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Predictive equations for the defluoridation by electrocoagulation technique using bipolar aluminum electrodes in the absence and presence of additives: a multivariate study

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ABSTRACT

The adverse public health problem due to the fluoride that is found in drinking water and waste water is of great concern. In the present work, the effect of different variables on the defluoridation by electrocoagulation (EC) process was studied. The variables were analar and commercial sodium fluoride solutions, different fluoride concentrations, pH of solution, temperature, speed of agitation, electrode spacing, type of comprising water, electrolyte additives (NaCl, KCl, NH_4Cl, and CH_3COONH_4), and mono and bipolar configurations. The present data indicated that the time required to reach the highest % extractions for the different concentrations of fluoride solutions (57.90, 42.30, 29.0, 21.50, 11.60, and 6.44 mg/L) was 5–15 min. Among the studied variables that significantly affected the maximum defluoridation efficiency, the type of comprised water was the only variable that did not pose observable effect. Statistically, a multivariate study was applied to get a set of predictive multiple regression equations, those were under constant and variable conditions of the fluoride removal process. Interestingly, these equations significantly represented the EC defluoridation technique under the studied variables. Due to the high economic value, the low applicable energy, as well as the saving of time that belong to the process of fluoride removal by EC, it is advisable to use the predictive equations for the EC defluoridation of different waters and wastewaters under the same conditions .

Keywords: Sodium fluoride solutions; Defluoridation; Electrocoagulation; Bipolar aluminum electrodes; Multivariate analysis

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1. Introduction

The presence of fluoride in high concentrations in drinking water is a public health problem; consequently, its removal is a very essential process and has been the focus of many studies all over the world [1–6]. If the fluoride concentration increases to more than 4 mg/L in drinking water, skeletal fluorosis and fluorosis deformity in hips, knees, and other joints can be observed [7]. However, the main source of fluoride

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for the human body is usually from the drinking water which covers about 75–90% of the daily intake [8]. Natural and anthropogenic activities are the major sources of fluoride pollution in water ecosystems. Naturally, fluoride becomes available for surface species due to the erosion and the weathering of fluoride-bearing minerals. Industries that result in discharged waste waters, such as the production of semiconductors, manufacturing of aluminum, and processing of glass are some examples of the anthropogenic sources that contribute in fluoride pollution, especially in ground water [9].

Globally, several defluoridation methods were studied. These methods included adsorption [10–12], chemical precipitation [13–19], electrodialysis [17], and electrochemical methods [20,21]. These approaches can be divided in two categories including the precipitation and the sorption methods [21].

Performance of a parallel-plate electrocoagulation (EC) process with aluminum electrodes was investigated by Khatibikamal et al. [18]. This process is used in the removal of fluoride from treated industrial wastewater that has originated from steel industry. The effect of various parameters such as: pH, voltage, hydraulic retention time, and the number of aluminum plates between anode and cathode was studied. EC process was carried out for initial fluoride concentrations 4.0–6.0 mg/L, and 93% of fluoride removal was obtained after 5 min. The kinetic analysis showed that the adsorption system followed the second-order model.

Continuous EC experiments were designed and operated by Emamjomeh and Sivakumar [22]. They investigated the effects of the different parameters including current density, initial fluoride concentration, initial pH, residence time, and the flow rate on the fluoride removal efficiency by the EC process. The highest treatment efficiency was obtained by the largest current input when the flow rate was kept constant. The fluoride removal efficiency increased to 99% at 50 A/m^2 when the flow rate and initial fluoride concentration were kept at 150 mL/min and 10 mg/L, respectively. Both researchers concluded that at a constant flow rate, higher initial fluoride concentrations needed higher current inputs for more treatment. The experimental mass ratio Al^{3+}/F^- was 13–17.5 in the EC when the residual aluminum concentrations in the effluent were <0.2 mg/L. The residual fluoride concentration fluctuated from 10 to 1 mg/L when the total aluminum concentrations were between 120 and 155 mg/L at optimum charge density (60,000–70,000 C/m^2). The experimental results showed a more efficient defluoridation process at final pH 6–8. X-ray diffraction (XRD) analysis of the dried sludge reflected the formation of aluminum fluoride hydroxide complexes $[Al_nF_m(OH)_{3n-m}]$.

Drouiche et al. [13] stated that the quality of the electrocoagulation treatment depended on the amount of coagulant produced. The amount was affected by the applied potential and the electrolysis time. The addition of supporting electrolyte had a positive effect on the removal of fluoride; it also caused a rise in electrical conductivity of the water that lead to less passing of current through the circuit. The XRD, fourier transform infrared spectroscopy analysis, scanning electron microscope, and the energy dispersive X-ray analysis for the sludge, concluded the formation of aluminum fluoride complexes, hydroxide, and/or aluminum oxyhydroxides.

Un et al. [23] investigated an electrochemical reactor with a unique design for defluoridation of water and wastewater using a rotating impeller aluminum cathode and a cylindrical aluminum anode. Various operating parameters, such as the electrode material (aluminum and iron), the current density (0.5–2 mA/cm^2), the duration of electrolysis, the supporting electrolyte dosage (0.01–0.03 M Na_2SO_4), the initial pH (4–8), and the presence of other ions (Ca^{2+}, Mg^{2+}, PO_4^{3-} and SO_4^{2-}), were examined to achieve optimal performance of the process. The experimental results revealed that fluoride removal was enhanced at pH 6, higher current density, and higher EC time when the aluminum electrode was used. The presence of Ca^{2+} and Mg^{2+} ions also enhanced the removal efficiency, while the presence of SO_4^{2-} and PO_4^{3-} ions affected adversely. The fluoride concentration was reduced from the initial value of 5.0–0.12 mg/L. This caused a removal of efficiency 97.6% after 30 min of treatment at the current density of 2 mA/cm^2, pH of 6, and the presence of 0.01 M Na_2SO_4. The required EC time to reach the WHO-recommended fluoride limit (1.2 mg/L) at 0.5 mA/cm^2 was 5 min, with an energy consumption of 0.47 kW h/m^3.

Behbahani et al. [9] employed the response surface methodology as an experimental design tool for the fluoride removal by EC process. The effect of the main operating parameters including, initial pH, initial fluoride concentration, current density, and reaction time of the removal process, along with its relative operating costs by EC was evaluated. The results showed that the efficiency in fluoride removal was severely affected by all the studied parameters except the initial pH, whereas the operating costs were influenced by current density and reaction time. The optimum initial pH, initial fluoride concentration, current density, and reaction time were 7, 25 mg/L, 0.0167 A/cm^2, and 25 min, respectively. This resulted in a defluoridation efficiency of 94.5%.

The present work dealt with the defluoridation by the EC technique in an attempt to get a set of equations which can represent the value of the defluoridation under constant parameters (initial solution volume, speed of agitation, and sometimes number of electrodes), and also under variable parameters (concentration of fluoride at initial and at progress time, time, number of electrodes, pH, temperature of solution, as well as the additive weight).

2. Materials and methods

2.1. Experimental setup

A laboratory bench-scale electrocoagulation flotation (ECF) reactor was designed and constructed to the dimensions shown in Fig. 1. In the electrochemical cell, seven aluminum electrodes (95% purity, product of copper company-Alexandria) with dimensions of 150 mm × 8 mm × 2 mm, in addition to cathode and anode, were connected using a bipolar configuration in the ECF reactor. The electrodes were then dipped in 150 mm of aqueous solution in the Perspex reactor. To attain uniform mixing, stirring was achieved using a magnetic stirrer with its bar placed at the bottom of the reactor. A draining tube was installed at the bottom of the cell, and a sampling valve was fit for drawing samples of treated water at different time (min) intervals. The anode and cathode were connected to a 12 V battery (product of El-Nasr Varta Germany; Alexandria) that provide a DC current. Two avometers (Sunwa, China) were used; one functioned as a voltmeter while the other functioned as an ammeter. A rheostat was connected in the circuit for the adjustment of voltage drop and current density.

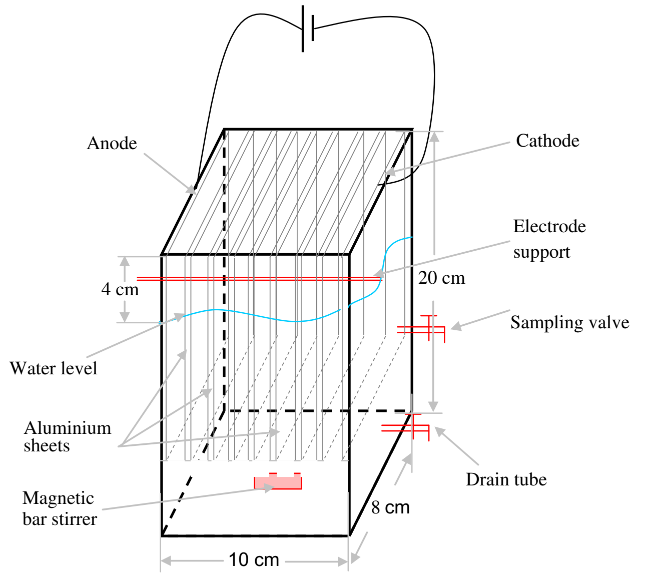

Fig. 1. Schematic diagram of setup.

2.2. Procedure

The 0.5 M stock sodium fluoride solutions (commercial or AR) were prepared using distilled water. The different desired F^- concentration solutions were made by adding proper amount of stock sodium fluoride solution (commercial or AR) into distilled water to reach certain volumes. Each sodium fluoride concentration was added to the aforementioned cell after washing the cell with distilled water. The battery was then connected and the magnetic stirrer was adjusted to the desired speed. Samples were taken at certain time intervals for analysis during the defluoridation process.

2.3. Variables investigated

The effects of different variables on the defluoridation process were studied. These variables included initial sodium fluoride solution concentration (analar or commercial), speed of magnetic stirring, electrode spacing, mono and bipolar configurations, presence of a additives (sodium chloride, potassium chloride, ammonium chloride and ammonium acetate), comprising water of the solution (tap or distilled waters), volume of solution, temperature during the process as well as the initial pH of solution.

2.4. Analysis of fluoride

Fluoride (F^-) concentration was determined following the colorimetric procedure of zirconium alizarin red S (Zr-ARS) using UV/Visible single beam Spectronic 21 D Milton Roy spectrophotometer [24,25]. The concentration of the unknown sample (mg/L) was obtained using the calibration curve in which the standard NaF was of 10 μg F^-/ml. The mean fluoride concentrations (triplicate measurements for each sample) were calculated. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations were determined by EDTA titration in the presence of murexide and eriochrome black T indicators, respectively [26]. Sodium (Na^+) determination was performed by flame atomic emission spectrophotometry. The sulfate (SO_4^{2-}) concentration was estimated using the turbidimetric method by measuring the absorbance of barium sulfate suspension in the presence of the condition reagent (glycerol mixed with concentrated HCl, distilled water, ethyl alcohol, and NaCl) [26]. The sample was diluted to a suitable dilution then was stirred. A spoonful of $BaCl_2$ crystals was added to the diluted sample while it is stirring for 1 min. Some of this solution is poured into the absorption cell, measured the turbidity at 30 s intervals for a minute. The maximum absorption obtained in 4 min intervals was recorded at $\lambda = 420$ nm. The required concentration was determined using a standard curve. Total carbonate (CO_3^{2-}) and silicate concentrations were estimated [27]. Throughout the study, all reagents used were of analytical grade.

3. Results and discussions

3.1. Effect of the initial AR grad fluoride concentrations

The % extraction of the different initial concentrations of AR grad fluoride solutions (57.90, 42.30, 29.0, 21.50, 11.60, and 6.44 mg/L) are 37.3, 52.9, 58.2, 64.3, 83.4, and 100%, respectively (Fig. 2). The highest initial concentration ($C_i = 57.9$ mg/L) drops rapidly within 5 min and then slowly increases once more (Fig. 2). Obviously, the rate of the fluoride removal increases when the C_i decreases. This proves the rapid defluoridation that takes place at the beginning of the process due to the concentration's driving force. At the beginning, the aluminum sheets are not able to dissolve at their anodic sides rapidly, therefore, defluoridation slowdown and become constant. In some cases, it increases after about 30 min especially, in case of a 57.9 mg/L. However, this lowering in the removal's efficiency can be explained by the consumption of alkalinity and the decrease of pH in the first 15 min by coagulant precursors and H^+ produced during the reactions [18,23]. Additionally, the defluoridation depletion indicates that the sampling port is not far from the cleaning port at the cell bottom. Accordingly, some of the colloidal precipitate may be gathered during the sampling procedure. The same observation was recorded previously, and it was accompanied with the oxidation of the aluminum electrodes that lead to the passivation and oxygen evolution at the electrodes [28]. It was also reported that capacity of flocs increased when the initial F^- concentration went up. That improved the chemical effect by increasing the fluoride concentration in bulk solution [29]. Also, Zhu et al. [29] related the increase in the efficiency of at the beginning of the process, to the removal by the aluminum electrodes. This procedure came along side the adsorption by hydroxide aluminum flocs, which gave a secondary effect. A similar result is observed in this study. The initial rates, however, increase with the increase in the initial concentrations (Fig. 2). Interestingly, the solution of fluoride concentration (6.44 mg/L) shows a complete removal of fluoride within 15 min. Generally, data indicate that the time required to reach an almost maximum extraction is almost in the thereabouts of 5–15 min (Fig. 2). This time range for the EC process was identified by previous studies [18,28].

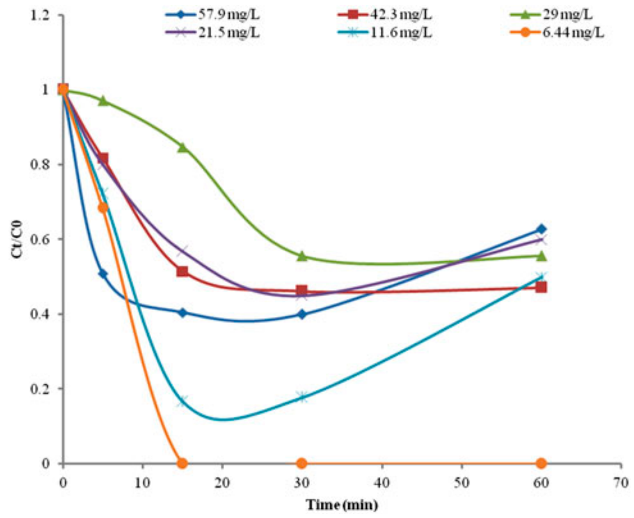

Fig. 2. Effect of initial concentration of fluoride in different AR grade NaF solutions on rate of defluoridation, $C_i = 57.9$–6.44 mg/L, volume of solution = 1 L, seven bipolar electrodes, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

3.2. Effect of the stirring speed

Fig. 3 shows the effect of the speed of agitation (100, 300, and 500 rpm) on the rate of the defluoridation procedure. The calculated % extractions of the stirring speeds 100, 300, and 500 rpm are 48.3, 91.08, and 30.3, respectively. It is clear that the medium speed of agitation (300 rpm) gives the highest fluoride removal followed by the lowest speed, then the highest speed. This observation can be explained by the lack of efficient mixing which is responsible for better contact between F^- and different aluminum hydroxides complexes. Those are formed in the vicinity of the electrodes to achieve defluoridation process. At the high speed of stirring, inefficient defluoridation takes place. That is due to the lack of the fluoride concentration's driving force which attributes to less liable contact between F^- and different aluminum hydroxides complexes formed in the vicinity of the electrodes [30]. This possibly refers to the destruction of fluoro-aluminum complexes on which F^- is adsorbed. This will be a result of the high degree of turbulence that will lead to separation of boundary layer and vortex

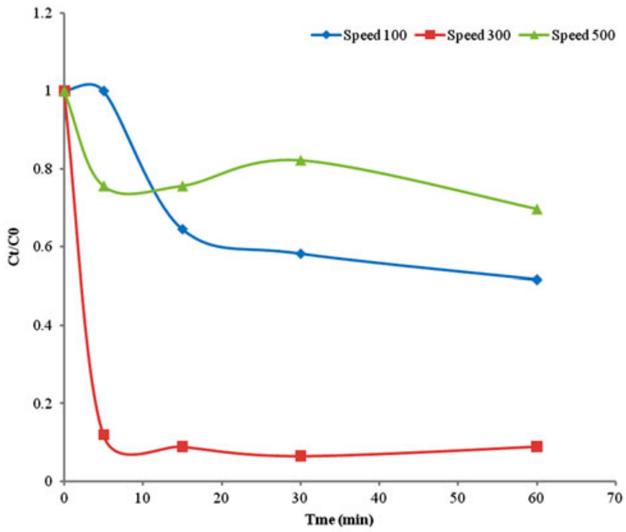

Fig. 3. Effect of speed of stirring on rate of defluoridation of NaF solution (AR grade), $C_i = 12.76$ mg/L, volume of solution = 1 L, seven bipolar electrodes, current = 250 mA, voltage = 10.5 V.

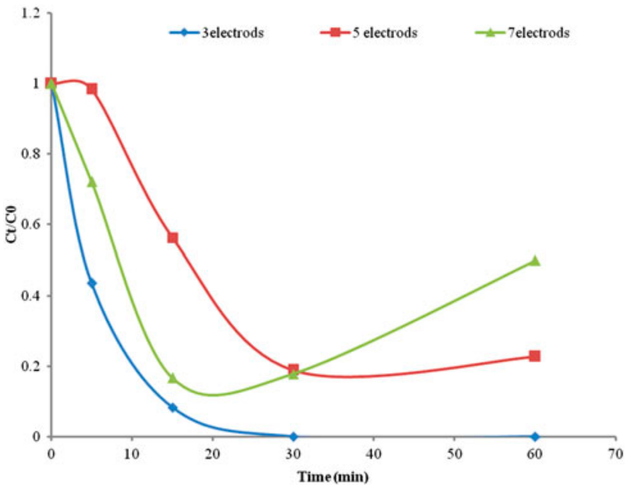

Fig. 4. Effect of number of electrodes on rate of defluoridation of NaF solution (AR grade), $C_i = 13.43$ mg/L, volume of solution = 1 L, seven bipolar electrodes, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

formation [28,31]. Additionally, at high speed, the hydrogen bubbles blown in cathode compartment induce high resistance to float the fluoro-aluminum complexes which limit the dissolution of aluminum anode, and accordingly decrease the complex formation. On the other hand, no vortex is formed at lower speeds, and the same time, poor mixing is attained.

3.3. Effect of the electrode numbers

Fig. 4 shows the effect of distance between electrodes on the rate of defluoridation. Clearly, the highest rate of defluoridation is recorded in the application case of 3 electrodes followed by 5 then 7 electrodes, those that are inserted between the anode and the cathode with % extractions of 100, 77.3, and 50%, respectively. Although aluminum anode's dissolution of 7 electrodes is less liable than of 5 electrodes, there is a higher extraction observed in the case of the 5 electrodes. This may be attributed to the larger aluminum anode dissolution obtained by 5 electrodes. This is relatively sufficient to the C_i of fluoride ion to attain a higher extraction. It is also observed that, the lowering of defluoridation rate with the increasing of the electrode numbering (decreasing the inter-electrode distance), is due to the formation of the gas in the cathode compartment which induces the great floating phenomenon of the fluoro-aluminum complexes. This latter operation permits the further dissolution of the aluminum anode, and increases the complex formation at the metal–solution interface [32]. Therefore, the efficient contact between F^- and different aluminum hydroxides complexes that are formed in the vicinity of the electrodes, achieve higher extraction. On the other hand, the resistance to float the formed complexes increases at a small inter-electrode distance. This limits both the anodic dissolution and the complex formation.

3.4. Effect of the different additives

Fig. 5 shows the effect of different doses of the NaCl that are added to the solution bath at the rate of defluoridation. The highest defluoridation rate is obtained in the presence of 0.5, 0, 1, and 1.5 g NaCl with % extractions of 100, 91.1, 84.3, and 51.2, respectively. Obviously, the defluoridation rate increases with the increasing of the NaCl dosage to a certain limit above which the performance of the defluoridation process is reduced. This proves that the defluoridation takes place rapidly due to the ionic conductivity of the solution which is enhanced with the different doses of NaCl. The dose of NaCl acts as a supportive electrolyte. Chloride ions of NaCl increase the solution's conductivity by the rapid decreasing of the cell voltage due to the ohmic potential drop in the solution, which facilitate the passage of the electrical current [33]. Also, chloride ions decrease the passivity of the electrodes by removing the formed passivating oxide layer on electrode surface. Those permit further aluminum anode dissolution due to its catalytic action (corrosion pitting

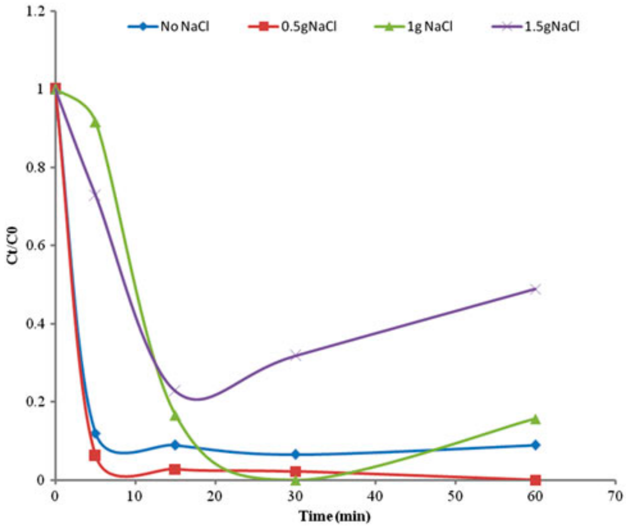

Fig. 5. Effect of amount of NaCl added as electrolyte on rate of defluoridation of NaF solution (AR grade), $C_i = 12.24$ mg/L, volume of solution = 1 L, seven bipolar electrodes, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

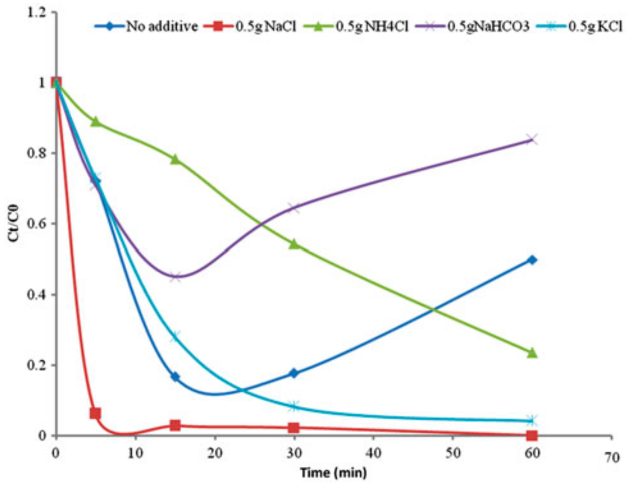

Fig. 6. Effect of using different additives rather than NaCl added as electrolyte on rate of defluoridation of NaF solution (AR grade), $C_i = 11.7$ mg/L, volume of solution = 1 L, seven bipolar electrodes, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

phenomenon at the EC electrode [32]). Therefore, the fluoride removal can be improved by the availability of aluminum hydroxide in the solution on which F^- can be adsorbed [34]. It seems that the fluoride removal rate, after using different doses of NaCl (0, 0.5, and 1 g) is higher than 1.5 g. This can be attributed to the decrease in the speed of the ions as a result of the retardation force of the inter-ionic attraction, and the competitive adsorption effect between Cl^- and F^-; especially in high sodium chloride dosage. Therefore, the crowding between ions and the action of Cl^- increases the conductivity and consequently, increases the cell resistance of the solution [13,21]. Also, these counters can balance the corrosion pitting phenomenon effect. Accordingly, in this case, the hydrogen bubbles become less able to float the formed fluoro-aluminum complexes and both further anodic dissolution and complex formation, as well as the decrease in the area of the anodic part due to the lack of floatation is limited [18,34,35].

The comparative investigation of some additives, including sodium chloride (NaCl, NH_4Cl, CH_3COONH_4, and KCl), is done in order to determine the effect of the electrolyte nature on fluoride removal (Fig. 6). Generally, the competitive adsorption between the anions and F^- reduce the fluoride removal efficiency, except in the case of Cl^- as discussed before [21,35,36]. Fig. 6 shows that increasing the defluoridation rate takes the following order 0.5 g NaCl > 0.5 g KCl > 0.5 g NH_4Cl > no additive > 0.5 g ammonium acetate with % extractions of 100, 95.8, 76.4, 50.1, and 16.15, respectively. Although potassium chloride and ammonium chloride salts contain the same common anion part (Cl^-), they give different fluoride removal results. This observation reflects the effect of the cation part on the defluoridation process. However, K^+, is smaller than NH_4^+, and therefore, K^+ has higher ionic mobility than NH_4^+. Accordingly, the ionic conductivity in the presence of KCl is higher than that of NH_4Cl, and the first salt can easily permit the current to pass through the bulk solution between electrodes [37,38].

Interestingly, among the additives, ammonium acetate is found to have the lowest defluoridation rate. That is due to three reasons: firstly, due to the competitive adsorption effect between CH_3COO^- and F^-; secondly, it decreases the solutions' conductivity since it is a weak electrolyte (is not completely ionized), and finally, the acetate ion has the greatest size. Conclusively, NaCl additive can be considered as the most optimum electrolyte; however, it has achieved complete defluoridation, and also has been found to be available in nature with a reasonable cost.

3.5. *Effect of solution volume*

Fig. 7 shows the effect of the volume of solution on the rate of defluoridation. The figure displays that a smaller volume of solution (1 L) has given a better extraction than the larger one (1.25 L). However, in the larger volume (1.25 L), the speed of agitation is less

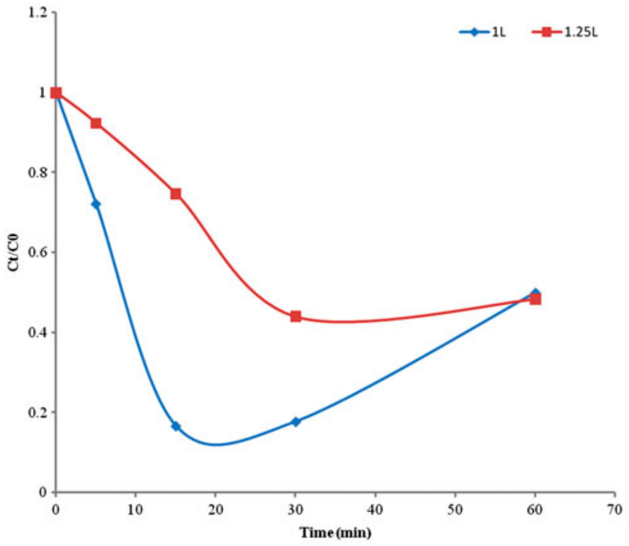

Fig. 7. Effect of volume of solution on rate of defluoridation of NaF solution (AR grade), $C_i = 11.9$ mg/L, seven bipolar electrodes, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

able to achieve efficient mixing, and to contact between F^- and different formed aluminum hydroxides complexes in the whole vicinity of the electrodes. Also, the higher volume may have lead to the destruction and the explosion of fluoro-aluminum complexes where F^- could have been adsorbed. It also makes the hydrogen bubbles less liable to achieve excellent flotation of destructed precipitate.

3.6. Effect of initial pH

The pH of a solution is one of the most important parameters that direct the removal of fluoride in the EC procedure [39]. It is difficult to control the pH of the solution during the defluoridation by EC process; however, the pH values changed during its internal reactions [37,40]. Furthermore, controlling the initial pH in the EC system is not possible due to the change in the final pH. It was stated that the final pH and the residual fluoride solutions of the EC process remained within a pH of 4–8 due to the buffering capacity of aluminum hydroxide [20].

Fig. 8 shows the effect of the initial pH of solution (1, 4, and 6) on the rate of the defluoridation process. Obviously, the rate of defluoridation exhibits a descending order pH 6 > pH 4 > pH 1 with % extractions of 83.4, 53.5, and 29.1, respectively. Clearly, the highest initial (pH 6; for the original solution) gives better extraction than the lowest one (pH 1). The highest pH, however, is closer to the value (pH 7.6) that corresponds to the formation of the strong aluminum complexes [22]. Generally, as previously discussed, the presence of H^+ increases the conductivity of the solution due to its very small size and its high ionic mobility. Accordingly, at low pH, low fluoride extraction is attained because of the retarding force among the great number of hydrogen ions, and the presented ions in the bulk solution. The pH is adjusted at the beginning of the defluoridation process by H_2SO_4 to reach pH 1 and pH 4 (Fig. 8). It is observed that the defluoridation efficiency decreases with the increase of H_2SO_4's concentration (i.e., increase of H^+). This negative effect of SO_4^{2-} on the defluoridation process is attributed to the inhibition of the localized corrosion of aluminum electrodes, according to the competition effect by lyotropic series of SO_4^{2-} and F^- for Al^{3+} [32,35]. However, the increase of the concentration of sulfate ion, which has a strong affinity with Al^{3+}, decreases the adsorption capacity of fluoride onto hydrous alumina [35]. Thus, as the SO_4^{2-} concentration increases, the ion exchange reaction shifts to the right side and causes further increase in the effluent of fluoride concentration [10]. So, SO_4^{2-} leads the cell resistance of the solution to increase and causes inadequate fluoride removal.

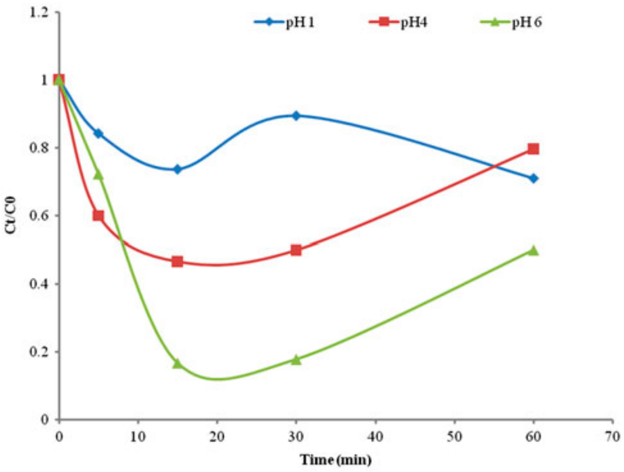

Fig. 8. Effect of pH on rate of defluoridation of NaF solution (AR grade), $C_i = 11.53$ mg/L, volume of solution = 1 L, seven bipolar electrodes, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

The mechanism of the removal of the fluoride process was confirmed as a competitive adsorption between fluoride and hydroxyl ions at pH range 6–7.5, where strong fluoro-aluminum complexes such as: AlF_3, $AlOHF_3^-$ and $Al(OH)_2F_2^-$ were present. These complexes induced an effective aluminum complexation by fluoride [22,41]. Also, it was documented that the initial pH and the final pH of the solution were converged to the value of 7.6 due to the blowing of the hydrogen bubbles at the cathode compartment [41]. Accordingly, the time required for the low pH (pH 1) to reach pH 7.6 (best extraction) is longer than that for pH 4. Therefore, pH 6 is the optimum in this study due to three reasons: (1) very strong aluminum complexes are present and that will cause the highest fluoride extraction. (2) There is no need to use acid or base to adjust the pH, since it is already the original pH of the solution. (3) Finally, its final pH value is the most closest to 7, in comparison to the studied lower initial pH values, that is, the readjustment of pH of solution is not required [10].

3.7. Effect of the electrode configurations

Fig. 9 shows the effect of electrode configuration (monopolar and bipolar) on the rate of defluoridation. It is obvious that bipolar configuration gives a higher defluoridation rate than the monopolar configuration. Monopolar configuration suffers a passivation, since the reversible polarity of it prevents the anodic passivation [21]. However, in the monopolar configuration, the two faces of the aluminum sheet acts as anodes so aluminum dissolution takes place on the two faces. On the other hand, the bipolar configuration of one face of the sheets only acts as an anode. Thus, the anode's over potential is increased and aluminum dissolution at the initial stage is limited. Consequently, the solution's conductivity in the monopolar system decreases. The thickness of the oxide film layer on one sheet in monopolar system is larger than that found in the bipolar system. Accordingly, its cell resistance increases due to the difficulty encountered in the electrical current which passes through the solution. Additionally, in the monopolar configuration, the floated layer of aluminum fluoride has certain shape with a thickness of zero at the anode's surface, and the maximum one at the cathode's surface. In the defluoridation process, the hydro-fluoro-aluminum complexes are obtained in two forms (negatively and positively charged complexes). The negatively charged complexes move toward the anode, which suffers from passivation, and high resistance when encountered by the vicinity of anodes. In contrast, at the cathode, most of the defluoridation takes place, and accordingly, the thickness of floated layer zero is observed at the anode. On the other hand, the positively charged complexes are also attracted to the adjacent area of cathode. Moreover, the liberated hydroxide ions near the cathode neutralize the positively charged complexes to form colloid flocs where fluoride ions are adsorbed. Accordingly, no resistance is encountered in the cathodes' compartments when compare to those of the anodes. So the defluoridation process mainly occurred in the vicinity of cathodes, and consequently, the thickness of floated layer is maximized on the cathode's surface.

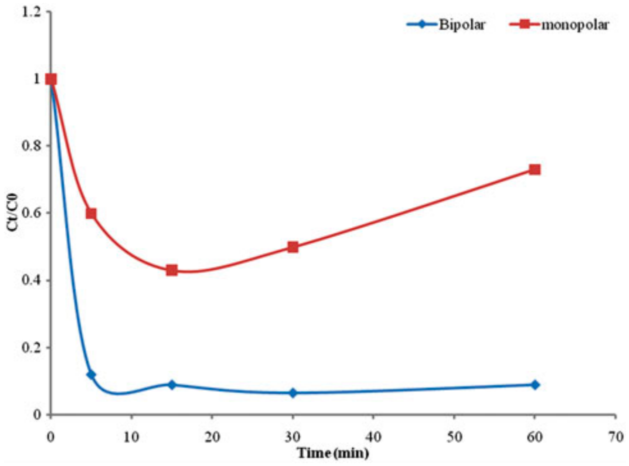

Fig. 9. Effect of electrode configurations on rate of defluoridation of NaF solution (AR grade), $C_i = 11.5$ mg/L, volume of solution = 1 L, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

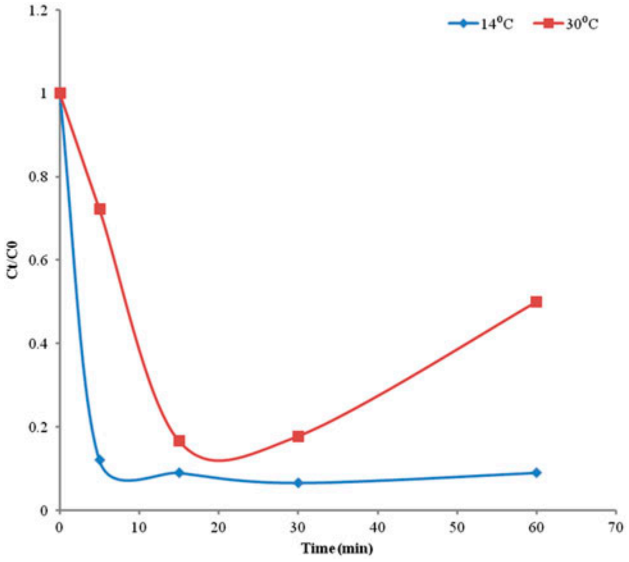

Fig. 10. Effect of temperature on rate of defluoridation of NaF solution (AR grade), $C_i = 11.9$ mg/L, volume of solution = 1 L, seven bipolar electrodes, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

3.8. Effect of the temperature

Fig. 10 demonstrates the effect of temperature on the defluoridation process at 14 and 30°C. The initial rate of defluoridation decreases with the increasing of temperature. The fluoride concentration drops rapidly especially at the lowest temperature. The defluoridation process, however, possesses a rapid concentration driving force at low temperatures. While at high temperatures, lower fluoride removal is obtained by desorption of fluoride ions, and the destruction of the fluoro-aluminum complexes [21]. Therefore, it is recommended to work at the ambient temperature for defluorination by the EC process using aluminum electrodes [32].

3.9. Effect of the comprising water purity used in the preparation of NaF solution

The effects of comprising water (distilled and tap (tap water characteristics, Table 1)) that is used in the preparation of NaF solution (6.4 and 4.0 mg/L) at the rate of defluoridation is studied (Fig. 11). It seems that rate of defluoridation is faster when distilled water is used than when tap water is used. The complete removal of fluoride from both kinds of water under similar conditions is obtained within 15 and 30 min, respectively. However, the difference in the fluoride removal in the two composite types of waters is attributed to the confliction between F^- and other anions in tap water during the adsorption process on aluminum hydroxide, and the reduction in the solution conductivity as discussed before. Interestingly, distilled water can be replaced by tape water since it results in complete removal within 30 min. It is also preferable to be done at the industrial field for its low cost and minimum consumption of time and energy.

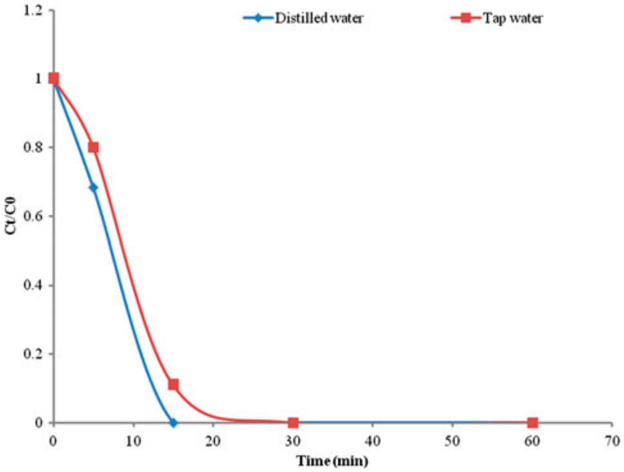

Fig. 11. Effect of purity of water used to prepare NaF solution on rate of defluoridation of NaF solution (AR grade), $C_i = 5.23$ mg/L, volume of solution = 1 L, seven bipolar electrodes, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

3.10. Effect of the NaF purity

Fig. 12 reflects the effect of purity of sodium fluoride (AR and commercial) solutions on the defluoridation rate. Clearly, AR solution gives a higher fluoride removal rate than commercial one. The main chemical composition of sodium fluoride commercial grade solid is 53.4% F^-, 37.2% Na^+, 3.7% Ca^{2+}, 4.7% Mg^{2+}, and 0.6% CO_3^{2-}. The initial defluoridation rate of commercial solution is lower than the AR solution. This is attributed to the competitive adsorption effect among the constituent anions in the commercial solution and F^- [21]. Furthermore, this competitive adsorption increases the resistance and decreases the opportunity for the reaction of F^- and Al^{3+} to take place. This, therefore, decreases the formation of fluoro-complexes. In contrast, Ca^{2+} is widely used for high removal of

Table 1
Tap water characteristics according to "Holding company for water and waste water, Alexandria Water Company, Siouf water treatment"

Ions	Concentration (ppm)	Metals	Concentration (ppm)	Physical properties	
Ca^{2+}	41.6832	Al	0.411	Temperature	26°C
Mg^{2+}	16.53964	Fe	0.001	pH	7.27
Na^+	76.949	F^-	0.452	Turbidity	0.9
CO_3^{2-}	104.4	PO_4^{3-}	0.031		
SO_4^{2-}	80.132	NO_2^-	0.002		
Cl^-	66	Mn	0.001		
NO_3^-	12.102	Ammonia free	0.04		
SiO_2	1.720	Ammonia albuminoid	0.05		
		Abs. O_2 from $KMnO_4$ at 37°C	0.36		

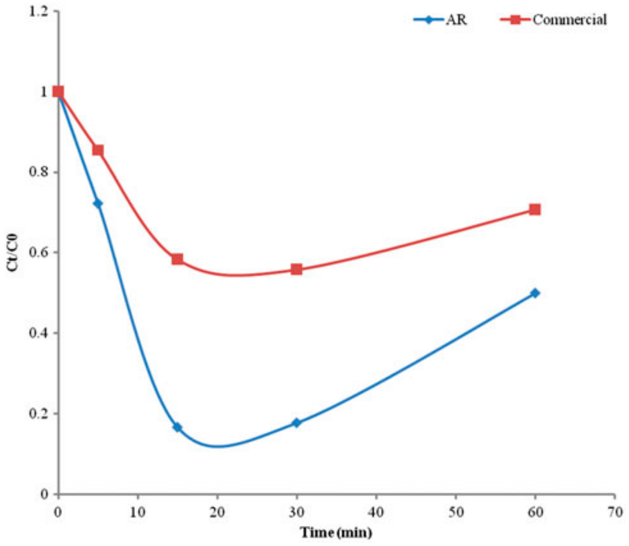

Fig. 12. Effect of purity of NaF solution on rate of defluoridation of NaF solution, $C_i = 13.02$ mg/L, volume of solution = 1 L, seven bipolar electrodes, speed of stirring = 300 rpm, current = 250 mA, voltage = 10.5 V.

fluoride due to the formation of CaF_2. The % extractions of the removal of fluoride from AR and commercial solutions within 30 min are 83.4 and 44.3, respectively.

3.11. The predictive equations for the defluoridation process in absence and in the presence of additive (NaCl)

The equations for the fluoride removal by the EC technique using bipolar aluminum electrodes in the absence and in the presence of additive (NaCl) are evaluated by multivariate analysis (multiple regression). Multiple regression equations are calculated by the program of STATISTICA version 5. The value of fluoride removal (C_t/C_o) can be calculated from different predictive multiple equations concerning the effect of some parameters (Table 2). These equations represent the value of defluoridation by EC technique under constant parameters (current, voltage, initial solution volume, speed of agitation, and sometimes number of electrodes) and variable parameters (concentration of fluoride at initial and at progress time, time, number of electrodes, pH and temperature of solution as well as the additive weight). The regression constant (R) proves that the removal of fluoride can be calculated from these equations at any time. This can be done by applying the values of the independent parameters in the equations with high significant concentrations; these resemble the experimental removal values.

4. Conclusions

The present work explored the simplicity and effectiveness of electrocoagulation defluoridation technique. The effect of different variables (analar and commercial sodium fluoride solutions, different fluoride concentrations, pH of solution, temperature, speed of agitation, electrode spacing, volume of solvent, type of comprising water, electrolyte additives (NaCl, KCl, NH_4Cl, and CH_3COONH_4), and mono and bipolar configurations on the defluoridation method were evaluated. The experimental results showed complete fluoride removal from 6.44 mg/L analar sodium fluoride solution within 15 min. It was also noticed that the different concentrations of analar NaF solutions gave higher percentage extractions than those of similar contents of commercial NaF solutions. On the other hand, the high initial concentrations of NaF solutions showed faster initial rate of defluoridation. The present results reflected that the defluoridation efficiency increased with the increase of the distance between electrodes. To improve the performance of the process, different electrolytes (NaCl, KCl, NH_4Cl, and CH_3COONH_4) were used. The competitive adsorption between the anions and F reduced the fluoride removal efficiency except for Cl^-. Thus, it was found that NaCl was the only additive that led to the excellent extraction. However, the fluoride removal rate increased with the increase of the NaCl weight to reach a maximum definite value. Then, it decreased with the further addition of sodium chloride. 0.5 g was the optimum minimum weight of NaCl which led to complete defluoridation of the solution that contained 10 mg F^-/L. Additionally, bipolar configuration gave better rates of fluoride removal than that of the monopolar, which suffered from the problem of passivation. The medium speed of agitation (300 rpm) was the best speed for fluoride removal. Moreover, the defluoridation efficiency decreased with the increase in temperature. The preferable pH used for the optimum fluoride removal was 6. The presented data indicated that the defluoridation efficiency was not affected by the comprised water type of water used (tap or distilled). The usage of multivariate analysis could help in the prediction of the preferable conditions which can be used in the fluoride removal without consuming time. Accordingly, this technique could be reasonably applied in different fields including treatment of drinking water and industrial wastes due to its low cost, fast progress, low effort, as well as its low used energy. In the future, the usage of the multivariate analysis for the defluoridation can be extended to further work using other variables to be applied in each industrial field.

Table 2
The predictive equations for the defluoridation by EC technique using bipolar aluminum electrodes in the absence and presence of additive (NaCl)

Effective parameter	Constant parameters	Equations	*R*
Time (min)	Speed, initial volume, 7 electrodes	$C_t/C_o = 1.25 - \mathbf{0.34\ Time} + \mathbf{0.82}\ \boldsymbol{C_t} - \mathbf{0.55}\ \boldsymbol{C_o} - 0.14\ \mathbf{Solvent\ volume} - \mathbf{0.31}\ \mathrm{Temperature}$	0.87214714
pH	Speed, initial volume, 7 electrodes	$C_t/C_o = 0.09 - 0.02\ \mathrm{Time} + \mathbf{0.97\ C_t} - \mathbf{0.09\ pH}$	0.99944084
Number of electrodes	Speed, initial volume	$C_t/C_o = 1.36 - 0.14\ \mathrm{Time} + \mathbf{1.30}\ \boldsymbol{C_t} - \mathbf{1.10}\ \boldsymbol{C_o} - 0.22\ \mathrm{Temperature} + 0.14\ \mathrm{Electrode\ number}$	0.90306232
Additive NaCl (g)	Speed, initial volume, 7 electrodes	$C_t/C_o = 0.25 + 0.00\ \mathrm{Time} + \mathbf{0.99}\ \boldsymbol{C_t} - 0.04\,C_o - 0.07\ \mathrm{Temperature} + 0.04\ \mathrm{NaC1}$	0.99721909

Notes: Significant beta are in bold font at $p < 0.05$.
Dependent parameter is C_t/C_o,
Independent parameters are time, C_t, C_o, solvent volume, temperature, pH, electrode number, NaCl.

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