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Technical Note

Defluoridation of drinking water by combined electrocoagulation: Effects of the molar ratio of alkalinity and fluoride to Al(III)

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ABSTRACT

The defluoridation efficiency (ε_F) of electrocoagulation (EC) is closely related to the pH level of the F^--containing solution. The pH level usually needs to be adjusted by adding acid in order to obtain the highest ε_F for the F^--containing groundwater. The use of combined EC (CEC), which is the combination of chemical coagulation with EC, was proposed to remove fluoride from drinking water for the first time in this study. The optimal scheme for the design and operation of CEC were obtained through experiments on the treatment of F^--containing groundwater. It was found, with OH^- being the only alkalinity of the raw water, that the highest efficiency would be obtained when the molar ratio of alkalinity and fluoride to Al(III) ($\gamma_{Alkalinity+F}$) was controlled at 3.0. However, when the raw water contained HCO_3^- alkalinity, a correction coefficient was needed to correct the concentration of HCO_3^- to obtain the optimal defluoridation condition of $\gamma_{Alkalinity+F} = 3.0$ for CEC. The correction coefficient of HCO_3^- concentration was concluded as 0.60 from the experiment. For the practical F^--containing groundwater treatment, CEC can achieve similar ε_F as an acid-adding EC process. The consumption of aluminum electrode was decreased in CEC. The energy consumption also declined greatly in CEC, which is less than one third of that in the acid-adding EC process.

1. Introduction

Fluorine is an essential element in the human body. Low-dose fluoride (<1 mg L^{-1}) in drinking water will prevent dental caries, but high-dose fluoride (>1.5 mg L^{-1}) will accumulate in the human body and lead to fluorosis (WHO, 2004). Defluoridation of drinking water has long been a focus of studies. This has led to the application of numerous techniques and methods to remove fluoride from drinking water (He and Cao, 1996; Lounici et al., 1997; Amor et al., 2001; Fan et al., 2003; Ghorai and Pant, 2005; Zhang et al., 2005; Meenakshi, 2006; Gopal and Elango, 2007). Chemical coagulation (CC) and electrochemical coagulation (EC) are two such normal defluoridation techniques (Mameri et al., 1998; Abdessemed and Nezzal, 2003; Pinon-Miramontes et al., 2003; Emamjomeh and Sivakumar, 2006; Meenakshi, 2006). These two processes can remove fluoride ions from water by coprecipitation or adsorption through the use of aluminum or iron coagulants, or the electrochemical technique (“sacrificial anode”) in order to generate aluminum or iron ions (Buffle et al., 1985; Hao and Huang, 1986; Parthasarathy et al., 1986; Mollah et al., 2001; Shen et al., 2003; Holt et al., 2005).

Defluoridation efficiency (ε_F) is related to the pH, alkalinity, coexisting ions, and other characteristics of the solution regardless of whether CC or EC was used in the process (Hao and Huang, 1986; Hu et al., 2005). The highest ε_F can be obtained through CC and EC when the pH value is 5.5–6.5 (Sujana et al., 1998; Shen et al., 2003; Hu et al., 2005). In practical operations, the pH level is usually controlled by adding acid or base to the water. The pH of the F^--containing water is sensitive to the addition of acid or base in the aforementioned pH range. Fluoride ions coordinate with aluminum ions or are adsorbed by aluminum hydroxide, which will always result in the change of effluent pH (Hu et al., 2005). Therefore, it is difficult to control the pH of the system. Over addition of acid or base is an ordinary occurrence in practical operations. The pH of the solution is related to the concentrations of hydroxide ions, fluoride ions, and aluminum doses. The terms of γ_{OH}, γ_F, and γ_{OH+F}, used in the research on defluoridation by CC or EC, are defined by Eqs. (1)–(3):

$$\gamma_{OH} = \frac{[OH^-]}{[Al^{3+}]_T} = \frac{[OH^-]_0 + [OH^-]_{EC} - [H^+]_0}{[Al^{3+}]_T} \tag{1}$$

$$\gamma_F = \frac{[F^-]_0}{[Al^{3+}]_T} \tag{2}$$

$$\gamma_{OH+F} = \gamma_{OH} + \gamma_F = \frac{[OH^-]_0 + [OH^-]_{EC} + [F^-]_0 - [H^+]_0}{[Al^{3+}]_T} \tag{3}$$

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where γ_{OH} is the molar ratio of OH^- to Al(III), γ_F is the molar ratio of the initial F^- to Al(III), and γ_{OH+F} is the molar ratio of OH^- and F^- to Al(III). $[OH^-]_0$ is the initial OH^- concentration, $[OH^-]_{EC}$ is the concentration of OH^- generated in the electrolysis process, and $[H^+]_0$, $[F^-]_0$, and $[Al^{3+}]_T$ are the initial concentration of H^+, F^-, and the total concentration of Al(III), respectively.

Hu et al. (2005) suggested that it was more convenient to control γ_{OH+F} than to control the pH level. They found that the highest ε_F could be obtained by controlling $\gamma_{OH+F} = 3.0$ for the CC or EC.

In the EC process, the molar ratio of OH^- to Al(III) generated by electrolysis is 3 (Mollah et al., 2004). For raw water with a certain content of F^- and a higher pH, acid should be added to the system in order to control $\gamma_{OH+F} = 3$. The amount of acid needed would be calculated after the initial concentrations of OH^- and F^- were measured. In this acid-adding process, the OH^- generated by electrolysis would be consumed insignificantly, which could result in an increase in treatment cost. Moreover, some ions or impurities would be introduced to the water causing secondary pollution.

If aluminum salt coagulants were used instead of the common acid, the goal to control $\gamma_{OH+F} = 3.0$ would also be achieved. Qu and Liu (2004) electrolyzed $AlCl_3$ solution to produce polyaluminum chloride. Based on the known concentration of the $AlCl_3$ solution, the γ_{OH} of polyaluminum chloride can be controlled by adjusting the amount of Al(III) and OH^- released in the electrolysis process. For raw water with a known initial concentration of OH^- and F^-, the goal for achieving $[Al^{3+}]_T$ and γ_{OH+F} would be achieved by changing the ratio of Al(III) from the Al salt coagulant to that generated by electrolysis. This process is actually the combination of CC with EC, which is known as combined EC (CEC). Can et al. (2006) used the CEC process to remove COD from textile wastewater. At a fixed Al dose from EC, they sought for the best removal efficiency by changing the dose of polyaluminum chloride. Polyaluminum chloride is a prehydrolyzed Al coagulant with a certain basicity, and its γ_{OH} is usually more than 2, even 3 (Zhao et al., 2004). Consequently, polyaluminum chloride has a weak capability for pH adjustment in the CEC process. Some traditional Al coagulants, for instance $AlCl_3$, are the better choice.

Many studies attribute the higher ε_F of EC as compared to CC to the electrocondensation effect existing in the EC process (Ming et al., 1987; Hu et al.,2003, 2005; Zhu et al., 2007). The electrocondensation effect also exists in the CEC process. However, since chemical aluminum coagulant is added, the required dosage from the CEC process will be declined greatly. Moreover, it is not necessary to add acid to adjust the pH level. Therefore, the CEC process would reduce operational cost to some extent, including the consumption of electric energy and aluminum electrode.

Zhu et al. (2007) considered that the cooperation between EC and CC could occur inside an EC process. Unfortunately, so far, there have been no related reports on the CEC defluoridation process and the optimal scheme for its design and operation. The study of Hu et al. (2005) showed that ε_F was the highest at $\gamma_{OH+F} = 3.0$. However, it is not clear whether this principle is suitable for the CEC process. Furthermore, F^--containing groundwater usually has a high concentration of bicarbonate alkalinity (Meenakshi, 2006). Its water quality characteristics differ from those with OH^- as initial alkalinity. If this F^--containing water with bicarbonate alkalinity is to be treated by the CEC process, the issue of how to operate conveniently and obtain the highest ε_F in the process must be addressed first.

In this paper, a CEC process was proposed for the first time to remove F^- from drinking water. The relationship between ε_F and γ_{OH+F}, and its change with the initial alkalinity were also investigated. A scheme was proposed to optimize the performance of the CEC process to treat F^--containing groundwater with HCO_3^- as the initial alkalinity. In accordance with the scheme, the ε_F of the CEC process for treating F^--containing groundwater was investigated, and its power consumption was evaluated.

2. Materials and methods

2.1. Raw water

Two types of F^--containing water were used in the experiment. The simple one was prepared by adding 2.0 mM NaCl and a certain amount of NaF into deionized water, as well as adding a certain amount of NaOH and $NaHCO_3$ to obtain the required alkalinity. The other sample was groundwater obtained from Peking University and prepared by adding a certain amount of NaF to meet the required initial fluoride concentration for the test. The groundwater had a pH range of 7.80–7.95, and its composition is shown in Table 1.

2.2. Determination of the operational parameters for the CEC process

First, the initial fluoride concentration, alkalinity, and pH (for the calculation of $[H^+]_0$) of water were measured. The $[OH^-]_{EC}$ would then be calculated using Eq. (3) based on the predetermined $[Al^{3+}]_T$ and γ_{OH+F}.

The molar ratio of OH^- to Al(III) produced in the EC process is 3:1. Consequently, the dosage of aluminum from electrolysis ($[Al^{3+}]_{EC}$) and from the chemical agent ($[Al^{3+}]_{CC}$) can be determined using Eqs. (4) and (5), respectively.

$$[Al^{3+}]_{EC} = \frac{1}{3} \times [OH^-]_{EC} \tag{4}$$

$$[Al^{3+}]_{CC} = [Al^{3+}]_T - [Al^{3+}]_{EC} \tag{5}$$

$[Al^{3+}]_{EC}$ is related to the operation parameters of electrolysis. $[Al^{3+}]_{EC}$ would be regulated by changing the current intensity if the other parameters are constant.

$$I = \frac{zFV}{\varepsilon_c T}[Al^{3+}]_{EC} \tag{6}$$

where I is the current intensity, Z is the valence of aluminum ($Z = 3$), F is the Faraday constant (96486 C mol^{-1}), V is the volume of reaction (L), T is the time of electrolysis (s), ε_c is the current efficiency, and 1.11 of ε_c was chosen in this experiment (Zhu et al., 2007).

2.3. Defluoridation by CEC

An aluminum electrode with a purity of 99.9999% was used as the anode, while a copper electrode was used as the cathode. The purpose of this was to avoid the dose deviation of Al(III) resulting from the cathode dissolution. The electrodes were 90 mm × 60 mm, and the distance between the electrodes was 10 mm. Batch CEC processes were used for the defluoridation experiment, and 300 mL of raw water and 10 min of electrolysis time were adopted for each batch. The dosage of $AlCl_3$ and the applied I would be calculated according to the predetermined $[Al^{3+}]_T$ and γ_{OH+F}. Once the $AlCl_3$ was added, electromagnetic agitation was

Table 1
Water quality of F^--containing groundwater.

Item	Concentration (mg L^{-1})
F^-	9–10
Cl^-	20
SO_4^{2-}	30–31
NO_3^-	11
HCO_3^-	144
Na^+	25
K^+	2
Ca^{2+}	41
Mg^{2+}	13–14
Al^{3+}	0.006–0.012

used to keep the solution homogeneous. At the same time, a regulated power supply (DJS292, Leici instrumental Co. Shanghai, China) was turned on to supply constant *I*. The electrodes were removed immediately after batch electrolysis was completed. After gentle mixing for 10 min, the samples were drawn and filtrated by syringe filter (0.22 μm, PSE membrane) for the water quality analysis (Zhu et al., 2007).

2.4. Analysis methods

The anions including F^-, Cl^-, SO_4^{2-} and NO_3^-, and the cations including Na^+, K^+, Ca^{2+}, and Mg^{2+} were measured by ion chromatograph (Diane, ICS2500). The sample was filtered through 0.22 μm film before analysis. Alkalinity was determined by potentiometric titration.

3. Results and discussion

3.1. Effect of γ_{OH+F}

For a CEC process with a constant $[Al^{3+}]_T$, γ_{OH} can be changed by adjusting the ratio of Al(III) generated in the electrolysis process to those from dosed $AlCl_3$. When the F^--containing water with no initial alkalinity was treated by CEC, the ε_F were changed with γ_{OH} at a different $[Al^{3+}]_T$ (Fig. 1a). It was observed from Fig. 1a that for each $[Al^{3+}]_T$, there was always a γ_{OH} at which the ε_F was the highest. This γ_{OH} was defined as the optimal γ_{OH}, which increased with the increase in $[Al^{3+}]_T$. From Eq. (2) it can be seen that γ_F decreased with the increase in $[Al^{3+}]_T$. Thus, γ_{OH+F}, the sum of the optimal γ_{OH} and γ_F, can possibly be constant at a different $[Al^{3+}]_T$. The variation of ε_F with γ_{OH+F} at a different $[Al^{3+}]_T$ is shown in Fig. 1b It can be found from Fig. 1b that the highest ε_F would be achieved when γ_{OH+F} is close to 3.0 for each $[Al^{3+}]_T$. It was demonstrated that although some Al(III) were added through the chemical method, $\gamma_{OH+F} = 3.0$ would still be the control criterion to optimize the parameters for the CEC defluoridation process.

3.2. Effect of initial alkalinity

If the initial alkalinity of raw water was bicarbonate alkalinity, $[OH^-]_0$ in Eq. (3) could be replaced by $[HCO_3^-]_0$ (the initial concentration of HCO_3^- according to the relationship that the molar ratio of HCO_3^- to OH^- is 1:1. γ_{OH+F} was expressed correspondingly as $\gamma_{Alkalinity+F}$.

$$\gamma_{Alkalinity+F} = \frac{[HCO_3^-]_0 + [OH^-]_{EC} + [F^-]_0 - [H^+]_0}{[Al^{3+}]_T} \tag{7}$$

when the F^--containing water with different types (OH^- and HCO_3^-) and the same concentration (2 mM) of alkalinity was treated by CEC process, there is a variation of ε_F with $\gamma_{Alkalinity+F}$ as shown in Fig. 2. It was observed in Fig. 2 that the optimal $\gamma_{Alkalinity+F}$ ($\gamma_{Alkalinity+F(opt)}$) for defluoridation was close to 3 when the initial alkalinity was OH^-. From the results in Figs. 1a and b and 2 conclusion can be drawn that $\gamma_{Alkalinity+F} = 3.0$ would be the control criterion to optimize the parameters for the CEC defluoridation process.

However, when the initial alkalinity was bicarbonate (2 mM), the $\gamma_{Alkalinity+F(opt)}$ was close to 3.6 rather than 3.0. The reason is that, differing from the initial OH^- alkalinity, the initial bicarbonate alkalinity would not be consumed completely when the system pH decreased to the optimal pH (5.5–6.5) for defluoridation. Therefore, it is not appropriate to adopt $\gamma_{Alkalinity+F} = 3.0$ as the control criterion to optimize the CEC parameters when bicarbonate was the initial alkalinity.

By changing the initial concentration of bicarbonate alkalinity, the defluoridation efficiencies were investigated. As seen in Fig. 2, the $\gamma_{Alkalinity+F(opt)}$ for defluoridation was dependent on the bicarbonate concentration and rose with the increase of bicarbonate concentration. It would be more convenient in the application

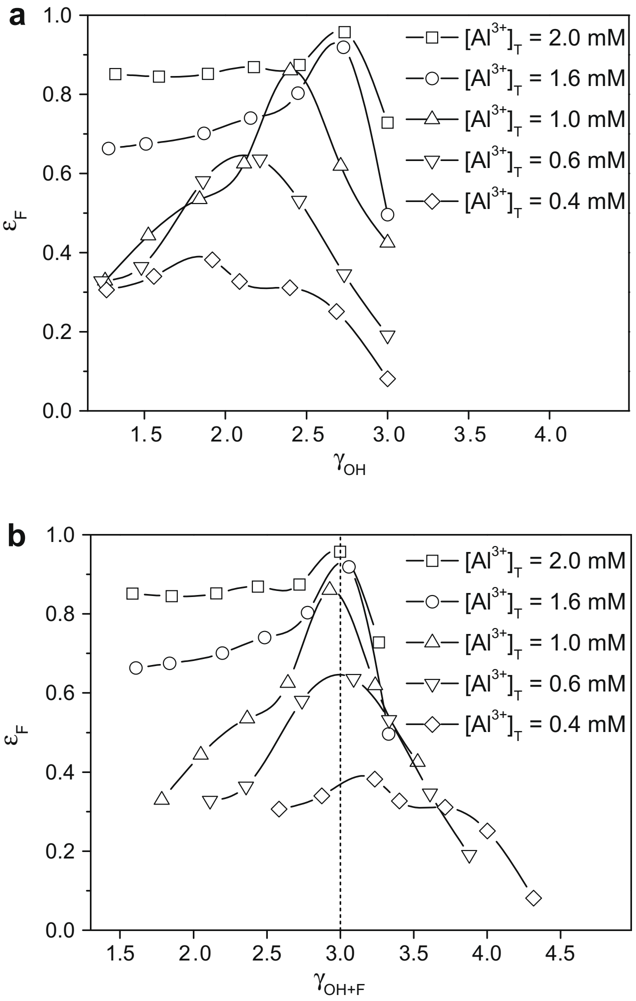

Fig. 1. Variation of ε_F with γ_{OH+F} (a) and γ_{OH+F} (b) at different $[Al^{3+}]_T$ ($[F^-] = 10\ mg\ L^{-1}$; $[OH^-]_0 = 0\ mg\ L^{-1}$).

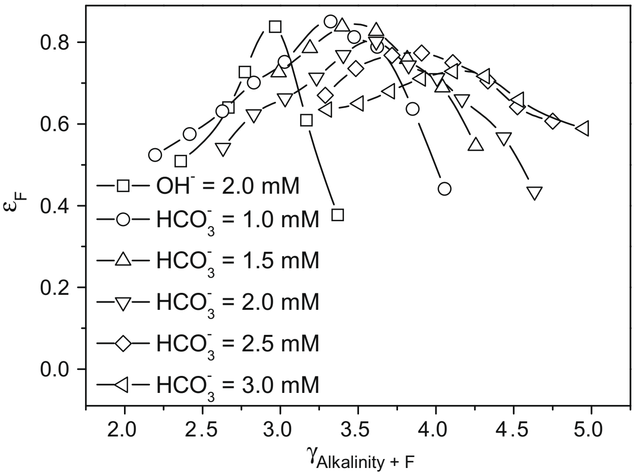

Fig. 2. Variation of ε_F with $\gamma_{Alkalinity+F}$ for the F^--containing water with initial alkalinity of OH^- and HCO_3^-, respectively ($[F^-] = 10\ mg\ L^{-1}$, $[Al^{3+}]_T = 1.2$ mM).

if the $\gamma_{\mathrm{Alkalinity+F(opt)}}$ was adjusted at 3.0 by correcting the bicarbonate alkalinity.

3.3. Correction of bicarbonate alkalinity

To obtain the correction coefficient of bicarbonate alkalinity, some assumptions were made: (1) $\gamma_{\mathrm{Alkalinity+F(opt)}}$ equates to 3.0 at a varied concentration of bicarbonate. (2) The difference between bicarbonate and hydroxide alkalinity can be expressed by Eq. (8), where α is the correction coefficient and is a constant

$$[\mathrm{OH}^-]_0 = \alpha[\mathrm{HCO}_3^-]_0 \tag{8}$$

(3) The correction calculation of $\gamma_{\mathrm{Alkalinity+F}}$ is conducted using Eq. (9) if the initial alkalinity is bicarbonate.

$$\gamma_{\mathrm{Alkalinity+F(cor)}} = \frac{\alpha[\mathrm{HCO}_3^-]_0 + [\mathrm{OH}^-]_{\mathrm{EC}} + [\mathrm{F}^-]_0 - [\mathrm{H}^+]_0}{[\mathrm{Al}^{3+}]_{\mathrm{T}}} \tag{9}$$

where $\gamma_{\mathrm{Alkalinity+F(cor)}}$ is the corrected $\gamma_{\mathrm{Alkalinity+F}}$. According to the first assumption, $\gamma_{\mathrm{Alkalinity+F(cor)}}$ is 3.0, and it is at this point that the highest ε_{F} will be achieved. For the different bicarbonate concentrations, $\gamma_{\mathrm{Alkalinity+F(opt)}}$ must comply simultaneously with Eqs. (7) and (9). Eq. (10) will be obtained by subtracting Eq. (9) from Eq. (7).

$$(\gamma_{\mathrm{Alkalinity+F(opt)}} - 3.0) \times [\mathrm{Al}^{3+}]_{\mathrm{T}} = (1 - \alpha)[\mathrm{HCO}_3^-]_0 \tag{10}$$

By substituting the results in Fig. 2 to Eq. (10) and linear fitting to the values of $(\gamma_{\mathrm{Alkalinity+F(opt)}} - 3.0) \times [\mathrm{Al}^{3+}]_{\mathrm{T}}$ at different bicarbonate concentrations, the following equation will be obtained:

$$y = 0.40x, \; R^2 = 0.9731$$

where 0.40 is the slope of $(1 - \alpha)$ in Eq. (10). Thus, the correction coefficient of bicarbonate alkalinity (α) is 0.60.

Based on the experimental data in Fig. 2, the values of $\gamma_{\mathrm{Alkalinity+F(cor)}}$ can be calculated after substituting the correction coefficient of 0.60 to Eq. (9). The variation of ε_{F} with $\gamma_{\mathrm{Alkalinity+F(cor)}}$ at different initial bicarbonate concentrations is shown in Fig. 3. As seen in the figure, when initial bicarbonate concentration is 1.0–3.0 mM, the optimal defluoridation efficiencies were achieved at $\gamma_{\mathrm{Alkalinity+F(cor)}}$ close to 3.0.

For natural F^--containing groundwater, it was measured using potentiometric titration that the initial alkalinity was bicarbonate with a concentration of 2.362 mM. When $[\mathrm{Al}^{3+}]_{\mathrm{T}} = 1.2$ mM, the ε_{F} of CEC increased with the increase of $\gamma_{\mathrm{Alkalinity+F(cor)}}$, and decreased after the maximum value was reached at $\gamma_{\mathrm{Alkalinity+F(cor)}}$ close to 3.0. It was proven that the correction coefficient of bicarbonate obtained from the above experiment was also suitable for the bicarbonate alkalinity in F^--containing groundwater.

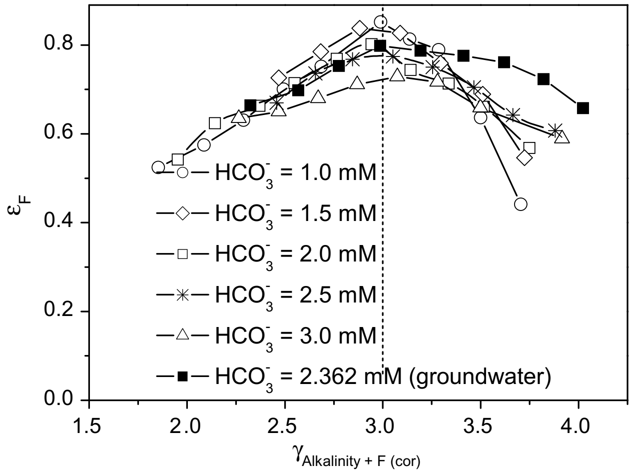

Fig. 3. Variation of ε_{F} with $\gamma_{\mathrm{Alkalinity+F(cor)}}$ at different bicarbonate concentrations ($[\mathrm{F}^-] = 10$ mg L^{-1}, $[\mathrm{Al}^{3+}]_{\mathrm{T}} = 1.2$ mM).

3.4. Analysis for performance and energy consumption

The bicarbonate alkalinity of F^--containing groundwater was corrected using the correction efficient, and the $\gamma_{\mathrm{Alkalinity+F(cor)}}$ was adjusted to 3.0. The defluoridation efficiencies of CEC and acid-adding EC were then tested. It was observed from Fig. 4a that the defluoridation efficiencies of the two processes rose with the increase in Al(III) dosage. When the Al(III) dosage exceeded 1.5 mM, the defluoridation efficiencies of the two processes exceeded 90%, and the effluent F^- became less than 1 mg L^{-1}. In the CEC process, only a part of Al(III) was from electrolysis, while in the acid-adding EC process, all the Al(III) was from electrolysis. Thus, the effect of the electric field was stronger in the acid-adding EC process than in the CEC process at the same $[\mathrm{Al}^{3+}]_{\mathrm{T}}$. In the range of low-Al(III) dosage ($[\mathrm{Al}^{3+}]_{\mathrm{T}} < 1.2$ mM), the electrocondensation caused by the electric field had a great contribution to defluoridation, and the fluoride removal occurred mainly near the electrode (Zhu et al., 2007). Therefore, the ε_{F} of the acid-adding EC was slightly higher than that of the CEC. With the increase in Al(III) dosage, the effect of electrocondensation was no longer significant. The fluoride removal not only occurred near the electrode but also depended largely on the adsorption from the aluminum hydroxide dispersed in the bulk solution (Mameri et al., 1998; Emamjomeh

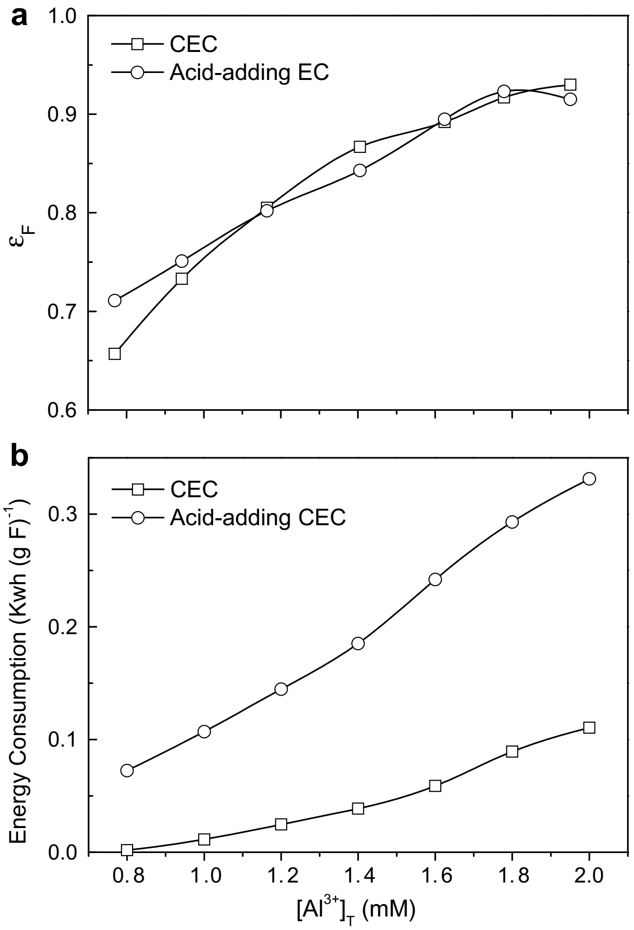

Fig. 4. Comparison of performance and energy consumption between CEC and acid-adding EC in treating F^--containing groundwater (initial $\mathrm{F}^- = 10$ mg L^{-1}). (a) ε_{F} and (b) energy consumption.

and Sivakumar, 2006). Therefore, the defluoridation efficiencies of the two processes had little difference in the range of high-Al(III) dosage ($[Al^{3+}]_T > 1.2$ mM).

Fig. 4b presents the energy consumption (energy required to remove 1 g of F^-) of the two processes. Only a part of aluminum was needed to be produced from the electrolysis in the CEC process, and all in the acid-adding EC process. Therefore, the energy consumption of CEC was evidently less than that of the acid-adding EC process (Can et al., 2006), and the difference between them increased with the increase in aluminum dosage. While the two processes had similar defluoridation efficiencies, energy consumption in CEC was less than one third of that in the acid-adding EC (Fig. 4b). Moreover, it is believed that the cost of electrode consumption in the CEC process would decrease substantially.

4. Conclusions

In this paper, a CEC was proposed for the first time, and the method to optimize the design and operation of the process was explored in the experiments. The results showed that for the F^--containing water with OH^- as the only initial alkalinity, CEC would reach the highest ε_F at $\gamma_{\text{Alkalinity+F}} = 3.0$. If there was bicarbonate alkalinity in raw water, the bicarbonate concentration should be corrected to meet the criterion of $\gamma_{\text{Alkalinity+F}} = 3.0$, which was the optimal defluoridation condition for CEC. The correction coefficient of bicarbonate alkalinity was 0.60 from the experiments. There was little difference in the ε_F between CEC and the acid-adding EC process. When the Al(III) dosage exceeded 1.5 mM, the defluoridation efficiencies of both processes exceeded 90%. Little energy was consumed in CEC, which was less than one third of that consumed in the acid-adding EC process. The CEC process not only decreased the energy and aluminum consumption but also retained the advantages from the electric field of EC, showing that the CEC process has promising application prospects.

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