



# Effect of organic acids on adsorption and desorption of rare earth elements

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## Abstract

Effect of citric, malic, tartaric and acetic acids on adsorption of La, Ce, Pr and Nd by and desorption from four typical Chinese soils was studied. Generally, adsorption capacities of rare earth elements (REEs) were significantly correlated with the cation exchange capacity (CEC) of soils. In the presence of acetic acids adsorption of REEs was similar to that in the presence of  $\text{Ca}(\text{NO}_3)_2$ . However, in the presence of citric, malic and tartaric acids adsorption of REEs by Heilongjiang, Zhejiang and Guangdong soils decreased to varying extents if compared with that in the presence of nitrate and acetic acid. The significance of suppression followed the order of citric acid > malic acid > tartaric acid > acetic acid, which was consistent with the order of stability of complexes of REEs with these organic acids. However, the adsorption increased with increasing equilibrium solution pH. For Jiangxi soil with low soil pH, CEC and organic matter these organic acids exerted an even more serious suppression effect on the adsorption of REEs. Another feature of the relationship between the adsorption of REEs and equilibrium solution pH was that the adsorption of REEs decreased with increase of pH from 2 to 4.5 and then slightly increased with further increase of pH. Desorption of REEs varied with soils and with organic acids as well. REEs were released easily from Heilongjiang, Zhejiang and Guangdong soils in the presence of organic acid. Generally, desorption of REEs decreased with increasing equilibrium solution pH. Effect of organic acids on desorption of REEs from Jiangxi soil was more complicated. In the presence of citric and malic acids no decrement and/or slight increase in desorption of REEs were observed over the equilibrium solution pH from 3 to 6.5. The reasons for this were ascribed to the strong complexing capacity of citric and malic acids and low soil pH, CEC and organic matter of Jiangxi soil. © 2002 Published by Elsevier Science Ltd.

*Keywords:* Adsorption; Desorption; Organic acids; Rare earth elements

## 1. Introduction

In recent years, more and more rare earth elements (REEs) enter the environment through various pathways because of the rapid increase of the exploitation of REE resources and its applications to modern industry and daily life (Volokh et al., 1990). Moreover, millions of tons of fertilizers containing REEs are used world-

wide for increasing agricultural productivity (Bremmer, 1994). In China, the fertilizer containing REEs for agriculture use was estimated to cover  $(16\text{--}20) \times 10^6$  ha in 1995 (Tu et al., 1994). It has been forecasted that the agricultural usage of the fertilizers containing REEs might result in environmental problems in the next few decades (Volokh et al., 1990). REEs from anthropogenic sources usually get into the environment in biologically available forms, which are of particular concern because they may dislocate the balance of the biogeochemical cycle of these species. A comprehensive study is needed to determine the behavior of REEs in different soils.

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It is well established that the bioavailability, and potential toxicity or deficiency of trace metal ions in soils depend on their concentrations in the soil solution and on the soil's ability to release trace metal ions from the soil phase to replenish those removed from solutions by plants (Backes et al., 1995). The concentrations of metals in soil solutions are most likely to be controlled by sorption–desorption reactions (Hogg et al., 1993). From this point of view, study on the sorption–desorption reactions of REEs is important. Jones (1997) reported that adsorption of La, Y, Pr and Gd depended on soil pH and cation exchange capacity (CEC). The adsorption appeared to conform well to the single Langmuir equation. Equilibrium release experiments (Cao et al., 2001) demonstrated that the release of La, Ce, Gd and Y increased with decreasing pH or Eh. It was also reported that the release of REEs were correlated with the release of Fe and Mn, suggesting that the release of REEs originated from dissolution of Fe–Mn oxyhydroxides under the reduced and low soil pH conditions (Li et al., 1998). The adsorption of REEs increased with increasing soil pH (Ran and Liu, 1992, 1993). Li et al. (2001) studied the kinetics of adsorption and desorption of Ce(III) on soil using a batch method and isotope  $^{141}\text{Ce}$ . It was indicated that the Elovich equation proved to fit the data on desorption of Ce(III) from fluvoaquic and black soils well, while the parabolic-diffusion equation were the best models for red earth and loess soils.

It is well recognized that the rhizosphere is a zone of increased microbial activity and biomass under the influence of the plant roots, which can secrete substances such as carbohydrates and low-molecular-weight-organic-acids (LMWOAs). In addition, LMWOAs can also be produced due to breakdown of plant residues. Thus, this zone is distinguished from bulk soil by this root influence (Anderson et al., 1993). LMWOAs are involved in many interactions with the physicochemical properties of soils and capable of forming complexes with metal ions (Robert and Berthelin, 1994; Stevenson and Fitch, 1994). Therefore they play an important role in the sorption and desorption processes of heavy metals (Harter, 1983; Bruemmer et al., 1988; Backes et al., 1995). The leaching procedures and bioavailability of heavy metals have also

been affected by LMWOAs (Zhang et al., 2000; Wang et al., 2001).

It seems that there is no report in the literature on the effect of LMWOAs on sorption and desorption behavior of REEs. Indeed, such a comprehensive knowledge allows one to predict transformation, bioavailability and mobilization of REEs in soils, thus it helps to predict the long-term effect on the environment. To our knowledge this is the first time to address the effect of LMWOAs such as citric, malic, tartaric and acetic acids on adsorption by and desorption behaviors of REEs from soils.

## 2. Materials and methods

### 2.1. Soils and soil characterization

Four surface soils were collected from Jiangxi and Guangdong Provinces (southern China), Zhejiang Province (eastern China), and Heilongjiang Province (northeastern China). All the soil samples were taken from the surface layer (0–20 cm) of cultivated soils. The soils were air dried, sieved to pass through a 20-mesh sieve, homogenized, and stored in polyethylene bags for the further analysis. Soil pH values were measured in soil to water ratio of 1:1 (w/v). CECs were determined by the Rhoades' method (1982) and organic matter contents were determined by the Walkley-Black' method (Nelson and Sommers, 1982). Amorphous iron (Fe) and aluminum (Al) oxides were determined by ammonium oxalate extraction (McKeague and Day, 1966). Crystalline Fe and Al oxides were determined by the oxalate–ascorbic acid extraction method of Shuman (1982). These properties of the soils are given in Table 1. Fertilizer containing La, 27.4%; Ce, 50.8%; Pr, 5.4% and Nd, 15.3% in nitrate form was used as exogenous REEs in this study.

### 2.2. Organic acids

Citric, malic, tartaric and acetic acids were chosen as the representatives of LMWOAs present in the rhizosphere soils. The stability constants of organic acids–REE complexes were different from one to another.

Table 1  
Selected properties of studied soils

Sampling site	Order	CEC (cmol/kg)	pH (1:1)	Organic matter (%)	Fe (%)		Al (%)	
					Crystal.	Amorp.	Crystal.	Amorp.
Jiangxi	Ultisol	14.24	4.63	1.53	3.52	0.72	1.39	0.28
Zhejiang	Ultisol	19.76	7.02	3.28	2.50	0.97	1.07	0.18
Guangdong	Alfisol	15.92	7.56	1.37	2.30	0.36	0.79	0.13
Heilongjiang	Mollisol	21.57	6.00	5.38	2.01	0.35	1.36	0.28

### 2.3. Adsorption isotherms

Adsorption isotherms were performed by batch equilibrium experiments. A portion of 0.500 g of soils was placed in 40 mL of polypropylene centrifuge tubes, then 20 mL of background electrolyte solution of 0.01 mol/L of  $\text{Ca}(\text{NO}_3)_2$  containing different amounts of REE fertilizer were added depending on the adsorption capacity of individual soil.  $\text{Ca}(\text{NO}_3)_2$  was used as supporting electrolyte to eliminate non-specific adsorption of REEs since low affinity sites would be saturated by calcium ions. The mixtures were shaken by end-over-end for 24 h, then centrifuged for 0.5 h at 6000 rpm, and finally filtered through a 0.45  $\mu\text{m}$  of cellulose nitrate membrane. Adsorbed amounts of REEs were calculated from the difference between the amounts added to and the amounts remained in the solution.

### 2.4. Effect of organic ligands and equilibrium solution pH on adsorption of REEs

Effect of organic ligands and equilibrium solution pH on the adsorption of REEs by Heilongjiang and Jiangxi soils was investigated. Different organic acids were prepared at their final concentration of 0.01 mol/L in background electrolyte of 0.01 mol/L  $\text{Ca}(\text{NO}_3)_2$  and their pH values were adjusted with dilute  $\text{Ca}(\text{OH})_2$  in the range of 2.6–7.8. After pH adjusting, certain amount of REEs was added to make the final concentrations of REEs in one supporting electrolyte solutions to be 2.91, 5.39, 0.58 and 1.62  $\mu\text{g}/\text{mL}$  of La, Ce, Pr and Nd, respectively. In another supporting electrolyte the concentrations of La, Ce, Pr and Nd were defined as 10.55, 26.98, 2.29 and 8.12  $\mu\text{g}/\text{mL}$ , respectively. A portion of 0.500 g of soil samples were equilibrated with 20 mL of 0.01 mol/L of organic acid–0.01 mol/L of  $\text{Ca}(\text{NO}_3)_2$  solutions containing REEs at the above mentioned concentration levels under the conditions of continuous shaking for 24 h. Then, the samples were centrifuged at 6000 for 0.5 h, the pH values of equilibration solutions were determined again, and the concentrations of REEs in the equilibration solutions remained were determined as well by using inductively coupled plasma mass spectrometry (ICP-MS) (Wen et al., 1999).

### 2.5. Effect of organic ligands and pH on extractable REEs

Subsamples of 100 g of soils were mixed with 100 mL of 200  $\mu\text{g}/\text{mL}$  of REE fertilizer, and shaken for 48 h. Then, the soils were incubated for three weeks, during this process they were periodically weighed and any weight loss was made up with regular addition of distilled, deionized water. After the soils were incubated for various periods, the supernatant was removed and the concentrations of REEs remained in the supernatants were determined. Then, the soils were air dried, ground

to pass through a 20-mesh sieve, homogenized, and stored in polyethene bags. Duplicate 0.500 g samples of the incubated air-dried soils were placed in polypropylene centrifuge tubes and 20 mL of 0.01 mol/L organic acids were added. The samples were shaken on an end-over-end shaker for 16 h, centrifuged for 0.5 h at 6000 rpm, and filtered through a 0.45  $\mu\text{m}$  membrane. After filtration, the concentrations of REEs in the filtrates were determined by ICP-MS. In addition, pH values of the filtrates were also measured. Since the  $\text{p}K_{\text{a}}$ s of the organic acids vary considerably, the nature of organic acids is different at any given pH with different organic acids. REEs adsorbed in the incubated soils for three weeks were extracted with various organic acids at the pH range between 3.1 and 7.0. The pH values of all organic acids were monitored, and pH variations were only 0.1–0.4 units before and after extraction. REEs in the extracts were determined by ICP-MS.

### 2.6. Determination of REEs

REE concentrations in the extracts were determined by ICP-MS. The instrumental operation parameters were optimized. Indium was added as an internal standard to monitor matrix effects and signal drift. The details were reported previously by Wen et al. (1999).

## 3. Results and discussion

### 3.1. Adsorption isotherms

Owing to the similar physicochemical properties of REEs, adsorption and desorption behaviors of REEs were somewhat alike (Brown et al., 1990). Therefore, only the adsorption isotherms of La were schematically shown in Fig. 1. As can be seen that adsorption amounts of La by various soils increased with increasing concentration of La in the equilibrium solutions. Two isotherm models were used to described adsorption behaviors of REEs by soils. They are the Langmuir equation:  $x/m = K_1 K_2 C / (1 + K_1 C)$  and the Freundlich equation:  $x/m = KC^{1/n}$ , where  $x/m$  is the adsorption amount of La by soil ( $\mu\text{g}/\text{g}$ );  $C$  is the La concentration remained in the equilibrium solution ( $\mu\text{g}/\text{mL}$ );  $K_1$ ,  $K$  and  $n$  are parameters (constants) for the equations.  $K_2$  is the maximum adsorption capacity of La ( $\text{mg}/\text{g}$ ). The results showed that the adsorption of La corresponded to the two equations well ( $\gamma^2 > 0.91$ ,  $p < 0.05$ ). Maximum adsorption capacities of REEs for all soils were shown in Table 2, together with the relationship between the maximum adsorption capacity and soil characteristics. As it was shown that Heilongjiang soil had the highest adsorption capacity, while Jiangxi soil had the least. A significant relationship between maximum adsorption capacity of REEs and CEC of soils was found, with the

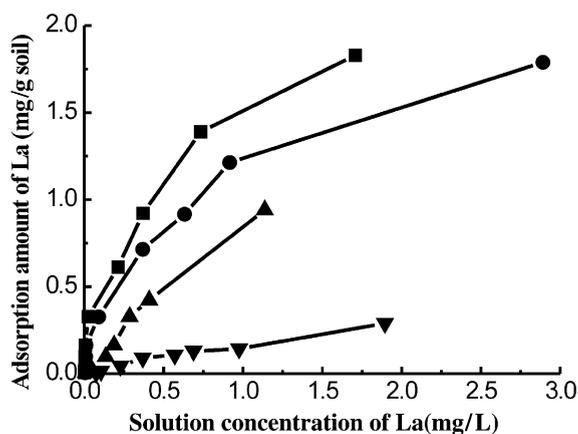


Fig. 1. Adsorption of La in soils in the presence of 0.01 mol/L  $\text{Ca}(\text{NO}_3)_2$  Heilongjiang soil (■); Zhejiang soil (●); Guangdong soil (▲); Jiangxi soil (▼).

range of  $\gamma$  from 0.939 to 0.989. However, only a poor relationship between maximum adsorption capacity and organic matter or total amounts of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  existed.

### 3.2. Effect of organic acids and pH on adsorption of REEs by soils

The concentrations of LMWOAs were reported to be in the range of  $10^{-7}$ – $10^{-4}$  mol/L in the soil pore solutions, even higher in the rhizosphere soils (Stevenson, 1994; Krishnamurti et al., 1997). The concentrations of 1–10 mM of organic acids were used in the sorption and desorption of cadmium (Krishnamurti et al., 1997; Naidu and Harter, 1998). Therefore, a concentration of  $10^{-2}$  mol/L of LMWOAs was chosen in this study to simulate the adsorption of REEs by and desorption from the rhizosphere soils.

The effect of different organic acids and equilibrium solution pH on adsorption of REEs at its various concentration levels by Heilongjiang and Jiangxi soils were shown in Figs. 2 and 3, respectively. Compared the

profiles of the left side with that of the right side (Figs. 2 and 3), one may concluded that when higher amounts of REEs added, total adsorbed REEs increased while adsorption percent decreased. For Heilongjiang soil, in the presence of both  $\text{Ca}(\text{NO}_3)_2$  and acetic acid, near 100% of REEs can be sorbed in the experimental pH range. It seemed that pH did not affect the adsorption behavior of REEs. However, for Jiangxi soil, in the presence of  $\text{Ca}(\text{NO}_3)_2$ , with the pH increase, the sorbed REEs increased from 40% to more than 90%. It was indicated that the affinity between Heilongjiang soil and REEs was larger than that between Jiangxi soil and REEs. In the presence of citric, malic and tartaric acids, adsorption of REEs for both soils decreased obviously. In the mean time, with the pH decreased, the amount of adsorption decrease gradually from Heilongjiang soil. This pH-dependent behavior of heavy metal sorption is generally recognized (Tiller et al., 1979; Naidu and Harter, 1998). Effect of different organic acid on the decrease of REEs adsorption was dissimilar. Among the organic acids studied, effect of citric acid on the decrease of REE adsorption is the most significant, while that of acetic acid is the least. For example, at pH 5 in Heilongjiang soil, the decrease in La adsorption is 20%, 24% and 48% in the presence of tartaric, malic and citric acid, respectively (Fig. 2), while almost no decrement of adsorption occurred when acetic acid was added. The reduction of adsorption of REEs followed the orders: citric acid > malic acid > tartaric acid > acetic acid. This order is in consist with the stability constants of REEs with these organic ligands ( $\log K_1$  for four La-organic acid complexes, Martell and Smith, 1977), indicating the formation of aqueous REEs-organic ligands complexes is one of the important reasons for the adsorption decrease. In the absence of organic ligands system with only electrostatic attraction and repulsion existing, the adsorption of REEs was a function of soil characteristics, while in the presence of organic ligands, there existed a competitive effect for REEs between soil adsorption sites and aqueous organic ligands. The affinity of organic ligands, which causes the decrement of adsorption, was related to the REEs-organic ligand

Table 2

Maximum adsorption capacity  $K_2$  (mg/g) for REEs in four soils and correlation matrix ( $\gamma$ ) for  $K_2$  of REEs and CEC, organic matter (OM), total content of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  (%)

Element	$K_2$ (mg/g)				$\gamma$		
	Heilongjiang	Zhejiang	Guangdong	Jiangxi	CEC	OM	$\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$
La	2.106	2.039	1.249	0.191	0.939 <sup>a</sup>	0.774	-0.779
Ce	4.338	3.963	1.465	0.382	0.989 <sup>b</sup>	0.889	-0.587
Pr	0.467	0.405	0.137	0.046	0.981 <sup>b</sup>	0.876	-0.554
Nd	1.214	1.171	0.386	0.083	0.982 <sup>b</sup>	0.873	-0.537

<sup>a</sup> Significance at 10% level.

<sup>b</sup> Significance at 5% level.

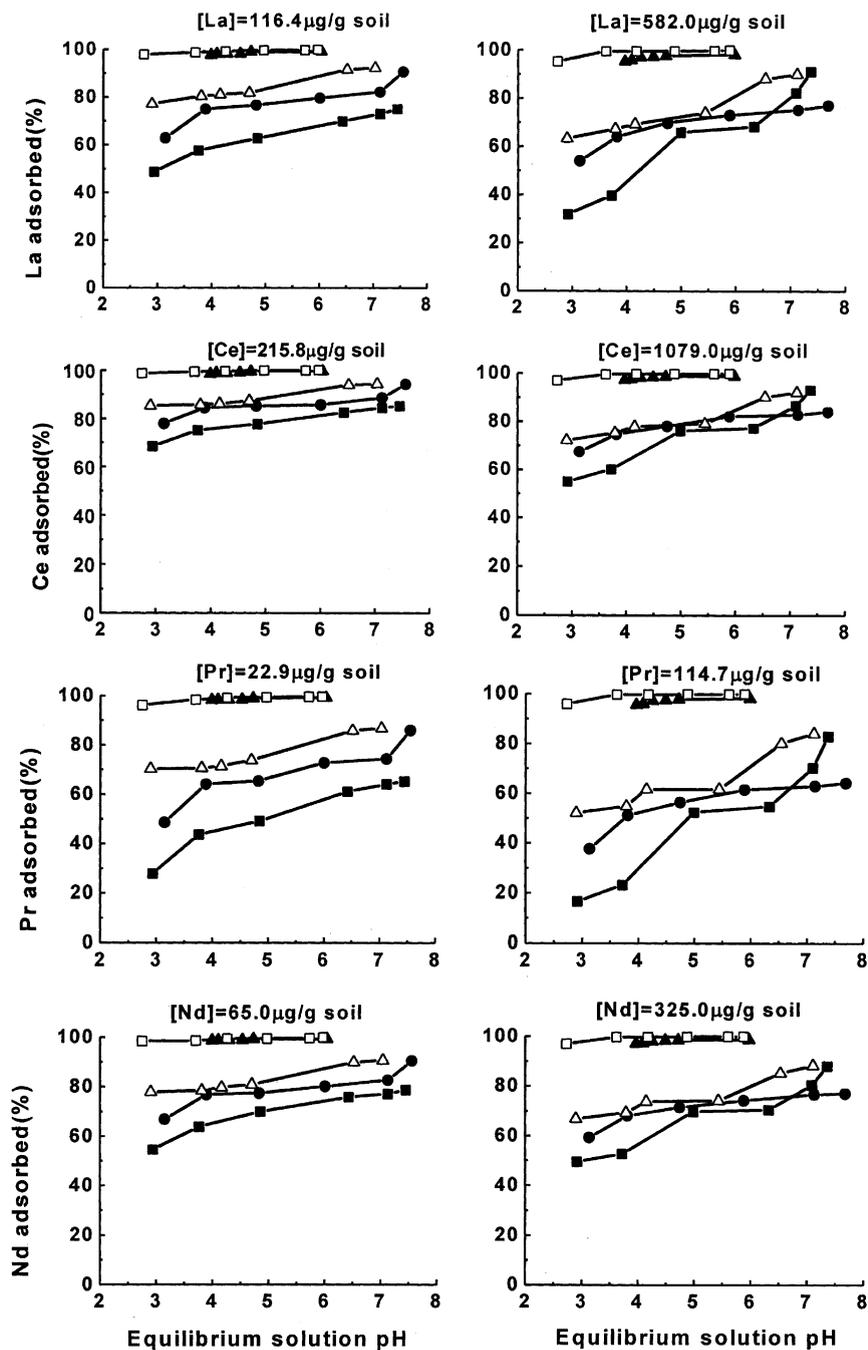


Fig. 2. Effect of organic acids and pH on adsorption of REEs in Heilongjiang soil, organic acids: citric acid (■); malic acid (●); tartaric acid (Δ); acetic acid (▲); nitrate (□).

stability constants and concentration of organic ligand. Soils are a heterogeneous complex system with organic matter; iron-, aluminum-, and manganese-oxides; clay minerals, and miscellaneous other minerals. Each component of soils exhibits its different influence on REEs

entering the soil, precisely quantification of the soil affinity is quite difficult. In many systems, the valence of the adsorbate and adsorbent surface charge influences the heavy metal adsorption strongly (Dalang and Stumm, 1976; Elliott and Huang, 1979). Elliott and

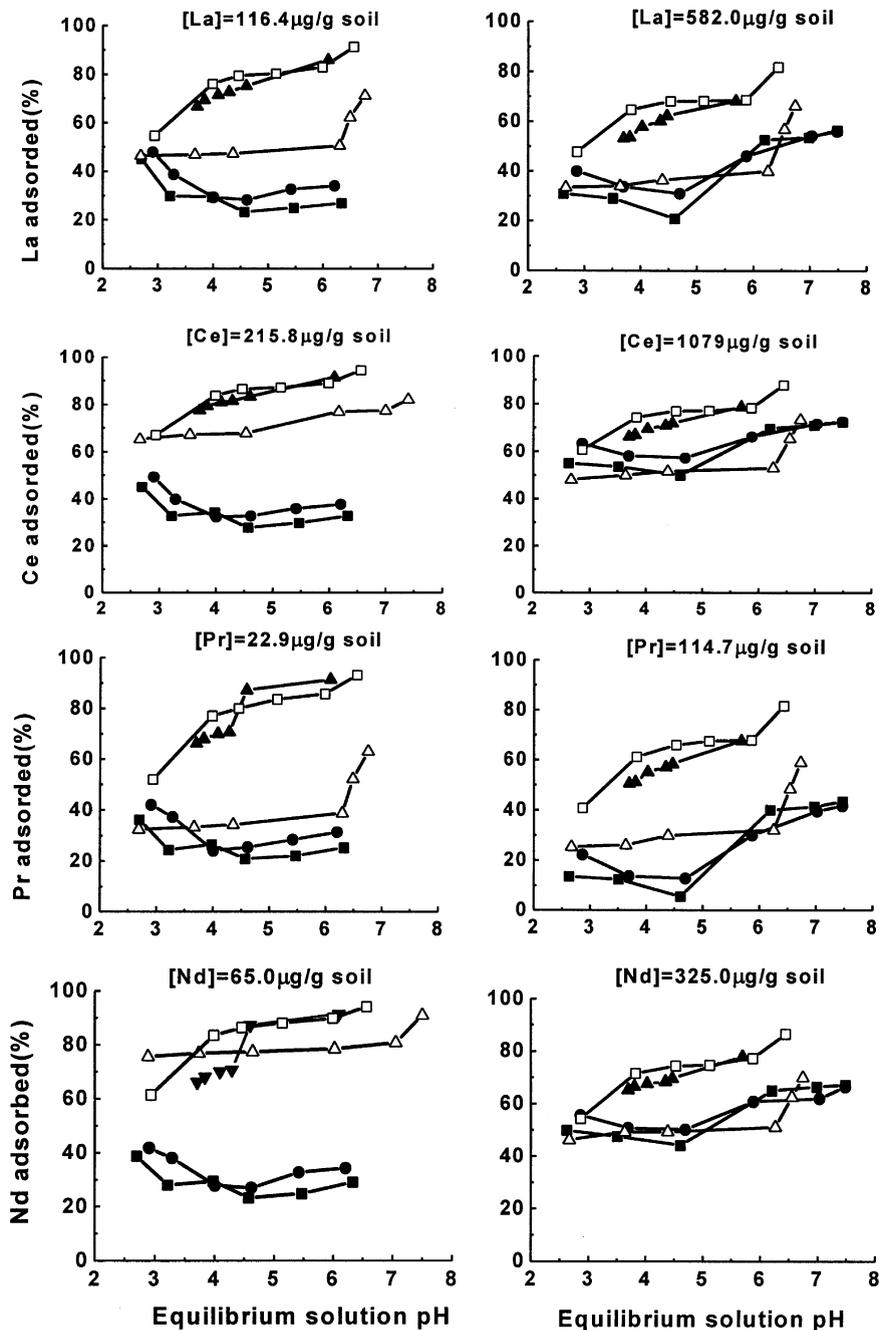


Fig. 3. Effect of organic acids and pH on adsorption of REEs in Jiangxi soil, organic acids: citric acid (■); malic acid (●); tartaric acid (△); acetic acid (▲); nitrate (□).

Denneny (1982) determined the pH of zero net surface charge (zero point of charge, ZPC) in three soils. Their results showed that the  $\text{pH}_{\text{zpc}}$  of all the studied soils was low, so the surface charges were therefore electronegative. Thus the electrostatic attraction with the cationic complexes would be expected. Wang et al. (2000) in-

vestigated the pH at the zero point charge using electrophoresis and further calculated the stability constant of metal-sludge complex. Generally, biological and other organic materials have low  $\text{pH}_{\text{zpc}}$  values, while inorganic adsorbents have higher  $\text{pH}_{\text{zpc}}$  values. For examples, the  $\text{pH}_{\text{zpc}}$  of *Aspergillus oryzae* and *Saccharomyces*

*cerevisiae* were lower than 2 (Westman, 1988), whereas, the  $pH_{zpc}$  values for iron oxide and aluminum oxide are 5.3 and 9.1, respectively (Park, 1987). From the soil properties one can deduce that the  $pH_{zpc}$  value of Heilongjiang soil is much lower than that of Jiangxi soil. It was reported that the  $pH_{zpc}$  of Jiangxi soil was 3.00 (Yuan, 1981) while that of Heilongjiang was less than 2.2 (Xiong and Chen, 1990).

For Jiangxi soil, the effect of pH values on adsorption of REEs was more complicated than that of Heilongjiang soil. It varied from one organic acid to another. For acetic acid the adsorption of REEs increased with increasing pH, no matter what concentrations of REEs were added. For tartaric acid, there was a plateau for the adsorption of REEs over a range of pH 2–6, and then a rapid increase occurred from pH 6 to pH 7. For malic and citric acids, the adsorption of REEs decreased first with pH increasing from 2.5 to 4.5, then there was no further change or increased slightly when pH value exceeded 4.5 (Fig. 3). These phenomena might be due to the relatively high amount of ferric oxide and alumina, and relatively high value of  $pH_{zpc}$  of Jiangxi soil. When the soil pH below 5.2, reaction (1) may occur. Furthermore, when the soil pH below 3.2, reaction (2) would be happen, thus resulting in the formation of positive-charge ligand of  $Al(OH)_2^+$  and  $Fe(OH)_2^+$  on the soil surface (Zhu, 1983)



The lower pH was, the more positive charge had. When the soil surfaces are positively charged, adsorption of strong organic ligand ions may lead to charge reversals. Such charge reversals could enhance adsorption of metal ions. Positive-charged surfaces could adsorb ligands ions or negative-charged REE–organic complexes, then increased REE adsorption. However, there is no more precise information about Jiangxi soil available, this is just our speculation.

### 3.3. Effect of organic ligands and pH on extractable REEs from soils

Effect of organic ligands and pH on REE desorption from Heilongjiang, Zhejiang, Guangdong and Jiangxi soil is shown in Fig. 4. As can be seen clearly that over the experimental pH range, almost no REEs can be extracted by  $NO_3^-$  or acetic acid except for Jiangxi soil. However, in the presence of other organic acids, desorption behavior of each REEs was different from different soils. Almost all REEs followed the following release order: Jiangxi > Guangdong > Zhejiang > Heilongjiang soils. This difference is consisted with CEC of these soils. For Heilongjiang, Zhejiang and Guang-

dong soils, in the presence of citric, malic and tartaric acids, desorption of REEs decreased with increasing pH values, so it did for Jiangxi soil in the presence of  $NO_3^-$ , acetic acid and tartaric acid. A similar phenomenon was also reported for other metal ions such as  $Cu^{2+}$  (Padmanabham, 1983),  $Cd^{2+}$  (Gray et al., 1998) and  $Zn^{2+}$  (Pardo and Guadalix, 1996). It is generally recognized that pH can affect desorption of heavy metal from two aspects. On one hand, it changed the affinity of soils for REEs due to pH-dependent surface-charge density on soil colloids (Cao et al., 2001), leading to the less desorption of heavy metals with increasing pH value. On the other hand, pH changes the species of organic ligands, which affect the REE desorption further. Because different organic acid has different  $pK_a$  (Table 3), the concentrations of organic ligand ions should be different at a given pH. The order of pH for  $10^{-2}$  mol/L organic acid solutions was: tartaric acid < citric acid < malic acid < acetic acid. If pH was the main factor responsible for the release of REEs from soils, at a given pH condition, relatively high amounts of organic ligands ions should be exist in the presence of tartaric acid, thus resulting high amount of REEs desorption. However, this phenomenon was not observed. Instead, a trend was observed in desorption of REEs from soils in the order of: citric acid > malic acid > tartaric acid > acetic acid, which was consistent with the order of the complex stability of the organic acids with REEs. This indicated that organic acids are the main controlling factor that influenced the REE desorption.

For Jiangxi soil, in the presence of citric and malic acids, desorption behavior of REEs appeared to be quite different (Fig. 4d). No desorption decrement, and even slight increase was found when pH increased from 3.5 to 6.5. Desorption of REEs dropped down with further increasing pH value. As mentioned before, there was a competitive reaction for REEs with soil adsorption sites and/or with aqueous organic ligands. The affinity between Jiangxi soil and REEs was lower than those of other soils because of the lower pH, CEC and organic matter of Jiangxi soil (Table 1), thus resulting in a lower REE adsorption capacity of Jiangxi soil. In the meantime, the affinity between citric or malic ligands was higher than that of acetic or tartaric ligands. On one hand, when pH increased, the affinity of soils for REEs increased, thus the desorption of REEs decreased consequently. On the other hand, with the pH increasing, the species of organic ligand ions increased, leading to the increase in desorption of REEs which effect is prevailing over, which can determine the desorption of REEs. Since the CEC of Heilongjiang, Guangdong and Zhejiang soils were relatively high, the effect of pH on the desorption decrement was predominant in the presence of citric or malic acid. Similarly, the stability of REE–organic acid complexes is relatively low in the presence of acetic acid or tartaric acid. However, for

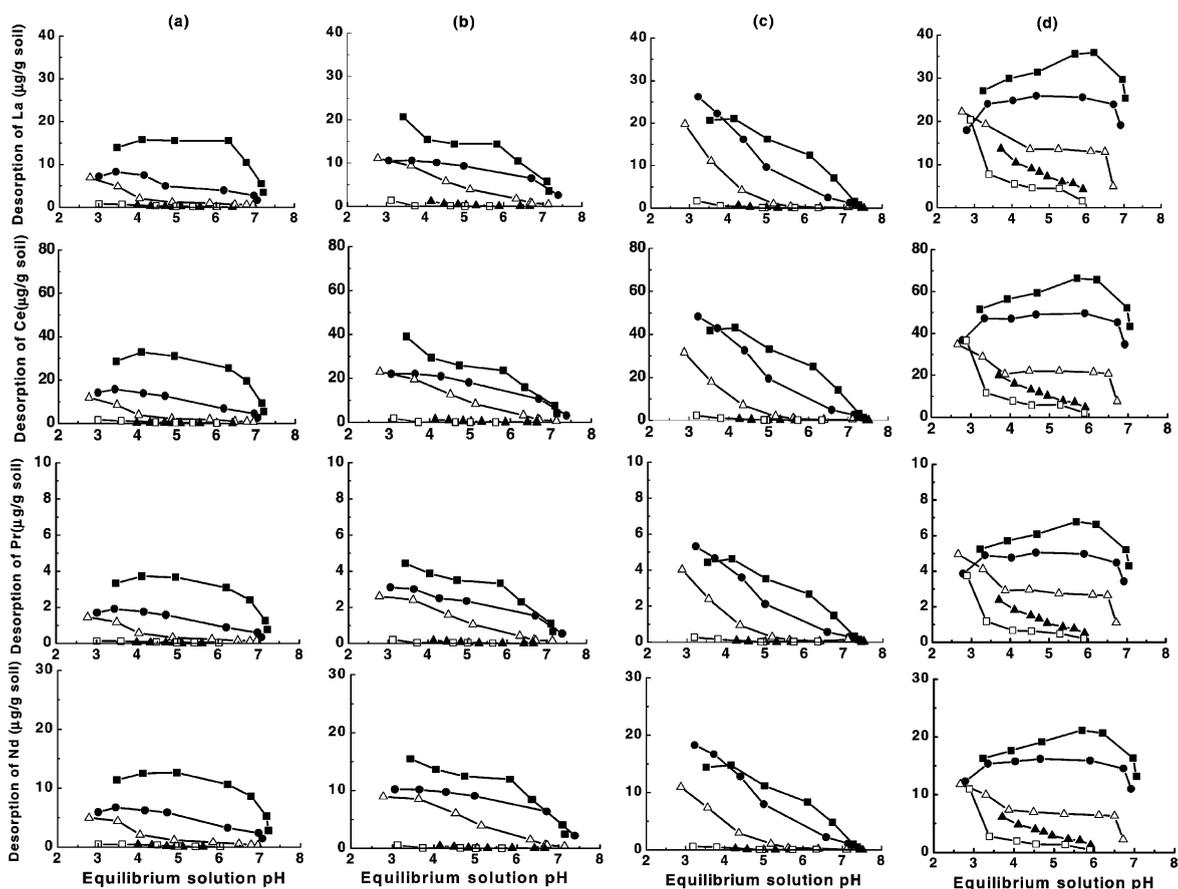


Fig. 4. Effect of organic ligands and pH on desorption of REEs from soils (a) Heilongjiang; (b) Zhejiang; (c) Guangdong; (d) Jiangxi, organic acids: citric acid (■); malic acid (●); tartaric acid (△); acetic acid (▲); nitrate (□).

Table 3  
Low molecular weight organic acids used in this study

Organic acid	Formula	Ligand form	$pK_a^a$
Acetic acid	$CH_3CO_2H$	HL	4.76
Citric acid	$HO_2CCH=C(CO_2H)(OH)CH_2CO_2H$	$H_3L$	3.13, 4.78, 6.43
Malic acid	$HO_2CCH_2CH(OH)CO_2H$	$H_2L$	3.46, 5.10
Tartaric acid	$HO_2CCH(OH)CH(OH)CO_2H$	$H_2L$	3.03, 4.46

<sup>a</sup>  $pK_a$  values were adopted from Serjeant and Dempsey (1979).

Jiangxi soil in the presence of citric or malic acid, a complex reaction can take place with REEs strongly, the effect of pH on the REE desorption due to increase in soil positive charge was not significant. Under the higher pH conditions organic ligand ions increased in the equilibrium solution the desorption of REEs increased. The functions of these two reactions are opposite each other. However, none of these reactions predominated and the integrated action of these reactions resulted in desorption of REEs remained unchanged at the pH range of 3.5–6.5. With pH further increasing, more and more positive hydroxyl REEs, such as  $REE(OH)^{2+}$ ,

$REE_3(OH)_4^{5+}$  and  $REE_2(OH)_3^{3+}$  (Ran and Liu, 1992), would adsorb on the negative surface, which caused reduction of the desorption of REEs obviously.

Based on effect of organic ligand concentration on desorption one can obtain the same conclusion that at any pH investigated there was no exception, i.e., desorption of REEs increased with increasing concentrations of organic acids, which meant that competition reactions between soil surfaces and organic acids more favored organic acids by formation of complex in aqueous solution. Therefore, organic acid was responsible for the REE desorption (Fig. 5).

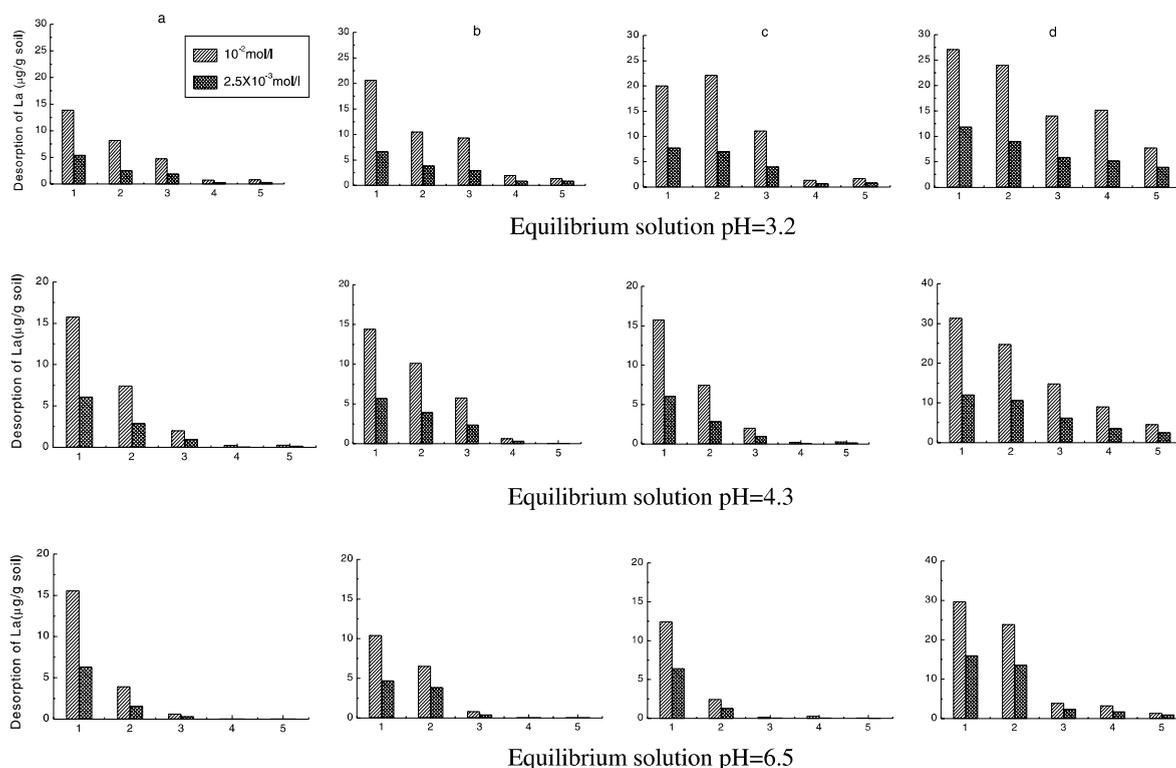


Fig. 5. Effect of different concentrations of organic acids on desorption of REEs at different pH: (a) Heilongjiang soil; (b) Zhejiang soil; (c) Guangdong soil; (d) Jiangxi soil and (1) citric acid; (2) malic acid; (3) tartaric acid; (4) acetic acid; (5) nitrate.

#### 4. Conclusion

Based on the above data obtained under the experimental conditions specified, it could be inferred that the adsorption and desorption of REEs were affected by soil pH, and LMWOAs as well. pH is an important factor affecting the adsorption and desorption of REE in soils as it can change the affinity of sorption sites for REEs and the species of organic acids. However, adsorption by and desorption of REEs from soils were closely relevant to the stability constants of complexes formed between REEs and LMWOAs. In addition, physico-chemical properties of soils such as CEC, organic matter, iron-, manganese- and aluminum-oxides also affect the adsorption and desorption behavior of REEs. The information about the adsorption and desorption of REEs in the presence of LMWOAs can mimic the interactions taking place in the rhizosphere soil, and it can also provide a clue to the study on the bioavailability of REEs.

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