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Effect of Ionic Strength and Mechanism of Cu(II) Adsorption by Goethite and γ-Al_2O_3

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In the present investigation, the enhancement of Cu(II) adsorption on goethite and γ-Al_2O_3 by increasing ionic strength under acidic conditions was observed. The decrease of the electrostatic potential at the adsorption plane on the Fe/Al oxides with increasing ionic strength was responsible for the enhanced adsorption of Cu(II) by the oxides. The ζ-potential of goethite and γ-Al_2O_3 obtained under different ionic strengths gave evidence to support the interpretation. The value of the ζ-potential of goethite and γ-Al_2O_3 indicated that the potential at the adsorption plane decreased with the increase in ionic strength when the pH was less than the PZSE (point of zero salt effect) of the Fe/Al oxides, which was exactly opposite to the changing trends of surface charge of these oxides with ionic strength. Therefore, the decrease of the potential at the adsorption plane on these Fe/Al oxides with increasing ionic strength favored the Cu(II) adsorption.

Introduction

Sorption−desorption reactions on the surfaces of soils and oxides are two important processes controlling the concentration of heavy metals in solution,[1] hence affecting their bioavailability, leaching, and toxicity.[2] Fe/Al oxides such as goethite, hematite, and gibbsite are important components of acid soils in tropical and subtropical regions.[3] It was noted that Cu(II) could be adsorbed specifically by goethite and gibbsite,[4−6] since the adsorption process accompanied by the release of one to two moles of protons per mole of cation adsorbed[4] is unaffected by a change in ionic strength.[6] Recently, the formation of inner-sphere complexes of Cu(II) on goethite and gibbsite was confirmed by X-ray absorption fine structure (EXAFS) spectroscopy.[7,8]

The formation of inner-sphere complexes is apparently unaffected by a change in ionic strength, whereas the presence of outer-sphere complexes is likely to be influenced significantly by a change in ionic strength because of competitive adsorption with counterions.[9] However, Zhou et al. reported that the adsorption of Cu(II) by goethite under acidic conditions was increased with increasing ionic strength.[10] This was ascribed to the decline of the diffuse layer with the increase of ionic strength and OH^- release as incoming anions adsorbed on the surface of goethite.[10] The increase of Cu(II) adsorption onto TiO_2 with increasing ionic strength was also reported when $NaClO_4$ was used as a background electrolyte.[11] The adsorption of Cd(II) and Pb(II) onto alumina and hematite also exhibits increases with increasing ionic strength.[12] The increase of ionic strength increased the adsorption of Cu(II) and Zn(II) by δ-MnO_2 at low pH, while opposite trends were observed for Ni(II) and Co(II).[13]

In addition to the adsorption of heavy metals on oxides investigated in simple electrolyte systems, the adsorption of these metal cations was also studied in complex solutions resembling seawater. As the system changes from simple $NaNO_3$ solutions to synthetic solutions containing seawater ions (Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, and SO_4^{2-}), there is an overall increase in Cu(II) adsorption on goethite, an increase in Pb(II) adsorption at low pH, and a slight decrease in Pb(II) adsorption for the higher concentrations at higher pH; however, the adsorption of Cd(II) and Zn(II) on the goethite decreased significantly.[14] Similar decreases in the adsorption were observed for Co(II), Ni(II), and Zn(II) on amorphous FeOOH and β-FeOOH.[15,16] The decreases in heavy metal adsorption induced by increasing ionic strength have been ascribed to the competition of electrolyte cations for adsorption sites on Fe/Al oxides with heavy metals.[15] However, the mechanisms for the increase in adsorption of heavy metals induced by increasing ionic strength are not well-understood.

Moreover, the anionic systems showed that a characteristic pH usually occurs above which the adsorption of anions (phosphate) by goethite and variable charge soils increased with the increase in ionic strength, and below this a reverse trend occurred.[17,18] Recently, similar results were shown for arsenate adsorption by variable charge soils.[19] Earlier, an adsorption model was developed by Bowden et al. to describe the adsorption mechanism of anions by goethite.[20] This model was applied to explain the effect of ionic strength and pH on the adsorption of phosphate on goethite and soils.[17,18] According to the model, the effect of ionic strength on the adsorption operated through its effect on electrostatic potential at the plane of adsorption, rather than through its effect on surface charge.[20] The interpretation was confirmed with the measurement of the ζ-potential of soil colloids.[21] The results of the ζ-potential suggested that the potential at an adsorption plane became less negative with increasing ionic strength above the soil PZNC (point of zero net charge) and decreased with increasing ionic strength below the soil PZNC.[21] It can be predicted that the change of electrostatic potential at the adsorption plane of goethite and variable charge soils with ionic strength not only affect the specific adsorption of anions such as phosphate and arsenate, but also the specific adsorption of cations, that is, toxic heavy metal ions. Therefore, the adsorption model given by

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Bowden et al. can perhaps be used to interpret the effect of ionic strength on adsorption of heavy metals by Fe/Al oxides.

Hence, the objectives of this investigation are: (1) to use the adsorption model of Bowden et al. to interpret the effect of ionic strength on Cu(II) adsorption by goethite and γ-Al_2O_3 and (2) to test the hypothesis of the adsorption model with ζ-potential measurements in the systems of Fe/Al oxides.

Experimental Section

Fe/Al Oxides. γ-Al_2O_3 was a commercial product obtained from the Dalian Luming Light Science and Technology Co., Ltd. (Dalian, China) with diameter of < 2 μm.

Goethite was synthesized using the procedure reported earlier.[22] The pH of a 0.5 $mol \cdot L^{-1}$ $Fe(NO_3)_3$ solution was adjusted to 12 with NaOH under stirring, and then the precipitate was aged at 60 °C in an oven for 24 h. The synthetic goethite was electrodialyzed at a potential gradient of 15 $V \cdot cm^{-1}$ until a constant specific electrical conductance was achieved. Finally, the treated sample was dried at 60 °C using an IR lamp and ground to pass through a 100 mesh sieve.

Experiments for Cu(II) Adsorption. A stock solution of Cu(II) (0.1 M) was prepared using reagent-grade $Cu(NO_3)_2 \cdot 3H_2O$ followed by a series of $Cu(NO_3)_2$ solutions with various concentrations of (0.50, 0.75, 1.0, 1.25, 1.88, and 2.50) mM prepared by successive dilution for adsorption isotherm experiments. The background electrolyte was kept constant as 0.001 M of $NaNO_3$. The solution pH was adjusted to 4.4 by dropwise addition of NaOH (5.0 M) or HNO_3 (6.0 M).

Samples of goethite (0.200 g) in duplicate were weighed into centrifugation bottles, and then 25 mL of $Cu(NO_3)_2$ solution was added into each of the bottles. Suspensions were shaken in a constant-temperature water bath at (25 ± 1) °C for 2 h. After standing overnight, the solution was separated from the solid phase by centrifugation at 4499 g for 10 min, and further it was filtered using a 0.45 μm pore membrane filter. The Cu(II) present in the bulk solution was determined by an atomic absorption spectrophotometric method (TAS-990, Pgeneral, China). The same adsorption experiment was repeated with the background electrolytes of (0.1 and 1.0) M $NaNO_3$, separately. The adsorption isotherm experiments were also conducted for the γ-Al_2O_3 system. However, prior to the addition of the γ-Al_2O_3 sample, the pH of the $Cu(NO_3)_2$ solutions was adjusted to 5.1 by dropwise addition of NaOH (5.0 M) or HNO_3 (6.0 M). Other steps were exactly the same as those for the goethite system. The amount of Cu(II) adsorbed by goethite or γ-Al_2O_3 was calculated from the difference between the total amount added and the amount remaining at equilibrium. When the effect of ionic strength on Cu(II) adsorption in binary systems containing Cu(II) and Cd(II) was investigated, a series of mixed solutions with various concentrations of (0.50, 0.75, 1.0, 1.25, 1.88, and 2.50) mM $Cu(NO_3)_2$, 1 mM $Cd(NO_3)_2$, and 1 mM $NaNO_3$ (or 1 M $NaNO_3$) were prepared. Then the same procedures were executed to obtain Cu(II) adsorption isotherms in the binary systems of Cu(II) and Cd(II).

The effect of pH on Cu(II) adsorption was investigated using 2 mM $Cu(NO_3)_2$ solution prepared from the stock solution of 0.1 M $Cu(NO_3)_2$ with the $NaNO_3$ of (0.001, 0.1, and 1.0) M as background electrolytes separately. The solution pH was then adjusted to the different values in the range from 3.0 to 5.5. Similar adsorption procedures were adopted as described earlier to obtain the amount of Cu(II) adsorbed by goethite or γ-Al_2O_3 at different pH values and ionic strengths.

Determination of the Point of Zero Salt Effect (PZSE). The potentiometric titrations were performed with the TIM854 autopotential titration system (Radiometer, France) to obtain the PZSE for Fe/Al oxides.[23] Exactly 0.2 g of sample was taken in a plastic beaker. A portion of 40 mL of 0.001 M $NaNO_3$ was then added, and the suspension was agitated continuously for about 5 min using a bar magnet followed by measuring the suspension pH. An automatic titrimeter along with a combined electrode assembly was used to titrate the suspension with 0.1 M HCl and 0.1 M NaOH at a regulated addition of HCl (or NaOH), that is, 0.05 mL/2 min. The procedure was repeated with 0.01 and 0.1 M $NaNO_3$ solutions as well. The adsorption of H^+ and OH^- ions by these oxides was calculated, and the intersection of H^+ and OH^- adsorption−pH curves at different ionic strengths was reported as the PZSE of the Fe/Al oxides.

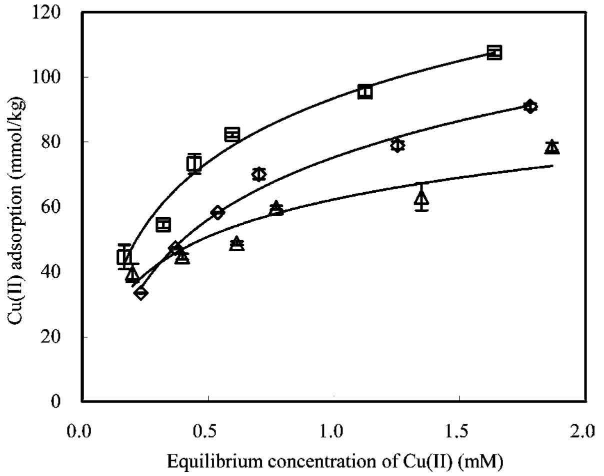

Figure 1. Adsorption isotherms of Cu(II) on goethite from (△, 0.001; ◇, 0.1; and □, 1) M $NaNO_3$ solutions at pH 4.4. The goethite concentration is 8.0 $g \cdot L^{-1}$.

ζ-Potential Determination. The electrokinetic potential (ζ-potential) was measured using a JS94G+ microelectrophoresis apparatus made in China.[24] The colloidal suspension was agitated and transferred to the electrophoresis vessel. The electrophoresis vessel was wetted properly prior to use to avoid any disturbance due to the presence of air bubbles. An average of the electrophoretic velocity was obtained with the computer by timing 10 particles, first in one direction, and then in the reverse direction by the reversal of the polarity of the applied electrical field. The values of the ζ-potential were calculated using dedicated computer software based on the Helmholtz−Smoluchowski equation:

$$\zeta = \frac{Ku\eta}{\varepsilon} \tag{1}$$

where u is the electrophoretic mobility, ε is the permittivity of the medium, and η is the viscosity of the liquid phase. K is a constant relative to the shape of the colloid particle. The radii of colloidal particles (a) are much higher than the thickness of electrical double layer ($1/\kappa$) and $\kappa a \gg 1$, so $K = 4\pi$. This step was repeated 10 times, and an average value of the ζ-potential from 10 replicates is reported in this paper. The measurement error is found to be ± 2 mV and at the temperature (25 ± 0.5) °C.

Results and Discussion

Effect of Ionic Strength on Cu(II) Adsorption. The adsorption isotherms of Cu(II) by goethite at different ionic strengths and pH 4.4 are shown in Figure 1. The results indicated that

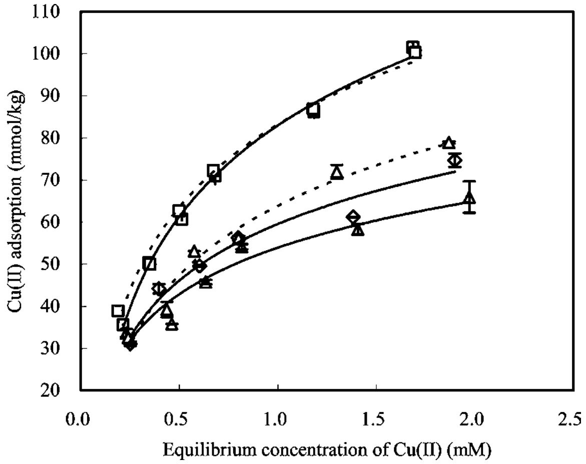

Figure 2. Adsorption isotherms of Cu(II) on γ-Al_2O_3 from (△, 0.001; ◇, 0.1; and □, 1) M $NaNO_3$ solutions at pH 5.1 in single Cu(II) system (solid lines) and the binary systems containing Cu(II) and Cd(II) (dashed lines). The γ-Al_2O_3 concentration is 8.0 g·L^{-1}.

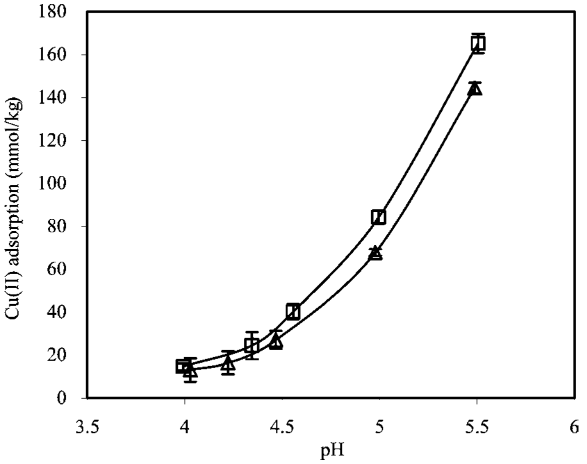

Figure 3. Effect of ionic strength on Cu(II) adsorption by γ-Al_2O_3 at different pH values (△, 0.001 M $NaNO_3$; and □, 1 M $NaNO_3$). The initial concentration of Cu(II) is 2.0 mM, and the γ-Al_2O_3 concentration is 8.0 g·L^{-1}.

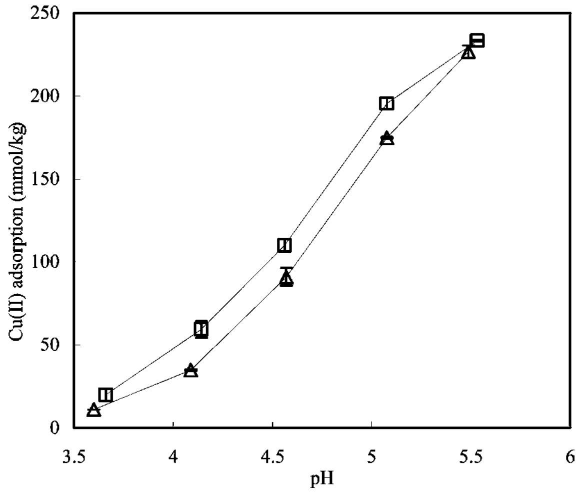

Figure 4. Effect of ionic strength on Cu(II) adsorption by goethite at different pH values (△, 0.001 M $NaNO_3$; and □, 1 M $NaNO_3$). The initial concentration of Cu(II) is 2.0 mM, and the goethite concentration is 8.0 g·L^{-1}.

the amount of Cu(II) adsorbed by goethite increased with the increase in its equilibrium concentration as well with the concentrations of the background electrolyte ($NaNO_3$). The similar trends for the adsorption isotherms of Cu(II) were observed for the γ-Al_2O_3 system under similar conditions as shown in Figure 2. By increasing the concentration of $NaNO_3$ from (0.001 and 0.1 to 1.0) M, Cu(II) adsorption onto goethite increased from (51.0 and 56.5 to 74.0) mmol·kg^{-1} at Cu(II) equilibrium concentration of 0.5 mM and from (69.5 and 86.5 to 100.5) mmol·kg^{-1} at Cu(II) equilibrium concentration of 1.5 mM. Similarly, for the γ-Al_2O_3 system, the amount of Cu(II) adsorbed was increased from (43.0 and 46.0 to 61.0) mmol·kg^{-1} and from (60.2 and 67.5 to 95.5) mmol·kg^{-1} at its equilibrium concentrations of (0.5 and 1.5) mM, respectively, for the increase in $NaNO_3$ concentrations from (0.001 and 0.1 to 1.0) M. The increase was observed at a higher equilibrium concentration of Cu(II) for both the goethite and the γ-Al_2O_3 systems.

In addition to single Cu(II) systems, the effect of ionic strength on Cu(II) adsorption by γ-Al_2O_3 was also investigated in binary systems containing Cu(II) and Cd(II), and the obtained data are presented in Figure 2. In the presence of 0.001 M Cd(II), the adsorption of Cu(II) onto γ-Al_2O_3 increased with increasing concentration of $NaNO_3$, which was similar to the trends in single Cu(II) systems. In the system of Cu(II) + 0.001 M $NaNO_3$, the presence of Cd(II) increased the amount of Cu(II) adsorbed by γ-Al_2O_3 due to the increased ionic strength by $Cd(NO_3)_2$. However, in the system of Cu(II) + 1 M $NaNO_3$, the presence of Cd(II) did not change Cu(II) adsorption significantly. In this system, the contribution of 0.001 M $Cd(NO_3)_2$ to ionic strength can be neglected, and the ability of Cd(II) to compete for adsorption sites on Fe/Al oxides with Cu(II) is much weaker[25] and thus did not affect Cu(II) adsorption under this condition.

The effect of pH on Cu(II) adsorption by γ-Al_2O_3 at different ionic strengths is shown in Figure 3. The adsorption of Cu(II) was increased sharply by increasing the sorptive pH from pH 4.0 to 5.5 for γ-Al_2O_3, and similar trends were observed for goethite systems (Figure 4). These results are consistent with previous reports.[26,27] It is evident from the Cu(II)−pH adsorption curves obtained at two different background electrolyte concentrations, that is, (1.0 and 0.001) M $NaNO_3$ for these two oxides, the adsorption of Cu(II) was higher at 1.0 M $NaNO_3$ than at 0.001 M $NaNO_3$. These results suggested that the increasing ionic strength of a system enhanced the adsorption of Cu(II) by Fe/Al oxides under the prevailing acidic conditions.

Mechanism of Cu(II) Adsorption by Fe/Al Oxides at Different Ionic Strengths. The amount of H^+ and OH^- adsorbed by goethite as a function of pH during acid−base titration at three different ionic strengths is presented graphically in Figure 5. The amount of H^+ and OH^- adsorbed indicates respectively the positive and negative surface charge on the oxide surfaces. The intersection of H^+ and OH^- adsorption−pH curves at different ionic strengths virtually gives the PZSE of the oxide. It is found to be 7.92. Similar changing trends of adsorption of H^+ and OH^- with pH at different ionic strengths are observed for γ-Al_2O_3 systems (Figure 6). The PZSE for γ-Al_2O_3 calculated from Figure 6 is 8.15. Figures 5 and 6 show that, when pH is higher than the PZSE of the oxides, the oxides carry net negative surface charge and the surface charge becomes more negative with increasing ionic strength; when pH is less than the PZSE of the oxides, the oxides carry a net positive surface charge, and the value of the surface charge increases with increasing ionic strength.

Under acidic conditions, both goethite and γ-Al_2O_3 carry net positive surface charges on their surfaces, and the value of the

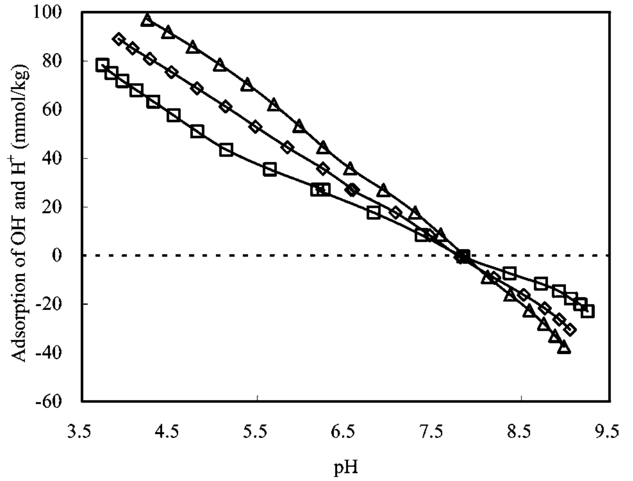

Figure 5. Amount of H^+ and OH^- adsorbed by goethite as a function of pH during acid−base titration in (□, 0.001; ◇, 0.01; and △, 0.1) M $NaNO_3$ solutions. The goethite concentration is 5 g·L^{-1}.

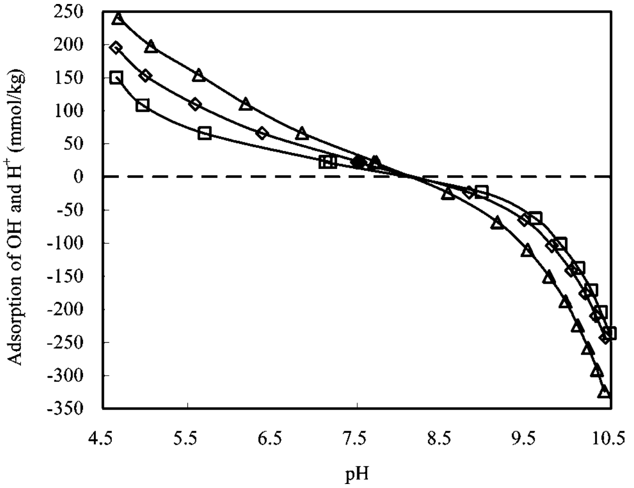

Figure 6. Amount of H^+ and OH^- adsorbed by γ-Al_2O_3 as a function of pH during acid−base titration in (□, 0.001; ◇, 0.01; and △, 0.1) M $NaNO_3$ solutions. The γ-Al_2O_3 concentration is 5 g·L^{-1}.

positive surface charge increases with increasing ionic strength (Figures 5 and 6). Therefore, Cu(II) was mainly adsorbed specifically by goethite and γ-Al_2O_3 under acidic conditions, and the change of surface charge on goethite and γ-Al_2O_3 cannot be used to explain the change of Cu(II) adsorption by these Fe/Al oxides with the changing ionic strength of the systems.

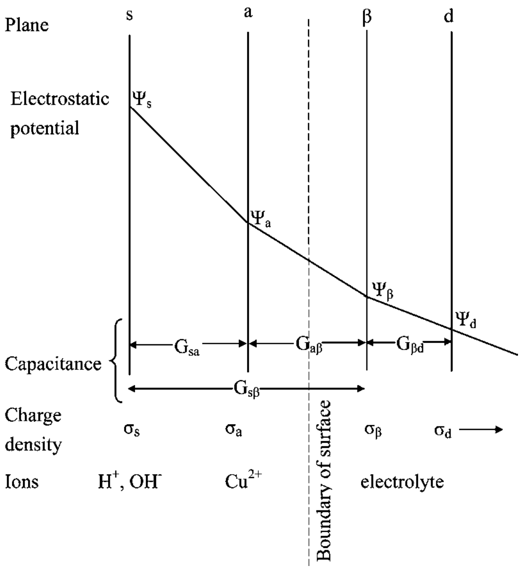

Figure 7. Schematic representation of the charge distribution and the change in potential when phosphate is adsorbed on an idealized planar surface (the figure was reproduced from Bowden et al.,[20] and phosphate in the original figure was replaced by Cu^{2+}).

The adsorption model developed by Bowden et al.,[20] which was used for the specific adsorption of anions previously, is used to interpret the mechanism involved in the adsorption of Cu(II) by goethite and γ-Al_2O_3 as a function of ionic strength in this paper. The outline of the model is presented in Figure 7. According to the model, the specific adsorption of Cu(II) on the surfaces of goethite and γ-Al_2O_3 takes place in a separate plane, "a" in Figure 7. Because Cu(II) has a high binding constant, it coordinates to the surface and is nearer the surface than electrolyte cations. The electrolyte ions can reach the boundary of surface, and plane "a" is between plane "s" and plane "β" as shown in Figure 7. The variation in the number of electrolyte ions in plane "β" and in the diffuse layer (d) will affect the potential (Ψ_a) developed in the adsorption plane (plane "a") and thus affect the adsorption of Cu(II). Under acidic conditions, both goethite and γ-Al_2O_3 possess a net positive surface charge, and thus the surface potential and the potential in the adsorption plane were positive. With increasing ionic strength, the positive surface charge of goethite and γ-Al_2O_3 increased for the pH values less than the PZSE of the oxides. Under this condition, the counterion in plane "β" and the diffuse layer was an anion (NO_3^-),and the number of anions per unit area apparently increased with an increase in background electrolyte concentration. Therefore, the increase in the number of anions in plane "β" and the diffuse layer caused the decrease in potential at the adsorption plane (plane "a"), thus allowing the increase of Cu(II) adsorption by goethite and γ-Al_2O_3. The increase in Cu(II) adsorption by goethite and γ-Al_2O_3 with increasing concentration of $NaNO_3$ (Figures 1 to 4) was attributed to the enrichment of nitrate in plane "β" and the diffuse layer, followed by the decrease of the potential at the adsorption plane. The decrease of electrostatic potential at the adsorption plane favors the specific adsorption of Cu(II) occurring on Fe/Al oxides because of the decrease in electrostatic repulsion of positively charged Fe/Al oxide surfaces to Cu^{2+}.

Confirmation of the Adsorption Model for the Effect of Ionic Strength on Cu(II) Adsorption. The adsorption model can be used to interpret the effect of ionic strength on Cu(II) adsorption by goethite and γ-Al_2O_3. McBride pointed out that such complex model applications were generally not subject to direct experimental confirmation because they employed several fitting parameters that could not be analytically measured.[28] However, the present communication is to testify the hypothesis of the model with the help of ζ-potential measurements.

The ζ-potential is an electrical potential at the shear plane of the electric double layer on colloid particles. Although the exact location of the shear plane in the electric double layer cannot be ascertained, it is generally considered that it is located near the interface between the Stern layer and the diffuse layer.[3] In Figure 7, the location of the shear plane is the boundary of the surface as shown by the dashed line. Therefore, the shear plane is near the adsorption plane (plane "a") in the model described previously. Hence, the change trends of ζ-potential with pH at different ionic strengths should be similar to that on the adsorption plane for goethite and γ-Al_2O_3. The ζ-potential−pH curves for goethite and γ-Al_2O_3 at different ionic strengths are shown in Figures 8 and 9. Similar to surface charge−pH curves

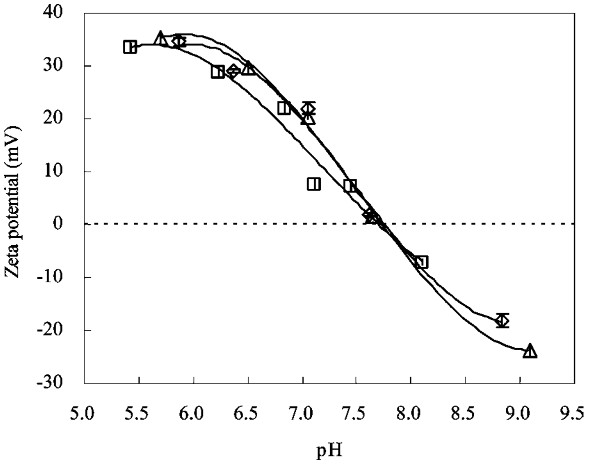

Figure 8. Effect of ionic strength on the ζ-potential of goethite (△, 0.1 mM $NaNO_3$; ◇, 1 mM $NaNO_3$; and □, 10 mM $NaNO_3$). The goethite concentration is 0.25 g·L^{-1}.

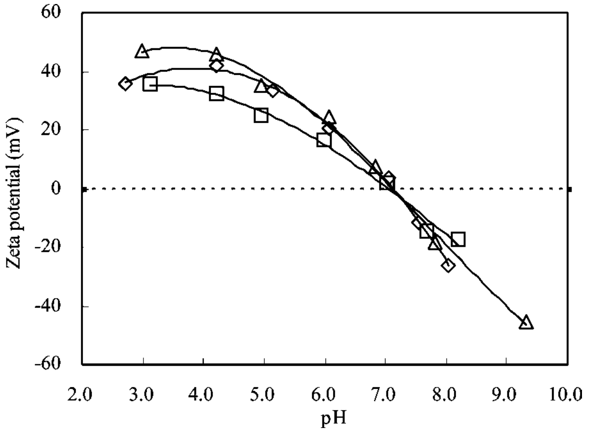

Figure 9. Effect of ionic strength on ζ-potential of γ-Al_2O_3 (△, 0.1 mM $NaNO_3$; ◇, 1 mM $NaNO_3$; and □, 10 mM $NaNO_3$). The γ-Al_2O_3 concentration is 0.25 g·L^{-1}.

at different ionic strengths, the ζ-potential−pH curves at different ionic strengths also intersect at one point. The point of intersection is obviously the isoelectric point (IEP) for the oxides. The value of IEP is 7.7 for goethite and 7.3 for γ-Al_2O_3. It is clear from Figures 8 and 9 that, when pH is less than the IEP, the value of ζ-potential is positive and decreases with increasing ionic strength. Therefore, the change of surface charge with ionic strength is exactly opposite in nature to that for ζ-potential with ionic strength for both oxide systems. These results suggest that, when the pH is less than the IEP, the potential at the adsorption plane on goethite and γ-Al_2O_3 is also positive and decreases with increasing ionic strength and thus is opposite to the change in surface charge with ionic strength. The change of the potential at the adsorption plane is consistent with that predicted by the adsorption model mentioned above. The results of the ζ-potential provide direct support to the interpretation that the change of potential at the adsorption plane with ionic strength was responsible for the effect of ionic strength on Cu(II) adsorption by goethite and γ-Al_2O_3, because the change of ζ-potential and the potential at the adsorption plane with ionic strength are ascribed to the change in the distribution of counterion in the shear plane with ionic strength, which was opposite to the change in surface charge of these Fe/Al oxides with ionic strength.

Conclusion

The results can be summarized as the following: (1) Cu(II) adsorption on goethite and γ-Al_2O_3 increased with increasing ionic strength both in a simple Cu(II) system and the binary system containing Cu(II) and Cd(II) under acidic conditions. (2) The effects of ionic strength on Cu(II) adsorption by Fe/Al oxides were well-interpreted by the adsorption model developed by Bowden et al.[20] The effect of ionic strength on the adsorption was closely related to the electrostatic potential induced at the adsorption plane. (3) The results of ζ-potential suggested that the electrostatic potential in the adsorption plane changed with ionic strength as an opposite trend to the surface charge of the Fe/Al oxides. When the pH is less than the IEP, the potential at the adsorption plane on goethite and γ-Al_2O_3 is positive and decreases with increasing ionic strength, thus allowing the increase of Cu(II) adsorption onto goethite and γ-Al_2O_3 because of the decrease in electrostatic repulsion of positively charged Fe/Al oxide surfaces to Cu^{2+}.

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