Competitive adsorption of copper(II), cadmium(II), lead(II) and zinc(II) onto basic oxygen furnace slag

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ABSTRACT

Polluted and contaminated water can often contain more than one heavy metal species. It is possible that the behavior of a particular metal species in a solution system will be affected by the presence of other metals. In this study, we have investigated the adsorption of Cd(II), Cu(II), Pb(II), and Zn(II) onto basic oxygen furnace slag (BOF slag) in single- and multi-element solution systems as a function of pH and concentration, in a background solution of 0.01 M NaNO$_3$. In adsorption edge experiments, the pH was varied from 2.0 to 13.0 with total metal concentration 0.84 mM in the single element system and 0.21 mM each of Cd(II), Cu(II), Pb(II), and Zn(II) in the multi-element system. The value of pH$_{50}$ (the pH at which 50% adsorption occurs) was found to follow the sequence Zn > Cu > Pb > Cd in single-element systems, but Pb > Cu > Zn > Cd in the multi-element system. Adsorption isotherms at pH 6.0 in the multi-element systems showed that there is competition among various metals for adsorption sites on BOF slag. The adsorption and potentiometric titrations data for various slag–metal systems were modeled using an extended constant-capacitance surface complexation model that assumed an ion-exchange process below pH 6.5 and the formation of inner-sphere surface complexes at higher pH. Inner-sphere complexation was more dominant for the Cu(II), Pb(II) and Zn(II) systems.

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1. Introduction

The existence of heavy metals in the aquatic system can be detrimental to a variety of living species. Many industrial processes discharge aqueous effluents containing heavy metals [1]. Heavy metals are non-biodegradable and tend to accumulate in living organisms, causing various disorders for living organisms. Accordingly, improved and innovative methods of water and wastewater treatment are continuously being developed to treat water-containing metals [2]. Precipitation and ion exchange are the most widely used methods for cleaning water contaminated with metal pollutants. However, these methods are unable to achieve the standards which are recommended by international water standards bodies [3]. In recent years, many natural adsorbents have been investigated for the removal of heavy metals from water. A review of more than 70 natural and synthetic adsorbents and their potential uses for metal removal has been reported [2].

Contaminated water often contains more than one heavy metal, which can potentially impact the adsorption behavior of each metal present as a result of competition among various ions present in the system. Heavy metals such Cd, Cu, Pb, and Zn occur commonly at elevated concentrations in contaminated water [4]. Metals such as Cu and Zn are known to be essential to plants, humans, and animals, but they can also have adverse effects if their availability in water exceeds certain threshold values. Other heavy metals, such as Cd, Pb, and Hg, which are not essential to plants or animals, are known to be hazardous to health, even at low concentrations. Among the important heavy metals, Pb is reportedly the least mobile. Copper has been shown to remain bound up as insoluble complexes, whereas Zn and Cd are considerably more mobile. Cd and Zn have a greater tendency to dissociate from insoluble inorganic and organic complexes to form soluble ionic species that remain stable at neutral or slightly alkaline pH [5].

Adsorption is arguably the most important of the physicochemical processes responsible for the retention of inorganic and organic substances in the aqueous environment [6]. Factors such as pH [7,8], nature and concentration of substrate and adsorbing ion [9,10], ionic strength [11], and the presence of competing and complex ions [12], affect the extent of adsorption. Adsorption of heavy

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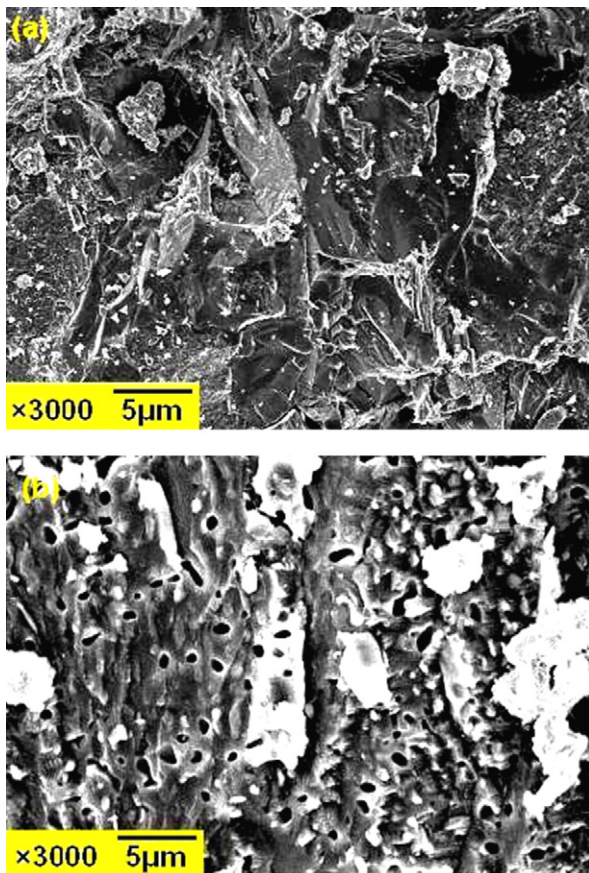E-mail address: xueyj@mail.whut.edu.cn (Y. Xue).

Table 1
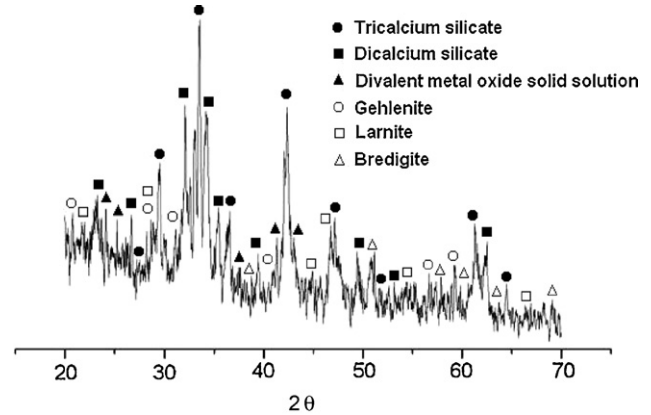Physical properties and chemical compositions of BOFS

Chemical composition	Content (%)
Silica (as SiO_2)	13.7
Calcium (as CaO)	45.4
Iron (as Fe_2O_3 and FeO)	17.8
Magnesium (as MgO)	7.3
Alumina (as Al_2O_3)	6.8
H_2O at $105\,^\circ C$	1.1
H_2O at $950\,^\circ C$	2.4
BET–N_2 surface area (m^2/g)	1.15

Fig. 2. XRD spectrum of BOF slag.

metals has been modeled on various minerals such as natural adsorbents [6], fly ash [13], blast furnace slag, and clay minerals [14] in single-element systems. However, little work has been done to model the adsorption of heavy metals onto basic oxygen furnace slag which generated from steel making process in multi-element systems.

Basic oxygen furnace slag (BOF slag in short) is a final waste material in the basic oxygen furnace steel making process [15]. In recent years, the management of BOF slag has become a significant issue in environmental engineering due to the enormous quantities generated and the associated disposal costs and constraints. BOF slag is heterogeneous oxide materials which are compounded by some main oxides such as CaO, Fe_2O_3, SiO_2, Al_2O_3, and MgO due to their mass percentage. These oxides are going to change with different steel making process, raw materials, even cooling and crash methods, and all these factors will lead to BOF slag show

the heterogeneity characters which may affect the new application way for BOF slag like removal of heavy metal from aqueous solution. It is known that BOF slag shows strongly heterogeneous surfaces. The heterogeneity of the BOF slag surface stems from two sources, namely geometrical and chemical. The geometrical heterogeneity (porosity) is the result of differences in the size and shape of pores, as well as pits, vacancies and steps. Chemical heterogeneity is associated with different functional groups at a surface, and with various surface contaminants. Besides, it reported that BOF slag can show very stronger acid neutralization capacity and chemical precipitation capacity. Both the chemical and geometrical heterogeneities contribute to the unique adsorption properties of BOF slag [16].

In the present work, we have studied adsorption behavior of four divalent metals (Cd, Cu, Pb, and Zn), which occur most commonly in contaminated water and have different hydrolysis behavior. The objective of this study was to examine the adsorption of heavy metals (Cd, Cu, Pb, and Zn) onto basic oxygen furnace slag in single- and multi-element systems. This is very useful to investigate and discuss a new kind of heavy metal adsorbents. We used an extended constant-capacitance surface complexation model to describe the sorption, as it allows for both inner sphere and outer sphere complexation, but requires fewer adjustable parameters than triple layer models.

Fig. 1. SEM micrographs: (a) original BOF slag and (b) 3 h ground by mill.

Table 2
Extent constant-capacitance surface complexation model parameter for adsorption of Cu, Cd, Pb and Zn using GRFIT [21]

	Cu(II)	Cd(II)	Pb(II)	Zn(II)
Equilibrium constants, $\lg K_W$				
$M^{2+} + H_2O = MOH^+ + H^+$	−8.00	−9.60	−7.71	−8.96
$2M^{2+} + 2H_2O = M_2(OH)_2{}^{2+} + 2H^+$	−10.36	–	–	–
$M^{2+} + 2H_2O = M(OH)_2 + 2H^+$	−17.30	−18.80	−17.12	−16.90
$M^{2+} + 3H_2O = M(OH)_3{}^- + 3H^+$	−21.88	−30.15	−28.06	−28.40
$3M^{2+} + 4H_2O = M_3(OH)_4{}^{2+} + 4H^+$	−25.28	–	−23.88	–
$6M^{2+} + 8H_2O = M_6(OH)_8{}^{4+} + 8H^+$	–	–	−35.72	–
Surface reactions, $\lg K_S$				
$2XNa + M^{2+} = X_2M + 2Na^+$	4.45	4.13	4.28	4.73
$2SOH + M^{2+} = (SO)_2M + 2H^+$	–	−8.79	–	−7.06
$SOH + MOH^+ = SOMOH + H^+$	−8.13	–	−8.65	–
Concentration of sites (mM)				
X^-	0.82			
SOH	0.154			
Specific capacitance ($F\,m^{-2}$)				
C_{inner}	7			
C_{outer}	3			

2. Materials and methods

2.1. Materials, chemicals and equipments

BOF slag used in this study generated from the Wuhan steel-making company in China with 2 years setting time. Adsorbents were made by such slag with further treatment. The sieve size of BOF slag was controlled under 0.6 mm first, and then slag was treated by acid (0.1 M HCl) and washed by deionised water. After been dried, the slag was ground for 3 h by vertical plane-tary ball mill. Physical properties and chemical compositions of BOF slag used in this study are shown in Table 1. Morphological structure of the BOF slag was showed in Figs. 1 and 2 by scan electron microscope (SEM) and X-ray diffraction (XRD) spectrum. Scanning photo shows BOF slag is more porous materials after ground. The XRD spectrums are complex in spectrum and some of them overlapped. Major miner products were RO phase (diva-lent metal oxides solid solution), dicalcium silicate and tricalcium silicate.

All chemicals and reagents used were of analytical grade and obtained from Merck, Germany Stock solutions of Cd, Cu, Pb, and Zn were prepared from analytical grade chemicals, $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Pb(NO_3)_2$ and $Zn(NO_3)_2$. Solution of 0.1 M NaOH and 0.1 M HNO_3 were used for pH adjustment. Constant ionic strength of 0.1 M $NaNO_3$ of solution for background electrolyte was used in all experiments. All working solutions were prepared by diluting the stock solutions with deionised water.

Elemental, physical and chemical analyses of the BOF slag were carried out using inductively coupled plasma-atomic emis-sion spectrometer (ICP-AES, IRIS Advantage). The morphological structure of the dewatered BOF slag was examined by X-ray diffractometer (XRD, D/Max-RB Model XRD Analyzer) and scan-ning electron microscope (SEM, JSM-5610LV Model). The specific surface areas SBET of the samples were determined by the ther-mal desorption method using a "Chrom4" gas chromatograph fed with nitrogen as adsorbate. The pH control measurement (PHS-3C Model), a thermo-stated shaker (Orbital Model SHZ-88) and a centrifuge (Sigma Model 3E-1) were used in adsorption batch experiments. A vertical planetary ball mill (QM-1SP2 Model) was used for modification of BOF slag. The concentration of metal ions was determined by using a Varian flame atomic absorption spec-trophotometer (FAAS, TAS 990 Model).

2.2. Batch adsorption experiments

Adsorption experiments as a function of pH (adsorption edge), contact time (adsorption kinetics) and concentration (adsorption isotherm) were conducted in a borosilicate reaction vessel at con-trolled room temperature under nitrogen atmosphere.

A sufficient mass of slag was added to give a surface area concen-tration of 10.6 m²/L (solid/solution ration, 13.6 g/L) and adsorption edge experiments were conducted at 0.84 mM metal concentration in the single-element systems and at 0.21 mM metal concentration each of Cd, Cu, Pb, and Zn (i.e., total metal concentration of 0.84 mM)
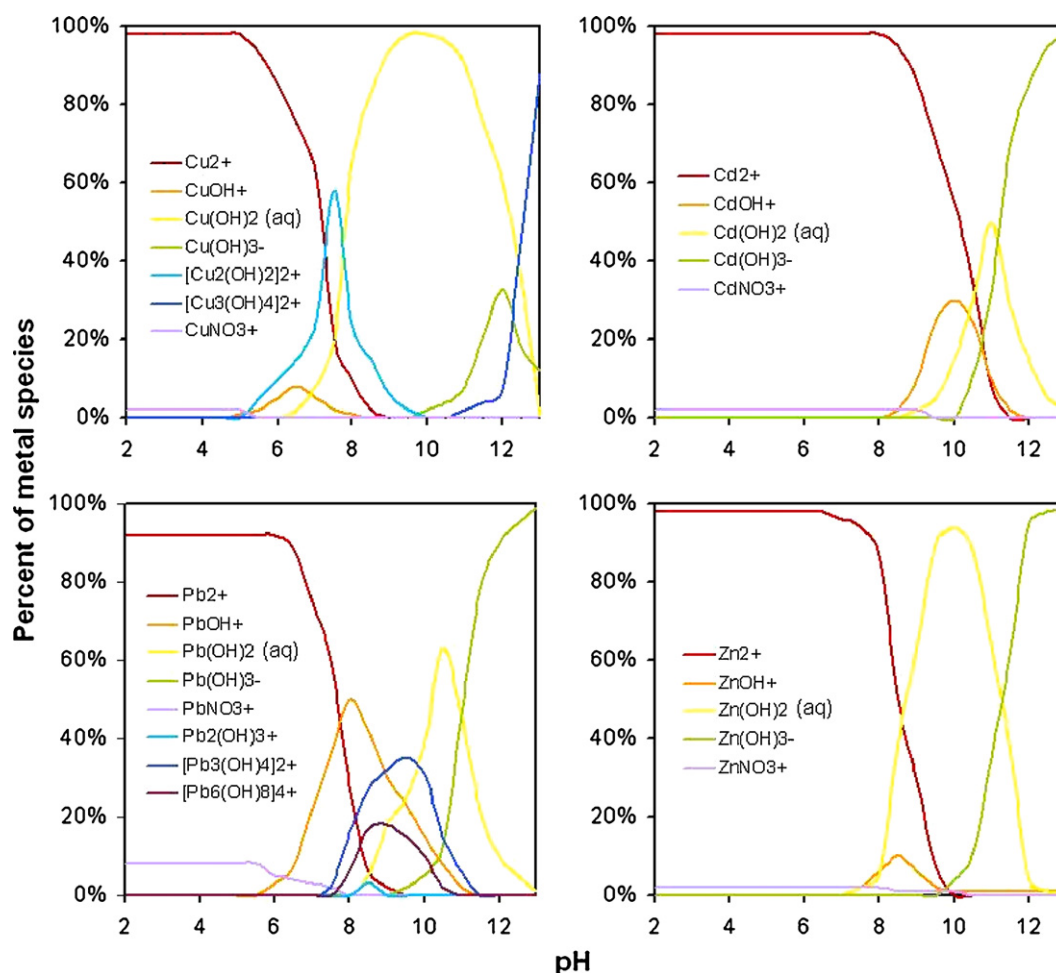

Fig. 3. Aqueous speciation of Cu, Cd, Pb and Zn as a function of pH in the single-element system.

in multi-element systems. The equilibrium pH of the suspension was varied from 2.0 to 13.0. The suspension was equilibrated for metal adsorption for 1 h and an aliquot was collected every hour. The aliquots were centrifuged and filtered and the supernatant was analyzed for the respective metal(s) using FAAS. The amount of metal adsorbed was calculated as the difference between the initial and equilibrium metal concentrations. Kinetic experiments were completed to establish the time required for the sorption system to reach equilibrium. 1.00 mM metal concentration in the single-element systems and 0.25 mM metal concentration each of Cd, Cu, Pb, and Zn was added at pH 6.0. Samples were taken at intervals over a period of 24 h and supernatants were analyzed after centrifuged for metal concentration at determined time. Adsorption isotherm experiments were conducted at pH 6.0 with the metal concentrations from 0.40 to 4.00 mM in the single-element systems and from 0.10 to 1.00 mM each of Cd, Cu, Pb, and Zn (i.e., total metal concentration from 0.40 to 4.00 mM) in multi-element system. The pH was maintained by addition of 0.1 M NaOH and 0.1 M HNO_3.

Potentiometric titrations were performed on suspensions in the absence and presence of metal ion(s) at the same mineral and metal concentrations as in the adsorption edge experiments to determine the proton stoichiometry of the various surface reactions. After the BOF slag suspension was equilibrated overnight, the metal ion(s) was/were added and the system was titrated between pH 2.0 and 13.0 using 0.1 M HCl and 0.1 M NaOH, respectively, using the automatic titrator (Metrohm 719S Titrino). After each addition of acid or

base, the suspension pH was stable until the pH drift was less than 0.01 units per minute. All experiments were performed in triplicate and average results were kept.

2.3. Aqueous speciation of metals

Aqueous speciation of metals as a function of pH was studied using the computer program Visual MINTEQ, Version 2.30 [17], which is a modified version of the original MINTEQA2/PRODEFA2 program [18]. The solution speciation of the metals was modeled because the hydrolysis behavior of metal ions has been found to influence sorption processes [19].

2.4. Adsorption model

The data from potentiometric titration, adsorption edge, and adsorption isotherm experiments were modeled using an extended constant-capacitance surface complexation model by setting the ionic strength in the triple layer model to 10^9 M, which has the effect of eliminating the diffuse layer [20]. Extended constant-capacitance models have been used previously to describe the adsorption of various ionic species onto a number of different substrates. Parameters for surface protonation reactions were obtained by modeling the titration data of slag suspensions without metal ions. The values for equilibrium constants and site densities (Table 2) were estimated by modeling adsorption and titration data using the computer program GRFIT [21]. The equi-
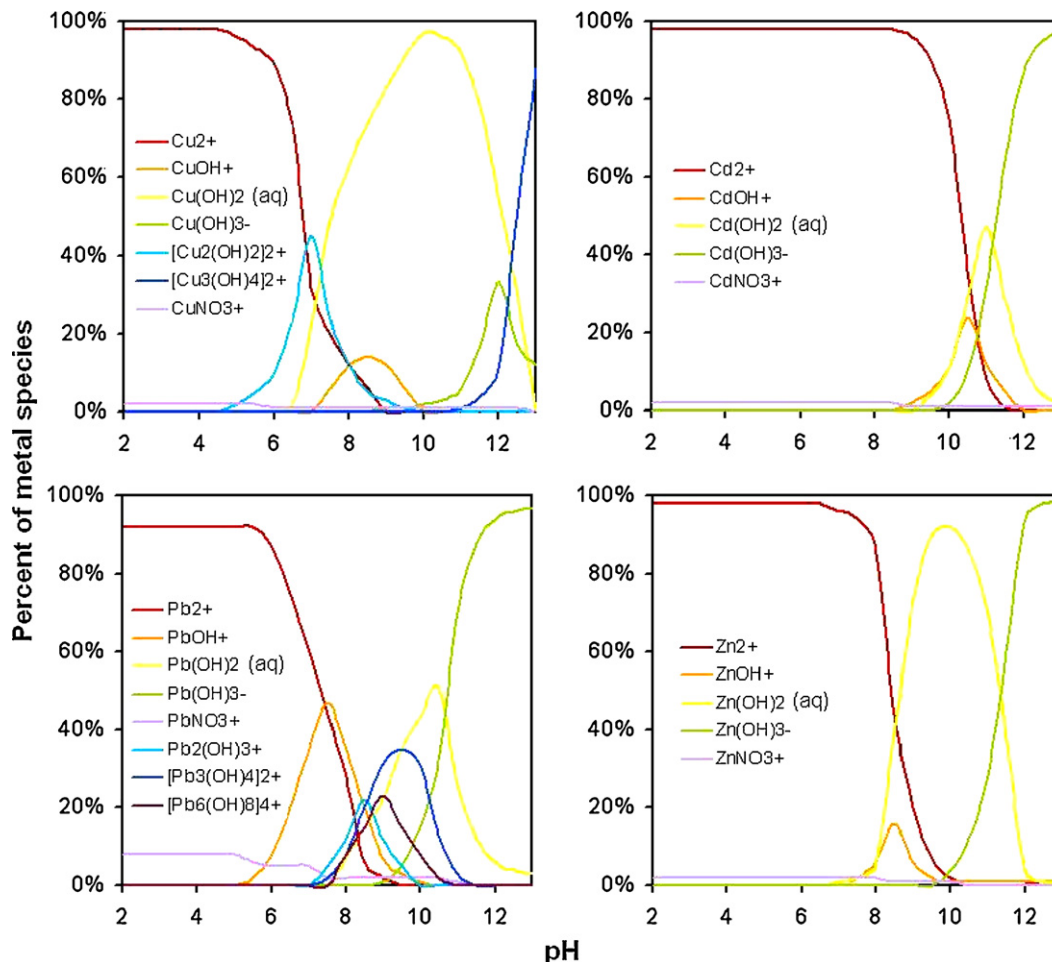

Fig. 4. Aqueous speciation of Cu, Cd, Pb and Zn as a function of pH in the multi-element system.

librium constants for surface site densities were then used as fixed values for modeling the data from adsorption experiments and potentiometric titrations of suspension in the presence of metal ions. The equilibrium constants for these adsorption reactions were deemed acceptable only when these constants closely fitted the data from all three experiments.

Earlier modeling [22] suggests that transition metals adsorb at permanent- and variable-charge sites. The permanent, negatively charged sites, represented by X^-, can undergo an exchange reaction:

$$X^- --Na^+ + H^+ \rightarrow X^- --H^+ + Na^+ \tag{1}$$

In the absence of metal ions, the X^- sites are assumed to be occupied by Na^+ ions from the background electrolyte at higher pH values. The variable charge sites can undergo both protonation and de-protonation reactions:

$$SOH + H^+ \rightarrow SOH_2^+ \tag{2}$$

$$SOH \rightarrow SO^- + H^+ \tag{3}$$

where SOH represents a surface hydroxyl group. Although no distinction is made between aluminol and silanol surface groups, it is likely that the SOH groups involved in adsorption are mostly aluminol (AlOH) [23]. For permanent charge sites, one reaction was sufficient to model adsorption of all metals on BOF slag (4):

$$M^{2+} + 2X^- --Na^+ \rightarrow MX_2 + 2Na^+ \tag{4}$$
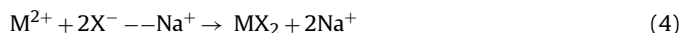
where M^{2+} represents Cd(II), Cu(II), Pb(II), or Zn(II), X^- is a permanent charge site and MX_2 is an outer-sphere complex in the model. For variable charge sites, inner-sphere complexes of the form SOMOH were required to give adequate fits to potentiometric titration, adsorption edge, and isotherm experiments involving Cu and Pb (5). Bidentate inner sphere complexes of the $(SO)_2M$ were required for Cd and Zn uptake (6):

$$2SOH + M^{2+} \rightarrow SOMSO + 2H^+ \tag{5}$$

$$2SOH + M^{2+} \rightarrow (SO)_2M + 2H^+ \tag{6}$$

3. Results

3.1. Aqueous speciation of metals

The aqueous speciation of metals was determined by the hydrolysis constant from Baes and Mesmer [24]. Figs. 3 and 4 show the speciation of each of the metals in the single- and multi-element solution systems, respectively. Curves from figures are similar. Copper appears predominantly as Cu^{2+} species at pH < 5.0, after which its concentration decreases. Concentration of various Cu hydroxyl species such as $CuOH^+$, $[Cu_2(OH)_2]^{2+}$, $[Cu(OH)_4]^{2-}$, $Cu(OH)_2(aq)$ and $[Cu(OH)_3]^-$, increases at pH > 5.0 in both the solutions. Concentration of other Cu species such as $CuNO_3^+$, $[Cu(OH)_4]^-$ and $[Cu_2(OH)]^{3+}$ is negligible in solution and does not significantly change with the pH. Cadmium appears predominantly as Cd^{2+} species over pH 2–9. At pH 10, concentration of $CdOH^+$ reaches maximum 30%, whereas the concentration of $Cd(OH)_2(aq)$ and $[Cd(OH)_3]^-$ increases with the decrease of concentration of Cd^{2+} and $CdOH^+$ at higher pH. Concentration of $CdNO_3^+$, $[Cd(OH)_4]^-$ and $[Cd_2(OH)]^{3+}$ is lower in solution and does not change results over the pH range. Similarly, lead also appears predominantly as Pb^{2+} species up to pH 6 in both systems. It is slight different with Cu and Cd, even Zn, that the concentration of nitrate species $PbNO_3^+$ is a significant amount at pH < 6.0, after which its concentration decreases. As compared to the single-element system, concentration of $PbOH^+$ and $Pb(OH)_2(aq)$ decreases while concentration of $[Pb_2(OH)_3]^+$ and $[Pb_6(OH)_8]^{4+}$ increases. Concentration
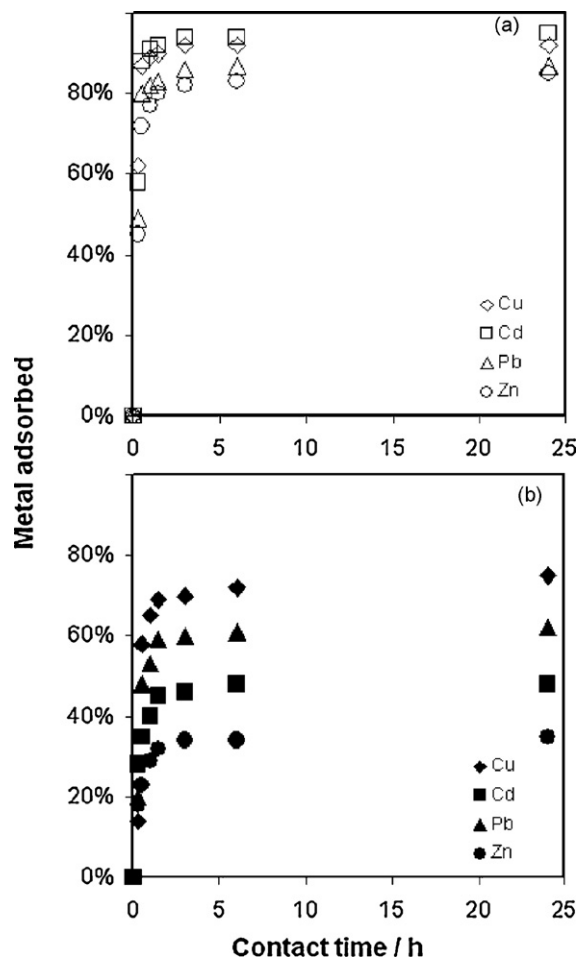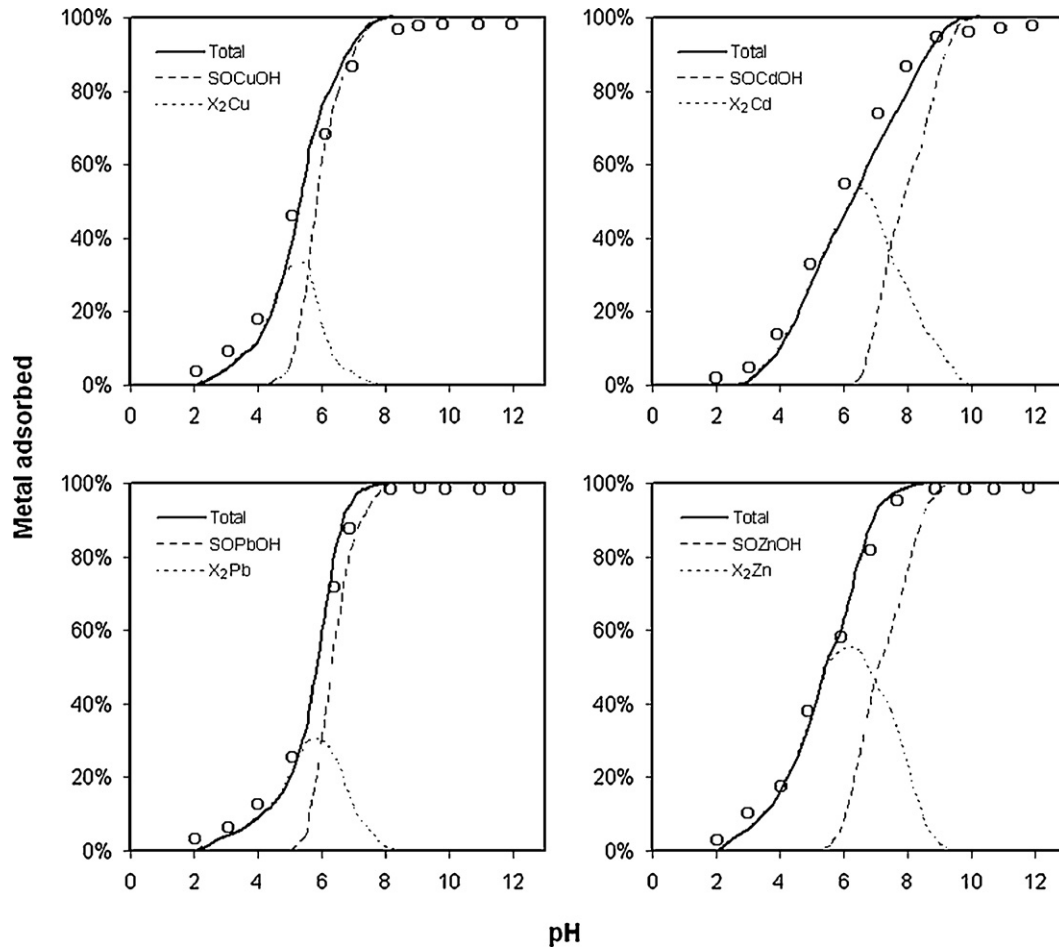

Fig. 5. Adsorption of Cu, Cd, Pb and Zn as a function of contact time in the single-element system (a) and multi-element system (b).

of Pb^{2+}, $[Pb_3(OH)_4]^{2+}$ and $[Pb(OH)_3]^-$ does not change with pH range. Zinc appears predominantly as Zn^{2+} species which concentration sharply decreases at pH > 8. Concentration of $Zn(OH)_2(aq)$ and $[Zn(OH)_3]^-$ is similar in both systems while concentration of $ZnOH^+$ increases as compared to single-element solution system. Other Zn species such as $ZnNO_3^+$, $[Zn(OH)_4]^{2-}$ and $[Zn_2(OH)]^{3+}$ is negligible and does not affect results at experiment condition. For Cu, Cd, Pb and Zn, the concentration of $Cu(OH)_2(aq)$, $Cd(OH)_2(aq)$, $Pb(OH)_2(aq)$ and $Zn(OH)_2(aq)$ reaches the maximum value at high level pH 10.0, 11.5, 10.5 and 10.0, respectively, after which its concentration decreases. At pH 13.0, concentration of $Cu(OH)_2(aq)$, $Cd(OH)_2(aq)$, $Pb(OH)_2(aq)$ and $Zn(OH)_2(aq)$ is close to zero while concentration of Cd, Pb and Zn hydroxyl species, $[Cd(OH)_3]^-$, $[Pb(OH)_3]^-$ and $[Zn(OH)_3]^-$ increases up to 98, 99 and 98% in single-element system while 98, 97 and 98% in multi-element system. It is different to Cu species that concentration of $[Cu_3(OH)_4]^{2+}$ increases up to 88% while concentration of $[Cu(OH)_3]^-$ is 12% at pH 13.0.

3.2. Adsorption kinetics

The results of adsorption kinetic measurements are shown in Fig. 5. These indicate that sorption onto BOF slag at pH 6.0 reached equilibrium after about 30 min, with no evidence of further adsorption up to 24 h. Available adsorption results reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In

Fig. 6. Surface speciation showing adsorption of Cd, Cu, Pb, and Zn onto BOF slag as a function of pH in the single-element system (the circles represent the actual experimental data and the lines represent the modeled adsorption calculated from the extended constant-capacitance surface complexation model).

between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Figs. 5 and 6 show the plot of metal removal rate versus contact time in single- and multi-element solution. All curves of metals adsorption appear nearly similar trend. At first 30 min, metals are adsorbed rapidly. For example, at 30 min, around 80% of the metals are adsorbed in single-element system except Zn. And final equilibrium concentration of metals increases up to 85%. This initial fast reaction is characteristic of heavy metal sorption on BOF slag and has been attributed on adsorption on high affinity surface sites or on sites with higher bonding strength with the metal [25]. However, some differences are observed between the systems. As compared to single-element system, the amount of single metal adsorbed decreases in the multi-element system. This is attributed on the effect of competitive adsorption of metals. Metals adsorbed are similar and higher in single-element system, while lower in multi-element system. The selectivity is Cu > Pb > Cd > Zn.

3.3. Adsorption edges

Adsorption edges of Cu, Cd, Pb and Zn were studied between pH 2 and 13 for both solution systems. The adsorption of the heavy metals on BOF slag increased with increasing pH, with the shape

of the curves dependent on the metal (Figs. 6 and 7). In single-element systems, the adsorption edges for Cu and Pb were sigmoid, whereas those for Cd and Zn were characterized by two distinct adsorption stages, with each stage in Cd adsorption edge separated by a plateau in the pH range 6.0–6.5. The plateau was more evident in the Cd adsorption edge compared to Zn. A plateau in the middle of adsorption edges was not observed for any metal in the multi-element system. The value of $pH_{1/2}$ (Table 3), corresponding to the pH value where 50% of metal are adsorbed, varied from metal to metal and increased in a relatively narrow range (1–2 pH units) and showed that the selectivity sequence was Zn > Cu > Pb > Cd in single-element systems, whereas the sequence was Pb > Cu > Zn > Cd in the multi-element system. The $pH_{1/2}$ for metals also showed that, in the multi-element system, adsorption edges for Pb and Cd were shifted to lower pH, while Cu and Zn to higher pH. The surface speciation of the adsorption edges shows that at lower pH, uptake of all four metals first occurred on permanent charge sites (X^-), and thereafter on variable charge sites in both single- and multi-element systems. Adsorption at permanent charge sites predominated up to pH 5.6 and 6.2 for Cu and Pb and pH 7.1 and 7.8 for Zn and Cd, respectively, in the single-element systems.

3.4. Adsorption isotherms

Isotherms were conducted to study metal adsorption onto slag sample as a function of adsorbate concentration at pH constants. The adsorption isotherms at pH 6.0 indicate that the amount of
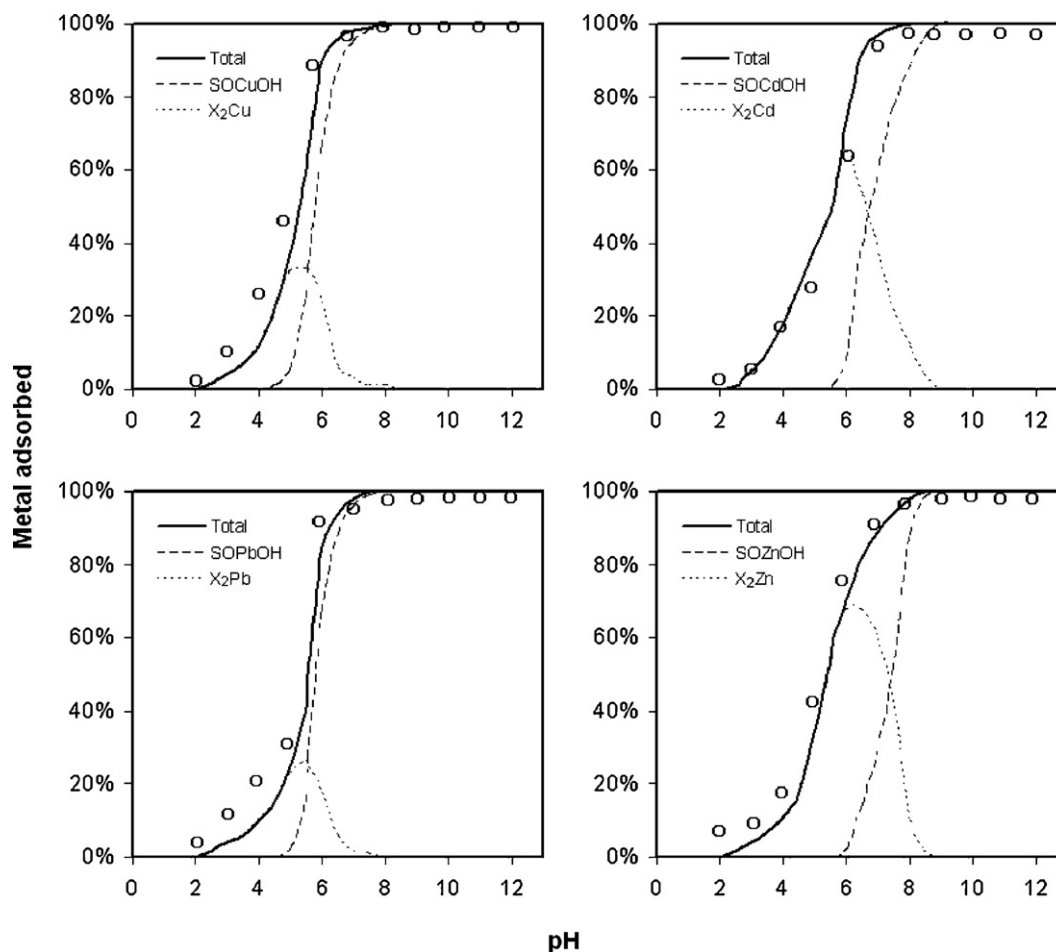
Fig. 7. Surface speciation showing adsorption of Cd, Cu, Pb, and Zn onto BOF slag as a function of pH in the multi-element system (the circles represent the actual experimental data and the lines represent the modeled adsorption calculated from the extended constant-capacitance surface complexation model).

each metal adsorbed increased as the equilibrium concentration of the metal increased in both single- and multi-element systems (Figs. 8 and 9). The isotherms showed that Cu, Cd and Zn had similar but relatively higher adsorption capacity compared to Pb in single-element system. However in multi-element system, Cu showed higher adsorption capacity compared to Cd, Pb and Zn. The selectivity sequence in the adsorption isotherm experiments was Cu > Zn > Pb > Cd in single-element system and Cu > Cd > Pb > Zn in multi-element system.

The surface speciation of the isotherms showed that at pH 6.0, adsorption of Cu and Zn occurred predominantly on the variable charge sites in both single- and multi-element systems; with a greater proportion being adsorbed in single element systems than in the multi-element system. In contrast to Cu and Zn adsorption, the adsorption of Cd and Pb occurred predominantly on permanent charge sites in both systems. The adsorption of Zn on variable charge sites was greater in the single-element system, while adsorption of Cd and Pb on variable charges sites was negligible in both systems.

Table 3
Values of $pH_{1/2}$ for adsorption of Cd, Cu, Pb, and Zn onto BOFs in single- and multi-element systems

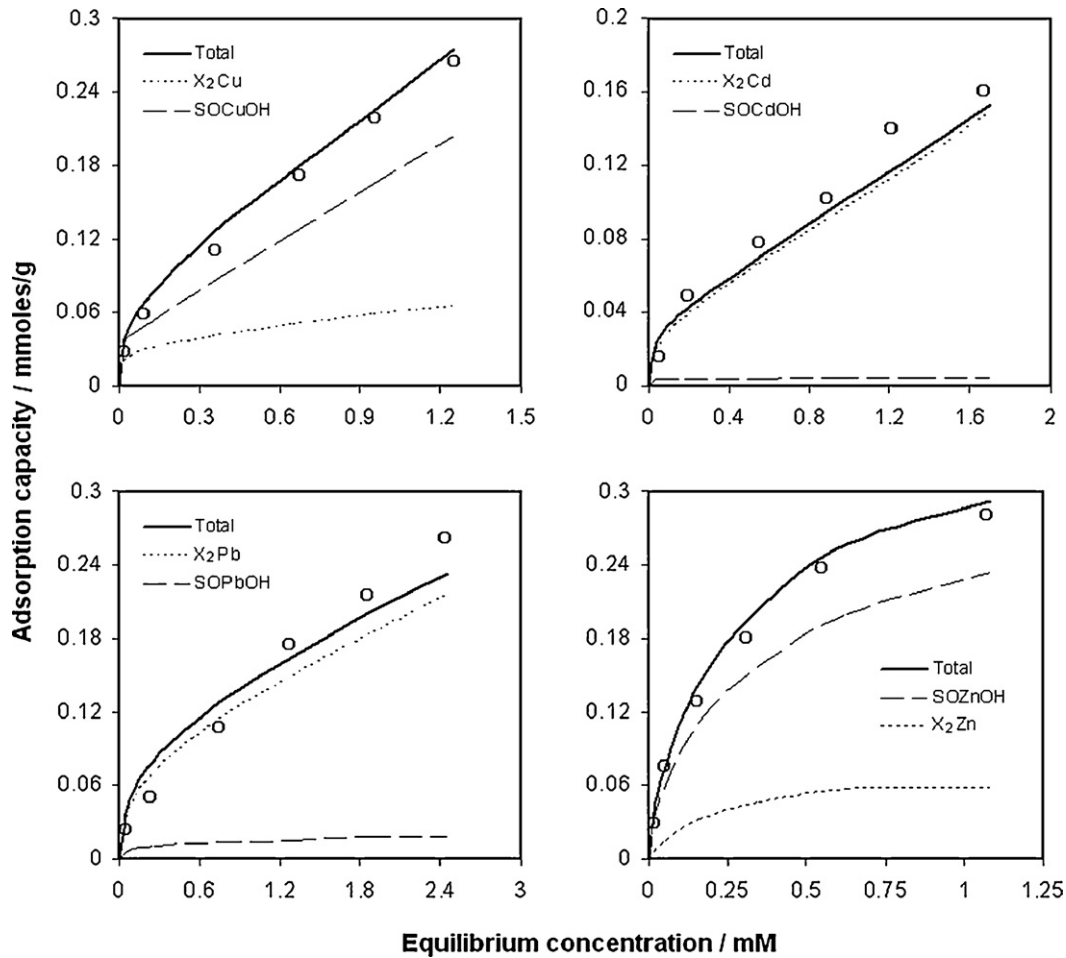| Metal	Single-element system	Multi-element system
Cu	5.35	5.45
Cd	6.35	6.15
Pb	5.40	4.95
Zn	5.15	5.70

3.5. Potentiometric titrations

Fig. 10 shows potentiometric titrations for the three montmorillonite samples with, and without, added 0.4 mM metal and 0.1 mM each of metals in single- and multi-element systems, respectively. The lines in Fig. 10 represent the best fit of the extended constant-capacitance surface complexation model to the experimental data. Values of the intrinsic equilibrium constants for protonation and de-protonation of the surface groups depend on the value chosen as the pH_{zpc}. For BOF slag suspensions, in which no metal was added, the surface reactions assumed were ion exchange between H^+ and Na^+ on permanent charge (X^-) sites, together with protonation and de-protonation of variable charge (SOH) sites. After added metal(s), a bidentate exchange reaction (Eq. (4)) was required to account for the sorption below pH 6.0, where as reactions involving surface complexation with hydroxyl groups (Eqs. (5) and (6)), were required to model the adsorption of the metals at higher pH.

4. Discussion

4.1. Adsorption in single-element system

The adsorption edges investigated have a similar shape and occur across a pH range similar to those reported previously for the adsorption of Cu, Cd, Pb and Zn. In modeling these systems, this study assumed that ion exchange is the dominant mechanism at low pH, and that an exchange process represented by Eq. (4) is

Fig. 8. Surface speciation showing adsorption of Cd, Cu, Pb, and Zn onto BOF slag as a function of equilibrium concentration in single-element system (the circles represent the actual experimental data and the lines represent the modeled adsorption calculated from the extended constant-capacitance surface complexation model).

responsible for metal uptake. This view is supported by the effects of the cation exchange capacity and the saturating cation on adsorption. The surface species X_2M is an outer-sphere complex, with the best fit obtained when the complex is bidentate; a monodentate species XM^+ could not model the data as effectively.

It is probably unrealistic to think of this species as a divalent metal ion specifically coordinated to two sites; rather it represents the electrostatic attraction between a divalent ion that neutralizes an opposite, but diffuse, charge at the surface. The surface speciation given in Fig. 6 shows that interaction with permanent charge is more significant in the Cd systems. This may be because Cu, Pb and Zn hydrolyze at lower pH and are more likely to interact with edge hydroxyl sites than Cd. The adsorption edges for the metal ions in single-element system showed that the Cu, Pb and Zn edges occurred at lower pH than the Cd edge. The stronger interaction of Cu, Pb and Zn at lower pH is also reflected by the greater amounts adsorbed in the isotherm experiments at pH 6.0 in Fig. 8. In addition, the Values of $pH_{1/2}$ (Table 3) measured in the adsorption edge experiments was significantly higher for Cu, Pb and Zn and supported the suggestion that adsorption of Cu, Pb and Zn involves significant hydrolysis and interaction with surface hydroxyls at pH values where Cd interact only with exchange sites. The selectivity series for these metals followed the tendency for the metal to hydrolyze. Cu, Pb and Zn hydrolyze more readily and hence are more likely to interact with a hydroxylated surface. Several investigations have shown that metals that hydrolyze more readily have a lower

$pH_{1/2}$ [7,9,26]. The selectivity sequence concluded in this study was slightly different from previous research work. Puls and Bohn [27] found that Zn adsorbed to the kaolinite surface at a lower pH than Cd. A study of metal adsorption onto goethite by Forbes et al. [28] showed a selectivity sequence Cu > Pb > Zn > Cd, which was slightly different with Zn > Cu > Pb > Cd from this study. On the other hand, Benjamin and Leckie [29], who studied metal uptake by amorphous iron oxyhydroxide, and Cho et al. [13], in a study on removal characteristics of heavy metals from aqueous solution by fly ash, found that Pb had a higher affinity for the surface than Cu, with the selectivity sequence Pb > Cu > Zn > Cd. The difference in the selectivity between this present study and previous researches is probably a function of the different surfaces investigated.

The modeling generally fitted to the adsorption edges, isotherms and potentiometric titrations. However, there is no research work about using an extended constant-capacitance surface complexation model to describe competitive adsorption of heavy metals onto BOF slag. This study referred to other heavy metal-adsorbents systems, such as adsorption of heavy metals onto kaolinite, goethite, fly ash. The constant-capacitance model assumed that all complexes were inner-sphere and was perhaps not an ideal representation of the ion exchange process that occurred on the slag surfaces. In this study we applied an extended constant-capacitance model that assumes outer sphere complex formation in the exchange reactions in a similarity to Lackovic et al. [30]. However, the model proposed here is simple, it provides an adequate fit to the three different sets
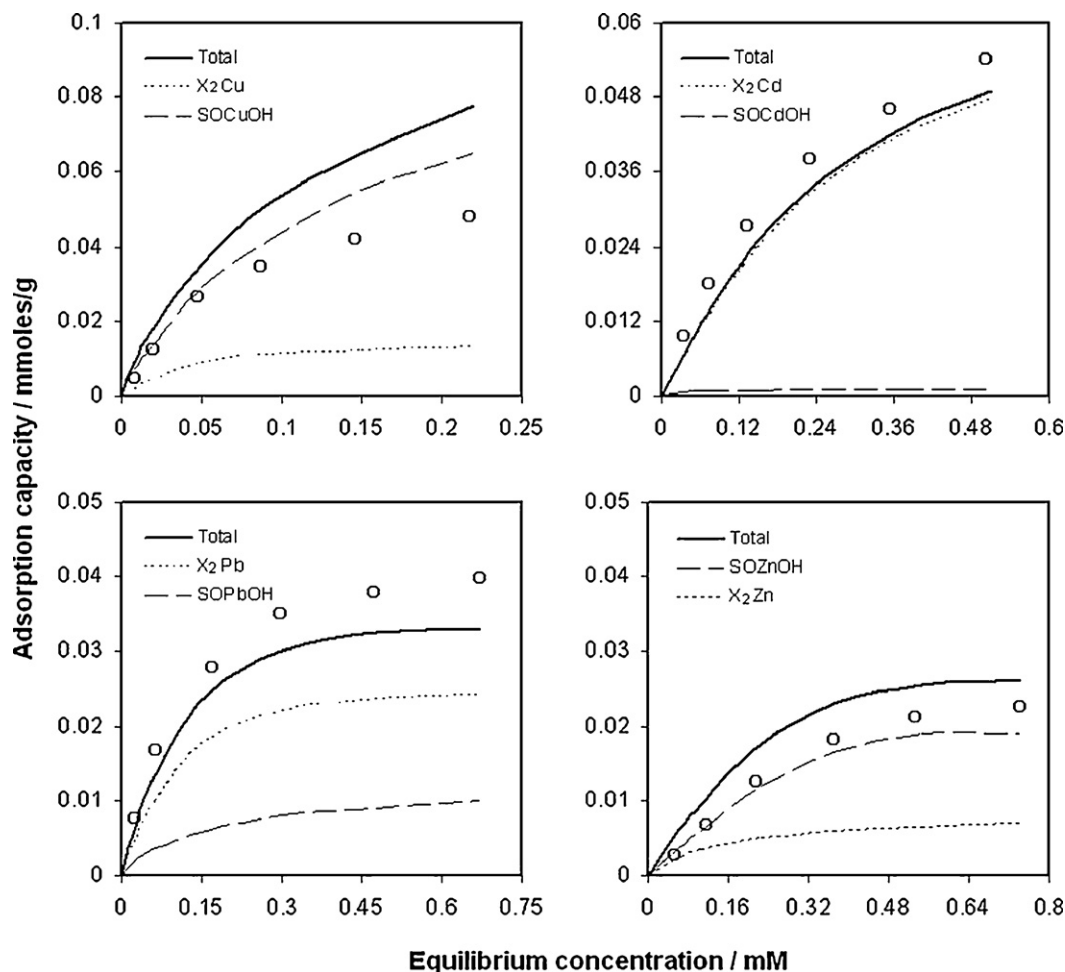
Fig. 9. Surface speciation showing adsorption of Cd, Cu, Pb, and Zn onto BOF slag as a function of equilibrium concentration in multi-element system (the circles represent the actual experimental data and the lines represent the modeled adsorption calculated from the extended constant-capacitance surface complexation model).

of experiments for all metals studied with minimum adjustable parameters. The fit for the Cd and Pb adsorption isotherm was not as good as observed for other metals, as the model slightly under-estimated the Cd and Pb adsorption.

An interesting aspect of the modeling was the different reaction schemes that were required to model the sorption of the metals. For Cu, Pb and Zn, the best fits were obtained by assuming a complex SOMOH. Fig. 6 shows that this surface species becomes significant at pH values above 5.0. For Cd, the model required a surface complex of the form SO_2M, which becomes important above pH 6.5. This difference in the surface speciation reflected the different hydrolysis behavior of the metals, with the Cu, Pb and Zn surface species occurring as hydrolyzed complexes, while Cd adsorb as divalent ions.

4.2. Adsorption in multi-element system

The adsorption of the metals in the multi-element system differed from their corresponding behavior in single-element systems. The surface speciation curve for Cd adsorption showed that the adsorption in single-element systems predominantly occurred on permanent negatively charged sites in the first stage up to pH 6.0 (Fig. 6). The adsorption of Cd onto the variable charged hydroxyl edges began at pH 6.5 in the single-element system. In the multi-element system, however, Cd adsorption occurred predominantly on the permanent charge surface down to pH 5.8. The decreased

uptake of Cd by the permanent charge surface in the multi-element system might be explained by considering the behavior of the presence of the other metals. Modeling in the multi-element system revealed that metals (Cu, Pb and Zn) that form hydrolysis products more readily adsorbed to variable charge surfaces from about pH 5.0. Atanassova [31] reported that, in a multi-component system, an increase in the Cu concentration resulted in a reduction in the uptake of other heavy metals such as Ni, Cd, and Zn. Since Cu is predominantly specifically adsorbed (inner-sphere complexation), and it can be expected that increasing the amounts of the more strongly bonded Cu reduced the number of sites available for Cd, Pb and Zn adsorption. Figs. 8 and 9 undoubtedly showed the presence of Cu suppressed the uptake of Cd and Zn by variable charge surface, while the presence of Cd decreased the uptake of Cu and Pb onto exchange sites. The model provided a good fit to the adsorption edge data for all metals. However, the lack of fit in the multi-element system suggests that the chemistry of the sorption process for Cu and Pb is not simple in the adsorption isotherm experiments. For example, it could be that a multi-element adsorbate or co-precipitate forms at the surface. Direct methods such as extended X-ray absorption fine structure spectroscopy (EXAFS) might be useful to ascertain the mechanism of heavy metal adsorption in multi-element systems. This technique might provide useful information on how the surface speciation might change when competing metals were present, and if species involving two or more different metal cations also formed.
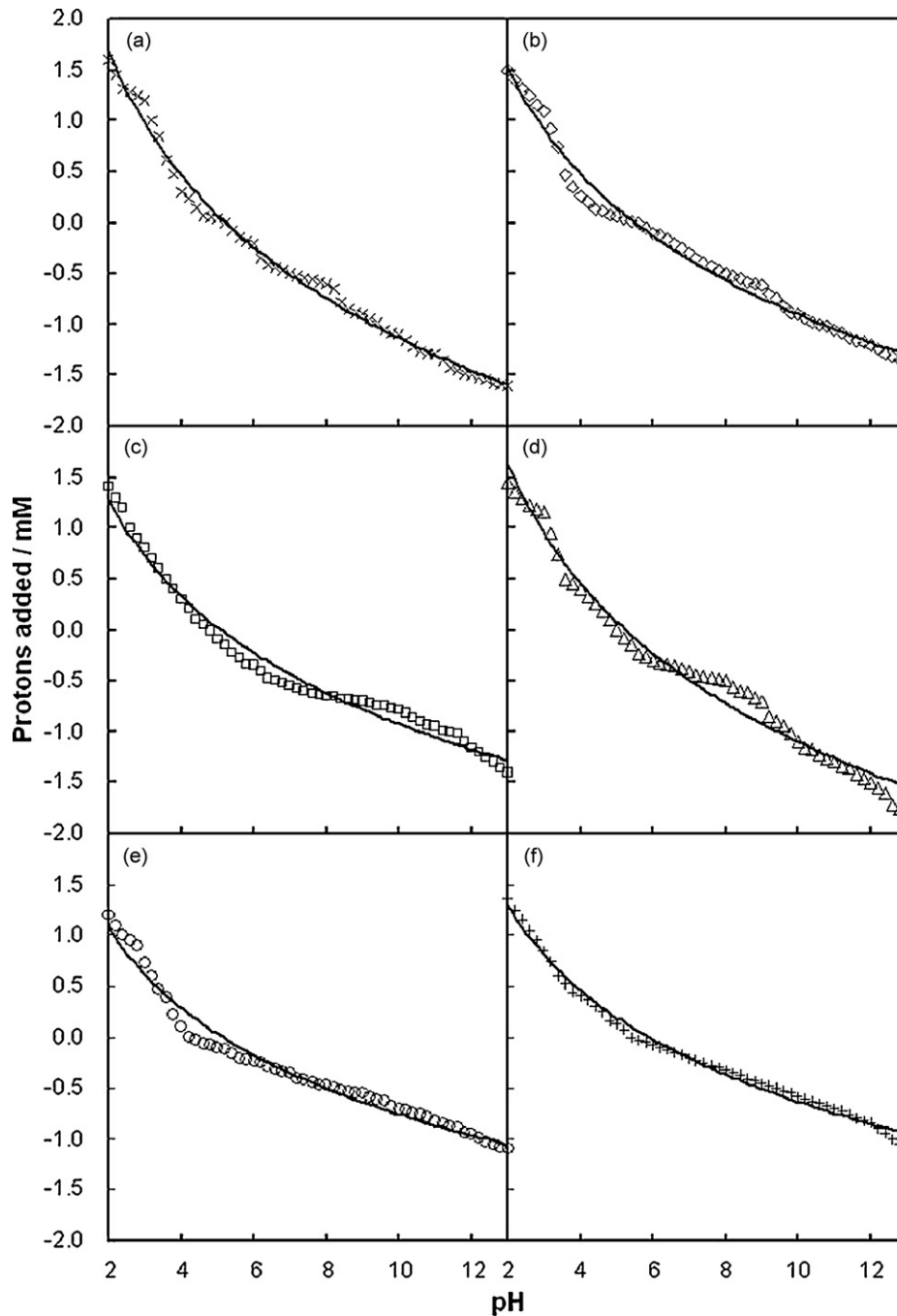
Fig. 10. Potentiometric titrations of slag suspension, without (a) and with added metals, Cu (b), Cd (c), Pb (d), Zn (e), and all four metals (f) (the circles represent the actual experimental data and the lines represent the modeled adsorption calculated from the extended constant-capacitance surface complexation model).

5. Conclusions

This study has investigated that competitive adsorption of Cu, Cd, Pb and Zn onto surface of basic oxygen furnace slag. The adsorption reached equilibrium within 30 min. The adsorption behaviors of metals onto slag in single- and multi-element systems were different. The selectivity sequence of the adsorption edges of these metals was Zn > Cu > Pb > Cd in single-element systems, whereas the sequence was Pb > Cu > Zn > Cd in the multi-element system. For adsorption isotherms, the selectivity sequence was Cu > Zn > Pb > Cd in single-element system and Cu > Cd > Pb > Zn in multi-element system. It is first time to use the extended constant-capacitance

surface complexation model to describe adsorption of heavy metals onto BOF slag. This model proposed three kinds of possible reaction mechanism to explain the adsorption behaviors. At low pH, all these metals adsorb onto permanent charge sites by ion exchange reactions. Adsorption onto variable charge sites occurred at higher pH by forming inner-sphere complexes at the crystal edges and octahedral alumina faces. The hydroxyl species of Cu, Pb and Zn were adsorbed by forming monodentate inner-sphere complexes, whereas adsorption of Cd on variable charges occurred by forming bidentate complexes.

The extended constant-capacitance surface complexation model fitted the data adequately to different kinds of adsorption

and potentiometric titration experiments with the exception of the Cd adsorption isotherm in the multi-element system. The model probably needs to include for more complex speciation to account for the Cu and Pb adsorption isotherm in the multi-element system. Direct methods such as EXAFS and other spectroscopic techniques might be required to ascertain the mechanism for adsorption of heavy metals onto slag particularly in multi-element systems.

Acknowledgments

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