Abatement of toxic heavy metals from highway runoff using sawdust as adsorbent

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ABSTRACT

The possible use of sawdust as biosorbent has been successfully utilised to remove heavy metal ions from highway runoff. It is noted that increase in Pb^{2+} concentration and pH, caused the increase in adsorption capacity of sawdust. In relation to this, a decrease in sawdust dose results in a higher metal loading on the sawdust. The adsorption isotherms of heavy metals fit the Langmuir or Freundlich model reasonably well. The order of heavy metal adsorption is $Pb^{2+} > Cu^{2+} > Zn^{2+}$. A high concentration of co-existing ions such as Ca^{2+} and Mg^{2+} depresses the adsorption of heavy metal. Dissolved organic matter (DOM) has a significant influence on metal adsorption. In studies involving column, a long breakthrough time is observed for heavy metals according to the ion selectivity on sawdust. The metal adsorption capacity per sawdust mass in column is lower than that obtained in batch equilibrium tests, which is possibly due to the insufficient residence time and diffusion limitation of the metal. Flushing of the column saturated with heavy metals by 0.1M $CaCl_2$ solution results in the elution of a highly concentrated metal within shortened pore volumes, implying that sawdust could be re-used for the treatment of heavy metals.

Keywords: Adsorption, Sawdust, Heavy metal, Isotherm, Breakthrough.
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INTRODUCTION

Highway runoffs have various pollutants such as heavy metals, oil and grease, and particulates from vehicles such as fuels, brake pad wear, and tire wear. In particular, various types of heavy metals are observed in highway runoffs, posing environmental concerns due to their toxic and persistent characteristics. When there is a storm, the highly polluted runoff from the highway is washed off, directly affecting the water quality near the site [1]. Among them, significant concentrations of copper, lead, and zinc were reported in most literature [2-5].

Many types of structural best management practice (BMP) technologies including porous pavement, catch basins, detention ponds, wetlands, infiltration trenches, complexation, solvent extraction and membrane processes and vegetated swales have been developed for the treatment of runoff containing heavy metals [3, 5-7]. Meanwhile, adsorption processes have shown many advantages over these physicochemical methods. They are quite selective, effective, and are able to remove very low levels of soluble heavy metals in solution. Therefore, the treatment of highway runoff through a specially constructed filtration/adsorption system can be a promising alternative.
The adsorption of metals has been studied using low-cost sorbents including carbonaceous materials, waste by-products, weathered soils, and natural products such as activated carbon, iron-oxide-coated sand, and zeolites [8-11]. Biological materials are also recently gaining attention as simple, effective, and economical means for the treatment of heavy metals in runoff because they provide effective adsorption capacity and cheaper regeneration cost as compared to conventional sorbents such as activated carbon and ion-exchange resins [7, 9, 12-18]. The adsorption of heavy metals by these biological sorbents is attributed to their constituents which are mainly proteins, carbohydrates, and phenolic compounds containing functional groups such as carboxyl, hydroxyl, and amine groups which are responsible for the binding of metal ions [19]. Conclusively, bio-sorbents would be a feasible option for metal removal in order to develop a suitable highway runoff treatment system. Significantly, sawdust has advantages over other media due to its low cost as well as environmental benefits in terms of reuse of solid waste.

The objective of this study is to investigate the feasibility of utilizing sawdust for the adsorption of heavy metals such as copper, lead, and zinc in solution typically contained in highway runoff. In this work, the adsorption of metals, especially lead on sawdust, was studied using batch kinetic and equilibrium techniques. The equilibrium adsorption data were described by isotherm models.. Column tests were also performed to investigate the applicability of the sawdust adsorption system for the treatment of highway runoffs.

EXPERIMENTAL SECTION

2.1. Sorbent and Sorbates
Sawdust was collected from Shivam Saw Mill, Chunar, Mirzapur and washed with deionized water for three times to ensure that all fines were removed. The cleaned materials were dried in an oven at temperature of 70°C for 12 hours. The dried materials were then sieved with a #30 mesh (0.6mm) to be used for adsorption tests. The elements C, H, O, and N were determined with an Elemental Analyzer equipped with an inductive furnace analyzer (CE Instruments). The

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cation exchange capacity of sawdust was measured by a method of NH_4Ac exchange [20]. Other physico-chemical properties of sawdust were analyzed and are given in Table 1.

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.

Table 1. Physical and chemical properties of sawdust

Properties	Value
Particle size (mm)	< 0.6
Water content (%)	4.4 ± 0.10
Volatile matter (%)	98.9 ± 0.12
CEC (meq/100g)	72.3 ± 3.25
Total acidity (meq/g)	0.108
Elemental analysis (%)	
Carbon	48
Hydrogen	6
Oxygen	39.9
Nitrogen	0.1

2.2. Adsorption tests

Adsorption experiments for heavy metals on the sawdust were carried out in batch reactors. A known weight of sawdust (2.0 g) was added to the solution (1000 mL) with an initial metal concentration of 3–20 mg/L. 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.). All the bottles were mixed using a fixed agitation speed at room temperature. Samples were taken at predetermined sampling times. 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 filtrates were analyzed by an inductively coupled plasma atomic emission spectroscopy analyzer (ICP-AES, Leeman Abs. Inc.) to measure metal concentration. No correction for volume change was made because the percentage of total volume removed was considered sufficiently small (less than 0.5%).

Adsorption studies were carried out at various initial sorbate concentrations, sorbent doses, and pH values. Additionally, the effects of other ions on the adsorption were evaluated considering the real conditions occurring at the storm water runoff from the highway. Ions of Na^+, K^+, Mg^{2+}, and Ca^{2+} concentration varied from 0 M to 0.5 M. Dissolved organic matter (DOM) was obtained by purification of Aldrich humic acid according to the method of Hur and Schlautman [21]. The DOM concentration used in this study was 0, 10, 50, 100 mg/L based on total organic carbon content, respectively. 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 were presented.

Column experiments were carried out using a glass column (0.015 m long, 0.025 m i.d.) with an adjustable plunger. The column was packed with 7.2 g of sawdust, and the bed length was kept at 0.03 m. After packing the column, helium gas was used to remove the entrapped air in the

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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. 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 metal solution. Conservative tracer tests were carried out using a sodium bromide solution. The tracer solution was regularly taken from the outflow, and its concentration was measured by an ion chromatography (ACME, Younglin Inc.).

The solution of heavy metal mixture (i.e., Pb^{2+}, Cu^{2+}, Zn^{2+}) with an initial concentration of 10 mg/L was pumped through the column at a flow rate of 30 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 0.1M $CaCl_2$ solution followed, and the samples were collected for analysis.

RESULTS AND DISCUSSION

3.1 Effect of sorbate and sorbent concentration

The adsorption of Pb^{2+} as a function of its initial concentration ranging between 3 to 20 mg/L on sawdust is shown in Fig. 1. The adsorption rate was relatively fast at the initial stage, showing that approximately 90% equilibrium was attained within 30 min. This result suggests that the adsorption of Pb^{2+} mainly occurred 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. Storm water containing high initial pollutant load is called the first flush, a phenomenon commonly observed at highly impervious sites such as the highway. Initially, high pollutant concentrations in the first flush rapidly decreases after 20-50 min, thereby maintaining relatively low concentrations [22]. Over 90% of metal removal was obtained within the first 30 min of the run, indicating that the sawdust can be an effective adsorption material for the treatment of first flush. The equilibrium time for the adsorption of Pb^{2+} on sawdust at different sorbate concentrations was found to be 360 min, which implies that equilibrium time is independent of initial adsorbate concentration.
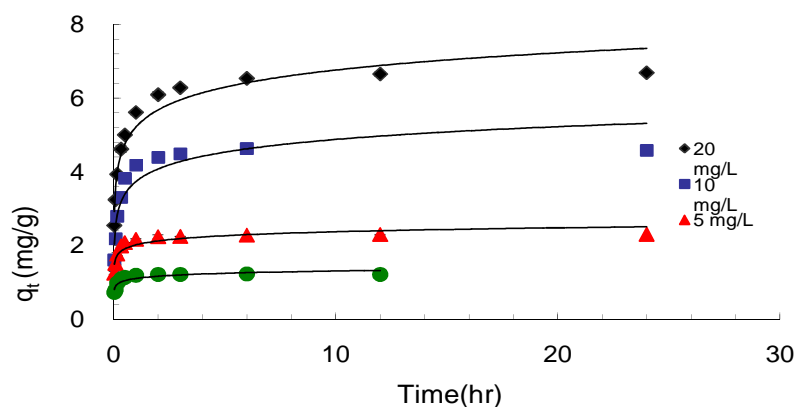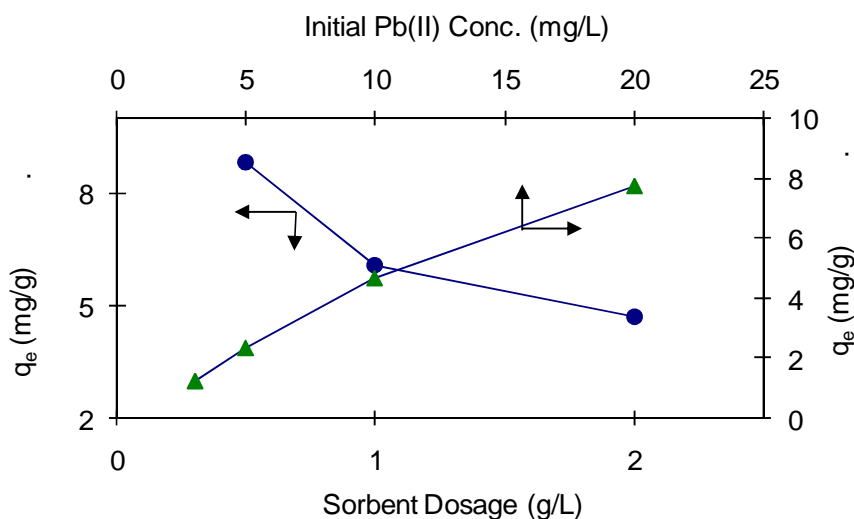

Fig. 1. Adsorption rate of Pb (II) on sawdust (Sawdust dose = 2 g/L, pH = 4.5).

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The results shown in Fig. 2 and Table 2 indicate that the adsorption capacities of sawdust increased as Pb^{2+} concentration increased. This is possibly due to the gradual increase in electrostatic interactions between sawdust surface sites and increased Pb^{2+} molecules [19]. The dosages of sawdust varying from 0.5 to 2 g/L were studied using solutions of 10 mg/L Pb^{2+} to evaluate the influence of the sorbent dose on the adsorption capacity. The adsorption capacity of sawdust was obtained after a 24 h adsorption process (Fig. 2, Table 2). The adsorption capacity of the sawdust decreased as the sorbent dose increased. However, the removal efficiencies of Pb^{2+} increased, since the equilibrium concentration of the Pb^{2+} in solution was lower in the presence of high concentrations of sorbent. More than 90% of the Pb^{2+} could be removed from the solution when the dosage of the sorbent was 2 g/L at the pH of 4.5.

Table 2. Effect of sorbent dose, initial sorbate concentration, and solution pH on the adsorption of Pb (II) by sawdust

Sorbent	pH	Sorbent dose (g/L)	Initial Pb(II) concentration (mg/L)	Sorption capacity, q_e (mg/g)	Removal efficiency (%)
Sawdust	4.5	0.5	10	8.84	44.2
		1.0	10	8.56	85.6
		2.0	3	1.40	93.3
			5	2.31	92.4
			10	4.68	92.2
			20	7.92	79.2
	3.0	2.0	10	1.64	32.8
	7.0	2.0	10	4.94	98.8

Fig. 2. Adsorption capacities of Pb (II) sawdust as a function of sorbent dose and initial Pb(II) concentration (pH = 4.5).

3.2 Effect of pH
The effect of pH on the adsorption of Pb^{2+} on sawdust was studied by varying the pH of metal solution from 3.0 to 7.0. The results in Table 2 indicate that the adsorption of Pb^{2+} on sawdust was strongly pH dependent, as has been commonly observed for heavy metal adsorption on bio-

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sorbents [13, 23, 24]. The adsorption of heavy metal on sawdust is attributed to ion exchange with hydrogen ions. Additionally, a number of anionic ligands such as carboxyl and hydroxyl group may take part in the complexation with metal ions at the sawdust surfaces. It was also observed that Pb^{2+} removal increased as pH increased. At a low pH, the existence of a relatively large number of hydrogen ions resulted in the depression of the exchange between the metal and the hydrogen ion. Also, the complexes formed via interaction between the metal ions and acidic functional groups were destabilized at a low pH because the stability constants decreased with pH, and therefore, the metal ions eluted into the solution. Also, physical adsorption on the lipophilic part of the sawdust occurred at certain pH ranges where metal was associated with hydroxide and became neutral [25].

3.3 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 linear 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 for 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. The adsorption isotherms of heavy metals were determined for various concentration ranges and fixed mass of sawdust (1g/L of solution). The linear plot of the Langmuir equation was drawn, and the values of S_m and K_L were determined by Fig. 3 and also from the slope and intercept of the linear plot of $\log q_e$ vs. $\log C_e$ corresponding to 1/n and log K_F (Fig. 4).
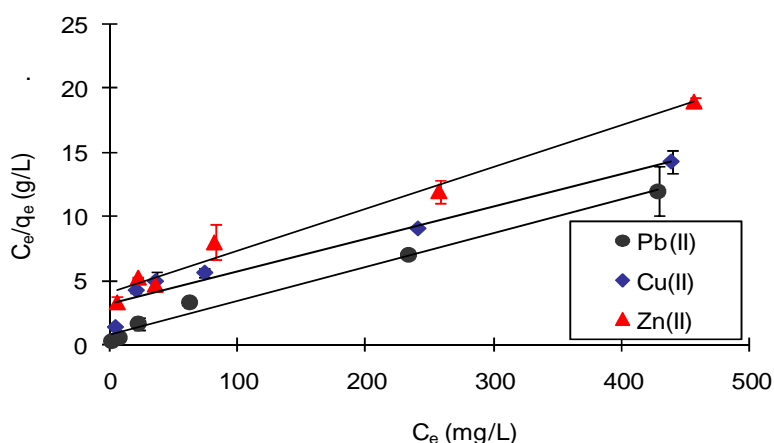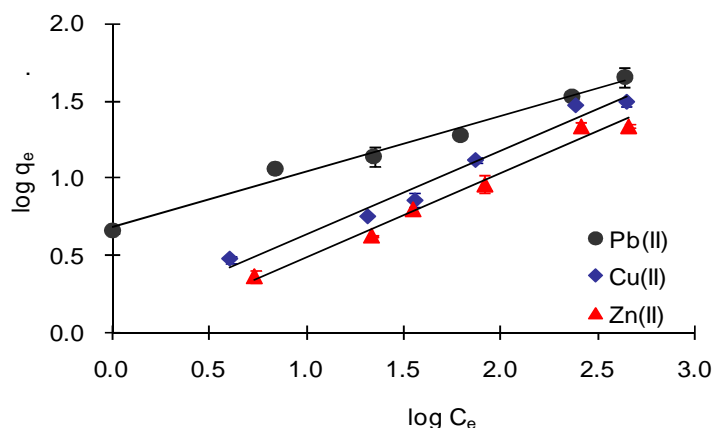

Fig. 3. Langmuir isotherm plot for the adsorption of heavy metals on sawdust (Sawdust dose = 1g/L, pH = 4.5).

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**Fig. 4. Freundlich isotherm plot for the adsorption of heavy metals on sawdust (Sawdust dose = 1g/L, pH = 4.5).**

The equilibrium adsorption of three heavy metals (i.e., Pb^{2+}, Cu^{2+}, and Zn^{2+}) were well represented by the Langmuir or the Freundlich model with high R^2 values, as described in Table 3. The suitability of both isotherm models in representing the equilibrium data of three heavy metals indicated that there was the formation of a monolayer of metal ions on the sawdust surface [13]. The order of adsorption affinity on sawdust was $Pb^{2+} > Cu^{2+} > Zn^2$, and it was related to the differences in electronegativity of the atom. Considering that the adsorption of heavy metals on sawdust is mainly due to ion-exchanges at the surface level, and found that more electronegative metals show a higher adsorption tendency.

**Table 3. Langmuir and Freundlich adsorption isotherm parameters of heavy metal on sawdust**

Sorbent	System	Metal type	Langmuir constant			Freundlich constant		
			S_m	K_L	R_L^2	K_F	$1/n$	R_F^2
Sawdust	Metal ion in single	Pb(II)	30.48	0.0137	0.999	2.67	0.382	0.982
		Cu(II)	30.90	0.0073	0.986	1.19	0.495	0.973
		Zn(II)	26.74	0.0071	0.999	1.00	0.500	0.999
	Metal ion in mixture	Pb(II)	35.10	0.0052	0.985	0.95	0.535	0.999
		Cu(II)	28.30	0.0059	0.999	0.80	0.538	0.999
		Zn(II)	28.10	0.0042	0.991	0.42	0.625	0.976

3.4 Effects of Co-existing ions

As highway runoff usually contains a mixture of ions and dissolved organic matter [3, 26], the effects of these compounds on the adsorption of heavy metals on sawdust need to be evaluated. In the mixture system of metals, the order of the metal adsorption was $Pb^{2+} > Cu^{2+} > Zn^{2+}$, which was consistent to the order of the single metal system (Table 3). It was found that in mixed metal solutions, the adsorption of a particular metal ion on sawdust was less than those if it were present alone, which corresponded to a decrease in removal efficiency (Fig. 5). Also, our results showed that the presence of Na^+, K^+, Mg^{2+}, and Ca^{2+} partially depressed the adsorption of Pb^{2+} by sawdust (Fig. 6). In Fig. 6, the control represented the Pb^{2+} adsorption in a single system without any other ions. Divalent ions such as Ca^{2+} and Mg^{2+} exhibited a stronger inhibition of Pb^{2+} adsorption than Na^+ and K^+.

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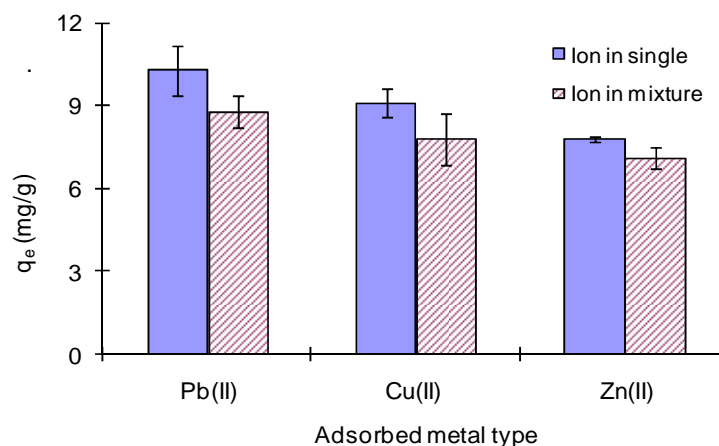
Fig. 5. Comparison of Pb^{2+} adsorption in single and mixture system by sawdust (Initial metal concentration = 100 mg/L, sawdust dose = 2 g/L, pH = 4.5)
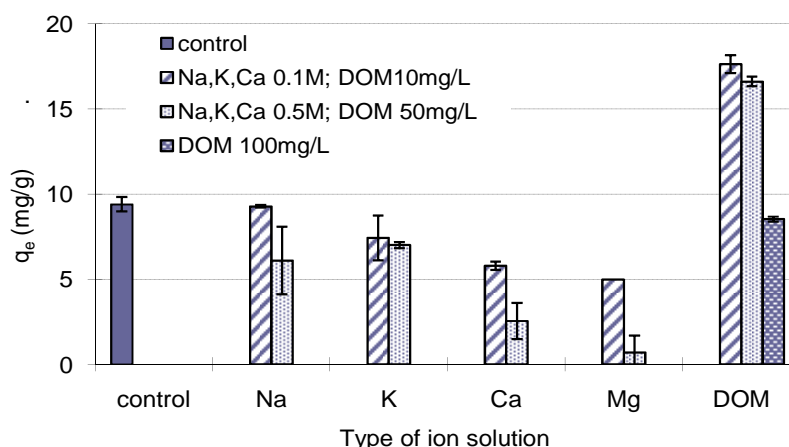
Fig. 6. Effect of inorganic ions and dissolved organic matter on the Pb^{2+} adsorption by sawdust (Initial Pb^{2+} concentration= 100 mg/L, sawdust dose= 2 g/L, pH = 4.5)

This was in agreement with other studies which showed that the inhibition was stronger with higher valent ions than with lower ones [19]. As the concentrations of these ions increased from 0.1M to 0.5M, 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 the Pb^{2+} adsorption on sawdust. At a low concentration of DOM, an enhanced adsorption of Pb^{2+} was observed. Generally, DOM strongly affect heavy metal adsorption, since the structure of these compounds contains a large proportion of functional groups such as carboxyl, hydroxyl, sulfate, phosphate, and amino groups [26]. Added DOM was adsorbed on the available surface sites of 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 sawdust became saturated. DOM in aqueous phase then competed with sawdust surface sites and sorbed DOM for Pb^{2+} partitioning. Correspondingly, the increased

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interaction between DOM in aqueous phase and Pb^{2+} at a high dose of DOM resulted in the decreased enhancement of Pb^{2+} adsorption on solid phase (sawdust).

3.5 Column Studies

The results of metal adsorption on sawdust in column were described using breakthrough curves (BTCs) where the concentration ratio (C_t/C_o) was plotted versus pore volumes (time). Figure 5 shows that an observed BTC of conservative tracer (Br^-) and a concentration ratio of $C_t/C_o = 0.5$ was reached at 1.0 pore volume, implying that the sawdust layer in column was relatively homogeneous. The BTCs of metals showed a large extent of retardation (Fig. 7). The breakthrough curves occurred at about 150, 500, and 800 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 column. Therefore, less favorably sorbed metals such as Cu^{2+} and Zn^{2+} showed more rapid breakthrough. Also, the slope of the Zn^{2+} and Cu^{2+} curve was steeper than that of the Pb^{2+} curve. This observation implied that the adsorption of Zn^{2+} and Cu^{2+} on sawdust resulted mainly from the ion exchange, while the adsorption of Pb^{2+} was not only based on ion exchange, but might likewise involve some physical adsorption [25]. 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 0.89 for Zn^{2+}, 2.17 for Cu^{2+}, and 5.15 mg/g for Pb^{2+}, respectively. These values were lower than those obtained from batch equilibrium tests, in which maximum Q_e was 17.1 for Zn^{2+}, 20.2 for Cu^{2+}, and 24.5 mg/g for Pb^{2+}, respectively. This difference might be due to the intra particular diffusion-limited adsorption rate [16, 17]. Mostly, high flow rate results in the insufficient residence time of the solute and the diffusion limitations of the solute into the pores of the sorbent. It implies that the retention capacity of the adsorption system utilizing sawdust is largely dependent upon the intensity of rainfall by which the flow rate of highway runoff coming into the treatment facility is determined.
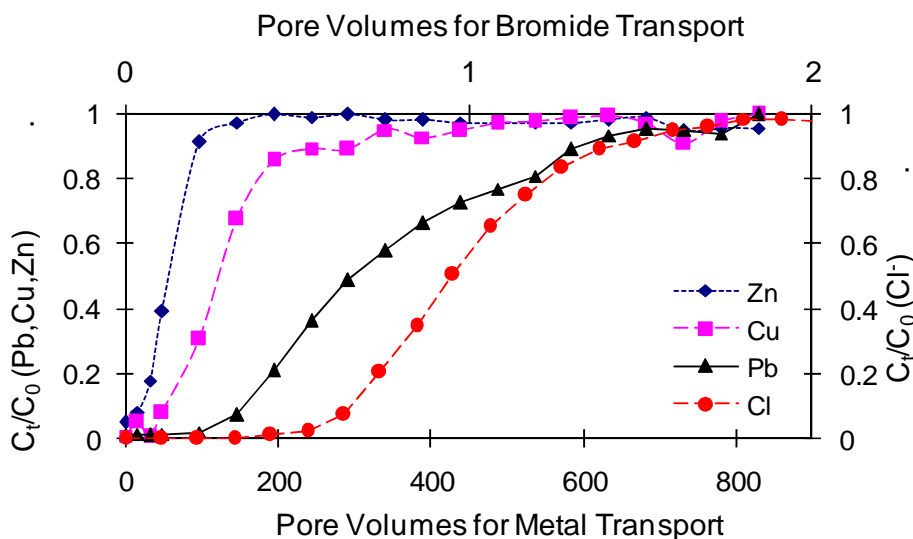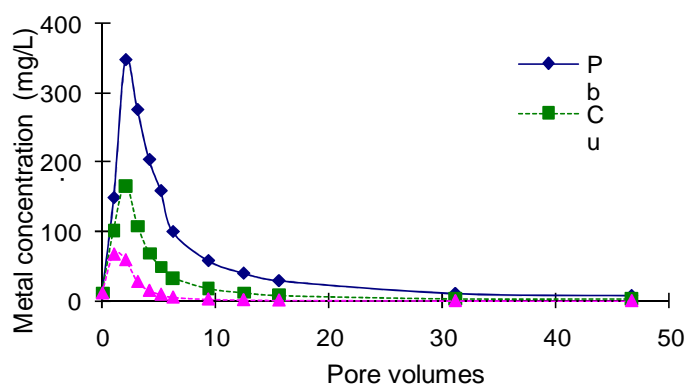

Fig. 7. Breakthrough curves of heavy metals from sawdust-packed column (Metal concentration of feed solution = 10mg/L).

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The column regeneration was carried out to evaluate the re-utilization of the adsorption system with sawdust. A solution of 0.1M $CaCl_2$ was used to elute the heavy metals adsorbed inside the column. The elution curves of the three heavy metals are shown in Figure 8. The curves showed 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 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, and thus the sawdust could be re-utilized for the repetitive adsorption of metals.

Fig. 8. Breakthrough curves of heavy metals from sawdust-packed column flushed with 0.1M $CaCl_2$ solution.

CONCLUSION

Sawdust was found to be an effective bio-sorbent for the removal of heavy metals in highway runoff. Based on our findings, the adsorption capacity of sawdust increased along with increases in sorbate concentration and pH. The increase in the sawdust dose resulted in the increased removal rate of heavy metal. The removal of Pb^{2+} was rapid at the initial stages, but it became slower afterward. The equilibrium adsorption of heavy metals on sawdust fitted well the Langmuir or Freundlich model . The adsorption capacity of metal varied from one metal system to another, and depended upon the presence of other metal(s) in the solution. Divalent ions (Ca^{2+}, Mg^{2+}) were more efficient in depressing the metal adsorption on sawdust than monovalent ions (Na^{+}, K^{+}). DOM showed a significant effect on the metal adsorption on sawdust via the complexation reaction. The enhancement or depression of metal adsorption in the presence of DOM might be largely dependent upon the relative amounts of DOM existing at the aqueous and solid phase (sawdust surface). The results of the column experiments indicate that the sawdust layer exhibited a retarded breakthrough of metals due to high adsorption capacity. The value of adsorption capacity per sorbent mass in column was less than those from equilibrium batch tests. Conclusively, the results of this study suggest that the adsorption system utilizing sawdust is an economically feasible technique for the treatment of highway runoff.

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