

Copper(II) Removal from Aqueous Solution by Organosolv Lignin and Its Recovery

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ABSTRACT: In this study the removal of Cu(II) ions from aqueous solution was performed at different concentrations, temperatures, and pHs using ethanol-based organosolv lignin as the adsorbent. The results indicated that the amount of Cu(II) ions adsorbed onto the lignin increased with increasing concentration and pH; however, it decreased with an increase in temperature. It was possible to remove 40.74% (maximum removal) of Cu(II) ions from aqueous solution by using organosolv lignin within 10 min under certain conditions (3×10^{-4} M and 20°C). The adsorption process was

determined to be consistent with the Freundlich isotherm. Furthermore, it was found that 40% (maximum recovery) of the Cu(II) ions adsorbed on the organosolv lignin could be recovered using HCl with an initial concentration of 3×10^{-4} M and a contact time of 10 min. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1537–1541, 2003

Key words: organosolv lignin; ethanol; adsorption; Cu(II) ions; isotherm, metal recovery

INTRODUCTION

Potential sources of toxic copper metal ions are, essentially, the industrial waste streams of metal-cleaning and -plating baths; mills employing pulp, paper, paperboard, and wood preservatives, the fertilizer industry, and so forth.^{1,2} When there is excessive intake of copper (more than 1.0 mg/L in drinking water) by humans and animals, it is accumulated in the liver, which results in hemochromatosis and gastrointestinal catarrh disease. When available, copper is especially toxic to fish, even in small quantities in natural water.³

The most common methods for removing heavy metal ions from municipal and industrial waste streams involve ion exchange and adsorption.⁴ Even though the efficient removal of heavy metals can be successful via their adsorption onto activated carbons, adsorption is not a suitable method for developing countries.^{5–7} Therefore, experiments have been conducted worldwide in order to find cheap, readily available, and effective sorbents for the removal of heavy metal ions using various raw materials from the plant kingdom^{4,8–14} and other inorganics.^{1,2,15–18} For binding heavy metal ions, appreciable results have

been obtained by applying sorbents with a high content of polyphenols such as lignin, tannin, and humic acid.¹⁹ Although lignin is a natural polymer and does not have significant selectivity for magnesium and sodium, its adsorption capacity for heavy metals is very high,²⁰ a result of its negatively charged surface. Moreover, it is believed that metal cation removal via lignin is related mainly to the activity of phenolic hydroxyl groups.

Lignin is known to adsorb many toxic heavy metal ions, and its molecules are very large and complex, constituting about 20% of green plants and consisting of hundreds of interlinked phenolic ring subunits, most of which are phenylpropanelike structures with various methoxyl ($-\text{OCH}_3$) and hydroxyl ($-\text{OH}$) groups attached.²¹ The well-known industrial lignin, the so-called kraft lignin, and lignosulfonate have been largely produced from the pulp and paper industries and rejected into streams and rivers as waste byproducts.²² Every year about 50 million tons are accumulated.²²

Low-molecular-weight organosolv lignin (produced through delignification of wood and other lignocelluloses in organic solvents such as methanol, butanol, and ethanol) has been found to be quite similar to natural lignin but to be a more attractive polymer because it does not contain sulfur^{22,23} and therefore is considered an environmentally friendly and cheap industrial byproduct. The phenolic monomers (about 12%, based on total lignin) obtained by nitrobenzene

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oxidation of ethanol-type organosolv lignin under acidic conditions are syringic acid, vanillic acid, vanillin, syringylaldehyde, *p*-cumaric acid, ferulic acid, *p*-hydroxybenzaldehyde, gallic acid, and protocatechuic acid, which are all effective compounds in the adsorption process.²³ Organosolv lignin has also been reported to have a lower polysaccharide content (4%–5%).²²

So far, kraft lignin as well as hydrolysis lignin and modified hydrolysis lignin have been used for the removal of heavy metal ions.²³ However, no study in the literature has been found in which the use of organosolv lignin (natural) was associated with being a remover of metal ions from aqueous solutions. Therefore, in this research, the aim was to investigate the removal of Cu(II) ions through ethanol-based organosolv lignin and their recovery.

EXPERIMENTAL

Materials

Organosolv lignin, which was obtained as described below (15% moisture content, 100 mesh), was used as adsorbent for the removal of Cu(II) ions from aqueous solution. Cu(II) stock solutions were prepared from an analytical-grade sulfate salt: copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). In preparing the aqueous solution of the cation, distilled water was used. Moreover, diluted sulfuric acid was used to adjust the pH values of the aqueous solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with a pH meter (WTW pH Meter 320, Germany).

Preparation of organosolv lignin

The wood chips (20 g; 12% moisture content) of black poplar (*Populus nigra* L.), an ethanol–water mixture [800 mL; 60:40 (v/v)], and 0.02N H_2SO_4 (as a catalyst; 0.2%, based on the solvent mixture) were refluxed at 75°C for 2 h. The mixture thus obtained was diluted with water and filtered. After refluxing the pulp containing the solution above was washed with the corresponding organic solvent [60:40 (v/v)] and eventually washed with distilled water. The filtrate was concentrated under reduced pressure at 40°C. The lignin (dark brown color) that remained in the black liquor was precipitated by diluted HCl and then dried in an oven at 40°C for 24 h.

Batch adsorption

Batch adsorption experiments were conducted using 0.25 g of organosolv lignin with 35 mL of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ aqueous solution in 250-mL Erlenmeyer flasks at various concentrations, temperatures, and pHs. The samples were shaken at a constant rate of 125 rpm in a water bath equipped with a temperature controller.

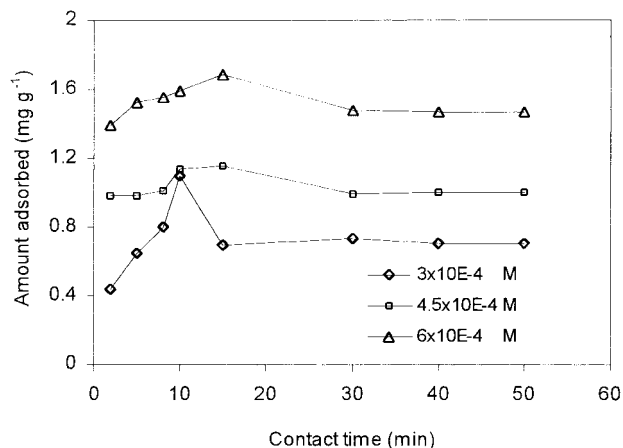


Figure 1 Effect of initial adsorbate concentrations on the adsorption of Cu(II) ions onto organosolv lignin at 20°C.

After reaching the desired contact time, suspensions were filtered by filter paper (Selecta filter, 589²; Weißband, Germany). The filtrate was analyzed for Cu(II) ions by using an atomic absorption spectrometer (Perkin–Elmer spectrometer 3110). Blank solutions without cations were used for each series of experiments. The amounts of Cu(II) adsorbed onto organosolv lignin were calculated by subtracting both concentration of Cu(II) ions adsorbed onto the filter paper used here and the final solution concentration from the initial concentrations of aqueous solutions. For each adsorption process the average of two replicates is reported.

RESULTS AND DISCUSSION

Effect of initial concentration

Figure 1 shows the adsorption of Cu(II) ions onto organosolv lignin for different initial concentrations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from 3×10^{-4} M to 6×10^{-4} M at 30°C and pH 5.5 as a function of contact time. The absolute amount of Cu(II) ions adsorbed by organosolv lignin first increased when increasing the treatment time from 2 min to about 10 min, then desorption of some of the copper ions adsorbed occurred, and finally the amount of copper(II) ions adsorbed on organosolv lignin became constant. It can also be seen in Figure 1 that the adsorption processes reached equilibrium at a contact time of about 40 min for all concentrations studied. With a change in the initial concentration of the aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from 3×10^{-4} M to 6×10^{-4} M, the absolute amount of Cu(II) ions adsorbed per unit of the adsorbent obviously increased. For example, the maximum amount of Cu(II) ions adsorbed rises from 1.10 mg/g (40.74% removal) to 1.683 mg/g (29.33% removal) at a temperature of 20°C. As can be seen in Figure 2, this can also be observed on the adsorption isotherm of the amount of

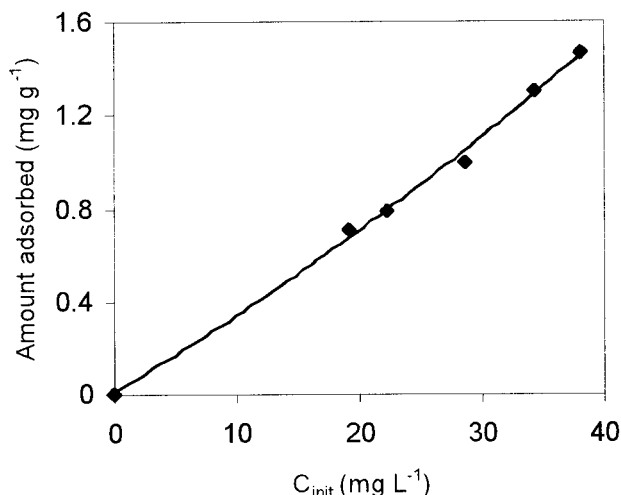


Figure 2 Adsorption isotherm of the amount of Cu(II) ions adsorbed versus the initial concentrations of Cu(II) at 20°C.

Cu(II) ions adsorbed versus the initial concentration of the metal ions used.

However, the percent removal of Cu(II) ions via organosolv lignin shows a decrease with an increase in the initial concentration of the copper solution. This is consistent with previous studies on the removal of heavy metals by using various adsorbents, such as fly ash,¹ wollastonite,² cellulose,⁸ and bentonite,²⁴ for Cu(II) ions.

Effect of temperature

Figure 3 presents the effect of temperature on adsorption for the initial concentration of 3×10^{-4} M as a function of contact time. It is obvious from Figure 3 that the maximum amount of Cu(II) ions adsorbed significantly decreased when increasing temperature from 20°C to 50°C. That is, the maximum amount and percentage of Cu(II) ions adsorbed onto organosolv

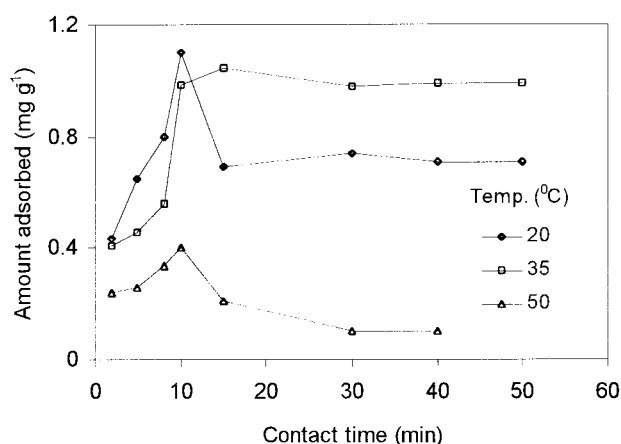


Figure 3 Effect of temperature on the adsorption of Cu(II) ions onto organosolv lignin for a concentration of 3×10^{-4} M.

TABLE I
pH Values after Adsorption for Different Concentrations at 20°C

Contact time (min)	pH ^a		
	3×10^{-4} M	4.5×10^{-4} M	6×10^{-4} M
2	4.42	3.84	3.94
5	4.31	3.80	3.89
10	4.17	3.74	3.82
15	3.90	3.77	3.86
30	3.78	3.82	4.07
40	3.90	3.79	3.92

^a pH of initial solution of aqueous CuSO₄ · 5H₂O was 5.5 and pH of organosolv lignin in water was 4.63.

lignin went down from 1.10 mg/g (40.74% removal) to 0.40 mg/g (14.83% removal) when the temperature changed from 20°C to 50°C. As with the effect of concentration on adsorption (see Fig. 1), after maximum adsorption, some copper ions adsorbed had a tendency to escape from the surface of lignin to the solution medium at all temperatures. This can be explained by the pH dropping during the adsorption process (as shown in Table I) and weak van der Waals binding of Cu(II) ions on the active sites of the lignin.

Effect of pH

Metal removal by adsorption is usually dependent on the pH of a solution because of its remarkable effect on the surface of the adsorbent. In this study, in the experiments on Cu(II) removal, the maximum pH was kept at 5.5 because various hydrolyzed copper species such as Cu₂(OH)₂²⁺, Cu₂(OH)₂⁰, and Cu(OH)⁺ are formed at pH values greater than 5.5.^{1,2,7,14,16} The relationship between pH and the percentage of Cu(II) ions adsorbed on the organosolv lignin for an initial concentration of 3×10^{-4} M at 20°C is given in Figure 4. It is clear from this figure that the amount of Cu(II) ions adsorbed steadily increased from 0.081 mg/g (2.97% removal) to 1.10 mg/g (40.74% removal) per unit of the adsorbent when the pH value was increasing from 3.5 to 5.5. Also, no adsorption was found below a pH of 3.5.

Moreover, as can be seen from Table I, it is obvious that pH values of samples decrease during the course of the adsorption at 20°C for all the initial concentrations as a function of time. For instance, as average, a 23% decrease in pH is determined for all the adsorption conditions studied. The reason of this decrease has not been exactly known. However, this phenomenon may be attributed to the removal of protons from phenolic hydroxyl sites on lignin, which may form copper-lignin complexes.²⁵

Analysis of adsorption isotherm

To determine the adsorption capacity, the experimental data points were fitted to Langmuir and Freundlich

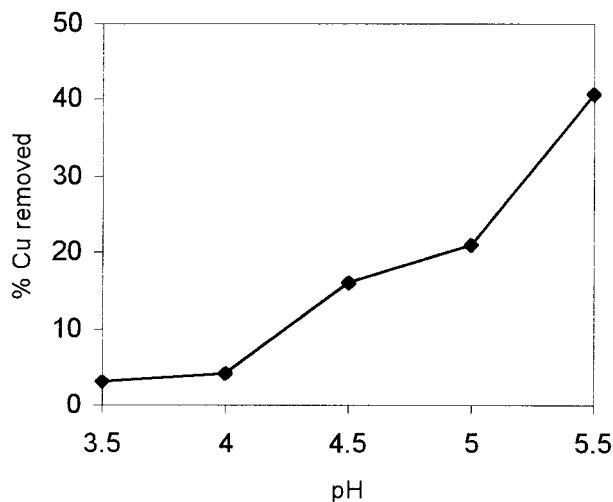


Figure 4 Effect of pH on the adsorption of Cu(II) ions onto organosolv lignin for $3 \times 10^{-4} M$ and $20^{\circ}C$.

equations. It was determined that the adsorption of Cu(II) ions from the aqueous solution onto the lignin complied with the Freundlich isotherm; however, it did not comply with the Langmuir adsorption isotherm. This phenomenon suggests that the adsorption isotherm has no plateau. Thus, it can be said that no formation exists on a full monolayer of Cu(II) ions covering the surface of the lignin.

The Freundlich adsorption isotherm at $20^{\circ}C$ is shown in Figure 5, and its equation is expressed as

$$\ln x/m = \ln k + 1/n \ln C_e \quad (1)$$

where x/m is the amount of metal ions adsorbed per unit weight of the adsorbent (mg/g), C_e is the equilibrium concentration of metal ions in solution (mg/L), and k (mg/g) and n (g/L) are Freundlich constants.

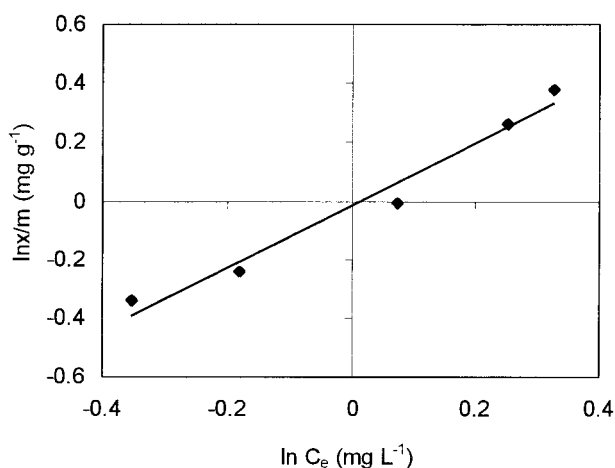


Figure 5 Freundlich isotherm of Cu(II) adsorption at $20^{\circ}C$ ($r^2 = 0.97$).

TABLE II
Recovery Percentage of Cu(II) Ions Adsorbed onto Organosolv Lignin

Contact time (min)	Recovery (%)		
	$3 \times 10^{-4} M$	$4.5 \times 10^{-4} M$	$6 \times 10^{-4} M$
2	34.08	38.30	15.32
10	29.05	21.44	14.93
40	18.01	18.20	5.37

The values of k and n were calculated from the slope and intercept of the plot of $\ln x/m$ versus $\ln C_e$. The constant values (k and n) for the Freundlich isotherm at $20^{\circ}C$ were determined to be 0.982 (mg/g) and 0.933 (g/L), respectively.

Copper recovery from organosolv lignin

After the adsorption experiment with the initial concentrations of solution of $3 \times 10^{-4} M$, $4.5 \times 10^{-4} M$, and $6 \times 10^{-4} M$ at $20^{\circ}C$, a certain quantity of sediments remaining on the filter paper was mixed with 10 mL of 0.1M HCl for 15 min using a magnetic stirrer.¹⁴ The samples were then centrifuged for 10 min, and supernatants were analyzed to determine the quantities of copper recovered by the AAS.

Table II presents the recovery percentage of the copper ions adsorbed onto organosolv lignin for all the initial concentrations studied as a function of three contact times: 2, 10, and 40 min. It is possible to recover the Cu(II) ions from Cu(II)-bearing organosolv lignin with a 10-min contact of 40.0%, 16.7%, and 8.5% 0.1M HCl for the $3 \times 10^{-4} M$, $4.5 \times 10^{-4} M$, and $6 \times 10^{-4} M$, respectively.

In addition, as can be seen in Table II, the recovery percentage decreased with an increasing initial concentration of copper solution for all the contact times. This could be explained by the greater penetration and fixation probability of Cu(II) ions onto organosolv lignin at higher initial concentrations. This was also confirmed by the greater decreases in pH values at higher initial concentrations, which was evident for a higher ion-exchange capacity (see Table I). Therefore, as is also clear from Table II, the recovery percentage of Cu(II) ions increased as the Cu(II) absorbed per unit weight of the lignin decreased.

CONCLUSIONS

It was found that the amount of Cu(II) ions adsorbed onto the organosolv lignin decreased with temperature and increased with increasing concentration and pH. Using the organosolv lignin, 40.74% of Cu(II) ions were removed from the aqueous solution. The adsorption process was found to comply with the Freundlich isotherm. Also, it was found that 40% (maximum re-

covery) of the Cu(II) ions adsorbed on the organosolv lignin could be recovered using HCl.

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