Adsorption of copper (II) ions to peanut hulls and *Pinus brutia* sawdust

H. Duygu Özsoy*, Halil Kumbur and Zafer Özer

Engineering Faculty, Department of Environmental Engineering, 33360, Mersin University, Turkey
Fax: 90 324 361 00 99 E-mail: ozsoyhd@mersin.edu.tr
*Corresponding author

Abstract: Adsorption of copper (II) ions to untreated peanut hulls and untreated *Pinus brutia* sawdust was investigated as a function of the contact time, amount of adsorbents, initial pH, temperature and initial metal ion concentration. Adsorption efficiency was increased by increasing contact time, amount of adsorbents and decreasing initial metal ion concentration. The optimum adsorption conditions were obtained at pH 5.0. Experimental results indicate that peanut hulls are a more effective adsorbent than *Pinus brutia* sawdust for the removal of Cu (II) from aqueous solutions. The isothermal data of peanut hulls could be well described by the Langmuir and Freundlich equations.

Keywords: adsorption; copper (II) ions; peanut hulls; *Pinus brutia* sawdust.


Biographical notes: H. Duygu Özsoy is a Research Assistant and her research interests are heavy metal and dye removal from industrial wastewaters, adsorption studies, biotechnology treatment with fungi and bacteria) and noise pollution. She has been a PhD student at University of Mersin, Faculty of Engineering, Department of Environmental Engineering since 2001 and the project entitled *Removal of Chromium Ions from Aqueous Solutions with Agricultural Residues*. She received her MS Degree from the University of Mersin, Faculty of Engineering, Department of Environmental Engineering with *Decolorisation of Textile Industry Wastewaters by White Rot Fungi* project in 2001. She received her Bachelor’s Degree from the University of Mersin, Faculty of Engineering, Department of Environmental Engineering in 1997 and her project title was *Biodegradation of Orgaprin 2R which is a Textile Dye by White Rot Fungi Phanerochaete chrysoseporium*.

Halil Kumbur is one of the Professors of Mersin University, Engineering Faculty, Department of Environmental Engineering. His research interests are GIS, water and wastewater treatment systems, noise pollution, heavy metal and pesticide residue analysis. Since 1978–1982 he received his PhD Degree from the University of Ankara, Faculty of Science, Department of Chemical Engineering and his MS Degree from the University of Ankara, Faculty of Science, Department of Chemical Engineering since 1977–1978. Since 1973–1977 he received his Bachelor’s Degree from the University of Ankara, Faculty of Science, Department of Chemical Engineering.
1 Introduction

Heavy metal pollution is spreading throughout the world with the expansion of industrial and agricultural activities; copper is known to be a commonly used heavy metal. Although copper is an essential element for many living organisms, it is very harmful when it is discharged in high concentrations into natural water resources. Finally, it may pose a serious health hazard (Öztürk et al., 2004).

The toxicity of copper in living organisms has been comprehensively investigated by some researchers (Vinot and Pihan, 2005; Utgikar et al., 2004). No chronic copper poisoning has been described in humans. Acute copper poisoning after ingestion may show systemic effects such as haemolysis, liver and kidney damage, and fever with influenza syndrome. Local effects include irritation of upper respiratory tract, gastrointestinal disturbance with vomiting and diarrhoea and a form of contact dermatitis (Rengaraj et al., 2004). Therefore, treatment of copper containing wastewaters before they are discharged into water streams is necessary.

The potential sources of copper containing wastewaters are metal cleaning and plating baths, pulp, paper board mills, wood pulp production, the fertiliser industry, etc. The conventional methods used for treatment of wastewaters containing copper (II) ions are precipitation, ion exchange, electrolysis, adsorption on activated carbon, etc. (Monahar et al., 2002; Ho, 2003). Because the activated carbon is expensive, alternative low cost sorbents have been investigated. Low cost sorbents are defined as ones, which are abundant in nature, or they are byproducts or waste materials from any other industry. Some researchers reported that the agricultural byproducts such as peat (Ma and Tobin, 2004), pine bark (Hanzlik et al., 2004), sawdust (Garg et al., 2004), banana pith (Kadirvelu et al., 2003) have been widely investigated for metal removal from wastewaters. Previous studies have also shown that heavy metals have bined to peanut hulls, sawdust and to other agricultural materials. Various chemical treatments of agricultural materials might improve the heavy metal binding capacity of these materials. However, chemical treatments increase the cost of removal process.

The aim of the present study was to investigate the adsorption of copper (II) ions to the untreated agricultural byproducts such as peanut hulls and residues of the timber industry Pinus brutia sawdust. In order to achieve our objectives the effects of contact time, initial pH, initial metal ion concentration, temperature and different amounts of adsorbent were investigated.
2 Materials and methods

2.1 Materials

The peanut hulls and Pinus brutia sawdust used in this study were supplied from Mersin City, Turkey. Raw peanut hulls and Pinus brutia sawdust were washed with about 2L of distilled water and dried in an oven for 24 h at 105°C. Materials were ground into appropriate particle size using a mill and then sieved through a US standard 14 mesh sieve.

2.2 Chemicals

The stock solution of copper (II) was prepared in 1.0 g/l concentration using CuSO₄·5H₂O purchased from Merck and then diluted with distilled water to appropriate concentrations. HNO₃ and NaOH were obtained from Merck.

2.3 Experimental

The effects of contact time, initial pH, initial metal ion concentration, temperature and different amounts of adsorbent were investigated. To optimise the contact time, it was varied from 24 h to 168 h while other experimental conditions were kept constant (copper solution concentration 100 mg/l, amount of adsorbent 10 g/l, pH 5.0, 30°C). The effect of the pH on the Cu (II) adsorption was studied at different pH values (2.0–7.0), at constant copper solution concentration (100 mg/l), amount of adsorbent (10 g/l) and temperature (30°C). For the determination of the effects of initial copper concentration, 20–100 mg/l solution concentrations were studied at pH 5.0, 30°C and 10 g/l adsorbent. Temperature effect experiments were performed using 100 mg/l Cu (II) ion solution and 10 g/l adsorbent. The temperature was varied from 20°C to 50°C and pH was 5.0. To determine the effect of amounts of adsorbent on adsorption of Cu (II) ions, 1–10 g/l adsorbent was used and other experimental conditions were fixed (copper solution concentration 100 mg/l, pH 5.0, 30°C).

Adsorption studies were performed in 250 ml erlenmeyer flasks by addition of adsorbent (peanut hulls, sawdust) to 100 ml of copper solutions. The pH was adjusted with 1 M HNO₃ and 1 M NaOH before the addition of adsorbents. In all experiments, the flasks were shaken at 150 rpm on a rotary shaker. Contact time was 24 h except for the contact time experiments. After shaking, samples were filtered and the final metal concentration of the filtrate was determined by flame atomic absorption spectrometry (Perkin Elmer A Analyst 700 Atomic Absorption Spectrophotometer). The same procedure was applied for different amounts of adsorbent added to 100 ml of distilled water. They served as a control (blank). All experiments were performed in triplicate.

The amount of adsorbed copper at equilibrium, \( q_{eq} \) (mg/g) and the efficiency of adsorption (%) were calculated as follows (Ozer et al., 2004):

\[
q_{eq} = \frac{[(C_o - C_{eq})V]}{X}.
\]
Efficiency of adsorption

\[
\text{Efficiency} = \left(\frac{C_o - C}{C_o}\right) \times 100
\]  

(2)

where \(C_o\) and \(C_{eq}\) are the initial and equilibrium concentrations of copper (mg/l), \(V\) is volume of the solution, \(x\) is the weight of the sorbent (g) and \(C\) is the concentration of copper in the solution at the end of adsorption.

The Langmuir isotherm was used to describe observed sorption phenomena. The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules (Yu et al., 2001). For a single solute, it is calculated as:

\[
\frac{x}{m} = \frac{q_{\text{max}} b C_{eq}}{1 + b C_{eq}}
\]

(3)

The linear form of the equation can be written as

\[
\frac{C_{eq}}{q_{eq}} = \frac{1}{b q_{\text{max}}} + \frac{C_{eq}}{q_{\text{max}}}
\]

(4)

where \(C_{eq}\) is the equilibrium concentration of copper, \(q_{eq}\) is the amount of adsorption at equilibrium, \(q_{\text{max}}\) is the monolayer capacity, and \(b\) is an equilibrium constant of Langmuir.

The Freundlich isotherm (empirical model adsorption in aqueous systems) was also tested with our experimental data. This isotherm is shown in the following equation;

\[
\frac{x}{m} = K_f C_{eq}^{1/n}
\]

(5)

The linear form of the equation can be written as

\[
\ln q_{eq} = \ln K_f + \frac{1}{n} \ln C_{eq}
\]

(6)

where \(K_f\) is the measure of sorption capacity, \(1/n\) is sorption intensity.

3 Results and discussion

3.1 The effects of the contact time

The effects of contact time on adsorption of copper (II) ions (100 mg/l) to the peanut hulls and \textit{Pinus brutia} sawdust are presented in Figure 1. The efficiency of adsorption was increased for both adsorbents with increasing contact time from 24 h to 168 h. The blank samples were below the limit of detection 0.077 mg/l. Experimental data indicated that after 24 h, 79\% of Cu (II) was removed by peanut hulls and 32\% by \textit{Pinus brutia} sawdust. After seven days, Cu (II) removal was 95\% for peanut hulls and only 44\% for \textit{Pinus brutia} sawdust. These results indicate that untreated sawdust has lower adsorption efficiency for Cu (II) ions in a concentration of 100 mg/l compared to
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peanut hulls. However, this efficiency may be increased due to chemically activation. Saravanane et al. (2001) reported that heavy metal adsorption capacity of sawdust was increased with chemical modification.

Figure 1 The effect of the contact time on adsorption of copper (II) ions in concentration of 100 mg/l by peanut hulls (a) and Pinus brutia sawdust and (b) at 30°C, 150 rpm shaking, pH 5.0 and amount of adsorbent 10 g/l

3.2 The effect of the initial pH

Results of the experiments using 100 mg/l copper (II) solutions and 10 g/l adsorbent showed that efficiencies of adsorption were increased for both adsorbents with increasing pH from 2.0 to 5.0. The results are presented in Figure 2. At pH values above pH 5.0, a sharp increase of Cu adsorption was observed. This can be explained by precipitation of copper ions in the solution. At the optimal pH of 5.0, 79% of Cu (II) ions in concentration of 100 mg/l were removed by peanut hulls and 32% by Pinus brutia sawdust.

Figure 2 The effect of the pH on adsorption of copper (II) ions in a concentration of 100 mg/l by peanut hulls (a) Pinus brutia sawdust and (b) at 30°C, 150 rpm shaking, amount of adsorbent 10 g/l and the contact time 24 h
Similarly, Basci et al. (2004) reported that pH has a significant role on Cu removal. The sorption efficiency of Cu (II) was optimal at pH of 5.0. They reported also that at pH’s above 7.0, copper (II) ions (50 mg/l) were precipitated as hydroxides.

The effect of pH on the adsorption of copper (II) has been extensively investigated also by other researchers. Optimal adsorption capacity of copper (II) ions (5–200 mg/l concentrations) at pH of 5.0–5.5 has been reported on pecan shell activated carbon (Dastgheib and Rockstraw, 2001), peat (Ma and Tobin, 2004) and *Streptomyces coelicolor* A3 (Öztürk et al., 2004).

### 3.3 The effect of temperature

The effect of temperature on metal removal was less significant than that of pH (Figure 3). The maximal adsorption efficiencies were found at temperatures between 30 and 40°C for peanut hulls from 79% to 84%. Although adsorption efficiency of peanut hulls was decreased with temperatures higher than 50°C, the increasing trend of adsorption was observed for *Pinus brutia* sawdust (from 32% to 59%) with increasing temperature from 20°C to 50°C. Temperatures above 50°C were not investigated because they are economically inefficient.

![Figure 3](image)

Öztürk et al. (2004) also reported that adsorption of Ni (II) and Cu (II) on *Streptomyces coelicolor* A3 was affected by temperature, but less than by pH value.

### 3.4 The effect of the amount of adsorbent

The removal of the copper (II) ions from aqueous solutions (100 mg/l) was significantly dependent on the amount of adsorbent. Efficiencies of adsorption were increased for both adsorbents (from 7% to 79% for peanut hulls; from 3% to 32% for *Pinus brutia* sawdust) with increasing of the amount of adsorbent from 1.0 g/l to 10 g/l (Figure 4). The reason for that is the availability of more binding sites for complexation of copper (II) ions. Similarly, Yu et al. (2003) reported that the adsorption of Cr (VI) ions in a concentration of 10 mg/l increases with increasing weight of the sawdust from 10 g/l to 50 g/l.
3.5 The effect of the copper (II) ion concentration

The adsorption of Cu (II) by peanut hulls and sawdust was studied at different copper concentrations in the range from 20 mg/l to 100 mg/l. Results are presented in Figure 5. Adsorption efficiencies decreased with the increasing of the copper concentration at constant adsorbent amount 10 g/l. Ma and Tobin (2004) reported that sorption of Cu (II) from aqueous solutions was increased with increasing solution concentration (5–200 mg/l) at amount of adsorbent 1 g/l. Similarly, at solution concentrations from 25 mg/l to 200 mg/l with 50 g/l adsorbent, Hanzlik et al. (2004) showed that adsorption of Cu (II) ions increased as a function of increasing Cu (II) concentration.

3.6 Adsorption isotherms

Our experimental results indicate that peanut hulls are a more effective adsorbent than Pinus brutia sawdust for removing Cu (II) from aqueous solutions. Therefore adsorption isotherms were analysed only for peanut hulls. The analysis of isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes (Rengaraj et al., 2004). In order to investigate the sorption isotherm for peanut hulls, two equilibrium models were employed: The Langmuir and Freundlich isotherm equations.
Langmuir and Freundlich isotherms were tested at Cu (II) ions concentrations in the range of 100–200 mg/l, at the constant amount of the peanut hulls (10 g/l).

The adsorption constants of Langmuir isotherms $q_{\text{max}}$ and $b$ was estimated from the intercept and slope of $C_{\text{eq}}/q_{\text{eq}}$ vs. $C_{\text{eq}}$, according to equation (4) and obtained as 33.9 mg/g and 0.054 (l/g), respectively. The correlation coefficient of the Langmuir isotherm ($R^2$) was 0.9889 (Figure 6).

Figure 6  Plot of Langmiur isotherm for the biosorption of Cu(II) ions in concentration of 100 mg/l by peanut hulls 30°C, 150 rpm shaking, pH 5.0 and amount of adsorbent 10 g/l

In this study, Freundlich was the best fit isotherm for biosorption of Cu(II) to the peanut hulls. The adsorption constants of Freundlich isotherms $K_f$ and $n$ was estimated from the intercept and slope of $\ln q_{\text{eq}}$ vs. $\ln C_{\text{eq}}$, according to equation (6) and obtained as 2.95 mg/g and 1.67 (l/g) respectively. The correlation coefficient of the Freundlich isotherm ($R^2$) was 0.9965 (Figure 7).

Figure 7  Plot of Freundlich isotherm for the biosorption of Cu(II) ions in concentration of 100 mg/l by peanut hulls 30°C, 150 rpm shaking, pH 5.0 and amount of adsorbent 10 g/l

4 Conclusions

The adsorption efficiencies of copper (II) ions on the untreated peanut hulls and untreated Pinus brutia sawdust were investigated as a function of the contact time, initial pH, amount of adsorbent, temperature and various Cu (II) ion concentrations. The results indicated that:
Efficiency of adsorption of Cu (II) ions in a concentration of 100 mg/l was increased with increasing contact time from 24 h to 168 h. After 144 h, 95% of Cu (II) ions were removed by peanut hulls and 44% by Pinus brutia sawdust.

The pH significantly influences the adsorption of Cu (II) ions by the peanut hulls and the sawdust. The adsorption efficiency was increased with increasing pH values. It was maximal at pH 5.0. At pH’s higher than 5.0, precipitation of Cu (II) ions was observed.

The increase in the amount of adsorbent resulted in an increase of adsorption efficiency. At 10 g/l of adsorbent, 79% adsorption efficiency for 100 mg/l of Cu (II) was found using peanut hulls and 32% using Pinus brutia sawdust respectively.

The effect of temperature on the Cu (II) ions removal from the solutions (100 mg/l) was less significant than pH.

The adsorption efficiencies of Cu (II) ions from aqueous solutions by the peanut hulls and sawdust were found to be higher at lower concentrations of Cu (II) ions.

The isothermal data of peanut hulls better fitted the Freundlich equation than the Langmuir model.

Our results showed that untreated peanut hulls are more effective adsorbents for removal of Cu (II) ions from solutions than untreated Pinus brutia sawdust. However, both peanut hulls and Pinus brutia sawdust, can be used for low cost adsorbents for removing of Cu (II) ions from waters and wastewaters.

References


