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Kinetics of lead adsorption by iron oxides formed under the influence of citrate

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Abstract—The presence of organic acids greatly affects the formation of Fe oxides and surface properties; however, the subsequent effect on the kinetics and mechanisms of Pb adsorption by the Fe oxides formed under the influence of organic acids remains obscure. The kinetics of Pb adsorption on the Fe oxides formed in the presence of citrate ligands at initial citrate/Fe(II) molar ratios (MRs) of 0, 0.001, 0.01, and 0.1 was studied at the initial Pb concentration of 8.33 μM and pH 5.0 at 278, 288, 298, and 313 K using macroscopic batch method. The results indicate that the Pb adsorption followed multiple first-order kinetics and the rate coefficient, activation energy, and pre-exponential factor in the Arrhenius equation of the adsorption varied greatly with the surface properties of the Fe oxides formed at various citrate/Fe(II) MRs. The alteration of surface properties of Fe oxides formed at the citrate/Fe(II) MR of 0.1 and the effect on the rate coefficient of the fast and slow reactions of Pb adsorption were especially significant. The rate-limiting step of Pb adsorption reactions on the Fe oxides was predominantly a diffusion process, except for the slow reaction of Pb adsorption on the Fe oxides formed at the initial citrate/Fe(II) MR of 0.1, where the rate-limiting process was evidently a chemical process, which may involve bond breaking between the coprecipitated citrate ligand and Fe oxide. The rate coefficients of Pb adsorption by the Fe oxides formed at various citrate/Fe(II) MRs cannot be explained by the activation energy alone. The pre-exponential factor plays an important role in influencing the rate coefficient of Pb adsorption by the Fe oxides. The role of organic acids such as citric acid in influencing the crystallization and the resultant alteration of surface properties of Fe oxides, and the impact on the dynamics of Pb in terrestrial and aquatic environments, thus merit close attention. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

Lead and Pb compounds are highly toxic to plants and animals. With the increase in industrial development, Pb pollution is of increasing concern. It is reported that the Pb concentration in garden soils in London can be as high as 20,000 $\mu\text{g g}^{-1}$ (OECD, 1993), whereas Pb occurs naturally in the earth's crust at average levels of 5 to 50 $\mu\text{g g}^{-1}$ (US EPA, 1989). The use of leaded gasoline for automobiles has declined in most countries, and Pb is no longer used as an ingredient in paint. However, many anthropogenic activities have resulted in widespread Pb contamination of surface soils through past use of Pb-containing compounds, sewage sludge, and dust (Harrison and Laxen, 1984; Haygarth and Jones, 1992; Maynard et al., 1993; Kabata-Pendias and Pendias, 2001). Severe Pb pollution of agricultural and urban soils can originate from heavy emitters of airborne particles. Major fallout problems result from mines, old smelters and foundries, battery recycling, municipal incinerators, coal-burning power plants, and facilities related to gasoline antiknock additives (Maynard et al., 1993; Page and Chang, 1993; Wixson and Davies, 1994). After Pb enters soil environments, the fate of the Pb pollutant can be modified through adsorption-desorption processes by soil colloidal particles. The mobility and toxicity of Pb are largely controlled by chemical reactions that take place at the hydrous oxide/water interface (Manceau et al., 1992). Soils polluted at the surface with Pb deposited from aerial contaminants show little indication of metal leaching over many years (McBride, 1994).

Iron (hydr)oxides, which are the most abundant of the metallic oxides in soils, have long been recognized as playing a vital role in controlling the fate of heavy metals in soils and sediments (Schwertmann and Taylor, 1989; Cornell and Schwertmann, 1996) and in the regulation of Pb in natural waters (Angino et al., 1972; Benes et al., 1985; Manceau et al., 1992) due to their very reactive -OH and/or -OH₂ functional groups exposed on the surface. The Pb adsorption on Fe oxides has been studied intensively by equilibrium approaches in the last three decades (Forbes et al., 1976; McKenzie, 1980; Barrow et al., 1981; Muller and Sigg, 1992; Ainsworth et al., 1994; Gunneriusson et al., 1994). The fast kinetics and mechanisms of Pb adsorption/desorption at Fe oxide/aqueous interfaces on millisecond time scales were investigated using pressure-jump relaxation spectrometry (Hayes, 1987; Liu and Huang, 2001). The Pb adsorption involves two parallel elementary reactions: (1) bimolecular adsorption of a Pb²⁺ ion to a surface hydroxyl site and (2) bimolecular adsorption of a Pb²⁺ ion to a surface site at which a nitrate ion is bound as an ion-pair when sodium nitrate is used as a background electrolyte. The first adsorption reaction takes place faster than the second adsorption reaction. Further, Liu and Huang (2001) found that the intrinsic equilibrium and rate constants of Pb sorption on Fe oxides vary greatly with the surface properties of the Fe oxides such as specific surface area and surface charges. The proposed Pb surface complexes (Hayes, 1987; Liu and Huang, 2001) are in accord with the conclusions derived from synchrotron-based X-ray absorption fine-structure spectroscopy (XAFS) (Roe et al., 1991; Bargar et al., 1997, 1998). Recently, Eick et al. (1999) studied the Pb adsorption on a well crystalline goethite over a 12-week sorption period. Their results showed that Pb adsorp-

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Table 1. Characteristics of Fe oxide formed at various initial citrate/Fe(II) molar ratios.

	Citrate/Fe molar ratio			
	0	0.001	0.01	0.1
Dominant mineral [†]	G, M, L	L	L	non-crystalline
Specific surface area (m ² g ⁻¹)	135.2 ± 0.5	102.8 ± 0.3	189.3 ± 0.4	209.6 ± 1.4
Micropore area (m ² g ⁻¹)	0	0	22.2 ± 0.1	136.1 ± 0.9
Average pore diameter (nm)	10.2 ± 0.1	18.4 ± 0.2	5.4 ± 0.0	2.6 ± 0.0
PZSE	7.0 ± 0.2	6.0 ± 0.0	5.6 ± 0.1	3.9 ± 0.1
Organic C (g kg ⁻¹)	0.2 ± 0.0	1.1 ± 0.1	6.2 ± 0.4	55.7 ± 0.9

[†] G - goethite, M - maghemite, L - lepidocrocite.

tion is very rapid within 1 h, and there is essentially no change in the quantity of Pb sorbed by goethite after a 20-h sorption period. Scheinost et al. (2001) compared the kinetics and mechanisms of Pb sorption by fresh and freeze-dried ferrihydrite using batch method in combination with synchrotron-based XAFS.

Pure Fe oxides were used in almost all of above-mentioned studies. However, pure Fe oxides rarely exist in natural environments. Pedogenic Fe oxides are formed under the influence of the common soil-forming factors, including ionic factors in soil solutions. Once formed, the mineral phases and composition of Fe oxides may be subjected to continual modifications with changing soil environment. Various ions and molecules can be incorporated into the structure of Fe oxide. The influence of various organic and inorganic ligands on the formation and transformation of Fe oxides has been substantially studied for more than two decades (Schwertmann and Thalmann, 1976; Lewis and Schwertmann, 1979; Schwertmann and Fischer, 1982; Schwertmann and Fechter, 1984; Krishnamurti and Huang, 1989, 1991, 1993).

Citric acid is very common in natural environments, especially in rhizosphere soils, and usually ranges from 10⁻⁵ to 10⁻³ M (Robert and Berthelin, 1986). The presence of citrate ligands during the formation of Fe oxides can significantly modify the structural and surface properties of the Fe oxides formed (Liu and Huang, 1999a, 1999b). These surface properties include surface area, surface porosity, surface charge, and surface geometry. The surface of Fe oxides is the region of their interaction with the soil solution and with other solid phases, plant roots, and the soil biota (Schwertmann and Taylor, 1989). Therefore, the surface properties directly govern the behavior of Fe oxides in the soil and associated aquatic environments. Citrate greatly affects the formation of Fe oxides and the surface properties; however, the subsequent effect on the kinetics of Pb adsorption by the Fe oxides has never been reported. Therefore, the objective of this study was to investigate the kinetics of Pb adsorption by the Fe oxides that were formed under the influence of citrate at various concentrations common in natural environments.

2. MATERIAL AND METHODS

2.1. Formation and Characteristics of Iron Oxides

Iron oxides were formed at pH 6.00 ± 0.05 and 25°C at an initial Fe(II) concentration of 10⁻² M in the presence of citrate ligands at initial citrate/Fe(II) molar ratios (MRs) of 0, 0.001, 0.01, and 0.1. Citric acid concentration ranged from 10⁻⁵ to 10⁻³ M. The synthesis proce-

dures is the same as the method reported before (Liu and Huang, 1999a). The sample was freeze-dried at -40°C. The minerals of Fe oxides were identified by X-ray powder diffraction (XRD) on a Philips (Model PW 1031) X-ray diffractometer using Mn-filtered FeK α radiation at 35 kV and 16 mA and by infrared spectrometry (IR) on a Perkin Elmer infrared spectrophotometer (Model 983) using the KBr pellet technique (1 mg of sample mixed with 250 mg of KBr).

The specific surface area of Fe oxides was measured by using a multiple point BET-N₂ adsorption isotherm obtained with a Quantachrome Autosorb-1 apparatus (Quantachrome). Before N₂ adsorption, ~100-mg samples were outgassed for 24 h at 10 mTorr. During N₂ adsorption, the solids were thermostated in liquid N₂ (77–78 K). The pore-specific surface area of the Fe oxides was determined from the 93-point N₂ adsorption isotherms using the t-plot method of de Boer, and the average pore diameter was estimated using the Kelvin equation (assuming cylindrical pores) (Gregg and Sing, 1982) with the Quantachrome Autosorb-1. The point-of-zero salt effect (PZSE) was determined in 0.01, 0.1, and 1 mol/L NaCl solutions by the potentiometric titration method on a Metrohm titroprocessor (model 682). The organic carbon content of the Fe oxides was determined with a Leco CR12 C analyzer at 1123 K (Wang and Anderson, 1998).

The basic characteristics of the Fe oxides formed at various initial citrate/Fe(II) MRs are given in Table 1.

2.2. Kinetic Experiment

The kinetics of Pb adsorption by the Fe oxides formed at citrate/Fe(II) MRs of 0, 0.001, 0.01, and 0.1 was studied by the conventional batch method. The freeze-dried Fe oxides were dispersed as suspensions by ultrasonification (Sonifier, Model 350) at 150 W for 2 min. An aliquot of the suspension containing 7.8 mg of the Fe oxides was transferred to a series of 250-mL flasks, which contained 80-mL deionized distilled water, and then shaken overnight at 278, 288, 298, or 313 K in a shaker with a constant-temperature water bath. The pH of the suspension was then adjusted to 5.0 with 0.1-mol/L HNO₃ or NaOH. An aliquot of 25 mL of 40- μ M Pb stock solution (pH 5.0), containing Pb(NO₃)₂ and NaNO₃, was added to each flask to obtain the initial concentrations of Pb and NaNO₃ of 8.33 μ M and 0.01 mol/L, respectively. The final volume of the suspension was 120 mL. The concentration of Fe oxides in the suspension was 0.065 g L⁻¹. The suspension was shaken for 0.033, 0.083, 0.25, 0.5, 0.75, 1, 2, 4, 8, 12, and 24 h at 278, 288, 298, and 313 K by placing the flask into the same shaker with constant-temperature water bath. The pH of the suspension was measured during the reaction period and was kept constant (5.0) by adding 0.001-mol/L NaOH. The suspensions at the end of each adsorption period were filtered through a 0.1- μ m Millipore membrane within 10 s. The Pb concentration of the filtered solution was determined by atomic absorption spectrophotometry at a wavelength of 283.3 nm on a Perkin Elmer atomic absorption spectrophotometer (Model 3100). The amount of Pb adsorbed was determined by taking the difference between the initial and final concentrations of Pb in the solution. The experiment was conducted in duplicate.

Table 2. The amounts of Pb adsorbed in the Fe oxide systems at the end of a 24-h reaction period at different temperatures.

Initial citrate/Fe(II) molar ratio	278 K	288 K	298 K	313 K
	cmol of Pb kg ⁻¹ oxide			
0	6.90	7.42	7.72	8.09
0.001	5.57	6.61	6.98	7.35
0.01	6.53	7.65	7.87	8.17
0.1	6.68	9.13	10.10	10.69

LSD_{0.05} = 0.21 and LSD_{0.01} = 0.29 for different temperatures and various Fe oxides. The LSD is the least significant difference.

3. RESULTS AND DISCUSSION

3.1. Amount of Lead Adsorbed by Iron Oxides

The amounts of Pb adsorbed on the Fe oxides, which were formed at the different initial citrate/Fe(II) MRs, at the end of a 24-h reaction period at different temperatures are presented in Table 2. The amounts of Pb adsorbed on the different Fe oxides increased with increasing temperature, since the higher temperature provided more energy to enhance the diffusion of Pb ions and to break and form the bonding on the oxide surface. Except for the data obtained at 278 K, the sequence of Pb adsorption by the Fe oxides formed at different MRs was 0.1 > 0.01 ≥ 0 > 0.001. This sequence in the amounts of Pb adsorbed by the Fe oxides is generally in accord with the increase in the N₂-BET-specific surface area of the Fe oxides (Table 1).

The differences in mineralogical composition of the Fe oxides formed at different initial citrate/Fe(II) MRs may affect their Pb adsorption behavior. In the absence of citrate ligands, a mixture of goethite, maghemite, and lepidocrocite was formed. The presence of citrate ligands at the initial citrate/Fe(II) MR of 0.001 improved the crystallization of lepidocrocite at the expense of goethite and maghemite and decreased the surface area of the precipitation products (Table 1). Although lepidocrocite was still formed at an initial citrate/Fe(II) MR of 0.01, the degree of crystallinity of lepidocrocite was reduced (Liu and Huang, 1999a), and the surface area was increased (Table 1). The atomic force micrograph showed that some X-ray noncrystalline Fe oxide was also formed at this citrate/Fe(II) MR (Liu and Huang, 1999b). As the initial citrate/Fe(II) MR was further increased to 0.1, only X-ray noncrystalline Fe oxide was formed.

No micropores were formed in the precipitates at the citrate/Fe(II) MRs of 0 and 0.001. When the citrate/Fe(II) MR was increased to 0.01 and 0.1, the specific surface area of the Fe oxides formed, especially that from micropores, greatly increased (Table 1). At 278 K, the Fe oxides formed at the MRs of 0 and 0.001 adsorbed the most and least Pb, respectively; the amounts of Pb adsorbed by the Fe oxides formed at the citrate/Fe(II) MRs of 0.01 and 0.1 were not significantly different and smaller than that sorbed by the Fe oxides formed at the MR of 0. The Fe oxides formed at the citrate/Fe(II) MR of 0.01 and 0.1 developed micropores and had a much smaller average pore diameter in comparison with the Fe oxides formed at the MRs of 0 and 0.001 (Table 1). The effective diameter of Pb²⁺ ions in aqueous solutions is 0.9 nm (Dean, 1992). The diameter of a micropore is < 2 nm (Lowell and Shields, 1991). The steric

effect of the micropores on the Pb adsorption was apparently more pronounced at 278 K than at the higher temperatures.

Further, the amount of Pb adsorbed by the Fe oxides at 288, 298, and 313 K (Table 2) increased with the decrease in the PZSE of the oxides (Table 1), except for the Fe oxides formed at the initial citrate/Fe(II) MR of 0.001. The Fe oxides with a lower PZSE had more net negative surface charges at the same pH and would, thus, enhance the attraction of the Pb cations. The smaller specific surface area of the Fe oxides formed at the initial citrate/Fe(II) MR of 0.001 apparently counteracted the influence of their lower PZSE on Pb adsorption in comparison with the Fe oxides formed at the MR of 0.

3.2. Rate Coefficients of Lead Adsorption

The concentration of Pb in the solutions greatly decreased with time (Fig. 1). The time required to reach the reaction equilibrium decreased with increasing temperature. For example, Pb adsorption by the Fe oxides reached equilibrium at the end of a 12-h reaction period at 278 and 288 K. The adsorption reaction at 298 and 313 K approached equilibrium before the end of a 12-h reaction period. While the concentration of Pb in the solution decreased rapidly in the 0.033- to 2-h reaction period at reaction temperatures of 278 and 288 K, the concentration of Pb in solution decreased rapidly in the 0.033 to 1 h at 298 K. The Pb concentration in the solution decreased greatly at 313 K even in a shorter reaction period such as 0.033 to 0.75 h.

The Pb concentration in the solution decreased more slowly after the rapid reaction period, indicating possible multiple rate processes. The processes of Pb adsorption by the Fe oxides included chemical adsorption processes and diffusion processes. Any factors affecting those processes will influence the observed rate of the adsorption reactions. The multiple-rate character of Pb adsorption is possibly related to the heterogeneity of adsorption sites on the Fe oxides (Benjamin and Leckie, 1981). The different accessibility of surface pores results in an apparent heterogeneity of the surface (Madrid and de Arambarri, 1985) and could cause differences in the adsorption rate. The adsorbed Pb also tends to lower the surface potential and increase the positive charge. The electrostatic repulsion becomes stronger as adsorption proceeds.

The kinetic equations, including the zero-order, first-order, and second-order kinetic models, overall diffusion parabolic equation, Elovich equation, and modified Freundlich equation (Stumm and Morgan, 1996), were used to fit the Pb adsorption data. The rate curves were divided into the fast and slow reactions based on the degree of the fit of the kinetic equations to the experimental data. The degree of fit of the kinetic equations to the data was examined by the correlation coefficient (r^2) and probability (p) of the slope of the simple linear regression analysis as well as the standard error (SE). The values of r^2 , p , and SE for the Pb adsorption by the Fe oxides formed at the citrate/Fe(II) MR of 0 are given as an example in Table 3. The data revealed that the zero-order, first-order, and second-order kinetic equations generally fitted the data better than the Elovich, modified Freundlich, and overall parabolic diffusion equations. The same trend was observed in the Pb adsorption by the Fe oxides formed at the citrate/Fe(II) MRs of 0.001, 0.01, and 0.1 (not shown).

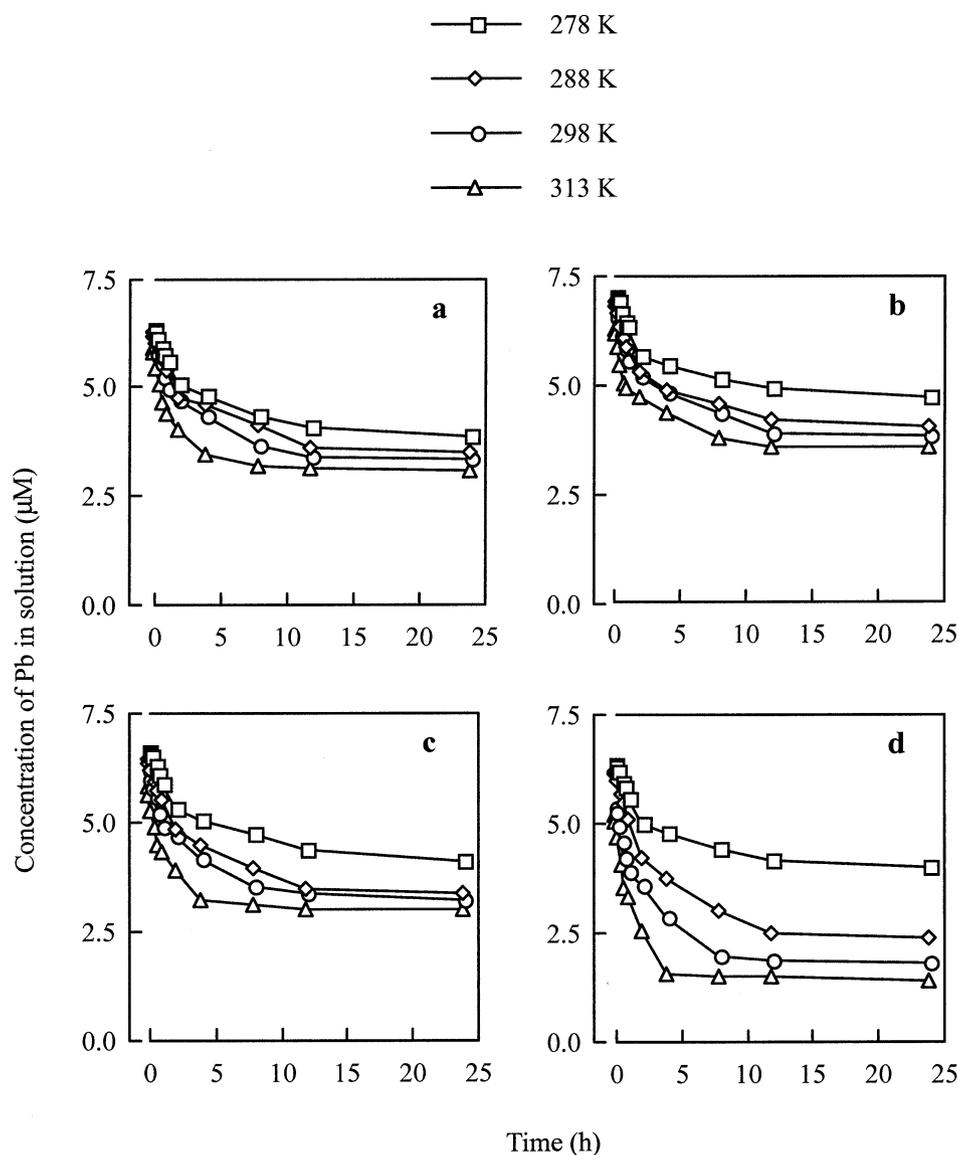


Fig. 1. Time function of the Pb^{2+} concentration remaining in the solution after reaction with Fe oxides formed at initial citrate/Fe(II) molar ratios of (a) 0, (b) 0.001, (c) 0.01, and (d) 0.1.

It has often been found that in heterogeneous systems, a number of rate equations seem to equally well describe the kinetics of a particular reaction if correlation coefficients, probability, and standard errors of the estimates are the indices that are used to evaluate the data (Chien and Clayton, 1980; Martin and Sparks, 1983; Sparks, 1989; Aharoni et al., 1991). In heterogeneous systems, the order of a kinetic equation in describing the reaction does not have the meaning of molecularity. Based on the values of the correlation coefficient, probability, and standard error for the multiprocesses, overall, the first-order rate equation is judged to be the best among the rate equations examined for all the systems studied. Therefore, the first-order kinetic model was chosen to describe the Pb adsorption by the iron oxides formed at various citrate concentrations:

$$\ln C = \ln C_0 - kt \quad (1)$$

where C is the Pb^{2+} concentration remaining in the solution

(mol L^{-1}) at time t , C_0 is the initial Pb^{2+} concentration in the solution (mol L^{-1}), k is the rate coefficient (h^{-1}), and t is time (h).

Based on the first-order kinetic plottings for the Pb adsorption on the Fe oxides at different temperatures, the rate coefficients for the fast and slow adsorptions of Pb on the Fe oxides at different temperatures can be calculated from Eqn. 1 (Table 4). The first-order kinetic plottings for the Pb adsorption on the Fe oxide formed at the citrate/Fe(II) MR of 0.01 were used as an example and presented in Figure 2.

The first-order rate coefficients of Pb adsorption by the Fe oxides generally increased with increasing temperature from 288 to 313 K (Table 4). Compared with the Fe oxides, which were formed at the citrate/Fe(II) MRs of 0, 0.001, and 0.01, the rate coefficients of the fast and slow reactions of Pb adsorption by the Fe oxides formed at the citrate/Fe(II) MR of 0.1 were higher, especially at the temperatures of 288, 298, and 313 K.

Table 3. The comparison of the degree of fit of various kinetic models to the data of Pb adsorption by the Fe oxides.[†]

Model	r^2		p		SE [‡] (cmol kg ⁻¹)	
	f [‡]	s [§]	f	s	f	s
0-order	0.990	0.996	3.57×10^{-5}	1.90×10^{-3}	0.072	0.067
1-order	0.991	0.999	2.85×10^{-5}	2.55×10^{-4}	0.071	0.041
2-order	0.991	0.999	3.09×10^{-5}	3.22×10^{-4}	0.194	0.039
Overall parabolic diffusion equation	0.972	0.994	2.97×10^{-4}	2.76×10^{-3}	0.123	0.080
Elovich	0.881	0.950	5.57×10^{-3}	2.52×10^{-2}	0.253	0.239
Modified Freundlich	0.913	0.968	2.91×10^{-3}	1.59×10^{-2}	0.225	0.193

[†] The Fe oxide was formed at the initial citrate/Fe(II) molar ratio of 0; the kinetic experiment was conducted at 298 K; r^2 is the correlation coefficient; p is the probability; SE is the standard error.

[‡] Fast reaction.

[§] Slow reaction.

[¶] Standard error. $SE = [\sum(A - A^*)^2/(n - 2)]^{1/2}$, where A is the experimental value; A* is the theoretical value based on modeling; n is the number of the data.

Apparently, the temperature greatly affected the adsorption of Pb onto Fe oxides formed at various citrate/Fe(II) MRs. As mentioned above, the higher temperature provided more energy to enhance the diffusion of Pb ions and to break and form the bonding on the oxide surface.

At low temperatures such as 278 K, the diffusion of Pb ions in the micropores of the Fe oxide, formed at the citrate/Fe(II) MRs of 0.01 and 0.1, would be retarded as discussed above, and the formation of the Pb ion-surface complexes in the micropores would, thus, be hindered. This accounts for the observation that the rate coefficient of the fast and slow reactions of Pb adsorption did not systematically vary with the citrate/Fe(II) MRs at which the Fe oxides were formed. The Fe oxides formed at the citrate/Fe(II) MR of 0 and 0.001 only had mesopore surfaces. Mesopores refer to the pores with diameters between 2 and 50 nm (Lowell and Shields, 1991). Besides mesopores, the Fe oxides formed at the citrate/Fe(II) MRs of 0.01, and especially 0.1, had substantial amounts of micropores (Table 1).

The rate coefficient of Pb adsorption was also influenced by other surface properties of the Fe oxides formed such as specific surface area, PZSE and surface charge, and the coprecipitated citrate ligands. The rate coefficient of Pb adsorption (Table 4) generally increased with the N₂-BET-specific surface area of the Fe oxides (Table 1). The amount of citrate ligands coprecipitated with Fe oxides increased with the increase in the initial citrate/Fe(II) MR, which caused the decrease in the PZSE (Table 1). The lower PZSE and greater net negative charge increased the electrostatic attraction between Pb ions and the oxide surface and, thus, increased the rate of Pb adsorption on the Fe oxides formed at the initial citrate/Fe(II) MR of 0.1 (Table 4). Further, since Pb forms the chelate with citrate at the stability constant of $10^{4.44}$ (Martell et al., 1998), at the higher citrate/Fe(II) MRs, the exposed carboxylate groups of the citrate ligands, coprecipitated with the Fe oxides, should have the ability to chelate with Pb²⁺ ions (Liu, 1999) to increase the Pb adsorption. Although this mechanism needs to be corroborated in the future study, it may explain that the Fe oxide formed at the initial citrate/Fe(II) MR of 0.1 had the highest amount and rate of Pb adsorption.

Scheinost et al. (2001) reported that the addition of fulvic acid into ferrihydrite gel does not change significantly the kinetics of Pb sorption. This is apparently different from the

influence of citrate ligand on the formation of Fe oxides and the resultant effect on their surface properties and the subsequent impact on the Pb adsorption in the present study. The addition of fulvic acid into ferrihydrite gel before adding Pb only results in the adsorption of fulvic acid on the external surface of ferrihydrite (Scheinost et al., 2001). However, the presence of citric acid during the formation of Fe oxides can modify the structure of the Fe oxides formed and cause the resultant alteration of their surface properties (Liu and Huang, 1999a, 1999b). The citrate ligands not only can be adsorbed on the external surface, but also can be incorporated into the structural network of Fe oxides (Liu and Huang, 1999a). All of these factors significantly changed the kinetics of Pb adsorption by the Fe oxides.

3.3. Activation Energy and Preexponential Factor of Lead Adsorption

The temperature dependence of the rate coefficients of Pb adsorption by the Fe oxides is illustrated in Figure 3. The same

Table 4. The reaction rate coefficients of Pb adsorption on the Fe oxides formed at various initial citrate/Fe(II) molar ratios (MRs) based on the first-order rate equation.[†]

	MR	278 K	288 K	298 K	313 K	LSD _{0.05}	LSD _{0.01}
		Rate coefficient (h ⁻¹) × 10 ³					
Fast reaction	0	113	137	200	331	24	40
	0.001	112	134	181	310	24	39
	0.01	113	144	230	344	41	68
	0.1	120	198	324	534	21	35
LSD _{0.05}		11	16	29	41		
LSD _{0.01}		19	26	48	68		
Slow reaction	0	22	28	43	89	22	36
	0.001	14	22	34	48	11	18
	0.01	20	33	47	98	10	17
	0.1	19	52	100	261	10	16
LSD _{0.05}		5	9	17	19		
LSD _{0.01}		9	15	28	32		

[†] The first-order rate equation is $\ln C = \ln C_0 - kt$, where C is the Pb²⁺ concentration remaining in the solution (mol L⁻¹) at time t, C₀ is the initial Pb²⁺ concentration in the solution (mol L⁻¹), k is the rate coefficient (h⁻¹) and t is time (h).

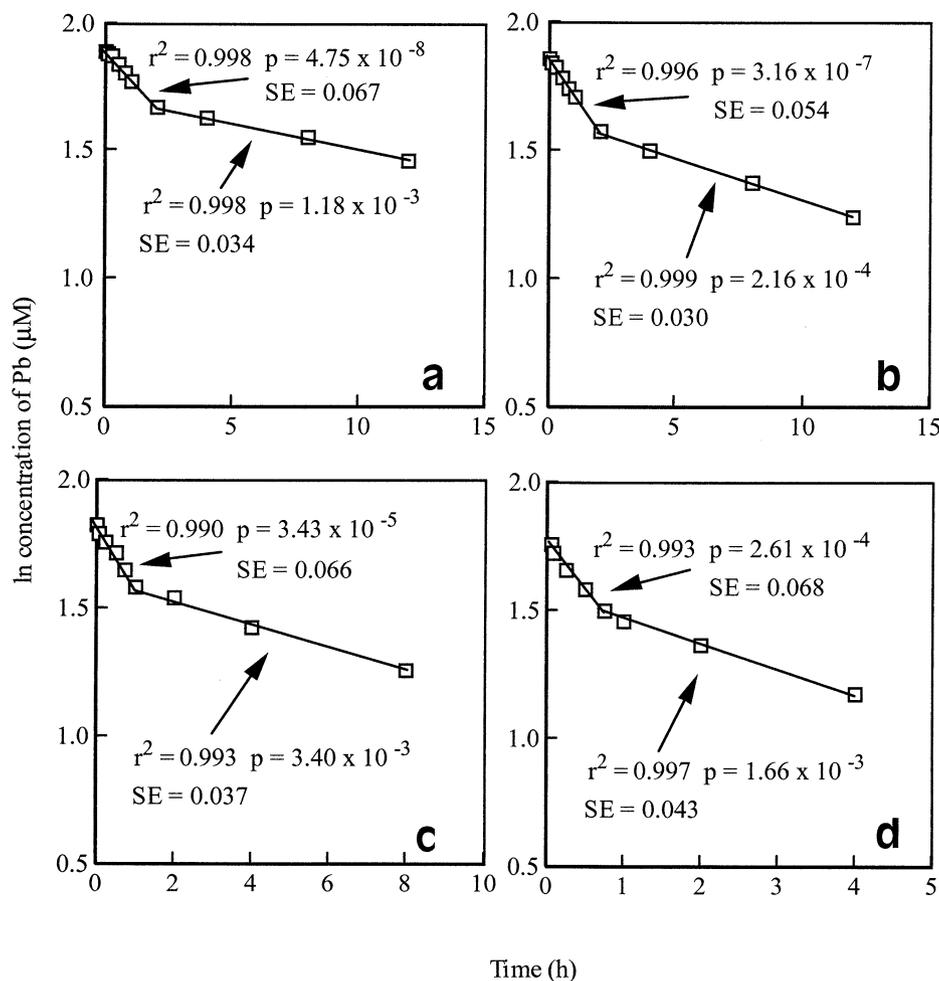


Fig. 2. The first-order plottings of Pb adsorption on the Fe oxides, which were formed at the initial citrate/Fe(II) molar ratio of 0.01, at (a) 278 K, (b) 288 K, (c) 298 K, and (d) 313 K.

trend was true for all the Fe oxide systems studied (Table 5). This indicates that the rate coefficients of both fast and slow Pb adsorption reactions by the Fe oxides were of the Arrhenius temperature dependence (Moore and Pearson, 1981). The Arrhenius equation was used to calculate the activation energy (E_a) and the preexponential factor:

$$k = Ae^{-E_a/RT} \quad (2)$$

where k is the rate coefficient, A is the preexponential factor (frequency factor), E_a is the Arrhenius activation energy, R is the universal gas constant, and T is the absolute temperature (K).

The activation energy and preexponential factor can be calculated from the slope and intercept of the plotting of $\ln k$ vs. $1/T$, respectively. The activation energy (E_a) of Pb adsorption on the Fe oxides formed at different citrate/Fe(II) MRs ranged from 21 to 53 kJ mol^{-1} Pb adsorbed (Table 6). Low E_a values ($<42 \text{ kJ mol}^{-1}$) indicate diffusion-controlled processes, whereas higher E_a values ($>42 \text{ kJ mol}^{-1}$) indicate chemically controlled processes (Sparks, 1989). The rate-limiting step of the Pb adsorption reactions on the Fe oxides involved predominantly diffusion processes, except for the slow reaction of Pb

adsorption on the Fe oxides formed at the initial citrate/Fe(II) MR of 0.1, where the rate-limiting process was evidently a chemical process. The activation energies of Pb adsorption on the Fe oxides formed under the influence of various citrate/Fe(II) MRs were not significantly different, except that Pb adsorption by the Fe oxides formed at the citrate/Fe(II) MR of 0.1 had a higher activation energy for the slow reaction.

Scheinost et al. (2001) estimated the apparent activation energy of Pb adsorption by freshly prepared and freeze-dried ferrihydrite, based on the data at two temperatures. Their activation energies are in the similar range ($14\text{--}53 \text{ kJ mol}^{-1}$). Their data showed that the activation energy of Pb adsorption on freshly prepared ferrihydrite gel (52 kJ mol^{-1}) is much higher than that of Pb adsorption on freeze-dried dense ferrihydrite (19 kJ mol^{-1}). In the present study, the Fe oxide samples were freeze-dried. However, the activation energy of the slow reaction of Pb adsorption on the Fe oxides formed at the initial citrate/Fe(II) MR of 0.1, which was X-ray noncrystalline, was 53 kJ mol^{-1} . This indicates that citrate incorporated with Fe oxides may prevent the aggregation of noncrystalline Fe oxides during freeze-drying. Further, the Fe oxides formed at the citrate/Fe(II) MR of 0.1 had substantial micro-

Table 5. The degree of fit of the Arrhenius equation to the temperature dependence of the rate coefficient of Pb adsorption by the Fe oxides formed at various citrate/Fe(II) molar ratios (MRs).

Citrate/Fe(II) MR	r^2		p		SE [§] (h ⁻¹)	
	f [†]	s [‡]	f	s	f	s
0	0.981	0.972	1.01×10^{-2}	1.46×10^{-2}	1.086	1.136
0.001	0.971	0.984	1.51×10^{-2}	8.75×10^{-3}	1.106	1.090
0.01	0.986	0.996	7.35×10^{-3}	2.73×10^{-3}	1.077	1.036
0.1	0.996	0.994	2.59×10^{-3}	3.34×10^{-3}	1.083	1.058

[†] Fast reaction.

[‡] Slow reaction.

[§] Standard error. $SE = [\sum(A - A^*)^2/(n - 2)]^{1/2}$, where A is the experimental value; A* is the theoretical value based on modeling; n is the number of the data.

pores (Table 1), which apparently resulted in the increase of the activation energy of Pb adsorption.

Lead adsorption onto the Fe oxides formed at citrate/Fe(II) MR of 0.1 had the highest rate coefficient among the slow reactions at 288, 298, and 313 K. However, the slow reaction of Pb adsorption by the Fe oxides formed at the citrate/Fe(II) MR of 0.1 had the highest activation energy. This is attributed to the preexponential factor for Pb adsorption on the Fe oxides (Table 6). The preexponential factor values for Pb adsorption differed by five orders of magnitude for the different Fe oxide systems studied and increased with the increase of the specific surface of the Fe oxides formed (Tables 1, 6). The higher the specific surface area, the more reaction sites were available. Consequently, this resulted in the higher accessibility of Pb ions to reactive sites of the oxide surface, and, therefore, both the activation energy and preexponential factor must be considered in interpreting the rates of Pb adsorption on the Fe oxides.

At the initial citrate/Fe(II) MR of 0.001, lepidocrocite crystallization was improved by catalysis, and the specific surface of the precipitation products decreased (Table 1). A smaller surface area of Fe oxides corresponds to fewer -OH and -OH₂ functional groups exposed on the surface and, thus, fewer adsorption sites, such as the case of Pb adsorption by the Fe oxides formed at the citrate/Fe(II) MR of 0.001. At the initial citrate/Fe(II) MRs of 0.01 and 0.1, the crystallization of the precipitation products was perturbed, resulting in the increase of their specific surface (Table 1). Krishnamurti and Huang (1993) stated that Fe-citrate complexation formed at the optimal citrate/Fe(II) MR such as 0.001 possibly influences the oxygen coordination and plays a positive role in the way the double rows of [Fe(O,OH)₆] octahedra of lepidocrocite are linked during the crystallization of the precipitation products. However, when the initial citrate/Fe(II) MR was increased from 0.001 to 0.01 and 0.1, the crystallization of lepidocrocite was perturbed apparently due to the incorporation of citrate ligands into the growing fragments of Fe oxides. Therefore, the regular linkage of these structural fragments was hampered. The citrate ligands coprecipitated with Fe oxides may exist both on the surface and in the internal structural network of Fe oxides and, thus, distort their crystal structure, leading to the formation of poorly crystalline to noncrystalline Fe oxides.

The proposed model for the structural perturbation of Fe oxyhydroxides caused by coprecipitation of citrate ligands is illustrated in Figure 4. The model for the structural perturbation of Fe oxyhydroxides caused by the coprecipitation of citrate

ligands is based on the X-ray diffraction, specific surface, microporosity, PZSE, organic C data (Table 1), atomic force microscopy (Liu and Huang, 1999b), and the FTIR spectroscopic evidence on the presence of bond at 1385 cm⁻¹, which was attributed to COO⁻ bending vibration of the citrate complexed with Fe(III) in the precipitates (Liu and Huang, 1999a). This structural model could be further refined in the future study by using molecular modeling and synchrotron-based radiation techniques such as X-ray absorption spectroscopy and infrared spectroscopy. A larger surface area of Fe oxides corresponds to more -OH and -OH₂ functional groups exposed on the surface and more adsorption sites such as the case of the Fe oxides formed at the citrate/Fe(II) MRs of 0.01 and 0.1. However, significant amounts of citrate were coprecipitated with the Fe oxides formed at the initial citrate/Fe(II) MRs of 0.01 and 0.1 (Table 1). Citrate ligands can complex with Fe oxides through one carboxylate group and/or one hydroxyl group (Fig. 4). When only one carboxylate group of citrate ligands is complexed with one Fe of Fe oxides and occupies one adsorption site, the two exposed free carboxylate groups of the same citrate ligand can react with Pb ions. Therefore, the coprecipitation of citrate ligands in this case would increase the amount and rate of Pb adsorption. However, when one carboxylate and one hydroxyl functional groups of one citrate ligand are chelated with two reaction sites of one Fe of the Fe oxide, two free carboxylate groups are exposed and, thus, compensated for the loss of the adsorption sites of the Fe oxides for Pb, which were caused by citrate chelation.

By increasing the citrate/Fe(II) MR, more citrate ligands were coprecipitated with Fe oxides, as indicated by the organic carbon content of the Fe oxides (Table 1). In the case of the fast reaction of Pb adsorption by the Fe oxides formed at an initial citrate/Fe(II) MR of 0.1, Pb ions would occupy the exposed Fe-OH or -OH₂ sites of the Fe oxides and the exposed carboxylate groups of the citrate ligands coprecipitated with the Fe oxides. Most of the exposed Fe-OH and -OH₂ or COOH groups could have been depleted by reaction with Pb ions in the fast reaction. In the slow reaction, in addition to the diffusion of Pb ions to the reaction sites of the micropores to form chemisorbed Pb species, Pb ions could be adsorbed by the Fe oxides through breaking the bonds between the Fe oxides and the coprecipitated citrate ligands and replacing citrate if the affinity of Pb ions to the surface of Fe oxides is higher than that of citrate ions to the surface of Fe oxides. Scheinost et al. (2001) pointed out that Pb seems to have a higher affinity for the ferrihydrite

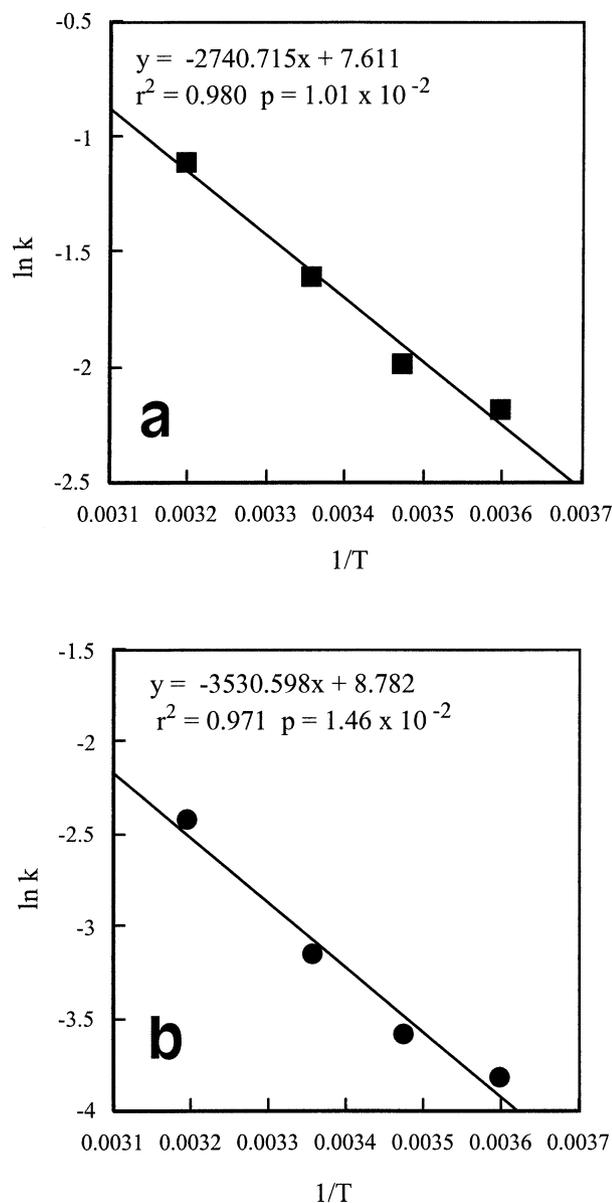


Fig. 3. Temperature dependence of the rate coefficients of (a) the fast reaction and (b) the slow reaction of Pb adsorption by the Fe oxide formed at the initial citrate/Fe(II) molar ratio of 0.

surface than fulvic acid. Similarly, Pb may have a higher affinity for the surface of Fe oxides than citrate ligands. These factors may explain why the activation energy in the slow reaction of Pb adsorption on the Fe oxides formed at the initial citrate/Fe(II) MR of 0.1 was substantially increased (Table 6) and the rate-limiting step was a chemically controlled process.

The noncrystalline oxides formed at the initial citrate/Fe(II) MR of 0.1 had a much higher value of mean surface roughness and surface fractal dimension (Liu and Huang, 1999b). Their surface was much rougher compared with the Fe oxides formed at the MRs of 0, 0.001, and 0.01. More edges and corners exist on the rougher surface. More Fe-OH and Fe-OH₂ groups should be present per unit area of edges and corners than per unit area of faces. The noncrystalline Fe oxides formed at the

Table 6. The activation energy and pre-exponential factor of Pb adsorption on Fe oxides formed at various initial citrate/Fe(II) molar ratios (MRs).

MR	Activation energy (kJ/mol)		Pre-exponential factor (h ⁻¹)	
	Fast reaction	Slow reaction	Fast reaction	Slow reaction
0	23	29	2.02×10^3	6.52×10^3
0.001	21	26	1.06×10^3	1.01×10^3
0.01	24	32	3.35×10^3	2.39×10^4
0.1	31	53	8.71×10^4	2.18×10^8

LSD_{0.05} = 10 and LSD_{0.01} = 15 for the activation energy.
LSD_{0.05} = 2.56×10^2 and LSD_{0.01} = 3.84×10^2 for the pre-exponential factor.

initial citrate/Fe(II) MR of 0.1 should, thus, have more exposed Fe-OH and Fe-OH₂ functional groups per unit area. Compared with the Fe oxides formed at lower initial citrate/Fe(II) MRs, the higher specific surface area and more-exposed Fe-OH and -OH₂ groups of the noncrystalline Fe oxides rendered a higher accessibility of Pb ions to the reactive surface, resulting in the higher preexponential factor.

In the general form instead of the simplified form of Arrhenius equation, preexponential factor is related to the average overall participating internal energy states (Moore and Pearson, 1981). Entropy is a state property and can be interpreted as a measure of disorder of a system (Shriver et al., 1990). Therefore, the preexponential factor may contain information about the reaction entropy. Incorporation of citrate to the Fe oxides (Fig. 4) would result in more disorder of the Fe oxide surface and change in the energy state.

4. CONCLUSIONS

The Pb adsorption on the Fe oxides formed at various initial citrate/Fe(II) MRs can be described by the multiple first-order kinetic model. The alteration of the surface properties of the Fe oxides by coprecipitation of citrate and the resultant effect on the rate coefficient of the Pb adsorption was especially pronounced in the Fe oxide system formed at the citrate/Fe(II) MR of 0.1. The coprecipitation of citrate ligands with the Fe oxides increased the rate coefficient of Pb adsorption on the Fe oxides by increasing their specific surface area and negative charge. The rate-limiting step of Pb adsorption reactions on the Fe oxides was predominantly a diffusion process, except for the slow reaction of Pb adsorption on the Fe oxides formed at the initial MR of 0.1, where the rate-limiting process was evidently a chemical process. For the Fe oxides formed at the initial citrate/Fe(II) MR of 0.1, the activation energy for the slow reaction of Pb adsorption on the Fe oxides was substantially increased; however, its preexponential factor was also significantly increased. Therefore, compared with the Fe oxides formed at other citrate/Fe(II) MRs, the higher rate coefficient of Pb adsorption on the Fe oxides formed at the initial citrate/Fe(II) MR of 0.1 was evidently due to the high preexponential factor, which apparently resulted from the higher specific surface, and more exposed Fe-OH and -OH₂ groups of noncrystalline Fe oxides formed. The rate coefficients of Pb adsorption by the Fe oxides formed at various citrate/Fe(II) MRs cannot be explained by the activation energy alone. The preexponential

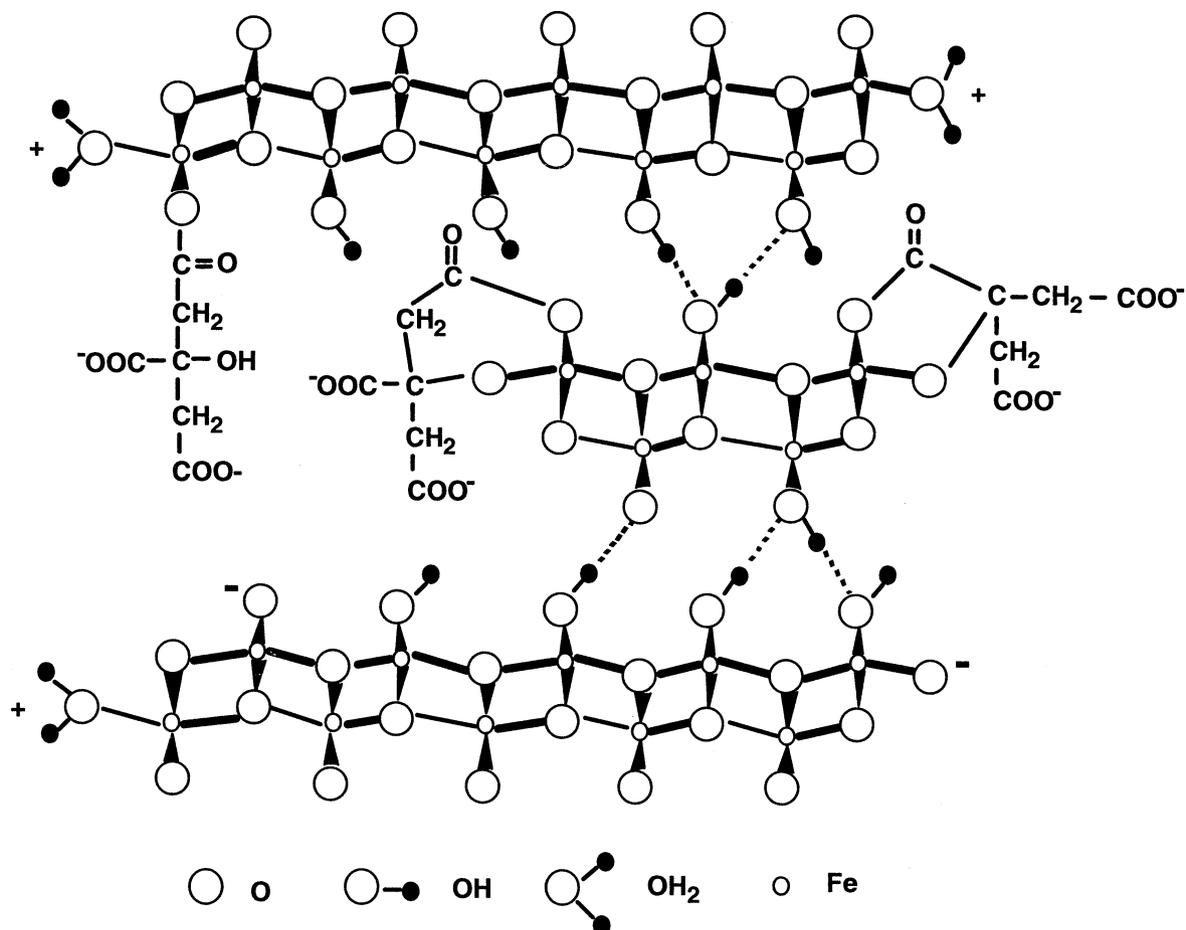


Fig. 4. Proposed model for the structural perturbation of Fe oxyhydroxides caused by the coprecipitation of citrate ligands.

factor plays an important role in influencing the rate coefficient of Pb adsorption by the Fe oxides. The results indicate that the role of organic acids, which are commonly present in natural environments, especially in the soil rhizosphere, in modifying the structural configuration and the resultant surface properties of the Fe oxides formed and their impact on kinetics of Pb adsorption, warrants in-depth study.

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