

Short communication

Effect of low-molecular-weight organic acids on the adsorption of norfloxacin in typical variable charge soils of China

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Abstract

Batch equilibrium experiments were used to study the adsorption of norfloxacin (NOR) onto three kinds of variable charge soils in China, namely Rho-Udic Ferrallic soils collected from Yunnan, Ali-Perudic Ferrallic soils collected from Jiangxi and Typ-Hap-Udic Ferrallic soils collected from Guangdong. Results show that NOR is strongly adsorbed by the soils, with $\lg K_d$ -values (linear model) of 4.41 ± 0.01 , 4.50 ± 0.02 , 4.44 ± 0.01 and $\lg K_f$ -values (Freundlich model) of 4.32, 4.45, 3.08 for the three tested soils, respectively. Both curves of the Freundlich equation and Langmuir equation for the three soils were in excellent linear correlation. Low-molecular-weight (LMW) organic acids, including citric acid, malic acid and salicylic acid were added in the presence of acetate buffer (pH 4.5) to test their effects on NOR adsorption. It was observed that the addition of LMW organic acids inhibited the NOR adsorption process. It was assumed that several effects, including soil pH, solid surface charge and competitive adsorption of co-existing cations, dominated the NOR sorption processes onto variable charge soils. Further studies should be performed to reveal the mechanism of the adsorption.

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1. Introduction

Scientific researchers are greatly concerned about the impact of pharmaceuticals on the environment [1]. A large number of drugs are used extensively in both human and veterinary treatments. Furthermore, a large percentage (from 25% to 75%) of veterinary medicines, including their metabolites, pass through animal bodies [2–4] and then spread into both the aquatic and terrestrial environments via several different pathways [4,5]. Antibiotics may enter soil matrices during the application of manure and slurry as fertilizers. However, not very much is known about the occurrence, fate, effect and risk associated with the release of antibiotics into the environment [6].

In China, fluoroquinolones (FQs) are administered widely in the treatment of animal disease. Among them, norfloxacin

(NOR), ciprofloxacin (CIP) and ofloxacin (OFL) account for approximately 98% of the total production of FQs. For example, the yield of NOR is about 3500 tons per year.¹

Studies by Golet et al. [7] showed that FQs are adsorbed onto solid matrices and may accumulate in the environment, but little is known about its adsorption behavior in soil. Acidic and variable charge soils are widely distributed in the tropical and subtropical areas of South China, which are characterized by high content of iron and aluminum oxides and dominated by 1:1-type clay minerals, such as kaolinite. These factors make the surface charge properties of variable charge soils distinctly different from those of the constant charge soils in temperate regions, which may greatly affect the environmental behaviors of veterinary medicines [8]. Additionally, low-molecular-weight (LMW) organic acids, which exist widely in soils, have been

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¹ Available at (in Chinese): <http://www.nanhui.org/ShowNews.asp?id=95350&newstype=%D0%D0%D2%B5%BE%DB%BD%B9>.

Table 1
Characteristics of the three tested soils

Soil type	Organic matter (OM) (g/kg)	pH in CaCl ₂	CEC (cmol/kg)	Fe ₂ O ₃ (g/kg)	Texture (v/v) (%)			Composition of minerals
					Clay	Silt	Sand	
Rho-Udic Ferralisols	6.9	4.91	5.28	211.4	38.3	15.0	46.7	Kaolinite, ferric oxide
Ali-Perudic Ferrisols	4.2	4.81	6.05	48.9	31.5	17.2	47.1	Kaolinite
Typ-Hap-Udic Ferralisols	4.4	4.88	8.91	51.1	15.2	43.2	41.6	Poor-crystalized kaolinite

implicated in many soil processes, such as nutrient availability, translocation of metals, fate of heavy metals and mineral weathering [9–13].

The objective of this paper was to obtain the sorption coefficients of NOR in three variable charge soils, and to investigate how anions of LMW organic acids influence the adsorption process of NOR.

2. Materials and methods

2.1. Materials

NOR (CAS 70458-96-7, 97.8% purity) was supplied by the National Institute for the Control of Pharmaceutical and Biological Products, China. Acetonitrile (HPLC grade) was purchased from Tedia, USA. All other chemicals were analytical reagents. Milli-Q organic-free water (Millipore, Bedford, MA) was prepared as the solvent.

The batch equilibrium test was performed by utilizing 50 mL polypropylene test tubes. To avoid adsorption of NOR onto silanol groups of the glassware surface, all glassware was rinsed with 6% dimethyldichlorosilane in methanol, dried at 60 °C and rinsed again with methanol before use.

Three kinds of variable charge soils, namely Rho-Udic Ferralisols, Ali-Perudic Ferrisols and Typ-Hap-Udic Ferralisols were collected from Yunnan, Jiangxi and Guangdong Province in China, respectively, and were air-dried and sieved prior to their use in the experiments [14]. The physical–chemical properties of the three soils are listed in Table 1.

2.2. Sorption experiments

NOR sorption behavior in the three soil types was investigated. Batch equilibrium experiments were performed in accordance with the Organization for Economic Co-operation and Development (OECD) test Guideline 106 [15]. For pre-equilibration, 1–2 g aliquots of soil sample were mixed with 25 mL 0.01 M CaCl₂ as the aqueous phase in 50 mL polypropylene plastic tubes and then equilibrated by shaking for 48 h. In a preliminary test, sorption kinetics of NOR had shown that there was only a minor difference between the amounts adsorbed after 8 h and 48 h, respectively, and thus, 12 h was found to be a sufficient equilibration time. In order to inhibit microbial activity, the soil suspension was adjusted to 0.01 M NaN₃.

Triplicate samples of 1 g of soil and different amounts of NOR, dissolved in small amounts of MeOH:H₂O, were made for each soil sample to a final volume of 25 mL with NOR

concentrations of 1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L and 5 mg/L, respectively in the test tubes. A blank for each soil and a control for each concentration were made. Blanks contained 25 mL of CaCl₂ solution, while controls contained 25 mL NOR solution without soil. All samples were shaken for 12 h. After centrifugation at 4000 × g for 10 min, samples of the supernatants were subsequently analyzed by high performance liquid chromatography (HPLC) with fluorescence detection.

Given that NOR is a zwitterionic compound with pK_a-values shown below in Fig. 1 [16,17] and that results by Boxall et al. [18] have shown that the sorption of sulfachloropyridazine is influenced by pH, it was predicted that NOR sorption onto soils would also be pH-dependent. It has been shown that the concentration of acetic acid in soils reaches 116.7–166.7 μmol/kg [19]. Therefore, in order to eliminate the effect of soil pH on sorption, 0.5 mL of 0.5 M acetate buffer (pH 4.5) in 25 mL soil solution was added to obtain stable pH values. The effect of LMW organic acids on sorption of NOR to the three soils was examined by performing sorption experiments using three LMW

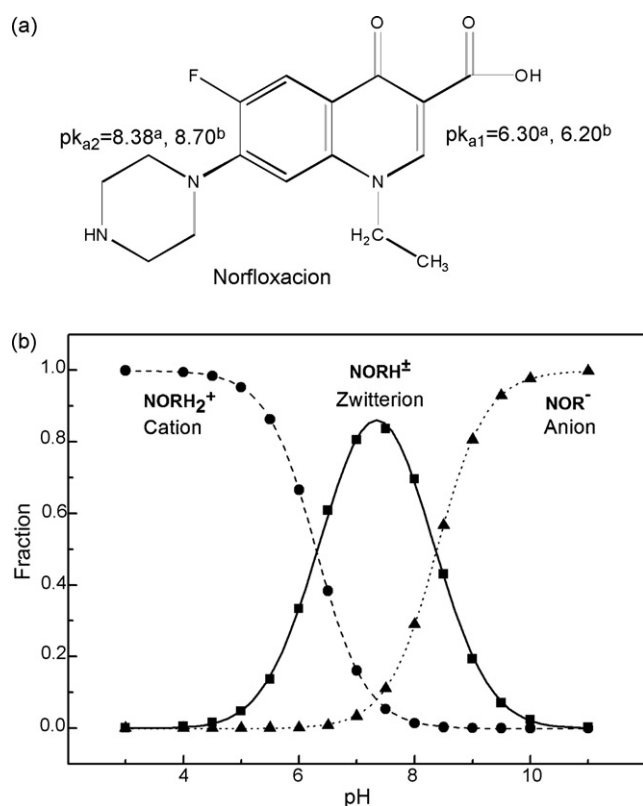


Fig. 1. (a) Structure of NOR molecule (a: Ref. [16]; b: Ref. [17]) and (b) pH-dependant speciation of NOR.

Table 2
Parameters of the adsorption models fitted

Soil type	Freundlich model			Langmuir model		
	$\lg K_f$	$1/n$	r	K_L	Q_m (mg/kg)	r
Rho-Udic Ferralisols	4.32	0.9832	0.9874	21.46	1150	0.9837
Ali-Perudic Ferralisols	4.45	0.9895	0.9867	14.9	2090	0.9816
Typ-Hap-Udic Ferralisols	3.08	0.7594	0.9881	125	297	0.9972

organic acids including citric acid, malic acid and salicylic acid. With the addition of acetate buffer, the soil suspensions containing 5 mg/L NOR were adjusted to 0.5 mM, 1 mM, 1.5 mM, 2 mM and 2.5 mM concentrations of LMW organic acids, respectively. Following the procedures described above, the sorption coefficients for NOR were then determined.

2.3. Chemical analysis

A 2695 Waters Alliance system (Milford, MA, USA) equipped with a Waters 2475 Fluorescence Detector (FLD) together with an autosampler controlled the binary gradient system. The FLD excitation and emission wavelengths were 278 nm and 445 nm, respectively. A Phenomenex Gemini C18 column (150 mm \times 4.6 mm I.D., 5 μ m) was coupled to a Phenomenex Gemini C18 guard cartridge (4.0 mm \times 3.0 mm I.D.). The column temperature was set to 40 $^{\circ}$ C.

The separation was performed by gradient elution. Mobile phase A was acetonitrile and mobile phase B was prepared by diluting 0.5 mL phosphoric acid into 1 L water. The flow rate was 1 mL/min. To eliminate the influence of impurities from the soils to NOR peak shape, a gradient elution program with a 15 min run per sample was applied. Elution started with 3% mobile phase A, followed by a 6 min linear gradient to 15% mobile phase A, and ended with a 3 min isocratic elution at 15% mobile phase A. To reestablish the initial conditions, a 1 min linear gradient to 3% mobile phase A was followed by an equilibration time of 5 min. The retention time for NOR was 7.8 min.

3. Results and discussion

3.1. Sorption characteristics of NOR onto the soils

Freundlich isotherms ($\lg c_s = \lg K_f + 1/n \times \lg c_w$) and Langmuir isotherms ($1/q_e = 1/Q_m + 1/K_L Q_m c_w$) obtained for NOR in the three soils are shown in Fig. 2a and b and the parameters of adsorption equations are listed in Table 2. Our results indicated that NOR was greatly adsorbed onto all three soils. As the values of $1/n$ were close to unity, sorption in Rho-Udic Ferralisols and Ali-Perudic Ferralisols can be reasonably well approximated by the linear sorption coefficient K_d . Fitting of a linear model to the data ($c_s = K_d \times c_w$) resulted in the distribution coefficients $\lg K_d$ -values of 4.41 ± 0.01 , 4.50 ± 0.02 and 4.44 ± 0.01 for Rho-Udic Ferralisols, Ali-Perudic Ferralisols and Typ-Hap-Udic Ferralisols, respectively. It is clear that the $\lg K_f$ -value for Typ-Hap-Udic Ferralisols was slightly different from its $\lg K_d$ -value because of its nonlinear sorption process. The maximum adsorption amount of 2090 mg/kg for Ali-Perudic Ferralisols exceeded that for Rho-

Udic Ferralisols and Typ-Hap-Udic Ferralisols by a factor of about two and seven, respectively.

The adsorption of pharmaceuticals is a complex process and the adsorption capacity of FQs is related to different soil properties, including organic matter content, type and amount of clay, ion-exchange capacity and pH, and several physicochemical properties of FQs [20–23]. For the three soils examined, strong adsorption of NOR may be due to the presence of kaolinite. It had been proven by Nowara [24] that several FQs are strongly adsorbed onto pure kaolinite with K_d -values of 3550 L/kg. However, the presence of kaolinite should not be

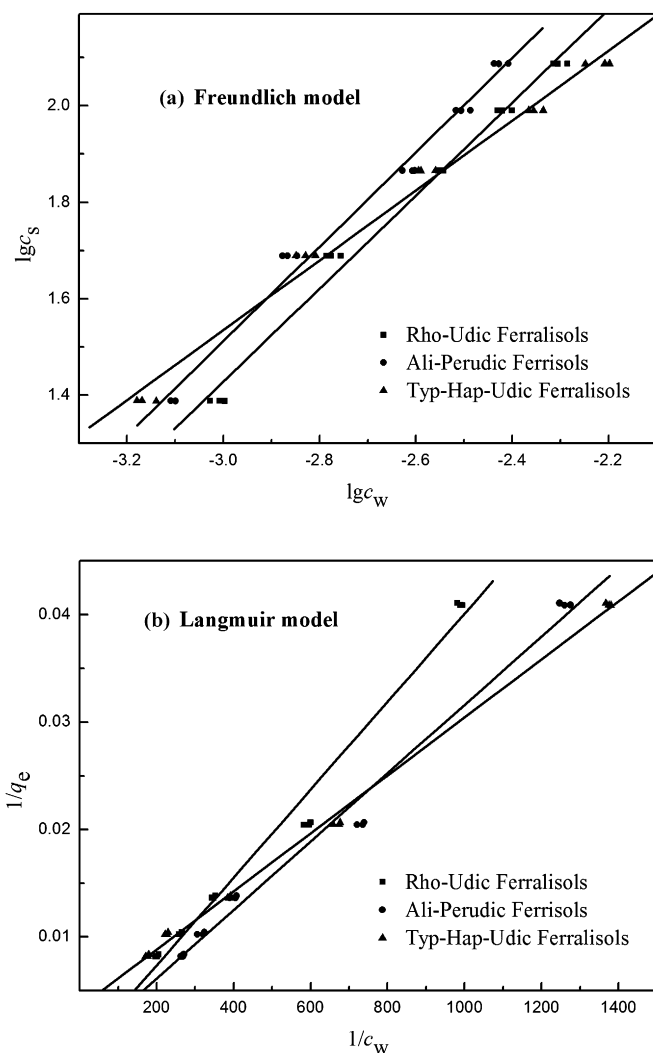


Fig. 2. Fitting curves of (a) Freundlich isotherm and (b) Langmuir isotherm for the three soils.

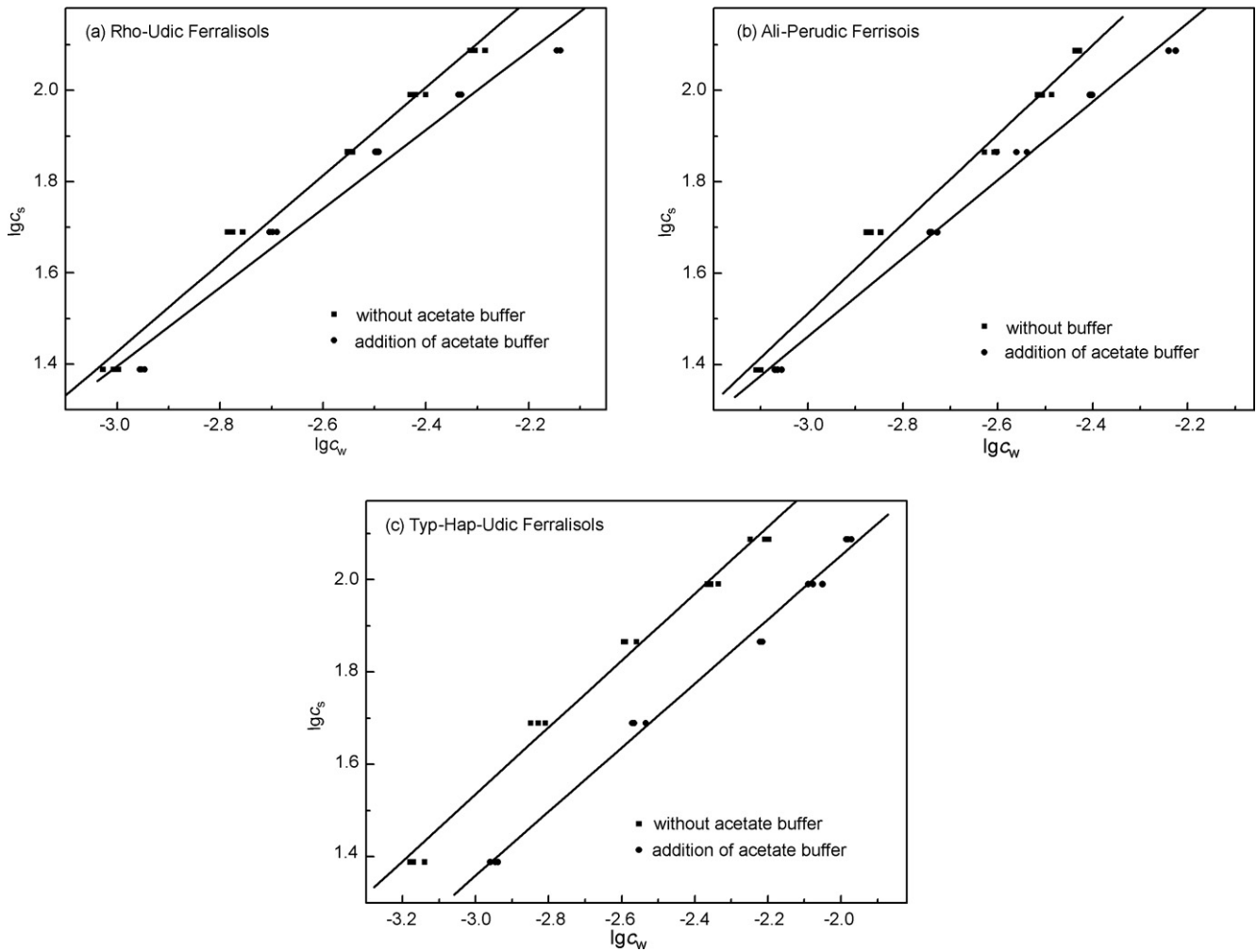


Fig. 3. Fitting curves of Freundlich isotherm before and after addition of acetate buffer of the three soils.

the only reason why such high adsorption coefficients were observed. Sorption coefficients for sulfachloropyridazine in two soil types increased as pH decreased [18]. As well, soil pH values in CaCl_2 solution for the three tested soils were in significantly negative correlation to their K_d -values with a r value of -0.9992 ($K_d = -59029 \times \text{pH} + 315567$, $P < 0.01$), which means less NOR was adsorbed onto soils with a high pH value. This is in accordance with the results obtained in other soils by Zhang and Dong [25]. Zhang and Dong [25] also reported the nonlinear relationship between soil pH and NOR K_d -values in Ali-Perudic Ferrisols and Gleyic-Stagnic Anthrosols at different pHs (5–9). Thus, such a linear relationship cannot be simply extrapolated to the pH interval of 4–7, even though to some extent NOR sorption is a pH-dependant process.

It had been previously assumed that at low pH, NOR sorption onto soils was predominated by cationic adsorption [25]. Zhao and Zhang [26] had reported that for variable charge soils the quantity of surface positive charge increased with decreasing pH. Consequently the sorption process could be correlated with the changes in surface charge. With an increased quantity of positive surface charges, the number of active sorption sites decreased so that less NOR cations adsorbed onto the soil's

surface. Moreover, other factors, like complexation with trivalent or divalent metal ions and cation bridging at clay surfaces, might also affect adsorption of NOR [21,23].

3.2. Effect of acetate buffer on NOR sorption

In the fitting curves of the Freundlich isotherm (Fig. 3), the addition of acetate buffer decreased NOR $\lg K_f$ -values to 3.68, 3.96, 2.65 and $\lg K_d$ -values to 4.33, 4.42, 4.17 for Rho-Udic Ferralisols, Ali-Perudic Ferrisols and Typ-Hap-Udic Ferralisols, respectively, in accordance with the previously described fact that sorption amounts of NOR dropped as pH decreased. All data were had good correlation to the Freundlich model and the Langmuir model, but not to the linear model.

The addition of acetate buffer was to keep the pH value of the sorption system steady while simultaneously increasing the ionic strength of the solution. Co-existing and extraneous cations could competitively adsorb onto the soil surface so as to weaken NOR sorption [27]. In general, it could be concluded that the decrease of the amount of sorption was the combination of pH and ionic strength effects induced by the addition of acetate buffer.

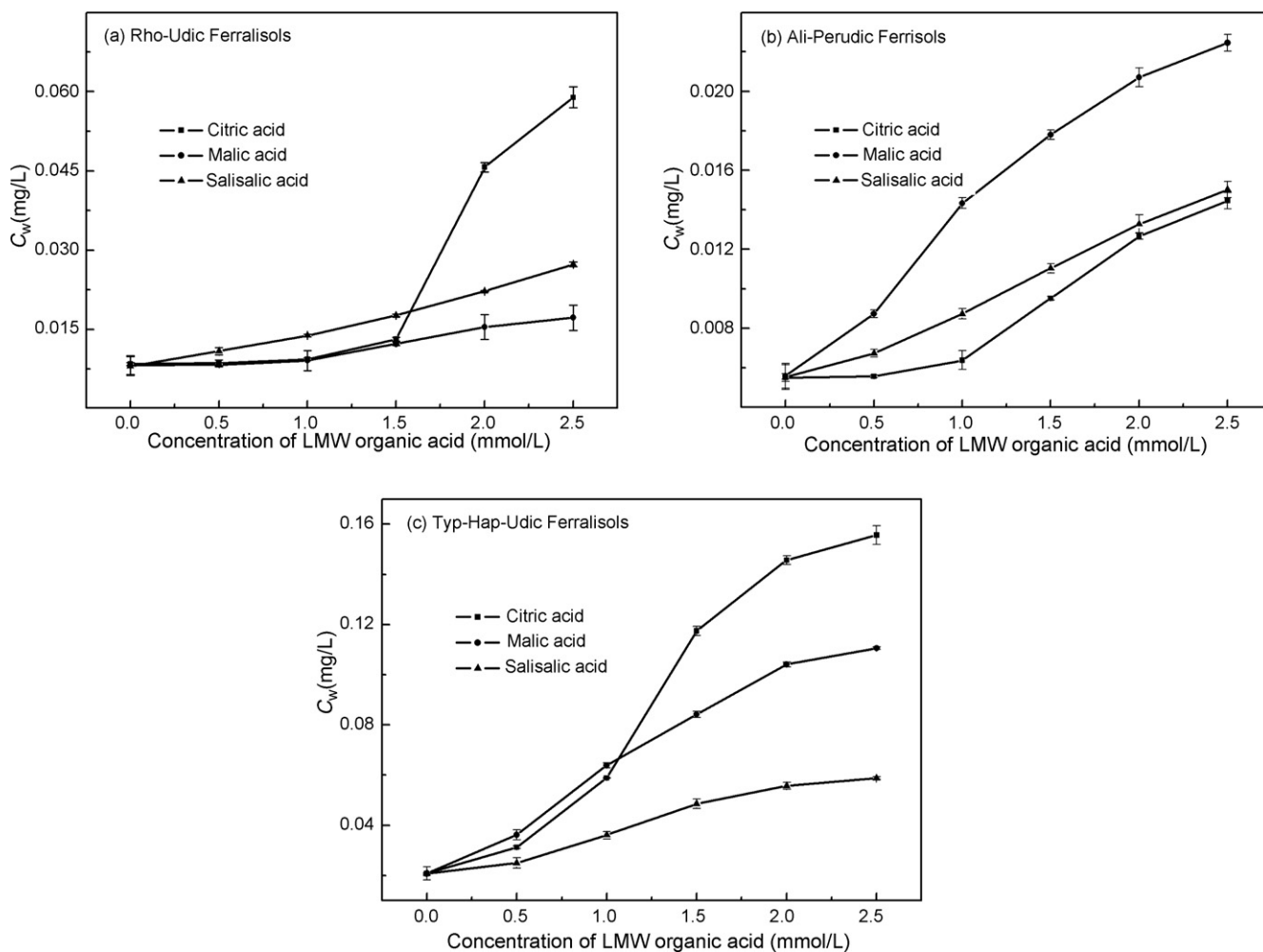


Fig. 4. Effects of addition of three LMW organic acids on adsorption of NOR on the three tested soils.

3.3. Effects of LMW organic acids on NOR adsorption

With the presence of an acetate buffer, the addition of LMW organic acids (citric, malic and salicylic acid) resulted in the release of more NOR into the aqueous solution (Fig. 4). With increasing concentrations of the three LMW organic acids, the concentration of NOR in solution increased, but with different trends. For Typ-Hap-Udic Ferralisols, NOR sorption gradually reached equilibrium. While for Rho-Udic Ferralisols and Ali-Perudic Ferralisols, more NOR was detected in solution with increasing concentrations of organic acid. For Rho-Udic Ferralisols, an abrupt increase of NOR concentration occurred at higher concentration of citric acid.

At low concentrations of LMW organic acids, organic anions adsorbed onto soils so that the surface negative charges increased, resulting in a change in the amount of surface charge [28]. It has been reported that the presence of several LMW organic acids caused an increase of surface negative charge and a decrease of positive charge in variable charge soils with the following order: citric acid > malic acid > axalic acid > acetate acid [29,30]. At the working pH of 4.5, the cationic form of NOR was predominant in solution (Fig. 1). However, no adsorption

amount increase was observed. On the contrary, more NOR was detected in the solution. Thus, it can be assumed that the surface negative charge should not be the only factor to increase NOR sorption amounts.

Previous studies have shown that different cations result in different amounts of NOR sorption and that the competitive adsorption by aluminum ion (Al^{3+}) greatly affects NOR sorption onto soils [27]. In variable charge soils, LMW organic acids promoted the dissolution of aluminum by acidity and complexation. Acetate buffer had little influence on the release of aluminum in variable charge soils [31]. It had been reported that organic acids greatly increased the concentration of active aluminum in solution by forming organic–aluminum complexes [32,33]. For instance, at pH 4.5, organic acids dissolve the aluminum best with the following order: citric acid > malic acid > salicylic acid [34]. However, in Fig. 4a–c, no such trend was observed except at the high concentration of LMW organic acid for Typ-Hap-Udic Ferralisols.

In variable charge soils, the presence of LMW organic acids leads to a change of solid surface. At low pH, LMW organic acids possessing three or more active functional groups (citric acid and malic acid) formed the soil–organic anion–Al com-

plex [35]. To some extent, the forming and steric hindrance of this complex inhibited the competitive adsorption of NOR. Additionally, organic acid anions might combine with NOR cations so as to increase NOR concentration in solution.

This study shows that a large proportion of adsorption sites on the solid surface of soils are occupied by organic anions (citrate, malate and salicylate) and that when they are combined with metal ions, the adsorption process of NOR is hindered. Several effects discussed above all inhibited the sorption process of NOR. The effects of pH, surface negative charge and aluminum release varied with different concentrations of the three LMW organic acids, resulting in different inhibition on NOR sorption.

4. Conclusion

The results of the present studies illustrated a strong adsorption of NOR into the three variable charge soils. This appears to be mainly due to the minerals composition and pH of the three tested soils. The sorption coefficient K_d -values were found to be in a significantly negative correlation to soil pH in CaCl_2 solution. The addition of LMW organic acids inhibited the NOR adsorption process, mainly because of the competitive adsorption on active adsorption sites of the solid surface. Several effects, including soil pH, solid surface charge and competitive adsorption of co-existing cations were involved in NOR sorption onto variable charge soils. In order to reveal the mechanism of the adsorption process an investigation of other factors affecting the adsorption of organic compounds in soil will need to be performed.

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