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Defluoridation of commercial and analar sodium fluoride solutions without using additives by batch electrocoagulation-flotation technique

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ABSTRACT

Electrocoagulation-flotation (ECF) process evades many of the defects of chemical processes and considered as a simple low coast one for fluoride removal. The present work deals with defluoridation of different sodium fluoride solutions of both analar (AR) and commercial grades using bipolar and monopolar ECF. The effect of different variables on the defluoridation process; the initial fluoride solution concentration, speed of agitation, number of electrodes and distances between them, volume of solution, time of experiment, presence of additives and coexisting anions were studied. Complete removal is obtained after 5 min for AR grade (5 mg l^{-1}) and for commercial (4.93 mg l^{-1}) solutions without adding any additives. Monopolar configuration showed more effective removal than the bipolar one. This method is considered as a perfect one in the removal of high concentrations of fluoride in AR and commercial solutions in short time with no environmental risk and can be used in the industrial field. Data was analyzed using statistical programs trying to derive a modeling equation representing the conditions of defluoridation process.

Keywords: Commercial and analar NaF solutions; Tap water; Electrocoagulation-flotation; Defluoridation; Monopolar; Bipolar

1. Introduction

Fluoride levels in surface waters vary according to location and proximity to emission sources. Fresh water concentrations generally range from 0.01 to 0.3 mg l^{-1}. However, seawater contains more fluoride than fresh water, with concentrations ranging from 1.2 to 1.5 mg l^{-1} [1]. The recorded unpolluted water range for fluoride is of 0.5–1.5 mg l^{-1}. Fluoride compounds are widely used in aluminum, fertilizers, glass manufacturing and nuclear applications [2–4]. Actually, the long term exposure or intake of fluoride can lead to fluorosis with symptoms such as changes in the bone structure and it may also lead to enzyme inhibition [1,5,6]. Acute oral exposure to fluoride may produce effects including nausea, vomiting, abdominal pain, diarrhea, fatigue, drowsiness, coma, convulsions, cardiac arrest and even death. Calcification of muscles, osteosclerosis and decreased production of erythrocytes may also develop as a result of long term exposure. It can also affect the metabolism, growth and reproduction and other physiological process. Therefore, there is an urgent need to develop more inexpensive and effective treatment techniques of wastewater. Amongst these techniques, electrocoagulation (EC), the

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low cost and efficient one for treatment [7]. This process is used for the treatment of heavy metals [8,9], organics [10,11], bacteria [12], turbidity [13] and inorganic anions [14–16]. Also, it was re-examined as potential treatment technology [17]. Generally, the fluoride removal from industrial waste waters involves the chemical precipitation process [2–4,18–20]. The kinetics of EC defluoridation process was reported to follow the exponential function with time [21,22]. However, Emamjomeh and Sivakumar [23] developed an empirical model using critical parameters to evaluate the rate constant (K) for fluoride removal by a monopolar ECF process. The mechanism of fluoride removal process was a chemical adsorption process with the F^- replacing by OH^- group from the $Al_n(OH)_{3n}$ flocs [22]. Also, fluoride ions and hydroxide ions can coprecipitate with Al^{+3} ions to form $Al_nF_m(OH)_{3n-m}$ [24]. It was reported that EC system performed better than chemical coagulation (CC) system in defluoridation efficiency [21,25–28]. Hu et al. [21] reported that defluoridation efficiency in the ECF system was almost 100% in solutions without co-existing anions (Cl^-, NO_3^-, SO_4^{-2}). Shen et al. [22] reported that the combination of EC and electroflotation (EF) process was successfully applied in treating fluoride-containing waste water. Lui et al. [25] stated that the defluoridation efficiency of the EC system may exceed that of the traditional coagulation process because of the electrocondensation. Shen et al. [22] demonstrated that the optimal final pH in EC was about 6. Zhu et al. [28] explored that the inside mechanism of EC for fluoride removal was divided into three parts; remained in water, removed by electrodes, and adsorbed on hydroxide aluminum flocs. The result indicated that the flotation ability was insufficient when gas/solid ratio ($\Gamma G/S$) was under 0.1 l g^{-1} and the flow of waste water became discontinuous when ($\Gamma G/L$) was over 0.4. Both of these situations would lead to the increase of suspended solids [29,30] proposed a successful kinetic (VOK) model derived from the Langmuir equation for the fluoride removal reaction for EC in a system in which the initial concentration of the acid was lesser than the initial fluoride concentration [30].

The objective of this study is to explore the optimum conditions of initial concentration, time, distance between electrodes, speed of agitation, etc. for fluoride removal from industrial byproducts and tap water using EC technique. Additionally, the evaluation of an experimental model for the removal process has to be done.

2. Materials and methods

2.1. Experimental set-up

A laboratory bench-scale 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 dipped 150 mm in the 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; 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) providing a DC current. Two avometers (Sunwa, China), were used in which 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.

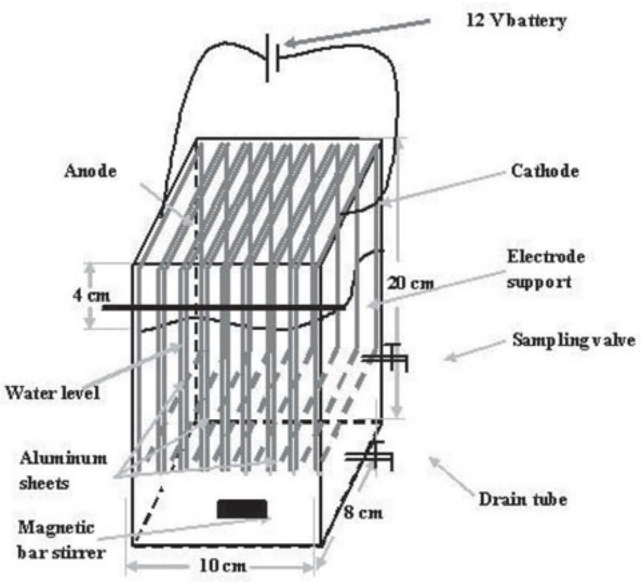

Fig. 1. Schematic diagram of set-up.

2.2. Procedure

Different concentrations of sodium fluoride stock solutions (commercial and AR) were prepared from standard 0.5 M sodium fluoride, each one was added to the aforementioned cell after washing it with distilled water. The battery was then connected and the magnetic stirrer adjusted to the desired speed. Samples were taken at certain time intervals for analysis.

2.3. Variables investigated

The effects of different variables on the defluoridation process were studied and they were: initial fluoride solution concentration, purity of sodium fluoride used, electrode spacing, speed of agitation, mono and bipolar configurations, NaCl addition, number of electrodes, volume of solution and finally distilled and tap water.

2.4. Methods used for analyses

Fluoride (F^-) concentration was determined following the procedure of zirconium alizarin red S (Zr-ARS) [31,32] and the mean concentrations (triplicate measurements for each sample) were calculated. Calcium (Ca^{+2}) and magnesium (Mg^{+2}) concentrations were determined by EDTA titration in presence of murexide and Eriochrome black T indicator, respectively [33] Sodium (Na^+) determination was performed by flame atomic emission spectrophotometry. The sulphate (SO_4^{-2}) concentration was estimated by turbidimetric method [33]. Total carbonate (CO_3^{-2}) and silicate concentrations were estimated gravimetrically [34].

3. Effect of initial concentration on fluoride removal

3.1. Commercial sodium fluoride grade solution

EC is a complex electrochemical process, which comprises chemical and physical processes involving many surface and interfacial phenomena. The technology lies at the intersection of three more fundamental technologies-electrochemistry, coagulation and flotation [17,28]. Many spontaneous processes are performed including oxidation, reduction, hydroxides and gases evolution [35]. To avoid all these incorporated processes, 45–60 min is selected as the maximum time for the examined experiments. Additionally, this removal time is chosen to overcome the competition of the different present ions with fluoride in the commercial sodium fluoride solutions during the defluoridation process [24].

The % extraction for the different initial concentrations of commercial fluoride solutions (chemical characteristics are listed in Table 1) 30.40, 21.27 and 4.93 mg l^{-1} are of 75.0%, 78.6% and 100.0%, respectively (Fig. 2). However, the maximum time of fluoride removal for the examined initial fluoride concentrations is about 5–10 min (Fig. 2). The observed fluoride concentration increase in the prolonged time (<10 min) may relate to the oxidation of the aluminum electrodes that leads to the passivation and oxygen evolution at the electrodes.

Table 1
Percentage of the chemical composition of sodium fluoride commercial grade solid

Component	Ca^{+2}	Mg^{+2}	Na^+	SO_4^{-2}	F^-	CO_3^{-2}
Percentage composition	23.71	4.79	0.22	0.48	0.19	60.59

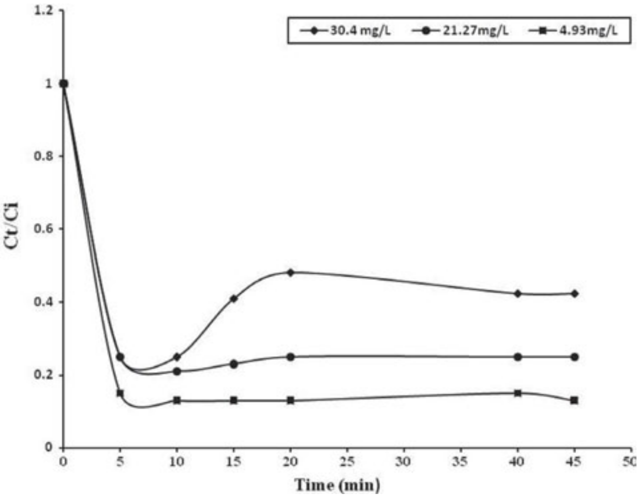

Fig. 2. Effect of initial concentration of fluoride in different commercial NaF solutions on rate of defluoridation, C_i = 30.4–4.93 mg l^{-1}, volume of solution = 1 l, seven bipolar electrodes, speed of agitation = 400 rpm, current = 250 mA, voltage = 10.5 V.

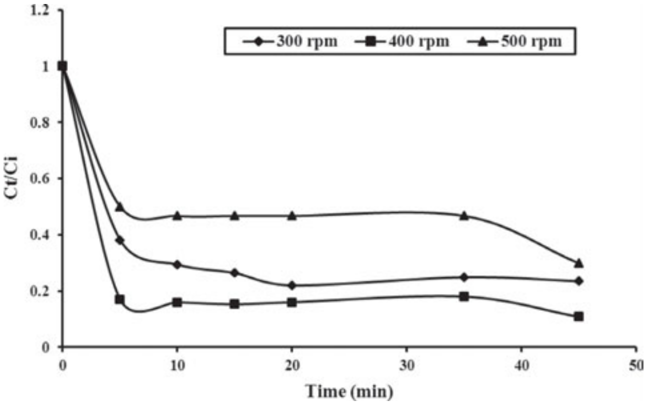

Fig. 3. Effect of speed of agitation on rate of defluoridation of NaF solution (AR grade), C_i = 42.17 mg l^{-1}, volume of solution = 1 l, seven bipolar electrodes, current = 250 mA, voltage = 10.5 V.

Also, during EC defluoridation process, pH can be flocculated not only because of hydrogen generation at the cathodes, but also the liberation of hydroxide ions due to the substitution of fluoride [24]. The adsorbed fluoride on flocs declined quickly to be neglected as the influent pH was rising above 7.5. Since aluminum hydroxide is amphoteric hydroxide and high pH will lead to the formation of $Al(OH)^{-4}$, the influent pH implied the different interactions might exist around the electrodes, such as electrophoresis, adsorption and precipitation of hydrofluoroaluminium complexes, which in turn lead to the change of fluoride content removed by electrodes. Also, the presence of some ions in the commercial sodium fluoride solution may compete with the fluoride ions. However, it was stated that the lyotropic series of anions for Al^{+3} is $F^- > SO_4^{-2}$ [21]. Sulphate is the only possible species, which is able to replace F^- ions coordinating with aluminum. By applying the following equation [21] concerning the calculations of theoretical aluminum content in all the experiments (commercial grade solutions), it was found that the aluminum concentration doesn't pose any effect towards the % extraction (%Ex) (Table 2):

$$m_{Al(T)} = \frac{n \times I \times t \times M_{Al}}{Z \times F}$$

where n is the number of electrodes, I is the current (A, ampere), t is the time (min), M_{Al} is the molecular weight of aluminum (g mol^{-1}), Z valency (three for aluminum) and F is Faraday constant, $F = 96{,}487$ (C mol^{-1}).

3.2. AR grade sodium fluoride solution

For AR grade solution, it is clear that the final fluoride concentration (C_f) increases when the initial fluoride concentrations (C_i) increases (Table 3). This phenomenon agrees with the pervious results [23,30]. The comparison between the same initial concentrations of AR grade and the commercial sodium fluoride solutions shows that the % extractions of different commercial sodium fluoride solutions are relatively lower than those of AR grade ones. This probably reflects the competition of the coexisting ions with fluoride ion adsorption in the commercial solution [21]. Accordingly, all the fluoride could readily be reacted with the available aluminum that dissolves in the solution especially in case of low concentrations of NaF leading to complete extraction (0.756 and 5.69 mg l^{-1}). Also, by applying the previous equation for the theoretical calculated aluminum content [21], it was found that the aluminum content in the solution plays a very important role in the defluoridation process of the AR grad solutions. Interestingly, aluminum concentration seems to be affected by the initial of fluoride concentration (Table 3). As the initial fluoride concentration increases the aluminum content increase. Although, the defluoridation process is related to the aluminum liberation that remove fluoride ions from the solution, the fluoride extract percentage decreases with the initial fluoride increase. This is possibly due to insufficient of aluminum hydroxide complex formation in higher concentrated solutions [23]. Interestingly, monopolar EC system containing four electrodes shows complete fluoride removal at low (15.96 mg l^{-1}) and high (28.9 mg l^{-1}) initial fluoride concentrations and this system isn't affected by the released aluminum concentration (Table 3). This is possibly related to many factors including the type of electrode connection, the number of aluminum electrodes, the Al^{+3} dosages and the produced aluminum hydroxide complex [23,24].

Table 2
Aluminum concentration and percentage extraction for the defluoridation of different commercial sodium fluoride solutions at variable time [initial (i), removal (t) and final time (f)]

C_i (mg l^{-1})	C_f (mg l^{-1})	C_t (mg l^{-1})	Al^{+3} (mg l^{-1})	% Ex
30.40	14.67	7.60	3.16E + 04	75.0
21.27	5.39	4.55	3.16E + 04	78.6
4.93	0.76	0.00	3.16E + 04	100.0

3.3. Effect of electrode spacing on fluoride removal

For seven electrodes bipolar EC system of an electrode spacing of 1.2 cm, poor fluoride extraction of 65% is obtained. In contrast, high fluoride extraction of 100% is performed when three electrodes are used (electrode space = 2.4 cm). However, it is clear that the residual fluoride concentration increases when the electrode

Table 3
Aluminum concentration and percentage extraction for the defluoridation of different of AR grade sodium fluoride solutions at variable time [initial (i), removal (t) and final time (f)] in 1 l and seven electrodes bipolar and four electrodes monopolar EC system

EC system	Number of electrodes	C_i (mg l^{-1})	C_f (mg l^{-1})	C_t (mg l^{-1})	Al^{+3}(mg l^{-1})	% Ex
Bipolar electrode	7	0.76	0.00	0.00	7.91E + 03	100.0
		5.69	1.14	0.00	2.38E + 04	100.0
		42.17	4.56	3.42	3.16E + 04	91.9
		62.68	10.63	6.84	7.14E + 04	89.1
Monopolar electrode	4	2.89	0.00	0.00	7.91E + 02	100.0
		15.96	0.00	0.00	7.91E + 02	100.0

distance is increased [23]. This high extraction may be attributed to the better mixing of fluoride solution, the wider distance which enhanced turbulence and the better stirring with high resistance to the passing electric current in the solution. Also, this is perhaps because of the electro-condensation effect which induced the accumulation of fluoride ions and its coprecipitation on the anode surface [26–29]. However, it was recorded that most of defluoridation processes took place on the surface of the anode in the solution [36].

3.4. Effect of speed of magnetic agitation on fluoride removal

The usage of 500, 400, and 300 rpm magnetic agitation speed in the EC fluoride defluoridation system give % extraction of 91.89, 70.18 and 77.94, respectively (Fig. 3). It seems that the used medium speed (400 rpm) is the most appreciable one for the applied EC technique. Since the lowest speed is insufficient to renew the solution, whereas, the highest speed may cause a vortex in the solution between the electrodes. Also, it was reported that the released hydrogen gas is affected by the speed of agitation and subsequently, the fluoride removal process [29].

3.5. Effect of solution volume on fluoride removal

The comparison between 1 and 1.25 l have the same initial fluoride concentration C_i (21.27 mg l^{-1}) give % extractions of 78.6 and 62.5, respectively (Fig. 4). This reflects the less opportunity of the liquid agitation among the upper parts of the bipolar electrodes and the smaller mass ratio of F/Al in case of the large volumes.

3.6. Effect of presence of additives on fluoride removal

The effect on fluoride removal in presence and absence of NaCl as additive is studied. The addition of 0.5 g of NaCl to 1.25 l of 42.17 mg l^{-1} initial fluoride concentration is very effective and leads to a complete removal during 20 min. The ECF process takes place and a white precipitate layer of about 3 cm height floats on the solution surface is formed, however, after leaving the cell over night, the float sinks completely to the bottom. This proves that flotation of the formed particles takes place by the evolved gases [21,37]. Also, it was recorded that the lower NaCl concentration in the solution produced smaller amount of sorbent and led to more energy consumption for aluminum adsorption [38]. Additionally, large electric energy is consumed in producing oxygen by water electrolysis [38].

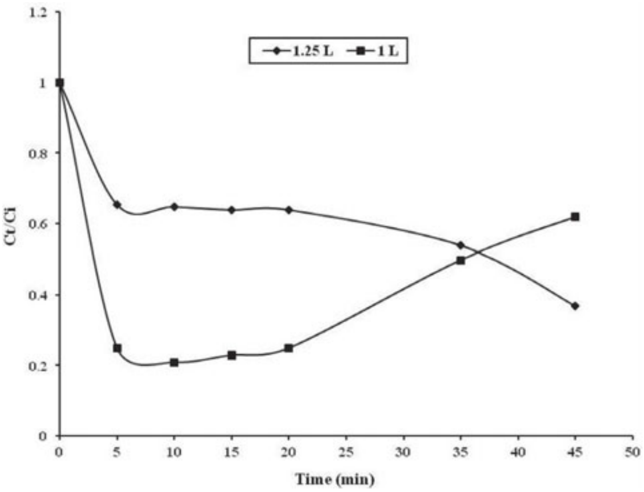

Fig. 4. Effect of volume of solution on rate of defluoridation of NaF solution (AR grade), C_i = 21.27 mg l^{-1}, seven bipolar electrodes, speed of agitation = 400 rpm, current = 250 mA, voltage = 10.5 V.

3.7. Effect of co-existing anions on fluoride removal

The effect of removing fluoride ions from tap water (tap water characteristics, Table 4) containing co-existing

Table 4
Tap water characteristics according to "Holding company for water and waste water, Alexandria Water Company, Siouf water treatment"

Ions	Concentration P.P.M.	Metals	Concentration P.P.M.	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		

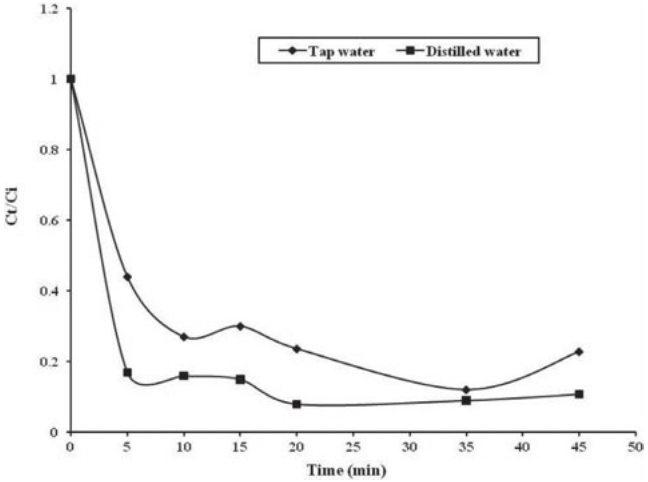

Fig. 5. Effect of presence or absence of coexisting ions on rate of deflouridation of NaF solution (AR grade), C_i = 42.17 mg l^{-1}, volume of solution = 1 l, seven bipolar electrodes, speed of agitation = 400 rpm, current = 250 mA, voltage = 10.5 V.

anions and from AR standard solution is given in Fig. 5. During almost 35 min. the concentration dropped from 46.6 mg l^{-1} to 6 mg l^{-1}, with 90% extraction for tap water. While almost the same % extraction is attained using standard solution in a shorter time (20 min). The presence of different anions affects the defluoridation process. It was demonstrated that the % reduction was in the following orders of $Cl^- > F^- > HCO_3^- > SO_4^{-2}$ and $Ca^{+2} > Mg^{+2} > K^+ > Na^+$ for anions and cations of brackish water by electrodialysis [39].

3.8. *Effect of using monopolar system on fluoride removal*

The comparison between using monopolar and bipolar systems in fluoride removal is studied. Monopolar system shows a very rapid defluoridation with a complete removal within 5 min. As agreed in the previous results, monopolar system can be considered as the more effective configuration than bipolar one for the defluoridation process [21,37]. Although, monopolar EC technique is the more effective one, it is not preferable to be used because of its higher energy consumption [21].

4. Computed results

Mass transfer coefficients are calculated according to the following equation:

$$-L_n \frac{C_t}{C_i} = \frac{Ka}{V} t$$

where, C_t and C_i are the removal time and initial concentrations (mg l^{-1}), K is the mass transfer coefficient (cm s^{-1}), a is the surface area (cm^2) and V is the initial volume (l). Generally, the mass transfer ($-\text{Ln}\ C_t/C_i$) values for the set of experiments are directly related to C_i as illustrated previously [23,30]. Also, the calculated mass transfer values of the set experiments for the effect of agitation speed proves the same aforementioned results, however, the medium speed (400 rpm) gives the fastest deflouridation rate of the highest mass transfer coefficient. For the set experiments of electrode spacing effects on defluoridation process, the largest space of 2.4 cm (three electrodes) shows higher rate of removal than that of lowest space of 1.2 cm (seven electrodes). This possibly reflects the difficulty of the renewal of the solution between the electrodes. Accordingly, the largest spacing electrode experiment provides efficient solution mixing and the least dissolved aluminum concentration. According to the electrode spacing effect the fluoridation process the mass transfer coefficient values of fluoride removal follow the order of 2.4 > 4.8 > 1.2 cm. The computed results for the fluoride removal experiments indicate that the rate of defluoridation and mass transfer coefficients are higher in presence of NaCl salt. However, the conductivity is improved in the presence of Na^+ and Cl^- ions [28]. The mass transfer coefficient value for 1 l volume is higher than 1.25 l volume of the same initial fluoride concentration C_i (21.27 mg l^{-1}). This probably due to the available competitions between the formed fluoroaluminum complexes within the solution media [23,40].

5. Statistical analysis

5.1. *Correlation matrix*

Correlation matrices among % Extraction, C_i, C_f, C_t, time, and Al for commercial and AR grades are performed. Commercial NaF solutions show good and significant relation between initial concentration, (C_i) and both fluoride concentrations at any time (C_t) and at the end of each experiment (C_f) [correlation coefficients (r) are 0.9448 and 0.9556 with probability values (p) of 0.004 and 0.003, respectively]. Interestingly, the correlation matrix of AR NaF solutions illustrates high significant correlations between all variables, (Table 5). However, % extraction is related to the aluminum content, progressed time and both C_f and C_t fluoride concentrations.

5.2. *Multiple regression equation*

Multiple regression equations for both commercial and AR grades are studied. Commercial solution of NaF is given in the following equation:

Table 5
Correlation matrix between %Ex, C_i, C_f, C_t, time, and Al for the defluoridation of AR NaF solution ($p < 0.05$, $n = 15$)

Variables	C_i	C_f	C_t	Time	Al	% Ex
C_i	$r = 1.000$					
	$p = 0.000$					
C_f	$r = 0.5171$	$r = 1.000$				
	$p = 0.048$	$p = 0.000$				
C_t	$r = 0.5497$	$r = 0.8626$	$r = 1.000$			
	$p = 0.034$	$p = 0.000$	$p = 0.000$			
Time	$r = 0.4604$	$r = 0.3346$	$r = 0.5188$	$r = 1.000$		
	$p = 0.084$	$p = 0.223$	$p = 0.048$	$p = 0.000$		
Al	$r = 0.3838$	$r = 0.2477$	$r = 0.527$	$r = 0.8748$	$r = 1.000$	
	$p = 0.158$	$p = 0.373$	$p = 0.044$	$p = 0.000$	$p = 0.000$	
%Ex	$r = -0.1346$	$r = -0.6601$	$r = -0.7675$	$r = -0.6121$	$r = -0.6208$	$r = 1.000$
	$p = 0.632$	$p = 0.007$	$p = 0.001$	$p = 0.015$	$p = 0.014$	$p = 0.000$

$$C_f = -0.69 + 0.96\, C_i \; (R = 0.95564)$$

On the other hand, AR solution is described by the following equation:

$$\%\,\mathrm{Ex} = 97.56 + 0.54\, C_i - 0.42\, C_f - 0.43\, C_t - 0.27\,\mathrm{Time} - 0.27\, Al \; (R = 0.92645)$$

Accordingly, these two equations can be used to calculate both C_f and % extraction of fluoride in the two systems (commercial and AR solutions).

6. Conclusions

Defluoridation of alalar and commercial solutions series as well as tap water was performed using the ECF technique in bipolar and monopolar systems. The effect of different variables on the defluoridation process including; the initial fluoride solution concentration, speed of agitation, the electrode space, solution volume, time of experiment, presence of additives and coexisting anions were studied. The study showed a complete fluoride removal in short time (5–10 min) without adding any additives in low fluoride concentration solutions. The statistical analyses showed that the fluoride removal is affected by the different studied variables and the percentage of extraction can be calculated at any experiment time. This method is considered as a perfect one in the removal of high concentrations of fluoride in AR and commercial solutions in short time with no environmental risk and can be used in the industrial field, however, it doesn't use any chemical additives. This study can be extended in the future work to include the energy consumption within the defluoridation process.

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