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Single- and Multi-component Adsorption of Pb, Cu, and Cd on Peat

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Heavy metals have long been recognized as ecotoxicological hazardous substances, and their chronic toxicities and accumulation abilities in living organisms have been of great interest for many years. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products and, to worsen matters, can be accumulated in the organisms. Lead, as well as copper and cadmium, are in the group of serious hazardous heavy metals. They are released into aquatic environments mostly as a result of various anthropogenic activities, and have posed serious environmental problems. Removal of heavy metals from waters has been a major preoccupation for many years.

Among various treatment methods for removing heavy metals from waters, adsorption is the most widely used process. The severe limitation of this process lies in the high cost of substrate material and the difficulty of its recycling. Therefore, numerous approaches have been studied for the development of cheaper metal adsorbents, such as fly ash, peat, minerals, and various biomass (Ringqvist and Oborn, 2002; Machida et al., 2004). The application of peat in water purification and waste treatment has received increasing attention (Ho and Mckay, 2004). Peat, with lignin, cellulose, and humic acids as its major constituents, is relatively inexpensive and possesses characteristics that make it effective for adsorption (Yonebayashi et al., 1994).

Many studies involve the removal of only one kind of metal ion by peat from solutions (Ho et al., 2002; Ho and Mckay, 2004). However, the presence of only one heavy metal ion is a rare situation in nature. Most systems are multicomponent ones generated by pollutants. Therefore, adsorption studies from multicomponent systems are of interest with a view to environmental preservation. In this study, we examined the competitive adsorption isotherms of Pb, Cu, and Cd in binary and ternary systems. The Langmuir one-site model, the Langmuir two-site model, and the Freundlich model were applied to simulate the experimental data.

Materials and Methods

The experiments were conducted with peat obtained from Hebei (China). It was first dried at 105°C and then passed through a 100-mesh sieve. The typical characteristics of peat were determined by conventional methods (Nelson and Sommers, 1996; Thomas, 1996) and summarized in Table 1.

Batch adsorption experiments were performed using 0.100 g of peat with 20 ml of $Pb(NO_3)_2$, $Cu(NO_3)_2$, or $Cd(NO_3)_2$ solutions in 50 ml polypropylene centrifuge tubes. The samples were shaken end-over-end for 24 h, and then filtered through a 0.45 μm membrane. The concentrations of Pb, Cu, and Cd in the filtrates were determined by ICP-MS. The detailed operating conditions of ICP-MS followed those reported by Wang et al. (2003). All the measurements were made in duplicate and only the means are reported. Pb, Cu, and Cd adsorption isotherms on peat

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Table 1 Some typical characteristics of the peat used in the study

Characteristics	Values
pH	4.45
C (%)	29.7
N (%)	1.87
O and H (%)	17.1
CEC (cmol kg^{-1})	85.2
Organic matter (%)	48.6
BET surface area (sq. mg^{-1})	15.9

both in binary and ternary mixtures followed the procedure detailed above for the single-component systems.

Results and Discussion

Three models were used to describe the adsorption experimental results, namely the Langmuir one-site model, the Langmuir two-site model and the Freundlich model. The above three models can be expressed respectively by the following equations:

$$q_e = \frac{bq_mC_e}{1 + bC_e} \tag{1}$$

$$q_e = \frac{b_1q_{m,1}C_e}{1 + b_1C_e} + \frac{b_2q_{m,2}C_e}{1 + b_2C_e} \tag{2}$$

$$q_e = K_FC_e^{1/n} \tag{3}$$

where C_e and q_e are the equilibrium adsorbate concentrations in the aqueous (mmol L^{-1}) and solid (mmol g^{-1}) phases, respectively; q_m is the maximum loading capacity (mmol g^{-1}); $q_{m,1}$ and $q_{m,2}$ are the maximum numbers of adsorption sites for the two different sites; b, b_1, and b_2 are adsorption equilibrium constants; K_F is the equilibrium constant indicative of adsorption capacity and $1/n$ is the adsorption constant whose reciprocal is indicative of adsorption intensity. In order to determine the validity of models, the standard error of estimation (S.E.) (Alves and Lavorenti, 2004) was calculated,

$$S.E. = \left[\sum (q - q^*)^2 \Big/ (n - 2)\right]^{1/2} \tag{4}$$

where q is measured metal adsorption; q* is predicted metal adsorption by models; and n is number of experimental points.

The Langmuir one-site, two-site, and Freundlich isotherms of Pb, Cu, and Cd on peat in single-component systems are shown in Figs. 1a, 1b, and 1c, respectively. Isotherm parameters obtained by non-linear least-square regression analysis together with the standard error of estimation (S.E.) calculated from Eq.4 are listed in Table 2. From Table 2 and Fig. 1, Langmuir two-site model best describes the adsorption of Pb, Cu, and Cd on peat with highest R^2 (0.999) and lowest S.E. (3.02×10^{-3}–2.86×10^{-3}). The Freundlich model showed the poorest fit, which was in agreement with the work of Sharma and Forster (1993) also describing the peat-metal system. The Langmuir two-site model has been successfully applied to represent equilibrium adsorption data of lead and zinc onto goethite (Rodda et al., 1996), cadmium onto bone char (Cheung et al., 2001), and lead onto activated carbon (Machida et al., 2004). The adsorption capacity followed the order Pb (0.562 mmol L^{-1}) > Cu (0.516 mmol L^{-1}) > Cd (0.422 mmol L^{-1}), which may explain the different adsorption affinities of metals for peat surface according to their different properties, such as metal hydrolysis (negative log of first hydrolysis constant, pK_H, and hydrated radius), electronegativity, and softness (Saha et al., 2002).

The competitive adsorption isotherms of Pb, Cu, and Cd in binary mixtures Pb-Cu, Pb-Cd, and Cu-Cd, and in a ternary mixture Pb-Cu-Cd on peat are shown in Fig. 2. The Langmuir one-site model and the Langmuir two-site model were used to simulate experimental data, and the fit of the Langmuir two-site model is presented in Fig. 2. Based on R^2 and S.E., shown in Table 2, the Langmuir two-site model describes the adsorption of Pb and Cu on peat better than the Langmuir one-site model, even in binary and ternary systems. In the case of Cd in binary and ternary systems, both the Langmuir one-site model and the Langmuir two-site model fell off, especially in the ternary system. Compared with their adsorption in single-component systems, the individual adsorption capacity of all the three metals showed obvious decrease both in the binary and the ternary system. The adsorption capacity decreased even more in the ternary system as compared to binary systems. However, the total adsorption capacity for the two metals in the binary systems, and that for the three metals in the ternary system, was significantly higher than for a single metal ion in a monometallic system. The suppressing effect of one metal on adsorption capacity of peat for the other(s) with the simultaneous substantial increase of the total sorption capacity for both/all metals combined, indicated, on the one hand, a competition for the same adsorption sites. On the other hand, it suggested simultaneous non-competitive binding of metals onto peat matrices either by different mechanisms or at sites with undersaturated binding capacities, which are capable of

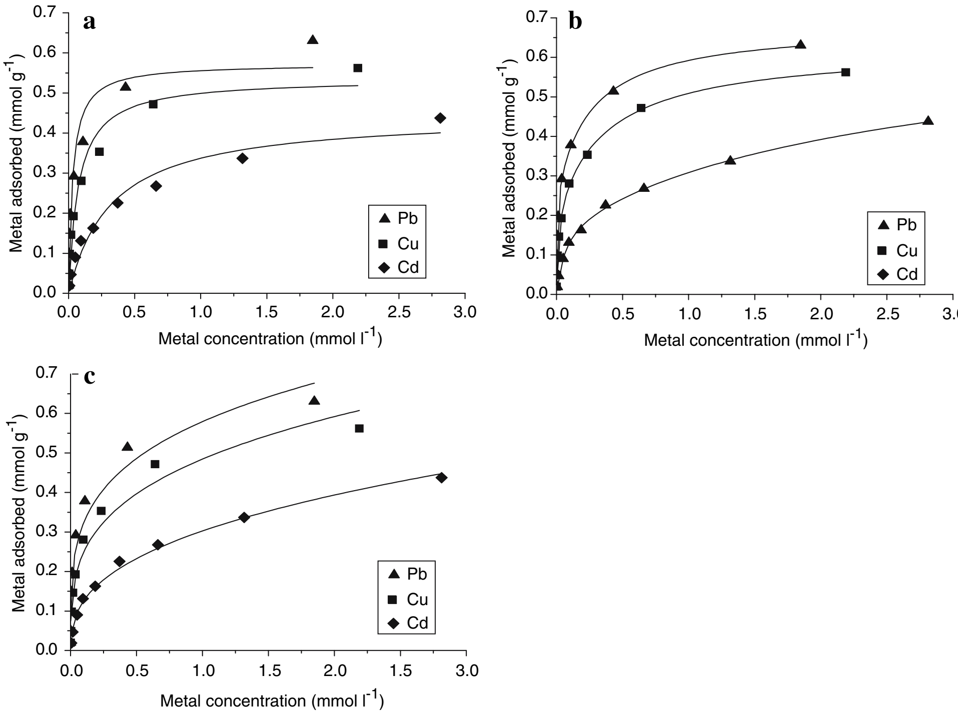

Fig. 1 Isotherms of Pb, Cu, and Cd adsorption in single-component system on peat. Experimental data are reported as points. Data fit by Langmuir one-site model (a), Langmuir two-site model (b), and Freundlich model (c) are reported as solid curves

Table 2 Langmuir and Freundlich parameters for Pb, Cu, and Cd adsorption on peat in single-component systems together with R^2 and S.E

Model		Parameters	Pb	Cu	Cd
Langmuir model	Single-site model	q_m (mmol g^{-1})	0.562	0.516	0.422
		b (L mmol^{-1})	31.3	13. 1	3.01
		R^2	0.951	0.976	0.961
		S.E.	3.23×10^{-2}	2.22×10^{-2}	1.85×10^{-2}
	Two-site model	$q_{m,1}$ (mmol g^{-1})	0.264	0.219	0.189
		b_1(l mmol^{-1})	199	72.8	15.6
		$q_{m,2}$ (mmol g^{-1})	3.60	2.48	0.364
		b_2 (L mmol^{-1})	0.416	0.401	0.510
		R^2	0.999	0.999	0.999
		S.E.	3.02×10^{-3}	2.15×10^{-3}	2.86×10^{-3}
Freundlich model		K_F	0.581	0.488	0.315
		$1/n$	0.255	0.285	0.380
		R^2	0.956	0.958	0.991
		S.E.	4.01×10^{-2}	2.55×10^{-2}	8.65×10^{-3}

binding metals non-competitively within the applied concentration range.

As can be seen from Fig. 2 and Table 3, Pb always adsorbed more favorably on peat than Cu and Cd, and Cu more than Cd in binary and ternary systems, which was consistent with the result of isotherms in single-component systems. Moreover, Pb, Cu, and Cd had different competitive effects. Compared to its adsorption in single-solute system, the adsorption capacity (q_m) of Pb on peat was reduced by 25.8% in Pb-Cu-Cd, by 24.4% in Pb-Cu and by 1.42% in Pb-Cd systems. Similarly, the adsorption capacity (q_m) of Cu on peat was decreased by 47.3% in Pb-Cu-Cd, by 44.2% in Pb-Cu and by 6.20% in Cu-Cd systems, compared to Cu adsorption capacity in single-solute system. As shown in Fig. 2, the Cd adsorption decrease was more pronounced in binary and ternary solute systems than Pb and Cu. The above results indicate that Pb was the metal that experienced the least reduction in the competitive adsorption process. Ma et al. (1994) also reported similar results, i.e., Cu and Cd had little influence on the Pb adsorption in the presence of peat. Conversely, Pb significantly inhibited the retention of Cu and Cd. Cd was most

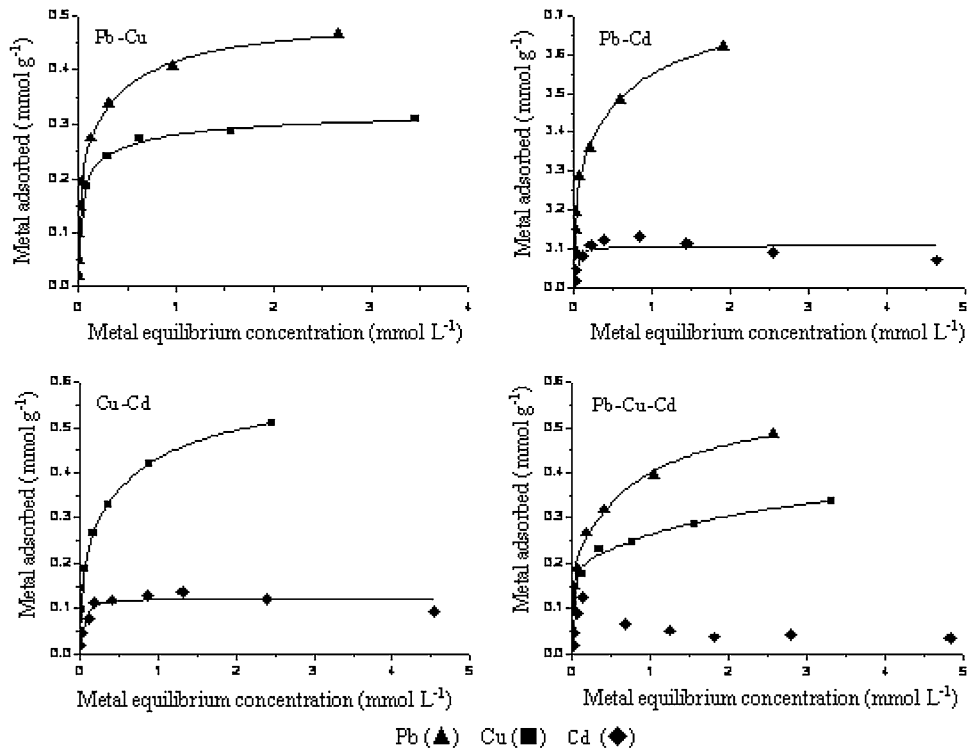

Fig. 2 Competitive adsorption isotherms of binary and ternary metal ions on peat. Experimental data are reported as points. Data fit by Langmuir two-site model are reported as solid curves

Table 3 Adjustable parameters and correlation coefficients of the Langmuir one-site equation for Cu, Cd, and Pb adsorption by peat in binary and ternary systems

Metal species	q_m	b	R^2	R^{2a}	S.E.	S.E.[a]
Pb (Pb-Cd)	0.554	20.0	0.936	0.999	0.0576	0.0314
Pb (Pb-Cu)	0.425	37.9	0.922	0.996	0.106	0.0937
Pb (Pb-Cu-Cd)	0.417	12.8	0.814	0.990	0.0603	0.0176
Cu (Cu-Cd)	0.484	9.37	0.961	0.997	0.0357	0.0165
Cu (Pb-Cu)	0.288	33.6	0.975	0.990	0.189	0.0327
Cu (Pb-Cu-Cd)	0.272	53.6	0.843	0.986	0.0582	0.0352
Cd (Cu-Cd)	/	/	/	0.875	/	0.0457
Cd (Pb-Cd)	0.108	41.7	0.718	0.718	0.0424	0.0424
Cd (Pb-Cu-Cd)	/	/	/	/	/	/

[a] Parameters calculated from Langmuir two-site model; the units are same as in Table 2

affected in the competitive adsorption. Such different competitive effects were also observed in natural carbonaceous materials (Hanzlík et al., 2004), and in activated carbon (Xiao and Thomas, 2004).

As can be seen from Fig. 2, the adsorption of Cd reached a maximum and then decreased with increasing equilibrium solution concentration, while the adsorption of Pb and/or Cu increased with increasing Pb and/or Cu solution equilibrium concentration. This phenomenon was also observed by Lv et al. (2005), who studied the competitive adsorption of Pb, Cu, and Cd on microporous titanosilicate ETS-10. At low concentrations, the amounts adsorbed for both/all metal ions increased with increasing concentration of metal ions in solution due to the abundant adsorption sites on peat. As the concentration of both/all metal ion species increased further, the adsorption sites that were also available to both/all adsorbed species were occupied to an increasing extent by the more strongly adsorbed species, resulting in a decrease in the amount of the more weakly adsorbed species. Moreover when metals were competing for the same type of adsorbent, metals with a greater affinity (strongly adsorbed species) will displace others with a lower affinity (weakly adsorbed species) (Christophi and Axe, 2000). Among the three metal ions, Cd was the weakest one. Therefore when the stronger competitive species Pb and/or Cu in solution compete with the weakest adsorbed species Cd, Cd may undergo displacement, while Pb and/or Cu in solution was reduced in the presence of Cd.

The adsorption isotherms of Pb, Cu, and Cd on peat in single, binary, and ternary systems were successfully simulated with the Langmuir two-site model, with the exception of Cd in the binary and ternary systems. The adsorption capacity of Pb, Cu, or Cd on peat in single-component systems followed the order: Pb > Cu > Cd. In the binary and ternary systems, the total adsorption increased, whereas adsorption capacity of peat for individual metal ions decreased and the extent of the decrease depended in the other metal ion(s) present.

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