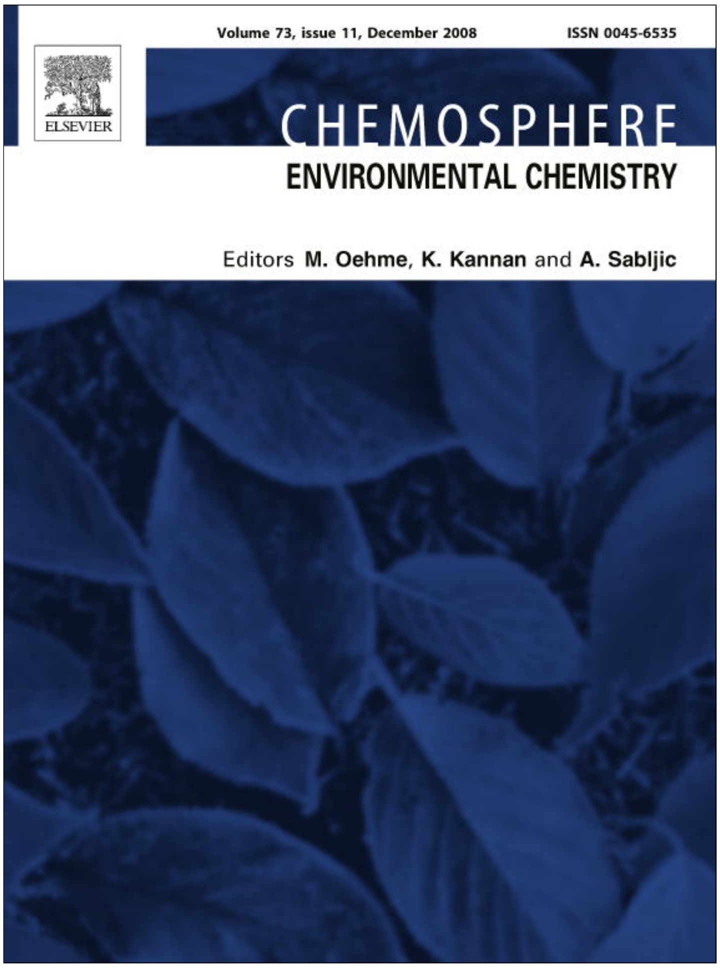

Volume 73, issue 11, December 2008 ISSN 0045-6535

ELSEVIER

CHEMOSPHERE
ENVIRONMENTAL CHEMISTRY

Editors M. Oehme, K. Kannan and A. Sabljic

Chemosphere 73 (2008) 1757–1764

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Comparison of monometal and multimetal adsorption in Mississippi River alluvial wetland sediment: Batch and column experiments

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ARTICLE INFO

Article history:
Received 9 May 2008
Received in revised form 28 August 2008
Accepted 2 September 2008
Available online 16 October 2008

Keywords:
Monometal adsorption
Multimetal adsorption
Langmuir isotherm
Freundlich isotherm
Thomas model
Wetland sediment

ABSTRACT

Monometal and multimetal adsorption of selected heavy metals in a sediment from a coastal Louisiana forested swamp used for wastewater treatment was studied. Results from the batch experiments show that the maximum adsorption capacities of the metals by the sediment were in the order of $Pb \gg Hg > Cr > Cd \geqslant Cu \geqslant Zn \gg As$ based on monometal adsorption isotherm, and $Hg > Cr > Cu \geqslant Cd \approx Pb \gg As \approx Zn$ based on multimetal adsorption isotherm, respectively. Batch experimental data best fit the Langmuir model rather than the Freundlich isotherms. In the column experiments, the maximum adsorption capacities of the metals were in the order of $Pb \gg Hg > Cr > Cd > Cu > Zn \gg As$ in monometal conditions, and $Hg \gg Cr \gg Pb > Cu \geqslant Zn \approx Cd > As$ in multimetal conditions. The metals became more mobile in multimetal than in monometal conditions. Results from both the batch and column experiments show that competitive adsorption among metals increases the mobility of these metals. Particularly, in this study, Pb in multimetal conditions lost it adsorption capacity most significantly. In both monometal and multimetal conditions, the maximum adsorption capacity of the metals in the column experiments was higher than that in the batch experiment indicating other metal retention mechanisms rather than adsorption may be involved. Therefore, both column and batch experiments are needed for estimating retention capacities and removal efficiencies of metals in sediments.

1. Introduction

Wetlands are a sink for heavy metals via adsorption and sedimentation processes (Williams et al., 1994). Wetlands in the Mississippi deltaic plain can be used to treat municipal wastewater (Day et al., 2004), a potential sourced of heavy metals. The point sources in Louisiana also include the cities of New Orleans, Baton Rouge, Lafayette and their vicinities, where the electronic and metalwork industries are well developed (Presley et al., 1980).

Heavy metal adsorption does not only depend on soil characteristics, but also on the nature of metals involved, and on their competition for soil sorption sites. Usually, when competitive sorption of metals is compared with their monometal behaviour, it is shown that their adsorption is lower in the competitive systems (Harter, 1992). Competitive adsorption of heavy metals has been indirectly assessed either by single sorbate ion or by binary system experiments using pure phases or synthetic minerals (Brümmer et al., 1988) and soil samples (Harter, 1992; Pardo, 2000). The consensus reached in these studies is that Pb, Cu and Cr are more strongly retained as compared to Zn, Ni and Cd.

There are many studies on competitive sorption and selectivity sequences of heavy metals by various sorbents and soils, however, few studies have examined competitive sorption of heavy metals by sediments. Some reported studies have compared batch and column/centrifugation experiments (Celorie et al., 1989; Filius et al., 1998; Voegelin et al., 2003; Antoniadis et al., 2007), providing valuable information on adsorption mechanisms.

Information from batch experiment on metal adsorption capacity can be used to estimate the maximum immobilization of metals. However, batch experiment cannot provide an accurate estimation of the longevity of soils and sediments in heavy metal removal. Therefore, batch experiments should be coupled with longer-term investigation performed in columns for estimating heavy metal removal and retention capacities. In practical applications, longevity of metal removal by wetland sediments is an important factor. Design and construction of a wetlands system must also consider the longevity of the system for metal removal to obtain efficient and cost-effective performance.

The goal of this study was to evaluate the monometal and multimetal adsorption to the sediment from a swamp forest used for wastewater treatment, and to compare the adsorption behaviour between batch and column experiments for accurately estimating metal removal capacity. The specific objectives were: (1) to compare monometal and multimetal adsorption isotherms in a batch experiment using both the Freundlich and Langmuir adsorption isotherm; (2) to identify the optimum adsorption isotherm (Freundlich or Langmuir adsorption isotherm) for

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doi:10.1016/j.chemosphere.2008.09.003

predicting metal removal; (3) to compare monometal and multimetal adsorptions in a column experiment; (4) to compare the measured breakthrough curves in the column experiment with the calculated results using the Thomas model; and (5) to compare the maximum adsorption capacity of the metals between the batch and column experiments.

2. Materials and methods

2.1. Materials

The sediment (Mississippi River alluvial) used in the investigation was collected in June 2007 from a forested wetland (N29°52.36′, W90°21.25′) adjacent to the Luling wastewater treatment pond, St. Charles Parish, Louisiana, USA (Fig. S1, Supplementary material). Three major plant species, Water Tupelo (*Nyssa aquatica*), Red Maple (*Acer rubrum*), and Cypress (*Taxodium distichum*) in the study area were indentified. The sediment was sampled from 0 to 20 cm layer, air-dried and passed through a 2-mm sieve. The sediment was from a representative swamp forest in the Louisiana Mississippi River deltaic plain. Major sediment characteristics were analyzed, and the results are shown in Table 1. The following group of metals was used in the studies (As, Cd, Cr, Cu, Hg, Pb and Zn). Stock solutions (1000 mg L^{-1}) of As ($NaAsO_2$), Cd ($Cd(NO_3)_2 \cdot 4H_2O$), Cr ($Cr(NO_3)_3 \cdot 9H_2O$), Cu ($Cu(NO_3)_2 \cdot 2.5H_2O$), Hg ($HgCl_2$), Pb ($Pb(NO_3)_2$) and Zn ($Zn(NO_3)_2 \cdot 6H_2O$) were prepared by dissolving exact quantity of respective salts (GR grade, Fisher Scientific, USA) in double distilled water, and then immediately adjusting the solution pH to 6.0. This stock solution pH was chosen to make the same pH as in the sample sediment. The stock solution was further diluted to the required experimental concentration.

2.2. Batch experiment

Both monometal and multimetal adsorption experiments were conducted to determine the adsorption characteristics of the sediment for the selected heavy metals (As, Cd, Cr, Cu, Hg, Pb and Zn). Adsorption behaviours of the metals by the sediment were evaluated using both the Freundlich and Langmuir adsorption isotherm equations. Monometal adsorption isotherms of As, Cd, Cr, Cu and Zn except for Hg and Pb were obtained by weighing 5 g of sediment in each test into glass Erlenmeyer flasks. Only 1 g of the sediment was used for Hg and Pb in monometal adsorption isotherm, because a pilot study showed that the adsorption capacity of Hg and Pb was much higher than other metals. Then, 50 mL solution containing specific concentrations of each metal was added to the corresponding flask.

Multimetal adsorption isotherms were determined using the same procedure as for the monometal experiment with the same concentration ratio for the seven metals. For each metal, concentration levels of 0, 2.5, 5, 10, 20, 40, 80, 160 and 320 mg L^{-1} were evaluated, respectively. All samples were equilibrated for 24 h (providing sufficient time for the system to reach equilibrium, as determined by the pilot test) on a 25 mm sway gyratory shaker at constant room temperature (25 °C). After settling, a 30 mL aliquot of the supernatant was filtered through a Whatman GF/C filter (0.45 μm) and then analyzed for metal concentrations. The amount of metal adsorption by the sediment was calculated from the concentration decrease in solution.

Adsorption isotherms were determined using the Freundlich and Langmuir model (see the Supplementary material for the Freundlich and Langmuir model). The Freundlich equation (Bohn et al., 1979), in its original form, can be written as

$$q = KC_e^{\frac{1}{n}} \tag{1}$$

Table 1
Major characteristics of the sediment used for this study

	pH	Eh (mV)	O.M. (%)	Fe (%)	Mn (mg kg^{-1})	S (mg kg^{-1})	As (mg kg^{-1})	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Hg (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Salinity (‰)	Bulk density (g cm^{-3})	Particle size (%)		
																Sand	Silt	Clay
Mean	6.1	72	8.0	1.7	269	725	8.9	1.2	29.5	17.5	30.0	1.1	57.2	0.3	0.9	20.2	21.5	58.3
SD[a]	0.0	19	0.1	0.04	7	26	4.5	0.1	1.3	1.5	7.6	0.2	1.2	0.0	0.15	–	–	–

[a] Standard deviation. According to particle size analysis, the sediment texture is silt loam (United States Department of Agriculture).

where q is the metal concentration in the sorbent material (adsorption capacity), K is a constant related to the sorption capacity, C_e (mg L^{-1}) is the concentration in solution, and n is an empirical parameter related to the intensity of sorption, which varies with the heterogeneity of the material.

The Langmuir equation (Bohn et al., 1979), in its original form, can be written as

$$q = \frac{abC_e}{1 + bC_e} \tag{2}$$

where C_e (mg L^{-1}) is the concentration of metal in solution at equilibrium, q (mg kg^{-1}) is the mass of metal adsorbed to the sediment, a (mg kg^{-1}) is the maximum adsorption capacity of metal, and b is a constant related to the binding strength of metal, which represents the inverse of the equilibrium concentration of adsorption at one-half saturation.

According to Alloway (1995), distribution coefficients (K_d) is a useful parameter for comparing the sorptive capacities of different soils or materials for any particular ion, when measured under the same experimental conditions. The distribution coefficients (K_d) were calculated according to Alloway (1995)

$$(K_d) = \frac{\text{Equilibrium metal concentration adsorbed}}{\text{Equilibrium metal concentration in solution}} \tag{3}$$

where the equilibrium metal concentration adsorbed is given per unit weight of soil and the equilibrium metal concentration in solution per unit volume of liquid.

2.3. Column experiment

Column experiments were conducted for determining both monometal and multimetal adsorption characteristics of the seven heavy metals. Eight columns were constructed from a PVC cylinder (inside diameter: 25 mm, height: 150 mm) and each column was packed with 10.25 g of wet sediment (water content 51.2%). Metal solutions containing 50 mg L^{-1} of each metal for the monometal columns and mixed metal solution (containing 50 mg L^{-1} of all seven metals with the same concentration ratio) for the multimetal columns were supplied continuously at a rate of approximately 30 mL d^{-1} using a constant-head feeding tank, respectively. The solution level in the feed tank was kept constant by continuously stirring the storage tank which was kept at ground level. The solution in the storage tank was renewed each day. The columns were kept saturated with the effluent level of the columns set just above the surface of the sediment. The effluent and its volume from each column were measured daily to estimate actual loading. Samples of the effluent were collected each day over a 4 week period. The samples were filtered through a 0.45 μm syringe filter, and the metal concentrations in filtrate were analyzed.

Successful design and evaluation of a column adsorption process requires prediction of a breakthrough curve and determining the maximum adsorption capacity of an adsorbent for estimating longevity of the column (see the Supplementary material for the breakthrough curve). Traditionally, the Thomas model is used to fulfill this purpose. The Thomas model is one of the most general and widely used method for determining column performance (see the Supplementary material for the Thomas model).

The Thomas model has the following form (Thomas, 1944)

$$\frac{C}{C_o} = \frac{1}{1 + \exp\left(\frac{k_{Th}}{Q}(q_o M - C_o V)\right)} \tag{4}$$

where C_o and C are metal ion concentrations (mg L^{-1}) in the influent and effluent, respectively, k_{Th} is the Thomas rate constant (L d^{-1} mg^{-1}), Q is the flow rate (L d^{-1}), q_o is the maximum adsorption capacity (mg g^{-1}), M is the total mass of the adsorbent loaded in the column (g) and V is the volume of metal solution passed through the column (L) (Aksu and Gönen, 2004).

Average percentage error (ε%) calculated according to Eq. (5) indicates the performance of the best fit between the experimental and predicted breakthrough curves

$$\varepsilon\% = \frac{\sum_{i=1}^{N}\left|\frac{(C/C_o)_{exp}-(C/C_o)_{theo}}{(C/C_o)_{exp}}\right|}{N} \times 100 \tag{5}$$

where the subscripts ‘exp’ and ‘theo’ indicate the experimental and calculated values, and N is the number of measurements.

2.4. Statistical analysis

Statistical analysis of the data was conducted using SAS software (version 8.02, 1999–2001, SAS Institute, Cary, NC). Simple linear regression using PROC REG (SAS 9.1, SAS Institute Inc. Cary, NC, USA) was conducted to determine if the slope of a regression was significantly different from a theoretical model ($p < 0.05$).

3. Results and discussion

3.1. Batch experiment

3.1.1. Distribution coefficients and selectivity sequences

The monometal and multimetal adsorption isotherms for the seven metals in the batch experiment is summarized in Fig. S2 in Supplementary material. A concentration of 20 mg L^{-1} was chosen to compare the difference in metal adsorption because the amount of metal adsorbed decreased above this concentration for the seven metals. Supplementary material shows the distribution coefficients (K_d) for the monometal and multimetal adsorption of the metals by the sediment based on the added metal concentrations. The distribution coefficients (K_{d20}; L kg^{-1}) of all metals indicated that the order of metal sorption was Pb (48463) $\gg$ Hg (910) > Cr (757) > Cd (495) $\approx$ Cu (467) > Zn (117) > As (13) for the monometal adsorption isotherms. For the multimetal adsorption isotherms, the distribution coefficients (K_{d20}; L kg^{-1}) was in the order of Hg (174.8) $\gg$ Cr (51.4) > Pb (20.8) $\approx$ Cu (17.7) > Cd (8.6) $\gg$ Zn (0.8) $\approx$ As (0.7). Lead presented the highest K_{d20} value in the monometal adsorption isotherm, showing that it was the most retained cations, whereas, the metals with the lowest K_{d20} values was As, which suggests As could be easily exchanged and substituted by other metals such as Pb, Hg and Cr. It is worthwhile to mention that metal adsorption isotherm can be case specific. Schwertmann and Taylor (1989) reported the selectivity sequence of heavy metal adsorption for goethite was in the order Cu > Pb > Zn > Cd > Co > - Ni > Mn, while for hematite the same sequence was found except for an exchange in positions of Cu and Pb.

The metal adsorption sequence did not follow the order of their electronegativity (Evans, 1966), As (2.0), Hg (1.9), Cu (1.9), Pb (1.8), Cd (1.7), Cr (1.7) and Zn (1.6). For both the monometal and multimetal adsorption isotherms in this study, Cr, in spite of its lower electronegativity value, was one of the most retained cations. The presence of Cr seems to be related to the fact that this metal was applied in its trivalent form, the dominant form in soils (Smith and McGrath, 1990). McBride et al. (1997) found Cr, with a very high K_d value, to be the least mobile element, supporting their initial decision to use Cr as the reference of marker element in the sludge-amended soil where K_d values were determined to indicate the leaching loss potential for some elements. On the other hand, results of Gao et al. (1997) showed that Cr as CrO_4^{2-} instead of Cr^{3+} was the last element in the sequence of adsorption with the lowest K_d values. Moreover, As showed one of the lowest measured K_{d20} values, in spite of its higher electronegativity. In addition, based on monometal adsorption isotherms, Pb had one of the

Table 2
Determination of the parameters for the Freundlich and Langmuir adsorption isotherm by best fit approach in batch experiment of monometal and multimetal adsorption to the sediment

Metals		Freundlich adsorption isotherm			Langmuir adsorption isotherm		
		K[a]	1/*n*[b]	Equation	*a*[c]	*b*[d]	Equation
As	Monometal	48	0.50	$y = 0.51x + 1.69$ ($R^2 = 0.98^{**}$)	769	0.03	$y = 1.3 \times 10^{-3}x + 4.5 \times 10^{-2}$ ($R^2 = 0.99^{**}$)
	Multimetal	13	0.13	$y = 0.14x + 1.12$ ($R^2 = 0.99^{**}$)	22	0.22	$y = 4.5 \times 10^{-2}x + 2.0 \times 10^{-1}$ ($R^2 = 0.90^{**}$)
Cd	Monometal	467	0.35	$y = 0.36x + 2.67$ ($R^2 = 0.95^{**}$)	2896	0.09	$y = 3.5 \times 10^{-4}x + 3.7 \times 10^{-3}$ ($R^2 = 0.99^{**}$)
	Multimetal	31	0.55	$y = 0.55x + 1.51$ ($R^2 = 0.86^{*}$)	413	0.04	$y = 2.4 \times 10^{-3}x + 5.7 \times 10^{-2}$ ($R^2 = 0.80^{*}$)
Cr	Monometal	701	0.42	$y = 0.42x + 2.85$ ($R^2 = 0.88^{*}$)	4897	0.28	$y = 2.0 \times 10^{-4}x + 7.2 \times 10^{-4}$ ($R^2 = 0.85^{*}$)
	Multimetal	201	0.40	$y = 0.41x + 2.30$ ($R^2 = 0.96^{**}$)	1051	0.17	$y = 9.5 \times 10^{-4}x + 5.7 \times 10^{-3}$ ($R^2 = 0.98^{**}$)
Cu	Monometal	453	0.34	$y = 0.34x + 2.66$ ($R^2 = 0.95^{**}$)	2579	0.11	$y = 3.9 \times 10^{-4}x + 3.6 \times 10^{-3}$ ($R^2 = 0.99^{**}$)
	Multimetal	107	0.38	$y = 0.39x + 2.03$ ($R^2 = 0.95^{**}$)	637	0.09	$y = 1.6 \times 10^{-3}x + 1.7 \times 10^{-2}$ ($R^2 = 0.95^{**}$)
Hg	Monometal	730	0.46	$y = 0.47x + 2.86$ ($R^2 = 0.91^{**}$)	6422	0.19	$y = 1.6 \times 10^{-4}x + 8.3 \times 10^{-4}$ ($R^2 = 0.99^{**}$)
	Multimetal	266	0.57	$y = 0.57x + 2.43$ ($R^2 = 0.97^{**}$)	3020	0.07	$y = 3.3 \times 10^{-4}x + 4.4 \times 10^{-3}$ ($R^2 = 0.93^{**}$)
Pb	Monometal	3640	0.30	$y = 0.31x + 3.56$ ($R^2 = 0.90^{**}$)	25 380	0.04	$y = 3.9 \times 10^{-5}x + 1.1 \times 10^{-3}$ ($R^2 = 0.93^{**}$)
	Multimetal	111	0.35	$y = 0.36x + 2.05$ ($R^2 = 0.87^{*}$)	350	0.42	$y = 2.9 \times 10^{-3}x + 6.8 \times 10^{-3}$ ($R^2 = 0.99^{**}$)
Zn	Monometal	381	0.34	$y = 0.35x + 2.58$ ($R^2 = 0.98^{**}$)	2408	0.08	$y = 4.2 \times 10^{-4}x + 5.2 \times 10^{-3}$ ($R^2 = 0.98^{**}$)
	Multimetal	8	0.20	$y = 0.20x + 0.90$ ($R^2 = 0.83^{*}$)	20	0.24	$y = 4.9 \times 10^{-2}x + 2.0 \times 10^{-1}$ ($R^2 = 0.99^{**}$)

*, ** denote significance at 5.0% and 1.0% levels, respectively.

[a] *K*: adsorption capacity of heavy metal.

[b] 1/*n*: an empirical parameter related to the intensity of sorption.

[c] *a*: maximum adsorption capacities of heavy metal (mg kg^{-1}).

[d] *b*: binding strength constant of heavy metal.

highest K_{d20} values, whereas for the multimetal adsorption isotherm the K_{d20} value for Pb rapidly decreased due to competition among the metal cations.

In the multimetal adsorption isotherm, the positions of Pb and Cu in the adsorption sequence were reversed with respect to that expected based on electronegativity values. But the preference for Pb over Cu in the sediment agrees with predictions on the basis of the Misono softness parameter as postulated by Sposito (1989), as well as predictions based on the first hydrolysis constant, both of which are greater for Pb. The Misono softness parameter is an index usually determined from ionic radius and ionization potential of a metal (Sposito, 1989. Based on softness parameter, Basta and Tabatabai (1992) reported that Cu was sorbed preferentially to Zn by soils. Copper and Pb exchanging places is not unusual as reported by Brümmer et al. (1988) and Schwertmann and Taylor (1989) for the synthetic minerals goethite and hematite. According to Schwertmann and Taylor (1989), Zn is always adsorbed to a greater extent than Cd by synthetic samples. However, this is not the case for the sediment used in our study, which shows that Cd was adsorbed more than Zn. The result agrees with the observations by de Matos et al. (1996) and Gomes et al. (2001) for the retention of these two heavy metals in Brazilian soils.

3.1.2. Application of the Freundlich and Langmuire models

The adsorption capacities (*K*) for the metals determined by the Freundlich isotherms were in the order of $\text{Pb} \gg \text{Hg} \geqslant \text{Cr} \gg \text{Cd} \approx \text{Cu} \geqslant \text{Zn} \gg \text{As}$ in the monometal condition, and $\text{Hg} > \text{Cr} \gg \text{Pb} \approx \text{Cu} \gg \text{Cd} > \text{As} \approx \text{Zn}$ in the multimetal condition (Table 2). The adsorption capacity (*K*) of each metal in the multimetal condition was lower than the monometal condition. Especially, the *K* value of Pb determined by the monometal adsorption was 33 times higher than that determined by the multimetal adsorption isotherm.

The maximum adsorption capacities (*a*; mg g^{-1}) of the metals determined by the Langmuir isotherms were in the order of Pb (25.4) ≫ Hg (6.4) > Cr (4.9) > Cd (2.9) ⩾ Cu (2.6) ⩾ Zn (2.4) ≫ As (0.8) in monometal condition, and Hg (3.0) > Cr (1.1) > Cu (0.6) ⩾ Cd (0.4) ≈ Pb (0.4) ≫ As (0.02) ≈ Zn (0.02) in multimetal condition (Table 2). Each maximum adsorption capacity (*a*) of the seven metals was lower in multimetal condition than in monometal condition. The a_{metal} (monometal adsorption)/a^{*}_{metal} (multimetal adsorption) ratios were generally greater than unity suggesting that the simultaneous presence of multimetal reduced adsorption capacity for each metal through competition for the sorption sites in solid phases. The $a_{\text{metal}}/a^{*}_{\text{metal}}$ ratio was in the order of $a_{\text{Zn}}/a^{*}_{\text{Zn}}$ (120.4) > $a_{\text{Pb}}/a^{*}_{\text{Pb}}$ (72.5) > $a_{\text{As}}/a^{*}_{\text{As}}$ (35.0) > $a_{\text{Cd}}/a^{*}_{\text{Cd}}$ (7.0) > $a_{\text{Cr}}/a^{*}_{\text{Cr}}$ (4.7) > $a_{\text{Cu}}/a^{*}_{\text{Cu}}$ (4.0) > $a_{\text{Hg}}/a^{*}_{\text{Hg}}$ (2.1). This suggests that Zn, Pb and As adsorption were more affected by the competing metals than Cd, Cr, Cu and Hg. In other words, Hg, Cu and Cr showed effective competition for the sorption sites of the sediment in presence of As, Cd, Pb and Zn in this study.

Fontes and Gomes (2003) and Christl and Kretzschmar (1999) reported that Pb in the presence of Cd and Cu could effectively compete for the sorption sites on different colloidal surfaces. Saha et al. (2002) reported that there was no competition between Pb, Cd and Zn were observed at low concentrations. They explained that metals are mainly adsorbed onto specific adsorption sites at low metal concentrations, while at higher metal inputs soils lose some of their ability to bind heavy metals as the adsorption sites overlap, becoming thus less specific for a particular metal. This in turn induces a reduction in metal sorption (Saha et al., 2002).

The maximum adsorption capacity (*a*) of Pb was higher than Cd in the monometal condition, but in the multimetal condition, *a* values for Pb and Cd were similar. The ratio of $a_{\text{Pb}}/a_{\text{Cd}}$ (monometal adsorption) and $a^{*}_{\text{Pb}}/a^{*}_{\text{Cd}}$ (multimetal adsorption) was 8.76 and 0.84, respectively. In this study, the results showed higher ratio of $a_{\text{Pb}}/a_{\text{Cd}}$ than $a^{*}_{\text{Pb}}/a^{*}_{\text{Cd}}$ in the sediment. A different result was reported by Serrano et al. (2005) using three soils. They found that the $a_{\text{Pb}}/a_{\text{Cd}}$ ratios (ranging from 1.2 to 1.8) for single metal solution were lower than $a^{*}_{\text{Pb}}/a^{*}_{\text{Cd}}$ rations (ranging from 2.1 to 3.4) for binary metal solutions.

The binding strength constant (*b*) of the metals (determined by the Langmuir isotherms) in the sediment were in the order of $b_{\text{Cr}} > b_{\text{Hg}} > b_{\text{Cu}} > b_{\text{Cd}} > b_{\text{Zn}} > b_{\text{Pb}} \geqslant b_{\text{As}}$ for the monometal adsorption, and $b^{*}_{\text{Pb}} > b^{*}_{\text{Zn}} > b^{*}_{\text{As}} > b^{*}_{\text{Cr}} > b^{*}_{\text{Cu}} > b^{*}_{\text{Hg}} > b^{*}_{\text{Cd}}$ for the multimetal adsorption. This suggests that Pb in multimetal condition lost some of its adsorption ability as a result of competition with other metals. The sediment showed much lower relative affinity for Pb^{2+} ions than for other metals in multimetal condition. The binding strength constants of Pb and Cd varied with metal solution in both monometal and multimetal conditions. Although the sediment showed greater affinity for Pb than for Cd ($b^{*}_{\text{Pb}} \gg b^{*}_{\text{Cd}}$) in the multimetal adsorption isotherm, whereas, in the monometal adsorption isotherm, the sediment showed slightly greater affinity for Cd than for Pb ($b_{\text{Cd}} \geqslant b_{\text{Pb}}$).

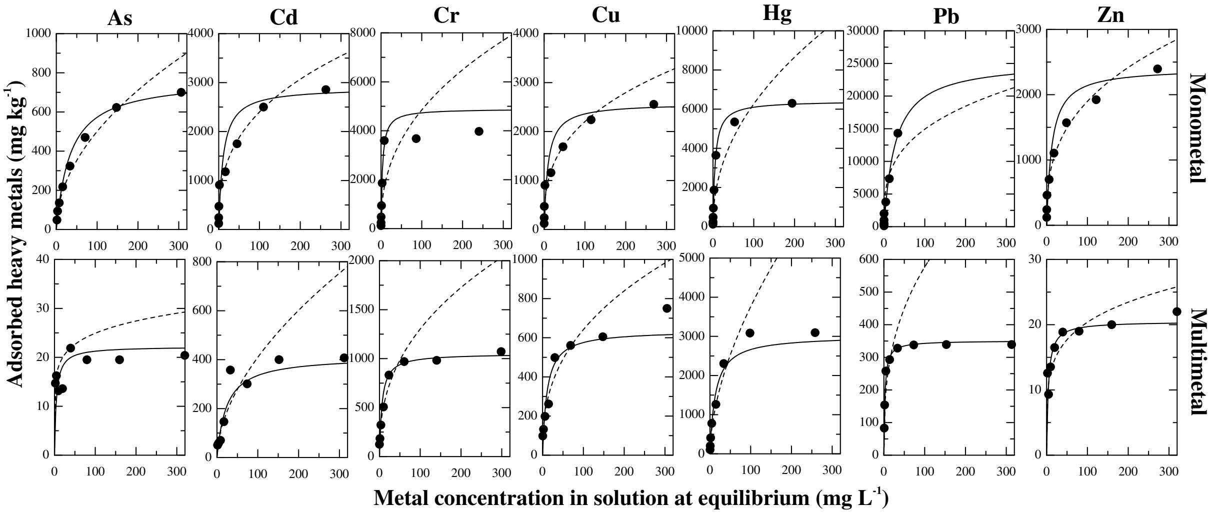

Fig. 1. Experimental and calculated values from the Freundlich and Langmuir adsorption isotherms for the monometal and multimetal conditions. ●: Experimental data; —: Langmuir equation (Eq. (3)); - - -: Freundlich equation (Eq. (1)).

Serrano et al. (2005) reported that the binding strength constant (b_{Pb} and b_{Cd} for single metal solutions, and b^*_{Pb} and b^*_{Cd} for binary metal solutions) of all soil showed greater affinity for Pb than for Cd ($b_{Pb} > b_{Cd}$ and $b^*_{Pb} > b^*_{Cd}$). Rodríguez-Maroto et al., 2003 found a similar result for both single and binary solution. However, in contrast to these authors but in agreement with Masquita and Viera e Silva (2002) and Serrano et al. (2005) for competitive sorption of Cu and Zn, our study found $b_i \leqslant b^*_i$ for As, Pb and Zn except for Cd, Cr, Cu and Hg in the sediment.

While binding strength constant (b) estimated from sorption isotherms should only be considered qualitatively (Sparks, 1995). They have been compared to the free energy change of adsorption of different species (Van Riemsdijk et al., 1985). Higher b values have been related to specifically sorbed metals at high energy surfaces with low dissociation constants. Alternatively, lower b values apper to be releated to sorption at low energy surfaces with high dissociation constants (Ma and Rao, 1997; Adhikari and Singh, 2003). The multimetal isotherm b values in the sediment may indicate that competition promotes the retention of the seven metals on more specific sorption positions. As a result, although the maximum adsorption capacity (a) decreases for As, Pb and Zn, the metals are held more strongly. Therefore, the estimated b^*_i values increased as a consequence of the decreased adsorption levels (Serrano et al., 2005).

Generally, Zn and Cd retention is more dependent on electrostatic interactions with solid phase exchange sites. In contrast Cr, Cu and Pb retention is less dependent on this type of adsorption and more dependent on covalent interactions with the mineral structures (McBride, 1994).

3.1.3. Selection of the optimum adsorption isotherm

Comparison of the experimental and calculated values using the Freundlich and Langmuir isotherms for the monometal and multimetal adsorption of the seven metals is shown in Fig. 1. The Langmuir isotherm models for both monometal and multimetal adsorption isotherms fitted well with the adsorption equilibrium data at all stages. At the initial stage, the Freundlich isotherm model fitted very well with the adsorption equilibrium data from both the monometal and multimetal adsorption experiments. But the Freundlich adsorption isotherm equation did not fit the adsorption equilibrium data at higher added metal concentrations. The experimental data best fitted the Langmuir model rather than the Freundlich isotherms for all operation stages. The Langmuir equation rather than the Freundlich equation for determining the adsorption of Zn in bentonite was also suggested by Kaya and Ören (2005). However, Sheta et al. (2003) showed that the Langmuir and Freundlich isotherms corresponded well with the experimental results of Zn and Fe.

3.2. Column experiment

3.2.1. Monometal and multimetal adsorption in the column

The breakthrough curves for the seven metals are shown in Fig. 2. Table 3 summarizes the analysis results of the breakthrough curves. The breakthrough adsorption capacity of the metals by the sediment in monometal adsorption column was in the order of Pb $\gg$ Hg $\gg$ Cr > Cd $\geqslant$ Cu $\geqslant$ Zn $\gg$ As. In multimetal adsorption column, the order was Hg $\gg$ Cr > Pb > Cu $\geqslant$ Cd > Zn > As.

The maximum adsorption capacity (mg g^{-1}) of the metals by the sediment was in the order of Pb (96.5) $\gg$ Hg (56.6) > Cr (31.3) > Cd (17.5) > Cu (13.4) > Zn (9.3) $\gg$ As (1.1) in monometal column, and Hg (36.0) $\gg$ Cr (12.3) $\gg$ Pb (3.9) > Cu (2.5) $\geqslant$ Zn (1.5) $\approx$ Cd (1.3) > As (0.6) in the multimetal column.

The breakthrough point and the maximum adsorption capacity of Pb using the monometal columns were more than 25 times higher than in the multimetal columns. This suggests that Pb in multimetal column lost adsorption capacity significantly as the result of other metals binding to the sediment.

The throughput volume for breakthrough of the heavy metals was calculated. The throughput volume (L) was in the order of Pb (8.47) $\gg$ Hg (4.49) $\gg$ Cr (1.64) > Cd (0.91) > Cu (0.70) > Zn (0.57) $\gg$ As (0.02) in monometal column, and Hg (2.83) $\gg$ Cr (0.38) > Pb (0.22) > Cu (0.12) > Cd (0.07) > Zn (0.04) > As (0.01) in multimetal column.

The longevity of the wetland sediment to remove a specific metal can be estimated using the throughput volume for breakthrough in the columns. If the sediment were used in a constructed wetland system [with the design criteria of inflow: 10 m^3 d^{-1}; heavy metal (As, Cd, Cr, Cu, Hg, Pb and Zn) concentration: 50 mg L^{-1}; area: 100 m^2; depth: 1 m], the Pb saturation in monometal pollution would be 96.5 mg g^{-1}, and the longevity for Pb removal would be about 47.6 years. At the same condition, the Pb saturation in multimetal pollution would be 3.9 mg g^{-1}, and the longevity for Pb removal would be about 1.9 years.

3.2.2. Application of the Thomas model

The breakthrough curves were analyzed using the Thomas model to determine the Thomas rate constant (k_{Th}) and the

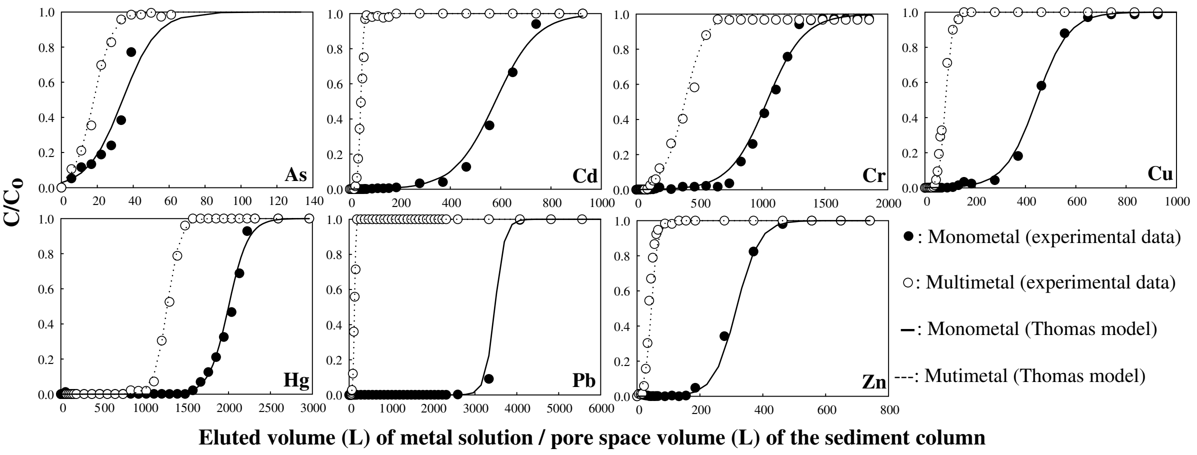

Fig. 2. The experimental and predicted breakthrough curves using the Thomas model in the monometal and multimetal columns.

Table 3
Analysis of the breakthrough curves, determination of the parameters for the Thomas model and model deviations in the column experiment of monometal and multimetal adsorption to the sediment

Heavy metal	Condition	Breakthrough adsorption capacity (mg g^{-1})	Maximum adsorption capacity (mg g^{-1})	Throughput volume to breakthrough (L)	Throughput volume to exhaustion (L)	k_{Th}[a] (L d^{-1} mg^{-1})	q_o[b] (mg g^{-1})	ε%[c]
As	Monometal	0.2	1.1	0.02	0.21	2.31×10^{-2}	0.9	2.0
	Multimetal	0.1	0.6	0.01	0.11	4.26×10^{-2}	0.5	0.7
Cd	Monometal	9.1	17.5	0.91	2.58	2.70×10^{-3}	15.6	6.4
	Multimetal	0.7	1.3	0.07	0.19	3.97×10^{-2}	1.2	0.5
Cr	Monometal	16.4	31.3	1.64	4.63	1.51×10^{-3}	28.1	36.6
	Multimetal	3.8	12.3	0.38	2.09	2.65×10^{-3}	10.5	3.5
Cu	Monometal	7.0	13.4	0.70	1.98	3.54×10^{-3}	12.0	2.2
	Multimetal	1.2	2.5	0.12	0.38	1.75×10^{-2}	2.2	2.8
Hg	Monometal	44.9	56.6	4.49	6.84	1.93×10^{-3}	54.0	1.9
	Multimetal	28.3	36.0	2.83	4.37	2.93×10^{-3}	34.3	3.4
Pb	Monometal	84.7	96.5	8.47	10.83	1.92×10^{-3}	93.9	35.5
	Multimetal	2.2	3.9	0.22	0.55	1.35×10^{-2}	3.5	8.1
Zn	Monometal	5.7	9.3	0.57	1.30	6.20×10^{-3}	8.5	9.5
	Multimetal	0.4	1.5	0.04	0.25	2.12×10^{-2}	1.2	7.3

All results were statistically significant at 1% level ($R^2 > 0.88$).

[a] k_{Th}: Thomas rate constant (L d^{-1} mg^{-1}).

[b] q_o: maximum adsorption capacity of heavy metal (mg g^{-1}).

[c] ε%: average percentage errors.

maximum adsorption capacity (q_o). Fig. 2 shows both the experimental and the predicted breakthrough curves for both the monometal and multimetal adsorption columns. The regressions indicate that the Thomas model was a suitable fit with the experimental data ($R^2 > 0.89$, $\varepsilon\% < 36.6$). The values of k_{Th} and q_o (mg g^{-1}) are presented in Table 3. For the monometal columns, the k_{Th} value for the sediment was in the order of As > Zn > Cu > Cd > Hg > Pb > Cr, whereas the q_o value was in the order of Pb (93.9) ≫ Hg (54.0) > Cr (28.1) > Cd (15.6) > Cu (12.0) > Zn (8.5) ≫ As (0.9). In the multimetal columns, the k_{Th} value for the sediment was in the order of As > Cd > Zn > Cu > Pb > Hg > Cr, whereas the q_o value (mg g^{-1}) was in order of Hg (34.3) ≫ Cr (10.5) ≫ Pb (3.5) > Cu (2.2) ⩾ Zn (1.2) ≈ Cd (1.2) > As (0.5).

The Thomas model has been used for analysis of breakthrough curves in other adsorption and biosorption studies without soils and sediments. According to Yan and Viraraghavan (2001), the Thomas model fitted ($R^2 \geqslant 0.85$) the breakthrough curves for biosorption of Pb^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+} by immobilized *Mucor rouxii*. Due to various experimental conditions employed in different studies, comparison of their results is difficult, because the Thomas model has not been used for the sediments.

In our study the maximum adsorption capacity (q_o) of Cr, Hg and Pb by the sediment in the monometal adsorption was higher than other metals, and the q_o value for Cr and Hg in the multimetal adsorption were also higher than that for other metals.

In our study the maximum adsorption capacity (q_o) of Cr and Hg by the sediment in both the monometal and multimetal adsorption column was higher than other metals. Unlike the Cr and Hg, the q_o value for Pb in the monometal adsorption compared with the multimetal adsorption was higher than that for other metals. Therefore, the sediment used in this study could be a good sorbent for use in wastewater treatment system for treating Hg and Cr. In addition, the sediment could be a good sorbent for treating Pb for monometal adsorption. Due to competition with other metals, the sediment might not be a good sorbent for Pb because its maximum adsorption capacity decreases dramatically in multimetal conditions. Lead contamination is a great concern for the environment, because it has a long residence time compared with most other pollutants.

3.3. Comparison between the batch and column experiments

In both the monometal and multimetal adsorptions, the maximum adsorption capacity of the metals in the column experiments was higher than that in the batch experiment (Fig. S3, Supplementary material). This suggests that the metals were retained by the sediment mainly in the mechanism of adsorption in the batch study. However, in the column study, besides adsorption other additional retention mechanism, such as surface precipitation, may be involved. In our study, the batch experiment was conducted in aerobic condition starting with air-dry sediment. In the field, the sediment was in anoxic condition when sampled ($Eh < 100$ mV, Table 1) where a large part of sulfate could be reduced to H_2S. The column study was conducted in anaerobic conditions as in the field with water saturation. Thus, the metals in the column could be precipitated as insoluble metal sulfides in such ananerobic condition. This is probably the major reason for the "higher" maximum sorption capacity in the column experiment compared to the batch experiment.

In monometal adsorption, the maximum sediment adsorption capacity of the metals was in the order of $Pb \gg Hg > Cr > Cd \geqslant Cu \geqslant Zn \gg As$ in the batch experiment, and $Pb \gg Hg > Cr > Cd > Cu > Zn \gg As$ in the column experiments. In multimetal adsorption, the maximum sediment adsorption capacity for the metals was in the order of $Hg > Cr > Cu \geqslant Cd \approx Pb \gg As \approx Zn$ in the batch experiment, and $Hg \gg Cr \gg Pb > Cu \geqslant Zn \approx Cd > As$ in the column experiments. Therefore, the adsorption of individual metal by the sediment in both the batch and column experiments showed the same tendency. However, the maximum adsorption capacity of the metals by the sediment was different between the batch and column experiments.

Saha et al. (2002) reported that competition in batch experiments seems to affect the metal adsorption only when high concentrations of metal are introduced to the soil. According to Antoniadis et al. (2007), in column experiments, where the steady-state condition is adsorption site saturation by the given metal, competition affects metal adsorption even if the added metal concentration is low. Moreover, in batch experiments, all soil surfaces are exposed to ion exchange reactions, even those in the soil micropores, thus equilibrium can be achieved within a few hours. In column experiments, nonequilibrium conditions are common for both chemical (easily and noneasily accessible sorption domains) and physical (stagnant and flowing water phases) natures, which affect rate-limited diffusive mass transfer. The two nonequilibrium types are practically indistinguishable in evaluating macroscopic metal transport with column tests (Seuntjens et al., 2001).

In our column experiments, the sediment was not exposed for interaction with metal ions, due to such nonequilibrium conditions. However, this situation better represents metal movement under field conditions, especially through clays (Harter and Naidu, 2001). Therefore, based on measurements in the batch tests, metal mobility may not be successfully assessed, because overestimation of K_d by the batch techniques may lead to inappropriate optimistic judgments on metal retention (Plassard et al., 2000; Antoniadis et al., 2007). However, opposite conclusion was found by Atia et al. (2005) that heavy metal uptake obtained by a column experiment was relatively higher than that obtained by a batch experiment.

4. Conclusions

This study investigates the monometal and multimetal adsorptions of selected seven metals by a wetland sediment, and compares batch and column experiments in the removal and sequestration of the metals. In the batch experiments, the adsorption sequences were in the order of $Pb \ggg Hg > Cr > Cd \approx Cu > Zn > As$ based on monometal adsorption, and $Hg \gg Cr > Pb \approx Cu > Cd \gg Zn \approx As$ based on multimetal adsorption. The maximum adsorption capacity ($mg\,g^{-1}$) of the metals by the sediment was in the order of Pb (25.4) $\gg$ Hg (6.4) > Cr (4.9) > Cd (2.9) $\geqslant$ Cu (2.6) $\geqslant$ Zn (2.4) $\gg$ As (0.8) in monometal adsorption isotherm, and Hg (3.0) > Cr (1.1) > Cu (0.6) $\geqslant$ Cd (0.4) $\approx$ Pb (0.4) $\gg$ As (0.02) $\approx$ Zn (0.02) in multimetal adsorption isotherm, respectively. In the batch experiment, the data best fit the Langmuir model rather than the Freundlich isotherms. In the column experiments, the maximum adsorption capacity ($mg\,g^{-1}$) of the metals was in the order of Pb (96.5) $\gg$ Hg (56.6) > Cr (31.3) > Cd (17.5) > Cu (13.4) > Zn (9.3) $\gg$ As (1.1) in the monometal adsorption condition, and Hg (36.0) $\gg$ Cr (12.3) $\gg$ Pb (3.9) > Cu (2.5) $\geqslant$ Zn (1.5) $\approx$ Cd (1.3) > As (0.6) in the multimetal adsorption condition. Results from both the batch and column experiments show that Pb in the multimetal adsorption column lost its adsorption capacity significantly as the result of competition with other metals. In the sediment, the maximum adsorption capacity of the metals was higher in the column experiments than in the batch experiments. Results demonstrate that both column and batch experiments are necessary for estimating heavy metal removal efficiencies and retention capacities by wetland sediments. Column studies are necessary for accurately predicting the longevity of sediments in removal of heavy metals.

Acknowledgment

The research was supported in part by Louisiana Department of Environmental Quality.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.09.003.

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