Removal of Heavy Metals by Sawdust Adsorption: Equilibrium and Kinetic Studies

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Abstract

Adsorption of heavy metals by sawdust was investigated to evaluate the effectiveness of using sawdust to remove heavy metals from aqueous solutions. Kinetic and isotherm studies were carried out by considering the effects of initial concentration and pH. The adsorption isotherms of heavy metals fitted the Langmuir or Freundlich model reasonably well. The adsorption capacity of metal was in the order $Pb^{2+} > Cu^{2+} > Zn^{2+}$. A high concentration of co-existing ions such as Ca^{2+} and Mg^{2+} depressed the adsorption of heavy metal. Adsorption data showed that metal adsorption on sawdust follows a pseudo-second-order reaction. Kinetic studies also indicated that both surface adsorption and intraparticle diffusion were involved in metal adsorption on sawdust. Column studies prove that sawdust could be effective biosorbent for the removal of heavy metals from aqueous phase.

Keywords: Adsorption, Breakthrough, Heavy metal, Isotherm, Kinetics, Sawdust

1. Introduction

Heavy metals are toxic pollutants released into aqueous system as a result of various activities such as industry, mining, and agriculture. There are many methods for the removal of metal ions from solutions including, chemical precipitation, complexation, solvent extraction, and membrane processes. However, most of these methods are either economically prohibitive or too complicated for the treatment of metals.[1] Meanwhile, adsorption processes have shown many advantages over these physicochemical methods. They are quite selective, effective, and are able to remove various levels of soluble heavy metals in solution. In recent years, considerable attention has been focused on the removal of heavy metals using biosorbents derived from low-cost materials. Several biosorbents such as peat, sawdust, sewage sludge, and crop waste have been used for the treatment of metals in aqueous solution.[1-7] In this study, sawdust, which has environmental benefits in terms of the reuse of solid waste, was tested to evaluate its potential for the treatment of heavy metals. The adsorption rate and capacity per unit mass of sawdust may be

important parameters in the treatment process. It determines the sorbent replacement frequency and the economics of operation. Therefore, the parameters and mechanisms affecting the metal adsorption of sawdust must be identified prior to the application of adsorption system.

The objective of this study is to investigate the feasibility of utilizing sawdust for the adsorption of heavy metals in aqueous solution. Kinetics and isotherms of metal adsorption on sawdust were studied and described by several models. The effects of various parameters such as initial concentration and pH are evaluated. Column tests were also performed to investigate the applicability of the sawdust adsorption system for the treatment of heavy metals in aqueous system.

2. Materials and Methods

2.1. Sorbent and Sorbates

The sawdust of *Pinus koraiensis* used as an adsorbent was purchased from Jaeda, Inc., Korea, and was washed with deionized water three times to ensure that all fine particles were removed. The cleaned materials were dried at an oven temperature of 60°C for 24 hr. The dried materials were then sieved with a #30 mesh (0.6 mm) to be used for adsorption tests. The

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cation exchange capacity (CEC) of sawdust measured by an NH4Ac exchange method[9] was 71.9±3.28 meq/100 g. The analytical grades of $Pb(NO_3)_2$, $Cu(NO_3)_2 \cdot 2.5H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$ were purchased from Aldrich Chemicals. All heavy metal solutions were prepared in stock solutions of up to 1000 mg/L of metal. Concentrated stock solution was used to make various required dilutions for the adsorption experiments.

2.2. Adsorption Tests

Kinetic studies were carried out in batch reactors. Solutions (1000 mL) of different Pb^{2+} concentrations (i.e., 3-20 mg/L) were prepared from the stock solution and then transferred into the reactor containing sawdust (2.0 g). The initial pH of the metal solution was adjusted to the desired value (pH 3.0, 4.5, or 7.0) with HCl or NaOH. The pH value was measured using a digital pH meter (920A, Orion Inc.). Blank solutions containing no sawdust were also included. All reactors were mixed using a shaker bath at 21±1°C. Five milliliters of the sample was withdrawn at predetermined time intervals, and was filtered using a 0.45 μm syringe filter (PVDF, Millex HV). The metals in filtrates were analyzed by an inductively coupled plasma atomic emission spectroscopy analyzer (ICP-AES, Leeman Abs., Inc.). No correction for volume change was made because the percentage of total volume removed was sufficiently small (~ 0.5%). For adsorption isotherm tests, solutions with different metal concentrations ranging from 10 to 500 mg/L were prepared in reactors containing sawdust. After equilibrium, the sample was withdrawn and filtered for analysis. The quantity of adsorbed heavy metal on sawdust was calculated by a mass balance relationship. Duplicate tests were carried out for all experiments, and the mean values are presented. The effects of other cations on the adsorption of each single metal were evaluated considering the real conditions. First, adsorption isotherm tests were carried out for ternary combinations of heavy metals, maintaining equal concentrations of each metal ion. Next, the effect of a co-ion such as Na^+, K^+, Mg^{2+}, and Ca^{2+} on the adsorption of metal was evaluated. The concentration of Na^+, K^+, Mg^{2+}, and Ca^{2+} was varied from 0 M to 0.5 M. Dissolved organic matter (DOM) was obtained by purification of humic acid (Aldrich) according to the method of a previous study.[10] The DOM concentration used in this study was 0, 10, 50, or 100 mg/L based on total organic carbon content.

Column experiments were carried out using a glass column (0.15 m long, 0.025 m i.d., Ace glass, Inc.) with an adjustable plunger. The column was packed with 4.8 g of sawdust, and the bed length was maintained at 0.03 m. After packing the column, helium gas was used to remove the air trapped in the sorbent pores. Deionized water was then passed through more than 100 pore volumes to condition the column. The bulk density and porosity were determined gravimetrically as 510 g/L and 0.64, respectively. An HPLC pump (Alltech Inc.) was connected to the column, with a three-way valve placed in-line to facilitate switching between solutions with and without heavy metals. Conservative tracer tests were carried out using a sodium bromide solution. The tracer solution was regularly taken from the out-

flow, and its concentration was measured using ion chromatography (ACME, Younglin Inc.). The solution of heavy metal mixture (i.e., Pb^{2+}, Cu^{2+}, and Zn^{2+}) with the same concentration (10 mg/L) was pumped through the column at a flow rate of 30.0 mL/min. The samples were collected at the end of the column at different time intervals, and they were analyzed for metal concentration using ICP-AES. After the adsorption test, flushing of the column with 0.1 M $CaCl_2$ solution was followed, and the samples were collected for analysis.

3. Results and Discussion

3.1. Adsorption Isotherms

The equilibrium adsorption of heavy metals, q_e (mg/g), can be related to the equilibrium concentration of these metals, C_e (mg/L), either by the linearized form of the Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m} \tag{1}$$

or the Freundlich isotherm model:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

where S_m and K_L are the Langmuir constants, representing the maximum adsorption capacity of the solid phase loading and the energy constant related to the heat of adsorption, respectively. K_F is the Freundlich constant related to the adsorption capacity, where $1/n$ is related to the adsorption intensity. A linear plot of the Langmuir equation was drawn, and the values of Sm and K_L were determined using the least squares method (Fig. 1). Also, the slope and intercept of the linear plot of $\log q_e$ against $\log C_e$ corresponds to $1/n$ and $\log K_F$, respectively (Fig. 2). The equilibrium adsorption of each metal and mixture of metals (i.e., Pb^{2+}, Cu^{2+}, and Zn^{2+}) are well represented by the Langmuir or the Freundlich model with high R^2 values, as described in Table 1. The suitability of both isotherm models in representing the equilibrium data of three heavy metals indicates that a monolayer of metal ions formed on the sawdust surface.[11] The order of adsorption affinity on sawdust is $Pb^{2+} > Cu^{2+} > Zn^2$, which is related to the differences in electronegativity of the atoms. Considering that the adsorption of heavy metals on sawdust is mainly due to ion exchanges at the surface level, it is expected that more electronegative metals will show a higher adsorption tendency. The electronegativity of each metal is 2.33, 1.9, and 1.65 for Pb^{2+}, Cu^{2+}, Zn^{2+}, respectively.[12] The adsorption affinity of heavy metal observed here is in agreement with the order of electronegativity. It is also known that the adsorption of heavy metal with a larger ionic radius is greater than those with a smaller ionic radius.[13] The ionic radius of each metal, namely, Pb^{2+}, Cu^{2+}, and Zn^{2+} is 1.33, 0.87, and 0.88, respectively. However, the adsorption of Cu^{2+} onto the sawdust was greater than that of Zn^{2+}, implying that other factors might play important roles in the adsorption

Table 1. Langmuir and Freundlich adsorption isotherm parameters of heavy metal on sawdust

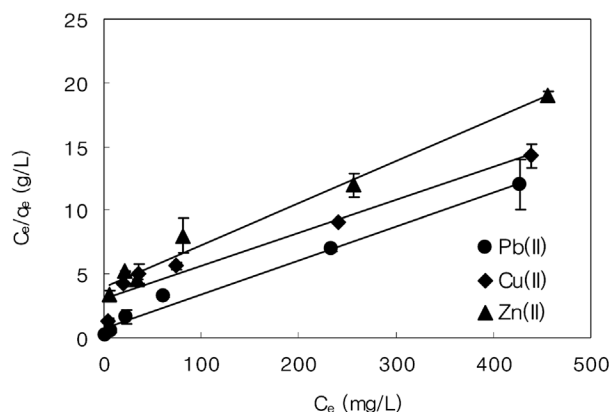| System	Metal type	$q_{e,exp}$ (mg/g)	Langmuir constant			Freundlich constant		
			S_m (L/mg)	K_L (mg/g)	R_L^2	K_F (mg^{1-n} · L^n/g)	$1/n$	R_F^2
Metal ion in single	Pb(II)	26	30.48	0.0137	0.999	2.67	0.382	0.982
	Cu(II)	22.5	30.9	0.0073	0.986	1.19	0.495	0.973
	Zn(II)	19.75	26.74	0.0071	0.999	1.0	0.5	0.999
Metal ion in mixture	Pb(II)	24.5	35.1	0.0052	0.985	0.95	0.535	0.999
	Cu(II)	20	28.3	0.0059	0.999	0.80	0.538	0.999
	Zn(II)	18	28.1	0.0042	0.991	0.42	0.625	0.976

Fig. 1. Langmuir isotherm plot for the adsorption of heavy metals on sawdust.
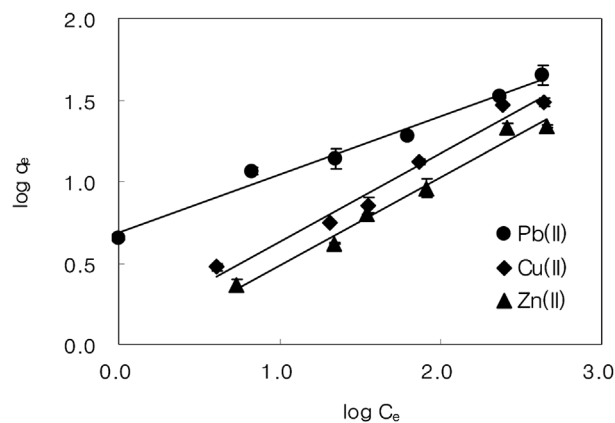

Fig. 2. Freundlich isotherm plot for the adsorption of heavy metals on sawdust.

process. It could be concluded that electronegativity and other factors including the ionic radius of the metal might be well correlated with its selectivity on sawdust.

3.2. Effects of Co-existing Cations

In the mixed system of metals, the order of metal adsorption was $Pb^{2+} > Cu^{2+} > Zn^{2+}$, which is consistent with the order of the single metal system (Table 1). The adsorption of a particular metal ion on sawdust in mixed metal solutions was less than that in single metal system resulting in a decrease in removal efficiency. Also, our results showed that the presence of Na^+, K^+, Mg^{2+}, and Ca^{2+} partially depressed the adsorption of Pb^{2+} on sawdust.

In Fig. 3, the control represents the Pb^{2+} adsorption in a single system without any other cations. Divalent ions such as Ca^{2+} and Mg^{2+} exhibit a stronger inhibition of Pb^{2+} adsorption than monovalent Na^+ and K^+ ions. This is in agreement with other studies that showed stronger inhibition with higher valent ions than that with lower ones.[11] As the concentrations of these ions increased from 0.1 M to 0.5 M, the effects of Ca^{2+} and Mg^{2+} were much more pronounced than those of K^+ and Na^+. Additionally, it was observed that DOM significantly affects Pb^{2+} adsorption on sawdust. It was known that DOM forms complexes with metals, because its structure contains a large proportion of functional groups such as carboxyl, hydroxyl, sulfate, phosphate, and amino groups.[14] At a low concentration of DOM, an enhanced adsorption of Pb^{2+} was observed. Added DOM was prefer-
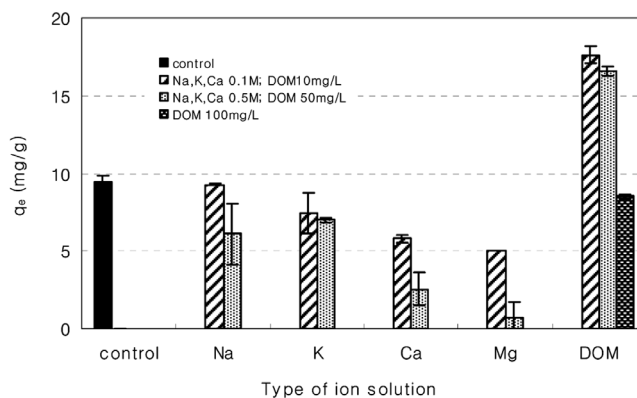
Fig. 3. Effect of inorganic ions and dissolved organic matter on the Pb^{2+} adsorption by sawdust.

ably adsorbed on the available surface sites of the sawdust, and sorbed DOM reacted with Pb^{2+} via complexation, resulting in the increased adsorption of Pb^{2+}. As DOM dosage increased, a relative amount of DOM in aqueous phase also began to increase as the surface sites of the sawdust became saturated. DOM in the aqueous phase then competed with sorbed DOM and surface sites for Pb^{2+} partitioning. Correspondingly, the increased interaction of Pb^{2+} with DOM in aqueous phase at a high dose of DOM resulted in decreased enhancement of Pb^{2+} adsorption on sawdust.

3.3. Effect of Contact Time and Initial Sorbate Concentration

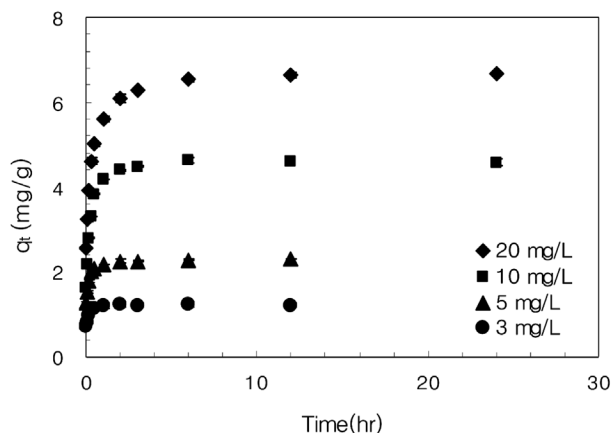The amount of Pb^{2+} adsorbed increased with the increase in-

Fig. 4. Adsorption rate of Pb(II) on sawdust.

initial concentration and remained nearly constant after equilibrium (Fig. 4). Equilibrium was attained within 360 min and the equilibration times were found to be independent of all concentrations studied. The adsorption rate was relatively fast in the initial stage, showing approximately 90% equilibrium attained within 30 min. This result indicates that adsorption of Pb^{2+} is mainly occurring at the surface of the sawdust. After this stage, the adsorption rate became slower, which was probably due to the diffusion of the metal ion into the sawdust.

3.4. Effect of pH

The effect of pH on the adsorption of Pb^{2+} on sawdust was described in Table 2. It indicates that the adsorption of Pb^{2+} on sawdust is strongly pH dependent, as has been commonly observed for heavy metal adsorption on biosorbents.[11,15,16] It is observed that Pb^{2+} removal decreases as pH decreases. The adsorption of heavy metal on sawdust is mainly attributed to ion exchange with hydrogen ions. Additionally, a number of anionic ligands such as carboxyl and hydroxyl groups may take part in the complexation with metal ions at the sawdust surfaces. At a low pH, the existence of a relatively large number of hydrogen ions resulted in a depression of the exchange between metal and hydrogen ions. Also, the complexes formed via interaction between the metal ions and acidic functional groups were destabilized at a low pH.[16]

3.5. Kinetic Studies

The kinetic parameter, which is helpful for the prediction of

the adsorption rate, gives important information for designing the processes. The kinetics of the adsorption data are analyzed using different kinetic models such as pseudo-first-order and pseudo-second-order kinetic models.[17] The kinetic rate expression of the first-order model is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (3)$$

where q_t and q_e are the amounts of adsorbate (mg/g) at time t (min) and at equilibrium, respectively. The constant k_1 can be obtained from the slope of the plot of $\log(q_e - q_t)$ vs. time. The values of k_1 at different sorbate concentrations and pH were calculated and are represented in Table 2. The R^2 values in Table 2 indicate that the first-order model is not appropriate to describe the adsorption process. The pseudo-second-order model[17] for adsorption kinetics is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (4)$$

where k_2 (g/mg·hr) is the second-order rate constant determined from the plot of t/q_t vs. t, as shown in Fig. 5. The second-order rate constants are used to calculate the initial sorption rate, given by

$$h = k_2 q_e^2 . \qquad (5)$$

The second-order rate constants and the calculated initial sorption rates are shown in Table 2. From Table 2, it was observed that the pseudo-second-order rate constant (k_2) decreased with increasing initial concentration and the initial sorption rate (h) decreased with higher initial Pb^{2+} concentration. As pH increased, the rate constant and initial sorption rate increased. The calculated q_e values agree well with the experimental values, and high R^2 values indicate that the pseudo-second-order model can be applied for the entire adsorption process.

Prediction of the rate-limiting step is an important factor to be considered in the design of an adsorption process. For a solid-liquid sorption process, the solute transfer is usually characterized by external mass transfer (boundary layer diffusion), or intraparticle diffusion, or both.[18] To identify the mechanism involved in the adsorption process, an intraparticle diffusion plot has been utilized. The rate constant of intraparticle diffu-

Table 2. Kinetic parameters under different conditions

| Parameters		First-order kinetics			Pseudo-Second-order kinetics				Intraparticle diffusion parameter
Conc. (mg/L)	pH	$q_{e,exp}$ (mg/g)	k_1 (1/hr)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg·hr)	h (mg/g·hr)	R^2	k_{id} (mg/g·hr$^{1/2}$)
3	4.5	1.214	5.37	0.973	1.22	3.31	4.926	0.999	0.0217
5	4.5	2.307	0.58	0.767	2.31	0.752	4.013	0.999	0.0434
	3	1.636	0.46	0.765	1.65	0.137	0.373	0.999	0.0991
10	4.5	4.679	1.08	0.899	4.68	0.15	3.285	0.999	0.0302
	7	4.942	1.96	0.950	4.95	0.399	9.776	1.0	0.0596
20	4.5	7.756	0.05	0.692	7.61	0.015	0.869	0.997	0.1913
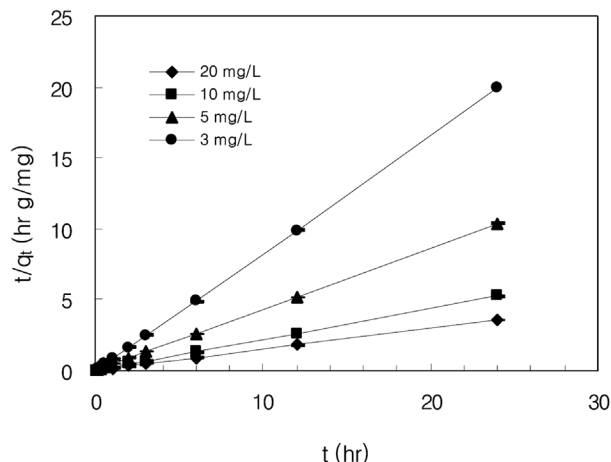
Fig. 5. The second-order rate constant plot for Pb(II) adsorption on sawdust at different adsorbate concentrations.

sion (kid) is given by the following equation.[18,19]

$$q_t = k_{id} t^{0.5} \qquad (6)$$

The plot of q_t vs. $t^{0.5}$ as shown in Fig. 6 represents the different adsorption stages. The initial curved portion is related to boundary layer diffusion and the latter linear curve represents intraparticle diffusion. The two regions in the plot indicate that both surface adsorption and intraparticle diffusion are involved in metal adsorption on sawdust. The slope of the second linear portion of the plot (k_{id}) represents the intraparticle diffusion coefficient. The calculated coefficient values are listed in Table 2. Meanwhile, the intercept of the plot indicates the boundary layer effect. The larger the intercept, the greater the contribution of surface adsorption was observed. It indicates that high initial concentration has relatively strong tendency for surface adsorption.
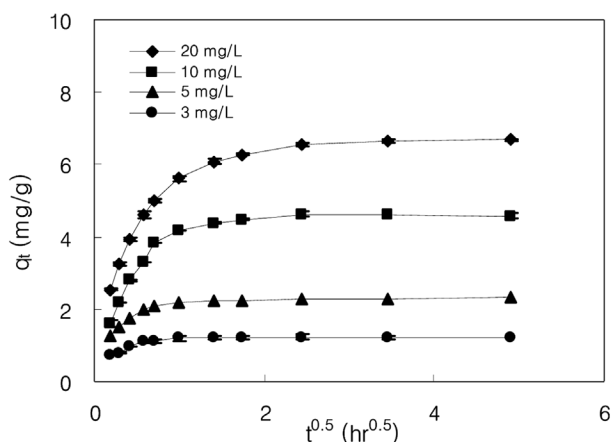

Fig. 6. Intraparticle diffusion plots for Pb(II) adsorption on sawdust at different adsorbate concentrations.

3.6. Column Studies

The results of metal adsorption on sawdust in the column are described using breakthrough curves (BTCs) where the concen-
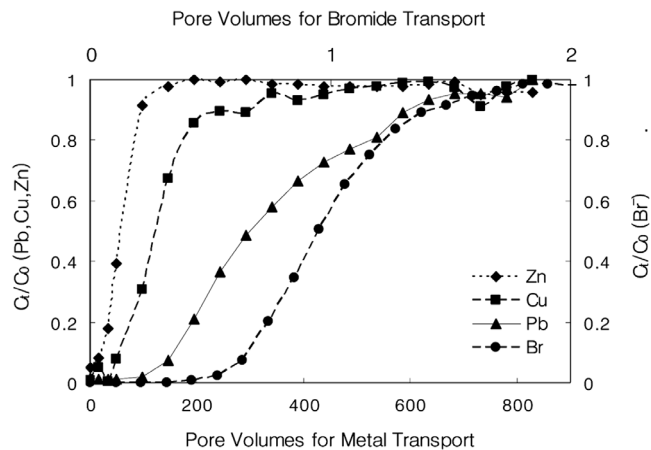

Fig. 7. Breakthrough curves of heavy metals from a sawdust-packed column (Metal concentration of feed solution = 10 mg/L).

tration ratio (C_t/C_o) is plotted versus pore volumes (time). Fig. 7 shows an observed BTC of a conservative tracer (Br⁻). A concentration ratio of $C_t/C_o = 0.5$ was reached at 1.0 pore volume, implying that the sawdust layer in the column was relatively homogeneous. The BTCs of metals show a large extent of retardation (Fig. 7). The breakthrough occurred at about 800, 500, and 150 pore volumes for Pb^{2+}, Cu^{2+}, and Zn^{2+}, respectively. As proven from batch tests, the most favorably sorbed metal, Pb^{2+}, occupied most of the adsorption sites on the sawdust in the column. Therefore, less favorably sorbed metals such as Cu^{2+} and Zn^{2+} showed more rapid breakthrough. Also, the slopes of the Zn^{2+} and Cu^{2+} curves were steeper than that of the Pb^{2+} curve. The quantity of Pb^{2+} adsorbed in the column was obtained by numerical integration of the area above the BTC. The adsorption capacity per sorbent mass (q_e) was determined to be 1.34 for Zn^{2+}, 3.26 for Cu^{2+}, and 7.73 mg/g for Pb^{2+}, respectively. These values are lower than those obtained from batch equilibrium tests. This difference might be due to the diffusion-limited adsorption rate.[8,15] A flow condition mostly results in an insufficient residence time and diffusion is limited inside the sorbent pores.

A solution of 0.1M CaCl₂ was used to elute the heavy metals adsorbed inside the column. The elution curves of the three heavy metals are shown in Fig. 8. The curves show a sharp increase in the beginning followed by a gradual decrease. Also, highly concentrated metal solutions were eluted within shortened pore volumes (time). Opposite the order of the adsorption process, the order of the elution of heavy metals was Zn > Cu > Pb, respectively. The mass of eluted metal was calculated using the elution curve, and it measured 37.8, 10.6, and 6.8 mg for Pb^{2+}, Cu^{2+}, and Zn^{2+}, respectively. Most of the heavy metals adsorbed onto the sawdust were eluted.

4. Conclusions

Sawdust was found to be an effective biosorbent for the removal of heavy metals in aqueous system. The adsorption on sawdust increased with increases in sorbate concentration and pH. The equilibrium adsorption of heavy metals on sawdust fit the Langmuir or Freundlich model reasonably well. The adsorption
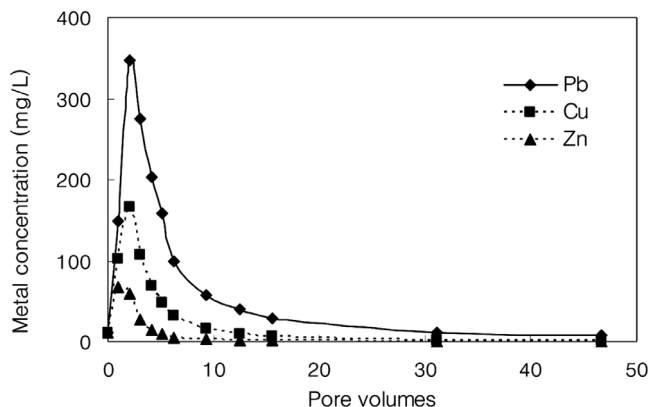
Fig. 8. Breakthrough curves of heavy metals from a sawdust-packed column flushed with 0.1M CaCl₂ solution.

capacity of metal varied from one metal system to another, and depended upon the presence of other metals in the solution. Divalent ions (i.e., Ca^{2+}, Mg^{2+}) were more efficient in depressing the metal adsorption on sawdust than monovalent ions (i.e., Na^+, K^+). DOM showed a significant effect on the metal adsorption on sawdust via the complexation reaction. The removal of Pb^{2+} was rapid at the initial stages, but it became slower afterward. Kinetic studies indicate that adsorption follows a pseudo-second-order model. Also, intraparticle diffusion plots indicate that both surface adsorption and pore diffusion are involved in metal adsorption on sawdust. The results of the column experiments showed retarded breakthrough of metals due to the high adsorption capacity of sawdust. The results of this study suggest that an adsorption system utilizing sawdust can be an economically feasible technique for the treatment of heavy metals in aqueous solution.

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