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Dejan Tanikić

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Mg/Fe-MODIFIED HYDROCHAR WITH PROMOTED ADSORPTION PERFORMANCES

**Jelena Petrović, Marija Ercegović, Marija Simić,
Marija Koprivica, Jelena Dimitrijević, Marija Marković**

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Abstract

This study examined Mg/Fe-pyro-hydrochar produced from grape pomace as potential sorbent for Cu^{2+} ions. Obtained results show that the Mg/Fe-modification increases the adsorption capacity for five times. To evaluate the effectiveness of produced sorbent, Langmuir, Freundlich, Sips and Redlich-Peterson isotherm models were applied to batch adsorption results. According to applied models Cu^{2+} adsorption at equilibrium fitted the Sips isotherm model, with a maximum achieved capacity of 75 mg/g. Spectroscopic analysis reveal that oxygenated active sites and aromatic groups on pyro-hydrochar surface participate in Cu^{2+} ions binding. In general, preliminary findings from this paper offers perspective to effective utilization of waste biomass as an efficient adsorbents for Cu^{2+} ions removal.

***Keywords**: waste biomass, pyro-hydrochar, heavy metal removal, adsorption mechanism.*

1. INTRODUCTION

Over the years, rapid development of industrial activities caused accelerated production of industrial effluents contaminated with heavy metals. The inadequate management of polluted wastewater and its release into water bodies poses a serious threat to the environment and human health [1,2]. Besides other heavy metals, copper (Cu^{2+}) is classified as an essential micronutrient, however numerous anthropogenic activities are the significant contributors to the detrimental levels of Cu^{2+} in the environment, thus its concentration exceeds the permissible limits [3]. For this reason, removal or reduction of Cu^{2+} ions to standards defined acceptable quantity from the various industrial effluents become essential. Until now, various physical and chemical strategies (chemical precipitation, ion exchange, coagulation, oxidation, membrane filtration, adsorption, etc.) have been widely used for this purpose [4]. Among aforementioned techniques, adsorption is currently considered as a simple, efficient, low energy demand, and cost-effective method for wastewater purification. Along with adsorption, the development of novel adsorbents is on the rise. A movement toward greener methods proposes utilization of waste agricultural biomass as a chip, renewable and highly available as adsorbent material in adsorption technique. Furthermore, conversion of agricultural waste to carbonaceous materials has made their practical application even more attractive. Carbon-rich adsorbents can be produced from various waste biomasses by gasification, pyrolysis or hydrothermal carbonization (HTC).

The latter conversion process offers significant advantages over dry pyrolysis, such as milder reaction conditions (180-260°C) and high conversion efficiency of wet waste biomass into a carbon-rich product, hydrochar [2]. Although produced material exhibit smaller active surface and porosity compared to activated carbon, hydrochars shows significant potential for application in wastewater treatment due to a large number of functional groups on their surface [5]. Regarding improvement of adsorption potential, numerous studies have examined various physical and chemical modifications or functionalization of hydrochars. Previous experiences have shown that the treatment with hydrogen peroxide, different alkalis or metal salts can significantly increase their adsorption efficiency [2,5].

Within this study, the potential application of Mg/Fe doped grape pomace hydrochar as a potential adsorbent of Cu^{2+} ions from aqueous solutions will be investigated for the first time. In order to detail examine the binding mechanism and the metal adsorption process, characterization of hydrochar before and after Cu^{2+} removal, as well as isothermal study was performed.

2. EXPERIMENTAL

2.1 Preparation and modification of hydrochar

Waste pomace was collected from an open landfill site after processing of grapes into confectionery products. Pomace was air-dried, ground, and hydrothermally carbonized in an autoclave (Carl Roth, model II), in water as a reaction medium (1:15 m/v ratio) at 220°C, for one hour. The resulting hydrochar (GPHC) was filtered and dried at 105°C. The impregnation of the obtained hydrochar with MgO and FeO was carried out by a two-step co-precipitation procedure during which 1g of the HC-GP was stirred with Mg and Fe salts for 4 h at 60°C. Thereafter, the material was subjected to pyrolysis (Nabertherm 30-3000°C, Germany) at 300°C, within 1h, in an inert atmosphere. Obtained Mg/Fe-activated pyro-hydrochar was labeled as Mg/FeGPHC.

2.2 Characterization of obtained Mg/Fe-pyro-hydrochar and adsorption test

To gain insight into the influence of modification process onto adsorbent surface, and to reveal participation of functional groups in the binding of Cu^{2+} ions, the spectroscopic analyses using Thermo Scientific Nicolet iS50 FT-IR spectrometer were performed. The KBr pastilles that include 0.8 mg of powdered Mg/Fe-HC and 80 mg of KBr have been recorded in transmission mode under spectral range from 4000 to 400 cm^{-1}.

The influence of the initial Cu^{2+} concentration on the removal efficiency and the evaluation of the equilibrium adsorption capacity were examined under batch adsorption test. For this reason, 25 mL of Cu^{2+} solutions (pH 5.0) of different concentrations (100-500 mg/L) were stirred with 0.5 g/L of the Mg/FeGPHC during 24 h at room temperature (298±0.5 K), and 250 rpm. The content of Cu^{2+} in the resultant filtrates was measured using Atomic Absorption Spectrophotometer (AAS) (Analytic Jena Spekol 900T). The amounts of Cu^{2+} removed by tested Mg/FeGPHC were calculated by following equation:

$$q_{eq} = \left(\frac{C_0 - C_{eq}}{m} \right) xV \quad (1)$$

where C_0 and C_{eq} are the initial and equilibrium concentrations of the Cu^{2+} solution (mg/L); V represents the volume of the Cu^{2+} solution (L), m is the amount of adsorbent (Mg/FeGPHC) (g), respectively.

3. RESULTS AND DISCUSION

3.1 Spectroscopic assay

In order to gain insight into the involvement of functional groups on the Mg/FeGPHC surface, and therefore the reveal potential mechanism of Cu^{2+} ion removal, a spectroscopic analysis of the adsorbent material before and after adsorption was performed. The obtained results (Figure 1a.) reveal that Mg/FeGPHC showed the peaks common to hydrochars, which indicate an aromatic structure rich in oxygen functional groups. Thus, the FTIR diagrams of modified GP hydrochar display a broad peak at around 3300 cm^{-1}, attributed to stretching vibrations of hydroxyl and carboxyl groups, aromatic C=C at around 1590 cm^{-1}, band at around 1380 cm^{-1} corresponding to stretching vibrations of carboxylate $–CH_2$ or C-O, as well as correlated bands (1200 to 1000 cm^{-1}) attributed to stretching vibrations of aromatic and aliphatic C-O groups [2]. The peaks notable in spectral range from 750 to 500 cm^{-1} indicating the presence of MgO and FeO incorporated onto

the hydrochar surface during the modification process [6]. Obtained findings suggest that the Mg/FeGPHC display surface abundant with functional groups, which contribute to heavy metal removal.

As a result of Cu^{2+} ions adsorption, certain changes are notable through all spectral range. A broad intense peak that occurs at about 3300 cm^{-1} after adsorption shows a significant decrease in intensity. Similarly, the other bands notable on the FTIR spectrum become less pronounced and shifted to lower wavenumbers after the adsorption of Cu^{2+} ions. This observation indicates that the potential mechanisms responsible for metal ions binding include Cu-π reaction between aromatic groups of Mg/FeGPHC (C=C) and Cu^{2+} ions, surface complexation with oxygen-containing functional groups (-OH, C-O), as well as exchange with Mg and Fe ions.

3.2 Preliminary adsorption test

3.3 Isothermal study

Preliminary adsorption test reveal that modified hydrochar exhibited significantly higher adsorption capacity (71 mg/g) towards Cu^{2+} ions in comparison to unmodified (14 mg/g). In order to gain insight into the nature of the interaction between Cu^{2+} ions and modified Mg/FeGPHC surface, and to determine a theoretical maximum adsorption capacity, four isotherm models were applied to the experimental results [2,7].

The Langmuir isotherm model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

The Freundlich isotherm model:

$$q_e = K_F C_e^{1/n} \tag{3}$$

The Sips isotherm model:

$$q_e = q_m \frac{K_S C_e^{n_S}}{1 + K_S C_e^{n_S}} \tag{4}$$

and Redlich-Peterson (R-P) isotherm model:

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta}} \tag{5}$$

Where C_e represents the equilibrium concentration (mg/L), q_m is the maximum quantity of adsorbed Cu^{2+} ions (mg/g), K_L, K_F, K_S, and K_{RP} are model constants, 1/n adsorption intensity, n_S is the Sips model exponent, and a_{RP} (L/mg) represents the R-P equilibrium constant.

The obtained results are presented and summarized in Figure 1b, and Table 1.

Table 1- Parameters and determination coefficients of the isotherm models for Cu^{2+} removal

Models	Parameters	Value	Models	Parameters	Value
Langmuir	q_m (mg g^{-1})	83.28	Freundlich	K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	17.95
	K_L (L mg^{-1})	0.14		1/n	0.41
	R^2	0.9755		R^2	0.9828
Sips	q_m (mg g^{-1})	75.0	R-P	K_{RP} (L g^{-1})	35.54
	K_S (L mg^{-1})	0.14		a_{RP} (L mg^{-1})	1.23
	n_s	0.62		β	0.72
	R^2	0.9930		R^2	0.9900

Based on results of correlation coefficients (R^2) displayed in Table 1 can be concluded that the Sips isotherm model best described nature of the interaction. Thus, adsorption occurs as multi-layered adsorption on a heterogeneous surface. Furthermore, according to Sips isotherm model the maximum adsorption capacity (q_m) was 75 mg/g. In addition, summarized parameters from applied isothermal models (K_L<1, K_F>1, the 1/n, and n_s values are in range from 0 to 1, and β<1) suggesting that the removal of Cu^{2+} ions onto investigated material are favorable.

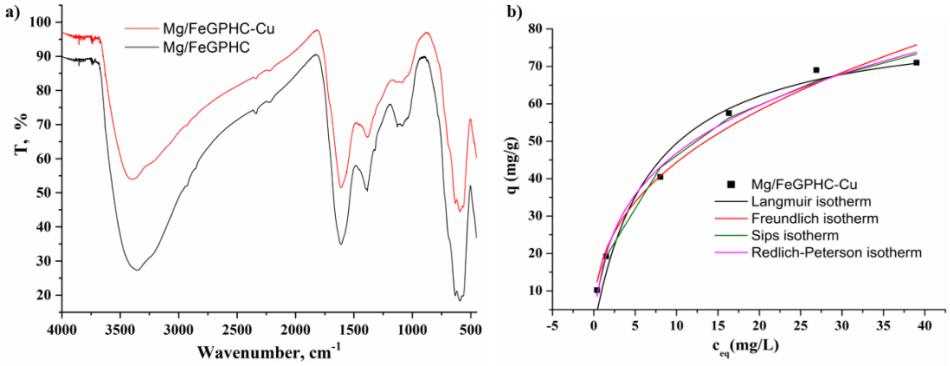

Figure 1- FTIR spectra (a) before and after adsorption onto Mg/FeGPHC, and applied isotherm models (b)

4. CONCLUSION

In this study, Mg/Fe doped grape pomace hydrochar was investigated as potential adsorbent of Cu^{2+} ions from aqueous solution. The prepared Mg/FeGPHC was subjected to spectroscopic analysis before and after adsorption, as well as isothermal study tests. Based on the results, oxygen-containing functional groups and aromatic functional groups from Mg/FeGPHC surface participate in the binding of Cu^{2+} ions from aqueous solutions, with maximum adsorption capacity of 75 mg/g. Moreover, removal of Cu^{2+} ions onto investigated material is favorable process.

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