

## Zinc and Cadmium Adsorption to Aluminum Oxide Nanoparticles Affected by Naturally Occurring Ligands

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Nanoparticles of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) are efficient in removing Cd, Zn, and other heavy metals from wastewaters and soil solutions due to their high specific surface area and surface area to volume ratio. Naturally occurring ligands, such as phosphate ( $\text{PO}_4$ ), citrate, and humic acid (HA), may affect the efficiency of  $\text{Al}_2\text{O}_3$  nanoparticles in adsorption of Cd and Zn. The objective of this study was to investigate Zn and Cd adsorption to  $\text{Al}_2\text{O}_3$  nanoparticles as influenced by  $\text{PO}_4$ , citrate, and HA. Adsorption of Zn and Cd was performed in mono-metal and binary-metal systems at pH 6.5 with initial metal concentration of  $1.0 \text{ mmol L}^{-1}$  and varying ligand concentration at a solid:solution ratio of 1:1000. Adsorption isotherms showed that Zn had higher affinity to the  $\text{Al}_2\text{O}_3$  nanoparticle surface than Cd and that adsorption of Zn and Cd in the binary-metal system was lower than in the respective mono-metal systems. Phosphate and HA enhanced Zn and Cd adsorption in all systems, whereas citrate reduced Zn adsorption in the mono-metal system by 25% and increased adsorption in the other metal systems. Removal of Zn or Cd from the systems was generally accompanied by enhanced removal of  $\text{PO}_4$  and HA, which may indicate enhanced adsorption due to ternary complex formation or metal-ligand precipitation. Phosphate was the most effective among the three ligands in enhancing Zn and Cd adsorption. Overall,  $\text{Al}_2\text{O}_3$  nanoparticles are suitably used for Zn and Cd adsorption, which can be significantly enhanced by the presence of  $\text{PO}_4$  or HA and to a lesser degree by citrate at low concentrations.

CADMIUM (Cd) and Zinc (Zn) are heavy metals that pose serious threats to soil and water if present in quantities exceeding allowable limits. The critical soil values of Cd and Zn are  $3 \text{ to } 8 \text{ mg kg}^{-1}$  and  $70 \text{ to } 400 \text{ mg kg}^{-1}$ , respectively (Kabata-Pendias and Pendias, 2000). These elements are released into the environment through numerous sources, such as manure, smelter emissions, mine wastes, and fertilizers, where they find their way into the food chain through plant and animal uptake (McBride, 1994; Wang and Harrell, 2005; Schroder et al., 2011; Stietiya and Wang, 2011). Cadmium acts as an enzyme inhibitor and affects the liver, kidney, and bones. Zinc is essential for human growth, but excess quantities result in lung disorders, growth retardation, and malady mental fever (Sharma et al., 2009). It is therefore essential that Cd- and Zn-contaminated soils and waters be remediated to prevent metal access into the food chain (Wang and Evangelou, 1995). Wastewaters contaminated with these and other heavy metals may be remediated using technologies such as ion exchange ultrafiltration, reverse osmosis, chemical precipitation, membrane filtration, coagulation-flocculation, vacuum evaporation, solvent extraction, electrochemical deposition, and adsorption (Pacheco et al., 2006; Sharma et al., 2009; Zhang and Fang, 2010). Many of these remediation technologies are expensive and time consuming and have limitations (Pacheco et al., 2006). For example, chemical precipitation is not always the best approach, particularly if the precipitated fines cannot be settled or collected via flotation (Hao et al., 2010). Adsorption, on the other hand, is a simple and cost-effective technology that has been widely used for remediation of numerous contaminants in waters, wastewaters, and soils. Numerous phyllosilicate and oxide clay minerals have been investigated as adsorbents for remediation purposes over the past decades. Recently, attention has been focused on the use of nanoparticle minerals as adsorbents. Nanoparticle minerals have better efficiency in removing metal ion pollutants from soil solutions and wastewaters than bulk-size particles of the same minerals, mainly due to their high surface area and high surface area to volume ratio (Savage and Diallo, 2005; Waychunas et al., 2005; Sharma et al., 2009). The use of alumina nanoparticles for the removal of heavy metals has been investigated due to its low cost, high surface area, surface reactivity, porosity, mechanical strength,

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**Abbreviations:** HA, humic acid.

and thermal stability (Kasprzyk-Hordern, 2004; Pacheco et al., 2006; Afkhami et al., 2011). Alumina nanoparticles were found to be effective for the removal of Cd, Cr, Cu, Hg, Pb, and Zn from wastewaters (Pacheco and Rodriguez, 2001; Pacheco et al., 2006; Afkhami et al., 2010; Rahmani et al., 2010).

The adsorption of Cd and Zn to alumina nanoparticles could be affected by numerous factors, including the presence of naturally occurring ligands, which are ubiquitous in the soil and water environment and in various wastewaters. They include low-molecular-weight organic acids such as citric and oxalic acid, high-molecular-weight acids such as humic acid (HA), and important inorganic ligands such as phosphate, sulfate, and carbonate. Previous research on bulk-sized minerals showed that varying inorganic and organic ligands may enhance Cd or Zn adsorption to goethite or kaolinite by forming metal–ligand–surface ternary complexes, by increasing the surface electrostatic potential, or by formation of metal–ligand precipitates (Davis and Bhatnagar, 1995; Collins et al., 1999; Stietiya et al., 2011). On the other hand, Pb adsorption in soil decreased when the formation of Pb–mineral surface complexes in the presence of citrate was unable to compete with stable Pb–citrate complexes in solution (Schwab et al., 2005). Furthermore, citrate enhanced Cd adsorption to goethite and montmorillonite when present at low concentrations but inhibited it at high concentrations (Lackovic et al., 2004; Huang et al., 2010). Phosphate enhanced Zn or Cd adsorption to iron oxide surfaces due to electrostatic interaction (Diaz-Barrientos et al., 1990; Collins et al., 1999; Wang and Xing, 2004), whereas it was found to reduce Cd adsorption to hematite and soils due to formation of Cd–P complexes in solution (Krishnamurti et al., 1999; Li et al., 2006). Clearly, different results have been observed regarding the impact of ligands on metal adsorption by minerals and soils. In addition, although previous studies were primarily focused on metal adsorption by bulk-sized minerals, few studies have investigated ligand effects on nanoparticle mineral surfaces. Limited studies have reported reduced Cu adsorption onto hydroxyapatite nanoparticles in the presence of low-molecular-weight organic acids (Wang et al., 2009). On the other hand, chemical or physical surface modification of  $\text{Al}_2\text{O}_3$  nanoparticles with functional groups containing donor atoms such as oxygen, nitrogen, and sulfur enhanced adsorption of various metals (Savage and Diallo, 2005; Afkhami et al., 2010). It is imperative to understand the conditions under which adsorption of heavy metals is enhanced in the presence of ligands to optimize the adsorption efficiency of  $\text{Al}_2\text{O}_3$  nanoparticles for various heavy metals. To the best of our knowledge, this is the first investigation that compares the impact of  $\text{PO}_4$ , citrate, and HA, three common inorganic and organic ligands, on the adsorption of Cd and Zn to  $\text{Al}_2\text{O}_3$  nanoparticles at various ligand:metal ratios. The objective of the study was to investigate Zn and Cd adsorption to  $\text{Al}_2\text{O}_3$  nanoparticles as influenced by varying concentrations of  $\text{PO}_4$ , citrate, and HA in mono-metal and binary-metal systems at pH 6.5. In support of the primary objective, the adsorption of  $\text{PO}_4$ , citrate, and HA to the nanoparticles was characterized in the absence and presence of Cd and Zn.

## Materials and Methods

### Materials and Reagents

Aluminum oxide nanopowder ( $\gamma\text{-Al}_2\text{O}_3$ ) was obtained from Sigma-Aldrich (catalogue #544833). The main characteristics of this product as provided by the supplier are: particle size <50 nm, melting point 2040°C, and density 3.97 g cm<sup>-3</sup>. The BET surface area was measured as 185 m<sup>2</sup> g<sup>-1</sup>. Zinc, Cd,  $\text{PO}_4$ , and citrate were prepared from  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{NaH}_2\text{PO}_4$ , and trisodium citrate dihydrate, respectively. Humic acid was obtained from Sigma-Aldrich (H16752) and was purified by acid washing and subsequent removal of ash content according to the International Humic Substance Society method (Swift, 1996). Humic acid was then dialyzed until free of  $\text{Cl}^-$  (as tested using  $\text{AgNO}_3$ ), freeze dried, and homogenized before use (Stietiya et al., 2011). All reagents used in the present investigation were of analytical reagent grade. Ultra-pure water with resistivity of 18.2 M $\Omega$  was used throughout experimentation and was obtained from a Milli-Q Water System (Millipore Corp.).

### Adsorption Isotherms

Adsorption experiments were conducted to obtain the equilibrium isotherms for Cd and Zn. Three Zn and Cd adsorption systems were constructed: Zn mono-metal (adsorption of Zn only), Cd mono-metal (adsorption of Cd only), and Zn/Cd binary-metal (adsorption of Zn and Cd) systems. The initial Zn and Cd concentrations ranged from 0.05 to 1 mmol L<sup>-1</sup> as nitrate salts at an adsorbent dosage level of 1 g L<sup>-1</sup> or as a solid:solution ratio of 1:1000. In the binary-metal system, the concentration of Zn was identical to that of Cd at each initial concentration. The background electrolyte concentration for the systems was 10 mmol L<sup>-1</sup>  $\text{NaNO}_3$  to dominate ionic strength, and pH was fixed at 6.5 using 0.1 mol L<sup>-1</sup>  $\text{HNO}_3$  or 0.1 mol L<sup>-1</sup>  $\text{NaOH}$ . After 1 wk of equilibration, the samples were centrifuged, and equilibrium concentrations of Cd and Zn were determined using ICP–AES (Spectro Analytical Instruments). The equilibrium data obtained were then fit to the Langmuir and Freundlich adsorption isotherms. The Langmuir model is expressed as:

$$q_e = Q^0 b C_e / (1 + b C_e)$$

where  $q_e$  is amount of Zn or Cd adsorbed per unit weight of  $\text{Al}_2\text{O}_3$  (mmol kg<sup>-1</sup>),  $C_e$  is the equilibrium concentration (mmol L<sup>-1</sup>),  $Q^0$  is the monolayer adsorption capacity (mmol kg<sup>-1</sup>), and  $b$  is the constant related to the free energy of adsorption (L mmol<sup>-1</sup>). The Freundlich model is expressed as:

$$q_e = K_F C_e^N$$

where  $K_F$  is the constant indicative of the relative adsorption capacity of  $\text{Al}_2\text{O}_3$  nanoparticles (mmol kg<sup>-1</sup>), and  $N$  is the constant indicative of the intensity of adsorption. Isotherms were also constructed for citrate, HA, and  $\text{PO}_4$  in the absence of Cd or Zn, in the presence of 1 mmol L<sup>-1</sup> Cd, in the presence of 1 mmol L<sup>-1</sup> Zn, and in the presence of 1 mmol L<sup>-1</sup> Zn and Cd. Experiments were performed in triplicate.

## Ligand Effect

Zinc and Cd adsorption to  $\text{Al}_2\text{O}_3$  nanoparticles in the absence and presence of varying concentrations of  $\text{PO}_4$ , citrate, and HA was studied. The impact of ligand concentrations on metal adsorption was studied in three metal systems: Zn mono-metal, Cd mono-metal, and Zn/Cd binary-metal systems. The initial concentrations of Zn and Cd in the systems were  $1 \text{ mmol L}^{-1}$  as nitrate salts, and ligand concentrations were 0, 0.25, 0.5, 1.0, and  $2.0 \text{ mmol L}^{-1}$ . This resulted in ligand-to-metal molar ratios of 0:1, 0.25:1, 0.5:1, 1:1, and 2:1 in each of the systems investigated at an adsorbent dosage level of  $1 \text{ g L}^{-1}$  or a solid:solution ratio of 1:1000. Ligands were added to the systems 24 h before the addition of Zn or Cd metal solution to eliminate the possibility of metal-ligand precipitate formation, particularly with  $\text{PO}_4$ . Citrate and  $\text{PO}_4$  concentrations were expressed in  $\text{mmol L}^{-1}$ , and HA was expressed in  $\text{mg L}^{-1}$ . The background electrolyte concentration was  $10 \text{ mmol L}^{-1} \text{ NaNO}_3$ , and pH was fixed at 6.5. The pH was continuously checked and adjusted using  $0.1 \text{ mol L}^{-1} \text{ HNO}_3$  or NaOH. After 1 wk of equilibration, samples were centrifuged at  $47,893 \times g$  for 10 min, and the supernatant was filtered using  $0.45\text{-}\mu\text{m}$  membrane filters. Equilibrium concentrations of Zn, Cd, and P were determined using ICP–AES (Spectro Analytical Instruments). A preliminary experiment confirmed the sufficiency of settling  $\text{Al}_2\text{O}_3$  nanoparticles in  $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$  and found no Al (by ICP) in the supernatant after filtering with a  $0.45\text{-}\mu\text{m}$  membrane filter. Equilibrium concentrations of citrate and HA were determined using a total organic carbon analyzer (Shimadzu). The amounts of Zn, Cd, citrate, HA, and  $\text{PO}_4$  adsorbed were calculated by the difference between the initial and equilibrium concentrations. Adsorption experiments were performed in triplicate.

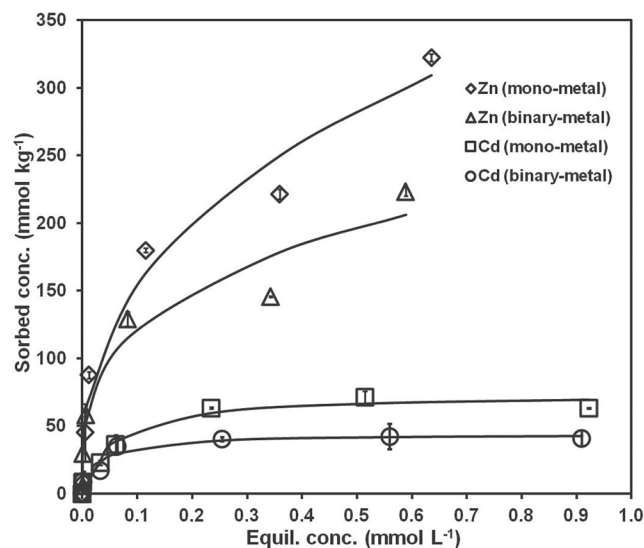
## Statistical Analysis

Analysis of variance was performed using SPSS 17 (SPSS, Inc.), and comparison of means was undertaken using a Bonferroni test to determine any significant differences at  $P \leq 0.05$ .

## Results and Discussion

### Zn and Cd Adsorption Isotherms

Figure 1 shows Zn and Cd adsorption isotherms in mono-metal and binary-metal systems. The equilibrium data for Zn and Cd adsorption gave generally satisfactory fits to the Freundlich and Langmuir models ( $R^2 > 0.90$ ), although Zn adsorption was a slightly better fit using the Freundlich model in both metal systems, and Cd adsorption gave slightly better fits to the Langmuir model (Table 1). The Freundlich model assumes that the uptake of Zn and Cd occurs on a heterogeneous  $\text{Al}_2\text{O}_3$



**Fig. 1.** Zinc and Cd adsorption isotherms in mono-metal and binary-metal systems. The solid lines represent best fits of adsorption data for Zn using the Freundlich model and for Cd using the Langmuir model. Experimental conditions: pH 6.5;  $10 \text{ mmol L}^{-1} \text{ NaNO}_3$  background electrolyte;  $1.0 \text{ g L}^{-1} \text{ Al}_2\text{O}_3$  nanoparticles.

nanoparticle surface, whereas the Langmuir model assumes uptake on a homogeneous surface by monolayer adsorption with no interaction between sorbed species (Sharma et al., 2009). Zinc adsorption was greater than Cd adsorption in both mono-metal and binary-metal systems (Fig. 1). The greater affinity of  $\text{Al}_2\text{O}_3$  nanoparticles for Zn adsorption was likely attributed to chemical characteristics of ions, such as ionic radii, and hydrolysis constants ( $\text{p}K_h$ ). The smaller unhydrated ionic radius of Zn ( $0.074 \text{ nm}$ ) as compared with that of Cd ( $0.097 \text{ nm}$ ) suggests stronger electrostatic adsorption of the former (McBride, 1994; Antoniadis et al., 2007). The first hydrolysis products of Zn and Cd are 9.0 and 10.1, respectively. Metal ions having lower hydrolysis constants are characterized by higher electrostatic attraction to exchange sites (Bosso and Enzweiler, 2002; Yavuz et al., 2003; Yang et al., 2006; Unuabonah et al., 2007; Abollino et al., 2008; Srivastava et al., 2008; Huang et al., 2010). If chemisorption is the dominant adsorption mechanism, the more electronegative Cd ion would form stronger covalent bonds with O atoms of the  $\text{Al}_2\text{O}_3$  surface than Zn and would hence be expected to adsorb preferentially over Zn (McBride, 1994; Mahdavi et al., 2012). Because this was not the case in our study, it is likely that adsorption to surface sites was mainly electrostatic in nature. On the other hand, we could not rule out the possible formation of inner-sphere surface complex (chemisorption) or surface precipitation because other research based on extended X-ray absorption fine structure spectroscopy showed that Zn sorption to bulk-sized ( $>100 \text{ nm}$ )  $\alpha$ -phase-dominated  $\text{Al}_2\text{O}_3$

**Table 1.** Parameters of Langmuir and Freundlich adsorption isotherms for Zn and Cd in mono-metal and binary-metal systems.

Metal ion	System	Freundlich isotherm			Langmuir isotherm			$Q_{\text{bin}}^0/Q_{\text{mon}}^0$
		$K_F$	$N$	$R^2$	$Q^0$	$b$	$R^2$	
		$\text{L kg}^{-1}$			$\text{mmol kg}^{-1}$	$\text{L mmol}^{-1}$		
Zn	mono-metal	366.9	0.4	0.98	298.2	19.0	0.94	–
	binary-metal	241.1	0.3	0.96	187.4	47.7	0.90	0.63
Cd	mono-metal	75.8	0.3	0.92	73.4	18.0	0.97	–
	binary-metal	51.9	0.2	0.91	44.0	32.5	0.94	0.60

minerals formed inner-sphere surface complexes at low sorption densities and formed a precipitate phase at higher concentrations (Trainor et al., 2000). Previous studies also reported that Zn formed outer-sphere complexes with ferrihydrite irrespective of pH or surface loading (Trivedi et al., 2001).

Zinc and Cd adsorption rates were higher in their respective mono-metal systems than in the binary-metal system, especially at higher equilibrium concentrations (Fig. 1). The distribution coefficient ( $K_F$ ) for Zn adsorption in mono-metal system was  $366.9 \text{ L kg}^{-1}$ , as compared with  $241.1 \text{ L kg}^{-1}$  in the binary-metal system (Table 1). Higher  $K_F$  values indicate stronger adsorption and lower metal solubility (Antoniadis et al., 2007). The lower  $K_F$  value in the binary-metal system indicates that Zn adsorption was suppressed in the presence of Cd (Unuabonah et al., 2007). The selectivity of Zn and Cd adsorption to  $\text{Al}_2\text{O}_3$  nanoparticles based on  $K_F$  values was in the order of Zn mono-metal > Zn binary-metal > Cd mono-metal > Cd binary-metal. Competition between Zn and Cd for the same binding sites was likely the cause of reduction in adsorption in the binary-metal systems. The adsorption rates of Zn and Cd were favorable as indicated by the Freundlich model, where values of  $N$  between 0 and 1 represent favorable adsorption (Antoniadis et al., 2007; Sheela et al., 2012) (Table 1).

Similar to Zn, Cd adsorption was higher in the mono-metal system than in the binary-metal system (Fig. 1). The value of adsorption capacity, or the maximum uptake for Cd in mono-metal system ( $Q_{\text{mon}}^0$ ), was  $73.4 \text{ mmol kg}^{-1}$ , as compared with  $44.0 \text{ mmol kg}^{-1}$  in the binary-metal system ( $Q_{\text{bin}}^0$ ). The value of  $Q_{\text{bin}}^0/Q_{\text{mon}}^0$  being less than unity indicates the suppression of Cd adsorption in the presence of Zn (Adebowale et al., 2006; Unuabonah et al., 2007). The feasibility of fitting the Langmuir isotherm can be expressed using the separation factor,  $R_L$ , defined as:

$$R_L = 1/(1 + bC_0)$$

where  $C_0$  is the initial concentration ( $\text{mmol L}^{-1}$ ) of Cd and Zn in solution, and  $b$  is the Langmuir constant. The shape of the isotherms is unfavorable at  $R_L > 1$ , favorable at  $0 < R_L < 1$ , or linear at  $R_L = 1$  (Hao et al., 2010; Sheela et al., 2012). The  $R_L$  values for adsorption of Zn and Cd in mono-metal and binary-metal systems at all initial concentrations are  $< 1$  (Fig. 2), indicating the suitability of  $\text{Al}_2\text{O}_3$  nanoparticles for the removal of Zn and Cd from solution (Doğan et al., 2000; Sheela et al., 2012).

The competitive effects of metal adsorption in bulk-sized minerals have been widely documented. For example, the presence of Cu was found to reduce Zn adsorption to goethite, whereas Pb was shown to reduce Cd adsorption to kaolinite (Juang and Chung, 2004; Adebowale et al., 2006). Adsorption of Cu, Ni, Cd, and Pb to nano-size particles of  $\text{Fe}_3\text{O}_4$ , ZnO, and CuO was also found to be lower in competitive-metal systems than in the respective mono-metal system of each metal (Mahdavi et al., 2012). Mahdavi et al. (2013) reported that Cd adsorption by  $\text{Al}_2\text{O}_3$  nanoparticles in the competitive system of Cu, Ni, and Pb decreased by as much as 80% in comparison with Cd in the mono-metal system. Our results in this study also showed that Cd adsorption decreased by 60% from  $73.4$  to  $44 \text{ mmol kg}^{-1}$ , whereas Zn adsorption decreased by 37% from  $298.2$  to  $187.4 \text{ mmol kg}^{-1}$  (Table 1). Although the magnitude

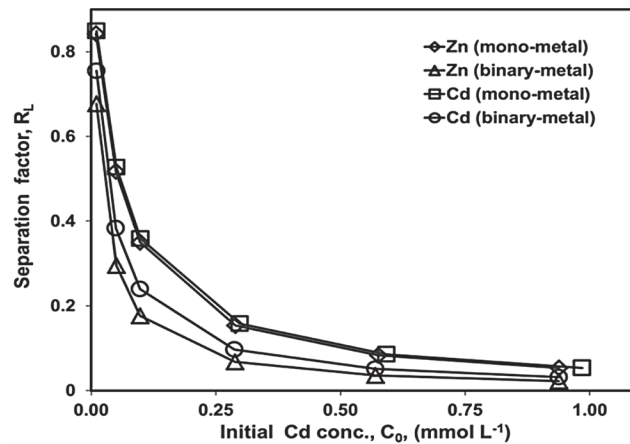


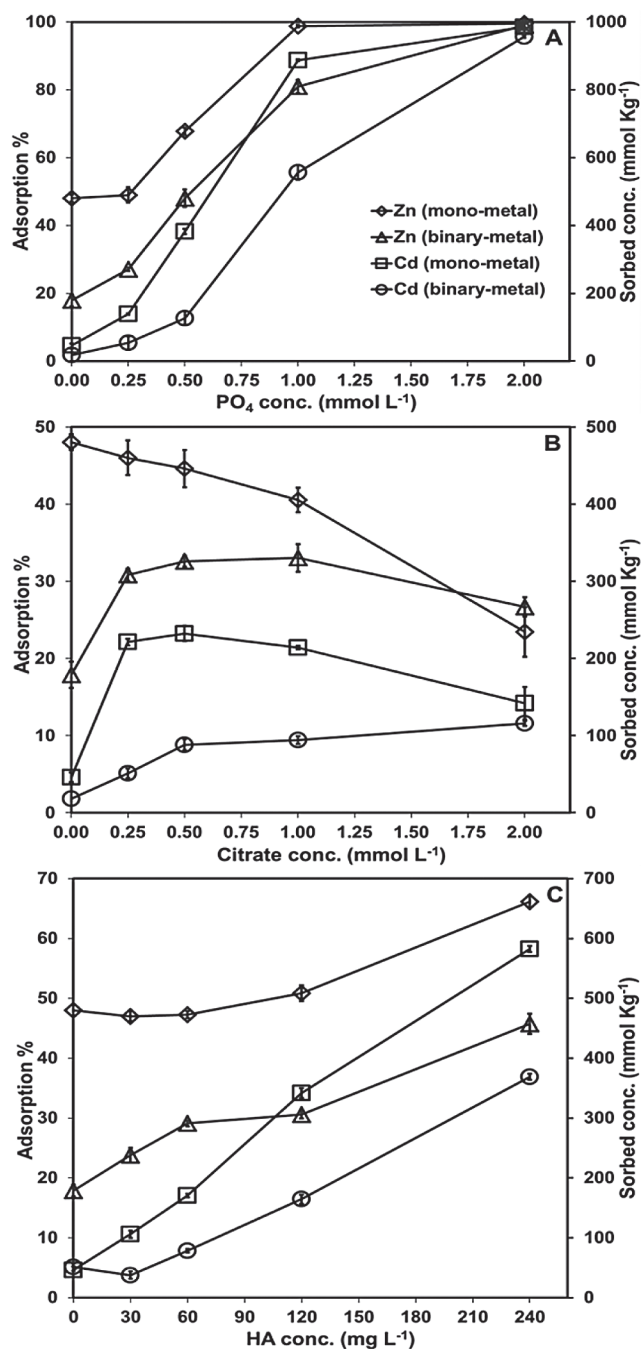
Fig. 2. Effect of initial Zn and Cd concentration on separation factor,  $R_L$ .

of competition among metals may be different depending on metal and mineral types, the general phenomenon of competitive effect of metal adsorption in nano-sized mineral systems appears to be consistent with that observed in bulk-sized mineral systems.

The surface area of  $\text{Al}_2\text{O}_3$  nanoparticles has been reported to range from  $43$  to  $411 \text{ m}^2 \text{ g}^{-1}$  depending on the method of preparation (Hua et al., 2012), which is generally larger than that of bulk-size  $\text{Al}_2\text{O}_3$  particles ( $9.3$ – $16 \text{ m}^2 \text{ g}^{-1}$ ) (Chen et al., 1973; Boily and Fein, 1996; Trainor et al., 2000). As shown in this study,  $\text{Al}_2\text{O}_3$  nanoparticles yielded 10 to 30 and 40 to 100 times higher adsorption capacities of Zn and Cd, respectively, in mono-metal systems as compared with those reported for bulk-sized  $\text{Al}_2\text{O}_3$  (Hachiya et al., 1984; Benjamin and Leckie, 1980; Trainor et al., 2000). These Zn and Cd adsorption capacities of  $\text{Al}_2\text{O}_3$  nanoparticles were also much greater (2–100 times) than those reported for bulk-sized gibbsite or bayerite (Kinniburgh et al., 1976; Shuman, 1977; Weerasooriya et al., 2002) as the surface of  $\text{Al}_2\text{O}_3$  was known to generally hydroxylate in aqueous solution, forming gibbsite or bayerite-like surfaces (Laiti et al., 1998; Eng et al., 2000). The higher surface area of nanoparticles was likely the cause for the increased Zn and Cd adsorption capacity. Recently, Rahmani et al. (2010) reported a maximum Zn adsorption capacity of  $899 \text{ mmol kg}^{-1}$  for  $\text{Al}_2\text{O}_3$  nanoparticles with an even higher surface area of  $206 \text{ m}^2 \text{ g}^{-1}$  and a smaller mean nanoparticle size of  $7.21 \text{ nm}$ . In this study, we did not examine the possibility of conglomeration of  $\text{Al}_2\text{O}_3$  nanoparticles during the adsorption experiment, which could reduce the adsorption capacity of metals (Mahdavi et al., 2013). However, the experimental dosage of  $\text{Al}_2\text{O}_3$  nanoparticles in this study was not high (i.e., it was less than the critical limit of dosage of  $< 4 \text{ g L}^{-1}$  for potential conglomeration) (Rahmani et al., 2010), and therefore the likelihood of this happening was low. Conglomeration of nanoparticles could be controlled using stabilizers such as carboxylic acids and polymers (Bahrami et al., 2012). Additionally, decreasing  $\text{Al}_2\text{O}_3$  nanoparticle adsorbent dosage below critical limits reduces conglomeration (Mahdavi et al., 2013).

### Impact of Ligands on Zn and Cd Adsorption

Figure 3 shows Zn and Cd adsorption to  $\text{Al}_2\text{O}_3$  nanoparticles in the presence of increasing  $\text{PO}_4$ , citrate, and HA in mono-



**Fig. 3.** Zinc and Cd adsorption to  $\text{Al}_2\text{O}_3$  nanoparticles at various concentrations of (A) phosphate ( $\text{PO}_4$ ), (B) citrate, and (C) humic acid (HA) in Zn mono-metal, Cd mono-metal, and binary-metal systems. Experimental conditions:  $1 \text{ mmol L}^{-1}$  Zn or Cd; pH 6.5;  $10 \text{ mmol L}^{-1}$   $\text{NaNO}_3$  background electrolyte;  $1 \text{ g L}^{-1}$   $\text{Al}_2\text{O}_3$  nanoparticles.

metal and binary-metal systems where initial concentrations of Zn and Cd were at  $1 \text{ mmol L}^{-1}$ . In the absence of any of the complexing ligands (control), the amount and trend of Zn and Cd adsorption in both the mono-metal and the binary-metal systems were consistent with those in isotherms (Fig. 1). The impact of ligands on adsorption of Zn and Cd by  $\text{Al}_2\text{O}_3$  nanoparticles varied by ligand type, ligand concentration, and metal system (Fig. 3). In general, the presence of  $\text{PO}_4$  and HA enhanced Zn and Cd adsorption in all systems, whereas citrate had both inhibitory and beneficial effects on adsorption, depending on metal system and citrate concentration. Zinc

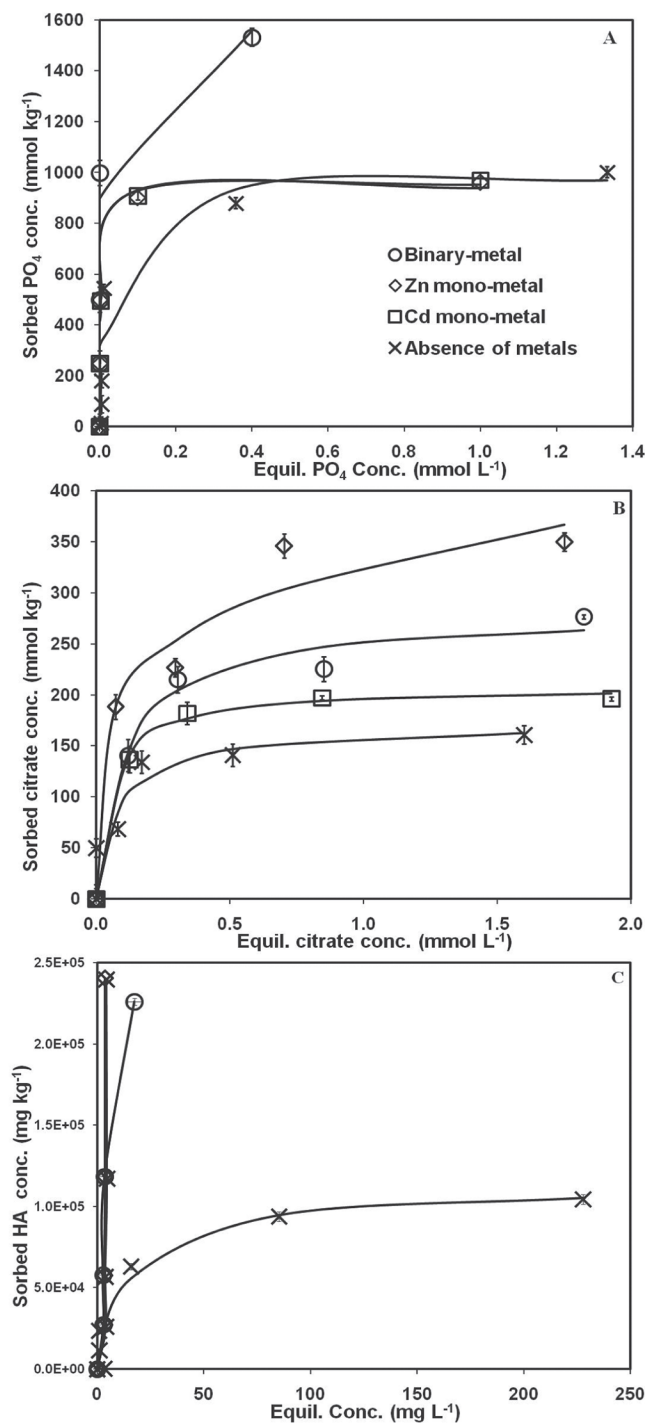
reached near-complete adsorption ( $996 \text{ mmol kg}^{-1}$ ) at  $1.0 \text{ mmol L}^{-1}$   $\text{PO}_4$  in the mono-metal system and at  $2.0 \text{ mmol L}^{-1}$   $\text{PO}_4$  in the binary-metal system. Cadmium also reached near-complete adsorption at  $2 \text{ mmol L}^{-1}$   $\text{PO}_4$  ( $\text{PO}_4$ :Zn ratio of 2:1) in the mono-metal and binary-metal systems (Fig. 3A). Although HA had similar effects to  $\text{PO}_4$  in enhancing metal adsorption, complete adsorption of Zn and Cd was not observed in any of the systems at these HA concentrations (Fig. 3C). With HA, the largest increase in adsorption was for Cd in the mono-metal system (from  $5\%$  [ $46 \text{ mmol kg}^{-1}$ ] to  $58\%$  [ $583 \text{ mmol kg}^{-1}$ ]), and the smallest increase in adsorption was for Zn in mono-metal system (from  $48\%$  [ $480 \text{ mmol kg}^{-1}$ ] to  $66\%$  [ $661 \text{ mmol kg}^{-1}$ ]) at HA concentrations ranging from 0 (control) to  $240 \text{ mg L}^{-1}$  HA. In the citrate systems where adsorption of Zn and Cd was enhanced, adsorption had not exceeded  $33 \text{ mmol kg}^{-1}$  (33%) of the total initial concentration of Zn (Fig. 3B). Thus,  $\text{PO}_4$  was the most effective ligand in comparison with HA and citrate for promoting Zn and Cd adsorption.

Previous studies on bulk-size minerals had shown enhanced adsorption of Zn, Cd, and other metals to mineral surfaces by  $\text{PO}_4$  due to ternary complex formation or due to increases in negative charge of the inner Helmholtz plane of the mineral surface as a result of specific adsorption of  $\text{PO}_4$  (Diaz-Barrientos et al., 1990; Collins et al., 1999; Wang and Xing, 2004; Stietiya et al., 2011; Ren et al., 2012) and HA (Davis and Leckie, 1978; Vermeer et al., 1999; Lai et al., 2002; Lai et al., 2002; Arias et al., 2002; Stietiya et al., 2011). Conversely, Cd adsorption on hematite and in soils was lower in the presence of  $\text{PO}_4$  likely due to the formation of soluble  $\text{PO}_4$  complexes like  $\text{CdHPO}_4$  or due to  $\text{PO}_4$  blocking Cd sorption sites (Krishnamurti et al., 1999; Li et al., 2006). In addition,  $\text{PO}_4$  was found to increase Cu adsorption capacity of bulk-size  $\gamma\text{-Al}_2\text{O}_3$  from  $52.7$  to  $129.6 \text{ mmol kg}^{-1}$  at low concentration, but  $\text{PO}_4$  concentrations  $>2.4 \text{ mg L}^{-1}$  P (or  $0.03 \text{ mmol L}^{-1}$   $\text{PO}_4$ ) had little influence on Cu adsorption capacity (Ren et al., 2012). Humic acid, which binds directly on iron oxide surfaces, may block surface sites, thus decreasing metal adsorption (Zuyi et al., 2000; Lai et al., 2002). Fulvic acid did not affect Zn adsorption to bulk-size  $\text{Al}_2\text{O}_3$  surface at pH  $<7$  (Zuyi et al., 2000). The effect of humic substances on metal sorption appears to be dependent on the nature of the metal oxides and the humic substance (Zuyi et al., 2000). Nonetheless, our results showed strong  $\text{PO}_4$  enhancement of Zn and Cd adsorption with concentration up to  $2 \text{ mmol L}^{-1}$ , indicating the significant impact of  $\text{PO}_4$  on Zn and Cd adsorption to  $\text{Al}_2\text{O}_3$  nanoparticle surface (Fig. 3A). These results also confirmed the general positive impact of HA in enhancing Zn and Cd adsorption to  $\text{Al}_2\text{O}_3$  nanoparticle surfaces at the studied solid to solution ratio and HA concentration ranges (Fig. 3C).

Contrary to  $\text{PO}_4$  and HA, the impact of citrate on Zn and Cd adsorption varied among the systems (Fig. 3B). Citrate had a positive impact on Zn adsorption in the binary-metal system and on Cd adsorption in both metal systems (Fig. 3B). In these systems, adsorption was enhanced specifically at low citrate concentrations between  $0.25$  and  $1.0 \text{ mmol L}^{-1}$  or at a citrate:metal ratio between 1 and 2. At the highest citrate concentration of  $2.0 \text{ mmol L}^{-1}$ , adsorption of Zn in the binary-metal system and Cd in the mono-metal system was lower than at any other concentration. Enhancement of heavy metal

adsorption at low organic acid concentration and suppression at high concentration has been reported for  $\text{Al}_2\text{O}_3$  and goethite bulk-size minerals (Liao, 2006; Huang et al., 2010). For instance, Huang et al. (2010) reported that  $\text{Cd}^{2+}$  adsorption to goethite was enhanced at low citric acid concentrations ( $1.0 \text{ mmol L}^{-1}$ ) and was suppressed at  $1.0$  to  $3.0 \text{ mmol L}^{-1}$ . The current study showed similar behavior of citrate in  $\text{Al}_2\text{O}_3$  nanoparticles for Zn in binary-metal system and for Cd in both systems. In the Zn mono-metal system, however, the presence of citrate reduced Zn adsorption at all levels (Fig. 3B). The results suggest that the trend of enhanced metal adsorption to bulk-size mineral surfaces at low citrate concentrations does not apply to Zn adsorption to  $\text{Al}_2\text{O}_3$  nanoparticles when present alone in the system (Zn mono-metal system). This may be due to the weak adsorption of citrate by nano-sized  $\text{Al}_2\text{O}_3$  and the formation of a strong solution citrate-Zn complex that prevents Zn from bonding to  $\text{Al}_2\text{O}_3$  nanoparticle surfaces. On the other hand, the fact that Zn in the binary metal system was enhanced by citrate at the low concentration ( $<2 \text{ mmol L}^{-1}$ ) could indicate that the surface-bonded Cd may further bind solution citrate-Zn species and could therefore enhance Zn adsorption in the binary metal system in the presence of citrate.

To better understand the effects of ligands on Zn and Cd adsorption to  $\text{Al}_2\text{O}_3$  nanoparticles, adsorption isotherms of  $\text{PO}_4$ , citrate, and HA in the mono-metal systems and binary-metal system are presented in Fig. 4. Adsorption of these ligands was generally better fit to the Langmuir model than to the Freundlich model in all systems except for HA in both metal systems, which did not fit due to too strong HA adsorption by  $\text{Al}_2\text{O}_3$  nanoparticles (Table 2). The separation factor confirmed the favorable adsorption of  $\text{PO}_4$ , citrate, and HA to  $\text{Al}_2\text{O}_3$  nanoparticle surface (Fig. 5). The isotherms revealed that the presence of Zn or Cd enhanced the adsorption of  $\text{PO}_4$ , citrate, and HA to the  $\text{Al}_2\text{O}_3$  nanoparticle surface in these systems because the absence of both metals showed generally lower ligand adsorption (Fig. 4). The comparison of  $\text{PO}_4$  adsorption capacity ( $Q^0$ ) in different metal systems showed that the presence of both Zn and Cd enhanced adsorption of  $\text{PO}_4$ , whereas the presence of Zn alone had the greatest adsorption of citrate and Zn or Cd alone had the greatest adsorption of HA (Fig. 4; Table 2). These results indicated that the enhanced adsorption of Zn and Cd in the metal systems (Fig. 3) was accompanied by generally enhanced adsorption of  $\text{PO}_4$ , citrate, and HA (Fig. 4). Accordingly, the different impact of  $\text{PO}_4$  and HA on Zn and Cd adsorption from that of citrate may be explained by differences in the ligand adsorption (Fig. 4). Most of the  $\text{PO}_4$  and HA was adsorbed to  $\text{Al}_2\text{O}_3$  nanoparticle surfaces, especially at low ligand concentrations, whereas large portions of citrate remained nonadsorbed, specifically at high concentrations. Considerable equilibrium concentrations of citrate indicate that  $\text{Al}_2\text{O}_3$  surface sites were saturated with the ligand, which would typically allow excess citrate to compete with surface sites for Zn or Cd complexation (Boily and Fein, 1996; Liao, 2006). Citrate has three  $\text{pK}_a$  values (3.13, 4.76, and 6.39) and would be in the dissociated  $\text{Cit}^{3-}$  form at pH 6.5, which would provide high chelating ability for Zn and Cd as compared with the partially dissociated  $\text{H}_2\text{Cit}^-$  and  $\text{HCit}^{2-}$  species (Qin et al., 2004; Johnson and Loeppert, 2006; Abollino et al., 2008). Therefore, the dominant Cd and Zn solution species in the presence of



**Fig. 4.** Adsorption isotherms of (A) phosphate ( $\text{PO}_4$ ), (B) citrate, and (C) humic acid (HA) to  $\text{Al}_2\text{O}_3$  nanoparticles in absence of metals, Zn mono-metal system, Cd mono-metal system, and binary-metal system. Experimental conditions: pH 6.5;  $10 \text{ mmol L}^{-1}$   $\text{NaNO}_3$  background electrolyte;  $1 \text{ g L}^{-1}$   $\text{Al}_2\text{O}_3$  nanoparticles.

citrate are likely  $\text{CdCit}^{-1}$  and  $\text{ZnCit}^{-1}$ , respectively (Boily and Fein, 1996). The same complexes with carboxyl groups would be assumed for HA because carboxyls account for more than 50% of total acidity and have  $\text{pK}_a$  in the range of 4 to 6, whereas phenols range from 9 to 11 (Lai et al., 2002). Nevertheless, the impact of these two ligands on Zn and Cd adsorption was quite different, indicating the varying interaction with  $\text{Al}_2\text{O}_3$  nanoparticle surface groups. Stietiya et al. (2011) also showed

**Table 2. Parameters of Langmuir and Freundlich adsorption isotherms for PO<sub>4</sub>, citrate, and humic acid in the absence of metals and in mono-metal, and binary-metal systems.**

Metal ion	System	Freundlich isotherm			Langmuir isotherm		
		K <sub>F</sub> L kg <sup>-1</sup>	N	R <sup>2</sup>	Q <sup>0</sup> mmol kg <sup>-1</sup>	b L mmol <sup>-1</sup>	R <sup>2</sup>
PO <sub>4</sub>	absence of metals	999.4	0.28	0.86	983.6	1.66	0.93
	Zn mono-metal	1030.0	0.12	0.93	939.0	1129.1	0.98
	Cd mono-metal	1047.6	0.14	0.93	954.7	355.6	1.00
	binary-metal	1757.6	0.13	0.86	1557.9	2712.5	0.99
Citrate	absence of metals	157.2	0.21	0.82	171.0	11.8	0.89
	Zn mono-metal	326.3	0.21	0.96	352.2	12.4	0.97
	Cd mono-metal	191.3	0.12	0.98	208.0	16.6	1.00
	binary-metal	243.8	0.21	0.98	280.0	8.8	0.98
Humic acid	absence of metals	–	–	–	1.13 × 10 <sup>5</sup> mg kg <sup>-1</sup>	0.06	0.93

that citrate suppressed adsorption at pH >5.7, whereas HA and PO<sub>4</sub> increased Zn adsorption to kaolinite.

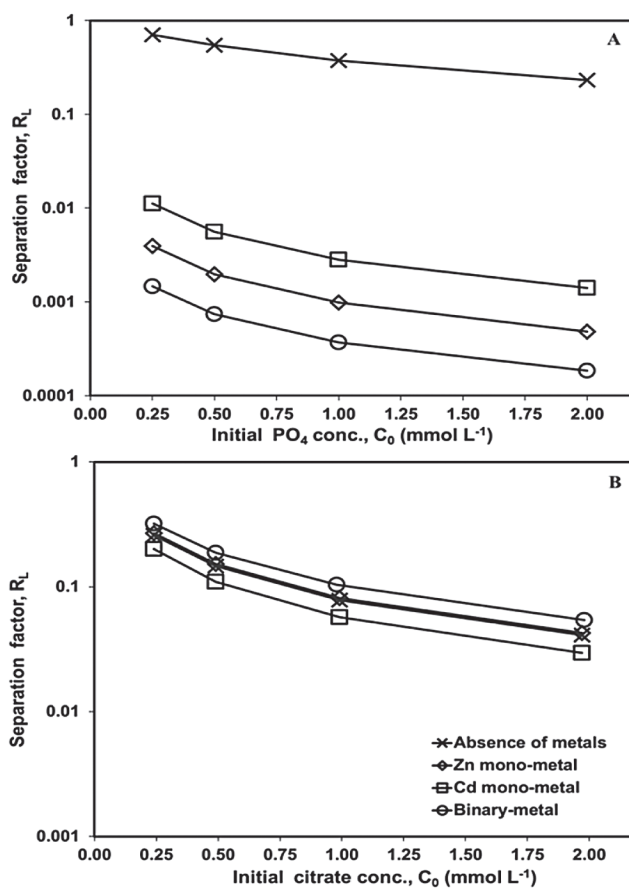
The expected adsorption complexes formed in the absence of ligands were likely ≡Al-OCd<sup>+</sup> and ≡Al-OZn<sup>+</sup> despite the high pH<sub>PZC</sub> (8.9–9.1) of Al<sub>2</sub>O<sub>3</sub> (Pacheco et al., 2006). Previous modeling attempts of coadsorption of Cd and citrate by α-Al<sub>2</sub>O<sub>3</sub> suggested that the surface species ≡AlCitCd<sup>0</sup> was likely dominant between pH 5 and 7.9, whereas ≡AlOCd<sup>+</sup> was at pH >8.0 due to increasing Al surface deprotonation and reduced citrate adsorption at high pH (Boily and Fein, 1996). Although similar surface species could be expected in this study for Cd and Zn adsorption by γ-Al<sub>2</sub>O<sub>3</sub> nanoparticles, the formation Cd- and Zn-citrate precipitates has been reported (Collins et al., 1999). The exact formation of surface complex species in the presence of these ligands would require confirmation of detailed solid speciation (Stietiya et al., 2011).

The fact that adsorption of both Zn and Cd was generally enhanced as a result of the presence of these ligands and vice versa suggests that several mechanisms may be at work. Although it is possible that adsorption of PO<sub>4</sub>, citrate, and HA reduced the overall positive charge of the nano-sized Al<sub>2</sub>O<sub>3</sub> surface, the beneficial impact of these ligands on metal adsorption would indicate the following processes: (i) PO<sub>4</sub>, citrate, and HA formed soluble complexes with Cd and Zn, and such complexes had high affinity for an Al<sub>2</sub>O<sub>3</sub> nanoparticle surface; (ii) ternary complex formation; or (iii) surface precipitation of HA with Zn and Cd as shown for bulk-size minerals (Collins et al., 1999; Arias et al., 2002; Ren et al., 2012). Regardless of the unconfirmed underlining mechanisms, our results showed enhancing Zn and Cd adsorption in mono- and binary-metal systems with increasing PO<sub>4</sub> concentration up to 2 mmol L<sup>-1</sup> or HA concentration up to 240 mg L<sup>-1</sup>. On the other hand, citrate only exhibited increased metal adsorption in Cd mono- or Zn and Cd binary systems with optimal concentration between 0.5 and 1.0 mmol L<sup>-1</sup> but decreased Zn adsorption in a mono-metal system throughout the citrate concentrations studied.

## Conclusion

This study demonstrated that Zn and Cd adsorption by nano-sized Al<sub>2</sub>O<sub>3</sub> was generally much higher than the reported adsorption capacities of these metals by bulk-sized alumina. Zinc had higher affinity to the γ-Al<sub>2</sub>O<sub>3</sub> nanoparticle surface than Cd. For both Zn and Cd, the adsorption in the

binary-metal system was lower than in their respective mono-metal systems, indicating competition for the same surface sites of nano-Al<sub>2</sub>O<sub>3</sub> minerals, a trend that was similar to that reported for bulk-sized Al<sub>2</sub>O<sub>3</sub>. The presence of PO<sub>4</sub> and HA enhanced Zn and Cd adsorption in all systems, whereas citrate reduced Zn adsorption in the mono-metal system but increased adsorption in the other metal systems at low citrate concentrations (0.5–1 mmol L<sup>-1</sup>). Removal of Zn or Cd from the systems by nano-Al<sub>2</sub>O<sub>3</sub> minerals was generally accompanied by enhanced removal of PO<sub>4</sub> and HA, suggesting the formation of a ternary surface complex or metal-ligand



**Fig. 5. Effect of (A) initial phosphate and (B) initial citrate concentration on separation factor, R<sub>L</sub>, for adsorption in absence of metals, and in Cd mono-metal, Zn mono-metal, and binary-metal systems.**

precipitation. Overall,  $\text{Al}_2\text{O}_3$  nanoparticles are suitable for use as a sorbent for removing Zn and Cd from solution systems, which can be significantly enhanced by the presence of  $\text{PO}_4$  or HA. Citrate, on the other hand, can also promote solution Cd and Zn removal, especially the former, by  $\text{Al}_2\text{O}_3$  nanoparticles at low citrate concentrations or at citrate:Cd concentration ratios between 1 and 2.

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