

REMOVAL OF Cd²⁺ AND Pb²⁺ FROM AQUEOUS SOLUTIONS USING BIO-CHAR RESIDUES

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Abstract: In this paper, wheat straw and rapeseed residues before and after microwave pyrolysis during bio-oil production were studied as potential sorbents of heavy metals. The sorbents were characterized by elemental analysis and FTIR spectroscopy. Sorption properties of the materials were investigated using batch adsorption-equilibrium experiments and the effect of initial Cd and Pb concentration was studied. The experimental data fit Langmuir adsorption isotherm. The maximum sorption affinity of studied materials was observed in the case of rapeseed and its sorption capacity was 31.6 and 83.5 mg/g for Cd and Pb, respectively.

Key words: biomass, microwave pyrolysis, char, cadmium, lead, sorption

1. Introduction

Water pollution is one of the most important environmental problems. Among the aquatic pollutants, heavy metals have gained relatively more significance in view of their persistence, bio-magnification and toxicity. The main sources of heavy metal contamination are e.g. metal plating, mining operations, tanneries, radiator manufacturing, smelting, alloy industries and storage batteries manufactures (KADIRVELU *et al.*, 2001). Treatment processes for heavy metals removal from wastewaters include precipitation, membrane filtration, ion exchange, adsorption and co-precipitation/adsorption. Cost-effective alternative technologies for the treatment of metal-containing wastewaters are needed. Adsorption has evolved as one of the most used treatment techniques for removing metal ions to lowers from water which cannot be removed by other techniques (MOHAN *et al.*, 2007).

In recent years, considerable attention has been focused on the removal of heavy metals from aqueous solution using adsorbents derived from low-cost materials, such as agricultural waste and by-products. Natural materials that are available in large quantities, or certain waste products from agricultural operations, may have potential as inexpensive adsorbents. Due to their low cost, after these materials have been expended, they can be disposed of without regeneration. In general, adsorbents can be assumed as low cost if they require little processing, are abundant in nature, or are a by-product or waste material from another industry (BAILEY *et al.*, 1998). Several methods have been studied over the years, for the production of low-cost adsorbents. Pyrolysis is one of the methods that can be used for production of low-cost adsorbents (CHEN *et al.*, 2011; LIU *et al.*, 2011; LIU *et al.*, 2012; MOHAN *et al.*, 2007)

Pyrolysis can be described as the direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid, liquid and gas products.

Microwave heating technology has been shown to be more energy efficient than conventional methods in many applications. Microwave irradiation is rapid and volumetric with the whole material heated simultaneously. In contrast, conventional heating is slow and the heat is introduced into the sample from the surface. Microwave pyrolysis has gained momentous attraction because of the merits mentioned above. Existing research works on microwave pyrolysis of biomass includes pyrolysis of wheat straw (BUDARIN *et al.*, 2009), corn stover (YU *et al.*, 2007), rice straw (HUANG *et al.*, 2008), biomass (WAN *et al.*, 2009), coffee hulls (DOMÍNGUEZ *et al.*, 2007), and pine wood sawdust (CHEN *et al.*, 2008).

The main purpose of this study was the evaluation of Pb and Cd adsorption from aqueous solutions onto straw and rapeseed char. Sorption properties of the materials were studied before and after their conversion into biochars through microwave pyrolysis treatment.

2. Materials and methods

2.1 Sorbent preparation

Samples of the wheat straw and rapeseed (Palma Sečovce, s.r.o) were crushed by (Air Grinder MC – FDV), sieved to granulometric fraction under 1 mm and washed with deionized water and dried at temperature of 100°C. The material were press to briquettes and used for pyrolysis. After pyrolysis samples were crushed, sieved and dried again. Microwave pyrolysis experiments were carried out at nitrogen atmosphere and power 900 W. Samples were characterized by elemental analysis (CHNS Elementar Vario Macro Cube) and FTIR spectroscopy (FT-IR Bruker Tensor 27).

2.1 Adsorption experiments

The sorption properties of raw materials and biomass char residues were tested under batch conditions. The initial Cd and Pb concentration was 10-200 and 10-250 mg/L, respectively. Model solutions of Cd and Pb were prepared by dissolving Cd(NO₃)₂·4H₂O and Pb(NO₃)₂ in deionized water, respectively. The sorbent concentration was 2 g/L. The pH of the solutions was adjusted to value of 5.0 with 0.01 and 0.1 M NaOH and HNO₃.

The experiments were performed at constant temperature of 25°C in a rotary shaker set at 30 rpm and equilibrium time 24 hours. The metal quantity in solutions was determined by AAS (Varian 240 RS/240 Z, Australia) before and after the sorption experiments. The amount of the metal sorbed (mg) per unit mass of sorbents (g) q_{eq} , was calculated using the Eq. (1)

$$q_{eq} = \frac{C_0 - C_{eq}}{C_s} \quad (1)$$

where C_0 and C_{eq} are initial and equilibrium metal concentration (mg/L), respectively and C_s is the sorbent concentration in solution (g/L).

3. Results and discussion

3.1 Characterization of sorbents

The results of the elemental analysis of tested materials are given in Table 1 and 2. During the conversion of biomass to biochar the original carbon is retained in the biochar, which offers a significant opportunity for creating a carbon sink. As a consequence of the pyrolysis process, the carbon content of the carbonized residue increased with regard to the original biomass, along with a deoxygenation as a consequence of the loss of functional groups during the process. There was also a noticeable decrease in the hydrogen content, probably due to the great proportion of hydrogen compounds in the volatile matter.

Table 1. Characterization of biomass samples (A – ash, V – volatile matter, W – moisture; Superscripts: d – dry basis, a – analytical specimen, O^d – by difference - according to 100 - (A^d + C^d + H^d + N^d + S^d).

Sample	A ^d	W ^a	V	N ^d [%]	C ^d [%]	H ^d [%]	S ^d [%]	O ^d [%]
rapeseed	7.0	4.2	74.6	5.44	46.07	6.59	0.79	34.11
wheat straw	7.3	4.7	74.8	1.7	39.67	5.96	0.24	45.13

Table 2. Characterization of biomass samples after microwave pyrolysis.

Sample	Recovery [%]	Time of pyrolysis [min]	N[%]	C[%]	H[%]	S[%]
rapeseed	27	25	4.26	59.83	1.237	0.414
wheat straw	24	30	1.56	63.92	1.635	0.315

FTIR spectroscopy was used to characterize the functional groups responsible for heavy metals adsorption. The FTIR spectra of rapeseed and wheat straw before and after pyrolysis are given in Fig. 1 and 2, respectively. It is important to note that visible vibrations presented in the spectrum represent not only one structure, but there are several group/bond vibration, which are often overlapped. The broad peak at maximum of 3287 cm⁻¹ represents hydroxyl groups (vibration frequencies of water, alcohols, and phenols) and N–H stretching vibrations (ABDEL-NASSER and EL-HENDAWY, 2006). The peaks at 2924 and 2854 cm⁻¹ can be assigned to CH₂ (asymmetric) and CH₃ (symmetric) stretch of aliphatic structures. Vibration frequency at 1743 cm⁻¹ can be assigned to esters. Theoretical vibration frequencies C=O functional group of aldehydes and ketones are shifted to lower values (around 1725 - 1700 cm⁻¹), even though these compounds also contribute to this absorbance. Next peak at 1634 cm⁻¹ can be associated with weaker H-O-H bending vibration of water. Moreover, in this region, there are also C=C bond of alkenes and aromatic compounds and C=O stretching vibration of carbonyl group. The aromatic skeletal C=C bonds are visible in the region at 1517 cm⁻¹ and 1443 cm⁻¹, respectively. C–O stretching

vibration can be also presented in this region (around 1423 cm^{-1}) (BARKA *et al.*, 2010). Asymmetric stretching vibration of C-O-C in esters and/or organic acids is presented at 1234 cm^{-1} . Absorption bands at 1132 cm^{-1} and 1023 cm^{-1} are assigned to deformation vibrations of C-H bonds in aromatic ring and deformation vibrations of C-O bonds in alcohols and carboxylic acids (TUZEN *et al.*, 2009).

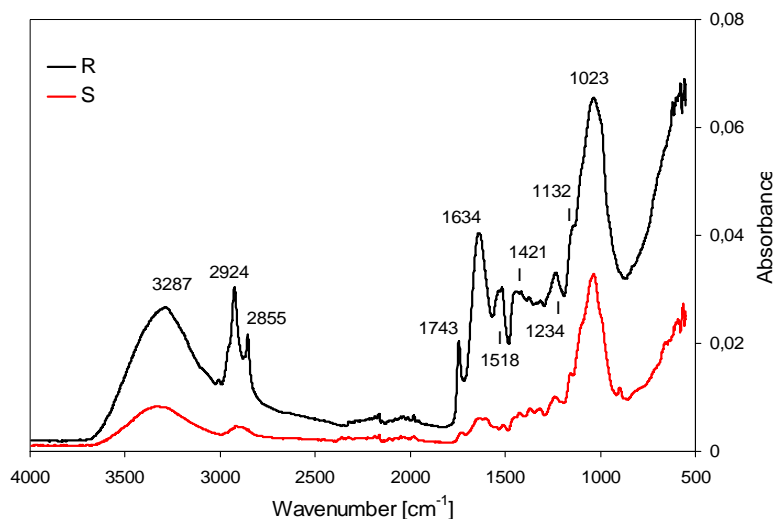


Fig. 1. FT-IR spectroscopy of wheat straw and rapeseed.

Degradation of the organic phase was observed in both samples after process of pyrolysis (Fig. 2). Decreasing in the band intensities is visible in all regions and only some peaks are presented in the FT-IR spectrum. For example, a visible intensity was recorded at 1010 cm^{-1} in the case of wheat straw residue.

3.2 Adsorption

The effect of initial metal concentration on sorption by tested materials is shown in Fig. 3-6. Isotherm studies provide information on the capacity of sorbent. Adsorption isotherms are characterized by certain constants and describe the mathematical relationship between the quantity of adsorbate and concentration of adsorbate remaining in the solution at equilibrium. The experimental data were evaluated using Langmuir isotherm (Eq. 2).

$$q_{eq} = q_{max} \frac{bC_{eq}}{1 + bC_{eq}} \quad (2)$$

where q_{eq} (mg/g) is the weight adsorbed per unit mass of adsorbent at equilibrium, q_{max} (mg/g) is the theoretical monolayer adsorption capacity, b (L/mg) is the Langmuir constant related to the energy of adsorption and C_{eq} (mg/L) is the equilibrium concentration.

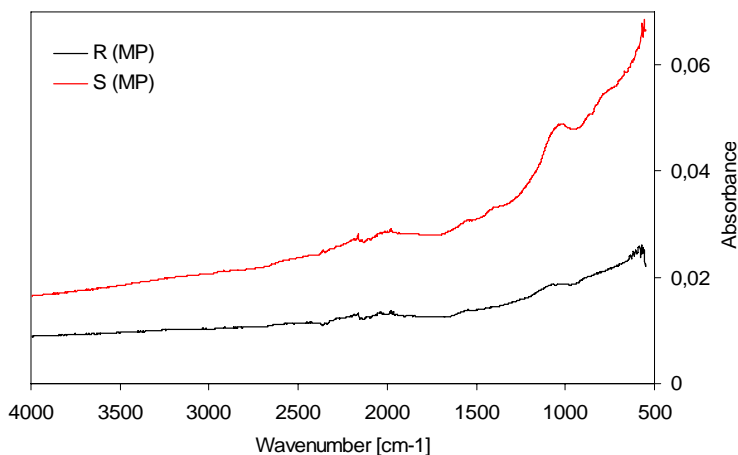


Fig. 2. FT-IR spectra of char residues (wheat straw and rapeseed) after microwave pyrolysis.

The effect of initial Cd and Pb concentration on sorption capacity of tested sorbents is shown in Fig. 3-6. It was observed that the increase of initial metal concentration caused increasing of the metal amount adsorbed per mass unit. The maximum obtained sorption capacity of wheat straw was 5.5 and 14.0 mg/g for Cd and Pb, respectively. Microwave pyrolysis of straw caused a considerable increase of sorption capacity of material. The maximum sorption capacity of wheat straw after pyrolysis was 10.5 and 33.5 mg/g for Cd and Pb, respectively. The sorption capacity of rapeseed was 31.6 and 83.5 mg/g for Cd and Pb, respectively. Microwave pyrolysis of rapeseed caused a decrease of sorption affinity of material toward Cd and Pb ions. The sorption capacity of rapeseed after microwave pyrolysis was 4.8 and 26.2 mg/g for Cd and Pb, respectively. Experimental data were in good agreement with Langmuir isotherms. Langmuir adsorption parameters are given in Table 3.

Table 3. Langmuir adsorption parameters.

	Cd			Pb		
	$q_{\max}[\text{mg/g}]$	$b[\text{L/mg}]$	R^2	$q_{\max}[\text{mg/g}]$	$b[\text{L/mg}]$	R^2
S	6.71	0.02	0.98	14.24	0.12	0.99
S_{MP}	11.99	0.04	0.99	23.91	0.72	0.97
R	49.36	0.02	0.98	88.53	0.24	0.99
R_{MP}	5.60	0.08	0.98	26.89	0.41	0.97

The sorption of Cd and Pb by biomass char residues has been studied by several authors, as well. MOHAN *et al.* (2007) studied Cd and Pb sorption by chars produced from pyrolysis of pine wood, pine bark, oak wood and oak bark during bio-oil production. The most efficient sorbent was oak bark char with sorption capacity

2.9 and 11.3 mg/g for Cd and Pb ($C_0=10$ mg/L), respectively. TANGJUANK *et al.* (2009) studied removal of Cd and Pb by activated carbon prepared from cashew nut shells. The maximum sorption capacity of sorbent was 14.3 and 28.9 mg/g for Cd and Pb ($C_0=40$ mg/L), respectively.

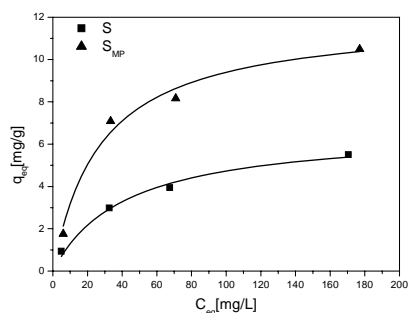


Fig. 3. Cd adsorption on wheat straw (S) and wheat straw char residues (S_{MP}).

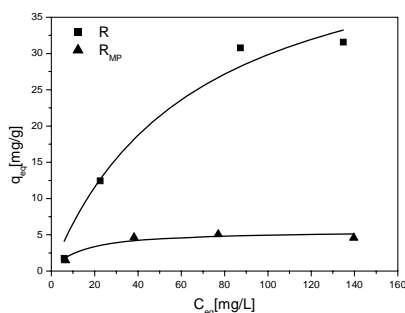


Fig. 4. Cd adsorption on rapeseed (R) and rapeseed char residues (R_{MP}).

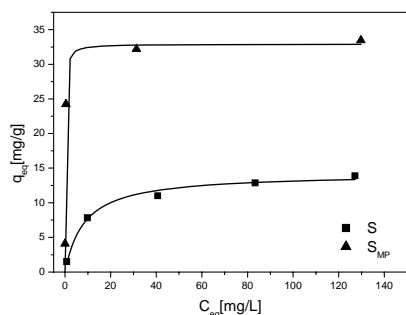


Fig. 5. Pb adsorption on wheat straw (S) and wheat straw char residues (S_{MP}).

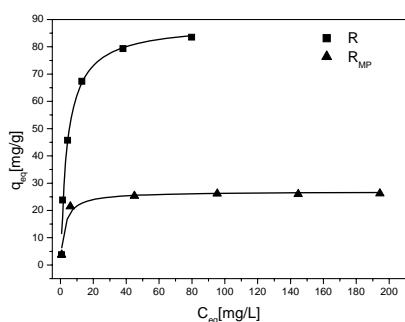


Fig. 6. Pb adsorption on rapeseed (R) and rapeseed char residues (R_{MP}).

4. Conclusions

In this work straw and rapeseed before and after microwave pyrolysis were studied as Pb and Cd sorbents. The chars produced from microwave pyrolysis of straw and rapeseed during bio-oil production were characterized and used successfully without activation for the removal of Cd and Pb from water. Microwave pyrolysis caused significant changes in sorption properties of materials. After pyrolysis the sorption capacity of straw increased while in the case of rapeseed it decreased. The Cd sorption on the sorbents followed the order: $R \gg S_{MP} > S \sim R_{MP}$. The Pb sorption on the sorbents followed the order: $R \gg S_{MP} > R_{MP} > S$. The sample of untreated rapeseed has shown the highest sorption affinity toward Cd and Pb ions. The maximum sorption capacity of the untreated rapeseed was 31.6 mg and 83.5 mg/g for Cd and Pb, respectively.

Acknowledgements: This work has been supported by Science and Scientific Grant Agency VEGA, project No. 0141 and the Slovak Research and Development Agency under the contract No. APVV-0252-10.

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Presented at the 2nd International Conference "Biotechnology and Metals - 2011", September 22-23, 2011, Košice, Slovak Republic.