A Study on Adsorption of Pb, Cu, Zn and Cd Onto Natural Clay

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ABSTRACT: The effect of temperature on the adsorption of heavy metals on not only natural bulk clay, but also for the individual phases that composed the bulk clay sample, was investigated. Combined Adsorption-Sequential extraction Analysis (CASA) for Pb, Cu, Zn and Cd were conducted under various temperatures that ranged from 15^0C to 55^0C. As a result, it was found that heavy metals adsorption for bulk clay increased about 12% when the temperature increased from 15^0C to 55^0C. The effect of temperature on the individual phases was mainly observed in oxide, including Fe-and Mn-oxide, and the organic phases of all of the metals. As for the Phase Concentration Factors (PCFs) of the metals, the largest increase of the values was observed in the oxide phase. Based on the thermodynamic parameters of the individual phases, the adsorption of metals on natural clay was an endothermic reaction with the exception of exchangeable phase adsorption. This shows that adsorption affinity and capacity tend to increase when the temperature increase for all adsorption phases of soil, except for adsorption in the exchangeable phase. In the case of Pb, Zn, and Cu adsorption, the considerable enthalpy changes were observed in carbonates, Fe-oxides, and organic phases, which means the adsorption affinity for those phases were largely affected by temperature change. On the other hand, relatively small enthalpy changes in the Cd adsorption were observed in bulk and all individual phases when it was compared with the other metals enthalpy changes for the same phases. This means that Cd adsorption mainly occurred in the exchangeable phase, which was affected a little by temperature change.

Key words: Pb, Cu, Zn, Cd, Combined Adsorption-Sequential Extraction Analysis (CASA), Temperature effect

INTRODUCTION

Mining and industrial activities have caused extensive heavy metal contamination by introducing heavy metals directly into the surrounding environment (Ernst, 1995; Li and Li, 2001; Al-Juboury, 2009, Ahmad *et al.,* 2010). Heavy metals, such as arsenic (As), lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), and chromium (Cr) constitute one of the contaminant groups considered noxious to human health and are commonly found in several kinds of waste and landfill leachates (Yong and Phadungchewit, 1993; Salim and Munekage, 2009, Uba *et al.,* 2009). Compacted clay soils are widely used as landfill liners that isolate hazardous and other waste materials from surrounding environments and to prevent the heavy metals commonly found in landfill leachates from migrating into groundwater. Conventional clay liners are designed with the focus on minimizing permeation of leachate through the liner.

However, many heavy metals can pollute the groundwater by diffusing through a block liner. In order to evaluate the potential application of clay as barrier material, some parameters, such as sorption and diffusion coefficients, need to be clarified. There are relatively few studies on adsorption characteristics of heavy metal ions in natural soils and landfill clay liner systems. Furthermore, although temperatures at the base of the landfill have been reported to range from 20^oC to 60^oC, studies on the effect of temperature on the adsorption capacity of heavy metals onto landfill liners are quite rare (Matsumoto *et al.,* 1987; Southern and Rowe 2002; Koerner and Koerner 2006). Many researchers have focused on the effects of temperature on adsorption for merely pure minerals, such as kaolinite, bentonite or oxide minerals (Rodda *et al.,* 1993; Bereket *et al.,* 1997; Angove *et al.,* 1998; Angove *et al.,* 1999). The problem is that information

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gained from pure mineral or metal oxides is not suitable to apply to natural clay, in which various clay minerals, oxides, and organic matters are mixed together, because the interaction among phases cannot be determined and nothing is learned about the actual partitioning of metals in various phases (Yong, 2001; Salim *et al.,* 1996, Yong *et al.,* 1995). In order to predict the mobility and retention mechanism of heavy metals from a various temperature pollution source around soil and ground water systems, the effects of temperature on the adsorption of a bulk soil sample and on each constituent of the soil sample should be considered. The objectives of this study are (1) to evaluate the effect of temperature on the adsorption behavior of metals (Pb, Cu, Zn, and Cd), not only for the bulk clay sample, but also for individual soil phases, which are comprised of five different adsorption sites in the bulk clay sample and (2) to identify the potential mobility of metals in landfill liner-natural clay by analyzing the thermodynamic and adsorption isotherm of the metals with the variation of temperature.

MATERIALS & METHODS

In this study, natural clay samples obtained from Mokpo, a coastal area in southwestern Korea, were used. In order to investigate effect of temperature on the adsorption characteristics of the metals for the natural clay, the adsorption experiments for the metals (Pb , Cu , Zn, and Cd) were conducted at different temperatures(15, 25, 40, and 55^0C). After adsorption experiments, sequential extraction experiments were performed for residual samples to evaluate the effects of temperature on the adsorption of metals in each of the operationally defined individual phases.

The properties of the clay sample, which was air-dried and grounded in order to pass through a 2mm sieve, are presented in Table 1. The Soil pH was measured in a 1:1 soil-water solution ratio according to ASTM D4972-95a, and specific gravity, Atterberg limits, and the amount of materials finer than the No. 200 sieve were measured by ASTM D854-92, D4318-95a, and D1140-92, respectively. Hydraulic conductivity was calculated from the results of a consolidation test (ASTM D2435-96). Soil buffer capacity was measured by pouring 10 g of dry soil and 25 mL of deionized water into 50 mL polypropylene tubes, adding 0.1 M HCl of 0, 0.5, 1, 1.5, ... 16 mL. Then, after shaking for 24 hr, the pH of the soil suspensions was measured (Rowell, 1994; Yong *et al.,* 1990). The buffer capacity of a soil prevents pore water pH from dropping to a value at which the mobility of heavy metals in leachate is maximized (Yong *et al.,* 1990; 1992).

The carbonate content of soil was determined by dissolving the carbonate by using 2M HCl and back-

Table 1. Physical and chemical properties of clay sample

% passing # 200 sieve	99.8%
Specific gravity	2.68
Liquid limit	54
Plastic limit	26
Plastic Index	28
Unified Soil Classification System	CH
Permeability(cm/s)	$2.1 \times 10^{-7} \sim 4.8 \times 10^{-9}$
Soil pH(1:5)	8.5
CEC(meq/100g)	18.7
Organic carbon content(% by wt)	0.8
Soil buffer capacity(mmolH$^+$kg^{-1}pH^{-1})	62.5
FeOOH(wt. %)	0.1
MnO_2 (wt. %)	<0.01
$CaCO_3$ (wt. %)	0.95
Mineral composition	Quartz: 52.2%; Albite: 18.6% Illite: 17.9%; Chlorite:6.1% Kaolin: 2.2%; Microcline: 1.8% Tremolite: 1.3%

titrating the remaining acid by using 0.1 M of NaOH (Rowell, 1994). Fe- (Chester and Hughes, 1967) and Mn-oxide (Chao, 1972) contents were determined by using 1 M and 0.1 M of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), respectively. Organic carbon content and cation exchange capacity were measured by the Walkely Black and ammonium acetate methods (Rowell, 1994), respectively. The mineralogical composition was determined by X-ray diffraction analysis in range of $2\theta = 3 \sim 65^0$.

Initial concentrations of each metal solution ranged from 20~500 mg/L for Zn, and 5~300 mg/L for Pb, Cu, and Cd. Adsorption characteristics of the metals (Pb, Cu, Zn, and Cd) with variation of their initial concentration were observed at each temperature of 15, 25, 40, and 55^0C, respectively (Table 2). The initial pH of each solution was adjusted to 4 by using 0.1 and 0.01 M of both HNO_3 and NaOH. One gram of air-dried soil and 40 mL of metal solution were put into a 50 mL capacity polypropylene tube. In all cases, metal solutions, adsorbents (clay samples), and all instruments used were adapted to each determined temperature for a period of 24 hours. The samples were shaken in a shaking incubator at each determined temperature for 48 hours and the suspended solutions were then centrifuged while the clear supernatants were analyzed to obtain a solution concentration after the reaction with natural clay adsorbents.

Table 2. Thermodynamic parameters for adsorption of metals onto natural clays

	Pb		Cu		Zn		Cd	
	ΔH^0 kJ/mol	ΔS^0 J/mol K	ΔH^0 kJ/mol	ΔS^0 J/mol K	ΔH^0 kJ/mol	ΔS^0 J/mol K	ΔH^0 kJ/mol	ΔS^0 J/mol K
Exchangeable	-0.3	-10.67	-9.65	-59.9	-1.7	-35.11	3.95	-14.66
Carbonate	10.32	26.38	11.83	31.75	16.18	37.04	4.9	2.15
Mn-Oxide	8.52	24.54	5.9	17.74	14.16	36.07	4.6	3.03
Organic	16.56	51.21	7.89	27.53	12.92	31.47	4.37	4.21
Fe-Oxide	18.96	64.0	6.74	22.89	18.28	52.72	5.71	9.68
Bulk sorption	10.06	27.8	11.26	21.04	15.0	26.93	1.15	-17.26

After the 48 hours adsorption experiment, the residues of the experiment were washed with 8 mL of distilled water. The samples were centrifuged again and the washing water was discarded. This washing step was repeated at the end of each extraction step. The volume of washing water used was kept to a minimum to avoid excessive solubilization of solid materials, particularly for organic matter (Tessier *et al.,* 1979).

The following sequences were used for analyzing heavy metals that were released from each soil phase (Salim *et al.,* 1996).

1) Exchangeable phase: The residue from the adsorption experiment was extracted in 20 mL of 1 M $MgCl_2$ (pH=7). The suspension was shaken for 1 hour at 20^0C.

2) Carbonate occluded phase: The residue from Step 1 was extracted in 20 mL of 1 M NaOAc (pH=5). The suspension was shaken for 5 hours at 20^0C.

3) Mn-oxide occluded phase: The residue from Step 2 was extracted in 20 mL of 0.1 M $NH_2OH \cdot HCl + 0.01$ M HNO_3. The suspension was shaken for 30 minutes at 20^0C.

4) Organic occluded phase: The residue from Step 3 was extracted in 20 mL of 0.1 M $K_4P_2O_7$. The suspension was shaken for 24 hours at 20^0C.

5) Fe-oxide occluded phase: The residue from Step 4 was extracted in 20 mL of 1 M $NH_2OH \cdot HCl + 25\%$ (v/v) HOAc. The suspension was shaken for 4 hours at 20^0C.

The adsorption isotherms of the clays for the metals were expressed mathematically in terms of the Langmuir adsorption isotherm and it can be expressed in the following simple model in which the attachment of adsorbate to the surface is represented (Angove *et al.,* 1999, Stumm and Morgan, 1996; Gaur and Dhankhar, 2009):

$$M_{(aq)} + S \;\rightleftharpoons\; S - M \qquad (1)$$
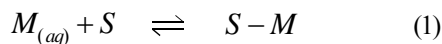
where $M_{(aq)}$ denotes any soluble form of metal or adsorbate, S denotes a surface site, and $S - M$ denotes the adsorbed metal in a form.

Equation (2) represents the Langmuir adsorption isotherm, which can be derived from the simplified adsorption process of Equation (1):

$$q_e = \frac{Q^0 K_{ads} C_e}{1 + K_{ads} C_e} \qquad (2)$$

where q_e is the solid phase concentration at equilibrium (mg/g), C_e is the solution phase concentration at equilibrium (mg/L), Q^0 is the adsorbed solute concentration on the adsorbent that corresponds to complete monolayer coverage (mg/g), and K_{ads} is the adsorption equilibrium constant (l/mg).

To investigate the influence of temperature as the driving force of the adsorption reaction in a soil-water environment, thermodynamic parameters (adsorption enthalpy and entropy change) were analyzed. The thermodynamic parameters are convenient for characterizing adsorbing reactions because the parameters are calculated by using the Langmuir model parameter, which represents the combined effects of all the solutions and surface reactions that contribute to the adsorption of metals under the experimental condition (Angove *et al.,* 1999). The adsorption enthalpy represents the heat of adsorption while entropy change stands for the order or disorder produced in a system during a given reaction (Bereket *et al.,* 1997; Jurinak and Bauer, 1956).

Using the van Hoff equation (Eq.3), the thermodynamic parameters can be finally calculated (Mohan and Singh, 2002; Mohan *et al.,* 2001; Angove *et al.,* 1998; Bereket *et al.,* 1997; Stumm and Morgan, 1996; Johnson, 1990):

$$\ln K_{ads} = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (3)$$

where ΔH^0 is the standard adsorption enthalpy

change, ΔS^0 is the standard adsorption entropy change, K_{ads} is the adsorption equilibrium constant for the reaction, R is the universal gas constant, and T is the temperature.

RESULTS & DISCUSSION

In this study, the effects of temperature on the adsorption characteristics of heavy metals (Pb, Cu, Zn, Cd) on the natural clay were investigated. Figs 1 to 4 show the results of the adsorption experiments for each metal (Pb, Cu, Zn, Cd), including the amount of adsorption at each temperature. Solid lines were obtained by curve fitting the experimental data based on the Langmuir model.

In Fig. 5, the parameter values of the Langmuir adsorption isotherm obtained through curve fitting from Fig. 1. to Fig 4 are shown with the variation of temperatures. In accordance with increasing the temperature from 15^0C to 55^0C, the adsorption equilibrium constants (K_{ads}) showed a tendency to increase for all the individual phases of soil except for adsorption in the exchangeable phase. In the case of Pb, Zn, and Cd adsorption (see Fig. 5(a), (b), and (c)), the magnitude of the value in the Fe-and Mn-oxide phase was relatively larger than those of the other phases. However, for the case of Cu (see Fig. 5(b)), the largest value of K_{ads} was observed in the organic occluded phase.
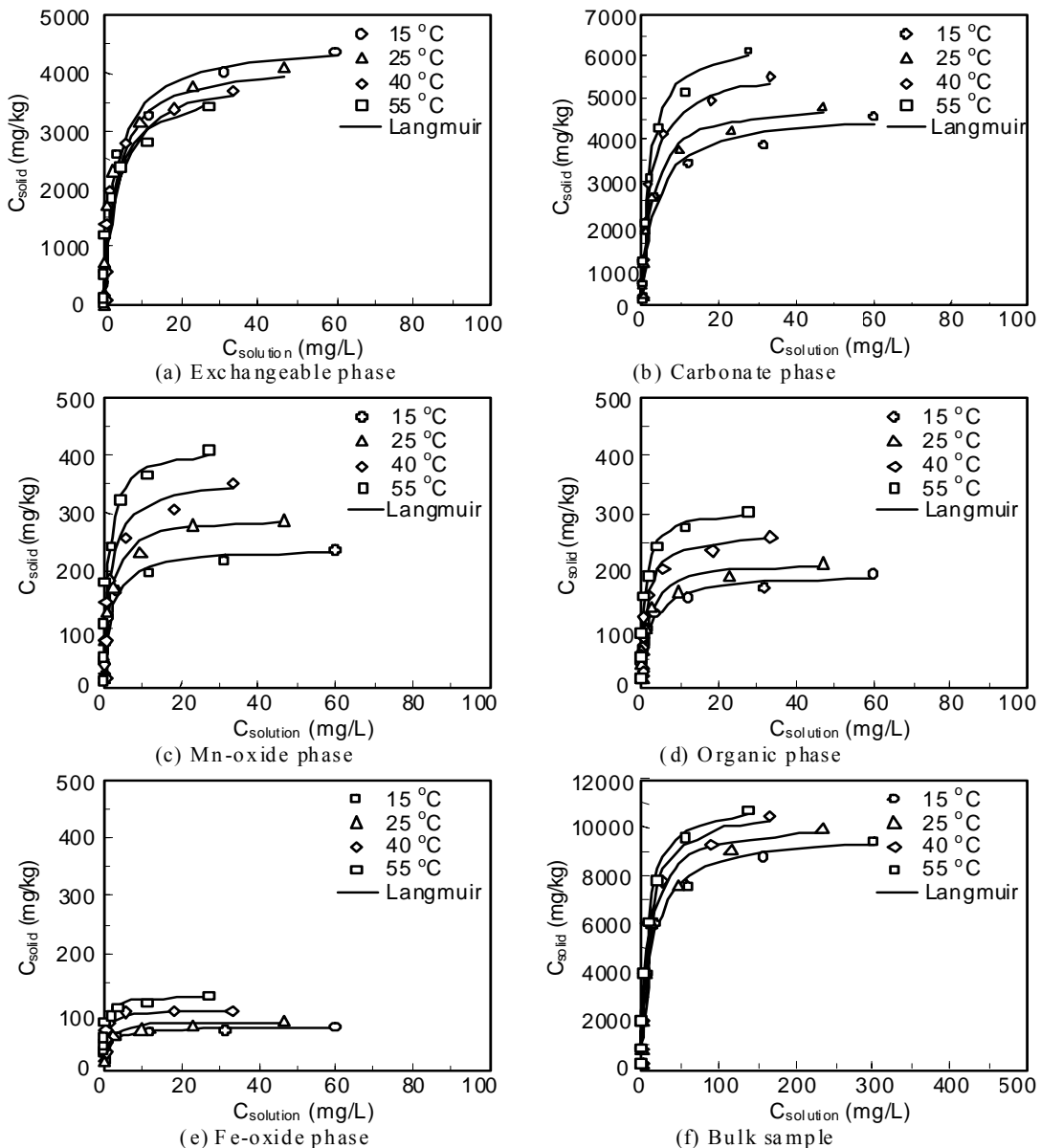

(a) Exchangeable phase

(b) Carbonate phase

(c) Mn-oxide phase

(d) Organic phase

(e) Fe-oxide phase

(f) Bulk sample

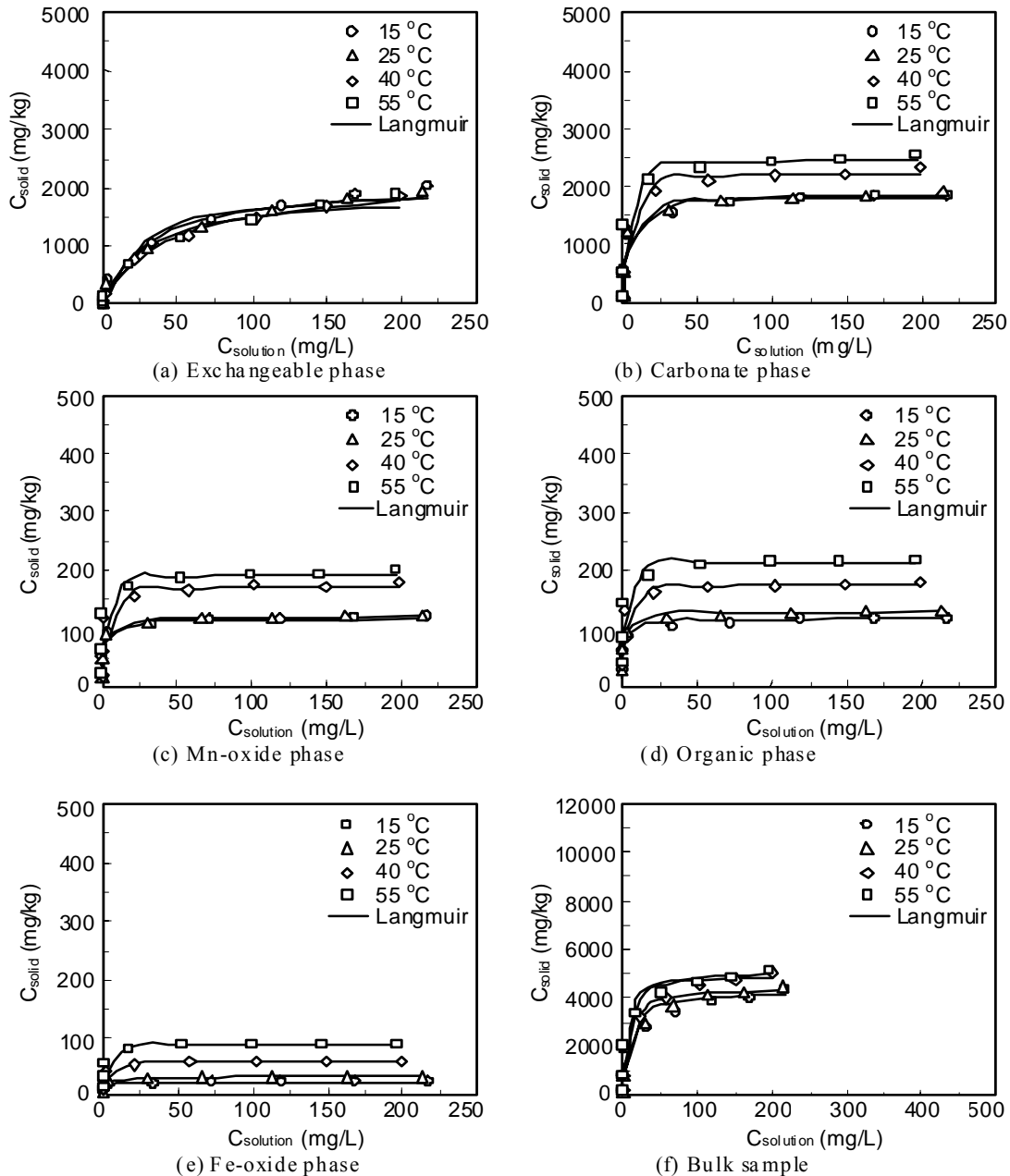**Fig. 1. Langmuir adsorption isotherms of the each phase for Pb**

Fig. 2. Langmuir adsorption isotherms of each phase of Cu

In the case of Pb, the maximum value of adsorption capacity (Q^0) was observed in the carbonate phase while in the case of Zn and Cd, the maximum value was observed in the exchangeable phase. As for the adsorption of Cu, the maximum value of adsorption capacity changed from the exchangeable phase to the carbonate phase following an increase of temperature.

The values of absorption capacity (Q^0) for all of the metals showed little variation with an increase in temperature. This result can be interpreted that since most of the adsorbing metals were adsorbed in the exchangeable or carbonate phase, which has enough

adsorption capacity to attach the metals but have little adsorption energy on the metals, the adsorption capacity (Q^0) of the metals for the bulk sample has not changed much with temperature variations. However, temperature dependency of the metals adsorption for each soil phase was observed in the Mn-and Fe-oxide and organic phase, which have a larger adsorption affinity for metal adsorption.

With the exception of the exchangeable phase, most of the relative magnitudes of adsorption equilibrium constants (K_{ads}) for each adsorption
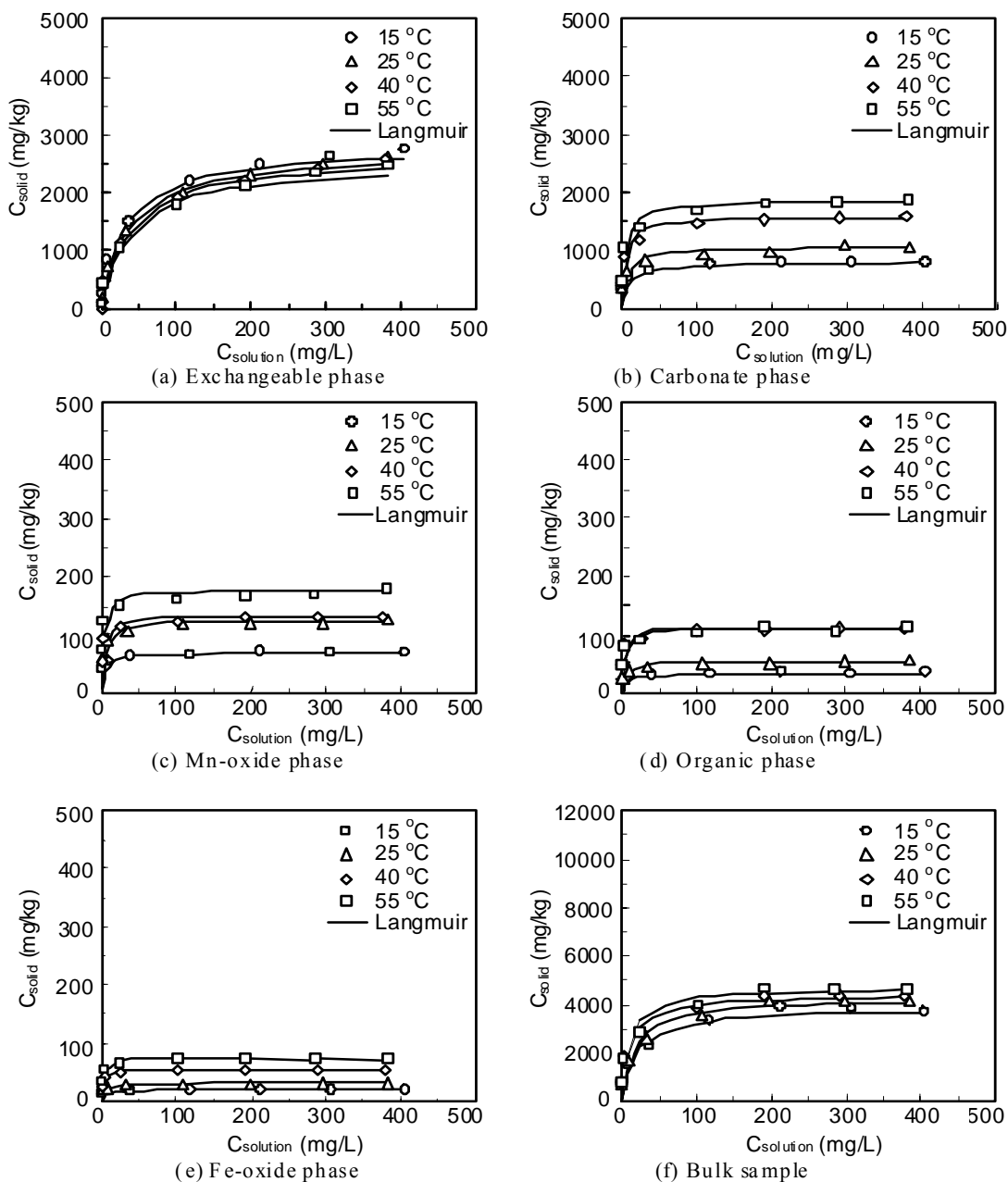
Fig. 3. Langmuir adsorption isotherms of each phase of Zn

phases have an order of Cu > Pb > Zn > Cd. On the other side, the relative magnitudes of adsorption equilibrium constants for the exchangeable phase were observed in Pb > Cd > Cu > Zn, which means the relative affinity of cadmium in the exchangeable phase has a higher value than the other phases. The relative magnitudes of the adsorption capacities (Q^0) of the metals in each adsorption phase were Pb > Cu > Zn > Cd, excluding the exchangeable phase. In the case of Cd, the adsorption capacity of the exchangeable phase was larger than the other individual phases. It was also reported that a selectivity order of Pb and Cu under various kinds of soils and environments is larger than

that of other metals, such as Zn and Cd (Yong and Phadungchewit 1993; Elliot *et al.,* 1986). This fact is similar to present experimental results where the adsorption capacity of Pb and Cu on natural clay had a higher value than that of other metals (Zn and Cd).

The adsorption thermodynamic parameters (adsorption enthalpies and entropies) calculated by using Equation (3) for each metal are shown in Table II. The adsorption reaction of the metals (except for Cd) to the exchangeable phase was observed in the exothermic reaction, in which the adsorption enthalpy was under zero and the amount of adsorption to the phase decreased when the temperature increased. However, the adsorption characteristics in the
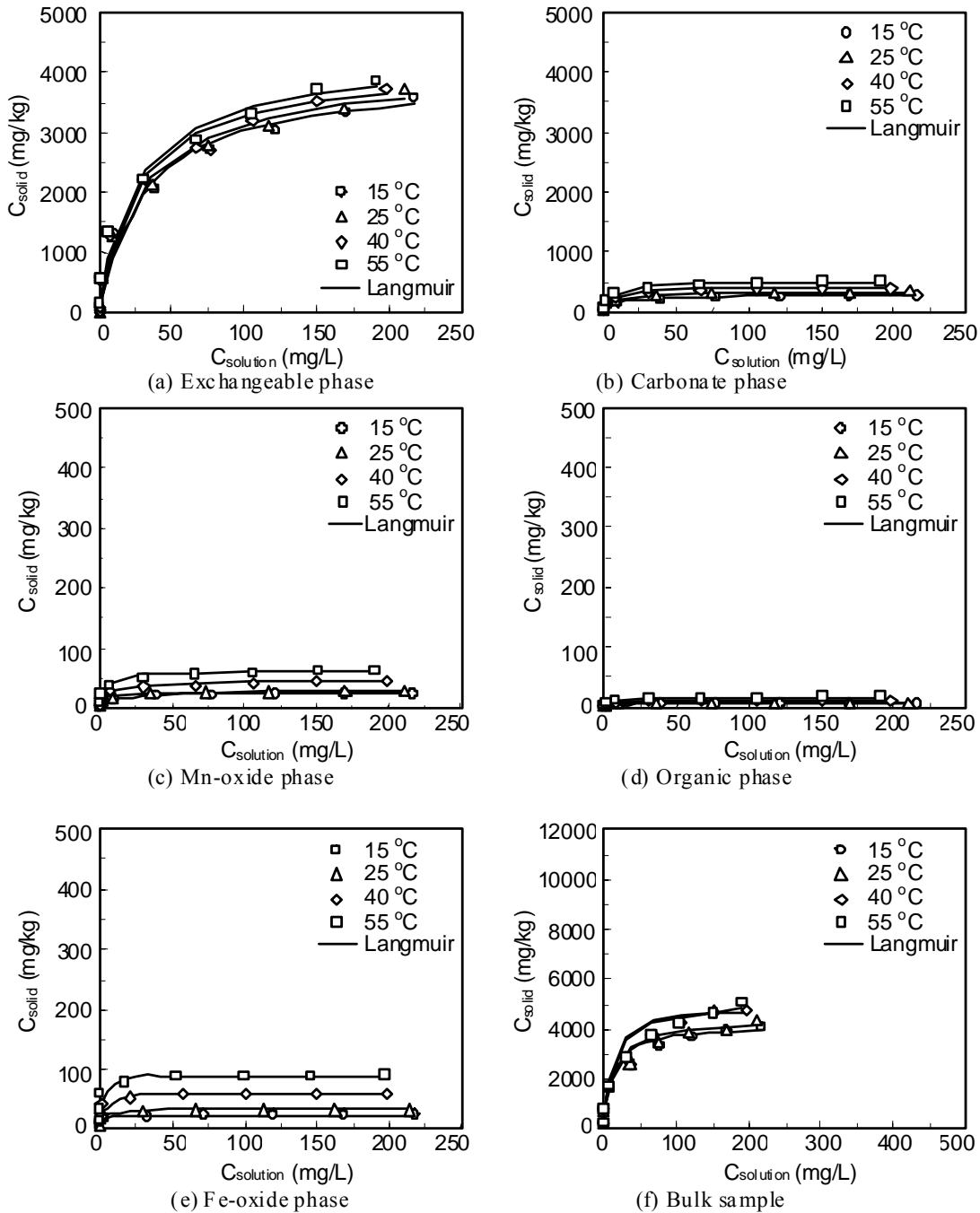
Fig. 4. Langmuir adsorption isotherms of each phase of Cd

exchangeable phase were observed with a relatively small enthalpy change when it was compared with the adsorption enthalpy change of the other phases. Angove et al. (1998) and Yong et al. (1992) also reported that an ion exchange reaction, which is the major reaction in the exchangeable phase, was only affected a little by temperature change. Therefore, the decrease in the exchangeable phase adsorption of Pb, Cu, and Zn with the increase in temperature can be interpreted that an increase of adsorption in the other phases affected the adsorption of metals in the exchangeable

phase. In the case of Cd, major adsorption occurred in the exchangeable phase, which was not affected much by temperature change, so that the enthalpy change in the exchangeable and other soil phases were relatively small compared to the enthalpy change of the other metals for those individual phases.

In the case of Pb and Zn adsorption, considerable adsorption enthalpy changes were observed in the Fe-oxide phase, and in the case of Cu, the changes were also observed in the carbonate occluded phase. It means that adsorption equilibrium constants for
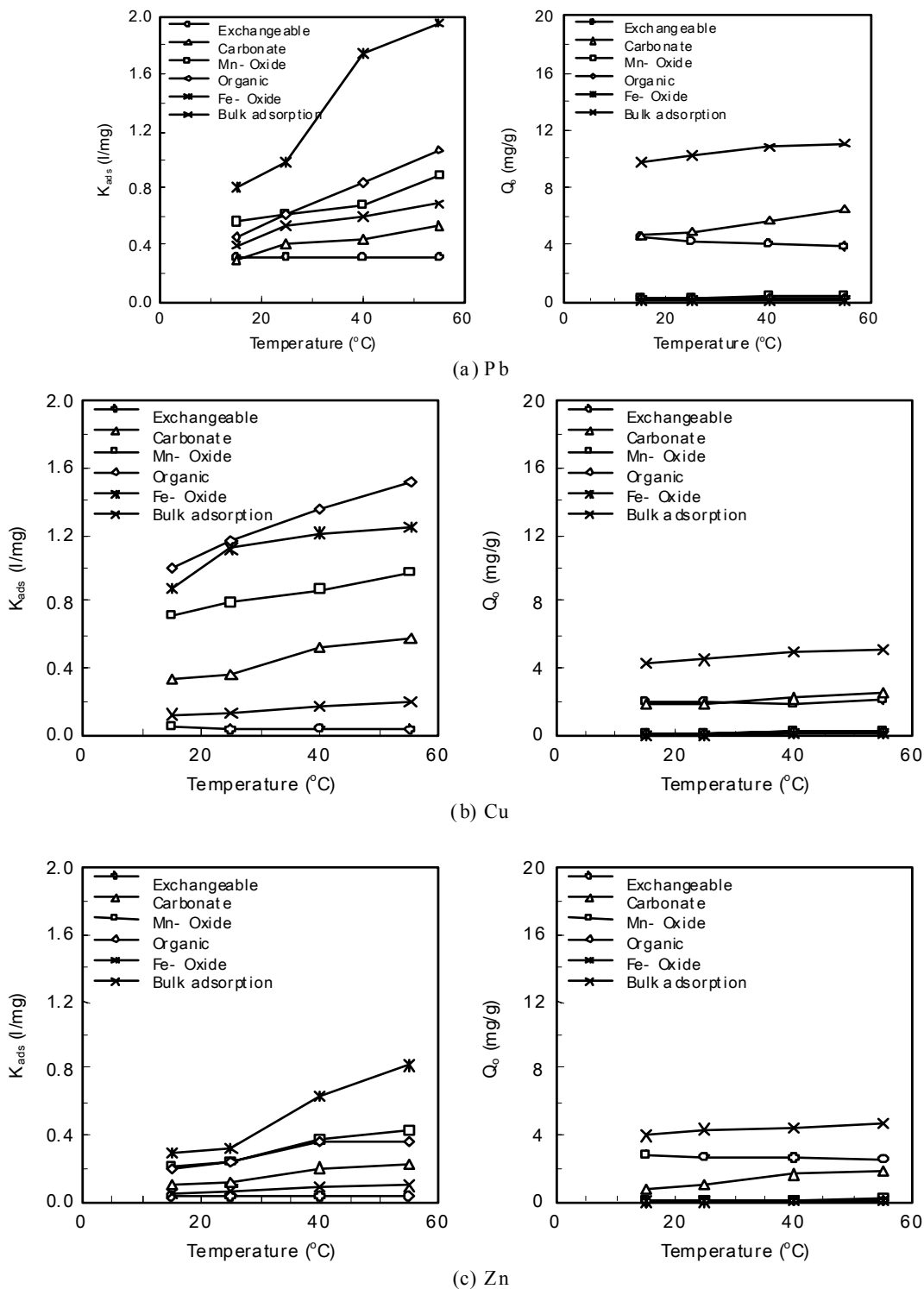
(a) Pb

(b) Cu

(c) Zn

Fig. 5. Variation of Langmuir model parameter values with an increase in temperature (Continued)

those phases were affected appreciably by temperature change. In the present study, the adsorption enthalpy change in the Fe- and Mn-oxide phases was less than 30 kJ/mol. It was reported that the enthalpy change of the hydrogen bond was 8.4 ~50.2 kJ/mol and that of the chemical bond was 210 kJ/mol (Trivedi and Axe, 2000; Stumm and Morgan, 1996). This shows that the

metals adsorbed in this study should be not chemically bonded (inner-sphere complex), but should be a physical type of reaction where the cations do not lose their hydration and form an outer-sphere complex (ion-pair).

Phase Concentration Factors (PCFs) were calculated (Table 3) as the ratio of weight percentage of metal in a
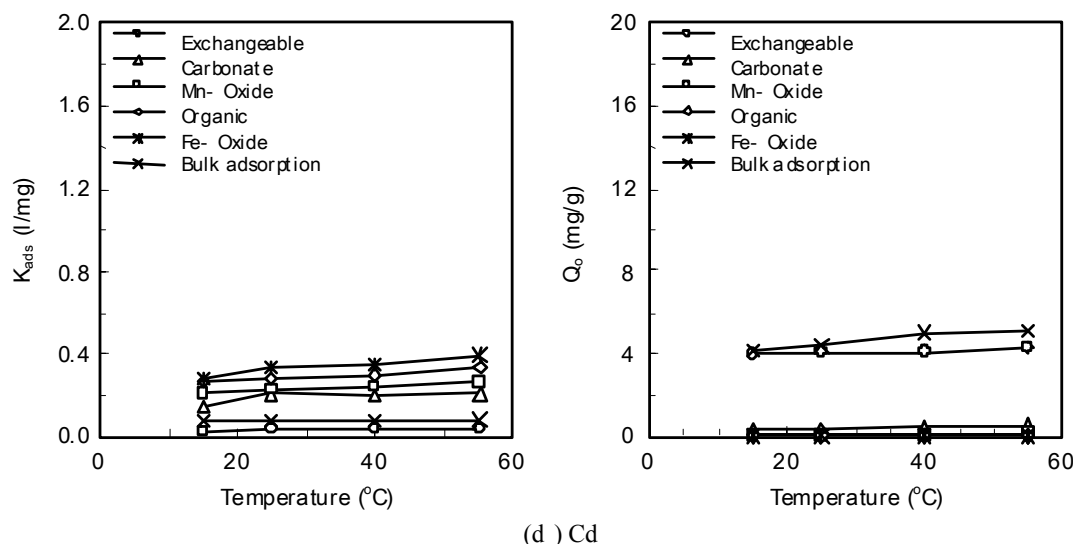
(d) Cd

Fig. 5. Variation of Langmuir model parameter values with an increase in temperature

given form (determined by sequential extraction) to the weight percentage of the form in a soil sample, as follows (Howard and Sova, 1993; Forstner and Patchineelam, 1980). According to this method, the metal enrichment of a phase is indicated by PCFs>1, whereas PCFsd"1 indicates no enrichment (Howard *et al.*, 1993; Forstner and Patchineelam, 1980).

PCFs = (wt. % of metal in a given form) / (wt. % of the form in a sample)   (4)

Using the weight percentage of the form in the soil sample, the values of the heavy metals' PCFs at the carbonate, organic, and oxide (Fe- + Mn-oxide) phases were calculated, as shown in Table 3. A considerable increase of PCFs values was observed in the oxide phase for all of the metals when the temperature increased from 15^0C to 55^0C. This indicates that the largest enrichment occurred in the oxide phase with an increase in temperature. Besides, the absolute PCF values of the oxide phase were larger than the carbonate phase in all of the heavy metals when the temperature increased. This implies that chemical affinity of the metals in the oxide phase was larger than that of the carbonate phase. This fact is in agreement with the results shown in Fig. 5, in which the adsorption equilibrium constants (K_{ads}) of the metals in the oxide phase have higher values than that of the carbonate phase.

Fig. 6 shows the measured pH of the metals solution at equilibrium condition. To investigate the relation between the measured pH variation of the metals solution and the metals speciation after reaching equilibrium condition in the reaction, the USEPA geochemical model MINTEQA2 (Allison *et al.,* 1991)

was applied. In the MINTEQA2 model analysis, it was assumed that Ca^{2+} and CO_3^{2-} components were set at the same concentration as measured in the soil as the calcite ($CaCO_3$) (see Table 1) (Yong and MacDonald, 1998). The metal speciations in pore water, which were obtained from the geochemical model analysis, were calculated with the variation of pH, as shown in Table I After increasing the temperature and concentration, a larger pH drop was observed in the case of adsorption of Cu compared to the pH drop in other adsorption of metals (See Fig. 6). It seems that Cu precipitation as a malachite ($Cu_2(OH)_2CO_3$) affected the pH drop (Table 4).

From the results of MINTEQA2 analysis, it can be seen that most of Pb and Cu were precipitated in cerrisite ($PbCO_3$) and ($Cu_2(OH)_2CO_3$) at a pH of 6 (see Table IV), respectively. These results are in good agreement with present experimental results, in which the partitioning of Cu and Pb was presented in the carbonate-occluded phase.

It might be found from the model analysis that Zn was mostly present in the dissolved form of Zn^{2+} under a pH of 7, whereas from the Zn adsorption results, a part of Zn adsorption occurred in the carbonate phase. These diverse results of experiment and model analysis suggest that it might be easier for Zn to precipitate as a carbonate form because soil particle surfaces provide good nucleation sites where precipitation can grow at a faster rate (Yong *et al.,* 1995). In the case of Cd, the model analysis results show that most of Cd over a pH of 5 was precipitated in the otavite ($CdCO_3$), whereas, in the result from adsorption experiment most of the Cd partitioning occurred in the exchangeable phase. This different result may show that the adsorption reaction rate of Cd for the exchangeable phase was faster than the rate of precipitation.

Table 3. Phase Concentration Factors (PCFs) of three different phases at different temperatures

		Carbonate	Organic	Oxide
Pb	15°C	54.8	3.7	48.7
	25°C	54.2	3.6	54.2
	40°C	60.0	4.5	57.6
	55°C	62.7	5.3	72.9
Cu	15°C	57.7	5.1	47.4
	25°C	59.6	5.7	51.6
	40°C	63.8	7.3	70.2
	55°C	65.0	8.1	78.9
Zn	15°C	31.9	1.8	37.5
	25°C	37.0	2.5	59.4
	40°C	47.6	4.8	63.3
	55°C	51.5	4.4	78.1
Cd	15°C	9.4	0.24	9.9
	25°C	12.1	0.3	12.1
	40°C	13.45	0.5	18.4
	55°C	15.3	0.6	23.9

CONCLUSION

In this study, the effect of temperature that ranged from 15^0C to 55^0C on the adsorption characteristics of Pb, Cu, Zn and Cd for bulk natural clay and for each individual phase that the bulk clay is composed of was investigated by using combined sequential extraction procedures. The following results can be deduced from this experimental study.

1. Based on the analyses of adsorption equilibrium constants (K_{ads}) and Phase Concentration Factors (PCFs), representative temperature dependency of the metals (Pb, Cu, Zn, and Cd) adsorption for each individual phase was observed in the oxide (Fe-and Mn-oxide) and organic phases. It can be interpreted that the effect of temperature on the strongly bonded phases (organic and oxide phase) was larger than the weakly bonded phases (exchangeable and carbonate phase) that were more easily desorbed under the variation of the soil-water environment, such as temperature, pH, or concentration.

2. However, the value of adsorption capacity (Q^0) for all of the metals showed little variation when the temperature increased. It can be interpreted that the
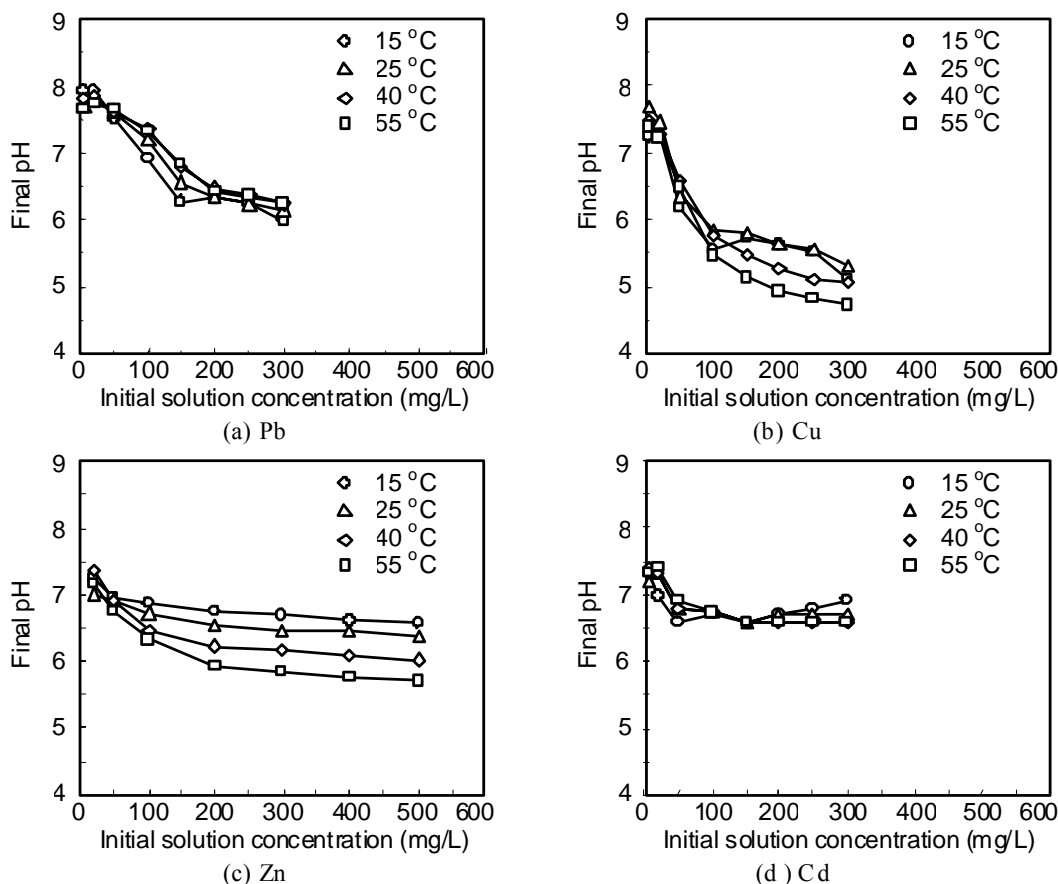

Fig. 6. Final pH profiles after single adsorption of metals at four different temperatures

Table 4. Calculated results of metal species distribution by MINTEQ2A

Metal	pH			
	4	5	6	7
Pb precipitation (%)	0	47.5	98.7	99.7
Precipitated Pb species (%)				
$PbCO_3$		100	100	100
Pb dissolved (%)	100	52.5	1.3	0.3
Dissolved Pb species (%)				
Pb^{2+}	99.4	94.3	59.2	9.6
$PbOH^+$				1.5
$PbCO_3(aq)$			20.1	80.8
$PbHCO_3^+$		5.0	19.8	8.0
Cu precipitation (%)	0	0	98.1	99.8
Precipitated Cu species (%)				
$Cu_2(OH)_2CO_3$	0	0	100	100
Cu dissolved (%)	100	100	1.9	0.2
Dissolved Cu species (%)				
Cu^{2+}	99.6	96.3	77.5	19.1
$CuCO_3(aq)$			6.8	41.8
$CuOH^+$				1.5
$Cu(OH)_2(aq)$			1.2	29.1
$CuHCO_3^+$		3.4	13.8	8.4
Zn precipitation (%)	0	0	0	84.8
Precipitated Zn species (%)				
$ZnCO_3$	0	0	0	100
Zn dissolved (%)	100	100	100	15.2
Dissolved Zn species (%)				
Zn^{2+}	99.9	99.1	93.9	88.0
$ZnHCO_3$			5.6	6.4
$ZnCO_3(aq)$				4.7
Cd precipitation (%)	0	91.0	99.9	100
Precipitated Cd species (%)				
$CdCO_3$	0	100	100	100
Cd dissolved (%)	100	9.0	0.1	0
Dissolved Cd species (%)				
Cd^{2+}	99.9	99.4	95.6	
$CdHCO_3^+$			4.0	
$CdCO_3(aq)$				

most of the adsorbing metals were adsorbed in the exchangeable or carbonate phase, which has little adsorption energy for the metals and was affected a little by temperature change.

3.With the exception of the exchangeable phase, the adsorption reaction of the metals in the adsorption phases was endothermic ($\Delta H^0 > 0$) which means that the quantities of adsorbed metals increase with increasing of the temperature. However, in the case of the exchangeable phase, the adsorption enthalpy changed for the adsorption of metals was below zero or had small enthalpy change, which means the adsorption quantity of the metals for the phase decreased or did not change nearly as much with the increase in temperature.

4.Based on the magnitude of the adsorption enthalpy change of the metals in the oxide phase, which was less than 30 kJ/mol, the metals adsorption should be a physical type of reaction where the cations do not lose their water hydration and form an outer-sphere complex.

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