Inhibition of acidification of kaolinite and an Alfisol by aluminum oxides through electrical double-layer interaction and coating

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Summary

Soil chemical properties are affected significantly by surface charge characteristics of the soil. Interaction between oppositely charged particles in variable-charge soils plays an important role in variation of soil electrochemical properties. In this study, the effects of Al oxides on surface charge and acidity properties of kaolinite and an Alfisol during electrodialysis were investigated. The results indicated that Al oxides, when mixed into kaolinite or the Alfisol, decreased the effective cation exchange capacity (ECEC) and exchangeable acidity and inhibited the decrease in pH. Gibbsite had less effect than γ-Al_2O_3 and amorphous $Al(OH)_3$ in reducing the ECEC and acidity of kaolinite and the Alfisol; γ-Al_2O_3 and amorphous $Al(OH)_3$ displayed comparable effects. However, this effect is inconsistent with the order of the surface positive charge per unit mass that the Al oxides carried. Their effect on the ECEC of kaolinite and Alfisol varied irreversibly with ionic strength of the bathing solutions. X-ray diffraction spectra indicated that amorphous $Al(OH)_3$ and γ-Al_2O_3 were more effective than gibbsite in decreasing peak intensity of electro-dialyzed kaolinite when mixed with these Al oxides at the same rate. The results demonstrated that Al oxides could decrease the effective negative charge and inhibit acidification of kaolinite and an Alfisol through diffuse-double-layer overlapping between oppositely charged particles and coating of Al oxides on these materials. Both mechanisms intensified with increasing rate of added Al oxides, which can therefore act as anti-acidification agents in variable-charge soils.

Introduction

Variable-charge soils develop under intensive weathering and leaching. In this type of soil kaolinite and iron (Fe)/aluminum (Al) oxides are the dominant mineralogical components (Qafoku *et al*., 2000, 2004). Under normal soil pH conditions, kaolinite carries a net negative surface charge, while Fe and Al oxides have a positive one (Yu, 1997). These oppositely charged particles interact with one another through the overlap of diffuse layers of electric double layers. This interaction causes a neutralization of opposite charges and decrease in effective surface charge density of these charged particles in variable-charge soils (Barber & Rowell, 1972; Qafoku & Sumner, 2002; Qafoku *et al*., 2004) (Figure 1). Thus, this interaction results in changes in the ion concentration and potential distribution of charged particles and affects the surface chemical properties of the soils (Usui, 2008; Schießl *et al*., 2012). Overlapping of diffuse layers on oppositely

charged particles has been reported to be an important mechanism that is responsible for many chemical properties of variable-charge soils, such as ion adsorption and desorption, colloidal aggregation and precipitation (Kim & Berg, 2000; Qafoku & Sumner, 2002; Li *et al*., 2009; Wang *et al*., 2011; Xu *et al*., 2011). This interaction increases with increasing charge per unit mass on the colloid particles and increasing content of Fe/Al oxides in their mixtures with phyllosilicates (Hou *et al*., 2007a,b; Li & Xu, 2008). Because the thickness of the diffuse layer of electric double layers increases with decreasing ionic strength of the bathing solution and *vice versa*, the overlapping of diffuse layers and its effect on charge neutralization intensifies with declining ionic strength and weakens with increasing ionic strength of the system. That is to say, this effect is completely reversible with changes in ionic strength of the contacting solution (Qafoku & Sumner, 2002; Li *et al*., 2009) (Figure 1).

Moreover, Fe and Al oxides, released from weathering of primary minerals or from deposition of translocated materials, may coat to a greater or lesser extent phyllosilicate mineral particles in variable-charge soils (Hendershot & Lavkulich, 1983). These
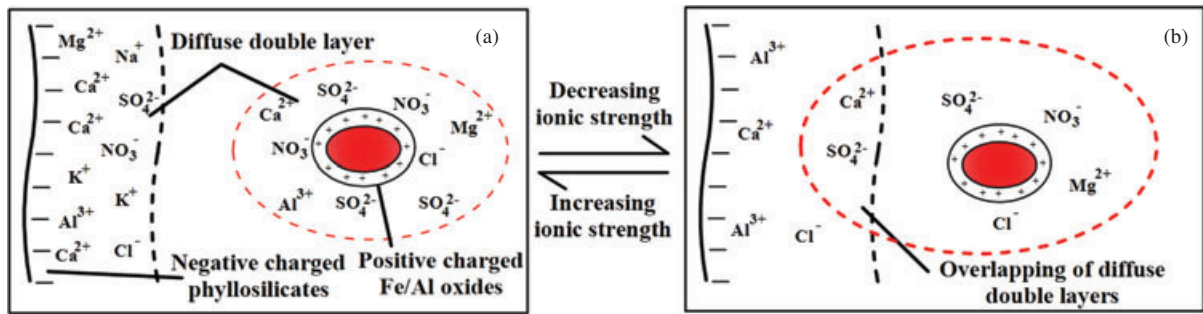
Figure 1 Schematic diagram of coexistence status of oppositely charged phyllosilicates and Fe/Al oxides in soil suspensions with large (a) and small (b) ionic strength.

sesquioxides are considered to be important cementing agents in the formation of soil aggregates in variable-charge soils (Goldberg, 1989). The coating of Fe and Al oxides on phyllosilicates increases the amount of positive charge, but decreases that of negative charge at low pH. This coating reduces significantly the negative potential on the clay surfaces, and shifts the point of zero charge to a higher pH value (Sumner, 1963; Zhang & Zhang, 1992; Zhuang & Yu, 2002). Therefore, the sesquioxide coating also evidently changes the electrochemical properties of phyllosilicates in acidic variable-charge soils. Coating occurs through the formation of chemical bonds, such as hydrogen bonds and coordination bonds, between the sesquioxides and phyllosilicates (Beauvais & Bertaux, 2002; Orolínová & Mockovčiaková, 2009; Villalba *et al.*, 2010). Once formed, these coatings are stable in moderately changing environments, such as a change in pH or ionic strength in variable-charge soils (Goldberg, 1989).

Intensive leaching also leads naturally to acidification of variable-charge soils. According to the traditional acidification principle, highly weathered soils are characterized by small concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+}, weak ionic strength and relatively large contents of Fe and Al oxides. They have negatively charged sites that are saturated with exchangeable acidity, thus becoming strongly acidic (Jackson & Sherman, 1953; Reuss & Johnson, 1986). Therefore, soil acidity characteristics are mainly determined by the electrochemical properties of the soil. Iron and Al oxides can decrease the effective negative charge of phyllosilicates through overlapping of diffuse layers and coating and they would also affect soil acidity properties of the variable-charge soils. Iron oxides have been observed to be natural anti-acidification agents through electric double-layer overlapping and coating on phyllosilicates in highly weathered soils, which is not involved in the traditional acidification principle (Li *et al.*, 2012). However, little is known about the effect of Al oxides on natural soil acidification in variable-charge soils.

The content of Al oxides is generally less than that of Fe oxides in variable-charge soils. However, Al oxides, such as amorphous $Al(OH)_3$ and gibbsite, carry a greater positive charge per unit mass than do Fe oxides (amorphous $Fe(OH)_3$, hematite and goethite) (Hou *et al.*, 2007a; Wang *et al.*, 2011). They also exhibit stronger interactions with kaolinite and soil colloids through diffuse layer overlapping and more effectively decrease the effective negative charge of kaolinite and soil colloids (Hou *et al.*, 2007a; Li & Xu, 2008; Wang *et al.*, 2011). Oades (1984) reported that Al oxides were also more effective than Fe oxides in blocking the negative charge of phyllosilicates through coating, because Al oxides generally have greater amounts of hydroxyls on their surfaces than Fe oxides. Therefore, Al oxides should also be important agents in influencing acidification of variable-charge soils. To test this hypothesis, we investigated the effects of added Al oxides on acidification of kaolinite and an Alfisol with a small content of Fe and Al oxides during electrodialysis. Because leaching-induced acidification is a very slow process, electrodialysis was used to simulate natural soil acidification in tropical and sub-tropical regions in the present study, because it is considered to be a highly intensified reproduction of the natural leaching process (Mattson, 1933; Li *et al.*, 2012). Because of the completely different responses of the mechanisms of diffuse layer overlapping and coating with change of ionic strength in the bathing solution, experiments to determine the effect of changing ionic strength on the effective cation exchange capacity (ECEC) were conducted to differentiate the contributions of diffuse layer overlapping and coating to the effect of Al oxides on the charge properties of kaolinite and Alfisol.

Materials and methods

Kaolinite and Alfisol samples

The kaolinite used was collected from Suzhou, Jiangsu Province of China. Subsoil samples from an Alfisol (87–150 cm) were collected from Nanjing, Jiangsu Province, with hydrous mica being the dominant clay mineral and vermiculite and kaolinite present in appreciable quantities. The soil is classified as a Calciorthidic Paleustalf, an Alfisol in the US Soil Taxonomy (Soil Survey Staff, 1999). Only subsoil samples were used in this study to reduce the effect of organic matter, which is also an important charged component in soils. The clay fractions (<2 µm in diameter) of the kaolinite and the soil were obtained using the sedimentation method (Pansu & Gautheyrou, 2006). Their basic properties are presented in Table 1.

Table 1 Basic properties of kaolinite and Alfisol tested

Mineral or soil	pH[a]	Free Fe_2O_3[b] / g kg^{-1}	Free Al_2O_3[b]	Organic matter[c]	CEC[d] / mmol$_c$ kg^{-1}	Exchangeable base cations / CEC / mmol$_c$ kg^{-1}			
						Ca^{2+}	Mg^{2+}	K^+	Na^+
Kaolinite	6.44	—	—	—	64.4	14.9	1.3	0.8	43.7
Alfisol	6.74	22.1	19.6	3.67	218.0	163.5	39.8	10.2	2.5

[a]Soil:water 1:2.5.
[b]DCB method.
[c]Dichromate method.
[d]Ammonium acetate method (1 M, pH 7.0).

Preparation of Al oxides

γ-Al_2O_3 is a commercial product obtained from Dalian Luming Light Science and Technology Co., Ltd (Dalian, China), with particle size being less than 2 μm. We chose γ-Al_2O_3 in this study because the surface of well-hydrated γ-Al_2O_3 is structurally similar to that of aluminum oxides such as bayerite in soils (Arai *et al*., 2001).

Gibbsite was prepared according to the method described by Kyle *et al*. (1975). Four molar NaOH was added slowly to 1.0 M $AlCl_3$ solution under stirring until its pH reached 4.6, and the suspension was allowed to stand for 2 hours at 40°C. The synthetic gibbsite was electro-dialyzed at a potential gradient of 15 V cm^{-1} until a constant specific electrical conductance was achieved. Finally, the treated sample was dried at 60°C using an IR lamp and then ground to pass a 60-mesh sieve.

Amorphous $Al(OH)_3$ was synthesized following the procedure reported by Huang *et al*. (1977). One litre of 0.5 M $AlCl_3$ solution was titrated gradually with 0.5 M NaOH to pH 7.0. The suspension was aged at room temperature for 48 hours and then centrifuged. The precipitate was washed once with H_2O and then with 95% ethanol until it was free of Cl^-. The washed precipitate was freeze-dried and gently ground into powder using a mortar and pestle, to pass through a 60-mesh sieve.

The X-ray diffraction (XRD) analysis verified that the synthesized gibbsite had good crystallinity but contained a little bayerite. γ-Al_2O_3 had excellent purity but poor crystallinity. No peak was found in the XRD spectra of the amorphous $Al(OH)_3$, indicating that it was completely non-crystalline (Figure 2). The specific surface areas, measured by the N_2 adsorption method, were 32.3, 131.3 and 156.5 m^2 g^{-1} for the gibbsite, γ-Al_2O_3 and amorphous $Al(OH)_3$, respectively.

Determination of surface charge

Surface charge of Al oxides was determined using the potentiometric titration method (Parks & de Bruyn, 1962). For charge determination, 0.4 ml 0.1 M HNO_3 was added to 25 ml of the suspension containing 0.10 g Al oxide, using either 1 mM or 100 mM $NaNO_3$ as supporting electrolyte. Then, all the treatments including the control ($NaNO_3$ solution) were titrated with 0.1 M NaOH solution at 25°C using an automatic titration system (TIM 854, Radiometer Analytical, Lyon, France) to cover the pH range of
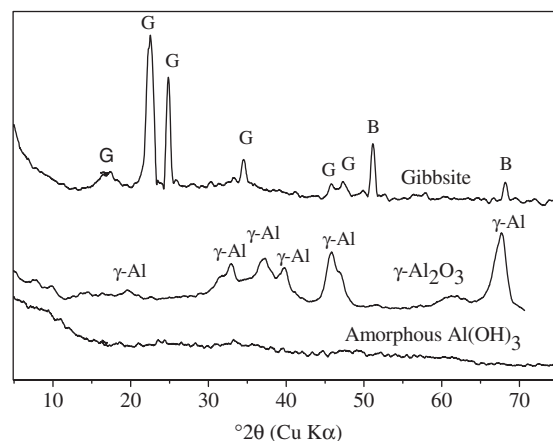

Figure 2 X-ray diffraction spectra of aluminum oxides. G = gibbsite; B = bayerite; γ-Al = γ-Al_2O_3.

4–10 in a nitrogen atmosphere. The adsorption of OH^- by Al oxides at different pH was determined by subtracting the value of the control from that of the samples. Net surface charge was calculated from the amount of OH^- adsorbed relative to the point of zero charge, and the point of zero charge was located at the intersection of the titration curves obtained at various ionic strengths. The surface charge of kaolinite and Alfisol was determined with the modified Schofield method (Pansu & Gautheyrou, 2006).

Electrodialysis procedure

The electrodialysis procedure was used to accelerate acidification of kaolinite and the Alfisol and purification of the samples by increasing the removal rate of base cations from soil surfaces using an applied electrical field, as in the procedure described elsewhere (Li *et al*., 2012). The electrodialysis cell was composed of three chambers, separated from each other with a cellophane membrane. The chamber in the middle was packed with soil samples and the cathode- and anode-chambers, separately on the two sides, were filled with deionized water. During electrodialysis, cations in the soil solution and on the surface exchange sites migrated to the cathode chamber (increasing pH) and anions to the anode chamber (decreasing pH), and mobile anions and cations on the soil surface were replaced by OH^- and H^+, respectively. The

water in the two side-chambers was renewed frequently until a small and constant electrical conductivity (EC) of the water was reached after 8–12 hours of electrodialysis. Therefore, the electro-dialyzed aluminosilicates in the soil were more or less saturated with H$^+$, containing few other exchangeable cations (Wilson, 1929; Mattson, 1933). Exchangeable H$^+$ on clay minerals is reactive and can dismantle the mineral lattices by reacting with structural Al^{3+}. This reaction eventually leads to release of Al^{3+} ions to soil surface cation exchange sites and subsequently soil acidification occurs (Coleman & Craig, 1961; Zhang *et al*., 1991). The whole process is identical to that of natural acidification of the soil in tropical and sub-tropical regions (Yu, 1997; Li *et al*., 2012).

In the electrodialysis experiment, samples of kaolinite or Alfisol, 60 g each, mixed with varying amounts of Al oxides were first dispersed ultrasonically (40 kHz in frequency and 300 W in power) in 500 ml of deionized water for 30 minutes, and then electrodialyzed at a potential gradient of 15 V cm^{-1}. Finally, the treated samples were dried at 60°C under an IR lamp (except for those containing amorphous Al(OH)$_3$, which were freeze-dried) and ground to pass a 60-mesh sieve.

In order to investigate how Al oxides affect properties of kaolinite and Alfisol during electrodialysis, kaolinite or Alfisol with and without γ-Al$_2$O$_3$ was prepared as described above and was sub-sampled four times during the period of electrodialysis. The first and fourth sub-samples were collected at the beginning and the end of electrodialysis, respectively. For kaolinite and the Alfisol samples, the end came after 360 and 720 hours, respectively, which was mainly determined by properties of the sample, such as pH, CEC and sample suspension concentration. The second and third sub-samples were collected at 24 and 120 hours, respectively, after the start of electrodialysis for the kaolinite systems, and at 72 and 360 hours for the Alfisol. All treated samples were dried at 60°C under an IR lamp and then ground to pass a 60-mesh sieve.

Soil pH was measured in suspension (1:2.5 soil:water ratio), using deionized water. Exchangeable base cations were extracted with 1.0 M ammonium acetate solution, and Ca^{2+} and Mg^{2+} were analysed by atomic adsorption spectrophotometry and K$^+$ and Na$^+$ by flame spectrophotometry. Samples not subjected to electrodialysis, were washed three times with deionized water and then three times with 95% ethanol to remove soluble salts before exchangeable base cations were determined. Exchangeable acidity (sum of exchangeable Al^{3+} and H$^+$ extracted with 1 M KCl solution) was determined by alkaline titration. Effective cation exchange capacity (ECEC) (sum of exchangeable acidity and exchangeable base cations) represents effective negative counter-ion charge of soils (Li *et al*., 2012). Exchangeable acidity, exchangeable base cations and ECEC were all calculated using the quantities of kaolinite and the Alfisol in the mixtures. As the content of Al oxides in the mixtures was very small and the negative charge carried by Al oxides was also small, their contributions to the exchangeable acidity, exchangeable base cations and ECEC were negligible.

Effect of ionic strength on effective cation exchange capacity

Each electrodialyzed sample, 1.00 g in weight, was put into a plastic bottle with 24 replicates each. The samples were dispersed in solutions of KNO$_3$ varying in concentration at a soil: water ratio of 1:25 and KNO$_3$ in the solution was added as ionic strength adjustor at 0, 0.5, 1.0, 2.0, 5.0 and 10.0 mM for the kaolinite systems, and at 0, 2.0, 5.0, 10.0, 15.0 and 20.0 mM for the Alfisol systems. Each treatment had four replicates. The suspensions were shaken in a constant-temperature water bath at 25($\pm$1)°C for 4 hours. During this period, the samples were taken out twice for adjusting pH with 0.01 M HNO$_3$ or NaOH solution to the same value as that of the suspensions of the samples without KNO$_3$.

After standing overnight at 25 ($\pm$1)°C, the suspensions were centrifuged at 2204 *g* for 5 minutes. The supernatants were filtered after centrifugation and stored for determination of EC, active acidity and soluble base cations (Ca^{2+}, Mg^{2+}, K$^+$ and Na$^+$). Ionic strength (I) was calculated as I = 0.013 EC (Griffin & Jurinak, 1973).

The bottle containing the sample and the residual solution was weighed again to obtain the quantity of the residual solution. Of the four treatment replicates, two were used for measurement of exchangeable acidity and the other two for determination of exchangeable base cations. For the former, exchangeable acidity was extracted with 50 ml 1 m KCl solution and then analysed by using the alkaline titration method. It is obvious that the exchangeable acidity measured in this way includes active acidity in the residual solution. Thus the active acidity in the residual solution was also determined with the alkaline titration method and should be deducted in the calculation of exchangeable acidity.

Exchangeable base cations were measured as described, but the content of the soluble base cations in the residual solution was deducted. The soluble base cations were measured using the same method as for measurement of the exchangeable base cations. Effective CEC is given as the sum of the exchangeable acidity and exchangeable base cations and represents the amount of effective negative charge of kaolinite and the Alfisol. Exchangeable acidity, exchangeable base cations and ECEC were all calculated on the basis of the quantity of kaolinite and the Alfisol in the mixtures.

X-ray diffraction analysis

Fifty milligrams of the electrodialyzed kaolinite or its mixture with Al oxides was placed on a glass slide with several drops of acetone to make a slurry, which was then dried and subjected to XRD using Co Kα radiation generated at 40 kV and 20 mA with a Rigaku X-ray diffractometer (Rigaku Rotaflex Model RU-200, Tokyo, Japan) equipped with an incident beam graphite monochromator. XRD patterns of γ-Al$_2$O$_3$, gibbsite and amorphous Al(OH)$_3$ were also measured with Cu Kα radiation. The XRD spectra were recorded from 2 to 70° 2θ with 0.01° 2θ steps at a scanning rate of 2° 2θ minute^{-1} in continuous mode.
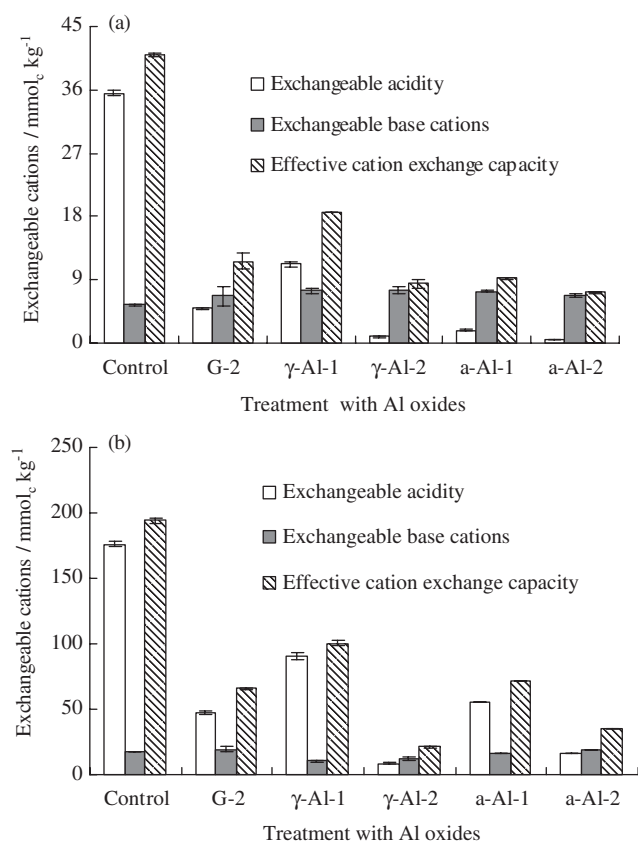
Figure 3 Effect of Al oxides on the exchangeable cations of kaolinite (a) and an Alfisol (b) after electrodialysis. Error bars denote standard deviation ($n = 2$). G = gibbsite; γ-Al = γ-Al$_2$O$_3$; a-Al = amorphous Al(OH)$_3$; 1 and 2 represent the percentages of Al oxides in their mixtures with kaolinite (7.5 and 15%) or with an Alfisol (10 and 20%), respectively.

Results

Effect of Al oxides on acidity and ECEC of kaolinite and an Alfisol

Both kaolinite and the Alfisol were close to neutral in pH and saturated with exchangeable base cations before electrodialysis (Table 1). Electrodialysis released more than 83.1% of the exchangeable base cations from the surface exchange sites of kaolinite in the control system, and the corresponding value in the Alfisol system was 92.3% (Figure 3). Electrodialyzed kaolinite and Alfisol became strongly acidified with pH lowered to about 4.5 and were almost saturated with exchangeable acidity. The exchangeable acidity occupied 86.7 and 90.7% of their surface cation exchange sites, respectively (Figures 3 and 4). These findings demonstrate that all the samples were electrodialyzed thoroughly to reach an ultimate acidification status.

However, the addition of Al oxides evidently inhibited the decrease of pH and decreased the content of exchangeable acidity of electrodialyzed kaolinite and the Alfisol mixed with Al oxides (Figures 3 and 4). For example, after electrodialysis, the exchangeable acidity was 35.56 mmol$_c$ kg^{-1} for the control
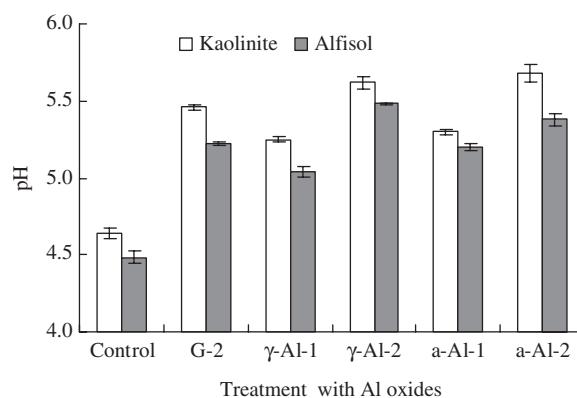

Figure 4 Effect of Al oxides on the pH of kaolinite and Alfisol after electrodialysis. Error bars denote standard deviation ($n = 2$). G = gibbsite; γ-Al = γ-Al$_2$O$_3$; a-Al = amorphous Al(OH)$_3$; 1 and 2 represent the percentages of Al oxides in their mixtures with kaolinite (7.5 and 15%) or with an Alfisol (10 and 20%), respectively.
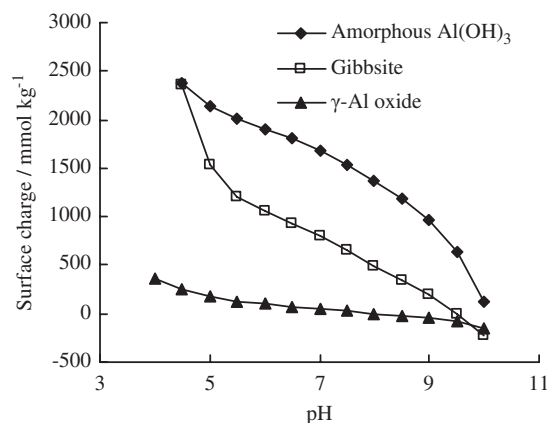

Figure 5 Surface charge of aluminum oxides measured in 0.1 M NaNO$_3$ with the acid-base titration method. γ-Al oxide: γ-Al$_2$O$_3$.

kaolinite system, and for the systems of kaolinite mixed with 15% Al oxides it was 0.97 mmol$_c$ kg^{-1} for γ-Al$_2$O$_3$, 4.97 mmol$_c$ kg^{-1} for gibbsite and 0.49 mmol$_c$ kg^{-1} for amorphous Al(OH)$_3$. This shows that the addition of Al oxides decreased exchangeable acidity by 97.3, 86.1 and 98.6%, respectively. The pH values in corresponding binary systems containing kaolinite and Al oxide increased by 0.98 for γ-Al$_2$O$_3$, 0.81 for gibbsite and 1.04 for amorphous Al(OH)$_3$, as compared with the control kaolinite system. The same phenomena were observed in the Alfisol systems when mixed with 20% Al oxides. Therefore, Al oxides effectively inhibited acidification of kaolinite and the Alfisol during electrodialysis, and their efficiency followed the order of γ-Al$_2$O$_3$ ≈ amorphous Al(OH)$_3$ > gibbsite. This effect is inconsistent with the order of the surface positive charge per unit mass that the Al oxides carried in the range of pH 3–7 (Figure 5).

The addition of Al oxides decreased the ECEC of kaolinite and the Alfisol after electrodialysis. Compared with ECEC in the control kaolinite system, the ECECs of kaolinite in the binary

systems with 15% Al oxides decreased by 79.3% for γ-Al$_2$O$_3$, 71.5% for gibbsite and 77.5% for amorphous Al(OH)$_3$. The corresponding values in the binary systems containing the Alfisol and 20% Al oxides were 89.2% for γ-Al$_2$O$_3$, 66.1% for gibbsite and 82.0% for amorphous Al(OH)$_3$. The effect of Al oxides on decreasing the ECEC of kaolinite and the Alfisol followed the same order as their abilities to inhibit acidification of the two samples.

Effect of amount of Al oxides added on acidity and ECEC of kaolinite and Alfisol

Figures 3 and 4 show that the effect of Al oxides on acidification of kaolinite and Alfisol was related to the amount of Al oxides added. In suspensions of kaolinite and the Alfisol mixed with a large amount of Al oxides, their pH was high and exchangeable acidity small. Hence, a greater amount of Al oxides added led to a greater reduction of acidity of kaolinite and the Alfisol after electrodialysis. In the meantime, the greater amount of Al oxides added also resulted in the greater decrease in the ECEC of electrodialyzed kaolinite and the Alfisol. Aluminium oxides not only decreased the exchangeable acidity of kaolinite and Alfisol, but also reduced the ratio of exchangeable acidity to ECEC.

Comparison between electrodialyzed kaolinite and Alfisol systems showed that Al oxides induced a greater decrease in exchangeable acidity and ECEC in the latter than in the former (Figure 3). For example, the addition of 10% γ-Al$_2$O$_3$ decreased the exchangeable acidity by 86.06 mmol$_c$ kg^{-1} and ECEC by 93.91 mmol$_c$ kg^{-1} for the Alfisol, while the addition of 15% γ-Al$_2$O$_3$ to kaolinite reduced these values by only 33.70 and 31.82 mmol$_c$ kg^{-1}, respectively.

Effect of γ-Al$_2$O$_3$ on dynamics of acidity and ECEC of kaolinite and the Alfisol during the electrodialysis process

The results presented in Figures 6 and 7 indicated that as the electrodialysis proceeded, exchangeable base cations decreased, exchangeable acidity increased and pH declined gradually in the control kaolinite or the Alfisol system and in the binary system containing kaolinite or the Alfisol and γ-Al$_2$O$_3$: this is similar to the process of natural acidification induced by intensive leaching in the tropical and sub-tropical regions. Compared with the control kaolinite or Alfisol system, γ-Al$_2$O$_3$ in the binary systems inhibited the production of exchangeable acidity and reduction of pH significantly. As γ-Al$_2$O$_3$ is weakly alkaline (pH 7.26 in deionized water), γ-Al$_2$O$_3$ in the binary systems of kaolinite or the Alfisol increased pH by 0.25 or 0.12, respectively, in the first sub-sample collected before electrodialysis. However, the corresponding value was 0.98 for kaolinite and 1.00 for the Alfisol, in the fourth sub-sample collected at the end of electrodialysis. Therefore, the direct contribution of γ-Al$_2$O$_3$ alkalinity to an increase in pH of the kaolinite and Alfisol suspensions was very limited.
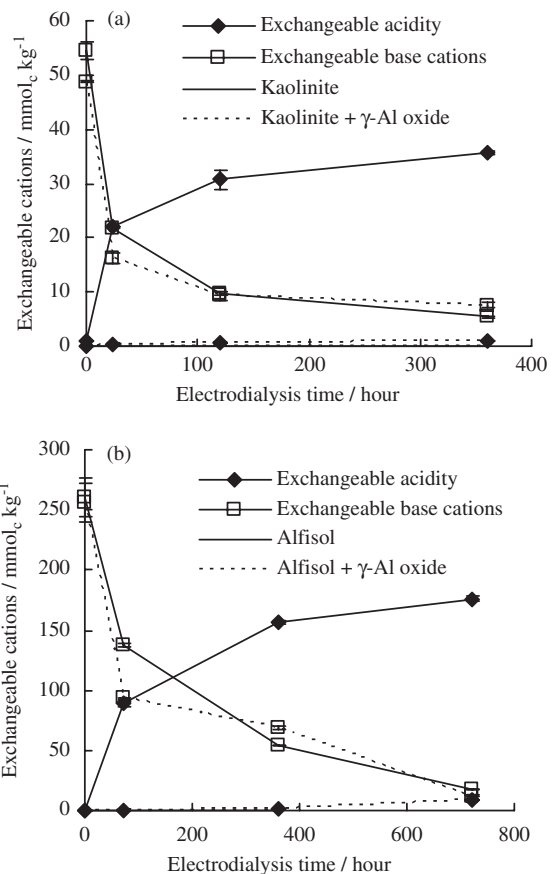

Figure 6 Dynamics of exchangeable acidity and exchangeable base cations of kaolinite (a) and an Alfisol (b) with or without γ-Al$_2$O$_3$ (γ-Al oxide) during electrodialysis process. Error bars denote standard deviation ($n = 2$).

The results in Figure 7 also display ECEC of kaolinite and the Alfisol, which decreased gradually as electrodialysis proceeded; the presence of γ-Al$_2$O$_3$ accelerated the decrease. For example, the differences in ECEC between the control kaolinite and the kaolinite with 15% γ-Al$_2$O$_3$ were 6.59, 28.04, 30.39 and 32.54 mmol$_c$ kg^{-1} after electrodialysis for 0, 24, 120 and about 360 hours, respectively; the corresponding values for the Alfisol systems with and without 20% γ-Al$_2$O$_3$ were 5.49, 132.24, 140.64 and 173.29 mmol$_c$ kg^{-1} after electrodialysis at 0, 72, 360 and about 720 hours, respectively.

Effect of ionic strength on ECEC of electrodialyzed kaolinite and Alfisol

Figure 8 shows the effect of ionic strength on ECEC of electro-dialyzed kaolinite and the Alfisol with or without Al oxides. The data indicate that the smaller the ionic strength, the greater the difference in ECEC between control kaolinite or the Alfisol system and their respective binary systems with Al oxides. Moreover, increase in ionic strength had little effect on ECEC in the control systems, but raised ECEC markedly in the binary systems with
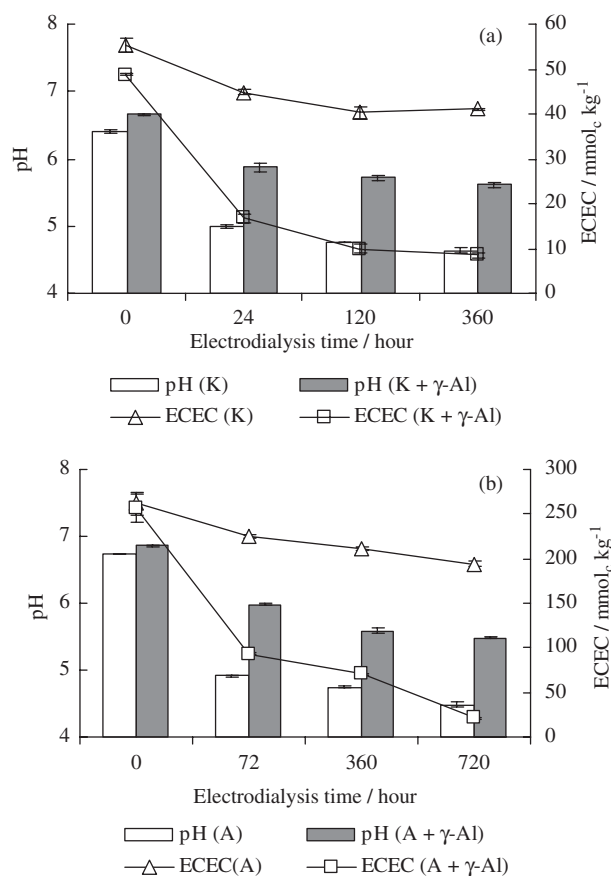
Figure 7 Effective cation exchange capacity (ECEC) and pH of kaolinite (a) and an Alfisol (b) with or without γ-Al$_2$O$_3$ when subjected to electrodialysis with different times. Error bars denote standard deviation ($n = 2$). K = kaolinite; A = Alfisol; γ-Al = γ-Al$_2$O$_3$.

Figure 8 Effect of ionic strength on effective cation exchange capacity (ECEC) of electrodialyzed kaolinite (a) and an Alfisol (b) mixed with Al oxides. The content of Al oxides accounted for 15 and 20% of their mixtures with kaolinite and Alfisol, respectively. Error bars denote standard deviation ($n = 2$). K = kaolinite; A = Alfisol; γ-Al = γ-Al$_2$O$_3$; G = gibbsite; a-Al = amorphous Al(OH)$_3$.

Al oxides. For example, with ionic strength increasing from 0.56 to 26.46 mM, ECEC of electrodialyzed kaolinite in the control system increased by only 1.27 mmol$_c$ kg^{-1}; when ionic strength rose from 0.31 to 27.04 mM, the ECEC of electrodialyzed kaolinite in the binary system mixed with 15% γ-Al$_2$O$_3$ increased by 28.76 mmol$_c$ kg^{-1}. However, an increase in the already large ionic strength induced little increase in ECEC of the binary systems, especially those with γ-Al$_2$O$_3$ or amorphous Al(OH)$_3$. For instance, when ionic strength increased from 12.94 to 27.43 mM, the ECEC of electrodialyzed kaolinite in the binary system with 15% amorphous Al(OH)$_3$ increased only by 1.57 mmol$_c$ kg^{-1}; when ionic strength increased from 40.95 to 53.47 mM, ECEC of electrodialyzed Alfisol in the binary system with 20% amorphous Al(OH)$_3$ increased only by 2.90 mmol$_c$ kg^{-1}. These results demonstrate that a further increase in ionic strength would not have much further effect in increasing ECEC. The data in Figure 8 and Table 2 show that there was still a big difference in ECEC of kaolinite or the Alfisol between control systems and their respective binary systems with Al oxides at a large ionic strength. These results indicate that the changes in ECEC of electrodialyzed kaolinite or Alfisol in the binary systems with Al oxides were not
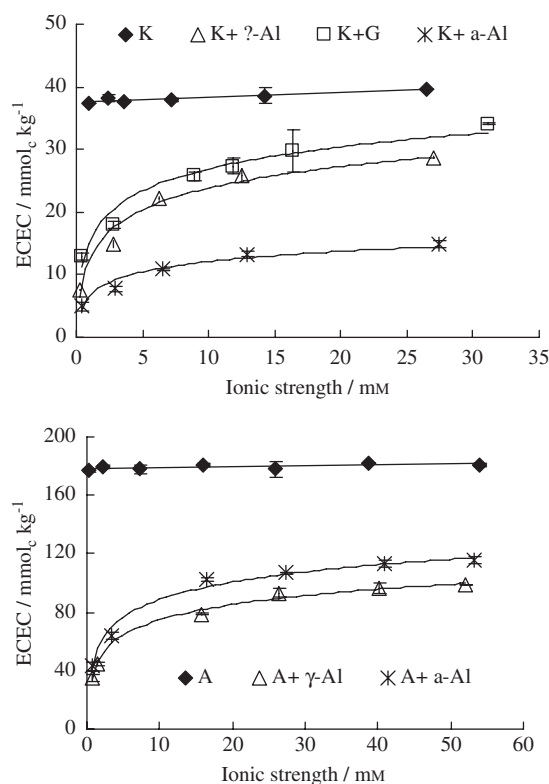
completely reversible with the change in ionic strength of the bathing solution.

Discussion

Mechanisms for inhibition of acidification by Al oxides

When kaolinite and the Alfisol were electrodialyzed to a final acidity, their negatively charged sites were primarily saturated with exchangeable H$^+$ and Al^{3+}. Thus, soil exchangeable acidity (the total amount of exchangeable H$^+$ and Al^{3+}) should be closely correlated with the negative charge properties of the soil. Effective CEC is the sum of exchangeable acidity and exchangeable base cations and our results (Figure 3) demonstrate that Al oxides reduced the acidity of kaolinite and the Alfisol mainly by decreasing the effective negative charge on surfaces of these materials.

Aluminium oxides carried a positive charge when pH varied within the range of 4–7 (Figure 5), while kaolinite and the Alfisol generally carried a net negative charge when pH was greater than 4. When charged particles of kaolinite and Alfisol are dispersed in water, electric double layers form on the surfaces of these charged particles. Moreover, when oppositely charged

Table 2 Changes in effective cation exchange capacity (ECEC) of the electrodialyzed kaolinite or the Alfisol mixed with different amounts of Al oxides in KNO_3 solutions different in ionic strength (IS)

Aluminum oxides added	Addition rate[a] / %	IS_1[b]	IS_2[b]	$ECEC_1$[c]	$ECEC_2$[c]	$\Delta ECEC_1$[d]	$\Delta ECEC_2$[d]
		/ mм		/ $mmol_c$ kg^{-1}			
Kaolinite							
Control	—	0.95	26.4	37.3	39.6	1.3	—
Gibbsite	15	0.46	31.2	12.9	34.1	21.2	5.5
γ-Al_2O_3	7.5	0.17	27.6	14.1	32.0	17.9	7.6
	15	0.31	27.0	7.5	28.8	21.3	10.8
Amorphous	7.5	0.29	28.0	9.2	22.6	13.4	17.1
Al (OH)$_3$	15	0.30	27.4	4.9	14.9	10.0	23.7
Alfisol							
Control	—	0.30	53.9	177	181	4	—
Gibbsite	20	0.82	52.1	93	143	50	38
γ-Al_2O_3	10	0.38	52.3	103	127	24	54
	20	0.65	52.1	36	99	63	82
Amorphous	10	0.86	51.7	76	132	56	48
Al(OH)$_3$	20	0.61	53.2	44	116	72	65

[a]Addition rate = the percentage of Al oxides in the mixtures with kaolinte or Alfisol.
[b]IS_1 was measured in the sample solution without KNO_3 electrolyte, and IS_2 was measured in sample solutions with 10.0 mм KNO_3 for kaolinite and 20.0 mм KNO_3 for the Alfisol, respectively.
[c]$ECEC_1$ and $ECEC_2$ of kaolinite or the Alfisol with and without Al oxides were determined under the conditions of IS_1 and IS_2, respectively.
[d]$\Delta ECEC_1$ was the difference between $ECEC_1$ and $ECEC_2$ of each sample; $\Delta ECEC_2$ represented the difference between the $ECEC_2$ of the kaolinite or the Alfisol mixed with Al oxides and the $ECEC_2$ of pure kaolinite or the Alfisol, respectively.

particles co-exist in the same suspension, they move towards each other *via* electrostatic attraction. Aluminum oxide particles and kaolinite or phyllosilicates present in the Alfisol acted in the same way, and when they are close to each other, the diffuse layers on oppositely charged particles may overlap to some extent. This interaction caused a decrease in the effective negative charge (Wang *et al.*, 2011; Xu *et al.*, 2011). Therefore, compared with the control kaolinite or the Alfisol systems, the binary systems containing Al oxides needed less exchangeable acidity to balance the negative charge even when most of their exchangeable base cations were removed after electrodialysis. The smaller content of exchangeable acidity led to higher pH of the systems containing Al oxides than the control systems of both materials. This is possibly an important mechanism for Al oxides to decrease the effective negative charge and acidity of kaolinite and the Alfisol during electrodialysis and thus inhibit their acidification.

Generally, the greater the positive or negative charge per unit mass carried by oppositely charged particles led to the more extensive overlapping of diffuse layers, and the sharper the decrease in opposite effective charge (Hou *et al.*, 2007a; Li & Xu, 2008). However, the effects of Al oxides in reducing effective negative charge did not follow exactly the same order as that of positive charge per unit mass carried by Al oxides (Figures 3 and 5). This phenomenon did not conform to the characteristics of overlapping of diffuse layers of electric double layers on oppositely charged particles. Therefore, as well as overlapping of diffuse layers between oppositely charged particles, there is another factor, such as coating, that may also contribute to the

decrease in effective negative charge of kaolinite and Alfisol during electrodialysis.

The first dissociation constant (pKa_1) of Al^{3+} in water is about pH 5 and pH in this study varied between 4.5 and 7.0. Aluminium oxides under this condition are very active and reactions of hydrolysis, polymerization, precipitation and transformation can occur with changes of environmental conditions (Sposito, 1996). For example, diffuse reflectance Fourier-transformed infrared spectroscopic investigation shows that the surface of γ-Al_2O_3 was transformed into a bayerite polymorph upon ageing in solution (Arai *et al.*, 2001). Thus, the abundant hydroxyl groups on Al oxide surfaces create a layer of coating on silicates with hydrogen and coordination bonds (Goldberg, 1989; Beauvais & Bertaux, 2002; Orolínová & Mockovčiaková, 2009; Villalba *et al.*, 2010). McAtee & Wells (1967) verified with electron microscopy that, when kaolinite was mixed with gibbsite, the clay particles were coated by Al oxides. Aluminium oxides carry positive charge under acid conditions; the coating of Al oxides blocks the negative charge sites and decreases the effective negative charge of silicates (Zhang & Zhang, 1992; Zhuang & Yu, 2002). In addition, the Alfisol also contained vermiculite (an open 2:1 phyllosilicate). Aluminium oxides may be inserted into the interlayer of vermiculite to form hydroxyl Al-interlayers. This insertion also blocks the negative charge sites, and decreased the effective negative charge of the Alfisol (Goldberg, 1989). Therefore, less exchangeable acidity was needed to balance the negative charges and this resulted in the less acidity with Al oxides after electrodialysis. Because the vermiculite in the Alfisol was present in only small

quantities and the effect of hydroxyl Al-interlayer formation on the charge and acidity properties of the Alfisol may be limited and not easily distinguishable from surface coating, this mechanism is not discussed further in any detail.

Kaolinite and the Alfisol both contained variable charge. The charge magnitude and sign on their surfaces depend on chemical characteristics of the bathing solution such as pH and ionic strength (Chorover & Sposito, 1995; Yu, 1997). During the electrodialysis process, pH and ionic strength of the sample suspensions decreased gradually over time. The decline of pH and ionic strength led to the reduction of negative charge of these materials and was the main cause of the gradual decrease in their ECEC during electrodialysis. Moreover, decrease in ionic strength also favours the expansion of the diffuse layers on positively charged γ-Al_2O_3 and negatively charged kaolinite or the Alfisol. The expansion enhances overlapping of the diffuse layers on oppositely charged particles. The greater extent of the overlapping led to more opposite charges being neutralized (Li & Xu, 2008; Li *et al.*, 2009). Thus, the decreasing ECEC induced by γ-Al_2O_3 became more evident during electrodialysis (Figure 7). Of course, the effect of coating cannot be ignored. Because electrodialysis induced a decline in the pH of the binary systems containing γ-Al_2O_3 and kaolinite or the Alfisol from 6.8 to about 5.5, γ-Al_2O_3 would also become more active at lower pH and the effect of coating on blocking negative charge become stronger. This coating in turn led to a gradual decrease in ECEC of both materials mixed with γ-Al_2O_3 during electrodialysis. Therefore, the sharp decrease in ECEC of kaolinite or the Alfisol induced by γ-Al_2O_3 had the substantial effect of inhibiting the production of exchangeable acidity and reduction of pH during electrodialysis.

The overlapping of diffuse layers between positively charged Al oxides and negatively charged kaolinite or the Alfisol becomes greater with a greater amount of added Al oxide (Hou *et al.*, 2007a,b). Coating of Al oxides would also increase with the amount of Al oxides added, intensifying their effect of decreasing ECEC and acidity. The Alfisol had a larger CEC than kaolinite (Table 1) and thus carried a greater negative charge per unit mass. Therefore, the effect of Al oxides in decreasing effective negative charge through diffuse layer overlapping and coating was also more significant in the Alfisol than in kaolinite. The larger decrease in ECEC led to a greater drop in exchangeable acidity of the Alfisol.

Relative contribution of diffuse layer overlapping and coating of Al oxides

Overlapping of the diffuse layers on oppositely charged particles and its effect on neutralizing opposite charge are completely reversible with change of ionic strength (Qafoku & Sumner, 2002; Li *et al.*, 2009). However, coating is irreversible and its effect on blocking negative charge of silicates changes less with changing ionic strength (Goldberg, 1989). The changes in ECEC of kaolinite and the Alfisol in the binary systems containing Al oxides were not completely reversible with ionic strength. This

result demonstrates the occurrence of overlapping of diffuse layers and coating, underlying the interaction of Al oxides with kaolinite or Alfisol.

The ionic strength experiments were conducted to differentiate the contributions of the two mechanisms to decreasing ECEC in the binary systems containing Al oxides during electrodialysis. The restoration of the amount of ECEC of electrodialyzed kaolinite or the Alfisol mixed with Al oxides with increasing ionic strength ($\Delta ECEC_1$ in Table 2) was ascribed to the effect of diffuse layer overlapping. The difference in ECEC between the control systems and their respective binary systems containing Al oxides, both with large ionic strength ($\Delta ECEC_2$ in Table 2), was ascribed to the effect of coating. The data in Table 2 indicate that in the kaolinite binary systems, overlapping of diffuse layers contributed more than the coating to the decrease in ECEC in the case of gibbsite or γ-Al_2O_3; an opposite trend occurred in the case of amorphous $Al(OH)_3$. In the Alfisol binary systems, the two mechanisms showed comparable effects, regardless of type of Al oxides, in decreasing ECEC. The two mechanisms for decreasing ECEC in the binary systems intensified with increasing amounts of Al oxides added and the effect was greater in the Alfisol. These findings confirm the inferences made earlier. What is more, gibbsite was less effective than γ-Al_2O_3 and amorphous $Al(OH)_3$ in decreasing the ECEC of kaolinite and the Alfisol through coating and this may be because gibbsite was more crystalline than γ-Al_2O_3 and amorphous $Al(OH)_3$ (Figure 2). These findings also explain why gibbsite, with more positive charge per unit mass than γ-Al_2O_3, is less effective than γ-Al_2O_3 in decreasing ECEC and acidity of kaolinite and the Alfisol during electrodialysis.

The results in Figure 9 indicate that the addition of 15% Al oxides apparently decreased the peak intensity of kaolinite; this decrease was attributed to the smaller content of kaolinite and surface coating on kaolinite in its mixtures with Al oxides (Ioannou & Dimirkou, 1997). Because the contents of kaolinite in the mixtures with three different types of Al oxides were the same,
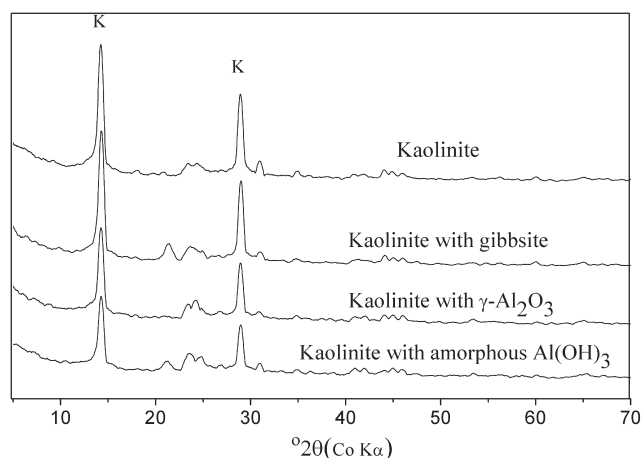

Figure 9 X-ray diffraction spectra of kaolinite mixed with gibbsite, γ-Al_2O_3 or amorphous $Al(OH)_3$ (15% in proportion) after electrodialysis. K = kaolinite.

different peak intensities of kaolinite in these mixtures reflected the extent of coating of these Al oxides on the surface of kaolinite. Based on peak intensities of kaolinite, it can be concluded that the three types of Al oxides followed the order gibbsite $< \gamma\text{-}Al_2O_3 <$ amorphous $Al(OH)_3$ in terms of extent of coating; this was consistent with their effects of decreasing ECEC of kaolinite through coating (Table 2). These results demonstrated that coating was also an important mechanism for inhibiting acidification of kaolinite and the Alfisol during electrodialysis.

Conclusions

According to the traditional acidification theory, variable-charge soils are supposed to be strongly acidified because they have been subjected to intensive leaching. Moreover, intensive weathering results in large contents of free Al and Fe oxides in variable-charge soils. The results in this study indicate that Al oxides can very effectively inhibit acidification of kaolinite and an Alfisol. The overlapping of diffuse layers of electric double layers between positively charged Al oxides and negatively charged kaolinite or Alfisol and coating of Al oxides on kaolinite or Alfisol were responsible for inhibition of the acidification by Al oxides, because diffuse layer overlapping and coating markedly decreases effective negative charge and exchangeable acidity of kaolinite and Alfisol during electrodialysis. As electrodialysis can simulate leaching-induced soil acidification in tropical and sub-tropical regions very well, Al and Fe oxides can act as important agents in inhibiting natural acidification of variable-charge soil under intensive weathering and leaching (Li *et al.*, 2012). However, the traditional acidification theory did not involve the interaction between oppositely charged particles and its effect on the charge properties and soil acidity. Therefore, it cannot explain the phenomenon of soil acidification in variable-charge soils (Li *et al.*, 2012). The mechanism of Al oxides in inhibiting natural acidification of variable-charge soils through interaction of electric double layers and coating may offer an important supplement to the traditional theory of natural acidification of soils.

Acknowledgements

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