The Roles of the Surface Charge and Hydroxyl Group on a Fe–Al–Ce Adsorbent in Fluoride Adsorption

Hai-Xia Wu, Ting-Jie Wang,* Lin Chen, and Yong Jin

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Yu Zhang

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Xiao-Min Dou

School of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China

The roles of the surface charge and hydroxyl group on a Fe–Al–Ce adsorbent in fluoride adsorption were studied. Fluoride adsorption at different initial solution pH was investigated. An external voltage was applied to an adsorbent-coated electrode to examine the adsorption characteristics due to the surface charge. The capability of accepting or providing H^+ of the hydroxyl on the adsorbent surface was determined through the titration of NaOH solution, and the change of the hydroxyl before and after adsorption was analyzed by FTIR. Fluoride adsorption was rapid during the initial stage but slowed down later. Fluoride ions were transferred to the adsorbent surface by Coulombic attraction and/or thermal motion, forming a temporary and nonspecific adsorption. The enriched fluoride ions reacted with the hydroxyl groups on the adsorbent surface, forming a stable adsorption. The surface charge on the adsorbent and ion exchange between surface hydroxyl groups and fluoride ions have a large effect on the adsorption rate and efficiency.

1. Introduction

Of all chemical elements, fluorine is the most electronegative and most reactive. Because of its high reactivity, fluorine is not found in nature in its elemental state and exists as fluorides,¹ and is harmful to human health because a high concentration of fluoride in drinking water causes dental and skeletal fluorosis,² etc. The guideline values for fluoride in drinking water are 2.0 mg/L in the United States,³ 1.5 mg/L by the World Health Organization, and 1.0 mg/L in China.⁴ Adsorption is considered one of the most efficient technologies for fluoride removal in drinking water when compared to other technologies like reverse osmosis,⁵ nanofiltration, electrodialysis,⁶ and Donnan dialysis.⁷

The development of socially acceptable and economical adsorbents to meet local community needs has become a focus of water treatment in the world.⁸ Rare earth metal hydroxides/oxides are potential adsorbents because of their strong affinity for fluoride.^{9,10} However, rare earth metals are usually expensive, which restricts their use in the treatment of drinking water. Because of the high electronegativity and small ionic size of the fluoride ion, it has strong affinity toward multivalent metal ions including Al(III), Fe(III), and Zr(IV).¹¹ So, a hybrid of a rare earth metal with the cheaper metals, Al(III), Fe(III), or Zr(IV), is an economical way for a high fluoride adsorption capacity. One of the most important factors in designing an adsorption material is the understanding of the adsorption mechanism. In the data fitting to kinetic models, usually a rate-limiting step is assumed and used,^{9,12} with the result that the kinetic equation that gives the best fit is often empirical, and the physical meaning of the rate parameters is unclear. Thus, a deeper understanding of the adsorption mechanism is important.

Fluoride adsorption depends on many variables such as solution pH, surface charge, surface groups, etc., and no single property appears to be dominant in anion adsorption from aqueous solutions.¹ Some researchers have used a mechanism of Coulombic electric attraction, ion exchange, and ion adsorption competition.⁴ Ions transferred to the adsorbent surface through directional transfer caused by the surface potential and ion diffusion caused by the thermal motion. This article studied the mechanism of fluoride adsorption onto a Fe–Al–Ce adsorbent surface, and the influences of the solution pH, surface charge, and surface hydroxyl. An external voltage was used to examine the adsorption characteristics due to the surface charge. The hydroxyl properties on the adsorbent surface were studied by NaOH solution titration and FTIR. Batch adsorption experiments were carried out on the adsorption of fluoride from aqueous solution by a Fe–Al–Ce hydroxide adsorbent under various experimental conditions.

2. Experimental Section

2.1. Preparation of the Fe–Al–Ce Adsorbent. $FeSO_4 \cdot 7H_2O$, $Al_2(SO_4)_3 \cdot 12H_2O$, and $Ce(SO_4)_2 \cdot 4H_2O$ (analytical grade, Chemical Engineering Co. of Beijing, China) were dissolved in deionized water at concentrations of 0.1, 0.2, and 0.1 M, respectively, to form a mixed solution. The pH of the mixed solution was adjusted slowly with 6 M NaOH solution until the final pH reached 9.5. The solution was stirred at 200 rpm during the process.⁴ The precipitates were centrifuged and washed with deionized water until the pH of the filtrate was 6.5 ± 0.2 . The Fe–Al–Ce hydroxide adsorbent particle cake obtained was dried at 55 °C under vacuum for 20 h and crushed into dispersed particles. The obtained Fe–Al–Ce trimetal hydroxide (Fe–Al–Ce) adsorbent was amorphous with Fe:Al:Ce at 1:4:1, 40 nm in diameter, 96 m²/g of BET surface area, and the product was kept in a capped bottle.^{4,13}

* To whom correspondence should be addressed. Tel.: +86-10-62788993. Fax: +86-10-62772051. E-mail: wangtj@mail.tsinghua.edu.cn.

2.2. Fluoride Adsorption Experiments. 2.2.1. Batch Adsorption. The concentration of the fluoride solution was 0.001 mol/L, and KNO₃ with a concentration of 0.2 M was used as the background electrolyte. The adsorbent dose was 1 g/L, and the fluoride solution volume was 100 mL. The pH of the test solution was adjusted by 0.05 M HNO₃ or 0.05 M NaOH solution. The solution was shaken at 100 rpm and 20 °C during adsorption. The fluoride ion concentration of the solution was measured with a fluoride selective electrode connected to an ion meter (PXS-450, Shanghai Kang-Yi Instruments Co., LTD, China). After 10 h of adsorption, the adsorbent was centrifuged and washed three times, and the adsorbent cake was dried at 55 °C under vacuum for 20 h and crushed into dispersed particles for FTIR analysis.

2.2.2. Adsorption under an External Voltage. A suspension of Fe–Al–Ce adsorbent with a binder of polymer latex at a set concentration was sprayed onto the surface of a stainless steel mesh and was dried by hot air to form an adsorbent-coated electrode. To avoid the effect of the other electrode to which a reverse voltage was applied, a copper wire with small surface area was used as the other electrode. The two electrodes were immersed in the fluoride solution for examining the change in fluoride adsorption due to the external voltage. The voltage was controlled and changed by a transformer. The solutions and the measurement of the fluoride concentration were the same as used in the batch adsorption.

2.3. Determination of the Surface Groups. For examining the capability of accepting or providing H⁺ of the hydroxyl on the adsorbent surface, titrations were carried out in a flask equipped with a pH meter and peristaltic pump described in our previous paper.¹⁴ The titrations were carried out at 20 °C under N₂ protection to avoid the influence of CO₂ dissolution into the suspension.

A blank experiment was carried out by titrating 0.010 M NaOH solution into a mixture of 5 mL of oxalic acid solution (0.010 M) and 70 mL of deionized water. The titration rate was kept at 0.5 mL/min. The titration for the Fe–Al–Ce adsorbent was operated as follows: (1) 50 mg of adsorbent was dispersed into 70 mL of deionized water to form a suspension, (2) 5 mL of oxalic acid solution (0.010 M) was uniformly mixed into the suspension, and (3) 0.010 M NaOH solution was titrated into the suspension at a constant titration rate of 0.5 mL/min.

2.4. Characterization. A FTIR spectrometer (Nicolet 5DX, USA) with 2 cm^{−1} resolution was used for sample analysis. The scans were repeated 200 times in the spectral range from 4000 to 400 cm^{−1}. KBr was used as the mulling agent, and the fraction of the sample in the KBr is about 0.5%. An accessory of “Qwik Handi-Press” was used to press a KBr pellet in diameter of 7 mm.

3. Results and Discussion

3.1. Adsorption Efficiency at Different pH. The effect of the solution pH on adsorption efficiency was investigated by measuring the amount of residual fluoride with a fluoride ion meter. The initial concentration of the fluoride solution was set at 0.001 M, and the pH was kept constant by titrating HNO₃ or NaOH solution during adsorption. The experiments showed that the fluoride adsorption reached equilibrium after 10 h. Fluoride adsorption efficiency was defined as adsorbed fluoride divided by initial fluoride, which is shown as eq 1.

$$F^- \text{ adsorption efficiency} = \frac{\text{adsorbed } F^-}{\text{initial } F^-} = \frac{\text{initial } F^- \text{ concentration} - \text{residual } F^- \text{ concentration}}{\text{initial } F^- \text{ concentration}} \quad (1)$$

The efficiency change with pH is shown in Figure 1. Figure 1 shows that the fluoride adsorption efficiency decreased with increased solution pH, and the trend coincides with the reported results.^{4,9}

It is assumed that the adsorbent adsorbed anions through electrical attraction and the exchange of anions and hydroxyl groups on the adsorbent surface; therefore, the negative surface charge and the competition from the OH[−] ions in the basic solution resulted in a decreased adsorption capacity.⁴ However, the literature did not discuss the effects of the surface charge and the ion exchange with the surface hydroxyl.

In addition, the groups on oxide particle surfaces accept or provide different amounts of protons at different pH's.¹⁵ There are two reactions at the interface of the oxide particles and water in the aqueous solution, that is:

where M indicates the metal element (Fe, Al, or Ce), and ≡MOH, ≡MOH₂⁺, and ≡MO[−] indicate the different surface groups and charges. In an acidic condition, the concentration of H⁺ is higher than that of OH[−], and the equilibrium of eq 2 shifts to the right easily. In a basic condition, the equilibrium of eq 3 shifts to the right easily. Therefore, in an acidic solution, the adsorbent surface accepts more protons from the solution than it provides to the solution, producing more ≡MOH₂⁺ than ≡MO[−] and carrying a positive charge. In a basic solution, the adsorbent surface produces more ≡MO[−] than ≡MOH₂⁺ and carries a negative charge. No matter in acidic or basic solution, the ≡MOH, ≡MOH₂⁺, and ≡MO[−] groups all exist on the adsorbent surface, but their amounts are different.

The detailed effects of the surface charge and groups on anion adsorption will be discussed as follows.

3.2. Examination of the Effects of the Surface Charge.

To examine the effects of the particle surface charge on the adsorption, experiments were designed to change the particle surface charge. The Fe–Al–Ce adsorbent was coated onto a stainless steel mesh to form an electrode whose charge can be changed by an external voltage. The voltage was changed from 0 to 1.2 V and 0 to −1.0 V, and in 1 min intervals for each change. Considering the electrolysis voltage for pure water is about 1.229 V,¹⁶ the electrolysis phenomenon is not obvious until 1.5 V. To avoid the effects of electrolysis, the external voltage of <1.3 V was used.

The coated mesh was immersed in the 0.001 M fluoride solution at pH 6.5. The choosing of pH 6.5 is mainly because of the pH of the drinking water and for weakening the effects of the electrode reaction, which happens obviously at higher or lower pH of the solution. After 10 h adsorption, an external voltage was added onto the coated mesh. The residual fluoride concentration in the solution was measured as the voltage changed. The fluoride adsorption efficiency change versus the external voltage is shown in Figure 2. It can be seen that the fluoride adsorption efficiency was about 80% without the external voltage. When the voltage reached −1.0 V, the adsorption efficiency almost decreased to 0, and when the voltage reached 0.5 V, the fluoride adsorption efficiency

Figure 1. Effect of solution pH on fluoride adsorption efficiency (Fe–Al–Ce adsorbent, 10 h).

Figure 2. Effect of external voltage on fluoride adsorption efficiency.

almost increased to 100%. Overall, fluoride adsorption efficiency increased with voltage increase from -1.0 to 0.5 V, and then became stable. This indicated that a positive voltage promoted anion adsorption while a negative voltage inhibited adsorption, and the effect due to the copper wire electrode can be ignored.

The prompt response of adsorption efficiency to a switched on/off external voltage is shown in Figure 3. Figure 3a shows that fluoride was completely adsorbed when a positive voltage of 1.0 V was switched on, and the adsorption efficiency returned to the value of about 80% when the voltage was switched off. When a negative voltage of -1.0 V was switched on, adsorbed fluoride was released completely, and when the voltage was switched off the adsorption efficiency returned to the value of about 80%, which is shown in Figure 3b. Figure 3 also shows that the adsorption efficiency reached 100% or 0% promptly once an external voltage of 1.0 or -1.0 V was applied, which indicates that the directional ion transfer caused by external voltage dominates the adsorption process, and the effect of the thermal motion is weakened. When the external voltage was removed, the adsorption efficiency slowly approached a value of about 80%, which results from the surface potential of the adsorbent and thermal motion of the ions.

It is deduced that a positive voltage caused anions to move to the adsorbent surface, and when the voltage is high enough, all of the fluoride ions in the solution can move to the adsorbent surface. When the voltage was switched off, the efficiency returned to the original value, which indicated that the external voltage led to a temporary adsorption. Also, the temporary adsorption is nonspecific, corresponding to outer-sphere adsorption. A negative voltage inhibited the anions from moving to

Figure 3. The response of adsorption efficiency with an external voltage: (a) positive external voltage; (b) negative external voltage.

Figure 4. FTIR spectra of Fe–Al–Ce adsorbent before and after fluoride adsorption (pH 6.5).

the surface, and when the voltage was low enough, the fluoride ions in the solution could hardly move to the adsorbent surface, and even caused adsorbed fluoride ions to be released from the surface. In addition, Figure 2 shows that adsorption can still occur even at a negative voltage, which indicated that the thermal motion also brings fluoride ions to the adsorbent surface in addition to the motion due to electrostatic attraction.

3.3. Hydroxyl Groups on the Adsorbent Surface. The FTIR spectra of the adsorbent before and after adsorption (at pH 6.5) are shown in Figure 4. The adsorption bands at 3550 – 3200 , 1641 , and 1120 cm^{-1} were assigned to the hydroxyl stretching vibration of water, bending mode of water, and the bending vibration of the surface hydroxyl group ($\equiv\text{M}-\text{OH}$),¹⁷ respectively.

Figure 4 shows that the 1120 cm^{-1} peak present before adsorption disappeared after fluoride adsorption. It can be

Figure 5. NaOH titration curve of solution with Fe–Al–Ce adsorbent and blank solution with oxalic acid.

Figure 6. Fluoride adsorption on Fe–Al–Ce adsorbent versus time at different initial solution pH.

deduced that the disappearance of the 1120 cm^{-1} peak is due to fluoride adsorption on the corresponding hydroxyl site. Because $-\text{OH}$ and F^- have nearly the same size, they can exchange for each other,⁸ and F^- can be stably adsorbed.

The capability of accepting or providing H^+ of the hydroxyl on the adsorbent surface can be determined through the titration of NaOH solution, and the results are shown in Figure 5. It shows that the adsorbent suspension needed less NaOH solution to reach a pH than did the blank oxalic acid solution. Supposing that the adsorbent adsorbs oxalate ions, it would promote the oxalic ionization, produce more H^+ in the solution, and consume more NaOH for a fixed pH as compared to the titration of the blank solution, which is the reverse of the experimental result. So it is deduced that the adsorbent surface accepts H^+ , leading to the decrease of NaOH consumption for a fixed pH, as compared to the titration of the blank solution. The difference of the consumed NaOH between the adsorbent suspension and blank solution was shown in the inset in Figure 5, which decreased with pH increase. It is inferred that the capability of the adsorbent surface accepting H^+ decreases with pH increase, leading to less $\equiv\text{MOH}_2^+$ forming on the adsorbent surface, and this trend is consistent with the adsorption efficiency decrease with pH increase in Figure 1.

3.4. The Adsorption Process. Figure 6 shows the fluoride adsorption efficiency versus time at different initial pH at 20°C and an initial fluoride concentration at 0.001 M . Here, the initial pH indicates that the pH was not controlled during the adsorption process. The slopes of the curves indicate the adsorption rate at different conditions. The steeper is the curve,

Figure 7. Solution pH change during fluoride adsorption at different initial pH.

the higher is the adsorption rate. There was a high adsorption rate in the initial stage but a slower rate later, especially at low initial pH. For different initial solution pH, it is shown that the lower is the pH, the more fluoride was adsorbed in the initial stage.

It can be deduced that at a lower pH, the adsorbent surface had more positive charges and attracted fluoride ions by Coulombic attraction, which led to a high adsorption rate. After adsorption had proceeded for some time, the surface charge was reversed, and the Coulombic force on the fluoride ions in the solution changed into a repulsive force, and the available sites on the surface and the concentration of F^- ions decreased, all of which led to a sharp decrease in the adsorption rate during the later stage. At a higher pH, the adsorbent surface had more negative charges and inhibited the movement of fluoride ions to the adsorbent surface by electrical repulsion, such that there was little adsorption and the adsorption rate did not change much during the later stage. It was only when the fluoride ions were in a solution that was above the threshold of the electric repulsion that they can reach the adsorbent surface and be adsorbed. Thus, the adsorption rate at a high pH was lower than that at a low pH.

The pH changes during adsorption at different initial pH were recorded and are shown in Figure 7. It was found that the pH changed to neutral quickly ($<20\text{ min}$) regardless of the initial pH.

In aqueous solution, $\equiv\text{MOH}$, $\equiv\text{MOH}_2^+$, and $\equiv\text{MO}^-$ groups existed on the adsorbent surface. $\equiv\text{MOH}_2^+$ groups adsorbed anions easily and OH^- was released, by the reaction shown as eq 4.^{1,9,18} $\equiv\text{MO}^-$ groups adsorbed cations easily and released H^+ , by the reaction shown as eq 5.

In acidic condition, mainly

In basic condition, mainly

where X^+ represents cation; here the cation mainly is Na^+ .

In acidic condition, the adsorbent surface has mainly $\equiv\text{MOH}_2^+$ groups, and the adsorbent surface absorbs the fluoride ions easily and quickly and releases OH^- . Meanwhile, the adsorbent surface also has $\equiv\text{MO}^-$ species, and where cations

that have kinetic energies and that are above the repulsion threshold can get to the adsorbent surface and complex with the $\equiv\text{MO}^-$, there is H^+ release. However, because the amount of released OH^- was much higher than the released H^+ , the pH increased quickly when adsorption occurred in an acidic solution, as shown in Figure 7.

In basic condition, the adsorbent surface has mainly $\equiv\text{MO}^-$ groups, and the adsorbent surface absorbs cations easily and quickly and releases H^+ . There are only two kind of cations in the solution, Na^+ and H^+ ; supposing $\equiv\text{MO}^-$ adsorbs H^+ , it would lead pH increase, which is the contrary to the experimental phenomena shown as in Figure 7, so the cations mainly are Na^+ . Meanwhile, the adsorbents surface also has $\equiv\text{MOH}_2^+$ groups, and where fluoride ions that have kinetic energies and that are above the repulsion threshold can get to the adsorbent surface and complex with the $\equiv\text{MOH}_2^+$, there is OH^- released. However, because the amount of released OH^- was much less than the released H^+ , the pH decreased when adsorption occurred in a basic solution, as shown in Figure 7.

In neutral condition, the amounts of released OH^- and H^+ were about equal, so the pH changed little in the adsorption.

At high pH, the adsorbed fluoride ions can exchange with the solution OH^- , and the process was used to regenerate the used adsorbent, which was verified in our previous work.⁴

According to the above analysis, the fluoride adsorption process has two steps: ion transfer to the surface and ion exchange at the surface. The ion transfer, that is, the first step, is due to Coulombic attraction and/or thermal motion and increases the ion concentration at the adsorbent surface. The experiments to which an external voltage was applied showed that the ion transfer results in a temporary and nonspecific adsorption, which corresponds to outer-sphere adsorption. The ion exchange, that is, the second step, is the enriched ions at the surface exchange with the hydroxyl groups on the adsorbent surface. This ion exchange results in a stable and specific adsorption, which corresponds to inner-sphere adsorption.

4. Conclusion

Fluoride adsorption efficiency decreased with increased solution pH. The adsorption rate was high in the initial stage but slowed later, especially at low initial solution pH. As adsorption progressed, the solution pH will become neutral regardless of the initial solution pH. The hydroxyl amount on the adsorbent surface decreased with increased solution pH.

The adsorption process occurs in two steps: ion transfer and ion exchange. In the ion transfer step, fluoride ions are transferred to the adsorbent surface by Coulombic attraction and/or thermal motion, resulting in an increased concentration at the adsorbent surface, forming a temporary adsorption. In the ion exchange step, these enriched fluoride ions exchange with the hydroxyl groups on the adsorbent surface, which results in a stable adsorption.

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