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Foreword to Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 2

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Foreword / Avant-propos

## Foreword to Sustainable Biomass Resources for Environmental, Agronomic, Biomaterials and Energy Applications 2

Avant-propos à Ressources de biomasse durables pour des applications environnementales, agronomiques, de biomatériaux et énergétiques 2

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The concept of sustainable development is placed at the center of the problematic issue of economic growth versus the scarcity of natural resources. Even if several signs seem to indicate that the international dynamic is running out of steam (fragmentation of institutions, failure of international collective action, non-involvement of private actors ...), this topic is still on the political agendas from the local use of resources until their more generalized exploitation. Indeed, the various societies on the globe are facing the same challenges:

- meet the needs (especially in terms of water, food and energy) of a global population of around 9 billion people in 2050, with some regional populations experiencing strong economic development;
- · control, limit and reduce greenhouse gas

- emissions in order to ensure a neutral development in terms of atmospheric carbon.
- develop substitutes for fossil hydrocarbons (and their derivatives) whose reserves, for a given cost, will be increasingly scarce;
- Sustainably manage natural resources, under the pressure of climate change and related socio-economic and geopolitical purposes;

In this context, biomass stands as an excellent candidate to promote energy independence, stimulate carbon neutral development and develop a bio / agro-industry, with a view to (re) structuring, (re) localization and (re) industrialization. As a matter of fact, in view of the rapid evolution of the sector and the need for a synthesis, which would allow the implementation of (inter)national strategies as well as of industrial units, the sustainable management

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of the biomass deserves to be supplemented by an examination of the main questions posed today to scientific and technological research both on the biomass resource side and on its transformation and use. Indeed, the exploitation of resources from biomass involves different sectors, corresponding to many conversion technologies such as heat, electricity, biofuels (by thermal or enzymatic processes), biomaterials (fibrous polymers, biocomposites, biosorbents, pulp paper, etc.), amendments, organic fertilizers, etc. In this perspective, this special issue aims to collect scientific articles, comprehensive reviews and engineering research focused on the abovementioned contents, while meeting various regional and international requirements (i.e. UN-SDG, IPCC, etc.).

This special issue contains ten peer-reviewed papers that have the opportunity to increase the attractiveness of large scale biomasses use by increasing their conversion efficiency to viable products (fuels, energy carriers, biomaterials, biofertilizers, biochars, etc.).

The first paper is entitled: "Investigations on lignite use for lead removal from aqueous solutions under static and dynamic conditions: adsorption properties and mechanism exploration" [1]. This research work proposed the use of lignite, an abundant and low-cost material, to remove lead (Pb(II)) from aqueous solutions in static (batch) and dynamic (column) modes and, by varying the experimental conditions. Results showed that rising the initial concentration, the aqueous pH, and the adsorbent initial dose increased the removal efficiency during the static assays. Adsorption kinetic and isothermal data were fitted with the pseudo-second-order and Freundlich models, respectively, suggesting that Pb (II) removal by lignite was mainly governed by chemical processes and occurs heterogeneously on multilayer surfaces. In comparison to many other natural materials, the maximum Langmuir's adsorption capacity was high as it reached 61.4 mg/g. In the laboratory column experiments, the adsorption capacity was lower (the highest recorded value was about 21%). This was attributed to the short time contact between Pb(II) and the lignite particles inside the column. It was also mentioned that the height of the bed in the column highly influences the Pb(II) adsorption efficiency by lignite. Still, the adsorption capacity of lead removal, under dynamic conditions, is considered high compared to other adsorbents, which promotes the use of lignite as a low-cost and efficient material for Pb(II) and other heavy metals removal from wastewaters.

The second paper is entitled: "Anaerobic codigestion of dairy raw by-products and Ulva sp. macroalgae: effect of organic and inorganic additives" [2]. The main objective of this work was producing biogas from dairy raw materials (DRM) and Ulva sp. macroalgae as a co-substrate. In order to optimize methane yield, some nutrient media were selected. While using a single-stage anaerobic process, the effect of the mineral additive medium (medium I), based on bicarbonate compound, and the organic additive medium (medium II), based on glucose, on the anaerobic digestibility of DRM was assessed. Four batch experiments were performed and, correspond respectively to DRM without inoculum, DRM with additive medium I, DRM with additive medium II and, DRM and *Ulva* sp. with additive medium I. During the tests, methane produced, chemical oxygen demand (COD), proteins, lipids, carbohydrates and volatile fatty acids were measured. Many interesting results were then obtained. For instance, it was found that the mineral additive medium provided a higher specific methane yield (0.208 LCH<sub>4</sub>/g<sub>VS</sub>) compared to the organic additive one and, that the co-digestion of DRM with Ulva sp. yielded 0.118  $LCH_4/g_{VS}$ . It was also revealed that the use of *Ulva* sp. as co-substrate reduced the concentration of volatile fatty acids, and enhanced the biogas quality, which contained 96% of methane and only 0.5 to 2% of hydrogen sulphide. Besides, a first-order kinetic model was applied to describe proteins, lipids and carbohydrates biodegradation. The model indicated that these last three compounds followed different kinetics, according to the composition of the medium and the presence or not of additive medium.

The third paper is entitled: "Energy analysis of a micro-cogeneration unit fed by biogas as a function of pyrolysis operating parameters" [3]. The main objective of this study was to evaluate the energy performance of a micro-cogeneration unit fed by biogas. To do so, the authors proposed a model that included an accurate characterization of the initial feedstock material and predicted the yield and the composition of the pyrolysis products in order to estimate to what extent the produced pyro-gas can be exploited for energetic purposes. In comparison to

existing numerical pyrolysis models, which provide a simplified composition of the produced pyrogas, the presented model proposed a very detailed analysis of the chemical species originating from the pyrolysis process. The decomposition of the feedstock material was set as a two-stage process: firstly, in the reactor, the biomass was decomposed into a residual solid fraction (char) and a gaseous mixture; then, the condensable gases were divided from permanent gases generating the pyro-oil. As a further added value, the decomposition model took into account both the dependence of degradation on temperature (500-900 °C) and the kinetics of reactions involved during the process. The gas fraction obtained at the end of the cycle was characterized and used to feed a micro-CHP system. The related results showed a great potential in terms of thermal recovery; more than 60% of the initially fed biogas and about 30% power output can be derived.

The fourth paper is entitled: "Bioremediation of hexavalent chromium by an indigenous bacterium Bacillus cereus S10C1: optimization study using two level full factorial experimental design" [4]. This study focused on chromium removal by indigenous chromium-resistant microorganisms isolated from polluted soils and sludge of an industrial site. For that purpose, a mathematical model was established allowing fixing experimental conditions for each desired degradation of chrome by the selected bacterial strain. Then, the effect of the crucial environmental parameters such as temperature, Cr(VI) initial concentration, pH and time as well as their interaction terms such as (T°-pH), (T°-time) and (Cr(VI) initial concentration-pH), on chromium removal using a full factorial design at two levels was investigated and optimized. The results showed, for the first objective, that from the 54 bacterial strains, S10C1 identified as Bacillus cereus 4080 LBK (NCBI:txid1396) was the most efficient strain in removing Cr(VI). As for the second goal of the study, the optimum conditions for chromium biodegradation were found to be a pH of 3, a temperature of 55 °C, a Cr(VI) initial concentration of 0.5 mM and a contact time of 20 h. Under these conditions the experimental Cr(VI) removal percentage was about 92.9%.

The fifth paper is entitled: "Optimization of a cationic dye desorption from a loaded-lignocellulosic biomass: factorial design experiments and investigation of mechanisms" [5]. In this research work, the

desorption of methylene blue (MB) from a saturated orange tree sawdust (ROS) was followed under different experimental conditions in batch mode. The main targeted objectives were: (i) to investigate the effect of the solution's pH, the sodium chloride concentration and the MB-loaded biomass content on the desorbing yield efficiencies, (ii) to determine the possible interactions between these parameters and their statistical significance by the means of a full factorial design composed of 24 experiments and finally (iii) to explore the probable mechanisms governing the recovery of MB. The maximum desorption yield was around 82.4% obtained for an aqueous pH of 3, an eluent (NaCl) concentration of 0.2 M and MB-loaded-ROS dosage in the desorbing solution of 1 g/L. A good fit was reached between the experimental data and the used statistical model. Moreover, multiple analysis techniques conducted by the authors led to the conclusion that MB desorption from ROS's particles was mainly driven by a counter chemisorption process based on cationic exchange with the sodium and hydronium ions present in the desorbing solutions.

The sixth paper is entitled: "Optimal parameters and structural composition of bio-oil and biochars from intermediate pyrolysis of red algal biomass" [6]. This work aims to assess the potential of red algal biomass for the production of bio-oil and biocoal from intermediate pyrolysis in a fixed-bed tubular reactor. In the search of excellent red algal based fuel properties, different temperatures (400-600 °C) and different heating rates (15, 30 and 50 °C/min) were applied and many characterization techniques (proximate and ultimate analysis, FTIR, 1HNMR, GC-MS analysis, SEM, BET, etc.) were used. The results were promising as, at 450 °C temperature and while applying 50 °C/min as a heating rate, an interesting bio-oil yield of 45% was obtained. Its higher heating value and density were 20.11 MJ/kg and 1289 kg/m<sup>3</sup>, respectively. Besides, the characterization of the bio-oil showed a high percentage of aliphatic functional groups and presence of phenolic, ketone- and nitrogen-containing groups, making it potentially valuable as a source of value-added chemicals. As for the yielded biochar, the characterization showed its suitability to be used as an adsorbent as well as a solid fuel.

The seventh paper is entitled: "Thermocatalytic Degradation of Lignin Monomer Coniferyl Aldehyde by Aluminum-Boron-Oxide Catalysts" [7]. In this work, two aluminum-boron oxide catalysts were produced via a sol-gel method at pH 3 and 4 during the solution mixing step of the synthesis. The two synthesized catalysts were mostly amorphous and mesoporous, aiding in permeability and percolation of coniferyl aldehyde (CA). In comparison with a commercial catalyst (Pt/alumina at 1 wt%), this last showed higher activity than the aluminum-boron oxide catalysts, but the synthetic catalysts presented a wider variety of organic products than the commercial catalyst. In particular, two high-value products, isomers of eugenol and isoeugenol, were yielded in higher percentages. The experimental reaction rate data was well fitted to the Langmuir-Hinshelwood model and, the calculated kinetic parameters were analyzed, revealing how the adsorbed CA molecules on the catalytic surface had higher mobility with the synthesized catalyst compared to the commercial catalyst.

The eighth paper is entitled: "Optimization of Formulation for Surrogate fuels for Diesel-Biodiesel mixtures" [8]. The authors of this paper proposed to reproduce a fossil diesel in mixtures at different proportions with biodiesel, which was prepared by a transesterification reaction of local cooking oil wastes, by optimizing a surrogate fuel considering the density, the viscosity and the cetane number as the target properties. More precisely, it was aimed to reproduce as close as possible these properties (of the diesel, the biodiesel and the mixtures of the two fuels) considering a large range in molar biodiesel percentages, namely 5%, 10%, 20%, 50% and 80%. To overcome the difficulty of the variety of number and nature of components of the proposed surrogates, the objective was to suggest surrogates with a minimum number of hydrocarbons and the same components that differ in composition to emulate all the studied target fuels and blends. The findings of this study showed that it was possible to optimize alternative fuel formulations that emulate the required properties. The objective of minimizing the number of components in the optimized surrogates was achieved using the same three components for all the studied target fuels: Isocetane, 1-methylnaphthalene and n-eicosane. This result would allow managing increased complexicity when developing kinetic models.

The ninth paper is entitled: "Catalytic hydrodeoxygenation of acetic acid, 4-ethylguaiacol, and furfural from bio-oil over Ni2P/HZSM-5 catalysts" [9]. This work was dedicated to easily understanding the Hydro-deoxygenation (HDO) mechanism of bio-oil by studying the HDO of various model molecules over Ni<sub>2</sub>P/HZSM-5 catalysts. Catalytic HDO of biooil's model molecules (acetic acid, 4-ethylguiacol, and furfural) using Ni<sub>2</sub>P/HZSM-5 catalyst was carried out to better identify the products and make the modeling work of HDO process more reliable. Results showed that low temperatures favored the formation of acetaldehyde and acetone during acetic acid HDO. Acetone was produced via the self-ketonization reaction of acetic acid. In most cases of 4-ethylguaiacol HDO, phenol, cresol, and 2, 4-dimethylphenol were the primary products. For furfural HDO, the major furan and CO products proved that the direct decarbonylation of furfural was the main reaction. Accordingly, the main pathways of acetic acid, 4ethylguaiacol, and furfural HDO were proposed, which could provide significant guidance for the upgrading of crude bio-oil.

The last paper is entitled: "Thermal Behaviour of Impregnated Olive Stones with Phosphoric Acid via TGA-MS" [10]. This paper explored the thermal behaviour of raw and phosphoric acid impregnated olive stone via coupled Thermogravimetric analysis-Mass spectrometry (TGA-MS) during pyrolysis, with the ultimate goal of improving the activated carbon production. The impregnated material was prepared at different H<sub>3</sub>PO<sub>4</sub>/precursor weight ratios and for various impregnation times. The thermal degradation of olive stones was observed to be occurring in three stages; dehydration, main degradation and slow pyrolysis. Two main degradation steps were detected for the raw olive stones in the temperature interval from 210 °C to 425 °C, whereas the H<sub>3</sub>PO<sub>4</sub> impregnated olive stones involved a single step in the range 110 °C to 230 °C. The authors noticed that the impregnation by H<sub>3</sub>PO<sub>4</sub> reduced sharply the temperature onset of the main decomposition step and the by about 100 °C due to its catalytic power. They concluded that the presence of phosphoric acid appreciably accelerated the activated carbon production, the impregnation rate and time effects being more significant than the time for pyrolysis. The main products of gas emissions during pyrolysis were H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub>. Acid activation

favoured  $\mathrm{CH_4}$ ,  $\mathrm{H_2O}$ ,  $\mathrm{C_2H_6}$  and  $\mathrm{CO}$  emissions while reducing  $\mathrm{CO_2}$  emissions. Mass degradation behaviour and analysis of evolved gas demonstrated that kinetic scenario of pyrolysis of raw olive stones were different from impregnated ones. Indeed, while the former were likely to be controlled by simultaneous or competitive reactions, the latter seemed to be controlled by consecutive reactions.

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