MME SEE
CONGRESS 2023

5th Metallurgical & Materials Engineering Congress of South-East Europe
Trebinje, Bosnia and Herzegovina
7-10th June 2023

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CONGRESS PROCEEDINGS - MME SEE 2023
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Mg/Fe-PYRO-HYDRO CHAR DERIVED FROM CORN COB AS EFFECTIVE ADSORBENT OF LEAD REMOVAL FROM AQUEOUS SOLUTIONS

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The corn cob was investigated as available agrowaste material for the production of potential efficient material for heavy metals removal. The hydrothermal carbonization (HTC) technology is one of the appropriate methods for biomass transformation into high-value carbonaceous products than can be utilized as adsorbents. In this study, modified pyro-hydrochar derived from corn cob (MCC) was effectively prepared by modification with Mg-Fe solution and pyrolysis. This material was used for Pb ions removal from aqueous solutions. The effect of solution pH, contact time and initial Pb concentration were examined in batch system. The achieved results revealed that the most effective Pb adsorption take place at pH 5. The experimental results were fitted to Langmuir, Freundlich, Sips and Redlich-Peterson isotherm models. The best data fit was achieved with the Sips isotherm model with maximum adsorption capacity for Pb removal of 214.9 mg/g. Additionally, the experimentally results from kinetic study were fitted by pseudo-first and pseudo-second order models. According to kinetic parameters, the Pb removal using MCC follows pseudo-second order model, which assumes that chemical interaction between Pb ions and functional groups on the MCC surface was involved in metal adsorption. According to data from this investigation and in comparisons to other adsorbents can be concluded that investigated material can be used as potential suitable adsorbent of Pb from aqueous solutions.

Keywords: hydrothermal carbonization; modification; corn cob utilization; heavy metals removal; adsorption.

Introduction

Rapid industrialization and technological development caused prompt pollution of the environment. Factories, as the main polluters, emit pollutants through waste water and exhaust gases in environment. These sources of pollution contaminate water with organic and inorganic waste. Before disposal, most organic matter is neutralized and decomposed by various physical, chemical and biological processes. However, inorganic waste represents a big problem because it contains high concentrations of heavy metals that are very toxic, non-degradable, have the ability to bioaccumulate in living organisms and thus end up in the food chain, which can cause many health problems in humans.

In the conditions of global development, taking care of water is a question of civilization. Therefore, it is understandable that there is an effort in the world to protect water from any form of pollution and to find the most acceptable solutions for the protection and preservation of the planet. There are a large number of different processes for wastewater treatment, such as: chemical precipitation, oxidation-reduction processes, coagulation and flotation and effective, but very expensive procedures, such as: ion exchange, reverse osmosis, electro-dialysis, ultra-filtration, electrolysis etc. These methods are limited because of high costs or disposal of large amounts of secondary waste (eg sludge after precipitation). Also, a very effective technology for removing heavy metals from industrial wastewater is their treatment using activated carbon. However, the high cost of obtaining activated carbon and the loss during regeneration limit its use.

Adsorption process has proven to be an effective method for removing heavy metals from wastewater. In recent years, various alternative agro waste materials for the adsorption treatment of polluted waters have been increasingly investigated.

Besides, biomass transformation into high-value carbonaceous products via the hydrothermal carbonization (HTC) technology is used to obtain materials with improved adsorption characteristics.

Conversely, low porosity and specific surface area might limit utilization of hydrochars as the efficient adsorbents. In order to improve adsorption performance, different modification techniques can be used. Thus, Petrović et al used alkali modified hydrochar of grape pomace for lead removal (Petrović et al., 2016). Kojić et al showed that a calcium-pyro-hydrochar can be applied as efficient adsorbent of Pb^{2+} and Cd^{2+} from an aqueous solution (Kojić et al., 2022). Additionally, Lu et al. study the effect of different modifiers on the sorption and structural properties of biochar derived from wheat stalk (Lu et al., 2022).

In this study, hydrothermally treated corn cob (CC) was activated in order to produce effective adsorbent of Pb^{2+} ions removal from aqueous solutions. As modifier agent magnesium chloride was used and pyrolysis under oxygen-limited condition at 300C was done. The effect of solution pH, contact time and initial Pb concentration on adsorption process were examined in batch system. Obtained results were fitted by two and three parameter isotherm models: Langmuir, Freundlich, Sips and Redlich-Peterson as well as two kinetic models: pseudo-first and pseudo-second order models.

Materials and methods

Chemicals and Materials preparation

All chemical used for experiments were of analytical grade. Standard Pb solution was prepared by dissolving of desired amount of $Pb(NO_3)_2x3H_2O$ in double distilled water. Working solutions were prepared daily by dilution of prepared standard solution.

Corn cob was collected after harvesting from the local cornfield near the Belgrade, Serbia, in 2022. Collected CC was washed, dried, grinded and sieved. About 10 g of prepared CC was mixed with 150 ml double distilled water and hydrothermally carbonized in an autoclave (Carl Roth, Model II) during 120 min at 220°C. The content from the autoclave was filtered, rinsed and dried at 105°C until constant weight. About 1g of prepared sample was modified by stirring with 0.2M $MgCl_2x6H_2O$ and 0.4M $FeCl_2x4H_2O$ at pH 10 during 4h at 60°C. Modified hydrochar was rinsed and dried at 100°C during 24h afterward pyrolised in furnace at 300°C in inert atmosphere (N_2 flow 25 mL/min) with heating rate 7°C/min during 1h. Modified material (MCC) was filtered, rinsed, dried in an oven at 105°C until constant weight and used for further experiments.

Batch experiments

All adsorption experiments were done in a batch system. Effect of the initial pH was studied in pH range from 2.0 to 5.0. Solution pH was adjusted by adding of small volume of 0.01M HNO_3 and NaOH solutions. In 25 ml of Pb solution (200 mg/L) was added 0.025 g of MCC, shaken at an orbital shaker (Heidolph, Unimax) for 4 h at 250 rpm and room temperature. After reaction period, the suspensions were filtered and residual Pb concentration in filtrate was measured by Atomic Absorption spectrometry (AAS) at PerkinElmer PinAAcle 900T. Effect of the contact time was studied in interval range from 10 to 300 min. In 25 ml of Pb solution (pH 5) was added 0.025 g of MCC, shaken at an orbital shaker at 250 rpm and room temperature, filtered and residual Pb concentration in filtrate was measured by AAS.

Effect of the initial meal concetration was studied at different Pb concentrations (100 to 500 mg/L). In 25 ml of Pb solution (pH 5) was added 0.025 g of MCC, shaken at an orbital shaker at 250 rpm and room temperature, filtered and residual Pb concentration in filtrate was measured by AAS. The adsorption capacity of MCC was calculated by following equation:

$$qe = \frac{(Ci - Cf)}{m} * V \tag{1}$$

where: q_e is the amount of adsorbed Pb ion in equilibrium (mg/g); C_i and C_f are the initial and the final Pb concentration in solution (mg/L), respectively; *m* is a mass of MCC (g) and *V* is the volume of metal solution (L).

Experimental results from the effect of contact time were fitted by two kinetic models: pseudo first and pseudo second order kinetic models and calculated by equations (2) and (3), respectively (Ho and McKay, 1999; Lagergren, 1989):

$$\frac{1}{qt} = \frac{1}{qe} + \frac{k1}{qet} \tag{3}$$

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{t}{qe} \tag{4}$$

where: q_t is the amount of adsorbed Pb ion at the time *t* (mg/g); k_1 and k_2 are the pseudo first and pseudo second order rate constant (1/min), respectively and *t* is a reaction time (min).

Experimental results from the effect of initial metal ion solution were fitted by two and three parameter isotermic models: Langmuir, Freundlich, Sips and Redlich-Peterson (Redlich and Peterson, 1959; Sips, 1948; Langmuir, 1918; Freundlich, 1906).

$$qe = \frac{q\max KlCe}{(1 + KlCe)} \tag{5}$$

$$qe = KfCe1/nf \tag{6}$$

$$qe = \frac{q\max(KsCe)1/ns}{[1 + (KsCe)1/ns]} \tag{7}$$

$$qe = \frac{KrpCe}{(1 + arpCeg)} \tag{8}$$

where: q_{max} is the maximal adsorbed amount of Pb on the MCC (mg/g); K_L (L/mg), K_F (mg g^{-1}(mg $L^{-1})^{-1/nf}$), K_S ((mg $L^{-1})^{-1/ns}$) and K_{RP} (L/g), a_{RP} (mg/L)/g are the Langmuir, Freundlich, Sips and Redlich-Petrrson constants, respectively and 1/nf, 1/ns and g are empirical Freundlich, Sips and Redlich-Peterson parameters, respectively.

Results and discussion

The effect of initial pH value of metal solution on adsorption properties of MCC was investigated. According to experimental data MCC has higher affinity toward lead ions at higher pH values and reaches its maximum at pH 5.

In order to obtain information about the rate of adsorption processes and mechanisms, a kinetic study was performed. Pseudo first and pseudo second order models were used for this study. Obtained kinetic parameters are presented in Table 1, and plots are shown at Figure 1.

Table 1 Kinetic parameters for Pb adsorption on MCC

	MCC		MCC
Pseudo first order		**Pseudo second order**	
$q_{eq,\,cal}$ (mg/g)	152.44	$q_{e,cal}$ (mg/g)	166.39
k_1 (1/min)	3.14	k_2 (g/mg/min)	0.00067
R^2	0.7367	R^2	0.9981

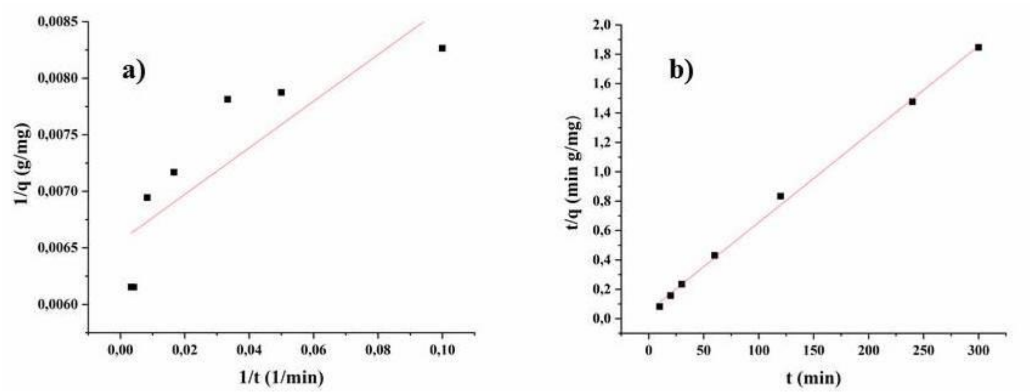

Figure 1 Kinetic models for Pb adsorption on MCC

According to R^2 value, pseudo second order model is more suitable for kinetic explanation of Pb adsorption on the MCC. This indicates that chemisorption is involved in Pb adsorption on the MCC.

In order to examine equilibrium of adsorption process of Pb and MCC the isotherm study was done. Experimental data were calculated by Langmuir, Freundlich, Sips and Redlich-Petrson isotherm models. Calculated parameters are presented in Table 2, while used models are graphically presented at Figure 2.

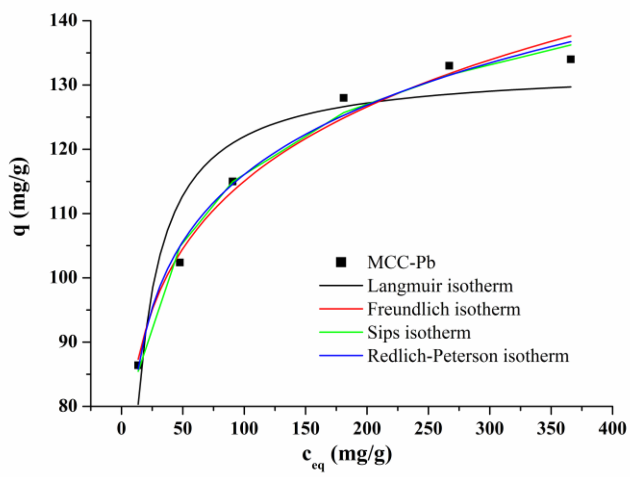

Figure 2 Isotherm models for Pb adsorption on MCC

Table 2 Isotherm parameters for Pb adsorption on MCC

Models	Parameters	MCC
Langmuir	q_{max} *(mg/g)*	132.84
	K_L*(L/mg)*	0.112
	χ^2	50.862
	R^2	0.888
Freundlich	*Kf (mg/g)(L/mg)1/n*	60.892
	1/n	0.138
	χ^2	7.437
	R^2	0.984
Redlich-Peterson	k_{RP}*(L/g)*	82.526
	a_{RP}*(L/mg)*	1.211
	β	0.881
	χ^2	8.005
	R^2	0.987
Sips	q_m *(mg/g)*	214.9
	K_s *(L/g)*	0.307
	n_s	3.415
	χ^2	6.421
	R^2	0.989

According to obtained values (Tab. 1) the Sips model best described adsorption Pb on the MCC the adsorption of Pb on the MCC. Based to this model, maximal adsorption capacity for Pb removal is 214.9 mg/g. Additionally, based on the values of R_L and n_F from Lagmuir and Freundlich models, respectively, it can be conclude that adsorption process of Pb on the MCC is favorable. In comparison to other investigated similar materials for Pb removal, MCC has a good ability for Pb removal from water solutions. The maximum adsorption capacities for Pb removal of other investigated materials are tabulate presented in Table 3.

Table 3 The maximal adsorption capacities of different hydrochars

Used hydrochars	q_{max} (mg/g)	Ref.
Calcium pyro-hydro char from spent mashroom substrate	297	Kojić et al., 2022
Hydrochar of grape pomace	137	Petrović et al., 2016
Activated hydrochar of bamboo	151.5	Li et al., 2020
Pinewood activated hzdrochar	46.7	Madduri et al., 2020
Activated hydrochar of sawdust	92.8	Xua et al., 2019
This study	214.9	

Conclusion

In this study modified pyro-hydrochar derived from corn cob was investigated as new adsorbent for Pb removal from water solutions. Modification step was done with Mg-Fe solution and pyrolysis afterward the batch adsorption experiments were done. Experimentally obtained results were calculated by pseudo second and pseudo second order kinetics models as well as Langmuir, Freundlich, Sips and Redlich-Peterson isotherms models. According to obtained data, maximum adsorption capacity of investigated material for Pb ions removal was 214.9 mg/g. Besides, results from this study indicate that chemisorption is responsible for the binding of lead ions to the surface. This study confirms that the modification procedure used is very effective in obtaining a suitable adsorbent for lead removal.

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