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Mercury Adsorption with Bio-Chars Produced from Waste Biomass

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Highlights
- Study of two waste biomasses as feedstock for bio-char production.
- Bio-char production through an innovative slow pyrolysis process.
- Assessment of bio-char performance as adsorbent for mercury removal from wastewater.

1. Introduction

Mercury is identified as a pollutant of primary concern that may derive from natural and anthropogenic sources and is spread through atmosphere, water and soil in different forms. Mercury pollution is often unrelated to any emission spot, and it has a long persistence in the environment. Mercury tends to bioaccumulate and main intake for humans is through inhalation and water and food consumption [1]. Mercury removal from wastewater has been successfully proven by means of adsorption [2].

Pyrolysis is a thermochemical process involving the conversion of carbon-based materials, in absence of an oxidizing agent, into gas, bio-oil and bio-char. Pyrolysis fed by waste biomass may be defined "2nd generation" biorefinery process (compared to 1st generation biorefinery routes, based on specifically cultivated crops), and it is fully consistent with EU strategy about Circular Economy. Moreover, pyrolysis is a carbon negative system; up to 50% carbon in biomass is converted into bio-char, and carbon can remain sequestered in soils for hundreds of years. The net result is a reduction of CO_2 emissions. Bio-char gained attention in the last years as adsorbent for organic and inorganic pollutants, showing performances analogous to conventional Granular Activated Carbon (GAC) and undeniable environmental and economic revenues [3]. This study is aimed at two main objectives. First, the assessment of two significant waste biomasses, Kraft lignin (from wood pulp industry) and olive oil production residues, as feedstock for bio-char production. Second, the investigation of the bio-chars as adsorbent for mercury removal from wastewater, considering commercial GAC as reference.

2. Methods

A novel reactor developed at ICFAR, the Jiggled Bed Reactor (JBR) was employed in a two-step process. Bio-chars were produced in slow pyrolysis mode (500°C for 5 min) and then activated (850°C for 60 min with CO_2). Bio-chars were characterized through elemental analysis (AN634 Flash 2000 CHN Analyzer), surface area and pore volume (TriStar II 3020 BET Surface Area and Pore Analyzer Micromeritics). Adsorption batch tests were performed at 25°C and 400 rpm, on 1 g of biochar in 10 mL of aqueous phase. Tests were firstly aimed at determining equilibrium contact time and then adsorption isotherms were generated. Mercury was analyzed in aqueous samples through Rhodamine 6G colorimetric method [4] at 575 nm using an Evolution 220 LC UV-VIS spectrophotometer and concentrations of 50-1000 mg/L.

3. Results and discussion

The main features of the two activated bio-chars (see Table 1) show analogous carbon contents and a more significant ash content for olive residue bio-char. Sulfur was detected only in Kraft lignin activated bio-char. Bio-char yield was higher for Kraft lignin, however surface area and micropore and mesopore areas were considerably higher for olive residue activated bio-char.

Equilibrium contact time values were different: activated bio-chars deriving from Kraft lignin and olive residue reached equilibrium after 8 and 3 hours, respectively, while GAC needed 11 hours. Concerning

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adsorption capacity, similar results were achieved with Kraft lignin bio-char (70 mg/g) and GAC (80 mg/g), while olive residue bio-char gave a lower value (40 mg/g).

Table 1. Physico-chemical characteristics of the bio-chars compared to commercial GAC (n.d.: not detected)

activated biochar	% C	% N	% H	% S	% ash	% yield	Surface Area (m^2/g)	micropore area (m^2/g)	mesopore area (m^2/g)
Kraft lignin	75	0.5	0.4	1.1.	2.3	31	529	440	89
Olive residue	79	0.6	1.6	n.d.	11.7	21	735	636	99
Commercial GAC	58	0.1	0.5	n.d.	2.2	-	1339	1083	256

The experimental data gathered during equilibrium contact time investigation were fitted with different kinetic model equations (first order, pseudo-second order, particle diffusion) to better understand the kinetics of the adsorption process. The parameters obtained (data not displayed) were calculated by linear regression of the linearized forms of the different kinetic model equations. The pseudo-second order kinetic model equation provided the best fit for both cases, leading to hypothesize that mercury adsorption on the activated bio-chars used in this work happens through the formation of complexes between the adsorbate and the adsorbent. The positive influence of sulfur (detected in Kraft lignin biochar) in such complexes formation during mercury adsorption was already demonstrated [5].

Considering the adsorption isotherms (see Table 2), the Langmuir model (usually related to mono-layer adsorption) better represents the experimental data derived from the Kraft lignin activated bio-char. (because of lower value of SSE, even in with higher R^2). The Freundlich model (usually related to multi-layer adsorption) was the best for olive residue activated bio-char.

Table 2. Adsorption isotherm parameters calculated for the activated biochars (SSE: sum of squared errors)

Activated biochar	Langmuir		Freundlich	
Kraft Lignin	Q^0	82.6	k_f	2.9
	b	0.017	n	1.7
	R^2	0.92	R^2	0.98
	SSE	55	SSE	491
Olive residue	Q^0	64.5	k_f	0.9
	b	0.0026	n	1.7
	R^2	0.95	R^2	0.99
	SSE	22.7	SSE	6

4. Conclusions

Bio-chars derived from Kraft lignin and olive residue exhibited inferior structural characteristics compared to commercial GAC. However, the contact time was shorter in both cases and the adsorption capacity of Kraft lignin bio-char was analogous to that of GAC. Considering the experimental results of batch adsorption tests for mercury removal from aqueous samples, the adsorption process was better represented by a pseudo second order kinetic model for both activated bio-chars, by the Langmuir isotherm model for Kraft lignin activated bio-char and by the Freundlich isotherm model for olive residue activated bio-char.

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