



INSTITUT DE FRANCE
Académie des sciences

Comptes Rendus

Chimie

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Volume 25, Special Issue S2 (2022), p. 1-5

Published online: 4 August 2022

<https://doi.org/10.5802/crchim.190>

Part of Special Issue: Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 3

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Les Comptes Rendus. Chimie sont membres du
Centre Mersenne pour l'édition scientifique ouverte
www.centre-mersenne.org
e-ISSN : 1878-1543



Foreword: Recent Advances in Sustainable Biomass Valorization

Avant-propos : Récentes Avancées dans la Valorisation Durable de la Biomasse

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Published online: 4 August 2022

Huge amounts of biomasses are annually generated in the world by several sectors including agriculture, industry, tourism etc. The sustainable management of these organic wastes has been pointed out as an urgent challenge to be urgently taken into consideration in order to avoid any negative effects onto human health and environment and to dispose of a supplementary resource that can be valorized in several domains. Indeed, some biomasses have high volatile matter contents allowing them to be used as a source for renewable energy extraction. Other biomasses contain high contents of valuable nutrients that can be used as low cost and eco-friendly biofertilizers in agriculture instead of synthetic fertilizers. Besides, some treated biomasses

could exhibit promising properties permitting them to act as efficient adsorbents for pollutants removal from aqueous and gaseous effluents. Finally, some specific biomasses have interesting physical, chemical and biological properties allowing them to be precious source of various biomaterials.

In this context, the current special issue entitled: **“Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 3”** aims to collect the most recent scientific works related to biomasses sustainable management and valorization in the domain of energy, agriculture, environment and biotechnology. This special issue aims to contribute to the international efforts deployed in order to make progress in the achievement of several related worldwide initiatives such as: “2030 United Nations Sustainable Development Goals” (UN-SDGs), the “4 per 1000” aiming to boost

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the annual carbon storage in agricultural soils by 0.4%, the “Greenhouse Gas Emissions reduction” as recommended by the Intergovernmental Panel on Climate Change (IPCC).

This special issue contains 10 peer-reviewed papers dealing with the valorization of several types of biomasses in various domains including energy, environment, and biotechnology.

The first paper is entitled: “*Pharmaceutical pollutants adsorption onto activated carbon: isotherm, kinetic investigations and DFT modeling approaches*” [1]. In this work, the removal of pharmaceutical pollutants, i.e., oxytetracycline (OTC) was studied through adsorption onto activated carbon (ACT) produced from households or agricultural wastes under various experimental conditions. The physicochemical properties of the produced carbon were investigated using multiple techniques. The characterization analysis highlighted an essential concentration of surface functional groups and a very developed porous structure. The adsorption process onto activated carbon occurs with a high yield at a large range of pH values varying between 4 and 8 at an optimum contact time of 2 h. It was established that the pseudo-second-order kinetic model fitted well OTC adsorption onto ACT. Moreover, the adsorption isotherm data showed that the pollutant removal process followed the Langmuir model with high regression coefficients (R^2) values and important adsorption efficiency of 80% for $100 \text{ mg}\cdot\text{L}^{-1}$ of OTC. Consequently, the use of ACT could be considered an efficient, sustainable, and low-cost alternative for pharmaceuticals-loaded wastewater treatment.

The second paper is entitled: “*Competitive biosorption of basic dyes onto petiole palm tree wastes in single and binary systems*” [2]. This work aimed to study petiole palm tree wastes (PTW) efficiency in removing two basic dyes: Rhodamine B (RB) and Victoria blue B (VBB) from aqueous solutions in single and binary systems under various experimental conditions including the effect of contact time, pH, initial concentration, and temperature. The PTW characterization shows that the PTW is a lingo-cellulosic material. The experimental results indicate that the removal of both dyes was relatively fast, spontaneous, exothermic and occurred on monolayers. Moreover, the adsorption competition between these two dyes on the adsorbent particles surface was im-

portant since the Langmuir’s adsorption capacities were evaluated to 260.1; 440.1; 168.0; and 417.4 mg/g for RB and VBB in single and binary systems, respectively. These adsorption capacities, even in binary systems, are interesting compared to other raw materials and prove that this abundant agricultural waste can be considered as a promising material for an efficient dyes removal from aqueous effluents.

The third paper is entitled: “*Industrial dye removal from tannery wastewater by using biochar produced from tannery fleshing waste: a road to circular economy*” [3]. In this study, the capacity of biochars, derived from the pyrolysis of tannery fleshing waste (TFW) at 400 °C; 500 °C and 600 °C, in removal of red dye Sella Fast Red (SFR) from aqueous solutions and tannery wastewater was investigated under various experimental conditions in batch mode. Results show that for all applied biochars, the removed kinetics data were well fitted by the pseudo-second-order model, and the equilibrium state was obtained after 240 min of contact time. For an aqueous pH of 6 and a red dye concentration of $75 \text{ mg}\cdot\text{L}^{-1}$, the removed amounts increased from $26 \text{ mg}\cdot\text{g}^{-1}$ to $39.86 \text{ mg}\cdot\text{g}^{-1}$ when the used pyrolysis temperature was increased from 400 °C to 600 °C. Moreover, SFR adsorption data at equilibrium were well fitted by Langmuir model suggesting a probable monolayer adsorption process with a maximal removal capacity of $62.7 \text{ mg}\cdot\text{g}^{-1}$ for BTFW-600 °C. The thermodynamic study demonstrated that SFR adsorption was endothermic for the three tested biochars. Desorption experiments with distilled water proved that SFR was significantly desorbed from the tested biochars, which offers possible reusability. On the other hand, BTFW-600 °C has demonstrated an important ability in removing SFR from real wastewater since only one dosage of $15 \text{ g}\cdot\text{L}^{-1}$ was enough to ensure more than 97% of dye removal. According to pHZC and FTIR analysis, the possible mechanism toward SFR dye removal was attributed to electrostatic interactions that occurred between biochar and functional groups of SFR. This work could provide guidance for the value-added utilization of tannery solid waste and a practical way to remove dyes from tannery wastewater.

The fourth paper is entitled: “*Cationic dye removal using Pergularia Tomentosa L. fruit: kinetics and isotherm characteristics using classical and advanced models*” [4]. In this study, different techniques

were used to characterize the powdered *pergularia tomentosa* fruit. After that, the biomaterial was exploited to investigate the adsorption of methylene blue in batch mode. The effects of initial pH, contact time, dye concentration, biosorbent dose, and temperature on the biosorption capacity have been performed. The fit of the adsorption isotherms was performed by means of several classical models and advanced models derived from statistical physics. The two-energy monolayer model proves to be the more suitable. It appears that two functional groups of the biosorbent are involved in the dye biosorption. The adsorption energy ranges from 14 to 18 kJ·mol⁻¹ which indicates a physisorption mechanism. The maximum adsorption capacity is 152 mg·g⁻¹. *Pergularia tomentosa* fruit proves to be attractive for the efficient removal of cationic dyes from polluted water.

The fifth paper is entitled: “*Investigations on potential Tunisian biomasses energetic valorization: thermogravimetric characterization and kinetic degradation analysis*” [5]. During this work, six Tunisian local biomasses, namely ziziphus wood (ZW), almond shells (AS), olive stones (OS), vine stems (VS) and date palm leaflets (DPL) and trunks (DPT) were slowly pyrolyzed under inert atmosphere at a heating rate of 5 °C/min through thermogravimetric (TG) analyses. The thermal degradation of samples involves the interaction in a porous media of heat, mass and momentum transfer with chemical reactions. Heat is transported by conduction, convection and radiation and, mass transfer is driven by pressure and concentration gradients. Thermal degradation curves have been studied with minute details for each degradation step. The Coats–Redfern model was used to extract the kinetic parameters from the TG data, then the kinetic parameters such as the activation energy, the pre-exponential factor and the order of the reaction were calculated. Results showed that the total mass losses amounts and kinetics are dependent on the type of the used biomass. Moreover, the devolatilization could be described by the first order model, while the char formation stage was better described by the second and third order reactions model. The physicochemical characteristics of these samples were also determined. The volatile matter (VM) content varies considerably, with values ranging from 67.19% for AS to 77.4% for ZW. The maximum values were obtained for ZW

and VS with values of 77.4% and 71.9%, respectively. The lowest value (67.19%) was determined for AS. In addition, the ash contents vary between 0.8% for OS and 5.66% for DPT. The ashes vary significantly from one sample to another, with the values being even lower than 1% for OS, whereas the higher values in the DPT is 5.66%. Further, activation energies corresponding to main devolatilization regions were 59.5, 47.0, 55.8, 41.1, 89.1, 45.2 kJ/mol for ZW, AS, OS, VS, DPL, and DPT respectively. Among all the tested biomasses, the ZW and VS appear to have an important potential to be used for energy production.

The sixth paper is entitled: “*D-optimal design optimization of unsaturated palm fatty acid distillate and trimethylolpropane esterification for biolubricant production*” [6]. In this work, polyol ester of green biolubricant base oil was synthesized through the esterification of unsaturated palm fatty acid distillate (USFA-PFAD) with polyhydric alcohol, trimethylolpropane (TMP) in the occurrence of sulphuric acid catalyst. The optimization process was conducted by using D-optimal design of the response surface methodology (RSM). The results showed that the highest yield percentage of resultant polyol ester, USFA-TMP ester was obtained at 96.0 ± 0.5% with 99.9 ± 0.9% of tri-ester selectivity. These were obtained at the esterification optimal condition at reaction temperature of 150 °C for 6 h with 5% H₂SO₄. The polyol ester chemical structure was characterized by using spectroscopy analysis techniques of infrared (FTIR), proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR). The resultant USFA-TMP ester recorded viscosity index of 163, pour points at -45 °C, flash points at 298 °C, and thermal oxidative stability temperatures at 215 °C. It was found that the ester product as a Newtonian fluid with viscosity grade lubricant ISO VG 46. In overall, the resultant polyol ester has shown good lubrication properties that make it conceivable to be used for many industrial green biolubricant applications.

The seventh paper is entitled: “*CFD multiphase combustion modelling of oleic by-products pellets in a counter-current fixed bed combustor*” [7]. In this research work, a transient two-dimensional multiphase model was built to study the combustion of pellets of oleic by-products (Olive Pits (OPi)) in a cylindrical counter-current 40 kW fixed bed combus-

tor. The fixed bed is modelled as a porous medium, which is randomly packed with spherical particles of equal size. A $\kappa - \varepsilon$ model for low Reynolds number flows was used for turbulence Modelling. Primary and secondary air injections were supplied at the bed (solid phase combustion) and at the freeboard zone (gas phase combustion), respectively. The mass loss history, the temperature distribution at different heights inside the reactor and the gas emissions of CO, CO₂, O₂, H₂, CH₄ and C_{org} were computed. Key parameters related to the reaction front velocity, the mass conversion rate and the progress of ignition were also computed. We show that computational results are in good agreement with experimental measurements obtained using a similar reactor fed with the same pellet types. These results also motivate the implementation of the present formulation and its extension to industrial scale furnaces, having established the results for the comparison with pilot-scale experiments.

The eighth paper is entitled: “*Biohydrogen production by Thermotoga maritima from a simplified medium exclusively composed of onion and natural seawater*” [8]. In this work, biohydrogen production by the anaerobic hyperthermophilic and halophilic bacterium, *Thermotoga maritima* (TM) was conducted using a mixture of Onion Waste Juice (OWJ) and seawater (SW). The highest production of biohydrogen (H₂) with OWJ, as the exclusive source of carbon and energy, was obtained for an optimum volume of 50% (v/v), with the highest overall productivity of biohydrogen (15.6 mM/h) and a maximum yield of 2.6 (molH₂/molH_{exose}). This was mainly due to the presence of organosulfur compounds and the natural presence of ammonium contained in OWJ. The addition of inorganic nitrogen and iron sources in the mixture of SW and OWJ has improved biohydrogen production, achieving productivity yield (23.0 mM/h for 3.2 molH₂/molH_{exose}) close to the maximum obtained for TM. Above 600 mL, the high concentration of substrate (>30 g COD/L) led the metabolism to deviate towards lactate production at the expense of H₂ production. A fed-batch culture with the sequential addition of concentrated OWJ mixed with only sea salt was investigated for the prevention of substrate-associated growth inhibition by controlling the nutrient supply. The total cumulative biohydrogen produced was about 300 mM after 30 h of incubation.

The ninth paper is entitled: “*Enhanced transesterification of rapeseed oil to biodiesel catalyzed by KCl/CaO*” [9]. In this work, a series of supported solid based catalysts were prepared by impregnation of chloride salts over CaO. The catalytic activity of the prepared catalysts was tested for the transesterification reaction of biodiesel from rapeseed oil and methanol. The KCl/CaO catalyst containing 15% KCl exhibited the highest catalytic activity after calcination at 600 °C for 6 h. A reaction optimization study was carried out using KCl/CaO as catalyst leading to operation conditions for achieving a 98.3% yield of fatty acid methyl ester (FAME) at 2.5 h and 65 °C, a catalyst amount of 10%, and a mole ratio of methanol to rapeseed oil of 15:1. It was found that the highest FAME yield at 2.5 h was faster than that at 6 h for commercial CaO catalysts under the same reaction conditions. The characterization results showed that the pore size of CaO particles was greatly improved by the addition of KCl, which facilitated better access of the reactive molecules to the active sites of the catalyst.

The last paper is entitled: “*H₂-rich syngas production by sorption enhanced steam gasification of palm empty fruit bunch Catalytic*” [10]. In this work, hydrogen-rich syngas from palm empty fruit bunch has been produced in the presence of CaO and bentonite as absorbent and catalyst, respectively. The gasification process is carried out at 550–750 °C at atmospheric pressure in a fixed bed gasifier with steam to biomass ratio (S/B) of 0–2.5 and Ca/C ratio of 0–2. The results showed that CaO only acts as CO₂ absorber during the process. Increasing the ratio of Ca/C and S/B have increased the concentration of H₂ and absorption of CO₂ in the syngas. The addition of CaO did not significantly increase the production of CH₄ and CO in the syngas. The H₂ concentration reaches about 78.16 vol% at 700 °C and Ca/C ratio of 2.

Guest Editors of this special issue are grateful to all the authors for their valuable contribution and to the reviewers for their comments that contributed to the quality improvement of the above-cited accepted papers. Many thanks to the Editor-in-Chief of Comptes Rendus Chimie, Professor Pierre Braunstein for renewing his confidence and support. Special thanks to the entire production team of the journal for their constructive collaboration.

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