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BIOSORPTION OF Cu^{2+} FROM AQUEOUS SOLUTION BY HYDROCHAR OF GRAPE POMACE

Jelena Petrović[1], Mirjana Stojanović[1], Jelena Milojković[1], Marija Petrović[1], Zorica Lopičić[1], Tatjana Šoštarić[1], Marija Mihajlović[1]*

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1. Introduction

Copper is one of the toxic metals commonly found in industrial effluents [1, 2]. Although low concentrations of copper are essential, its excessive levels in waters can be detrimental [3]. Conventional wastewater treatments such as chemical precipitation and reduction, filtration, flocculation, ion exchange, electrochemical treatment, are insufficiently selective, oftentimes polluting, expensive, and have various technical limitations especially at low concentrations of contaminants [4].

In recent years, increase of environmental awareness has resulted in the development of new, eco-friendly technologies for the removal of wastewater contaminants. One approach has been the use of different biological materials as adsorbents of pollutants from aqueous solutions [4-6]. Compared to the conventional methods, biosorption has numerous advantages: selectivity, low-price, high efficiency and sustainability [4]. Expended biomass can be regenerated, or subsequently reused in different ways. Also, the adsorption efficiency of biomass can be increased by physical, chemical, thermal or combined modifications [7-9].

Along with the biosorption, development of new methods for conversion of waste biomass, focused on design of novel multifunctional materials, become very attractive. One of such technologies is hydrothermal carbonization (HTC) [10-12]. HTC is a thermochemical process for converting of lignocellulosic feedstock into lignite-like product at elevated temperatures (180-280°C) and high pressure (2-10 MPa) in the presence of water [13]. The process converts all the carbon from biomass to the coal, with no methane or CO_2 release into the atmosphere [11]. Unlike gasification or pyrolysis, HTC does not require intensive and expensive pre-drying of raw material. The resulting product-hydrochar, created via reactions between subcritical water and lignocellulosic residues, is hydrophobic, porous, solid material with high carbon content [14]. So far, HTC has been utilized on a wide range of different feedstock [13-16].

One of raw materials that is highly suitable for HTC is grape pomace (GP), produced in the course of winemaking [13, 17]. According to the statistic, grape production in Serbia takes place on about 58,000 hectares, with a total annual production of about 430,000 tons of fruit [18]. However, up to 25% of the used amount of raw material, in form of pomace, remains after grape processing stored on permanent or makeshift dumps [18]. This waste biomass with a high water content (>60%), composed of grape seeds, skins, and stems, due to degradation of organic matter, drainage and evaporation, has a negative impact on the environment. Therefore, appropriate utilization of GP is necessary.

The aim of this research was to investigate the ability of GP hydrochar (HC-GP) to remove copper ions (Cu^{2+}) from aqueous solution, simulating wastewater with low toxic metal concentrations. Particular interest of this study was to evaluate the suitability of GP as a precursor for preparation of adsorbent, because this type of biomass is largely available in Serbia. The effect of sample dose on Cu^{2+} sorption for the adsorbent prepared from the GP using HTC was determined using different initial metal concentrations. Equilibrium sorption isotherms were assessed together with the modeling of the obtained experimental results. Binding mechanism of copper for HC-GP surface was implied using FTIR spectroscopy.

2. Material and Methods

2.1 Biomass

The used GP was randomly collected from landfill sites, which have left behind after processing of red grape grown on a test plot Radmilovac, property of the Faculty of Agriculture in Belgrade, Serbia. Biomass was air-dried to constant weight and grinded in order to obtain homogeneity of samples. Grinded material was sieved and fraction size of 0.5 mm was used in further HTC experiments.

2.2 HTC experiment

Preparation of HC-GP at 220°C we have previously described elsewhere [13]. Briefly, 250 g of selected GP was carbonized in 2000 mL autoclave (Model 10253, Deutsch & Neumann), at 220°C within one hour. After cooling of the reactor to room temperature, HTC process streams (solid HC and process water) were divided by filtration. Obtained HC-GP was rinsed several times with distilled water and dried at 105°C in the oven. Sorption experiments were performed with HC-GP particle size between 0.1 and 0.5 mm.

2.3 Chemicals

Copper solutions and standards were prepared using analytical grade copper nitrate salt ($Cu(NO_3)_2$, Sigma-Aldrich). A stock copper nitrate solution (1mM $Cu(NO_3)_2$ x $3H_2O$) was prepared with deionized water. The copper (II) solutions of varying concentrations were prepared by diluting the stock solution with deionized water.

2.4 Batch adsorption experiments

The sorption tests were conducted by contacting weighed amounts of HC-GP samples (0.01-0.05 g) and 50 ml of copper ion solutions of different initial concentrations (0.1, 0.5 and 1mM) placed in 100 ml glass flasks. Erlenmeyer flasks were then located on orbital shaker (Heidolph, model Unimax 1010) and shaken at room temperature (25±0.5 °C) for 180 min at 250 rpm. The pH value of all solutions was adjusted to pH 5, using 0.1 M KOH and/or 0.1 M HNO_3 solutions. The pH value was selected based on reported results indicating that the highest sorption of copper ions has been attained at pH 5 [4]. The pH was monitored using SensION MM340, Hach pH meter, with integrated magnetic stirrer. All experiments were performed in duplicates and average values of obtained results were shown. The concentration of copper ions was determined using atomic adsorption spectrometry (AAS) (Perkin Elmer Analyst 300).

Equilibrium isotherms for Cu^{2+} were obtained using sample dose of 0.5 g L^{-1} HC-GP in a range of initial metal concentrations between 0.001-1 mM. The general procedure depicted above was followed, applying the same experimental conditions. The suspensions were stirred for 120 min to attain equilibrium.

The amount of metal adsorbed by the HC-GP was calculated using Eq. (1):

$$q = \frac{V(C_i - C_e)}{m} \quad (1)$$

where sorption capacity, q, is the amount of metal adsorbed by adsorbent (mmol g^{-1}), C_i and C_e are the initial and equilibrium metal concentrations (mmol L^{-1}), V is the volume of metal solution (L) and m is the mass of the adsorbent (g).

Metal removal efficiency (%) was calculated from Eq. (2):

$$R = \frac{C_i - C_e}{C_i} x100 \quad (2)$$

Non-linear fitting method using Origin 9.0 software was employed to investigate applied isotherm models.

2.5 FTIR spectroscopy

FTIR analysis of samples before and after adsorption was performed in transmission mode using Thermo Scientific Nicolet iS50. The spectra were obtained in the spectral range of 4000-400 cm^{-1}.

3. Results and discussion

3.1 Effect of hydrochar dose on biosorption

The dose response for Cu^{2+} was studied by varying amount of HC-GP from 0.2 to 1 g L^{-1} at different initial metal concentrations (0.1, 0.5 and 1 mM) (Fig. 1). Sorption experiment was performed at constant pH 5, since at pH values higher than 6.1, precipitations of metal hydroxides occurs [19]. Also, the pH value of the zero-point charge for HC-GP of 4.5 (data not shown), indicate that the repulsion of positively charged metal ions at lower pH values might take place together with a possible competition with hydrogen ions towards active sites [19].

Fig. 1 clearly shows that regardless of the initial metal concentration, HC-GP removes up to 85% of Cu^{2+} from the solution. As it was expected, at constant initial concentration of Cu^{2+}, increasing of the sample dose up to 0.5 g L^{-1} provides a greater surface area and number of available sorption sites for metal ions uptake. Increase of dose above this threshold did not increase the percentage of Cu^{2+} removal, and thus dose of 0.5 g L^{-1} of adsorbent was chosen for further experiments.

<Figure 1>

3.2 Effect of contact time

The effect of contact time was studied using selected dose of HC-GP (0.5 g L^{-1}) and initial Cu^{2+} concentration of 1 mmol L^{-1} at constant pH 5.0 and contact time up to 180 min (Fig. 2). Contact time of 90 min was enough to reach equilibrium. Therefore, in order to ensure sorption equilibrium, the contact time of 120 min was chosen in further experiments. Copper adsorption capacity of 0.206 mmol g^{-1}, indicated efficient removal of Cu^{2+} from water solution by HC-GP.

<Figure 2>

3.3 Equilibrium isotherm models

In this study, Langmuir and Freudlich isotherm models were applied for analyzing the Cu^{2+} adsorption process on HC-GP surface in accordance to the obtained experimental data.

The Langmuir isotherm model, based on the assumption of a monolayer adsorption process onto a homogeneous surface, is represented by the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where the C_e is the equilibrium concentration (mmol L^{-1}), q_m is the maximum amounts of Cu^{2+} ion adsorbed on the HC (mmol g^{-1}) and K_L is the Langmuir constant (L $mmol^{-1}$), related to the affinity of the binding sites [20].

The Freundlich isotherm model that assumes a heterogeneous sorption surface with different sites energies can be expressed in non-linear form as:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where q_e, represents the amount of the adsorbate per unit weight of the adsorbent (mmol g^{-1}), K_F the Freundlich constant, ($L^{1/n}$ $mmol^{1-1/n}$ g^{-1}), C_e the equilibrium Cu^{2+} concentration in the solution (mmol L^{-1}) and 1/n, the adsorption intensity (Freundlich parameter) [21]. Both applied isotherm curves are shown in Fig. 3.

< Figure 3 >

According to the values of the resulted correlation coefficients R^2, the Langmuir isotherm (R^2=0.999) gave slightly better description of the experimental data than the Freundlich isotherm model (R^2 = 0.998), with a maximum adsorption capacity for Cu^{2+} of 0.211 mmol g^{-1}. Adsorption isotherm parameters for Cu^{2+} are given in Table 1.

<Table 1>

3.4 FTIR analysis

The FTIR spectra of analyzed HC-GP samples before and after adsorption of copper ions are presented in relevant spectral regions (3700-2800 cm^{-1} and 1850-500 cm^{-1}) in Fig. 4. Detailed spectroscopic analysis of the used HC-GP was given elsewhere [13].

Binding of copper for HC surface resulted in a reduction of the O-H stretching band intensity (3346 cm^{-1}) and its shift to higher wavenumbers. This may be ascribed to the complexation between the oxygen-containing functional groups on HC surface and metal ions [22]. Also, notable weakening of aromatic C-H band at 783 cm^{-1} and slightly decrease of peaks at 1613 cm^{-1} and 1515 cm^{-1} (attributed to C=C stretching of aromatic rings) after interaction with Cu^{2+}, may indicate the formation of coordination bonds between the d-electron of copper and π -electron of C=C bond of aromatic rings [22, 23].

<Figure 4>

4. Conclusion

Hydrochar produced by HTC from grape pomace have been studied as an adsorbent of Cu^{2+} from aqueous solutions. Resulted copper adsorption capacity of 0.206 mmol g^{-1}, indicated efficient copper removal using HC-GP. The sorption isotherms of Cu^{2+} onto HC-GP were well described by the Langmuir model, with a maximum theoretical adsorption capacity for Cu^{2+} of 0.211 mmol g^{-1}. The differences in FTIR spectra of HC-GP samples before and after adsorption of copper ions seem to correlate well with the proposed mechanisms of metal binding for the oxygen-containing functional groups present on HC surface. Our findings suggest that the GP is a promising precursor for production of quality adsorbents for copper removal from wastewaters using HTC.

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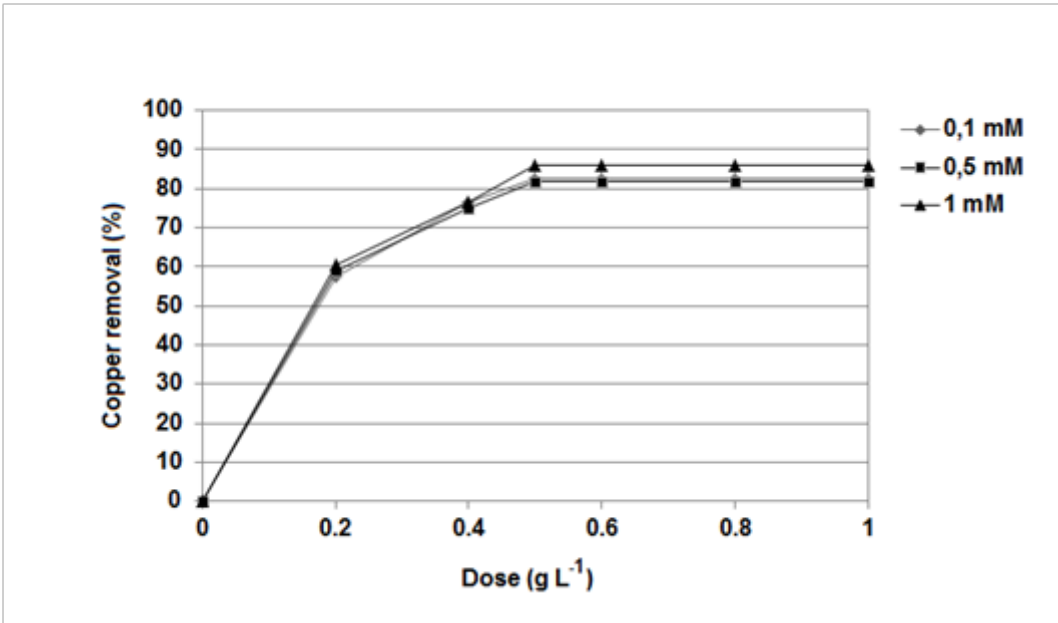

Figure 1. Effect of the HC-GP dose on the equilibrium sorption of copper at different initial metal concentrations (pH=5.0, T=25°C, t=180 min).

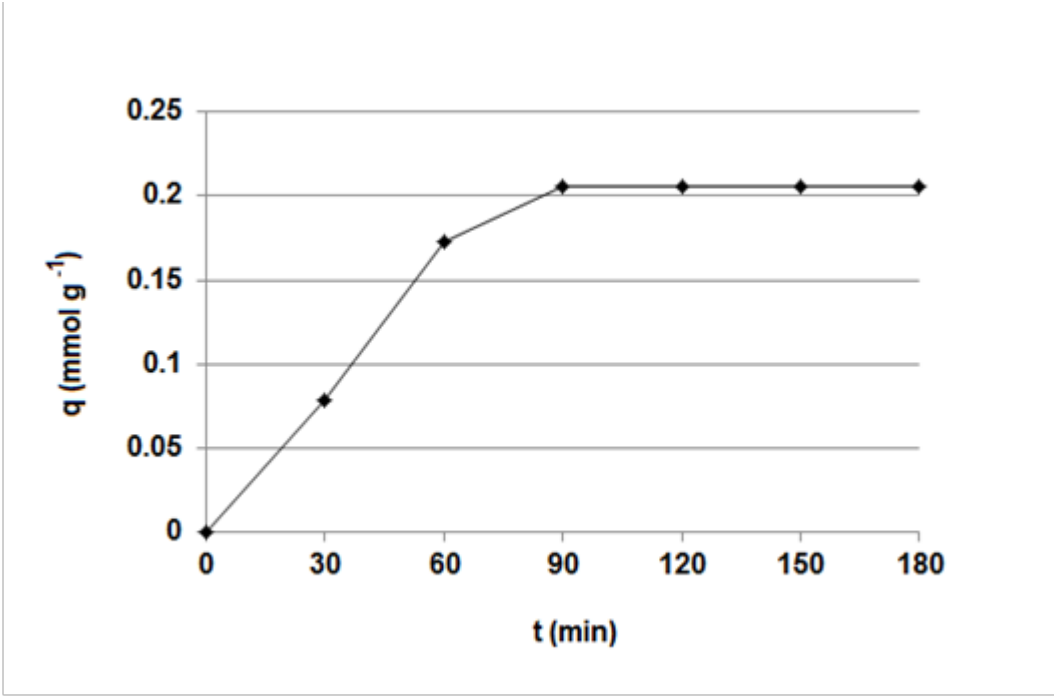

Figure 2. Effect of contact time on adsorption of copper by HC-GP (pH=5.0, sorbent dose 0.5 g L^{-1}, initial metal concentration 1mM, T=25°C).

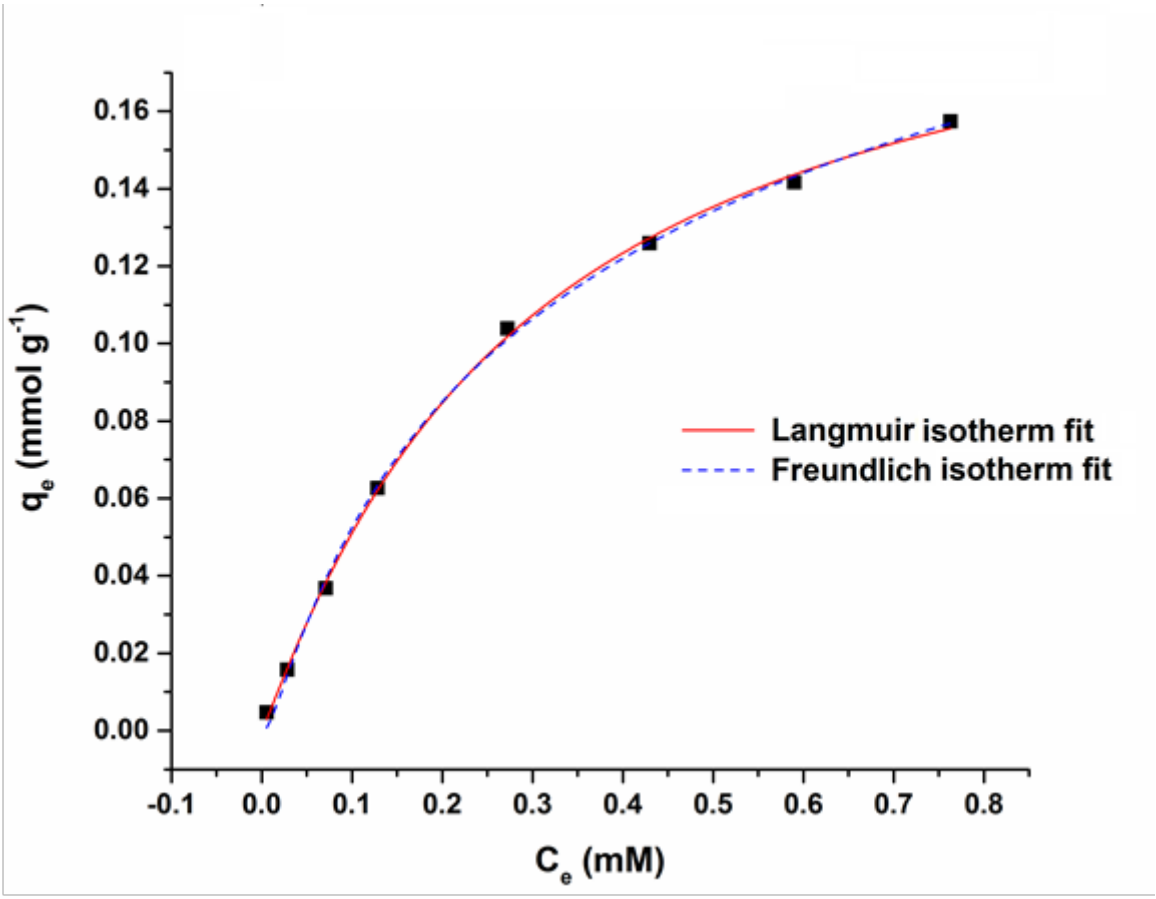

Figure 3. Adsorption isotherms of Cu^{2+} onto HC-GP (pH=5.0, sorbent dose 0.5 g L^{-1} T=25°C, t=120 min)

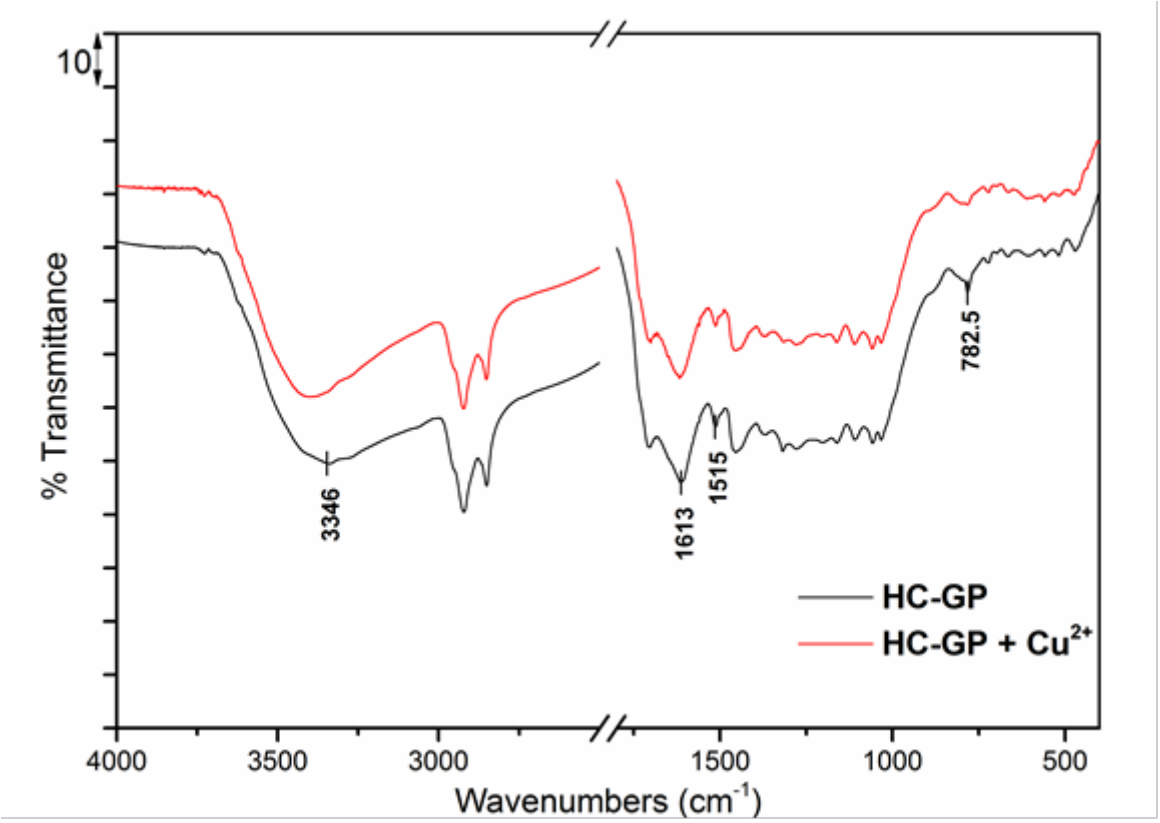

Figure 4. FTIR spectra of HC-GP before and after adsorption of copper (pH=5.0, sorbent dose 0.5 g L^{-1}, C_e= 0.206 mM, T=25°C, t=120 min)

Table 1. Calculated parameters of applied isotherm models for copper biosorption by HC-GP

Langmuir	*Freundlich*
q_{max} = 0.211 mmol g^{-1}	K_F = 0.171 $L^{1/n}$ $mmol^{1-1/n}$ g^{-1}
K_L = 3.77 L $mmol^{-1}$	1/*n* = 0.294
R^2 = 0.999	R^2 = 0.998