Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Polymers 72 (2008) 144–150

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Fluoride removal by Fe(III)-loaded ligand exchange cotton cellulose adsorbent from drinking water

Yaping Zhao [a,*], Xiuyan Li [a], Lu Liu [b], Fuhua Chen [b]

[a] *Department of Environmental Science, East China Normal University, 200062 Shanghai, China*
[b] *College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China*

Received 27 March 2007; received in revised form 27 July 2007; accepted 31 July 2007
Available online 14 August 2007

Abstract

A novel bead adsorbent, Fe(III)-loaded ligand exchange cotton cellulose adsorbent [Fe(III)LECCA], was prepared, for fluoride removal from drinking water. The influence of pH, reaction time, temperature, foreign ions, flow rate, and regeneration were determined in batch and column systems. Adsorption–desorption–readsorption results indicated that Fe(III)LECCA has the potential to act as an adsorbent for the removal of fluoride because of its adsorption capacity and mechanical stability. The adsorption mechanism of fluoride removal was elucidated clearly by Fourier Transform Infra Red (FTIR) spectrum and chemical analysis. The results showed that Fe(III)LECCA would be a cost-effective and environmental benign adsorbent for fluoride removal from drinking water.

Keywords: Fluoride removal; Fe(III)LECCA; Drinking water; Ligand exchange mechanism

1. Introduction

High concentrations of fluoride occur naturally in ground water throughout many parts of the world. Long-term ingestion of high fluoride drinking water causes serious toxic effects. In 1993, 25 million people in 15 of India's 32 states were identified as endemic for fluorosis (Gandhi, 1993). In Mexico, 5 million people (about 6% of the population) were affected by fluoride in groundwater (Amor, Taky, Malki, Nicolas, & Elmidaoui, 2001) Fluorosis is also threatening some parts of central and western China. The WHO guideline value is 1.5 mg/l for fluoride in water (WHO, 1984). India lowered its permissible upper limit from 1.5 to 1.0 mg/l. China also adopted 1.0 mg/l as the upper limit.

For a long time, the treatment methods employed in removing high concentration fluoride from drinking water have received significant attention. A standard treatment for removing fluoride from surface water uses Ca^{2+}, which reacts with fluoride to create a solid that precipitates from the water. However, this treatment system produces a fluoride-contaminated solid with limited solubility. The adsorption method seems to be one of the most promising methods for fluoride removal from drinking water. However, the traditional adsorbents and adsorption methods have many limitations. For example, activated alumina (AA) (Bulusu & Nawlakhe, 1988; Fink & Lindsay, 1936; Swope & Hess, 1937; Trejo Vazquez, Bonilla Petriciolet, Custanon Ayala, Ruvalcaba Luna, & Juarez Medina, 1999) shows low adsorption capacity, has a short use life span, slow adsorption rate, and decrease of adsorption capacity after regeneration. It also requires adjusting pH of influent and effluent solution and dissolved aluminum may be undesirable for health. These disadvantages may make this approach impractical for water systems serving a few thousand people. Recently, several types of materials have been proposed as adsorbents for fluoride removal. Their better adsorption performances of fluoride have received increasingly significant attention. There are modified materials, such as La(III)-loaded chelating resin (Kanesato, Yokoyama, & Suzuki, 1988), Al(III)- and

---

[*] Corresponding author. Tel.: +86 21 62238393; fax: +86 21 62233670.
E-mail address: ypzhao@des.ecnu.edu.cn (Y. Zhao).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2007.07.038

List of symbols

c_o	concentration of fluoride at initial (mg/l)
c_t	concentration of fluoride at any time (mg/l)
R'	rate constant of film diffusion (min^{-1})
K	rate constant of particle diffusion ($\text{min}^{-1/2}$)
q_m	the maximum amount of fluoride adsorbed by adsorbent (mg/g)
b	Langmuir constant (l/mg)
V_B	the effluent volume at breakthrough point (ml)
V_T	the effluent volume at saturation point (ml)
C_0	concentration of fluoride solution in initial influent (mg/l)
C	concentration of fluoride solution at any time in effluent (mg/l)
m	the amount of the adsorbent (g)
$\overline{Q_B}$	the mean adsorption capacity in column at breakthrough for fluoride (mg/g)
$\overline{Q_T}$	the mean adsorption capacity in column at saturation point for fluoride (mg/g)
q_z	adsorption capacity of adsorption zone (mg/g)
f	fraction of the utilized adsorbent in adsorption zone formed (%)
H_Z	the height of adsorption zone (cm)
H_T	the height of the adsorbent bed (cm)
N	the number of series column

Fe(III)-loaded amino methylene phosphonic acid resin (Zhang, Qian, & Xu, 1988), Yttrium-loaded poly(hydroxamic acid) resin (Haron, Wan Yunus, Wasay, Uchiumi, & Tokunaga, 1995), Spherical Adsorbent Loaded with $TiO_2 \cdot nH_2O$ (Song, Yan, Huo, Wang, & Jia, 1996), and polymer complex of zirconium(V) (Yuchi, Matsungaga, Niwa, Terao, & Wada, 1999). But for most of them, there is a problem in either efficiency or cost. In order to meet the needs of people in fluoride-contaminated regions, alternative techniques are required that can effectively reduce fluoride concentration in drinking water to environmentally acceptable level at affordable costs.

In this paper, a novel adsorbent, Fe(III)-loaded ligand exchange cotton cellulose adsorbent [Fe(III)LECCA], is synthesized for selective adsorption and removal of fluoride from drinking water. The availability of an inexpensive and biodegradable carrier – a macroporous cellulose material with a high surface area – further enhanced our interest in choosing this path for our research. The adsorbents are basically modified cotton cellulose through crosslinking, activation, and function to improve the three-dimensional chelating ability of introduced ligands. The improvement in metal affinity is thought to be structurally mediated, which indicates a more flexible ligand arrangement to satisfy different coordination geometries in the adsorbents. For the metal of concern, Fe(III) is primarily considered due to its strong affinity toward fluoride anions, environmental safe, and low cost. This work aims at employing Fe(III)LECCA to perform a series experiments and evaluate the performances and removal mechanism of fluoride removal in batch and column experiments.

2. Materials and methods

2.1. Chemicals

Sodium fluoride was prepared in a 2000 mg/l stock solution stored in polyethylene bottle at 0 °C. Sodium chloride and sodium sulfate were employed to study the influence of the foreign ions. Deionized water was used throughout the experiments. All other reagents were of analytical reagent grade and purchased from Tianjin Chemical Reagent No. 1 and No. 2 Company (China).

2.2. Preparation of adsorbent

Cotton cellulose beads were made into cotton beads through anti-phase polymerization. The cellulose xanthate viscose was prepared by reacting 45 g alkali-treated and aged degreasing cotton with 20 ml CS_2 and then dissolving into 6% (w/w) NaOH solution. One hundred gram of viscose was dispersed in a solution of 200 ml chlorobenzene in 400 ml pump oil in a 1 L flask with agitation at 350 rpm for 0.5 h at 25 °C. The suspension was heated up to 95 °C and keep for 1 h under continuous stirring, then cooled down and filtered. The resulting particles were washed successfully with benzene and methanol after washing with water and sieving with standard test sieves in water.

The cotton cellulose beads were activated by epoxy chloropropane and 2 M NaOH at 25 °C for 24 h then ammonified through ammonia water at 65 °C for 12 h (Popat, Anand, & Dasare, 1994; Xu, Yan, & Xia, 1986). The amino cotton cellulose beads reacted with phosphorous acid and chloride acid at 75 °C for 8 h to get the phosphonomethy amino group adsorbent carrier, i.e. ligand exchange cotton cellulose adsorbent, LECCA (Kanesato et al., 1988; Zhang et al., 1988) After being washed with alcohol, 5% NaOH solution, deionized water, 5% HCl solution, and deionized water in series. LECCA was shaken with a excessive volume 0.6 mol/l $FeCl_3$–0.2 mol/l CH_3COONa solutions for 8 h at room temperature, yielding Fe(III)-loaded LECCA, Fe(III)LECCA. It was washed with deionized water until residual ferric ions can not be detected. Surface was measured by B.E.T. method-N_2 gas adsorption using a QS-7 Quantasorb surface area analyzer. The topology of adsorbent surface was examined by Hitachi S-4000 scanning electron microscope. IR spectrum was performed by FT-

IR Nieolet 50 X IR spectrometry. P was analyzed by PE 2400 II elemental analysis instrument (Perkin Elmer Co., USA).

2.3. Operating conditions and instruments

The batch adsorption experiments were carried out using the completely mixed batch reactor techniques. The adsorbent Fe(III)LECCA 0.0691 g was put in conical flasks containing 10 ml 20 mg/l fluoride solution. The contents at the desired concentration and pH were agitated in a shaking thermostat at 105 rpm. Solution pH was adjusted by 1 M HCl or NaOH solution. At the end of the desired period, the content was taken out and filtered with 0.45 μm membrane and the filtrate was analyzed for leaking Fe(III) by a colorimetric method with a detection limit of 0.03 mg/l and residual fluoride by ion selective electrode method with a detection limit of 0.05 mg/l (The Committee of " Standard methods of examination water and wastewater" in State Environmental Protection Administration of China, 1997) and the instrument used was a pH 2 acidity meter (Shanghai Analysis Instrument Company, China).

The column adsorption experiments were carried out using fixed-bed minicolumn techniques (Lounici et al., 1997). The adsorbent Fe(III)LECCA 0.4353 g was packed into a water-jacked glass column (φ 9.5 × 300 mm) with the ratio of height to diameter of 10:1, bed volume of 6.7 ml and the water-jacked column temperature was maintained by thermostat. The fluoride solution of certain concentration was continuously fed from the top side of the column at a constant rate and the effluent was collected at the column bottom at regular intervals and analyzed. The breakthrough point of column was chosen as 1 mg/l fluoride concentration (living drinking water quality of China, GB5749-85) and saturation point was chosen as the concentration of influent fluoride.

The regeneration or desorption experiments were simply column adsorption experiments in reverse. The elution and regeneration of adsorption saturated Fe(III)LECCA for fluoride were carried out at the flow rate of 26.0 BV/h using 1 mol/l NaOH solution. After each regeneration cycle, adsorption capacity of the regenerated adsorbent for fluoride was measured.

3. Results and discussion

3.1. Characterization of Fe(III)LECCA

Phosphonomethy amino Cotton cellulose beads are the carriers of Fe(III)LECCA. Fe(III) ions are chelating centers which decided adsorption ability for the fluoride ions for Fe(III) ions hve a high affinity towards fluoride ions. The physiochemical properties of the adsorbent were listed in Table 1. The SEM showed that Fe(III)LECCA had a lot of large pores among adsorbents' inner part which greatly improved its contact surface with fluoride ions in water solutions.

Table 1
Physicochemical properties of Fe(III)LECCA

Parameters	Properties
Surface area	2.23 m^2/g
Particle size	20–40 mesh
Fe(III) content	6%
P content	0.5%
Moisture (w/w)	87%

3.2. Batch adsorption experiments

3.2.1. Effect of pH

Fig. 1 illustrated the effect of pH on fluoride adsorption by Fe(III)LECCA at 25 °C with shaking for 8 h. The amount of fluoride adsorbed increased with the pH of the systems, and leveled off from pH 4 to 9. The adsorption decrease took place at pH less than 4 and fluoride existed mainly as undissociated HF, which accounted for very little adsorption. The leakage of Fe(III) from the adsorbent, below 0.3 mg/l (GB5749-85) can be neglected over the whole pH range because of strong complex action between phosphonomethy amino group of LECCA and chelating center Fe(III). Popat et al. (1994) reported Al(III)-loaded chelating resins showed better adsorption ability towards fluoride in the range of pH 2.6–6.9. Compared the pH is outside this range. Kanesato et al. (1988) reported that the uptake of fluoride by La(III)-loaded chelating resin having phosphonomethy amino groups increased from 7.6 to 30.4 mg/g when pH increased from 3 to 6. This means the leaking of La(III) was influenced by the lowering pH. While the adsorption capacity dropped in high pH, because deprotonization of coordination water within chelating center increased the negative charge around the La(III), leading to repulse of the fluoride anions. It is noteworthy that significant adsorption of fluoride by

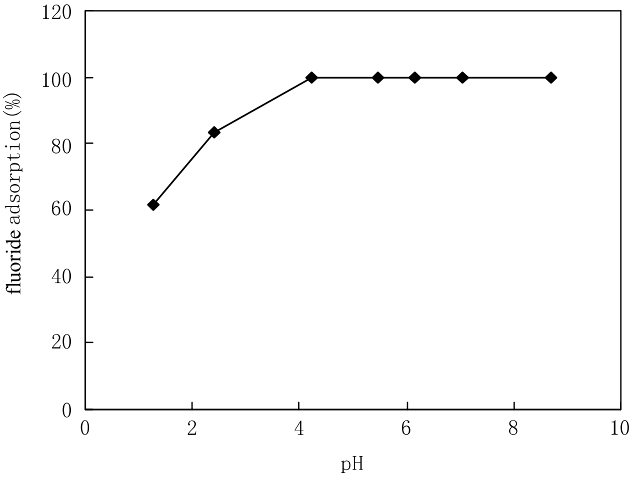

Fig. 1. The effect of pH on fluoride adsorption (adsorbent: 0.0691 g; fluoride concentration: 20 mg/l; shaking time: 8 h; temperature: 25 °C).

Fe(III)LECCA in aqueous solution takes place at a wide pH range, which maybe caused by different ligand complexation sites of Fe(III)LECCA comparing with Al(III)- or La(III)-loaded chelating resins.

3.2.2. Kinetic study

Fig. 2 showed the effect of time on fluoride removal by Fe(III)LECCA under different temperatures. It has been observed that the extent of uptake and rate of adsorption increased with increasing in temperature from 25 to 45 °C. It took 2 min to adsorb half amount of fluorides; the adsorption can reach equilibrium at 8 min then the curve levels off. The adsorption kinetics are much faster than those of the common adsorbents, i.e. activated alumina (Li et al., 2001).

Adsorption from solution involves the transfer of soluble species from the liquid phase to the surface of the adsorbent. The uptake of the solute involves four basic steps: first, bulk transport of the solute to the hydrodynamic boundary layer surrounding the adsorbent particle; second, diffusive film transport through the boundary layer (film diffusion); third, intraparticle transport, which may be diffusive transport within the fluid inside the pores (pore diffusion); forth, attachment of the solute onto the adsorbent surface (adsorption). Fick's first and second law combined with the equilibrium of mass was used to describe the rate limitation step in dynamics process.

From Fick's first law and the equilibrium of mass, film diffusion control equation (Popat et al., 1994; Xu et al., 1986) can be obtained:

$$(c_t - c_0)/(c_0 - c_\infty) = \exp(-R't) \tag{1}$$

As c_∞ decreased to 0, Eq. (1) can be simplified as

$$c_t/c_0 = \exp(-R't) \tag{2}$$

From Fick's second law and the equilibrium of mass, particle diffusion control equation can be obtained:

$$c_t/c_0 = 1 - Kt^{1/2} \tag{3}$$

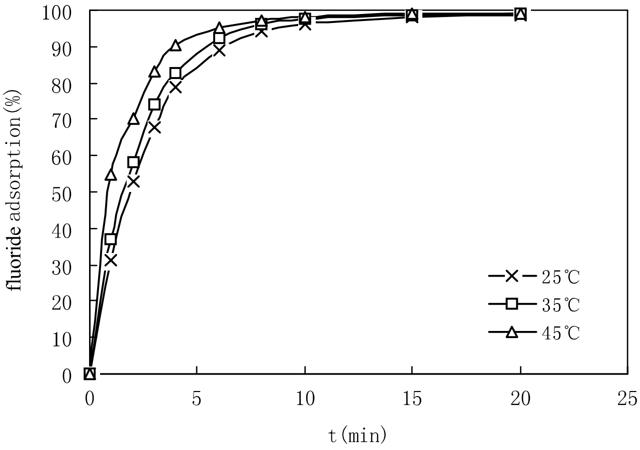

Fig. 2. The effect of temperature on fluoride adsorption (adsorbent: 0.0691 g; fluoride concentration: 20 mg/l; pH: 5.6).

where c_o and c_t are concentration of fluoride at initial and at any time (mg/l); R' and K are rate constants of film and particle diffusion, respectively. If the experimental data fit well with the Eq. (2) and have good linear relationship under certain circumstance, the adsorption can be described by film diffusion control. If the experimental data fit well with the Eq. (3) and have good linear relationship under certain circumstance, the adsorption can be described by particle diffusion control.

Based on the data for uptake of fluoride with time at 25, 35, and 45 °C in Fig. 2, the rate constants of film diffusion R', rate constants of particle diffusion K, and correlation coefficient R^2 can be calculated by Eqs. (2) and (3), respectively. R', K, and R^2 are listed in Table 2. The linear plot of $\mathrm{Ln}(c_t/c_o)$ versus t confirmed the validity of $c_t/c_o = \exp(-R't)$, showing that the film diffusive control was the rate limitation step of the adsorption. Usually, the sharp initial adsorption curves (in Fig. 2) indicated that the adsorption of fluoride might occur on the surface of the adsorbent. The curve model in Fig. 2 was consistent with film diffusion control equation (2).

3.2.3. Adsorption capacity

The effect of temperature on fluoride removal by Fe(III)LECCA with different fluoride concentrations, such as 10, 20, 40, 80, and 200 mg/l, were also studied. The results were described by Langmuir isotherm equation (Du, 2005):

$$c_e/q_e = c_e/q_m + 1/q_m b \tag{4}$$

where c_e and q_e are equilibrium concentration of fluoride and equilibrium and maximum amount of fluoride adsorbed by Fe(III)LECCA. Where q_m are the maximum amount of fluoride adsorbed by Fe(III)LECCA and b is Langmuir constant which were shown in Table 3. At a certain temperature, the adsorption capacity of fluoride was increased with fluoride initial concentration. At the same time the fluoride adsorption capacity increased with the working temperatures which suggested the adsorption was endothermic reaction.

3.3. Column experiments

3.3.1. Effect of flow rate

The effects of flow rate, 5.3, 10.0, 15.5, 26.0, and 35.2 BV/h, on the column performance at 25 °C were shown in Fig. 3. The relevant parameters shown in Table 4 which have been calculated with following equations of the adsorption zone theory (Jiang, Qing, & Song, 1992):

Table 2
The parameters of diffusion

Temperature (°C)	R' (min^{-1})	R^2	K ($\mathrm{min}^{-1/2}$)	R^2
25	0.35	0.988	0.32	0.688
35	0.40	0.981	0.33	0.488
45	0.46	0.928	0.34	−0.887

Table 3
The parameters of fluoride adsorption isotherm

Temperature (°C)	Langmuir constants		Correl. coeff. R^2
	q_m (mg/g)	b (l/mg)	
25	18.55	0.47	0.999
45	19.26	0.28	0.992
65	21.05	0.30	0.993

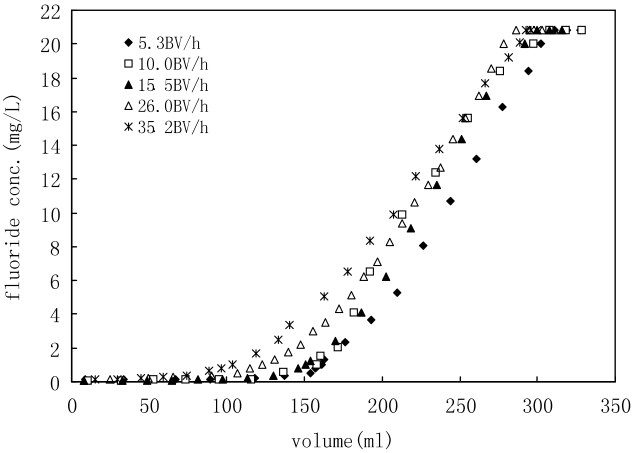

Fig. 3. The effect of flow rate on column adsorption fluoride (adsorbent: 0.4353 g; fluoride concentration: 20 mg/l; temperature: 25 °C).

Table 4
The parameters of flow rate on column absorption of fluoride

Flow rate (BV/h)	5.3	10.0	15.5	26.0	35.2
V_B (ml)	160.7	157.5	150.7	122.8	103.0
V_T (ml)	302.4	297.2	291.6	278.4	288.0
$\overline{Q_B}$ (mg/g)	7.4	7.2	6.9	5.6	4.7
$\overline{Q_T}$ (mg/g)	10.5	10.3	9.9	9.7	9.6
N	1.6	1.6	1.7	1.7	1.9

$$\overline{Q_B} = (C_0 \times V_B)/m \tag{5}$$

$$\overline{Q_T} = q_z/m + \overline{Q_B} \tag{6}$$

$$f = \frac{q_z}{C_0 \times (V_T - V_B)} \tag{7}$$

$$H_Z = \frac{H_T \times (V_T - V_B)}{V_T - (1-f) \times (V_T - V_B)} \tag{8}$$

$$N = \frac{H_Z}{H_T} + 1 \tag{9}$$

where V_B and V_T are the effluent volume at breakthrough and saturation point separately, C_0, C are concentration of fluoride solution in initial influent and at any time in effluent, respectively, m is the amount of the adsorbent, $\overline{Q_B}$ and $\overline{Q_T}$ are the mean adsorption capacity in column at breakthrough and saturation point for fluoride, respectively, q_Z is adsorption capacity of adsorption zone, f is fraction of the utilized adsorbent in adsorption zone formed, H_Z and H_T are the height of adsorption zone and the adsorbent bed respectively, N is the number of series column. Table 4 indicated that $\overline{Q_B}$ and $\overline{Q_T}$ of fluoride tended to decrease with the increase of influent flow rate. When the flow rate was 15.5 and 26.0 BV/h, the column kept both the rather high flow rate and the rather great breakthrough mean adsorption capacity 6.9 and 5.6 mg/g and saturation mean adsorption capacity 9.9 and 9.7 mg/g. While Lounici et al. (1997) has reported that the mean adsorption capacity at breakthrough and saturation point of activated Alumina (AA) were 1.75 and 2.2 mg/g in optimum condition. Compared with AA, Fe(III)LECCA still showed high adsorption velocity, high adsorption capacity and stable performance. So the flow rate 26.0 BV/h was adopted in the following experiments.

The effects of temperature and fluoride concentration on the column adsorption were also investigated. With increasing temperature (such as from 25 to 45 °C) or increasing fluoride concentrations (such as from 20 to 80 mg/l), it would cause fluoride ions to breakthrough the column ahead of time comparing with that of 20 mg/l fluoride at 25 °C.

3.3.2. Fluoride removal from tap water spiked with fluoride

Table 5 indicated decrease of the column adsorption capacity for fluoride when the influent is tap water spiked with fluoride. But the breakthrough adsorption capacity of the column of fluoride spiked tap water still preserved 89% of fluoride aqueous solution. The N, number of the column in series, was 3 and reasonable in practical operation. The water qualities of influent and effluent tap water are listed in Table 6. The effluent tap water qualities are fitted well with living drinking water quality of China (GB5749-85). It was suggested that the adsorbent was

Table 5
The parameters of column absorption of fluoride from tap water

	Aqueous solution 20 mg/l	Tap water spiked with fluoride 20.45 mg/l
V_B (ml)	122.8	106.0
V_T (ml)	278.4	361.0
$\overline{Q_B}$ (mg/g)	5.6	5.0
$\overline{Q_T}$ (mg/g)	9.7	6.3
N	1.7	2.9

Table 6
Influent and effluent drinking water quality (mg/l)

	Influent water	Effluent water	Standards[a]
F^-	20.45	0.96	⩽1.0
Total As	<0.0001	<0.0001	<0.05
Hardness	202.4	182.6	250
pH	7.9	6.3	6.5–8.5
Cl^-	24.8	149.7	250
SO_4^{2-}	65.0	5.4	250

[a] Living drinking water quality of China (GB5749-85), hardness calculated as $CaCO_3$.

Table 7
Column experiment parameters of adsorption–regeneration–readsorption cycles ($T = 25$ °C)

Adsorption–regeneration–readsorption cycles	1	2	3	4	5	6	7	8	Average	Relative standard deviation (%)
V_B (ml)	229	267	278	273	253	252	252	255	257	5.94
V_T (ml)	428	479	478	479	479	479	453	453	466	4.07
$\overline{Q_B}$ (mg/g)	5.497	6.409	6.673	6.553	6.073	6.049	6.049	6.121	6.178	5.97
$\overline{Q_T}$ (mg/g)	8.072	8.599	8.969	8.977	8.513	8.576	8.710	8.244	8.633	3.31

highly selective for the adsorption of fluoride in drinking water. The sulfate concentration decreased from 65.0 to 5.4 mg/l. According to the results of selectivity in batch experiment, the decrease of the column adsorption may be noted that the interference is mainly caused by the high concentration sulfate in tap water. While chloride concentration in effluent tap water increased from 24.8 to 149.7 mg/l which may cause by fluoride ions substituting the chloride ligands of Fe(III)LECCA.

3.3.3. Regeneration

A consideration of practical interest with regard to the application of a new adsorbent is its regeneration ability. The column was regenerated with 1 M NaOH aqueous solution at 26.0 BV/h at room temperature. Sharp stripping curve of fluoride indicated that more than 98% fluoride ions fed into the column was eluted only with the 30 ml stripping solution. The column performance after several adsorption–desorption–readsorption cycles was investigated using 10.45 mg/l fluoride ions at 26.0 BV/h flow rate. Table 7 indicated results of successively readsorption of fluoride ions by Fe(III)LECCA. In regeneration, the adsorption capacity of Fe(III)LECCA for fluoride ions tended to increase slightly with regeneration cycles. This was mainly because the adsorbent reacted with NaOH to form some colloid ferric hydroxide, which coated on the adsorbent surface in varying degree. The hydroxide itself favored the fluoride adsorption through increasing its adsorption sites.

After eight adsorption–regeneration–readsorption cycles, the relative standard deviations of column $\overline{Q_B}$, $\overline{Q_T}$, V_B, and V_T were below 6%, which indicated that the column has stable and better adsorption ability. Though the first adsorption capacity was lower, after two times the adsorption capacity of adsorbent and the column' dilation was gradually stable. Moreover, the capacity of the adsorbent reached its original level again and kept basically constant in the following adsorption–regeneration–readsorption cycles. This similar phenomenon was reported elsewhere (Zhang et al., 1988). From the microscopic examination, it was found that there was no broken Fe(III)LECCA after more than 8 times adsorption–desorption–readsorption cycles on the same adsorption column. This mechanistic stability can be a good character in practical application in drinking water treatment.

3.4. Adsorption mechanism

From batch experiments and physiochemical characteristics of adsorbent Fe(III)LECCA, the ligand exchange mechanism was suggested as following:

$$\mathrm{X{\equiv}Fe(III){-}L} + \mathrm{F^-} = \mathrm{X{\equiv}Fe(III){-}F} + \mathrm{L^-}$$

$$\mathrm{X}: \text{cotton cellulose adsorbent carriers}, \quad \mathrm{L}: \text{ anions ligands}$$

Fe(III) belongs to $3\mathrm{d}^{\cdot 5}$ metal ion and is easy to accept electron pairs of ligands to form stable complexes (Wu, 1986). Far-IR spectrum of Fe(III)LECCA in Fig. 4 showed that the main characteristic absorbance peak of Fe–Cl were 555, 442, 377, and 314 cm^{-1}. After adsorbing fluoride by Fe(III)LECCA, the main characteristic absorbance peak of Fe–Cl disappear and main characteristic absorbance peak of Fe–F, 621, 604, and 310 cm^{-1}, occur. The exchange of chloride of Fe(III)LECCA by fluoride showed that the reaction mechanism was ligand exchange mechanism. From Table 6, the changes of chloride and sulfate quality index, can also demonstrate this ligand exchange mechanism. In regeneration process, OH$^-$ exchange with F$^-$ to achieve the stripping aim. It can be concluded that the adsorption process is ligand exchange mechanism from chemical analysis and Far-IR spectrum results.

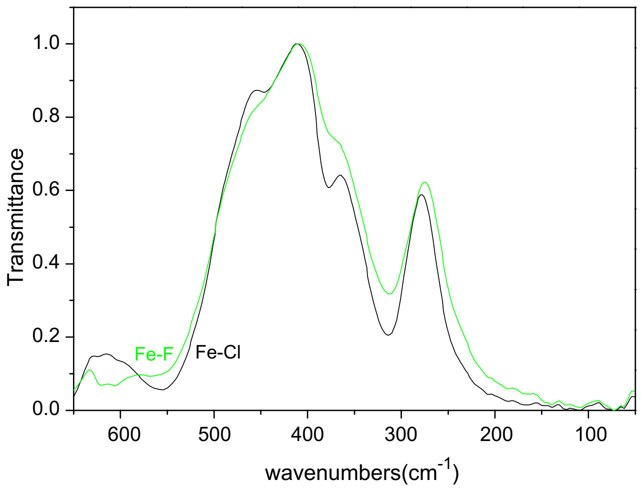

Fig. 4. Far-IR of Fe(III)LECCA before (Fe–Cl) and after (Fe–F) adsorbents adsorbing fluorides.

4. Conclusion

Fe(III)LECCA exhibited good performances in fluoride removal under varying conditions in batch experiments. The adsorption followed first-order rate reaction. The saturation adsorption capacity was 18.6 mg/g at 25 °C. Coexistent common anions hardly affected the adsorption of fluoride. In column experiment, with 20 mg/l influent fluoride at 26.0 BV/h flow rate under 25 °C, the column can gain 5.6 mg/g breakthrough adsorption capacity and 9.7 mg/g saturation adsorption capacity, which is more than half of the saturation adsorption 18.6 mg/g in batch, such high capacity was rarely reported. Fe(III)LECCA had a high selectivity towards fluoride anions, even in tap water, the adsorbent still preserved 89% breakthrough adsorption capacity of that for fluoride aqueous solution. The NaOH regeneration was effective in column stripping. Fe(III)LECCA was not broken and deviation of saturation adsorption was less than 3.5% after 8 times adsorption–desorption–readsorption cycles.

The carrier of the Fe(III)LECCA has wide sources and biodegradable characteristic. The chelating center is low price Fe(III) and nontoxic. Fe(III) also coordinate with strong electron donating groups of methyl aminophosphonic cotton carriers, showing high selectivity. These properties made the novel adsorbent more attractive and competitive in drinking water treatment. Lab-scale experiment showed that Fe(III)LECCA also had good adsorption capacity, selectivity, and adsorption rate for fluoride removal from drinking water. So it can be conclude that Fe(III)LECCA would be an alterative novel adsorbent for fluoride removal from drinking water.

Acknowledgement

Financial support of the research from National Natural Science Foundation of China (Grant No. 29977010) is greatly acknowledged.

References

Amor, Z., Taky, M., Malki, S., Nicolas, S., & Elmidaoui, A. (2001). Fluoride removal from brackish water by electrodialysis. *Desalination, 133*(3), 215–223.

Bulusu, K. R., & Nawlakhe, W. G. (1988). Defluoridation of water with activated alumina: Batch operations. *Indian Journal of Environmental Health, 30*(3), 262–299.

Du, Q. (2005). *Physiochemistry* (2nd ed.). China: Chongqing University Publication.

Fink, G. J., & Lindsay, F. K. (1936). Activated alumina for removing fluorides from drinking water. *Industrial Engineering Chemistry, 28*(8), 947–948.

Gandhi, Rajiv (1993). Water Board, Ministry of Resources, Government of India. Rajiv Gandhi National Drinking Water Mission. Prevention and Control of fluorosis in India.

Haron, M. J., Wan Yunus, W. M. Z., Wasay, S. A., Uchiumi, A., & Tokunaga, S. (1995). Sorption of fluoride ions from aqueous solutions by Yttrium-loaded poly(hydroxamic acid) resin. *International Journal of Environmental Studies, 48*, 245–255.

Jiang, Z., Qing, C., & Song, Z. (1992). *Engineering of ion exchange and separation*. China: Tianjing University Publication.

Kanesato, M., Yokoyama, T., & Suzuki, T. M. (1988). Selective adsorption of fluoride ion by La(III)-loaded chelating resin having phosphonomethyamino groups. *Chemistry Letters, 2*, 207–210.

Li, Y., Wang, S., Cao, A., Zhao, D., Zhang, X., Wei, J., Xu, C., Luan, Z., & Wu, D. (2001). Adsorption of fluoride from water by alumina supported on carbon nanotubes. *Chemical Physics Letters, 350*(5–6), 412–416.

Lounici, H., Addour, L., Belhocine, D., Grib, H., Nicolas, S., Bariou, B., & Mamerj, N. (1997). Study of a new technique for fluoride removal from water. *Desalination, 114*, 241–251.

Popat, K. M., Anand, P. S., & Dasare, B. D. (1994). Selective removal of fluoride ions from water by the aluminium form of the aminomethylphosphonic acid-type ion exchanger. *Reactive polymers, 23*, 23–32.

Song, K., Yan, X., Huo, M., Wang, J., & Jia, X. (1996). Study on porous structure of spherical adsorbent loaded with $TiO_2{\cdot}nH_2O$ and their absorption properties for fluoride anions. *Ion Exchange and Adsorption, 12*(6), 557–562, [Ch].

Swope, G. H., & Hess, R. H. (1937). Removal of fluoride from natural water by defluorite. *Industrial Engineering Chemistry, 29*(4), 424–426.

The Committee of "Standard methods of examination water and wastewater" in State Environmental Protection Administration of China (1997). Standard methods of examination water and wastewater, 3rd ed. Beijing, China.

Trejo Vazquez, R., Bonilla Petriciolet, A., Custanon Ayala, L., Ruvalcaba Luna, J. M., & Juarez Medina, H. (1999). Activated alumina for removal of fluoride from water II. Results. *Ingenieria Quimica (Madrid), 31*(361), 382–385, [Span].

WHO (1984). Fluorine and fluorides *Environmental Health*, IPCS international program on chemical safety, Criteria 36.

Wu, J. (1986). *Modern Fourier Transform Infrared Spectroscopy technology and application*. China: Science and Technology Publication.

Xu, R., Yan, J., & Xia, Y. (1986). Investigation of phosphonomethy amino resin by Fourier Transform Infrared Spectroscopy. *Ion Exchange and Adsorption, 3*, 25–29.

Yuchi, A., Matsungaga, K., Niwa, T., Terao, H., & Wada, H. (1999). Separation and preconcentration of fluoride at the ng ml^{-1} level with a polymer complex zirconium (IV) followed by potentiometric determination in a flow system. *Analytic Chemica Acta, 388*, 201–208.

Zhang, Z., Qian, T., & Xu, G. (1988). The synthesis of amino methylene phosphonic acid resin and the removal of fluoride from drinking water. *Ion Exchange and Adsorption, 4*(1), 42–48, [Ch].