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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

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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 biofertilizer 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 sus-

tained 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 con-

cerned 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 °C·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 pyrolysis 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 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 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 con-

ducted 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 adsorptive removal of cationic and anionic dyes from aqueous solutions by olive stone activated carbon*” [7]. In this work, four activated carbons were synthesized from natural olive stones wastes (NOS) using $ZnCl_2$ as activating agent. These activated car-

bons (OSAC), were synthesized for a constant mass ratio of $ZnCl_2$: 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 N_2 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 $mg\cdot g^{-1}$ 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 an-

ionic 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 water-to-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.

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