



**HAL**  
open science

## Fluoride removal from water by electrocoagulation: Effect of the type of water and the experimental parameters

Naila Ben Grich, Anis Attour, Marie Le Page Mostefa, Senoussi Guesmia,  
Mohamed Tlili, François Lapticque

### ► To cite this version:

Naila Ben Grich, Anis Attour, Marie Le Page Mostefa, Senoussi Guesmia, Mohamed Tlili, et al.. Fluoride removal from water by electrocoagulation: Effect of the type of water and the experimental parameters. *Electrochimica Acta*, 2019, 316, pp.257-265. 10.1016/j.electacta.2019.05.130 . hal-02892388

**HAL Id: hal-02892388**

**<https://hal.science/hal-02892388>**

Submitted on 25 Oct 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

## **Fluoride removal from water by electrocoagulation: Effect of the type of water and the experimental parameters**

Naila Ben Grich<sup>a</sup>, Anis Attour<sup>a,b</sup>, Marie Le Page Mostefa<sup>c</sup>, Sirine Guesmi<sup>a</sup>, Mohamed Tlili<sup>d</sup> and François Lapicque<sup>c\*</sup>

<sup>a</sup>Laboratoire de Traitement des Eaux Naturelles - Centre de Recherche et des Technologies des Eaux (CERTE), Technopole de Borj-Cedria, BP 273, 8020 Soliman, Tunisia.

<sup>b</sup>Institut Supérieur des Sciences et Technologies de l'Environnement, Université de Carthage, Technopole de Borj-Cedria, BP 1003, 2050 Bordj-Cedria, Tunisia.

<sup>c</sup>Reactions and Chemical Engineering Laboratory, CNRS-Univ. Lorraine, BP 20451, 54000 Nancy, France.

<sup>d</sup>Department of Chemistry, College of Sciences – King Khalid University, 9033 Abha, Saudi Arabia

### **Abstract**

Contamination of the ground water with fluoride is a great problem worldwide. Removal of fluoride (F<sup>-</sup>) ions from simulated natural waters containing fluoride by electrocoagulation (EC) using aluminum electrodes, has been investigated in a discontinuous lab cell. Two types of water have been studied: local tap water and deionized water-based fluoride solutions of sodium fluoride with addition of sodium chloride to reach the desired conductivity. The effect of four operating parameters has been followed for a current density fixed at 5 mA/cm<sup>2</sup> within the following ranges: fluoride concentration (5-50 mg/L), temperature (25-55°C), conductivity (1-6 mS/cm) and initial pH (4-8.5). In accordance with recently published data, the presence of 61 mg/L buffering hydrogencarbonate ions in the tap water was found to substantially reduce the Al(III) amount required for a given abatement in comparison with deionized water. Performance comparison of the discontinuous electrocoagulation treatment between the two types of water has been discussed for 90% abatement of F<sup>-</sup> introduced, in terms of the amount of Al(III) dissolved over the initial fluoride concentration, the parameters of a previous adsorption model and the fraction of Al(III) flocs not involved in the adsorption. EC performances were shown to be governed by the solution pH for the two types of water, with little effect of the other operating conditions: at initial pH 6, F<sup>-</sup> abatement was found to require two or three times less trivalent aluminium than at initial pH 8.5.

**Keywords:** Adsorption equilibrium; Aluminum; Electrocoagulation; Fluoride removal; Hydrogencarbonate.

(\* ) Dr. Francois Lapicque

francois.lapicque@univ-lorraine.fr

## 1- Introduction

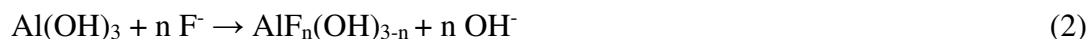
The benefit and the hazard inherent to the presence of fluoride water have been described in numerous papers dealing with health and medical sciences or environment protection [1-4]: fluoride can be beneficial in drinking water at levels below 1 mg/L [3, 5, 5]. Although often reported as contributing to maintain good calcification in humans, it has been shown to exhibit nearly contrary effects for concentrations larger than 1 mg/L, with dental fluorosis, numerous reported cases of teeth decay, over-calcification of ligaments and degenerative deceases in joints and bones in human skeleton [3, 5, 7]. Therefore, recent papers recommend fluoride-free drinking water [8]. Excessive concentrations of fluoride can be encountered in ground waters, in particular in sub-tropical areas e.g. Central America, China, India, Japan and Northern Africa and Tanzania, with concentrations reported up to 20 mg/L or beyond [8 9-15]. Besides, fluoride ions are present in industrial wastewaters from electronic manufacturing plants, photovoltaic manufacturing process, or particular etching processes, at concentrations up to 1500 mg/L [16-20]. For these reasons, fluoride must be removed from waste waters as well as in ground waters

Removal of fluoride had been carried out at industrial scale by precipitation upon addition of calcium or barium salts [4, 16, 17], adsorption on specific porous solids [21-23], ion-exchange by resins [4, 13, 24], reverse osmosis [25], electro dialysis [5], micro-filtration [26], or coagulation [4, 12]. Electrocoagulation (EC), another electrochemical technique, has been proven to be efficient for fluoride removal while requiring moderate energy consumptions [11, 27-32]: this technique relies upon the generation of trivalent metal species from sacrificial Al or Fe electrodes accompanied with water electrolysis at the cathode to produce hydrogen and hydroxide ions, and electromigration of the various charged species [31,33]. With Al electrodes, the trivalent aluminium species form predominantly solid  $\text{Al}(\text{OH})_3$  between pH 5 and 8: this little soluble hydroxide polymerizes to form large solid Al oxo-hydroxy networks (flocs) with various complex hydration states and molecular stoichiometries. All these solid forms are called  $\text{Al}(\text{OH})_3$  in this paper.

In the case of fluoride ion removal, the water treatment involves the formation of little soluble, neutral mixed metal species  $\text{AlF}_n(\text{OH})_{3-n}$  where n may be a non-integer number. This formation is usually described as being the fact of co-precipitation of Al species with  $\text{F}^-$  species after [29, 31]:



or chemical adsorption by integration of this anion onto solid  $\text{Al}(\text{OH})_3$  upon ion-exchange process with release of  $\text{OH}^-$  ions:



Here,  $\text{AlF}_n(\text{OH})_{3-n}$  species are neutral, solid species forming in the treatment flocs or gels, that can be mechanically separated. In this paper, “adsorption” covers the various physicochemical processes involved in the removal of fluoride ions to form  $\text{AlF}_n(\text{OH})_{3-n}$  species. The stability of  $\text{AlF}_n(\text{OH})_{3-n}$  forms coming from chemical adsorption is limited in slightly alkaline solutions because of the lower affinity of Al species to  $\text{F}^-$  than with  $\text{OH}^-$  ions [31, 32, 34]. In such solutions,  $\text{F}^-$  is back released into the water upon formation of F-free  $\text{Al}(\text{OH})_3$  or  $\text{Al}(\text{OH})_4^-$  species:



It is often considered that the optimal pH range for  $\text{F}^-$  removal is in the range 6-7 for Al(III) flocs [29, 32, 34]. In addition to the above hydrolysis of  $\text{AlF}_n(\text{OH})_{3-n}$ , the zero charge potential of solid Al hydroxide was measured at  $\text{pH} = 7.4$  [32], so  $\text{F}^-$  species are less prone to adsorb on Al hydroxide flocs, which exhibit a negative surface charge over this pH: this effect is to be observed in the initial pH range considered. In addition to the initial pH of the water, hydrogencarbonate ions can change the course of the treatment by electrocoagulation, since these ions exhibit buffering properties (pKa of  $\text{CO}_2/\text{HCO}_3^-$  couple near 6.37 [35], so their presence hinders too significant increase in pH during electrocoagulation. This property has been exploited in previous investigations [36, 37]. In particular, we recently demonstrated that treatment of  $\text{HCO}_3^-$  containing tap water at 61 mg/L, could be carried out by EC with lower Al dosages than  $\text{F}^-$  solutions prepared with deionized water [36], for various current density levels, when the pH of the water to be treated was set to 6. In addition to its buffering role, hydrogencarbonate species were observed to result in formation of calcium carbonate (calcite) on the cathode surface [36], but without clear effect on adsorption equilibrium of fluoride ions on  $\text{Al}(\text{OH})_3$  flocs. In the present paper, the effect of experimental parameters other from current density, namely initial pH, fluoride concentrations, temperature and solution conductivity has been thoroughly examined for the two types of water. The observations gained were first discussed from the raw data, then with the assistance of a previously

developed model [36, 38] relying upon the Langmuir-derived equilibrium between dissolved/suspended and adsorbed pollutants: this model had been shown to hold for F<sup>-</sup> adsorption on the Al(OH)<sub>3</sub> flocs [36]: this original model-based approach of discussion allowed the effects of operating parameters to be quantified in a physically meaningful manner. Defined features deduced from the adsorption model and criteria of EC performance could be well correlated to water pH, thus confirming that the main beneficial effect of hydrogen carbonate ions is that of pH levelling agent.

## **2- Experimental sections and interpretation techniques**

### **2.1. Experimental setup**

Experiments were carried in a double-walled vessel with a volume near 1.2 L, as reported in a previous paper [36]. The two facing electrodes out of aluminum alloy (AU4G) 5 x 10 cm<sup>2</sup> in dimensions, were immersed in the solution with a 5 mm gap. This narrow gap was actually shown to yield higher phosphate removal [39], with moderate cell voltage and energy consumption. Before each EC run, the two electrodes were polished with 400 mesh grit papers, degreased with ethanol then rinsed with deionized water. The solution, with a volume of one litre was gently homogenized by a magnetic stirrer at 150 rpm. Temperature was set at 25°C within 1°C by water circulation in thermostatic bath. The cell current was fixed at 0.25 A (5 mA/cm<sup>2</sup>) by a direct current supply (ALR 3002M). Cell voltage and pH of the solutions were continuously monitored in the 90 min. tests.

### **2.2. Solutions and analytical techniques**

Fluoride solutions were prepared by dissolving sodium fluoride (Qualikems) in water: Water was either deionized water or the local tap water. In both cases, the pH was set to 6 by addition of hydrochloric acid aliquots (Novachim). Moreover, for the sake of acceptable ohmic drop between the two electrodes, the conductivity was usually increased to 2.0 mS/cm upon addition of sodium chloride (Chemi-Pharma): the composition of the two types of solutions with 10 mg/L fluoride is given in Table 1. The behaviour of more conducting solutions has been investigated, with accordingly increased amounts of sodium chloride. To study its effect on the treatment, the initial pH was adjusted either by 0.1 M hydrochloric acid or 0.1 M sodium hydroxide (Chemi-Pharma).

Five mL samples were taken from the solution at regular intervals and then filtered from formed Al(III) hydroxide, whose solubility in the pH range 5 - 8 is below  $10^{-6}$  M and is near  $10^{-5}$  M (0.27 mg/L) at pH 9 [36]. Fluoride was assayed using a specific electrode (Metrohm 6.0502.750F) with an Ag/AgCl reference electrode according to the procedure reported in [36]. Calcium and magnesium concentrations from the tap water were determined by complexometry, hydrogencarbonate ions were analysed by titration with 0.01 M HCl solution. Sodium and potassium were assayed by flame spectrometry (Elico CL 378), sulfate ions by gravimetry and chloride species by titration using Mohr method [36].

### 2.3. Criteria for performance assessment of EC treatment

#### *Physicochemical criteria*

Removal efficiency defined as the concentration ratio of removed fluoride over the initial content, is often used in EC investigations. In addition to the efficiency of the treatment, another criterion of interest is the Al dosage required for a given performance of the treatment,  $D_{Al}$ . For instance, considering a 90% removal efficiency, the criterion:

$$D_{Al}^{90} = \frac{[Al(III)]^{90}}{[F^-]_0} \quad (5)$$

compares the amount of Al(III) required for 90%  $F^-$  abatement to the fluoride content of the water to be treated: because of the cost of sacrificial aluminum and the potential hazard of this metal in disposal areas, lower  $D_{Al}^{90}$  values are to be preferred.

Moreover, because the treatment relies upon adsorption equilibrium of  $F^-$  on  $Al(OH)_3$  flocs, it can be wondered how large is the fraction of Al sites “hosting” fluoride ions – or conversely what is the fraction of free, vacant Al sites. For this purpose, a simple adsorption model [36, 38] involving two parameters has been used:

(i) Adsorption equilibrium constant K defined as:

$$K = \frac{[Al-F]}{[Al]_f [F]} \quad (6)$$

where Al-F refers to the “complex” formed between Al flocs and  $F^-$  ions, regardless of the molar or weight ratio between Al and F elements in the “complex”,  $[Al]_f$  denotes the concentration of free Al in the form of solid hydroxide, and  $[F]$  is the fluoride concentration over time;

(ii) Coefficient  $n$  compares the amount of  $F^-$  adsorbed per unit amount Al-F:

$$n = \frac{[F]_0 - [F]}{[Al - F]} \quad (7)$$

Subscript 0 corresponds to initial time.  $n$  is defined in mg F per mg solid Al, but this ratio could also be defined in terms of molar amounts or concentrations.

Mass balance in solid Al(III) can be written as:

$$[Al]_t = [Al]_f + [Al - F] \quad (8)$$

Upon rearrangement of Eqs (6) and (8), the following Eq. has been obtained:

$$\frac{[Al - F]}{[Al]_t} = \frac{K [F]}{1 + K [F]} \quad (9)$$

This equation is equivalent to the Langmuir expression for the sorbed  $F^-$ .

Mass balances in both Al and F species developed elsewhere [36], allow to calculate the fraction of “free” (unused) Al for a treatment efficiency,  $X_{Al,f}$ :

$$X_{Al,f} = \frac{[Al]_f}{[Al]_t} = \frac{1}{1 + K[F]} \quad (10)$$

As done previously for  $D_{Al}^{90}$ , 90 % fluoride efficiency has been considered in this work:

$$X_{Al,f}^{90} = \frac{[Al]_f^{90}}{[Al]_t^{90}} \quad (11)$$

For the sake of efficient presence of trivalent Al in the sludge formed by the treatment,  $X_{Al,f}^{90}$  has to be as low as possible, but a high value of coefficient  $n$  can be also appreciated for lower Al-content in the sludge produced.

### *Electrochemical variables*

The amount of Al(III) generated per coulomb passed is given by the faradaic efficiency of Al dissolution  $\Phi_{Al}$ : this efficiency is usually larger than unity because of side corrosion of the Al plates. Moreover, the cell voltage at a given value of the current applied,  $U_c$ , is linked to the energy requirement, in addition to  $\Phi_{Al}$  and the above “physicochemical” criteria.

## **3- Results**

Experiments have been conducted to follow the effect of the water used on fluoride removal, depending on four operating parameters, i.e. initial fluoride concentration, temperature, conductivity of the solution treated, and initial pH. Before describing the effect of the operating conditions, the variations of electrochemical variables  $\Phi_{Al}$  and  $U_c$  are presented.

### 3.1. Electrochemical variables

As expressed above, the presence of  $Cl^-$  ions induces corrosion of aluminium, resulting in apparent faradaic yields of Al dissolution larger than unity, as shown in Figure 1a where all the data obtained are plotted versus the solution pH after 90%  $F^-$  abatement,  $pH(90\%)$ , with no direct correlation to this pH. For treatment of tap water-based fluoride solutions, the current yield ranged from 1.45 to 2.1, whereas this yield varied from 2.0 to 3.2 with deionized water: less aluminium is dissolved in tap water-based fluoride solutions than with deionized waters. As expected, for both types of water, the highest values were obtained at high chloride concentrations, in highly conducting media.

The cell voltage varied in the range 1.2 – 2.95 V depending on the operating conditions, and in particular on the solution conductivity. For possible comparison and discussion of the values, the voltage values have been corrected for the ohmic drop ( $i \cdot d / \kappa$ ), which was estimated theoretically from the electrode gap  $d$ , the conductivity  $\kappa$  and the current density  $i$ . The obtained data shown in Figure 1b shows that the corrected voltage lays in the range 0.4 – 1 V in most cases, with no clear effect of  $pH(90\%)$  or the water type used. Closer examination of the data below 1 V does not allow to interpret these moderate differences which are presumably due to different passivation state of the Al electrodes in the various runs. In contrast, for two experiments with tap water (Figure 1b), the larger cell voltage was attributed to the formation of a calcium carbonate (calcite) film at the cathode: already reported in previous papers [36, 37]. For long-term operation with such waters, use of alternating current as suggested in [40] could limit the importance of this inhibiting film. The observed film renders hydrogen evolution more sluggish, resulting in higher voltages in the cell operated at constant current density.

### 3.2. Effect of operating conditions

The operating conditions were varied from the common reference conditions: 10 mg/L fluoride ions, 25°C,  $\kappa = 2$  mS/cm and initial  $pH = 6$ .

*Fluoride concentration*



This concentration was varied from 5 to 50 mg/L  $F^-$ : for the sake of clarity, the ratio of  $F^-$  concentration over the initial concentration,  $[F^-]/[F^-]_0$ , was considered in the graphs. For the same water used for preparation of the solutions, it can be observed in Figure 2a and b, that the treatment of concentrated solutions requires more Al dissolved than that of more dilute solutions. However, the amount of Al required does not vary linearly with the initial concentration of fluoride: for instance, 80%  $F^-$  abatement with deionized water can be obtained upon dissolution of approx. 70 ppm Al for  $[F^-]_0 = 5$  mg/L, and 270 mg/L with the most concentrated solution (Fig. 2a). Comparable observations can be made with tap water-based solutions (Fig. 2b). This behaviour could be the fact of synergetic adsorption of fluoride with high Al dosages. Besides, as reported previously [36] with different current densities,  $F^-$  removal from tap water in the presence of hydrogencarbonate requires far less Al(III) than that with deionized water. At the end of the 90 min runs with increasing  $[F^-]_0$  values, the pH of the solution varies from 7.0 to 8.3 with tap water, and from 9.2 to 9.9 with deionized water (data not shown): hydrogencarbonate strongly limits the increase in pH during the treatment which indirectly facilitates the treatment because of the higher affinity of  $F^-$  to  $Al(OH)_3$  as explained above.

The analysis of the data can be discussed in terms of the above physicochemical criteria. First, the required Al dosage per mg  $F^-$  for 90% abatement is reported in Figure 3a: in accordance to the direct above observations,  $D_{Al}^{90}$  decreases with the initial  $F^-$  concentration, and is approx. 2 - 3 times lower with tap water than with deionized for  $[F^-]_0$  larger than 5 mg/L. For the same type of water, it was not possible to fit the various data with the same couple (K, n) of the adsorption model, so fitting was carried out for each  $[F^-]_0$  value. As shown in Figure 3b and c, values for both parameters K and n are usually larger with tap water than with deionized water: adsorption equilibrium is facilitated by the presence of  $HCO_3^-$  species, and the Al-F entities formed have also a larger amount of  $F^-$  with tap water (coefficient n), in the range 0.21 – 0.59, than with deionized water for which n remains near 0.20 for all  $[F^-]_0$  values. Adsorption constant K was the same with 10, 25 and 50 mg/L fluoride in deionized water, near 0.35, and found at 0.70 with 5 mg/L, in most cases below the values obtained with tap water, decreasing from 1.8 down to 0.21 with increased initial fluoride dosages. Finally, from the sorption model, the fraction of “free” aluminium,  $X_{Al,f}^{90}$ , is globally larger with low initial fluoride concentrations than with larger  $[F^-]_0$  values (Figure 3d). Moreover, with deionized water,  $X_{Al,f}^{90}$  is larger than with tap water for 5, 10 and 25 mg/L fluoride. For the 50 mg/L

solution, the reverse trend observed is due to the low  $K$  value obtained with tap water - expressing difficult adsorption, but with a far larger  $n$  value: In this case, 50 % of Al(III) flocs do not accommodate  $F^-$  species, but the sorbing flocs have an appreciable  $F^-$  concentration (0.59 mg F/mg Al, i.e. 0.84 mol F/mol Al).

### *Temperature*

For both types of water, the faradaic yield of Al dissolution is increased by 50% when the temperature is passed from 25 to 55°C, from the reference values at 25°C at 1.52 and 2.10 with tap water and deionized water, respectively (data not shown). Corrosion was presumably more accelerated than faradaic dissolution by temperature increase, as revealed by compared variations of anode and cathode weights with time: from 25 to 55°C, cathode dissolution rate was increased by a factor of 2.5 with deionized water and nearly 4 with tap water, at least three times more than the rate increase at the anode (data not shown). With deionized water, temperature appears to facilitate the treatment as shown in Figure 4a: 90%  $F^-$  abatement can be obtained with 198 mg/L Al (III) at 25°C and only 140 mg/L at 55°C. This positive effect could be linked to the lower increase in pH during the run, attaining only 7.5 at 55°C, instead of 9.0 at 25°C (data not shown). The temperature effect at constant Al(III) dosage is scarcely visible with tap water – in relation with very little changed pH(90%) values - for which comparable treatment is achieved with 50 mg/L within 10 mg F/L whatever the temperature in the range considered (Figure 4b).

The Al dosage  $D_{Al}^{90}$  is near 18 mg Al/mg F with deionized water at temperatures below or equal to 45°C and only at 13 at 55°C (Figure 5a). Tap water allows lower Al dosage, with  $D_{Al}^{90}$  values ranging from 5 to 6 mg Al/mg F, except at 55°C where slightly higher dosage was required (7 mg Al/mg F). Parameters of the sorption model are reported in Figure 5b and c. As for the effect of  $F^-$  concentration, the adsorption equilibrium constant  $K$  with deionized water is low in the range 0.20 - 0.32 in comparison with that with tap water, which varies from 0.75 to 1.12. Increasing temperature seems to enlarge coefficient  $n$  with deionized water from 0.2 to 0.50 mgF/mgAl, in accordance with the favorable effect of the temperature; with tap water, coefficient  $n$  is of comparable order of magnitude, around 0.3 mgF/mgAl which explains the low dependence of fluoride removal on temperature. Besides, the fraction of free Al(III) in deionized water  $X_{Al,f}^{90}$ , appears to increase slightly with temperature, from 0.73 to 0.81 (Figure 5d), but this is compensated by the fact that the

sorbing Al(III) flocs have a far larger content of F species ( $n = 0.50$  for  $T = 55^\circ\text{C}$ ), resulting globally in improved treatment at higher temperatures. For tap water,  $X_{Al,f}^{90}$  varies weakly in the range of 0.57-0.59, confirming that temperature have a limited effect for natural waters.

### *Conductivity*

As expected, increasing the solution conductivity upon larger sodium chloride content, results in larger faradaic yield of Al dissolution, passing from approx. 2.0 at 2 mS/cm to 2.3 - 2.5 at 6 mS/cm for the two waters used (data not shown): this is directly linked to the catalytic effect of chloride on Al pitting corrosion [41-43]. Solution pH after 90% fluoride abatement was found to be reduced in more concentrated NaCl solutions, from approx. 9 in the reference solution with deionized water to 7.9 at 6 mS/cm. This phenomenon is far more limited with tap water with pH(90%) values at 6.6 for  $\kappa = 2$  mS/cm to 6.2 at 6 mS/cm because of the buffering effect of hydrogen carbonate (data not shown). The lower pH in deionized water-based fluoride solutions corresponds to easier treatment, as shown in Figure 6a, for which the required Al dosage at 6 mS/cm is less than the half of that at 2 mS/cm. With tap water, fluoride removal by EC is not visibly affected by the sodium chloride concentration (Figure 6b).

Interpretation of the data yields comparable trends for the Al dosage at 90% fluoride abatement: Whereas  $D_{Al}^{90}$  passed from 17 mg Al/mg F for  $\kappa = 2$  mS/cm to only 6.7 for 6 mS/cm with deionised water, the dosage remains in the range 6 - 7 mg Al/mg F with tap water (Figure 7a). The adsorption equilibrium constant for the case of deionized water remains approximately constant near 0.36 in the conductivity range, but in the meanwhile, coefficient  $n$  passes from 0.20 at 2 mS/cm to 0.45 mg F/mg Al at 6 mS/cm (Figure 7b), corresponding to significant improvement in the treatment efficiency mentioned above. Interaction of  $\text{F}^-$  with Al flocs might be favoured by higher ionic strength, in addition to neutral solution pH, but this could not be evidenced here. With tap water, the adsorption equilibrium constant  $K$  increases with the conductivity (from 0.9 at 2 mS/cm to 1.65 at 6 mS/cm), however, with lower values of coefficient  $n$ , passing from 0.3 at 2 mS/cm to 0.20 at 6 mS/cm (Figure 7c): adsorption equilibrium is facilitated but the hosting Al flocs have a lower fluoride content which results in little changed fluoride removal rates reported above with tap water, presumably because of the moderate change in pH (from 6.6 to 6.2). Finally, the fraction of “free” (useless)  $\text{Al}(\text{OH})_3$  species is high in the treatment of solutions prepared with deionized

water, slightly larger than 70%. Because of the fair K values,  $X_{Al,f}^{90}$  is lower with tap-water based solution, decreasing from 0.54 to 0.31 in the conductivity range investigated. This is due to the presence of the pH leveler at the optimal pH range. As expressed above, this last criterion has to be considered jointly with n for evaluation of the treatment efficiency.

### *Initial pH*

Three levels of initial pH have been considered: 4, 6 and 8.5. With tap water-based fluoride solutions, it is likely that part of hydrogen carbonate ions turned to carbon dioxide upon acidification before the EC run started immediately afterwards, but this likely loss could not be evaluated. Nevertheless, the tap water-based solutions were observed to behave differently from deionized water-based fluoride solutions. With initial pH at 4, pH(90%) was in the order of 6 for the two waters (data not shown). Likewise, with  $pH_i = 8.5$ , the two solutions have a final pH near 9. For this series of experiments, aluminum was dissolved at yields slightly larger with deionized water than with tap water (data not shown). Fluoride abatement is shown to be highly dependent on initial pH (Figure 8), with far faster abatement for moderate pH, i.e. with initial pH at 4 for deionized water, and at 4 and 6 for tap water, than in other cases: more alkaline solutions require at least two times more Al(III) than acidic/neutral solutions for comparable abatement (Figure 8a and b).

Figure 9a shows that the required Al dosage for treatment of deionized water-based fluoride solutions increase greatly with the initial pH, for approx. 5 mg Al/mg F for  $pH_i = 4$  to 29 mg Al/mg F for the most alkaline solution. In the meanwhile,  $D_{Al}^{90}$ , was found to be near 4.5 mg Al/mg F for initial pH of tap water solutions at 4 or 6, but reached 17.5 mg Al/mg F for  $pH_i = 8.5$ , presumably because of the high pH of the medium during the run. In fact, alkaline media are to accelerate the cathode corrosion [41, 42], and thus to increase the dissolution rate of aluminum in the solution. Parameters K and n for deionized waters were kept at moderate levels for  $pH_i = 6$  or 8.5 (K near 0.3, n = 0.2). Nevertheless, with the most acidic solution  $pH_i = 4$ , n attained 0.31 and K was found larger than 1 (Figure 9b). With tap water, parameters K and n are at fairly high level for acid and neutral initial pH but far lower with the most alkaline solution (Figure 9c). The fraction of free Al(III) varies regularly with the initial pH, expressing a more efficient use of Al(III) flocs for acidic  $pH_i$ , than with initial pH at 8.5 for which the fraction of “free” Al(III) exceeds 80% expressing the more difficult treatment of the water, regardless of the water nature (Figure 9d).

### 3.3. Discussion: a global effect of pH on fluoride removal efficiency by EC

Although presumably not the only influencing variable, the above presentation of the results in accordance with previous papers [36, 37] suggests the governing effect on pH on EC efficiency and treatment behavior. In order to better demonstrate this point, the above four criteria were plotted versus pH(90%) for the two waters investigated and for all operating conditions: Regression was carried out for each criterion over 28 data to estimate the statistical relevancy of the trend observed. The parameters of the regression used were not presented here, since being dependent on other factors such as cell design or stirring rate, then being of moderate importance only.

First, the required amount of Al(III) for 90% fluoride abatement is shown to increase with pH(90%) (Figure 10a): the dotted line corresponds to the exponential regression with pH(90%), holding for the two types of water with a regression coefficient near 0.66: the higher the liquid pH(90%), the higher the amount of aluminum to be dissolved from the electrodes (Figure 10a). Regarding the adsorption parameters, equilibrium constant  $K$  appears clearly to vary linearly with pH(90%) with a high negative slope (Figure 10b): the indicative regression lets appear that  $F^-$  species cannot adsorb on  $Al(OH)_3$  flocs for pH(90%) larger than 10. In the pH domain investigated (5.0 – 9.4), the regression exhibits a coefficient regression larger than 0.76, demonstrating the clear tendency. For the case of coefficient  $n$ , the set of data may suggest the existence of a flat maximum near 0.4 for neutral pH(90%) (Figure 10c). However, the second-order polynomial function tested has to be considered with care, because of the low regression coefficient found ( $R^2 = 0.397$ ), thus the existence of the above maximum for  $n$  could not fully be demonstrated. Finally, the fraction of free Al(III) for 90% fluoride abatement,  $X_{Al,f}^{90}$ , seems to be an increasing function of the solution pH(90%), as indicated by the linear regression tested with a fair regression coefficient, near 0.57 (Figure 10d): according to the model, higher solution pH results in larger fractions of Al(III) flocs which do not accommodate  $F^-$  ions. The fraction of free Al is overall lower with tap water than with deionized water expressing facilitated adsorption equilibrium, as indicated by the higher equilibrium constants  $K$ .

## 4- Conclusions

For abatement of fluoride ions contained in water by electrocoagulation, a methodological approach has been developed on the basis of several criteria: (i) how much Al(III) per unit F<sup>-</sup> is required for a given abatement? (ii) how can adsorption equilibrium be characterized in terms of non-involved (free) Al(OH)<sub>3</sub> flocs and amount of F<sup>-</sup> ions adsorbed per unit Al(III)? (iii) how large is the fraction of free Al(OH)<sub>3</sub> flocs? Although partly linked to each other, these criteria help to better understand how electrocoagulation proceeds depending on various operating conditions, with or without the presence of hydrogencarbonate ions, in view to limiting the consumption of energy and sacrificial metal aluminium, and to maximizing the fluoride content in the sludge produced, for easier and safer disposal afterward. Beyond the influence of factors e.g. F<sup>-</sup> concentration, temperature, initial conductivity and pH, treatment of the set of data indicates the governing effect of the pH of the medium for the considered abatement efficiency. As a matter of fact, pH values in the course of the treatment larger than 7.5 have to be avoided for the sake of reduced amounts of dissolved Al, and because of the lower affinity of F<sup>-</sup> to Al(III) flocs beyond this pH value, in accordance with the conclusions reported in [32].

In complement to nearly systematic investigations of the effect of operating conditions often made in the area, the approach proposed could be applied to the treatment of other pollutants, with the help of complementary knowledge on the interactions between the species to be removed and the Al(III) flocs, for the sake of better-mastered, designed and operated EC processes.

### **Acknowledgements**

Thanks are due to the Tunisian Ministry of Higher Education and Scientific Research for funding of N. Ben Grich's PhD grant, and PHC-Utique programme through 15G1119 Project. Some facilities used in the work have been funded through SusChemProc project, with the joint French Ministry of Research and Region Lorraine CPER programme (2015-2020).

## References cited

- [1] WHO (World Health Organization), Guidelines for Drinking Water Quality, Recommendations, 3<sup>rd</sup> ed., World Health Organization, Geneva, 2004.
- [2] J. Fawell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell, Y. Magara, Fluoride in Drinking-water, World Health Organization (WHO) ISBN: 1900222965 (2006). Published by IWA Publishing, London, UK, 2006.
- [3] S. Meenakshi, R.C. Maheshwari, Fluoride in drinking water and its removal, Journal of Hazardous Materials B137 (2006) 456-463.
- [4] M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, P. Singh, Review of fluoride removal from drinking water, Journal of Environmental Management 91 (2009) 67–77.
- [5] L.L. Terry, Public health service drinking water standards, U.S. Department of health, education and welfare, U.S. Government printed office, Washington (1962)
- [6] J.J. Schoeman, Performance of a water defluoridation plant in a rural area in South Africa, Water S.A. 35 (2009) 97-101.
- [7] A.A. Ismail, R.R. Bandeker, Fluoride supplements and fluorosis: a meta-analysis, Community Dentistry and Oral Epidemiology 27 (1999) 48-56.
- [8] A.I. Ndé-Tchoupé, R. Tepong-Tsindé, M. Lufingo, Z. Pember-Ali, I. Logodisha, R.I. Mureth, M. Nkinda, J. Marwa, W. Gwenzi, T. Burton Mwamila, M.A. Rahman, C. Noubactep, K.N. Njau, White teeth and healthy skeletons for all: the path to universal fluoride-free drinking water in Tanzania, Water 11 (2019) paper 131, 1-22.
- [9] M.H. Dehghani, G.A. Haghghat, M. Yousefi, Data on fluoride concentration in drinking water resources in Iran: A case study of Fars province, Larestan region, Data in Brief 19 (2018) 842-846.
- [10] C. B. Dissanayake, The fluoride problem in the ground water of Sri Lanka - environmental management and health, Intern. Journal of Environmental Studies 38 (1991) 137-156.
- [11] 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 plates, Water Research 32 (1998) 1604-1612.
- [12] E. Mulugeta, F. Zewge, C. A. Johnson, B. S. Chandravanshi, Aluminium hydro(oxide)-based (AO) adsorbent for defluoridation of drinking water: Optimisation, performance comparison, and field testing, Water SA 41(2015) 121-128.
- [13] A. Ben Nasr, C. Charcosset, R. Ben Amar, K. Walha, Fluoride removal from aqueous solution by Purolite A520E resin: kinetic and thermodynamics study, Desalination and Water Treatment 54 (2015) 1604–1611.

- [14] A. Ben Nasr, K. Walha, C. Charcosset, R. Ben Amar, Removal of fluoride ions using cuttlefish bones, *Journal of Fluoride Chemistry* 132 (2011) 57-62.
- [15] L. Ming, S.R. Yi, Z.J. Hua, B. Yuan, W. Lei, L. Ping, K.C. Fuwa, Elimination of excess fluoride in potable water with coagulation by electrolysis using aluminum anode, *Fluoride* 20 (2) (1987) 54-63.
- [16] E.I. Reardon, Y.X. Wang, A limestone reactor for fluoride removal from wastewaters, *Environmental Science and Technology* 34 (2000) 3247-3253.
- [17] M.F. Chang, J.C. Liu, Precipitation removal of fluoride from semiconductor waste water, *Journal of Environmental Engineering* 33 (4) (2007) 419-525.
- [18] S. Aoudj, A. Khelifa, N. Drouich, M. Hecini., Removal of fluoride and turbidity from semiconductor industry wastewater by combined coagulation and electroflotation. *Desalination and Water Treatment* 57(39) (2015) 18398 - 18405.
- [19] T. Ouslimane, Aoudj S., Amara M., Drouiche N., Removal of Copper and Fluoride from Mixed Cu-CMP and Fluoride-Bearing Wastewaters by Electrocoagulation. *International Journal of Environmental Research* 11 (2017) 677-684.
- [20] N. Drouiche, S. Aoudj, M. Hecini, N. Ghaffour, H. Lounici, N. Mameri, Study on the treatment of photovoltaic wastewater using electrocoagulation: Fluoride removal with aluminium electrodes—Characteristics of products, *Journal of Hazardous Materials* 169 (2009) 65–69.
- [21] N. Hamdi, E. Srasra, Retention of fluoride from industrial acidic wastewater and NaF Solution by three Tunisian clayey soils, *Fluoride* 42 (1) (2009) 39-45.
- [22] Q. Guo, Q. Guo, Water defluoridation by hydrocalcite and takovite and subsequent formation of new fluoride-bearing phases, *Environmental Technology* 34 (8) (2013) 1053–1062.
- [23] S. Bibi, A. Farooqi, K. Hussain, N. Haider, Evaluation of industrial based adsorbents for simultaneous removal of arsenic and fluoride from drinking water, *Journal of Cleaner Production* 87 (2015) 882-896.
- [24] K.M. Popat, P.S. Anand, B.D. Dasare, Selective removal of fluoride ion from water by the aluminium from of the aminomethylphosphonic acid type ion exchange, *Reactions of Polymers* 23 (1994) 23-32.
- [25] R. Trikha, B.K. Sharma, Studies on factors affecting fluoride from water using passive system, *Journal of Environmental Chemical Engineering* 2 (2014) 172-176.
- [26] D. Ghosh, M.K. Sinha, M.K. Purkait, A comparative analysis of low-cost ceramic membrane preparation for effective fluoride removal using hybrid technique, *Desalination* 327 (2013) 2–13.



- [27] M. Bennajah, M. Maalmi, Y. Darmane, M. Ebn Touhaim, Defluoridation of drinking water by electrocoagulation/electroflotation: kinetic study, *Journal of Urban and Environmental Engineering* 4 (1) (2010) 36-44.
- [28] M. Bennajah, B. Gourich, A.H. Essadki, Ch. Vial, H. Delmas, Defluoridation of Morocco drinking water by electrocoagulation/electroflotation in an electrochemical external-loop airlift reactor, *Chemical Engineering Journal* 148 (2009) 122–131.
- [29] C.Y. Hu, S.L. Lo, W.H. Kuan, Simulation the kinetics of fluoride removal by electrocoagulation (EC) process using aluminium electrodes, *Journal of Hazardous Materials* 145 (2007) 180-185.
- [30] H-Z. Zhao, W. Yang, J. Zhu, J-R. Ni, Defluoridation of drinking water by combined electrocoagulation: effects of the molar ratio of alkalinity and fluoride to Al(III), *Chemosphere* 74 (2009) 1391-1395.
- [31] 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 Research* 37 (2003) 4513-4523
- [32] S. Hamamoto, N. Kishimoto, Characteristics of fluoride adsorption onto aluminium(III) and iron(III) hydroxide flocs, *Separation Science and Technology* 52 (2017) 42-50.
- [33] P.K. Holt, G.W. Barton, C.A. Mitchell, The future for electrocoagulation as a localised water treatment technology, *Chemosphere* 59 (2005) 355-367.
- [34] J. Zhu, H. Zhao, J. Ni, Fluoride distribution in electrocoagulation defluoridation process, *Separation and Purification Technology* 56 (2007) 184–191.
- [35] *Handbook of Chemistry and Physics*, R.C. Weast Ed., 66<sup>th</sup> Edition, CRC Press, Boca Raton (1986)
- [36] N. Ben Grich, A. Attour, M. Le Page Mostefa, M. Tlili, F. Lapique. Fluoride removal from water by electrocoagulation with aluminium electrodes: Effect of the water quality, *Desalination and Water Treatment* 144 (2019) 145-155.
- [37] A. Doggaz, A. Attour, M. Le Page Mostefa, K. Côme, M. Tlili, F. Lapique, Removal of heavy metals by electrocoagulation from hydrogenocarbonate-containing waters: Compared cases of divalent iron and zinc cations, *Journal of Water Process Engineering* 29 (2019) 100796.
- [38] M. Khemis, J.P. Leclerc, G. Tanguy, G. Valentin, F. Lapique, Treatment of industrial liquid wastes by electrocoagulation: Experimental investigations and an overall interpretation model, *Chemical Engineering Science* 61 (2006) 3602-3609.
- [39] A. Attour, M. Touati, M. Tlili, M. Ben Amor, F. Lapique, J-P. Leclerc, Influence of operating parameters on phosphate removal from water by electrocoagulation on aluminium electrodes, *Separation and Purification Technology* 123 (2014) 124-129.

- [40] S. Vasudevan, J. Lakshmi, G. Sozhan, Effects of alternating and direct current in electrocoagulation process on the removal of cadmium from water, *Journal of hazardous Materials* 192 (2011) 26-34.
- [41] T. Picard, G. Cathalifaud-Feuillade, M. Mazet, C. Vandensteendam, Cathodic dissolution in the electrocoagulation process using aluminium electrodes, *Journal of Environmental Monitoring* 2 (2000) 77-80.
- [42] V. Landolt, *Traité des Matériaux: Corrosion et Chimie de Surface des Métaux*, Presse Polytechniques et Universitaires Romandes, Lausanne (1993) [in French].
- [43] 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 plates, *Water Research* 32 (1998) 1604-1612.

**Table 1:** Composition of the fluoride solutions (10 mg/L), initial pH = 6, initial conductivity = 2.0 mS/cm at 25°C prepared with deionized water and the local tap water. Concentrations in mg/L.

Ions	F <sup>-</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>
With deionized water	10.1	607	0	0	0	0	399	0
With the local tap water	10.6	550	61	56	60.2	48.6	298	5.3

## Legends of the Figures

Figure 1: Electrochemical variables for the treatment of deionized water- or tap water-based fluoride solution depending on the solution pH after 90% abatement: a) Cell voltage corrected for the ohmic drop; b) Apparent current efficiency of Al dissolution.

Figure 2: The reduced F<sup>-</sup> concentration versus the dissolved aluminium concentration for different initial fluoride amounts: a) Deionized water-based fluoride solutions; b) Tap water-based fluoride solutions.

Figure 3: a) Aluminium dosage for 90% F<sup>-</sup> abatement,  $D_{Al}^{90} = [Al(III)]/[F^-]_0$ ; b) Parameters of the adsorption model for deionized water solutions and c) for tap water; d) Fraction of free Al(III) flocs at 90% F<sup>-</sup> abatement,  $X_{Al,f}^{90}$ , versus initial fluoride concentration.

Figure 4: Fluoride concentration versus dissolved aluminium concentration for different temperatures: a) deionized water-based fluoride solutions; b) tap water-based fluoride solutions.

Figure 5: a) Aluminium dosage for 90% F<sup>-</sup> abatement,  $D_{Al}^{90} = [Al(III)]/[F^-]_0$ ; b) Parameters of the adsorption model for deionized water solutions and c) for tap water; d) Fraction of free Al(III) flocs at 90% F<sup>-</sup> abatement,  $X_{Al,f}^{90}$ , versus temperature.

Figure 6: Fluoride concentration versus dissolved aluminium concentration for different conductivities: a) Deionized water-based fluoride solutions; b) Tap water-based fluoride solutions.

Figure 7: a) Aluminium dosage for 90% F<sup>-</sup> abatement,  $D_{Al}^{90} = [Al(III)]/[F^-]_0$ ; b) Parameters of the adsorption model for deionized water solutions and c) for tap water; d) Fraction of free Al(III) flocs at 90% F<sup>-</sup> abatement,  $X_{Al,f}^{90}$ , versus conductivity.

Figure 8: Fluoride concentration versus dissolved aluminium concentration for different initial pH: a) Deionized water-based fluoride solutions; b) Tap water-based fluoride solutions.

Figure 9: a) Aluminium dosage for 90% F<sup>-</sup> abatement,  $D_{Al}^{90} = [Al(III)]/[F^-]_0$ ; b) Parameters of the adsorption model for deionized water solutions and c) for tap water; d) Fraction of free Al(III) flocs at 90% F<sup>-</sup> abatement,  $X_{Al,f}^{90}$ , versus initial pH.

Figure 10: a) Aluminium dosage for 90% F<sup>-</sup> abatement,  $D_{Al}^{90} = [Al(III)]/[F^-]_0$ ; b) Equilibrium constant K of fluoride adsorption; c) Coefficient n of the adsorption model; d) Fraction of free Al(III) flocs at 90% F<sup>-</sup> abatement,  $X_{Al,f}^{90}$ , versus initial pH.(90%)

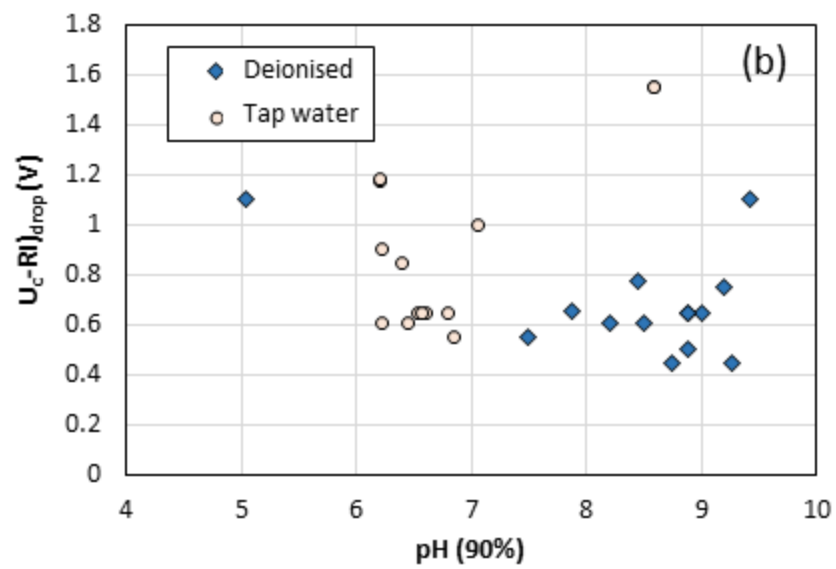
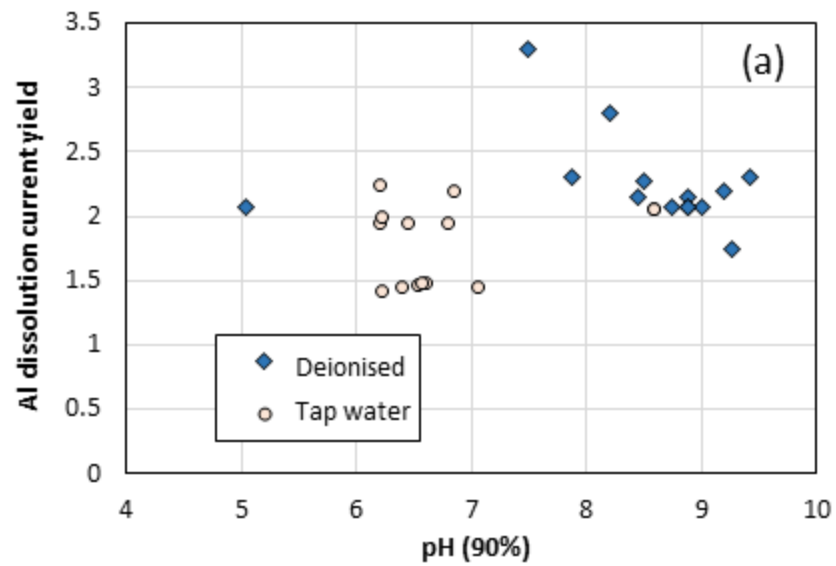


Figure 1

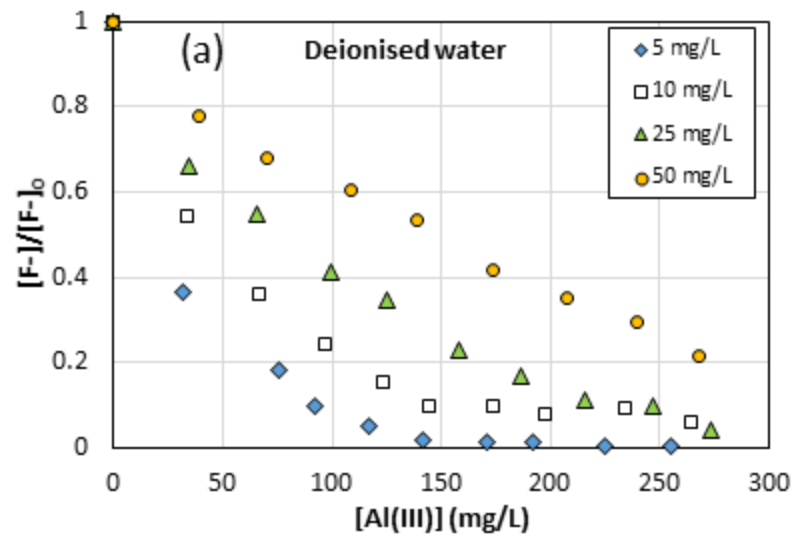


Figure 2

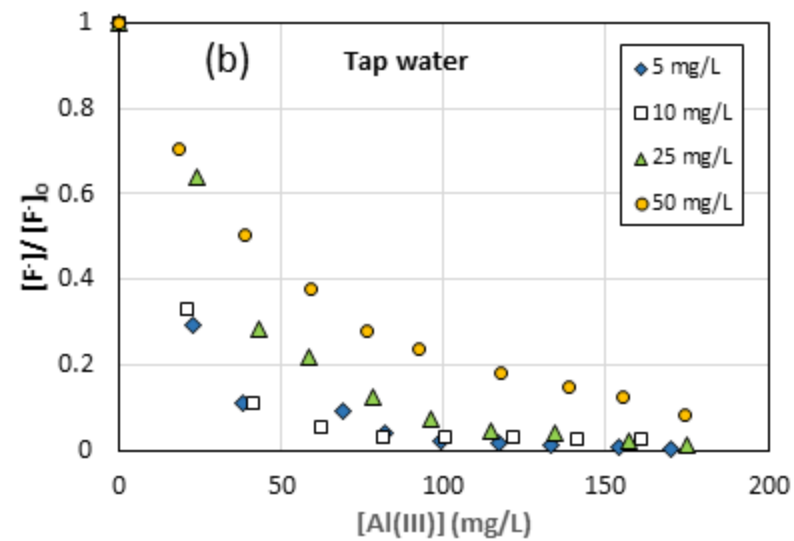
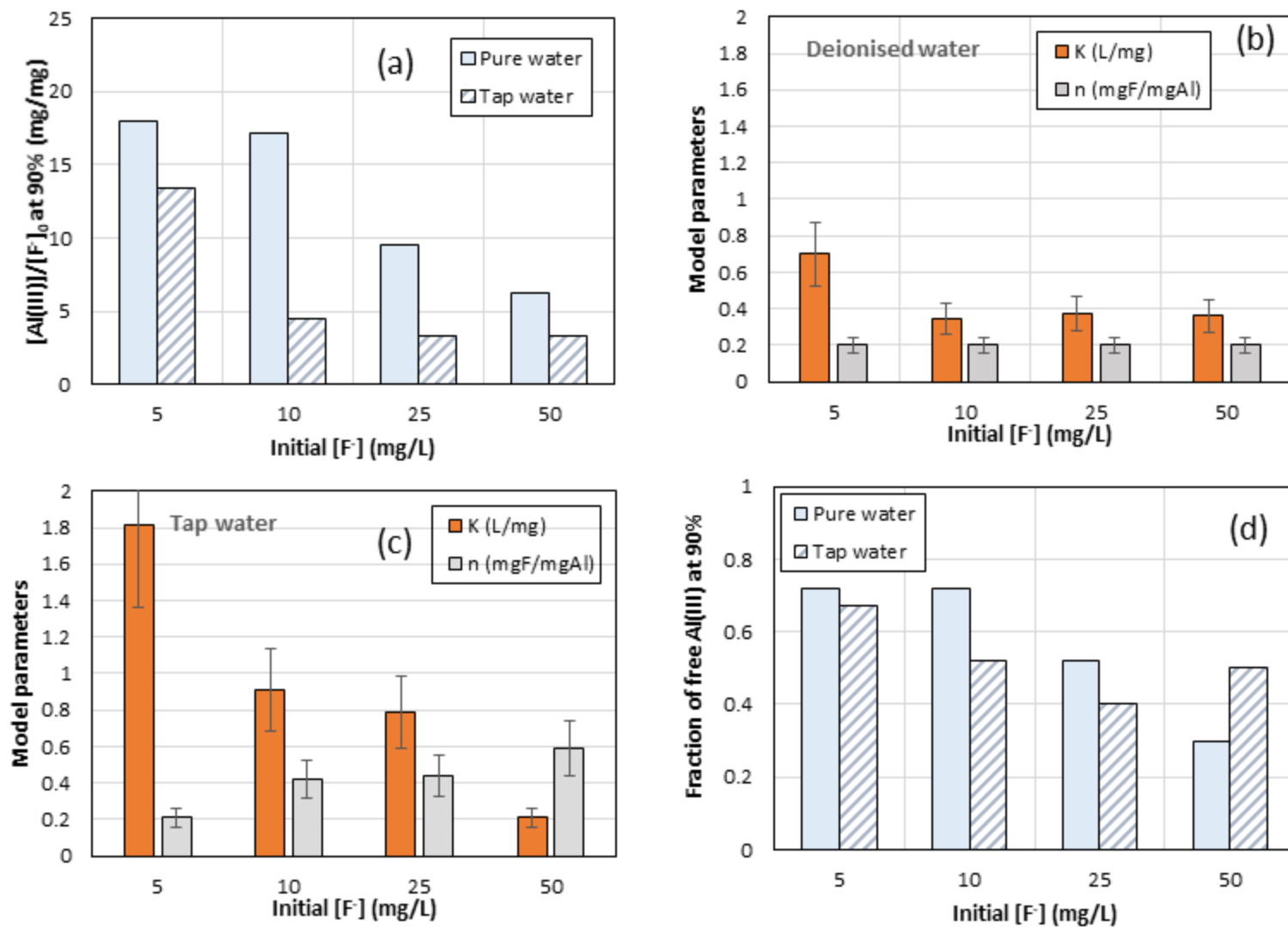


Figure 3



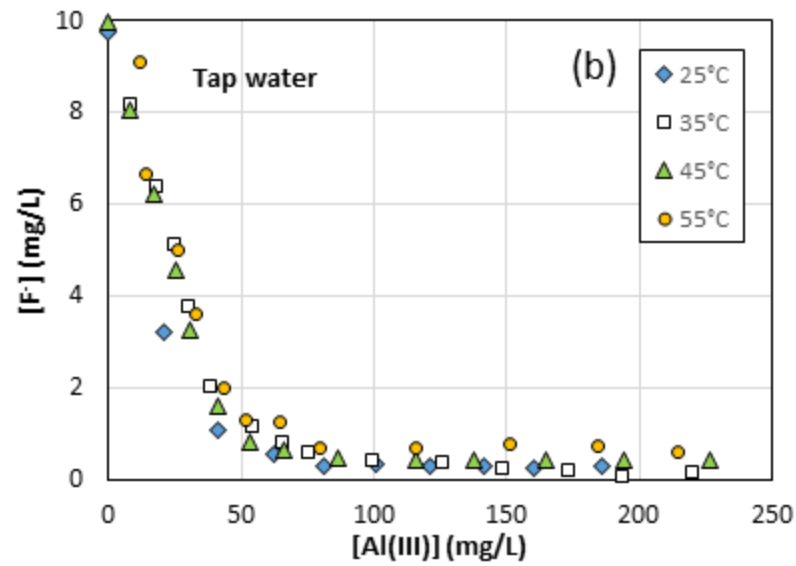
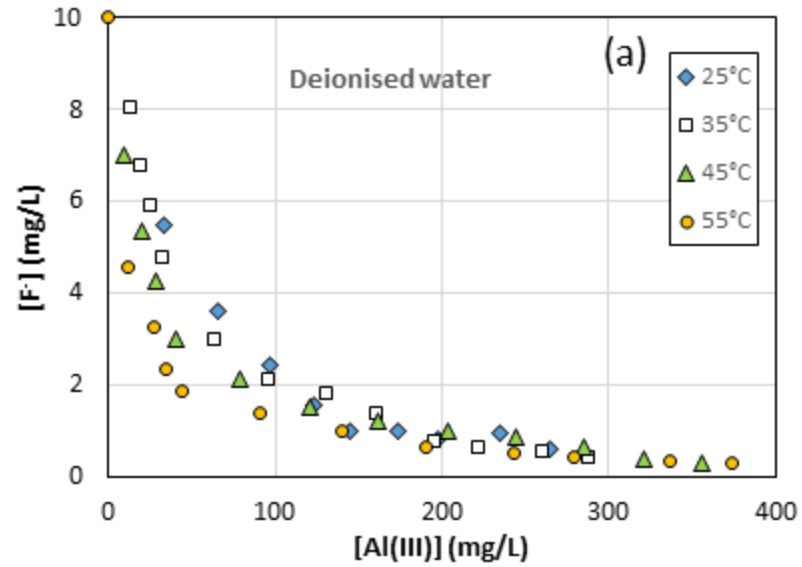
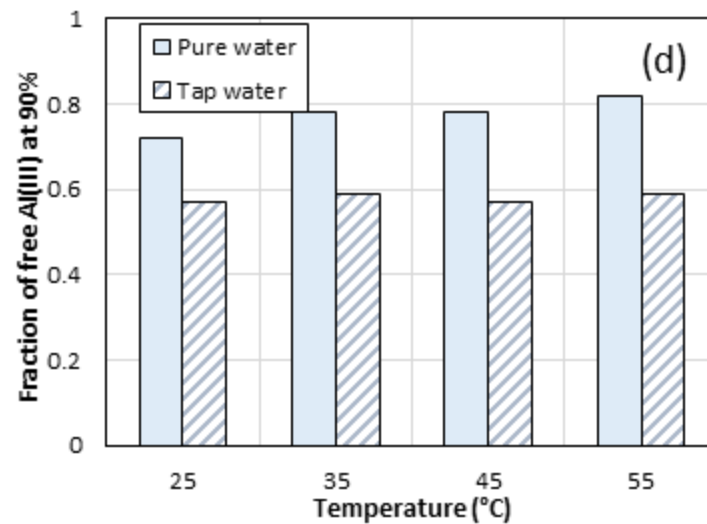
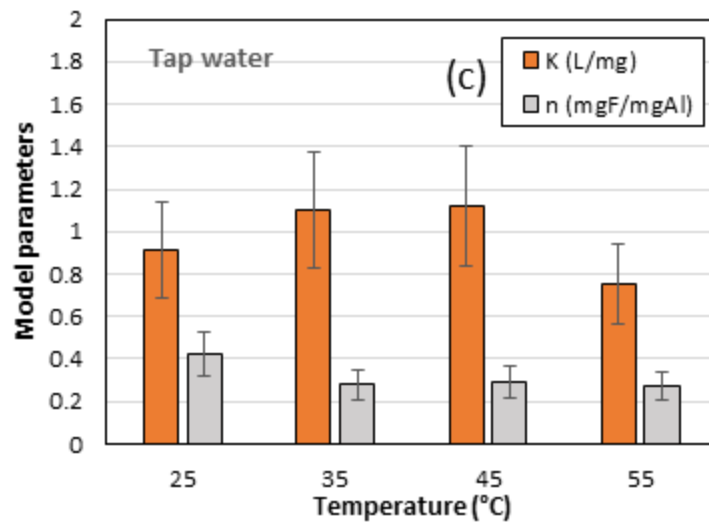
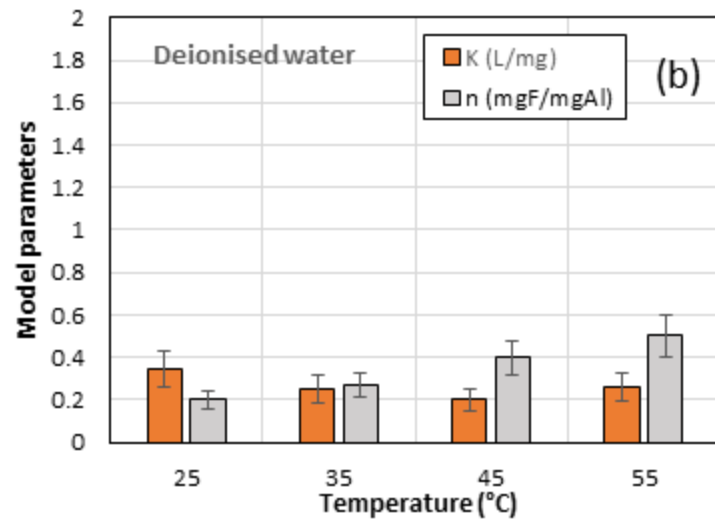
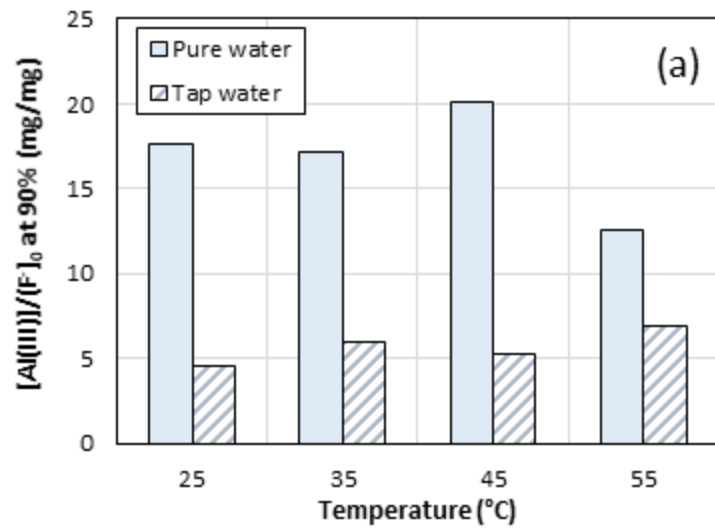


Figure 4



Figure 5



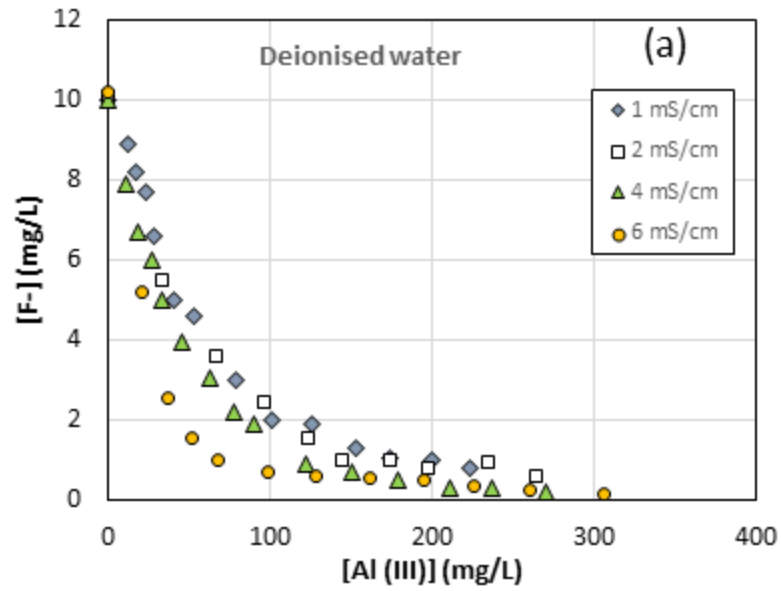


Figure 6

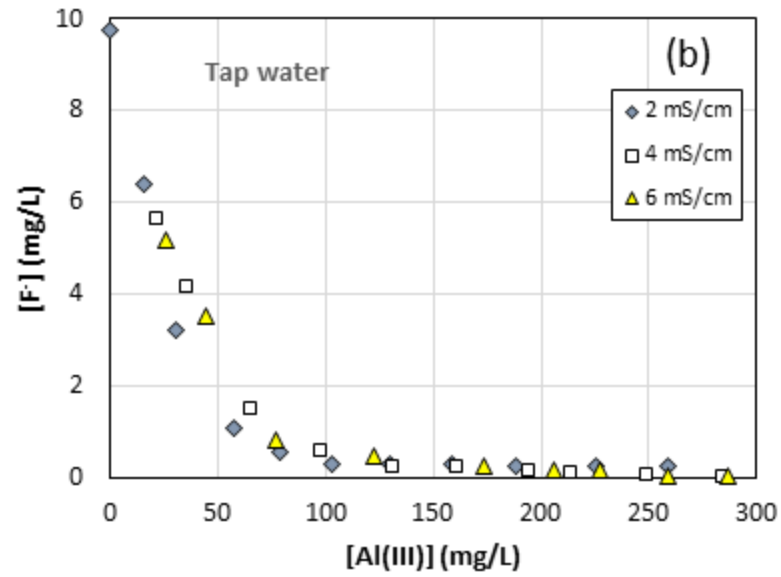
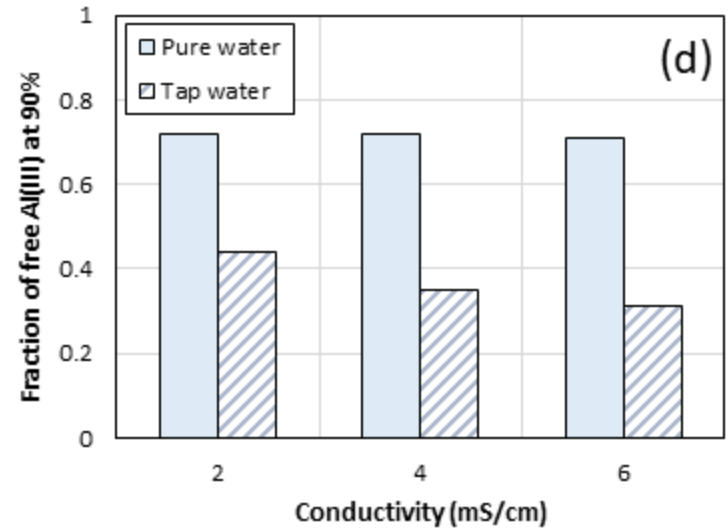
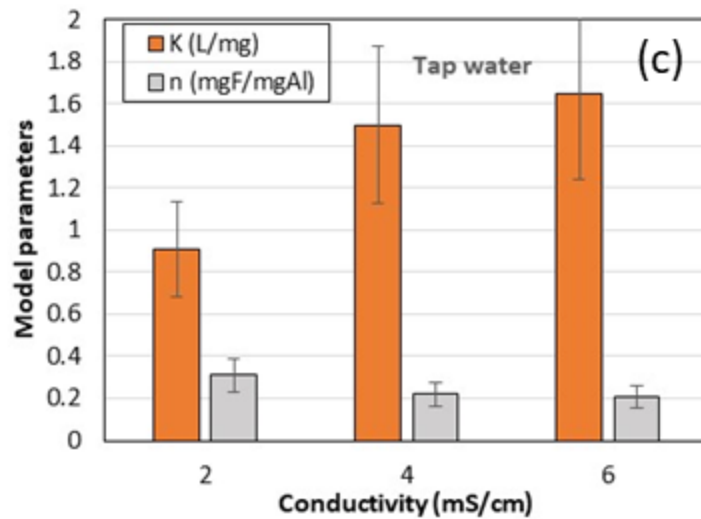
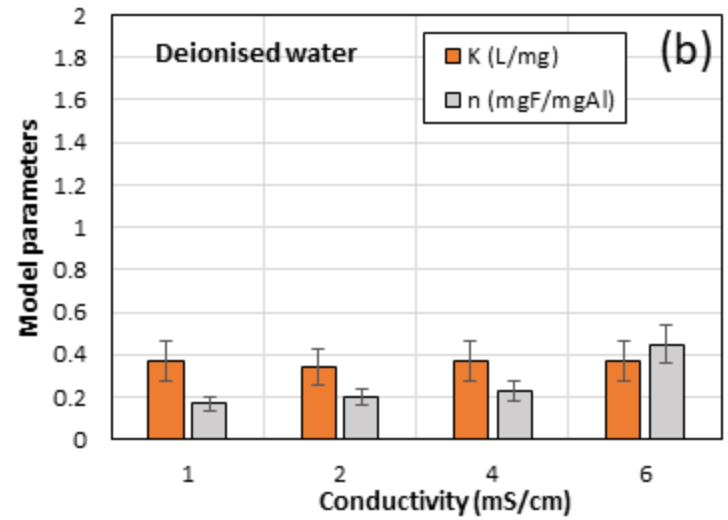
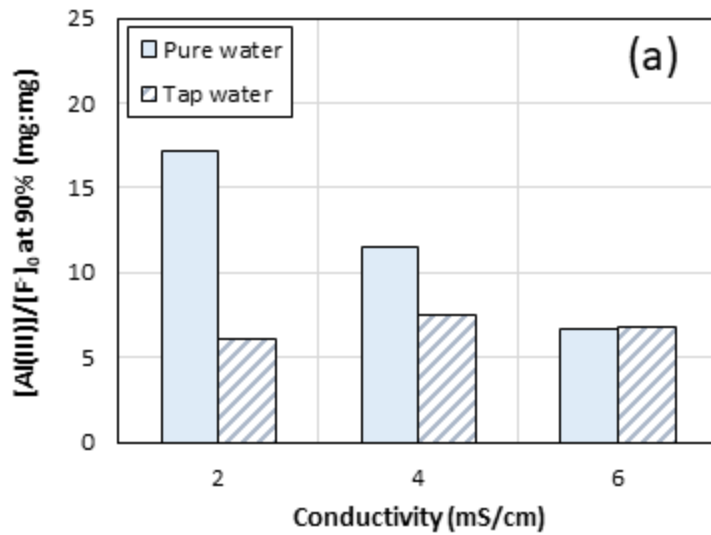


Figure 7



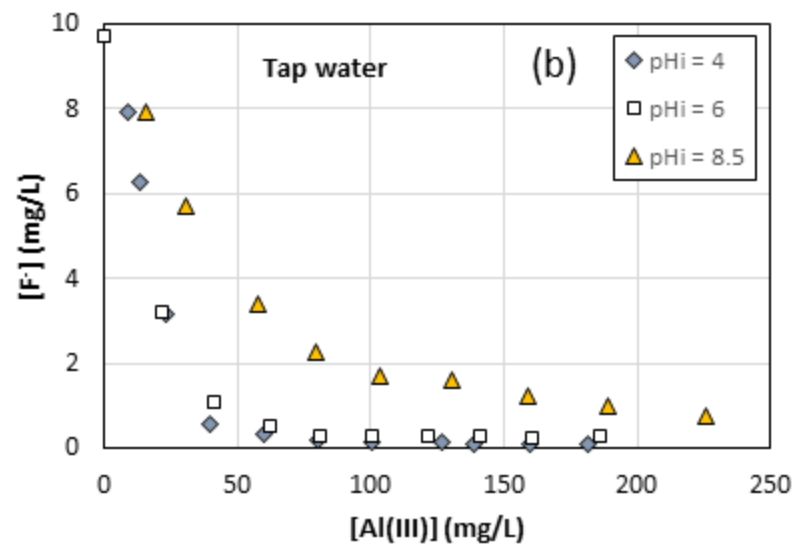
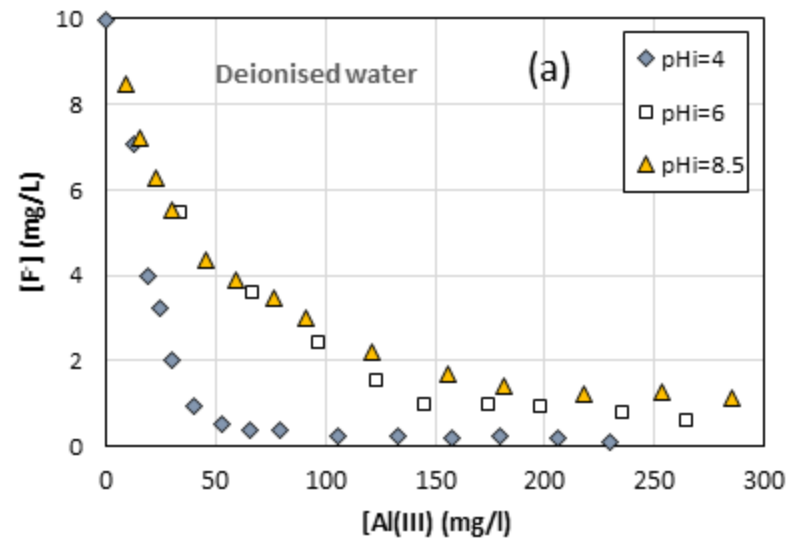


Figure 8

Figure 9

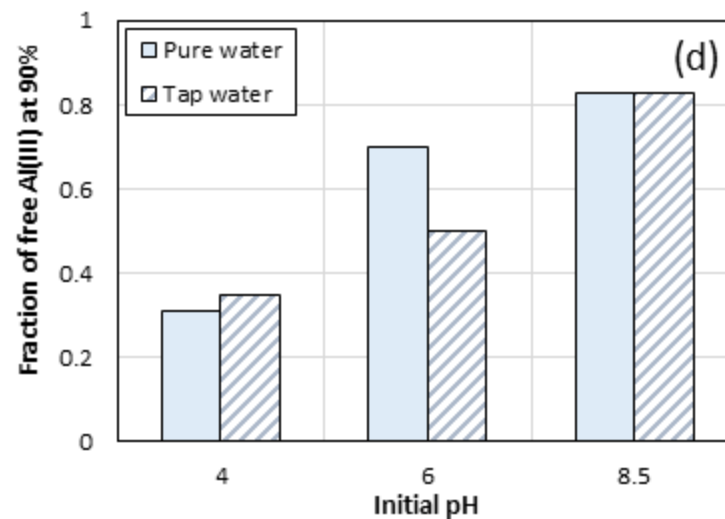
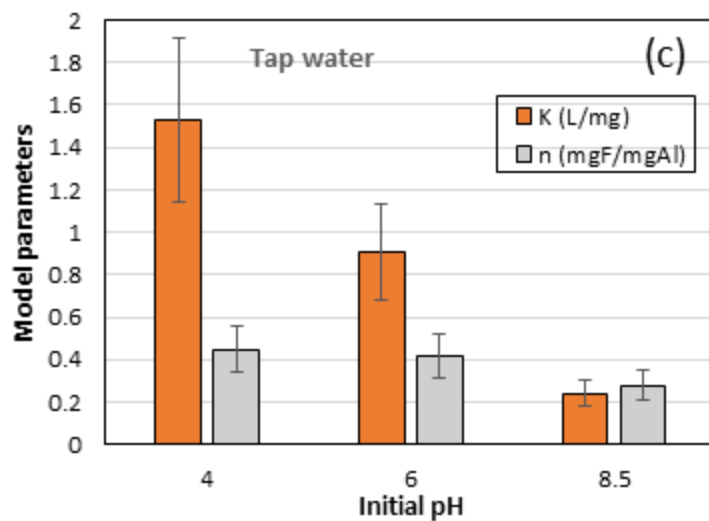
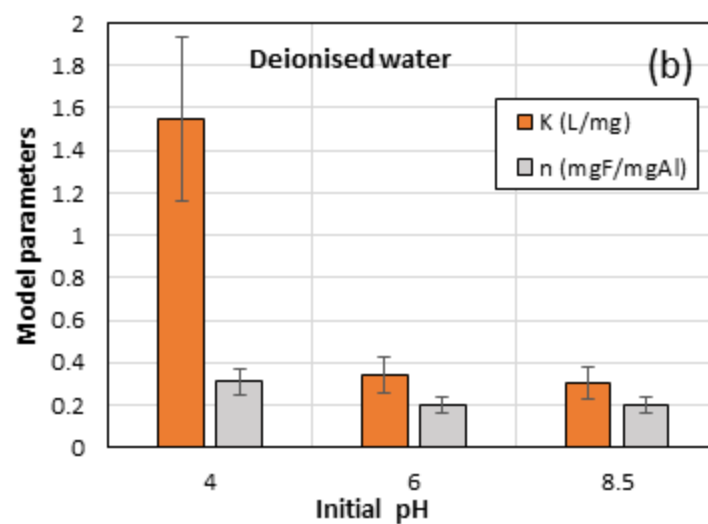
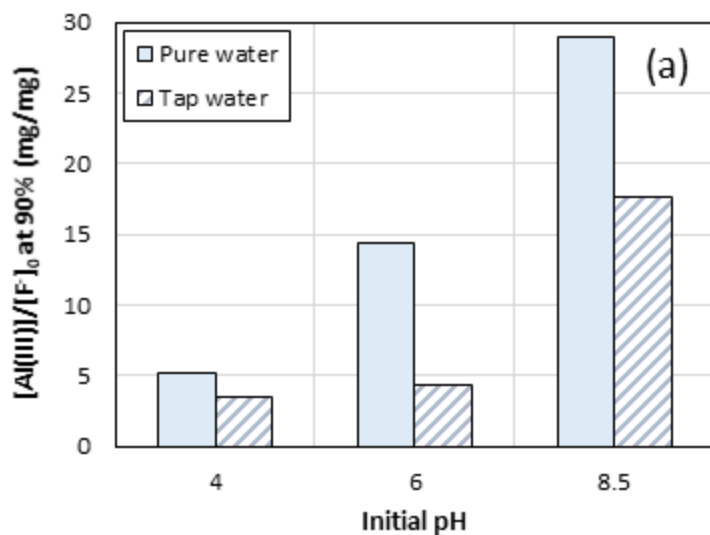


Figure 10

