DEFLUORIDATION OF DRINKING WATER BY ELECTROCOAGULATION/ELECTROFLOTATION: KINETIC STUDY

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Abstract: A variable order kinetic (VOK) model derived from the langmuir-freundlish equation was applied to determine the kinetics of fluoride removal reaction by 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 in Airlift reactor in comparison with the experimental results. In this study two EC cells with the same capacity (V = 20 L) were used to carry out fluoride removal with aluminum electrodes, the first is a stirred tank reactor (STR) the second is an airlift reactor (ALR). The comparison of energy consumption demonstrates that the (ALR) is advantageous for carrying out the defluoridation removal process.

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INTRODUCTION

An excess amount of fluoride anions in drinking water has been known to cause adverse effects on human health. To prevent these harmful consequences, especially problems resulting from fluorosis, the World Health Organization (WHO) fixed the maximum acceptable concentration of fluoride anions in drinking water to 1.5 mg L^{-1}. Differents techniques have been used to carry out water defluoridation: Membrane separation techniques were also investigated for the effective separation of fluoride using electrodyalysis (Amor *et al.*, 1998; Amor *et al.*, 2001), nanofiltration (Hu *et al.* 2006; Cohen & Conrad, 1998), ion exchange membrane (Singh *et al.*, 1999, Castel *et al.*, 2000, Chubar *et al.*, 2007; Tor, 2007), chemical treatment (Huang *et al.*, 1999; Hu *et al.*, 2005; Menakshi *et al.*, 2006) and adsorption into materials (Srimulari *et al.*, 1999; Fan *et al.*, 2003; Wu *et al.*, 2007).

As an example, Garmes .*et al.* (2002) performed defluoridation of ground water by a hybrid process containing adsorption and donna dialysis. Integrated biological and physicochemical treatment process for nitrate and fluoride removal was investigated by Mekonen *et al.* (2001).

A common problem of the processes mentioned above is their poor selectivity. Moreover, these processes not only remove the beneficial content present in water during defluoridation, but also increase the operational cost. Therefore, membrane processes are only suitable for treatment of brackish industrial water containing high content of fluoride which needs simultaneous defluoridation and desalination.

Although, EC may be cost effective at chemical dosing (Bayramoglu *et al.*, 2007; Hansen *et al.*, 2007; Holt *et al.*, 2005; Danshvar *et al.*, 2004; Kobaya *et al.*, 2003; Sheng *et al.*, 2003; Lounici *et al.*, 1997), its main deficiency is the lack of sufficient reactor design and modelling procedures. Mollah *et al.* (2001) and Mollah *et al.* (2004) described six typical configurations for industrial EC cells, and report their respective advantages and drawbacks. Bennajah *et al.* (2009) demonstrated that airlift reactors are suitable units to carry out EC with complained flotation, using only electrochemically generated bubbles, to achieve an overall liquid circulation and good mixing conditions.

Emamjomeh & Sivakumar (2006) and Mameri *et al.* (1998) reported that the defluoridation rate of the EC follows first order kinetics with respect to fluoride concentration:
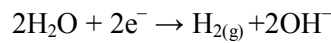
$$[F] = [F]_0 e^{(-k_1 t)} \qquad (1)$$

were k_1 represents the first order rate constant and t the reaction time. According to the following chemistry:
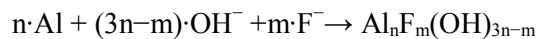
Anode:

$$Al_{(s)} \rightarrow Al^{3+} + 3e^-$$

Cathode:

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-$$

Adsorption on Al(OH)$_3$ particles:

$$Al_n(OH)_{3n} + m \cdot F^- \rightarrow Al_nF_m(OH)_{3n-m} + m \cdot OH^-$$

Coprecipitation:

$$n \cdot Al + (3n-m) \cdot OH^- + m \cdot F^- \rightarrow Al_nF_m(OH)_{3n-m}$$

If the inference is true, k_1 should be independent of the initial fluoride concentration and other system parameters (i.e. hydrodynamic). However, many experimental results demonstrate that k_1 decline as the initial fluoride concentration increases (Emamjomeh, 2006). The defluoridation of the EC process, therefore, should be a pseudo first order reaction. According to Hu *et al.* (2008), the defluoridation reaction can also follow Langmuir law if good mixing, which can minimize external transfer of adsorbent, is assumed. Consequently, the defluoridation model kinetics depends of EC cells hydrodynamic configuration.

In the present work, the EC mechanisms effect of defluoridation is studied in order to develop a kinetic model to simulate defluoridation in a specific EC cell based on Langmuir-Freundlich adsorption model, which takes into account mixing degree and coagulation beyond monolayer deposition which takes place in large reactors.

The objective of the present investigation is also to evaluate the removal of fluoride from drinking water, and assess the influence of operating parameters on removal efficiency dosage, in order to define the kinetic defluoridation model that can be applied in airlift reactor (used in previous work as EC cell) to predict operating time for realizing an effective flouride removal.

MATERIAL AND METHODS

The defluoridation of drinking water was studied in two types of electrocoagulation reactors working under batch flow conditions: an electrochemical, mechanically-stirred reactor (STR) and an external-loop airlift reactor (ALR). Both had the same clear liquid volume V = 20 L. The ALR is an innovative reactor for Electro-Coagulation/Electro-Flotation process (EC/EF): its geometrical configuration and its operating
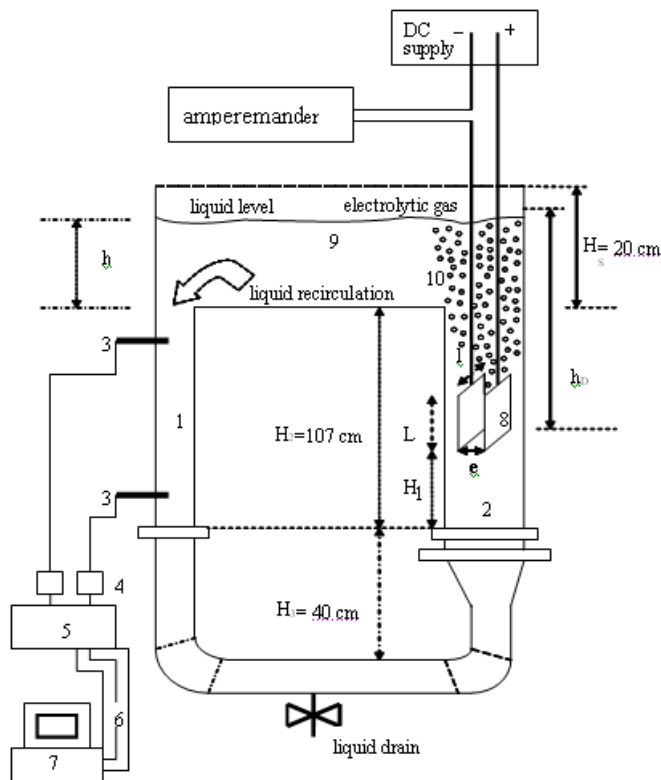
Fig. 1 External-loop airlift reactor (1: downcomer section; 2: riser section; 3: conductivity probes; 4: conductimeter; 5: analog output/input terminal panel (UEI-AC-1585-1); 6: 50-way ribbon cable kit; 7: data acquisition system; 8: electrodes; 9: separator; 10: electrochemically-generated bubbles).

Table 1. Water properties

Properties	Values
pH	7.85
Alkalinity ($\circ$f)	15
Total hardness ($\circ$f)	35
Turbidity (NTU)	0.15
Conductivity (μS)	1600 (20°C)
Chloride $[Cl^-]$ (mg L^{-1})	400

between the bottom of the reactor and the liquid level and placed 6.5 cm from the shaft of the impeller to maintain an equal distance between the wall and the center of the impeller blades. The effective area of the electrodes was 175 cm^2.

The same electrodes were used in the ALR, but the distance between electrodes was $e = 20$ mm. Further details on the role of the axial position of the electrodes are available in a previous work on the decolourization of textile dye wastewater in a similar setup (Essadki *et al.*, 2008). Previous results showed that flocs erosion could be prevented when the liquid velocity in the downcomer U_{Ld} was less than 8–9 cm s^{-1} in the presence of dispersive dyes. This corresponds to the maximum possible velocity that could be correlated to current density and dispersion height h_D.

In both reactors, all experiments were conducted at room temperature (20 $\pm$ 0,1°C) and atmospheric pressure. The desired potential (U) between electrodes was monitored by a digital DC power supply (Didalab, France) and the current intensity was measured by an amperemeter. Current density values (j) between 2.8 and 17 mA cm^{-2} were investigated, which corresponded to current ($I = j \cdot S$) in the range of 0.5–3 A. Conductivity and pH were measured using a CD810 conductimeter (Radiometer Analytical, France) and a ProfilLine pH197i pHmeter (WTW, Germany). Samples were filtered and the concentration measurements of the remaining fluoride were determined in the solution by means of a combined selective fluoride electrode ISEC301F and a PhM240 ion-meter (Radiometer Analytical, France), using the addition of a TISAB II buffer solution to prevent interference from other ions. The pH could be adjusted by minute addition of either HCl or NaOH aqueous solutions. The evolution of turbidity over time was measured on non-filtered samples in order to follow floc separation by flotation using a 550 IR turbidimeter (WTW, Germany). The quality of water used to carry out the experiments was drinking water of Casablanca (Morocco), the characteristics of this water are given in **Table 1**.

The initial fluoride concentration $[F^-]_0$ of this water was between 10–20 mg L^{-1} and was obtained by adding sodium fluoride NaF (Carlo Erba Réactifs, France). The efficiency of fluoride removal could be calculated as follows:

conditions are presented in **Fig. 1**. The desired liquid volume corresponded to a clear liquid level (h) of 14 cm in the separator section as shown in **Fig. 1**.

The overall liquid circulation velocity in the riser U_{Lr} can be predicted from an energy balance using the following Equation (Chisti, 1989).

Contrary to conventional operations in airlift reactors, no gas phase was injected at the bottom of the riser; only electrolytic gases (H$_2$ microbubbles) induced the overall liquid recirculation resulting from the density difference between the fluids in the riser and the downcomer as shown by **Eq. 2**.

$$U_{Lr} = \left[\frac{2gh_D\left(\varepsilon_r - \varepsilon_d\right)}{K_T / \left(1-\varepsilon_r\right)^2 + \left(A_r / A_d\right)^2 K_B / \left(1-\varepsilon_d\right)^2} \right]^{0.5} \quad (2)$$

The STR consisted of a dished-bottom cylindrical tank of internal diameter D=23 cm and ratio H/D=2.4 equipped with a two-blade marine propeller of 6 cm diameter placed 6 cm from the bottom in order to avoid settling and to favour EC/EF. The anode and cathode were both flat aluminium electrodes of rectangular shape (250 $\times$ 70 $\times$ 1 mm), they were vertically centred

$$Y(\%) = 100 \times \frac{\left[F^-\right]_0 - \left[F^-\right]}{\left[F^-\right]_0} \qquad (3)$$

The remaining concentration of fluoride $[F^-]$ was measured over time by means of the combined selective electrode.

The specific electrical energy consumption per kg F^- removed (E) was calculated as follow:

$$E\left(kWh/kg\ F^-\right) = \frac{UI \cdot t}{VY \cdot \left[F^-\right]_0} \qquad (4)$$

RESULTS AND DISCUSSION

Adsorption equilibrium isotherms (STR)

The experimental adsorption equilibrium isotherms are useful for describing the adsorption capacity of a specific adsorbent. Moreover, the isotherm plays a vital role for the analysis and the design of adsorption systems as well as for model prediction. Several models have been used in the literature to describe the experimental data of adsorption isotherms. Two general purpose models and a modified combined model were used in an attempt to fit the experimental data: (a) the Langmuir model (**Eq. 5**), (b) the Freundlich model (**Eq. 5**), and (c) the Langmuir-Freundlich model **Eq. (6)**:

$$q_e = \frac{q_{max}k_L C_e}{1 + k_L C_e} \qquad (5)$$

$$q_e = k_F C_e^{\frac{1}{p}} \qquad (6)$$

$$q_e = \frac{q_{max}k_{LF} C_e^n}{1 + k_{LF} C_e^n} \qquad (7)$$

In these above equations q_e is defined as the mole of removed fluoride anions per mole of Al(III) cations (Al(OH)$_3$) at equilibrium, q_{max} is the maximum fluoride adsorption, k_L is the Langmuir constant related to the strength of adsorption, k_F and p are the Freundlich constants and C_e is the equilibrium fluoride concentration.

The experiments data of defluoridation by electrocoagulation in mechanically-stirred reactor (STR) were used in order to obtain adsorption equilibrium isotherm at N = 200 rpm. The experiments were conducted by changing initial fluoride concentration from 0.33 to 1.05 mM, keeping all other experimental

conditions unchanged (N = 200 rpm, initial pH = 7.0, conductivity κ = 7.5 mS cm^{-1}, current density j = 17.1 mA cm^{-2}. The flocs recovered correspond exactly to the first point of equilibrium, these flocs were dried and weighed leading to the amount of Al(OH)$_3$. The fluoride concentration retained in the flocs was calculated by the following equation:

$$q = \frac{\left(\left[F^-\right]_0 - \left[F^-\right]_{eq}\right)V}{m_{Al(OH)_3}} M_{Al(OH)_3} \qquad (8)$$

where [F-]$_0$ and [F-]$_e$ are initial and equilibrium fluoride concentrations respectively, m and M are mass quantity and molecular weight of Al(OH)$_3$ respectively, and V is the volume of solution.

The results for the test of the three models of fluoride adsorption described in **Eqs 4**, **5** and **6** are discussed below.

Langmuir-Freundlich model

For the model of Langmuir-Freundlich (LF), q_e was directly plotted against C_e as shown in **Eq. (6)**, and the three parameters (q_{max}, k_{LF} and n) were determined by nonlinear regression.

The comparison between the models was made on the basis of regression coefficients and Chi-square test for non-linear χ^2 is given by the following **Eq. (9)**:

$$\chi^2 = \sum \frac{\left(q_{exp} - q_{mod}\right)^2}{q_{mod}} \qquad (9)$$

Small number of χ^2 indicates that data from the model is close to the experimental and this test can confirm the best fit.

Table 2 summarizes all the coefficient of the three models, from which we can conclude that L-F model is the one that fits well the experimental results (x^2 = 0.0003, R_F^2 = 0.998). This result is in fact, expected because the equilibrium concentrations are relatively weak (**Fig. 2**). Thus, as predicted by L-F model **Eq. (7)** and n is closer to unity.

Table 2. Comparaison between the three adsorption models Langmuir, Freundlich and Langmuir-Freundlich

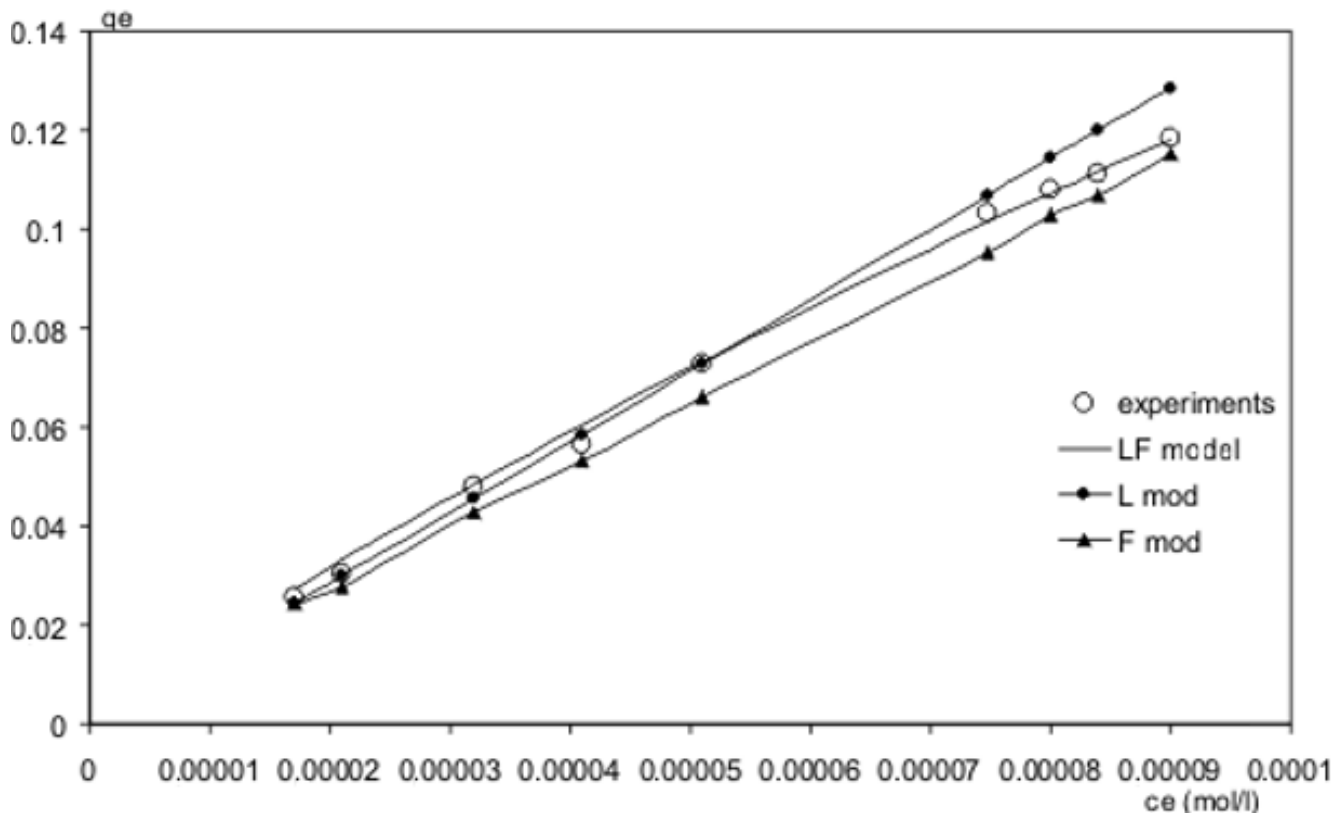| Parameter	Langmuir	Freundlich	Langmuir-Freundlich
q_{max}	0.885 ± 0.06	–	0.75 ± 13
k_L (L mol^{-1})	1614 ± 15	–	–
k_F (L mol^{-1})		697 ± 6.5	
k_{LF} (L mol^{-1})$^{-n}$	–	–	1600 ± 9.8
P	–	1.07 ± 0.05	–
N	–	–	1.15 ± 0.03
R^2	0.799	0.969	0.998

Fig. 2 Non linear representation of the three adsorption models.

Hu *et al.* (2008) limited their VOK model to the particular situation in which q_e could be fitted using Langmuir isotherm. This approach was tested, but again, it did not fit the experimental data of Essadki *et al.* (2009). It must be reminded that Hu *et al.* (2008), as Emamjomeh & Sivakumar (2006), used small laboratory electrolytic cells with magnetic stirring, whereas a 20 L mechanically stirred reactor was used in this work. This may explain why their and our results do not agree.

Similar trends were, however, observed when the Freundlich isotherm was introduced in **Eq. (10)**, even though it was retained in Section 1.1: neither Langmuir, nor Freundlich isotherms were able to represent adequately the experimental results. Another difference with the literature was that the S/V ratio was lower both in the Airlift and the STR (0.875 m^2 m^{-3}) than in the conventional EC cells in which the S/V ratio ranged between 10 and 40 m^2 m^{-3} (Mameri *et al.,* 2001; Hu *et al.*, 2005). At high S/V ratios, Zhu *et al.* (2007) demonstrated that fluoride adsorption/attachment on the electrode was primarily responsible for defluoridation efficiency, while other mechanisms played only a secondary role.

Conversely, fluoride removal by attachment on the electrodes was negligible when S/V = 0.875 m^2 m^{-3} and the prevailing mechanisms were in the bulk, i.e. the simultaneous formation of soluble fluoroaluminium compounds, their coprecipitation with Al(OH)$_3$ and the simultaneous adsorption of fluoride anions on the insoluble species.

This may also explain why the conventional isotherms are not able to fit experimental data, as the quantity of adsorbent was close to zero at the beginning of EC in the STR, while it was not negligible due to electrode attachment at high S/V ratio. As a result, only the VOK model based on the Langmuir–Freundlich isotherm will be developed in this section.

Variable Order Kinetic approach (ALR)

The kinetics of the defluoridation by electrcoagulation in (ALR) needs to be examined for estimating the time required for defluoridation. This kinetics was established by some authors in stirred reactor, they agreed roughly on the following expression (Mameri *et al.*, 1998):

$$[F] = [F]_0 e^{(-k_1 t)} \tag{10}$$

where, k_1 represents the first-order rate constant. However, the kinetic constant k_1 was reported to depend on the initial fluoride concentration, current and electrode distances for a constant temperature and pH. On the other hand, Hu *et al.* (2008) proposed a variable order kinetic (VOK) based on Langmuir isotherm in order to estimate the time required to defluoridation by EC in a 1L stirred cell.

Our experimental results were firstly confronted to the VOK with Langmuir model, and to the VOK with Freundlich model, but neither fitted well the experimental results. In this work, we consider that

fluoride adsorption by aluminium compounds follows the Langmuir-Freundlich adsorption isotherm instead of the Langmuir isotherm model or Freundlich model. Generally the defluoridation rate is related to the aluminium liberation, as follows:

$$-\frac{d\left[F^-\right]}{dt} = \varphi_{Al} q_e \frac{d\left[Al\right]_{tot}}{dt} \qquad (11)$$

where ϕ_{Al} and $[Al]_{tot}$ are the efficiency of hydro-fluoro-aluminium formation and the total aluminium dosage liberated from the anode, respectively. The rate of Al liberation from anode can be determined from Faraday's law:

$$\frac{d[Al]_{Tot}}{dt} = \phi_c \cdot \frac{I}{Z.F.V} \qquad (12)$$

where, ϕ_c is the current efficiency, I is the applied current, Z is the valence of the Al ($Z = 3$), F is Faraday's constant and V is the volume of the reactor. Combining **Eqs (12)** and **(13)** gives:

$$\frac{d\left[F^-\right]}{dt} = \phi_{Al}\phi_c \frac{q_{max} k\left[F^-\right]^n}{1 + k\left[F^-\right]^n} \cdot \frac{I}{ZFV} \qquad (13)$$

According to **Eq. (14)**, the pseudo-first-order rate constant is then deduced and can be expressed as follows:

$$k = \phi_{Al}\phi_c \frac{q_{max} k\left[F^-\right]^{n-1}}{1 + k\left[F^-\right]^n} \cdot \frac{I}{ZFV} \qquad (14)$$

The retention time required (t_N) for a targeted residual fluoride concentration $[F^-]_e$ can be determined by integrating **Eq. (15)**:

$$t_N = \frac{ZFV}{\phi_c\phi_{Al} I q_{max}}\left[\left(\left[F^-\right]_0 - \left[F^-\right]_e\right) + \frac{1}{k(1-n)}\left(\left[F^-\right]_0^{1-n} - \left[F^-\right]_e^{1-n}\right)\right] \qquad (15)$$

Effect of current density:

The effects of current density and initial fluoride concentration on the kinetics of the EC process in ALR are studied below. The initial pH and initial fluoride concentration were fixed respectively at 7.4 and 15 mg L^{-1}, i.e. 0.8 mol l^{-1}.

Figure 3 shows the effect of the current density on the evolution of the fluoride concentration for the Airlift reactor.

For $I = 0.5$ A corresponding to a current density of 2.86 mA cm^{-2}, the concentration reaches only 4 mg L^{-1} for an electrolysis time of 30 minutes, whereas, for I exceeding 2 A (i.e. for a current density higher than 8.6 mA cm^{-2}), the concentration reaches a value of 1.5 mg L^{-1} after 15 minutes and decrease more especially as the density of current increases.
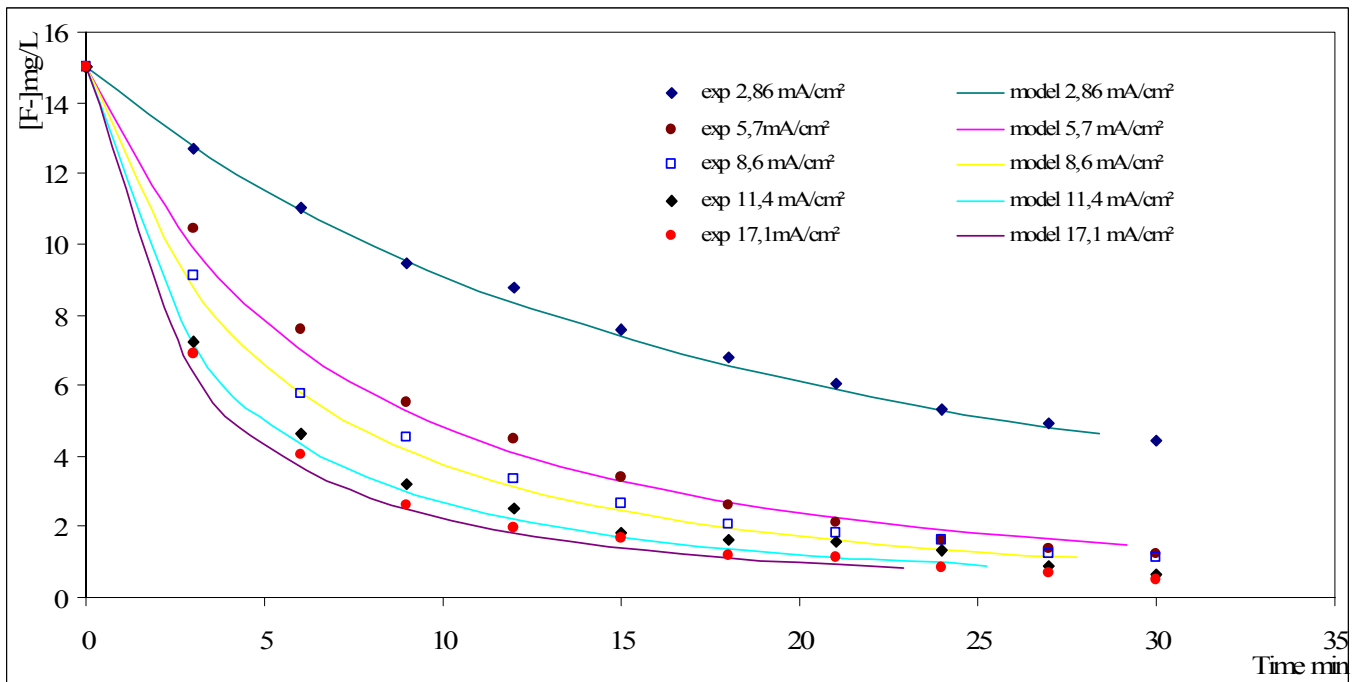

Fig 3 Evolution of fluoride ions during EC: influence of current intensity (initial pH = 7.4, κ = 7,5 mS cm^{-1}) on the ALR : VOK Model and experiments ($n = 1.15$, $K = 1600$, $q_{max} = 0.75$).

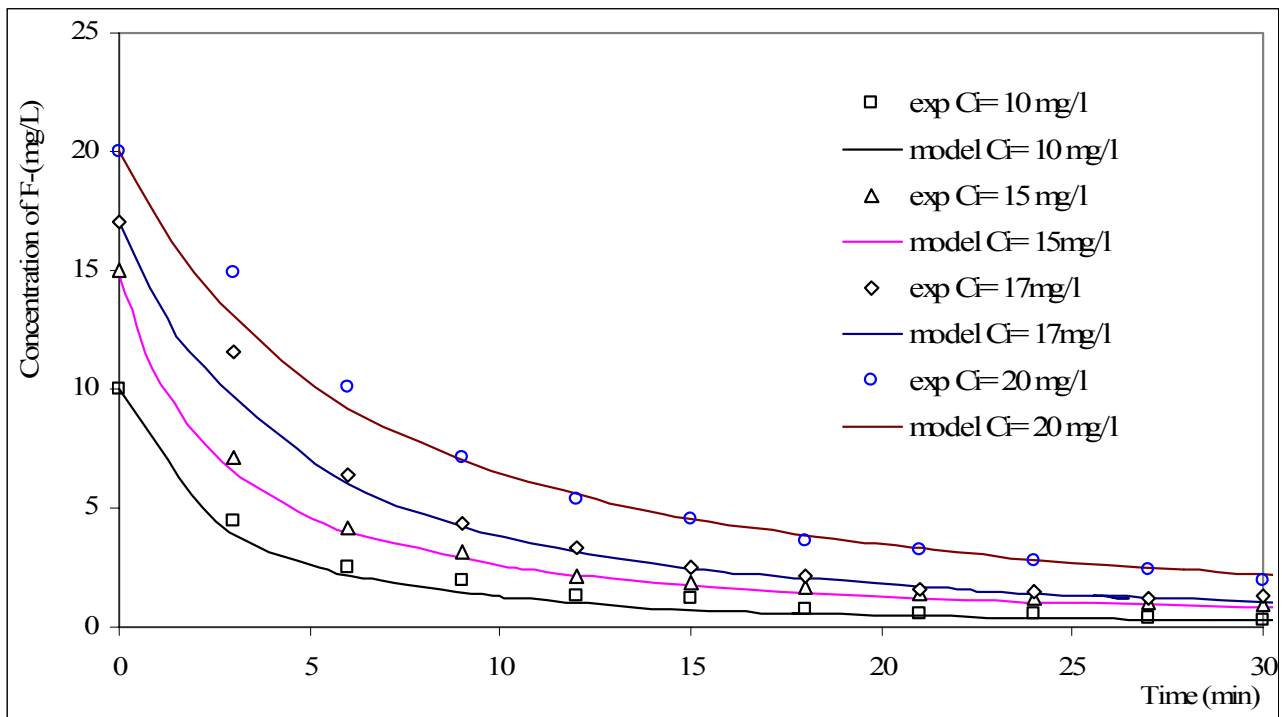**Fig 4** Influence of the initial concentration ($pH_i = 7.4$, $\kappa = 6.1$ mS cm^{-1}, $j = 17.1$ mA cm^{-2}).

The relative weak efficiency concerning 0.5 A is attributed to the weak charge loading produced in this case; 0.47 F m^{-3}. Thus, the quality of EC depends of the amount of coagulant produced in situ. More than 0.47 F m^{-3} is needed to have a better efficiency; in this study it is shown that this amount is 0.9 F m^{-3}. A comparison with the data of Mollah *et al.* (2001) showed that 5–6 F m^{-3} is required to achieve 1.5 mg L^{-1} with [F$^-$]$_0$ between 10–15 mg L^{-1}.

We can see also from **Fig. 4** that the model of VOK with Langmuir-Freundlich fits the experimental data very well. Thus, the expected values of q_{max} are close to 1 as found in the adsorption isotherms study (**Table 2**).These values are used to fit experimental data. The coefficient n is greater than 1 indicating that positive cooperativity is assumed (Prauss *et al.*, 2007). The adsorption on the floc takes place on the external surface and intercalation into the interlayer space at the same time.

Effect of initial concentration

The experiments were conducted in ALR by changing initial fluoride concentration from 10 to 20 mg L^{-1}, keeping all other experimental conditions unchanged ($j = 17.1$ mA cm^{-2}, pH = 7.4, $\kappa = 7.5$ mS cm^{-1})**.**

Figure 4 demonstrates that the rate of defluoridation was significantly influenced by the initial concentration of fluoride. The retention time (t_N) required for an acceptable residual fluoride concentration decreases when the initial concentration increases. This figure presents also the results of simulation using the VOK

model for various initial fluoride concentrations. The same tendency of the simulation result is obtained as for the case of the influence of current density (**Fig. 4**). The figure shows that the model represents very well the experimental data for all initial concentrations with identical parameters ($n = 1.15$, $K = 1600$, $q_{max} = 0.75$).

It should be noted that our results were modelled for a time ranging from 0 to 24 minutes, whereas for the simulation of Hu *et al.* (2008) and Hu *et al.* (2003) the operating time does not exceed 9 minutes. Moreover, our work, both in airlift and stirred reactor, the S/V ratio used is lower (0.875 m^2 m^{-3}) than that used in conventional EC cells, in which the *S/V* ratio is high, between 10 and to 40 m^2 m^{-3} (Mameri *et al.*, 2001). HU *et al.* (2003) and Hu *et al.* (2007) have demonstrated that in this case, electrode removal was primarily responsible for defluoridation efficiency, while other mechanisms gave only a secondary effect. In our case, the mechanisms involved are in the bulk, i.e. coprecipitation and adsorption.

The mode of adsorption is so complicated to be represented by the Langmuir model because the quantity of adsorbent changes with time contrary to the conventional adsorption, and because adsorption takes place also in multi-layers.

CONCLUSION

A variable order kinetic (VOK) derived from the Langmuir-Freundlich equation was developed to simulate the kinetics of the defluoridation with EC using bipolar aluminium electrodes in the airlift reactor. The results showed good agreement between the predictive

equation and the experimental data. The critical parameters (maximum fluoride adsorption q_{max} and kinetic constant K) for VOK model stay constant when the initial fluoride concentration and current varies. Other critical parameters, current efficiency and efficiency of hydro-fluoro aluminium formation were shown to be depending on initial fluoride concentration, but vary with current density and needed to be experimentally determined. The external-loop reactor is confirmed as an efficient tool to achieve complete flotation using only electrochemically-generated bubbles without the need for surfactants or compressed air to induce overall liquid circulation. Another advantage for the external-loop reactor is the instantaneous recovery of the floc, compared to the case of the stirred reactor where the recovery of the floc obtained by the EC needs a long time or an additional secondary treatment (like filtration or sedimentation).

Nomenclature

A	Total anode surface (m^2)
A_d	Cross-sectional area of the downcomer (m²)
A_r	Cross-sectional area of the riser (m²)
E	Specific energy (kwh kg F$^-$)
F	Faraday constant, F = 96 478 (C mol^{-1})
$[F^-]$	Fluoride concentration at any time (mol L^{-1})
$[F^-]_0$	Initial fluoride concentration (mol L^{-1})
g	Acceleration of gravity (m s^{-2})
h_D	Dispersion height (m)
I	Current (A)
j	Current density (A m^{-2})
K	Constant of variable order kinetic model (L mol^{-1})
K_B, K_T	Friction factors in **Eq. (1)**.
k_l	Pseudo-first-order rate constant (min)
k_L	Langmuir constant (L mol^{-1})
k_F	Freundlich constant
k_{LF}	Langmuir-Freundlich constant (L mol^{-1})$^{-n}$
pH_i	Initial pH
q	Mole of removed fluoride ions per mole Al^{3+} ions at given equilibrium pH
q_{max}	Maximum q
t	Reaction time (min)
t_N	Retention time required for $[F^-]_e$
U_{Lr}	Overall liquid recirculation in the riser (cm s^{-1})
V	Volume (L)
Y	Defluoridation efficiency (%)
Z	Valence (Z = 3 for aluminium)

Greek letters

ϕ_{Al}	Efficiency of hydro-fluoro-aluminum formation (%)
ϕ_c	Current efficiency (%)
ε_d	Gas hold-up in the downcomer
ε_r	Gas hold-up in the riser

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