Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Combined electrocoagulation and electroflotation for removal of fluoride from drinking water

Qianhai Zuo^a, Xueming Chen^{a,*}, Wei Li^a, Guohua Chen^b

^a Environmental Engineering Department, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China ^b Chemical Engineering Department, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

ARTICLE INFO

Article history: Received 24 October 2007 Received in revised form 14 February 2008 Accepted 14 February 2008 Available online 19 February 2008

Keywords: Defluoridation Drinking water Electrocoagulation Electroflotation

ABSTRACT

A combined electrocoagulation (EC) and electroflotation (EF) process was proposed to remove fluoride from drinking water. Its efficacy was investigated under different conditions. Experimental results showed that the combined process could remove fluoride effectively. The total hydraulic retention time required was only 30 min. After treatment, the fluoride concentration was reduced from initial 4.0–6.0 mg/L to lower than 1.0 mg/L. The influent pH value was found to be a very important variable that affected fluoride removal significantly. The optimal influent pH range is 6.0–7.0 at which not only can effective defluoridation be achieved, but also no pH readjustment is needed after treatment. In addition, it was found that SO_4^{2-} had negative effect; Ca^{2+} had positive effect; while CI^- had little effect on the fluoride removal. The EC charge loading, EF charge loading and energy consumption were 3.0 Faradays/m³, 1.5 Faradays/m³, and 1.2 kWh/m³, respectively, under typical conditions where fluoride was reduced from initial 4.0 to 0.87 mg/L.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Fluoride has beneficial and detrimental effects on human body. It can help prevent dental cavities. However, long-term consumption of water containing excessive amounts of fluoride can lead to dental fluorosis and even to skeletal damage. According to the World Health Organization (WHO) guidelines for drinking water quality, the fluoride concentration should be ≤ 1.5 mg/L. Unfortunately, many countries in the world are suffering from the problem that the fluoride concentration in some groundwater is much higher than the guidelines value. Such groundwater should be defluorinated when used as drinking water. In China, the upper limit of fluoride concentration in drinking water is only 1.0 mg/L. Therefore, more effective defluorination techniques should be used.

Nowadays, the most popular processes for drinking water defluoridation are the adsorption using activated alumina [1–3], bone char [4,5], activated carbon [6,7] and other adsorbents [8,9], and the coagulation using aluminum salts [10]. Adsorption is effective in defluoridation, but its operation is complex. Coagulation is simple in equipment and effective in defluoridation under proper conditions, but large amounts of contaminants such as SO_4^{2-} are introduced to the water, especially when the fluoride concentration is high. Other major processes for defluoridation include electrodialysis [11], reverse osmosis [12], and nanofiltration [13]. These membrane processes are known to be effective means for defluoridation. However, a common problem is their poor selectivity. This not only removes the beneficial contents present in water during defluoridation, but also increases the operational cost. Therefore, membrane processes are only suitable for treatment of brackish water containing high content of fluoride, which needs both defluoridation and desalination simultaneously.

In recent years, there is growing interest in EC. This technique can be used to treat restaurant wastewater [14], textile wastewater [15], electroplating wastewater [16], and fluoride-containing wastewater [17,18] effectively. It has also proven its good efficacy for drinking water defluoridation [19,20]. EC is attractive in that no contaminants are introduced and beneficial contents present in raw water can be remained during defluoridation. The main reactions involved are as following:

 $Al \rightarrow Al^{3+} + 3e$ at the anode (1)

 $Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$ (2)

$$Al(OH)_3 + xF^- \rightarrow Al(OH)_{3-x}F_x + xOH^-$$
(3)

$$2H_2O + 2e \rightarrow H_2 + 2OH^-$$
 at the cathode (4)

Defluoridation is achieved by forming $Al(OH)_{3-x}F_x$. The fine hydrogen gas bubbles generated at the cathode can enhance $F^$ mass transfer and float the $Al(OH)_{3-x}F_x$ flocs to the top of the EC unit. Since fluoride in the water is transferred to $Al(OH)_{3-x}F_x$, $Al(OH)_{3-x}F_x$ must be separated effectively from the water in order

^{*} Corresponding author. Tel.: +86 571 87951239; fax: +86 571 87952771. *E-mail address:* chenxm@zju.edu.cn (X. Chen).

^{0304-3894/\$ -} see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2008.02.039

Nomenclature		
Е	energy consumption (kWh/m ³ water)	
EC	electrocoagulation	
EF	electroflotation	
HRT	hydraulic retention time (min)	
Ι	current (A)	
п	number of electrodes for the bipolar electrodes sys-	
	tem	
Q	water flowrate (m ³ /h)	
q	charge loading (Faradays/m ³ water)	
$q_{\rm EC}$	EC charge loading (Faradays/m ³ water)	
$q_{ m EF}$	EF charge loading (Faradays/m ³ water)	
$U_{\rm EC}$	electrolysis voltage between two neighboring alu-	
	minum electrodes of EC (V)	
$U_{\rm EF}$	electrolysis voltage between an anode and a cathode	
	of EF (V)	
V	total volume of the EC-EF apparatus (m ³)	

to achieve effective defluoridation. Nevertheless, we observed that the hydrogen gas produced at the cathodes of an EC unit could float only about two-thirds of the total flocs [21]. Therefore, further effective separation of the residual flocs is very important. In our previous work [22], a combined EC and EF process was examined for removing fluoride from industrial wastewater. The results were encouraging. The fluoride concentration could be reduced from initial 15 to 2 mg/L without filtration.

In the present work, the combined EC and EF was proposed for removal of fluoride from drinking water. The major objectives of this study are to examine the defluoridation efficacy under different conditions, and to estimate the energy consumption required.

2. Experimental

The experimental setup is schematically shown in Fig. 1. The defluoridation apparatus consisted of an EC chamber, a flocculation-enhanced chamber and an EF chamber, with effective volumes being 0.4, 0.5, and 0.85 L, respectively. The EC chamber had three aluminum electrodes, each with a dimension of 160 mm \times 47 mm \times 4 mm and an effective area of 64 cm². The alu-



Fig. 1. Diagram of the experimental setup ((1) EC cell, (2) flocculation-enhanced chamber, (3) EF cell, (4) sludge chamber, and (5) DC power supply).

minum electrodes were installed vertically, and connected in a bipolar mode. The net spacing between the aluminum electrodes was 4 mm. In order to enhance flocculation, four pieces of PVC plates with holes were installed in the flocculation chamber. The diameter of the holes varied from 1 mm at the bottom to 2 mm at the top.

The EF chamber had two rod $Ti/IrO_2-SnO_2-Sb_2O_5$ anodes and three rod Ti cathodes with a diameter of 3 mm. These electrodes were installed horizontally. It should be noted that $Ti/IrO_2-SnO_2-SbO_5$ electrodes can only serve as anodes. When used as cathodes, they will fail very quickly. Therefore, the EF electrode system was connected in a monopolar mode instead of a bipolar mode. The net spacing between a $Ti/IrO_2-SnO_2-SbO_5$ anode and a Ti cathode was 5 mm. The anodes were prepared using a conventional thermal decomposition method. The detailed preparation procedure can been found elsewhere [23,24].

The testing water was prepared artificially by dissolving a proper amount of NaF and other chemicals such as NaCl, Na₂SO₄ and CaCl₂ into deionized water. After aggregated and floated up to the surface of water in EF process, the $Al(OH)_{3-x}F_x$ scum was removed manually.

The pH values of water were measured with a pH meter (420A, Orion, MA). Fluoride concentrations were analyzed using a spectrophotometer (DR/2500, Hach, USA) at 620 nm according to the standard methods [25]. Total ionic strength adjustment buffer (TISAB) at pH 4.1 was used to maintain constant ionic strength and to prevent the interference from other ions such as Al³⁺ and Ca²⁺. Residual Al species in effluent were measured using inductively coupled plasma (ICP, X Series II, Thermo, USA).

3. Results and discussion

3.1. Effect of Influent pH

It has been established that the influent pH is an important operating factor influencing the performance of the EC and EF processes [26,27]. To investigate its effect on defluoridation, the water was adjusted to the desired pH values using 0.1 M sodium hydroxide or 0.1 M hydrochloric acid solution. The result is shown in Fig. 2. It was found that fluoride removal was highly dependent on the influent pH value. Low initial pH value was beneficial to fluoride removal. The fluoride concentration could be reduced effectively from initial 4.0 to 0.55–0.87 mg/L in the influent pH range of 3.4–7.0. As the influent pH value increased, the effluent fluoride concentration



Fig. 2. Effect of influent pH on defluoridation (initial $F^- = 4.0 \text{ mg/L}$, EC charge loading = 3.0 Faradays/m³, EF charge loading = 1.5 Faradays/m³, hydraulic retention time = 30 min).



Fig. 3. Change of pH after treatment (initial $F^- = 4.0 \text{ mg/L}$, EC charge loading = 3.0 Faradays/m³, EF charge loading = 1.5 Faradays/m³, hydraulic retention time = 30 min).

increased quickly. When the influent pH value reached about 7.4, the effluent fluoride concentration increased to 1.25 mg/L. When the influent pH increased further to about 8.0, the effluent fluoride was beyond 1.60 mg/L.

Fluoride removal can be taken as the ion exchange of F^- with OH^- in $Al(OH)_3$ as shown in Eq. (3). When OH^- concentration decreases, the ion exchange equilibrium shifts toward the right side. This explains why low pH value is beneficial to fluoride removal.

It is necessary to point out that the determination of the influent pH should be based not only on its effect on defluoridation, but also on other considerations. Although low pH is beneficial to defluoridation, the effect trends to be small when the influent pH values are lower than \sim 6.0–7.0. In addition, if the influent pH is controlled at a lower pH value, more acid will be added and readjustment of pH will be necessary. Therefore, it is believed that the optimum influent pH is about 6.0–7.0.

Fig. 3 shows the variation of the effluent pH with the influent pH. Like the case for wastewater defluoridation [22], there was an increase in pH value after treatment. When the influent pH value was 3.4, the effluent pH value was 6.3. When the influent pH values increased to 6.0–7.0, the effluent pH values were \sim 7.0–8.0. This indicates that as the influent pH is controlled at the optimal range recommended previously, no pH readjustment is needed after treatment.

The pH increase was mainly attributed to CO_2 transfer [14]. At acidic medium, CO_2 was oversaturated in water and thus could release from water due to the disturbance of H_2 and O_2 bubbles produced at the electrodes, which caused a pH increase. In addition, fluoride ions exchanged partly with OH⁻ in Al(OH)₃ to free OH⁻, which also caused a pH increase [22].

3.2. Effect of charge loading and initial fluoride concentration

Charge loading is defined as the charges transferred in electrochemical reactions for a given amount of water treated, and can be calculated using Eq. (5) for a monopolar electrodes system, or using Eq. (6) for a bipolar electrodes system:

$$q = \frac{3,600I}{96,500Q} \tag{5}$$

$$q = \frac{3,600(n-1)I}{96,500Q} \tag{6}$$



Fig. 4. Effects of charge loading and initial fluoride concentration on defluoridation (influent pH 7.0, hydraulic retention time = 30 min).

where *q* is the charge loading (Faradays/m³ water); *n* is the number of electrodes for the bipolar electrodes system; *I* is the current (A); and *Q* is the water flowrate (m³/h). As mentioned before, EC electrodes were connected in a bipolar mode, while EF electrodes were connected in a monopolar mode in the present work. In addition, the EC electrodes system and the EF electrodes system shared a DC power supply together and were connected in series. Therefore, the ratio of the EC charge loading to the EF charge loading was fixed to be (n - 1): 1 = (3 - 1): 1 = 2: 1 in the present work.

Fig. 4 shows the variation of the effluent fluoride concentration with EC charge loading under different initial fluoride concentrations. As expected, the fluoride concentration in the effluent depended strongly on the initial fluoride concentration and on the charge loading. At the same charge loading, the effluent fluoride concentration increased when the influent fluoride concentration increased. This is consistent with the batch result reported by Emamjomeh and Sivakumar [28]. High effluent fluoride level was observed for both cases at low charge loading. As the EC charge loading increased to about 3.0 Faradays/m³, the effluent fluoride concentrations were reduced from 4.0 and 6.0 mg/L to 0.87 and 1.35 mg/L, respectively. As the EC charge loading increased further to 3.4 Faradays/m³, the effluent fluoride concentrations were reduced to only 0.20 and 0.95 mg/L, respectively.

The importance of charge loading for fluoride removal is understandable. According to Faraday's law, the amount of the aluminum dissolved electrochemically is proportional to the charge loading. When the charge loading was low, the aluminum dose was not sufficient. In that case, only a small amount of $Al(OH)_3$ flocs were formed, which could not adsorb the fluoride effectively. As the charge loading increased, the aluminum dose increased accordingly. In such a case, more $Al(OH)_3$ flocs were formed, which could adsorb more fluoride. As a result, the fluoride concentration in the effluent decreased.

The main role of EF is to separate the $AI(OH)_{3-x}F_x$ flocs from EC. It was observed that the effluent was clear, indicating the high separation efficiency of EF. In addition, it was found that the effect of charge loading to the separation efficiency was small. This was essentially attributed to the fact that the amount of $AI(OH)_{3-x}F_x$ flocs formed in EC was proportional to that of hydrogen and oxygen bubbles generated in EF because the ratio of the EC charge loading to the EF charge loading was fixed to be 2:1 in the present work.

In addition to the solid–liquid separation, EF also plays an important role in enhancing mass transfer. Usually, the residual fluoride concentration decreases fast initially, and then slowly as aluminum



Fig. 5. Effects of coexisting ions on defluoridation (initial $F^- = 4.0 \text{ mg/L}$, influent pH 7.0, EC charge loading = 3.0 Faradays/m³, EF charge loading = 1.5 Faradays/m³, hydraulic retention time = 30 min).

dose increases [28]. In the present work, it is found, however, that the fluoride concentration in effluent drops linearly as the charge loading increases as shown in Fig. 4. This is attributed to the mass transfer enhancement occurred in the EF chamber where the small hydrogen and oxygen bubbles generated at the Ti and $Ti/IrO_2-SnO_2-SbO_5$ electrodes can cause a strong turbulence.

3.3. Effect of coexisting ions

Hu and coworkers [17] reported that coexisting anions such as SO₄^{2–} could affect wastewater defluoridation in the EC process. Since some raw water, especially underground water, may contain high concentrations of coexisting ions, it is necessary to quantify the effects of the coexisting ions on drinking water defluoridation in the combined EC and EF process. Fig. 5 shows the dependence of the effluent fluoride concentration on the concentrations of three typical coexisting ions. It was found that SO_4^{2-} could affect fluoride removal dramatically. When no SO_4^{2-} was present in water, the fluoride concentration in the effluent was 0.87 mg/L. But when the SO_4^{2-} concentration increased to 250 mg/L, the fluoride concentration in the effluent rose to 1.85 mg/L. Hu and coworkers [17] attribute the negative effect of SO_4^{2-} on defluoridation to the inhibition of the localized corrosion of aluminum electrodes. When the corrosion of aluminum electrodes is inhibited, the current efficiency decreases. This leads to a decrease in defluoridation efficiency. Additionally, in our previous study for wastewater defluoridation [22], we have analyzed the sludge produced in the combined EC-EF process using X-ray photoelectron spectroscopy (XPS), and found the atomic concentration of S in the dried sludge was as high as 1.03% when the concentrations of F^- and SO_4^{2-} in the influent were 15 and 96 mg/L, respectively. Therefore, we believe that the negative effect of SO_4^{2-} on defluoridation is also associated with the ion exchange competition between SO_4^{2-} and F^- , that is:

$$Al(OH)_{3-x}F_x + ySO_4^{2-} = Al(OH)_{3-x}F_{x-2y}(SO_4)_y + 2yF^-$$
(7)

As the SO_4^{2-} concentration increases, the ion exchange reaction (7) shifts to the right side, which causes a further increase in the effluent fluoride concentration.

It can be seen from Fig. 5 that the effect of Cl⁻ on fluoride removal is small. Actually, Cl⁻ can affect defluoridation in two different ways. On one hand, Cl⁻ is known to be able to rupture the passive films of aluminum electrodes [17]. As Cl⁻ concentration

increased, the current efficiency of EC increased also, and therefore, more aluminum species were generated. This was beneficial to defluoridation. On the other hand, there was an ion exchange competition between Cl⁻ and F⁻ just like the case between SO_4^{2-} and F⁻. As the Cl⁻ concentration increased, defluoridation was inhibited slightly. The positive role could be offset by the negative role, and therefore, Cl⁻ had only little effect on the defluoridation.

It was found that Ca^{2+} could enhance defluorination. When no Ca^{2+} was present in water, the fluoride concentration in the effluent was 0.87 mg/L. But when Ca^{2+} concentration increased to 250 mg/L, the fluoride concentration in the effluent was reduced to 0.23 mg/L. The mechanisms of enhancement of fluoride removal by Ca^{2+} are complex. It is well known that fluoride is able to form the precipitate of CaF_2 with Ca^{2+} :

$$Ca^{2+} + 2F^{-} = CaF_2$$
 (8)

In fact, chemical precipitation with lime is the most common approach currently available for treatment of fluoride-laden industrial wastewaters. Therefore, when a large amount of Ca²⁺ was added to the water, insoluble CaF₂ formed, which caused an enhancement in fluoride removal. However, it should be noted that the fluoride concentration in the influent was 4.0 mg/L in experiments, which corresponded to an equilibrium concentration of 150 mg/L for Ca²⁺ on the basis of the solubility product of CaF₂ (1.7 × 10⁻¹⁰ at 25 °C). Apparently, no CaF₂ was formed when Ca²⁺ < 150 mg/L. In that case, the positive effect of Ca²⁺ on fluoride removal was probably associated with the coprecipitation of Al³⁺ and Ca²⁺:

$$\begin{split} & mAl^{3+} + nCa^{2+} + (3m+2n)H_2O = Al_mCa_n(OH)_{3m+2n} \\ & + (3m+2n)H^+ \end{split} \tag{9}$$

Since Ca^{2+} has strong affinity to F^- , incorporation of Ca^{2+} into the aluminum hydroxide can enhance fluoride removal.

3.4. Effect of hydraulic retention time

Hydraulic retention time is defined as below:

$$HRT = \frac{60V}{Q}$$
(10)

where HRT is the hydraulic retention time (min); V is the total volume of the EC–EF apparatus including the EC chamber, the flocculation-enhanced chamber and the EF chamber (m³); and Q is the same as mentioned before. Since the charge loading can



Fig. 6. Effect of hydraulic retention time on defluoridation (initial $F^- = 4.0 \text{ mg/L}$, influent pH 7.0, EC charge loading = 3.0 Faradays/m³, EF charge loading = 1.5 Faradays/m³).

affect the fluoride removal significantly, the HRT effect was investigated at a constant charge loading by varying the applied current in proportion to the water flowrate. The result is shown in Fig. 6. It was found that there was small effect of HRT on defluoridation. When HRT was 20 min, the fluoride concentration in the effluent was 1.02 mg/L. When HRT increased to 30 min, the fluoride concentration decreased to 0.87 mg/L. Beyond 30 min, the effect of HRT on fluoride removal was insignificant. Therefore, the optimal HRT was about 30 min.

The slight decrease in fluoride removal efficiency at short HRT was mainly attributed to the relatively low mass transfer rate. Essentially, the formation of $Al(OH)_{3-x}F_x$ flocs involved a series of steps, including the direct complex of Al³⁺ with F⁻ during the initial period of time, hydrolysis of the aluminum species, mass transfer of F⁻ from the bulk solution to the Al(OH)₃ flocs, and ion exchange. Usually, most steps could be completed quickly. However, due to the limited number of the Al(OH)₃ flocs, the mass transfer of F⁻ from the bulk solution to the Al(OH)₃ flocs was relatively low. This caused a decrease in fluoride removal at short HRT. In addition, short HRT was not beneficial to flocs separation either. In the EF unit, water flowed downward, while the Al(OH)_{3-x} F_x flocs attached by tiny hydrogen and oxygen bubbles moved upward. Obviously, only when the upward velocity of a floc exceeded the downward velocity of the water flowrate, could the floc be separated from the water. When HRT was short, the velocity of some small flocs was lower than that of the water flow. As a result, these flocs moved out together with the water flow, and the effluent fluoride concentration increased.

3.5. Energy consumption

The energy consumption of the combined EC and EF process can be calculated according to Eq. (11):

$$E = \frac{(n-1)U_{\rm EC}I + U_{\rm EF}I}{1,000Q}$$
(11)

where *E* is energy consumption (kWh/m³ water); U_{EC} is electrolysis voltage between two neighboring aluminum electrodes of EC (V); U_{EF} is electrolysis voltage between an anode and a cathode of EF (V). The other symbols are the same as mentioned before. Eq. (11) can be rearranged as

$$E = \frac{96,500}{1,000 \times 3,600} \left[\frac{3,600(n-1)U_{EC}I}{96,500Q} + \frac{3,600U_{EF}I}{96,500Q} \right]$$

or $E = 0.0268(U_{EC}q_{EC} + U_{EF}q_{EF})$ (12)

where $q_{\text{EC}} = (3,600(n-1)I)/96,500Q$, the EC charge loading, Faradays/m³ water; $q_{\text{EF}} = (3,600I)/96,500Q$, the EF charge loading, Faradays/m³ water.

Eq. (12) reveals that the energy consumption is determined by charge loadings and electrolysis voltages. In the present work, the charge loadings of EC and EF were 3.0 and 1.5 Faradays/m³, respectively, and the voltages of EC and EF were measured to be 7.6 and 14.0 V, respectively, under typical conditions where fluoride was reduced from initial 4.0 to 0.87 mg/L at a conductivity of 200 µs/cm, a CE current density of 22 A/m², and an average EF current density of 75 A/m². Therefore, $E = 0.0268(U_{EC}q_{EC} + U_{EF}q_{EF}) = 0.0268(7.6 \times 3.0 + 14.0 \times 1.5) = 1.2 kWh/m³ water.$

3.6. Residual Al in effluent

For any drinking water treatment process using Al, residual Al is an important consideration. In order to know the Al level in effluent, three samples were taken after the EC–EF apparatus run normally for 1-2 h, and the measuring results are shown in Table 1. It can be

Table 1

Residual Al in effluent (initial $F^- = 4.0 \text{ mg/L}$, influent pH 7.0, EC charge loading = 3.0 Faradays/m³, EF charge loading = 1.5 Faradays/m³, hydraulic retention time = 30 min)

Samples	Residual Al in effluent (mg/L)
1#	0.83
2#	1.10
3#	0.90

seen that the residual Al in the effluent ranges from 0.83 to 1.1 mg/L, higher than the permit value, 0.2 mg/L, of Chinese Standards for Drinking Water Quality. In industrial application, therefore, EC–EF should be followed by filtration, which can remove the residual Al effectively.

4. Conclusions

The combined EC and EF process could remove fluoride from drinking water effectively. The total hydraulic retention time required was only 30 min. After treatment, the fluoride concentration was reduced from initial 4.0-6.0 mg/L to lower than 1 mg/L. It was found that the influent pH value could affect fluoride removal significantly. The optimal influent pH is 6.0-7.0. In this influent pH range, not only can effective defluoridation be achieved, but also no pH readjustment is needed after treatment. In addition, it was found that SO₄²⁻ had negative effect; Ca²⁺ had positive effect; while Cl⁻ had little effect on the fluoride removal. The EC charge loading, EF charge loading and energy consumption were about 3.0 Faradays/m³, 1.5 Faradays/m³, and 1.2 kWh/m³, respectively, under typical conditions where fluoride was reduced from initial 4.0 to 0.87 mg/L at a conductivity of about 200 µs/cm, a CE current density of 22 A/m², and an average EF current density of $75 \,\text{A/m}^2$.

References

- S. Ghorai, K.K. Pant, Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina, Sep. Purif. Technol. 42 (2005) 265– 271.
- [2] S.S. Tripathy, J.L. Bersillon, K. Gopal, Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina, Sep. Purif. Technol. 50 (2006) 310–317.
- [3] V.S. Chauhan, P.K. Dwivedi, L. Iyengar, Investigations on activated alumina based domestic defluoridation units, J. Hazard. Mater. 139 (2007) 103–107.
- [4] H. Mjengera, G. Mkongo, Appropriate deflouridation technology for use in flourotic areas in Tanzania, Phys. Chem. Earth 28 (2003) 1097–1104.
- [5] V. Hernandez-Montoya, M.P. Elizalde-Gonzalez, R. Trejo-Vazquez, Screening of commercial sorbents for removal of fluoride in synthetic and groundwater, Environ. Technol. 28 (2007) 595–607.
- [6] A.A.M. Daifullah, S.M. Yakout, S.A. Elreefy, Adsorption of fluoride in aqueous solutions using KMnO₄-modified activated carbon derived from steam pyrolysis of rice straw, J. Hazard. Mater. 147 (2007) 633–643.
- [7] S. Kumar, A. Gupta, J.P. Yadav, Fluoride removal by mixtures of activated carbon prepared from Neem (*Azadirachta indica*) and Kikar (*Acacia arabica*) leaves, Ind. J. Chem. Techn. 14 (2007) 355–361.
- [8] K. Biswas, S.K. Saha, U.C. Ghosh, Adsorption of fluoride from aqueous solution by a synthetic Iron(III)-Aluminum(III) mixed oxide, Ind. Eng. Chem. Res. 46 (2007) 5346–5356.
- [9] S. Samatya, U. Yuksel, M. Yuksel, N. Kabay, Removal of fluoride from water by metal ions (Al³⁺, La³⁺ and ZrO²⁺) loaded natural zeolite, Sep. Sci. Technol. 42 (2007) 2033–2047.
- [10] M. Pinon-Miramontes, R.G. Bautista-Margulis, A. Perez-Hernandez, Removal of arsenic and fluoride from drinking water with cake alum and a polymeric anionic flocculent, Fluoride 36 (2003) 122–128.
- [11] M. Tahaikt, I. Achary, M.A. Menkouchi Sahli, Z. Amor, M. Taky, A. Alami, A. Boughriba, M. Hafsi, A. Elmidaoui, Defluoridation of Moroccan groundwater by electrodialysis: continuous operation, Desalination 189 (2006) 215– 220.
- [12] M. Arora, R.C. Maheshwari, S.K. Jain, A. Gupta, Use of membrane technology for potable water production, Desalination 170 (2004) 105–112.
- [13] K. Hu, J.M. Dickson, Nanofiltration membrane performance on fluoride removal from water, J. Mem. Sci. 279 (2006) 529–538.

- [14] X.M. Chen, G.H. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Sep. Purif. Technol. 19 (2000) 65–76.
- [15] M. Bayramoglu, M. Kobya, O.T. Can, M. Sozbir, Operating cost analysis of electrocoagulation of textile dye wastewater, Sep. Purif. Technol. 37 (2004) 117–125.
- [16] N. Adhoum, L. Monser, N. Bellakhal, J.E. Belgaied, Treatment of electroplating wastewater containing Cu²⁺, Zn²⁺ and Cr(VI) by electrocoagulation, J. Hazard. Mater. 112 (2004) 207–213.
- [17] C.Y. Hu, S.L. Lo, W.H. Kuan, Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes, Water Res. 37 (2003) 4513–4523.
- [18] C.Y. Hu, S.L. Lo, W.H. Kuan, Effects of the molar ratio of hydroxide and fluoride to Al(III) on fluoride removal by coagulation and electrocoagulation, J. Colloid Interf. Sci. 283 (2005) 472–476.
- [19] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhocine, H. Grib, B. Bariou, Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrode, Water Res. 32 (1998) 604–612.
- [20] N. Mameri, H. Lounici, D. Belhocine, H. Grib, D.L. Piron, Y. Yahiat, Defluoridation of Sahara water by small plant electrocoagulation using bipolar aluminium electrodes, Sep. Purif. Technol. 24 (2001) 113–119.

- [21] G.H. Chen, X.M. Chen, P.L. Yue, Electrocoagulation and electroflotation of restaurant wastewater, J. Environ. Eng-ASCE 126 (2000) 858– 863.
- [22] F. Shen, X.M. Chen, P. Gao, G.H. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci. 58 (2003) 987–993.
- [23] X.M. Chen, G.H. Chen, P.L. Yue, Stable Ti/IrO_x-SnO₂-Sb₂O₅ anode for O₂ evolution with low Ir content, J. Phys. Chem. B 105 (2001) 4623–4628.
- [24] X.M. Chen, G.H. Chen, Investigation of Ti/IrO₂-SnO₂-Sb₂O₅ electrodes for O₂ evolution, J. Electrochem. Soc. 152 (2005) J59–J64.
- [25] APHA, Standard Methods for the Examination of Water and Wastewater, 17th edition, American Public Health Association, Washington, DC,1989.
- [26] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electro-coagulation (EC)—science and applications, J. Hazard. Mater. 84 (2001) 29– 41.
- [27] G.H. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.
- [28] M.M. Emamjomeh, M. Sivakumar, An empirical model for defluoridation by batch monopolar electrocoagulation/flotation (ECF) process, J. Hazard. Mater. B131 (2006) 118–125.