COMPTES RENDUS de l'Académie des sciences

1878-1543 (electronic)





Volume 23, Special Issue 11-12, novembre-décembre 2020

Special issue / Numéro thématique

Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

> **Guest editors /** *Rédacteurs en chef invités* Mejdi Jeguirim, Salah Jellali, Besma Khiari

Académie des sciences — Paris



INSTITUT DE FRANCE Académie des sciences



Comptes Rendus

Chimie

Objective of the journal

Comptes Rendus Chimie is a peer-reviewed electronic journal of international standing, covering all areas of the discipline. It publishes mainly thematic issues, but also original research articles, preliminary announcements, review articles, historical perspectives, pedagogical texts or conference proceedings, without length limit, in English or in French. Comptes Rendus Chimie is published according to a virtuous policy of diamond open access, free for authors (no publication fees) as well as for readers (immediate and permanent open access).

Editorial director: Pascale Cossart

Editors-in-Chief: Pierre Braunstein

Advisory Board: Rick D. Adams, Didier Astruc, Guy Bertrand, Azzedine Bousseksou, Bruno Chaudret, Avelino Corma, Janine Cossy, Patrick Couvreur, Stefanie Dehnen, Paul J. Dyson, Odile Eisenstein, Marc Fontecave, Pierre Grandclaudon, Robert Guillaumont, Paul Knochel, Daniel Mansuy, Bernard Meunier, Armando J. L. Pombeiro, Michel Pouchard, Didier Roux, João Rocha, Clément Sanchez, Philippe Sautet, Jean-Pierre Sauvage Patrice Simon, Pierre Sinaÿ

Scientific secretary: Julien Desmarets

About the journal

All journal's information, including the text of published articles, which is fully open access, is available from the journal website at https://comptes-rendus.academie-sciences.fr/chimie/.

Author enquiries

For enquiries relating to the submission of articles, please visit this journal's homepage at https://comptes-rendus.academie-sciences.fr/chimie/.

Contact

Académie des sciences 23, quai de Conti, 75006 Paris, France Tel: (+33) (0)1 44 41 43 72 CR-Chimie@academie-sciences.fr



The articles in this journal are published under the license Creative Commons Attribution 4.0 International (CC-BY 4.0) https://creativecommons.org/licenses/by/4.0/deed.en



Contents / Sommaire

Mejdi Jeguirim, Salah Jellali, Besma Khiari Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1	583-587
H. Hammani, M. El Achaby, K. El Harfi, M. A. El Mhammedi, A. Aboulkas Optimization and characterization of bio-oil and biochar production from date stone pyrolysis using Box–Behnken experimental design	589-606
Mouzaina Boutaieb, Monia Guiza, Silvia Román, Beatriz Ledesma Cano, Sergio No- gales, Abdelmottaleb Ouederni	
Hydrothermal carbonization as a preliminary step to pine cone pyrolysis for bioenergy production	607-621
Nourelhouda Boukaous, Lokmane Abdelouahed, Mustapha Chikhi, Chetna Mohab-	
EVALUATE: Investigations on Mediterranean biomass pyrolysis ability by thermogravimetric analyses: thermal behaviour and sensitivity of kinetic parameters	623-634
Ahmed Amine Azzaz, Mejdi Jeguirim, Evan A. N. Marks, Carlos Rad, Salah Jellali, Mary-Lorène Goddard, Camelia Matei Ghimbeu Physico-chemical properties of hydrochars produced from raw olive pomace using olive mill wastewater as moisture source	635-652
Carole Tanios, Yara Saadeh, Madona Labaki, Maya Boutros, Cédric Gennequin, Hain- gomalala Lucette Tidahy, Antoine Aboukaïs, Edmond Abi-Aad Methane catalytic reforming by carbon dioxide on Mg–Al oxides prepared by hydrotal- cite route with different surfactants (CTAB, glucose, P123) or with intercalation of SBA- 15 and impregnated by nickel	653-669
Manel Wakkel, Besma Khiari, Fethi Zagrouba Comprehensive study of simultaneous adsorption of basic red 2 and basic violet 3 by an agro-industrial waste: dynamics, kinetics and modeling	671-687
Khaled Mahmoudi, Noureddine Hamdi, Mahassen Ben Ali, Salah Jellali, Ezzeddine	
Enhanced adsorptive removal of cationic and anionic dyes from aqueous solutions by olive stone activated carbon	689-704
Maria K. Doula, Antonis Papadopoulos, Chronis Kolovos, Olga Lamnatou, Antonis A. Zornas	
Evaluation of the influence of olive mill waste on soils: the case study of disposal areas in Crete, Greece	705-720

Antonis V. Papadopoulos, Maria K. Doula, Antonis A. Zorpas, Stavros Kosmidis, Anna	
Assimakopoulou, Chronis Kolovos	
Pepper cultivation on a substrate consisting of soil, natural zeolite, and olive mill waste sludge: changes in soil properties	721-732
Latifa Morjène, Fadhel Aloulou, Mongi Seffen	
Effect of organoclay and wood fiber inclusion on the mechanical properties and ther-	
mal conductivity of cement-based mortars	733-746

Foreword / Avant-propos



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1

Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1

Mejdi Jeguirim^{*a*}, Salah Jellali^{*b*} and Besma Khiari^{*c*}

^a Institut de Science des Matériaux de Mulhouse, France
 ^b Sultan Qaboos University, Oman
 ^c Water Research and Technologies Centre, Tunisia
 E-mails: mejdi.jeguirim@uha.fr (M. Jequirim), s.jellali@squ.edu.om (S. Jellali), besmakhiari@yahoo.com (B. Khiari)

This Special Issue of the journal Comptes Rendus Chimie is entitled: "Sustainable biomass resources management for environmental, agronomic, biomaterials and energy applications 1". It is motivated by the net decline of the current use of fossil resources due to both their economic exploitation viability and also the climate change mitigation requirements. Natural biomasses, that are worldwide produced with large amounts, have been pointed out as promising, attractive and sustainable materials for green energy recovery. Furthermore, these biomasses in their raw state or modified through mastered physical/chemical/thermal techniques could be used in environmental, agricultural and building applications including low-cost adsorbent for the treatment of wastewaters, eco-friendly organic biofertlizer for the amendment of agricultural soils and green materials for construction, respectively. However, the optimization of biomass valorization as a sustainable pathway is a complex issue that still require sustained research and development activities. Therefore, this special issue seeks to collect the latest scientific/engineering research on the suitable pathways for biomasses sustainable management that fulfill the United Nations sustainable development goal, the Intergovernmental Panel on Climate Change requirement and various other regional and international initiatives.

This special issue contains ten peer-reviewed papers covering important subjects related to biomasses thermochemical and biochemical conversion processes, the application of biomasses and their derived carbonaceous materials for wastewaters treatment, the biomass impacts on soil properties and plants growth and their application in the construction sector.

The first paper is entitled: "Optimization and characterization of bio-oil and bio-char production from date stone pyrolysis using Box–Behnken experimental design" [1]. This research work concerned production of bio-oil and biochar from olive stones using a fixed-bed pyrolyzer under various experimental conditions: temperature (400-600 °C), heating rate (10–50 $^{\circ}C \cdot min^{-1}$), and particle size (0.5-1.5 mm). The modeling and optimization of the pyrolysis process' parameters were conducted by using the Box-Behnken experimental design method. Results indicated that the maximum value of the desirability function was obtained at a pyrolysis temperature of 500 °C, a heating rate of 10 °C·min⁻¹, and a particle size of 1.5 mm. An in depth physico-chemical characterization of the produced bio-oil and biochar at these optimal conditions was performed by using various analytical apparatus including mainly Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, gas chromatography-mass spectrometry, and scanning electron microscopy. The corresponding results showed that the generated bio-oil can be used as a bio-fuel owing to its high content of aliphatic hydrocarbon compounds. Moreover, the produced biochar has high carbon content making it a promising candidate for the production of activated carbon.

The second paper is entitled: "Hydrothermal carbonization as a preliminary step to pine cone pyrolvsis for bioenergy production" [2]. The main objective of this work was to elucidate the benefits of including hydrothermal carbonization (HTC) as a preliminary step of traditional fast pyrolysis of Tunisian pine cone (PC). The results indicated that increasing the HTC temperature from 180 °C to 240 °C led to a net decrease in the solid yield and an increase in the gas yield. However, increasing the HTC time led to a decrease in both solid and gas yields. The optimum HTC conditions (240 °C and 60 min) yielded in a carbon content and a higher heating value of 92.5% and $34.28 \text{ MJ} \cdot \text{kg}^{-1}$, respectively, producing a material that might be utilized as a category-A briquette for domestic use. Under these conditions, the gas production was also found to be maximum.

The third paper is entitled: "Investigations on Mediterranean biomass pyrolysis ability by thermogravimetric analyses: thermal behaviour and sensitivity of kinetic parameters" [3]. In this study, thermal and kinetic studies are carried out for five different biomasses of Mediterranean origin: C. monspeliensis, Olive and date kernels, Aleppo pine husks and Wheat straw through thermogravimetric analyses. Results indicated that despite the different origins of biomasses, the initial and final ranges of pyrolysis temperatures are globally included in the ranges of 171–215 °C and 375–463 °C, respectively. Moreover, parameters such as the activation energy and the pre-exponential factor of the pyrolysis reaction were determined by different methods (Kissinger, Kissinger–Akahira–Sunose [KAS], Coats–Redfern, nonlinear least-squares minimization [NLSM] and distributed activation energy model [DAEM]). The related results showed that for all biomasses, the activation energy remains between 150 and 200 kJ·mol⁻¹ except for the Coats–Redfern method, where the value is in the range of 50 and 100 kJ·mol⁻¹.

The fourth paper is entitled: "Physico-chemical properties of hydrochars produced from raw olive pomace using olive mill wastewater as moisture source" [4]. This study concerned the hydrothermal carbonization (HTC) of Raw Olive Pomace (ROP) by using Olive Mill Wastewater (OMWW) and distilled water as two different liquid medium. Results showed that the use of OMWW as a liquid matrix enhances the yield of hydrochar production, but volatile matter, fixed carbon contents, O/C and H/C ratios had a decreasing trend. Furthermore, for an HTC temperature of 220 °C, the use of OMWW considerably increased the high heating value (HHV) of the hydrochars from about 24.2 MJ/kg to 31.6 MJ/kg. According to the Van Krevelen diagram of feedstock and derived hydrochars, dehydration was the predominant carbonization reaction for both liquid sources. Morphological characterization of both sets of hydrochars suggests the appearance of specific carbon nuclei when using distilled water while OMWW led to creation of hydrochars with a less homogeneous surface. Structural analysis emphasized the heterogeneous aspect of the hydrochars' surface with an abundance of crystallized metal-based inorganic salts.

The fifth paper is entitled: "*Methane catalytic reforming by carbon dioxide on Mg–Al oxides prepared by hydrotalcite route with different surfactants (CTAB, glucose, P123) or with intercalation of SBA-15 and impregnated by nickel*" [5]. In this research work, four magnesium-aluminum mixed oxides were synthesized by the hydrotalcite route using four modifying agents (three surfactants: glucose, CTAB, and P123, as well as silica SBA-15), and then calcined at 550 °C. Physicochemical characterizations were conducted before and after calcination through various techniques including XRD, DTA/TGA, and FTIR. Analytical results showed that the hydrotalcite structure was obtained even in the presence of a modifying agent. This structure was converted into mixed oxides upon calcination where the pore size distribution was more homogeneous in the presence of a modifying agent. Nickel was impregnated on these oxides and then the catalytic performances of the obtained catalysts were tested in the dry reforming of methane as a model for biogas reforming. Under the used experimental conditions, good catalytic activities and high carbon balances were obtained for the samples prepared with the three surfactants. Surfactant appear to slightly enhance the carbon balance due to higher nickel species dispersion.

The sixth paper is entitled: "Comprehensive study of simultaneous adsorption of basic red 2 and basic violet 3 by an agro-industrial waste: dynamics, kinetics and modelling" [6]. This work aims to assess the simultaneous adsorption of basic red 2 (BR2) and basic violet 3 (BV3) in a binary system in a batch mode using date stones as a low-cost adsorbent. For both dyes, experimental kinetic data were well fitted to the Brouers Sotolongo model ($R^2 = 0.99$) and the intraparticle diffusion seems to be the controlling step in mass transfer mechanisms. The equilibrium study revealed lower adsorption capacities for both dyes in binary system (41.95 and 88.91 mg/g for BR2 and BV3 respectively) compared to the individual sorption results (92.00 and 136.00 mg/g for BR2 and BV3 respectively). To assess the extent of competition and the preference of dyes for functional sites, competition and separation factors were calculated suggesting an antagonistic effect as well as a greater affinity for BV3 than for BR2 to adsorption sites. The equilibrium adsorption results were best fitted by modified Langmuir and P-Factor Langmuir isotherms for BR2 and BV3 respectively. Besides, based on enthalpy values (16.30 and 30.26 kJ/mol for BR2 and BV3 respectively), the simultaneous adsorption of both dyes was endothermic while the entropy revealed a higher affinity of the investigated adsorbent to BV3.

The seventh paper is entitled: "*Enhanced ad*sorptive removal of cationic and anionic dyes from aqueous solutions by olive stone activated carbon" [7]. In this work, four activated carbons were synthetized from natural olive stones wastes (NOS) using ZnCl₂ as activating agent. These activated carbons (OSAC), were synthetized for a constant mass ratio of ZnCl₂: NOS of 2:1, a contact time of 2 h and four different heating temperatures (300; 400; 450 and 500 °C). The physico-chemical characterization of these activated carbons by various analyses including N2 adsorption-desorption measurements, surface charges evolution versus pH, Boehm titration, FTIR and SEM. They showed that the activated carbon produced at a temperature of 400 °C (OSAC 400 °C) exhibited the best structural and textural properties. The test of this activated carbon for the adsorption of a cationic (methylene blue (MB)) and anionic (methyl orange (MO)) dye under various experimental conditions, showed that OSAC 400 °C could be considered as an effective, attractive and promising adsorbent for the both tested dyes. The Langmuir's adsorption capacities of this adsorbent were assessed to 303.0 and 277.8 mg·g⁻¹ for MB and MO, respectively which are significantly high compared to other various activated carbons. The retention of the pollutants seems to be mainly chemical including hydrogen bond and electrostatic attraction between the dyes and the activated carbon surface.

The eighth paper is entitled: "Evaluation of the influence of Olive Mill Waste on soils; The case study of disposal areas in Crete, Greece" [8]. In this research work, the risks of OMWW disposal on soil quality was carried out. It has resulted in the definition of eight soils indicators, namely pH, organic matter, electrical conductivity, total nitrogen, polyphenols, exchangeable potassium, available phosphorus and available iron. In order to confirm the validity of this indicators set, nine OMWW disposal areas were randomly selected and studied in Rethymno, Crete, without knowing their history, details of OMWW production and disposal or other activities of the areas. Soil samples were collected and analyzed for particle size distribution, pH, electrical conductivity, organic matter, carbonates, total N, available P, exchangeable cations (K, Ca, Mg), polyphenols, boron and available Mn, Fe, Cu, and Zn. The results indicated that all soil parameters were affected but at different magnitudes. Changes were evaluated considering the number of ponds for which (a) changes in soil parameters were observed; (b) a parameter value was measured above the excessive threshold; and (c) the change of the parameters' values was >100%. It was revealed that organic matter, nitrogen, polyphenols, potassium,

phosphorus and iron are the properties for which all three evaluation factors showed the highest values while zinc could be also considered as a potential indicator although it is not included in the evaluated indicators set. For pH and electrical conductivity, although no substantial changes were observed, they should always be included in a indicators' set because they are valuable for evaluating soil buffering capacity and salinization threat, respectively.

The ninth paper is entitled: "Pepper cultivation on a substrate consisting of soil, natural zeolite, and olive mill waste sludge: changes in soil properties" [9]. The aim of this research work was to investigate the potential of the natural zeolite clinoptilolite as a soil additive for using OMW sludge for vegetable cultivation and for eliminating the risk of soil and underground water degradation. For this purpose, a pot experiment was conducted under greenhouse conditions in which pepper seedlings were transplanted and grown onto different substrates containing combinations of 0%, 2.5%, and 5.0% zeolite and 0%, 2.5%, and 5.0% OMW sludge (v/v). The plants were irrigated twice a week, while leachates were collected on a weekly basis for testing. The experimental results indicate that the use of OMW sludge significantly improved the soil properties. The use of clinoptilolite as a substrate did not cause any significant variations in the cultivation process although it led to an increase in exchangeable Na at phytotoxic levels. The substrate consisting of 2.5% clinoptilolite and 2.5% OMW sludge exhibited the best results in terms of substrate and leachate properties. The results are considered to be useful in effectively treating OMW when combined with natural zeolite additives as this process enhances the physicochemical characteristics of soil without leading to major irreversible negative consequences.

The last paper is entitled: "*Effect of organoclay and wood fiber inclusion on the mechanical properties and thermal conductivity of cement-based mortars*" [10]. This paper explored the use of organic clay (OC) and a common biomass (wood fibers) treated with NaOH (WFsT) as reinforcement materials in cement mortars. The compressive strength, porosity, hydration rate and thermal conductivity of different formulations of reinforced cement were recorded. It was found that the best dispersion and the stabilization of WFsT in the composite materials are achieved by the addition of 6% WFsT in the presence of an anionic surfactant sodium dodecylbenzene sulfonate. Moreover, experimental results revealed that the optimal composite material was a mixture of water with ordinary Portland cement and 1 wt% modified with Cetyltrimethylammonium bromide at a waterto-solid ratio of 0.65. For OC contents from 2% and up to 18%, compressive strength results were higher than that of the plain cement paste. A decrease of the thermal conductivity was obtained by the addition of 2 wt% of WF from 2.26 to 0.8 W/m·°C. The presence of WFsT influenced the hydration of the cement while promoting the formation of more portlandite and more calcium silicate gel.

The Guest Editors of this special issue are thankful to all the authors for their innovative contribution and also to the reviewers for their constructive comments which have significantly contributed to the improvement of the quality of the accepted papers. Big thanks to the Editor-in-Chief of Comptes Rendus Chimie, Professor Pierre Braunstein for providing this great opportunity to publish the current peer reviewed papers. Special thanks to M. Julien Desmarets and Mrs Marie Christine Brissot, Editorial Scientific Secretaries and the entire production team of the journal for their valuable collaboration and support.

Mejdi Jegurim Co-Guest Editor Institut de Science des Matériaux de Mulhouse, France mejdi.jeguirim@uha.fr

Salah Jellali Co-Guest Editor Sultan Qaboos University Oman s.jellali@squ.edu.om

Besma Khiari Co-Guest Editor Water Research and Technologies Centre Tunisia besmakhiari@yahoo.com

References

- H. Hammani, M. El Achaby, K. El Harfi, M. A. El Mhammedi, A. Aboulkas, C. R. Chim., 2020, 23, no. 11-12, 589-606.
- [2] M. Boutaieb, M. Guiza, S. Román, B. L. Cano, S. Nogales, A. Ouederni, C. R. Chim., 2020, 23, no. 11-12, 607-621.
- [3] N. Boukaous, L. Abdelouahed, M. Chikhi, C. Mohabeer, A. H. Meniai, B. Taouk, C. R. Chim., 2020, 23, no. 11-12, 623-634.
- [4] A. A. Azzaz, M. Jeguirim, E. A. N. Marks, C. Rad, S. Jellali, M. L. Goddard, C. Matei Ghimbeu, *C. R. Chim.*, 2020, 23, no. 11-12, 635-652.
- [5] C. Tanios, Y. Saadeh, M. Labaki, M. Boutros, C. Gennequin,

H. L. Tidahy, A. Aboukaïs, E. Abi-Aad, C. R. Chim., 2020, 23, no. 11-12, 653-670.

- [6] M. Wakkel, B. Khiari, F. Zagrouba, C. R. Chim., 2020, 23, no. 11-12, 671-687.
- [7] K. Mahmoudi, N. Hamdi, M. Ben Ali, S. Jellali, E. Srasraa, C. R. Chim., 2020, 23, no. 11-12, 689-704.
- [8] K. M. Doula, A. Papadopoulos, C. Kolovos, L. Olga, A. A. Zorpas, C. R. Chim., 2020, 23, no. 11-12, 705-720.
- [9] A. V. Papadopoulos, M. K. Doula, A. A. Zorpas, S. Kosmidis, A. Assimakopoulou, C. Kolovos, C. R. Chim., 2020, 23, no. 11-12, 721-732.
- [10] L. Morjene, F. Aloulou, M. Seffen, C. R. Chim., 2020, 23, no. 11-12, 733-746.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Optimization and characterization of bio-oil and biochar production from date stone pyrolysis using Box–Behnken experimental design

H. Hammani^{*a*, *b*, *c*}, M. El Achaby^{*d*}, K. El Harfi^{*b*}, M. A. El Mhammedi^{*a*} and A. Aboulkas^{*, *b*}

^a Laboratoire de Chimie et Modélisation Mathématique (LCMM), Faculté Polydisciplinaire, Univesité Sultan Moulay Slimane, BP 145, 25000 Khouribga, Morocco

^b Laboratoire des Procédés Chimiques et Matériaux Appliqués (LPCMA), Faculté Polydisciplinaire, Univesité Sultan Moulay Slimane, BP 592, 23000 Béni Mellal, Morocco

 $^{\it c}$ Laboratoire des Sciences Appliquées et Didactiques (LASAD), Ecole Normale Superieure, Université Abdelmalek Essaadi, Tetouan, Morocco

^d Materials Science and Nano-engineering Department, Mohammed VI Polytechnic University, Lot 660, Hay Moulay Rachid, 43150 Ben Guerir, Morocco

E-mails: hasnaahammani@gmail.com (H. Hammani), mounir.elachaby@um6p.ma (M. El Achaby), K.elharfi@usms.ma (K. El Harfi), elmhammedi@yahoo.fr (M. A. El Mhammedi), a.aboulkas@usms.ma (A. Aboulkas)

Abstract. In Morocco, large quantities of agricultural residues such as date stones are generated annually during the processing of date palm fruit. This waste is usually discarded although it can be used as an attractive energy source or can be converted into chemical products using thermochemical conversion processes. Among these processes, pyrolysis has attracted attention since it enables the production and chemical recovery. In this context, the use of date stones as a raw material for the production of bio-oil and biochar using a fixed-bed reactor is investigated. The pyrolysis process was performed by varying three parameters: temperature (400–600 °C), heating rate (10–50 °C·min⁻¹), and particle size (0.5–1.5 mm). The modeling and optimization of the process parameters were conducted using the Box-Behnken experimental design. The maximum value of the desirability function was obtained at a pyrolysis temperature of 500 °C, a heating rate of 10 °C/min, and a particle size of 1.5 mm. Under these conditions, the bio-oil and biochar produced were successfully characterized using different analytical techniques including elemental analysis, chemical composition, Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, gas chromatography-mass spectrometry, and scanning electron microscopy. The results show that the bio-oil can be used as a biofuel owing to its high content of aliphatic hydrocarbon compounds. The biochar having a high carbon content is a promising candidate for the production of activated carbon.

Keywords. Date stone, Optimization, Pyrolysis, Box–Behnken, Characterization.

^{*} Corresponding author.

1. Introduction

Currently, energy plays an important role in the world. Socioeconomic development depends on its production and on its long-term availability in increasing quantity from reliable, safe, and environmental friendly sources. Over millennia, humans have found ways to extend various sources of energy ranging from wood, coal, oil, and petroleum to nuclear. Renewable energy sources such as biomass, hydropower, geothermal, solar, and wind energy have a share of 14% in total world energy consumption of which 62% is biomass [1]. Biomass is considered an interesting energy source due to several reasons. The main one is that bioenergy can make a substantial contribution to sustainably meeting future energy demand. Resources are often locally available as is waste. Hence, biomass allows not only waste management but also energy and chemical recovery using thermochemical conversion processes.

Thermochemical processes can be categorized into gasification, combustion, and pyrolysis. Pyrolysis has attracted more attention than the other thermochemical processes due to the possibility of optimizing its conditions to produce high energy density pyrolytic bio-oil as well as derived biochar and gas [2-4]. The liquid product (bio-oil) can be upgraded or used directly in heat boilers, drive diesel engines, or turbines. As it is in liquid form, it can be easily transported and stored more efficiently than the original biomass. The combustion of pyrolysis oils results in zero net contribution to carbon dioxide (CO₂) emissions as the burned carbon is fixed by biomass during its lifetime. Furthermore, during the burning of bio-oils, there are no sulfur oxide (SO_x) emissions and very low nitrogen oxide (NO_x) emissions when compared to fossil fuels. Therefore, it may be a potential fuel replacement in the future [5-7]. The use of the solid product (biochar) in various environmental applications including adsorption (for water and air pollutants), catalysis (for syngas upgrading, biodiesel production, and air pollutant treatment), and soil conditioning have been discussed. The recent research trend for biochar in other applications, such as fuel cells, super capacitors, and hydrogen storage, has also been reviewed.

The main sources of biomass are agricultural residues such as olive and date wastes. These agri-

cultural wastes are available in large quantities, and their use does not compromise food crops. In addition, they may be a potential fuel replacement in the future [8]. The date palm is one of the main fruit crops in arid and semi-arid regions in Morocco. About 105 million date palms are currently being grown around these regions. The production of dates has seen considerable expansion over the last decade, rising from 0.4 million tons in 2006 to 2.4 million tons in 2018 [9]. The expansion of fruit production has naturally led to the increase in waste every year. For this reason, exploitation of this palm waste would help us to (i) improve waste disposal, (ii) produce new value-added materials, and (iii) provide livelihoods for people in these areas. Therefore, a systematic and comparative investigation of the distribution of pyrolysis products was performed using a fixed-bed reactor. It is important to note that the effects of distinct conditions on pyrolysis product yields from date stone have not yet been reported in detail in the literature. However, the use of date stones for pyrolysis has been reported in the literature [10-12]. However, all these works investigated the pyrolysis of date stones in N2 atmosphere and did not examine the effect of pyrolysis conditions such as temperature, heating rate, and other parameters on the bio-oil and the biochar yield and properties. Besides, the effect of pyrolysis conditions on the production of bio-oil from date stones via pyrolysis was only reported by Fadhil et al. [13], who investigated the effect of individual parameters and did not examine the combined effect of all process parameters. It is time-consuming and requires several experiments to determine the optimal levels. This process could be unreliable. These limitations of the classical method can be eliminated by optimizing all the process parameters using a statistical experimental design such as the Box-Behnken experimental design (BBD). The objective of this optimization study is to gain the optimal amount (quantity) of bio-oil and biochar by the pyrolysis process.

This work aims to study the combined effect of three process parameters, namely, pyrolysis temperature, heating rate, and particle size, on the biochar and bio-oil yield from date stones based on the BBD. Under the optimal condition, the pyrolytic bio-oil and biochar were characterized using elemental analysis, Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (¹H-NMR), gas chromatography–mass spectrometry (GC–MS), and scanning electron microscopy (SEM).

2. Materials and methods

2.1. Chemicals and reagents

To evaluate the local by-products in terms of energetic valorization, biomass-based date stones from the region of Errachidia in Morocco as the feedstock was used in this present study.

All the used chemicals were of analytical grade. They were used without any further pre-treatment. Iodine (I₂), sodium thiosulfate (Na₂S₂O₃ \cdot 5H₂O), Na₂CO₃, NaHCO₃, and HCl (37%) were purchased from Sigma-Aldrich (Germany). NaOH was purchased from Merck (Germany), potassium iodide (KI) from Pharmac (Morocco), and methylene blue (C_{16H18}ClN₃S) (85%) from Panreac (Spain). All the instruments and apparatus used in this work are mentioned in Section 2.3.

2.2. Pyrolysis procedure

The pyrolysis experiments were carried out in a fixedbed reactor. An electric furnace was used to heat the reactor externally. Then, the reactor was cooled down to a temperature equal to 0 °C with an icesalt bath. The condensed liquid products did not only contain the oil phase product but also the aqueous phase products. They were separated by decantation after being washed with dichloromethane. Pyrolytic oil or bio-oil was dried using anhydrous sodium sulfate and was collected by evaporating the solvent at a temperature of 60 °C followed by calculating its yield. After cooling the pyrolysis reactor, the solid (biochar) was removed and weighed. The amount of gas released was then calculated by subtracting the amount of solid and liquid products from the amount of initial raw material. Repeatability expressed using the relative standard deviation was less than $\pm 0.5\%$, which was obtained thrice.

2.3. Characterization of raw materials and biooil and biochar

2.3.1. Proximate and ultimate analyses

The proximate analysis was conducted using a thermogravimetric analyzer (METTLER TOLEDO TGA/DSC 3+). The moisture content was determined by mass loss after the sample was heated to 105 °C in N₂. Volatile matter corresponds to the mass loss between 105 and 900 °C in N₂. Fixed carbon is the solid combustible material that leads to the mass loss at 900 °C when the atmosphere is switched from N₂ to air; the residue left is the ash content.

The ultimate analysis for C, H, N, and S content was performed using an elemental analyzer (vario MICRO cube V4.0.2). The H/C and O/C molar ratios and empirical formula were calculated from elemental composition. The higher heating value (HHV) of the samples was experimentally measured using a bomb calorimeter (Model 1261, Parr Instrument) according to ASTM D5865-04.

2.3.2. Infrared spectroscopy

Surface functional groups were determined by using an FTIR spectrometer (FTIR-2000, PerkinElmer). The spectrum was recorded in the range $400-4000 \text{ cm}^{-1}$.

2.3.3. Scanning electron microscopy

Surface morphologies of the optimally prepared activated carbon were studied by SEM and energydispersive X-ray spectroscopy. The SEM images were recorded using TESCAN VEGA3 at an accelerating voltage of 20 kV.

2.3.4. Iodine number

The iodine number is the most fundamental parameter used to characterize the performance of activated carbon. It is a measure of the micropore (0–20 Å) content of activated carbon by the adsorption of iodine from solution according to the ASTM D4607-94 method. The experiment consists in treating 1 g

of activated carbon with 10 mL of 5% HCl. This mixture is boiled for 30 s and subsequently cooled. Soon afterward, 100 mL of 0.1 mol·L⁻¹ iodine solution is added, shaken for 30 min, and filtered. The resulting solution is filtered and 50 mL of the filtrate is titrated with 0.1 mol·L⁻¹ sodium thiosulfate by using starch as an indicator.

2.3.5. Methylene blue index

The methylene blue index (MBI) is a measure of mesoporosity (2–5 nm) present in activated carbon. It is defined as the maximum amount of dye adsorbed by 1 g of adsorbent. It is also determined according to the standard method (JIS K 1470-1991). In this assay, 0.1 g of activated carbon was placed in contact with 100 mL of methylene blue solution at different concentrations (20–500 mg·L⁻¹) for 24 h at room temperature (approximately 25 °C). After shaking for 24 h, the suspensions were filtered and the remaining concentration of methylene blue in the solution was determined by a spectrophotometric method at a λ max value of 665 nm. Standard solutions of methylene blue were used for calibration.

2.3.6. Boehm titration

The Boehm titration method was used to quantify the basic and oxygenated acidic surface groups on activated carbons. Generally, carboxyl, phenolic hydroxyl, and lactonic groups are acidic, while the basicity of activated carbon derives primarily from delocalized π -electrons of graphene structure with a small contribution from oxygen-containing surface functionalities (such as pyrene, chromene, and quinone). These surface functional groups were quantified by back-titration with NaOH solution for acidic groups and with HCl solution for basic groups.

Experimentally, approximately 0.1 g of each sample was mixed with 50 mL of 0.01 mol·L⁻¹ aqueous reactant solution (NaOH, or Na₂CO₃, or NaHCO₃). The mixtures were stirred for 24 h at room temperature. Then, the solid phase was filtrated by a 0.45 mm membrane filter. To determine the oxygenated group's content, titrations of the filtrate approximately 10 mL were performed with standardized HCl (0.01 mol·L⁻¹). The numbers of all acidic sites were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups. Basic groups' contents were also determined by titration of the filtrate with NaOH (0.01 mol·L⁻¹).

2.3.7. Point of zero charge (pH zpc)

The pHzpc is an important characteristic of any activated carbon as it indicates the acidity/basicity of the adsorbent and the net surface charge of the carbon in solution. To measure the pHzpc, 0.1 mg of activated carbon was added to 100 mL of solution of $0.01 \text{ mol}\cdot\text{L}^{-1}$ NaCl with pH varying from 2 to 12 and stirred for 6 h. The final pH was measured and plotted against the initial pH. The pH_{zpC} was determined at the value for which pH_{final} = pH_{initial}.

2.3.8. ¹H-NMR spectroscopy and GC-MS

¹H-NMR spectroscopy was recorded on 600 MHz Bruker spectrospin instruments. The oil samples were diluted using CDCl₃. The GC–MS analysis of bio-oil was carried out using a Thermo Scientific ISQ Single Quadrupole. The temperature program adopted is as follows: initial and final temperatures were 60 and 300 °C, respectively; the total time was 20 min at a heating rate of 10 °C·min⁻¹. The injector and detector temperatures were 250 °C and 300 °C, respectively. The gas sample was injected by a Hamilton syringe of 50 mg/mL.

3. Results and discussion

3.1. Physicochemical characterization of date stone

3.1.1. Ultimate and proximate analyses

Table 1 presents the proximate and ultimate characterization of the date stone and its empirical structure. The results show that the date stone has high volatile matter content and a low amount of ash, moisture, and fixed carbon as compared to the results in the literature [14,15].

The percentages of carbon, hydrogen, nitrogen, sulfur, and oxygen present in the date stone are determined by elemental analysis. The analysis shows that the tested samples are rich in carbon, hydrogen, and oxygen contents (43.81%, 6.41%, and 46.9%, respectively). On the contrary, the relative contents of nitrogen and sulfur are low (0.15% and 0.19%, respectively). The high carbon and oxygen contents give the material a high calorific value. This value showed that the biomass could be considered suitable for pyrolysis, gasification, or combustion processes. Moreover, the knowledge of ratios of H/C and O/C is important for thermochemical conversion processes.

Characteris	tics	Percentage
Proximate analysis (wt%)	Moisture content	6.59
	Volatile matter	73.46
	Ash	2.24
	Fixed carbon	24.3
Ultimate analysis (wt%)	Carbon	46.9
	Hydrogen	6.41
	Nitrogen	0.45
	Sulfur	0.19
	Oxygen	43.81
H/C molar	atio	1.64
O/C molar i	atio	0.70
Empirical for	mula	$CH_{1.640}O_{0.700}N_{0.008}$
Higher heating valu	$(MJ \cdot kg^{-1})$	18.77
pH _{pzc}		6.13
Carboxylic group	s (meq/g)	0.465
Lactonic groups	0.538	
Phenolic groups	0.535	
Acidic groups (meq/g)	1.538
Basic groups (1	0.282	

Table 1. Proximate and ultimate analyses and chemical groups on the surface of date stone

In most cases, biomasses have higher O/C and H/C ratios than those of fossil fuels. The high values of the atomic H/C ratio (1.64) in date stone agree with the high volatile content found by proximate analysis (73.46%). The values obtained for these parameters are relatively similar to those reported for date stone in the literature [14,16]. The HHV was 18.7 KJ·kg⁻¹. These values are of the same order of magnitude as the results obtained for sawdust, olive solid waste, oil palm fruit bunches, wood pellets, and wood chips. A comparison with the data from the literature for wood biomass and energetic crops shows that the investigated biomass has a typical composition [17,18] with a significant HHV value.

3.1.2. Infrared spectroscopy

The raw date stone was also characterized by FTIR in the middle region (Figure 1), including the wavenumbers between 4000 and 400 cm⁻¹. The aim of the analysis was to identify the functional groups of the raw material and then compare any structural

changes after the pyrolysis experiments. The bands in the spectra of raw date stone indicate that it is mainly composed of lignin, cellulose, and hemicelluloses [19–21]. The band at 3335 cm⁻¹ is caused by the OH⁻ group of lignin in the date stone. The absorption peak at wavenumber 1736 cm⁻¹ is characteristic of hemicellulose. The absorption peaks at approximately 3362, 2900, 1365, and 1143 cm⁻¹ are characteristic of cellulose. Generally, similar absorption peaks are observed in the spectrum of lignin. The absorption peaks at 2900, 1600–1500, 1416, 1314, and 830–750 cm⁻¹ are attributed to lignin [22,23]. The characteristic absorption peaks of raw date stone prove the presence of lignin, cellulose, and hemicelluloses.

3.1.3. Boehm titration

The functional groups of date stone were estimated by the Boehm titration (Table 1). The results show that the date stone mainly contains more acidic groups than basic groups. This indicates that the date



Figure 1. FTIR spectra of date stone and its bio-oil and biochar obtained at 500 °C, 10 °C/min, and 1.5 mm.

Table 2. Process factors and their levels

Factors	Unidimensional variables	Leve	ls of fa	ctors
		-1	0	1
Pyrolysis temperature (°C)	А	400	500	600
Heating rate (°C/min)	В	10	30	50
Particle size (mm)	С	0.5	1.0	1.5

stone has an acidic character. Thus, the high content of oxygenated groups is due to the presence of a large quantity of phenolic, lactonic, and carboxylic groups. Therefore, these results are in agreement with the $(pH_{ZPC}$ value of 6.29, which indicates the acidity of the date stone.

3.2. Study of the factors influence on pyrolysis product yields

3.2.1. Response surface methodology

Pyrolysis experiments were conducted to aid in the design of response surface methodology based on the BBD. Box and Wilson introduced this method in 1951. It is a regression method for exploring the correlation between some explanatory factors and one or more responses. The BBD consists of three factors, the pyrolysis temperature (A), heating rate (B), and particle size (C), as the independent variables. Thus, the pyrolysis product yields consisting of the solid product (biochar), the liquid product (bio-oil), and the gaseous product (gas) are the dependent variables. All the responses are listed in Table 2. These variables with their respective domain are chosen based on the data from the literature and preliminary experiments [24–28]. The experiments were conducted according to the BBD at three levels, -1, 0, and +1, for 16 experiments. The number of experiments was calculated by using (1):

$$N = 2n(n-1) + n_c = 16,$$
 (1)

where *n* is the number of variables and n_c is the replicate number of experiment.

The mathematical model associated with this design is generally a quadratic equation or secondorder model. The model can be written as in (2) (X_i are the unidimensional variables corresponding to the above described A, B, and C variables):

$$Y = b_0 + b_1 A + b_2 B + b_3 C + b_{12} A B + b_{13} A C + b_{23} B C + b_{11} A^2 + b_{22} B^2 + b_{33} C^2,$$
(2)

-

Exp.	p. Coded level		evel	Actual level			Experimental responses		
	А	В	С	Pyrolysis temperature	Heating rate	Particle size	Y ₁ (%)	Y ₂ (%)	Y ₃ (%)
				(°C)	(°C/min)	(mm)			
1	-1	-1	0	400	10	1.0	44.12	09.26	46.62
2	1	-1	0	600	10	1.0	31.76	15.16	53.08
3	-1	1	0	400	50	1.0	42.69	10.75	46.56
4	1	1	0	600	50	1.0	30.48	15.79	53.73
5	-1	0	-1	400	30	0.5	43.22	10.06	46.72
6	1	0	-1	600	30	0.5	30.02	14.96	55.02
7	-1	0	1	400	30	1.5	43.06	10.32	46.62
8	1	0	1	600	30	1.5	30.92	15.16	53.92
9	0	-1	-1	500	10	0.5	36.76	15.05	48.19
10	0	1	-1	500	50	0.5	36.60	16.10	47.30
11	0	$^{-1}$	1	500	10	1.5	37.55	15.26	47.19
12	0	1	1	500	50	1.5	36.46	16.26	47.28
13	0	0	0	500	30	1.0	37.13	15.05	47.82
14	0	0	0	500	30	1.0	37.19	15.10	47.71
15	0	0	0	500	30	1.0	37.12	15.05	47.83
16	0	0	0	500	30	1.0	37.10	15.08	47.82

 Table 3. Experimental design matrix and dependent variables attributed to the factors of Box–Behnken design

where Y denotes the responses of the yields of biochar (Y_1) , bio-oil (Y_2) , and gaseous products (Y_3) . These product yields are estimated as in (3)–(5) [29]:

$$Y_1 = \frac{W_{\text{bio-char}}}{W_0} \times 100,\tag{3}$$

$$Y_2 = \frac{W_{\text{bio-oil}}}{W_0} \times 100,\tag{4}$$

$$Y_3 = 100 - Y_1 - Y_2. (5)$$

Here, W_0 , $W_{\text{bio-char}}$, and $W_{\text{bio-oil}}$ represent the weights of the raw biomass (g), biochar (g), and bio-oil (g), respectively.

3.2.2. Experimental results

Table 3 lists the coded and actual values of the three important factors together with the response values and the observed results for the three responses: biochar, bio-oil, and gas yields.

From these results, it appears that for the biochar and bio-oil yield responses, the pyrolysis temperature and the heating rate have a strong impact on the development of response during the pyrolysis step. Therefore, a yield of bio-oil from the date stone varies between 9.26% and 16.26%, which represents a high value at a carbonization temperature of 600 °C, a heating rate of 50 °C/min, and a particle size of 1.5 mm. Therefore, these date stones have a medium bio-oil yield. Moreover, it could be noted that the maximum value of biochar is approximately 44.12%. It is obtained for date stone pyrolysis at 400 °C, a heating rate of 10 °C·min⁻¹, and a grain size of 1 mm. Finally, the yield of pyrolysis gases released during the thermal decomposition of date stone reaches a maximum of 55.02%, and it is obtained at 600 °C, 30 °C, and 0.5 mm for pyrolysis temperature, heating rate, and particle size, respectively.

In addition, a regression analysis was performed to fit the response functions with the experimental data. The effect values of regression coefficients are shown in Table 4.

According to this table, the pyrolysis temperature presents a negative effect on the biochar yield and a positive effect on other responses. In contrast, the heating rate has a positive effect on bio-oil and

	Source	Main coefficients	Sum of squares	df	Mean squares	<i>F</i> -value	p-value Prob > F	
Y1	Model	37.135	315.171019	9	35.019002	1059.32462	3.977×10^{-10}	Significant
	А	-6.364	311.0018	1	311.0018	9407.80277	3.2626×10^{-12}	
	В	-0.557	2.5200125	1	2.5200125	76.2303645	5.1942×10^{-5}	
	С	0.111	0.4465125	1	0.4465125	13.5070007	0.00790982	
	AB	-0.213	0.0036	1	0.0036	0.10889998	0.75105599	
	AC	0.265	0.2809	1	0.2809	8.49722348	0.27561155	
	A^2	0.108	0.04620026	1	0.0462002	1.39755771	0.27572917	
	B^2	0.207	0.00125289	1	0.0012528	0.03790006	0.85117362	
	C^2	-0.438	0.84412658	1	0.8441265	25.5348245	0.00147453	
	Residual		0.231405	7	0.0330578			
	Cor. total		315.402424	16				
	Model	15.07	86.4954668	9	9.61060742	366.128341	1.6244×10^{-8}	Significant
	А	2.585	53.4578	1	53.4578	2036.54304	6.8551×10^{-10}	-
	В	0.521	2.1736125	1	2.1736125	82.806539	3.9702×10^{-5}	
	С	0.104	0.0861125	1	0.0861125	3.28056546	0.11301055	
Y_2	AB	-0.215	0.1849	1	0.1849	7.0440012	0.03274845	
	AC	0.015	0.0009	1	0.0009	0.03428665	0.85834927	
	A^2	-2.686	30.3376761	1	30.3376761	1155.75244	4.9384×10^{-9}	
	B^2	0.356	0.54039184	1	0.54039184	20.5869161	0.00267636	
	C^2	0.243	0.24913921	1	0.24913921	9.49127581	0.01779559	
	Residual		0.183745	7	0.02624929			
	Cor. total		86.6792118	16				
	Model	47.79	136.943931	9	15.2159924	175.113559	2.1161×10^{-7}	Significant
	А	3.65	106.799113	1	106.799113	1229.09977	3.9861×10^{-9}	
	В	0.036	0.0105125	1	0.0105125	0.12098332	0.73819512	
	С	-0.34	0.9248	1	0.9248	10.6430797	0.01381903	
	AB	0.177	0.126025	1	0.126025	1.45036129	0.26760568	
	AC	-0.25	0.25	1	0.25	2.8771301	0.13366307	
	A^2	2.58	28.0976024	1	28.0976024	323.36183	4.0637×10^{-7}	
	B^2	-0.37	0.58188658	1	0.58188658	6.69665357	0.03606072	
Y_3	C^2	0.196	0.16968658	1	0.16968658	1.95284146	0.20497622	
	Residual		0.608245	7	0.08689214			
	Cor. total		137.552176	16				

Table 4. Analysis of variance of biochar yield (Y₁), bio-oil yield (Y₂), and bio-gas yield (Y₃)

bio-gas yields and has a negative effect on the biochar yield. Furthermore, the particle size has a positive impact on the yields of bio-oil and biochar and a negative effect on the yield of gas. Besides, an analysis of interaction effects indicates greater interaction between the pyrolysis temperature and the particle size with a positive effect on the biochar yield. Moreover, for the yields of bio-gas and biooil, the most important interaction is the quadratic combination of pyrolysis temperatures.

3.2.3. Analysis of variance

To determine the main and significant interaction effects in the responses, the analysis of variance (ANOVA) was used at a confidence level of 95%. After removing the insignificant terms, the ANOVA data for the three responses are presented in Table 4.

According to the ANOVA analysis, the significant effects are the pyrolysis temperature (A), heating rate (B), particle size (C), interactions AB and AC, and quadratic interactions A^2 , B^2 , and C^2 (Equations (6)–(8); Table 4):

$$\begin{split} Y_1 &= 37.148 - 6.238A + 0.495B + 0.173C - 0.03AB \\ &\quad + 0.265AC + 0.038A^2 + 0.076B^2 - 0.038C^2, \quad (6) \\ Y_2 &= 15.066 + 2.585A - 0.521B + 0.103C + 0.215AB \\ &\quad - 0.015AC - 2.684A^2 + 0.358B^2 + 0.243C^2, \quad (7) \\ Y_3 &= 47.786 + 3.653A + 0.026B - 0.277C - 0.177AB \\ &\quad - 0.25AC + 2.645A^2 - 0.432B^2 + 0.1382C^2. \quad (8) \end{split}$$

In fact, the biochar yield increased with increase in the pyrolysis temperature, heating rate, interaction between the pyrolysis temperature and the heating rate, and the quadratic interaction of particle sizes. On the other hand, the particle size of the date stone, the interaction between the pyrolysis temperature and the particle size, and the quadratic interactions of two other factors increased the biochar yield.

Furthermore, the pyrolysis temperature (A), heating rate (B), and particle size (C) and AB, B^2 , and C^2 interaction terms have significant effects on the responses, implying that the increase in these terms enhances the bio-oil yield. In contrast, the interactions AC and A^2 have a negative effect on the response of the bio-oil yield.

Moreover, the particle size and the interaction between the pyrolysis temperature and the particle size had a negative effect on the gaseous product yield. Besides, an increase in the yield of noncondensable gases occurred for A and B and interactions AB, A^2 , and C^2 . As a result, the yield of the gaseous product increased at higher pyrolysis temperatures.

3.2.4. Response surface analysis

In this step, the response surface methodology and the optimal conditions of this process were determined on the basis of mathematical models for the yield of pyrolysis products. Figure 2 shows the three-dimensional response surface plots for the significant interactions. For the yields of biochar, biooil, and bio-gas, the most significant interactions were the pyrolysis temperature/heating rate and pyrolysis temperature/particle size.

For the biochar yield, it can be seen from Figure 2A that the surface area increases with decrease in pyrolysis temperature and increase in heating rate for a constant particle size (1 mm). The maximum biochar yield is obtained at 400 °C regardless of heating rate. Moreover, Figure 2B shows that the yield increases at low pyrolysis temperatures regardless of particle size. The maximum biochar yield is obtained at a pyrolysis temperature of 50 °C·min⁻¹, and a particle size of 1 mm.

It can be seen from Figure 2C that the bio-oil yield increases with increase in pyrolysis temperature and decrease in heating rate when the particle size is 1 mm. A maximum yield is observed at a pyrolysis temperature of 500 °C at a heating rate of 10 °C·min⁻¹. However, Figure 2D shows that the bio-oil yield increases regardless of particle size. Then, a maximum value appears at pyrolysis temperature, heating rate, and particle size values of 500 °C, 10 °C·min⁻¹, and 1.5 mm, respectively.

On the other hand, Figures 2E and F show that the efficiency of non-condensable gases increases with increase in pyrolysis temperature. A high gas efficiency value is obtained at the pyrolysis temperature of 600 °C regardless of heating rate and particle size, indicating that the gas efficiency is necessarily dependent on the pyrolysis temperature.

3.2.5. Diagnostic model

The graphs of the normal probability of residues are shown in Figures 3A–C. It is seen from the figure that the data points for the performance of pyrolysis products (biochar, bio-oil, and gas) are close to the straight line, which shows that the experiments are at the origin of a normally distributed population.

3.2.6. Optimal values and discussion

The desirability function was used for optimizing the three responses studied, including biochar, biooil, and gas yields. The maximum value of the desirability function was obtained at a pyrolysis temperature of 500 °C, a heating rate of 10 °C·min⁻¹, and a particle size of 1.5 mm. Under these conditions, the



Figure 2. Surface response plots for biochar yield (A, B), bio-oil yield (C, D), and bio-gas yield (E, F).

predicted responses for biochar, bio-oil, and bio-gas yields were $36.64 \pm 2.03\%$, $16.12 \pm 0.98\%$, and $47.24 \pm 3.21\%$, respectively.

All the obtained results can be analyzed as follows. At temperatures below 500 °C, the lowest yields are attributed to the incomplete conversion of organic compounds. At temperatures above 500 °C, the decrease in the bio-oil yield may be due to the secondary cracking of pyrolysis vapors at higher temperatures. At intermediate temperatures, there is a compromise between secondary reactions and the final temperature, which leads to an optimal bio-oil yield. The optimal yields of bio-oil and biochar were obtained at 500 °C.



Figure 3. Normal probability plots of residuals for three responses: (A) biochar yield, (B) bio-oil yield, and (C) bio-gas yield.

The heating rate also plays a significant role in the destruction and reforming of biochar and bio-oil.

It is well known from a survey of the literature and previous studies that the heating rate plays an important role in product distribution [30–33]. In this work, faster heating rates maximized the yield of bio-oil, while low heating rates favored the formation of biochar [30,34–36]. However, at low heating rates, secondary cracking remained low and the flow of locally produced gases was insufficient to break the organic molecules outside the grain of the date stone. On the other hand, it can be explained that bio-oil yields increased with increase in organic and specific products and secondary cracking of volatiles at higher heating rates. At a heating rate of $10 \, ^{\circ}\text{C} \cdot \text{min}^{-1}$, a good compromise among the effects of the abovementioned parameters is obtained. Furthermore, we obtained optimal bio-oil and biochar yields.

The particle size of the date stone has a slight influence on the yield of the pyrolysis product. It is a parameter that controls the drying rate and primary pyrolysis and the extent to which these processes overlap during thermal decomposition. The effect of particle size is explained in terms of the heating rate at which bigger particles heat up more slowly resulting in a lower temperature for average particles, which

Properties	Grape bagasse [37]		Residual chañar [38]		Eastern giant fennel [39]		Date stone [this work]	
	Bio-oil	Biochar	Bio-oil	Biochar	Bio-oil	Biochar	Bio-oil	Biochar
Carbon	71.72	72.09	56.7	35.5	53.96	63.92	67.38	69.63
Hydrogen	8.69	3.05	7.1	7.8	7.41	3.268	7.24	3.54
Nitrogen	2.69	1.4	0.2	< 0.1	1.227	0.949	0.304	0.421
Oxygen	16.90	23.46	35.9	56.6	37.403	31.86	22.65	23.89
Empirical formula	$CH_{1.45}O_{0.17}\;N_{0.03}$	$CH_{0.51}O_{0.24}N_{0.02}$	$CH_{1.5}O_{0.46}N_{0.003}$	CH _{2.63} O _{0.47}	$CH_{1.65}O_{0.52}N_{0.02}$	$CH_{0.61}O_{0.37}N_{0.013}$	$CH_{1.289}O_{0.252}N_{0.004}$	$CH_{0.61}O_{0.258}N_{0.005}$
H/C molar ratio	1.45	0.51	0.46	2.63	1.647	0.61	1.289	0.610
O/C molar ratio	0.17	0.24	0.46	0.47	0.52	0.37	0.252	0.258
HHV (MJ/kg)	32.95	28.40	23.0	13.1	22.20	20.59	25.1	23.25

Table 5. Comparison of physicochemical characteristics of date stone biochar and bio-oil obtained at 500 °C, 10 °C/min, and 1.5 mm with other biomasses' biochar and bio-oil

leads to less amounts of volatile yields. Uniform heating could be established with sufficiently small particle size samples. The results of our study show that 1.5 mm particle size samples are the most suitable for obtaining optimal yields from the pyrolysis of date stone.

3.3. *Physical and chemical characterization of the pyrolysis product*

In this step, only bio-oil and biochar that were obtained under the most suitable conditions, a temperature of 500 °C, a heating rate of 10 °C/min, and a particle size of 1.5 mm, were retained for the next characterization.

The analytical methods we used to characterize the liquid fraction (bio-oil) and the solid fraction (biochar) are as follows. For elemental analyses, SEM, FTIR, ¹H-NMR spectroscopy, and GC–MS were carried out.

3.3.1. Bio-oil characterization

a. Physical property and elemental composition

Table 5 lists the results of elemental analysis of bio-oil produced by the pyrolysis of date stone at a temperature of 500 °C, a heating rate of 10 °C·min⁻¹, and a particle size of 1.5 mm. We note that the values for carbon (67.38%) and hydrogen (7.420) contents and the HHV (25.10 MJ/kg) of bio-oil are higher than those of the raw date stone. Furthermore, the average chemical composition of the pyrolysis oil is $CH_{1,289}O_{0,252}N_{0,004}$. The significant decrease in oxygen content of the oil (22.65%) compared to that of the original feedstock (43.81%) is important because the high oxygen content is not conducive to the production of transport fuels. The cause of this

decrease is decarboxylation and dehydration reactions of molecules in the biomass.

Table 5 presents the characteristics of the pyrolysis oil derived from date stone in comparison with other biomass-derived oils [37–39]. It is evident that the HHV of date stone oil is favorable than that of other pyrolysis oils. Furthermore, the oil from the date seed may be considered as an important potential source of alternative fuel.

b. FTIR spectroscopy

FTIR spectroscopy was used to analyze the functional group composition of bio-oil (Figure 1 and Table 6). The FTIR spectra indicate the presence of O– H group stretching vibrations between wavenumbers 3200 and 3400 cm⁻¹ and C–H deformation vibrations between 1350 and 1450 cm⁻¹, which shows the existence of alkane groups. The C=O stretching vibrations between 1680 and 1750 cm⁻¹ confirm the presence of ketones, quinones, and carboxylic acid or aldehyde groups. The wavenumbers 1645–1678 cm⁻¹ show C=C stretching vibrations, which indicate the presence of alkenes. Besides, mono- and polycyclic and substituted aromatic groups can be identified by the absorption peaks between 690 and 900 cm⁻¹ and 1350 and 1450 cm⁻¹, respectively [40,41].

All these absorption bands suggest the presence of a wide variety of chemical groups such as phenols, aromatics, alcohols, esters, ethers, carboxylic acids, aldehydes, and ketones. This heterogeneity arises from the thermal degradation of the constituents of the date stone during secondary pyrolysis reactions such as polymerization, polycondensation, and etherification or esterification.

c. ¹*H*-*NMR* spectroscopy

To have a better understanding of the complete chemical composition of bio-oil, an analysis using



Figure 4. GC-MS spectrum of bio-oil obtained at 500 °C, 10 °C/min, and 1.5 mm.

Table 6.	FTIR bands	and functional	groups of bio	-oil obtained at 5	00 °C, 10	°C/min,	and 1.5 mm
			/ · · · · · ·			/	

Peak (cm ⁻¹)	Bond	Attribution	
3200-3600 О-Н		Polymer O–H	
2850 and 2930 C-1		Aliphatic stretching band	
1700	C=O	Ketones, aldehydes, lactones, and carboxylic group	
1600–1680	C=C	Olefinic	
1200-1350	C–H	Aromatic	
1000-1200	C–O	Alcohol, ester, and ether	
3150	N–H	Heteroatoms	

nuclear magnetic resonance (NMR) spectroscopy was performed. ¹H-NMR spectrum (Figure 4) was used to obtain information about functional groups and quantify integration areas. On this spectrum, it is therefore also possible to distinguish the percentages of proton types, which can be calculated from the chemical deviation values (Table 7).

The resonances of a proton between chemical shift 0.5 and 1.5 ppm correspond to the presence of 66.66% of aliphatic protons attached to paraffinic CH₃. Peaks in the following region between 1.5 and 3.0 ppm are attributed to the proton of an aromatic ring or acetylenic (24.0%). The region 3.0-4.0 ppm is due to hydroxyls, ring-joining methylene, methine, or methoxy (0.67%). We observed phenols and non-conjugated olefins in the bio-oil, and they resonate

in the range of 4.0–6.0 ppm (4%). Finally, a region between 6.0 and 9.5 corresponds to aromatic protons, aldehyde protons, and also protons in heteroaromatics containing oxygen and nitrogen. The content of this region was 4.67%.

A higher number of aliphatic protons (90%) from date stone are due to the destruction of side chains of date stone compounds in pyrolysis processes. As a result, the bio-oil produced from the date stone can be used as a bio-fuel.

d. Gas chromatography-mass spectrometry

The GC–MS spectrum of bio-oil produced by the pyrolysis of date stone at a temperature of 500 °C, a heating rate of 10 °C·min⁻¹, and a particle size of 1.5 mm is given in Figure 5. As we can see, the



Figure 5. ¹H-NMR spectrum of bio-oil obtained at 500 °C, 10 °C/min, and 1.5 mm.

Table 7. Chemical composition of bio-oil obtained at 500 °C, 10 °C/min, and 1.5 mm from 0	GC-M	48
---	------	----

Chemical shift (ppm)	Type of proton	Area (%)
0.5–1.5	\circ CH_3 γ or farther from aromatic ring and paraffinic CH_3	66.66
	\circ CH ₃ , CH ₂ , and CH β to aromatic ring	
1.5-3.0	• CH ₂ and CH attached to naphthenes	24.00
	\circ CH ₃ , CH ₂ , and CH α to aromatic ring or acetylenic	
3.0-4.0	• Hydroxyls, ring-joining methylene, methine, or methoxy	0.67
4.0-6.0	 Phenols, nonconjugated olefins 	4.00
6.0–9.5	 Aromatics, conjugated olefins 	4.67

bio-oil produced consists of a complex mixture of hundreds of compounds. However, the identification of the main peaks has been made in the first 40 peaks in terms of relative areas. For these identifications, structural formula, chemical name, and GC peak areas of compounds with more than 0.4% of the total area identified in this fraction are listed in Table 8. The volatile fraction of bio-oil is mainly composed of heavy compounds, in particular, fatty acids and their derivatives. They represent almost half of the total area of the detected peaks. Among these compounds are long-chain amides and fatty acid esters. These derivatives of fatty acids are obtained by the hydrolysis of the lipids present in the date stone. Fatty acids are released by the hydrolysis of triglycerides. The fatty acids then react with alcohols by esterification or with amino acids to form amides [42,43].

Other molecules in small quantities such as phenolic derivatives were detected. These compounds are obtained from lignin degradation. A significant diversity of nitrogen compounds is also found in biooil. The structures identified are long-chain amides and also aromatic molecules: pyridine derivatives, pyrazine, pyridinol, indole, and so on. These molecules are assumed to be derived from protein degradation.

As can be seen clearly, the results obtained by GC–MS are highly consistent with those obtained by infrared spectroscopy. This is because all classes of identified chemical compounds are similar to those obtained by infrared spectroscopy. Furthermore, we note that the vast majority of the compounds identified are rich in hydrogen (particularly aliphatic hydrocarbons) in accordance with the results of elemental analysis. In addition, the aliphatic hydrocarbons detected are mainly alkylated fatty acid esters, ethers, and alkenes with a large number of protons, which is consistent with the ¹H-NMR analysis.

No.	Retention time	Compounds	Molecular	Surface (%)
	(min)		formula	
1	7.67	Nonane, 2-methyl-5-propyl	$C_{13}H_{28}$	0.90
2	8.62	Tetradecane	$C_{14}H_{30}$	0.51
3	9.53	Hexadecane	$C_{16}H_{34}$	1.17
4	9.82	Benzyl nonyl maleate	$C_{20}H_{28}O_4$	1.69
5	10.03	2-Cyclopenten-1-one, 3-methyl	C_6H_8O	0.40
6	10.37	2-Furancarboxaldehyde, 5-methyl	$C_6H_6O_2$	1.81
7	10.60	Carbonic acid, ethyl octadecyl ester	$C_{21}H_{42}O_3$	0.88
8	10.78	N,N'-bis(carbobenzyloxy)-lysine methyl(ester)	$C_{23}H_{28}N_2O_6$	0.75
9	10.93	3-Furanmethanol	$C_5H_6O_2$	1.10
10	11.22	Eicosane	$C_{20}H_{24}$	0.80
11	11.42	8-Heptadecene	$C_{17}H_{34}$	3.28
12	11.81	(Z)6-Pentadecen-1-ol	$C_{15}H_{30}O$	0.86
13	12.39	1,2-Cyclopentanedione, 3-methyl	$C_6H_8O_2$	1.38
14	12.70	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	8.28
15	13.08	5,8,11-Heptadecatriynoic acid, methyl ester	$C_{18}H_{24}O_2$	0.57
16	13.38	Decanoic acid, 2-propenyl ester	$C_{13}H_{24}O_2$	1.71
17	13.48	5-Methylcytidine	$C_{10}H_{15}N_3O_5$	1.10
18	13.61	Phosphonic acid, (p-hydroxyphenyl)-	$C_6H_7O_4P$	2.69
19	13.86	Oxiraneoctanoic acid, 3-octyl-, cis	$C_{18}H_{34}O_3$	0.82
20	14.19	Phenol, 4-methyl	C_7H_8O	3.16
21	14.77	5,8-Decadien-2-one, 5,9-dimethyl-, (E)-	$C_{12}H_{20}O$	1.31
22	15.01	Pentadecanoic acid, 13-methyl-, methyl ester	$C_{17}H_{34}O_2$	0.51
23	15.14	Heptaethylene glycol monododecyl ether	$\mathrm{C_{26}H_{54}O_8}$	0.42
24	15.28	n-Decanoic acid	$C_{10}H_{20}O_2$	0.60
25	15.51	Heptaethylene glycol monododecyl ether	$\mathrm{C_{26}H_{54}O_8}$	0.57
26	15.76	Heptaethylene glycol monododecyl ether	$\mathrm{C}_{26}\mathrm{H}_{54}\mathrm{O}_{8}$	1.04
27	16.19	Octadecanoic acid, 2-propenyl ester	$C_{21}H_{40}O_2$	1.13
28	16.46	Cyclododecanol, 1-aminomethyl	$C_{13}H_{27}NO$	1.02
29	16.64	Methyl 11-octadecenoate	$C_{19}H_{36}O_2$	1.04
30	16.78	Dodecanoic acid	$C_{12}H_{24}O_2$	14.55
31	17.16	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	$C_6H_6O_3$	1.31
32	17.53	Octadecanoic acid	$C_{18}H_{36}O_2$	3.47
33	17.81	Octadecanoic acid, 2-propenyl ester	$C_{21}H_{40}O_2$	0.54
34	18.04	cis-Vaccenic acid	$C_{18}H_{34}O_2$	3.11
35	18.31	cis-13-Octadecenoic acid	$C_{18}H_{34}O_2$	15.37
36	18.43	cis-13-Octadecenoic acid	$C_{18}H_{34}O_2$	0.41
37	18.58	Tetradecanoic acid	$C_{14}H_{28}O_2$	11.72
38	18.76	cis-13-Octadecenoic acid	$C_{18}H_{34}O_2$	0.51
39	18.95	cis-13-Octadecenoic acid	$C_{18}H_{34}O_2$	0.42
40	19.83	Ethyl 9,12-hexadecadienoate	$C_{18}H_{32}O_2$	0.84

Table 8. 1 H-NMR analysis results of bio-oil obtained at 500 °C, 10 °C/min, and 1.5 mm

3.3.2. Biochar characterization

a. Physical property and elemental composition

Table 5 presents the elemental composition and calorific value of biochar obtained by the pyrolysis of date stone under optimized experimental conditions. The analysis findings show that the biochar is rich in 69.63%, 3.54%, 0.21%, and 23.98% of carbon, hydrogen, nitrogen, and oxygen contents, respectively.

The obtained results show that the biochar of date stone has a high carbon content and low oxygen and hydrogen contents in comparison to its raw material. The decrease in H and O contents and increase in C content are due to dehydration, decarbonylation, and decarboxylation reactions of biomass. It appears that the pH_{PZC} value of biochar is neutral.

These results show that the biochar obtained has interesting physical and chemical properties, which make it suitable for soil remediation. Moreover, with some functionalization, biochar can be converted into functional materials, finding applications in catalysis, energy storage and conversion, and environmental protection. Biochar production and applications for soil remediation and pollutant removal have been discussed and reviewed extensively [44– 46]. Biochar is also used in metallurgy and as a feedstock for the production of activated carbon, which has many uses. For example, it is used as an adsorbent to remove odorants from airstreams and both organic and inorganic contaminants from wastewater streams.

The properties of the biochar from date stone were evaluated by comparison with other biomass samples reported in the literature (Table 5) [37–39]. The date stone stood out among the other biomass samples when the published HHV values were compared as it had an HHV value higher than 23 MJ/kg. The biochar has an HHV comparable to biomass samples because of its lower proportion of H and O than C. This considerably increases the energy value of the fuel as more energy is present in C–C bonds than in C–O and C–H bonds.

b. Characterization of surface functional groups

The functionality of biochar is evaluated by characterization with Boehm titration and FTIR methods. The Boehm titration method is applied to determine the acidic and basic sites in the biochar. The results show that the biochar produced at 500 °C, 10 °C/min, and 1.5 mm has 1.423 meq·g⁻¹ of acidic groups and 0.334 meq·g⁻¹ of basic groups. These results indicated that the biochar obtained has an acidic character.

These results are confirmed by infrared spectroscopy. As can be seen from the FTIR spectra of biochar (Figure 1), remarkable changes are present compared to that of the raw material, which indicates an effective conversion of date stone under optimal pyrolysis conditions. The hydroxyl group band O-H at 3100–3600 cm^{-1} in the FTIR spectra of the biochar sharply decreases after pyrolysis, probably due to the dehydration of the date stone with the release of an amount of water. The bands observed at 2860–2970 cm⁻¹, which can be attributed to C-H alkyl functional groups, are almost absent in the biochar. The bands occurring on the spectrum at 875 cm⁻¹ and 1400 cm⁻¹ are attributed to the vibrations of the C=C and C=O bonds in the aromatic rings. The high intensity of the C=O band in the biochar and the decrease in carboxylic groups. as previously observed from Boehm titrations, suggest the presence of a higher amount of ketone compared to the raw material. A wide band at 900-1200 cm⁻¹ shows the presence of aromatic functional groups C-O and phenolic groups O-H. Between 700 and 900 cm⁻¹, another band is observed. This band is attributed to aromatic C-H stretching vibrations, which indicate the presence of an adjacent aromatic hydrogen in the biochar [47].

c. Scanning electron microscopy

The morphology of the biochar obtained by SEM is shown in Figure 6. From this micrograph, it can be seen that the morphology of the biochar shows the presence of empty spaces and greater porosity on its surface compared to that of the raw material. This confirms that the biochar produced has a larger surface area than the raw date stone. This behaviour is attributed to the fact that the heat treatment improves the porous structure of the biochar due to the loss of mass of some of the volatile matter from the date stone.

d. Iodine number and methylene blue index

The iodine number (I_2) and MBI are widely used parameters for biochar testing due to their simplicity and their rapid assessment of adsorbent quality. The values obtained are 100.83 mg/g and



Figure 6. SEM micrograph of the date stone (A) and its biochar (B).

51.28 mg/g for the iodine number (I_2) and MBI, respectively. These values indicate that the surface of the biochar has a low porosity, which may be less significant for adsorption or catalysis. Therefore, it is recommended to activate the surface of biochar to improve its porosity. This result is verified by the calculation of the surface area specific to biochar, which is of the order of 8.083 m²·g⁻¹.

4. Conclusion

In sum, this work is devoted to the valorization of the date stone by converting it to bio-oil and biochar by pyrolysis using a fixed-bed reactor. All the experimental results obtained show that the best yields of bio-oil, biochar, and bio-gas are approximately $36.64 \pm 2.03\%$, $16.12 \pm 0.98\%$, and $47.24 \pm 3.21\%$, respectively, at a pyrolysis temperature of 500 °C, a heating rate of 10 °C/min, and a particle size of 1.5 mm. However, the characterization of the liquid phase shows that the bio-oil produced under these optimal conditions consists mainly of aliphatic hydrocarbon in the form of alkylated fatty acids and their derivatives. This preliminary study shows that the bio-oil can be used as a bio-fuel or as a source of value-added chemicals. In addition, the biochar has good properties suitable for its use as a solid fuel and as a carbon source for the production of activated carbon.

References

[1] A. Demirbas, Prog. Energy Combust. Sci., 2005, 31, 171-192.

- [2] İ. Demiral, S. Şensöz, Energy Sources A, 2006, 28, 1149-1158.
- [3] M. Francavilla, P. Manara, P. Kamaterou, M. Monteleone, A. Zabaniotou, *Bioresour. Technol.*, 2015, 184, 305-313.
- [4] J. Mabrouki, K. Guedri, M. A. Abbassi, A. Omri, M. Jeguirim, C. R. Chim., 2016, 19, 466-474.
- [5] A. E. Pütün, B. B. Uzun, E. Apaydin, E. Pütün, *Fuel Process. Technol.*, 2005, 87, 25-32.
- [6] N. Q. Bui, P. Fongarland, F. Rataboul, C. Dartiguelongue, N. Charon, C. Vallee, N. Essayem, C. R. Chim., 2018, 21, 555-562.
- [7] K. Frikha, L. Limousy, J. Bouaziz, S. Bennici, K. Chaari, M. Jeguirim, C. R. Chim., 2019, 22, 206-219.
- [8] C. Sambusiti, A. Licari, A. Solhy, A. Aboulkas, T. Cacciaguerra, A. Barakat, *Bioresour. Technol.*, 2015, 181, 200-206.
- [9] A. Bouaziz, A. Hammani, M. Kuper, *Cahiers Agric.*, 2018, 27, 14001-14005.
- [10] M. W. Azeem, M. A. Hanif, J. N. Al-Sabahi, A. A. Khan, S. Naz, A. Ijaz, *Renew. Energy*, 2016, **86**, 124-132.
- [11] F. Jamil, H. Ala'a, L. Al-Haj, M. A. Al-Hinai, P. Hellier, U. Rashid, Energy Convers. Manage., 2016, 117, 264-272.
- [12] M. A. Amani, M. S. Davoudi, K. Tahvildari, S. M. Nabavi, M. S. Davoudi, *Ind. Crops Prod.*, 2013, **43**, 40-43.
- [13] A. B. Fadhil, M. A. Alhayali, L. I. Saeed, Fuel, 2017, 210, 165-176.
- [14] S. Ceylan, Waste Manage. Res., 2015, 33, 345-352.
- [15] H. H. Sait, A. Hussain, A. A. Salema, F. N. Ani, *Bioresour. Technol.*, 2012, **118**, 382-389.
- [16] M. Jeguirim, S. Dorge, G. Trouvé, R. Said, *Energy*, 2012, 44, 702-709.
- [17] M. G. Grønli, G. Várhegyi, C. Di Blasi, Ind. Eng. Chem. Res., 2002, 41, 4201-4208.
- [18] L. Wilson, W. Yang, W. Blasiak, G. R. John, C. F. Mhilu, *Energy Convers. Manage.*, 2011, **52**, 191-198.
- [19] M. Jeguirim, S. Dorge, G. Trouvé, *Bioresour. Technol.*, 2010, 101, 788-793.
- [20] M. Jeguirim, G. Trouvé, *Bioresour. Technol.*, 2009, 100, 4026-4031.

H. Hammani et al.

- [21] Z. Liu, E-S. Zhang, Energy Convers. Manage., 2008, 49, 3498-3504.
- [22] P. Sun, M. Heng, S.-H. Sun, J. Chen, Energy Convers. Manage., 2011, 52, 924-933.
- [23] H.-M. Liu, X.-A. Xie, M.-F. Li, R.-C. Sun, J. Anal. Appl. Pyrolysis., 2012, 94, 177-183.
- [24] A. Bacaoui, A. Dahbi, A. Yaacoubi, C. Bennouna, F. Maldonado-Hódar, J. Rivera-Utrilla, F. Carrasco-Marín, C. Moreno-Castilla, *Environ. Sci. Technol.*, 2002, **36**, 3844-3849.
- [25] A. Bacaoui, A. Yaacoubi, A. Dahbi, C. Bennouna, J. Ayele, M. Mazet, *Environ. Technol.*, 1998, **19**, 1203-1212.
- [26] T. V. Tran, D. T. C. Nguyen, H. T. N. Le, H. L. Ho, T. T. Nguyen, V.-D. Doan, T. D. Nguyen, L. G. Bach, C. R. Chim., 2019, 22, 794-803.
- [27] S. Akbari, N. H. Abdurahman, R. M. Yunus, C. R. Chim., 2019, 22, 714-727.
- [28] M. Azizkhani, H. Faghihian, C. R. Chim., 2019, 22, 562-573.
- [29] Y. Song, A. Tahmasebi, J. Yu, Bioresour. Technol., 2014, 174, 204-211.
- [30] A. Aboulkas, H. Hammani, M. El Achaby, E. Bilal, A. Barakat, *Bioresour. Technol.*, 2017, 243, 400-408.
- [31] D. Pradhan, R. K. Singh, H. Bendu, R. Mund, *Energy Convers. Manage.*, 2016, **108**, 529-538.
- [32] M. Kılıç, A. E. Pütün, B. B. Uzun, E. Pütün, Energy Convers. Manage, 2014, 78, 461-467.
- [33] A. Aboulkas, T. Makayssi, L. Bilali, M. Nadifiyine, M. Benchanaa, *Fuel Process. Technol.*, 2012, 96, 209-213.

- [34] S. Zhang, Y. Yan, T. Li, Z. Ren, *Bioresour. Technol.*, 2005, 96, 545-550.
- [35] B. B. Uzun, N. Sarioğlu, Fuel Process. Technol., 2009, 90, 705-716.
- [36] X. Wang, S. R. Kersten, W. Prins, W. P. van Swaaij, Ind. Eng. Chem. Res., 2005, 44, 8786-8795.
- [37] I. Demiral, E. A. Ayan, Bioresour. Technol., 2011, 102, 3946-3951.
- [38] M. Bertero, H. A. Gorostegui, C. J. Orrabalis, C. A. Guzmán, E. L. Calandri, U. Sedran, *Fuel*, 2014, **116**, 409-414.
- [39] T. Aysu, M. M. Küçük, *Energy*, 2014, **64**, 1002-1025.
- [40] D. Zhou, L. Zhang, S. Zhang, H. Fu, J. Chen, *Energy Fuels*, 2010, 24, 4054-4061.
- [41] S. Şensöz, M. Can, Energy Sources, 2002, 24, 357-364.
- [42] P. Das, T. Sreelatha, A. Ganesh, *Biomass Bioenergy*, 2004, 27, 265-275.
- [43] S. Chiaberge, I. Leonardis, T. Fiorani, G. Bianchi, P. Cesti, A. Bosetti, M. Crucianelli, S. Reale, F. De Angelis, *Energy Fu*els, 2013, 27, 5287-5297.
- [44] K. Qian, A. Kumar, H. Zhang, D. Bellmer, R. Huhnke, *Renew-able Sustainable Energy Rev.*, 2015, 42, 1055-1064.
- [45] S. Meyer, B. Glaser, P. Quicker, Environ. Sci. Technol., 2011, 45, 9473-9483.
- [46] S. P. Sohi, E. Krull, E. Lopez-Capel, R. Bol, Adv. Agronomy, 2010, 105, 47-82.
- [47] P. Fu, S. Hu, L. Sun, J. Xiang, T. Yang, A. Zhang, J. Zhang, Bioresour. Technol., 2009, 100, 4877-4883.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Hydrothermal carbonization as a preliminary step to pine cone pyrolysis for bioenergy production

La carbonisation hydrothermale comme préalable étape à la pyrolyse traditionnelle. Changements globaux sur le chemin du processus et les charbons obtenus

Mouzaina Boutaieb^{*, a}, Monia Guiza^a, Silvia Román^b, Beatriz Ledesma Cano^b, Sergio Nogales^c and Abdelmottaleb Ouederni^a

^{*a*} Laboratory of Process Engineering and Industrial Systems (LR11ES54), National School of Engineering, University of Gabes, Medenine Street 6029, Tunisia

^b Applied Physics Department, Industrial Engineering School, University of Extremadura, Avda. Elvas, s/n, 06006, Badajoz, Spain

^c Chemical Engineering and Physical Chemistry Department, Faculty of Sciences, University of Extremadura, Avda. Elvas, s/n, 06006, Badajoz, Spain

E-mails: mouzainaboutaieb@gmail.com (M. Boutaieb), monia.guiza@enig.rnu.tn (M. Guiza), sroman@unex.es (S. Román), beatrizlc@unex.es (B. Ledesma Cano), senogalesd@unex.es (S. Nogales), mottaleb.ouederni@enig.rnu.tn (A. Ouederni)

Abstract. The main objective of this work was to elucidate the benefits associated with including hydrothermal carbonization (HTC) as the previous step to traditional fast pyrolysis of Tunisian pine cone (PC). The pyrolysis was performed in a fixed-bed reactor, while the HTC was carried out in an autoclave plus the subsequent carbonization step in the former reactor. The comparison of the two methods was based on the fraction yields, the molar composition of gas, the chemical composition, the surface characteristics, and the higher heating value.

The pyrolysis of PC hydrochars (600 °C) was carried out using hydrochars prepared at various HTC temperatures (180–240 °C) and times (30, 60, and 180 min). Results showed that increasing the HTC temperature from 180 °C to 240 °C led to a decrease in the solid yield and an increase in the gas yield while increasing the HTC time led to a decrease in both solid and gas yields. The optimum HTC conditions (240 °C and 60 min) yielded a carbon content and a higher heating value of 92.5% and 34.28 MJ·kg⁻¹, respectively, producing a material that might be utilized as a category-A briquette for domestic use. Under these conditions, the gas production was also maximum.

^{*} Corresponding author.

Keywords. Hydrothermal carbonization, Pyrolysis, Hydrochars, Bioenergy, Biochars, Optimisation, High-added value.

1. Introduction

Many investigations into the development of alternative resources and renewable energy are aimed at addressing the growing demand for energy as well as the continuing rise in energy prices and the persistent shortage of hydrocarbon resources [1]. Switching to a scenario with a greater share of renewable energies involves the use of biomass since this resource is certainly effective in providing energy in diverse forms such as heat, electricity, fuel for transportation, and so on depending on the thermochemical process used. Furthermore, zero carbon dioxide emissions associated with biomass and its availability in many areas of the world can be cited as an additional advantage.

A variety of thermochemical or biological processes can be used to convert biomass in the absence of oxygen to products with higher degrees of carbon content than the original biomass.

Traditional pyrolysis processes have been largely used to convert biomass in the absence of oxygen to products with a higher proportion of carbon content than in the original biomass. Recently, hydrothermal carbonization (HTC), also known as wet pyrolysis or autohydrolysis or wet torrefaction [2], has attracted much attention as a sustainable, eco-friendly, and costless thermochemical process to convert organic biomass, in the presence of water, into bio-oil and a carbon-rich solid product (called hydrochar [HC]) [3] and, unlike traditional pyrolysis, to recover nutrients from biomass [4]. The HTC temperature is much lower, ranging from 180 °C to 300 °C compared to the pyrolysis temperature (between 500 °C and 900 °C) [5]. As a result of the hermeticism of the system and the presence of liquid water under these conditions, autogenous pressures in the range 2-6 MPa are associated with HTC [6]. Besides, a variety of dwell times have been reported from several minutes to hours [7] although most of the reaction seems to occur within the first 20 min [8]. The distributions of the final products as well as its properties are strongly influenced by the reaction temperature of hydrothermal conversion processes [9,10].

During biomass pyrolysis, the organic matter is thermochemically decomposed by heating in the absence of oxygen. Differently, during HTC processes, the biomass is submerged in subcritical liquid water and transformed into an HC; so prior costly drying of high-moisture biomass is not an issue [11], making the HTC process cheaper and more environmentfriendly as compared to the traditional pyrolysis process [12]. As a result of HTC, the biomass structure is broken down, and an energy-rich carbonaceous HC is obtained, with a high calorific value, suitable as a renewable solid fuel or for value-added material applications [13–15].

Waste materials such as lignocellulosic biomass [16–18], algae [19], and food waste [20,21] have been commonly used as starting materials for energy and resource recovery by HTC. In addition, HTC has recently attracted considerable interest from the research field, but only few authors have analyzed the HTC as a pretreatment stage and used HCs as a precursors for the traditional pyrolysis.

Aleppo pine (*Pinus halepensis*) forests cover a high area along North Africa and the Mediterranean basin. According to Ayari [22], pine forests cover more than 3.5 million ha with the highest surface area (2.5 million ha in the Mediterranean region). In Tunisia, the Aleppo pine forest is the most important woodland in the country; it extends from its subhumid zone in the north to the arid zone in the south [23]. Forests cover 1.1 million ha, where about 300 000 ha of Aleppo pine is found [24]. In fact, more than 10% of the Tunisian population live within the forest area, where they earn a good part of their resources [25].

The multiple functions and products extracted from Aleppo pine forests make this tree species one of the most appreciated ones in the Mediterranean basin. In Tunisia, their uses are related to different types of industries: seed (zgougou/food) and wood production, tannins (skin industry), soil protection, biodiversity, programs for reforestation of degraded areas, and as an anti-erosion species. Among these applications, pine seed production is an economically important food subsector in Tunisia.

Pine cones (PCs) are one of the most important products of Aleppo pine trees; these are mainly used in decoration applications. According to Ayari *et al.* [22], an average tree produces about $51 \pm (7)$ cones per tree weighing a total of 921.6 \pm (151.2) g/tree. After being emptied of seeds for food, the PCs are also

used for decoration handcrafts.

Recently, a variety of thermochemical or biological treatments of PCs have been investigated in several studies such as pyrolysis [26,27] and combustion [28], but they have been barely investigated during the HTC process. The high degree of heterogeneity and complexity of the PC structure makes its use as a raw material a tough challenge for HTC treatment.

The previous research of Boutaieb *et al.* [27], on the effect of the pyrolysis temperature on biochar characteristics and gas production, showed that under optimum conditions (at 600 °C for 30 min using 100 mL·min⁻¹ of nitrogen flow rate) a high heating value (HHV) as high as 30.95 MJ·kg⁻¹ was obtained, allowing its possible use as a briquette biofuel.

To the best of our knowledge, the HTC of PCs has been scarcely studied, and in particular, the influence of experimental conditions (temperature and residence time) on the process have not been analyzed so far. Moreover, the pyrolysis of HCs produced from PCs has not been reported in the literature.

The main objective of the present work is to provide deep insight into the HTC of PC, and to compare it to fast pyrolysis, as well as to evaluate the synergies of combining both processes. The fast pyrolysis was performed in a fixed-bed reactor and HTC was performed in an autoclave, while two-step reactions combined both processes. The comparison of the two treatments was based on the fraction yields, the molar composition of gases, the chemical composition, the surface characteristics, and the thermal stability.

2. Experimental procedure

2.1. Materials

Mature PCs (*P halepensis*) were collected from southern Tunisia and then brushed to remove all seeds and soil particles. After the separation of the cone scales from the axis, the scales were sieved to obtain samples with particle size diameters ranging from 1.25 to 1.6 mm. The samples were then stored in sealed ziplock bags for further processing.

The PCs were investigated in terms of proximate and elemental analyses following suitable technical specifications as reported in Section 2.3. Their HHV was determined using a bomb calorimeter (Parr). These results are collected in Table 1.

2.2. Preparation of pyrochar

2.2.1. Pyrolysis process

Pyrolysis was carried out in a fixed-bed vertical cylindrical stainless steel reactor equipped with a heating system (electronic furnace). The experimental setup was described in detail in our previous work [27]. At each run, 15 g of PC was filled in the basket, which was then placed inside the preheated electronic furnace. All experiments were carried out isothermally in a fast pyrolysis regime at 600 °C, based on a previous optimization study [27].

Each experiment was carried out at least twice, and the values reported in this study correspond to their average.

2.2.2. Hydrothermal carbonization process

The HTC assays were performed in a 0.25 L stainless steel autoclave (Berghof Digestec DAB-3, Germany) as shown in Figure 1. In a 0.2 L Teflon vessel (unstirred), an appropriate amount of the sample (15 g) and 0.120 L of deionized water at room temperature were added to obtain the targeted biomass/water ratio R (1:8) at the same time that the biomass was completely submerged in water. Then, the Teflon vessel was sealed and placed into the autoclave, and the system remained overnight at room temperature. Thereafter, the system was heated in a preheated electric furnace at the required temperatures (180, 200, 220, and 240 °C). Based on previous research, the authors determined the time it took for the reactor to reach the target temperature using a simulation model. The heating period was considered for each temperature, and then 30 min (proper processing time) was added. After the reaction, the heater was turned off. The autoclave was removed from the oven and subsequently placed in a coldwater bath and allowed to cool down to room temperature (for about 15 min). After cooling, the resulting solid was separated from the liquid by filtration, washed with abundant distilled water until the filtrate was clean, and subsequently dried at 105 °C overnight to remove residual moisture. The resulting liquid was collected and stored in a glass beaker at 4 °C in a freezer. The dried HC was stored in a ziplock



Figure 1. HTC Teflon vessel and stainless steel autoclave.

Table 1. Proximate and elemental analyses (wt%) and HHV (MJ·kg⁻¹) of raw scales and Spanish PC [28]

Precursor	Proximate analysis (wt%)					Elemental composition (wt%)			
	Moisture	Volatile matter	Fixed carbon	Ash	С	Ν	Η	0*	
Raw-Sc	10	79.2	10.2	0.6	50.5	0.29	5.86	43.35	18.0563
Spanish PC [28]	8.9	-	-	0.8	54.2	0.3	6.8	38.7	18.782

* The sulfur content in the hydrochars was not measured due to its negligible content in the raw biomass (<0.01 wt%).

* Balanced (O% = 100 - (%C + %N + %H)).

bag until the start of the analysis and pyrolysis process.

The effectiveness of HTC as a pyrolysis pretreatment was then tested. For this task, HC samples were pyrolyzed in the same reactor used for the previously described pyrolysis process [27] at 600 °C for 30 min under nitrogen atmosphere. The biochar derived from the pyrolysis of HCs is referred to as pyrochar (PYC), and the solid yield values were determined as follows.

 HC_y (wt%) is the solid yield of HTC processes and is calculated by (1), where m_{HC} (g) is the mass of HC and m_i (g) is the mass of the initial feedstock (15 g of raw scales):

$$HC_y = \frac{m_{\rm HC}}{m_i} * 100. \tag{1}$$

 PYC_y (wt%) is the total solid yield (PYC) corresponding to the pyrolysis of HC and is calculated by (2):

$$PYC_y = \frac{m_{PYC}}{m_i} * 100, \qquad (2)$$

where m_{PYC} (g) is the final mass of the product PYC.

2.3. Solid characterization

2.3.1. Elemental analysis

Elemental analyses were carried out using a LECO CHNS (EA 1108) elemental analyzer to quantify the carbon (C), hydrogen (H), and nitrogen (N) contents of raw PC scales (Raw-Sc), biochars, HCs, and PYCs, following the corresponding technical specification CEN/TS 15104 [29]. Specification CEN/TS 15289 [30] was used to determine sulfur (S) content. Oxygen (O) content was determined by difference using expression (3):

$$O\% = 100\% - (\%C + \%N + \%H + \%S).$$
(3)

2.3.2. Textural characterization

Nitrogen adsorption isotherms at 77 K were performed by AUTOSORB equipment (Quantachrome). Before analyses, the selected samples were outgassed at 250 °C for 12 h. Characteristic parameters such as the apparent Brunauer–Emmet–Teller (BET) surface S_{BET} (m²·g⁻¹), the micropore volume V_{mi} (cm³·g⁻¹), and the external surface S_{EXT} (m²·g⁻¹) were estimated using the BET theory, the Dubinin– Radushkevich method, and the α -method, respectively.

2.3.3. Thermogravimetric analysis

The thermogravimetric behavior under inert atmosphere was analyzed by a thermobalance (TGA/DTG) (STA 449 F3 Jupiter–Netzsch) coupled with mass spectrometry (QMS 403D Aëolos III—Netzsch) using a flow rate of 100 mL·min⁻¹ of argon and a heating rate of 20 °C·min⁻¹ from 30 °C to 800 °C.

2.3.4. Surface chemistry

The surface chemistry of selected samples was studied by means of Fourier transform infrared (FT-IR) spectroscopy. The FT-IR spectra were recorded by a PerkinElmer model (PerkinElmer, 1000 PC), and bands were assigned according to suitable results from the literature [8,12,27].

2.3.5. Surface morphology analysis

Surface morphology studies were carried out by scanning electron microscopy (SEM, Quanta 3D FEG, FEI). The samples were prepared by depositing about 50 mg of the sample on an aluminum stud covered with conductive adhesive carbon tape and then coated with Rh–Pd for 1 min to prevent charging during observations. Imaging was carried out under high-vacuum conditions ($<6 \times 10^{-4}$ Pa) at an accelerating voltage of 30 kV by using secondary electrons for high vacuum (ETD).

3. Results

3.1. Precursors

Table 1 presents the proximate and elemental composition (wt%) of the Raw-Sc as well as their HHVs $(MJ \cdot kg^{-1})$.

The results obtained here are similar to data presented by other authors [28] for Spanish PCs. As seen in Table 1, PC has a high amount of volatile matter content, greater than 79%, and a low moisture content <15%. This result is as expected for lignocellulosic materials [31] and most of the agricultural and forest wastes [32].

The elemental analysis showed that the raw material was mainly composed of carbon (>50%) and oxygen (>40%) with a low percentage of nitrogen (<0.29%) and a negligible amount of sulfur (<0.01%). From an environmental point of view, a low N content (<1%) is advantageous for minimizing toxic NO_x emissions during combustion processes [33]. Besides, a low content of S is also important to prevent the formation of SO₂ [32] and hence the corrosion of equipment [33].

3.2. Fraction yield and gas production

The influence of different process conditions on both Raw-Sc and HCs prepared at different temperature and residence time conditions is observed from the results in Table 2. It is noted that both variables influence the value of yields significantly.

First, compared to pyrolysis, HTC produces higher solid yields, fewer liquid yields, and a smaller quantity of gases. The HTC of raw feedstock under mild conditions is associated with a solid yield of 84.07%; the solid yield from pyrolysis is 27.07%. It may also be inferred that the liquid yields follow an inverse trend as compared to the solid yields—41.47% of liquid produced from raw feedstock pyrolysis as compared to 27.87% produced from HTC. This result is consistent with a more pronounced thermal decomposition of the feedstock during pyrolysis [34].

On the other hand, from Table 2, it can be observed that the reaction temperature has a major effect on the HTC process. The HC yields decrease as the reaction temperature increases from 84.07% at 180 °C to 76.13% at 240 °C. According to Lucian *et al.* [34], this decline in HC yield with temperature is due to the enhancement of a series of dehydration and decarboxylation reactions, which at higher temperatures become more effective and lead to an increase in the gaseous phase with a decrease in solid yield.

Moreover, it can be seen that different residence times have the same effect as the reaction temperature. They decrease with increase in residence time, from 76.13% for 30 min to 62.2% for 180 min (at the

Samples	HTC	HTC	Pyrolysis	SY	LY	GY
	T (°C)	t (min)	<i>T</i> (°C)	(wt%)	(wt%)	(wt%)
HC-180-30	180	30	-	84.07	15.17	0.76
HC-200-30	200	30	-	80.13	9.87	10.00
HC-220-30	220	30	-	80.47	7.93	11.6
HC-240-30	240	30	-	76.13	11.00	12.87
HC-240-60	240	60	-	66.47	24.06	9.47
HC-240-180	240	180	-	62.20	27.87	9.93
PY-600	-	-	600	27.07	41.47	31.46
PYC-180-30-600	180	30	600	23.93	43.58	32.49
PYC-200-30-600	200	30	600	23.53	43.34	33.13
PYC-220-30-600	220	30	600	22.00	43.20	34.80
PYC-240-30-600	240	30	600	21.67	42.39	35.94
PYC-240-60-600	240	60	600	20.47	50.8	28.73
PYC-240-180-600	240	180	600	20.20	57.87	21.93

Table 2. Fraction yield of derived chars at different conditions

HC = hydrochar; PYC = pyrochar; PY = biochar.

SY = solid yield; LY = liquid yield; GY = gas yield.

same temperature 240 °C). A larger amount of HCs was obtained at shorter residence times.

This decrease in HC yields at longer reaction times could be explained in terms of the formation of permanent gases and lighter organic compounds by prolonging the carbonization time [35].

As shown also in Table 2, the pyrochar yields tend to decrease from 23.93% to 21.67% with rising HTC temperature, while the gas yield increases from 32.49% to 35.94%. However, an increase in the HTC time leads to a decrease in the pyrochar yield from 21.67% to 20.2% and a decrease in the gas yield from 35.94% to 21.93%. In addition, an increase in HTC temperature has a negative effect on the formation of liquid yield due to a more pronounced thermal decomposition of the raw biomass and the liquid product at a high amount of gas and solid yields.

The effect of the temperature process on pyrochar production can be explained in terms of the decrease in volatile matter during HTC, which leads to the increase in carbon content after HTC and then after pyrolysis [36]. These results are in agreement with the results of thermogravimetric analysis in Section 3.3.

This decline in pyrochar yield and the increase in gas yield with rising HTC temperature or time are due to the previous decrease in volatile components [32].

Figure 2 shows the molar accumulation of gases with time. In general, at the beginning of the pyrolysis process, there is a negligible increase in the production of all gases followed by a significant gas release during the first 15 min at the maximum decomposition rate. However, after 20 min, cumulative molar gas is produced at a relatively slower rate until the end of the process to the end of the pyrolysis reaction.

The composition of gas was mainly CO₂, CH₄, which are the dominant components, H₂, and a small fraction of CO. Figure 2 indicates that the production of gases is affected by the reaction time and the temperature. The more severe the reaction conditions, the greater the maximum gas yield. The figure also highlights the fact that under severe conditions, HTC maximizes gas production almost twice as that compared to conventional pyrolysis. A larger amount of gases was obtained at a higher HTC temperature 240 °C and pyrolysis temperature 600 °C for 60 min (0.86 mol·kg⁻¹ of H₂, 0.58 mol·kg⁻¹ of CO₂ with higher LHV = 562.46 kJ·L⁻¹).

As shown in Figure 3, the CO and CO₂ yields were reduced with increase in time and temperature. This



Figure 2. Effect of process conditions on gas molar cumulative.

could be related to the decomposition of the hemicellulose with rise in temperature since CO_2 (and CO) was mainly produced as a consequence of the rearrangement of cellulose and hemicellulose during the early stages of thermal degradation [37].

These results were confirmed later from the thermogravimetric behavior of the chars.

In contrast to the release of CO and CO_2 , H_2 emission increases with increase in process parameters. This rise can be related to secondary reactions in the liquid phase, which is greater in amount [38].

3.3. Thermogravimetric behavior of different chars

An analysis of the thermal behavior of chars was carried out from the thermogravimetric and dTG curves that are plotted in Figure 3.

The Raw-Sc showed three mass-loss peaks in pyrolysis. The first phase, ranging from 58.65 °C to 163.29 °C, corresponds to dehydration reaction and a release of volatile products. The second massloss peak (79.2%), between 160 °C and 400 °C, cor-



Figure 3. Thermogravimetric analysis of raw material and different chars.

responds to the degradation of hemicellulose and cellulose. A small shoulder peak was observed in the dTG profile at approximately 290 °C due to the decomposition of hemicellulose. Finally, the third phase begins at a temperature of 400 °C, and it can be associated with the degradation of lignin [39].

In contrast, the chars exhibited only two peaks. The second mass loss and the small shoulder peak in dTG at 290 °C disappeared, which indicates the decomposition of hemicellulose in both processes. These results are in agreement with the trends found by other authors for the HTC process [16,40].

Moreover, the initial decomposition temperature of both pyrochars and HCs was higher than that of biochars and raw scales, respectively, which could be related to the reduction in volatile matter during the HTC step [35].

An interesting observation is that the rise in pyrolysis and HTC temperatures resulted in a slight shift of the loss peak to a higher temperature (up to 700 °C), which explains the thermally stable structures in chars (pyrochars). In turn, this means a significant advantage in terms of subsequent combustion applications. Correa *et al.* [40] and Wang *et al.* [41] related the presence of inorganic content in the HC to changes in the mass-loss velocity as a consequence of inhibition of particular decomposition reactions.

This can promote the HTC step, which therefore results in the stability of the char when used as a combustible.

3.4. Elemental and proximate analyses

The process temperature and reaction time are the main factors influencing the char composition. Table 3 presents the elemental composition of chars from pyrolysis, HTC, and HTC–pyrolysis as well as their HHV values:

$$\frac{H}{C} = 1.4265 \frac{O}{C} + 0.5845.$$
(4)
As compared to the HCs, the pyrochars and the biochars showed higher carbon and nitrogen contents and lower hydrogen and oxygen contents. In general, carbon content is higher than 85%, nitrogen content is lower than 1%, hydrogen content is up to 3%, and the oxygen content is close to 9%.

In addition, the carbon content of the pyrochar treated under different HTC process conditions and pyrolyzed at 600 °C (\approx <92%) decreased by about 4% compared to the corresponding biochar (91.4%).

The higher the HTC temperature (240 °C) and residence time (180 min), the higher the carbon (66.6%) and nitrogen (0.47%) contents and the lower the oxygen (27.18%) and hydrogen (5.75%) contents of the HCs produced. By comparison with the biochars produced from the raw material, it could be concluded that the HTC step improves the elemental content of the pyrochars except for carbon content.

The carbon enrichment was explained by Zhang *et al.* [42], who related it to a greater degree of aromatization and condensation during the HTC and the reduction in the H and O contents to dehydration and decarboxylation reactions. In addition, Chen *et al.* [43] related this drop in H and O contents to the cracking and decomposition of biomass, which was coupled with gas emission. The fact that most of the carbon in the biomass is retained in HC suggests that the HTC is beneficial to the enrichment of the pyrochar carbon content compared with that of the conventional pyrolysis process. This is one of the strengths of this work.

Using the elemental composition data (Table 3), the H/C and O/C atomic ratios were calculated and then plotted in Figure 4 (Van Krevelen diagram). From this diagram, it can be clearly found that both H/C and O/C atomic ratios of the HCs closely resemble the initial raw material and biomass unlike pyrochars and biochars, which both exhibit lower H/C and O/C atomic ratios similar to those of natural coal. These results could be explained by the higher rate evolution of H_2O and CO_2 in the dehydration and decarboxylation reactions during HTC and then in pyrolysis [15].

As illustrated in Figure 5, where the correlation between H/C and O/C atomic ratios of the HCs is given, it can be clearly observed that the HC points lie almost on a straight line ($R^2 = 0.9951$), with a slope close to 1.4, showing that 1.4 atoms of H are lost for each atom of O. In addition, the straight line corre-



Figure 4. Van Krevelen diagram of different chars produced at different conditions.



Figure 5. Correlation between H/C and O/C atomic ratios of hydrochar samples.

sponds to dehydration reactions. Therefore, it can be concluded that decarboxylation and dehydration reactions are dominant in the PC HTC under different experimental conditions.

Energy production is a crucial element in determining the feasibility of a biomass conversion process. For this reason, the comparison of the HHVs of solid products from both processes is necessary. Both processes convert PC to a coal-like material that has potential for energy production. The HHVs of the HCs are in the range from 20.3 to 24.72 MJ·kg⁻¹, while 30.63 MJ·kg⁻¹ is reported for pyrolysis. Moreover, similar measurements for the combined process (pyrolysis with HTC) produced values up to 34.28 MJ·kg⁻¹.

From these results, it can be observed that HTC increases the HHV of pyrochars compared to that of biochars. Furthermore, there is an optimum temperature for which the HHV of char is maximum. This occurs at the highest HTC temperature and

Samples	HTC	HTC	Pyrolysis	C (%)	N (%)	H (%)	O (%)	H/C	0/C	HHV
	T (°C)	t (min)	<i>T</i> (°C)							
Raw-Sc	-	-	-	50.5	0.29	5.86	43.35	1.38	0.64	18.06
HC-180-30	180	30	-	-*	_*	_*	_*	_*	-*	20.30
HC-200-30	200	30	-	53.7	0.27	6.19	39.84	1.37	0.56	21.79
HC-220-30	220	30	-	55.2	0.35	6.20	38.25	1.34	0.52	20.89
HC-240-30	240	30	-	56.2	0.33	6.14	37.33	1.30	0.50	20.99
HC-240-60	240	60	-	58.1	0.33	6.02	35.33	1.23	0.46	22.54
HC-240-180	240	180	-	66.6	0.47	5.75	27.18	1.03	0.31	24.72
Pyro-600	-	-	600	91.4	0.88	2.65	5.07	0.35	0.04	30.63
PYC-180-30-600	180	30	600	90.7	1.01	2.64	5.65	0.35	0.05	29.77
PYC-200-30-600	200	30	600	86.0	0.85	2.74	10.41	0.38	0.091	31.99
PYC-220-30-600	220	30	600	91.4	0.96	2.80	4.84	0.36	0.040	31.85
PYC-240-30-600	240	30	600	87.0	0.99	2.71	9.30	0.37	0.080	32.81
PYC-240-60-600	240	60	600	92.5	0.98	2.81	3.71	0.36	0.030	34.28
PYC-240-180-600	240	180	600	87.1	0.89	2.84	9.17	0.39	0.080	34.17

Table 3. Elemental composition and higher heating value of different chars

time (240 °C for 60 min) and pyrolysis temperature (600 °C).

In addition, the HHV of the final chars $(34.28 \text{ MJ}\cdot\text{kg}^{-1})$ is equivalent to the HHV of anthracite, indicating that the chars derived from hydrothermally treated PC have the potential to be used as solid fuels for combustion applications [33]. According to French standards [44], this pyrochar, with an HHV of 34.28 MJ·kg⁻¹ and high fixed carbon content of 92.5% (>70%) could be utilized as a category-A briquette for domestic use. Thus, it is important to keep in mind that complex reaction mechanisms are involved in the calorific nature of the process reactions and highly dependent on reaction conditions. In fact, although the overall reaction is exothermic, the initial phases of both pyrolysis and HTC are endothermic.

3.5. Characterizing pore structure of chars

The N₂ adsorption isotherms of selected chars (biochars prepared at 600 °C, HCs [HC-200-180, HC-240-180, and HC-240-30], and pyrochars [PYC-200-180-600, PYC-240-180-600, and PYC-240-30-600]) are plotted in Figure 6. The N₂-BET surface area of the same biochars and pyrochars are also listed in Table 4. These samples were chosen to compare both the effect of the HTC temperature (HC-200-180 and HC-240-180) and the effect of HTC residence time (HC-240-30 and HC-240-180) as well as to analyze the effect of pyrolysis of the HCs produced.

As shown in Figure 6, where the N_2 adsorption isotherms of selected chars at -196 °C have been plotted, the isotherms of HCs have the same shape, indicating that the HTC temperature and time had no significant influence on the pore-size distribution [33]. The isotherms are of type II according to the IU-PAC classification [45], indicating that the HCs have a mesoporous structure [46] with weak adsorbate– adsorbent interactions. Furthermore, the adsorbed N molecules are clustered around the most favorable sites on the surface of the pores, which makes the amount adsorbed at the saturation pressure finite and reduces the BET surface area [36].

In contrast to HCs, pyrochar and biochar isotherms exhibit a gradual increase in the adsorbed volume, and most of the uptake of N₂ adsorption occurs in low relative pressure regions ($P/P_0 < 0.1$), indicating the presence of micropores [16]. This is consistent with a rearrangement of carbon layers during the creation of small pores, which is more evident for the sample obtained from one-step pyrolysis and also for the pyrolysis of high-temperature HCs.



Figure 6. Nitrogen adsorption isotherms of selected chars at -196 °C.

Samples	S_{BET} (m ² ·g ⁻¹)	$V_{\rm mi}~({\rm cm}^3{\cdot}{\rm g}^{-1})$	$V_{\rm me}~({ m cm}^3{ m \cdot}{ m g}^{-1})$	S_{EXT} (m ² ·g ⁻¹)
PY-600	123	0.077	0.027	154
PYC-200-180-600	135	0.009	0.01	65
PYC-240-180-600	237	0.152	0.024	227
PYC-240-30-600	64	0.052	0.024	207

Table 4. Physical characteristics of selected chars

These results confirm the observations made during the SEM analysis, which is further described in Section 3.6.

The results of physical characteristics listed in Table 4 show that char samples have a moderate apparent BET surface area, which in general is lower than 240 m²·g⁻¹. Compared to biochars, pyrochars have a significantly greater surface area.

Considering the pyrolysis process, there is a very significant increase in the BET specific surface area of both chars that are prepared with (PYC) and without (PY) HTC.

A similar observation is made as follows. When the HTC temperature is increased, the pyrochar sample prepared at a higher HTC temperature (PYC-240-180-600) has a surface area 1.75 times larger (237 m²·g⁻¹) than the pyrochar prepared at a lower HTC temperature (PYC-200-180-600).

Since pores can be formed by the loss of volatiles [35], it can be suggested that the increase in pores on the PYC surface compared to that on the biochars can be caused by the loss of total volatiles during the HTC process.

These results confirm the observations made during the SEM analysis in Section 3.6.

3.6. External surface morphology of chars by SEM

The surface morphology of selected samples was studied by SEM. Figures 7 and 8 show representative micrographs corresponding to the selected biochar (PY-600) and the pyrochar (PYC-240-180-600). First, it is important to note that the cellular morphology of the feedstock is maintained after both processes.

From these figures, it can be observed that the surface structure of the pyrochar differs substantially from that of the biochar.

In contrast to the biochar, the pyrochars are covered with carbon microspheres on the surface with a distinctive size distribution. The carbon microspheres are mainly produced by the breakup of cellulose molecules [47] that might be decomposed during the HTC process and then during the pyrolysis process as well as by the recombination of carbon products from decarboxylation reactions [2]. Az-



Figure 7. SEM for biochar (PY-600).



Figure 8. SEM for pyrochar (PYC-240-180-600).

zaz *et al.* [12] also explained that these carbon microspheres are formed due to a change in the crystalline arrangement associated with the condensation of cellulose and hemicellulose in the carbon content.

On the other hand, in all samples, the fibrous structure of the starting material is maintained. The distinctive differences in the char structures result from a shift in the reaction mechanisms governing the processes.

From the EDX surface composition analysis of the two chars, it was reported that their outer surface is mainly made up of carbon with very low oxygen content [48]. These results confirm the observations made during the elemental analysis (Section 3.4).

As a result of hydrolysis, cellulose breaks up into small-chain polymers and monomers, which later can polymerize as higher molecular weight compounds (this is the second solid phase as was previously indicated by thermogravimetric profiles). After hydrolysis, dehydration is assumed to take place. This process can be both physical (rejection of water from the solid precursor) and chemical (removal of hydroxyl groups). The spherical configuration is related to their limited solubility and hydrophobicity as it minimizes the interfacial surface HC-solvent [8].

3.7. FT-IR analysis

To study the surface chemistry transformations that take place in both processes, only the IR spectra of selected samples (PY-600, HC-240-30, PYC-240-30-600, HC-240-180, and PYC-240-180-600) have been included in this part. The spectra are shown in Figure 9.

From Figure 9, the FT-IR spectra indicate that the biochars and HCs share similar functional groups.

In all cases, a large peak at 3454 cm^{-1} can be attributed to O–H stretching vibration in the hydroxyl and carboxyl groups, indicating the presence of a large number of hydroxyl groups in the chars. The intensity of this peak is gradually weakened as the HTC and pyrolysis temperature and time increase, which is due to the dehydration and decarboxylation reactions in both processes [48,49]. These results are in agreement with those from elemental analysis (Figure 5) in Section 3.4.

From the HC spectrum, it can be observed that small peaks appear at 2920 cm⁻¹, which represent C–H stretching vibrations of aliphatic compounds. This indicates the presence of aliphatic and aromatic structures. These peaks present in the HC spectrum disappear in the pyrochar and biochar spectra (after pyrolysis). This implies the destruction of hemicellulose and cellulose during pyrolysis.

Another peak is characteristic of cellulose and lignin and is associated with different C–O–C (carbonyl) linkages and primary alcohols within the structure of these materials. These bands are found in the aromatic $(1450-1650 \text{ cm}^{-1})$ and nonconjugated carbonyl (1730 cm^{-1}) regions.

The peak at 1730 cm^{-1} can be attributed to the C=O stretching vibration of acetyl in hemicellulose [8,49]. It can be observed that with the rise in the pyrolysis and HTC time and temperature, the peaks are substantially diminished, indicating an increase in the destruction of hemicellulose.

The peak at 1650 cm⁻¹ is attributed to the stretching vibration of C=C in the aromatic structure [8,27]. The peak at 1386 cm⁻¹ is assigned to the stretching vibration of C–H bonds in cellulose or C–O bonds in syringyl derivatives [8].

At the highest HTC and pyrolysis temperatures (240 °C and 600 °C, respectively), the intensity of peaks at 1030 cm⁻¹ associated with the stretching vibrations of C–O and C–C in cellulose and hemicellulose [27,36] is gradually weakened. This indicates

that the cellulose in biomass is degraded during both processes, but there is still a fraction of it that did not react [27]. On the other hand, [36] explained that during the HTC process, aliphatic and aromatic hydrocarbons are formed and suggested that this increase in aromaticity is confirmed by the decrease in H/C atomic ratios. This result is in good agreement with the elemental analysis result presented in Table 3.

4. Conclusions

This work has focused on the study of pyrolysis and HTC of PC for converting it into a carbon-rich material. The resulting chars have been characterized in terms of their composition, energetic power, and morphology and surface chemistry. It can be concluded that the HTC of PC leads to an increase in the fixed carbon content of the material. This is accompanied by a reduction in volatile matter, compared to the pyrolysis process, which results in an increase in the calorific value of the material. This is one of the strengths of this work. Especially influential is the temperature variable followed by the HTC time. Results show that increasing the HTC temperature from 180 °C to 240 °C leads to a decrease in the solid yield and an increase in the gas yield, while increasing the HTC time leads to a decrease in both solid and gas yields. The optimum HTC conditions (240 °C and 60 min) yield a carbon content and a higher heating value of 92.5% and 34.28 MJ·kg⁻¹, respectively, leading to a material that might be utilized as a category-A briquette for domestic use.

Moreover, the adsorbed heat modified the surface morphology of the HCs with the appearance of carbon microspheres related to the breakup of cellulose and the condensation of hemicellulose in the carbon content.

Finally, the chemical structure of pyrochars more closely resembles natural coal than charcoal with respect to the types of chemical bonds and their relative quantity as well as their elemental composition.

Highlights

• The pyrochar yield decreases and gas production increases with increment in HTC temperature.





- The HTC maximizes gas production almost twice as much as conventional pyrolysis.
- A larger amount of gases is obtained at the highest HTC temperature with a higher PCI to produce heat and electricity.
- The pyrochar generated at the highest HTC temperature and time has the highest HHV.
- The biomass is transformed into a coal-like material to be utilized as briquettes for domestic use.

Conflict of interest

The authors certify that they have *no* affiliations with or involvement in any organization or entity with any financial interest in the subject matter or materials discussed in this manuscript.

Acknowledgments

This work has received funding from Junta de Extremadura through projects GR15034 and IB16108 and from Ministerio de Economía y Competitividad via project CTM2016-75937-R. Furthermore, the authors thank the Service "SAIUEX" (Servicios de Apoyo a la Investigación de la Universidad de Extremadura) for surface characterization analyses.

References

 D. Kim, K. Y. Park, K. Yoshikawa, "Conversion of Municipal Solid Wastes into Biochar through Hydrothermal Carbonization", in *Engineering Applications of Biochar*, IntechOpen, 2017.

- [2] W. Gu, Z. Yu, S. Fang, M. Dai, L. Chen, X. Ma, *BiomassConvers. Biorefinery*, 2019, **10**, 1221-1236.
- [3] R. Victor, P. Antero, A. Cristina, F. Alves, S. Botelho, D. Oliveira, S. A. Ojala, S. S. Brum, *J. Clean. Prod.*, 2019, article no. 119899.
- [4] S. Román, B. Ledesma, A. Álvarez-Murillo, E. Sabio, J. F. González, M. Olivares-Marín, M. Boutaieb, "Hydrocarbonization. Does It Worth to Be Called a Pretreatment?", in *Analytical Pyrolysis*, IntechOpen, 2018.
- [5] H. S. Kambo, A. Dutta, *Renew. Sustain. Energy Rev.*, 2015, 45, 359-378.
- [6] M. Kumar, A. Olajire Oyedun, A. Kumar, *Renew. Sustain. Energy Rev.*, 2018, 81, 1742-1770.
- [7] M. Lucian, L. Fiori, *Energies*, 2017, 10, 211.
- [8] M. T. Reza, J. Andert, B. Wirth, D. Busch, J. Pielert, J. G. Lynam, J. Mumme, *Appl. Bioenergy*, 2014, 1, 11-29.
- [9] D. Basso, D. Castello, M. Baratieri, L. Fiori, 21st Eur. Biomass Conf. Exhib., 2013, 1478-1487.
- [10] A. Jain, R. Balasubramanian, M. P. Srinivasan, *Chem. Eng. J.*, 2016, **283**, 789-805.
- [11] S. Román, J. Libra, N. Berge, E. Sabio, K. Ro, L. Li, B. Ledesma, A. Álvarez-Murillo, S. Bae, *Energies*, 2018, 11, 216.
- [12] A. A. Azzaz, M. Jeguirim, V. Kinigopoulou, C. Doulgeris, M.-L. Goddard, S. Jellali, C. M. Ghimbeu, *Sci. Total Environ.*, 2020, 733, article no. 139314.
- [13] A. T. Yuliansyah, T. Hirajima, Waste Biomass Valor, 2010, 1, 395-405.
- [14] M. Mäkelä, J. Forsberg, C. Söderberg, S. H. Larsson, O. Dahl, *Bioresour. Technol.*, 2018, 263, 654-659.
- [15] J. Libra, K. S. Ro, C. Kammann, A. Funke, *Biofuels*, 2011, 2, 89-124.
- [16] L. P. Xiao, Z. J. Shi, F Xu, R. C. Sun, *Bioresour. Technol.*, 2012, 118, 619-623.
- [17] M. Mäkelä, V. Benavente, A. Fullana, Appl. Energy, 2015, 155, 576-584.
- [18] M. Wilk, A. Magdziarz, K. Jayaraman, M. Szymańska-Chargot, I. Gökalp, *Biomass and Bioenergy*, 2019, **120**, 166-175.
- [19] K. Y. Park, K. Lee, D. Kim, *Bioresour. Technol.*, 2018, **258**, 119-124.
- [20] K. Zhao, Y. Li, Y. Zhou, W. Guo, H. Jiang, Q. Xu, *Bioresour*. *Technol.*, 2018, 267, 9-16.

- [21] L. Li, R. Diederick, J. R. V. Flora, N. D. Berge, *Waste Manag.*, 2013, **33**, 2478-2492.
- [22] A. Ayari, Glob. J. Bot. Sci., 2017, 5, 39-49.
- [23] M. Meftahi, M. Khouja, F. Zammeli, A. Ayari, *Glob. J. Bot. Sci.*, 2016, 4, 20-23.
- [24] A. Ayari, D. Moya, A. Zubizarreta-gerendiain, "Influence of Environmental Factors on Aleppo Pine Forest Production", in *Tunisia: Economic, Political and Social Issues*, Nova Publishers, 2012, 93-118.
- [25] T. Sghaier, Y. Ammari, Ecol. Medit., 2012, 38, 39-57.
- [26] C. Quan, N. Gao, Q. Song, J. Anal. Appl. Pyrol., 2016, 121, 84-92.
- [27] M. Boutaieb, M. Guiza, S. Román, S. Noglas, B. Ledesma, A. Ouederni, *Environ. Prog. Sustain. Energy*, 2020, **39**, article no. e13272.
- [28] R. Font, J. A. Conesa, J. Moltó, M. Muñoz, J. Anal. Appl. Pyrol., 2009, 85, 276-286.
- [29] E. C. for Standardization, "CEN/TS 15104, Solid biofuels method for the Determination of total content of carbon, hydrogen and nitrogen. Instrumental methods", 2005.
- [30] E. C. for Standardization, "CEN/TS 15289, Solid biofuels method for the determination of total content of sulfur and chlorine", 2006.
- [31] M. A. Martin-Lara, G. Blazquez, A. Ronda, M. Calero, *Renew. Energy*, 2016, 96, 613-624.
- [32] A. I. Almendros, A. Ronda, A. Pérez, G. Blázquez, M. Calero, Bioresour. Technol., 2015, 196, 406-412.
- [33] A. Bedoui, S. Souissi-Najar, A. Ouederni, *Fuel Process. Technol.*, 2016, **18**, 938-950.

- [34] M. Lucian, M. Volpe, L. Gao, G. Piro, J. L. Goldfarb, L. Fiori, *Fuel*, 2018, 233, 257-268.
- [35] X. Chen, X. Ma, X. Peng, Y. Lin, J. Wang, C. Zheng, *Bioresour. Technol.*, 2018, 267, 167-174.
- [36] R. K. Garlapalli, B. Wirth, M. T. Reza, *Bioresour. Technol.*, 2016, 220, 168-174.
- [37] D. Chen, X. Chen, J. Sun, Z. Zheng, K. Fu, *Bioresour. Technol.*, 2016, **216**, 629-636.
- [38] X. He, Z. Liu, W. Niu et al., Energy, 2018, 143, 746-756.
- [39] S. Uçar, S. Karagöz, Fuel, 2014, 137, 85-93.
- [40] C. R. Correa, T. Hehr, Y. Rauscher, M. J. Alhnidi, A. Kruse, J. Anal. Appl. Pyrolysis, 2019, 140, 137-147.
- [41] Z. Wang, F. Wang, J. Cao, J. Wang, Fuel Process. Technol., 2010, 91, 942-950.
- [42] S. Zhang, X. Zhu, S. Zhou, H. Shang, J. Luo, *Biochar Biomass Waste*, 2019, 275-294.
- [43] X. Chen, X. Ma, X. Peng, Y. Lin, Z. Yao, Bioresour. Technol., 2018, 249, 900-907.
- [44] F. A. for Standardization, "Charcoal and charcoal briquettes for household use: name, specifications, tests", AFNOR. 1985;84361:NF B55-NF B101.
- [45] M. Thommes, K. Kaneko, A. V. Neimark *et al.*, *Pure Appl. Chem.*, 2015, 87, 1051-1069.
- [46] A. Abdedayem, M. Guiza, A. Ouederni, C. R. Chim., 2015, 18, 100-109.
- [47] S. Román, J. M. V. Nabais, C. Laginhas, B. Ledesma, J. F. González, Fuel Process. Technol., 2012, 103, 78-83.
- [48] C. Dupont, J. M. Commandré, P. Gauthier, G. Boissonnet, S. Salvador, D. Schweich, *Fuel*, 2008, 87, 1155-1164.
- [49] E. Sabio, B. Ledesma, S. Rom, Energy, 2016, 94, 600-608.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Investigations on Mediterranean biomass pyrolysis ability by thermogravimetric analyses: thermal behaviour and sensitivity of kinetic parameters

Étude de la pyrolyse de la biomasse méditerranéenne par analyse thermogravimétrique: comportement thermique et sensibilité des paramètres cinétique

Nourelhouda Boukaous^{*a*, *b*}, Lokmane Abdelouahed^{*a*}, Mustapha Chikhi^{*b*}, Chetna Mohabeer^{*a*}, Abdeslam Hassen Meniai^{*, *b*} and Bechara Taouk^{*a*}

^{*a*} Normandie Univ, INSA Rouen Normandie, UNIROUEN, Laboratoire de Sécurité des Procédés Chimiques LSPC-EA 4704, 76000 Rouen, France

 b Faculté de Génie des Procédés, Université Salah Boubnider Constantine 3, Constantine, Algérie

E-mails: nourelhouda.boukaous@insa-rouen.fr (N. Boukaous), lokmane.abdelouahed@insa-rouen.fr (L. Abdelouahed), chikhi_mustapha@yahoo.fr (M. Chikhi), chikirsha.mohabeer@insa-rouen.fr (C. Mohabeer), meniai@yahoo.fr (A. H. Hassen), bechara.taouk@insa-rouen.fr (B. Taouk)

Abstract. A comparison of the thermal behaviours of different Mediterranean biomasses, based on the evaluation of their pyrolysis characteristic temperatures, their reactivity and kinetic parameters is presented. Parameters such as the activation energy and the pre-exponential factor of the pyrolysis reactions are determined by different methods (Kissinger, Kissinger–Akahira–Sunose [KAS], Coats–Redfern, nonlinear least-squares minimization [NLSM] and model distributed activation energy model [DAEM]). Furthermore, a sensitivity analysis of the kinetic parameters based on different methods is conducted. The comparison of this work with the literature, showed that thermal characteristic parameters determined using the thermogravimetric analysis (TGA) are often neglected and not used in biomass pyrolysis at laboratory scale. The kinetic parameters seem to be highly sensitive to the used kinetic methods. For a given biomass, such as the Aleppo pine husk residue, for example, the activation energy can vary from 65.80 to 197.08 kJ·mol⁻¹ depending on the used method. For this biomass, the highest average activation energy (190 kJ·mol⁻¹) was estimated by the KAS and DAEM methods. The Kissinger method yields to an activation energy close to that of cellulose calculated by

^{*} Corresponding author.

the NLSM method. For all biomasses, the activation energy remains between 150 and 200 kJ·mol⁻¹ except for the Coats–Redfern method, where this value is in the range of 50-100 kJ·mol⁻¹. Therefore, it is important to have a means of recommending the most appropriate method for the determination of kinetic parameters.

Keywords. Biomass, Pyrolysis, Thermogravimetric analysis, Kinetic parameters, Bio-oil.

1. Introduction

The incessant increase for energy demand and the important widespread of environmental pollution in relation with the depletion of fossil fuels has stressed the need for a green transition to renewable energy resources [1]. Green energy sources are considered as the best alternative to fossil fuels use. Green energy can meet the world's energy demands and reduce greenhouse gas emissions and air pollution. As regards the utilization of alternative energy sources, the use of agricultural residues and organic wastes as biomass is a major challenge for the future and has attracted much attention. Biomass is an inexhaustible source and can exist over wide geographical regions in contrast to fossil fuels. Biomass has also a low impact on the environment due to its low sulphur and nitrogen contents [2,3]. By the year 2050, the the use of biofuel and green electricity from biomass is expected to be approximately 38% and 17%, respectively [4].

Various agricultural residues are essentially composed of holocellulose (cellulose and hemicellulose) and lignin. These residues have high heating values (HHV) [5–7]. The thermochemical conversion process is one of the best and favoured methods for the turning of biomass into biofuels due to their high energy values under acceptable thermal conditions [8,9]. Among these thermochemical conversion processes, pyrolysis has received special attention since it produces solid, liquid and gaseous products that could be recovered by different techniques [10]. The selection of a suitable recovery strategy depends strongly on the physical and chemical characteristics of the feedstock [10].

The climate conditions in the Mediterranean basin contribute to its diverse forests and natural and agricultural resources and consequently affect the variety of agricultural residues. Olive trees, palm trees and wheat fields are the major agricultural products in this region. *Cistus monspeliensis* and Aleppo pine trees are two of the most abundant natural species in the Mediterranean basin. The olive

trees are essentially cultivated in the Mediterranean region. They are present in all the regions bordering the Mediterranean area from Madeira and the Canaries to Arabia and Mesopotamia. Spain is the world's leading producer and exporter of olive oil and table olives. It also has the largest area of olive groves and the largest number of olive trees. Moreover, it is estimated that the number of date palm trees worldwide is about 105 million [11]. This number explains the global production of dates, which has undergone considerable expansion over the past decade, increasing from 6 million in 2004 to approximately 7.5 million tons in 2009 [12]. Egypt is the leading producer and Tunisia is the leading exporter of dates [13]. Regarding Aleppo pine trees, palaeogeography studies show that it is indeed North Mediterranean. It remains mainly native to semi-arid Mediterranean climate, and it is considered as a typical fruit in the French Mediterranean basin [14]. C. monspeliensis is mainly native to Spain and the Mediterranean Rim; it has the characteristics of easy regeneration and multiplying even after fires.

Several investigations have examined the characterization and the pyrolysis of various lignocellulosic materials such as palm kernel shells, corn cob, peanut shell, coffee husk [15], spent coffee grounds [16], *Posidonia oceanica* [17], kenaf stems [18] and grape marc [19]. Although the energy valorization values of olive [20,21], date waste [4,22,23], wheat straw [24,25] and Aleppo pine husks [26–28] are found in the literature, no information is available about the determination of reaction kinetics of *C. monspeliensis* using thermogravimetric analysis (TGA).

The biomass reactivity is often dependent on the content of holocellulose and lignin, the average size of the pellet and the presence of minerals [13].

It is well known that the distribution of the product of biomass pyrolysis varies according to operating conditions [29–33] and the nature of the biomass. Imam and Capered [34] examined the effect of temperature from 400 to 600 °C on the yield of pyrolytic products of switchgrass and found that an increase in the pyrolysis temperature led to an increase in the bio-oil and gas yields and a decrease in the the biochar yield. The optimization of this process therefore requires a better knowledge of the thermal and kinetic behaviour of biomass pyrolysis on the one hand and the characteristics of pyrolysis products on the other [22,35-37]. The chemical valorization of bio-oil as a source of acids and sugars has been applied in the chemical industry. Acetic acid can be used in various industrial applications for the production of drugs, dyes and textures, while levoglucosan finds application in the pharmaceutical field such as in the synthesis of antibiotics. Phenol has various useful applications as an important chemical compound. Phenolic resins and caprolactam, for example, are used in nylon and synthetic fibres, and in the production of adhesives [38].

Several methods of biomass valorization can be found in the literature. The present work aims to study the production of a second-generation biofuel that can replace a conventional fuel such as gasoline or diesel by the pyrolysis of different biomasses.

The main objective of this study is to present a detailed characterization of some important parameters of pyrolysis reaction such as temperature, kinetics and product composition, which are required for the design of processes for thermochemical valorization. The pyrolysis of five biomasses of different origin (*C. monspeliensis*, olive and date kernels, Aleppo pine husks and wheat straw) was carried out in a thermogravimetric analyser.

2. Materials and methods

2.1. Biomasses

Five different biomasses were used in this work:

- *C. monspeliensis* (CM): This wild shrub is often found in Mediterranean forests and especially in southern Europe and North Africa. This plant can be a potential source of energy in mountainous and remote areas.
- Olive and date kernels (OK and DK, respectively): Olives are a typical Mediterranean product. They grow especially in the south of Europe and the north of Africa.
- Aleppo pine husks (APH) or *Pinus halepensis*: This is a type of woody biomass available in

mountainous areas of Mediterranean countries.

• Wheat straw (WS): This is one of the most abundant agricultural residues in the Mediterranean region.

2.2. Sample preparation and characterization

After drying and crushing, the samples were sieved to an average size of 200 μ m to avoid any constraints in heat and mass transfer according to the recommendations of Van de Velden *et al.* [39]. The characterization of the different biomass samples based on proximate and ultimate composition. For all of the samples, humidity was evaluated to 4%. The TGA was also used to conduct the proximate analysis following the process given by Garcia *et al.* [40]. This process involved carrying out pyrolysis and then a combustion of the sample (see Supporting Information for protocol details). The ultimate analysis was conducted using a CHNS analyser. A Parr bomb calorimeter (model 1356) was used for the determination of the calorific values of biomasses (HHV).

2.3. Experimental methods and modelling

The TGA is a useful tool for a wide variety of studies, including kinetic and thermal degradation of complex chemicals [41,42]. An SDT/Q6000-TA analyser was used for thermogravimetric experiments, which were carried out at different heating rates ranging from 2 to 40 °C·min⁻¹ under a nitrogen flowrate of 50 mL·min⁻¹ and at atmospheric pressure. This gas flowrate allows a similar residence time of vapour pyrolysis in the laboratory-scale reactor (approximately 10 min). The weight of the initial samples was in the range of 5±0.5 mg. The samples were introduced into the analyser at ambient temperature and then heated to 600 °C.

2.4. Thermal and kinetic study

The thermal pyrolysis of the biomass is usually expressed by the general equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(t)f(\alpha),\tag{1}$$

where *k* is the kinetic rate constant and *f* is the kinetic model function.

626

Sample	C (%)	H (%)	O (%) ⁽¹⁾	VM (%) ⁽²⁾	FC (%) ⁽³⁾	Ash (%)	HHV $(MJ \cdot kg^{-1})^{(4)}$
СМ	46.46	5.87	47.67	72.38	26.17	1.45	19.20
OK	45.56	5.8	48.64	75.42	23.79	0.79	20.86
APH	47.6	5.75	46.65	72.10	26.90	1.00	20.34
WS	47.35	5.74	46.91	70.44	28.83	0.74	19.10
DK	45.22	6.47	48.31	70.22	28.64	1.13	20.64

Table 1. Ultimate and proximate analysis and HHV of the studied biomasses

 $^{(1)}$ Oxygen content was calculated by difference; $^{(2)}$ volatile matter fraction; $^{(3)}$ fixed carbon; $^{(4)}$ high heating value.

The conversion rate α is calculated based on the mass loss of the sample:

$$\alpha = 1 - \frac{m_T - m_f}{m_0 - m_f},\tag{2}$$

where m_0 and m_f are the weights of the sample at the beginning and the end of the experiments, respectively, and m_T is the mass at temperature *T*.

The Arrhenius equation shows the dependence of the temperature and the rate constant as follows:

$$k(T) = A \cdot \exp\left(-\frac{E_a}{RT}\right),\tag{3}$$

where *A* is the pre-exponential factor, E_a represents the activation energy, and *R* denotes the ideal gas constant.

The kinetic model function mostly used [43] for biomass pyrolysis is

$$f(\alpha) = (1 - \alpha)^n, \tag{4}$$

where *n* denotes the reaction kinetic order.

Combining Equations (1), (3) and (4), leads to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \cdot \exp\left(-\frac{E_a}{RT}\right) (1-\alpha)^n. \tag{5}$$

It should be noted that the first order is usually considered for the pyrolysis of biomass [44,45]. The first order was considered in the present work, and several methods were used to determine the preexponential constants and the activation energies of the pyrolysis of five biomasses.

2.4.1. Kissinger method

The Kissinger relation [46] is widely used for solid and liquid decomposition under nonisothermal conditions. For biomass decomposition, the pyrolysis reaction is considered as a single reaction that produces bio-oil, gas and char. The Kissinger relation can be simplified as follows:

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E_a}{RT_m} + \ln\left(\frac{AR}{E_a}\right),\tag{6}$$

where β represents the heating rate and T_{max} denotes the maximum temperature of the $d\alpha/dt$ curve related to the maximum reaction rate.

2.4.2. Kissinger-Akahira-Sunose method (KAS)

Isoconversional methods are widely used for studying kinetic parameters [47] and are recognized as the most appropriate approach for calculating the activation energy of reactions. These methods assume that the mechanism of biomass pyrolysis involves infinitely independent and parallel reactions with different kinetic rate constants and activation energies [48]. The KAS method is the most widely used approach for studying biomass pyrolysis kinetics in the literature [49]. After rearrangement and integration of (5), the KAS process can be written as:

$$\ln\left[\frac{\beta}{T_{\alpha}^{2}}\right] = \ln\left[\frac{A_{\alpha}R}{E_{\alpha}g(\alpha)}\right] - \frac{E_{\alpha}}{RT_{\alpha}},$$
(7)

where A_{α} and E_{α} are the pre-exponential factor and activation energy, respectively, for a given conversion rate, *R* is the gas constant and *g* is a complex integral function.

The plot of $\ln[\beta_i/T_{\alpha,i}^2]$ versus 1/T for a given value of the conversion rate (α) yields a straight line. The slope of this line is used for determining the activation energy. Due to the complexity of the function *g*

(relation (7)), the Kissinger relation is combined with the KAS method to determine the pre-exponential factor A_{α} .

2.4.3. Coats-Redfern method

This is a fitting method that is based on optimization of the order of the reaction, pre-exponential factor and activation energy. This method is well described in the literature [50,51]. However, in the present case, the first order was already assumed for biomass pyrolysis as discussed above. The Coats– Redfern relation [52] is:

$$\ln\left|\frac{\ln(1-\alpha)}{T^2}\right| = \ln\left[\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT_a}.$$
 (8)

The $\ln |\ln(1 - \alpha)/T^2|$ plot of (8) versus the inverse of temperature gives a straight line whose slope is $-E_a/R$. Equation (8) is applied in the temperature range $[T_i, T_f]$ for different heating rates. In the literature, the term $2RT/E_a$ is usually neglected in relation (8) [53]. The parameters E_a and A are calculated as average values based on different heating rates.

2.4.4. Distributed activation energy model (DAEM)

DAEM is the most recent method. It is based on the same principle as the KAS method: the distribution of activation energies. In general, a Gaussiantype distribution function is considered. Miura [54] developed a derivative equation that is simple to use and gives the same results as the real DAEM. The relation used by Miura is the following:

$$\ln \left| \frac{\beta}{T^2} \right| = \ln \left(\frac{AR}{E_a} \right) + 0.6075 - \frac{E_a}{RT_a}.$$
 (9)

As described for the KAS method, this method requires plotting a straight line and then calculating the kinetic parameters.

2.4.5. Fitting method based on nonlinear leastsquares minimization (NLSM)

This method is based on the minimization of error between the differential thermogravimetry (DTG) curves from the experiment and the curves estimated and optimized from the kinetic parameters (E_a and A). This method has also been compared to a method based on genetic algorithms [55], which in turn is

based on the optimization of the following numerical system:

$$\left\{\begin{array}{l}
\frac{\mathrm{d}\alpha_{j}}{\mathrm{d}t} = A_{j} \cdot \exp\left(-\frac{E_{\alpha_{j}}}{RT}\right)(1-\alpha_{j})^{n_{j}}, \quad j = 1, 2 \text{ and } 3\\
\frac{\mathrm{d}\alpha_{\mathrm{tot}}}{\mathrm{d}t} = \sum_{j=1}^{3} x_{j} \frac{\mathrm{d}\alpha_{j}}{\mathrm{d}t}, \\
t = 0, \quad \alpha_{\mathrm{tot}} = 0, \quad \alpha_{j} = 0, \\
\sum_{j=1}^{3} x_{j} = 1.
\end{array}\right.$$
(10)

Here, x_j represents the evolution of the mass fraction of three biopolymers.

The convergence criterion is defined as

$$S = \sum_{T=T_0}^{T_f} \left(\left(\frac{\mathrm{d}\alpha_{\mathrm{tot}}}{\mathrm{d}t} \right)_{\mathrm{exp}} - \left(\frac{\mathrm{d}\alpha_{\mathrm{tot}}}{\mathrm{d}t} \right)_{\mathrm{sim}} \right)^2.$$
(11)

3. Results and discussion

3.1. Characterization of biomass products

Despite the different origins of biomasses, their ultimate and proximate analyses and HHVs show close values (Table 1). The analysis of mineral content in each sample is carried out using inductively coupled plasma atomic emission spectroscopy. According to these analyses, the major minerals in biomasses are K, Ca, Al, Na and Mg in different amounts (see Table S.1, Supporting Information).

3.2. Evaluation of thermal degradation and kinetic parameters

3.2.1. Evaluation of thermal degradation parameters

The kinetic derivative $(d\alpha/dt)$ for the five samples, at a heating rate of 10 °C·min⁻¹ is shown in Figure 1. During pyrolysis, the weight loss associated with moisture evaporation occurs between room temperature and approximately 150 °C [56]. Above this temperature, the thermal degradation of the biomass samples shows three successive stages representing the decomposition of three biopolymers: hemicellulose, cellulose and lignin [57]. The temperature and the intensity of each of these steps (the shoulder or peak of the $d\alpha/dt$ curve) depend on the biomass and its biopolymer composition.

At a medium heating rate of 10 $^{\circ}$ C·min⁻¹, the devolatilization of CM, DK, APH, WS and OK starts at

approximately 210 °C, 174 °C, 200 °C, 171 °C and 215 °C (T_i or T_{onset}) and ends at 395 °C, 463 °C, 405 °C, 375 °C and 400 °C (T_f), respectively. These temperatures correspond to the initial temperature (T_i or T_{onset}) and the final temperature (T_f) of the pyrolysis reaction, respectively. The observed differences between these temperatures can be attributed to the biomasses composition in terms of holocellulose and lignin fractions as well as their mineral contents [8,45].

The lowest initial temperature for biomass pyrolysis is 160 °C, which is exhibited for the WS pyrolysis at a heating rate of 2 $^{\circ}C \cdot min^{-1}$. The highest final temperature (T_f) is approximately 495 °C and observed for the DK pyrolysis at a heating rate of 40 °C·min⁻¹ (see Table S.2). It should be noted that T_i and T_f increase with the increase of the used heating rate. The major phenomenon that occurs at this temperature range is the pyrolysis of hemicellulose, cellulose and lignin [58]. It can be observed from the $d\alpha/dt$ curves in Figure 1 that in this range, the thermal degradation of biomasses consists of several overlapping steps. The first overlapping shoulder in the $d\alpha/dt$ curve represents the devolatilization of hemicellulose, whereas the second shoulder corresponds to cellulose devolatilization at T_{max} [55]. The last shoulder, which also overlaps, corresponds to the decomposition of lignin at high temperatures. The temperature at which the decomposition rate of biomass is maximum is denoted by T_{max} . At a heating rate of 10 °C·min⁻¹, it was determined to 359, 296, 344, 322 and 330 °C for the CM, DK, APH, WS and OK samples, respectively, (see Table 2). The maximum rates R_{max} (expressed in %·min⁻¹) of weight loss are as follows—DK: 1.58 > APH: 1.42 > OK: 1.26 > CM: 0.98 > WS: 0.73. The differences in the maximum rate and T_{max} are usually due to the reactivity of the biomass; the more volatile the matter, the more reactive the biomass. The evolution of the above-cited temperatures (T_i , T_f and T_{max}) and the maximum pyrolysis rates with heating rate for the different samples based on principal component analysis (PCA) is shown in Figure 2 [59].

As shown in Figure 2(a), a strong linear correlation can be observed between the maximum rate R_{max} and the heating rate β on the one hand and between T_{max} and T_i on the other. Figure 2(b) shows a global comparison of the different thermal parameters (T_i ,



Figure 1. Kinetic rate curves of the studied biomasses ($\beta = 10 \text{ °C} \cdot \text{min}^{-1}$).

 T_f and T_{max} and R_{max}) for the different biomasses. This figure provides information about the similarity of biomass behaviour with respect to the different parameters depicted in Figure 2(a). The index behind each biomass name in Figure 2(a) represents the value of the heating rate (°C·min⁻¹).

The parallel profiles show that globally the heating rate has the same influence on the behaviour of all biomasses. By combining Figures 2(a) and (b), a different behaviour can be observed between CM and DK. This can be confirmed by a comparative analysis of the different characteristics listed in Table S.2 and more particularly in relation to T_{max} and T_i . On the other hand, the profiles of the APH and OK biomasses almost overlie each other and their behaviours are almost similar. Finally, the WS biomass exhibits an average behaviour between the different biomasses. This difference in behaviour can significantly influence the design of the pyrolysis process.

3.2.2. Evaluation of kinetic parameters

The Kissinger, KAS and Coats–Redfern methods are used in this work in order to determine the kinetic parameters. The linear correlation coefficients are high for all the methods used. In fact, in the Kissinger method, the coefficient of correlation varies between 0.995 and 0.999, confirming the existence of a strong linearization of the experimental points as shown in Figure 3.

Figure 4 shows a plot of the CM sample according to the Coats–Redfern method at different heating rates. The correlation coefficient for the Coats– Redfern method also remains high; it varies between

Table 2. Temperatures and maximum pyrolysis conversion rates of the studied biomasses at a heating rate of $10 \, \text{°C} \cdot \text{min}^{-1}$

T_i (°C)	T_{\max} (°C)	T_f (°C)	R_{\max} (%·min ⁻¹)
210	359	395	0.98
174	296	463	1.58
200	344	395	1.42
171	322	375	0.73
215	330	400	1.26
	T _i (°C) 210 174 200 171 215	$\begin{array}{c c} T_i (^{\circ}\mathrm{C}) & T_{\max} (^{\circ}\mathrm{C}) \\ \hline 210 & 359 \\ 174 & 296 \\ 200 & 344 \\ 171 & 322 \\ 215 & 330 \\ \end{array}$	T_i (°C) T_{max} (°C) T_f (°C)210359395174296463200344395171322375215330400

 $R_{\rm max}$ is the maximum rate of pyrolysis.



Figure 2. Behaviours of different characteristic temperatures and the maximum conversion rates of the studied biomasses according to PCA.

0.926 and 0.990.

For the KAS method, the coefficient of correlation varies between 0.955 and 0.986 for conversion rates between 0.05 and 0.8. Above this conversion rate, linearization cannot be ensured in the KAS method, and the correlation coefficient drops to values between 0.4 and 0.8. Figure 5(a) shows a plot of the CM sample according to the KAS relation.

The plot of the different biomass samples according to the Coats–Redfern and KAS methods for different heating rates are given in Supporting Information (Figures S.1 and S.2 and Table S.4).

As reported in previous works, the Flynn–Wall– Ozawa (FWO) approach, which is another isoconversional method, can yield almost the same results as the KAS method. Table 4 summarizes all kinetic parameters for the different biomasses using the four methods mentioned above.

For the DAEM method, the biomasses have a close distribution. Furthermore, the curve trend of this distribution is very similar to that of the one estimated by the KAS method (Figure 6). However, the values of the corresponding activation energies were different. Moreover, at a high conversion rate, this method generates aberrant activation energy values similarly to those calculated by the KAS method.

For the NLSM method, the determination of the kinetics of the pyrolysis reaction is based on the eval-

		Cellulose	Hemicellulose	Lignin
OV	$\ln(A) (s^{-1})$	15.15	10.46	1.84
ŰK	E_a (kJ/mol)	195.98	132.96	60.34
CM	$\ln(A) (s^{-1})$	11.25	10.14	2.16
СМ	E_a (kJ/mol)	165.20	135.69	65.65
ADII	$\ln(A) (s^{-1})$	10.99	8.79	2.31
АРП	E_a (kJ/mol)	154.50	118.60	68.15
MC	$\ln(A) (s^{-1})$	10.99	7.73	1.90
WS	E_a (kJ/mol)	148.10	101.48	60.86
DV	$\ln(A) (s^{-1})$	11.02	15.89	1.06
DK	E_a (kJ/mol)	154.85	193.85	53.87

Table 3. Cellulose, hemicellulose and lignin kinetic parameters for the studied biomasses according to the NLSM method



Figure 3. Kinetic plots of the studied biomasses by the Kissinger method.



Figure 4. Kinetic plots of the studied biomasses by the Coats–Redfern method.



Figure 5. (a) Kinetic plots and (b) activation energy evolution versus the conversion rates of the studied biomasses according to the KAS method.



Figure 6. Activation energy evolution versus the conversion rates of the studied biomasses according to the DAEM method.

uation and optimization of the kinetic parameters of the three biopolymers that constitute the biomass: cellulose, hemicellulose and lignin. From the kinetics of these three polymers, the overall biomass DTG curve can be reconstructed, which represents the pyrolysis reaction rate. The kinetic parameters are calculated from the DTG curves of the different heating rates and are presented in Table 3. Figure 7 shows experimental and modelled DTG curves superposed for a heating rate of 2 °C/min. As shown in this figure, the algorithm is able to reconstruct the DGT curve but only with a certain gap especially at the level of transition from one biopolymer to another (particularly for the biomasses CM and DK).

3.2.3. Discussion

Generally, the optimum temperature used for biomass pyrolysis is in the range 450-550 °C for increasing the bio-oil yield. As it can be seen from Table 2, this temperature range is higher than the characteristic temperatures estimated through TGA measurements (T_i , T_f and T_{max}). Theoretically, the $T_{\rm max}$ obtained by TGA is useful and essential for the design of pyrolysers. In fact, at this temperature (between 296 and 359 °C according to this work), the kinetic rate of pyrolysis is the highest. This allows better optimization of both the residence time of the biomasses' particles in the reactor and its energy consumption. Nevertheless, this parameter is often neglected in the biomass pyrolysis for the reasons mentioned above (bio-oil yield). In the literature, thermal characteristics are often used to compare the reactivity of different biomasses or their chars. Some authors have even defined new parameters based on these temperatures to compare the reactivity of biomasses [8]. Besides this advantage, T_i and T_f are usually used to limit the temperature interval for kinetic studies.

As shown in Table 4, the kinetic methods, especially the Coats–Redfern method, generate some differences in the values of the activation energy and the pre-exponential factor. According to the literature, the Kissinger method is the oldest and the most widely used approach for kinetic determination by TGA. It was initially developed for monomolecular substances. However, as the biomass is composed of three complex biopolymers (cellulose, hemicellulose and lignin), the use of the Kissinger relation might lead to errors.

The KAS and DAEM methods are very useful methods for kinetic determination using TGA curves, but they have some limitations particularly at high temperatures, where the accuracy of the weight notably decreases due to the low mass present in the thermobalance. Above a conversion rate of 0.75, the activation energy is either very high or very low, and it has no physical significance (Table S.3). The average activation energy is therefore calculated based on conversion rates between 0.05 and 0.75. Despite the differences in the origins of the biomass samples and their varying values of T_i , T_{max} and T_f , the KAS, Kissinger and DAEM methods provide close activation energies for the different samples.

The Coats–Redfern method provides activation energies in the range of $54.81-76.77 \text{ kJ} \cdot \text{mol}^{-1}$. They are much lower than those ones given in the literature (Table 4).

Contrary to the NLSM method, it is difficult to compare the kinetic parameters of the different biopolymers directly with the estimated values obtained when using the other four methods mentioned above. The advantage of this method is reproduction accuracy of the DTG curves and hence of the conversion rates as a function of temperature.

Figure 8 shows the evolution of activation energies calculated by different methods for the APH biomass. The KAS and DAEM methods exhibit an activation energy distribution almost overlying each other. The average activation energy estimated by these two methods is the highest (approximately 190 kJ·mol⁻¹). The Kissinger method produces an activation energy



Figure 7. Experimental and modelling DTG curves of the studied biomasses according to the NLSM method at heating rate of $2 \, {}^{\circ}\text{C} \cdot \min^{-1}$.

Table 4. Comparison of the assessed kinetic parameters of the studied biomasses with the literature $(E_a \text{ in kJ} \cdot \text{mol}^{-1} \text{ and } A \text{ in s}^{-1})$

			Thi	s work						Literatur	e	
Kis		ssinger	KAS (α	= 0.05-0.75)	Coat	Coats-Redfern		DAEM	Kinetic parameters		Mathad	Def
DIOIIIASS	E_a	Α	E_a	Α	E_a	Α	E_a	Α	E_a	Α	Method	Rel.
СМ	169.62	7.37×10^8	194.16	1.02×10^{21}	73.39	1.27×10^4	252.04	9.00×20	No data ava	ailable (N.A.)	for this biomass	
ОК	163.19	1.18×10^9	193.56	7.09 × 10 ²⁰	74.08	1.43×10^4	184.85	2.68×10^{15}	135.48 130.03 $(\alpha = 0.1-0.6)$	2.59×10^{14} 1.18×10^{10}	FWO KAS	[20]
APH	168.74	1.61×10^9	197.08	6.67×20	65.80	3.23×10^2	186.63	2.59×10^{16}	253	N.A.	DAEM	[60]
									$(\alpha = 0.3-0.9)$			
WS	159.10	8.64×10^8	197.27	1.03×10^{21}	54.81	4.57×10^3	213.89	7.71×10^{23}	130–175	N.A.	FWO	[24]
									$(\alpha = 0.15 - 0.85)$			
DK	180.41	3.79×10^{11}	190.17	3.48×10^{21}	76.77	1.27×10^4	208.32	4.66×10^{19}	20.24 192.12	$\begin{array}{c} 1.64 \times 10^3 \\ 1.12 \times 10^{14} \end{array}$	Coats-Redfern Kissinger	[22] [4]

close to that of cellulose by the NLSM method. This may be reasonable because the Kissinger method is dependent on the T_{max} of the DTG curve.

In general, this temperature corresponds to cellulose because it is the major component and the most reactive biopolymer of the biomass. Moreover, this figure shows that at a global scale, the activation energy remains essentially between 150 and 200 kJ·mol⁻¹ except for the Coats–Redfern method, where a value of 70 kJ·mol⁻¹ is obtained. This value is close to that of lignin determined by the NLSM method. Furthermore, hemicellulose generates an average activation energy of 118 kJ·mol⁻¹.



Figure 8. Activation energy distribution versus the conversion rate of the studied biomasses according to the methods used in this work.

4. Conclusion

Thermal and kinetic studies are carried out for five different biomasses of Mediterranean origin. Results highlight the crucial problem of choosing the most appropriate method for the determination of the corresponding kinetic parameters. In addition, different temperatures from the TGA curves are usually neglected in the case of biomass pyrolysis at laboratory scale. Despite the different origins of biomasses, the initial and final ranges of pyrolysis temperatures are globally 171–215 °C and 375–463 °C, respectively.

Except for the Coats-Redfern method, the estimated values of the activation energy and the preexponential factor are relatively close. It would be better to validate all these methods by means of a pilot-scale reactor. The idea is to design a device that applies the same conditions in the TGA devices (controlled heating rate, controlled residence time of solid and vapours, etc.). In addition to the kinetic analysis, extensive heat and mass transfer studies are also required to better understand the biomass pyrolysis reaction particularly when using biomass pellets. In further work, a comparison study between the results from a TGA and a laboratory-scale reactor will be attempted in order to better understand the kinetics of solid pyrolysis and the possible complementarity between the two devices.

Greek symbols

- α conversion rate (–)
- β heating rate (°C·min⁻¹)

Supplementary data

Supporting information for this article is available on the journal's website under https://doi.org/10.5802/ crchim.56 or from the author.

Nomenclature

Α	pre-exponential factor (s^{-1})
APH	Aleppo pine husk biomass
A_{α}	pre-exponential factor at a given con-
	version rate (s^{-1})
СМ	Ciste of Montpellier biomass
DAEM	distributed activation energy model
DK	date kernel biomass
DTG	differential thermogravimetry
E_a	activation energy (kJ·mol ^{-1})
E_{α}	activation energy at a given conversion (kJ·mol ⁻¹)
f	kinetic model function
FID	flame ionization detector
FWO	Flynn–Wall–Ozawa
g	complex integral function
HHV	high heating value (MJ·kg ⁻¹)
k	rate constant (s ⁻¹)
KAS	Kissinger–Akahira–Sunose model
m_0	initial mass (kg)
m_f	final mass (kg)
m_T	mass at temperature T (kg)
n	reaction order (–)
NLSM	nonlinear least-squares minimization
OK	olive kernel biomass
R	gas constant (8.314 J·K ⁻¹ ·mol ⁻¹)
R _{max}	maximum reactivity (%·min ⁻¹)
Т	temperature (°C)
T_f	final temperature (°C)
TGA	thermogravimetry analysis
T_i	initial temperature (°C)
T _{max}	maximum temperature (°C)
T_{α}	temperature at a given conversion
WS	wheat straw biomass

References

C. Quan, N. Gao, Q. Song, J. Anal. Appl. Pyrol., 2016, 121, 84-92.

- [2] A. V. Bridgwater, G. Grassi, *Biomass Pyrolysis Liquids Upgrading and Utilization*, Springer Science & Business Media, Switzerland GA, 2012.
- [3] R. F. Probstein, R. E. Hicks, Synthetic Fuels, Courier Corporation, Mineola, New York, USA, 2006.
- [4] S. S. Idris, N. A. Rahman, K. Ismail, A. B. Alias, Z. A. Rashid, M. J. Aris, *Bioresour. Technol.*, 2010, **101**, 4584-4592.
- [5] I. Boumanchar, K. Charafeddine, Y. Chhiti, F. E. M. Alaoui, A. Sahibed-dine, F. Bentiss, C. Jama, M. Bensitel, *Biomass Convers. Biorefin.*, 2019, 1-11.
- [6] J. K. Odusote, A. A. Adeleke, O. A. Lasode, M. Malathi, D. Paswan, *Biomass Convers. Biorefin.*, 2019, 1-9.
- [7] N. Worasuwannarak, T. Sonobe, W. Tanthapanichakoon, J. Anal. Appl. Pyrol., 2007, 78, 265-271.
- [8] S. Munir, S. Daood, W. Nimmo, A. Cunliffe, B. Gibbs, *Bioresour. Technol.*, 2009, **100**, 1413-1418.
- [9] X. Zhang, M. Xu, R. Sun, L. Sun, J. Eng. Gas Turb. Power, 2006, 128, 493-496.
- [10] I. Ghouma, M. Jeguirim, C. Guizani, A. Ouederni, L. Limousy, Waste Biomass Valor., 2017, 8, 1689-1697.
- [11] B. Agoudjil, A. Benchabane, A. Boudenne, L. Ibos, M. Fois, *Energy Build.*, 2011, **43**, 491-497.
- [12] Y. El may, M. Jeguirim, S. Dorge, G. Trouvé, R. Said, *Energy*, 2012, 44, 702-709.
- [13] A. Rhouma, Le palmier dattier en Tunisie, le patrimoine génétique, vol. II, Rome, Italie, IPGRI, 2005.
- [14] V. Mure, "Qui est vraiment ce pin d'Alep qui barbouille nos paysages méditerranéens ", https://www.botanique-jardins-paysages.com/ ce-pin-dalep-qui-barbouille-nos-paysages-mediterraneens/, 2020.
- [15] M. Jeguirim, J. Bikai, Y. Elmay, L. Limousy, E. Njeugna, *Energy Sustain. Dev.*, 2014, 23, 188-193.
- [16] M. Jeguirim, L. Limousy, P. Dutournie, Chem. Eng. Res. Des., 2014, 92, 1876-1882.
- [17] M. Jeguirim, Y. Elmay, L. Limousy, M. Lajili, R. Said, *Environ. Prog. Sustain. Energy*, 2014, **33**, 1452-1458.
- [18] B. Khiari, I. Ghouma, A. I. Ferjani, A. A. Azzaz, S. Jellali, L. Limousy, M. Jeguirim, *Fuel*, 2020, 262, article no. 116654.
- [19] B. Khiari, M. Jeguirim, Energies, 2018,, 11, article no. 730.
- [20] K. A. B. Alrawashdeh, K. Slopiecka, A. A. Alshorman, P. Bartocci, F. Fantozzi, *JEPE*, 2017, 11, 497-510.
- [21] M. Jeguirim, A. Chouchène, A. F. Réguillon, G. Trouvé, G. Le Buzit, *Resour. Conserv. Recycl.*, 2012, 59, 4-8.
- [22] H. H. Sait, A. Hussain, A. A. Salema, F. N. Ani, *Bioresour. Technol.*, 2012, **118**, 382-389.
- [23] Y. Elmay, G. Trouvé, M. Jeguirim, R. Said, Fuel Process. Technol., 2013, 112, 12-18.
- [24] J. Cai, L. Bi, J. Therm. Anal. Calorim., 2009, 98, 325-330.
- [25] S. C. Peterson, M. A. Jackson, Ind. Crops Prod., 2014, 53, 228-235.
- [26] M. Statheropoulos, S. Liodakis, N. Tzamtzis, A. Pappa, S. Kyriakou, J. Anal. Appl. Pyrol., 1997, 43, 115-123.
- [27] A. P. Dimitrakopoulos, J. Anal. Appl. Pyrol., 2001, 60, 123-130.
- [28] S. Liodakis, D. Bakirtzis, A. P. Dimitrakopoulos, *Thermochim. Acta*, 2003, **399**, 31-42.
- [29] A. Galadima, O. Muraza, Energy Convers. Manage., 2015, 105, 338-354.

- [30] T. Kan, V. Strezov, T. J. Evans, *Renew. Sust. Energ. Rev*, 2016, 57, 1126-1140.
- [31] S. W. Kim, J. Anal. Appl. Pyrol., 2016, 117, 220-227.
- [32] M. Morin, S. Pécate, M. Hémati, Y. Kara, J. Anal. Appl. Pyrol., 2016, 122, 511-523.
- [33] A. M. Zmiewski, N. L. Hammer, R. A. Garrido, T. G. Misera, C. G. Coe, J. A. Satrio, *Energy & Fuels*, 2015, **29**, 5857-5864.
- [34] T. Imam, S. Capareda, J. Anal. Appl. Pyrol., 2012, 93, 170-177.
- [35] S. Daneshvar, F. Salak, K. Otsuka, Int. J. Chem. Eng. Appl., 2012, 3, no. 4, 256-263.
- [36] M. Jeguirim, S. Dorge, G. Trouvé, R. Said, *Energy*, 2012, 44, 702-709.
- [37] K. Lazdovica, V. Kampars, L. Liepina, M. Vilka, J. Anal. Appl. Pyrol., 2017, 124, 1-15.
- [38] E. Lazzari, T. Schena, C. T. Primaz, G. P. da Silva Maciel, M. E. Machado, C. A. L. Cardoso, R. A. Jacques, E. B. Caramão, *Ind. Crops Prod.*, 2016, 83, 529-536.
- [39] M. Van de Velden, J. Baeyens, A. Brems, B. Janssens, R. Dewil, *Renew. Energy*, 2010, 35, 232-242.
- [40] R. García, C. Pizarro, A. G. Lavín, J. L. Bueno, *Bioresour. Technol.*, 2013, **139**, 1-4.
- [41] S. Dorge, M. Jeguirim, G. Trouvé, Waste Biomass Valorizat., 2011, 2, 149-155.
- [42] J. J. M. Orfão, F. J. A. Antunes, J. L. Figueiredo, Fuel, 1999, 78, 349-358.
- [43] M. V. Gil, D. Casal, C. Pevida, J. J. Pis, F. Rubiera, *Bioresour*. *Technol.*, 2010, **101**, 5601-5608.
- [44] A. Anca-Couce, A. Berger, N. Zobel, Fuel, 2014, 123, 230-240.
- [45] M. G. Grønli, G. Várhegyi, C. Di Blasi, Ind. Eng. Chem. Res., 2002, 41, 4201-4208.
- [46] H. E. Kissinger, Anal. Chem., 1957, 29, 1702-1706.
- [47] N. E. Gordina, V. Y. Prokof'ev, N. N. Smirnov, A. P. Khramtsova, J. Phys. Chem. Solids, 2017, 110, 297-306.
- [48] K. Mansaray, A. Ghaly, Energy Sources, 1999, 21, 773-784.
- [49] A. Chandrasekaran, S. Ramachandran, S. Subbiah, *Bioresour. Technol.*, 2017, 233, 413-422.
- [50] A. Álvarez, C. Pizarro, R. García, J. L. Bueno, A. G. Lavín, *Bioresour. Technol.*, 2016, **216**, 36-43.
- [51] S. Y. Yorulmaz, A. Atimtay, "Investigation of combustion kinetics of five waste wood samples with thermogravimetric analysis", in *Survival and Sustainability: Environmental Concerns in the 21st Century* (H. Gökçekus, U. Türker, J. W. LaMoreaux, eds.), Springer, Berlin, Heidelberg, 2011, 511-520.
- [52] A. W. Coats, J. P. Redfern, Nature, 1964, 201, 68-69.
- [53] M. A. Islam, M. Auta, G. Kabir, B. H. Hameed, *Bioresour. Technol.*, 2016, **200**, 335-341.
- [54] K. Miura, T. Maki, Energy Fuels, 1998, 12, 864-869.
- [55] L. Abdelouahed, S. Leveneur, L. Vernieres-Hassimi, L. Balland, B. Taouk, J. Therm. Anal. Calorim., 2017, 129, 1201-1213.
- [56] S.-S. Kim, J. Kim, Y.-H. Park, Y.-K. Park, Bioresour. Technol., 2010, 101, 9797-9802.
- [57] L. Wilson, W. Yang, W. Blasiak, G. R. John, C. F. Mhilu, *Energy Convers. Manage*, 2011, **52**, 191-198.
- [58] H. Yang, R. Yan, H. Chen, D. H. Lee, C. Zheng, *Fuel*, 2007, 86, 1781-1788.
- [59] N. Boukaous, L. Abdelouahed, M. Chikhi, A.-H. Meniai, C. Mohabeer, T. Bechara, *Energies*, 2018, 11, article no. 2146.
- [60] M. Navarro, R. Murillo, A. Mastral, N. Puy, J. Bartroli, AIChE J., 2009, 55, 2700-2715.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Physico-chemical properties of hydrochars produced from raw olive pomace using olive mill wastewater as moisture source

Ahmed Amine Azzaz^{*, a, b}, Mejdi Jeguirim^{a, b}, Evan A. N. Marks^c, Carlos Rad^d, Salah Jellali^e, Mary-Lorène Goddard^{f, g} and Camelia Matei Ghimbeu^{a, b}

 a Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse (IS2M) UMR 7361, F-68100 Mulhouse, France

^b Université de Strasbourg, F-67081 Strasbourg, France

^c CT BETA, Universitat de Vic – Universitat Central de Catalunya, Carrer de la Laura 13, 08500 Vic, Spain

 d Composting Research Group UBUCOMP, Universidad de Burgos, Faculty of Sciences, Pl. Misael Bañuelos s/n, 09001 Burgos, Spain

^e PEIE Research Chair for the Development of Industrial Estates and Free Zones, Center for Environmental Studies and Research (CESAR), Sultan Qaboos University, Al-Khoud 123, Oman

 f Université de Haute-Alsace, Université de Strasbourg, CNRS, LIMA UMR 7042, Mulhouse, France

^g Université de Haute-Alsace, LVBE, EA-3991 Colmar, France

E-mails: amine.azzaz@uha.fr (A. A. Azzaz), mejdi.jeguirim@uha.fr (M. Jeguirim), evan.marks@uvic.cat (E. A. N. Marks), crad@ubu.es (C. Rad), s.jellali@squ.edu.om (S. Jellali), mary-lorene.goddard@uha.fr (M.-L. Goddard), camelia.ghimbeu@uha.fr (C. Matei Ghimbeu)

Abstract. In this study, we assessed the transformation of raw olive pomace into carbon-rich material using olive mill wastewater (OMWW) as the liquid medium for the hydrothermal carbonization (HTC) process. The findings were compared accordingly with the use of distilled water (DW), which is the conventional practice. The use of OMWW as a liquid matrix enhanced the hydrochar yield, but volatile matter, fixed carbon content, and O/C and H/C ratios followed a decreasing trend. Furthermore, for an HTC temperature of 220 °C, the use of OMWW considerably increased the high heating value of the hydrochars from approximately 24.2 MJ/kg to 31.6 MJ/kg. According to the van Krevelen diagram of feedstock and derived hydrochars, dehydration was the predominant carbonization reaction for both liquid sources. Morphological characterization of both sets of hydrochars indicated the generation of specific carbon nuclei when using DW while OMWW led to the creation of hydrochar with a less

^{*} Corresponding author.

homogeneous surface. Structural analysis revealed the heterogeneous aspect of the hydrochar surface with an abundance of crystallized metal-based inorganic salts.

Keywords. Raw olive pomace, Olive mill wastewater, Hydrothermal carbonization, High heating value, Solid characterization, Liquid characterization.

1. Introduction

Over the past few decades, lignocellulosic biomasses have been valorized as precursor materials for energy (heat production), environmental technology (pollutant removal), and agronomic (nutrient recovery) applications [1,2]. The selection of a suitable conversion method for these biomasses depends strongly on the properties of the raw feedstock, the available pretreatment techniques, and logistics and targeted objectives. For instance, biological conversion is very sensitive to feedstock composition since the activity of microorganisms can be inhibited by toxic substances [3]. In addition, these processes require long residence times, resulting in higher volumes and operating costs [4]. On the contrary, the residence time of thermochemical processes varies from minutes to hours and does not rely on microorganisms [5]. This constitutes a significant advantage for the treatment of heterogeneous raw materials (e.g., organic wastes, sewage sludge, etc.).

Among thermochemical processes, slow pyrolysis has the advantage of producing three fractions: liquid (bio-oil) and gaseous (syngas) residues, which can be upgraded to biofuels, and a solid residue (biochar), which can be used in various applications such as soil amendment [6]. However, this solid fraction does not exceed 35%, limiting the economic viability of biochar production [7]. In addition, this process can be energy-intensive when the feedstock biomass has a high moisture content (greater than 70%). This property is common to industrial organic wastes of interest such as agrifood, paper, and woodcrafts. Therefore, a drying step is required [8].

As a consequence, hydrothermal carbonization (HTC) is a promising alternative to the pyrolysis process as it (i) avoids the costly drying step, (ii) reduces energy consumption due to the lower temperature range (180–350 °C) used, and (iii) generates in pressurized water higher yields of carbonrich solid residue, namely, hydrochars (up to 60% on dry basis (db, %)). These carbonaceous materials are biologically and chemically more stable with

a high carbon sequestration potential over decades compared to carbon products generated by slow pyrolysis [9]. Additionally, HTC usually leads to the formation of carbonaceous materials with significant mineral content, interesting concentrations of surface functional groups, and attractive morphological aspects [10]. In fact, hydrochars produced from lignocellulosic materials are characterized by a significant concentration of surface functional groups, which could be exploited either for pollutant uptake by different media or as initial feedstock for the production of high-rank carbonaceous materials. Therefore, and owing to such interesting properties, the use of hydrochars in multiple applications has been considered in other studies. These applications include supercapacitors; synthesis of Li-, S-, and/or Na-ion batteries [11]; CO₂ and H₂ gas storage [12]; soil amendment [13]; and wastewater treatment [9].

Olive oil by-products (raw olive pomace (ROP) and olive mill wastewater (OMWW)) are generated in significant amounts after the milling process. In particular, the Mediterranean region contributes to the annual generation of about 12.2 Mt solid ROP and 30 Mm³ OMWW [14]. In various countries, these wastes are usually discharged into natural water bodies, causing severe damage and threat to the ecosystem as well as being a source of social malaise [15,16]. The sustainable management of these wastes has emerged as an urgent challenge for the purpose of not only protecting the environment but also exploiting the energetic, environmental, and agronomic potential of these organic wastes [17–21].

The HTC of ROP wastes has been tested at the laboratory scale under various experimental conditions [22–25]. The main aims of these investigations were to (i) understand the synthesis of valuable syngas, (ii) test the pretreatment of biomasses leading to carbon materials with high energetic properties, and (iii) explore the generation of interesting surface characteristics for application as adsorbents in liquid or gaseous media. All these studies have used distilled water (DW) as the moisture source during the HTC process. In the current paper, in a novel application, OMWW is used as the liquid source for the ROP wastes. This new approach takes advantage of the huge amount of organic matter as well as minerals present in OMWW for a possible enhancement of the physico-chemical properties of the derived hydrochars. Therefore, the main objective of this work is to investigate OMWW as a liquid medium for the carbonization of ROP and to analyze its effect on hydrochar properties. This study includes an in-depth physico-chemical characterization comprising various complementary analyses. Such an understanding of the material properties is crucial to their ultimate application in agriculture in the form of fertilizers as well as efficient adsorbents of organic and mineral pollutants.

2. Materials and methods

2.1. Raw feedstock: ROP and OMWW

In this study, the ROP and OMWW were collected from a three-phase olive mill located in the city of Touta in North East Tunisia. The ROP was placed in airtight bags and aired periodically at ambient temperature. The liquid waste was kept in glass bottles during the experimental campaigns and was stored at 4 °C.

2.2. HTC experiments

The HTC experiments were performed in the presence of DW and OMWW as liquid sources. In these experiments, a solid-liquid mixture was prepared at a 1:9 ratio, corresponding to 1 g of ROP and 9 mL of the moisture source (DW or OMWW) and was placed in a 100 mL bomb calorimeter (Top Industrie, Vauxle-Pénil, France). In accordance with typical experimental conditions, the calorimeter vessel was sealed hermetically, heated at a 10 °C/min rate using a programmable stove (Memmert, Schwabach, Germany), and kept for an isotherm period of 24 h at the three designated experimental temperatures of 180, 200, and 220 °C. The experimental conditions were chosen according to an optimization study presented in our previous papers, where HTC was performed in autogenous inner pressure atmosphere [9,10]. The hydrochars produced were accordingly named as follows: T-ROP and T-ROP + OMWW when using DW and OMWW as the moisture source, respectively, where T is the process temperature (°C). After carbonization, the by-product was filtered using a vacuum pump through 0.45 µm Whatman[®] filter paper (VWR, Leuven, Belgium). The recovered solid fraction was dried overnight at 105 °C and then weighed and stored in a glass flask for later characterization. The liquid fractions were also recovered. They were filtered twice using 0.2 µm polypropylene syringe filters (VWR, Leuven, Belgium) and then stored in 10 mL glass vials at 4 °C. All experiments were performed in triplicate. Statistical analyses were conducted using R v3.6.1 [26]. An analysis of variance (ANOVA) of each testable parameter was carried out to establish differences between treatments, and then Tukey multiple comparisons (post hoc) were made using multcomp::glht.

2.3. Hydrochar characterization

2.3.1. Solid yield determination

To determine the solid yield (Y_{HC} , %), two methods were applied according to the liquid source used. In the case where DW was used as the carbonization medium, the final solid yield was calculated as follows:

$$Y_{\rm HC}(\%) = m_{\rm HC}/m_{\rm FS} \times 100.$$
 (1)

On the other hand, the use of OMWW implies the addition of further organic matter to the carbonization medium, which should be taken into account according to (2):

$$Y_{\rm HC}(\%) = m_{\rm HC} / (m_{\rm FS} + m_{\rm S,OMWW}) \times 100,$$
 (2)

where $m_{\rm HC}$ (g) is the dry solid mass recovered after carbonization, m_{FS} is the initial feedstock mass (g), and $m_{S,\rm OMWW}$ is the solid fraction present in the OMWW estimated as 7.9% (db, %) according to the TAPPI/ANSI T 412 om-16 method [27]. The resulting solid fraction is the subject of later solid-phase chemical characterizations.

2.3.2. Proximate and ultimate analysis

Proximate analysis was performed to determine fixed carbon, volatile matter, and ash contents of the hydrochars. The thermogravimetric analysis (TGA) procedure that was applied was described in our previous studies [10]. A Flash 2000 CHNS-O Elemental Analyzer (Thermo Fisher Scientific, Cambridge, UK) was used to determine the elemental composition. Furthermore, the mineral composition of ROP, OMWW, and the derived hydrochars was determined using multiple extraction methods. The total nitrogen contents were determined according to the modified Kjeldahl method (ISO 1995). Soluble contents of K⁺, Na⁺, Mg²⁺, Ca²⁺, N-NH₄⁺, and soluble phosphorus were assessed according to the analytical method described by Thomson and Leege [28].

2.3.3. Morphological and structural properties

A high-resolution scanning electron microscopy (SEM) analysis was performed using a Philips XL30 microscope coupled with an energy-dispersive X-ray spectroscope (EDS; Oxford Instruments, Oxfordshire, UK) to determine the atomic composition of the hydrochars. Powder X-Ray diffraction (XRD) was employed to identify the crystalline phases in the prepared hydrochars. It was carried out by a PANalytical X'Pert powder diffractometer (Malvern, UK) equipped with a copper anode. Phase identification was conducted using the database from the International Center for Diffraction data (Crystallography Open Database; Graulis *et al.* [29]) on the PANalytical HighScore software.

2.3.4. Bulk and surface chemistry

The bulk quantitative characterization of the hydrochars produced was performed by two methods. First, pH at zero-point charge (pH_{ZPC}) was determined to gain an overall idea of the dominating surface charge. Then, acidic groups were quantified using the Boehm titration method. Both methodologies are described thoroughly in the literature [30]. Second, the surface chemistry was analyzed using a spectroscopic method (Fourier transform infrared (FTIR)). The FTIR spectra were acquired by an Equinox 55 Bruker spectrometer (Ettlinger, Germany). For each sample, an exact biocharto-KBr mass ratio of 1/200 was ground in a mortar and pressed into a 1 cm diameter disk at a pressure of 3.5 tons. The disk-like sample was then analyzed at a spectral resolution of 4 cm^{-1} , which was measured between 4000 and 400 cm^{-1} .

2.3.5. Energy contents

The energy contents of the raw feedstock and the derived hydrochars were assessed by determining

the higher heating value (HHV) and the lower heating value (HHV). The HHV (MJ/kg) is defined as the amount of energy released by the complete combustion of a fuel unit, where the water vapor is assumed to be condensed and the heat recovered. The HHV (MJ/kg) is related to the energy released during the combustion of a solid without taking into account the energy of water condensation [10]. Analyses were performed using an IKA C 200 bomb calorimeter (Staufen, Germany) according to DIN 51900 in the isoperibolic reaction mode. The LHV was calculated on the basis of the values of the HHV and the percentages of moisture and hydrogen (at dry base).

2.4. Liquid characterization

The quality of the final liquid medium after HTC was assessed by determining the chemical oxygen demand (COD, g O_2/L). The dichromate titrimetric method was used according to the protocol given by Moore *et al.* [31].

The organic composition of the process water after HTC was determined by gas chromatography coupled with mass spectrometry (GC-MS). The equipment used consists of a GC-2010 gas chromatograph coupled with a GC-QP2010 mass spectrometer (Shimadzu, Tokyo, Japan). After filtration on 0.2 µm regenerated cellulose syringe filters, samples were diluted 10 times in ultra-pure water (resistivity 18.0 $\mu\Omega$ ·cm). As internal standard, 50 μ L of 10 μ g/mL phenoxyacetic acid aqueous solution was added to 30 µL of the diluted solution; then, the samples were freeze-dried. Afterward, they were chemically derivatized and immediately analyzed by GC-MS as stated by Jeguirim et al. [17]. The peak assignment was carried out using an internal compounds' library as well as by the mass spectral library NIST 17.

3. Results and discussion

3.1. Carbonization yield

The effect of temperature and variation in the carbonization medium on the final hydrochar yield is presented in Figure 1. The carbonization of ROP in water and in OMWW at increasing temperatures led to a progressive decrease in the final yields of hydrochars. In fact, the hydrochar percentage decreased from 54.90% to 37.50% and from 41.87%



Figure 1. Final solid yields of the hydrochars derived from ROP in the presence of distilled water and OMWW as carbonization media at different temperatures (reported error is standard deviation).

to 31.37% when the carbonization temperature increased from 180 to 220 °C for ROP + DW and ROP + OMWW, respectively. This loss of solid mass with increasing temperature is attributed to the degradation of the lignocellulosic matrix of both materials as the temperature increases. Moreover, higher temperatures induce major modifications in the moisture state inside the reactor, favoring the conversion of the biomass [32]. It is also seen that the type of liquid matrix significantly affects the hydrochar production yields. Here, at carbonization temperatures between 180 and 220 °C, the degradation rate of ROP in the solid fraction decreased from 17.5% to 10.5% when using DW and OMWW as moisture sources, respectively. Similar findings were reported by Li et al. [33] when studying the impact of liquid wastes on the HTC of different municipal wastes. In fact, reported results suggest that the carbonization of yard waste in the presence of landfill leachate containing significant contents of organic matter as the moisture source enhanced the dewaterability of solids as a function of time and decreased the recovery of the final solid fraction.

3.2. Proximate, ultimate, and elemental analyses

3.2.1. Proximate and ultimate analyses

Proximate analysis was performed for ROP and the produced hydrochars in the presence of DW and OMWW, respectively. The results depicted in Figure 2



Figure 2. Proximate analysis for ROP, OMWW's solid fraction, and derived hydrochars in the presence of distilled water and OMWW as carbonization media at different temperatures (reported error is standard deviation).

show that ROP is characterized by a high content of volatile matter (66%) with relatively low percentages of fixed carbon and ash of 20% and 14%, respectively. On the other hand, OMWW contains volatile matter, fixed carbon, and ash of approximately 84%, 6% and 10%, respectively [10]. When using DW, the produced hydrochars exhibit a decrease in volatile matter content from 64% to 49% for 180-ROP and 220-ROP, respectively. On the other hand, a significant increase in the fixed carbon content is observed, ranging from 28% to 41% for the same samples. This observation is attributed to the effect of temperature increase on the recombination and the polymerization of the light volatile matter into more condensed carbon content. Similar findings were reported by Missaoui et al. [22] when investigating the HTC of olive pomace at different temperatures. In this case, the volatile matter content decreased from 71.6% to 61.0% and the fixed carbon increased from 23.6% to 36.2% at treatment temperatures between 180 and 250 °C, respectively.

Conversely, the addition of OMWW as the moisture source for the carbonization of ROP did not enhance the quality of the final hydrochars. In fact, despite the increase in fixed carbon content of approximately 8%, the volatile matter contents remained relatively high and varied between 68% and 62% at carbonization temperatures between 180 and 220 °C, respectively (Figure 2). These results confirm that the slight decrease in the hydrochar yields when OMWW is added instead of DW is due to the difference in the volatile matter content (see Figure 1). The results suggest that the high content of volatile matter in both ROP and OMWW led to a decrease in their conversion rate into more stable carbon content. It is worth mentioning that in both cases, when using either DW or OMWW, the ash contents decreased with increasing temperature compared to that of the solid feedstock (Figure 2). Indeed, compared to ROP, these contents decreased by approximately 4% and 8% for an HTC temperature of 220 °C in the presence of DW and OMWW, respectively. Similar studies investigating the HTC of olive pomace suggested that an increase in treatment temperature enhances the ash content as minerals are more likely to be incorporated into the rearranged and more stable aromatic structure [22]. In our current study, it is possible that the degradation of the ROP as well as the physico-chemical properties of OMWW resulted in the production of highly scouring molecules, which contributed to the degradation of the lignocellulosic matrix and the release of minerals and organic contents from the solid fraction.

To have a clearer idea about the significance of the previous results, statistical tests were performed on the reported parameters (Figure S1-b). Regarding ash contents, there were generally no large or statistically significant differences between the measured samples. However, volatile matter—which was highest in the OMWW—showed a decreasing trend in values with increase in HTC temperature for both T-ROP and T-ROP + OMWW samples (Table 1). As expected, fixed carbon exhibited the exact opposite trends to those of volatile matter. It was lowest in OMWW and increased with treatment temperature (Figure S1-b).

Ultimate analysis was performed for ROP feedstock as well as the resulting hydrochars and the solid fraction of OMWW. The results are shown in Table 2. Initially, the ROP had percentages of carbon and oxygen of about 43% and 47%, respectively, which are similar to the majority of lignocellulosicbased feedstocks reported in the literature [34]. As for the solid fraction of OMWW, carbon and oxygen contents were 57% and 32%, respectively. When the carbonization temperature was increased for both moisture sources, an increase in C and a decrease in O percentages were observed. In fact, when using DW, C% increased from 43% to 64% and O% decreased from 47% to 27% for ROP and 220-ROP samples, respectively. On the other hand, this modification was further intensified when adding OMWW to the carbonization media as carbon and oxygen percentages for 220-ROP + OMWW were 68% and 20%, respectively. Nevertheless, the observed modifications in the H and N contents of the raw and carbonized materials were found to be low, with a maximum variation of $\pm 2.37\%$ and $\pm 1.02\%$, respectively. Such behavior could be ascribed to two synergistic effects. (i) Owing to its high carbon (Table 2) content, OMWW could have contributed to the impregnation of a small fraction of volatile organic compounds into the ROP. An increase in the carbonization temperature resulted in the condensation of the added carbon, which enhanced the final carbon content compared to the use of DW. (ii) The high acidity of the OMWW accelerated the defragmentation of cellulose and hemicellulose, which resulted in a noticeable reduction in the oxygen percentage.

3.2.2. NPK analysis

One of the most important methods for the characterization of hydrochars is the determination of their content in macroelements for eventual application in agriculture. As shown in Table 3, ROP is characterized by a total nitrogen, soluble phosphorus, and potassium (NPK) content of approximately 13.2 g/kg. When the HTC is performed at increasing treatment temperatures in the presence of DW, different tendencies in mineral concentrations were found. For instance, the potassium and sodium contents decreased from 6100 to 950 mg/kg and from 580 to 136 mg/kg for ROP and 220-ROP, respectively. Similarly, hydrochar contents of phosphorus and magnesium reduced considerably from 118 to 9 mg/kg and from 175 to 119 mg/kg for the same samples, respectively. However, an opposite trend was detected for the calcium content as it apparently increased from 560 to 860 mg/kg for ROP and 220-ROP, respectively. On the other hand, the hydrochars produced with OMWW as the carbonization medium showed the same global tendency in terms of mineral composition. Here, the global NPK soluble content decreased from 13.16 to 6.77 g/kg for ROP and 220-ROP + OMWW, respectively.

In contrast, a significant increase in the potassium contents was observed from 6100 mg/kg for ROP to 8000 and 9000 mg/kg when carbonization was carried out in the presence of OMWW at 180 and 200 °C,

Parameter	DF	Sum sq.	Resid. DF	Resid. sum sq.	F	Sig.
Solid yield	5	1040	12	17	143.4	***
Ash	7	113	16	71	3.6	*
Volatile matter	7	2086	16	42	111.2	***
Fixed carbon	7	2235	16	130	39.2	***
Phenolic	7	217088	16	76361	6.5	***
Carboxylic	7	232293	16	39230	13.5	***
Lactonic	7	681354	16	6403	243.2	***
pH_{ZPC}	7	13.7	16	0.8	40.7	***

Table 1. ANOVA table for study parameters with degrees of freedom (DF), sum of squares, residuals, *F*-test value, and significance

Significance codes are as follows: p < 0.0001, "***"; p < 0.05, "*".

Table 2. Ultimate analysis (wt.%) of the ROP, OMWW's solid fraction, and derived hydrochars in the presence of distilled water and OMWW as carbonization media at different temperatures

Samples	С	0	Η	Ν	S
	(%)	(%)	(%)	(%)	(%)
ROP	42.80	46.51	5.65	2.01	0.23
OMWW*	56.75	31.74	7.90	2.72	0.22
180-ROP	56.13	34.91	5.91	0.99	0.12
200-ROP	62.58	28.00	5.89	1.37	0.13
220-ROP	64.37	26.76	5.47	1.27	0.14
180-ROP + OMWW	62.73	25.19	8.02	1.88	0.18
200-ROP + OMWW	64.98	23.86	7.26	1.63	0.16
220-ROP + OMWW	67.90	20.24	7.64	1.86	0.07

*Analysis performed on the solid fraction of OMWW.

respectively (Table 3). The highest mineral content was found for the sample 200-ROP + OMWW with an estimated total of 11.851 g/kg. Although all the recovered hydrochars had a lower mineral content compared to the solid fraction of OMWW (total mineral content of 70.5 g/kg), they are still characterized by larger carbon contents and lower volatile matter. These properties could be beneficial in both energetic and agricultural applications [10].

When studying the fate of minerals in the solid fraction after HTC, controversial explanations and findings are encountered in the literature. The HTC of biomass is characterized by a very complex pro-

reactions, which depends mainly on the process temperature as well as the pH of the medium. Although the first parameter is permanently controllable, the solution acidity is contingent on the highly variable physico-chemical properties of the feedstock. Therefore, the impact of tuning these two parameters on the final mineral composition is relatively unpredictable. For instance, Chen et al. [35] reported an increase in nitrogen and phosphorus and a decrease in potassium solid concentrations with increase in carbonization temperature when the liquid pH varies between 3.52 and 4.83. The increase in solids in acidic media was ascribed to a possible deposition of soluble minerals on the hydrochar during the recombination reaction. Similarly, Smith et al. [36] reported an increase in the mineral composition of hydrochars produced from willow wood at two different temperatures. When the HTC is increased from 200 to 250 °C, they demonstrated an enhancement in magnesium, phosphorus, and calcium concentrations of approximately 11%, 31%, and 15%, respectively, while the potassium content decreased by about 46%. Conversely, Huang et al. [37] reported that the increase in the HTC temperature significantly reduced the presence of minerals in the final hydrochars produced from the cocarbonization of pine sawdust and plastic polymer granules. In fact, significant leaching of calcium, magnesium, potassium, and sodium in the liquid fraction was noted at the rates of 98.59%, 97.66%, 92.32%, and 87.43%, respectively, following the conversion of raw sawdust to hydrochar at 260 °C. The authors suggested that an increase in the carboniza-

cess that involves both synergistic and antagonistic

Samples	K	Na	Ca	Mg	Р	N _{Total}	Sum of minerals
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
ROP	6100.00	580.00	560.00	175.00	118.00	6950.00	14483.00
OMWW*	44000.00	3700.00	1421.00	1744.00	2034.00	17600.00	70499.00
180-ROP	1350.00	148.00	606.00	116.00	81.30	7330.00	19901.30
200-ROP	1650.00	156.00	438.00	103.00	52.20	7930.00	10329.20
220-ROP	950.00	136.00	860.00	119.00	9.21	9260.00	11334.21
180-ROP + OMWW	8000.00	620.00	283.00	347.00	110.00	1370.00	10730.00
200-ROP + OMWW	9000.00	840.00	293.00	448.00	50.80	1220.00	11851.80
220-ROP + OMWW	1450.00	148.00	22.10	11.40	31.40	5290.00	6952.90

Table 3. Elemental composition (wt.%) of ROP and hydrochars produced from HTC in the presence of distilled water and OMWW at different temperatures

*Solid fraction of OMWW.

tion temperature led to an acceleration in the autoionization of the water molecule toward an abundance of hydronium (H_3O^+) concentration in the media. It was presumed that H_3O^+ ions catalyzed the solubilization of the salts embedded in the lignocellulosic materials and their recovery in the liquid fraction.

Another observation that must be highlighted is the abrupt decrease in the contents of some minerals when the carbonization temperature increases from 200 to 220 °C for both media. As an example, in the case where OMWW is the moisture source, potassium, sodium, and calcium decreased by about 84%, 82%, and 92%, respectively. These minerals are generally incorporated into the biomass as part of their lignocellulosic matrix. According to the TGA results (Supplementary material, Figure S2), the degradation of cellulose and hemicellulose most likely started in the temperature range between 200 and 230 °C. The degradation of polymers led to the widening of matrix pores and then the liberation of the minerals from solid to liquid and gaseous phases.

3.3. Energy contents

Calorific measurements are considered as an important method for investigating the quality of the hydrochars produced. According to the results presented in Table 4, the ROP's HHV and LHV are 14.73 and 13.39 MJ/kg, respectively, which are similar to those of common biomasses such as eucalyptus wood (16.26 MJ/kg; Elaieb *et al.* [38]) and

chestnut shell (15.49 MJ/kg; Özçimen and Ersoy-Meriçboyu [39]). The HHV of the OMWW solid fraction is 26.55 MJ/kg. Increases in the process temperature of the ROP HTC in the presence of either DW or OMWW significantly increased its HHV and LHV. Indeed, the highest HHV and LHV values are shown for an HTC temperature of 220 °C (LHV 29.88 and HHV 31.62 MJ/kg) when DW and OMWW, respectively, are used as the moisture media. Thus, the use of OMWW instead of DW permits the production of hydrochar with an improved HHV (about 6% higher). The increase in calorific capacity is generally attributed to the significant increase in the O/C ratio for both liquid media [9]. Nevertheless, it has been reported that the increase in moisture acidity enhanced the final HHV of hydrochars. In fact, cellulose and hemicellulose are generally characterized by low calorific capacities (17.28 MJ/kg and 16.81 MJ/kg, respectively; Zhao et al. [40]). These were transformed into more stable components with lower oxygen contents when hydrothermally carbonized at low pH values [41]. The condensation and the repolymerization of the generated by-products lead to the formation of bitumen-like and humic-acid-like materials, which end up readhering to the highly calorific lignin matrix (25.51 MJ/kg; [40]). This hardly occurs at a carbonization temperature of 220 °C.

According to the literature, various possible mechanisms could be involved during the HTC of biomasses into hydrochars such as deamination, dehydrogenation, demethylation, deoxygenation, dehydration and/or decarboxylation [42,43]. To pre-

Samples	ROP	OMWW*	180-ROP	200-ROP	220-ROP	180-ROP +	200-ROP +	220-ROP +
						OMWW	OMWW	OMWW
HHV (MJ/kg)	14.73	26.55	22.80	24.06	24.21	27.74	29.58	31.62
LHV (MJ/kg)	13.39	24.76	21.43	22.70	22.94	25.91	27.92	29.88

Table 4. Calorific quantities for ROP and derived hydrochars in the presence of distilled water and OMWW as carbonization media produced at different temperatures

*Solid fraction of OMWW.

dict the possible mechanism, a van Krevelen diagram depicting the O/C versus H/C atomic ratios is presented in Figure 3. The atomic ratios corresponding to ROP suggest that long-chain polysaccharides such as cellulose and hemicellulose are its major components [44,45], which is further confirmed by its similarity to a pure cellulose composition (Figure 3). The increase in the carbonization temperature of ROP from 180 to 220 °C in the presence of water caused a decrease in both O/C and H/C ratios from 0.45 to 0.30 and from 1.26 to 1.02, respectively (Figure 3). A similar tendency was observed when OMWW was used as the moisture source since O/C and H/C ratios decreased from 0.28 to 0.22 and from 1.52 to 1.35 for the same carbonization temperatures, respectively. Moreover, it could be remarked that in the presence of OMWW, hydrochars exhibited higher H/C and lower O/C ratios compared to those produced using DW. It is possible that the addition of OMWW enhanced the organic charge as well as the acidity of the media by increasing the proton concentrations in the solution and subsequently on the surface of the carbonaceous materials, which explains the difference in H/C ratios. According to the evolution of H/C and O/C atomic ratios, it could be suggested that dehydration is the dominating mechanism for the HTC of ROP in the presence of DW or OMWW. This indicates the cleavage of surface functional groups of ROP in acid-catalyzed media, yielding water as the main carbonization by-product [46].

3.4. Morphological and structural properties of hydrochars

3.4.1. Morphological properties

The morphological structure of ROP after HTC with different liquid media was assessed using SEM imaging coupled with EDS analysis. Initially, ROP

C. R. Chimie, 2020, 23, nº 11-12, 635-652

presented a rough and kinky surface with no significant porosity (Figure 4). After HTC, the resulting solids showed significantly different structural characteristics. In fact, in the presence of DW, the ROP-derived hydrochars were sphere-like carbon structures of different diameters. According to SEM images, the sphere diameter varies between 0.49 and 1.69 µm for 180-ROP; 57% of these particles have a diameter between 0.67 and 0.84 µm (Figure 4). It has been reported that these structures possess an internal solid and porous morphology [50], where their size depends mainly on the carbonization temperature and time [51]. The formation mechanism of these spheres could be attributed to the degradation of hexose and pentose present in the lignocellulosic material at increasing temperatures through a dehydration reaction. The degradation of these two monosaccharides leads to the formation of 5hydroxymethylfurfural (5-HMF) and furfural, respectively. Studies suggest that for an extended reaction time where high temperatures are maintained, these organic compounds are polymerized and highly aromatized, which eventually allows the carbon to condense in the form of microspheres [49,52]. When the carbonization temperature is increased, the spherical structures become less obvious on the surface of the hydrochar at 200 °C with a relatively lower diameter varying between 0.14 µm and 1.11 µm until disappearing at 220 °C. It is worth noting that the hydrochar produced at 220 °C presented a similar apparent characteristic compared to the ROP with a very heterogeneous surface and without a porous structure.

On the other hand, the carbonization of ROP at increasing temperatures in the presence of OMWW resulted in a very different hydrochar morphology. At 180 °C, the hydrochar produced was characterized by deformed sphere-like particles. It appears that the addition of OMWW, which is more acidic than DW (pH = 4.86), affected the proper formation of the car-



Figure 3. Van Krevelen diagram for ROP and derived hydrochar produced at various temperatures in the presence of distilled water and OMWW versus carbonaceous materials present in the literature [47–49] (reported error is standard deviation).

bon spheres as compared to the use of DW. Similar results were described by Liang *et al.* [53] when performing the HTC of starch at different pH values of process water. They found that the carbonization of starch at a pH of 1 reduced significantly the growth of the carbon nanospheres compared to a solution pH varying between 3 and 7.

According to the LaMer model related to the nucleation-growth mechanism, the development of these particles is achieved when soluble polymers derived from the degradation of the cellulose and hemicellulose reach a certain saturation point and start segregating from the liquid medium [54]. The diffusion of these species through the solid is mainly ensured by the oxygen functional groups present on the surface, leading to the growth of carbon nuclei with a hydrophilic shell and a hydrophobic core [9]. However, the presence of strong acids at significant concentrations in the process water could change the dominating surface charge and composition and inhibit the diffusion of some oxygen functional groups through the solid either by complexation or electronic repulsion, thereby stopping the growth of carbon nuclei (180-ROP + OMWW; Figure 4) [52]. This could also explain the aspect of ROP and ROP + OMWW produced at 200 and 220 °C, as an increase in carbonization temperature has been known to increase the production of organic acids that hinders the diffusion of soluble free entities such as hydroxyl and carbonyl groups inside the hydrochar matrix [53].

The modification of the moisture source and the process temperature has an impact on the mineral composition of the hydrochars as well. Initially, EDS cartography related to ROP show a uniform partition of carbon and oxygen (Figure S3-a). For both moisture sources, EDS cartography suggest an increase in the carbon partition with increasing carbonization temperature (Figure S3). Moreover, a large variety of minerals are detected in the form of a homogeneous partition for the case of sodium, magnesium, potassium, and phosphorus, while some other elements such as silica, sulfur, and calcium exhibit a certain agglomerative property. When the carbonization temperature is increased and when the moisture source is modified, the carbon contents increase while oxygen constantly decreases due to the condensation of organic matter driven by dehydration mechanisms (Figure S3). Furthermore, mineral content appears to be highly affected by the increase in carbonization temperature as the general tendency suggests a significant decrease until the disappearance of certain minerals at an HTC process temperature of 220 °C. Such behavior is attributed to the combined impact of increasing temperature and solution acidity, which contributes to the release of minerals from the solid fraction [55]. These observations are in agreement with the elementary and proximate analyses.

3.4.2. Structural properties

In the presence of DW or OMWW, the impact of the HTC process on the structural properties of



Figure 4. SEM images of (a) ROP and derived hydrochars using (b–d) distilled water and (e–g) OMWW as carbonization media produced at 180, 200, and 220 °C, respectively, and the spherical particle size distribution for (h) 180-ROP and (i) 200-ROP.

the hydrochars produced was examined using the XRD technique. First, ROP showed a diffractogram typical of a lignocellulosic material with an amorphous cellulose I broad peak at 22.6° (2 θ) [30] as well as the existence of some minerals in crystalline form such as SiO₂, CaC₂O₄, CaCO₃, and KCl. After increasing the carbonization temperature up to 200 °C, no major modifications in the organic skeleton were noted. This suggests that the cellulosic structure was preserved (Figure 5). Moreover, peaks related to calcite (CaCO₃; at 32.35°, 36.40°, and 38.38° (2 θ)) disappeared, while others corresponding to calcium phosphate (Ca₃[PO₄]₂) emerged. This could be attributed to a rearrangement reaction as

calcium oxalate is usually found in lignocellulosic materials as monohydrates and dihydrates in a rare form [56]. It is presumed that H_2O molecules coordinate the crystalline structure between oxalate and calcium ions [57]. Therefore, the attenuation of calcium oxalate peaks along with other calciumbased crystals could be related to the dehydration reaction driving the carbonization process of ROP. When the carbonization temperature is further increased to 220 °C, the peak at 22.6° (2 θ) disappears, which suggests that the degradation of the cellulose in ROP takes place between 200 and 220 °C, confirming the reported TGA findings (Figure S2). Similar observations were made by Zhang *et al.* [58]



Figure 5. XRD diffractograms for the ROP and its derivative hydrochars in the presence of (a) distilled water and (b) OMWW as moisture sources at different hydrothermal carbonization temperatures.

when studying the HTC of corncob residues at different temperatures. They suggested that the cellulosic structure of the feedstock reached its integrity limit at 230 °C.

On the other hand, the use of OMWW as a carbonization medium accelerates the degradation process of the cellulose even at relatively low temperatures (Figure 5). The OMWW has a structure similar to that of the ROP with the exception of the characteristic cellulose I peak, where a slight shift is seen from 22.6° to 19.6° (2 θ), respectively. Despite the fact that this peak is attributed to the same amorphous structure as that which is present for ROP, the OMWW peak slightly precedes the ROP peak, which suggests a possible alteration in the hemicellulose structure related to the milling process. When the HTC is carried out at 180 and 200 °C, a small decay is noted at



Figure 6. FTIR spectra for ROP and derived hydrochars when using (a) distilled water and (b) OMWW as carbonization media produced at different temperatures.

19.6° (2 θ) related to the cellulosic fraction of OMWW. Moreover, when OMWW is used instead of DW, it can be clearly seen that the amorphous cellulose structure of ROP hydrochars becomes less relevant. Owing to its high acidity, the OMWW seems to accelerate the decomposition of cellulose into more amorphous forms.

3.5. Surface chemistry of hydrochars

To assess the impact of modifying the carbonization media on the surface chemistry of ROP and its derived hydrochars produced at different temperatures, a set of three characterization techniques were employed: FTIR, Boehm titration, and surface pH_{ZPC}.

The FTIR spectra of the feedstocks and their respective hydrochars produced at different temperatures are presented in Figure 6. The results suggest that the initial biomass and derived hydrochars possess a rather heterogeneous surface with multiple



Figure 7. Acidic functional groups and surface pH_{ZPC} of the ROP and the hydrochars produced from the HTC at different temperatures in the presence of distilled water and OMWW (reported error is standard deviation).

acidic and basic functional groups. For both cases, when DW or OMWW is used as the carbonization medium, common functional groups could be found: hydroxyl (–OH; 3600–3200 cm⁻¹), aliphatic (C–H; 3000–2700 cm⁻¹), carbonyl and acetyl esters (C=O and C–O stretching vibrations, respectively; 1650–1600 and 1180–980 cm⁻¹), methyl and methylene aromatic groups (–CH₂/–CH₃; 1465–1320 cm⁻¹), cellulose carbonyl (C–O–C symmetric stretching; 1160–1110 cm⁻¹), and out-of-plane aromatic groups (C–H; 896–809 cm⁻¹). After carbonization, various differences were observed.

After DW was employed, peaks corresponding to hydroxyl groups decreased in intensity with increase in carbonization temperature. It has been reported that this decrease indicates the tendency of the HTC toward dehydration [49]. An increase in the peak shift from -19 to -33 cm⁻¹ was detected when the carbonization temperature was increased between 180 and 220 °C, related to a vibration of the C=O hemicellulosic aromatic structure. Similar behavior was noted for aromatic C=C functional groups, where the related peak shifted by -16 to -18 cm⁻¹ for the same treatment temperatures. This could be attributed to stretching in the aromatic skeleton of the lignin matrix [59]. Some deformations could also be ascribed to -CH₂/CH₃ and carbonyl C-O aromatic groups as they shifted by +4 and +11 cm⁻¹ for ROP and 220-ROP, respectively.

In the case where OMWW was used as the mois-

ture source, similar tendencies were observed as the peak intensity of the O-H hydroxyl group decreased significantly until almost disappearing for the 220-ROP + OMWW sample (Figure 6). However, careful inspection of the peaks revealed a stabilization of the location of C=O, C=C, and -CH₂/-CH₃ functional groups. This result is in agreement with the outcome of the nucleation reaction as in the presence of OMWW, the ROP depolymerized structure fails to form any carbon nuclei (Figure 6b). In fact, the formation of carbon spheres is linked to a phenomenon of dehydration of specific polymers, namely, hemicellulose and polysaccharides, as this reaction implies a reduction in O/C and H/C ratios [49]. The diffusion of carbonization by-products with increasing temperature rate induces the rearrangement of condensed carbon in the form of benzene rings, which form stable groups with oxygen in the nucleus (e.g., ether, guinone, and pyrone). Moreover, the shell is composed of reactive oxygen hydrophilic functionalities (e.g., hydroxyl, carbonyl, carboxylic, and ester; Li et al. [52]).

To further understand the modification kinetics of the surface functional groups, Boehm titration and pH_{ZPC} techniques were carried out for the raw and carbonized solids. The results are shown in Figure 7. ROP had significant contents of acidic functional groups; a large content of phenolic and carboxylic groups and a low content of lactonic groups were present. When the HTC of ROP was conducted in the presence of DW, a slight increase in the concentration of phenols was detected from 594 to 661 µmol/g for ROP and 180-ROP, respectively. Moreover, carboxylic functional group contents decreased from 394 to 313 µmol/g for the same samples, respectively (Figure 7). When the carbonization temperature was increased, opposite trends were observed as concentrations of phenolic groups decreased by approximately 30% and carboxylic functionalities increased by 67% for the carbonization reaction between 180 and 220 °C, respectively (Figure 7). On the other hand, the content of lactonic groups increased by more than sixfold when the raw material was carbonized to 220 °C, which is attributed to the effect of degradation of cellulose on the formation of highly acidic functional groups. When OMWW was added to the carbonization media, similar outcomes were noted in terms of increase in the carboxylic group concentrations and a decrease in the phenolic groups. However, the content of lactonic groups increased remarkably from 190 to $556 \,\mu mol/g$.

From a statistical point of view, lactonic functional groups were practically absent in the feedstocks, but increases in HTC temperature had the strong effect of increasing these groups together with a very significant increase in 220-ROP – OMWW (Table 1; Figure S1-c). Carboxylic group density also appeared to be increased with temperature, whereas the highest densities were found not only in the 220 °C hydrochars but also in OMWW. Among phenolic groups, there appeared to be a trend toward decreased densities with increase in carbonization temperature (Table 1; Figure S1-c).

Such behavior could explain the tendency of the solid pH_{7PC} (Figure 7) where it constantly reduced with increasing carbonization temperature. The ROP had the highest value, which was statistically different from all other materials. The OMWW and hydrochars all had lower and similar pH_{ZPC} values, whereas this decreased with temperature (Figure S1-d). In fact, it decreased from 5.84 to 3.98 for ROP and 220-ROP, respectively. When OMWW was added, solid pH_{ZPC} varied from 5.84 to 3.32 for these samples, respectively. Therefore, it could be suggested that the enhancement of surface acidity was driven by both the effect of the acidic moisture source and the generation of highly protonated entities that contributed to the modification of the surface charge by adsorption, diffusion, or ion-exchange reaction between the solid and liquid fractions. In fact, a possible elimination of hydroxyl groups could be behind the relative stability of the final liquid pH, whereas it changed from 4.53 to 4.77 for 180-ROP + OMWW and 220-ROP + OMWW, respectively.

3.6. Liquid characterization

C. R. Chimie, 2020, 23, nº 11-12, 635-652

The characterization of the liquid fraction at the end of the HTC could be considered as an important parameter for understanding the ROP's degradation mechanism. This information is valuable when considering the possible application of ROP in agriculture. Although the reuse of the final process water in the irrigation of plants is economically very advantageous, it could pose some undesirable physicochemical hazards, leading to the irreversible alteration of soils and crops.



Figure 8. Chemical oxygen demand of the final liquid fraction (bio-oil) after the HTC of ROP in the presence of distilled water and OMWW at different temperatures (analysis performed in duplicate: n = 2; reported error is standard deviation).

The quality of the final process water has been assessed by studying the evolution of COD. The corresponding results are shown in Figure 8. When the carbonization of ROP in DW is carried out, a release of organic molecules is observed with increasing temperature since COD contents are 14.25, 17.85, and 17.55 g O_2/L for treatment temperatures of 180, 200, and 220 °C, respectively (Figure 8). This confirms our previous suggestion regarding the migration of soluble organic compounds such as fatty acids and phenols from the solid phase to the liquid fraction at increasing carbonization temperatures. These values are noticeably higher in the presence of OMWW since they reach 54.60, 64.05, and 64.20 g O_2/L for the same temperatures, respectively. Nevertheless, these COD concentrations are approximately 53% to 62% of the original OMWW content (103 g O_2/L). It is possible therefore that a significant fraction of the OMWW organic content has been incorporated into the ROP lignocellulosic matrix. This content is involved in the degradation mechanism during the HTC of the ROP. A similar outcome was noted by Li et al. [33] when studying municipal waste HTC in the presence landfill leachate.

To obtain proper information about the degradation mechanism of the feedstock in the presence of different moisture sources, a GC–MS analysis of final liquids was carried out following the method presented in Section 2.4. According to Table S4,

649



Figure 9. (a) GC–MS profile of 200-ROP (in pink) and 200-ROP + OMWW (in black) and (b) the relative Venn diagram representing the number of common and exclusive organic compounds for 200-ROP, 200-OMWW, and 200-ROP + OMWW [60].

a large variety of chemical species are detected such as phenolic and heteroaromatic compounds in addition to a major quantity of carboxylic acids and monosaccharides. The only types of compounds characterized in the literature after the HTC of ROP are generally furfural and 5-HMF obtained by lignin and cellulose degradation, respectively, and some phenolic compounds such as vanillin, 4-hydroxy-3-methoxyphenylacetone (guaiacylacetone), 2,6dimethoxyphenol (syringol), syringaldehyde, guaacetosyringone, phenol, 1-(4-hydroxy-3iacol. methoxyphenyl)-ethanone (acetovanillone), creosol, and 1-(2,4,6-trihydroxyphenyl)-2-pentanone [61,62]. In this paper, a comparison is performed for liquid fractions from HTC experiments at 200 °C. Here, the use of OMWW instead of DW for the HTC of ROP leads to a significantly different GC-MS profile as presented in Figure 9a. Moreover, as we compare these results with the 200-OMWW profile (data published previously [10]), we can note that among the 74 detected compounds, 30 are present in all three modalities and thus emerge from both OMWW and ROP after HTC (Figure 9b). Moreover, 29 compounds are present in 200-ROP and 200-ROP + OMWW samples and are specific to ROP. The five compounds found in 200-OMWW and 200-ROP + OMWW arise from OMWW, while 10 compounds arise from ROP. However, for these last compounds, we distinguish seven molecules, which are observed only when ROP HTC is conducted in the presence of OMWW. The remaining three are lost or transformed in the presence of OMWW.

The sum of relative areas for the 29 molecules detected only in 200-ROP and 200-ROP + OMWW is presented in Figure 10. Accordingly, higher contents are obtained in the different chemical classes, in particular for cyclic carboxylic acid and heterocyclic compounds. Such results suggest that a better HTC of ROP can be predicted in the presence of OMWW rather than DW. Similar outcomes are obtained at the other temperatures of 180 and 220 °C.

Moreover, seven molecules are detected only when HTC of ROP is performed in the presence of OMWW and, notably, the putative compound salidroside, which is a glucosylated form of tyrosol. It is well known that tyrosol is a major component of olive oil [63] and is abundant in OMWW-derived hydrochars [64]. We detected tyrosol in all T-ROP samples and in very higher proportions in raw OMWW, T-OMWW, and T-ROP + OMWW [10]. On the other hand, glucose is only identified in raw OMWW, suggesting that glucose is degraded via the HTC process. Therefore, the existence of salidroside can be explained in terms of the coupling between glucose and tyrosol when olive stones and raw OMWW are



Figure 10. Sum of normalized areas of the different chemical compound classes detected after HTC of ROP in the presence of distilled water and OMWW at 200 °C.

copresent. A similar explanation can be applied for the formation of monoacetin (glycerol monoacetate) since glycerol is much more abundant in OMWW than in ROP.

4. Conclusions

This research has investigated the possible conversion of hazardous OMWW to an environmentalfriendly substitute for water in the HTC of ROP into carbon-rich materials. The utilization of OMWW considerably enhanced some mineral contents, especially potassium and magnesium. Moreover, the carbonization of ROP in the presence of OMWW instead of DW at 220 °C enhanced the HHV by approximately 31%. This could be related to the significant increase in C contents and the decrease in O% owing to the acidic nature of the liquid waste. Furthermore, the coapplication of ROP and OMWW enhanced the quality of the final liquid fraction with a significant decrease in the COD value of approximately 53% to 62%. This feature, however, caused significant modifications of some chemical and morphological aspects of the hydrochars. In fact, the use of OMWW instead of DW led to decreases in ash and fixed carbon percentages of 4% and 10%. An increase of 14% in volatile matter contents was noted for 220-ROP and 220-ROP + OMWW, respectively. Moreover, the use of DW as the carbonization medium ensured the formation of spherical carbon structures with mean diameters varying between 1.09 and 0.62 µm for 180-ROP and 200-ROP, respectively. However, their formation is not favored in the presence of OMWW due to its low pH value. This work demonstrates a circular and environmental-friendly approach to waste management, which may open the door to several possible applications of the solid fractions obtained. Hydrochars produced with DW could be applied as adequate feedstock for the manufacture of high-valueadded carbon materials for energy storage applications or as adsorbents in liquid and gaseous media. On the other hand, OMWW-derived hydrochars have properties that make them not only apt for energy generation but also an appropriate source of fixed carbon content for agricultural applications.

Acknowledgments

This work was funded by the FERTICHAR project— European Union's Seventh Framework Programme for research, technological development and demonstration—under grant agreement number 618127. The authors gratefully acknowledge the funding agencies for their support. The authors also
wish to thank all the personnel operating the technical platforms of the IS2M for their scientific contributions and for their help in running the wellconducted experiments and analyses.

Supplementary data

Supporting information for this article is available on the journal's website under https://doi.org/10.5802/ crchim.61 or from the author.

References

- A. Méndez, G. Gascó, B. Ruiz, E. Fuente, *Bioresour. Technol.*, 2019, 275, 386-393.
- [2] A. A. Zorpas, V. J. Inglezakis, Appl. Environ. Soil Sci., 2011, 2011, 1-14.
- [3] J. Mata-Alvarez, Biomethanization of the Organic Fraction of Municipal Solid Wastes, Vol. 4, Water Intell. Online, 2015.
- [4] O. P. Karthikeyan, C. Visvanathan, *Rev. Environ. Sci. Bio/Technol.*, 2013, **12**, 257-284.
- [5] K.-H. Yeoh, S. A. Shafie, K. A. Al-attab, Z. A. Zainal, *Bioresour. Technol.*, 2018, 265, 365-371.
- [6] C. Karakaş, D. Özçimen, B. İnan, J. Anal. Appl. Pyrolysis, 2017, 125, 17-23.
- [7] S. O. Masebinu, E. T. Akinlabi, E. Muzenda, A. O. Aboyade, *Renew. Sustain. Energy Rev.*, 2019, 103, 291-307.
- [8] D. Bhatt, A. Shrestha, R. Dahal, B. Acharya, P. Basu, R. MacEwen, *Energies*, 2018, 11, article no. 2286.
- [9] A. A. Azzaz, B. Khiari, S. Jellali, C. M. Ghimbeu, M. Jeguirim, *Renew. Sustain. Energy Rev.*, 2020, **127**, article no. 109882.
- [10] A. A. Azzaz, M. Jeguirim, V. Kinigopoulou, C. Doulgeris, M.-L. Goddard, S. Jellali, C. Matei Ghimbeu, *Sci. Total Environ.*, 2020, **733**, article no. 139314.
- [11] F. Gao, G. Shao, J. Qu, S. Lv, Y. Li, M. Wu, *Electrochim. Acta*, 2015, **155**, 201-208.
- [12] S. Schaefer, V. Fierro, M. T. Izquierdo, A. Celzard, Int. J. Hydrogen Energy, 2016, 41, 12146-12156.
- [13] K. Reibe, K.-P. Götz, C.-L. Roß, T. F. Döring, F. Ellmer, L. Ruess, *Soil Biol. Biochem.*, 2015, 83, 84-87.
- [14] F. Valenti, C. Arcidiacono, G. Chinnici, G. Cascone, S. M. C. Porto, *Biofuels, Bioprod. Biorefining*, 2017, 11, 784-797.
- [15] M. Jeguirim, P. Dutournié, A. A. Zorpas, L. Limousy, *Energies*, 2017, **10**, article no. 1423.
- [16] M. K. Doula, A. A. Zorpas, V. J. Inglezakis, J. P. Navvaro, D. J. Bilalis, *Environ. Eng. Manag. J.*, 2019, **18**, 1297-1309.
- [17] M. Jeguirim, M. L. Goddard, A. Tamosiunas, E. Berrich-Betouche, A. A. Azzaz, M. Praspaliauskas, S. Jellali, *Renew. Energy*, 2020, **149**, 716-724.
- [18] P. Dutournié, M. Jeguirim, B. Khiari, M.-L. Goddard, S. Jellali, Water, 2019, 11, article no. 768.
- [19] A. Chouchene, M. Jeguirim, A. Favre-Reguillon, G. Trouvé, G. Le Buzit, B. Khiari, F. Zagrouba, *Energy*, 2012, **39**, 74-81.
- [20] M. Jeguirim, A. Chouchène, A. F. Réguillon, G. Trouvé, G. Le Buzit, *Resour. Conserv. Recycl.*, 2012, 59, 4-8.

- [21] A. Chouchene, M. Jeguirim, G. Trouvé, A. Favre-Reguillon, G. Le Buzit, *Bioresour. Technol.*, 2010, 101, 6962-6971.
- [22] A. Missaoui, S. Bostyn, V. Belandria, B. Cagnon, B. Sarh, I. Gökalp, J. Anal. Appl. Pyrolysis, 2017, 128, 281-290.
- [23] G. Ralf, J. J. Leahy, M. T. Timko, A. Trubetskaya, *Renew. Energy*, 2020, **155**, 347-357.
- [24] B. González, J. J. Manyà, Chem. Eng. Process. Process Intensif., 2020, 149, article no. 107830.
- [25] A. Chouchene, M. Jeguirim, B. Khiari, G. Trouvé, F. Zagrouba, J. Anal. Appl. Pyrolysis, 2010, 87, 168-174.
- [26] R Development Core Team, "R: a language and environment for statistical computing", 2020.
- [27] T-412, Moisture in pulp, paper and paperboard, Stand. Off. Method, Tappi, 2012.
- [28] W. Thompson, P. Leege, *Test Methods for the Examination of Composting and Compost*, Composting Council Research and Education Foundation, Raleigh, USA, 1998.
- [29] S. Graulis, D. Chateigner, R. T. Downs, A. F. T. Yokochi, M. Quirós, L. Lutterotti, E. Manakova, J. Butkus, P. Moeck, A. Le Bail, J. Appl. Crystallogr., 2009, 42, 726-729.
- [30] A. A. Azzaz, S. Jellali, H. Akrout, A. A. Assadi, L. Bousselmi, *Environ. Sci. Pollut. Res.*, 2016, 1-16.
- [31] W. A. Moore, R. C. Kroner, C. C. Ruchhoft, Anal. Chem., 1949, 21, 953-957.
- [32] T. Wang, Y. Zhai, Y. Zhu, C. Li, G. Zeng, *Renew. Sustain. Energy Rev.*, 2018, **90**, 223-247.
- [33] L. Li, M. Hale, P. Olsen, N. D. Berge, Waste Manag., 2014, 34, 2185-2195.
- [34] S. Başakçılardan Kabakcı, S. S. Baran, Waste Manag., 2019, 100, 259-268.
- [35] X. Chen, Q. Lin, R. He, X. Zhao, G. Li, *Bioresour. Technol.*, 2017, 241, 236-243.
- [36] A. M. Smith, S. Singh, A. B. Ross, Fuel, 2016, 169, 135-145.
- [37] N. Huang, P. Zhao, S. Ghosh, A. Fedyukhin, *Appl. Energy*, 2019, 240, 882-892.
- [38] M. T. Elaieb, A. Khouaja, M. L. Khouja, J. Valette, G. Volle, K. Candelier, *Waste Biomass Valorization*, 2018, 9, 1199-1211.
- [39] D. Özçimen, A. Ersoy-Meriçboyu, *Renew. Energy*, 2010, 35, 1319-1324.
- [40] C. Zhao, E. Jiang, A. Chen, J. Energy Inst., 2017, 90, 902-913.
- [41] A. Funke, F. Ziegler, Biofuels, Bioprod. Biorefining, 2010, 4, 160-177.
- [42] T. Mathimani, N. Mallick, J. Clean. Prod., 2019, 217, 69-84.
- [43] P. J. Arauzo, L. Du, M. P. Olszewski, M. F. Meza Zavala, M. J. Alhnidi, A. Kruse, *Bioresour. Technol.*, 2019, **293**, article no. 122117.
- [44] I. Miranda, R. Simões, B. Medeiros, K. M. Nampoothiri, R. K. Sukumaran, D. Rajan, H. Pereira, S. Ferreira-Dias, *Bioresour. Technol.*, 2019, **292**, article no. 121936.
- [45] S. Lammi, A. Barakat, C. Mayer-Laigle, D. Djenane, N. Gontard, H. Angellier-Coussy, *Powder Technol.*, 2018, 326, 44-53.
- [46] P. Biller, A. B. Ross, "Production of biofuels via hydrothermal conversion", in *Handbook of Biofuels Production*, Processes and Technologies, Woodhead Publishing, Oxford, UK, 2nd ed., 2016, 509-547.
- [47] S. Kang, X. Li, J. Fan, J. Chang, Ind. Eng. Chem. Res., 2012, 51, 9023-9031.

- [48] M. L. Hobbs, P. T. Radulovic, L. D. Smoot, Fuel, 1992, 71, 1177-1194.
- [49] M. Sevilla, A. B. Fuertes, Carbon N. Y., 2009, 47, 2281-2289.
- [50] Q. Wang, F. Cao, Q. Chen, C. Chen, *Mater. Lett.*, 2005, 59, 3738-3741.
- [51] J. Ryu, Y. W. Suh, D. J. Suh, D. J. Ahn, Carbon N. Y., 2010, 48, 1990-1998.
- [52] M. Li, W. Li, S. Liu, Carbohydr. Res., 2011, 346, 999-1004.
- [53] J. Liang, Y. Liu, J. Zhang, Proc. Environ. Sci., 2011, 11, 1322-1327.
- [54] V. K. Lamer, R. H. Dinegar, J. Am. Chem. Soc., 1950, 72, 4847-4854.
- [55] J. Xiong, Z. Pan, X. Xiao, H. Huang, F. Lai, J. Wang, S. Chen, J. Anal. Appl. Pyrolysis, 2019, 144, article no. 104692.
- [56] P. A. Nakata, *Plant Sci.*, 2003, **164**, 901-909.
- [57] V. R. Franceschi, P. A. Nakata, Annu. Rev. Plant Biol., 2005, 56, 41-71.
- [58] L. Zhang, Q. Wang, B. Wang, G. Yang, L. A. Lucia, J. Chen, *Energy Fuels*, 2015, 29, 872-876.
- [59] S. Guo, X. Dong, T. Wu, F. Shi, C. Zhu, J. Anal. Appl. Pyrolysis, 2015, 116, 1-9.
- [60] H. Heberle, V. G. Meirelles, F. R. da Silva, G. P. Telles, R. Minghim, *BMC Bioinformatics*, 2015, 6, article no. 169.

- [61] A. M. Borrero-López, E. Masson, A. Celzard, V. Fierro, Ind. Crops Prod., 2020, 151, article no. 112452.
- [62] A. M. Borrero-López, V. Fierro, A. Jeder, A. Ouederni, E. Masson, A. Celzard, *Environ. Sci. Pollut. Res.*, 2017, 24, 9859-9869.
- [63] G. Purcaro, R. Codony, L. Pizzale, C. Mariani, L. Conte, Eur. J. Lipid Sci. Technol., 2014, 116, 805-811.
- [64] J. Poerschmann, I. Baskyr, B. Weiner, R. Koehler, H. Wedwitschka, F. D. Kopinke, *Bioresour. Technol.*, 2013, 133, 581-588.
- [65] International Organization for Standardization, "Soil Quality: Determination of Total Nitrogen: Modified Kjeldahl Method", 1995, ISO 11261:1995.
- [66] A. R. K. Gollakota, N. Kishore, S. Gu, *Renew. Sustain. Energy Rev.*, 2018, 81, 1378-1392.
- [67] E. Atallah, W. Kwapinski, M. N. Ahmad, J. J. Leahy, A. H. Al-Muhtaseb, J. Zeaiter, *J. Environ. Chem. Eng.*, 2019, 7, article no. 102833.
- [68] V. Benavente, A. Fullana, N. D. Berge, J. Clean. Prod., 2017, 142, 2637-2648.
- [69] E. Atallah, W. Kwapinski, M. N. Ahmad, J. J. Leahy, J. Zeaiter, J. Water Process Eng., 2019, 31, article no. 100813.
- [70] J. Poerschmann, B. Weiner, I. Baskyr, *Chemosphere*, 2013, 92, 1472-1482.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Methane catalytic reforming by carbon dioxide on Mg–Al oxides prepared by hydrotalcite route with different surfactants (CTAB, glucose, P123) or with intercalation of SBA-15 and impregnated by nickel

Reformage catalytique du méthane par le dioxyde de carbone sur des oxydes Mg–Al préparés par voie hydrotalcite avec différents surfactants (CTAB, glucose, P123) ou avec intercalation de SBA-15 et imprégnés par le nickel

Carole Tanios^{*a*, *b*}, Yara Saadeh^{*a*, *b*}, Madona Labaki^{*, *b*}, Maya Boutros^{*b*}, Cédric Gennequin^{*a*}, Haingomalala Lucette Tidahy^{*a*}, Antoine Aboukaïs^{*a*} and Edmond Abi-Aad^{*a*}

> ^{*a*} Unité de Chimie Environnementale et Interactions sur le Vivant (UCEIV, *E.A. 4492), MREI*, Université du Littoral Côte d'Opale (ULCO), F-59140 Dunkerque, France

> ^b Laboratory of Physical Chemistry of Materials (LCPM)/PR2N, Faculty of Sciences, Lebanese University, Fanar, PO Box 90656 Jdeidet El Metn, Lebanon *E-mails:* caroletanios@outlook.com (C. Tanios), yarassaadeh@gmail.com (Y. Saadeh), mlabaki@ul.edu.lb (M. Labaki), maya.boutros@ul.edu.lb (M. Boutros), cedric.gennequin@univ-littoral.fr (C. Gennequin), lucette.tidahy@univ-littoral.fr (H. L. Tidahy), antoine.aboukais@univ-littoral.fr (A. Aboukaïs), edmond.abiaad@univ-littoral.fr (E. Abi-Aad)

Abstract. Four magnesium–aluminum mixed oxides were synthesized by the hydrotalcite route using four modifying agents (three surfactants: glucose, CTAB, and P123, as well as silica SBA-15), and then calcined at 550 °C. Physicochemical characterizations were conducted before and after calcination. X-ray diffraction (XRD), differential thermal and gravimetric analyses (DTA/TGA), and Fourier Transform Infrared Spectroscopy (FTIR) showed that the hydrotalcite structure was obtained even in the presence of a modifying agent. This structure was converted into mixed oxides upon calcination where the pore size distribution was more homogeneous in the presence of a modifying agent. Nickel was

^{*} Corresponding author.

impregnated on these oxides and then the catalytic performances of the obtained catalysts were tested in the dry reforming of methane as a model for biogas reforming. In our conditions, the catalyst based on SBA-15 did not show any catalytic activity whereas good catalytic activities and high carbon balances were obtained for the samples prepared with the three surfactants. The effect of a surfactant is mainly the slight enhancement of the carbon balance due to higher nickel species dispersion. It is suggested to put into evidence this slight enhancement by time on stream studies, where the formation of a lower amount of carbon and longer lifetime for catalysts elaborated with surfactants is expected.

Résumé. Quatre oxydes mixtes de magnésium et d'aluminium ont été préparés par voie hydrotalcite, avec introduction de surfactants (glucose, CTAB, P123) ou intercalation de SBA-15, et calcinés à 550 °C. Des caractérisations physico-chimiques ont été menées avant et après calcination. La Diffraction de Rayons X (DRX), les analyses thermiques différentielle et gravimétrique (ATD/ATG), la spectroscopie infrarouge à transformée de Fourier (IRTF) ont montré que la structure hydrotalcite a été obtenue même en présence de l'agent modifiant (surfactant ou SBA-15). Suite à la calcination, cette structure a été convertie en oxydes mixtes avec une distribution des tailles de pores plus homogène en présence du modifiant. Le nickel a été imprégné sur ces oxydes et les performances catalytiques ont été évaluées vis-à-vis de la réaction du reformage à sec du méthane comme modèle pour le reformage du biogaz. Le catalyseur contenant SBA-15 n'a pas montré d'activité catalytique dans nos conditions, alors que de bonnes activités avec de meilleurs bilans carbone ont été obtenus sur les catalyseurs préparés avec des surfactants. L'effet du surfactant est une légère amélioration du bilan carbone suite à une meilleure dispersion du nickel. Il est proposé de mieux mettre en évidence cette légère amélioration par des études de stabilité des catalyseurs sous flux réactionnel. Dans ce cas, il est prévu la formation d'une plus faible quantité de carbone et une plus longue durée de vie pour les catalyseurs préparés à partir de surfactants.

Keywords. Dry reforming, Mg–Al hydrotalcite, Methane, Nickel, SBA-15, Surfactants. Mots-clés. Reformage à sec, Hydrotalcite Mg–Al, Méthane, Nickel, SBA-15, Surfactants.

1. Introduction

Our dependence on fossil fuels as energy sources has caused global-energy crisis and serious environmental problems. These energy sources take millions of years to form naturally and are depleted much faster than the rate at which they are being produced. Moreover, the rapid growth in the world's population has increased further the demand for energy. It is expected that this demand will keep on increasing in the future. This is why this limited resource is going to run out eventually [1,2]. More importantly, the dependence on fossil fuels as energy vector has created environmental issues since their burning releases anthropogenic greenhouse gases to the atmosphere. Indeed, climate problems and the need to reduce greenhouse gas emissions has forced the politicians and industries to rethink of future energy and to favor the research on clean and energy-rich fuel for the future [1]. In this context, researches are being carried out in the aim of developing alternative solutions oriented toward minimizing the formation of polluting compounds and greenhouse gases. Hydrogen has been suggested as a clean and energy-rich fuel for the future. It can be produced from different methods, but lately studies are being conducted to derive hydrogen from natural gas due to its availability and low price. A good choice is dry reforming of methane (DRM) [3], which involves the reaction of the major component of natural gas, methane (CH₄), with carbon dioxide (CO₂) to produce hydrogen (H₂) and carbon monoxide (CO) as given by the following reaction [4]:

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta H_{298}^\circ = 247 \text{ kJ} \cdot \text{mol}^{-1}$$

The highly endothermic character of this reaction is the main problem. For it to be feasible in areas of temperature not too high, these reactions are carried out in the presence of a catalyst. However, it is important that the catalysts produced be cheap and resistant to the causes of deactivation (carbon deposition and sintering at high temperature) in order to be affordable for industrial applications. Nickelbased catalysts are not expensive, and were found to be of excellent activity and selectivity in DRM, but their stability to carbon deposition and sintering is poor [5]. Significant control can be achieved if well-defined structures (perovskites, spinels, oxides derived from hydrotalcites, etc.) are used as catalyst precursors or catalysts. Dedov et al. [6] found conversion about 90-97% associated to a better resistance to carbon formation on catalysts composed of Ni impregnated on MgAl₂O₄ spinel (derived from a hydrotalcite structure) pre-reduced with hydrogen at 550 °C. Also, well-controlled structured catalysts can be obtained by embedding the active phase into the pore channels of mesostructured materials [7]. Moreover, reduction of the crystalline oxide precursors (spinels, oxides derived from hydrotalcite, etc.) that contain active metal species homogeneously dispersed inside the bulk leads to the migration of some of the metal atoms to the surface [8-10]. A highly dispersed active phase could be obtained in this way with increased resistance to carbon formation. A recent method that gives catalysts with extremely high values of specific surface area is to immobilize the Ni nanoparticles in the pore channels of ordered mesoporous silica materials such as SBA-15, SBA-16, KIT-6, and MCM-41 [8,11-13]. Indeed, Kaydouh et al. [14] found that Ni is well dispersed in the pores of SBA-15 by a two-solvent deposition method. Also, Ni/SBA-15 are highly active and selective in DRM, with almost 100% CH4 and CO2 conversion at 600 °C.

For these reasons, in our work, nickel-based catalysts will be synthesized where nickel is dispersed on well-defined structures. These structures are composed of four supports, magnesium-aluminum oxides, prepared by a hydrotalcite route, where a surfactant (CTAB glucose, P123) or a mesoporous silica SBA-15 is introduced to enhance the hydrotalcite textural properties (porosity, specific surface area, etc ...). Indeed, the use of surfactants will affect the morphology, particle size, and some properties of hydrotalcites. This may help in improving its catalytic properties. Some previous works were performed on such structures [15-21] but did not concern applications in reforming reactions and did not use nickel as active phase. Some other works were carried out in DRM where surfactants were used with Ni-Mg-Al hydrotalcites. Tan et al. [22] prepared oxides derived from Ni-Mg-Al hydrotalcite with the use of the surfactants tetrapropylammonium hydroxide (TPAOH), pluronic P123, poly(vinylpyrrolidone) (PVP), and hexadecyltrimethylammonium bromide (CTAB). They evaluated their catalysts in DRM. They

found that the different surfactants influence the metal particle size and promote or inhibit specific crystal planes of Ni, therefore affecting the catalytic performance. Xu et al. [23] also prepared similar catalysts with P123 as surfactant and obtained promising results in DRM. In our work and in order to get more active phase (Ni) on the surface, we chose to introduce Ni by impregnation on different Mg-Al oxides supports. Hydrotalcite Mg-Al was prepared conventionally (no modifier) and with a modifier agent. After calcination, the oxide obtained will be impregnated by the active phase Ni. Ni is expected to be more dispersed on the supports prepared with a modifier than on the support without a modifier. So our target is to get more Ni on the surface with higher dispersion, taking benefit from the properties of the well-defined structure of Mg-Al oxides.

2. Experimental part

2.1. Preparation of catalysts

Three hydrotalcites were prepared using surfactants (CTAB, glucose, P123), and composite hydrotalcite was prepared by combining hydrotalcite (HT) with SBA-15. For the sake of comparison, a conventional hydrotalcite was synthesized as well. All these hydrotalcites prepared were calcined to give oxides that will be used as support for the active phase nickel.

2.1.1. Synthesis of conventional hydrotalcite by coprecipitation method

In order to combine several metals within the same homogeneous phase, the coprecipitation method at constant pH has been utilized [15,24,25]. A hydrotalcite with a molar ratio $Mg^{2+}/Al^{3+} = 3$ was synthesized. This sample is prepared by precipitating 50 mL aqueous solution containing the appropriate dissolved amounts of magnesium (II) nitrate hexahydrate Mg(NO₃)₂·6H₂O (UNI-CHEM, 98% purity) and aluminum (III) nitrate nonahydrate Al(NO3)3.9H2O (UNI-CHEM, 98% purity) with a basic solution of 1 mol·L⁻¹ sodium carbonate Na₂CO₃ (UNI-CHEM, 99% purity) and 2 mol·L⁻¹ sodium hydroxide NaOH (MERCK, 99% purity) at a temperature of 60 °C and a pH maintained between 9.5 and 10 with continuous stirring. The precipitate obtained is stirred for 1 h at 60 °C and then placed in an oven at 60 °C for 24 h. The solution obtained is filtered and washed

several times with deionized water until a neutral pH is obtained. The washing step is made in the aim of removing all soluble ions, such as excess of nitrates and Na⁺, since they could have a negative effect on the activity of the catalyst by blocking some pores or active sites. After that, the solid is placed in an oven at 60 °C for 48 h to dry and then ground to a fine powder form. The as-synthesized sample obtained is labeled HT-conventional.

2.1.2. Synthesis of hydrotalcites with surfactants

Three hydrotalcites were prepared with three carbon-based surfactants: glucose, hexadecyltrimethylammonium bromide (CTAB), and the copolymer triblock block-poly(ethylene glycol)block-poly(propylene glycol)-block-poly(ethylene glycol) pluronic P123. In each case, the surfactant was added to the basic precipitating solution as described hereafter.

Hydrotalcite with glucose. 2 g of glucose (D(+) glucose Sigma-Aldrich C₆H₁₂O₆, MW = 180.6 g·mol⁻¹, purity > 99.5%) were dissolved in 10 mL deionized water. The metal nitrate solution was added dropwise into a beaker containing the dissolved surfactant, while heating at 60 °C and adjusting the pH between 9.5 and 10 using the basic solution of Na₂CO₃ and NaOH. The suspension obtained was stirred for 1 h at 60 °C. The slurry was then poured into a teflon bottle and placed in an oven for hydrothermal treatment of 24 h at 100 °C. The mixture obtained was then filtered and washed with deionized water until a neutral pH of the filtrate was obtained. The solid obtained was brown in color after washing with deionized water, suggesting that glucose underwent aromatization and carbonization under the employed hydrothermal conditions [15]. The solid was then placed in an oven at 60 °C for 48 h to dry and after that it was ground to a fine powder form. The sample obtained is noted HT-glucose.

Hydrotalcite with CTAB. The same procedure detailed above was followed for this sample, with the following change: previous to the synthesis, 2 g of CTAB ($C_{19}H_{42}BrN$, SIGMA-ALDRICH purity \geq 96%, MW = 364.45 g·mol⁻¹) were dissolved in 60 mL deionized water at 40 °C and stirred for 3 h. The solid obtained after filtration was of white color. The powder obtained after drying and grinding is labeled HT-CTAB.

Hydrotalcite with Pluronic P123. For this sample, 2 g of Pluronic P123 (PEG-PPG-PEG, SIGMA-ALDRICH, MW \cong 5800 g·mol⁻¹) were dissolved in 60 mL deionized water while stirring at 60 °C overnight. The solution obtained after precipitating the metal nitrate solution was stirred for 20 h at 60 °C and then placed in a teflon bottle at 100 °C for 24 h. The obtained mixture was filtered, washed, then dried and ground as mentioned above. The obtained white powder was labeled HT-P123.

2.1.3. Synthesis of composite hydrotalcite-SBA-15

We followed the same procedure done by Baskaran *et al.* [16] to have the intercalation of SBA-15 molecular sieve in the interlayer of HT. The molar gel composition they used was respected (HT molar composition of $Mg^{2+}:Al^{3+}:CO_3^{2-}:NH_4^+:H_2O =$ 0.116:0.038:0.0769:0.379:30.6, the SBA-15 gel containing 0.04 mol·L⁻¹ of silica). What is important during this synthesis is to make sure that the two gels prepared separately are mixed together at room temperature in order to avoid the formation of foam resulting from the exothermicity of acid–base reaction between SBA-15 gel and HT gel. This sample is named HT-SBA-15.

All the above as-synthesized samples (also called uncalcined or dried samples) were calcined at 550 °C (5 °C·min⁻¹, 5 h) under air flow. The choice of calcination temperature was based on the thermal analysis results (presented later). After calcination, the samples will be marked by a (C) next to their names given above.

2.1.4. Nickel impregnation

The calcined samples were passed by porosimetry in order to determine their pore volume $(cm^3 \cdot g^{-1})$. Based on the value obtained, a corresponding solution to lead to a final content of 5 wt% Ni was prepared. A mass of calcined powder support was weighed, and a volume of the prepared Ni solution corresponding to this mass was added, then stirred gently and introduced in a round flask. In order to wash and wet the powder, 20–25 mL of deionized water were added. The flask containing the solution was then placed in a rotary evaporator (60 °C, 120 rpm) in order to homogenize well the catalyst and to evaporate the water. After that, the solid was placed in an oven to dry at 60 °C overnight. The obtained powder was then ground and calcined at 550 °C. The as-obtained samples will be denoted by "Ni-HT-X" where X represents the surfactant used (CTAB, glucose, or P123) or the SBA-15.

2.2. Physicochemical characterizations

Several physicochemical characterizations were performed on the prepared catalysts.

2.2.1. X-ray diffraction (XRD)

XRD analysis was conducted for the uncalcined samples as well as for the samples calcined after Ni impregnation in order to be able to characterize the different phases present in the structure. XRD analysis was performed, at room temperature, on a BRÜKER D8 advance diffractometer equipped with a copper anticathode emitting K α radiation (λ = 1.5406 Å), a goniometer $\theta/2\theta$, and a rotating sample holder to avoid preferential orientations. The general conditions of acquisition correspond to an angular range in 2θ from 5 to 70° with a measurement step of 0.02° for an integration time of 1 s. The crystalline phases are identified by comparing the diffractograms with those of reference compounds in the Joint Committee on Powder Diffraction Database Standards (JCPDS) established by the International Center for Diffraction Data (ICCD). This comparison is made by the EVA software.

2.2.2. Differential thermal and gravimetric analyses (DTA/TGA)

DTA/TGA were performed on the uncalcined samples as well as on samples after DRM. The measurements were carried out on a device SDT Q600 (TA instrument society) starting from ambient temperature up to 800 °C (temperature rise of 5 °C·min⁻¹) under an air flow of 100 mL·min⁻¹. For each analysis, the mass of test sample was about 10 mg. The software "Universal analysis" is used to process the results obtained.

2.2.3. Brunauer, Emmett, Teller (BET)

The specific surface areas of the samples before and after calcination were measured using a Q Surf

M1 (Thermo Electron) instrument (surface area analvser apparatus). The measurement was performed by the BET method by nitrogen adsorption, at its liquefaction temperature (-196 °C), on the solid. The BET method is based on the evaluation of the quantity of inert gas physisorbed. A mass of sample of 20–75 mg (depending on the specific area expected) is introduced into the BET cell. The sample, before measurement, is degassed for 30 min at 100 °C under nitrogen flow. The sample is weighed again after degassing in order to determine the mass lost during degasification. After this step, the measurement is performed. It is automated and takes place in two stages: adsorption and desorption, during which the variation of the thermal conductivity of a gaseous mixture consisting of 30% nitrogen (adsorbed gas) and 70% helium (carrier gas) is measured. The desorbed nitrogen is quantified by a thermal conductivity detector (TCD). We used a single-point analysis. This apparatus was used for the uncalcined samples.

2.2.4. Porosimetry

In order to examine the textural characteristic of the mixed oxides, N2 adsorption/desorption and BET calculation methods as well as Barrer, Joyner, and Halenda (BJH) model were used to determine the surface area as well as the pore volume and pore size distributions. Porosimetry was carried out on the calcined samples before and after Ni impregnation. The apparatus used is a Sorptomatic 1990 instrument. The adsorption step was carried out at -196 °C. Before measurement, the sample is heated in vacuum at 300 °C with an increase in temperature of 5 °C·min⁻¹, then kept for 5 h at 300 °C. After treatment, the sample is weighed again in order to determine the mass lost during degassing. After this step, the measurement is performed. It is automated and takes place in two stages: adsorption and desorption. When the analysis is done, the system in the apparatus gives the specific surface area $(m^2 \cdot g^{-1})$, pore volume $(cm^3 \cdot g^{-1})$, and pore distribution (nm) of the sample. By plotting the curve of pore distribution, one can conclude the homogeneity of formed pores in the sample: the more the pore distribution peak gets narrow, the more homogeneous is the size of pores formed. This is a multi-point analysis and therefore gives more accurate results than BET single-point analysis.

2.2.5. Temperature programmed reduction (TPR)

The reducibility of the calcined solids before and after Ni impregnation was studied by the TPR. The apparatus used is ZETON Altamira AMI 200 system. About 20 mg of sample were deposited in a quartz tube and pretreated under an argon flow of high purity. This argon (Ar) flow of 30 mL·min⁻¹ circulates under a temperature ranging from ambient to 150 °C with a rise of 5 °C·min⁻¹. The sample is then kept at 150 °C for 1 h to remove adsorbed moisture and air. After that, it is heated to 900 °C at 5 °C·min⁻¹ under a H₂ flow (5% H₂ in Ar, 50 mL·min⁻¹) followed by naturally cooling down under an Ar flow. The hydrogen consumed during the reduction was detected by a TCD.

2.3. Dry reforming of Methane (DRM)

2.3.1. Experimental conditions of test

Dynamic catalytic tests were carried out from 400 °C to 800 °C with an interval of 50 °C. For each test, a mass of 100 mg catalyst is introduced into a U-shaped quartz reactor (fixed bed). The reactor is fed by a gaseous mixture of CH₄/CO₂/Ar having 20%/20%/60% proportions under an atmospheric pressure with a CH_4/CO_2 molar ratio equal to 1. The total flow is 100 mL·min⁻¹ and the gas hourly space velocity (GHSV) is 32,000 h^{-1} . The effluent gas was analyzed using a micro gas chromatography Varian CP-4900 equipped with a Poraplot Q (PPQ) column, a molecular sieve, and a TCD. Before starting the test, the catalyst must undergo an activation step which consists of treating the catalyst by a reducing mixture 5% H₂ in Ar after an increase of the temperature from ambient till 800 °C (10 °C ⋅ min⁻¹). The latter temperature is maintained for 2 h in order to activate the catalyst. The reactor is then cooled at 400 °C under Ar flow to start the test. Many injections were done at each temperature studied. The analyses of the reactor effluents are done by gas chromatography every five minutes.

2.3.2. Calculation formulas

The general formulas given below are used to calculate the conversions of the reactants, the carbon balance, and H_2/CO ratio.

Conversion of reactants $R(X_R)$

$$X_R = \frac{R_{\rm in} - R_{\rm out}}{R_{\rm in}} \times 100.$$
(1)

 $R_{\rm in}$ and $R_{\rm out}$ correspond to the respective reactants amounts R at the inlet and the outlet of the reactor. In dry reforming, the reactants are methane (CH₄) and carbon dioxide (CO₂).

Carbon balance (CB)

$$CB = \frac{CH_{4 \text{ out}} + CO_{2 \text{ out}} + CO_{out}}{CH_{4 \text{ in}} + CO_{2 \text{ in}}} \times 100$$
(2)

H₂/CO ratio

ratio =
$$\frac{H_2}{CO}$$
 (3)

3. Results and discussions

3.1. Physicochemical characterization of uncalcined samples

3.1.1. X-ray diffraction

Figure 1 shows X-ray diffractograms of the dried solids. The patterns of all the prepared solids show the diffraction lines of the hydrotalcite structure (JCPDS 22-0700).

The diffraction peaks are observed at 2θ of 11.5°, 23.5°, 35.0°, 38.0°, 46.2°, 60.5°, and 61.8° and are respectively indexed to the lattice planes (003), (006), (012), (015), (018), (110), and (113) [24,26,27]. The inter-planar spacing (d) corresponding to these peaks is deduced from Bragg's law given by the relation:

$$2d\sin\theta = n\lambda.$$
 (4)

It is then concluded that the hydrotalcite structure was obtained in all our solids. The diffraction lines are less intense in the case of HT-SBA-15 due to the presence of a significant weight percentage of SBA-15 along with HT.

The different cell parameters are given in Table 1. Two parameters "*a*" and "*c*" should be evaluated for a hydrotalcite structure since it crystallizes in a 3R rhombohedral reticular system [26], with $a = b \neq c$ and $\alpha = \beta = \gamma \neq 90^{\circ}$.

Knowing the lattice planes (hkl) and the interplanar spacing d(hkl), the following relation is used to determine the cell parameters [28]:

$$d(hkl) = \frac{a}{\sqrt{\frac{4}{3}(h^2 + k^2 + hk) + l^2\left(\frac{a}{c}\right)^2}}.$$
 (5)

The crystallographic parameter "*a*" representing half of the cation–cation distance in a hydroxide sheet will be determined by the lattice plane d(110) at $2\theta =$



Figure 1. X-ray diffractograms of the uncalcined samples.*: hydrotalcite (JCPDS 22-0700).

Table 1. Crystallographic parameters and free interlayer space of uncalcined samples

Samples	2θ (°)	<i>d</i> (003)	<i>c</i> (Å)	2θ (°)	<i>d</i> (110)	<i>a</i> (Å)	Free interlayer space (Å)
HT-conventional	11.78	7.50	22.50	60.35	1.53	3.06	2.70
HT-CTAB	11.86	7.45	22.35	60.71	1.52	3.04	2.65
HT-glucose	11.78	7.50	22.50	60.35	1.53	3.06	2.70
HT-P123	11.92	7.42	22.26	60.71	1.52	3.04	2.62
HT-SBA-15	11.43	7.73	23.19	60.71	1.52	3.04	2.93

60.5° and calculated by the relation: $a = 2 \times d(110)$. Similarly, and according to the position of the two most intense lines at $2\theta^\circ = 11.5^\circ$ and 23.5° , the distances d(003) and d(006) can be used to determine the crystallographic parameter "c" ($c = 3 \times d(003) =$ $6 \times d(006)$). The d-spacing of the (003) reflection corresponds to the thickness of one layer constituting a brucite-like sheet and one interlayer, which is related to the electrostatic interactions between the brucite-like sheet and the interlayer and is strongly dependent on the ratio M^{2+}/M^{3+} [26]. The theoretical thickness of a brucite layer [29] being 4.80 Å, the length of the interlayer space could therefore be deduced from the following formula:

Free interlayer space = d(003) - 4.80.

The values obtained for the parameter "*a*" are in good agreement with the literature [15]. The basal spacing values d(003) and d(110) and the reflection

position for all HT-surfactant samples (Table 1) are the same as that of HT-conventional, indicating that during synthesis, the use of either surfactant (CTAB, glucose, or P123) has no significant effect on the basal space of the prepared hydrotalcite and the cationic composition of the sheets [15,20,21]. In addition, for the uncalcined samples, crystalline carbon-related diffraction lines are not detected, suggesting that the carbon exists in its amorphous form [15] or its content is below the detection limit of XRD.

Moreover, the composite sample HT-SBA-15 shows, in Figure 1, a slight deviation in the first peak at $2\theta = 11.7^{\circ}$ (in accordance with the literature) [16], resulting in a higher d(003) value due to the fact that the free interlayer distance obtained for this sample is slightly higher than that of the other samples. This might be attributed to the intercalation of SBA-15 in the interlayer space between two hydrotalcite brucite sheets to replace the CO_3^{2-} anions



Figure 2. BET values for the samples before and after calcination at 550 °C.

present. It is worthy to note that the decrease of 2θ value is more important in [16] than in our case. This may suggest a less intercalation of SBA-15 in hydrotalcite interlayers in our solid than in [16]. Further characterization should be carried out to check the extent of intercalation.

From XRD, based on the results obtained, we were able to detect the crystalline structure and determine the lattice cell parameters; therefore, we were capable of proving the formation of hydrotalcite layered structure even in the presence of surfactants or SBA-15.

3.1.2. Thermal analysis (DTA/TGA)

DTA/TGA curves (Figure S1) resulting from the calcination under air flow of dried samples exhibit three endothermic peaks accompanied with mass losses. According to the literature, these three peaks appear in the thermal profile of hydrotalcite and are ascribed to the loss of physisorbed and interlayer water (around 150–200 °C), to the loss of hydroxyl groups (HO⁻) in the brucite sheets (dehydroxylation of brucite-like sheets) (about 310 °C), and to the departure of interlayer CO_3^{2-} anions (around 410 °C) and therefore the destruction of hydrotalcite structure and formation of mixed oxides [18,20,21,27,30–33]. This observation confirms that the introduction of a surfactant did not alter the hydrotalcite structure and corroborates with the XRD results.

FTIR confirmed XRD and thermal analysis results since all the IR spectra (Figure S2) showed bands due to O–H, CO_3^{2-} , and M–O as well as M–O–M (M = Mg,

Al) of the brucite layer. These bands are characteristic of the hydrotalcite structure [15,16,20,21,26,27, 33–38]. A new IR band appeared around 1014 cm⁻¹ in the spectrum of HT-SBA-15, due to Si–O–Si vibrational stretching originating from the mesoporous silica present in the material [16,37].

3.2. Physicochemical characterization of the samples calcined at 550 °C

3.2.1. BET analyses for uncalcined and calcined samples

The different specific surface areas (ssa) obtained for the samples before and after calcination are given in Figure 2. Before calcination, the value of ssa obtained for the conventional HT did not change significantly with the introduction of the surfactants CTAB and P123. Conversely, it increased from 84 m²·g⁻¹ to 144 m²·g⁻¹ when glucose was used. As for the HT-SBA-15, it showed a surface area (378 m²·g⁻¹) significantly higher than that of conventional HT.

It is also noted that after calcination, a significant increase in the specific surface area is observed for all samples except for an SBA-15 based one. This increase is due to passing from a crystallized structure of hydrotalcite type to a mixed oxide type structure, in agreement with X-ray diffractograms (not shown for the calcined samples before Ni impregnation). It seems that despite the heat treatment at 550 °C, the mixed oxides retain an ssa greater than the hydrotalcite form. On the other hand, for the samples that contained surfactants, an ssa higher than that of



Figure 3. N₂ adsorption/desorption curves for samples calcined at 550 °C: (a) HT-conventional (C), (b) HT-CTAB (C), (c) HT-glucose (C), (d) HT-P123 (C), (e) HT-SBA-15 (C).

the oxide derived from conventional HT is obtained. This was expected due to the presence of surfactants whose role is to create more porous supports. As for the sample HT-SBA-15 in which the SBA-15 should be intercalated between the HT layers, a significant higher value for ssa is obtained, both before and after calcination. Indeed, SBA-15 alone has a surface area of 750–800 m²·g⁻¹ [39]; therefore, its intercalation within the HT interlayers will definitely lead to a much higher value of ssa than HT alone.

Samples	ssa $(m^2 \cdot \sigma^{-1})$	Pore volume ($cm^3 \cdot g^{-1}$)	Pore size distribution (nm)
Samples	33u (III g)		
HT-conventional (C)	76	0.40	—
HT-CTAB (C)	191	0.65	33
HT-glucose (C)	248	0.78	8
HT-P123 (C)	210	0.54	61
HT-SBA-15 (C)	281	1.05	7

Table 2. Different textural properties of the supports, given by the porosimetry

3.2.2. Porosimetry for calcined samples

The N₂ adsorption/desorption curves for calcined samples are shown in Figure 3. The appearance of a hysteresis loop in the samples is a sign of the presence of some mesoporosity in the structure. HTconventional (C) (graph a) followed a class IV(a) isotherm, with a H3 hysteresis loop. Isotherms with a H3 hysteresis do not generally have a limiting adsorption at high P/P_0 values which would imply that the pores are non-rigid aggregates of plate-like particles giving rise to slit-shaped pores [40]. Both HT-CTAB (C) and HT-P123 (C) (graphs b and d) showed a type IV(a) isotherm having H1 hysteresis loop. This type of hysteresis loop has steep parallel adsorption and desorption isotherms. At these steps all pores are filled (adsorption) and emptied (desorption). It is typical for mesoporous materials with uniform pores [40]. The curves obtained with P123 and CTAB are similar to those obtained in literature [19,21]. As for the sample HT-glucose (C) (graph c), the results obtained are compatible with the literature [15], where the isotherm is of type IV(a) and the hysteresis of type H2 (H2(b) in our case). However, in our case, the curve is always increasing after the loop, and does not show a saturation. The H2 hysteresis loop has a smooth adsorption step and a sharp desorption step. It is typical for materials with non-uniform pore shapes and/or sizes, such as metal oxides [40]. For HT-SBA-15 (C) sample (graph e), the isotherm is of type IV(a) and the hysteresis is rather of type H3. Such type of hysteresis loop is associated with slit-shaped pores as mentioned above, and might be due to the presence of agglomerates of plate-like particles [40]. However, in the literature, Baskaran et al. [16] obtained for HT-SBA-15 a type IV isotherm with a hysteresis loop that is a combination of H1 and H4 types, indicating the presence of uniform mesoporous channels in the interlayer.

In Table 2, the results obtained by porosimetry for all samples are presented. All supports, except for HT-P123 (C), are mesoporous since the pore diameters of the samples are all distributed in the range of 2-50 nm. Indeed, HT-P123 (C) contains mesopores and macropores (Figure S3), in accordance with the work of Petrolini et al. [21]. The HT-conventional (C) shows a non-uniform pore size distribution (Figure S3) indicating that the size of the pores of this HT structure is not uniform. As for the samples in which a surfactant was introduced, the pore distribution indicates that the distribution of pores is more uniform. For HT-glucose (C), in the literature [15] a pore size distribution around 7 nm was obtained. It is also to be noted that the peak obtained was narrow [15]. Our result was similar to that of the literature. HT-CTAB (C) has a porosity around 33 nm and HT-P123 (C) mainly around 61 nm (Table 2). HT-CTAB (C) was also found to be mesoporous by other authors [19]. For HT-SBA-15 (C), a pore distribution around 7 nm is obtained, which is in accordance with the literature [16]. It is concluded therefore that the use of a surfactant in the synthesis of a hydrotalcite will lead to the formation of more regular pore structure in the sample. It is also deduced from Table 2 that when a surfactant is added, the ssa of a sample increases considerably from 76 m²·g⁻¹ to values around 200–250 m²·g⁻¹ for all samples with a surfactant. Also, the pore volume increases from conventional HT to surfactantcontaining HT. HT-SBA-15 (C) shows a relatively high ssa (281 $m^2 \cdot g^{-1}$) compared to HT-conventional (C). This is expected, since as mentioned above, SBA-15 alone has a high ssa [39]. This sample also shows the highest pore volume, which is also attributed to the presence of SBA-15 in the interlayer of HT. Thus, due to the higher ssa obtained for the calcined samples modified by a surfactant or by SBA-15, it is expected



Figure 4. X-ray diffractograms of Ni-impregnated samples calcined at 550 °C (\blacktriangle : MgO-like phase (JCPDS N° 43-1022), •: MgAl₂O₄ spinel phase (JCPDS N° 75-1796), \blacklozenge : SiO₂).

that after Ni impregnation, stronger interactions between Ni and Mg–Al oxides will take place improving the dispersion of Ni and retarding the sintering of Ni particles during reforming process [41].

3.3. Physicochemical characterization of Niimpregnated samples calcined at 550 °C

3.3.1. X-ray diffraction (XRD)

XRD study was carried out on the calcined samples before Ni impregnation (curves not shown). After calcination at 550 °C, the hydrotalcite structure was transformed into mixed metal oxides MgAlOspinel phase and MgO-like phase [15,21,42,43].

The X-ray diffractograms of the Ni-supported catalysts are shown in Figure 4. After the impregnation of Ni, the XRD patterns remained the same. No line due to NiO diffraction was detected probably because of the overlapping between diffraction lines of periclase MgO and those of NiO. The oxide phase MgO periclase (JCPDS N° 43-1022) is present in all samples at $2\theta = 35$, 44, and 64°. The spinel MgAl₂O₄ (JCPDS N° 075-1796) phase was present in Ni-HTglucose at $2\theta = 46.5^{\circ}$ and in Ni-HT-CTAB at $2\theta =$ 40° [26,31]. As for Ni-HT-SBA-15 sample, the large intense peak present at $2\theta = 22.5^{\circ}$ is due to the presence of SiO₂ phase in the structure which comes from the intercalation of SBA-15 in the hydrotalcite structure [31,44]. The presence of a slight peak at $2\theta = 11.5^{\circ}$ for Ni-HT-glucose, as well as a peak at $2\theta = 22^{\circ}$ for Ni-HT-glucose (very slight), Ni-HT-P123, and Ni-HT-CTAB should also be noted. Till now we were not able to ascribe these peaks.

3.3.2. Porosimetry

Porosimetry for samples after Ni impregnation is done in order to be able to know whether the presence of nickel will modify the textural properties of the samples (will block some pores or decrease the ssa of the sample). While comparing the N₂-sorption curves of the samples as given in Figures 3 and 5, one observes a variation in the loop for some samples but always keeping type IV(a) isotherm. The samples containing glucose as surfactant and SBA-15 showed the same hysteresis type before and after nickel impregnation. After Ni impregnation, the hysteresis loop for the samples containing CTAB and P123 became type H3. This modification shows that the cylindrical pores present before impregnation became disordered lamellar with non-uniform (H3)



Figure 5. N₂ adsorption/desorption for Ni-impregnated samples: (a) Ni-HT-CTAB, (b) Ni-HT-glucose, (c) Ni-HT-P123, (d) Ni-HT-SBA-15.

Table 3. Different textural properties, given by the porosimetry, for the samples nickel impregnated on the supports

Samples	ssa (m ² ·g ⁻¹)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore size distribution (nm)
Ni-HT-CTAB	192	0.40	5.4
Ni-HT-glucose	179	0.25	3.9
Ni-HT-P123	174	0.41	3.6
Ni-HT-SBA-15	218	0.66	3.6

slits' size. Table 3 shows the ssa, pore volumes, and pore diameter values for the samples after Ni impregnation. The latter values decreased after nickel impregnation, except for Ni-HT-CTAB where the ssa remained the same. The decrease in the values of the textural parameters in the presence of nickel indi-



Figure 6. Temperature Programmed Reduction profiles of Ni-impregnated samples calcined at 550 °C.

cates some plugging of the pores by nickel species.

3.3.3. Temperature programmed reduction (TPR)

A TPR analysis was carried out to investigate the reducibility of the catalysts and in order to estimate the interaction between nickel species and the supports. TPR profiles of nickel impregnated on magnesium- and aluminum-based solids calcined at 550 °C are shown in Figure 6. It is worthy to note that no reduction peak is observed in the TPR profiles of the supports without nickel. Indeed, magnesium and aluminum oxides were not reduced in our experimental conditions. Conversely, nickel impregnated samples showed one or two reduction peaks, ascribed to the reduction of different nickel species. These peaks present low intensity probably due to the low amount of nickel impregnated (5 wt%).

The TPR profile of Ni-HT-glucose presents two peaks, indicating the presence of two different species of nickel oxide. The first peak is located at around 465 °C, and the second around 780 °C. The second peak is broad and has a very low intensity. The first peak is attributed to the reduction of nickel oxide in weak interaction with the support and the second one to the reduction of nickel species in strong interaction with the support [45,46].

As for the sample Ni-HT-P123, it showed a peak of higher intensity at temperatures within 450-550 °C.

This peak, as mentioned above, is related to the reduction of NiO in weak interaction with the support [4,46].

The absence of a reduction peak in the profile of Ni-HT-CTAB could be attributed to two reasons:

- Very strong interaction between nickel species and the support, and as a result the reduction of nickel will take place at temperatures above 900 °C.
- The low amount of nickel particles present are highly dispersed and thus their reduction, not easily detectable, does not lead to the appearance of a reduction peak.

In the profile of the sample Ni-HT-SBA-15, the graph shows one asymmetric reduction peak centered around 685 °C. This reduction peak is attributed to the reduction of nickel oxide strongly bonded and inserted in the structure [46,47].

3.4. Catalytic tests

The percentages of conversion of methane and carbon dioxide as a function of temperature, during the dry reforming of methane process, are presented in Figure 7. The increase of temperature will favor DRM thermodynamically and kinetically due to the DRM endothermic nature. As a result, an increase in the conversions of the reactants CH_4 and CO_2 is observed with the increase of the reaction temperature.



Figure 7. Conversion percentage of CH_4 and CO_2 versus reaction temperature in dry reforming of methane on the Ni-based catalysts.

It could be seen from Figure 7 that the catalysts show similar behaviors in both conversions of CH_4 and CO_2 , except Ni-HT-SBA-15 which shows null conversion of both methane and carbon dioxide. Based on the conversion of CH_4 and CO_2 , it appears that the order of catalytic activity varies with the reaction temperature. For the temperatures range 650–800 °C, according to CH_4 conversion, the order of catalytic activity is:

Ni-HT-conventional > Ni-HT-P123 > Ni-HT-glucose > Ni-HT-CTAB.

And according to CO₂ conversion, in the same range of temperature, this order is:

Ni-HT-conventional ~ Ni-HT-P123 > Ni-HT-glucose > Ni-HT-CTAB.

Furthermore, it is expected in our case, to have similar CO₂ and CH₄ conversions since the amounts used are stoichiometric. However, especially at 400–750 °C, a slight higher conversion for CO₂ than for CH₄ is noted. This fact is in line with the occurrence of side reactions that consume CO₂ such as methanation $(CO_2 + 4 H_2 \rightarrow CH_4 + 2 H_2O)$ at 400–550 °C, and reverse water gas shift $(CO_2 + H_2 \rightarrow CO + H_2O)$ at 600–750 °C.

Figure 8 shows the H_2/CO ratio and the carbon balance of the studied samples. H_2/CO ratio increases with the temperature increase and becomes close to 1 at T = 800 °C. In fact, in our case, equimolar amounts of the reactants CH₄ and CO₂ were used. Therefore, according to the stoichiometry of DRM reaction, the ratio H₂/CO should be equal to 1. A ratio lower than 1, as for our catalysts, suggests that side reactions are taking place along with the DRM such as reverse water gas shift reaction ($CO_2 + H_2$) \rightarrow CO + H₂O) which consumes H₂ and forms CO. H₂/CO ratio close to 1 reveals that almost only DRM reaction is taking place (at about 800 °C). However, in parallel, a carbon balance lower than 100% (at 800 °C) reveals that side reactions also take place, some of them produce H₂, some other CO, so that the overall ratio H₂/CO is slightly affected. Indeed, at 800 °C, the carbon balance is not 100% on our catalysts. This reveals that side reactions such as reverse water gas shift reaction and methane decomposition $(CH_4 \rightarrow C + 2 H_2)$ could take place with different extents. The latter reaction leads to carbon deposition and therefore to a deficit in carbon balance. Figure 8 also shows that the carbon balance is lower for Ni-HT-conventional than for Ni-HT-glucose and Ni-HT-P123. The higher carbon balance obtained for Ni-HT-CTAB is explained by its significant lower activity. The higher carbon balance for Ni-HT-glucose and Ni-HT-P123 indicates that the catalysts prepared with these surfactants have lower carbon deposition even if they show similar (for CO₂ conversion) or slightly lower (for CH₄ conversions) activities to those of Ni-HT-



Figure 8. H₂/CO ratio and carbon balance for the Ni-based catalysts in dry reforming of methane.

conventional. The higher carbon balance obtained in all catalysts that contained a surfactant reveals that the tendency to form carbon is less important on these catalysts than on Ni-HT-conventional. It is known that during DRM, the phenomenon of carbon deposition takes place and leads to the deactivation of the catalyst. It should be recalled that this carbon, in case present, comes from the decomposition of methane (CH₄ \rightarrow C + 2 H₂), Boudouard reaction, and reverse carbon gasification reaction (CO + H₂ \rightarrow C + H₂O), each of these reactions is favored at a given range of temperature. In fact, the high carbon balance, along with relatively high CH₄ and CO₂ conversions could be attributed to the presence of surfactants throughout synthesis, whose role is to increase the specific surface area of the support [48], therefore favoring the dispersion of the active phase nickel (active phase), improving the catalyst activity, and reducing carbon deposition as well as the catalyst deactivation [41].

The catalytic behavior of the catalyst containing SBA-15 could be explained by the fact that nickel species on its surface required some time to become active. Indeed, in the work of Tan *et al.* [22], different surfactants, tetrapropylammoniun hydroxide (TPAOH), P123, poly(vinylpyrrolidone) (PVP), and cetyltrimethylammonium bromide (CTAB), were used to prepare Ni–Mg–Al by hydrotalcite route. After calcination, the oxides were evaluated in DRM

at 800 °C under time on stream. The results showed that the oxides prepared with PVP and CTAB did not show catalytic activity before many hours under time on stream. Characterization studies showed that these oxides required some induction time to perform the growth of the plane Ni(200) that plays a key role in CH₄ activation for DRM. Conversely, TPAOH promoted the growth of Ni(200) plane and therefore, the corresponding oxide did not necessitate an induction period to become active. In fact, the crystallinity degree and the extent of exposure of Ni(200) play a crucial role in the catalytic behavior in DRM [22]. The effect of the surfactants was not the same in the work of Tan et al. [22]. It is thought that in our case, nickel species may necessitate some time under stream to become active in the oxide based on SBA-15, whereas in the other cases the formation of active nickel species is favored. Further characterization and catalytic tests studies should be performed on the SBA-15 based oxide to confirm our hypothesis.

3.5. Thermal analysis after test

DTA and TGA profiles of catalysts after DRM are shown in Figure 9. TGA curves for Ni-HT-CTAB (T), Ni-HT-glucose (T), and Ni-HT-P123 (T)—(T) designates the sample after test—showed weight losses between 5 and 8%, at around 300 °C accompanied



Figure 9. Thermal analysis after DRM for: (a) Ni-HT-CTAB (T), (b) Ni-HT-glucose (T), (c) Ni-HT-P123 (T).

by an exothermic peak in DTA corresponding to the oxidation of carbon present on the surface of materials. The results are in accordance with the carbon balance obtained in DRM (Figure 8) where the carbon balance was lower than 100% during the reaction.

4. Conclusion

The use of surfactants (CTAB, glucose, P123) or the intercalation of SBA-15 during the synthesis of MgAl hydrotalcite (HT) does not alter the structure. The oxides obtained after calcination evidenced more homogeneous pore distribution and higher specific

surface area than the oxide derived from conventional HT. These oxides were impregnated by 5 wt% nickel.

In our conditions, no activity is obtained in DRM on Ni-HT-SBA-15 (C), whereas good activities were obtained for all the other samples. However, the oxides derived from the surfactant-based samples showed a slightly higher carbon balance than on the oxide derived from conventional hydrotalcite revealing the formation of lower amount of carbon due to side reactions. High dispersion of nickel is responsible for this lower amount of carbon formed.

Finally, it is interesting to perform studies on the stability of the catalysts under time on stream. Such a study will evidence whether intercalation of SBA- 15 in Mg–Al hydrotalcite structure may show a catalytic activity in DRM after a given induction period. In addition, introduction of surfactants (CTAB, glucose, P123) in hydrotalcite structure results in a slight enhancement of the carbon balance. So, performing tests under time on stream may put more into evidence the stability with time of the catalysts with surfactants. Therefore, the longer time required to elaborate such catalysts and their higher cost will be justified by their significantly higher lifetime and lower carbon formation with time.

Conflict of interest

There is no conflict of interest to disclose.

Acknowledgments

The authors would like to thank the University of Littoral—Côte D'Opale (ULCO), the Agence Universitaire de la Francophonie (AUF)—Région du Moyen-Orient, and the Lebanese CNRS for funding this project. The authors would also like to thank the ARCUS E2D2 project, the French Ministry of Foreign Affairs, and the "Région Hauts de France" for financial support. The Lebanese University is also acknowledged for financing this work through the project: "Valorisation énergétique des déchets organiques par reformage catalytique du biogaz."

Supplementary data

Supporting information for this article is available on the journal's website under https://doi.org/10.5802/ crchim.49 or from the author.

References

- S. J. H. Rad, M. Haghighi, A.-A. Eslami, F. Rahmani, N. Rahemi, Int. J. Hydrogen Eng., 2016, 41, 5335-5350.
- [2] Z. Bian, S. Das, M.-H. Wai, P. Honfmanorom, S. Kawi, *Chem. Phys. Chem.*, 2017, 18, 3117-3134.
- [3] K. Mondal, S. Sasmal, S. Badgandi, D. R. Chowdhury, V. Nair, *Env. Sci. Poll. Res.*, 2016, 23, 22267-22273.
- [4] W.-C. Chung, M.-B. Chang, Eng. Conv. Manag., 2016, 124, 305-314.
- [5] Y. Zhu, S. Zhang, B. Chen, Z. Zhang, Z. Shi, *Catal. Today*, 2016, 264, 163-170.
- [6] A. G. Dedov, A. S. Loktev, V. P. Danilov, O. N. Krasnobaeva, T. A. Nosova, I. E. Mukhin, S. I. Tyumenova, A. E. Baranchikov, V. K. Ivanov, M. A. Bykov, I. I. Moiseev, *Petrol. Chem.*, 2018, **58**, 418-426.

- [7] M. M. Nair, S. Kaliaguine, New J. Chem., 2016, 40, 4049-4060.
- [8] C. Acar, I. Dincer, Int. J. Hydrogen Eng., 2014, 39, 1-12.
- [9] A. I. Tsyganok, T. Tsunoda, S. Hamakawa, K. Suzuki, K. Takehira, T. Hayakawa, J. Catal., 2003, 213, 191-203.
- [10] R. Dębek, K. Zubek, M. Motak, M. E. Galvez, P. Da Costa, T. Grzybek, C. R. Chim., 2015, 18, 1205-1210.
- [11] O. W. Perez-Lopez, A. Senger, N. R. Marcilio, M. A. Lansarin, *Appl. Catal. A*, 2006, **303**, 234-244.
- [12] D. Hu, J. Shan, L. Li, Y. H. Zhang, J. L. Li, J. Porous Mater., 2019, 26, 1593-1606.
- [13] Z. Roosta, A. Izadbakhsh, A. M. Sanati, S. Osfouri, J. Porous Mater., 2018, 25, 1135-1145.
- [14] M. N. Kaydouh, N. El-Hassan, A. Davidson, S. Casale, H. El Zakhem, P. Massiani, *Micropor. Mesopor. Mat.*, 2016, 220, 99-109.
- [15] X. Liu, B. Fan, S. Gao, R. Li, Fuel Process. Technol., 2013, 106, 761-768.
- [16] T. Baskaran, J. Christopher, T. G. Ajithkummar, A. Sakthivel, *Appl. Catal. A*, 2014, **488**, 119-127.
- [17] A. Pérez-Verdejo, A. Sampieri, H. Pfeiffer, M. Ruiz-Reyes, J.-D. Santamaría, G. Fetter, *Beilstein J. Nanotech.*, 2014, 5, 1226-1234.
- [18] J. Peng, D. Iruretagoyena, D. Chadwick, J. CO₂ Util., 2018, 24, 73-80.
- [19] H. K. D. Nguyen, H. V. Nguyen, V. A. Nguyen, J. Mol. Struct., 2018, 1171, 25-32.
- [20] P. Kurniawati, B. Wiyantoko, T. E. Purbaningtias, Muzdalifah, International Conference on Chemistry, Chemical Process and Engineering (IC3PE), AIP Conf. Proc., 2017, 1823, 020060-1-020060-7.
- [21] D. D. Petrolini, A. V. da Silva Neto, E. A. Urquieta-González, S. H. Pulcinelli, C. V. Santilli, L. Martins, *RCS Adv.*, 2018, 8, 6039-6046.
- [22] P. Tan, Z. Gao, C. Shen, Y. Du, X. Li, W. Huang, *Chin. J. Catal.*, 2014, **35**, 1955-1971.
- [23] L. Xu, H. Song, L. Chou, Appl. Catal. B, 2011, 108–109, 177-190.
- [24] R. Zăvoianu, R. Bîrjega, E. Angelescu, O. D. Pavel, C. R. Chim., 2018, 21, 318-326.
- [25] D. Chaillot, J. Miehé-Brendlé, S. Bennici, C. R. Chim., 2019, 22, 258-268.
- [26] D. Li, M. Koike, J. Chen, Y. Nakagawa, K. Tomishige, Int. J. Hydrog. Eng., 2014, 39, 10959-10970.
- [27] A. P. W. Kameni, H. L. Tcheumi, I. K. Tonle, E. Ngameni, C. R. Chim., 2019, 22, 22-33.
- [28] A. Pérez, J. F. Lamonier, J. M. Giraudon, R. Molina, S. Moreno, *Catal. Today*, 2011, **176**, 286-291.
- [29] F. Cavani, F. Trifirò, A. Vaccari, Catal. Today, 1991, 11, 173-301.
- [30] J. S. Valente, G. Rodriguez-Gattorno, M. Valle-Orta, E. Torres-Garcia, *Mater. Chem. Phys.*, 2012, 133, 621-629.
- [31] C.-R. Chen, H. Y. Zeng, S. Xu, X.-J. Liu, H.-Z. Duan, J. Han, J. Taiwan Inst. Chem. Engrs, 2017, 70, 302-310.
- [32] G. Lee, J. Y. Kang, N. Yan, Y.-W. Suh, J. C. Jung, J. Mol. Catal. A, 2016, 423, 347-355.
- [33] U. Sikander, S. Sufian, M. A. Salam, Procedia Eng., 2016, 148, 261-267.
- [34] I. Kirm, F. Medina, X. Rodríguez, Y. Cesteros, P. Salagre, J. Sueiras, *Appl. Catal. A*, 2004, **272**, 175-185.
- [35] L. A. Palacio, J. Velásquez, A. Echavarría, A. Faro, F. R. Ribeiro, M. F. Ribeiro, J. Hazard. Mater., 2010, 177, 407-413.

- [36] D. P. Debecker, E. M. Gaigneaux, G. Busca, *Chem. Eur. J.*, 2009, 15, 3920-3935.
- [37] C. V. Pramod, K. Upendar, V. Mohan, D. Srinivasa Sarma, G. Murali Dhar, P. S. Sai Prasad, B. David Raju, K. S. Rama Rao, *J. CO*₂ Util., 2015, 12, 109-115.
- [38] M. Abdollahifar, M. Hidaryan, P. Jafari, Boletín de la Sociedad Española de Cerámica y Vidrio, 2018, 57, 66-72.
- [39] M. Boutros, M. E. Gálvez, T. Onfroy, P. Da Costa, *Micropor. Mesopor. Mat.*, 2014, 183, 1-8.
- [40] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, *Pure Appl. Chem.*, 2015, 87, 1051-1069.
- [41] R. Dębek, M. Motak, M.-E. Galvez, T. Grzybek, P. Da Costa, *Appl. Catal. B*, 2018, **223**, 36-46.

- [42] G. Yang, J. Jiang, Y. Zhang, Prog. Org. Coat., 2015, 78, 55-58.
- [43] E. Dahdah, J. Estephane, R. Haydar, Y. Youssef, B. El Khoury, C. Gennequin, A. Aboukaïs, E. Abi-Aad, S. Aouad, *Renew. Eng.*, 2020, **146**, 1242-1248.
- [44] R. N. Widyaningrum, T. L. Church, A. T. Harris, *Catal. Commun.*, 2013, **35**, 40-45.
- [45] J. Guo, H. Lou, H. Zhao, D. Chai, X. Zheng, *Appl. Catal. A*, 2004, 273, 75-82.
- [46] H. M. Gobara, Egypt. J. Petrol., 2012, 21, 1-10.
- [47] H. Kamata, Z. Q. Tian, Y. Izumi, C. K. S. Choong, J. Chang, M. Schreyer, L. Chen, A. Borgna, *Catal. Today*, 2018, **299**, 193-200.
- [48] R. Guégan, C. R. Chim., 2019, 22, 132-141.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Comprehensive study of simultaneous adsorption of basic red 2 and basic violet 3 by an agro-industrial waste: dynamics, kinetics and modeling

Manel Wakkel^a, Besma Khiari^{*, b} and Fethi Zagrouba^a

^a Research Laboratory for Environment Sciences and Technologies, High Institute of Sciences and Technologies of Environment Borj Cédria, Hammam-Lif 2050, Tunisia

 b Wastewaters and Environment Laboratory, Water Research and Technologies Centre, 8020 Soliman, Tunisia

E-mails: manel.elwakkel@gmail.com (M. Wakkel), besmakhiari@yahoo.com (B. Khiari), fethi.zagrouba@isste.rnu.tn (F. Zagrouba)

Abstract. This paper aims to evaluate the simultaneous adsorption of basic red 2 (BR2) and basic violet 3 (BV3) in a binary system in a batch mode using date stones as low cost adsorbents. For both dyes, experimental kinetic data were well fitted by the Brouers–Sotolongo model ($R^2 = 0.99$) and intraparticle diffusion was the controlling step in mass transfer mechanisms. The intraparticle diffusion extent was found to be lower for BR2 $(1.13 \times 10^{-11} \text{ cm}^2/\text{s})$ than for BV3 $(1.11 \times 10^{-11} \text{ cm}^2/\text{s})$ when compared to individual solutions $(1.24 \times 10^{-10} \text{ cm}^2/\text{s} \text{ and } 1.76 \times 10^{-11} \text{ cm}^2/\text{s}$ for BR2 and BV3, respectively). The equilibrium study revealed lower adsorption capacities (41.95 and 88.91 mg/g for BR2 and BV3, respectively) compared to the individual sorption results (92.00 and 136.00 mg/g for BR2 and BV3, respectively) for both dyes. To assess the extent of competition and the preference of dyes for functional sites, competition and separation factors were calculated suggesting an antagonistic effect as well as a greater affinity for BV3 than for BR2 to the adsorption sites. The equilibrium adsorption results were best fitted by modified Langmuir and P-factor Langmuir isotherms for BR2 and BV3, respectively. Besides, based on enthalpy values (16.30 and 30.26 kJ/mol for BR2 and BV3, respectively), the simultaneous adsorption of both dyes was endothermic while the entropy revealed a higher affinity of the investigated adsorbent to BV3. The sorption process in separate systems (BR2 and BV3) was thermodynamically feasible for both dyes with negative free enthalpy values. The comparison to single systems showed an increase of affinity for BV3 contrarily to BR2 and, a decrease of spontaneity with higher extent for BR2.

Keywords. Date pits, Dyes, Binary system, Equilibrium, Kinetics, Modeling, Thermodynamic.

^{*} Corresponding author.

1. Introduction

Cationic or basic dyes are extensively used in textile industry processes [1,2]. The presence of dyes in water, even at very low concentrations, makes them unfit for human consumption [1]. The presence of small amounts of dyes in industrial waters is highly visible, due to their high stability and solubility in aqueous solutions [3]. Moreover, dyes as well as their degradation products could be toxic and carcinogenic, leading to serious hazards to aquatic organisms [4,5]. As for basic dyes, they are considered to be among the most toxic molecules due to the presence of metals in their structures [1, 6]. The wastewater containing dye molecules must, then, be treated before the discharge in the natural medium in order to overcome their negative environmental impacts [7]. Industrial wastewater treatment involves various methods: advanced oxidation processes, precipitation/coagulation, and biological treatment [8,9]. Such processes have some drawbacks, including high-energy requirement, consumption of chemicals, high operational cost, and the possible generation of toxic materials [10].

Nowadays, adsorption is emerging as an efficient method for dye removal from wastewaters [7,11,12]. Furthermore, adsorbents derived from agricultural crop residues, industrial by-products, etc. have received a particular attention due to their low cost [12-16]. Different types of modified and raw biosorbents such as rice husk, peat, pinus Sylvestris, red mud, sugarcane bagasse, etc. have been used for the removal of cationic dyes from aqueous solutions [9,17-21]. Date pits, which are agro-industrial solid wastes largely produced in MENA countries, are promising candidates as effective adsorbents [4,22]. Indeed, date stones are mainly composed of cellulose, hemicellulose, and lignin. These components are rich in hydroxyl and carbonyl groups which are implied during the dye adsorption process [4].

It is important to study the adsorption of dyes in a multi-component solution since industrial effluents are loaded with a mixture of numerous and different dyes. Indeed, at laboratory scale, few studies had focused on multi-solute system adsorption due to the complexity of wastewater composition and the possible interferences and competition between molecules [9,23]. In fact, Debnath *et al.* [23] studied the adsorption of safranine O (SO), brilliant green (BG), and methylene blue (MB) in a ternary dye system where the maximum adsorption capacities were estimated to be 67.9, 78.6, and 61.3 mg/g for SO, BG, and MB, respectively. Moreover, Mavinkattimath et al. [9] studied the adsorption of Remazol brilliant blue (RBB) and Disperse orange (DO) dyes by red mud on mixed dye system. The adsorption capacities were found to be 85 and 37 mg/g for DO and RBB, respectively. The presence of several dyes in a solution may mutually enhance or inhibit the adsorbent performance [9,24]. In general, a mixture of different adsorbates exhibits three possible behaviors: synergism (the effect of the mixture is more important than the individual adsorbates in the blend), antagonism (the effect of the individual solutes is greater than in the mix), or non-interaction [9,25].

During adsorption studies, kinetics, equilibrium, and thermodynamic data are necessary for the analysis and design of complex adsorption systems [9,26]. Various competitive multi-component models have been reported to describe the interaction, ranging from relatively simple models related only to individual parameters (non-modified models) to more complex ones with correction factors (modified models) [9].

As for date pits, there is presumably a lack of study on adsorption of cationic dyes which may be present simultaneously in a mixture solution. Thus, this research paper aims to investigate the sorption capacity of date pits in a bi-component system upon the contact with a mixture solution containing BR2 and BV3. The simultaneous adsorption is considered to assess the performance of date pits in a complex medium and to be near the conditions of real colored wastewaters.

2. Materials and methods

2.1. Preparation of dye solution mixture

The cationic dyes studied in this work, basic red 2 (BR2) known as safranin O and basic violet 3 (BV3) named also crystal violet, were provided by Sigma–Aldrich, USA. Their main chemical characteristics are summarized in Table 1. The stock solutions were prepared by dissolving 1 g of each dye powder in a volume of 1 L of distilled water, and were then diluted to get the desired concentration. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to

adjust the pH solutions to the optimum values of 7.28 and 7.7, respectively, for BV3 and BR2 allowing the highest removal efficiency [27]. These solutions were then mixed at one volumetric ratio 1:1 to obtain a bicomponent dye solution.

2.2. Preparation of date pit particles

Date pits were provided by a local industry of date transformation located in the city of Beni Khalled (North east of Tunisia). These wastes were washed, placed in an oven at 40 °C for 24 h, grounded and sieved to 125-250 µm size, and finally stored in a hermetically sealed container for later use in the adsorption experiments. The principal physicochemical properties of date stone particles were reported in our previous studies [4,27]. In fact, the average particle diameter and the pH at zero charge point (pH_{nzc}) were found to be equal to 187.5 µm and 6.8, respectively. Scanning electron microscopy (SEM) was used to study the surface morphology and structure of date pit particles. A rough surface with the presence of macropores was revealed. The amorphous nature of date stone powder was revealed by X-Ray Diffraction (XRD) analysis. Moreover, according to Fourier Transform Infrared (FTIR) spectroscopy analvsis, many bands were found ranging from 4000 to 400 cm⁻¹. In fact, a broad band of the O–H stretching vibration appears at 3396 cm⁻¹ which corresponds to hydroxyl groups and two adjacent bands were found at 2922 and 2852 cm⁻¹ and assigned to C-H stretching of aldehyde molecules. Moreover, a band of C=O stretching vibration located at 1745 cm⁻¹ was attributed to carbonyl groups. Carbonyl and hydroxyl groups are the main functional groups involved in the adsorption of BR2 and BV3 dyes from aqueous solutions [4,27].

2.3. Batch adsorption experiments

The adsorption measurements for binary systems were carried out by mixing 100 mg of date pit particles with 100 mL of BR2/BV3 mixture dye solution at a pH of 7.5. The samples of the reaction mixtures were put in a conical pyrex glass vessel and were agitated in batch experiments at a constant temperature of 35 °C using a horizontal thermostatic shaker at a speed of 125 rpm. After the stirring time, the liquid phase was separated from the adsorbent particles by a laboratory centrifuge type NÜVE[®] NF400 at a speed of 4000 rpm for 15 min. The residual concentrations were measured by using an ultraviolet-visible spectrometer at wavelengths (λ) of 518 and 584 nm for BR2 and BV3, respectively.

To investigate the kinetic, thermodynamic, and equilibrium uptake of BR2 and BV3 by date pits in the bi-component system, different experiments were carried out in which the contact time, the reaction temperature, and the initial concentration of the dye mixture were varied, respectively (Table 2).

The quantity of each adsorbed dye (q_t at time t and q_e at equilibrium) as well as the percentage adsorption (%) were calculated according to (1) to (4):

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

Adsorption rate at a given time,

$$t(\%)y_t = \frac{(C_0 - C_t)100}{C_0}(\%)$$
(2)

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{3}$$

Adsorption rate at equilibrium

$$(\%) y = \frac{(C_0 - C_e)100}{C_0} (\%), \tag{4}$$

where C_0 , C_t , and C_e (mg/L) are the dye concentrations in the mixture, initially, at time *t*, and when equilibrium is reached, respectively; *V* (L) is the volume of the solution and *W* is the dry date pit mass (g).

The total adsorption capacity in the mixture solution was also calculated, using (5):

$$q_T = \sum_{i=1}^n q_i.$$
⁽⁵⁾

The extent of the competition between the two dyes was assessed by the competition factor (CF), the expression of which is given by (6):

$$CF = \frac{q_{\rm mix}}{q_{\rm single}},\tag{6}$$

where q_{single} is the retention capacity in a singlesolute system while q_{mix} is that capacity in the binary-solute system.

This is an important parameter allowing to reveal the most affected component in the simultaneous adsorption system [28–30]:

- *CF* > 1: Adsorption is enhanced by the presence of other molecules (positive competition)
- *CF* < 1: Adsorption is reduced in the presence of other molecules (negative competition)

Characteristics	Basic red 2 (BR2)	Basic violet 3 (BV3)
Structural formula	$\mathrm{C_{20}H_{19}N_4Cl}$	$C_{25}H_{30}N_3Cl$
Dye category	Azine	Triarylmethane
Color Index (CI)	50,240	42,555
Wavelength (nm)	518	584
Molecular weight (g/mol)	353	407
Solubility in water at 25 °C (g·L ⁻¹)	50	16

Table 1. BR2 and BV3 chemical properties

Table 2.	Experimental conditions used for the kinetic, equilibrium, and thermodynamic studies in binary
system s	olutions

	Kinetic	Equilibrium	Thermodynamic
Initial dye concentration mixture (mg/L)	60	10-400	60
Contact time (min)	5-240	120	120
Temperature (°C)	35	35	15–50

• *CF* = 1: Adsorption is kept constant in the presence of other molecules (no competition).

2.4. Analytical procedure

Different concentrations of mixture solutions (BR2 + BV3) were prepared and the absorbance (optical density) of each dye in the mixture was measured at the same two wavelengths. The absorbance coefficients (also known by calibration constants) of each dye were obtained by plotting the absorbance against the dye concentration for each dye at each wavelength. The slope of the four linear regression lines gives the value of the absorbance coefficient for one dye at its wavelength of maximum absorption. These values are then used to calculate the dye concentrations in binary mixtures according to the following equations:

$$C_A = \frac{k_{B2}d_1 - k_{B1}d_2}{k_{A1}k_{B2} - k_{A2}k_{B1}} \tag{7}$$

$$C_B = \frac{k_{A1}d_2 - k_{A2}d_1}{k_{A1}k_{B2} - k_{A2}k_{B1}},$$
(8)

where, C_A and C_B (mg/L) are the concentrations of BR2 (A) and BV3 (B), respectively, in a binary solution. The absorbance coefficients are designated by (*k*) while the optical densities are called (*d*). The subscripts 1 and 2 are relative to λ_1 (518 nm) and λ_2 (584 nm), respectively.

2.5. Theoretical approach

2.5.1. Kinetic modeling

The simultaneous adsorption kinetics of BR2 and BV3 was fitted to several models as pseudo-firstorder [31], pseudo-second-order [32], Elovich [33], and Brouers–Sotolongo models [34,35] (Table 3).

The kinetic parameters gotten from the different theoretical models for the biosorption of BR2 and BV3 in the two-dye-component system were determined by non-linear fitting procedures using Excel (Microsoft) as a data-solver software. The suitability of kinetic models for describing the binary adsorption process was assessed by different error functions (see Section 2.6).

To determine whether the diffusion occurs through the pores of the adsorbent (pore flow diffusion) or across a boundary layer formed on the adsorbent (film diffusion), two diffusion kinetic models were used: Boyd's model, which determines if the main resistance to mass transfer is in the thin film (boundary layer) surrounding the adsorbent particle [36], while Webber's model highlights the extent of the resistance to diffusion inside the pores [37].

Boyd's equation allows to determine the film mass transfer constant (K_f) according to the following equation [36]:

$$\ln(1-F) = -K_f \cdot t, \tag{9}$$

674

Table 3. Kinetic model equations

Model	Equation		
Pseudo-first-order model	$q_t = q_e[\operatorname{Exp}(\ln q_e - k_1 t)]$		
Pseudo-second-order model	$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1}$		
Elovich model	$q_t = \frac{1}{\beta} \ln(\alpha \beta t)$		
Brouers–Sotolongo model	$q_t = q_e \left(1 - \left(1 + (n-1) \left(\frac{t}{\tau} \right)^{\gamma} \right)^{\frac{-1}{n-1}} \right)$		

where, *F* the fractional approach to equilibrium, defined as q_t/q_e , K_f is the film diffusion constant (min⁻¹), and *t* the Contact time (min).

The *F* value can be determined by the following equation

$$F = 1 - 6/\pi^2 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt)$$
(10)

where, *B* is the rate coefficient (s^{-1}) and *n* is the effective non-integer reaction order.

Based on the range of F value, Bt can be determined as follows:

For
$$F < 0.85$$
: $Bt = \left(\sqrt{\pi} - \sqrt{\pi - \left(\frac{\pi^2 F}{3}\right)}\right)^2$ (11)

For
$$F > 0.85$$
: $Bt = -0.498 - \ln(1 - F)$ (12)

The coefficients of film diffusion D_f were estimated according to the following equation:

$$D_f = \frac{Br^2}{\pi^2}.$$
 (13)

To identify the predominance of external intraparticle diffusion against surface film diffusion for both dyes in the binary adsorption system, the Biot numbers were calculated according to (14) [38].

$$Bi = \frac{k_f \cdot d \cdot C_0}{2 \cdot \rho_p \cdot D_{\rm ip} \cdot q_e},\tag{14}$$

where k_f (cm/s) is the film diffusion constant, $D_{\rm ip}$ (cm²/s) the intraparticle diffusion coefficient, C_0 (mg/L) the initial liquid-phase concentration, d (cm) the mean particle diameter, ρ_p (g/cm³) the adsorbent density, and q_e (mg/g) the solid-phase concentration at equilibrium.

Different intervals of Biot number can be distinguished:

> • When, *Bi* « 1, film diffusion is the controlling step

- When *Bi* ≫ 100, intraparticle diffusion is the limiting phenomenon
- When 1 < *Bi* < 100, film and intraparticle diffusion are the limiting steps.

2.5.2. Equilibrium modeling

Equilibrium during BR2 and BV3 simultaneous adsorption was modeled using eight isotherms including non-modified and modified Langmuir [17], Jain and Snoeyink (J-S) modified Langmuir [24], P-factor Langmuir [17,39], extended Freundlich [1,40], SRS model [41,42], and non-modified and modified Redlich-Peterson [43] (Table 4). The predictive multi-component adsorption isotherms were fed with mono-component parameters of the corresponding models due to the difficulty to predict multi-component equilibrium data and to the possible competitive effects [25]. The parameters of the investigated models were estimated following non-linear fitting procedures as indicated earlier. The optimum isotherm parameters were set, after calculating the error functions presented in Section 2.6.

2.5.3. Thermodynamic study

In order to highlight the effect of medium complexity on the thermodynamic parameters and especially on ΔH° and ΔS° , the following equations were used [44]:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$
(15)

$$K_d = \frac{q_e}{C_e}.$$
 (16)

 ΔH° and ΔS° values are extracted from the slope and the intercept of the Van't Hoff plot of $\ln(K_d)$ versus 1/T.

Model	Equation		
Non-modified Langmuir	$q_{e,i} = \frac{q_{\max,i} K_{L,i} C_{e,i}}{1 + \sum_{j=1}^{N} K_{L,j} C_{e,j}}$		
Modified Langmuir	$q_{e,i} = \frac{q_{\max,i} K_{L,i}(C_{e,i}/\eta_i)}{1 + \sum_{j=1}^{N} K_{L,j}(C_{e,j}/\eta_j)}$		
J–S Modified Langmuir	$q_{e,i} = \frac{(q_{\max,i} - q_{\max,j})K_{L,i}C_{e,i}}{1 + K_{L,i}C_{e,i}} + \frac{q_{\max,j}b_iC_{e,i}}{1 + K_{L,i}C_{e,i} + K_{L,j}C_{e,j}}$ $q_{e,j} = \frac{q_{\max,j}K_{L,j}C_{e,j}}{1 + K_{L,i}C_{e,i} + K_{L,j}C_{e,j}}$		
P-factor Langmuir	$q_{e,i} = \frac{1}{P_i} \left(\frac{k'_{L,i} C_{e,i}}{1 + a_{L,i} C_{e,i}} \right)$		
Extended Freundlich	$q_{e,1} = \frac{K_{F,1}C_{e,1}^{(1/n_1)+x_1}}{C_{e,1}^{x_1} + y_1C_{e,2}^{z_1}}$ $q_{e,2} = \frac{K_{F,2}C_{e,2}^{(1/n_2)+x_2}}{C_{e,2}^{x_2} + y_2C_{e,1}^{z_2}}$		
Sheindorf–Rebuhn–Sheintuch (SRS) model	$q_{e,i} = K_{F,i}C_{e,i}(C_{e,i} + a_{i,j}C_{e,j})^{(\frac{1}{n_i} - 1)}$		
Non-modified Redlich–Peterson	$q_{e,i} = \frac{K_{R,i}C_{e,i}}{1 + \sum_{j=1}^{N} \alpha_{R,j}C_{e,j}^{\beta_{R},j}}$		
Modified Redlich–Peterson	$q_{e,i} = \frac{K_{R,i}(C_{e,i}/\eta_{R,i})}{1 + \sum_{j=1}^{N} \alpha_{R,j}(C_{e,j}/\eta_{R,j})^{\beta_{R,j}}}$		

Table 4. Equilibrium models used for BR2 and BV3 adsorption in bi-component systems

2.6. Error functions

Different error functions are usually used to test the goodness of equilibrium and kinetic model parameters [45]. Table 5 lists the ones applied in this paper: the sum of the squares of the errors (SSE) [46], the hybrid fractional error function (HYBRID) [47], Marquardt's percent standard deviation (MPSD) [48], and the correlation coefficient (R^2) [49]. Models can be considered in good agreement with experimental data when R^2 is close to unity and when SSE, Hybrid, and MPSD values are as low as possible [50].

3. Results and discussion

3.1. Kinetic study and modeling

The experimental adsorption capacities of BR2 and BV3 in the binary system as a function of time are illustrated in Figure 1. For comparison reasons, the adsorption kinetics of each single-dyed solution is also presented; the initial concentration of this latter is the same as that in the mixture solution.

As it can be seen in Figure 1, the initial adsorption of BR2 and BV3 onto the date pits was faster in

Table 5. Applied error functions

Error function	Equation
Sum of squares of the errors (SSE)	$\sum_{i=1}^{N} (q_{e,\exp} - q_{e,\operatorname{cal}})_i^2$
Hybrid fractional error function (HYBRID)	$\sum_{i=1}^{N} \left[\frac{\left(q_{e,\exp} - q_{e,\text{cal}}\right)^2}{q_{e,\exp}} \right]_i$
Marquardt's percent standard deviation (MPSD)	$\sum_{i=1}^{N} \left[\frac{(q_{e,\exp} - q_{e,\text{cal}})}{q_{e,\exp}} \right]_{i}^{2}$
Correlation coefficient (R^2)	$\frac{\sum_{i=1}^{N} (q_{e,\text{cal}} - \overline{q_{e,\text{exp}}})_i^2}{\sum_{i=1}^{N} (q_{e,\text{cal}} - \overline{q_{e,\text{exp}}})_i^2 + \sum_{i=1}^{N} (q_{e,\text{cal}} - q_{e,\text{exp}})_i^2}$





the one-dye component than in the two-dye component systems. Thus, the adsorption kinetics of the two dyes affect each other but at different degrees. Indeed, the reduction of adsorption capacity was more important for BR2 than for BV3. In fact, at the beginning (t < 30 min), the difference between the uptake capacity of both dyes in single and binary systems could not be considered as negligible. However, at the final stage (t > 60 min), when equilibrium was almost reached, the q_t of BV3 was almost the same in the two cases (single and mixture solutions). These findings indicate that BV3 was not strongly affected by the presence of BR2, but the opposite was true.

The total adsorption capacity increased in contact with dye mixtures; its maximum was found to be equal to 97.49 mg/g, which is higher than in both the cases of BR2 and BV3 individual solutions. A possible explanation is that more than one dye in solution has increased the affinity of the date pits surface, either by a reorientation of the adsorbed molecules or through an alteration of the overall charge within the system [51].

The removal percentage was also determined (Figure 2). This was higher in one-dye solutions than in two-dyes' one. Besides, the reduction in intensity depended on the dye: only 66.58% of BR2 was removed in binary system versus 93.3% in mono system while the reduction was less significant for BV3 (from 98.85 to 95.90%). At the same time, the average adsorption percent of both dyes in the mixture solutions was found to be 81.24%. As highlighted earlier, this result can be explained by the antagonist effect of BV3 on the uptake of BR2. However, the former dye was not highly influenced by the presence of BR2.

In order to assess the extent of competition between BR2 and BV3, competition factors were calculated for a different time *t*. According to Figure 3, the competition factor varies during the adsorption process: in the first 30 min, the competition factor for both dyes increased exponentially with time. This result may be explained by the availability of adsorption sites in the date pit particles at the beginning of the adsorption process. Then, sites became saturated and the CF became almost constant (0.97 for BV3 and 0.71 for BR2). These values indicate that BR2 was relatively highly affected (0.71 < 1) by the existence of the BV3 in the same solution while the BV3 dye



Figure 2. Removal percentage of BR2 and BV3 at equilibrium in mono-dye and bi-dye solutions.



Figure 3. Competition factor variation as a function of time for BR2 and BV3 in a binary system.

was almost unaffected $(0.97 \approx 1)$ by the BR2. One can therefore conclude two different competition mechanisms: negative competition for BR2 and almost no competition for BV3.

A similar trend was reported by Issa *et al.* [29] when they investigated the kinetic biosorption of Allura Red (AR) and Sunset Yellow (SY) by activated pine wood. Authors reported that SY (CF = 0.76) dye manifested stable performance while AR (CF = 0.69) negatively competed with the other dye molecules. A reasonable explanation was attributed to the differences in the dyes' properties (solubility, molecular weight) as well as their affinity for adsorption sites.

Kinetics modeling

Table 6 gives the kinetic parameters extracted from different models applied to the biosorption of our two dyes on date stones in mixture solutions. Experimental adsorption data showed a poor fit for the Elovich model where R^2 exhibited the lowest values, and SSE, Hybrid, and MPSD exhibited the highest values for both dyes. This finding indicates that the chemisorption is not the mechanism that may explain the dyes' uptake and that the desorption reaction of dyes cannot be neglected in this system [4].

At the same time, the calculated values of R^2 , SSE, Hybrid, and MPSD indicated that the sorption of the two dyes from mixture solutions was better described by the pseudo-second order kinetics than by the pseudo-first order kinetics especially for BV3, for which R^2 is equal to 0.993 with the former model while it is equal to 0.967 with the latter model.

But, among the four investigated models, the Brouers–Sotolongo model showed the best match, based on all calculated error functions, for both cationic dyes in simultaneous adsorption systems.

This finding is strengthened by the predicted values of adsorption capacity (39.8 mg/g for BR2 and 58.7 mg/g for BV3) according to Brouers–Sotolongo model which were very close to the experimental q_t values (40.0 and 57.6 mg/g).

To visualize the different applied models during the whole process, the theoretical plots of kinetic data were displayed in Figure 4. As expected, Brouers–Sotolongo models follow perfectly the experimental uptake capacity upon all the studied range time, contrarily to Elovich and order-basedreaction models for both dyes.

Mechanistic study (mass transfer)

Boyd's and Webber's kinetic models were applied to determine the main resistance to mass transfer. The values of Bt were calculated as indicated earlier and then plotted against t (Figure not shown). The obtained graph shows a linear trend-line not passing through the origin and the slope is the mass transfer parameter K_f [52].

Mass transfer parameter (K_f) and coefficient of film diffusion (D_f) values obtained in mixture solutions were summarized in Table 7 and compared to those obtained in our previous study dealing with the adsorption of these dyes in mono-component dye solutions [4].

According to Table 7, the comparison of D_f values of BR2 in single $(3.99 \times 10^{-9} \text{ cm}^2/\text{s})$ and binary $(3.18 \times 10^{-9} \text{ cm}^2/\text{s})$ solution showed that the adsorption of this pigment slowed down in the mixture so-

	Model	Parameter	Value	SSE	HYBRID	MPSD	R^2
	$q_{e,\exp}$ (mg/g)		40.0				
	Pseudo-first order	$K_1 ({ m min}^{-1})$	0.103	7 029	0 338	0.018	0 988
		$q_e (\mathrm{mg}/\mathrm{g})$	39.131	1.025	0.520		0.000
	Pseudo-second order	$K_2 \text{ (mg/g·min)}$	0.004	30 555	79 961	3 373	0 989
BR2		$q_e (\mathrm{mg/g})$	41.994	00.000	10.001	0.010	0.000
	Elovich	α (mg/g·min)	45.67	120.444	5.615	0.319	0.802
		eta (g/mg)	0.17	1201111	0.010	0.010	0.002
		n	2.665				
	Brouers-Sotolongo	au (min)	6.136	0.558	0.015	0.0004	0.999
	0	γ	2.242				
		$q_e (\mathrm{mg/g})$	39.818				
	$q_{e,\exp}$ (mg/g)		57.6				
	Pseudo-first order	$K_1 ({ m min}^{-1})$	0.151	22 136	0 488	0.011	0 967
		$q_e (\mathrm{mg/g})$	55.888	22.100	0.100	0.011	0.001
	Pseudo-second order	$K_2 \text{ (mg/g·min)}$	0.004	4 305	12 149	0.339	0 993
BV3		$q_e (\mathrm{mg/g})$	58.810	1.000	12.110	0.000	0.000
	Elovich	α (mg/g·min)	781.02	90.169	2.1711	0.0558	0.849
		β (g/mg)	0.17	00.100	2.11.11	0.0000	0.010
		n	9.392				
	Brouers-Sotolongo	au (min)	2.622	0.6839	0.0139	0.0003	0.999
	0	γ	6.859				
		$q_e (\mathrm{mg/g})$	58.756				

Table 6. Parameters of kinetic models for the adsorption of BR2 and BV3 on date stones on mixture solution

Table 7. Internal and external mass transferparameters in mono- and bi-component system for BR2 and BV3

		K_f	$D_f (\mathrm{cm}^2/\mathrm{s})$
BR2	Single	4.48×10^{-4}	3.99×10^{-9}
	Mix	3.57×10^{-4}	3.18×10^{-9}
BV3	Single	3.06×10^{-4}	2.73×10^{-9}
	Mix	3.88×10^{-4}	3.46×10^{-9}

lution by a factor of 1.25 contrarily to BV3 where the film diffusion coefficient was raised by almost the same factor (1.27). The opposite trend of BR2 and BV3 can be explained by the electrostatic coupling effect where the faster molecule (BR2) was slowed down by BV3 and vice-versa. This phenomenon was reported during the adsorption of charged molecules such as proteins.

On another note, since the diffusion film coefficients were not in the range of 10^{-6} and 10^{-8} cm²/s, mass transfer mechanisms of BR2 and BV3 in mixture solutions cannot be controlled by the sole phenomenon of film diffusion [53]. These results are in accordance with the plot of Boyd's model which did not pass through the origin. The BR2 and BV3 sorption in this case was not governed only by external mass transfer controlled film diffusion, but also by intraparticle transport, i.e., pore diffusion.

To identify the importance of the intraparticle diffusion step of BR2 and BV3 in the binary adsorption process, the mathematical expression in the Weber and Morris model was used:

.

$$q_t = K_{\rm in} \cdot t^{\frac{1}{2}} + C, \tag{17}$$



Figure 4. Experimental and fitted kinetic curves describing the adsorption of BR2 (A) and BV3 (B) by date pits from binary solution.

where K_{in} is the intraparticle diffusion constant and the intercept *C* reflects the boundary layer effect [37].

The occurrence of intraparticle diffusion as the rate limiting step requires that the plot of q_e versus $t^{1/2}$ should be linear with a nil intercept.

However, the BR2 and BV3 plots, shown in Figure 4, are not linear over the whole time range and, instead, can be divided into three sections. The first sharper portion is the slowly rising stage where the external surface adsorption was implied. The second portion is a straight line reflecting the gradual sorption stage where the intraparticle diffusion is rate controlling. The final equilibrium stage is a plateau, where the intraparticle diffusion slows down due to the low solute concentration in the solution [54].

These non-linear sections indicate that surface adsorption and intraparticle diffusion processes occur simultaneously. This finding is similar to that reached in previous works [55,56].

The values of k_{in} and *C* parameters were calculated by minimizing the SSE errors using Solver EX-CEL and then compared to those obtained in single

solutions (Table 8).

The nonzero intercepts in each case indicate that the rate controlling process was not only due to the intraparticle diffusion but also due to some other mechanisms involved [57].

Moreover, *C* values for both dyes were lower in mixture solution revealing that less surface was available for the adsorption of BR2 and BV3 in the binary system and, the extent of mass transfer resistance due to boundary layers was reduced.

The diffusion coefficients (D_{ip}) in the binary mixture were obtained using the following equation [52,58]:

$$K_{\rm in} = \frac{6q_e}{r} \sqrt{\frac{D_{\rm ip}}{\pi}},\tag{18}$$

where r is the radius of the spherical adsorbent particle.

BR2 and BV3 have almost the same diffusion coefficients (D_{ip}) in binary mixtures which were 1.13×10^{-11} and 1.11×10^{-11} cm²/s, respectively (Table 8). But, when compared to mono systems, this parameter dropped for both dyes, more significantly for BR2 by a factor of 11.0 than for BV3 (factor of 1.6). These results indicate that the presence of BV3 dye affects significantly the diffusion rate of BR2 dye inside date pit particles. The competition between BR2 and BV3 to diffuse inside adsorbent and the possible poreblocking phenomena can be the cause of these observations.

Biot number was used to evaluate the predominance of film diffusion against intraparticle in binary adsorption system. Biot numbers were found to be greater than 100 for BR2 (389.77) and BV3 (300.26) indicating that the biosorption in binary systems was mainly controlled by internal diffusion mechanisms for both dyes. This behavior was different in the mono-component system for BR2 where the resistance to intraparticle diffusion was negligible in front of the resistance to film diffusion. This trend was reported in the recent study of Sharma et al. [1] dealing with the adsorption of Methylene blue (MB) and Safranin O (SO) in binary system. In fact, it was found that intraparticle diffusion was responsible for the transportation of MB and SO from aqueous solution to the adsorbent surface.

Thus, it can be concluded from this part that the medium complexity affects the rate of sorption of the diffusion coefficients and the controlling step on

		$K_{\rm in}~({\rm mg/g}\cdot{\rm min}^{0.5})$	<i>C</i> (mg/g)	$D_{\rm ip}~({\rm cm^2/s})$	$D_{\rm ipSingle}/D_{\rm ipMix}$	Bi
BDJ	Single	1.74	35.68	1.24×10^{-10}	10.00	31.92
BR2 0 Mix	Mix	0.38	34.92	1.13×10^{-11}	10.55	389.77
BV3	Single	0.70	51.00	1.76×10^{-11}	1.50	145.21
DVD	Mix	0.54	50.62	1.11×10^{-11}	1.59	300.26

 Table 8. Intraparticle diffusion model parameters and Biot numbers in mono- and bi-component systems for BR2 and BV3



Figure 5. Experimental isotherms of BR2 and BV3 in single and binary systems.

the kinetic adsorption reaction. In fact, it was found that BR2 was more affected by the presence of BV3 since it was hindered by this later dye. BV3 showed more affinity for adsorption sites compared to BR2. Intraparticle diffusion was the controlling step in the mass transfer of both dyes in a binary dye system. The intraparticle diffusion coefficients dropped significantly for BR2 in the mixture solution compared to single solution contrarily to BV3.

3.2. Equilibrium study

Adsorption isotherms would describe how BR2 and BV3 interact with the date pits and, therefore, help to approach the adsorption mechanism and to determine the equilibrium adsorption capacity. Figure 5 depicts then the experimental adsorption capacity (q_e) of BR2 and BV3 in single and binary systems as a function of dye concentration (C_e) when equilibrium is reached.

One can see that, for the low equilibrium dyes concentration, the concentrations of BV3 on the solid phase (q_e) in the mixture were almost equal to those when this dye was present individually in the solution. This behavior was different for BR2 where the adsorption capacity was clearly lower in binary systems compared to the single ones even for low dye concentrations. The uptake capacity of BV3 was more disturbed at higher dye concentrations (C_e). However, in higher solute concentrations, lower adsorption capacities were recorded for both dyes compared to the individual sorption results.

A deeper examination of the BV3 isotherms brings out that this latter is L-curve in the binary system, which is a sign of high affinity. The BV3 adsorption mechanism was not highly affected by the conditions of competition contrarily to BR2 dye. For this latter, a less regular shape of isotherm is noticed in the mixture solution compared to the mono-dye solution. Similar results were found by Al-Degs *et al.* [43] who indicated that the concentration of the dye being adsorbed increased before it decreased again. In our case too, BV3 may have displaced and replaced the BR2 dye which has less affinity to the adsorption date pit sites.

Figure 6 gives a comparison of individual BR2 and BV3 experimental adsorption capacities both in single and binary component systems as well as the total adsorption capacity.

It is clear that the adsorption capacity was reduced for both dyes in the binary system, which suggests a high competition between the dyes to occupy the active sites.

It should also be indicated that BR2 was more affected than BV3 in The mixture solution where the reduction percentage was 54.4% and 34.6% for BR2 and BV3, respectively.

In both cases, the drop of the adsorption capacities in the binary solutions can be the consequence of several factors including (i) interaction between dyes in solution; (ii) change of the sorbent surface charge



Figure 6. Experimental maximum adsorption capacities of BR2 and BV3 in mono- and bi-component solutions.

due to adsorption; (iii) displacement effects; and (iv) non-functional groups of an adsorbed dye blocking the active sites for the adsorption of other dyes [9].

The total adsorption capacity is apportioned as follows: 67.94% for BV3 and 32.06% for BR2. Thus, the available adsorption sites on date stones are preferentially occupied by BV3. This finding can be explained by the high molecular weight of BV3 (407 g/mol vs. 353 g/mol for BR2) and by its lower solubility (16 g/L vs. 50 g/L for BR2) [51,59,60]. Similar results were reported by Fernandez *et al.* [60] who studied the adsorption of Rhodamine B (RhB) and Methylene Blue (MB) by orange peels in binary system. In fact, it was showed that Rhodamine B exhibited higher adsorption capacity compared to Methylene Blue since the size of the former dye was higher (373.91 and 479.0 g/mol for MB and RhB, respectively).

Competition and separation factors

The extent of competition was assessed by the magnitudes of the competition factors (CF). Figure 7 displays the variation of the competition factor as a function of the initial dye concentration for both dyes.

In all cases, the competition factors were inferior to 1, demonstrating a negative competition between the solutes. The least affected was BV3, due to its high affinity toward the date pit particles. In all tests too, the removal of each of BR2 and BV3 decreased when these two solutes are both present in the solution. The serious inhibition of the adsorption of both dyes when they coexisted implied an antagonistic effect.



Figure 7. Competition factor variation as a function of initial concentrations of BR2 and BV3.

Moreover, besides the competition factor, the separation factor is generally adopted to assess the preference for the adsorption sites by mono- and bicomponent solutions [23]. The separation factor α_B^A is expressed by (19) and is calculated from the equilibrium sorption data [23]:

$$\alpha_B^A = \frac{q_A C_B}{q_B C_A}.$$
 (19)

If $\alpha_B^A > 1$, then the ion A (BR2) is preferred and, if $\alpha_B^A < 1$, then it is the ion B (BV3), which is preferred. The separation factor (0.42) was found lower than unity, which means that BR2 is not preferred and, BV3 had more affinity to the date pit particles, supporting the conclusions reached earlier.

Equilibrium modeling

The parameters obtained by the different applied models as well as the corresponding error functions are provided in Table 9.

All of the non-modified Langmuir model, the J–S modified Langmuir, the SRS model, and the non-modified Redlich–Peterson model exhibited a poor fit to the BR2 experimental data as indicated by the low R^2 values (0.441, 0.377, 0.251, and 0.442, respectively). Therefore, the assumption of non-competitive biosorption of BR2 was invalid. The *P*-factor Langmuir and extended Freundlich models could not fit the BR2 experimental data (R^2 equal to 0.872 and 0.803, respectively). Some previous researches also reported that the *P*-factor model did not account for competition nor for interactions between the metal ions [61]. The best match for BR2 was provided by the modified Langmuir and

	Model	Parameter	Value	SSE	HYBRID	MPSD	R^2
BR2	Non-modified Langmuir	$q_{ m max}$ (mg/g) K_L (L/mg)	97.893 0.1794	4445.818	305.984	34.102	0.441
	Modified Langmuir	$q_{\max} (mg/g)$ $K_L (L/mg)$	97.893 0.179 8 190	33.358	2.523	0.319	0.975
	J–S Modified Langmuir	$q_{\rm max} ({\rm mg/g})$ $K_L ({\rm L/mg})$	97.893 0.179	4004.346	268.070	29.358	0.377
	P-factor Langmuir	P K'_L (L/mg) a_L (L/mg)	2.240 7.358 0.070	165.638	10.691	1.302	0.872
	Extended Freundlich	$ \begin{array}{c} K_F (L/mg) \\ n \\ x \\ y \\ z \end{array} $	38.912 5.791 1.315 20.212 0.854	285.839	59.841	0.678	0.803
	SRS model	K_F (L/mg) n a	38.912 5.791 3.740	1495.565	108.537	12.785	0.251
	Non-modified Redlich–Peterson	$K_R (L/mg)$ α_R β_R	14.353 0.108 1.060	7240.304	177.216	4.445	0.442
	Modified Redlich–Peterson	$K_R (L/mg)$ $\alpha_R (L/mg)$ β_R η_R	14.353 0.108 1.060 6.151	35.077	2.513	0.303	0.973

Table 9. Equilibrium parameters for BR2 and BV3 adsorption in mixture solution by date pits

(continued on next page)

the modified Redlich–Peterson models which exhibited the highest correlation coefficient R^2 (0.975 and 0.973, respectively). Following SSE, Hybrid, and MPSD values, we can conclude that the modified Langmuir model described most accurately the adsorption behavior of BR2 in the binary dyes system. This finding may be due to the fact that this model considers the surface heterogeneity of the adsorbent and the mutual interaction effect of the different dye molecules [52]. As a matter of fact, the modified Langmuir model accounts for the influence of other competing solutes by means of the interaction factor (η). Similar previous results were explained by the fact that one adsorption site cannot be simultane-

ously occupied by two solutes, and competitive sorption between pollutants occur when they coexisted in wastewaters [29,51,62].

As for BV3, the *P*-factor model could match best the equilibrium adsorption data. Previous works have also successfully described binary adsorption by the *P*-factor model. This model is, in fact, a major enhancement over the modified Langmuir model [17,61], thanks to the lumped factor P_i , defined as the ratio between q_{max} on mono- and multicomponent systems. The calculus of this factor for BV 3 gives a *P*-value equal to 1.53 which is so close to the *P*-factor (1.55) provided upon the fitting using the *P*-factor model.

	Model	Parameter	Value	SSE	HYBRID	MPSD	R^2
	Non-modified Langmuir	$q_{\rm max}$ (mg/g)	117.357	6641.909	91.990	1.344	0.569
BV3		K_L (L/mg)	0.300				
	Modified Langmuir	$q_{ m max}$ (mg/g)	117.357	12,686.623	182.769	3.003	0.547
		K_L (L/mg)	0.300				
		η	9.438				
	J–S Modified Langmuir	$q_{ m max}$ (mg/g)	117.357	6641.909	91.990	1.344	0.569
		K_L (L/mg)	0.300				
	<i>P</i> -factor Langmuir	Р	1.552	281.863	9.534	0.371	0.928
		K_L' (L/mg)	42.795				
		a_L (L/mg)	0.301				
	Extended Freundlich	K_F (L/mg)	41.741	5304.276	59.841	0.676	0.727
		n	4.701				
		x	12.455				
		у	17,281.474				
		Z	0.001				
	SRS model	K_F (L/mg)	41.741	3575.884	50.150	0.787	0.736
		n	4.701				
		a	0.176				
	Non-modified Redlich–Peterson	K_R (L/mg)	347.391	7603.937	112.813	1.820	0.66
		α_R	7.695				
		β_R	0.803				
	Modified Redlich–Peterson	K_R (L/mg)	347.391	43,136.427	548.898	7 709	0.476
		α_R (L/mg)	7.695				
		β_R	0.803			1.103	
		η_R	170.311				

Table 9. (continued)

Among the eight tested models, the three equilibrium models fitting the best experimental data are (Figure 8):

- For BR2: Modified Langmuir > Modified Redlich–Peterson > *P*-factor Langmuir
- For BV3: *P*-factor Langmuir > SRS model > Extended Freundlich.

According to this summary, it is clear that the mechanisms of adsorption are different for each dye since they were represented by equilibrium models where the assumptions are different.

3.3. Thermodynamic study

A series of experiments were conducted at 15, 25, 35, 45, and 50 °C to approach the temperature effect on the equilibrium capacity of the date pits for the BR2 and BV3 cationic dyes in the binary system.

The quantities of BR2 and BV3 adsorbed on the date pit particles in single and mixture solutions as a function of solution temperature are depicted in Figure 9.

The rise in solution temperature increases the adsorbed quantities of BR2 and BV3 in bi-component systems. This trend was also observed in the onecomponent solutions and might be due to an in-



Figure 8. Equilibrium models of BR2 (A) and BV3 (B) in the binary adsorption system.



Figure 9. Variation of q_e as a function of temperature for BR2 and BV3 in mono- and bicomponent systems.

crease in dye mobility that may occur at higher temperatures. Moreover, the effect of temperature was more significant in the mono-component than in the bi-component systems, especially for BR2 (Figure 9).

Thermodynamic parameters, enthalpy (ΔH°), and entropy (ΔS°) values are given in Figure 10, together with those calculated in mono-dye solutions.



Figure 10. Comparison of enthalpy (A) and entropy (B) values for BR2 and BV3 in mono- and bi-component systems.

Several conclusions can be outlined. The adsorption in the mixture solution is endothermic since the value of enthalpy ΔH° is positive for BR2 (16.30 kJ/mol) and BV3 (30.26 kJ/mol) dyes (Figure 10-A). This is the result of two simple mechanisms [63]: (i) desorption of the solvent molecules previously adsorbed, and (ii) adsorption of the dye molecules. Each molecule of the colorant displaces more than one molecule of the solvent. The net result brings out an endothermic process. Comparison with the mono-component system showed that ΔH° was almost the same for BR2, contrarily to BV3, where the enthalpy was greater in mixture solution (30.26 against 24.98 kJ/mol). Similar results were reported by Sharma et al. [1] indicating the endothermic nature of simultaneous adsorption of methylene blue and Safranin O where the enthalpy values were 26.11 and 30.84 kJ/mol, respectively.

The positive values of ΔS° reflect the affinity of date pits for BR2 (57.63 J/mol·K) and BV3 (125.78 J/mol·K) and show the increasing of randomness at the solid/liquid interface during the adsorption of dyes in the binary system (Figure 10-B). By



Figure 11. Free enthalpy variation as function of temperature for BR2 and BV3 in mono- and bi-component systems.

comparison with the mono-dye solution, the entropy value relative to BR2 was dropped, suggesting that the randomness and the affinity also decreased. Contrary to BR2, the adsorption of BV3 is associated with a rise in entropy from 114.19 J/mol·K in mono to 125.78 J/mol·K in bi-component systems, which means that the adsorbed dye molecules are organized more randomly in this last case.

Debnath *et al.* [23] determined the entropy variation upon the simultaneous adsorption of dyes in ternary system which was found to be 54.51, 57.01, and 65.02 J/mol·K for Safranin O, brilliant green, and methylene blue. The positive entropy change indicate the increase in the number of species at the solid–liquid interface.

The free enthalpy ΔG° , the value of which is expressed by (20), is another calculated thermodynamic parameter (Figure 11) that gives information about the spontaneity of the adsorption reaction [44, 64]:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}. \tag{20}$$

Similar to single-component systems, ΔG° was negative which indicate that the overall adsorption processes in the mixture solution are also spontaneous. This spontaneity decreases with the increase of temperature in one hand and when adding a second dye in the solution on the other hand. This is truer for BR2 than for BV3.

Similar results were reported by Debnath *et al.* [23] where the free enthalpy variation was negative for the three studied dye in mixture solutions (Safranin O, brilliant green, and methylene blue).

4. Conclusions

This study investigated the kinetics, equilibrium, and thermodynamics of the biosorption of two cationic dyes (basic red 2 and basic violet 3) on date pit particles in a two-dye-component solution. The overall uptake capacity of the dyes in the binary system decreased due to the antagonistic interaction between dyes. Indeed, BV3 inhibited the adsorption of BR2. The comparison of different parameters between the mono- and the bi-component system revealed that the behavior of both dyes has changed.

Finally, based on the biosorption capacities of BR2 (41.95 mg/g) and BV3 (88.11 mg/g), the Tunisian annual amounts of date pits could eliminate simultaneously about 34 T of BR2 and 72 T of BV3 from textile industrial effluents.

References

- [1] K. Sharma, R. K. Vyas, K. Singh, A. K. Dalai, J. Environ. Chem. Eng., 2018, 6, 5732-5743.
- [2] T. W. Seow, C. K. Lim, Int. J. Appl. Eng. Res., 2016, 11, 2675-2679.
- [3] P. Zhang, S. Ouyang, P. Li, Y. Huang, R. L. Frost, *Chem. Eng. J.*, 2019, **360**, 1137-1149.
- [4] M. Wakkel, B. Khiari, F. Zagrouba, J. Taiwan Inst. Chem. Eng., 2019, 96, 439-452.
- [5] M. S. H. Mohd Shaid, M. A. A. Zaini, N. S. Nasri, J. Cleaner Prod., 2019, 223, 487-498.
- [6] J. Xiao, L. Wang, J. Ran, J. Zhao, M. Tao, W. Zhang, *Reactive Funct. Polym.*, 2020, **146**, article no. 104394.
- [7] S. Tian, S. Xu, J. Liu, C. He, Y. Xiong, P. Feng, J. Cleaner Prod., 2019, 239, article no. 117767.
- [8] A. H. Jawad, N. S. A. Mubarak, A. S. Abdulhameed, Int. J. Biol. Macromol., 2020, 142, 732-741.
- [9] R. G. Mavinkattimath, V. S. Kodialbail, S. Govindan, *Environ. Sci. Pollut. Res.*, 2017, 24, 18912-18925.
- [10] B. Kakavandi, A. Takdastan, S. Pourfadakari, M. Ahmadmoazzam, S. Jorfi, J. Taiwan Inst. Chem. Eng., 2019, 96, 329-340.
- [11] N. Abidi, J. Duplay, A. Jada, E. Errais, M. Ghazi, K. Semhi, M. Trabelsi-Ayadi, C. R. Chim., 2019, 22, 113-125.
- [12] A. A. Azzaz, S. Jellali, Z. Bengharez, L. Bousselmi, H. Akrout, *Int. J. Environ. Sci. Technol.*, 2019, **16**, 7393-7408.
- [13] J. Liu, F. Chen, C. Li, L. Lu, C. Hu, Y. Wei, P. Raymer, Q. Huang, J. Cleaner Production, 2019, 208, 552-562.
- [14] A. Chouchene, M. Jeguirim, G. Trouvé, *Clean Technol. Environ. Policy*, 2014, 16, 979-986.
- [15] A. A. Azzaz, S. Jellali, A. A. Assadi, L. Bousselmi, *Desalination Water Treatment*, 2016, 57, 22107-22119.
- [16] A. A. Azzaz, S. Jellali, R. Souissi, K. Ergaieg, L. Bousselmi, *Environ. Sci. Pollut. Res.*, 2017, 24, 18240-18256.
- [17] S. N. do Carmo Ramos, A. L. P. Xavier, F. S. Teodoro, M. M. C. Elias, F. J. Goncalves, L. F. Gil, R. P. de Freitas, L. V. A. Gurgel, *Ind. Crops Prod.*, 2015, **74**, 357-371.
- [18] S. N. do Carmo Ramos, A. L. P. Xavier, F. S. Teodoro, L. F. Gil, L. V. A. Gurgel, *Ind. Crops Prod.*, 2016, **79**, 116-130.
- [19] J.-X. Yu, J. Zhu, L.-Y. Feng, X.-L. Cai, Y.-F. Zhang, R.-A. Chi, Arab. J. Chem., 2019, 12, 2044-2051.
- [20] A. A. Azzaz, S. Jellali, H. Akrout, A. A. Assadi, L. Bousselmi, *Environ. Sci. Pollut. Res.*, 2017, 24, 9831-9846.
- [21] A. A. Azzaz, S. Jellali, H. Akrout, A. A. Assadi, L. Bousselmi, *J. Cleaner Prod.*, 2018, **201**, 28-38.
- [22] Z. Belala, M. Jeguirim, M. Belhachemi, F. Addoun, G. Trouvé, *Environ. Chem. Lett.*, 2011, 9, 65-69.
- [23] S. Debnath, N. Ballav, A. Maity, K. Pillay, J. Mol. Liq., 2017, 225, 679-688.
- [24] B. Noroozi, G. Sorial, H. Bahrami, M. Arami, *Dyes Pigments*, 2008, **76**, 784-791.
- [25] M. Turabik, J. Hazard. Mater., 2008, 158, 52-64.
- [26] B. Khiari, M. Wakkel, S. Abdelmoumen, M. Jeguirim, *Materials*, 2019, **12**, 365-388.
- [27] M. Wakkel, B. Khiari, F. Zagrouba, *Environ. Sci. Pollution Res.*, 2019, **26**, 18942-18960.
- [28] M. A. Al-Ghouti, A. A. Issa, B. S. Al-Saqarat, A. Y. Al-Reyahi, Y. S. Al-Degs, *Desalination Water Treatment*, 2016, 57, 27651-27662.
- [29] A. A. Issa, Y. S. Al-Degs, A. H. El-Sheikh, A. Y. Al-Reyahi, R. Z. A. Bakain, J. I. Abdelghani, A. P. Newman, *CLEAN–Soil, Air, Water*, 2017, 45, article no. 1600333.
- [30] A. A. Issa, Y. S. Al-Degs, M. A. Al-Ghouti, A. A. Olimat, *Chem. Eng. J.*, 2014, **240**, 554-564.
- [31] S. K. Lagergren, Sven. Vetenskapsakad. Handingarl, 1898, 24, 1-39.
- [32] Y. S. Ho, G. McKay, Process Biochem., 1999, 34, 451-465.
- [33] M. J. D. Low, Chem. Rev., 1960, 60, 267-312.
- [34] F. Brouers, J. Mod. Phys., 2014, 5, 1594.
- [35] F. Brouers, T. J. Al-Musawi, J. Mol. Liq., 2015, 212, 46-51.
- [36] G. E. Boyd, A. W. Adamson, L. S. Myers, J. Am. Chem. Soc., 1947, 69, 2836-2848.
- [37] W. Weber, J. Morris, Eng, 1963, 504, 2.
- [38] R. M. C. Viegas, M. Campinas, H. Costa, M. J. Rosa, Adsorption, 2014, 20, 737-746.
- [39] B. Wanassi, I. B. Hariz, C. M. Ghimbeu, C. Vaulot, M. B. Hassen, M. Jeguirim, *Environ. Sci. Pollution Res.*, 2017, 24, 10041-10055.
- [40] A. H. Ali, Chem. Eng. Commun., 2014, 201, 1620-1644.
- [41] T. Anirudhan, M. Ramachandran, Process Safety and Environmental Protection, 2015, 95, 215-225.
- [42] A. H. Sulaymon, W. M. Abood, J. Eng., 2013, 19, 655-667.
- [43] Y. Al-Degs, M. Khraisheh, S. Allen, M. Ahmad, G. Walker, *Chem. Eng. J.*, 2007, **128**, 163-167.

- [44] T. Markandeya, N. Dhiman, S. P. Shukla, D. Mohan, G. C. Kisku, S. Patnaik, J. Cleaner Prod., 2018, 182, 206-216.
- [45] K. Hedhili, P. Vauchel, K. Dimitrov, K. Kriaa, G. Chataigné, K. Hani, P. Dhulster, N. Nedjar-Arroume, *Bioprocess Biosyst. Eng.*, 2014, **37**, 1315-1323.
- [46] S. M. Miraboutalebi, S. K. Nikouzad, M. Peydayesh, N. Allahgholi, L. Vafajoo, G. McKay, *Process Safety Environ. Prot.*, 2017, **106**, 191-202.
- [47] J. F. Porter, G. McKay, K. H. Choy, Chem. Eng. Sci., 1999, 54, 5863-5885.
- [48] D. W. Marquardt, J. Soc. Ind. Appl. Math., 1963, 11, 431-441.
- [49] K. V. Kumar, K. Porkodi, F. Rocha, J. Hazard. Mater., 2008, 150, 158-165.
- [50] K. Foo, B. Hameed, Chem. Eng. J., 2011, 170, 338-341.
- [51] S. Allen, G. Mckay, J. F. Porter, J. Colloid Interface Sci., 2004, 280, 322-333.
- [52] S. Choudhury, S. K. Ray, *Carbohydr. Polym.*, 2018, 200, 305-320.
- [53] D. L. Michelson, J. A. Gideon, G. P. Griffith, J. E. Pace, H. L. Kutat, *Removal of Soluble Mercury from Water by Complexing Techniques*, Water Resources Center Bulletin 74, Virginia Polytechnic Institute, Blacksburg, Virginia, USA, 1975.
- [54] M.-S. Chiou, G.-S. Chuang, Chemosphere, 2006, 62, 731-740.
- [55] K. Mahmoudi, N. Hamdi, A. Kriaa, E. Srasra, Russian J. Phys. Chem. A, 2012, 86, 1294-1300.
- [56] H. Yu, T. Wang, W. Dai, L. Yu, N. Ma, Braz. J. Chem. Eng., 2018, 35, 253-264.
- [57] N. T. Abdel-Ghani, G. A. El-Chaghaby, F. S. Helal, J. Adv. Res., 2015, 6, 405-415.
- [58] I. Tsibranska, E. Hristova, Bulg. Chem. Commun., 2011, 43, 370-377.
- [59] A. A. Attia, B. S. Girgis, S. A. Khedr, J. Chem. Technol. Biotechnol. Int. Res. Process, Environ. Clean Technol., 2003, 78, 611-619.
- [60] M. E. Fernandez, G. V. Nunell, P. R. Bonelli, A. L. Cukierman, *Ind. Crops Prod.*, 2014, 62, 437-445.
- [61] K. K. Choy, J. F. Porter, G. McKay, J. Chem. Eng. Data, 2000, 45, 575-584.
- [62] B.-J. Ni, Q.-S. Huang, C. Wang, T.-Y. Ni, J. Sun, W. Wei, *Chemosphere*, 2019, **219**, 351-357.
- [63] C. Y. Shiau, C. C. Pan, Separation Sci. Technol., 2005, 39, 1733-1750.
- [64] N. Nabbou, M. Belhachemi, M. Boumelik, T. Merzougui, D. Lahcene, Y. Harek, A. A. Zorpas, M. Jeguirim, C. R. Chim., 2019, 22, 105-112.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Enhanced adsorptive removal of cationic and anionic dyes from aqueous solutions by olive stone activated carbon

Khaled Mahmoudi^{*, a}, Noureddine Hamdi^{a, b}, Mahassen Ben Ali^a, Salah Jellali^c and Ezzeddine Srasra^a

^{*a*} Laboratory of Composite Materials and Clay Minerals, National Center of Research in Materials Sciences (CNRSM), B.P.73–8020. Soliman, Tunisia

 b Higher Institute of Water Science and Techniques of Gabes, University of Gabes, Zrig 6072, Gabes, Tunisia

^c PEIE Research Chair for the Development of Industrial Estates and Free Zones, Center for Environmental Studies and Research, Sultan Qaboos University, Al-Khoud 123, Oman

E-mails: mahmoudikhaled1984@gmail.com (K. Mahmoudi), nouryhamdi@gmail.com (N. Hamdi), benalimahassen@gmail.com (M. Ben Ali), s.jellali@squ.edu.om (S. Jellali), srasra.ezzedine@gmail.com (E. Srasra)

Abstract. In this work, four activated carbons were synthetized from natural olive stone (NOS) wastes using ZnCl₂ as an activating agent. These activated carbons (OSAC) were synthetized for a constant mass ratio of ZnCl₂: NOS of 2:1, a contact time of 2 h and four different heating temperatures (300, 400, 450 and 500 °C). The physicochemical characterization of these activated carbons by various analyses including N₂ adsorption–desorption measurements, surface charge evolution versus pH. Boehm titration, Fourier transform (FTIR) and scanning electron microscopy (SEM) showed that the activated carbon produced at a temperature of 400 °C (OSAC 400 °C) exhibited the best properties. Indeed, it has the highest BET surface area, total pore and micropore volumes with values of 740 m²·g⁻¹, 0.57 cm³·g⁻¹ and 0.25 cm³·g⁻¹, respectively. Moreover, it is rich in various acidic and basic functional groups that could react with various common adsorbents.

The test of these activated carbons, for the adsorption of a cationic (methylene blue (MB)) and anionic (methyl orange (MO)) dye under various experimental conditions, showed that OSAC 400 °C could be considered as an effective, attractive and promising adsorbent for both the tested dyes. The Langmuir's adsorption capacities of this adsorbent were assessed to 303.0 and 277.8 $mg \cdot g^{-1}$ for MB and MO, respectively, which are significantly high compared to other various activated carbons. The retention of the pollutants is mainly chemical including hydrogen bond and electrostatic attraction between the dyes and the activated carbon surface.

^{*} Corresponding author.

Keywords. Olive stones, Activation, Zinc chloride, Characterization, Dyes, Adsorption.

1. Introduction

Dyes are among the most used substances in the world with a total production of 700,000-1000,000 tons [1]. Because of their chemical stability and the ease of their synthesis, dyes are widely used in a broad range of fields: food industry, paper, cosmetic and particularly in the textile industries [1]. They are generally discharged into the environment as dissolved components in industrial waste waters. Their excessive presence in water bodies could result in an important decrease of dissolved oxygen contents due to the reduction of sunlight penetration into deep areas. This eutrophication phenomenon could cause an important deterioration of the water bodies' physicochemical and biological quality and therefore a disturbance in the aquatic organisms' life [2]. When it comes in contact with humans, dyes can cause skin irritation and/or allergic dermatitis and also possible serious diseases for those considered as mutagenic and/or carcinogenic compounds [3].

Methylene blue is a cationic synthetic dye that is usually used in textile and pharmaceutical industries and in the coloring of various materials including wool, cotton, paper and silk. When discharged into the environment, MB can cause damaging impacts to fauna and flora. Exposure to these pollutants could induce severe damage to eyes (humans and animals) and even result in tissue necrosis, methemoglobinemia and mental confusion [4]. Methyl orange (MO) is an anionic dye widely used in textile printing, food and pharmaceutical industries. It can induce dangerous effects on flora and fauna, as well as human and animal health in case of inhalation, ingestion, and contact with eye and skin [5].

Given the confirmed negative impacts of dyes on human health and in water resources, removal of dyes from waste waters has become inevitable and necessary in order to ensure the related industry sustainable development [6]. Up to now, various technologies have been applied separately or as hybrid systems for an efficient elimination of dyes from industrial effluents. They include biological treatment, coagulation/flocculation, membrane separation and advanced oxidation processes [7]. However, these technologies have some drawbacks such as huge sludge production that has to be appropriately handled, low dye removal efficiency and high-energy consumption [6].

Dye removal from discharged industrial effluents through retention by low cost and abundant material-derived adsorbents has been recently pointed out as an attractive and promising technique [8,9]. The main advantages of this technique are its low cost, handling simplicity and good cost effectiveness [2]. Agricultural by-products, which are produced in huge quantities, have not only been tested as raw materials but also as activated carbons for the enhanced removal of dyes from industrial waste waters. In fact, activated carbons usually dispose of high specific surface area, have well-developed microporosity and richness in specific functional groups which favor the removal from aqueous solutions of dyes and other organic and inorganic pollutants [9]. Various agricultural precursors have been tested for the synthesis of activated carbons for dye removal from aqueous solutions. They include coconut husk, bamboo, jute fibers, rattan sawdust, orange sawdust and so on. [6,8,9]. In the Mediterranean region, olive oil extraction is well developed. This operation produces large amounts of solid olive stone by-products and also waste waters with possible negative impacts on the environment. According to Marks et al. [10], in 2017, the produced olive mill solid wastes were evaluated to 4.336, 0.450 and 1.050 million tons in Spain, Tunisia and Greece, respectively. The sustainable management of these wastes, therefore, represents an important challenge. Various management options have been tested and applied at laboratory scale for these by-products. They include their adapted treatment [11], their thermal conversion into biofuels and biochars for energetic, environmental and agronomic purposes [11-15] and also their turning into activated carbons for liquid and gaseous effluent treatment [16-18]. The characteristics of the olive stone derived activated carbons (OSAC) depend mainly on the used activating agent and concentration as well as the heating temperature and residence time [16,18,19]. ZnCl₂ represents one of the best activating agents permitting the derived activated carbon to have attractive physicochemical characteristics [20,21]. OSAC have exhibited important adsorption capacities of dyes [16], pharmaceuticals [18], heavy metals [20] and also gaseous pollutants [22]. However, the majority of these studies were realized in batch mode and generally focus on a single dye removal without a precise assessment of the involved mechanisms.

Therefore, the main aim of this work is to study, under various experimental conditions, the valorization of activated carbons generated from the activation of olive stones with an efficient impregnating agent, ZnCl₂, for the removal of cationic and anionic dyes. Practically, the specific objectives of this experimental investigation are: (i) assessment of the impact of heating temperatures on the properties of the generated activated carbons, (ii) investigation of the efficiency of these OSAC in removing both anionic and cationic dyes under different experimental conditions and (iii) exploration of the possible involved mechanisms for both cases.

2. Materials and methods

2.1. Adsorbent preparation

The natural olive stone (NOS) wastes used in this study were collected from an olive oil industry in Ben Guerdane city, south of Tunisia. They were washed with distilled water and then dried in an oven for 24 h at 110 °C. Afterward, they were grounded and sieved to obtain light brown particles with dimension between 0.05 and 0.25 mm. Four OSAC were then prepared at four different temperatures (300, 400, 450 and 500 °C) by using a professional Muffle Furnace (Nabertherm L24/11). They were baptized OSAC 300 °C, OSAC 400 °C, OSAC 450 °C and OSAC 500 °C, respectively. Based on preliminary experiments (data not shown), all these OSAC porous media were produced for a constant (ZnCl₂:NOS) mass ratio of 2:1 and a contact time of 2 h. The obtained activated carbons were washed several times with distilled water until a constant pH of the washing solutions. Finally, these samples were dried in a laboratory oven for 2 h at 80 °C.

2.2. Material characterization

The NOS as well as the generated OSAC were physicochemically characterized by using various methods and analyses with specific apparatus. They included

the assessment of the N2 adsorption-desorption profiles at 77 K according to the Brauner-Emmet-Teller (BET) method by using a Quantachrome Autosorb 1-MP apparatus. For each material, the specific surface area was assessed through the BET method and the pore volume was determined from the volume of nitrogen held at a relative pressure of P/Po =0.99. Besides, the micropores' surface and volume were estimated from the *t*-plot method. The impact of the NOS activation by ZnCl₂ on its morphology was assessed through scanning electron microscopy (Philips Fei Quanta 200). Furthermore, the surface chemistry of the materials was apprehended through complementary analyses including the assessment of: (i) the pH of zero-point-charge (pHzpc), and (ii) the main surface functional groups through Boehm titration and FTIR analysis. The pHzpc was determined according to the method given by Mohan et al. [23]. During these assays, the material (0.15 g) was mixed with 50 mL of distilled water containing 0.01 M NaCl at different initial aqueous pH values (pH_i) for 48 h. The used initial pH values were fixed to 2, 4, 6, 8, 10 and 12 by using 0.1 M HCl or NaOH solutions. The pHzpc of the materials were determined from the plateau of the curve of the measured final $pH(pH_f)$ versus (pH_i) .

The Boehm titration method aims to determine the oxygenic function contents in the studied materials [24]. During this titration, 1 g of each tested material was put in contact with 50 mL of sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) at 0.1 M for 24 h. This method was based on the fact that the strongest base, NaOH, neutralizes phenolic, lactonic and carboxylic groups. The NaHCO₃ neutralizes the lactonic and carboxylic groups, while the weakest base, Na_2CO_3 , neutralizes only the carboxylic acids. The acidic and basic functional groups were determined by titration of the filtrated aliquots against 0.05 M HCl and 0.05 NaOH solutions, respectively.

Furthermore, the Fourier transform infrared (FTIR) technique was used in order to identify the main functional groups present on the NOS and the derived activated carbon at different temperatures. For this aim, infrared spectra of these materials were assessed with a FTIR spectrometer (Perkin Elmer). The spectra were recorded within a wave number range of 4000–400 cm⁻¹ for a spectral resolution of 2 cm^{-1} .

2.3. Preparation and analysis of dye solutions

The used MB (chemical formula (CF): $C_{16}H_{18}ClN_3S$; molar weight (MW) = 319.852 g·mol⁻¹) and MO dyes (CF: $C_{14}H_{14}N_3 O_3S^-Na^+$; MW = 327.34 g·mol⁻¹) were purchased from Sigma-Aldrich (Figure 1). They were used during this adsorption study for the preparation of synthetic solutions.

During the adsorption tests, two stock MB and MO solutions of 1000 mg·L⁻¹ were prepared and used for the preparation of solutions at given concentrations. MB and MO removal efficiencies were assessed through the determination of their absorbance decline versus time at 664 nm and 460 nm, respectively, by using an UV spectrophotometer (Perkin Elmer, Model UV Lambda 20).

2.4. Adsorption experiments

Batch adsorption experiments have been performed in order to assess the efficiency of NOS and its derived activated carbon in removing MB and MO from aqueous solutions under various key experimental conditions. All these experiments were carried out at room temperature $(25 \pm 2 \,^{\circ}\text{C})$ in capped flasks. During these assays, a 0.1 g of the following materials was shaken in 50 mL of MB or MO solutions during a fixed time at 100 rpm by a magnetic shaker (Rotary agitator Reax2 (Heidolph)). The residual dissolved MB or MO concentrations were determined by using a UVvisible spectroscopy apparatus after centrifugation at 2500 rpm for 5 min with a Centrifuge Hermle Z300 apparatus.

All the experiments cited below were performed in triplicate and the mean values were given in this study. The standard deviation for all assays was lower than 5%.

2.4.1. Effect of contact time-kinetic study

The MB or MO removal kinetic by the NOS and the derived activated carbon was assessed at various times: 30, 60, 90, 120, 180, 240, 360, 480, 600, 720 and 1440 min. These assays were performed for constant adsorbents dosage of 2 g·L⁻¹ and a fixed pH of 8 and 5 for MB and MO, respectively.

The MB or MO adsorbed quantities at a given time "t", (q_t) and the related removal yield (Y_t) were assessed as follows:

$$q_t = \frac{(C_0 - C_t)}{D} \tag{1}$$

$$Y_t(\%) = \frac{(C_0 - Ct)}{C_0} \times 100,$$
 (2)

where C_0 and C_t (mg·L⁻¹) are the initial dye concentration and the dye concentration at a time "*t*", respectively, and *D* is the used adsorbent dosage (g·L⁻¹).

The MB and MO adsorption kinetics measured data were fitted to three well-known models, namely pseudo-first order (PFO), pseudo-second order (PSO), and intraparticle and film diffusion models. The original as well as the linearized equation of these models are widely cited in the literature [25,26]. The agreement between the measured and the calculated adsorbed amounts was determined according to the estimated values of the determination coefficients as well as the calculated average percentage errors ($APE_{kinetic}$):

$$APE_{\text{kinetic}}(\%) = \frac{\Sigma |(q_{t,\text{exp}} - q_{t,\text{calc}})/q_{t,\text{exp}}|}{N} \times 100, \quad (3)$$

where $q_{t,exp}$ and $q_{t,calc}$ (mg·g⁻¹) are the measured and the theoretical adsorbed amounts at the instant "*t*".

2.4.2. Impact of initial aqueous pH

The used initial pH values have a very important impact on ionic dye removal efficiency by adsorbents. In our case, MB and MO adsorption by the NOS and its derived activated carbon was performed for initial pH values of 2, 4, 5, 7, 8, 9, 10 and 12. The used adsorbent dose and contact time were fixed to 2 g·L⁻¹ and 6 h, respectively.

2.4.3. Effect of initial concentration-isotherm study

The effect of the initial dyes' concentrations on their removal efficiency by the NOS and OSAC were assessed at an equilibrium state for a contact time of 360 min, a pH = 9 for MB, a pH = 3.5 for MO and adsorbents dose of 2 g·L⁻¹. The tested dye concentrations were fixed to 30, 75, 125, 250, 500 and 1000 mg·L⁻¹. The measured data were confronted to famous models namely: Freundlich, Langmuir and Dubinin–Radushkevich (D–R) models. These model equations, assumptions and implications were widely cited in the bibliography [21,26,27]. The



Figure 1. Chemical structures of the used dyes: methylene blue and methyl orange.

Adsorbents	S_{BET} (m ² ·g ⁻¹)	$S_{\mu} (m^2 \cdot g^{-1})$	$V_{\rm T}$ (cm ³ ·g ⁻¹)	$V_{\mu} ({ m cm}^3 \cdot { m g}^{-1})$
NOS	16	0	0.03	0
OSAC 300 °C	200	160	0.11	0.10
OSAC 400 °C	740	595	0.57	0.25
OSAC 450 °C	400	320	0.18	0.15
OSAC 500 °C	300	250	0.137	0.11

Table 1. Textural properties of NOS and its derived ZnCl₂ activated carbon at different temperatures

(S_{BET} : total specific surface area; S_{μ} : micropores surface area; V_{T} : total pores volume; V_{μ} : micropores volume).

fitting goodness between the measured and theoretical adsorbed amounts by the three used models and the two tested dyes was calculated as follows:

$$APE_{\text{isotherm}}(\%) = \frac{\Sigma |(q_{e,\text{exp}} - q_{e,\text{calc}})/q_{e,\text{exp}}|}{N} \times 100, (4)$$

where $q_{e,\exp}$ and $q_{e,\operatorname{calc}}$ (mg·g⁻¹) are the measured and the theoretical adsorbed dye quantities at equilibrium.

3. Results and discussion

3.1. Adsorbents characterization

3.1.1. Textural and structural properties

 N_2 adsorption–desorption isotherms. The adsorption–desorption isotherms of N_2 at –196 °C by the NOS and its 4 derived activated carbons at 300, 400, 450 and 500 °C are shown in Figure 2. Based on the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC), the activated carbons exhibited the type I isotherms corresponding to microporous materials. It is important to underline that, by increasing the temperature up to

400 °C, the amount of N_2 adsorbed increases (this indicates the gradual development of the porous structure), then it decreases (which is explained by the deterioration of porous structure). A similar trend was found by Mojoudi *et al.* [28] when studying phenol adsorption onto activated carbons generated from oily sludge. Moreover, the activated carbons prepared with different temperatures present hysteresis loops indicating the existence of mesopores [29].

The textural characteristics of the tested materials are given in Table 1. Compared to the raw biomass, activation with ZnCl₂ has an important effect on the textural characteristics of the NOS-derived activated carbons. Indeed, this operation has significantly developed the pores structure. It appears that the values of the BET surface area, the surface area of the microporous pores, the total porous and microporous volumes significantly rise with the increase of the used heating temperature until a temperature of 400 °C, then, decrease even if the temperature increases. The highest values of these parameters (obtained at a temperature of 400 °C) were assessed to 740 m²·g⁻¹, 595 m²·g⁻¹, 0.57 cm³·g⁻¹ and 0.25 cm³·g⁻¹ for the



Figure 2. N₂ adsorption isotherms of NOS and its derived ZnCl₂ activated carbon at different heating temperatures.

 S_{BET} , the surface microporous area, the total porous and microporous volumes, respectively. These values were about 270%, 271%, 418%, 150% and "146%", "85%", "216%", "66%" higher than the values obtained at temperatures of 300 °C and "500 °C", respectively. This outcome might be attributed to the contraction of the porous structure, destruction of micropores and the decrease of the surface area for used temperatures higher than 400 °C [28].

Similar findings have been reported by Mojoudi *et al.* [28] and Mahmoudi *et al.* [21] when they studied the activation of oily sludge and lignite by potassium hydroxide and zinc chloride, respectively. For instance, when activating oily sludge by KOH (impregnation ratio of 1:1), the highest values of specific surface area, total porous volume and micropores were obtained at a heating temperature of 800 °C; these parameters then decreased when rising the used temperatures [28].

SEM analyses. The olive stones and its derived activated carbon at 400 °C surface morphology were investigated by SEM. The related images at different scales are presented in Figure 3. It can be deduced that the activation with ZnCl₂ has favored the development of cavities and micropores on the OSAC 400 °C. This activated carbon has cavities and cracks

on their external surfaces. Similar findings were registered by Ibn Ferjani *et al.* [30], Limousy *et al.* [18] and Eren *et al.* [31] for raw marc grapes pyrolyzed at various temperatures and olive stones activated by phosphoric acid and zinc chloride, respectively.

3.1.2. Surface chemistry

The point of zero charge. The determination of the pHzpc of the NOS and OSAC 400 °C was carried out with respect to the experimental protocol presented in Section 2.2. The ZnCl₂ activation of the NOS has decreased its pHzpc from 5.5 to 4.6. This decrease could be imputed to the acidification of the adsorbent surface. Similar behavior has been reported by Erdem *et al.* [32] and Uner *et al.* [33] when activating by zinc chloride vine shoots and waste watermelon rind, respectively. They found pHzpc values for their activated materials of 4.8 and 4.5, respectively. It is worth mentioning that for aqueous pH higher than pHzpc, adsorbent surfaces will be negatively charged and consequently adsorption of cationic dyes should be favored and *vice versa* [34].

Boehm titration. The functional groups existing on the surface of the NOS and the ZnCl₂-derived activated carbon at a heating temperature of 400 °C (having the best textural properties) were determined ac-



Figure 3. SEM images of NOS (a,b) and the derived ZnCl₂-activated carbon at a heating temperature of 400 °C (c,d).

cording to the explained protocol in Section 2.2. Experimental results (Table 2) showed that for natural olive stones, the total acidic and basic group contents were assessed to 3.30 and 2.03 mmol \cdot g⁻¹, respectively.

The use of zinc chloride in the activation process provides supplementary amounts of acidic groups on the OSAC 400 °C surface (especially carboxylic groups). After activation, the acidic functional groups increase by 12.1%, whereas the total basic sites decrease the OSAC by 50.7%. The formation of acidic surface groups is due to the reactions between zinc chloride and oxygen with the raw material [35]. Indeed, the ZnCl₂ oxidation can occur at a temperature range of 400–600 °C as follows:

$$\operatorname{ZnCl}_2(s) + 0.5O_2(g) \rightleftharpoons \operatorname{ZnO}(s) + \operatorname{Cl}_2(g)$$

A similar trend was registered by Bohli *et al.* [36] when studying date pits activation by zinc chloride. They found that the total acidic groups have increased from 2.5 to 5.9 mmol·g⁻¹ and the total basic contents decreased from 1.82 to 0.72 mmol·g⁻¹.

FTIR spectroscopy. The FTIR spectra of NOS and the generated ZnCl_2 activated carbons at different heating temperatures are given in Figure 4. For all the analyzed samples, the stretching vibrations of the OH groups (alcohols, phenols and carboxylic acids) observed at around 3430 cm⁻¹ was partly attributed to the residual presence of adsorbed water in the carbons [19]. The C–H stretching bands at about 2920 and 2850 cm⁻¹ were observed for all the samples [21, 37]. However, their intensities decrease with the in-

Adsorbents		Basic functions (mmol \cdot g ⁻¹)			
	Carboxylic groups	Phenolic groups	Lactonic groups	Total acid	
NOS	0.60	2.00	0.70	3.30	2.03
OSAC 400 °C	1.90	1.00	0.80	3.70	1.00

Table 2. Acidic and basic functional groups of NOS and its derived $ZnCl_2$ activated carbon at a temperature of 400 °C



Figure 4. FTIR spectra of NOS and its derived ZnCl₂-activated carbon at different heating temperatures.

crease of the heating temperature [29,38]. This behavior could be imputed to the volatilization, mineralization or degradation of the readily available molecules and metabolites [39]. The absorption band observed at 1650 cm⁻¹ correspond to C=O stretching vibration of carbonyl groups [37] and the ones at 3430 and 1060 cm⁻¹ are associated to O-H stretching vibration of hydroxyl groups [21,38] and C-O stretching vibrations in phenols, alcohols, ester or ether groups [37], respectively. For all the studied activated carbons, a band occurring at 1600 cm⁻¹ was observed; it corresponds to axial deformation of carbonyl groups [17]. Moreover, the bands observed at 1400 cm⁻¹ correspond to C=O stretching and C-O stretching in carboxylic groups [17,21]. The absorption band observed at 584 cm⁻¹ corresponds to inplane ring deformation [40]. These functional groups can significantly influence the adsorption of both the tested dyes. It is important to underline that the FTIR analyses confirm the abundance of acidic groups that were already highlighted by the Boehm titration analysis.

3.2. Dye adsorption

3.2.1. Kinetic studies of MB and MO removal

The effect of contact time on the adsorption of both dyes (MB and MO) by the NOS and its derived ZnCl₂-activated carbon at a temperature of 400 °C was determined for the experimental conditions cited in Section 2.4.1. The experimental results



Figure 5. MB (a) and MO (b) kinetic removal by NOS ($C_{0,\text{MB}} = 125 \text{ mg}\cdot\text{L}^{-1}$; $C_{0,\text{MO}} = 75 \text{ mg}\cdot\text{L}^{-1}$) and OSAC 400 °C ($C_{0,\text{MB}} = 500 \text{ mg}\cdot\text{L}^{-1}$; $C_{0,\text{MO}} = 500 \text{ mg}\cdot\text{L}^{-1}$) and their fitting with PFO and PSO (adsorbent dose = 2 g·L⁻¹; $T = 25 \pm 2$ °C).

(Figure 5a,b) showed that it is a time-dependent process. Indeed, MB and MO adsorption was very fast at the beginning of the experiments since about 90.3% and 91.3% of the totally adsorbed amounts of MB and MO by OSAC 400 °C were removed after a duration of only 2 h, respectively. This step is generally imputed to diffusion through the boundary layer. Then, MB and MO continue to be adsorbed by the used materials but with a slower rate. This phase could be attributed to intraparticle diffusion of the dyes inside the porous structure of the used adsorbents [41,42]. The equilibrium state which corresponds to quasiconstant adsorbed dye amounts was registered after about 6 h. This time is relatively higher than those determined by Gong *et al.* [43] when studying BM and MO removal by activated carbons derived from finger citron residue. It is, however, lower than the ones reported for the adsorption of MO and MB by activated carbons modified with silver nanoparticles [44]. It is worth mentioning that low equilibrium contact times

Adsorbent	Dyes		PFO model			PSO model				Diffusion model			
		$q_{e,\exp}$ (mg·g ⁻¹)	k_1 (h ⁻¹)	<i>R</i> ²	APE (%)	k_2 (g·mg ⁻¹ ·h ⁻¹)	$q_{e, calc}$ (mg·g ⁻¹)	R^2	APE (%)	$\begin{array}{c} D_{\rm f} \\ (\times 10^{-14} \\ {\rm m}^2 \cdot {\rm s}^{-1}) \end{array}$	<i>R</i> ²	D_{ip} (×10 ⁻¹⁴ m ² ·s ⁻¹)	<i>R</i> ²
NOS	MB	50.0	0.242	0.804	33.5	0.040	51.6	0.948	10.9	7.789	0.999	35.060	0.991
	MO	25.0	0.173	0.665	44.1	0.106	25.6	0.978	5.7	10.560	0.989	17.880	0.993
OSAC	MB	249.2	0.499	0.844	18.2	0.014	254.8	0.941	7.5	4.385	0.997	9.104	0.973
400 °C	MO	158.9	0.319	0.593	31.1	0.037	161.2	0.993	2.0	4.872	0.998	6.322	0.955

Table 3. Estimated kinetic model parameters during the adsorption of MB and MO onto NOS and derived activated carbon

 $(C_{0,\text{MB}} = 125 \text{ mg} \cdot \text{L}^{-1}; C_{0,\text{MO}} = 75 \text{ mg} \cdot \text{L}^{-1})$ and OSAC 400 °C ($C_{0,\text{MB}} = 500 \text{ mg} \cdot \text{L}^{-1}; C_{0,\text{MO}} = 500 \text{ mg} \cdot \text{L}^{-1};$ adsorbent dose = 2 g·L⁻¹; $T = 25 \pm 2$ °C).

is particularly important for the economic viability of the process when up-scaled to field conditions.

At equilibrium, the adsorbed MB and MO by OSAC 400 °C were determined to 249 and 158 $mg \cdot g^{-1}$, which are about 5.0 and 6.3 higher than the ones determined for NOS. This is attributed to the more interesting physicochemical characteristics of the OSAC compared to the NOS, especially its texture (see Table 1) and surface chemistry (see Table 2 and Figure 3). On the other hand, for both NOS and OSAC 400 °C, MB adsorbed amounts were higher than the ones for MO. This behavior will be discussed later in Section 3.2.3.

Table 3 gives the parameters of the three used kinetic models: PFO, PSO and diffusion models. It can be clearly deduced that the PFO model does not adequately fit to the experimental data. Indeed, the corresponding determination coefficients (R^2) are relatively low and the calculated *APE* between the experimental and the theoretical adsorbed amounts was very high. For instance, for OSAC 400 °C, the corresponding R^2 and *APE* were assessed to 0.844 and "0.593" and 18.2% and 31.1% for MB and "MO", respectively.

On the contrary, the PSO model fits very well the kinetic experimental data (Figure 5a,b). Indeed, the R^2 obtained for NOS or OSAC 400 °C and for the both studied dyes were higher than those obtained for PSO (Table 3). Moreover, the calculated *APE* values were relatively lower than the assessed ones for the case of PFO model. The worst case (*APE* = 10.9%) was observed for MB adsorption onto NOS but remains very low compared to the PFO model. This finding confirms the good concordance between the experimen-

tal data and the calculated ones by the PSO model (Figure 5). Besides the calculated adsorbed amounts of MB and MO at equilibrium for both NOS and OSAC 400 °C were close to the experimental values (Table 3). For instance, for OSAC 400 °C, these difference percentages between the experimental and the theoretical adsorbed amounts were determined to 2.3% and 1.5% for MB and MO, respectively. Therefore, under the tested experimental conditions, the PSO model is more suitable in fitting the MB and MO removal by NOS and the derived ZnCl2-activated carbon. This model suggests that the rate limiting step might be chemical adsorption including valency forces through sharing or exchange of electrons between these two tested dyes and olive stone derived adsorbents [41,45].

The adsorption of MB and MO by the NOS and OSAC 400 °C was analyzed through the application of film and intraparticle diffusion models. Results indicated that the dye adsorption process proceeds by surface interactions for times lower than 90 min for NOS and 120 min for OSAC 400 °C and by intraparticle diffusion at later stages (Figure 5a,b). According to the calculated film and intraparticle diffusion coefficients, it can be deduced that the intraparticle diffusion process might be the limiting factor during both MB and MO adsorption onto the two adsorbents (Table 3). A similar finding was reported by Wu et al. [46] when studying methylene blue, phenol and 4-chlorophenol removal by activated carbons from oil-palm shells. On the other hand, the activation of the OS has significantly reduced the film and intraparticle diffusion coefficients for MB and MO (Table 3). The values of film diffusion coefficient, $D_{\rm f}$



Figure 6. Impact of the initial aqueous pH on MB (a) and MO (b) removal efficiency by NOS ($C_{0,\text{MB}} = 30 \text{ mg}\cdot\text{L}^{-1}$; $C_{0,\text{MO}} = 30 \text{ mg}\cdot\text{L}^{-1}$) and OSAC 400 °C ($C_{0,\text{MB}} = 250 \text{ mg}\cdot\text{L}^{-1}$; $C_{0,\text{MO}} = 250 \text{ mg}\cdot\text{L}^{-1}$, adsorbent dose = 2 g·L⁻¹; contact time = 6 h; $T = 25 \pm 2$ °C).

were higher for NOS than for OSAC indicating that film diffusion was faster for NOS than for OSAC [47]. The calculus of the intraparticle diffusion coefficients showed that OSAC was a more favored medium than NOS for internal transfer of both the studied dyes.

3.2.2. Impact of initial aqueous pH

The impact of initial aqueous pH on MB and MO adsorption onto NOS and its derived ZnCl₂-activated

carbon at a temperature of 400 °C (OSAC 400 °C) was investigated under the experimental conditions presented in Section 2.4.2. The experimental results (Figure 6) indicated that the two used dyes exhibited opposite behaviors. Indeed, for example, for OSAC 400 °C the MB pollutant, which is a cationic dye, was preferentially adsorbed at higher used pH values. In fact, the adsorbed MB amount increased from 18 mg·g⁻¹ for an initial pH of 2 to more than

Adsorbents	Dye	Langmuir isotherm				Freundlich isotherm				D–R isotherm			
		K_L	q_m	R^2	APE	n	K_F	R^2	APE	$q_{m,\mathrm{D-R}}$	Ε	R^2	APE
		$(L \cdot mg^{-1})$	$(mg \cdot g^{-1})$		(%)				(%)	$(mg \cdot g^{-1})$	(kJ·mol⁻	-1)	(%)
NOS	MB	0.219	59.2	0.998	9.7	1.9	9.1	0.892	23.9	390.3	11.4	0.991	12.3
	MO	0.338	34.2	0.955	12.3	3.7	12.2	0.893	20.1	91.4	15.4	0.862	14.3
OSAC	MB	0.081	303.0	0.970	31.9	2.5	44.8	0.963	14.4	963.5	12.4	0.986	9.0
400 °C	MO	0.092	277.8	0.999	9.2	2.0	28.7	0.847	28.7	1380.0	11.1	0.993	16.9

Table 4. Calculated parameters of Langmuir, Freundlich and D–R models corresponding to MO and MB removal by natural olive stones and its ZnCl₂-derived activated carbon at a temperature of 400 °C

120 mg·g⁻¹ for an aqueous pH of 9. This finding could be explained by the fact that for aqueous pH higher than the pHzpc, which were determined to 5.5 and 4.6 for NOS and OSAC 400 °C, these materials should be negatively charged. Therefore, adsorption through electrostatic attraction of positively charged ions will be favored. A similar trend was reported for MB removal by activated carbons from globe artichoke leaves [48] and reed-derived biochar by tannic acid [49].

For the reason cited above, the opposite behavior was registered for the negatively charged MO dye. The MO adsorbed amount decrease from about 15 and 120 mg \cdot g⁻¹ for NOS and OSAC 400 °C at an aqueous pH of 4 to about 3.3 and 26.4 mg \cdot g⁻¹ at a pH of 12, respectively. Similar findings were reported for anionic dye removal by natural or modified adsorbents [50,51].

3.2.3. Impact of initial concentration-isotherm modeling

The impact of the initial concentrations on MB and MO removal efficiency by NOS and OSAC 400 °C has been determined under the experimental conditions presented in Section 2.4.3. The used pH for MB and MO solutions were fixed to 9.0 and 3.5, respectively. They correspond to their highest adsorbed amount during the kinetic study (see Figure 5). The obtained measured data were fitted to Freundlich, Langmuir and D–R models as explained in Section 2.4.3. Figures 7(a,b) give the comparison between the experimental and theoretical data regarding MB and MO adsorption by both adsorbents, respectively. The calculated constants of these three models are given in Table 4.

On the basis of Figure 7 and Table 4, it can be deduced that Langmuir isotherm fits the best to the

experimental data compared to the Freundlich and D-R results. Indeed, this model has the most interesting determination coefficients and APE. For instance, for MO onto OSAC 400 °C, the highest R^2 $(R^2 = 0.999)$ and the lowest APE (9.2%) were obtained for Langmuir isotherm. Even if the D-R isotherm's R^2 and APE are also satisfactory (Table 4), the corresponding predicted maximum adsorbed MB and MO amounts were very high compared to the calculated ones using the Langmuir model (Table 4). These unrealistic theoretical capacities could be imputed to the hypotheses taken into account by this model especially the presence of homogenous and uniform microporous structures in the studied material [2]. Besides, the highest Langmuir's parameter values " $R_L = 1/(1 + K_{L+C_0})$ " were estimated to 0.072 and 0.055 for MB and MO, respectively. All these values are less than 1 indicating a favorable adsorption of both dyes by the used adsorbents. This result suggests that dyes adsorption onto NOS and OSAC 400 °C occurs on uniform monolayer coverage at the outer surface of the adsorbents [52]. On the other hand, Freundlich parameter "n" was assessed to 2.5 and 2.0 for MB and MO adsorption onto OSAC 400 °C. They are in the range of 1-10, indicating that the adsorption of these two dyes by the used activated carbon is a favorable process. Values in the same range were determined by Tseng and Wu [53] when studying methylene removal by activated carbon from bamboo.

Concerning the D–R isotherm application, it is very important to mention that all the calculated free energy values ($E = 1/\sqrt{2}\beta$) for both dyes and the two adsorbents were higher than 8 kJ·mol⁻¹. This indicates that MB and MO removal process might occur mainly through cation exchange (Table 4). Comparable outcomes have been stated by Valliammai *et*



Figure 7. Isothermal experimental and fitted data with Freundlich, Langmuir and D–R models for MB (a) and MO (b) removal by NOS and OSAC 400 °C (initial pH for MB solutions = 9; initial pH for MO solutions = 3.5; adsorbent dose = $2 \text{ g} \cdot \text{L}^{-1}$; contact time = 6 h; $T = 25 \pm 2 \text{ °C}$).

al. [54] when investigating MB removal by activated carbons derived from agricultural by-products.

The Langmuir's maximum adsorption capacities of MB and MO by OSAC 400 °C were assessed to 303.0 and 277.8 mg·g⁻¹, which are about 5.2 and 8.1 times higher than the ones determined for NOS. This behavior is attributed to the improved structural and textural properties of the $ZnCl_2$ -generated activated carbon, especially its specific surface area, microporsity volume as well as functional group richness.

Table 5 compares the determined adsorption capacities (Langmuir's q_m) of MB and MO on NOS and

OSAC 400 °C with other activated carbons. It can be clearly seen that OSAC 400 °C can be considered as a promising material for dye removal from waste waters. Indeed, its MB adsorption capacity was about 28.5, 3.5 and 2.9 times higher than activated carbons generated from Macore fruit shells [55], cola nut shells [56] and cellulose biocomposite films [57]. Besides, MO adsorption capacity by OSAC 400 °C was about 2.5, 2.3 and 1.7 higher than those reported for activated carbons generated from Vitis vinifera [58], a copper sulfide nanoparticle-loaded activated carbon [59], and an activated carbon synthetized from





Figure 8. Probable adsorption mechanisms for MB and MO dyes onto olive stone activated carbon.

Adsorbent	Dye	Langmuir's adsorption capacity, q_m (mg·g ⁻¹)	Reference
Activated carbon from boiler residue	MO	161.81	[60]
Activated carbon prepared from Vitis vinifera L.	MO	111.11	[58]
Sisal activated carbon/cellulose biocomposite films	MB	103.7	[57]
Cola nut shells derived activated carbon	MB	87.12	[56]
Macore fruit shells derived activated carbon	MB	10.61	[55]
	MO	3.42	
Copper sulfide nanoparticles loaded activated carbon	MO	122	[59]
Activated carbon modified by three surfactants	MB	232.5	[61]
Activated carbon from olive stones	MB	303.0	Present work
	MO	277.8	

Table 5.	Comp	arison	of MB	and MO	adsor	ntion	onto	NOS	and	OSAC	400 °	Cwith	other	activated	carbons
Tuble 5.	Comp	u113011	OI MID	and mo	ausor	puon	onto	1100	ana	0010	100 0		outor	activated	carbons

3.2.4. Adsorption mechanism exploration

As illustrated in Figure 8, the adsorption mechanism is mainly attributed to hydrogen bonding and electrostatic interaction between dyes and oxygencontaining functional groups on the activated carbon surface [59,62]. For MB, the maximum adsorption occurs for alkaline pH values when the surface sites of the adsorbent become negatively charged. MB adsorption includes the electrostatic attraction between the positively charged amino groups and the negative charges available on the activated carbon surface, and the π - π interactions which occur between the localized π electrons in the conjugated aromatic rings of activated carbon and the aromatic rings of MB dye [63]. On the contrary, the adsorption capacity of methyl orange was maximum for acidic medium (pH = 3.5). At this pH range, the surface of the activated carbon is positively charged and that of MO is negatively charged. The electrostatic interactions between the methyl orange deprotonated groups (sulfonate ($-SO_3^-$)) and oxygen-containing groups on the activated carbon surface promote the adsorption of methyl orange [62]. Also, the hydrogen bonding and the π - π interactions in the structure of activated carbon are important factors in this dye adsorption process [63]. It is important to underline that given the fact that MB and MO adsorption was best fitted with Langmuir model, each active adsorption site will interact with only one dye molecule. Furthermore, all the adsorption sites are energetically equivalent and there were no interactions between adjacent adsorbed molecules [25,26].

4. Conclusions

This study investigated the synthesis of activated carbons from an abundant waste (olive stones) and its use as adsorbent for cationic and anionic dves. Results indicated that this raw material activation with ZnCl₂ at a temperature of 400 °C produces an activated carbon with attractive structural, textural and surface chemistry characteristics. These improved properties allowed the activated carbon to efficiently remove both cationic and anionic dyes under wide experimental conditions. Kinetic and isothermal data indicated that MB and MO adsorption onto the raw olive stone and its derived activated carbon occurs through chemical processes including mainly electrostatic attraction, hydrogen bonding and π - π interactions. Besides, the Langmuir's adsorption capacities of MB and MO onto the synthetized activated carbon were assessed to 303.0 and 277.8 $mg \cdot g^{-1}$, for aqueous pH values of 9.0 and 3.5, respectively. These adsorption capacities are relatively higher than various activated carbons which indicates that our synthetized material could be considered as an efficient and promising material for dyes and probably other organic/mineral pollutants removal from industrial effluents. Further investigations are required in order to assess these dyes removal abilities under dynamic conditions by using laboratory column or continuous stirring tank reactors. The optimization of these dyes' desorption and if possible, recovery for reuse, is also an important task to be undertaken.

References

- [1] V. K. Gupta, Suhas, J. Environ. Manag., 2009, 90, 2313-2342.
- [2] A. A. Azzaz, S. Jellali, A. A. Assadi, L. Bousselmi, *Desalin. Water Treat.*, 2015, **3994**, 1-13.
- [3] B. Lellis, C. Z. Fávaro-Polonio, J. A. Pamphile, J. C. Polonio, Biotechnol. Res. Innov., 2019, 3, 275-290.
- [4] B. Mokhlesi, J. B. Leikin, P. Murray, T. C. Corbridge, *Chest*, 2003, **123**, 897-922.

- [5] A. Mittal, A. Malviya, D. Kaur, J. Mittal, L. Kurup, J. Hazard. Mater., 2007, 148, 229-240.
- [6] A. A. Azzaz, S. Jellali, H. Akrout, A. A. Assadi, L. Bousselmi, AC SCJ. Clean. Prod., 2018, 9, article no. e00509.
- [7] H. Akrout, S. Jellali, L. Bousselmi, C. R. Chim., 2015, 18, 110-120.
- [8] A. Azari, R. Nabizadeh, S. Nasseri, A. H. Mahvi, A. R. Mesdaghinia, *Chemosphere*, 2020, 250, article no. 126238.
- [9] M. J. Ahmed, J. Environ. Chem. Eng., 2016, 4, 89-99.
- [10] E. A. N. Marks, V. Kinigopoulou, H. Akrout, A. A. Azzaz, C. Doulgeris, S. Jellali, C. Rad, P. S. Zulueta, E. Tziritis, L. El-Bassi, C. M. Ghimbeu, M. Jeguirim, *Sustain*, 2020, **12**, article no. 6081.
- [11] M. Bargaoui, S. Jellali, A. A. Azzaz, M. Jeguirim, H. Akrout, *Environ. Sci. Pollut. Res.*, 2020, 22, article no. IF 9.130.
- [12] K. Haddad, M. Jeguirim, B. Jerbi, A. Chouchene, P. Dutournié, N. Thevenin, L. Ruidavets, S. Jellali, L. Limousy, ACS Sustain. Chem. Eng., 2017, 5, 8988-8996.
- [13] P. Dutournie, M. Jeguirim, L. Limousy, S. Jellali, B. Khiari, "Olive mill wastewater controlled drying for material and water recovery", in 2019 10th International Renewable Energy Congress (IREC), IEEE, 2019, 1-4.
- [14] K. Haddad, M. Jeguirim, S. Jellali, N. Thevenin, L. Ruidavets, L. Limousy, *Sci. Total Environ.*, 2020, **752**, article no. 141713.
- [15] A. A. Azzaz, M. Jeguirim, V. Kinigopoulou, C. Doulgeris, M. L. Goddard, S. Jellali, C. Matei Ghimbeu, *Sci. Total Environ.*, 2020, **733**, article no. 139314.
- [16] M. A. Al-Ghouti, A. O. Sweleh, *Environ. Technol. Innov.*, 2019, 16, article no. 100488.
- [17] S. Larous, A. H. Meniai, Int. J. Hydrogen Energy, 2016, 41, 10380-10390.
- [18] L. Limousy, I. Ghouma, A. Ouederni, M. Jeguirim, *Environ. Sci. Pollut. Res.*, 2017, 24, 9993-10004.
- [19] M. Benallou Benzekri, N. Benderdouche, B. Bestani, N. Douara, L. Duclaux, J. Mater. Environ. Sci., 2018, 9, 272-284.
- [20] I. Kula, M. Uğurlu, H. Karaoğlu, A. Çelik, *Bioresour. Technol.*, 2008, **99**, 492-501.
- [21] K. Mahmoudi, N. Hamdi, E. Srasra, Surface Eng. Appl. Electrochem., 2015, 51, 427-433.
- [22] I. Ghouma, M. Jeguirim, S. Dorge, L. Limousy, C. Matei Ghimbeu, A. Ouederni, C. R. Chim., 2015, 18, 63-74.
- [23] D. Mohan, A. Sarswat, V. K. Singh, M. Alexandre-Franco, C. U. Pittman, *Chem. Eng. J.*, 2011, **172**, 1111-1125.
- [24] H. P. Boehm, Carbon N. Y., 2002, 40, 145-149.
- [25] S. Jellali, M. A. Wahab, R. B. Hassine, A. H. Hamzaoui, L. Bousselmi, *Chem. Eng. J.*, 2011, **169**, 157-165.
- [26] A. A. Azzaz, S. Jellali, H. Akrout, A. A. Assadi, L. Bousselmi, *Environ. Sci. Pollut. Res.*, 2017, 24, 9831-9846.
- [27] S. Jellali, E. Diamantopoulos, K. Haddad, M. Anane, W. Durner, A. Mlayah, J. Environ. Manag., 2016, 180, 439-449.
- [28] N. Mojoudi, N. Mirghaffari, M. Soleimani, H. Shariatmadari, C. Belver, J. Bedia, *Sci. Rep.*, 2019, 9, article no. 19352.
- [29] K. Mahmoudi, K. Hosni, N. Hamdi, E. Srasra, Korean J. Chem. Eng., 2014, 32, 274-283.
- [30] A. Ibn Ferjani, M. Jeguirim, S. Jellali, L. Limousy, C. Courson, H. Akrout, N. Thevenin, L. Ruidavets, A. Muller, S. Bennici, *Renew. Sustain. Energy Rev.*, 2019, **107**, 425-433.

- [31] O. Eren, S. Gul, E. Kusvuran, K. Cellat, F. M. Ertosun, Asian J. Chem., 2015, 11, 4106-4110.
- [32] M. Erdem, R. Orhan, M. Şahin, E. Aydın, Water Air Soil Pollut., 2016, 227, article no. 226.
- [33] O. Üner, Ü. Geçgel, Y. Bayrak, Arab. J. Chem., 2019, 12, 3621-3627.
- [34] K. Mahmoudi, N. Hamdi, E. Srasra, J. Mater. Environ. Sci., 2014, 5, 1758-1769.
- [35] F. Boudrahem, F. Aissani-Benissad, H. Aït-Amar, J. Environ. Manag., 2009, 90, 3031-3039.
- [36] T. Bohli, A. Ouederni, N. Fiol, I. Villaescusa, C. R. Chim., 2015, 18, 88-99.
- [37] S. Yapici, H. Eroglu, E. Varoglu, Appl. Radiat. Isot., 2011, 69, 614-622.
- [38] X. Song, Y. Zhang, C. Yan, W. Jiang, C. Chang, J. Colloid Interface Sci., 2013, 389, 213-219.
- [39] H. Wu, Y. Zhao, Y. Long, Y. Zhu, H. Wang, W. Lu, *Bioresour*. *Technol.*, 2011, **102**, 9403-9408.
- [40] A. C. Lua, T. Yang, J. Colloid Interface Sci., 2005, 290, 505-513.
- [41] A. A. Azzaz, S. Jellali, R. Souissi, K. Ergaieg, L. Bousselmi, *Environ. Sci. Pollut. Res.*, 2017, 24, 18240-18256.
- [42] S. Jellali, M. A. Wahab, M. Anane, K. Riahi, N. Jedidi, *Desalination*, 2011, **270**, 40-49.
- [43] R. Gong, J. Ye, W. Dai, X. Yan, J. Hu, X. Hu, S. Li, H. Huang, Ind. Eng. Chem. Res., 2013, 52, 14297-14303.
- [44] J. Pal, M. K. Deb, D. K. Deshmukh, D. Verma, Appl. Water Sci., 2013, 3, 367-374.
- [45] K. Haddad, S. Jellali, S. Jaouadi, M. Benltifa, A. Mlayah, A. H. Hamzaoui, C. R. Chim., 2015, 18, 75-87.
- [46] F. C. Wu, R. L. Tseng, R. S. Juang, Chem. Eng. J., 2009, 153, 1-8.
- [47] A. Pholosi, E. B. Naidoo, A. E. Ofomaja, South Afr. J. Chem. Eng., 2020, 32, 39-55.

- [48] M. Benadjemia, L. Millière, L. Reinert, N. Benderdouche, L. Duclaux, *Fuel Process. Technol.*, 2011, 92, 1203-1212.
- [49] Y. Wang, Y. Zhang, S. Li, W. Zhong, W. Wei, J. Mol. Liq., 2018, 268, 658-666.
- [50] E. Sharifpour, E. Alipanahpour Dil, A. Asfaram, M. Ghaedi, A. Goudarzi, *Appl. Organomet. Chem.*, 2019, **33**, article no. e4768.
- [51] F. Mbarki, A. Kesraoui, M. Seffen, P. Ayrault, Water Air Soil Pollut., 2018, 229, article no. 95.
- [52] J. Ndi Nsami, J. Ketcha Mbadcam, J. Chem., 2013, 2013, 1-7.
- [53] R. L. Tseng, F. C. Wu, J. Hazard. Mater., 2008, 155, 277-287.
- [54] S. Valliammai, Y. Subbareddy, K. S. Nagaraja, B. Jeyaraj, *Indian J. Chem. Technol.*, 2017, 24, 134-144.
- [55] K. N. Aboua, Y. A. Yobouet, K. B. Yao, D. L. Goné, A. Trokourey, *J. Environ. Manag.*, 2015, **156**, 10-14.
- [56] D. Angin, E. Altintig, T. E. Köse, *Bioresour. Technol.*, 2013, 148, 542-549.
- [57] N. Somsesta, V. Sricharoenchaikul, D. Aht-Ong, *Mater. Chem. Phys.*, 2020, 57, 25194-25206.
- [58] V. Yönten, N. K. Sanyürek, M. R. Kivanç, Surface Interfaces, 2020, 20, article no. 100529.
- [59] A. Mokhtar, S. Abdelkrim, A. Djelad, A. Sardi, B. Boukoussa, M. Sassi, A. Bengueddach, *Carbohydr. Polym.*, 2020, 229, article no. 115399.
- [60] B. K. Martini, T. G. Daniel, M. Z. Corazza, A. E. De Carvalho, J. Environ. Chem. Eng., 2018, 6, 6669-6679.
- [61] Y. Kuang, X. Zhang, S. Zhou, Water (Switzerland), 2020, 12, article no. 587.
- [62] L. Yu, Y. M. Luo, J. Environ. Chem. Eng., 2014, 2, 220-229.
- [63] H. Kim, S. O. Kang, S. Park, H. S. Park, J. Ind. Eng. Chem., 2015, 21, 1191-1196.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Evaluation of the influence of olive mill waste on soils: the case study of disposal areas in Crete, Greece

Maria K. Doula^{*, a}, Antonis Papadopoulos^a, Chronis Kolovos^a, Olga Lamnatou^a and Antonis A. Zorpas[©] ^{*, b}

^{*a*} Benaki Phytopathological Institute, Department of Phytopathology, Laboratory of Non-Parasitic Diseases, 8 Stef. Delta, 14561 Kifissia, Attiki, Greece

^b Open University of Cyprus, Faculty of Pure and Applied Science, Environmental Conservation and Management, Laboratory of Chemical Engineering and Engineering Sustainability, Giannou Kranidioti 33, 5220, Latsia, Nicosia, Cyprus

E-mails: mdoula@otenet.gr (M. K. Doula), a.papadopoulos@bpi.gr (A. Papadopoulos),

ch.kolovos@bpi.gr (C. Kolovos), o.lamnatou@bpi.gr (O. Lamnatou),

antoniszorpas@yahoo.com, antonis.zorpas@ouc.ac.cy (A. A. Zorpas)

Abstract. It is well known that soils where olive mill wastes (OMWs) are disposed of eventually become overloaded with organic matter of unknown and insufficient quality as well as inorganic nutrients and polyphenols. In European Mediterranean countries, the disposal of OMW is considered to be a major environmental issue. An extensive study on the risks of soil quality caused by the disposal of OMW, in the framework of the LIFE PROSODOL Project (http://www.prosodol.gr), resulted in the definition of eight soil indicators. The indicators specifically for soils that contain OMW are pH, organic matter, electrical conductivity, total nitrogen, polyphenols, exchangeable potassium, available phosphorus, and available iron. To confirm the validity of this set of indicators, nine OMW disposal areas were randomly selected and studied in Rethymno, Crete, without any knowledge of their history, details of OMW production and disposal, or other activities in those areas. Soil samples were collected and analyzed for particle size distribution, pH, electrical conductivity, organic matter, carbonates, total N, available P, exchangeable cations (K, Ca, and Mg), polyphenols, boron, and available Mn, Fe, Cu, and Zn. The results indicated that all soil parameters were affected but in different directions and by different magnitudes. Changes were evaluated considering the number of ponds for which (a) changes in soil parameters were observed; (b) a parameter value was measured above the excessive threshold; and (c) the change in the parameter values was >100%. It was revealed that organic matter, nitrogen, polyphenols, potassium, phosphorus, and iron are the constituents for which all three evaluation factors yielded the highest values. Moreover, zinc could be also considered as a potential indicator although it is not included in the evaluated set of indicators. With regard to pH and electrical conductivity, although no substantial changes were observed in this study, they should always be included in a set of indicators as they are valuable in evaluating soil buffering capacity and salinization threat, respectively.

Keywords. Olive mill waste, Soil, Indicators, Disposal, Evaporation ponds, Soil overloading, Metals.

^{*} Corresponding authors.

1. Introduction

Sustainable management of olive mill waste (OMW) in Mediterranean countries is a challenging issue [1]. A great deal of research has been devoted to studying the impact of various practices and methods for managing this type of waste worldwide [2,3].

Olive oil production is considered one of the oldest agricultural industries in the Mediterranean countries. Spain, Italy, Greece, and Tunisia are the largest oil producers worldwide, representing 73.5% of the overall olive oil production globally [4]. Furthermore, almost 98% of the world's olive tree cultivation involving approximately 900 million trees in 10 million hectares of land is concentrated in the Mediterranean Basin [5–8].

The production of olive oil from different types of olive mills (three-phase, two-phase, and traditional) is a seasonal process, which results in very large quantities of waste that must be managed in a short time. In ideal operating conditions, an oil production unit has its own waste management system (e.g., chemical or biological treatment) [9]. In most cases, however, mainly due to the small capacity of oil mills and the high cost of various waste treatment technologies, oil mills discharge untreated OMW into the environment. The main recipients are soils, surface water, and groundwater in addition to seas.

Untreated OMW can cause severe environmental degradation due to its very high organic and inorganic load, foul odour, and intense dark black/brown color [6,7,10–12]. Furthermore, landspreading and disposal into evaporation ponds without taking protective measures are practices that are observed in many olive producing areas and mainly small mills due to the low cost of these practices and also lenient control measures by competent authorities. Research works published so far report that discharge into soils (in ponds or directly on soil surfaces) degrades soils gradually [13] and may cause groundwater contamination through leaching [8].

As soil formation is an extremely slow process, the soil is considered a nonrenewable resource. Although, until recently, soil was the "poor relation" of air and water, its importance is now beginning to be recognized worldwide [14]. Significant strategies have been designed and implemented to protect soil [15,16]. Soil is now included directly and indirectly in the Sustainable Development Goals (Goal numbers 2, 3, 6, 11–13, and 15) [17].

Without ignoring the importance and contribution of various organic waste treatment technologies in maintaining environmental quality, the current approach focuses on the utilization of organic waste and moving to a more cyclic way of implementation as regards the management of materials and resources [3,18]. In light of these facts, many researchers and policy makers promote the reuse of OMW for irrigation and fertilization purposes [19]. Experiments with controlled addition of OMW to soils for usually a few years (1-3 years) have shown that a severe impact on soil electrical conductivity (EC), polyphenol content and pH is not expected although a significant increase is observed in potassium, phosphorus, nitrogen, and organic matter (OM) concentrations in soil [13,20]. Even though in most of these cases and after a sufficient time period, usually 4-6 months, or after harvesting of cultivated plants, the soil was restored in terms of increased value of its constituents, this is not the case for soils where untreated OMW is disposed of in an uncontrolled manner and for many years [10,11, 21]. Another important difference between these two cases is soil quality. In the case of field experiments, soils on experimental plots were healthy without prior waste disposal, while in the second case, soils had been receiving large amounts of waste for many vears. Therefore, it is obvious that soil behaviour in these two cases does not have much in common, especially in terms of persistence, resilience, and the degradation level of pollutants. Studies carried out in the framework of the European LIFE PROSODOL Project "Strategies to protect and improve soil quality from the disposal of olive mill waste in the Mediterranean region" have shown that in areas where untreated waste is disposed of, there are changes in soil properties, which are not reverted to normal conditions even after a 10-year cessation of waste disposal [10,11,21-23]. Although most of the soil properties were found to be affected to a greater or lesser degree, it was also found that some soil properties could be used as indicators for the assessment of soil quality at OMW disposal areas. These include soil pH, OM, EC, total nitrogen, polyphenols, exchangeable potassium, available phosphorus, and available iron [21]. This study aims to confirm the validity of these proposed soil indicators by evaluating the



Figure 1. Location of the five ponds studied in the LIFE PROSODOL project (blue markers) and the nine randomly selected ponds of this study in Crete (red markers).

results obtained after visiting and studying nine OMW disposal sites in Greece, which were randomly selected and without any knowledge of their history. Therefore, the importance and innovation of this study lie in verifying the ability of soil OMW indicators as proposed by Doula *et al.* [21]. This approach can be used as a framework for assessing soil quality not only in areas where the disposal of OMW is common practice but also in areas where OMW is applied for fertigation in accordance with current legislation.

2. Materials and methods

The study was based on the research work of Doula *et al.* [21] in the framework of the LIFE PROSODOL project [24], in which the authors reported their results regarding the definition of soil indicators specific to OMW disposal areas. In brief, the LIFE PROSODOL project was implemented in Rethymno, Crete, Greece, where a well-designed soil monitoring system was implemented to assess the impact of OMW disposal on soil properties.

The monitoring strategy was applied for almost two years. The process included bimonthly soil sampling and analysis of 23 soil parameters from five OMW disposal areas (blue markers in Figure 1), which were located in the prefecture of Rethymno, Crete. More than 16,200 samples were collected and analyzed. After processing the collected soil data, eight soil-quality indicators were defined and proposed.

2.1. Areas understudy

Nine OMW disposal areas were selected from Crete (red markers in Figure 1; Table 1). Soil and waste samples were collected once in June 2017 when evaporation ponds were full of OMW (after the oil production period, which ends in January, and before the hot Mediterranean summer when OMW partly evaporates). In all cases, OMW was produced from three-phase mills by the continuous centrifuge extraction process. The OMW management practice was the same for all sites, that is, disposal in evaporation ponds. The ponds were deep (up to 1.5–2 m) and were poorly constructed by using simple soil excavation methods (Figure 2) and without using any protective medium to prevent leaching to aquifers (e.g., geotextiles).

Soil and waste samples were collected by following the method of composite samples. Composite samples were prepared from discrete, equal quantities of specimens were taken from several locations at a constant depth (spatial composite). This type of



Figure 2. Typical OMW evaporation pond in Crete, Greece.

Disposal area	Latitude	Longitude	Clay (%)	Texture
Episkopi, Rethymno	35° 19′ 34.68″ N	24° 20′ 21.47″ E	28	Silty clay loam
Sellia, Rethymno	35° 12′ 08.21″ N	24° 22′ 39.64″ E	28	Silty clay loam
Akoumia, Rethymno	35° 10′ 8.72″ N	24° 34′ 48.99″ E	27	Silty clay loam
Agouseliana, Rethymno	35° 14′ 7.72″ N	24° 26′ 36.62″ E	14	Sandy loam
Koxare, Rethymno	35° 13′ 39.28″ N	24° 28′ 20.95″ E	10	Sandy loam
Asomatos, Rethymno	35° 11′ 26.00.″ N	24° 26′ 23.39″ E	29	Silty clay loam
Spili, Rethymno	35° 12′ 22.02″ N	24° 32′ 6.98″ E	16	Sandy loam
Adele, Rethymno	35° 21′ 57.17″ N	24° 33′ 39.70″ E	48	Clay
Achlada, Heraklion	35° 23′ 38.65″ N	24° 59′ 49.07″ E	20	Loam

Table 1. Coordinates, percentage of clay content, and texture of the nine OMW disposal areas in this study

sampling is considered as being representative of the mean composition of an area because in general it reduces the intrinsic variability of the final sample and allows the mean concentration of an area to be estimated with better accuracy [25].

Soil samples were collected from the inner area of the ponds and also from the surrounding area (control samples). The sampling interval was 25 cm, starting from the surface and ending at a depth of 1 m. However, in areas with shallow soils, samples were collected to a depth where it was possible for the auger to penetrate the soil. From inside the evaporation ponds, samples were collected from different points on the walls and the bottom (five points in each pond) and at different depths. Then, the samples of the same depth were mixed to form a single composite sample. As the soil inside the ponds was disturbed due to the excavation, the soil texture was determined from the undisturbed samples, which were the controls (Table 1).

Parameter	Value range	Mean	SD
pH	4.91-5.45	5.10	0.18
Electrical conductivity (mS/cm)	7.62-8.15	7.93	0.17
Total organic carbon (g/L)	34–37	35	1
BOD (g/L)	35-42	38	3
COD (g/L)	55-74	65	7
Total Kjeldahl nitrogen (mg/L)	750-790	775	15
Total polyphenols (g/L)	8.5-9.2	8.8	0.2
Potassium (g/L)	4.2-4.7	4.5	0.2
Phosphorus (mg/L)	430-480	463	17
Calcium (mg/L)	430-500	466	24
Sodium (mg/L)	106-118	111	4
Magnesium (mg/L)	152-170	162	6
Boron (mg/L)	5.1 - 5.4	5.3	0.1
Copper (mg/L)	30–33	32	1
Iron (mg/L)	210-260	238	14
Zinc (mg/L)	17–21	19	1
Manganese (mg/L)	9–13	11	1

Table 2. Chemical analysis results of the OMW collected from the nine ponds

2.2. Soil and OMW analysis

The collected soil samples were analyzed not only for the eight indicators defined by Doula et al. [21] but also for multiple parameters to determine whether other properties were affected by waste disposal. In particular, soil samples, after air drying and sieving, were analyzed for particle size distribution texture (only the control soils) by using the Bouyoucos method [26]; pH and EC in paste extract using a pH/EC meter [27,28]; OM by dichromate oxidation [29,30]; carbonates by using a Bernard calcimeter [27]; total N by the Kjeldahl method [31]; available P by sodium hydrogen carbonate extraction [32] and measured using a HITACHI U3010 Spectrophotometer; and exchangeable K⁺, Ca²⁺, and Mg^{2+} by BaCl₂ extraction [33] and measured using a Varian SpectrAA 220 Atomic Absorption Spectrometer. Methanol-extractable phenol compounds were quantified by means of the Folin-Ciocalteu colorimetric method [34]. Available Mn, Fe, Cu, and Zn were determined using extraction with diethylenetriaminepentaacetic acid according to the standard ISO 14870:2001 [35] and measured by a Varian SpectrAA 220 Atomic Absorption Spectrometer. Boron was extracted using boiling water and quantified by applying the azomethine-H method [36].

Moreover, nine mixed waste samples were collected from inside the nine ponds and analyzed for several parameters (Table 2) using accredited methods [6]. The initial digestion of the waste samples was carried out by using the EPA 3052 method with HNO₃ digestion in a microwave oven. The total phenol content was determined using the Folin–Ciocalteu method [34]. As can be seen in Table 2, the collected samples are characterized by low pH, high EC, and a high content of nutrients and polyphenols.

3. Results and discussion

3.1. Carbonate content and pH of pond soils

Regarding the effect on soil pH, as can be seen in Figure 3, the high percentage of carbonates acts protectively against the acidity of OMW. Thus, in soils with a low carbonate content, the reduction in pH is more probable (Achlada, Spili, and Akoumia). However, in some cases, there is an increase in the pH of pond soils in comparison to the controls (Sellia, Episkopi, Adele, and Asomatos). The common denominator of



Figure 3. pH values and CaCO₃ content of soil samples collected from the nine disposal areas in Crete.

the later cases appears to be the clay content of the soil, which in all these cases is higher than 28%. This is in agreement with the results by Regni et al. [20], who reported that soils with a high percentage of clay appear to be the best choice for fertigation with olive mill wastewater, while the carbonate content is important for providing efficient buffering power and avoiding extreme changes in the pH value. This is in line with the results from the main sampling campaign of the PROSODOL project, which indicate that for alkaline soils rich in CaCO₃, seasonal surface application of OMW does not markedly affect the soil pH in the long term since most of the acidity of OMW is neutralized by the CaCO₃ [23] in the soil. However, this study also reveals that OMW disposal may gradually reduce the CaCO₃ content in the soil as can be observed for Episkopi and Adele ponds. This is in agreement with the results of previous work [37], which reported that the low pH of OMW results in the long-term loss of carbonate from the topsoil.

Another interesting finding is that for some cases, the pH was found to increase (Sellia, Episkopi, Adele, and Asomatos). However, this result should not be considered unusual on the basis that because OMW has a low pH value, the expected effect on the soil pH is its reduction. As Tang and Yu reported [38], the direction and the magnitude of pH change depending on the concentration of organic anions in the residues, on the initial pH of the soil, and on the degree of residue decomposition. This suggestion was based on the findings of Yan *et al.* [39], who mentioned that the magnitude of change in soil pH involves the glycolytic pathway and the citric acid cycle. In particular, the decomposition of carbohy-



Figure 4. Electrical conductivity of soil samples collected from the nine disposal areas in Crete. Values in the red area are above the threshold of 4 mS/cm [21,23].

drates in the glycolytic pathway produces carboxylic groups, which after dissociation may decrease the soil pH. When these groups are decarboxylated in the citrate cycle, an equivalent number of protons is required, thereby inducing a rise in soil pH.

Apart from the above explanation, the pH increase has also been attributed to the production of ammonia from the microbial degradation of OMW [40].

3.2. Electrical conductivity of pond soils

In general, the ECs of all pond soils were significantly higher than the ECs of the respective control soils not only for the upper soil layers but also for the deeper layers (Figure 4). However, two of the nine cases had ECs lower than the threshold value for salinity (4 mS/cm) [21,23]. Moreover, for eight cases, there was a substantial increase in EC in comparison to the control soils. It should, however, be noted that the selected areas had not been monitored in the past and no further information such as years of disposal, pretreatment of wastes, and so on was available. Therefore it is not possible to correlate the results with the ponds' history. Nevertheless, the general conclusion drawn by Kavvadias *et al.* [23] after studying ponds where OMW disposal ceased for more than 8 years was that the increase in salinity appears to be irreversible when excessive amounts of OMWs were applied on soils, especially in the upper soil layers.

3.3. Organic matter and nitrogen in pond soils

High concentrations of OM were measured to a depth of 1 m in many areas (Figure 5), indicating a significant quantity of organic carbon as was also found for the five ponds in the main pilot area of the PROSODOL project [23]. For topsoils (0-25 cm), in all cases, the OM content was higher than 2%, while there were also cases of very high OM (up to 17%). Although the increase in OM content could be very beneficial to soils (increases fertility, sequesters carbon, provides nutrients, improves physical properties, protects against erosion, etc.), its extensive increase does not translate to more benefits. In fact, the addition of labile OM (not well stabilized) may decrease stocks of soil organic carbon. This happens because unstabilized OM decomposes quickly, which enhances the decomposition of native soil OM [41]. Saviozzi et al. [42] reported variable decomposition rates in soils amended with OMW, which are distinguished by a fast primary phase, in which the decomposable fraction is rapidly degraded, and a slower secondary phase, in which the more stable fraction is degraded. In addition, Pezzolla et al. [43] demonstrated that the application of organic fertilizer that is not well stabilized on the soil causes a significant increase in dissolved organic carbon and consequently CO₂ emissions. This is due to the rapid rise in microbial respiration resulting from the presence of available labile carbon. Therefore, this explains the small increase in OM observed in some of the ponds and a large increase in others. In addition, the excessive increase in OM is not necessarily beneficial to the soil system.

In general, OM and total nitrogen are well correlated (Figure 5). This is because the total nitrogen



Figure 5. Organic matter and total Kjeldahl nitrogen content in soil samples collected from the nine disposal areas in Crete. The upper threshold values for the parameters are circled in red [21,23].

content in the upper soil layer was very high (higher than the value considered as the upper threshold, which is 3 mgN/g [23]) for the majority of the examined cases (except two). Moreover, high values were also measured to a depth of 1 m. High levels of OM and residual N were also found in the control soils of some areas (e.g., Sellia) possibly due to sheep grazing since livestock farming is one of the main activities in the area of central Crete. Increased nitrogen concentration was detected also by Chartzoulakis *et al.* [13] after a controlled application of OMW in a plot experiment. This result was attributed to the increase in nitrogen-fixing microflora.

Evaluating the data from Figure 5, it can be observed that for the cases of a small increase in OM at Sellia, Episkopi, Asomatos, and Agouseliana ponds (probably for the reasons mentioned above), the nitrogen content is also low as compared to the other ponds. This could be due to the fact that OM is the main source of organic nitrogen. Therefore, low OM concentrations lead to low nitrogen concentrations in the soil. However, this effect may also be due to quick nitrogen mineralization and loss in soils amended with unstabilized OM [40].

3.4. *Phosphorus, polyphenols, potassium, magnesium, boron, and calcium in pond soils*

The available P (Figure 6) ranged between 0.4 and 13 mg/kg for control soils, while high values were measured in pond soils, ranging from 2.4 to 297 mg/kg across the soil profile. Different



Figure 6. Phosphorus and total polyphenol content in soil samples collected from the nine disposal areas in Crete. The upper threshold values for the parameters are circled in red [21,23].

thresholds for available phosphorus (Olsen P) have been proposed for soils to evaluate the P mobilization risk as, for example, the value of 50 mg/kg, above which phosphorus mobility increases considerably although the soil pH has an important role in this behavior [21,23]. In any case, phosphorus is a parameter that is significantly affected by the disposal of OMW, which was also reported in the survey of the PROSODOL project [21,23].

In general, the assessment of polyphenol concentration in soils is considered difficult and has a high degree of uncertainty due to the lack of generally accepted thresholds [21,23]. Thus, local and sitespecific thresholds are often adopted as in the case of the study by Sierra *et al.* [44]. These authors decided to consider as guideline values the concentrations of phenolic substances in the control soils of their study, which varied from 14 to 25 mg/kg. Other values have been proposed as thresholds such as the value of 10.0 mg/kg as a threshold concentration of phenols in paddy soil or the value of 40 mg/kg, which has been adopted by the Netherlands [10,11,21,23]. In the present study, a high percentage of the control samples (45%) had polyphenol values between 41 and 108 mg/kg, which are considered high, although the reason for that is unknown. This could be due to leakages during OMW transportation, the emptying of the solid residue from the ponds after the evaporation of wastewater, the discharge of other types of waste, or even the deposition of manure owing



Figure 7. Exchangeable potassium and available boron content in soil samples collected from the nine disposal areas in Crete. The upper threshold values for the parameters are circled in red [21,23].

to the presence of animals in these areas. Nevertheless, in most of the areas, pond soils have polyphenol concentrations higher than those in the control samples.

Figure 5 indicates also that high polyphenol concentrations can be detected in deeper soil layers, which is in line with the results obtained by Mekki *et al.* [45], who reported that phenolic compounds migrate in soil according to their molecular mass. Thus polyphenols are adsorbed in the upper layers of the soil, while phenolic monomers can be detected at a depth of 1.2 m 1 year after irrigation with untreated OMW. The increase in potassium concentration in soils that accept OMW has been reported by many researchers [10,11,13,20]. The very high exchangeable K content of the pond soils (Figure 7), especially in the upper soil layer, confirms also the observations about the main pilot area of the PROSODOL project. Namely, the 89% of K data in pond soils had values from >2 cmol(+)/kg up to 26 cmol(+)/kg, which were found throughout the soil profile.

Potassium in the control soils of the nine disposal areas of this study ranged below the threshold value of 2.0 cmol(+)/kg [23]. On the contrary, potassium accumulation was high in pond



Figure 8. Exchangeable magnesium and calcium in soil samples collected from the nine disposal areas in Crete. The upper threshold value is numbered red for Mg and is circled in red for Ca [21,23].

soils, and more than 80% of K data had values >2 cmol(+)/kg up to 12 cmol(+)/kg throughout the soil profile.

Therefore, the potential for accumulation of K in soils due to OMW disposal is high and can adversely impact soil properties. Furthermore, since excessive concentrations of the element were also found in deeper soil layers, the uncontrolled disposal of OMW in evaporation ponds may cause K leaching to groundwater, especially in soils with a high sand content. As is the case for potassium, the available boron was significantly higher in pond soils compared to control samples (Figure 7). However, to assess the potential risk from boron increase, one has to note that hot-water-soluble B levels higher than 5.0 mg/kg should be considered toxic for plants [10,11]. Furthermore, the phytotoxic threshold values above 2–3 mg/kg⁻¹ were given by Kelling [45] and Alloway [46].

For all the soils monitored, the exchangeable Mg content was determined to be in higher concentrations than those in the control samples (Figure 8). Approximately 25% of Mg data in pond soils ranged from 2.3 to 11 mg/kg throughout the soil profile;



Figure 9. Available iron and copper in soil samples collected from the nine disposal areas in Crete. The upper threshold values for the parameters are circled in red. [21,23].

the concentrations >2.2 mg/kg are characterized as high [10,11,21,23].

Regarding the presence of exchangeable Ca in pond soils, there is a decreasing tendency in relation to control soils. Soils with a high CaCO₃ content underwent a decrease in calcium (Episkopi, Adele, and Asomatos; Figure 3) because of CaCO₃ dissolution. Similarly, a decrease in Ca was observed for soils with a low carbonate content (Achlada, Spili, Koxare, Akoumia, and Agouseliana; Figure 3) for the same reason. Namely, carbonate dissolution buffers soil pH, which however does not appear to be successful since for these areas, the pH values of ponds finally decreased.

3.5. Iron, copper, zinc, and manganese in pond soils

Very high concentrations of available Fe and Cu were measured in soil samples collected from inside the disposal ponds (Figure 9), confirming the threat of severe soil degradation due to overloading of metals. According to the literature [21,23,47], normal available-Fe concentration is below 50 mg/kg, while the concentration values between 50 and 100 mg/kg are considered very high. Values higher than 100 mg/kg are considered excessive and toxic to plants. In addition, the release of other soil elements such as As and Al is possible [48]. In this



Figure 10. Available manganese and zinc in soil samples collected from the nine disposal areas in Crete. The upper threshold value for the metals are circled in red for Mn and numbered red for Zn [21,23].

study, it was found that the Fe concentrations of all pond samples were above 100 mg/kg, while most of the Fe data for control soils had values lower than 50 mg/kg.

Copper in control soils ranged from 0.3 to 4.7 mg/kg (Figure 9). A high accumulation of available Cu was recorded in pond soils, where the values ranged from 3 to 15 mg/kg across the soil profile, which are slightly lower than the toxicity limit (>15–16 mg/kg) [21,23].

Regarding Mn (Figure 10), there were two cases among the nine ponds for which the metal had a

measured value higher than the threshold value of 50 mg/kg [49]. There were also cases of Mn decrease in comparison to the control soils after OMW disposal, potentially due to waste acidity, which caused the dissolution of naturally occurring metals (e.g., Spili, Akoumia, Asomatos, and Agouseliana). Another reason could be the potential higher mobility of Mn in comparison to Fe, Zn, and Cu as Wang *et al.* [50] reported. On the contrary, available Zn (Figure 10) was significantly higher in pond soils than that in control soils; for many pond soils, the Zn content was higher than the threshold value of 8.1 mg/kg [21,23]. This



Figure 11. Number of ponds for which (a) changes in soil parameters were observed; (b) a parameter value was measured above the excessive threshold; (c) the change in the parameter values was >100%.

behavior was also detected in soils collected from the main pilot area of the PROSODOL project.

3.6. Evaluation of the proposed soil indicators

Figure 11 summarizes the changes that occur in all soil parameters measured for all the evaporation ponds to assess which of them would be suitable for soil-quality indicators and whether the outcomes of this study are in line with previous work regarding the definition of soil indicators for areas of OMW disposal [21]. For this purpose, the same evaluation factors as in the work of Doula *et al.* [21] were used: the number of ponds for which (a) changes in soil parameters were observed; (b) a parameter value was measured above the excessive threshold; and (c) the change in the parameter values was >100%.

From this figure, it is therefore concluded that OM, nitrogen, polyphenols, potassium, phosphorus, and iron are the properties for which all three evaluation factors yield the highest values. Electrical conductivity, although less variable compared to zinc, is nevertheless a very important property (quality indicator) of soil and is directly related to salinization, which is one of the soil threats described in the EU Thematic Strategy for Soil Protection [15]. It is therefore an important indicator that should be identified and evaluated even though it did not exhibit significant variations in the areas of this study. Zinc exhibits a dynamic profile although the number of ponds with values above the excessive value is relatively small compared to the values of the other two evaluation factors for this element. However, it could be further evaluated as a potential indicator in the future. Although the pH did not generally show significant fluctuations, a considerable change in this parameter indicates a decrease in the soil buffering capacity. Therefore, this parameter should be always determined.

4. Conclusions

An unsustainable practice for OMW management is discharge into evaporation ponds without following protective measures for soils and aquifers. Previous research reported benefits for soil when specific doses of OMW were applied followed by frequent monitoring of soil quality. The high content of OM and plant nutrients such as Fe, Mg N, K, P, and so on makes OMW not only a valuable material for agriculture but also a threat when used without regulations and precautionary measures. This study focused on confirming the results of previous research work, which suggested that pH, OM, total nitrogen, polyphenols, exchangeable potassium, available phosphorus, and iron are appropriate indicators for assessing soil quality at OMW disposal areas. Therefore, these indicators were tested at nine OMW disposal areas, which were selected randomly without any knowledge of their history or other details regarding current activities in the vicinity of the evaporation ponds. The study revealed that all

the tested soil parameters were affected, some to a large and some to a lesser extent. It was confirmed that a high carbonate content protects soils against the acidity of OMW. However, apart from a potential decrease in soil pH due to the acidic character of OMW, an increase in pH is also an anticipated behaviour due to decarboxylation of OM and ammonia production. From all the tested soil properties, iron and potassium were found to be affected to the greatest extent. Organic matter, nitrogen, phosphorus, and polyphenols were also affected. Therefore these, along with potassium and iron, are considered appropriate indicators for OMW disposal areas. Electrical conductivity, although not found to be affected to a similar extent as in previous works, is an important property (quality indicator) of soil and is directly related to salinization. Therefore, it should be identified and evaluated. A parameter that has not been proposed to belong to the set of indicators is zinc, which presented a dynamic profile as a potential indicator in this study. Therefore, it is proposed as a potential indicator to be further evaluated in the future. Finally, although the pH did not generally show significant changes, this parameter is strongly related to the buffering capacity of soils. Therefore, it should be always determined at such degraded areas.

References

- F. Galliou, N. Markakis, M. Fountoulakis, N. Nikolaidis, T. Manios, *Waste Manage.*, 2018, **75**, 305-311.
- [2] P. Gullon, B. Gullon, G. Astray, M. Carpena, M. Fraga-Corral, M. A. Prieto, J. Simal-Gandara, *Food Res. Int.*, 2020, **137**, article no. 109683.
- [3] C. Sánchez-Sánchez, A. González-González, F. Cuadros-Salcedo, F. Cuadros-Blázquez, J. Cleaner Prod., 2020, 274, article no. 1227892.
- [4] International Olive Oil Council, "Guide for the Determination of the Characteristics of Oil-olives", 2011, Guide COI/OH/Doc. No 1/2011,https://www. internationaloliveoil.org/wp-content/uploads/2019/11/ COI-OH-Doc.-1-2011-Eng.pdf.
- [5] M. Sesli, E. D. Yegenoglu, African J. Biotechnol., 2009, 8, 3418-3423.
- [6] A. A. Zorpas, N. C. Costa, Biores. Technol., 2010, 101, 7984-7987.
- [7] A. A. Zorpas, J. V. Inglezakis, *Appl. Environ. Soil Sci.*, 2011, 2011, article no. 537814.
- [8] M. Jeguirim, P. Dutournié, A. A. Zorpas, L. Limousy, *Energies*, 2017, 10, article no. 1423.
- [9] M. Niaounakis, C. P. Halvadakis, *Waste Manage. Ser.*, 2006, 5, 65-81.

- [10] V. Kavvadias, M. K. Doula, S. Theocharopoulos, *Environ. Forensics*, 2006, 15, 37-51.
- [11] V. Kavvadias, M. K. Doula, M. Papadopoulou, S. Theocharopoulos, *Soil Res.*, 2015, **53**, 461-473.
- [12] M. K. Doula, A. A. Zorpas, V. J. Inglezakis, J. N. Pedreno, J. Environ. Eng. Manage., 2019, 18, 1297-1309.
- [13] K. Chartzoulakis, G. Psarras, M. Moutsopoulou, E. Stefanoudaki, *Agricul. Ecosyst. Environ.*, 2010, **138**, 293-298.
- [14] M. K. Doula, A. Sarris, "Soil Environment", in *Environment and Development* (S. Poulopoulos, V. Inglezakis, eds.), Elsevier, 2016, 213-286.
- [15] COM. EU, "Communication from the Commission to the Council "Thematic Strategy for Soil Protection" COM", 2006, 231 final.
- [16] EN, "Combating desertification in the EU: a growing threat in need of more action", 2018, Special Report No 33 of European Court of Auditors, https://www.eca.europa.eu/Lists/ ECADocuments/SR18_33/SR_DESERTIFICATION_EN.pdf.
- [17] EEA, "Soil and United Nations Sustainable Development Goals".
- [18] Z. Guo, N. Yan, A. A. Lapkin, Curr. Opin. Chem. Eng., 2019, 26, 148-156.
- [19] M. Bargaoui, S. Jellali, L. El Bassi, A. Zorpas, M. Jeguirim, "Nutrients leaching from an agricultural Mediterranean soil amended with biochars derived from impregnated solid olive wastes by olive mill wastewaters: batch and column investigations", in 1st International Conference on OpenEarth On Climate Change Adaption and Mitigation, 12–15 February, 2020, Thessaloniki, Greece, Interreg, 2020, https://balkanroad.eu/ conference/.
- [20] L. Regni, G. Gigliotti, L. Nasini, E. Agrafioti, C. M. Galanakis, P. Proiett, "Reuse of Olive Mill waste as soil amendment", in Olive Mill Waste, Recent Advances for Sustainable Management (C. M. Galanakis, ed.), Elsevier; Academic Press, 2017, 97-117.
- [21] M. K. Doula, V. Kavvadias, K. Elaiopoulos, Water Air Soil Pollut., 2013, 224, 1621-1632.
- [22] K. Komnitsas, K. Modis, M. K. Doula, V. Kavvadias, D. Sideri, D. Zaharaki, *Desalin Water Treat.*, 2016, 57, 2982-2995.
- [23] V. Kavvadias, M. Doula, K. Komnitsas, N. Liakopoulou, J. Hazard Mater., 2010, 182, 144-155.
- [24] LIFE PROSODOL, 2020, https://ec.europa.eu/environment/ life/project/Projects/index.cfm?fuseaction=search.dspPage& n_proj_id=3297.
- [25] P. De Zorzi, S. Barbizzi, M. Belli, R. Mufato, G. Sartori, G. Stocchero, *Appl. Radiat Isotopes*, 2008, 66, 1691-1694.
- [26] G. J. Bouyoucos, J. Agron., 1962, 54, 464-465.
- [27] A. L. Page, R. H. Miller, D. R. Keeney, *Methods of Soil Analysis*, *Part 2: Chemical and Microbiological Properties*, American Society of Agronomy, Madison, Wisconsin, 1982.
- [28] A. G. Vlyssides, M. Loizidou, K. Gimouhopoulos, A. Zorpas, *Fresen Environ. Bull.*, 1998, 7, 308-313.
- [29] A. G. Vlyssides, M. Loizidou, A. A. Zorpas, J. Environ. Sci. Health (A), 1999, 34, 737-748.
- [30] International Standard Organisation (ISO), "Soil quality-Determination of Organic Carbon by Sulfochromic Oxidation", 1998, ISO 14235:1998, Geneva, Switzerland.
- [31] International Standard Organisation (ISO), "Soil quality-

Determination of Total Nitrogen—Modified Kjeldahl Method".

- [32] International Standard Organisation (ISO), "Soil Quality-Determination of Effective Cation Exchange Capacity and Base Saturation Level Using Barium Chloride Solution", 1994, ISO 11263:1994, Geneva, Switzerland.
- [33] International Standard Organisation (ISO), "Soil Quality-Determination of Effective Cation Exchange Capacity and Base Saturation Level using Barium Chloride Solution", 1994, ISO 11260:1994, Geneva, Switzerland.
- [34] J. D. Box, Water Res., 1983, 17, 511-525.
- [35] International Standard Organisation (ISO), "Soil Quality-Extraction of Trace Elements by Buffered DTPA Solution", 2001, ISO 14870:2001, Geneva, Switzerland.
- [36] F. T. Bingham, "Boron. In Methods of Soil Analysis, Part 2. Chemical and microbiological properties" (A. L. Page, R. H. Miller, D. R. Keeney, eds.), Agronomy Monograph, vol. 9, SSSA, Madison WI, 2nd ed., 1982, 431-447.
- [37] M. Mahmoud, M. Janssen, N. Haboub, A. Nassour, B. Lennartz, Soil Till Res., 2010, 107, 36-41.
- [38] C. Tang, Q. Yu., Plant Soil, 1999, 215, 29-38.
- [39] F. Yan, S. Stubert, K. Mengel, Soil Biol. Biochem., 1996, 4–5, 617-624.
- [40] A. C. Barbera, C. Maucieri, V. Cavallaro, A. Ioppolo, G. Spagna, Agr. Water Manage., 2013, 119, 43-53.
- [41] S. Molina-Herrera, J. Romany, Eur. J. Soil Biol., 2015, 70, 118-125.
- [42] A. Saviozzi, R. Levi-Minzi, R. Riffaldi, Agrochimica, 1990, 34, 157-164.
- [43] D. Pezzolla, G. Marconi, B. Turchetti, C. Zadra, A. Agnelli,

E Veronesi, A. Onofri, G. M. N. Benucci, P. Buzzini, E. Albertini, G. Gigliotti, *Soil Biol. Biochem.*, 2015, **82**, 9-20.

- [44] J. Sierra, E. Martí, G. Montserrat, R. Cruañas, M. A. Garau, Sci. Total Environ., 2001, 279, 207-214.
- [45] A. Mekki, A. Dhouib, S. Sayadi, *Microbiol. Res.*, 2006, 161, 93-101.
- [46] J. B. Alloway, *Heavy Metals in Soils*, Blackie Academic Professional, London, UK, 1995.
- [47] G. N. Mitra, S. K. Sahu, R. K. Nayak, "Ameliorating effects of potassium on iron toxicity in soils of Orissa. In the Role and Benefits of Potassium in Improving Nutrient Management for Food Production", in *Quality and Reduced Environmental Damage. IPI-OUAT-IPNI International Symposium, November* 5–7, OUAT, Bhubaneswar, Orissa, India, 2009.
- [48] M. Chen, L. Q. Ma, Y. C. Li, "Concentrations of P, K, Al, Fe, Mn, Cu, and As in Marl Soils from South Florida", in *Proceedings*, Proceedings of the Soil and Crop Science Society of Florida, vol. 59, Soil and Crop Science Society of Florida, 2000, 124-129.
- [49] M. M. Jordán, E. García-Sánchez, M. B. Almendro-Candel, J. Navarro-Pedreño, I. Gómez-Lucas, I. Melendez, *Environ. Earth Sci.*, 2009, **59**, 687-694.
- [50] D. Wang, M. Gong, Y. Li, L. Xu, Y. Wang, R. Jing, S. Ding, C. Zhang, *Int. J. Environ. Res. Public Health*, 2016, **13**, no. 9, article no. 884.
- [51] A. K. Kelling, Soil and applied boron (A2522), University of Wisconsin System Board of Reagents and University of Wisconsin Extension, Cooperative Extension, US Department of Agriculture, Madison, WI, 1999.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Pepper cultivation on a substrate consisting of soil, natural zeolite, and olive mill waste sludge: changes in soil properties

Antonis V. Papadopoulos^{*, a}, Maria K. Doula^a, Antonis A. Zorpas[®] ^{*, b}, Stavros Kosmidis^a, Anna Assimakopoulou^c and Chronis Kolovos^a

^{*a*} Laboratory of Non Parasitic Diseases, Department of Phytopathology, Benaki Phytopathological Institute, 8 Stef. Delta str, 14561 Kifissia, Greece

^b Open University of Cyprus, Faculty of Pure and Applied Sciences, Environmental Conservation and Management, Laboratory of Chemical Engineering and Engineering Sustainability, Giannou Kranidioti, 33, P.O. Box 12794, 2252, Latsia, Nicosia, Cyprus

^c Department of Agricultural Technology, TEI of Peloponnese, Kalamata, Greece

E-mails: a.papadopoulos@bpi.gr (A. V. Papadopoulos), mdoula@otenet.gr (M. K. Doula), antoniszorpas@yahoo.com, antonis.zorpas@ouc.ac.cy (A. A. Zorpas), s.kosmidis@bpi.gr (S. Kosmidis), a.assimakopoulou@teikal.gr (A. Assimakopoulou), ch.kolovos@bpi.gr (C. Kolovos)

Abstract. The distribution of olive mill waste (OMW) in soil under specific conditions and restrictions seems to be an advantageous choice considering that it is a low-cost method and it recycles nutrients and returns organic carbon to the soil. In addition, it is regarded as a practice that contributes to climate change mitigation. The aim of this research was to investigate the potential of the natural zeolite clinoptilolite as a soil additive for using OMW sludge for vegetable cultivation and for eliminating the risk of soil and underground water degradation. For this purpose, a pot experiment was conducted under greenhouse conditions in which pepper seedlings were transplanted and grown onto different substrates containing combinations of 0%, 2.5%, and 5.0% zeolite and 0%, 2.5%, and 5.0% OMW sludge (v/v). The plants were irrigated twice a week, while leachates were collected on a weekly basis for testing. The results indicate that the use of OMW sludge improved soil properties. Moreover, the use of clinoptilolite as a substrate did not cause any significant variations in the cultivation process although this led to an increase in exchangeable Na at phytotoxic levels. However, it was determined that the substrate consisting of 2.5% clinoptilolite and 2.5% OMW sludge produced the best results in terms of substrate and leachate properties. The results are considered to be useful in effectively treating OMW when combined with natural zeolite additives as this process enhances the physicochemical characteristics of soil without leading to major irreversible negative consequences.

Keywords. Olive mill waste, OMW, Clinoptilolite, Zeolites, Pepper cultivation, Soil quality, Nutrient leaching.

^{*} Corresponding authors.

1. Introduction

The total global yield of olive oil for the 2019/2020 season is estimated to reach 3.67 million tons as compared to 3.13 million tons for the previous season [1]. More specifically, according to reports by the European Union [2], recent forecasts indicate that "Spanish olive oil production is projected to reach 1.76 million tons at the end of 2018/19 season, up from 1.39 million tons the preceding season". 226,000 tons is expected to be produced by Italy (which is 50% less from the previous year's production). This is less than Greece's projected 248,000 tons (which is 35% less compared with the previous year's production for Greece). The main issues faced by Italy are attributed to climate change and *Xylella fastidiosa* infestation in some olive groves in the east.

According to many researchers [3-8], olive mill waste (OMW) management is an issue that has been of concern to the global research community for many years. This is because OMW management has significant environmental, social, and economic implications. Among the main issues for the treatment of OMW is the fact that OMW contains hazardous wastes having high concentrations of phenolic compounds (up to 10 $\text{g}\cdot\text{L}^{-1}$ depending on the type and origin of the effluent) that are difficult to biodegrade. Due to strong seasonality (between October and March), OMW cannot be transferred in a central unit due to the size of olive mills, which usually are spread close to agricultural areas. Moreover, the mills consist of plants with a daily OMW flow rate between 10 and 100 m³ and are distributed over large areas [3,4].

In recent years, apart from the significant achievements regarding different management technologies [9,10], there has been great improvement in the awareness level of citizens, especially of olive mill owners and farmers, in terms of rational management, minimization of environmental impacts, and reuse of OMW in agriculture. Moreover, the legislative framework of all Mediterranean countries, which are the main olive oil producers globally, permits the use of olive mill wastewater (OMWW) and also the remaining sludge after OMWW preliminary treatment for fertigation and use as a soil additive, respectively. For example, the Greek Common Ministerial Decision No. 3924 of 7th December 2016 sets the framework for OMW application on soils and defines the terms and preconditions for landspreading. According to this decision, and considering that all preconditions are fulfilled, the maximum permitted waste amount is 80 m³/ha/y. Furthermore, for Italy and according to Law No. 574 of 1996 with regard to the agronomic use of sewage sludge and other wastes such as OMWW, the maximum amount is $50 \text{ m}^3/\text{ha/y}$ for OMWW generated by traditional mills (discontinuous extraction systems) and 80 m³/ha/y for vegetable water generated by centrifugal extraction (continuous extraction systems).

Through research studies, it became clear that there are significant benefits from the reuse of OMW in agriculture [11–14]. However, despite the proven significant benefits in terms of environmental problems caused by nonrational OMW management (e,g., uncontrolled discharge into aquatic systems and soil as discussed in the technical study of the LIFE PROSODOL project [15]), it should be clear that it is ultimately waste reuse. For this reason, if landspreading has been decided for cultivation purposes, care should be taken not only to avoid phytotoxic effects on cultivated plants but also for the protection of soil and underground and surface water bodies [16,17]. As mentioned by several researchers [13,14,18,19], OMW can be a valuable source of nutrients, which has a direct effect on improving soil quality [20] affected due to the presence of phenol compounds, pH variations, and salts. López-Piñeiro et al. [21] suggested that OMW contains more than 90% organic matter (OM) and is free from heavy and toxic metals as well as pathogenic microorganisms. As a result, it enhances soil properties, especially those of soils containing limited OM. Moreover, it increases humified fractions, which constitute a major source of phytonutrients. Other studies have shown that the disposal of OMW on soils affect all soil properties, while more severe impacts have been observed for soil electrical conductivity (EC), OM, nitrogen, phosphorus, potassium, polyphenols, and iron [13,18,19, 22]. These properties have also been proposed by Doula et al. [22] as parameters that can be used as indicators for soil quality assessment in areas where OMWs are discharged. They were also considered for soil monitoring in Greek Common Ministerial Decision No. 3924 of 7th December 2016 (except iron). However, Di Bene et al. [23] stated that OMW application may affect the biological and chemical properties of soil. However, OMW can be considered
$$M_{n/m}^{m+} \bullet \left[Si_{1-n}Al_nO_2\right] \bullet nH_2O$$

extraframework cations · framework · sorbed phase



Figure 1. Primary building unit of the zeolite framework.

nontoxic after a certain period of application, especially on healthy soil. It is therefore important that all necessary measures are taken to avoid soil burden even from elements that are not considered to be pollutants in the classical sense of the term as for example, potassium and iron. A protective measure is the calculation of the appropriate waste amount to be distributed on soil by considering soil composition and nutritional needs of cultivated plants [24]. This is, however, a stricter but a safer measure than the process imposed by the laws of the Mediterranean countries, which define a specific amount of OMW for landspreading (e.g., 80 m³/ha/y).

Another protective measure is the use of active materials as soil additives, such as natural zeolites, which can mitigate the effects of waste addition to soil. The use of natural zeolites as soil additives has been extensively studied over the past several years by many researchers worldwide [13,25-35]. Its use has been proven not only beneficial in soils contaminated by heavy metals but also as a slow-release fertilizer [36]. Its ability to bind and release potassium and ammonium according to crop requirements and also to bind toxic elements, such as heavy metals, may be applicable in the case of OMW reuse in agriculture. However, as Doula et al. [37] has reported, besides the positive effects, sodium release during the first few weeks after its application on soil may cause severe problems such as phytotoxicity and overload of sodium ions in the soil if these issues are not taken into consideration during use.

The aim of this study is to identify the positive and negative effects of clinoptilolite as a soil additive together with residual sludge from OMW for the cultivation of pepper plants. The research focused on the effects on basic soil properties caused by the presence of these two materials in the cultivation substrate. This work also aims at determining the optimum mixing ratio that would be of low cost and ensuring high production without soil degradation and with a low risk of nutrient loss through leaching.

2. Materials and methods

2.1. Experimental design

To study the effects of OMW sludge and clinoptilolite addition on cultivated soil, an 11-week pot experiment was conducted under greenhouse conditions. The greenhouse system is considered a protected plant growth environment and further was chosen to avoid weather conditions such as rain and wind. No control of temperature, ventilation or relative humidity was integrated into the experimental process to better simulate field conditions. Pepper plant (Capsicum annuum) was selected for conducting the experiment, first because it is a species not so commonly found in the waste management research area and second because it is a rather nondemanding vegetable in terms of soil and management requirements. During the experiment, pepper seedlings were transplanted and grown onto different substrates containing combinations of 0%, 2.5%, and 5.0% zeolite and 0%, 2.5%, and 5.0% of OMW sludge (v/v) (Table 1). Each treatment was composed of 12 replicates arranged in a split-plot design using zeolite as the main treatment material. Plants were irrigated twice a week, and leachates were collected on a weekly basis and further analyzed. After estimating the nutrient requirements, the plants were fertilized during the 10th week of the experiment by adding 3.6 g of nitrogen and phosphorus and 5.4 g of potassium to each pot and by using a commercially available fertilizer. After the completion of the experiment, the substrates were collected and analyzed to evaluate OMW and clinoptilolite impacts on soil properties after harvesting.

2.2. Clinoptilolite

The natural zeolite used in this study was clinoptilolite (Na_{0.2}K_{0.6}Mg_{0.7}Ca_{2.0}Al_{6.2}Si_{29.8}O_{72}\cdot 19.6H_2O),

	OMW	Clinoptilolite
	(% v/v)	addition (% v/v)
Z0AP0	0	0
Z0AP1	2.5	0
Z0AP2	5	0
Z1AP0	0	2.5
Z1AP1	2.5	2.5
Z1AP2	5	2.5
Z2AP0	0	5
Z2AP1	2.5	5
Z2AP2	5	5

Table 1. Sample preparation

which originates from northern Greece. The material has also been used for experiments in previous studies. Moreover, its formula, X-ray diffraction spectrum, and physicochemical properties are well known and have been already published [25,33,37,38].

2.3. OMW sludge

The OMW sludge was obtained in February 2017 from a three-phase olive mill located in Peloponnese, Greece. The sludge was collected after the precipitation of OMW for 2 weeks in a tank. The main chemical parameters of OMW, namely pH, EC, total N, K, P, Na, Mg, Fe, Cu, and Zn, were determined in triplicate by using established methodologies [39–41]. The total phenol content was determined using the Folin-Ciocalteu method [42].

2.4. Analyses of soil and leachates

Leachates were collected on a weekly basis in plastic containers. They were further analyzed directly in the liquid phase after filtration for pH, EC, polyphenols, Na, and K. Analyses of soil and substrates were carried out using standard methodologies. The particle size distribution was estimated using the Bouyoucos method [43]; pH and EC were measured from a paste extract [44]; OM was determined by dichromate oxidation [45]; carbonates were estimated by using the Bernard calcimeter [44]; the total *N* was calculated by the Kjeldahl method [46]; the available phosphorus was estimated using sodium hydrogen carbonate extraction [47], exchangeable K, Na, Ca, and Mg using BaCl₂ extraction [48], and available Mn, Fe, Cu, and Zn by DTPA extraction [49]. Soil B was extracted by boiling water using the azomethine-H method [44]. Furthermore, methanol-extractable phenol compounds were quantified through the Folin–Ciocalteu colorimetric method [42].

2.5. Instrumentation

For the measurement of K and Na, a Sherwood (Corning) 410 Flame Photometer was used. For the estimation of Ca, Mg, Cu, Fe, and Zn, a Varian SpectrAA 220 Atomic Absorption Spectrometer was utilized. Polyphenols and phosphorus were estimated by using a Cary UV-Vis Spectrophotometer.

3. Results and discussion

Table 2 presents the physical and chemical properties of the material. This material is very rich in OM. Moreover, it has a low pH, and it is also rich in K, N, Fe, Cu, and Zn. The OMW contains OM up to $97 \pm 1.17\%$. It has a pH of 4.10 ± 0.12 (slightly acidic). The concentrations of polyphenols are $0.32 \pm 0.08\%$. Table 3 lists physicochemical properties of the soil used as the basic material for the formation of different substrates in this study. The soil is characterized by a low OM concentration ($5.65 \pm 1.12\%$) and a pH of 7.39 ± 0.05 (neutral). The exchangeable capacity of K, Ca, Mg, and Na is very good.

Pepper cultivation on substrates consisting of soil, clinoptilolite (Z), and sludge from olive processing (AP) causes changes in the substrate's physicochemical properties. Results obtained from this study clearly demonstrate the effect of each of the substrate's components as well as their combined synergistic effects on the substrate.

3.1. Substrates with soil and clinoptilolite

In the case of Z1AP0 and Z2AP0, it is clear from Table 4 that an increase in the Z percentage of the substrate led to an increase in the EC. For the case of 5% Z addition, the EC exceeded the threshold of 2 mS/cm [11,16]. The increase in EC recorded for these two treatments was the highest compared to

7	2	5
•	-	0

Parameters	Value
Organic matter (%)	97 ± 1.17
Electrical conductivity (mS/cm)	2.6 ± 0.05
pH	4.10 ± 0.12
Polyphenols (%)	0.32 ± 0.08
Nitrogen (%)	0.51 ± 0.12
Potassium (%)	1.10 ± 0.04
Calcium (%)	0.11 ± 0.02
Magnesium (%)	0.05 ± 0.02
Sodium (%)	0.04 ± 0.02
Phosphorus (%)	0.05 ± 0.03
Iron (mg/kg)	41.12 ± 3.41
Copper (mg/kg)	12.02 ± 1.33
Zinc (mg/kg)	4.30 ± 0.91

Table 2. Physical and chemical properties ofthe OMW sludge

Table 3. Physical and chemical properties ofsoil used for the formation of substrates

Parameters	Value
Texture	Sandy loam
pH	7.39 ± 0.05
Electrical conductivity (mS/cm)	1.22 ± 0.11
CaCO ₃ (%)	28.32 ± 5.61
Organic matter (%)	5.65 ± 1.12
Total nitrogen (mg/g)	3.47 ± 0.58
Exchangeable K (cmol(+)/kg)	0.80 ± 0.22
Exchangeable Ca (cmol(+)/kg)	30.59 ± 4.92
Exchangeable Mg (cmol(+)/kg)	1.87 ± 0.45
Exchangeable Na (cmol(+)/kg)	0.11 ± 0.02
Available P (mg/kg)	33.19 ± 7.82
Available Fe (mg/kg)	8.86 ± 2.23
Available Cu (mg/kg)	1.27 ± 0.32
Available Zn (mg/kg)	18.02 ± 4.31
Polyphenols (mg/kg)	114.98 ± 14.91

all other treatments with the same Z percentage (i.e., Z1AP1, Z1AP2 and Z2AP1, Z2AP2), indicating that the addition of AP improves the substrate and positively addresses the issue of salt increase.

The increase in the EC of the substrates is due to the ions present in zeolite exchangeable sites and mainly Na⁺ as seen from the results in Table 4. The



Figure 2. Plants harvested for different treatments. Z: zeolite; AP: sludge from olive processing; 0: no addition; 1: 2.5% addition; 2: 5% addition.

table lists the concentrations of exchangeable Na for all treatments.

Compared to the substrate consisting of only soil (Z0AP0), exchangeable Na was approximately 8 and 13 times higher for 2.5% (Z1AP0) and 5% (Z2AP0) of clinoptilolite addition, respectively. The increased sodium concentrations were also recorded during a soil remediation field experiment conducted with the addition of clinoptilolite to the soil at different percentages up to 10% [13]. In this case, it was observed that exchangeable sodium was significantly increased in the first two months after the zeolite application. After this period, limited Na amounts were detected in the pilot soils.

About plant harvesting (Figure 2), the Z2AP0 treatment yielded the worst result, probably due to sodium. As is known, the concentration of excessive salts may restrict plant growth and productivity and lead to plant death [50]. Two mechanisms have an impact on plant growth: osmotic stress and ionic toxicity. In the presence of excessive salt content, the osmotic pressure of the soil solution becomes higher than that in the plant cells, inhibiting water uptake by plants. Furthermore, ionic toxicity may arise when the salt concentration is imbalanced inside cells, inhibiting cellular processes and metabolism [51]. Sodium ions at the root zone inhibit nutrient uptake (e.g., potassium) as well as the enzymatic activities within cells. It was reported that sodium may cause stress at concentrations higher than 10 mM and that it is an inhibitor of many enzymes, thereby affecting metabolic processes [50,52].

The initial soil used for the cultivation experiments was rich in nitrogen (Table 3). However, during

Samples	EC	Total N	Organic	Polyphenols	Avai	ilable	Exchan	geable
	(mS/cm)	(mg/kg)	matter (%)	(mg/kg)				
					В	Fe	Na	Κ
					(mg/kg)	(mg/kg)	(cmol(+)/kg)	(cmol(+)/kg)
Z0AP0	1.29 ± 0.03	2.55 ± 0.39	4.12 ± 0.36	118.02 ± 13.23	1.10 ± 0.08	9.41 ± 2.12	0.11 ± 0.02	0.91 ± 0.07
Z0AP1	1.04 ± 0.02	2.88 ± 0.41	5.98 ± 0.22	169.85 ± 19.96	1.57 ± 0.11	14.79 ± 3.15	0.77 ± 0.08	1.12 ± 0.11
Z0AP2	1.38 ± 0.05	3.02 ± 0.63	7.02 ± 0.64	185.11 ± 21.07	1.62 ± 0.23	16.80 ± 2.09	0.89 ± 0.06	1.54 ± 0.18
Z1AP0	1.91 ± 0.07	2.81 ± 0.27	4.10 ± 0.19	127.56 ± 17.94	1.21 ± 0.15	9.61 ± 2.08	0.99 ± 0.07	1.15 ± 0.13
Z1AP1	1.76 ± 0.07	2.73 ± 0.58	6.22 ± 0.21	167.05 ± 22.12	1.47 ± 0.20	17.03 ± 3.11	1.01 ± 0.08	1.61 ± 0.17
Z1AP2	1.79 ± 0.08	2.95 ± 0.64	7.30 ± 0.66	189.29 ± 27.81	1.69 ± 0.19	18.49 ± 4.09	1.14 ± 0.05	1.89 ± 0.23
Z2AP0	2.39 ± 0.11	2.17 ± 0.29	4.19 ± 0.31	129.96 ± 17.33	1.21 ± 0.11	7.92 ± 1.98	1.62 ± 0.12	1.67 ± 0.12
Z2AP1	2.27 ± 0.07	2.91 ± 0.33	6.23 ± 0.47	178.21 ± 26.33	1.53 ± 0.18	17.88 ± 3.51	1.44 ± 0.11	1.80 ± 0.21
Z2AP2	2.32 ± 0.12	2.63 ± 0.19	7.49 ± 0.55	187.01 ± 30.15	1.76 ± 0.22	18.93 ± 3.01	1.40 ± 0.08	2.22 ± 0.34

Table 4. Variations in physicochemical characteristics of treated samples

plant growth, it was found that the addition of supplementary nitrogen was necessary. Therefore, nitrogen measured in the substrates after crop harvesting (Table 4) came, apart from the soil and AP, from the fertilizer added in the 10th week of the experiment. A slight increase in the substrate's nitrogen content can be seen for the case of 2.5% Z addition, while a decrease of almost 0.5 mgN/g substrate is seen for 5% Z, indicating that zeolite addition does not improve the N-holding capacity of the substrate. Nitrogen can be retained by the zeolite mainly as NH_4^+ . However, no significant activity is expected in retaining NO_3^- due to the negative charge of the ions, which are leached during irrigation if they are not used by plants. Leachates in the case of Z2AP0 had the highest EC (data not shown).

The capability of the substrate to retain nitrogen is strongly associated with OM, which for the case of only zeolite addition (Table 4) was the lowest among all other treatments and, as expected, similar to the ZOAPO treatment (i.e., substrate consisting of only soil). As previous studies mention, when OMW is applied to the soil, the leaching of nitrogen is avoided as it is present mainly in organic form or as ammonium, which is adsorbed by soil colloids. Thereafter, ammonium is oxidized to nitrate (negatively charged), which can easily be transported to soil solutions and to greater soil depths through leaching.

On the other hand, and as Kavvadias *et al.* [11,16] mentioned, the presence of AP in soils may lead to the immobilization of available nitrogen forms, resulting in an increased need for supplementary nitrogen addition as is also the case in this experiment.

The concentration of exchangeable potassium was increased with increase in zeolite percentage (Table 4) as expected. This is due to the characteristic property of clinoptilolite to retain cations at the exchangeable sites of its framework, preventing leaching and making them available to plants slowly on demand [13]. In this case, potassium came from the fertilizer and also from the zeolite itself and increased with the percentage of Z in the substrate. No significant (Table 4) effects and changes were observed for B, available Fe, and available Cu and Zn (data not shown).

3.2. Substrates with soil and sludge from olive processing

For the cases of only AP addition, which are Z0AP1 and Z0AP2, a significant improvement of 50% and 75% in substrate OM, respectively, was recorded. The percentage of OM content for both cases exceeds the value of 5%, which characterizes soils as very rich in OM [11,16]. This increase could be beneficial to soils and especially to Mediterranean soils, which are very poor in OM. However, it has to be mentioned that accumulation of insufficiently stable OM, which could be the case for part of the OM content of this waste type, may cause various negative effects on soil properties, including the generation of anaerobic conditions and release of phytotoxic substances [13,53]. Moreover, Pezzolla et al. [54] reported that the addition of a not well-stabilized organic fertilizer/additive to soil might cause a significant increase in dissolved organic carbon and therefore CO2 emissions due to a rapid rise in microbial respiration after soil amendment.

Compared to Z0AP0 and also to the Z1AP0 and Z2AP0 treatments, an increase in the capability of substrates to retain nitrogen was also observed (Table 4) due to the increase in organic-nitrogen forms. Similarly, B content (Table 4) was increased by almost 45%, however, without significant differences between the two AP treatments. Exchangeable K (Table 4) was also increased by approximately 22% for 2.5% AP content (which is similar to the increase caused by 2.5% zeolite) and by 72% for 5% AP content (which is slightly lower than the increase recorded for 5% zeolite addition; i.e., Z2AP0). A significant improvement in the substrate's available Fe content (Table 4) was also recorded, which is a known effect of AP addition to soils. This was confirmed also during the LIFE PROSODOL project [15] and by the work of Doula et al. [22] as regards the soil parameters that are mostly affected by OMW discharge into soils. The advantage of this type of treatment (i.e., only soil and AP) in comparison to only Z addition can be also confirmed by the improvement of the substrate's EC (Table 4). For the case of the 2.5% AP content, the EC was lower than that for the Z0AP0 treatment (corresponding to cultivation on only soil), while for the treatment of 5% AP, it was slightly higher than that for Z0AP0. Exchangeable Na (Table 4) was increased in the substrate compared to that in the Z0AP0 treatment. However, the increase was significantly lower compared to the treatments of only Z addition. No significant effects were observed for available Cu and Zn content (data not shown).

3.3. Substrates with soil, clinoptilolite, and sludge from olive processing

As regards harvesting, the Z2AP2 treatment (i.e., 5% Z and 5% AP) resulted in the largest mean number of harvested plants among all studied treatments (Figure 2). Organic matter content (Table 4) seems to depend solely on the percentage of the sludge content since no improvement of substrates' OM was observed with the increase in zeolite content. As regards nitrogen, no substantial effect of Z was observed (Table 4) because the AP content is the factor that determines the N-holding capacity of the substrate.

In the present work, in temporal terms, harvesting denoted the end of the experimental process in the greenhouse environment. In particular, the harvest did not concern tasks such as cutting the upper plant part and separating the leaves, the stems, and the fruits, which would have led to further tissue analyses, as these did not fall within the scope and objectives of the study. However, what was measured and referred to as "yield" (as indicated in Figure 2) was plant survival in terms of the number of plants that was actually collected per treatment at the end of the experiment. In this study, plant stress and mortality were only discussed in correlation to soil characteristics such as salt concentration and to the soil additives used. Finally, in Figure 2, the term "crops" is substituted by the term "plants".

Among all treatments, higher amounts of exchangeable K were measured for the treatments with Z and AP. The highest K content was recorded for the case of Z2AP2 treatment (Table 4). Although the K concentration exceeded the threshold of 2 cmol (+)/kg according to Kavvadias *et al.* [11,16], no phytotoxic effects were observed. This is mainly due to zeolite activity to retain cations at exchangeable sites and supply them to the substrate solution on plant demand. Therefore, the zeolite acts as a slow-release fertilizer. Further improvement in the Fe content (Table 4) compared to the results obtained for Z1AP0, Z2AP0, Z0AP1, and Z0AP2 was observed, which is attributed to the synergistic effect of the two materials.

Electrical conductivity (Table 4) was also affected, and it was found that the presence of AP decreased the ion concentration in the substrate solution in comparison to the cases of only Z addition. Even if the reduction in EC is not substantial, it is indicative of the improvement of substrates due to AP content. Similar behavior was observed for exchangeable Na (Table 4).

3.4. Polyphenols in substrates and leachates

The polyphenol content in soils amended using OMW is a well-known problem [12]. It has been reported [55] that the residual levels of polyphenols could remain significant even 6 years after OMW application on the soil. On the contrary, Chartzoulakis et al. [18] mentioned that despite a temporal increase in phenolic compound concentrations in soil soon after OMW application, their concentration is rapidly reduced with a few months. The same authors also mentioned that polyphenols do not move rapidly across the soil profile even if OMWs are applied on irrigated soil or during the rainy season. In addition, negligible leaching of polyphenols is expected from soils rich in carbonates and clay materials [56,57]. These findings were confirmed in this study also since no polyphenols were detected in the leachates, which is a very significant result that provides further assurance for the protection of groundwater and deeper soil profiles.

As presented in Table 4, there was an increase in polyphenol content due to the AP application, while Z did not affect polyphenol concentration significantly. It is worth noting, however, the disproportionate increase in the concentration of phenols when the amounts of AP and OM of the substrates are doubled (the cases of 5% AP). This could be due to the higher concentration of OM since, as Sierra *et al.* [58] and Saadi *et al.* [59] reported, decomposition or incorporation of phenolics into the humic fraction of OM might take place.

As regards polyphenol concentration, it is higher for all treatments with AP than the Z0AP0 treatment. However, it still can be characterized as medium compared to the findings of Sierra *et al.* [58], who have reported values up to 9926 mg/kg, and of Nikolaidis *et al.* [60], who measured a lower total phenol content (481 mg/kg) when only pre-treated OMW was applied on soils.

3.5. Leaching of Na and K

Leaching of Na and K can be observed in Figures 3 and 4, which demonstrate the important role of both materials, Z and AP. As regards K leaching, the absence of Z (Figure 3a) resulted in high leaching of the ion, which was affected by the AP percentage. That is, leaching increased with increase in AP percentage in the substrate. On the contrary, even for the highest percentage of AP, the presence of clinoptilolite restricted K leaching. However, for the cases of Z1AP2 and Z2AP2 also, potassium leaching was higher than the other treatments shown in Figures 3b and 3c. Among all treatments with Z and AP, Z1AP1 exhibited the optimum behavior as regards K leaching. It is also important to highlight the increase in K leaching detected during the 11th experimental week owing to plant fertilization, which indicates that fertilization may have a more significant impact with respect to nutrient leaching and consequently their loss and degradation of aquifers. However, in this case also, the presence of Z and AP (Figures 3b and 3c) could limit leaching compared to the case of Z0AP0 (Figure 3a).

According to Figure 3a, the addition of AP restricted Na leaching in comparison to the Z0AP0 treatment. This occurred due to the improvement in the cation-holding capacity of the substrate, resulting from the increase in OM. With an increase in Z percentage (Figures 3b and 3c), Na leaching was enhanced and higher concentration values were measured in the leachates. However, among treatments of the same Z percentage, higher leaching was recorded for the cases where the AP percentage was not increased, confirming the positive impact of the OMW in inhibiting Na leaching. Among treatments





Figure 3. Potassium measured in leachates for each experimental week and for all treatments.

10 11

9

(c)

with Z and AP, the optimum performance, as regards Na leaching, was exhibited by Z1AP1.

Finally, the increase in Na leaching during the first 5 weeks of the experiment is owing to the already reported problem of Na release by clinoptilolite [13], which however was limited after that period. The treatments with 2.5% Z (Z1AP1 and Z1AP2) showed the optimum behavior of smooth Na release from Z.

3.6. Other changes in substrate properties

Other parameters measured in the substrate were pH and exchangeable Ca and Mg. The pH measured for



Figure 4. Sodium measured in leachates for each experimental week and for all treatments.

Z0AP0 was 7.39 ± 0.12 , while for all other treatments, the pH values measured were within the range 7.00 ± 0.05 and 7.67 ± 0.11 . Although there are differences in pH values, this is not considered important for a pot experiment in which soil resilience and buffering capacity are limited. As regards exchangeable Ca, it was measured to be between 40.05 ± 1.22 and 42.11 ± 1.05 cmol(+)/kg for all treatments (for Z0AP0, exchangeable Ca was 41.02 ± 1.08 cmol(+)/kg). An increase in exchangeable Mg was recorded for all treatments, where the concentrations were between 2.80 ± 0.09 and 3.29 ± 0.12 cmol(+)/kg (for Z0AP0, exchangeable Mg was 2.41 ± 0.16 cmol(+)/kg).

The addition of clinoptilolite increased the EC; however, soil amendment by OMW equilibrated this increase. In any case, special caution should be exercised in monitoring and controlling salt concentration in amended substrates to avoid extreme values that lead to a potential burden in plant growth or even plant mortality. Furthermore [26,27,29,30, 35], clinoptilolite may improve the availability of exchangeable potassium, thereby acting as a slowrelease fertilizer. Moreover, the addition of OMW increased OM concentration in the substrate, indicating that poor- or low-fertility soils can be enriched using nutrient compounds. Attention should also be paid so that phytotoxic conditions do not arise at the root zone and consequently in the plants. It is reported that the clinoptilolite acts as a means of effective amendment for the remediation of heavymetal-polluted soils [61], which is not dealt with in the present study. This activity in conjunction with its capacity to reduce leaching phenomena may serve as a mitigation feature in soil-polluted or soil-degraded sites.

4. Conclusions

Olive mill wastes are still considered as a major problem in the Mediterranean region although many research works provide solutions for OMW treatment and production of clean or almost clean effluents that can be further used for irrigation or discharge. However, the issue that remains unresolved is the high cost for establishing such a treatment facility, which prevents the adoption of these solutions. The distribution of OMWs in soils has been extensively studied during the past years. In addition, it has been reported that such practices could provide a sustainable alternative methodology for OMW management provided that all appropriate measures are taken to avoid soil degradation.

This study demonstrated the benefits of using OMW sludge in the cultivation of pepper plants with respect to increase in OM, N, K, B, and Fe of the substrate and without serious effects on Cu and Zn and also pH, thereby resulting in higher yields. On the contrary, the addition of clinoptilolite to soil did not appear to have a positive effect on the above properties (except in the case of K). Moreover, it was found to cause phytotoxic effects due to increased Na concentration in the soil solution and increased sodium leaching. In addition to the positive effects of the OMW sludge, the zeolite's synergistic effect improves the stability of the substrate by reducing loss of potassium through leaching and enhancing the soil's ability to retain cations. Therefore, the zeolite acts as a slow-release fertilizer and also reduces the effect of soil salinity after fertilization, thereby reducing nutrient loss through leaching.

Even though polyphenols increased for all treatments with OMW sludge, they did not cause any adverse effect on plants and they were not detected in the leachates after irrigation. In this study, the overall best performance in terms of yield and substrate and leachate properties was observed for the Z1AP1 treatment, which corresponds to the addition of 2.5% zeolite and 2.5% sludge to the soil. However, further studies are needed for the assessment of more substrate parameters and the nutritional status of plant parts (roots, stems, and leaves) to finalize a potential cultivation protocol.

References

- C. Vasilopoulos, "First Estimates for 2019/2020 World Olive Oil Production Released in Spain", 2019, www.oliveoiltimes.com/business/first-estimates-for-2019-2020-world-olive-oil-production-released-in-spain.
- [2] C. Vasilopoulos, "E.U. to Allow Member States to Regulate Olive Oil Supply", 2020, www.oliveoiltimes.com/business/eu-to-allow-member-states-to-regulate-olive-oilsupply/84081.
- [3] A. A. Zorpas, C. N. Costa, "Combination of fenton oxidation and composting for the treatment of the olive solid residue and the olive mile wastewater from the olive oil industry in Cyprus", *Biores. Technol.*, 2010, **101**, 7984-7987.
- [4] A. A. Zorpas, J. V. Inglezakis, "Intergraded applied methodology for the treatment of heavy polluted waste waters from the olive oil industries", *Appl. Environ. Soil Sci.*, 2011, 2011, article no. 537814.
- [5] M. Jeguirim, P. Dutournié, A. A. Zorpas, L. Limousy, "Olive mill wastewater: From a pollutant to green fuels, agricultural water source and biofertilizer - 1. The drying kinetics", *Energies*, 2019, **10**, 1423.
- [6] D. Mantzavinos, N. Kalogerakis, "Treatment of olive mill effuents: Part I. Organic matter degradation by chemical and biological processes: an overview", *J. Environ. Int.*, 2004, **31**, 289-295.
- [7] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras, D. Mantzavinos, "Electrochemical oxidation of olive oil mill wastewaters", *Water Res.*, 2005, **39**, 4177-4187.
- [8] C. Galanakis, Innovation Strategies in the Food Industry: Tools for Implementation, Academic Press, Elsevier, 2016, ISBN: 978-0-12-805314-0, 29-56 pages.
- [9] M. K. Doula, J. L. Moreno-Ortego, F. Tinivella, V. Inglezakis, A. Sarris, K. Komnitsas, "Olive mill waste-recent advances

for the sustainable development of olive oil industry", in *Olive Mill Waste-Recent Advances for Sustainable Management* (G. Ch., ed.), Olive Mill Waste, Recent Advances for Sustainable Management, Elsevier, Academic Press, 2017, ISBN: 9780128092248, 29-56.

- [10] A. G. Vlyssides, A. A. Zorpas, P. K. Karlis, G. A. Zorpas, "Description of a pilot plant for the co-composting of the solid residue and wastewaters from the olive oil industry", *Hung. J. Ind. Chem.*, 2000, 2, 59-64.
- [11] V. Kavvadias, K. Komnitsas, M. K. Doula, "Long term effects of Olive Mill Wastes disposal on soil fertility and productivity", in *Hazardous Materials: Types, Risks and Control* (K. B. Satinder, ed.), NOVA Science Publishers, Inc., 2011, ISBN: 978-1-61324-425-8, Chapter 16.
- [12] S. Ayoub, K. Al-Absi, S. Al-Shdiefat, D. Al-Majali, D. Hijazean, "Effect of olive mill wastewater landspreading on soil properties, olive tree performance and oil quality", *Sci. Hort.*, 2014, **175**, 160-166.
- [13] M. K. Doula, A. A. Zorpas, V. Inglezakis, J. Navvaro Pedreno, D. J. Bilalis, "Optimization of heavy polluted soil from olive mill waste through the implementation of zeoilites", *J. Environ. Eng. Manage.*, 2019, **18**, 1297-1309.
- [14] N. Asses, A. Farhat, S. Cherif, M. Hamdi, H. Bouallagui, "Comparative study of sewage sludgeco-composting with olive mill wastes or greenresidues: Process monitoring and agriculture valueof the resulting composts", *Process. Saf. Environ.*, 2018, 114, 23-35.
- [15] M. K. Doula, V. Kavvadias, K. Komnitsas, F. Tinivella, M. O. J.L., S. A., PROSODOL 2012: Strategies to improve and protect soil quality from the disposal of Olive Oil Mill Wastes in the Mediterranean region: Results and Achievements of a 4-year demonstration project-What to consider; What to do, European Commission Environnement LIFE Programme, 2012, LIFE07 ENV/GR/000280, https://ec.europa.eu/environment/ life/project/Projects/index.cfm?fuseaction=home.showFile& rep=file&fil=PRODOSOL_Results_Achievements.pdf.
- [16] V. Kavvadias, M. Doula, K. Komnitsas, N. Liakopoulou, "Disposal of olive oil mill wastes in evaporation ponds: Effects on soil properties", *J. Hazard. Mater*, 2010, **182**, 144-155.
- [17] A. C. Barbera, C. Maucieri, V. Cavallaro, A. Ioppolo, G. Spagna, "Effects of spreading olive mill wastewater on soil properties and crops, a review", *Agric. Water Manag.*, 2013, **119**, 43-53.
- [18] K. Chartzoulakis, G. Psarras, M. Moutsopoulou, E. Stefanoudaki, "Application of olive mill wastewater to a Cretan olive orchard: effects on soil properties, plant performance and the environment", *Agric. Ecosyst. Environ.*, 2010, **138**, 293-298.
- [19] G. Ferarra, M. Fracchiolla, Z. Al Chami, S. Camposeo, C. Lasorella, A. Pacifico, A. Aly, P. Montemurro, "Effects of mulching materials on soil performance of cv. nero di troia grapevines in the Puglia region, southeastern Italy", *Am. J. Enol. Vitic.*, 2012, **63**, 269-276.
- [20] B. Lozano-García, L. Parras-Alcántara, M. del Toro Carrillo de Albornoz, "Effects of oil mill wastes on surface soil properties, runoff and soil losses in traditional olive groves in southern Spain", *CATENA*, 2011, 85, 187-193.
- [21] A. López-Piñeiro, S. Murillo, C. Barreto, A. Muñoz, J. M. Rato Angel, A. Arturo García, "Changes in organic matter and residual effect of amendment withtwo-phase olive-mill waste

on degraded agricultural soils", *Sci. Total Environ.*, 2007, **378**, 84-89.

- [22] M. K. Doula, V. Kavvadias, K. Elaiopoulos, "Proposed soil indicators for Olive Mill Waste (OMW) disposal areas", *Water Air Soil Pollut.*, 2013, **224**, 1621-1632.
- [23] C. Di Bene, E. Pellegrino, M. Debolini, N. Silvestri, E. Bonari, "Short- and long-term effects of olive mill wastewater land spreading on soil chemical and biological properties", *Soil Biol. Biochem.*, 2013, 56, 21-30.
- [24] M. K. Doula, A. Sarris, A. Hliaoutakis, A. Kydonakis, N. S. Papadopoulos, L. Argyriou, "Building a Strategy for soil protection at local and regional scale-the case of agricultural wastes landsprading", *Environ. Monit. Assess*, 2016, **188**, 1-14.
- [25] M. K. Doula, K. Elaiopoulos, P. Kouloumbis, A. A. Zorpas, "In situ application of clinoptilolite to improve compost quality produced from pistachio bio-wastes", *Fressen Environ. Bull.*, 2018, 27, 1312-1318.
- [26] J. V. Inglezakis, M. A. Stylianou, M. Loizidou, A. A. Zorpas, "Experimental studies and modelling of clinoptilolite and vermiculite fixed beds for Mn²⁺, Zn²⁺ and Cr³⁺ removal", *Desalin. Water Treat.*, 2016, 5, 11610-11622.
- [27] A. A. Zorpas, "Recycle and reuse of natural zeolites from composting process: A 7 years project", *Desalin. Water Treat.*, 2014, **52**, 6847-6857.
- [28] A. A. Zorpas, "Metals selectivity from natural zeolite in sewage sludge compost", Dyn. Soil, Dyn. Plant, 2011, 5, no. 2, 104-112, published in the special issue Compost III. A Function of Temperature and Contact Time.
- [29] A. A. Zorpas, V. Inglezakis, M. Stylianou, V. Irene, "Sustainable treatment method of a high concentrated NH3 wastewater by using natural zeolite in closed-loop fixed bed systems", *Open Environ. J.*, 2009, **3**, 70-76.
- [30] A. A. Zorpas, V. Inglezakis, M. Loizidou, H. Grigoropoulou, "Particle size effects on the uptake of heavy metals from sewage sludge compost using natural zeolite clinoptilolite", *J. Colloid. Interface Sci.*, 2002, **205**, 1-4.
- [31] A. A. Zorpas, T. Constantinides, A. G. Vlyssides, I. Haralambous, M. Loizidou, "Heavy metal uptake by natural zeolite and metal partitioning in sewage sludge compost", *Bioresource Technol.*, 2000, **72**, 113-119.
- [32] A. A. Zorpas A. A., "Contribution of zeolites in sewage sludge composting", in *Handbook on Natural Zeolite* (V. J. Inglezakis, A. A. Zorpas, eds.), Bentham Science Publishers Ltd. P.O. Box 294, 1400 AG Bussum, The Netherlands, 2012, 182-199.
- [33] M. K. Doula, V. A. Kavvadias, K. Elaiopoulos, "Zeolites in Soil Remediation processes", in *Handbook of Natural Zeolites* (A. Zorpas, V. Inglezakis, eds.), Natural Zeolites, Bentham Books, 2012, 519-568.
- [34] P. J. Leggo, B. Ledéser, G. Christie, "The role of clinoptilolite in organo-zeolitic soil systems used for phytoremediation", *Sci. Total Environ.*, 2006, 363, 1-10.
- [35] V. Inglezakis, A. A. Zorpas, M. D. Loizidou, H. P. Grigoropoulou, "Simultaneous removal of metals Cu^{2+} , Fe^{3+} , and Cr^{3+} with anions $SO_4{}^{2-}$ and $HPO_4{}^{2-}$ using clinoptilolite", *Microprocess. Mesop. Mater.*, 2003, **61**, 167-171.
- [36] D. W. Ming, E. R. Allen, "Use of natural zeolites in agronomy, horticulture, and environmental soil remediation", in *Natural Zeolites: Occurrence, Properties, Applications* (D. Bish, D. W.

Ming, eds.), vol. 45, The Mineral Soc America, Washington, DC, 2001, 619-654.

- [37] M. K. Doula, K. Elaiopoulos, V. A. Kavvadias, V. Mavraganis, "Use of Clinoptilolite to improve and protect soil quality from the disposal of Olive Oil Mills Wastes", *J. Hazard. Mater.*, 2012, 207–208, 103-110.
- [38] M. K. Doula, "Synthesis of a clinoptilolite-Fe system with high Cu sorption capacity", *Chemosphere*, 2007, **67**, 731-740.
- [39] L. C. Clesceri, A. E. Greenberg, D. Eaton, *Standard Methods for the Examination of Water and Wastewater*, 20th ed., APHA, AWWA, WEF, Washington, DC, 1998.
- [40] A. G. Vlyssides, M. Loizidou, A. A. Zorpas, "Characteristics of solid residues from olive oil processing as a bulking material for co-composting with industrial wastewater", *J. Environ. Sci. Health A*, 1999, **34**, 737-748.
- [41] A. G. Vlyssides, M. Loizidou, K. Gimouhopoulos, A. Zorpas, "Olive oil processing wastes production and their characteristics in relation to olive oil extraction methods", *Fresen Environ. Bull.*, 1998, 7, 308-313.
- [42] J. D. Box, "Investigation of the Folin–Ciocalteu phenol reagent for the determination of polyphenolic substances in natural waters", *Water Res.*, 1983, 17, 511-525.
- [43] G. J. Bouyoucos, "Hydrometer method improved for making particle and size analysis of soils", Agron J., 1962, 54, 464-465.
- [44] A. L. Page, R. H. Miller, D. R. Keeney, Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties, American Society of Agronomy, Madison, Wisconsin, 1982.
- [45] I. S. O. (ISO), "ISO 14235:1998: Soil Quality-Determination of Organic Carbon by Sulfochromic Oxidation", 1998, Geneva, Switzerland.
- [46] I. S. O. (ISO), "ISO 11261:1995: Soil Quality-Determination of Total Nitrogen—Modified Kjeldahl Method", 1995, Geneva, Switzerland.
- [47] I. S. O. (ISO), "ISO 11263:1994: Soil Quality-Determination of Effective Cation Exchange Capacity and Base Saturation Level Using Barium Chloride Solution", 1994, Geneva, Switzerland.
- [48] I. S. O. (ISO), "ISO 11260:1994: Soil Quality-Determination of Effective Cation Exchange Capacity and Base Saturation Level Using Barium Chloride Solution", 1994, Geneva, Switzerland.
- [49] I. S. O. (ISO), "ISO 14870:2001: Soil Quality-Extraction of Trace Elements by Buffered DTPA Solution", 2001, Geneva, Switzerland.

- [50] C. V. Malcolm, V. A. Lindley, J. W. O'Leary, H. V. Runciman, E. G. Barrett-Lennard, "Halophyte and glycophyte salt tolerance at germination and the establishment of halophyte shrubs in saline environments", *Plant Soil.*, 2003, 253, 171-185.
- [51] A. K. Parida, A. B. Das, "Salt tolerance and salinity effects on plants: a review", *Ecotox Environ. Safe*, 2005, 60, 324-349.
- [52] S. Yadav, M. Irfan, A. Ahmad, S. Hayat, "Causes of salinity and plant manifestations to salt stress: A review", *J. Environ. Biol.*, 2011, **32**, 667-685.
- [53] C. F. Cereti, F. Rossini, F. Federici, D. Quaratino, N. Vassilev, M. Fenice, "Reuse of microbially treated olive mill wastewater as fertiliser for wheat (Triticum durum Desf.)", *Bioresource. Technol.*, 2004, **91**, 135-140.
- [54] D. Pezzolla, G. Marconi, B. Turchetti, C. Zadra, A. Agnelli, F. Veronesi, A. Onofri, G. M. N. Benucci, P. Buzzini, E. Albertini, G. Gigliotti, "Influence of exogenous organic matter on prokaryotic and eukaryotic microbiota in an agricultural soil. A multidisciplinary approach", *Soil Biol. Biochem.*, 2015, 82, 9-20.
- [55] A. L. Feria, "The generated situation by the OMW", in Andalusia. Actas/Proceedings-Workshop Improlive, Annex A1, Universidad complutense de Madrid, 2000, FAIR CT96 1420, 55-63.
- [56] J. Sierra, E. Marti, M. A. Garau, R. Cruanas, "Effects of the agronomic use of olive oil mill wastewater: Field experiment", *Sci. Total Environ.*, 2007, **378**, 90-94.
- [57] S. Hanifi, I. El Hadrami, "Olive mill wastewaters fractioned soil-application for safe agronomic reuse in date palm (Phoenix dactylifera L.) fertilization", *J. Agron*, 2008, 7, 63-69.
- [58] J. Sierra, E. Marti, G. Montserrat, R. Cruanas, M. Garnu, "Characterisation and evolution of a soil affected by olive oil mill wastewater disposal", *Sci. Total Environ.*, 2001, 279, 207-214.
- [59] I. Saadi, Y. Laor, M. Raviv, S. Medina, "Land spreading of olive mill wastewater: effects on soil microbial activity and potential phytotoxicity", *Chemosphere*, 2007, 66, 75-83.
- [60] N. Nikolaidis, N. Kalogerakis, E. Psyllakis, O. Tzorakis, D. Moraitis, F. Stamati, K. Valta, E. Peroulaki, I. Vozinakis, V. Papadoulakis, "Agricultural Product Waste Management in Evrotas River Basin EnviFriendly", 2008, Technology Report #3 May 2008, LIFE05ENV/GR/00045, p 21.
- [61] W.-Y. Shi, H.-B. Shao, H. Li, M.-A. Shao, S. Du, "Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite", *J. Hazard. Mater.*, 2009, **170**, 1-6.



Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / *Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1*

Effect of organoclay and wood fiber inclusion on the mechanical properties and thermal conductivity of cement-based mortars

Latifa Morjène^a, Fadhel Aloulou^{*, a} and Mongi Seffen^a

 $^{\it a}$ Laboratory of Energy and Materials: LabEM-LR11ES34:, University of Sousse, Tunisia

E-mails: morjene.latifa@gmail.com (L. Morjène), alouloufadhel@gmail.com (F. Aloulou), mongiseffen@yahoo.fr (M. Seffen)

Abstract. Nowadays, there is an enormous demand for constructing housing that needs to be catered for a short span of time, with minimum transportation costs and in an ecological manner. Biobased materials are considered to be a promising resource for buildings in the twenty-first century due to their sustainability and versatility. This article discusses biopositive materials and low-cost renewable "green" technologies that are used in low-rise multi-functional architecture. It explores the use of organic clay (OC) and wood fibers treated with NaOH (WFsT) as reinforcement materials in cement mortars. The compressive strength, porosity, hydration rate and thermal conductivity of different formulations of reinforced cement were recorded. It was found that the best dispersion and the stabilization of WFsT in the composite materials are achieved with the addition of 6% WFsT in the presence of an anionic surfactant sodium dodecylbenzene sulfonate (SDBS). The results revealed that the optimal composite material was a mix of water with Ordinary Portland Cement (OPC) and 1 wt% modified with Cetyltrimethylammonium bromide (CTAB) at a water-to-solid ratio of 0.65. With OC contents from 2% up to 18%, compressive strength results were higher than that of the plain cement paste and a decrease of the thermal conductivity was obtained by the addition of 2 wt% of WF from 2.26 to 0.8 W/m·°C. The presence of WFsT influenced the hydration of the cement while promoting the formation of more portlandite and more calcium silicate gel.

Keywords. Composite, Compressive strength, Thermal conductivity, Organoclay, Natural clay, Wood fibers.

1. Introduction

The choices of materials used in constructions are of high importance. Cementitious building materials reinforced with vegetable fibers are the biomaterials needed for construction and building. This composite enhances the mechanical performance among other properties.

Clay-based composite along with natural fibers are being tested as cementitious composites in the building sector [1–4].

These formulations are aimed to help developing

^{*} Corresponding author.

cost-effective ecofriendly construction materials.

However, the stake of this composite formation is the cracks caused to the cement mortar, the weak interaction between natural fibers, organoclay (OC) and the cement matrix and the decline of the building thermal properties. As a solution, it is useful to incorporate several types of nanoparticles into the cement, ceramic and polymer matrixes of the building material in order to produce nanocomposites [5,6] with good mechanical and thermal conductivity properties. Several types of nanoparticles were used in the literature; e.g., TiO₂ [7], ZnO [8] and OC [9].

In recent studies, and in order to improve the quality, sustainability and cost of cement cellulose fibers have been extracted from several sources such as jute fibers [10], cellulosic fibers [11] and natural clay [12, 13]. The incorporation of these traditional fibers in polymer-based composite materials was aimed to enhance and to improve their mechanical flexibility as well as their thermal insulation [5].

Composites have been found to be the most promising material available nowadays.

Recently, several studies have focused on the dispersion and stability of cellulose nanofibers as reinforcing materials in a cement matrix.

These studies have shown that the addition of cellulose fibers (from 1 wt% to 5 wt%) enhances the bending strength up to 100% and the absorption energy of the cement up to 150% [14].

Other studies proved that the addition of cellulose (CNC) improves the flexural strength, specifically the resistance to bending due to the increase in hydration of cement pastes with the cellulose nanocrystals [6].

More recently, studies on the effect of date palm fibers added in cement-based formulations showed that the mechanical and thermal insulation properties were increased up to 52% in thermal properties.

Biobased materials of natural and OC [15] sources were used to reinforce cement, improve the mechanical properties and strength of cementitious materials and accelerate the formation and the precipitation of hydration [16,17]. Clay, who belongs to the group of phyllosilicates, could also replace other fibers in many applications. This material is considered to have a wide range of applications [8,9]. Modified clays such as chlorite, natural clay and Illite, are used as fillers in the composite material that enhance the cement properties. Results showed that the modified OC has enhanced the adhesion of fiber/clay inside the cement materials. Thus, the mechanical and thermal properties of the cement nanocomposites were improved. Modification of mineral clay is a necessity to obtain a homogenous material.

These clays have the merits of low cost, availability and excellent characteristics [18]. These fibers are also praised for being biodegradable, light-weight and abundant resources [19].

The industrial application of OC has been recognized in the literature due to the excellent performance that engendered on the physical properties of the elaborated composites [3,11,13,20]. Several obstacles are encountered which limit the application of natural fiber in cement composites [15]. One can cite several causes. First the interfacial bond existing between the fiber and the cement matrix is relatively weak. Second, the degradation of the fibers in a high alkaline cement adversely affects the mechanical properties and durability of such reinforced composites [16].

In this work, the wood fiber (WF) and OC supplementation in the cement matrix was aimed to improve the mechanical resistance and the microstructural characteristics of the matrix by strengthening the bonding existing between the matrix and the WFsT [17] and to reduce the alkalinity of the matrix.

2. Methods

2.1. Description of used materials

Ordinary Portland cement (OPC NF P 15-301) was used in all the cement formulation. More information about the chemical composition of OPC [21] is presented in Table 1.

Wood Fibers (abbreviated as WFsT) used in this study are chemically treated by following a TAAPI method in which the individual components (e.g., cellulose, hemicellulose and lignin) are separated and quantitatively determined (Table 2), [22].

The clay platelets used in this work were natural clay from Jemmel city (Tunisia).

The CTAB is a cationic surfactant (Mw 336.39 g·mol⁻¹), a quaternary alkyl ammonium salt soluble in H_2O and used in the preparation of OC. The SDBS (Mw 348.48 g·mol⁻¹) is sodium

Oxides	Cement (wt%)
CaO	65.47
SiO ₂	19.82
Al_2O_3	4.66
Fe ₂ O ₃	3.03
CaO	65.47
MgO	0.84
K ₂ O	0.64
Na ₂ O	0.10
TiO ₂	0.16
SO ₃	2.87
Loss ignition(LOI)	3.5
Density	3.2 g/cm^3
Surface area	355 m ² /kg
Particle size	18.54 µm

 Table 1. Constituents of Ordinary Portland cement [21]

dodecylbenzene sulfonate, an anionic surfactant used in the fabrication of composites.

The chemical composition of WFs is listed in Table 2.

2.2. Chemical treatment

2.2.1. Treatment of wood fibers

A mass of 5 g of the WFs were placed in 100 mL of aqueous solution of hydroxide (NaOH: 1 M) Sigma-Aldrich (98%), at pH = 12 for 1 h at 80 °C. They were then washed with distilled water. Finally, WFs with a diameter of <40 μ m, from Hammam Sousse, Tunisia [23], were dried in the oven at 80 °C for one day. The treatment of WFs enhances the homogeneity between C–WFsT–OC, which improves the mechanical properties of the matrix.

2.2.2. Treatment of natural clay

The natural clay was washed with distilled water to eliminate impurities. Then, the clay was attacked with sulfuric acid (2 M), and 500 g of clay was dispersed in 1 L of distilled water under stirring at 80 °C until complete dispersion. The solution was kept during 24h. After this time, the clay was washed three times with distilled water and filtered until a pH value of 7. At the end, the clay was treated with CTAB

Table	2.	Chemical	composition	of	wood
fibers	[22]				

Cellulosic	Hemicellulose	Lignin	(Pectin)
residue (wt%)	(wt%)	(wt%)	(wt%)
Wo wood fiber 40–50	25–40	15–35	1–8

and washed with distilled water following the same procedure applied with sulfuric acid.

2.2.3. Preparation of organoclay (OC)

To obtain organophile clays, pure clay was modified with CTAB for 3 h. In this context, different studies have shown that this surfactant [24] intercalation can change the hydrophilic character of the natural clay surface and increase the clay interlayer basal spacing.

The treatment of clay started by introducing 10 ml of hydrochloric acid (1 M). Then, this solution is heated to 80 °C. Then, we put 10 m moles of CTAB, for 3 h of stirring in 80 °C, and 10 g of clay was added. Finally, after 3 h of cationic exchange, the clay is filtered to eliminate the inorganic cations. At the end, the clay is dried at 80 °C.

2.3. Preparation of composites

Samples contained OPC alone or OPC–OC–WF with different formulations, with a water/OC–Cement ratio equal to 0.65. OPC and OC were slowly mixed for 5 min until homogenization.

Specimens with dimensions of $3.5 \times 7 \times 1.75$ (cm) were cast in the mechanical tests. The mix proportions are illustrated in Table 3. After 24 h, all samples were unmolded and immersed in water for 28 days. Bend experiment was controlled using an "MTS Insight" to examine the compressive strength. The compressive strength results are the average of the three test values.

The compositions of mixtures made with different rates of WFsT and OC that were used in the thermal conductivity and compressive strength tests are given in Table 3.

2.4. Physical properties

In order to define the quality of composite samples, different measurements of porosity and density were conducted following the ASTM standard (C-20) [25].

Composite recipes	Cement (%)	Wood fibers	Organoclay	W/C
Cement	115	-	-	0.5
C+WFsNT	99	6	-	0.6
C+ WFsT	114	1	-	0.65
	113	2	-	0.65
	111	4	-	0.65
	99	6	-	0.65
	97	8	-	0.65
	95	10	-	0.65
C+WFsT+OC	98.5	6	0.5	0.65
	98	6	1	0.65
	97.5	6	0.5	0.65

 Table 3. Mixture formulations

C: Cement; WFsNT: Wood Fibers Non-Treated; WFsT: Wood Fibers Treated; W: Water.

With the ethanol displacement method, the porosity of composites was evaluated. Ethanol can be adsorbed into the microstructure of composites without fissuration and cracks. After 28 days of curing, samples were crushed into particles and were immersed in ethanol. After that, these particles were dried at 40 °C until obtaining a constant weight. Then, they were placed in ethanol solution for 24 h, and the mass of samples immersed in ethanol was named m_i . The particles were then dried. Finally, the measurement mass was named m_s .

Measurement of porosity (Ps) was determined using the following Eq (1) [26]:

$$P_s\% = (m_s - m_d)/(m_s - m_i)$$
(1)

 m_i = mass of the sample saturated in ethanol.

 m_s = mass of the sample saturated in air.

 m_d = mass of the specimen dried (g).

In order to determine the bulk density, different parameters such as length, thickness, mass and width were determined by using Eq (2) [26]:

$$D = m_d / V, \tag{2}$$

where *D* is the density (g/cm³), m_d is the oven dried weight (g) and *V* is the volume of the test sample (cm³).

2.5. Characterization

The WFsT modified were characterized via Fourier transform infrared spectroscopy (FTIR). Further-

more, OC in powder form was characterized via structure X-ray diffraction. The effect of OC prepared by treating clay with Cetyltrimethyl ammonium bromide (CTAB) on the physical and mechanical properties of WF-reinforced composites was also investigated.

2.5.1. X-ray diffraction (XRD)

The XRD pattern was measured with an X-ray Diffractometer in the 2 Θ range between 9° and 60°, using CuK α ($\gamma = 1.54060$ Å) radiation at 40 KV and 30 mA. With an exceptional analysis speed, with a step size of 0.02°/s a collection time of 40 s per step and an incident angle of 1°. The crystallization degree is obtained by comparing the intensity of the crystalline and the amorphous curve.

The crystalline degree of OC was calculated from an XRD profile. X-ray measurements were made on sample sheets pushed in powder after the air-drying of the OC.

2.5.2. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) using a Perkin Elmer spectrometer (spectrum two, from 2011) with a resolution of 2 cm⁻¹ in the range of 400–4000 cm⁻¹ served to analyze the change of functional groups at the WFs and the natural clay after treatments with NaOH, sulfuric acid and CTAB, respectively. All FTIR measurements were done in transmittance mode after baseline correction. The



Figure 1. Size of wood fibers.

method is very classic, the sample is ground with transparent potassium bromide (KBr) then is pressed in pellet form to perform IR spectra analyzes.

2.5.3. Contact angle measurements

Contact angle is measured to study the capacity of a liquid spread out on a surface by wet ability. In this work, this technique was used to evaluate the hydrophilicity (small angle)/hydrophobicity (energy of the surface) character, to analyze the aspect of the composite surface, and to study the effect of WFs treated with NaOH and of SDBS on the absorbability of water. Contact angle measurements were modulated by using a goniometry coupled to an image analysis program. For the measurement of the contact angle, drops of calibrated distilled water were deposited on the pellets of modified cellulosic fibers. The contact angle device used was an OCA 15 from Dataphysics, equipped with a CCD camera, with a resolution of 752×582 square pixels, operating at an acquisition rate of 4 images per second. The data collected was processed using OCA software [27].

2.6. Thermal conductivity measurements

The thermal conductivity of composite samples of dimensions $(24.5 \times 1.5 \times 24.5 \text{ cm})$ was measured after 28 days of treatment using a "Heat Transmission Study Bench—PTC 100."

3. Results and discussion

3.1. Particle size determination of wood fibers

The WFsT (Figure 1) were in a distribution of monomodal size, which were narrow (PDI) around 0.2 μ m with a diameter of <40 μ m.

The particle size diameters of WFsT and their hydrodynamic diameters were measured at 20 °C using a Malvern Nano-zetasizer ZS (Malvern, UK) with a fixed scattering angle of 173°. The dispersions were not diluted before starting the measurements [22]. Dynamic light scattering measurements gave an Zaverage size that was used for comparison of the different particles.

3.2. XRD

3.2.1. Organoclay

The XRD patterns of natural clay and natural clay modified with the CTAB are shown in Figures 2a and b. Figure 2a shows the presence of pure natural clay characteristic peaks at specific reflection $2\theta = 6.4^{\circ}$ (d_{001}) and 19.83° (d_{020}) . The natural clay was identified by XRD measurement evidencing the characteristic diffraction peaks of quartz (26.9°) and Kaolinite (22.1°). These peaks refer to the presence of natural clay. Compared to other works, the peak at 2θ = 37.55° and 38.02° corresponds to natural clay [28]. Typical XRD patterns of natural clay, after the treatment with the CTAB show diffraction peaks at 5.13°. This result was due to the linear structure of CTAB (19 carbons) and reveals the existence of a smectite, which affirms that this clay belongs to the natural clay family. The CTAB natural clay matrix has a highest value of the interfoliar space $d_{020} = 19.83$ Å corresponding to the inter planar spacing [29]. From Figure 2, the (001) reflection, as it had shifted from $2\theta = 6.4^{\circ}$ corresponding to the spacing increasing from $d_{001} = 0.83$ to 1.23 nm, confirms that the CTAB surfactant has been interlayered between the layers of the pure natural clay. This result was accomplished by comparison with other researches using TiO_2 and not CTAB [30]. Added to these results, the reflection 001 is related to the number of mineral layers and the mode of stacking [31,32].

To explain the influence of WFsT, the phase composition of cement was determined through XRD of cement with a percentage variation of WFsT [27]. The corresponding XRD patterns, at one day of treatment, are shown in Figure 3. The XRD of the three composites show the hydration products, including portlandite, ettringite and unreacted calcium silicate phases (C_3S and C_2S). Moreover, as the calciumsilicate–hydrates (C–S–H gel) were poorly crystallized, in the patterns spectra, diffraction peaks could



Figure 2. XRD pattern of (a) natural clay and (b) natural clay with CTAB.

be clearly viewed. In addition, the evolution of C-S-H gel is evaluated referring to the unreacted anhydrous cement phases. The intensity of calcium silicate main peaks were reduced with WFsT supplementation, as a greater amount of anhydrous cement phases reacted in the presence of WFsT (C3S and C2S are transformed into C-S-H). Besides, higher amounts of portlandite and ettringite were formed in WFsT 1% and WFsT 2% samples, compared to the control paste WFsT 0%. The intensity of peak changes continued to increase as a function of WFsT. Compared to the pure cement sample, it can be confirmed that the presence of WFsT promotes the early hydration of cement by producing more portlandite, ettringite and C-S-H gel. As C-S-H is one of the major hydration products and the main binding phases in Portland cement controlling cement mechanical properties, the higher content in C-S-H phase is likely the main reason accounting for the strong enhancement in the compressive strength of the cement matrix.

3.3. FTIR spectroscopy

3.3.1. Infrared spectral characteristics of wood fibers

The FTIR spectra in the range $4000-500 \text{ cm}^{-1}$ of different samples are shown in Figure 4. The main characteristic bands of WFsT before and after treatment are listed as follows:

The presence of a large band at 3386 cm⁻¹ corresponds to hydroxyl group characteristic of polysaccharides [33].



Figure 3. XRD spectra of the WFsT 0%, WFsT 1% and WFsT 2% at one curing day.

The bands at 2930 and 2898 cm⁻¹ are due successively to sym and asym CH₂ in polysaccharides and fats [34]. The FTIR spectrum exhibits the presence of two carbonyl and acetyl groups existing in the xylan component (C=O stretching vibration) at 1732 cm⁻¹. However, this peak almost disappears when these fibers are treated with 2% NaOH.

The peak around 1635 cm^{-1} corresponds to stretching vibration of the hydroxyl group and characteristic to water molecules. Furthermore, the peak at 1436 cm^{-1} is assigned to the asymmetric CH deformation in lignin and hemicellulose structures.

Concerning the FTIR of non-treated WFsT, the band at 1512 cm⁻¹ confirms the presence of lignin and is due to the aromatic skeletal vibration (C=C). In the spectrum of WFsT treated 5% NaOH, the elimination of lignin after NaOH treatment confirmed the decrease of large band (1512 cm⁻¹). The small peaks at 1375 cm⁻¹ in the spectrum of non-treated WFsT, WFsT treated 0.5%, 2% are related to CH₂ vibration. In all the FTIR spectra, the band at 1168 cm⁻¹ is assigned to the hemicelluloses and lignin corresponding to the C–O–C asymmetric stretching.

The peak at 1042 cm⁻¹ is assigned to lignin or hemicelluloses (C–O–C linkage) [25]. The presence of CH rock vibrations band at 810 cm⁻¹ is attributed to the presence of cellulose.

Alkaline treatment is relatively conventional. Figure 4 shows the effect of NaOH on the fibers. A certain amount of lignin, wax and impurities was eliminated. Thus treatment promotes lignin extraction and partial degradation of hemicelluloses. It is noted that



90

80

Figure 4. FTIR spectra of the non-treated WFsT and of the treated WFsT with NaOH.



Figure 5. Effect of alkaline treatment on the surface of wood fibers [21].

when the WFsT are immersed in a basic NaOH solution, the ionization of the hydroxyl group OH can occur on the surface of the fibers (Figure 5).

3.3.2. Infrared spectral characteristics of organoclay

In the FTIR spectra of pure clay and of clay treated with H₂SO₄ and clay modified with CTAB (Figure 6), the band at $3624-3390 \text{ cm}^{-1}$ presented an OH stretching vibration. The treatment of clay with the CTAB led to the appearance of two peaks (2918-2849 cm⁻¹) assigned to the valence variations of the $-CH_2$ stretching vibration. The bond OH (1633 cm⁻¹) corresponds to water molecules adsorbed on the fiber surface [33] (Figure 6). The important band around 3539 cm⁻¹ during the treatment with sulfuric



Natural clay

natural clay, natural clay with CTAB and of natural clay treated with H₂SO₄.

acid is attributed to the vibrations of deformations of the H₂O molecules. The band at 3421 cm⁻¹ is attributed to the internal hydroxyls linked to aluminum. Similar results were reported in the literature [29].

In the 2000–500 cm⁻¹ range, the raw and modified clay spectra reveal several characteristic absorption bands. The band at 1018 cm⁻¹ confirms the existence of Si-O-Si bonds in crude clay. We note that the clay is known by the appearance of a peak at 3631 cm⁻¹ and shoulders at 3689 and 3401 cm⁻¹. This peak is

particularly characteristic of clay, and corresponds to stretching vibration of elongation of the OH groups of the octahedral layer band associated to the Si–O–Si stretching vibration of clay. The peaks at 1430 cm⁻¹ and 3421 cm⁻¹ are attributed to the presence of O–H stretching vibration.

3.4. Contact angle measurements

Contact angle measurements were performed to analyze the relation between the liquid drop and the surface (Figure 7). From these different curves, it is demonstrated that only the natural clay treated with the CTAB allows modifying the character of the composite (cement + fiber) from a hydrophobic character having a high contact angle (in the order of 130) to a hydrophilic character with a low contact angle (in the order of 46). Moreover, the addition of the SDBS in the elaboration of samples makes them more hydrophobic, which is explained by the electrostatic interactions [23].

The non-treated WFs added in the composites have a totally hydrophobic character but the addition of the treated WFs decreases the contact angle more precisely, which decreases the hydrophobicity and confirms that the value of contact angle decreases with the addition of WF-treated and (1 wt%) OC. On the other hand, the addition of SDBS surfactant increases the contact angle, and consequently the hydrophobicity of composites materials.

3.5. Density and porosity

3.5.1. Density

The study of the apparent density for the developed composite materials reinforced clay and fibers is presented in Table 4. The density value was measured by determining the mass and the dimensions of the prepared composites. The results of mixing natural clay and cement with variation of 1%, 2%, 4%, 6%, 8% and 10% of WFsT indicate that the addition of WFsT on C–OC creates porosity inside the composite material which makes it lighter and very practical in comparison with results in the literature [35]. The composite containing WFsT showed a lower density than pure composites. This could be due to the appearance of voids between the interfacial areas of WFsT and of the composite-based cement. For composites with 10 wt% of WFsT, the density decreased **Table 4.** The density and the porosity values ofWFsT reinforced cement

Samples	Density	Porosity
	(kg/m^{-3})	(%)
Composite	1300	3.99
Composite + 1% WFsT	1190	4.54
Composite + 2% WFsT	1110	2.03
Composite + 4% WFsT	990	1.82
Composite + 6% WFsT	840	3.05
Composite + 8% WFsT	800	4.36
Composite + 10% WFsT	730	3.82

by 43%. This result proves the filling effect of WFsT on the density of cement composites [26]. The density of composite with 10 wt% of WFsT decreased. Such behavior can confirm that WFT reduces density and offers a composite material with a consolidated microstructure.

3.5.2. Porosity

The results of porosity and absorbability values of cement, WFsT reinforced composite and WFsT-OC reinforced composites are shown in Figure 8. The porosity of composite is improved with WFsT inclusion. These results could be assigned to the formation of voids at the interfacial areas between WFsT and composite-based cement. For composites with 2 and 4 wt% of WFsT, the porosity decreased by 1.82% (4 wt% (WFsT)). We conclude that the addition of WFsT has a filling effect on the porosity of compositebased cement. The addition of 2 wt% and 4 wt% of WFsT are able to saturate the surface and to reduce pores. Figure 9 shows that the presence of OC in the composite has reduced the adsorbed water rate of the composite. The optimum percentage of OC was found at 1 wt%. The presence of OC decreased the porosity values of composite by 18.75% with comparison to the cement. This indicates that OC operates in the composite as a pore-filling agent to decrease the porosity values and saturate pores. However, adding less than 1 wt% of OC increased the porosity of all samples due to the agglomeration effect. This result is compared to the cement that is less dense, and contains more pores. Composites with 1 wt% of OC is more compact with few pores, as asserted by the literature [36].



Figure 7. Contact angles measurements.



Figure 8. The influence of percentage of wood fiber in the composite on the water absorbability.

3.6. Mechanical properties

3.6.1. Compressive strength

Pretreatment of wood fibers with NaOH. The study of compressive strength for WFsT treated with NaOH, and cement composite reinforced by non-treated WFsT are shown in (Figure 10). The effect of WFsT treated by NaOH on the compressive strength of cement composite was evaluated. The results of compressive strength of WFsT-reinforced cement was increased from 9.81 MPa to 18.41 MPa, with about 46.71% rise compared to cement composite reinforced by untreated WFsT. This enhancement is explained as follows: in sequence to enhance the



Figure 9. The effect of time on the water absorbability of composite samples.

links between fibers and the OPC, the composite could be modified by reducing or consuming the calcium hydroxide (CH). The low value of the compressive strength might be due to the high sugar and hemicellulose present in fast growing wood. Conversely, chemical treatment led to good mechanical properties [12].

Effect of organoclay. The effects of OC on the compressive strength of 0, 0.5, 1 and 1 wt%. WFsT–cement-composites after 28 days are given in Figure 11. It is clear that the compressive strength value was increased by the addition of OC after 28 days.

C+1%WFsT

C+ 2%WFsT

C+ 6%WFsT

C+10%WFsT

C+ 6%WFsNT

10

12.33

9.81

8

Figure 10. The effect of deformation on the compressive strength.

6

Deformation (mm)



Figure 11. The effect of deformation on compressive strength for the different composites.

After 28 days, the compressive strength of 1 wt% was 21.76 MPa, higher than that of 0.5 wt% of OC (10.11 MPa). The reasons for the enhancement in mechanical properties of composites are as follows. Firstly, the physical effects of 1 wt% of OC, including filling, can reduce the voids or the porosities in the cement matrix, in which the OC was inserted inside the composite-based cement. Thus, it improves the structure and microstructure of composites denser than the WFsT–composite-based cement. Secondly, in the cement matrix, a reaction between OC and calcium hydroxide (CH) produces calcium–silicate–hydrate (C–S–H). Nevertheless, the addition of OC (>1 wt%) led to a decrease in compressive strength. In fact, the compressive strength of 2 wt%



Figure 12. The influence of deformation on compressive strength.

OC was 11.47 MPa. This is due to the bad dispersion and agglomeration of the OC in the compositebased cement at a higher percentage of OC contents, which increases porosity and reduces the link between the fiber and the composite adhesion. In fact, the compressive strength was decreased in the cement-composite with a higher dosage of OC.

Effect of surfactant (SDBS/CTAB). The influence of SDBS on compressive strength of composite materials with non-treated WFsT is described in Figure 12. It shows that the presence of SDBS in composite-based cement increased the compressive strength from 9.81 MPa to 11.47 MPa. About 14.47% improvement can be explained by the adhesion and the collision of fibers in the matrix in the presence of the SDBS [21].

The SDBS has an essential role in the surface packaging of the fiber. It is defined as a super plasticizer that covers the surface of the fibers and renders them hydrophobic. In our case, anionic surfactants are able to agglomerate in the cement to fill the existing pores in the fibers.

Using an anionic surfactant as an adjuvant between the clay platelets treated with CTAB and the cement allows to react with calcium hydroxide Ca $(OH)_2$ by promoting the formation of additional hydration of the calcium–silica type (CSH) in the form of a gel.

Compressive strength (MPa)

25

20

15

10

5

0

0

2

4



Figure 13. Effect of the percentage of wood fibers on thermal conductivity and porosity.

3.6.2. Thermal conductivity

Thermal conductivity is a very important property of construction and building materials [37]. In this part, the relationship between WFsT contents in composite and thermal conductivity and porosity is studied.

The influence of wood fiber amount. The average thermal conductivities of composite material reinforced with WFsT are 2.26, 1.00, 1.08, 1.63 and 1.09 W/m·K. The mentioned results demonstrate that rising fibers amounts of 0%, 2%, 4%, 6% and 8% W·m⁻¹·K⁻¹, respectively, caused a decreasing thermal conductivity rate to 50% in comparison to the pure composite without WFsT. This reduction may be due to the quantity of WFsT added that is insufficient to favor the establishment of a homogeneous structure. Moreover, the thermal conductivity of a material depends on several parameters such as the nature of the constituent elements of the material, the water content, the temperature and the porosity [38].

The influence of porosity and thermal properties. We examined the relation between the thermal conductivity and the porosity as a function of the percentage of WFsT (Figure 13). In addition, we note that the supplementation of the WFsT in the cement increases the porosity of this material [17,39] (reinforcement by the natural and treated wood). Also, the thermal conductivity results showed a decrease

with the increase of percentage in the WFsT in comparison with the reference sample (Composite). In general, lower values of thermal conductivity were due to the high porosity of the WFs and the large amount of composite materials in the cement. In order to explain the decrease of different percentages of WFs, it can be concluded that 2 wt% of WFsT and 1% of OC contribute to good thermal conductivity of the composites materials compared to the reference sample. Hence, thermal conductivity of the composite increased with further incorporation of wood up to more than 6 wt%. In comparison with hybrid composites (see Figure 13), the reference showed better thermal conductivity results. These obtained results can be explained by the presence of WFsT in the composite [40]. Hence, the surface of the WFsT exhibited the presence of the pores, which may reduce the adhesion of the fibers with cement matrix. The WFsT-OC-matrix adhesion presents a necessity in the overall performance of the composite.

3.7. Interaction between the fibrous suspension modified by surfactant, the cement matrix and the clay

The interactions between the cement, WFs and clay modified by CTAB are summarized in Figures 14 and 15:

(a) An adsorption of molecules having SO_3^{2-} , COO⁻ type functions or a polar function such as OH.



Figure 14. Process describing the interaction between the composite and the surfactant.

- (b) The interaction describes an inter-granular repulsion; particularly due to the case of super plasticizers. It is an adsorption of charged polymers.
- (c) The formation of micelles at the solid-solution interface.
- (d) This mechanism explains the chemisorption of polynaphthalene sulfonate on specific reaction sites, such as these two aluminates.
- (e) This figure proposes the action of sugars or hydroxyl carboxylic acids by complexation in the interstitial solution. This complexation can then delay the precipitation of hydrates such as portlandite or C–S–H.
- (f) The mechanism (f) suggests that the CTAB surfactant plays the role of potentially inhibiting the growth of hydrates by adsorbing on specific crystallographic growth sites.
- (g) The figure (g) describes the insertion of the polymer into the structure of the hydrate.

4. Conclusion

In this paper, the enhancement and the testing of the properties of composite containing C–WFsT– OC were investigated. In particular, the effect of WFsT inclusion on the thermal, mechanical and physical properties of this type of material was evaluated.

The mechanical properties of this study showed that the optimum content of OC and WFsT in the composite is 1 wt% and 6 wt%, respectively. The thermal conductivity of cement composites could be enhanced by the addition of 2 wt% of treated WFs and 1 wt% of OC.

Due to the hydrophilic nature of WFsT, a reduction in porosity (15.78%) and density, the enhancement in compressive strength (18.11%) and the decrease of thermal conductivity are ameliorated by the addition of 1 wt% of OC. Moreover, introducing OC treated by the CTAB and WFs into cement matrix could lead



Figure 15. Dispersion of WF and state of the environment of cement grains.

to accelerate hydration and to reduce the thermal conductivity to ensure a good insulation.

Notation

C = Cement

- CTAB = Cetyltrimethylammonium bromide
- CSH = Calcium-silica-hydration
- NaOH = Sodium hydroxide
- OPC = Ordinary Portland cement NF P 15-301
- OC = Organoclay
- SDBS = Sodium dodecylbenzene sulfonate
- WFsT = Wood fibers treated
- WFsNT = Wood fiber non-Treated

Acknowledgments

Authors are grateful to the Laboratory of Energy and Materials (LABEM) for the financial support of this work and would also like to express their gratitude to the FP7 FP4BATIW Euro-Mediterranean project.

References

- M. Boumhaout, L. Boukhattem, H. Hamdi et al., Constr. Build. Mater, 2017, 135, 241-250.
- [2] A. Sadeghi-nik, J. Berenjian, A. Bahari *et al.*, Constr. Build. Mater, 2017, 155, 880-891.
- [3] R. Chihi, I. Blidi, M. Trabelsi-Ayadi, F. Ayari, C. R. Chim., 2019, 22, 188-197.
- [4] R. Guégan, C. R. Chim., 2019, 22, 132-141.
- [5] R. Demirbog, Constr. Build. Mater., 2017, 156, 208-218.
- [6] A. Hakamy, F. U. A. Shaikh, I. M. Low, *Cement Concrete Compos.*, 2014, **50**, 27-35.
- [7] A. Folli, I. Pochard, A. Nonat *et al.*, J. Am. Ceram. Soc., 2010, 93, 3360-3369.
- [8] J. Leitner, V. Barůtněk, D. Sedmidubský, O. Jankovský, App. Mater. Today, 2018, 10, 1-11.
- [9] H. Assaedi, F. U. A. Shaikh, I. M. Low, J. Asian Ceram. Soc., 2017, 5, 62-70.
- [10] J. Wei, S. Ma, D. G. Thomas, Corros. Sci., 2016, 106, 1-15.
- [11] J. Claramunt, R. Dias, T. Filho, Constr. Build. Mater., 2015, 79, 115-128.
- [12] J. Calabria-holley, S. Papatzani, B. Naden *et al.*, *Appl. Clay Sci.*, 2017, **143**, 67-75.
- [13] Y. Sun, P. Gao, F. Geng et al., Mater. Lett., 2017, 209, 349-352.
- [14] A. Rahman, Y. C. Ching, K. Y. Ching et al., BioResources, 2015, 10, 7405-7418.
- [15] N. Hamdi, I. Ben Messaoud, E. Srasra, C. R. Chim., 2019, 22, 220-226.

- [16] B. Feneuil, O. Pitois, N. Roussel, *Cement Concrete Res.*, 2017, 100, 32-39.
- [17] J. Calabria-Holley, S. Papatzani, B. Naden *et al.*, *Appl. Clay Sci.*, 2017, **143**, 67-75.
- [18] R. Cioffi, L. Maffucci, L. Santoro, F. P. Glasser, *Waste Manage.*, 2001, **21**, 651-660.
- [19] S. H. Ghaffar, Straw Fibre-Based Construction Materials, Elsevier Ltd, 2016.
- [20] Z. Grigale-Sorocina, I. Birks, C. R. Chim., 2019, 22, 169-174.
- [21] F Aloulou, S. Alila, H. Sammouda, J. Renew. Mater., 2019, 7, 763-774.
- [22] TAPPI, TAPPI Standards: Regulations and Style Guidelines, TAPPI Publications, 2018.
- [23] A. Fadhel, A. Sabrine, Int. J. Ind. Chem., 2018, 9, 265-276.
- [24] A. Mishra, J. Hanley, D. B. Tripathy, J. Clark, T. Farmer, "Synthesis, chemistry, physicochemical properties and industrial applications of amino acid surfactants: A review", This is a repository copy of White Rose Research Online URL for this paper at http://eprints.whiterose.ac.uk/133786. Accepted version available in *Comptes Rendus Chimie* journal, 2018.
- [25] G. B. Kankiliç, A. Ü. Metin, I. Tüzün, Ecol. Eng., 2016, 86, 85-94.
- [26] A. Hakamy, F. U. A. Shaikh, I. Low, Cement Concrete Compos., 2014, 50, 27-35.
- [27] F. Aloulou, S. Alila, J. Renew. Mater., 2019, 7, 557-566.

- [28] H. Bel Hadjltaief, S. Ben Ameur, P. Da Costa *et al.*, *Appl. Clay Sci.*, 2018, **152**, 148-157.
- [29] T. C. D. C. Costa, J. D. D. Melo, C. A. Paskocimas, *Ceram. Int.*, 2013, **39**, 5063-5067.
- [30] I. Fatimah, J. Mater. Environ. Sci., 2012, 3, 983-992.
- [31] C. W. Foley, J. Seitzman, T. Lieuwen, "Blowoff scaling of bluff body stabilized flames", in *Fall Technical Meeting of the Eastern States Section of the Combustion Institute 2011*, vol. 45, Combustion Institute, 2011, 606-614.
- [32] G. Goncalves, P. A. A. P. Marques, R. J. B. Pinto *et al.*, *Compos. Sci. Technol.*, 2009, 69, 1051-1056.
- [33] S. S. Bhattacharya, M. Aadhar, Res. J. Eng. Sci., 2014, 3, 10-16.
- [34] A. Fadhel, A. Sabrine, Int. J. Ind. Chem., 2018, 9, 265-276.
- [35] D. v. Westen, G. Skagerberg, J. Olsrud, P. Fransson, E.-M. Larsson, *Acta Radiol.*, 2005, **46**, no. 6, 599-609.
- [36] H. El-Sokkary, K. Galal, J. Compos. Constr., 2019, 23, article no. 04019032.
- [37] M. Ge, C. Cao, J. Huang et al., J. Mater. Chem. A, 2016, 18, 6772-6801.
- [38] J. Huo, Z. Peng, Q. Feng et al., Solar Energy, 2018, 169, 84-93.
- [39] S. Pilehvar, V. Duy, A. M. Szczotok *et al.*, *Cement Concrete Res.*, 2017, **100**, 341-349.
- [40] F. Balo, L. S. Sua, Int. J. Appl. Ceramic Technol., 2018, 15, 792-814.

Comptes Rendus

Chimie

Objet de la revue

Les *Comptes Rendus Chimie* sont une revue électronique évaluée par les pairs de niveau international, qui couvre l'ensemble des domaines de la discipline. Ils publient principalement des numéros thématiques, mais également des articles originaux de recherche, des annonces préliminaires, des articles de revue, des mises en perspective historiques, des textes à visée pédagogique ou encore des actes de colloque, sans limite de longueur, en anglais ou en français. Les *Comptes Rendus Chimie* sont diffusés selon une politique vertueuse de libre accès diamant, gratuit pour les auteurs (pas de frais de publications) comme pour les lecteurs (libre accès immédiat et pérenne).

Directeur de la publication : Pascale Cossart

Rédacteurs en chef: Pierre Braunstein

Comité scientifique : Rick D. Adams, Didier Astruc, Guy Bertrand, Azzedine Bousseksou, Bruno Chaudret, Avelino Corma, Janine Cossy, Patrick Couvreur, Stefanie Dehnen, Paul J. Dyson, Odile Eisenstein, Marc Fontecave, Pierre Grandclaudon, Robert Guillaumont, Paul Knochel, Daniel Mansuy, Bernard Meunier, Armando J. L. Pombeiro, Michel Pouchard, Didier Roux, João Rocha, Clément Sanchez, Philippe Sautet, Jean-Pierre Sauvage Patrice Simon, Pierre Sinaÿ

Secrétaire scientifique : Julien Desmarets

À propos de la revue

Toutes les informations concernant la revue, y compris le texte des articles publiés qui est en accès libre intégral, figurent sur le site https://comptes-rendus.academie-sciences.fr/chimie/.

Informations à l'attention des auteurs

Pour toute question relative à la soumission des articles, les auteurs peuvent consulter le site https://comptes-rendus.academie-sciences.fr/chimie/.

Contact

Académie des sciences 23, quai de Conti, 75006 Paris, France Tél. : (+33) (0)1 44 41 43 72 CR-Chimie@academie-sciences.fr



Les articles de cette revue sont mis à disposition sous la licence Creative Commons Attribution 4.0 International (CC-BY 4.0) https://creativecommons.org/licenses/by/4.0/deed.fr

COMPTES RENDUS de l'Académie des sciences

Chimie

Volume 23, nº 11-12, novembre-décembre 2020

Special issue / Numéro thématique

Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 / Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 1

Guest editors / Rédacteurs en chef invités

Mejdi Jeguirim (Institut de Science des Matériaux de Mulhouse, France), Salah Jellali (Sultan Qaboos University, Oman) Besma Khiari (Water Research and Technologies Centre, Tunisia)

Carole Tanios, Yara Saadeh, Madona Labaki, Maya

Mejdi Jeguirim, Salah Jellali, Besma Khiari

Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 1 H. Hammani, M. El Achaby, K. El Harfi, M. A. El Mhammedi, A. Aboulkas	583-587	Boutros, Cédric Gennequin, Haingomalala Lucette Tidahy, Antoine Aboukaïs, Edmond Abi-Aad Methane catalytic reforming by carbon dioxide on Mg–Al oxides prepared by hydrotalcite route with dif- ferent surfactants (CTAB, glucose, P123) or with inter- calation of SBA-15 and impregnated by nickel	653-669
Optimization and characterization of bio-oil and biochar production from date stone pyrolysis using Box–Behnken experimental design	589-606	Manel Wakkel, Besma Khiari, Fethi Zagrouba Comprehensive study of simultaneous adsorption of basic red 2 and basic violet 3 by an agro-industrial waste: dynamics, kinetics and modeling	671-687
Mouzaina Boutaieb, Monia Guiza, Silvia Román, Beatriz Ledesma Cano, Sergio Nogales, Abdelmot- taleb Ouederni Hydrothermal carbonization as a preliminary step to pine cone pyrolysis for bioenergy production	607-621	Khaled Mahmoudi, Noureddine Hamdi, Mahassen Ben Ali, Salah Jellali, Ezzeddine Srasra Enhanced adsorptive removal of cationic and anionic dyes from aqueous solutions by olive stone activated carbon Maria K. Doula, Antonis Papadopoulos, Chronis	689-704
Nourelhouda Boukaous, Lokmane Abdelouahed, Mustapha Chikhi, Chetna Mohabeer, Abdeslam Hassen Meniai, Bechara Taouk Investigations on Mediterranean biomass pyrolysis ability by thermogravimetric analyses: thermal be- haviour and sensitivity of kinetic parameters	623-634	Evaluation of the influence of olive mill waste on soils: the case study of disposal areas in Crete, Greece	705-720
Ahmed Amine Azzaz, Mejdi Jeguirim, Evan A. N. Marks, Carlos Rad, Salah Jellali, Mary-Lorène God- dard, Camelia Matei Ghimbeu Physico-chemical properties of hydrochars produced from raw olive pomace using olive mill wastewater as moisture source	635-652	Interpret culturation on a substrate consisting of soil,natural zeolite, and olive mill waste sludge: changesin soil propertiesLatifa Morjène, Fadhel Aloulou, Mongi SeffenEffect of organoclay and wood fiber inclusion on themechanical properties and thermal conductivity ofcement-based mortars	721-732

1878-1543 (electronic)





