

The removal of heavy metals in urban runoff by sorption on mulch

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“Capsule”: Hardwood bark had the best physicochemical properties for adsorption of metal ions.

Abstract

A series of adsorption experiments was conducted in order to assess the ability of three mulches to remove several of the heavy metal ions typically encountered in urban runoff. Three types of mulch, cypress bark (C), hardwood bark (H), and pine bark nugget (P), were selected as potential sorbents to capture heavy metals in urban runoff. The hardwood bark (H) mulch had the best physicochemical properties for adsorption of heavy metal ions. In addition, because of its fast removal rate and acceptably high capacity for all the heavy metal ions, it was concluded that the H mulch is the best of the three adsorbents for treatment of urban runoff containing trace amounts of heavy metals. In order to investigate the sorption isotherm, two equilibrium models, the Freundlich and Langmuir isotherms, were analyzed. The sorption of these metals on H mulch conformed to the linear form of the Langmuir adsorption equation. At pH 5 and 6, the Langmuir constants (S_m) for each metal were found to be 0.324 and 0.359 mmol/g (Cu); 0.306 and 0.350 mmol/g (Pb); and 0.185 and 0.187 mmol/g (Zn) at 25 °C.

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1. Introduction

The incidences of non-point source pollution that are detrimental to the environment have been gradually increasing over time due to rapid urbanization and industrialization (Thurston, 1999; Ngabe et al., 2000). Among the various non-point sources, stormwater runoff from urban areas has been recognized as a major contributor to a variety of water pollution problems in adjacent receiving bodies of water. It was reported that urban stormwater runoff alone ranks as the second most common source of water pollution for lakes and estuaries nationwide, and the third most common source for rivers in the United States (USEPA, 1995; Walker

et al., 1999). As a result of these investigations, legislation is pending under the United States' National Stormwater Program to control pollutants in stormwater discharges (Brown et al., 2000a,b).

In particular, urban stormwater runoff contains significant concentrations of heavy metals; nutrients; suspended, colloidal and volatile fractions of inorganic and organic particulates; and other anthropogenic compounds (Sansalone, 1996). It was reported that, although the potential exists for the occurrence of practically any metal ion in urban stormwater runoff, the types of metals most observed to have a negative effect on receiving waters are copper, lead and zinc (Marsalek et al., 1999; Roesner, 1999; Brown et al., 2000a,b). Walker et al. (1999) summarized the concentrations of heavy metals in urban runoff and reported them to be in the following concentration ranges: Cu (0.00006–1.41 mg/L), Pb (0.00057–26.0 mg/L) and Zn

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(0.0007–22.0 mg/L). From these studies, it was confirmed that runoff from small as well as large cities is typically contaminated with metals at several orders of magnitude above background levels (<10 µg/L for Cu and Zn, <1 µg/L for Pb; Sansalone, 1996).

Treatment of urban runoff containing low concentrations of heavy metals is of importance to many countries of the world, both for environmental quality and water reuse. Although various conventional and emerging methods (e.g. ion-exchange, electrolyte or liquid extraction, electrodialysis, precipitation, reverse osmosis) could be applied to treat stormwater runoff to acceptable levels before being discharged into water bodies, most of these available physicochemical technologies are either economically unfavorable or too technically complicated (Brown et al., 2000a,b). Adsorption of metals to filter materials has been studied using low-cost sorbents including carbonaceous materials, waste by-products, weathered soils, and agricultural/natural products such as activated carbon, iron-oxide-coated sand, zeolites, rice bran and hulls, soybean, peanut husk, saw dust, peat and leaves (Naidu et al., 1998; Brown et al., 2000a,b; Ricordel et al., 2001; Färm, 2002; Ho et al., 2002).

A number of structural best management practice (BMP) technologies (porous pavement, detention/retention ponds, wetlands, partial exfiltration trenches, infiltration trenches and vegetated swales) have been developed for urban runoff management (Sansalone, 1996; Shutes et al., 1997), one of which is bioretention. Filtration and sorption of runoff through a specially constructed bioretention filter system is one possible treatment method. Bioretention systems generally composed of layers of soil, a variety of plants, and mulch have the capacity to improve water quality by assimilating and transforming organic, inorganic and toxic constituents through processes such as infiltration, sorption, precipitation, and binding by organic colloidal material or adsorption of metal-ligand complexes (Davis et al., 2001). In a bioretention reactor, the soil layer is covered with a thin mulch layer where the filtration and sorption might mainly occur. Some plants also play important roles in bioretention systems for the removal of pollutants. They not only take up nutrients, but are also able to adsorb and accumulate metals. Mulch contains extensive organic materials composed mainly of humic substances, polysaccharides and poly-peptides (Petrović et al., 1999). Among the organic materials, humic substances strongly affect heavy metal sorption since the structure of these compounds contains a large proportion of functional groups such as carboxyl, hydroxyl, sulfate, phosphate and amino groups. Since mulches similar to leaf litter in a forest are plentiful, inexpensive and readily available, their utilization for the removal of heavy metals is gaining attention as a simple, effective and economical means of

urban runoff treatment. However, there are still questions to be answered regarding removal capacity and efficiency for heavy metals.

In order to achieve the development of an effective adsorber, the parameters and mechanisms affecting metal ion capture by mulches must be identified. Therefore, the major interest of this study was to investigate the possibility of utilizing mulches for the adsorption of heavy metals such as copper, lead and zinc in solutions typical of those found in urban runoff. Laboratory tests consisted of physicochemical tests to identify the structure and composition of mulches commercially available in the USA, flask-type batch extractions to determine the total content of heavy metals in mulch, and adsorption batch tests to compare the adsorption capacity for the different types of mulch.

2. Materials and methods

2.1. Sorbents and sorbates

Three types of mulch, cypress bark (C), hardwood bark (H), and pine bark nugget (P), were selected as potential sorbents to capture heavy metals in urban runoff. These mulches were purchased from Ohio Mulch, Cincinnati, OH, USA. Various sizes of raw mulch were washed several times with deionized water to remove easily leachable materials and fines. The rinsed materials left on shallow trays were subsequently dried at an oven temperature of 60 °C overnight. Each kind of dry sorbent was ground into appropriate particle sizes by placing a portion of each mulch into a blender, blending, and then sieving with #10 mesh (2 mm). The ground and sieved #10 mesh mulch particles were used for analysis of physicochemical characteristics and for the adsorption batch tests. The rehomogenized particles were packed in sealed polyethylene bags for further use.

All heavy metal solutions (divalent cations of Cu, Pb and Zn) for adsorption testing were prepared in stock solutions of up to 1000 mg/L of metal from the corresponding nitrate salts ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). All working solutions were prepared by diluting the stock solution with distilled water.

2.2. Surface and chemical composition of mulch

The specific surface areas of the mulches were determined using an N_2 volumetric gas adsorption analyzer (Coulter SA 3100) by applying the Brunauer, Emmett and Teller (BET) method to the N_2 isotherm. The microstructure of the mulch surface was monitored with an environmental scanning electron microscope,

ESEM (FEI XL-30 ESEM FEG). The working tension was 20 kV. Samples were prepared by depositing them on a support and then metallizing them with gold.

The elements C, H, O and N were determined with an Elemental Analyzer equipped with an inductive furnace analyzer (Perkin–Elmer). In order to determine the composition of metals in the mulch, the mulch was dissolved in an acid mixture (HNO_3 and HCl , 70:30) for the determination of Fe, K, Na and Ca; or in an alkaline solution (NaOH) for the analysis of Al and Si. The metals in the solution were analyzed using flame atomic absorption spectrophotometry, AAS (Perkin–Elmer AAnalyst 300).

2.3. Sorption tests

Sorption experiments for the different metal ions on the different mulches were carried out in batches as follows. All the metal ion solutions were prepared to give initial metal ion concentrations of 0.1–1.5 mM Cu^{2+} , Pb^{2+} and Zn^{2+} . Metal solutions (500 mL) were added to beakers already containing different weights (from 0.2 to 3 g) of mulch. The initial pH of the metal salt solutions was adjusted to the desired value (pH 6.0, 5.5 or 5.0) with dilute HCl or NaOH . All the beakers were sealed with foil caps to minimize evaporation and then were mixed at room temperature for 6 h with a magnetic stirrer at 200 rpm. No correction for volume change was made as the percent of total volume removed was considered sufficiently small (less than 3%). Samples were taken at predetermined sampling times (0, 1, 3, 5, 7, 10, 15, 30, 60, 180 and 360 min). The samples were filtered and stored in polyethylene bottles to which 0.1 mL of HCl (70%) had been added for sample preservation. The concentrations of the three metal species in the liquid were analyzed, either directly or after dilution (if necessary), by AAS using an acetylene–air flame. The net mass of the metal ions adsorbed onto the adsorbent was determined as the difference between the spiked mass measured in the blank series and the measured mass in the liquid phase. After adsorption, mulch containing its equilibrium metal content was extracted with a heated concentrated acid mixture (HNO_3/HCl ; 1:3 v/v) to determine the amount of metals adsorbed.

The amount of heavy metals retained in the sorbent phase (Q_e , mg/g) was calculated from the heavy metal mass balance yield expressed as: $m(Q_e - Q_0) = V(C_0 - C_e)$, where Q_0 is typically assumed to be zero. Hence, $Q_e = (C_0 - C_e)V/m$, where Q_0 is the initial metal ion concentration on the mulch (mg/g), C_0 and C_e are the initial and equilibrium concentrations of the metal ions in solution (mg/L), V is the volume of the metal solution (L), and m is the dry weight of the sorbent (g).

2.4. Analytical methods

The pH and conductivity values were separately measured in the supernatant of a mulch–distilled water mixture using a digital pH meter (Fisher Scientific, AR15) and a conductivity analyzer (Corning 311). Water content (WC) and biomaterial content (BC) of the mulches were determined according to APHA (1998). Cation exchange capacity (CEC) was calculated by the ammonium acetate method as reported by Ciesielski and Sterckeman (1997). The total metal contents of the mulches (1 g of dry weight) were extracted by heated concentrated acid digestion (HNO_3/HCl ; 1:3 v/v) based on SW-846 Method 3050A (USEPA, 1990). The filtrates were analyzed for these heavy metals using AAS. The absorbance of a sample was measured and the concentration was calculated from the calibration curve that was determined by previously recording the absorbance of standard concentration solutions of each ion. When samples of metal solutions without sorbent, which served as blanks, were filtered, the concentrations of the metals were the same before and after filtration. In order to remove possible metal complexes formed on the walls of the bottles, all the glasswares were washed in nitric acid (1 N HNO_3) overnight before use and rinsed with deionized water. All chemicals (Fisher Scientific) were of analytical reagent grade, and solutions were prepared with deionized water (17 M Ω). Each experiment was carried out in duplicate.

3. Results and discussion

3.1. Properties of the mulch

Three types of natural material mulches, cypress bark (C), hardwood bark (H), and pine bark nugget (P), were used as sorbents to adsorb heavy metals in solution. These are by-products of the paper and lumber industries and are the most common types in use in the United States. Although each of these differs in appearance and function, the common objectives of mulches are to hold moisture, retard weeds, maintain even soil temperatures and provide a decorative appearance. In general, mulch costs approximately 2.4 cents per kilogram, which can be considered relatively inexpensive compared to other materials for removal of heavy metals from wastewaters. For example, the costs of activated carbon and ion-exchanged resins are in the range of approximately \$2.0–\$4.0 per kilogram (Al-Asheh and Duvnjak, 1997). Being plentiful and inexpensive, mulch possesses several characteristics that make it a potentially effective sorbent for the removal of dissolved metals from urban runoff.

The physicochemical properties of the mulches used in this study are summarized in Table 1. Pine bark

Table 1
Physicochemical properties of the experimental mulches

Elements	Types of mulches		
	C	H	P
pH	5.15 ± 0.06	7.43 ± 0.28	4.26 ± 0.08
WC ^a (%)	36.9 ± 4.6	55.9 ± 6	49.4 ± 9.5
BC ^b (%)	5.3 ± 0.4	14.7 ± 0.4	11.2 ± 0.8
CEC ^c (meq/100 g)	20.5 ± 2.5	42.3 ± 3.4	10.8 ± 2.5
Conductivity (mS/cm), at 25 °C	0.25 ± 0.01	0.36 ± 0.01	0.17 ± 0.06
Surface area (m ² /g)	11–18	25–32	22–26

All the values except those for Surface area are Mean value ± standard deviation.

^a Water content.

^b Biomaterial content.

^c By BaCl₂ method proposed by Ciesielski and Sterckeman (1997).

nugget mulch has a reddish brown color and is relatively more acidic than the other mulches used. On the other hand, the hardwood bark mulch produced from hardwood trees has the highest pH and shows the highest values for the other physicochemical properties, which might be effective in increasing the sorption capacity of heavy metal ions. It is commonly believed that pH is one of the key factors, together with cation exchange capacity (CEC), the nature of adsorbent, and the presence of competing ions and complexing ligands on adsorption, controlling the adsorption of metal ions by various adsorbents (Dho and Lee, 2003). Thus, it can be assumed that the H mulch with a neutral pH might exhibit better ability to hold cations than the other mulches with their lower pH. In addition, it is generally understood that a material with a high CEC value has a tendency to hold a large amount of cations, and is also a good indicator of the high organic material content of the soil. The CEC of the H mulch was measured to be approximately 40 meq/100 g; the H mulch also contained the highest amount of biomaterials that are good for adsorbing the heavy metals. One of the potentially important biomaterials is organic material from the microbial biomass as a possible factor involved in metal adsorption. It is well known that the amount of biomass cells is related to that of extracellular polymeric substances (EPS) containing variable proportions of proteins, carbohydrates, nucleic acids, humic-like substances, lipids and heteropolymers (Jorand et al., 1998). The adsorption of heavy metals by bioavailability, in particular, can be caused by bridging mechanisms between metal cations and negative charge of acidic functional groups of EPS.

The chemical composition of mulch is central to its sorption characteristics. The H mulch, consisting of complex heterogeneous materials, is composed mainly of carbon (55.7%) and silicate (19.7%). The remaining chemical composition (by weight) is approximately H

(1.7%), O (19.5%), N (0.2%), K (1.3%), Na (1.4%), Ca (0.9%), Al (1.7%) and Fe (1.5%). At the initial stage of adsorption, the rapid loss of heavy metal ions from the solution in the presence of adsorbents might be due to adsorption on adsorbent surface and pores, and/or to attraction by surface charge. Among the mulches, the H mulch specific surface area (25–32 m²/g), measured by the BET/N₂ method, was high in comparison with montmorillonite that has a surface area of about 8.9 m²/g (Lin and Juang, 2002), and was lower than a seafood-processing factory waste sludge having a specific surface area of 80 m²/g (Lee and Davis, 2001). The specific surface area of C and P mulch was 11–18 and 22–26 m²/g, respectively.

The ESEM was used to confirm the adsorption of metals on the surface of the mulches. In Fig. 1, photograph (a) represents the surface of a virgin mulch before carrying out metal adsorption, while photograph (b) shows the surface after performing the adsorption. Although different pore sizes may be observed (Fig. 1(a)), many more small pores, with approximately

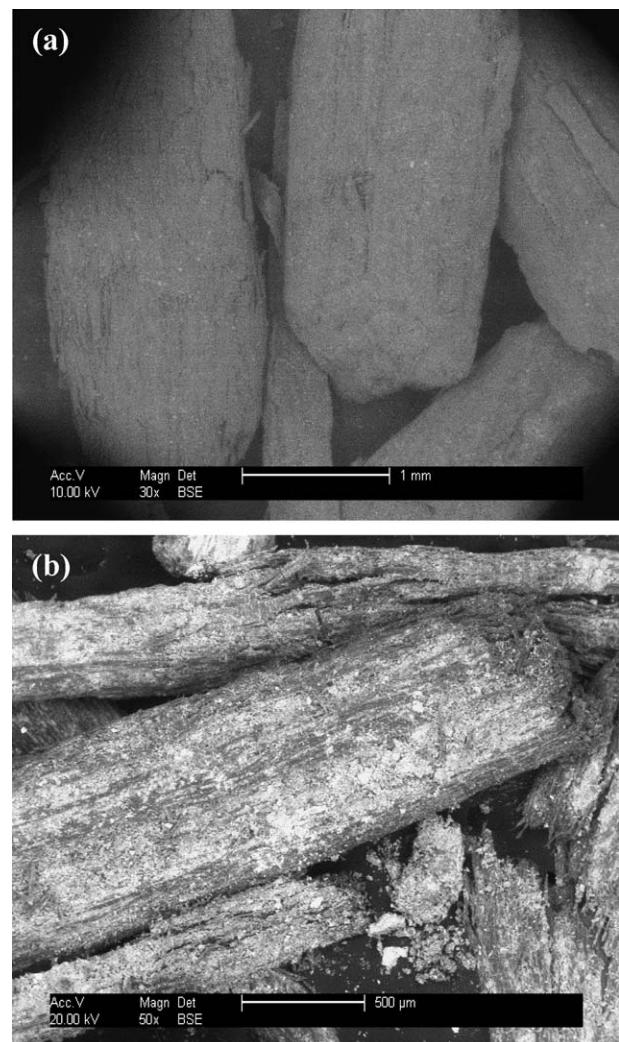


Fig. 1. Environmental scanning electron micrographs of H mulch before (a) and after (b) the adsorption experiment (1.5 Pb(II) mM).

Table 2

Extraction of metals, anions and TOC from three types of mulches according to the two extraction methods

Mulch	Extraction methods	Heavy metal ions (mg/kg)			TOC (g/kg)
		Cu(II)	Pb(II)	Zn(II)	
C	TCLP	ND	ND	4.1 ± 0.6	56.4 ± 2.0
	Aqua regia	0.6 ± 0.1	7.6 ± 0.0	61 ± 7.4	209.5 ± 16.5
H	TCLP	0.1 ± 0.0	ND	6.6 ± 2.1	58.9 ± 2.0
	Aqua regia	29.3 ± 5.6	10 ± 2.3	33.6 ± 5.2	216.3 ± 1.0
P	TCLP	1.9 ± 0.2	ND	3.5 ± 1.2	59.4 ± 3.2
	Aqua regia	36.8 ± 1.3	6 ± 2.3	46.2 ± 8.0	228.1 ± 21.3

Mean value ± standard deviation; Aqua regia ($\text{HNO}_3:\text{HCl}$, 1:3 v/v); ND means no detection (detection limit: 220 µg/L Cu(II); 169 µg/L Pb(II); 17 µg/L Zn(II)).

15 µm diameters, can be seen on the surface of the virgin mulch. It can be also observed that the surfaces of metal-laden mulches after the adsorption were choked up with the metal crystals (white color). Thus, it can be assumed that the surface areas of mulch contain most of the sorbed metal ions.

Knowing the content of heavy metal ions in a mulch is important for determining the adsorption capacity of that mulch. According to the results in Table 2, the three mulches evaluated contained various concentrations of heavy metals according to the mulch type and extraction method used. The levels of heavy metal extracted by the TCLP method are lower than those by aqua regia. This indicates that the total heavy metal concentrations may be determined more precisely using more acidic solutions. Among the heavy metals, the amount of Zn(II) extracted by aqua regia is a little high, which may raise environmental concerns. However, since some of the metal is present in a not easily extractable form, the total amount of heavy metals should not be used to predict the mobility and the bioavailability of metals in evaluating the risks to environmental quality and human health. According to data in Table 2, the total organic carbon (TOC) content extracted by the TCLP method was about 60 g/kg. The TOC concentrations of the three mulches were low in comparison with forest litter that has a carbon concentration of about 470 mg/g (Balabane et al., 1999).

3.2. Equilibrium sorption of single metal ions

Three mulches were tested for their ability to adsorb the three selected metal ions from aqueous solution, using adsorbent and initial metal ion concentrations of 2 mg/L and 1 mM, respectively, and maintaining the temperature at 25 °C and the initial pH at 5.5. In order to evaluate the equilibrium reaction time, the various reaction times were initially observed. As shown in Figs. 2(a1–a3), the time to sorption equilibrium can be considered relatively fast since approximately 90% equilibrium was attained within 30 min. However, to ensure complete equilibrium, in all subsequent

experiments samples with those adsorbents were left shaking for about 3 h. The time (3 h) was enough to reach an equilibrium state since there were small differences between before and after 3 h analyses.

Along with the sorption equilibrium time, the initial heavy metal removal rate is a very important factor in the design and optimization of a bioretention reactor to be used to remove heavy metals in urban runoff. Urbanization increases the amount of impervious surface in a region, which increases runoff volumes and decreases both infiltration and the time during which runoff occurs (Brezonik and Stadelmann, 2002). Fig. 2 (a1–a3) shows the concentration and uptake curves for each metal onto the different mulches. Uptake means the decreasing metal concentration in solution with respect to time. For all adsorption experiments in this study, over 80% of the total metal ion removal occurred within the first 10 min of the run. The initial metal ion removal rates could generally be divided into two steps. In the first step (less than 1 min), a rapid initial uptake of metal ions was observed. This is due to a rapid attachment of metal ions to the surface of the mulch by the increased amount of surface charges. It is generally understood that as the amount of mulch increases, the total surface charge of the mulch increases. In addition, penetration of ions into the mulch may occur as a consequence of irreversible chemical adsorption. In the second step (from 1 to 10 min), the metal ion removal rate follows a first-order reaction equation, which can be expressed generally as:

$$\ln C_t = \ln C_i - kt \quad (1)$$

where C_t is the concentration of metal ions at time t , C_i is the initial concentration of metal ions and k is the rate constant of adsorption at 25 °C. The plots of $\ln (C_t)$ versus time (t) in Fig. 2(b1–b3) show a straight line, indicating the applicability of assuming first-order kinetics.

After the initial second stage of the sorption (after 10 min), however, the results deviated from linearity, indicating that another kinetic process may be involved. The high initial interaction of mulch with heavy metal ions may form a relatively insoluble metal complex and/or may result in the adsorption of heavy metals mainly at the mulch surface, thus significantly reducing aqueous metal concentrations during the second stage of the sorption process. After this period of time, the adsorption rate became slower, which is probably due to diffusion of the ions into the porous structure of the mulch. However, although many different sorption studies have been carried out, the mechanism of the sorption reactions that occur in solution has not been clearly defined. This is probably because the various adsorbent types, the heterogeneous chemical composition, and the methodology used make the comparison of

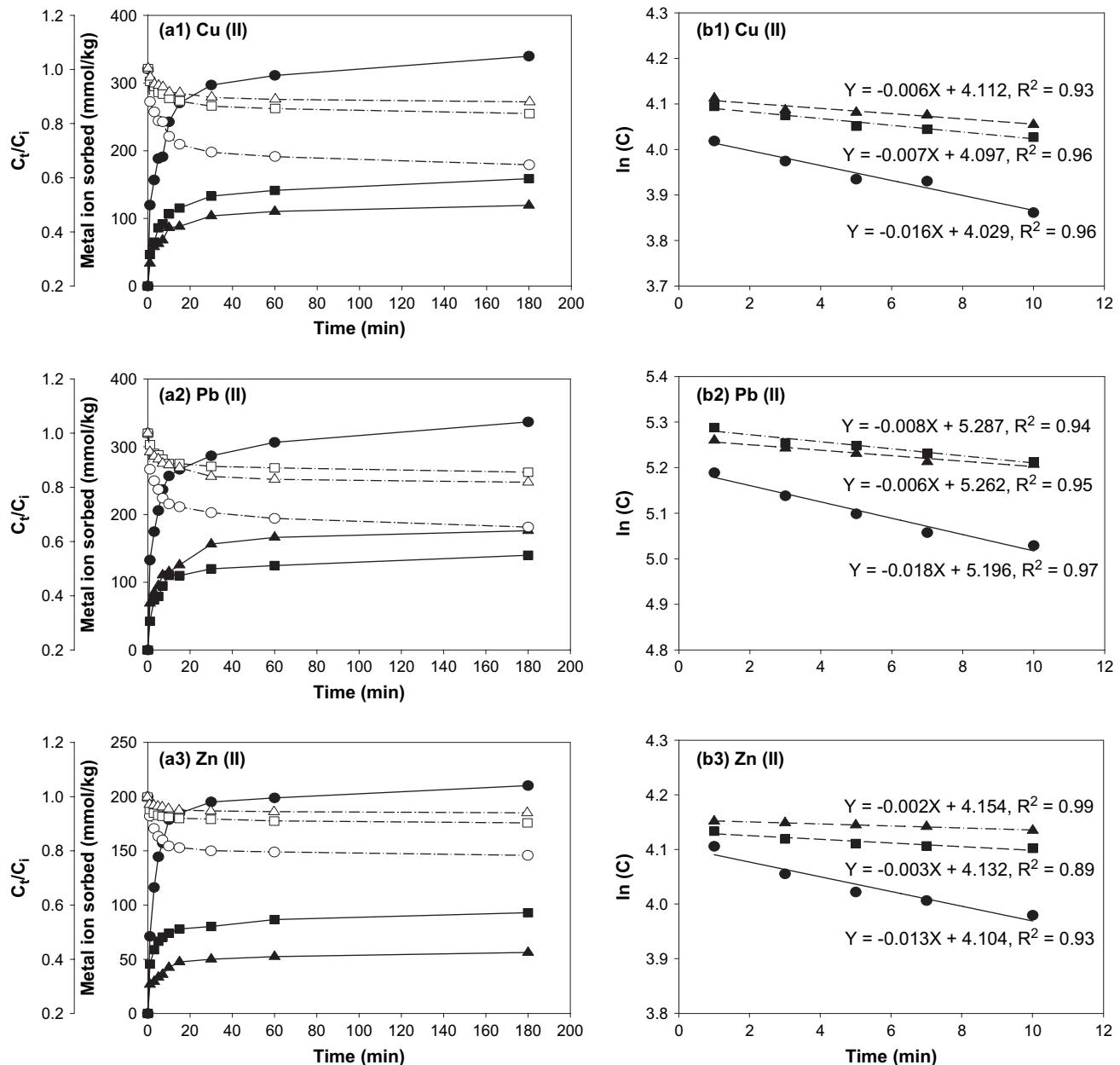


Fig. 2. Adsorption kinetics (a1, a2, a3) and the removal rates (b1, b2, b3) of metal ions during second step adsorption for the three mulches ((■, □) C, (●, ○) H and (▲, △) P).

results difficult (Brown et al., 2000a,b). For convenience, the sorption theories expressed in this study are inclusive of all phenomena at the solid–liquid interface including ion-exchange, surface adsorption, chemisorption, complexation, charge transfer, and ligand exchanges.

From results shown in Fig. 2, the adsorption capacities of the H mulch are shown to be the highest among the mulches for the three metal ions. Based on both the mulch characterization studies and equilibrium sorption testing, therefore, the H mulch was used in all further tests in this study.

The effect of the H mulch concentration on the initial removal rate of the three metal ions from aqueous

solutions was studied with respect to changes in initial pH and metal ion concentrations. The data in Table 3 show that the initial removal rate of the three metal ions increased with increasing adsorbent dose and higher pH. Under the same conditions (pH 6.0), on the other hand, the initial removal rate of the three metal ions decreased with respect to the increase of initial heavy metal concentration. It is also found that the order of the initial removal rates was Pb(II) > Cu(II) > Zn(II). Pb(II) was easily and rapidly adsorbed by H mulch regardless of the initial pH and metal ion concentrations. This order is possibly related to the differences in electronegativity and ionic radius of the atoms. The

Table 3

Effect of H mulch concentration on the removal rate of three metal ions during second step adsorption at 25 °C

Dose of H mulch (g)	Cu (II)			Pb (II)			Zn (II)		
	pH 5.0	pH 6.0	pH 6.0	pH 5.0	pH 6.0	pH 6.0	pH 5.0	pH 6.0	pH 6.0
	$k_{0.5}^a$	$k_{0.5}^a$	$k_{1.0}^b$	$k_{0.5}^a$	$k_{0.5}^a$	$k_{1.0}^b$	$k_{0.5}^a$	$k_{0.5}^a$	$k_{1.0}^b$
0.5	0.012	0.015	0.005	0.016	0.017	0.007	0.009	0.010	0.005
0.7	0.013	0.021	0.010	0.020	0.021	0.012	0.012	0.017	0.010
1.0	0.027	0.028	0.017	0.038	0.038	0.019	0.018	0.023	0.014
2.0	0.063	0.065	0.036	0.098	0.119	0.045	0.044	0.049	0.022

^a Rate constant of adsorption (min^{-1}) for 0.5 mM of heavy metal.^b Rate constant of adsorption (min^{-1}) for 1.0 mM of heavy metal.

values of atomic radius and electronegativity of Pb(II) are higher than those for the other metals. Al-Asheh and Duvnjak (1999) reported that the sorption (molar basis) of metals having a larger ionic radius was greater than for those with a smaller ionic radius.

3.3. Effect of H mulch dose on the adsorption capacity

To assess the influence of the adsorbent (mulch) dose on the adsorption capacity (amount of metal sorption per unit dry weight of H mulch), H mulch dosages varying from 0.4 to 6 g/L were studied using solutions of 0.5 mM Cu(II), Pb(II), and Zn(II). Sansalone (1996) reported that the pH of initial runoff at an urban highway was slightly acidic, in the range of 5.8–6.4, due to acid rainfall (typical pH range of 3.8–4.5). Therefore, the initial pH of sorption reactions in these studies was maintained at both 5.0 and 6.0.

As shown in Figs. 3 (a) and (b), the adsorption capacities of the H mulch decreased as the adsorbent dose increased. When the H mulch dose was increased to more than 6 g/L, the adsorption capacities for all metal ions were observed to somewhat decrease or to remain as constant values. However, the removal efficiencies, the percent mass of metal ions removed by the H mulch, increased since the equilibrium concentration of the metal ions in solution was lower in the presence of high H mulch concentrations. More than 90% of the Pb(II) could be removed from solution when the dosage of H mulch was 4 g/L and the pH was under 6. However, an H mulch dosage of above 6 g/L was required to achieve greater than 80% removal efficiency for Cu(II) and Zn(II). Comparing the adsorption capacities at pH 6.0 and 5.0, it can be seen that there is only a small difference, suggesting that the pH change had little apparent effect on the heavy metal removal capacity or the removal efficiency in the equilibrium state.

The order of the metal sorption capacity on a molar basis is Pb(II) > Cu(II) > Zn(II) regardless of changes in pH. It was difficult to compare this mulch with other sorbents described in the literature because of differing adsorbent characteristics and inconsistencies in data presentation. However, from the literature reviewed,

these results are in agreement with the results of Ho et al. (2002) who reported that for metal adsorption on tree fern the order of metal removal was the same and could be explained on the basis of ionic radius and specific surface area. However, the order of heavy metal removal by calcite was $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$ (Petrović et al., 1999) at pH 5.5, and the order by peanut hull pellet adsorbents was Pb > Zn > Cu > Cd (Brown et al., 2000a,b); these are slightly different from our results. These different orders are possibly related to the types of sorbents and metal ions, since the adsorption mechanism varies according to the chemical coordination characteristics between metal ions and sorbents.

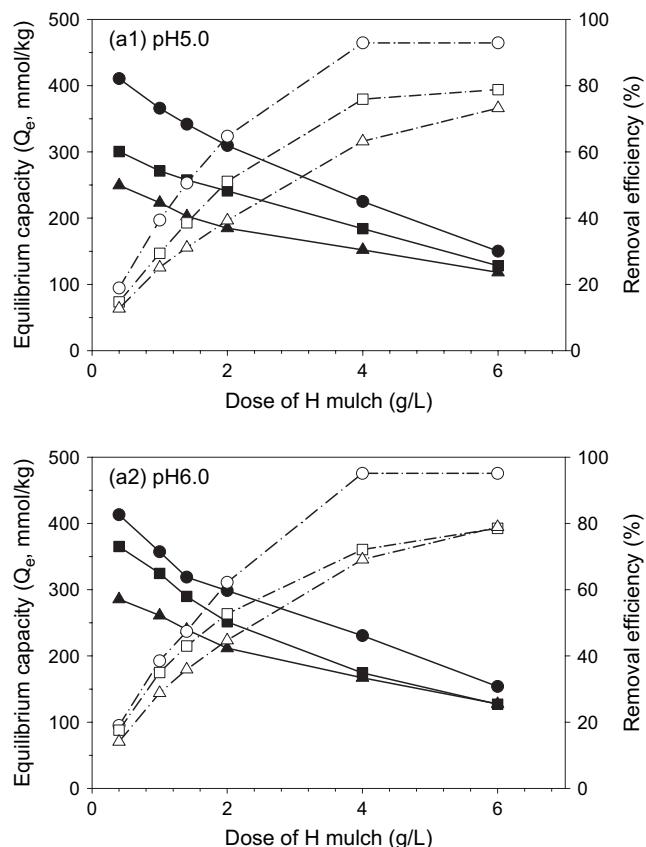


Fig. 3. Adsorption capacities of H mulch (filled symbols) and removal efficiencies of metal ions (open symbols) according to the adsorbent dose ((■, □) Cu, (●, ○) Pb, and (▲, △) Zn).

3.4. Equilibrium models

In order to investigate the effect of metal ion concentration on the adsorption capacity of the H mulch, an equilibrium experiment was performed using a dosage of H mulch (4 g/L) that was subjected to various initial concentrations of metal ions ranging from 0.2 to 1.5 mM. A comparison of adsorption capacities for the three metals on the H mulch under the various initial concentrations of metals in the solution is shown in Fig. 4. Under the given experimental conditions, the rate of heavy metal adsorption onto the H mulch decreased with increasing initial heavy metal concentration. The results also show that on comparing pH 5 with pH 6, the sorption capacities for Cu(II), Pb(II) and Zn(II) were favored with increasing pH. At lower pH, metal ions have greater competition with H^+ ions, thereby decreasing the adsorption capacity of the H mulch.

Unlike the removal efficiency trend, the adsorption capacities of the H mulch increased with increased equilibrium liquid-phase metal concentration. When the equilibrium liquid-phase metal concentration was more than 0.5 mM, the adsorption capacity for Zn(II) reached its equilibrium state at pH 5. In the cases of Pb(II) and Cu (II), the equilibrium adsorption capacities were

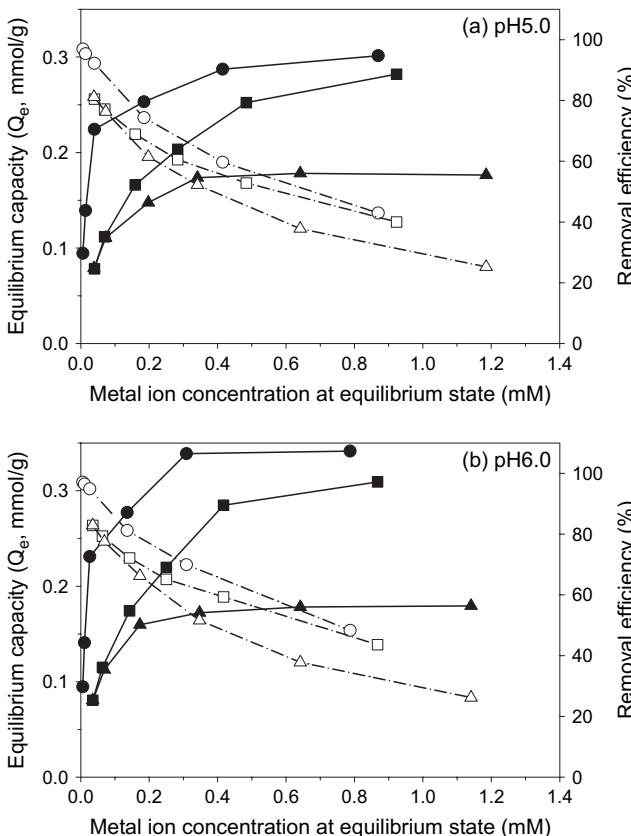


Fig. 4. Adsorption capacities of H mulch (filled symbols) and removal efficiencies of metal ions (open symbols) according to the concentration of metal ions ((■, □) Cu, (●, ○) Pb, and (▲, △) Zn).

maintained constant above 1 mM. It was observed that the adsorption of heavy metals on H mulch with the same equilibrium liquid-phase metal concentration decreased in the order Pb(II) > Cu(II) > Zn(II).

In order to quantify the adsorption capacity of the H mulch for removal of heavy metal ions, the experimental data corresponding to the isotherms were fitted according to the Langmuir and the Freundlich equations. These equilibrium isotherms were expressed by plotting the amount of metal ions held by the mulch versus the equilibrium concentration of metal ions left in solution:

$$\text{Langmuir isotherm : } Q_e = \frac{S_m K_L C_e}{1 + K_L C_e} \quad (2)$$

$$\text{Freundlich isotherm : } Q_e = K_F C_e^{1/n} \quad (3)$$

Eqs. (2) and (3) can be conveniently transformed to the following linearized forms:

$$\text{Langmuir model (I) : } \frac{C_e}{Q_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m} \quad (4)$$

$$\text{Langmuir model (II) : } \frac{1}{Q_e} = \frac{1}{K_L S_m C_e} + \frac{1}{S_m} \quad (5)$$

$$\text{Freundlich model : } \log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

where Q_e (mmol/g) is the amount of sorbed metal ion at the final equilibrium concentration C_e (mM), K_L (1/mmol) is the Langmuir isotherm constant related to the equilibrium constant or binding energy, S_m (mmol/g) is the amount of sorption corresponding to complete surface coverage, K_f (L/g) is the Freundlich empirical constant related to the sorption capacity, and n is related to the sorption intensity. Four isotherm constants, S_m , K_L , n and K_f , shown in Table 4, can be evaluated from the linear plots represented by Eqs. (4), (5) and (6),

Table 4
Comparison of Langmuir and Freundlich constants and correction coefficients (R^2 values) for the sorption of single-component metals onto H mulches at 25 °C

Metal type	Langmuir model (I)			Langmuir model (II)			Freundlich model	
	S_m	$K_{L,I}$	$R_{L,I}$	S_m	$K_{L,II}$	n	K_f	
Cu(II)	pH 5	0.324	7.052	0.09	0.297	8.781	2.424	0.325
	pH 6	0.359	7.354	0.08	0.328	9.063	2.298	0.379
Pb(II)	pH 5	0.306	47.155	0.01	0.288	75.445	4.505	0.352
	pH 6	0.350	54.784	0.01	0.344	64.463	4.026	0.429
Zn(II)	pH 5	0.185	23.994	0.03	0.192	18.114	4.219	0.196
	pH 6	0.187	26.877	0.02	0.195	20.192	4.425	0.200

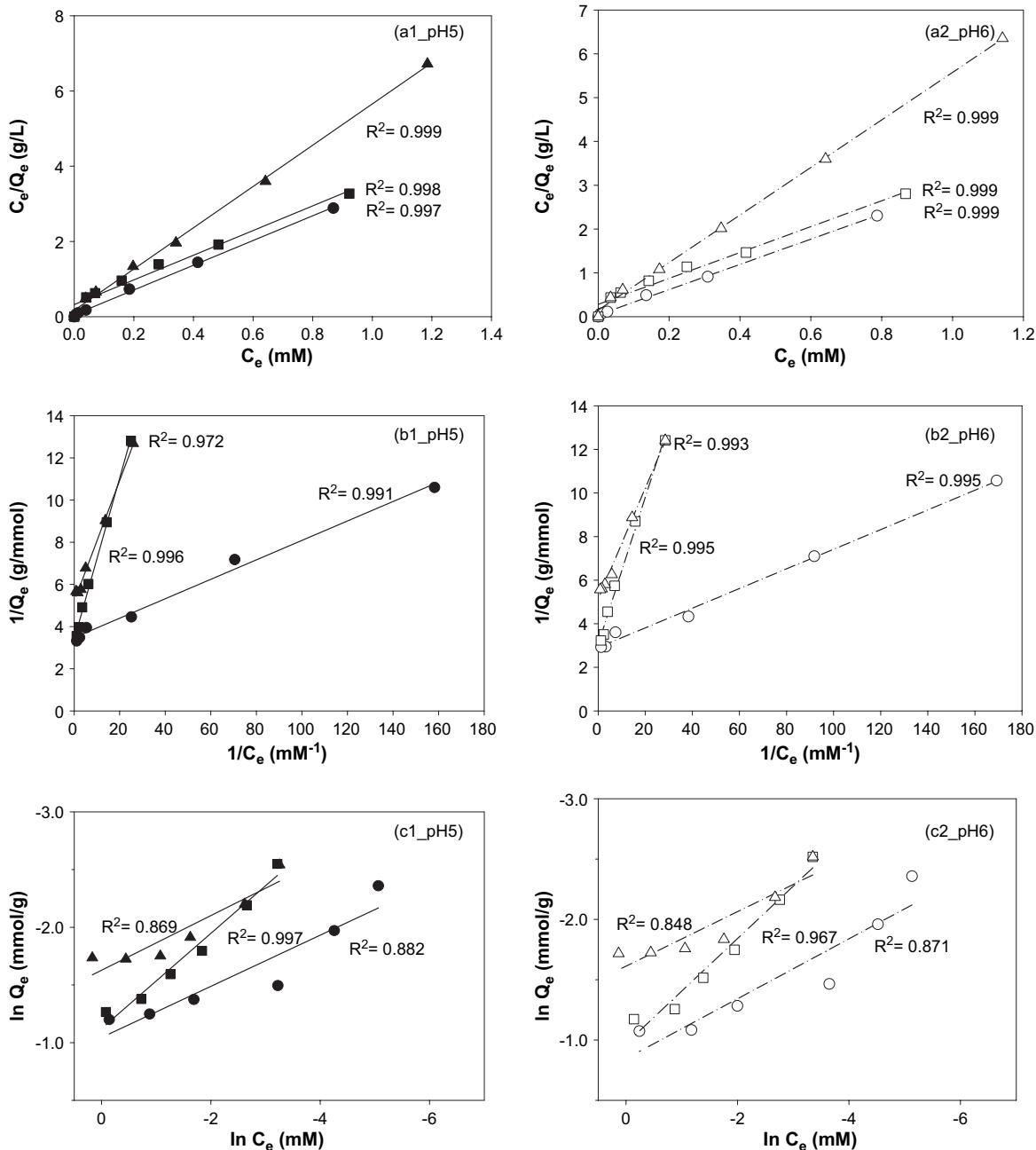


Fig. 5. Adsorption isotherm of metal ions ((■, □) Cu, (●, ○) Pb, and (▲, △) Zn) in linear forms of (a1, a2) Langmuir (I), (b1, b2) Langmuir (II) and (c1, c2) Freundlich model.

respectively. As can be observed in Fig. 5, the higher correlation coefficients indicate that there is a strong positive relationship for the data and that all experimental sorption data are better fitted to the Langmuir model (I) than to the Langmuir model (II). The exponentially increasing Freundlich model can be represented by plotting $\log(Q_e)$ versus $\log(C_e)$, but data are not in as good agreement as for the case of the Langmuir model. Consequently, although both Langmuir and Freundlich model approximations of the observed adsorption data in the linearized forms give

satisfactory correlation coefficients for most of the covered concentration range, the greater conformity of the adsorption data to the Langmuir isotherm (correlation coefficient > 0.99) implies that the sorption of metal ions on the H mulch follows the Langmuir isotherm. Consequently, it can be concluded that the metal ions adsorbed by the H mulch are adsorbed either in a monolayer or as a one-directional process; the Langmuir model is more suitable for analysis.

It was reported that one of the essential characteristics of the Langmuir equation is that it can be

Table 5

Adsorption capacity of H mulch in a mixed metal ion combination

System		Q_m (mg/g) ^a	Q_s (mg/g) ^a	x^b	y^c	K_{ij}^d	Q_m/Q_s
pH 5	(A) Cu(II)	3.58 (24.8)	10.6 (68.9)	0.42	0.10	(AB) 0.15	0.34
	(B) Pb(II)	33.9 (68.3)	46.5 (92.2)	0.58	0.90		0.73
	(A) Cu(II)	7.37 (48.9)	10.6 (68.9)	0.38	0.74	(AB) 4.63	0.70
	(B) Zn(II)	2.41 (17.1)	9.65 (61.4)	0.62	0.26		0.25
	(A) Pb(II)	29.3 (59.4)	46.5 (92.2)	0.60	0.93	(AB) 8.34	0.63
	(B) Zn(II)	2.04 (14.9)	9.65 (61.4)	0.40	0.07		0.21
	(A) Cu(II)	3.34 (23.3)	10.6 (68.9)	0.22	0.13	(AB) 0.34	0.32
	(B) Pb(II)	23.2 (47.3)	46.5 (92.2)	0.50	0.83	(BC) 9.95	0.50
	(C) Zn(II)	0.96 (8.3)	9.65 (61.4)	0.28	0.05	(AC) 3.38	0.10
pH 6	(A) Cu(II)	4.06 (27.8)	11.1 (72.1)	0.46	0.10	(AB) 0.13	0.37
	(B) Pb(II)	37.0 (74.3)	47.9 (94.9)	0.54	0.90		0.77
	(A) Cu(II)	8.32 (54.8)	11.1 (72.1)	0.35	0.77	(AB) 6.19	0.75
	(B) Zn(II)	2.29 (16.4)	10.4 (66.3)	0.65	0.23		0.22
	(A) Pb(II)	37.0 (74.3)	47.9 (94.9)	0.48	0.95	(AB) 19.8	0.77
	(B) Zn(II)	1.68 (12.7)	10.4 (66.3)	0.52	0.05		0.16
	(A) Cu(II)	3.10 (21.8)	11.1 (72.1)	0.23	0.12	(AB) 0.31	0.28
	(B) Pb(II)	23.2 (47.3)	47.9 (94.9)	0.50	0.84	(BC) 11.0	0.48
	(C) Zn(II)	0.84 (7.60)	10.4 (66.3)	0.28	0.04	(AC) 3.42	0.08

Initial concentration of each ion: 0.5 mM; H mulch concentration: 2 g/L.

^a Values in brackets indicate the removal efficiency.^b x is the equilibrium molar fraction of metal ion in solution.^c y is the equilibrium molar composition of metal ion on mulch.^d Selectivity index, $K_{ij} = (y_i x_j) / (y_j x_i)$ (i refers to the first symbol while j refers to the second one).

expressed in terms of a dimensionless constant called the equilibrium parameter ($R_{L,I}$), which can be beneficially used to predict whether a sorption system is favorable or unfavorable in batch processes (Lin and Juang, 2002). The parameter is described by the following equation:

$$R_{L,I} = \frac{1}{(1 + K_{L,I} C_i)} \quad (7)$$

where C_i is the highest initial solute concentration (mM), and $K_{L,I}$ is the Langmuir model (I) constant. The value of $R_{L,I}$ indicates whether the isotherm is irreversible ($R_{L,I} = 0$), favorable ($0 < R_{L,I} < 1$), linear ($R_{L,I} = 1$) or unfavorable ($R_{L,I} > 1$). The equilibrium parameter for the H mulch (see Table 4) shows that the sorption of metal ions on the H mulch is favorable, indicating that it is a good adsorbent for Cu(II), Pb(II) and Zn(II).

3.5. Co-ion effect

As runoff usually contains a mixture of metal ions, a mixed ion effect may also play an important role in sorption. Sorption experiments on the co-ion effect were carried out for binary and ternary combinations, maintaining equal concentrations of metal ion (0.5 mM). In all cases the pH was kept at 5 or 6. Al-Asheh and Duvnjak (1999) investigated the co-ion effect on sorption by means of the ratio of the sorption capacity for one metal in the presence of other metal ions, Q_m , to the sorption capacity for the same metal when it is alone in solution, Q_s . The value of the ratio

(Q_m/Q_s) indicates the sorption capacity to be promoted in the presence of other metal ions (>1), no observable net interaction effect ($=1$), or suppressed (<1). As seen in Table 5, it was found that in mixed metal solutions, the adsorption capacities of a particular metal ion were less than those if it were present alone, which corresponds to a decrease in removal efficiency. According to this classification, the adsorption capacity of the H mulch was suppressed by the presence of other metals in the solution. In the case of Zn(II), the adsorption capacity of the H mulch was always suppressed when Cu(II) or/and Pb(II) were present in the Zn(II) solution. In a mixed metal ion combination, the relative affinity of the mulch for different metal ions may also be expressed as the binary selectivity index, K_{ij} (Al-Asheh and Duvnjak, 1999). According to the results shown in Table 5, in mixed metal ion systems the order of preference of the mulch for metal ions in terms of adsorption capacity and binary selectivity index was the same as that for the single component: Pb(II) $>$ Cu(II) $>$ Zn(II).

4. Conclusions

The present study evaluated whether mulch has a potential use as a feasible alternative method for removing heavy metals commonly found in urban runoff. According to the physicochemical and batch adsorption experiments, it can be concluded that the H mulch would be effective for removing heavy metals such

as Cu, Pb and Zn. Both in single and mixed metal ion combination solutions, the order of preference of the H mulch was found to be Pb(II) > Cu(II) > Zn(II). The adsorption capacity of the H mulch was insignificantly suppressed by the presence of other metals in the solution. The equilibrium adsorption data for H mulch follows the Langmuir isotherm model, indicating that once a metal ion occupies a site, no further sorption can take place at that site. The results of batch studies, such as the adsorption capacity of the mulch for the metal ions and the rate of metal uptake, will be useful in reactor design by producing the design parameters necessary in the determination of reactor size, adsorbent usage amount, and breakthrough time prediction. Consequently, since mulches are plentiful, inexpensive and readily available, their utilization for the removal of heavy metals should gain attention as the simple, effective and economical means of urban runoff treatment.

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