



Characteristics of isothermal adsorption and desorption of aluminum ion to/from humic acids

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Abstract

The adsorption and desorption characteristics of Al^{3+} to/from humic acids at different pH, ionic strength, and temperature were studied by the C-25 glucosan-gel chromatography method. The results showed that the maximum adsorption amount (Q_{\max}) and adsorption constant (k) increased, whereas, the absolute value of standard thermodynamic molar free energy change (ΔG_m^0) decreased with the increase of pH at constant ionic strength and temperature. With ionic strength increasing from 0 to 0.15 mol/L, Q_{\max} and k increased and the absolute value of ΔG_m^0 decreased at constant pH and temperature. High temperature was unfavorable for the adsorption reaction, as indicated by the dramatic decrease of Q_{\max} and the absolute value of ΔG_m^0 with an increase in temperature. The standard thermodynamic molar free energy change (ΔG_m^0) and the standard thermodynamic enthalpy change (ΔH_m^0) of the adsorption reaction were both negative, suggesting that adsorption reaction was spontaneous and exothermic. The desorption rate of HA- Al^{3+} complex accelerated with the decrease of pH, and a significant linear relationship could be obtained between pH and the desorption rates of Al^{3+} from humic acids. These results demonstrated that the Al^{3+} adsorption reaction was a “biphase” reaction, and adsorption occurred at both the interior and exterior adsorption sites of humic acids.

Key words: adsorption and desorption characteristics; Al^{3+} ; humic acid

Introduction

Humic acid (HA) in soil is an important component influencing soil properties. It is a variably charged organic colloid, consisting of massive active functional groups, such as, carboxyl and hydroxyl groups. It has tremendous reactive competence and combining capacity with metal ions, in the environment (Xing *et al.*, 2005). Thus, it acts as an essential complexant and coagulator of metal ions in the environment, and plays an important role in adjusting the transformation, transportation, and bioactivity of metal ions (Li and Wei, 2003). Sibabda and Young (1986) and Kislenco and Oliynyk (2004), found a significant adsorption of humic substance on Al-rich tropical soil. Aluminum ion (Al^{3+}) is a vital contributor to the potential acid of soils, and its concentration in strongly acidified soils may be high enough to poison various animals and plants (Chen, 2002). Consequently, many studies with regard to its problems in acidic soil and acidified water environment were conducted.

However, the speciation of activated Al^{3+} has been enormously influenced by organic matter. As the main components of soil organic matter, humic acids can not only alter the dissolution equilibrium of sparingly soluble

aluminiferous minerals, but also directly decompose aluminiferous minerals and accelerate the dissolution of Al^{3+} from minerals. Therefore, adsorptions and desorptions are the inevitable reactions between metallic elements and HA. The study of Al^{3+} adsorption to and desorption from HA is of great significance for revealing its environmental behavior. However, few reports have been published concerning this aspect because of the difficulty in the measurements of free Al^{3+} concentration. In this article, C-25 glucosan gel chromatography has been employed to separate adsorptive Al^{3+} and dissociated Al^{3+} , thus the adsorption and desorption characteristics of Al^{3+} under various pH, ionic strength, and temperature have been studied in detail.

1 Materials and methods

1.1 Extraction and purification of humic acids

Humic acids were extracted from a surface soil (Al layer), taken from Mount Jingyun in Chongqing, China. After being air-dried, the soil samples were sifted through a 1-mm sieve pore. The method by Wang *et al.* (2005) was employed to extract, separate, and purify HA. Some of the basic properties of the final preparation of HA, such as, the number of functional groups and the content of metals and

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ash, were measured by using the method of Wang and Wei (2006). The results are shown in Table 1.

1.2 Methods

1.2.1 Isothermal adsorption experiment at different pH

In the batch experiment, every 2.0 ml of condensed HA solution (DOC, 5.0 mg/ml) was put into a series of 50-ml centrifugation tubes, adequate amounts of 1 mol/L of NaCl and 0.050 mol/L of AlCl₃ solutions were added to maintain an ionic strength of 0.10 mol/L, as well as a series of solutions with Al concentrations of 0.16, 0.32, 0.64, and 1.28 mmol/L, respectively. The pH of each series of the above-mentioned solutions was then adjusted to be 3.0, 4.0, 5.0, 6.0, and 7.0, respectively, by adding 0.1 mol/L of HCl or 0.1 mol/L of NaOH. The final solution volumes were kept at 20.0 ml by adding deionized water. The reaction solutions were shaken for 24 h at a temperature of 25 ± 0.5°C after 15 min of continuous pure argon bubbling under dark conditions. After the reactions approached an equilibrium, the reaction solutions were centrifuged at 4000 r/min for 10 min, and then the supernatants were taken, to determine the amount of total Al and adsorbed Al. The total amount of Al was analyzed by digestion of the supernatant with concentrated HNO₃-HClO₄ followed by the aluminum reagent method (Pekci and Miler, 1991). For the analysis of absorbed Al³⁺, 1 ml of supernatant was passed through an SP Sephadex C-25 gel chromatography column, the HA-Al³⁺ complex would easily pass through the column because of its large molecular, whereas, the free Al³⁺ would be kept at the capillary pore of the resin. Twenty milliliters of deionized water was passed through the column at a rate of 1 ml/min for the elution of absorbed Al³⁺, and then the same method for total Al measurement was used to analyze the absorbed Al³⁺.

1.2.2 Isothermal adsorption experiment at different ionic strengths

In the reaction systems, the ionic strengths of the reaction solutions were adjusted to 0, 0.05, 0.10, and 0.15 mol/L, respectively, at a constant temperature and pH. Then the same procedure as described earlier was used to examine the influence of ionic strength on the adsorption of Al³⁺ by HA.

1.2.3 Effect of temperature on adsorption

When pH and ionic strength were maintained at the same level as described earlier, the effect of temperature on Al³⁺ adsorption was studied at 25°C and 35°C, and subsequently a similar procedure was followed.

1.2.4 Isothermal desorption experiment

Twelve milliliters of HA solution (DOC, 5.0 mg/ml) was added into a 250-ml conical flask with a stopper. Subsequently about 90 ml of deionized water and an

adequate amount of 0.05 mol/L AlCl₃ solution were added to adjust the concentration of Al³⁺ to 0.16 mmol/L. The reaction system was maintained at pH 7.0 and 0.10 mol/L of ionic strength. When the reaction approached an equilibrium, the same adsorption procedure was followed, where every 20 ml solution was transformed into a 50-ml centrifugation tube, and then its pH adjusted to 7.0, 6.0, 5.0, 4.0, 3.0, and 2.0 with 1.0 mol/L of HCl, respectively. After aerated argon for 30 min, the centrifuge tube was capped and shaken for 24 h under dark conditions. The adsorption of Al³⁺ at different pH was measured using the method mentioned earlier. The desorption rate (θ) could be calculated using the following equation.

$$\theta = \frac{Q_7 - Q}{Q_7} \times 100\% \quad (1)$$

where, Q_7 was the adsorption amount of Al³⁺ at pH 7.0, and Q was the adsorption amount at other pH levels.

1.2.5 Data processing of characteristic parameters

Adsorption amounts (Q) of Al³⁺ on HA were calculated at different pH, ionic strength, and temperature. The experimental data were fitted with Langmuir isotherm model $Q = Q_{\max}C/(C + 1/k)$, after which the maximum adsorption amount (Q_{\max}) of Al³⁺ and adsorption constant (k) could be obtained. The standard thermodynamic molar free energy change (ΔG_m^0 , kJ/mol), the standard thermodynamic enthalpy change (ΔH_m^0), and the standard entropy change (ΔS_m^0) were also calculated according to the adsorption constant (k) at different temperatures, based on the following thermodynamics equations.

$$\Delta G_m^0 = -2.303RT \log(k\Phi) \quad (2)$$

Vant Hoff Equation:

$$\ln(k_2/k_1) = \Delta H_m^0/R(1/T_1 - 1/T_2) \quad (3)$$

Gibbs-Helmholtz Equation:

$$\Delta G_m^0 = \Delta H_m^0 - T\Delta S_m^0 \quad (4)$$

where, R is the gas constant, Φ is the conversion coefficient for concentration of HA from mol/L to a molar scale, $\Phi = \text{organic carbon content (\%)} \times \text{HA molecular weight (mg/mol)} \times \text{volume of reaction solution (L)}$; k_2 , k_1 are the adsorption constants at temperatures T_2 and T_1 , respectively.

2 Results and discussion

2.1 Effect of pH on the adsorption of Al³⁺ on HA

Figure 1 shows the effect of pH on the adsorption of Al³⁺ on HA. The results showed that Q_{\max} , k , and ΔH_m^0 were all

Table 1 Basic properties of pure humic acid

Total acidity	Function groups (mol/kg)		Organic carbon (g/kg)	Metal component (mg/L)					Ash (g/kg)
	Carboxyl	Phenolic hydroxyl group		Cu	Zn	Fe	Ni	Hg	
5.59	2.02	3.57	479.5	0.050	0.050	1.17	0.014	0.042	12.4

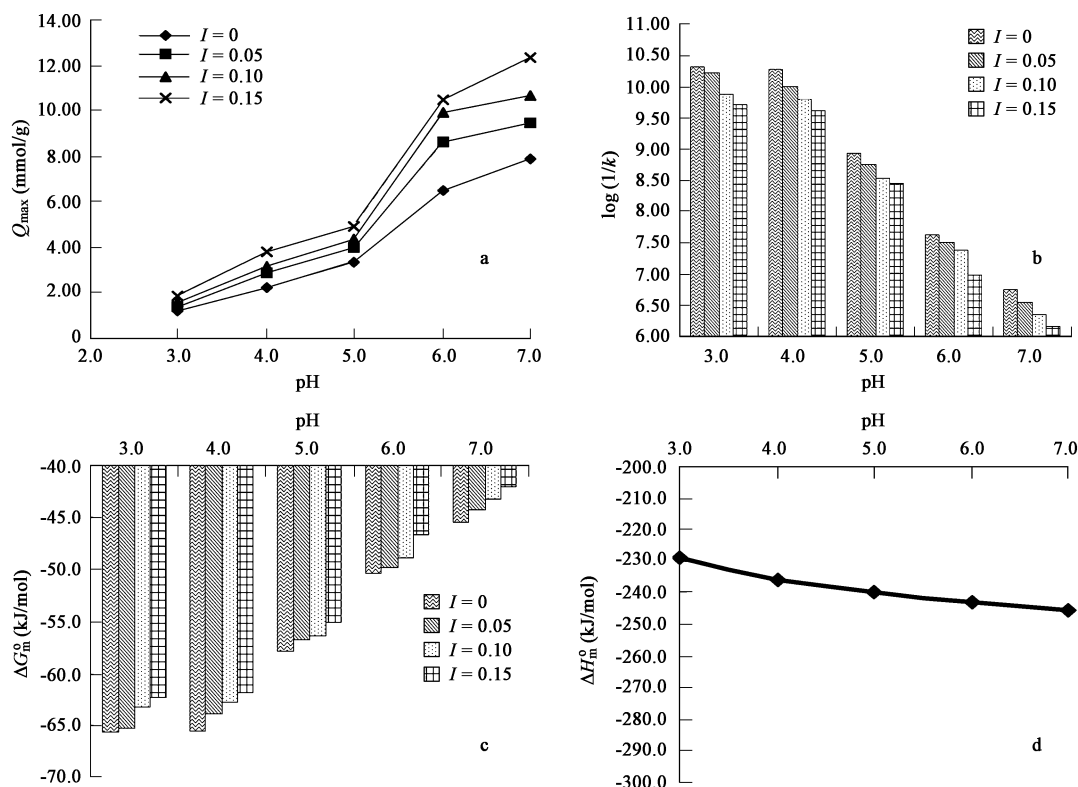


Fig. 1 Effect of pH on Q_{\max} (a), k (b), standard thermodynamic molar free energy change ΔG_m^0 (c), ΔH_m^0 (d) of Al^{3+} on HA.

increased with the increase of pH at constant ion strength and temperature, whereas, ΔG_m^0 decreased under the same conditions.

Models were used to fit the relationships between Q_{\max} , $\log(1/k)$, ΔG_m^0 , and pH. The results showed that linear relationships existed between these parameters and pH, and the correlation coefficients all reached 95% significance level.

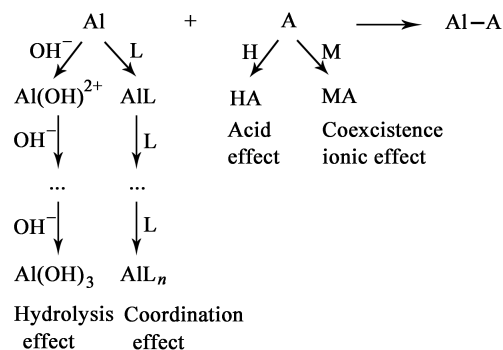
$$Q_{\max} = 2.503\text{pH} - 6.577 \quad n = 5, R^2 = 0.9212 \quad (5)$$

$$\log(1/k) = -0.944\text{pH} + 11.22 \quad n = 5, R^2 = 0.9539 \quad (6)$$

$$\Delta G_m^0 = 5.39\text{pH} - 71.05 \quad n = 5, R^2 = 0.9490 \quad (7)$$

These relationships were attributed to the acid effect of humic acid and the hydrolyzing effect of Al^{3+} (Wuhan University, 2000). In addition to reacting with HA, the reactions of Al^{3+} may include the hydrolysis effect of Al^{3+} and complex reactions between Al^{3+} and other ligands, such as Cl^- , in the reaction system. Besides the reaction of HA with Al^{3+} , the acid effect may also exist between HA and H^+ . If other metal ions (M) exist, the complex reactions may occur between HA and other metal ions (M). However, all these reactions are generally called side reactions. Owing to the interference of side reactions, the constants of the main reaction and the adsorption reaction will be influenced (Eq.(8)). It can be found from the results that the acid effect of HA plays a greater role than that of the hydrolysis effect of Al^{3+} obtained. When pH is low, HA has a very strong acid effect, which disassociates the Al-HA complex and the constant of the main reaction is reduced. The acid effect of HA becomes weak as pH

increases, which is beneficial to the complex reaction between Al^{3+} and HA, and so increases the adsorption amount and constant. Yu (1987) pointed out that when the pH is below 4, the group dissociated is mainly the carboxyl of HA. The coordination reaction mainly takes place on the carboxyl of HA. As pH increases, the phenolic hydroxyl group of HA also dissociates, leading to an increase in reaction sites, as the adsorption amount and adsorption constant are consequently increased. Similar conclusions have also been drawn by some researchers (Wang *et al.*, 2001). The possible reactions that occur in the solutions because of the influence of pH are as follows:



“L” denotes other ligands. “M” denotes other competitive metal ions. “A” denotes ligand in humic acid.

As the side reactions of the product (Al-A) are negligible, only the side reactions of the reactant are considered. The ionic electric charges of reactants and products have been neglected for convenience.

2.2 Effect of ionic strength on the adsorption of Al^{3+} on HA

Figure 2 shows the effect of ionic strength (I) on the adsorption of Al^{3+} on HA. The results show that Q_{\max} and k increase with the increase of ionic strength, at a constant pH, and temperature, whereas, the absolute value of ΔG_m^0 decreases slightly.

The data Q_{\max} , $\log(1/k)$, and ΔG_m^0 were fitted in terms of linear Eqs.(9)–(11), and the results showed that the correlation coefficients all reached 95% significance level.

$$Q_{\max} = 27I + 6.86 \quad n = 4, R^2 = 0.9328 \quad (8)$$

$$\log(1/k) = -0.208I + 7.895 \quad n = 4, R^2 = 0.9040 \quad (9)$$

$$\Delta G_m^0 = 1.19I - 51.9 \quad n = 4, R^2 = 0.9163 \quad (10)$$

Effect of ionic strength on the adsorption of HA to Al^{3+} reflected the complexity of its reaction mechanism. HA was a hydrophilic colloid with negative charge in the solution. Its structure and existing state was influenced by acidity and ionic strength of the solution. The reactions between HA and metal ions consisted of the reactions of the surface functional groups, as well as, the holding reaction between the interior binding sites of HA and the metal ions that penetrated into the HA particles. With the increase in ionic strength, the cations stuck to the agents, and with the negative charge of HA, the repulsion within the molecules reduced. Therefore, it was beneficial to the distortion and reunion of the HA macromolecule chain. On the one hand, the increase of steric hindrances inside the colloid, promoted the adsorption strength of the Al^{3+} that had penetrated into the HA particles, which led to the increase of the adsorption constant. On the other hand, the agglomerated HA colloids prevented the Al^{3+} in the solution from penetrating into HA, which led to the decrease of the adsorption constant. At the same time, quite a lot of Na^+ reacted with the exterior phenol group of HA–OH and the weak acid carboxyl (–COOH), and formed a sodium salt of weak acid, which competed with the combining sites of metal ions. These reactions also weakened the adsorption of Al^{3+} on HA.

Moreover, Cl^- may combine with Al^{3+} when its concentration is relatively high, which can influence the characteristic parameters of the adsorption of Al^{3+} on HA. Therefore, the effect of ionic strength on the characteristic parameters of the adsorption may be the integrated

reflection of the different impacts of the inner and outer combining sites and the coordination effect of Cl^- with Al^{3+} . The co-research of structure variation and the behavior of reaction characteristics in the adsorptive process will reveal the reaction nature, which also needs to be studied further.

2.3 Effect of temperature on the adsorption of Al^{3+} on HA

Figure 3 shows the effect of temperature on the characteristic parameters of the adsorption of Al^{3+} on HA. Regardless of the slight increase in the adsorption constant, with the temperature increasing, Q_{\max} and the absolute value of ΔG_m^0 decreased to a great extent. These results revealed that the adsorptive reaction was an exothermal reaction, and high temperature had an unfavorable influence on the reaction, which was in accordance with $\Delta H_m^0 < 0$. As the absolute value of ΔH_m^0 was higher than 230 kJ/mol, far greater than the physical adsorption heat (Fig.1d), it was deduced that quite a proportion of the adsorption of Al^{3+} on HA was chemical adsorption. The adsorption heat values usually suggested the type of adsorption reaction. Low absolute value of adsorption heat (< 25 kJ/mol) suggested that the initial phase adsorption was controlled by diffusion, which belonged to the physical adsorption. Although, high absolute value (> 25 kJ/mol) suggested that the adsorption reaction was a chemically controlled process, which belonged to a chemical reaction (Lakshmi-pathiraj *et al.*, 2006). Under the same condition, the higher the pH was, the larger the absolute value of ΔH_m^0 and ΔS_m^0 were. Therefore, the higher the pH was, the more favorable it was for the adsorptive reaction.

The standard thermodynamic free energy change (ΔG_m^0) was all negative at the experimental temperature, indicating that the adsorption reaction was a spontaneous process. The absolute value of ΔG_m^0 at 298.2 K was higher than that at 308.2 K, which demonstrated that low temperature was favorable for the adsorption reaction. The aluminum ion existed in the environment in a lower energy form, and the adsorbed Al^{3+} was more stable than the free ion. It was one of the reasons that the humic substance could fix metal ions, reduce their biological activity, and weaken their pollution in soil.

The thermodynamic standard entropy changes (ΔS_m^0) were all negative, indicating that the adsorption process

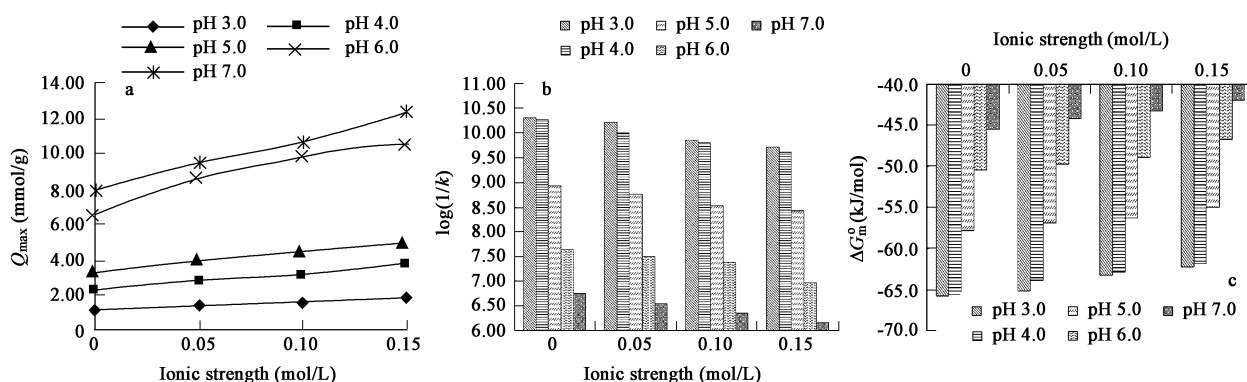


Fig. 2 Effect of ionic strength on Q_{\max} (a), k (b), and ΔG_m^0 (c) of Al^{3+} on HA.

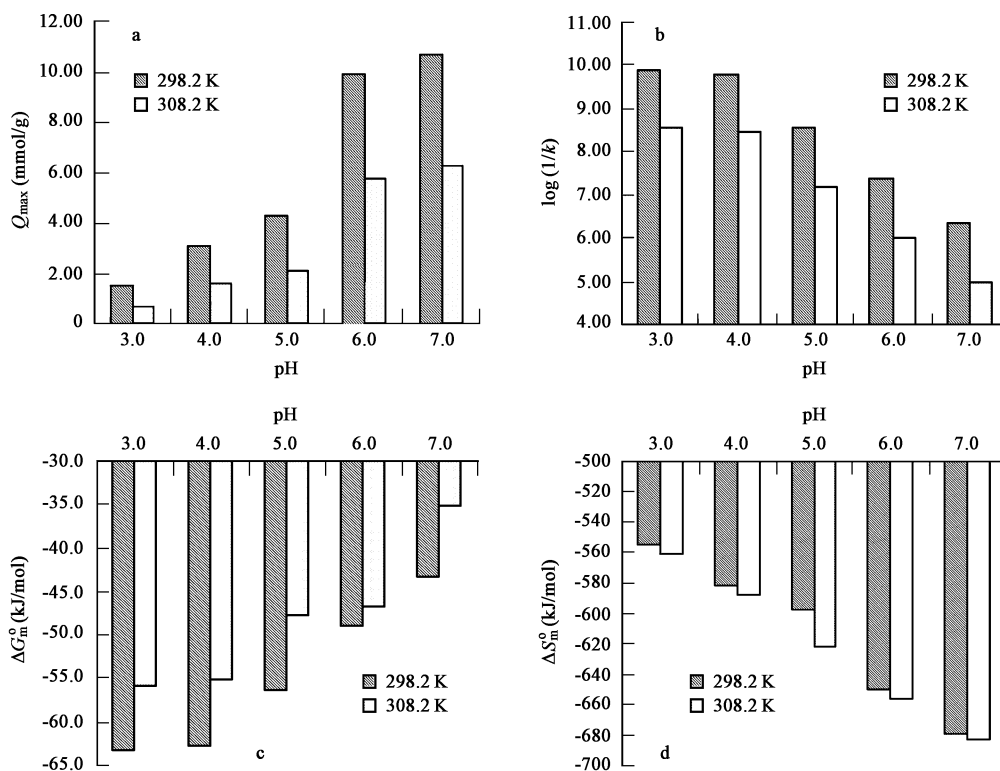


Fig. 3 Effect of temperature on Q_{\max} (a), k (b), ΔG_m^0 (c), and ΔS_m^0 (d) of Al^{3+} on HA.

was in a more systematical order, which was mainly caused by the transformation of Al^{3+} from a free form to an absorptive state. In the meantime the net structure of HA became tighter, so the order of the whole system had been reinforced.

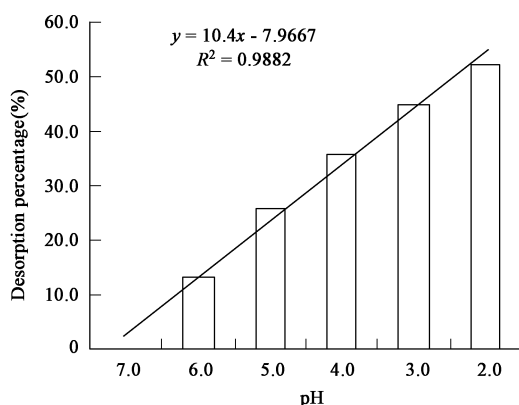


Fig. 4 Effect of pH on the desorption rate of HA-Al^{3+} .

2.4 Effect of pH on the desorption rate of HA-Al^{3+}

Figure 4 and Table 2 show the pH effect on the desorption rate of HA-Al^{3+} , at 0.10 mol/L of ionic strength and 298.2 K. These results show that both the desorption amount and desorption rate of HA-Al^{3+} increase with a decrease in pH. A significant linear relation between the desorption rate (θ) and pH exists as indicated by Eq.(12).

$$\theta = 0.104\text{pH} - 0.080 \quad n = 5, R^2 = 0.9882 \quad (11)$$

The reactions between HA and metal ions often involve more than one type of reaction site. Surface binding and chemical holding reaction between the interior binding sites of HA and metal ions, which penetrate into HA colloid particles may occur simultaneously. Because of greater interaction strength, the interior metal ion is difficult to desorb. On the contrary, the metal ion binding on the outer surface of humic acid, by a weak bond, may be easily desorbed. Thus, the adsorption amount on the HA surface may be estimated based on the desorption amount under certain conditions may occur simultaneously. The amount of interior metal ion through the chemical bond

Table 2 Adsorption and desorption rates of HA-Al^{3+} at different pH

pH	Adsorption (mg/g)	Al^{3+} combine interior (mg/g)	Al^{3+} combine exterior (mg/g)	Proportion of interior and exterior	Desorption (mg/g)	Desorption rate (θ)
7.0	25.67 ± 0.05	12.37 ± 0.01	13.30 ± 0.05	0.930 ± 0.003	0	0
6.0	22.34 ± 0.04	12.37 ± 0.01	9.97 ± 0.04	1.241 ± 0.005	3.33 ± 0.04	(13.0 ± 0.1)%
5.0	19.12 ± 0.03	12.37 ± 0.01	6.75 ± 0.03	1.833 ± 0.008	6.55 ± 0.03	(25.5 ± 0.1)%
4.0	16.51 ± 0.03	12.37 ± 0.01	4.14 ± 0.03	2.99 ± 0.02	9.16 ± 0.03	(35.7 ± 0.1)%
3.0	14.23 ± 0.02	12.37 ± 0.01	1.86 ± 0.02	6.65 ± 0.07	11.44 ± 0.02	(44.6 ± 0.1)%
2.0	12.37 ± 0.01	12.37 ± 0.01	0	–	13.30 ± 0.05	(51.8 ± 0.2)%

“±” denotes the standard error.

may be estimated based on the amount that is not able to be desorbed at a limited condition, for example, pH 2.0, as humic acid will become a deposit when pH is below 2.0.

Therefore, the amount of adsorption at pH 2.0 was used to approximately estimate the amount of the interior metal ion through the chemical bond. If on the assumption that the amount of interior metal ion was not changed with pH, then the adsorption amount on the HA surface at other pH levels was obtained, based on the total amount minus the amount of the interior metal ion. The calculation indicated that the amount of interior bonded aluminum through the chemical bond by humic acid was 12.37 mg/g under the given condition, whereas, that bonded through the surface adsorption decreased along with a decrease in pH, as shown in Table 2. Therefore, the proportion of interior and exterior also increased gradually from 0.930 to 6.65 with the decrease in pH from 7.0 to 2.0. The maximum desorption amount was 13.30 mg/g. It had been demonstrated that the adsorption reaction of HA to Al^{3+} had the characteristic of “biphase reactions”.

3 Conclusions

This study revealed that the adsorptive reaction of Al^{3+} on HA was much influenced by acidity, ionic strength, and temperature. (1) pH would influence the strength of HA and the hydrolysis effect of Al^{3+} . However, the influence direction and the influence extent on the two effects were different. Within the experimental pH range, the adsorption amount and adsorption constant increased with an increase in pH. Thus increase of pH was favorable to the adsorption process. (2) The increase of ionic strength was favorable to the adsorption process. (3) The adsorption reaction of HA to Al^{3+} could spontaneously take place, high temperature was unsuitable for the adsorption of Al^{3+} on HA as the adsorption reaction was exothermic. (4) ΔG_m^0 and ΔH_m^0 of the adsorption reaction were both negative, suggesting that the adsorption reaction was a spontaneous and exothermic reaction. (5) The adsorption reactions of HA adsorbing Al^{3+} were “biphase reactions” including the interior and exterior combinations. The Al^{3+} on the outer surface of HA bonded by weak physical adsorption was subject to the changing environment and happened to desorb. Although,

the Al^{3+} inside the HA held by chemical adsorption could not be desorbed even under very strong acidity (pH 2.0).

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