

The removal of heavy metal from aqueous solutions by sawdust adsorption — removal of copper

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Abstract

Locally available sawdust, a byproduct of the world industry, was found to be a low cost and promising adsorbent for the removal of copper(II) from wastewater. In this work, adsorption of copper on sawdust has been studied by using batch techniques. The equilibrium adsorption level was determined to be a function of the solution pH, contact time, and sorbate concentration. The equilibrium adsorption capacity of sawdust for copper was obtained by using linear Freundlich and Langmuir isotherms. Ion exchange is probably one of the major adsorption mechanisms for binding divalent metal ions to the maple sawdust. The results provide strong evidence to support the hypothesis of adsorption mechanism. It also supplies significant sawdust operation capacity data for engineering design. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The release of heavy metals into our environment is still large. In certain areas of the world it is even increasing. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. It is well known that some metals can have poisonous or otherwise harmful effects on many forms of life. The numerous metals, which are significantly toxic to human beings and ecological environments, include antimony (Sb), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), cadmium (Cd), etc.

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Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product such as food, water or drink. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well. For example, continued inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers.

Numerous techniques are available for water purification and metal recovery operations from wastewaters. Many of these are established methods, while others are still in the experimental stage. Often, only a combination of various treatment processes can provide the effluent quality desired. Inorganic heavy metals are usually removed from aqueous waste streams by chemical precipitation, electrodeposition and cementation [1]. Other methods, including activated carbon, ion exchange, and reverse osmosis, can be used to concentrate waste streams and remove the heavy metals. Activated carbon is effective in reducing hexavalent chromium, mercury, and many metals complexed by organic ligands. Similarly, various ion-exchange resins have been found to be effective in reducing metal ions from solution.

Interest has risen recently in removing heavy metals from solution by binding with agricultural materials such as waste wool, nut wastes, tree barks, modified cotton and sawdust. Many agricultural byproducts have little or no economic value, and some, such as bark and sawdust, which are in large quantities in lumber mills, are often present a disposal problem. If sawdust could be used, as an absorbent, both the environment and wood agriculture would benefit contaminated streams would be cleaned, and a new market would be opened for the sawdust.

Previous investigations have shown that heavy metals will bind to sawdust and other agricultural products [2–10]. The adsorption of acid and basic dyes from textile mill effluent onto sawdust has been investigated, and a significant amount of work has been done on the adsorptive capacity of various tree barks. However, the ash content of bark is about 10 times higher than that of sawdust for many species, which makes it less suitable for heavy metal recovery by combustion. Also, bark as produced from the lumber mill has a much larger average particle size than sawdust. It is likely that most of the bark would have to be processed through size-reduction equipment to make it suitable as an adsorbent, whereas only over-sized particles of sawdust, which could be separated by screening, would need to be processed through size-reduction equipment. Various chemical treatments of sawdust and other agriculture waste might improve the heavy metal binding capacity of these materials. However, because of the low costs of most agricultural wastes, it is unclear, whether this increase in adsorption will pay for the added cost associated with the chemical treatment. The purpose of this research was aimed to gain a fundamental understanding of the chemical and physical phenomena associated with the binding of copper to untreated sawdust.

2. Experimental

2.1. Instrumentation

Perkin Elmer model 2100 atomic absorption spectrometer (AAS) operating with an air-acetylene flame was used to analysis the concentrations of copper. The detection limits

were equal to or less than EPA requirement. Three standard solutions in the linear range of the instrument were used to construct each calibration curve. Samples reading beyond the linear range of the references were diluted to appropriate concentrations. All measurements were repeated three times and no results were accepted if the standard deviation was greater than 0.1 mg/l.

The pH measurements were performed with an Orion Research model 701A/digital ion analyzer and a combination electrode. The meter was standardized using buffer solutions with the following pH values: 4.00, 7.00 and 10.00.

A water bath shaker of American optical corporation (Buffalo, NY) was used for all the adsorption experiments. It was set to 70 cpm. The centrifugation was done with a model CL centrifuge machine made by International Equipment Co. to perform sampling after adsorption of metal ions with sawdust at 2000 rpm.

2.2. Chemicals

Analytical grade copper(II) nitrate was obtained from Fisher Scientific, and they were used for copper ion sources. ACS. reagent grade concentrated nitric acid and sodium hydroxide were obtained from Aldrich and used to adjust pH values of samples. The pH buffer solutions were obtained from Aldrich Chemical Company and Chemlab Supply Co. All experimental work used distilled water from running distilled water at lab.

2.3. Adsorbent

The sawdust samples with 30–60 mesh Maple wood flour used in these studies were obtained from P.J. Murphy Forest Products Corporation, Montville, NJ (courtesy of Mr. Fred A. Faehner). It was used directly for adsorption experiments without any treatment.

2.4. General procedures

The sorption of copper on sawdust was studied by batch technique. The general method used for this study is described as following.

A known weight (e.g. 0.5 g of sawdust) was equilibrated with 100 ml of the spiked copper solution of known concentration in a stopped Pyrex glass flask at a fixed temperature in a thermostatic shaker bath for a known period of time. After equilibration the suspension was centrifuged in a stopped tube for 2 min at 2000 rpm and the metal solution then was analyzed using the AAS.

The effect of several parameters such as pH, concentrations, contact time and quantity of sawdust etc. on the adsorption was studied. The pH of the suspension in one set of experiments was adjusted with NaOH and HNO₃. Adsorption of copper on the walls of glass flasks and centrifuge tubes, which was found negligible, was determined by running the blank experiments.

3. Results and discussion

Synthetic waste solutions containing copper was prepared, from stock solution to study their removal through adsorption on sawdust. Initial concentrations of copper used in this

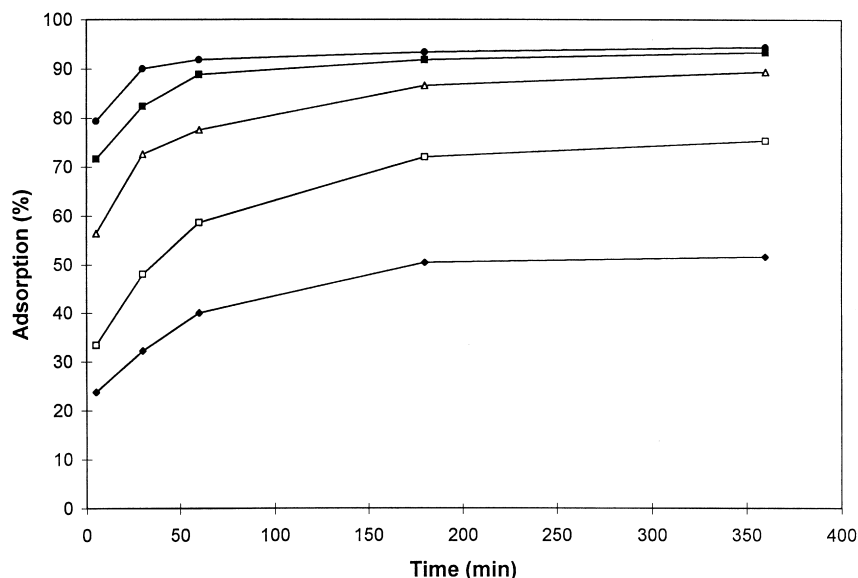


Fig. 1. Percent removal of copper vs. time, initial concentration of copper 5.0 mg/l: 40 g/l SD (◆); 30 g/l SD (□); 20 g/l SD (△); 10 g/l SD (■); 5 g/l SD (●).

investigation were kept at concentrations of 1.0, 5.0, 10.0, 25.0 and 50.0 mg/l. The 30–60 mesh maple sawdust was used as a sorbent in bench-scale studies. Sawdust of 0.5, 1.0, 2.0, 3.0 and 4.0 g were added, respectively, in five different flasks each containing 100 ml of the test solutions of copper without any pH adjustment. The mixture of the test solution and sawdust was stirred in a shaker at 70 rpm continuously for 6 h. Separate samples for copper were drawn after 5, 30, 60, 180 and 360 min intervals. The suspension was centrifuged in centrifuge test tubes for 5 min at 2000 rpm. The copper concentrations were then analyzed using AAS. The observations are shown in Fig. 1.

First of all, the plot reveals that the rate of percent copper removal is higher at the beginning. That is probably due to larger surface area of the sawdust being available at beginning for the adsorption of metals. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles.

Secondly, most of the maximum percent copper removal was attained after about 3 h of stirring time at different concentrations. There does not seem to be much benefit from a stirring time longer than 3 h. Therefore, equilibrium time of 3 h was selected for all further studies.

It is also observed that for low initial concentrations of copper (1.0–5.0 mg/l), the percent removal of it is greater in a given time when compared to the higher initial copper concentrations (10–50 mg/l), see Fig. 2. The availability of adsorptive sites of the sawdust is a possible explanation for this phenomenon.

It is necessary to point out that these tests were done under a condition without any pH adjustment. However, it is supposed that the pH of the metal solution may affect metal

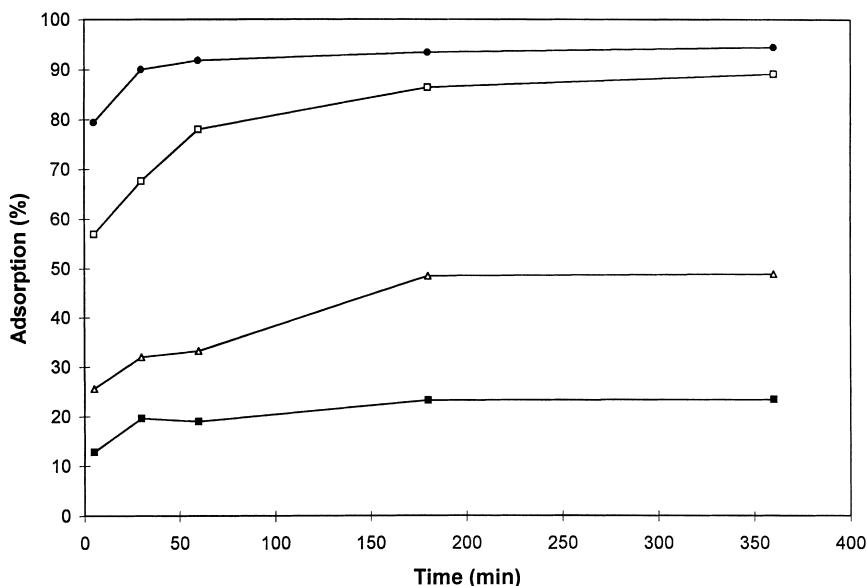


Fig. 2. The effect of initial concentrations of copper on adsorption, sawdust 40 g/l: 1.0 mg/l (□); 5.0 mg/l (△); 10 mg/l (■); 25 mg/l (●).

affinity for adsorption on the sawdust and that the process of metal adsorption may change the pH of an unbuffered solution. Anyway, pH may play an important role in the metals adsorption, which is an important aspect of our further studies.

3.1. Effect of pH

The effect of pH on copper sorption on sawdust was studied at room temperature by varying the pH of copper solution-sawdust suspension from 2.0 to 10. The results are shown in Fig. 3.

It can be observed that the removal of copper (II) by sawdust adsorption increases with increasing pH, from its minimum at pH 2.0 to its maximum at a pH of about 7.0. After that the percent adsorption decreases slightly in pH range of 8.0–10.0. The greatest increase in the sorption rate of copper ion on sawdust was observed in a pH range from 2 to 8.

3.2. Effect of sawdust or sorbate concentration

The dependence of copper sorption on sawdust concentration was studied at room temperature and fixed pH values by varying the sorbent amount from 0.5 to 4.0 g while keeping the volume (100 ml) of the metal solution constant. The results are shown in Fig. 4.

It is apparent that the percent removal of copper increases rapidly with increases in the concentration of the sawdust due to the greater availability of the exchangeable sites or surface area at higher concentration of the sorbent. This is certainly a capacity effect. From

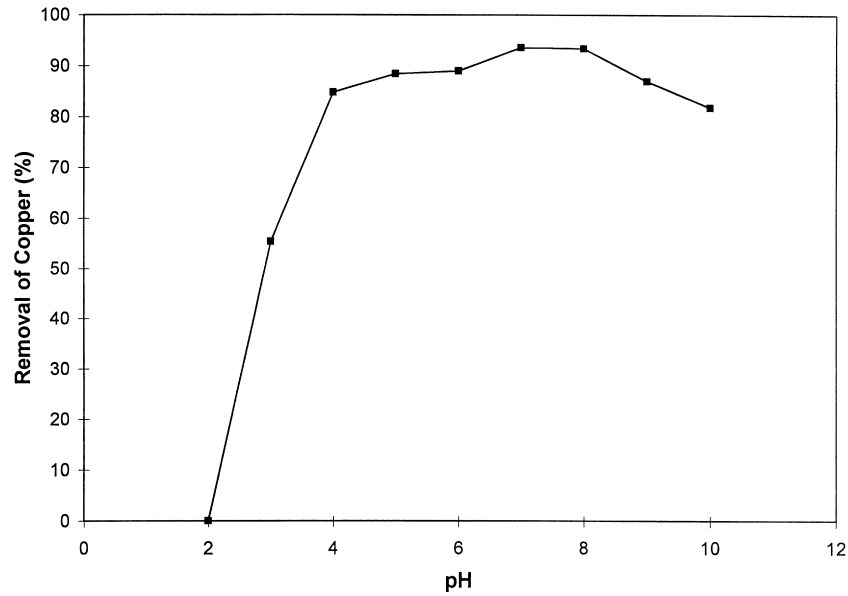


Fig. 3. The effect of pH on metal removal through sawdust adsorption. Temperature 23°C; equilibrium time 3 h; initial concentration of copper 10.0 mg/l; sawdust 10 g/l.

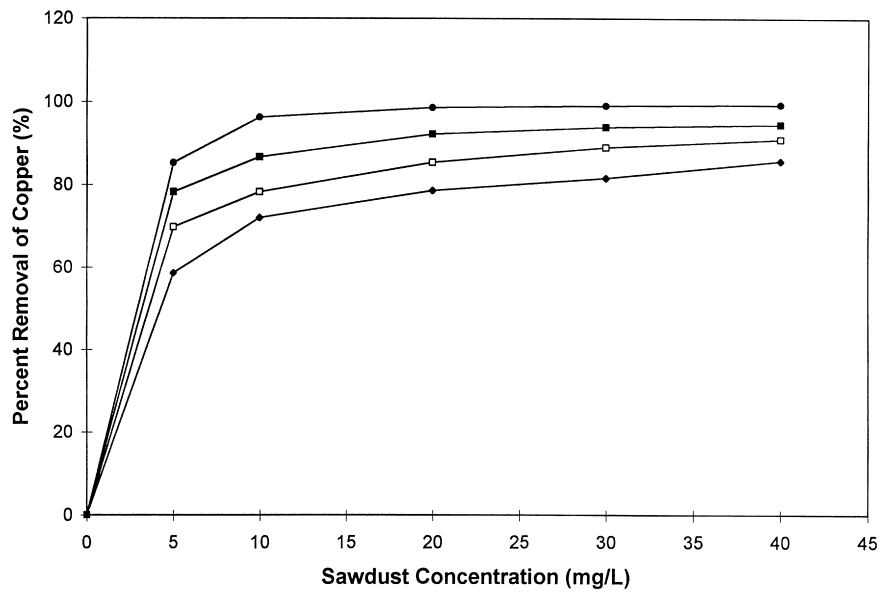


Fig. 4. Effect of sawdust concentration on the removal of copper(II) with different initial concentrations. Temperature 23°C; contact time 24 h: 5.0 mg/l (●); 10.0 mg/l (■); 25.0 mg/l (□); 50.0 mg/l (◆).

Table 1
The effect of sorbate concentration on the removal of copper(II)^a

Cu ²⁺ (mg/l)	Copper removal (%) at different sawdust (SD) concentrations				
	5 g/l	10 g/l	20 g/l	30 g/l	40 g/l
5.0	85.2	92.4	94.4	94.6	94.8
10.0	78.2	83.4	92.2	93.9	94.6
25.0	69.8	75.2	85.4	89.0	91.0
50	58.6	72.0	78.6	81.6	85.8

^a Contact time: 24 h, temperature: 23°C, and pH = 7.0.

this point of view, it is easily understandable that the initial concentration of copper gave some effect on its percent removal, see from Fig. 4 and Table 1.

From the results, it is revealed that within a certain range of initial metal concentration, the percentage of metal adsorption on sawdust is determined by the sorption capacity of the sawdust.

3.3. Adsorption isotherms

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 [11]. For a single solute, it is given by

$$\frac{x}{m} = \frac{V_m K C_e}{1 + K C_e} \quad (1)$$

However, the linear form of the equation can be written as

$$\frac{C_e}{x/m} = \frac{1}{K V_m} + \frac{C_e}{V_m} \quad (2)$$

where C_e is the equilibrium concentration of the solution, x/m is the amount adsorbed per unit mass of adsorbent, m is the mass of the sorbent, V_m is the monolayer capacity, and K is an equilibrium constant that is related to the heat of adsorption by equation

$$K = K_0 \exp\left(\frac{q}{RT}\right) \quad (3)$$

where q is the heat of adsorption. Linear Langmuir plot from Eq. (2) was drawn and the values V_m and K for the isotherms of copper were obtained by using least squares method. The linear Langmuir equation for copper on sawdust in distilled water system is then

$$\frac{C_e}{x/m} = 0.5583 C_e + 1.7428 \quad (4)$$

The Freundlich isotherm, which is an empirical model used to describe adsorption in aqueous systems, was also tested with our experimental data. The Freundlich isotherm is shown as the following equation:

$$\frac{x}{m} = K_f C_e^{1/n} \quad (5)$$

The linear form of the equation can be written as

$$\log \frac{x}{m} = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

where K_f is the measure of sorption capacity, $1/n$ is sorption intensity and other parameters have been defined as in Eq. (1). A plot of $\log(x/m)$ against $\log C_e$ gives a straight line, the slope and intercept of which correspond to $1/n$ and $\log K_f$, respectively. According to the plot of one set of data the K_f and $1/n$ values come out to be 0.956 mg/g and 0.601 respectively. The Freundlich isotherm equation for copper on sawdust is then

$$\frac{x}{m} = 0.956C_e^{0.601} \quad (7)$$

3.4. Adsorption mechanism

Ion exchange may be the principal mechanism for the removal of copper. It has been known for many years that cupric ion readily taken by Amberlite synthetic ion exchange resins. It is quite possible that the same mechanism controls with sawdust. The major components of the polymeric material in sawdust are lignin, tannins or other phenolic compounds. From the nature of the material which are efficient in capturing heavy metal ions, it can be speculated that lignin, tannins or other phenolic compounds are the active ion exchange compounds and that active sites are the phenolic groups of those compounds.

Based on the structure of these phenolic compounds, a possible mechanism of ion exchange could be considered as a divalent heavy metal ion (M^{2+}) attaches itself to two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution. Assuming pK of the phenolic group in sawdust being same as that of the free phenol, the phenolate ion population would be extremely small at pH less than 3 or 4. The adsorption may, therefore, fall rapidly as the pH falls.

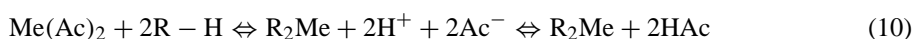
The equilibrium was quite dependent upon pH. In most cases, removal of Cu^{2+} from solution ceased as the pH of the solution in contact with the adsorbent dropped to 3.0–3.5. When the pH was further lowered by any case, for instance the introduction of acid, the equilibrium might be reversed. That is the metal ion was stripped from the solid into the acid.

As a verification of the hypothesis that a M^{2+} ion attaches itself to two phenolic groups, releasing two hydrogen ions into solution, the theoretical pH change of $Cu(NO_3)_2$ was calculated from the experimentally verified change in Cu(II) concentration as adsorption occurred. If 50 mg of Cu(II) disappeared from 1 l of solution, hypothetically, it would produce 57.5 mg HCl per liter, with a pH of about 2.82. The actual pH of the final solution in the experiment was 2.77, that is in good agreement with the calculated value. For comparable feed concentrations the sawdust removed heavy metal ions much more completely from acetate solution than from sulfate, chloride, or nitrate solutions. Comparisons of the data in Table 2 for $Cu(Ac)_2$ and $CuSO_4$ show this effect. The ion exchange hypothesis explains the better removal of copper from acetate solution than from chloride, nitrate, or sulfate solutions. In all cases, acid is formed with the liberation of hydrogen ions, but HCl, HNO_3 and H_2SO_4 are almost completely dissociated, while acetic acid is only partially dissociated.

Table 2
Effect of anions on the copper ion adsorption on sawdust

Compound	Initial cation concentration (mg/l)	Equilibrium cation concentration (mg/l)
Cu(NO ₃) ₂	25.0	11.8
Cu(Ac) ₂	25.0	6.42

Thus, the inorganic solution would have lower pH than HAc solution at equal concentrations of acid.



Since it has been established that removal of copper from solution is inhibited by low pH, copper ion could be removed from high pH acetate solution at an acid concentration where no further adsorption of copper from nitrate or sulfate solutions would take place. Table 2 shows this comparison.

4. Conclusions

The following conclusions can be drawn based on investigation of copper removal by sawdust adsorption.

First of all, sawdust appears to be a promising adsorbent for removal of copper from wastewater. At these adsorption levels, a process using sawdust for the removal and recovery of a heavy metal is potentially more economical than current process technology.

Secondly, adsorption of copper is dependent on its initial concentrations, the amount of sawdust, time of contact and pH of the metal solution. Maximum removal of copper on sawdust is at pH about 7.0. Since different metals have different properties with regard to acidity of the solution, optimized pH for different metals removal may be very different. A further study on some other metals will be needed.

Thirdly, isothermal data of copper sorption on sawdust can be modeled by both Freundlich and Langmuir isotherms. The capacity of sawdust for adsorption of certain metals can be calculated by using these models. The adsorption capacity of sawdust for copper, for instance, is 1.79 mg/g. For other metals it may be very different.

Acknowledgements

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