

# Simulation the kinetics of fluoride removal by electrocoagulation (EC) process using aluminum electrodes

Ching-Yao Hu<sup>a</sup>, Shang-Lien Lo<sup>a,\*</sup>, Wen-Hui Kuan<sup>b</sup>

<sup>a</sup> Research Center for Environmental Pollution Prevention and Control Technology, Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 106, Taiwan, ROC

<sup>b</sup> Research Center for Environmental Pollution Prevention and Control Technology, Department of Environmental and Safety Engineering, Ming-Chi University of Technology, Taishan, Taipei hsien 243, Taiwan, ROC

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## Abstract

A variable order kinetic (VOK) model derived from the Langmuir equation was applied to specify the kinetics of the fluoride removal reaction for electrocoagulation (EC). Synthetic solutions were employed to elucidate the effects of the initial fluoride concentration, the applied current and the initial acidity on the simulation results of the model. The proposed model successfully describes the fluoride removal reaction, except in a system in which the initial concentration of the acid is less than the initial fluoride concentration. The violent change of pH accompanying with the appearance of equivalence point in the titration curves should be the main reason the VOK model fails to simulate the defluoridation in the systems with an initial acidity higher than initial fluoride concentration.

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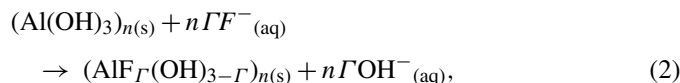
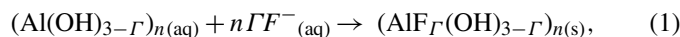
**Keywords:** Fluoride; Electrocoagulation; Aluminum; Langmuir equation

## 1. Introduction

Exceeding 1.5 mg/L of fluoride in drinking water may cause fluorosis that harms the bones and teeth [1]. Invertebrates and fish in fresh water are also very sensitive to fluoride toxicity [2]. Over 0.5 mg/L fluoride in fresh water can detrimentally influence the upstream migration of salmon [3]. Fluorine compounds are widely used in semiconductors, aluminum, fertilizers, glass-manufacturing and nuclear applications [4–7]. The effluent of those industries thus contains high levels of fluoride.

Several processes, including alum coagulation [8], adsorption with activated alumina [9], bone char or calcite [10], reverse osmosis (RO), electrodialysis [11], and selective ion exchange [12], can remove fluoride from water. Among these, coagulation with aluminum salt is one of the best. An electrochemical technique, electrocoagulation (EC), has been applied to yield aluminum ions with aluminum anodes as a coagulant for remov-

ing fluoride [13–15]. As the electric current passes through the anodes, the aluminum metal is oxidized to aluminum ions. Afterward, the aluminum ions are transformed to polymeric species or  $\text{Al}(\text{OH})_3$  flocs, which can co-precipitate or adsorb the fluoride ions, as presented by the following reactions [13–19]:



where  $\Gamma$  denotes the mole of removed fluoride ions per mole  $\text{Al}(\text{III})$  ions at a given equilibrium pH.

The kinetics of the EC defluoridation reaction needs to be examined for estimating the time required for defluoridation. Mameri et al. [14] and Emamjomeh et al. [20] reported that the defluoridation rate of the EC process is first-order with respect to fluoride concentration Eq. (3):

$$[\text{F}^-](t) = [\text{F}^-]_0 \exp(-K_1 t), \quad (3)$$

where  $K_1$  represents the first-order rate constant and  $t$  is the reaction time. If the inference is true, then  $K_1$  should be independent

\* Corresponding author at: Graduate Institute of Environmental Engineering, National Taiwan University, No.71 Chou-shan Road, Taipei 106, Taiwan. Tel.: +886 2 33664377; fax: +886 2 23928821.

E-mail address: [sll@ntu.edu.tw](mailto:sll@ntu.edu.tw) (S.-L. Lo).

### Nomenclature

$A$	active anode surface ( $\text{m}^2$ )
$[\text{Al}]_{\text{d}}$	dissolved Al(III) concentration
$[\text{Al}]_{\text{T}}$	total aluminum dosage liberated from the anodes ( $\text{mol L}^{-1}$ )
$[\text{Al}]_{\text{Theo}}$	theoretical concentration of Al liberated from anode ( $\text{mol L}^{-1}$ )
$B$	constant (A s)
$F$	Faraday constant, $F = 96,487$ ( $\text{C mol}^{-1}$ )
$[\text{F}^-]$	fluoride concentration ( $\text{mol L}^{-1}$ )
$[\text{F}^-]_{\text{e}}$	acceptable residual fluoride concentration ( $\text{mol L}^{-1}$ )
$[\text{F}^-]_0$	initial fluoride concentration ( $\text{mol L}^{-1}$ )
$i$	current density ( $\text{A m}^{-2}$ )
$I$	current (A)
$k$	Langmuir constant ( $\text{L mol}^{-1}$ )
$K_1$	first-order kinetic constant ( $\text{min}^{-1}$ )
$K_1'$	pseudo-first-order rate constant ( $\text{min}^{-1}$ )
$n$	cells number ( $n = 6$ in all systems)
$\text{pH}_i$	initial pH
$\text{pH}_f$	final pH
$t$	reaction time (s)
$t_{\text{N}}$	retention time required for $[\text{F}^-]_{\text{e}}$
$V$	volume (L)
$Z$	valence ( $Z = 3$ for aluminum)

### Greek letters

$\varepsilon_{\text{Al}}$	efficiency of hydro-fluoro-aluminum formation (%)
$\varepsilon_{\text{c}}$	current efficiency (%)
$\Gamma$	mole of removed fluoride ions per mole Al(III) ions at a given equilibrium pH
$\Gamma_{\text{max}}$	maximum $\Gamma$

upon the initial fluoride concentration. However, the experimental results of Mameri et al. [14] and Emamjomeh et al.'s [20] demonstrated that  $K_1$  declines as the initial fluoride concentration rise. The defluoridation of the EC process, therefore, should be a pseudo-first-order reaction.

The defluoridation rate is related to the aluminum liberation rate because Al(III) remove fluoride ions in the EC process, as shown in Eqs. (2) and (3). The fluoride adsorption by aluminum compounds follows the Langmuir adsorption isotherm model [8,19,21]. Therefore, a kinetic model inferred from the Langmuir equation was developed herein to describe EC defluoridation reaction. The effects of initial fluoride concentration, applied current and initial acidity on the kinetics of the EC process with aluminum electrodes were studied.

## 2. Model development

Defluoridation by aluminum flocs is ion exchange reaction proceeds as shown in reaction 2 or 3. The ion exchange equilibria

can be specified by the Langmuir equation [8,19,21], as shown in Eq. (4):

$$\Gamma = \frac{\Gamma_{\text{max}}k[\text{F}^-]}{1 + k[\text{F}^-]} \quad (4)$$

where  $\Gamma_{\text{max}}$  represents the maximum  $\Gamma$  and  $k$  is the Langmuir constant.

Sujana et al. [8] stated that the contact time for fluoride ions and the  $(\text{Al}(\text{OH})_3)_n$  flocs to reach equilibrium is approximately 2 h in conventional coagulation process. However, Mameri et al. [14] found that the liberation of Al(III) is the rate-determining step during EC defluoridation. They found that the liberation rate of Al(III) is less than the formation rate of hydro-fluoro-aluminum precipitate in EC defluoridation, when the current density is below  $200 \text{ A m}^{-2}$ . Therefore, the reaction is instantaneous if the current density is less than  $200 \text{ A m}^{-2}$ . Accordingly, if all of the Al(III) released form coprecipitate with fluoride, the fluoride removal rate is expressed as in Eq. (5):

$$-\frac{d[\text{F}^-]}{dt} = \varepsilon_{\text{Al}}\Gamma \frac{d[\text{Al}]_{\text{T}}}{dt} \quad (5)$$

where  $\varepsilon_{\text{Al}}$  is the efficiency of hydro-fluoro-aluminum formation,  $[\text{Al}]_{\text{T}}$  represents the total aluminum dosage liberated from the anodes. Combining Eqs. (4) and (5) yields Eq. (6).

$$-\frac{d[\text{F}^-]}{d[\text{Al}]_{\text{T}}} = \varepsilon_{\text{Al}} \frac{\Gamma_{\text{max}}k[\text{F}^-]}{1 + k[\text{F}^-]} \quad (6)$$

The rate of Al liberation from the anodes during EC can be determined from Faraday's law Eq. (7) [13,14,20,22,23]:

$$\frac{d[\text{Al}]_{\text{T}}}{dt} = \varepsilon_{\text{c}} \frac{nI}{Z F V}, \quad Z = 3 \text{ for Al}, \quad (7)$$

where  $\varepsilon_{\text{c}}$  represents the current efficiency;  $n$  is the number of cells;  $I$  is the applied current;  $Z$  is the valence of the metal of the electrode;  $F$  is Faraday's constant;  $V$  is the volume of the solution. Combining Eqs. (6) and (7) yields Eq. (8).

$$-\frac{d[\text{F}^-]}{dt} = \varepsilon_{\text{Al}}\varepsilon_{\text{c}} \frac{nI}{Z F V} \frac{\Gamma_{\text{max}}k[\text{F}^-]}{1 + k[\text{F}^-]} \quad (8)$$

According to Eq. (8), the defluoridation rate follows first-order kinetics if  $1/k \gg [\text{F}^-]$  and follows zero-order kinetics if  $[\text{F}^-] \gg 1/k$ . The order of reaction is variable. Therefore, the above model is called the variable order kinetic (VOK) model.

## 3. Materials and methods

### 3.1. EC apparatus

Experiments were performed in a bipolar batch reactor with seven aluminum electrodes, as displayed in the authors' previous work [17]. Only the outer electrodes were connected to the electric power source to form a bipolar system. The volume ( $V$ ) of the solution in each batch was 1 L. The active area of each electrode, excluding the outer electrodes, was  $72 \text{ cm}^2$  ( $8 \text{ cm} \times 9 \text{ cm}$ ),

and the dimensions of the outer electrodes (7cm × 7cm) were reduced to prevent the dispersion of the electric field. Accordingly, the area/volume ratio of each batch was 40.9 m<sup>-1</sup>, which exceeded the required value reported by Mameri et al. [14]. A constant current was maintained using a potentiostat in intensiostat mode. Magnetic stirring at 400 rpm helped to maintain a homogeneous solution in the batch reactor. The temperature of each system was controlled at 25 ± 1 °C.

### 3.2. Experimental protocol

The solution used in each reaction was prepared by diluting 0.2 M chloride or 1000 mg/L of F<sup>-</sup> stock solution. The chloride concentration in each reaction was 5 mM to prevent the rise in the voltage by the formation of a passive film [17]. Three different initial fluoride concentrations (25.0, 20.0, and 15.0 mg/L) were used to test the influence of the initial fluoride concentration. Six applied currents (4.00, 3.00, 2.00, 1.00, 0.50, and 0.25 A) were used to examine the effect of the applied current. Controlling the pH during defluoridation in electrocoagulation is very difficult because the defluoridation reaction releases OH<sup>-</sup> ions, which alter pH, and the applied current may interfere with the measurement of the pH by pH electrode. Because Al(III) itself is a buffer and it released after the EC process starts, the pH during EC should be closed to final pH (pH<sub>f</sub>) rather than initial pH (pH<sub>i</sub>). Controlling pH<sub>i</sub> in the electrocoagulation process is not very effective in varying pH<sub>f</sub> [14,15]. Hence, the initial acidity was varied to investigate the effect of so doing on the kinetics of fluoride removal. A 0.1 M HCl stock solution was used to adjust the set initial acidity (≈0, 0.5, 1.0, 1.5, and 2.0 mM).

### 3.3. Analytical techniques

Samples were extracted each minute and then immediately filtered through a 0.2 μm mixed cellulose ester membrane. The concentrations of fluoride were measured using an ion chromatography (Dionex, DX-100). After each reaction, [Al]<sub>T</sub> and the dissolved Al(III) concentration ([Al]<sub>d</sub>) were measured by an atomic absorption spectrophotometer (Perkin-Elmer, AAS 800) from a digested (standard method, Section3030E) and filtrated sample, respectively. The theoretical concentration of Al liberated from anode ([Al]<sub>Theo</sub>) is given by Faraday's law Eq. (9):

$$[\text{Al}]_{\text{Theo}} = \frac{nIT}{Z F V} \quad Z = 3 \text{ for Al}, \quad (9)$$

where  $T$  is the retention time. The current efficiency ( $\varepsilon_c$ ) is defined as follows:

$$\varepsilon_c = \frac{[\text{Al}]_T}{[\text{Al}]_{\text{Theo}}}, \quad (10)$$

and the efficiency of hydro-fluoride-aluminum formation ( $\varepsilon_{\text{Al}}$ ) is defined as follows:

$$\varepsilon_{\text{Al}} = 1 - \frac{[\text{Al}]_d}{[\text{Al}]_T}, \quad (11)$$

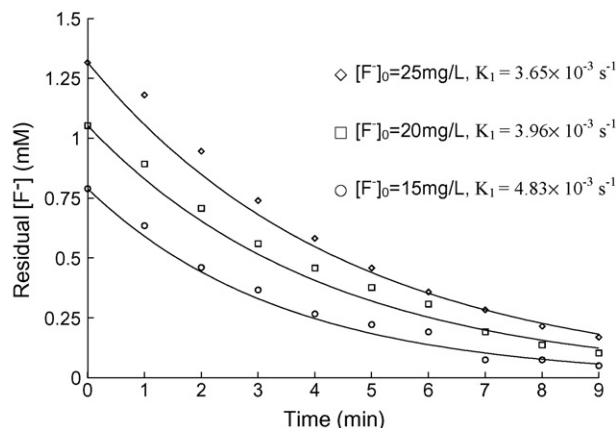


Fig. 1. Simulation results by FOK model in various initial fluoride concentration systems ( $I=0.4$  A,  $T=25$  °C,  $\text{pH}_i=5.2$ ).

All measurements herein in this work were undertaken in duplicate to ensure the reproducibility of the data.

## 4. Results and discussion

### 4.1. Effect of the initial fluoride concentration

Fig. 1 shows the results of the simulations using the first order kinetic (FOK) model with various initial fluoride concentrations. The values of  $K_1$  for systems with initial fluoride concentrations of 25, 20 and 15 mg/L, were  $0.65 \times 10^{-3}$ ,  $3.96 \times 10^{-3}$  and  $4.83 \times 10^{-3} \text{ s}^{-1}$ , respectively.  $K_1$  rose as the initial fluoride concentration decreased, so defluoridation by EC is a pseudo-first-order reaction. This phenomenon is in agreement with the results obtained by Mameri et al. [14] and Emamjomeh et al. [20].

Fig. 2 presents the results of the simulation using the VOK model for various initial fluoride concentrations. The data were correlated well ( $R^2 > 0.99$ ) by VOK model, revealing the model can successfully simulate the defluoridation in EC with various initial fluoride concentrations. The parameters ( $\Gamma_{\text{max}}$  and  $k$ ) for VOK model were not varied with initial fluoride. This fact makes the VOK model more convenient for simulating EC defluoridation kinetic.

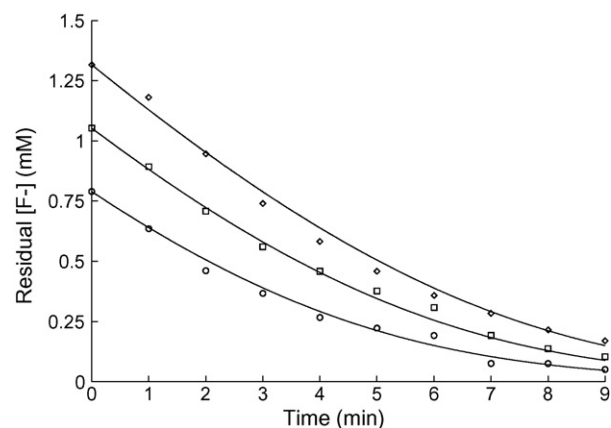


Fig. 2. Simulation results by VOK model in various initial fluoride concentration systems ( $I=0.4$  A,  $\Gamma_{\text{max}}=0.549$ ,  $k=1520 \text{ M}^{-1}$ ,  $T=25$  °C,  $\text{pH}_i=5.2$ ).

According to Eq. (8), the pseudo-first-order rate constant ( $K_1'$ ) can be expressed as Eq. (12):

$$K_1' = \varepsilon_{Al}\varepsilon_c \frac{nI}{Z F V} \frac{\Gamma_{max} k}{1 + k[F^-]}, \quad (12)$$

The fluoride concentration ( $[F^-]$ ) increases with the rise of initial fluoride concentration. Therefore,  $K_1'$  declines as the initial fluoride concentration rise.

#### 4.2. Effect of the current applied

Fig. 3 plots the simulation results obtained using the VOK model for various applied currents applied systems. The same parameters of the VOK model ( $\Gamma_{max}$  and  $k$ ) were used in various systems and the determination coefficients ( $R^2$ ) for all systems exceeded 0.99. The results revealed that the VOK model can accurately simulate the defluoridation of EC in systems with various applied currents as long as the current efficiency can accurately be predicated. The current efficiency, however, usually exceeds 100% due to the dissolution of Al metal from anodes [14,17,24] and cathodes [25] and is various with current density [14], distant between electrodes, types and concentrations of ions in solution [17], pH and temperature, etc. It can only be obtained by experiment.

The retention time required ( $t_N$ ) for an acceptable residual fluoride concentration ( $[F^-]_e$ ) can be determined from the integral form of Eq. (8), as follows:

$$t_N = \frac{Z F V}{\varepsilon_{Al}\varepsilon_c n I \Gamma_{max}} \left[ ([F^-]_0 - [F^-]_e) + \frac{1}{k} \ln \frac{[F^-]_0}{[F^-]_e} \right], \quad (13)$$

Fig. 4 plots the variation of  $t_N$  with current at various residual fluoride concentrations. The results were very similar to those obtained by Mameri et al. [14], which used Eq. (14) to estimate  $t_N$ :

$$t_N = \frac{B}{i}, \quad (14)$$

where  $i$  represents the current density ( $i = I/A$ ). Mameri et al. [14] claimed that  $B$  is a constant. Comparing Eqs. (13) and (14)

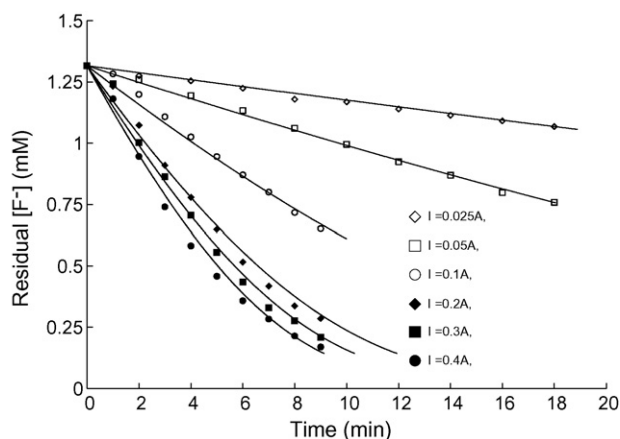


Fig. 3. Simulation results using VOK model in various current applied systems ( $[F^-]_0 = 25.0$  mg/L,  $\Gamma_{max} = 0.474$ ,  $k = 1520$  M $^{-1}$ ,  $T = 25^\circ$  C,  $pH_i = 5.2$ ).

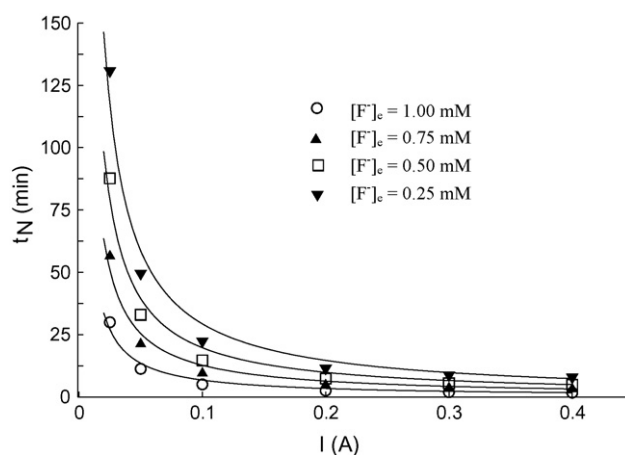


Fig. 4. The variation of  $t_N$  with various currents for various residual fluoride concentration. The curves are simulation results by Eq. (13) and the dots are the experimental data ( $[F^-]_0 = 25$  mg/L,  $T = 25^\circ$  C).

yielded the constant  $B$ :

$$B = \frac{Z F V}{\varepsilon_{Al}\varepsilon_c n A \Gamma_{max}} \left[ ([F^-]_0 - [F^-]_e) + \frac{1}{k} \ln \frac{[F^-]_0}{[F^-]_e} \right]. \quad (15)$$

Therefore,  $B$  is a function of the initial fluoride concentration ( $[F^-]_0$ ), the ideal residual fluoride concentration ( $[F^-]_e$ ), the number of cells ( $n$ ), the area of the electrodes ( $A$ ), the volume of the solution ( $V$ ) and the current efficiency ( $\varepsilon_c$ ).

#### 4.3. Effect of initial acidity

Fig. 5 plots the results of the simulation obtained using the VOK model for various initial acidities. Table 1 lists the parameters ( $\Gamma_{max}$ ,  $k$ ,  $\varepsilon_c$ ,  $\varepsilon_{Al}$ ) of the VOK model, initial and final pH and  $R^2$ . The results revealed that the VOK models could not successfully simulate the data for systems with an initial acidity of 0.5 or 1.0 mM.

During EC defluoridation, stoichiometrically equivalent amounts of aluminum and hydroxyl ions were added by electrolysis. If all of the hydroxyl ions react with aluminum ions to generate  $(Al(OH)_3)_n$  flocs, the pH of the solution should change very little. However, as presented in Eq. (2), defluoridation lead to the liberation of hydroxide ions, and the number of hydrox-

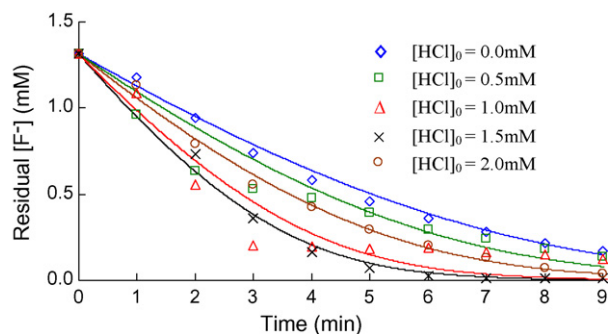


Fig. 5. Simulation results by VOK model in various initial acidity systems. The blue, green, red, black and brown curves are the simulation curves in the system with 0.0, 0.5, 1.0, 1.5 and 2.0 mM initial acidity, respectively ( $I = 0.4$  A,  $[F^-]_0 = 25.0$  mg/L,  $T = 25^\circ$  C, other operating conditions are shown in Table 1).



Table 1  
Variation of  $\Gamma_{\max}$ ,  $k$ ,  $R^2$ ,  $\text{pH}_i$ ,  $\text{pH}_f$ ,  $\varepsilon_c$  and  $\varepsilon_{\text{Al}}$  in the EC defluoridation system with various initial acidities

Initial acidity (mM)	$\approx 0.0$	0.5	1.0	1.5	2.0
$\Gamma_{\max}$	0.549	0.551	0.688	0.808	0.719
$k$ ( $\text{M}^{-1}$ )	1520	1520	1520	1520	1520
$R^2$ for VOK model	0.992	0.917	0.926	0.995	0.995
$\text{pH}_i$	5.2	3.3	3.0	2.6	2.4
$\text{pH}_f$	9.0	8.4	8.0	6.9	5.0
$\varepsilon_c$	1.25	1.42	1.53	1.46	1.47
$\varepsilon_{\text{Al}}$	0.863	0.970	0.992	0.993	0.763

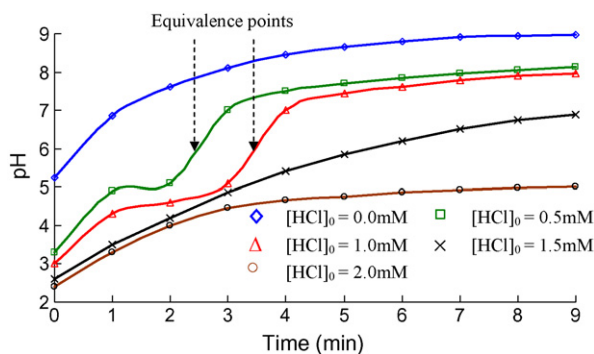


Fig. 6. Variation of pH with time in various initial acidity systems ( $I=0.4\text{A}$ ,  $[F^-]_0=25.0\text{ mg/L}$ ,  $T=25^\circ\text{C}$ ).

ide ions liberated equals the number of fluoride ions removed. Therefore, the defluoridation reaction in the EC process is an antacid reaction.

Fig. 6 presents the variation of pH during EC with various initial acidities. There was a clear equivalence point in the titration curves of the systems with an initial acidity of 0.5 and 1.0 mM, for which the simulation using the VOK model was rather unsuccessful. The basic assumption of the VOK model is that the parameters ( $\Gamma_{\max}$ ,  $k$ ,  $\varepsilon_{\text{Al}}$  and  $\varepsilon_c$ ) are constants during EC. If the equivalence point appears in the titration curve during EC defluoridation, then the pH of solution changes very violently and  $\Gamma_{\max}$  can not be regarded as a constant. Therefore, the VOK model cannot be used for systems in which the initial acidity is 0.5 or 1.0 mM.

The equivalence point appeared only if the concentration of liberated  $\text{OH}^-$  ions exceeds the initial concentration of acid in the solution. As stated above, the number of liberated hydroxyl ions equals the number of fluoride ions removed. Therefore, the VOK model can only be used for systems with very little acidity or with an acidity exceeding the initial fluoride concentration. Moreover, the pH change may also too violent if the fluoride is too high because the defluoridation leads to the liberation of hydroxyl ions. Therefore, VOK model may not be used for systems with high initial fluoride concentration.

## 5. Conclusion

A variable order kinetic (VOK) model derived from the Langmuir equation is developed to simulate the kinetic of the

defluoridation of EC using bipolar aluminum electrodes. The results reveal good agreement between the predictive equation and the experimental data. The critical parameters,  $\Gamma_{\max}$  and  $k$  for VOK model are constants when the initial fluoride concentration and current vary. Another critical parameter, current efficiency, is independent upon initial fluoride concentration but varies with current density and needed to be obtained by experiment.

The model cannot successfully simulate the defluoridation in EC process if pH changes too violently and the indicator of whether the pH changes too violently is whether the equivalence point appears in the tradition curve. If the equivalence point appears, it means pH changes too violently and the model can not be used to simulate the defluoridation in EC process. Furthermore, we can anticipate whether the equivalence point appears by the difference between initial acidity and initial fluoride concentration. The equivalence point appears only if the initial acidity is less than the initial fluoride concentration.

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## References

- [1] World Health Organization: Fluoride in Drinking Water, WHO Guidelines for Drinking Water Quality, 2004, Accessed on 3 April 2005. [http://www.who.int/entity/water\\_sanitation\\_health/dwq/chemicals/fluoride.pdf](http://www.who.int/entity/water_sanitation_health/dwq/chemicals/fluoride.pdf).
- [2] J.A. Camargo, Fluoride toxicity to aquatic organisms: a review, *Chemosphere* 50 (2003) 251–264.
- [3] D.M. Damkaer, D.B. Dey, Evidence for fluoride effects on salmon passage at John Day dam, Columbia river, *N. Am. J. Fish. Manag.* 9 (1989) 154–162.
- [4] J. Buffle, N. Parthasarathy, W. Haerdi, Importance of speciation methods in analytical control of water treatment processes with application to fluoride removal from waste water, *Water Res.* 19 (1985) 7–23.
- [5] N. Parthasarathy, J. Buffle, W. Haerdi, Combined use of calcium salts and polymeric aluminum hydroxide for defluoridation of wastewaters, *Water Res.* 20 (1986) 443–448.
- [6] C.J. Huang, J.C. Liu, Precipitation flotation of fluoride-containing wastewater from semi-conductor manufacture, *Water Res.* 33 (1999) 3403–3412.
- [7] T.C. Chuang, C.J. Huang, J.C. Liu, Treatment of semiconductor wastewater by dissolved air flotation, *J. Environ. Eng.* 128 (2002) 974–980.
- [8] M.G. Sujana, R.S. Thakur, S.B. Rao, Removal of fluoride from aqueous solution by using alum sludge, *J. Colloid Interf. Sci.* 206 (1998) 94–101.
- [9] O.J. Hao, C.P. Huang, Adsorption characteristics of fluoride onto hydrous alumina, *J. Environ. Eng.* 112 (1986) 1054–1069.
- [10] M. Hichour, F. Persin, J. Sandeaux, Fluoride removal from waters by Donnan dialysis, *Sep. Purif. Technol.* 18 (2000) 1–11.
- [11] Y. Min, H. Takayuki, H. Nobuyuki, M. Haruki, Fluoride removal in a fixed bed packed with granular calcite, *Water Res.* 33 (1999) 3395–3422.
- [12] K.M. Papat, P.S. Anand, B.D. Dasare, Selective removal of fluoride ion from water by the aluminium from of the aminomethylphosphonic acid type ion exchanger, *React. Polym.* 23 (1994) 23–32.
- [13] L. Ming, S.R. Yi, Z.J. Hua, B.Y.W. Lei, L. Ping, K.C. Fuwa, Elimination of excess fluoride in potable water with coacervation by electrolysis using aluminium anode, *Fluoride* 20 (1983) 54–63.
- [14] 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 electrodes, *Water Res.* 32 (1998) 1604–1612.

- [15] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, *Chem. Eng. Sci.* 58 (2003) 987–993.
- [16] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, *J. Hazard. Mater.* 100 (2003) 163–178.
- [17] C.Y. Hu, S.L. Lo, W.H. Kuan, Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminium 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] J.L.R. Bahena, A.R. Cabrera, A.I. Valdivieso, R.H. Urbina, Fluoride adsorption onto  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and its effect on the zeta potential at the alumina–aqueous electrolyte interface, *Separat. Sci. Tech.* 37 (2002) 1973–1987.
- [20] M.M. Emamjomeh, M. Sivakumar, A.I. Schafer, An empirical model for defluoridation by batch monopolar electrocoagulation/flotation (ECF) process, *J. Hazard. Mater.* 131 (2006) 118–125.
- [21] Y. Ku, H.M. Chiou, The adsorption of adsorption fluoride ion from aqueous solution by active alumina, *Water Air Soil Pollut.* 133 (2002) 349–360.
- [22] E.A. Vik, D.A. Carlson, A.S. Eikum, E.T. Gjessing, Electro-coagulation of potable water, *Water Res.* 18 (1984) 1355–1360.
- [23] O. Groterud, L. Smoczynski, Phosphorus removal from water by means of electrolysis, *Water Res.* 20 (1986) 667–669.
- [24] J.Q. Jiang, N. Graham, C. Andre, G.H. Kelsall, N. Brandon, Laboratory study of electro-coagulation flotation for water treatment, *Water Res.* 36 (2002) 4064–4078.
- [25] T. Picard, G. Cathalifaund-Feuillade, M. Mazet, C. Vandesteendam, Cathodic dissolution in the electrocoagulation process using aluminum electrodes, *J. Environ. Monit.* 2 (2000) 77–80.