The removal of heavy metals from aqueous solutions by sawdust adsorption — removal of lead and comparison of its adsorption with copper

Bin Yu [a], Y. Zhang [a], Alka Shukla [b], Shyam S. Shukla [c], Kenneth L. Dorris [c]

[a] *A&B Environmental Services, Houston, TX 77098, USA*
[b] *Southeast College, Houston, TX 77270, USA*
[c] *Department of Chemistry, Lamar University, Beaumont, TX 77710, USA*

Abstract

In this work, sorption of lead on sawdust (SD) has been studied by using batch techniques. Similar to the sorption of copper, the equilibrium sorption levels for lead is a function of the solution pH, contact time, sorbent and sorbate concentration. The equilibrium adsorption capacity of sawdust for lead was measured and extrapolated using linear Freundlich and Langmuir isotherms and compared with that for copper. Metal ions which are bounded to the sawdust could be stripped by acidic solution so that the sawdust can be recycled. Non-equilibrium experiments were done by using glass columns. The results indicate the potentially practical value of this method in industries and also provide strong evidence to support the adsorption mechanism proposed. Even though the focus of this work is on lead, some results from previous study for copper have been incorporated here for sake of comparison. © 2001 Published by Elsevier Science B.V. All rights reserved

Keywords: Sawdust; Metal ions; Lead; Adsorption; Wastewater

1. Introduction

Lead is a naturally occurring chemical element. Lead is a common industrial metal that has become widespread in air, water, soil, and food. The major uses of lead in the United States are in storage batteries (72%), gasoline additives and other chemicals (13%), ammunition (shot and bullets, 4%), solder (2%), and other uses (9%). World production exceeded 3 million tones per year. The vast increase in environmental lead has dramatically raised the measured blood concentration of lead in many people. Lead causes severe health effects even at relatively low levels in the body, including often irreversible brain damage and injury to the blood forming systems. At the typical levels to which individuals are exposed, lead can cross the placenta and damage developing fetal nervous systems.

Surveys of lead in the blood of children show typical concentrations already above the level at which changes in blood enzymes occur [1]. The margin of safety between measured blood levels and the levels causing clinical symptoms is remarkably small. In order to insure the quality of life and protect the environment, removing lead from industrial waste is of vital importance.

A number of investigations have shown that heavy metals will bind to sawdust and other agricultural products [2–11]. A previous study [12] showed that Maple sawdust is a promising material for the removal of copper from wastewater by adsorption. It was also found that the adsorption process was influenced by the matrix pH, the contact time and the capacity of the sawdust material. The focus of this research was centered on gaining more information to understand the chemical and physical phenomena associated with the binding of heavy metals to untreated sawdust. Another concern is to obtain significant data for the application of this technique in industrial scale.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer model 2100 atomic absorption spectrometer (AAS) was used for lead analysis. A digital ion analyzer of Orion Research model 701A was used for pH measurement. A water bath shaker of American Optical Corporation (Buffalo, New York) was used for all the adsorption experiments.

2.2. Chemicals

Analytical grade lead nitrate was obtained from Fisher Scientific, and used for heavy metal ion. The concentrated nitric acid and sodium hydroxide used for pH adjustment were all ACS reagent grade and obtained from Aldrich Chemical Company. pH buffer solutions were obtained from Aldrich Chemical Company and Chemlab Supply Co. Deionized water (DI H_2O) was used in all experimental work.

2.3. Adsorbent

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

2.4. Columns

Fifteen and twenty millimeters i.d. glass columns were packed with 39 or 40 cm high Maple sawdust with 30–60 mesh size for non-equilibrium experiments.

2.5. General procedures

Prepare experimental solutions of lead with varying pH and Pb concentrations (known initial concentrations) in stopped Pyrex glass flasks. Combine the experimental solutions

(e.g. 100 ml), respectively, with different amount of sawdust (e.g. 5, 10 g, etc.) and equilibrate them with stirring at a fixed temperature for a 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 effects of several parameters such as pH, concentrations, contact time and quantity of sawdust on the adsorption were studied. From experiment, it was found that the adsorption of lead on the walls of glass flasks and centrifuge tubes was negligible. Desorption and sorbent regeneration experiments were performed using acidic stripping solutions (0.1 M strong acid).

To carry out non-equilibrium tests, glass columns of 15 and 20 mm i.d. and 55 cm heights were filled with Maple sawdust to a height of 40 cm. The packing was periodically pressed down to increase bulk density. Liquid feed was added at the top of the column and the flow under gravity was controlled with a valve at the bottom.

3. Results and discussion

Synthetic waste solutions containing lead or copper were prepared, respectively, from stock solutions to study their removals through adsorption on sawdust. Initial concentrations of lead used in this investigations were kept at concentrations of 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. An amount of 5, 10, 20, 30 and 40 g sawdust were added, respectively, in five different flasks each containing 100 ml of the test solution lead without any pH adjustment. The mixture of the test solutions and sawdust were stirred in a shaker at 70 rpm continuously for 6 h. Separate samples each for copper and lead were drawn after 5, 30, 60, 180 and 360 min intervals. The suspension was centrifuged in centrifuge test tubes for 2 min at 2000 rpm. The metals concentrations were then analyzed using AAS. The observations are shown in Fig. 1.

From these experiment, a similar behavior for lead adsorption to sawdust was found as that for copper [6]. Firstly, the rate of metal removal is higher at the beginning in all cases, such as sawdust concentrations 40, 30, 20, 10 and 5 g/l, respectively. That is clearly due to the availability of the sawdust surface area. Secondly, in a certain time the percent metal removal reached maximum, say, about 3 h for both lead and copper. It is also found that the lower the initial concentration of the metal (1.0–5.0 mg/l) is, the greater the percent removal of the metal is when compared to the higher initial metal concentrations (10–50 mg/l), see Fig. 2.

Additionally, the results further show that the ultimate removal of the lead ranges from 80 to 99% for its lower initial concentrations (1–10 mg/l), while that of copper is seen in a little bit lower range (60–90% for 1–5 mg/l initial concentrations). Fig. 3 shows an example of this comparison indicating that lead has more affinity for adsorption on the sawdust than copper.

3.1. Effect of pH

The effect of pH on sorption of copper and lead on sawdust was studied at room temperature by varying the pH of metal solution-sawdust suspension from 2.0 to 10. The results are shown in Fig. 4.
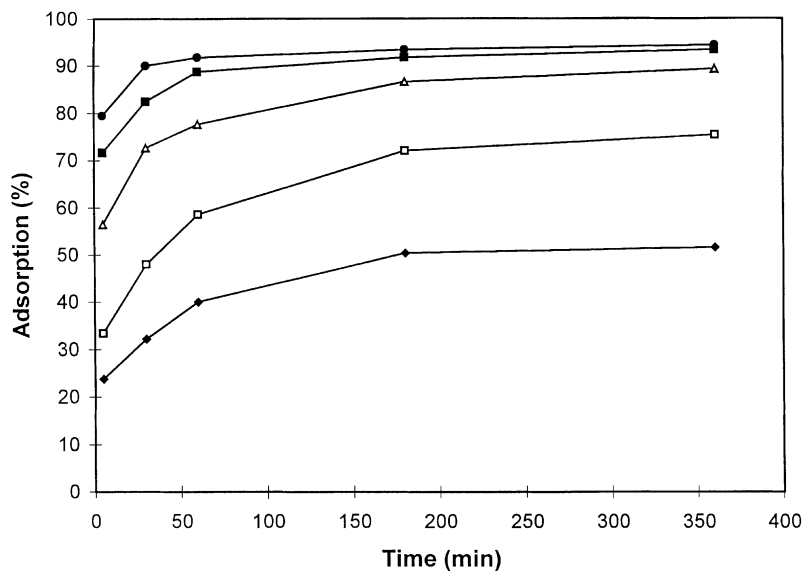
Fig. 1. Percent removal of lead vs. time. Initial concentration of lead: 5.0 mg/l; (●) 40 g/l SD, (■) 30 g/l SD, (△) 20 g/l SD, (□) 10 g/l SD, (◆) 5 g/l SD.
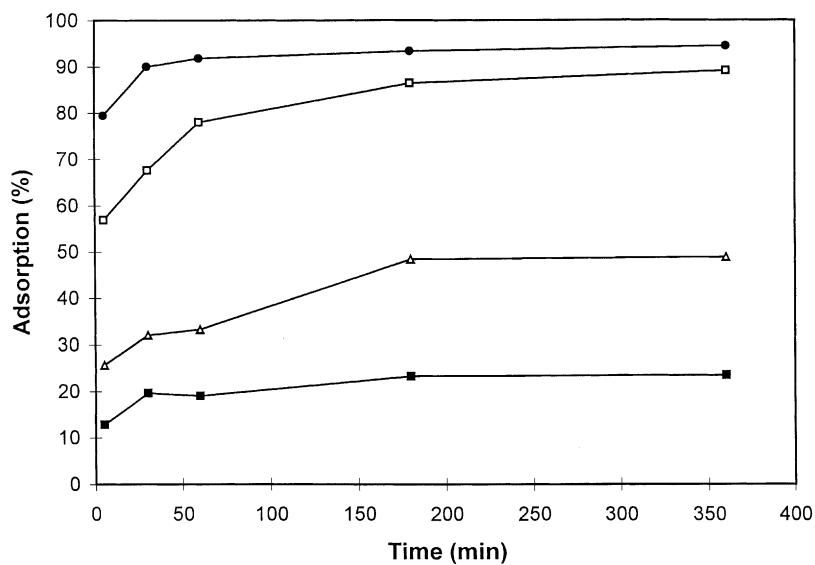

Fig. 2. The effect of initial concentrations of lead on adsorption. Sawdust: 40 g/l; (●) 1.0 mg/l, (□) 5.0 mg/l, (△) 10 mg/L, (■) 25 mg/l.
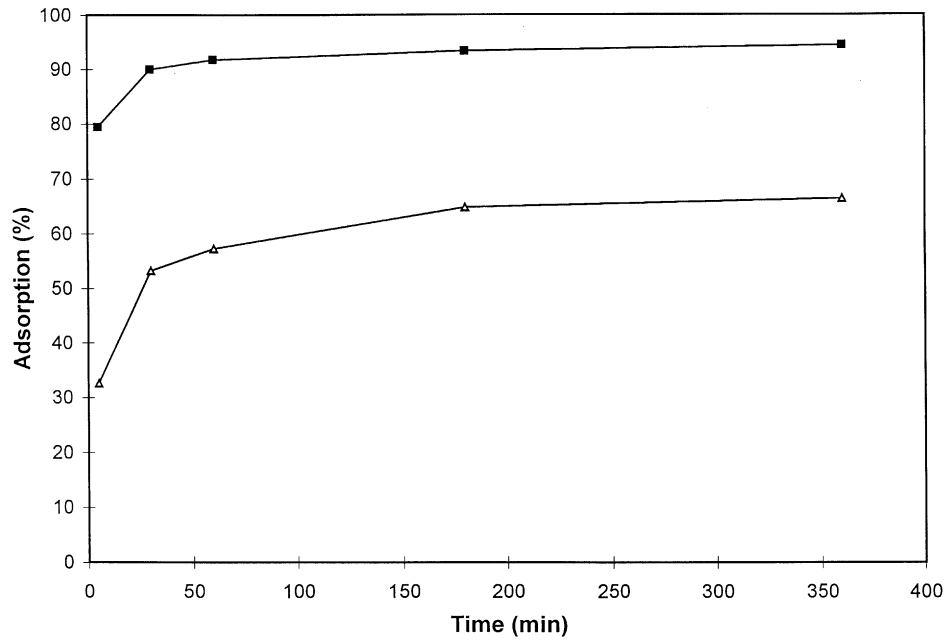
Fig. 3. A comparison of the adsorption of lead and copper. Sawdust: 40 g/l; (△) copper, initial concentration: 5.0 mg/l; (■) lead, initial concentration 5.0 mg/l.

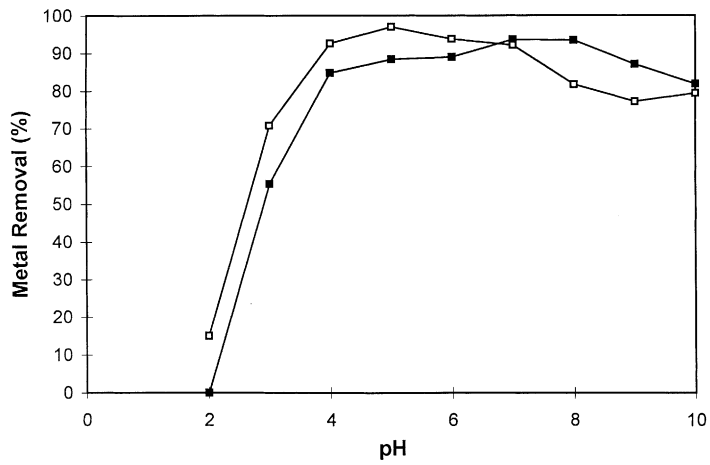
Fig. 4. The effect of pH on metal removal through sawdust adsorption. Temperature: 23°C, equilibrium time: 3 h, sawdust: 20 g/l; (□) lead, initial concentration: 5.0 mg/l; (■) copper, initial concentration: 5.0 mg/l.

It can be observed that the removal of Cu(II) and Pb(II) exhibits similar trend, i.e. it increases with increasing pH, from its minimum at lower pH to its maximum at a certain pH range. The maximum removal of Pb(II) by sawdust sorption occurs at a pH of about 5.0, while that of Cu(II) does at a pH of about 7.0. Unlike copper, there is still some adsorption for lead even when solution pH is as low as 2.0. The greatest increase in the sorption rate of metal ions on sawdust were observed in a range of pH from 2 to 8 for copper and 2–5 for lead. It is assumed from the results that the metal adsorption mechanism with maple sawdust is probably due to the ion exchange. At low pH, the existence of relatively large number of hydrogen ions may change the direction of reversible ion exchange equilibrium back to starting materials. In a higher pH range, existing of counter ions might result in lower efficiency of adsorption. Possibly some precipitation of metal could occur at higher pH.

3.2. Effect of sawdust or sorbate concentration

The dependence of lead sorption on sawdust concentration was studied at room temperature by varying the sorbent amount from 5 to 40 g, while keeping the other parameters, such as pH and metal solution volume (100 ml), constant. In all cases, the percent removal increased with increasing sawdust concentration. The sorption of lead as a function of their initial concentrations was also studied at room temperature. It is apparent that the percent removal of metals increases rapidly with increase in the concentration of the sawdust due to the greater availability of the exchangeable sites or surface area at higher concentration of the sorbent. Table 1 lists the results for lead removal by varying the concentration of sawdust. Fig. 5 demonstrates this effect and presents a comparison of the two metals, lead and copper.

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 and the selectivity of the sawdust to different metal ions. It is apparent that lead has more preference than copper for adsorption on the sawdust.

3.3. Desorption of metal ions

Desorption studies were performed for various lead loading concentrations. This was done by carefully decanting the remaining solution after sorption. The procedure is described below.

Table 1
The effect of sorbate concentration on the removal of Pb(II)[a]

Pb^{2+} (mg/l)	Lead removal (%) at different sawdust (SD) concentrations				
	5 g/l SD	10 g/l SD	20 g/l SD	30 g/l SD	40 g/l SD
5.00	96.2	96.8	97.0	97.8	98.8
10.0	96.3	97.5	97.9	97.9	98.8
25.0	91.7	95.9	96.3	96.7	98.2
50.0	88.1	93.1	95.6	96.1	97.6
100	62.9	86.0	88.5	92.2	96.4
500	17.3	33.9	42.8	54.2	55.7

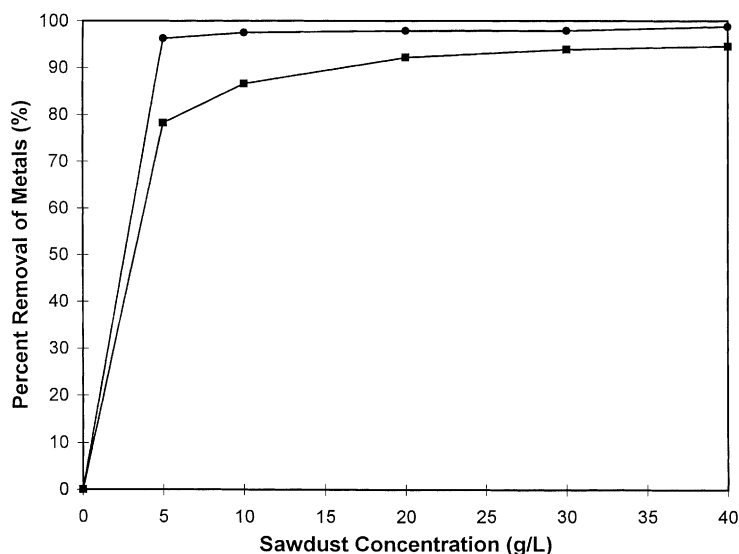[a] Contact time: 24 h, temperature: 23°C, pH: 5.0.

Fig. 5. Effect of sawdust concentration on the removal of Pb(II) and Cu(II). Initial concentration of lead (●) or copper (■): 10 mg/l, temperature: 23°C, contact time: 24 h.

In order to obtain the minimum residue concentration of metal ions after adsorption by sawdust, experiments were carried out at room temperature by using four different initial copper and lead concentrations at pH 7.0 for copper and 5.0 for lead, respectively. The amount of sawdust used for this type of test was 20 g/l and the contact time was 24 h. The pHs of the suspensions were checked periodically throughout the experiment. The loaded sawdust was filtered by vacuum pump and re-suspended in distilled water of the same volume with a pH adjusted to 2.0 using HNO_3. The sorption and loading of metal ions were determined by using the usual method. The results shown in Tables 2 and 3, reveal that the loading of ions on sawdust increases with the increase in bulk concentration of metals. In comparison, the percent recovery of copper is slightly higher than that of lead, that confirms the assumption that lead has more affinity for adsorption on sawdust compared to copper. It also suggests that there may be two major types of sorption mechanisms, the ion exchange and the mono ion-layer physical adsorption.

Table 2
Desorption of Cu(II) from sawdust (SD)[a]

Initial Cu(II) (mg/l)	ECS[b] (mg/l)	Loading of Cu(II) (mg/g SD)	Recovery from SD (%)
5.0	0.29	0.2355	98.3
10.0	0.72	0.4640	94.8
25.0	3.20	1.0900	97.2
50.0	9.70	2.0150	97.3

[a] Sawdust concentration: 20 g/l, temperature: 23°C, pH: 7.0 for sorption and 2.0 for desorption.
[b] Equilibrium concentration of sorption.

Table 3
Desorption of Pb(II) from sawdust (SD)[a]

Initial Pb(II) (mg/l)	ECS[b] (mg/l)	Loading of Cu(II) (mg/g SD)	Recovery from SD (%)
5.0	0.15	0.2425	86.6
10.0	0.21	0.4895	88.9
25.0	0.92	1.2040	89.3
50.0	2.21	2.3895	92.1

[a] Sawdust concentration: 20 g/l, temperature: 23°C, pH: 5.0 for sorption and 2.0 for desorption.
[b] Equilibrium concentration of sorption.

3.4. Regeneration of sawdust

The M^{2+} — H^+ ion exchange is easily reversible, depending upon pH. Sawdust samples which have been exposed to heavy metal solutions and adsorbed up to 97% copper and lead were stripped with 0.1 M HNO_3 (pH $\sim$ 1.3). The heavy metal cations were almost completely removed from the sawdust after 6 h. These concentrations represent almost a complete exchange of H^+ ions from the stripping acid to the sawdust. The generated sawdust samples were washed several times with distilled water until its pH reached the regular range. After dried in an oven at 101°C, the regenerated sawdust was employed to adsorb heavy metals again. The results shown in Table 4, indicates that the regenerated sawdust may have even higher capacity for heavy metals than the untreated material dose because of the impurities of sawdust being removed after regeneration and more exchangeable surface area becoming available.

3.5. Adsorption models and mechanism

The Langmuir and Freundlich isotherms described well the observed sorption phenomena for copper. In this study we again used them to describe the lead sorption on sawdust. For detailed information see reference [6]. Using the linear form of Langmuir isotherm

$$\frac{C_e}{x/m} = \frac{1}{KV_m} + \frac{C_e}{V_m} \tag{1}$$

Table 4
Percent removal of Cu(II) and Pb(II) comparing untreated sawdust to the regenerated one[a]

Initial metal concentration (mg/l)	Copper removal (%)		Lead removal (%)	
	Untreated sawdust	Regenerated sawdust	Untreated sawdust	Untreated sawdust
5.0	94.4	97.0	98.3	99.6
10.0	92.2	97.9	95.6	99.8
25.0	85.4	96.3	89.1	98.9
50.0	78.6	95.6	83.2	97.6

[a] Sawdust concentration: 20 g/l.

The models for the sorption of copper and lead were obtained as follows:

$$\text{Copper}: \quad C_e/(x/m) = 0.5583 C_e + 1.7428 \tag{2}$$

$$\text{Lead}: \quad C_e/(x/m) = 0.3138 C_e + 0.6459 \tag{3}$$

where C_e is the equilibrium concentration of the solution, x/m the amount adsorbed per unit mass of adsorbent, m is the mass of the sorbent, V_m the mono ion-layer capacity, and K an equilibrium constant that is related to the heat of adsorption.

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 and its linear form can be written as

$$\frac{x}{m} = K_f C_e^{1/n} \tag{4}$$

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \tag{5}$$

where K_f is the measure of sorption capacity, $1/n$ the 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. The equations for both copper and lead obtained, using our experimental data are given below

$$\text{Copper}: \quad \frac{x}{m} = 0.956 C_e^{0.601} \tag{6}$$

$$\text{Lead}: \quad \frac{x}{m} = 0.956 C_e^{0.769} \tag{7}$$

From these equations, the values of K_f come out to be 0.956 and 0.965 mg/g for copper and lead, respectively.

Ion exchange may be the principal mechanism for the removal of heavy metal ions such as Cu(II) and Pb(II). The major components of the polymeric material in sawdust are lignin, tannins or other phenolic compounds. These kinds of material possess the capability of 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. This hypothesis was verified by the sorption of copper on sawdust and again attested by the sorption data of lead.

As stated in previous study, a proof of this hypothesis is that for comparable feed concentrations the sawdust adsorbed heavy metal ions much more efficiently from acetate solution than from sulfate, chloride, or nitrate solutions. In all cases, the metal sorption was affected by the activity of hydrogen ions. The hydrogen ions in solution of strong acids like HCl, HNO_3 and H_2SO_4 are almost completely dissociated, while it is only partially dissociated in acetic acid. Comparisons of the data in Table 5 for $Cu(Ac)_2$ and $CuSO_4$, for $Pb(Ac)_2$ and $Pb(NO_3)_2$ show this effect.

Physical absorption can be another mechanism for the heavy metals removal. Sawdust is of course a kind of organic material that contains two important parts in its adsorption site. One is the lipophilic part to which some lipophilic substances or neutral compounds can be absorbed. The other part is hydrophilic part on which ion exchanges may take place.

Table 5
Effect of anions to the adsorption of metal ions 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
$Pb(NO_3)_2$	25.0	3.70
$Pb(Ac)_2$	25.0	0.60

As it is well known, heavy metals exist in acidic solution as cations. In this case, the main mechanism may be the ion exchange. At lower pH, the existing of relatively large quantity of hydrogen ion may change the direction of reversible ion exchange equilibrium back to start materials. With increasing pH the metal ions will be associated with hydroxide and become neutral at a certain pH range. A neutral compound possesses hydrophobicity makes the metal precipitated or lipophilicity that makes the metal easily absorbed by sawdust. Therefore, at this stage the adsorption mechanism can be the adsorption of affinity. In a higher pH range, existing of counter ions might result in lower efficiency of adsorption and ion exchange as well. This trend is clearly shown in Fig. 4. In addition, metal ions may also be adsorbed on sediment grains. The extent of sorption will therefore, depend upon experimental parameters that could affect the surface charge.
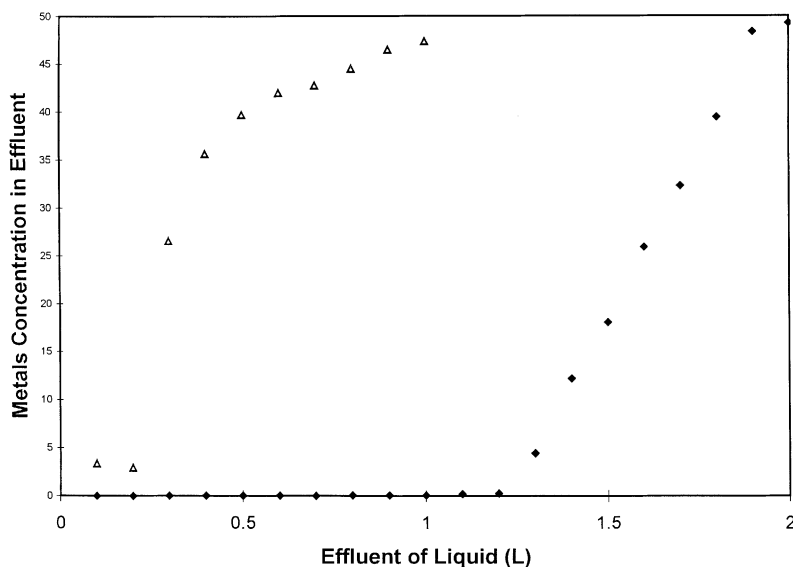

Fig. 6. Effluent of Cu(II) and Pb(II) from Maple sawdust in packed columns; (◆) feed solution: Pb(II) = 50 mg/l, pH = 5.0; column height: 39 cm, i.d. 20 mm; (△) feed solution: Cu(II) = 50 mg/l, pH = 5.4; Column height: 40 cm, i.d. 15 mm.
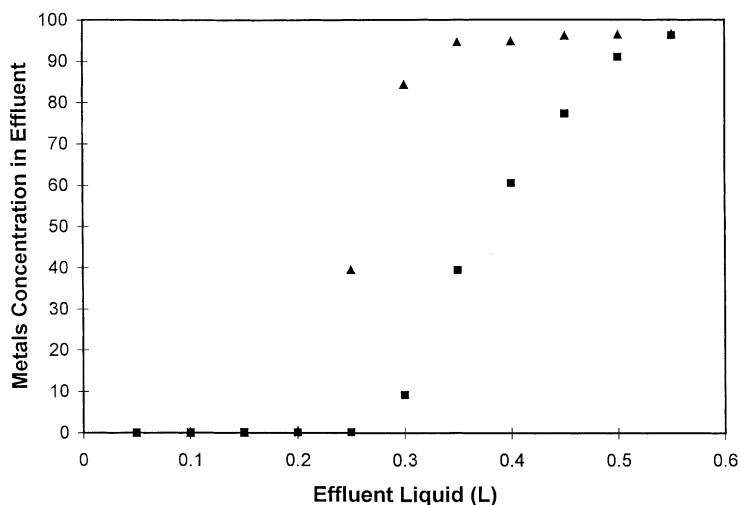
Fig. 7. Effluent of a mixed metal ions solution from maple sawdust in a packed column. Column height: 39 cm, i.d. 20 mm; (■) feed solution: Pb(II) = 100 mg/l, (△) feed solution: Cu(II) = 100 mg/l.

3.6. Packed columns

Packed columns are configured to study the removal of heavy metals by sawdust adsorption. The parameters and results are shown in Figs. 6 and 7. As shown in these Figures, the sorption curves of copper and lead are different. The breakthrough point of copper curve appears much earlier than lead, and the slope of the copper curve is steeper than lead curve. This observation provides convincing evidence for the explanation of the proposed adsorption mechanisms noted before. The adsorption of copper on sawdust results mainly from the ion exchange, while the adsorption of lead is not only based on ion exchange, but also involves some physical adsorption. This situation is also observed in the individual metal adsorption curves. The operation capacity of sawdust for copper and lead in mixture was calculated. Both 50 and 100 mg/l concentration gives out the same results. The capacity is 0.65 mg/g SD (0.02 meq/g SD) for copper, and 1.1 mg/g SD (0.01 meq/g SD) for lead. The total operation capacity is 0.03 meq/g SD.

Comparing the individual metal ion operation equivalent capacity (0.036 meq/g SD for copper, and 0.03 meq/g SD for lead) with the mixture metal ions, it shows that the sawdust capacity keeps consistent regardless of individual or mixture components. The competition to bind sawdust for each component in mixture depends on the ion selectivity to sawdust.

4. Conclusion

Significant data were obtained through this study for the removal of lead and copper by sawdust adsorption. Sawdust appears to be a promising adsorbent for the removal of copper

and lead. Based on the results noted for copper and lead, sawdust may also be suitable for other heavy metals. At these adsorption levels, a process using sawdust for the removal and recovery of heavy metals is potentially more economical than current process technology. The adsorption of metal ions is heavily dependent on the amount of sawdust, time of contact and pH of the metals solution. Maximum removal of copper and lead on sawdust is at pH about 7.0 and 5.0, respectively. Using isothermal data of metal sorption on sawdust, the adsorption process can be modeled by both Freundlich and Langmuir isotherms. Using these models, the adsorption capacity of sawdust for both copper and lead can be calculated. The adsorption capacities of the sawdust used in this study were 1.79 mg/g for Cu and 3.19 mg/g for lead, respectively.

Additionally, Metals stripping by acidic solution and column design were also studied in this work. The study indicates that maple sawdust is effective in heavy metals removal, and the sawdust column can be regenerated using acidic solution. Through this study, essential data was obtained for engineering design.

Acknowledgements

References

[1] J. Harte, C. Holdren, R. Schneider, C. Shirley, Toxic A to Z: A Guide to Everyday Pollution Hazards, University of California Press, Berkeley, 1991.
[2] J.G. Dean, F.L. Bosqui, K.H. Lanouette, Environ. Sci. Technol. 6 (1972) 520.
[3] J.M. Randall, For. Prod. J. 24 (1974) 80.
[4] J.M. Randall, For. Prod. J. 46 (1976) 46.
[5] J.M. Randall, For. Prod. J. 27 (1977) 51.
[6] C. Raji, T.S. Anirudhan, J. Sci. Ind. Res. 57 (1998) 10.
[7] M. Ajmal, A.H. Khan, S. Ahmed, Water Res. 32 (1998) 3085.
[8] P.S. Bryant, J.N. Patterson, J.M. Lee, T.M. Brouns, Appl. Biotechnol. 34/35 (1992) 777.
[9] C. Raji, J. Environ, Health 39 (1997) 230.
[10] C. Raji, T.S. Anirudhan, Ind. J. Chem. Technol. 4 (1997) 228.
[11] R.K. Weider, Water Air Soil Pollut. 53 (1990) 391.
[12] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, J. Haz. Mater. B80 (2000) 33.