Fluoride adsorption on carboxylated aerobic granules containing Ce(III)

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Abstract

Aerobic granules (AG) were carboxylated and Ce(III) was incorporated to obtain modified granules (Ce(III)–MAG) for removal of fluoride from aqueous solutions. The Ce(III)–MAG was characterized by SEM, FTIR, XRD and pHpzc, and the introduction of carboxyl groups and Ce(III) was confirmed. The adsorption capacity of Ce(III)–MAG for fluoride was 45.80 mg/g at neutral pH, an increase of 359% compared to the capacity of pristine AG. Adsorption was highest at pH range of 3.0–5.0. A positive effect on fluoride removal in the order of K+ > Mg2+ > Ca2+ > Na+ and a negative effect in the order of NO3− > Cl− > SO42− > HCO3− > PO43− was observed. Fluoride adsorption followed the Redlich–Peterson model and the pseudo-first order model with correlation factors of 0.999 and 0.950, respectively. Ce(III)–MAG held up to 790 bed volumes and the effluent fluoride concentration remained below 1.0 mg/L (influent fluoride 10 mg/L).

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1. Introduction

In concentrations above 1.5 mg/L, fluoride can be harmful to the environment and human health (WHO, 2006). Removal of fluoride from water sources is sometimes necessary and defluoridation has been achieved by adsorption, chemical precipitation, ion exchange, membrane separation and electrodialysis (Amor et al., 2001; Meenakshi et al., 2008; Reardon and Wang, 2000). Adsorption, especially biosorption is economical and efficient (Sun et al., 2010; Wu and Yu, 2008), and a wide variety of biosorbents such as algal and fungal biomass, and alginate have been explored for fluoride removal (Ramanaiyah et al., 2007; Venkata Mohan et al., 2007; Vijaya et al., 2011). However, a drawback of these biosorbents is their poor settling qualities, leading to washout of the active biomass.

Aerobic granules (AG), which are formed by self-aggregation of microorganisms in the absence of a carrier material, can be an attractive alternative biosorbents for fluoride removal due to their superior settling capability (Liu et al., 2005; Maszenan et al., 2011). AG have been used as biosorbents for the removal of pigments, dyes, and heavy metals (Sun et al., 2008a; Wang et al., 2010; Xu and Liu, 2008); however, biosorption of fluoride onto AG has apparently not been tested.

Amino, hydroxyl, and carboxyl groups on AG have been identified as binding sites for biosorption (Amor et al., 2001; Meenakshi et al., 2008; Reardon and Wang, 2000). Adsorption, especially biosorption is economical and efficient (Sun et al., 2010; Wu and Yu, 2008), and a wide variety of biosorbents such as algal and fungal biomass, and alginate have been explored for fluoride removal (Ramanaiyah et al., 2007; Venkata Mohan et al., 2007; Vijaya et al., 2011). However, a drawback of these biosorbents is their poor settling qualities, leading to washout of the active biomass.
Ce(III) with amino groups. SEM, FTIR, XRD and pH_{pzc} determination were used to characterize the granules. The fluoride sorption behaviors of Ce(III)–MAG was investigated by means of adsorption kinetics and isotherms under different initial pH and in the presence of other ions. Fixed-bed reactor tests were conducted to validate the feasibility for field application of Ce(III)–MAG.

2. Methods

2.1. Chemical

Ce(NO_{3})_{3}·6H_{2}O was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All other chemicals were of analytical grade and obtained from Sigma–Aldrich Company.

2.2. Preparation and surface modification of the adsorbent

AG were collected from a laboratory-scale sequencing batch reactor (SBR) fed with synthetic wastewater. The synthetic wastewater consisted of a medium with a composition (mg/L) of glucose, 235; sodium acetate, 320; KH_{2}PO_{4}, 15; Na_{2}HPO_{4}·2H_{2}O, 20; NaHCO_{3}, 200; CaCl_{2}, 60; MgSO_{4}·7H_{2}O, 25. The reactor was operated sequentially in a 4-h cycle, with 6 min of influent filling, 60 min of stirring, 168 min of aeration, 4 min of settling, and 2 min of effluent withdrawal. The range of AG sizes was from 0.8 to 1.0 mm. The AG were washed thrice by tap water and incubated in 0.5 M chloroacetic acid (pH 8.5, maintained using 0.1 M NaOH) for 10 h at 25 ± 1 °C, in order to exchange hydroxyl groups of the AG with carboxyl groups (Jeon and Holl, 2003). The thus modified AG (MAG) were washed to neutral pH with distilled water and mixed with 8% Ce(NO_{3})_{3}·6H_{2}O solution. After 24 h, the granules were washed with distilled water until the wash liquid was neutral, and the Ce(III)–MAG were stored in 4 °C refrigerator for further use. NaN_{3} (200 mg/L) was included throughout the modification process to inhibit microbial growth (Oleszczuk et al., 2009).

Fluoride adsorption was calculated by performing a mass balance using the following equation:

\[
q_t = \left( \frac{C_0 - C_t}{m} \right)V \tag{1}
\]

where \(q_t\) is the amount of fluoride adsorbed by adsorbent at time \(t\) (mg/g dry); \(V\) is the volume of solution (L); \(C_0\) (mg/L) and \(C_t\) (mg/L) are initial and residual fluoride concentration at time \(t\), respectively; and \(m\) is responding to the mass of adsorbent (g).

2.3. Material characterization and analyses

The surface morphologies of Ce(III)–MAG were observed qualitatively with scanning electron microscope (SEM) (HITACHI S-570, Japan). The granule samples were fixed with 3.0% glutaraldehyde in 0.1 M phosphate buffer at pH 7.2. The samples were then dehydrated with ethanol, silver-coated by a sputter and observed in the SEM. XRD (D/MAX-rA, Rigaku, Japan) was employed to characterize the crystalline structure of the AG, MAG and Ce(III)–MAG with Ni-filtered Cu Kα radiation and the data were matched with standard JCPDS data (Ma et al., 2009). The scanning region was from 10° to 70° in 2θ angle, with a scanning speed of 7°/min. FTIR spectra of the AG, MAG and Ce(III)–MAG were recorded on an FTIR spectrometer (Avatar 370, USA), in order to identify the changes in functional groups. Before XRD and FTIR, the biomass was freeze-dried and ground to a powder. In addition, pH_{pzc} (pH of point of zero charge) of AG and Ce(III)–MAG was determined by the batch equilibrium method (Babić et al., 1999).

2.4. Batch sorption experiments

Experiments were carried out in a series of 50-mL Teflon bottles, each of which contained 25 mL fluoride solution (prepared with NaF). Wet biosorbent (0.4 g) was added to a Teflon bottle and shaken in a thermostatic shaker for 3 h (160 rpm, 25 ± 1 °C), and samples were analyzed for the concentration of fluoride at the end of predetermined time intervals. The isotherm experiments were carried out with initial fluoride concentrations in the range of 4–20 mg/L with respect to fluoride. In order to examine the effect of pH, the concentration of fluoride was fixed at 10 mg/L and the desired pH values (3.0–11.0) were achieved by addition of HCl and NaOH. The effect of the presence of 200 mg/L of the sodium salts of PO_{4}^{3−}, Cl^{−}, SO_{4}^{2−}, HCO_{3}^{−}, NO_{3}^{−} and of the chloride salts of K^{+}, Ca^{2+}, Na^{+}, Mg^{2+} on the adsorption of fluoride (initial concentration of 10 mg/L of fluoride) were also determined. Experiments were conducted in duplicates, and the mean values are reported. A fluoride ion-selective electrode (PF-1, Shanghai Russoul Technology Ltd.) was used to measure the concentration of fluoride. In order to investigate the release of Ce(III) from Ce(III)–MAG, inductively coupled plasma emission spectrometry (ICP-AES) (IRIS Intrepid II XSP, Thermo Electron Corporation, USA) was applied. After 3 h of adsorption, the fluoride solutions were allowed to settle for 30 s and the vials were filtered with 0.45 μm membrane filter before the determination of Ce(III).

2.5. Fixed-bed reactor experiments

Fixed-bed adsorption tests were conducted in two separate Teflon columns (\(H \times D = 20 \times 1.2\) cm) packed with AG and Ce(III)–MAG, respectively. The solution with known concentration of fluoride was pumped upwards through the column. A Longer-Precision pump (Baoding, China) equipped with double soft tubes was used to control the flow rate of influent samples at about 0.7 mL/min and samples were collected at 12-h intervals. The experiments were carried out at room temperature (around 22 °C) and without pH adjustment. The bed height was set at 15 cm to investigate the breakthrough points of AG and Ce(III)–MAG.

3. Results and discussion

3.1. Characterization of Ce(III)–MAG

The surface morphology of AG before and after the modification was characterized using SEM. Based on the SEM images (Fig. 1a and b), the granules maintained intact after grafting, except for the appearance of some holes on the surface of AG. The surface modification loosened the physical structure (Fig. 1c and d). Ce(III)–MAG remained intact throughout the experiments. Fig. 1a displays the XRD patterns of AG, MAG and Ce(III)–MAG. Because the synthetic wastewater contained a large amount of Ca^{2+} and CO_{3}^{2−}, the peaks in XRD graph probably originated from CaCO_{3} (Ji et al., 2009, 2010). For MAG and Ce(III)–MAG, there were no marked changes for most of the peaks, indicating that there are no obvious changes in crystal structure after modification. Fig. 1b depicts the FTIR spectra of AG, MAG and Ce(III)–MAG. The broad and intense peak at 3431.02 cm\(^{-1}\) was assigned to \(\nu_{s}(O–H)\), the band at 2924.84 cm\(^{-1}\) is related to C–H vibration of C–H. The stretching vibration of 1650.70 cm\(^{-1}\) was due to asymmetric C–H stretching vibration of C–H. The stretching vibration of 1650.70 cm\(^{-1}\) was related to \(\nu_{as}(C=O)\) and C–N (I) (Teng et al., 2009). The strong peak at 1421.09 cm\(^{-1}\) was C–H bending vibration, and the peak at 1077.86 cm\(^{-1}\) corresponds to C–OH stretching vibration. For MAG, the band at 3431.02 cm\(^{-1}\) was shifted to 3436.02 cm\(^{-1}\), indicating that carboxyl groups were successfully incorporated. After
incorporating Ce(III), the spectrum of Ce(III)–MAG revealed marked changes. Peaks of –OH, –NH2 stretching at 3430.02 shifted to 3425.01 cm\(^{-1}\) from C–H of chloroacetic acid (Wang et al., 2010). Therefore, the charge characteristics of AG have no obvious change in the whole modification process.

The pH\(_{pzc}\) is an indicator of the surface charge of the biosorbent (Wang et al., 2010). The pH\(_{pzc}\) for AG and Ce(III)–MAG was around 7.0, which is similar to that of AG. After modification, there were unmarked changes on the charge characteristics of AG. The AG’s surface became the positive charge for Ce(III) and the negative charge for carboxyl group of chloroacetic acid (Wang et al., 2010). Therefore, the charge characteristics of AG have no obvious change in the whole modification process.

The pH\(_{pzc}\) for AG and Ce(III)–MAG was around 7.0. A lower wave number of the band at 1650.70 to 1649.48 cm\(^{-1}\) might display the formation of Ce–MAG complex. The new peaks emerging at 2958.84 and 2849.26 cm\(^{-1}\) originate from C–H of chloroacetic acid (Wang et al., 2010).

The pH\(_{pzc}\) is an indicator of the surface charge of the biosorbent and its preference for ionic species. In this study, the pH\(_{pzc}\) for Ce(III)–MAG was around 7.0, which is similar to that of AG. After modification, there were unmarked changes on the charge characteristics of AG. The AG’s surface became the positive charge for Ce(III) and the negative charge for carboxyl group of chloroacetic acid (Fig. 2). Therefore, the charge characteristics of AG have no obvious change in the whole modification process.

3.2. Effect of pH on fluoride retention

After 3 h of adsorption, the pH of solution increased at initial pH 3–7, while it decreased when the initial pH was 7–11. Fig. S2 exhibits the effect of the equilibrium pH on the adsorption of fluoride by AG and Ce(III)–MAG. The amount of fluoride adsorbed was higher for Ce(III)–MAG than AG over the pH range, especially in acid pH. Fluoride removal decreased with increasing pH. This result can be explained by the results of zero point charge studies (Fig. 2). The pH\(_{pzc}\) for Ce(III)–MAG was around 7.0. A lower pH is ideal for protonation of the amino groups in AG and Ce(III)–MAG, and thus resulted in increased positive charge on the surface of the biosorbents (Sun et al., 2010). The positively charged surface was favorable for the retention of negatively charged fluoride ions. The concentration of hydrogen ion was gradually decreased. Therefore, pH\(_4\) was increased after the adsorption of fluoride in the low pH range. At higher pH values, OH\(^-\) could compete with F\(^-\) for binding to Ce(III), and resulted in lower defluoridation capacity. The pH of equilibrated solution increased under acidic condition, while it decreased for basic solution. The phenomenon was also observed by Teng et al. (2009).

AG removes fluoride only by hydrogen bonding of F\(^-\) and the H\(^+\) of –COOH. Therefore, there are a small amount of fluoride was removed through electrostatic interaction. As for Ce(III)–MAG, the removal mechanism of fluoride by Ce(III) includes electrostatic interaction, strong Lewis acid–base interaction and complexation (Dahrowski et al., 2004; Viswanathan and Meenakshi, 2008). The Ce(III) could trap fluoride from solution related to the electrostatic adsorption and strong Lewis acid–base interaction. Meanwhile, the Ce(III)-chelated amino groups (Ce(III)–MAG) also removes fluoride through complexation. Therefore, Ce(III)–MAG shows greater defluoridation capacity than AG.

3.3. Effect of the presence of other ions

Fluoride-contaminated drinking water usually contains several common ions, which may interfere with fluoride removal by Ce(III)–MAG. Fig. 3 explains the influence of other ions including K\(^+\), Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), PO\(_4^{3-}\), SO\(_4^{2-}\), HCO\(_3^-\), NO\(_3^-\) and Cl\(^-\). It can be obviously observed that K\(^+\), Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) are advantaged for fluoride removal, whereas PO\(_4^{3-}\), SO\(_4^{2-}\), HCO\(_3^-\), NO\(_3^-\) and Cl\(^-\) are disadvantageous for fluoride removal. Fluoride removal in the presence of other ions increased in the order K\(^+\) = Mg\(^{2+}\) > Ca\(^{2+}\) > Na\(^+\) and decreased in the order NO\(_3^-\) > Cl\(^-\) > SO\(_4^{2-}\) > HCO\(_3^-\) > PO\(_4^{3-}\).
The positive effect of cations on fluoride removal may due to the presence of cation exchange sites on Ce(III)–MAG, or the presence of organic anion sites. For example, residue amino groups first combine with co-cations and then further remove fluoride through electrostatic interactions. Divalent metals Mg$^{2+}$ and Ca$^{2+}$ have more positive charge than monovalent ions Na$^+$. Thus, the effect of divalent metals is more significant than monovalent metal ions for the removal of fluoride. But K$^+$ and Mg$^{2+}$ displayed more positive influence on fluoride removal than Ca$^{2+}$. This may be attributed to their lower size, which promoted the removal of fluoride from water. Meanwhile, the solubility of CaF$_2$ is lower than that of MgF$_2$ in solution. The presence of Ca$^{2+}$ is more adverse to the removal of fluoride than Mg$^{2+}$.

The fluoride removal displayed different certain decrease in the presence of other anions. The effect of NO$_3^-$ and Cl$^-$ on the defluoridation capacity of sorbents had been recognized to be insignificant (Sundaram et al., 2009; Viswanathan and Meenakshi, 2008; Wang et al., 2009). SO$_4^{2-}$ had a greater negative effect on fluoride adsorption than NO$_3^-$ and Cl$^-$, partly attributed to its higher negative charge (Daifullah et al., 2007; Wang et al., 2009). HCO$_3^-$ showed obviously negative shift in the removal of fluoride, which may be due to the increase of pH after addition of this ion. PO$_4^{3-}$ had the most negative effect on the defluoridation capacity, indicating that both the fluoride and phosphate competed for the same active sorption sites of Ce(III) incorporated biosorbents. Haron et al. (2008) also reported that Ce(III) modified zeolite P has high affinity capacity for PO$_4^{3-}$.

3.4. Kinetic and isotherm study

The pseudo-first order, the pseudo-second order adsorption and intra-particle diffusion models were used to examine the adsorption kinetics of fluoride on AG and Ce(III)–MAG. As shown in Table 1, the kinetic data fit the pseudo-first order model better than the pseudo-second order model ($R^2$ of 0.95 vs. <0.9).

![Fig. 3. Fluoride removal by Carboxylated aerobic granules containing Ce(III) (Ce(III)–MAG) in the presence of other ions.](image)

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Measured $q_{e,exp}$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (1/min)</td>
<td>$q_e$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>AG</td>
<td>0.032</td>
<td>7.125</td>
<td>0.951</td>
</tr>
<tr>
<td>Ce(III)–MAG</td>
<td>0.051</td>
<td>31.817</td>
<td>0.955</td>
</tr>
</tbody>
</table>

Fig. 4a reveals the relationship between contact time and fluoride removal by AG and Ce(III)–MAG at an initial F$^-$ concentration of 10 mg/L. The adsorption of fluoride nearly reached equilibrium within 1 h for AG and Ce(III)–MAG. Evidently, Ce(III)–MAG has much higher sorption ability for fluoride removal than pristine AG (23.27 and 6.47 mg/g, respectively). When the intra-particle model is employed to predict the adsorption kinetics of fluoride ion on AG and Ce(III)–MAG at the same fluoride concentration of 10 mg/L, the adsorption of fluoride ion onto Ce(III)–MAG is attributed to film, or boundary layer diffusion, intra-particle diffusion, and equilibrium stage. The model described the linear portion perfectly ($R^2 = 0.999$). And the linear portion could be extended to pass through the origin, indicating that the adsorption process was complex and that surface sorption and intra-particle diffusion contributed to the rate-determining step. However, for AG, the linear portion of the curve passed through the origin with the relative coefficient of 0.962. Therefore, it could be concluded that intra-particle diffusion is the only rate-limiting step.

![Fig. 4a](image)

(a) Fluoride adsorption kinetics onto aerobic granules (AG) and Carboxylated aerobic granules containing Ce(III) (Ce(III)–MAG): 10 mg/L of F$^-$, natural pH, adsorbent dose 16 g/L; (b) Adsorption isotherm of fluoride on Carboxylated aerobic granules containing Ce(III) (Ce(III)–MAG) following with experimental data and fitting curves.
Influent:

The Redlich–Peterson isotherm (isotherm models for AG and Ce(III)–MAG are displayed in Table 2. Adsorption isotherm onto Ce(III)–MAG, various isotherms including Langmuir, Freundlich, and Redlich–Peterson were applied. Adsorption isotherm for AG and Ce(III)–MAG in fixed-bed columns. Fig. 5. Comparison of breakthrough curves for fluoride retention by Carboxylated aerobic granules containing Ce(III) (Ce(III)–MAG) in fixed-bed columns. Table 3.

Comparison among different adsorbents used for fluoride removal.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption potential (mg/g)</th>
<th>Particle size</th>
<th>Temperature (°C)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-HAp</td>
<td>1.845</td>
<td>Powder</td>
<td>30</td>
<td>Sundaram et al. (2008)</td>
</tr>
<tr>
<td>Na⁺ form of resin</td>
<td>0.445</td>
<td>0.30–0.50 mm</td>
<td>30</td>
<td>Viswanathan and Meenakshi (2009)</td>
</tr>
<tr>
<td>Al³⁺ form of resin</td>
<td>0.478</td>
<td>0.30–0.50 mm</td>
<td>30</td>
<td>Viswanathan and Meenakshi (2009)</td>
</tr>
<tr>
<td>HMOCA</td>
<td>7.090</td>
<td>0.45–0.90 mm</td>
<td>25</td>
<td>Teng et al. (2009)</td>
</tr>
<tr>
<td>La–CCB</td>
<td>4.711</td>
<td>Around 0.80 mm</td>
<td>30</td>
<td>Viswanathan and Meenakshi (2008)</td>
</tr>
<tr>
<td>Fe–Al–Ce trimetal oxide</td>
<td>178.0</td>
<td>Powder</td>
<td>25</td>
<td>Wu et al. (2007)</td>
</tr>
<tr>
<td>Modified kaolinite clay</td>
<td>0.609</td>
<td>&lt;2.0 μm</td>
<td>30</td>
<td>Meenakshi et al. (2008)</td>
</tr>
<tr>
<td>PCB</td>
<td>1.664</td>
<td>0.60–0.12 mm</td>
<td>30</td>
<td>Viswanathan et al. (2009)</td>
</tr>
<tr>
<td>Ce(III)–MAG</td>
<td>45.00</td>
<td>0.80–1.00 mm</td>
<td>25</td>
<td>This study</td>
</tr>
</tbody>
</table>

Fig. 5. Comparison of breakthrough curves for fluoride retention by Carboxylated aerobic granules containing Ce(III) (Ce(III)–MAG) in fixed-bed columns.

In order to describe the equilibrium characteristics of adsorption onto Ce(III)–MAG, various isotherms including Langmuir, Freundlich, and Redlich–Peterson were applied. Adsorption isotherm is also shown for AG for comparison. The parameters of the three isotherm models for AG and Ce(III)–MAG are displayed in Table 2. The Redlich–Peterson isotherm ($R^2 > 0.96$) best described the equilibrium adsorption of fluoride onto AG and Ce(III)–MAG. Fig. 4b shows the equilibrium data and fitting isotherm curves using these three relating isotherm models for Ce(III)–MAG. The fitting isotherm curves are shown in Fig. S3 for AG. The sorption isotherm for AG and Ce(III)–MAG resembled an L-type curve, which is normally observed when the adsorbate has a high affinity with increasing surface coverage (Gu and Karthikeyan, 2005; Sun et al., 2010). The removal by Ce(III)–MAG seemed to be controlled by electrostatic adsorption, complexation and hydrogen bonding mechanisms (Sundaram et al., 2008; Viswanathan and Meenakshi, 2008). The binding of fluoride to Ce(III)–MAG involves electrostatic interaction and strong Lewis acid–base interaction (Dabrowski et al., 2004). Simultaneously, the Ce(III)-chelated amino groups and fluoride could combine through complexation between Ce(III) - F and hydrogen bond between N–H - F (Sundaram et al., 2009; Viswanathan and Meenakshi, 2008).

Table 3 compares fluoride removal by different adsorbents with respect to maximum potential, particle size and temperature. Among these adsorbents, Fe–Al–Ce trimetal oxide had the highest capacities, but its powdery nature could cause operational problems. Ce(III)–MAG presents higher fluoride removal due to its stronger selectivity. The ICP-AES analysis demonstrated that the concentration of Ce(III) was hardly observed in aqueous solution after adsorption of fluoride (below the limit of detection of 5 μg/L), suggesting that Ce(III) could be steadily and tightly bound to the surface functional groups of MAG.

3.5. Fixed-bed reactor operation

The removal of fluoride was studied in separate fixed-bed reactors (packed with Ce(III)–MAG and AG, respectively). The pH was 7.0, which is not in the ideal value range (Fig. 5), but can be accepted according to natural drinking water conditions at 6.0–8.0. Based on China’s drinking water standard, the effluent concentration of fluoride cannot be higher than 1.0 mg/L. It is reasonable to set $C_t/C_0$ for 0.1 to examine the effective volume for comparing AG and Ce(III)–MAG in the separate volume. Fig. 5 shows that the breakthrough points for the two reactors occurred at 433 BV and 790 BV for AG and Ce(III)–MAG, respectively. Therefore, the removal of fluoride onto Ce(III)–MAG in the fixed-bed reactor demonstrates the encouraging prospect in the practical application. Before practical applications, regeneration of the Ce(III)–MAG will have to be studied.

4. Conclusions

Ce(III)–MAG as a novel biosorbent holds greater potential for the removal of fluoride than AG. The pseudo-first order model described the kinetic data well, indicating that physical sorption took place. The sorption isotherm can be well fitted by Redlich–Peterson isotherm model. Solution pH plays an important role in the removal of fluoride with the optimum pH range from 3.0 to 5.0. The presence of cation ions had positive effect on defluoridation and the negative effect for the anion ions. Fixed-bed reactor operation indicates the feasibility for practical application.
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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2012.09.127.

References