

INFLUENCE OF SELECTED ANIONS ON FLUORIDE REMOVAL IN ELECTROCOAGULATION/ELECTROFLOTATION

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SUMMARY: Fluoride removal by electrocoagulation/electrofloatation was investigated as an alternative defluoridation method. Batch experiments with aluminum electrodes were used to investigate, with response surface methodology (RSM), genetic algorithm (GA), and the artificial neural network approach (ANN), the effects on defluoridation by electrocoagulation/electrofloatation of the concentration of usual five co-existing anions (Br^- , Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{2-}), and the operational parameters of initial pH, applied electrical current intensity, initial fluoride concentration, and process time. The results demonstrated that the type and concentration of co-existing anions, as well as various operational parameters, had a significant effect on the efficiency of defluoridation by electrocoagulation/electrofloatation.

Keywords: Anions, co-existing; Artificial neural network approach; Electrocoagulation/ Electrofloatation; Fluoride removal; Genetic algorithm; Operational parameters; Response surface methodology.

INTRODUCTION

A major issue of groundwater contamination is the presence of various pollutants such as fluoride (F), pesticides, and heavy metals. F in the groundwater occurs through its presence in the earth's crust and industrial activities such as semiconductor manufacture which uses a large amount of hydrofluoric acid.^{1,2} According to WHO, the maximum permissible F level in drinking water is 1.5 mg/L and the long-term intake of water containing more than this may cause various adverse health effects including dental fluorosis and skeletal damage. The effluent discharge standard for F has been set at 4 mg/L and 2 mg/L by the US Environmental Protection Agency (EPA) and in the Iran national standard, respectively. Thus, treating high F-content wastewater and drinking waters is an important issue.²⁻⁹

Various treatment technologies have been proposed for the removal of F from water and wastewater. At present, the cheapest and usual way to remove F ions from wastewater is calcium precipitation by adding excess lime or other calcium salts, such as CaCl_2 , to form calcium fluoride (CaF_2). After the F level has been reduced by calcium precipitation, an additional process is then needed to remove the suspended solids.^{4,10-12} Recently, electrocoagulation-electrofloatation (EC/EF) has played a more prominent role in drinking water and wastewater treatment. Aluminum cations and related species along with hydrogen gas that are produced

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in EC/EF are useful absorbents and coagulants for the removal and co-precipitation of F.^{6,13-18} The present work aimed to elucidate the effects on defluoridation by the EC/EF process, by response surface methodology (RSM), genetic algorithm (GA), and the artificial neural network approach (ANN), of the concentration of the usual five co-existing anions (Br^- , Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{2-}), and the operational parameters of initial pH (pH_0), applied electrical current intensity (I), initial fluoride concentration (C_F), and process time (t_p).

MATERIAL AND METHODS

Synthetic wastewater was prepared by dissolving the desired amounts of potassium salts (Merck, Germany) of all the chosen anions in distilled water. The concentrations of the synthetic solutions were standardized using ion chromatography (US EPA standard). Aluminum plate electrodes were purchased from a local seller and prepared by cutting to the desired sizes. The pH_0 of the solutions was adjusted using NaOH and HBr (Merck, Germany).

Statistical design of experiments (DoE) is a useful technique to investigate a phenomenon by performing a minimum number of experiments. In the present study, a 27 run Taguchi design of experiments (Minitab 14) was applied to investigate the effects on defluoridation of the concentrations (C_{Br} , C_{Cl} , C_{NO_3} , C_{SO_4} , and C_{PO_4}), of the usual five co-existing anions (Br^- , Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{2-}), and the operational parameters of initial pH (pH_0), applied electrical current intensity (I), initial fluoride concentration (C_F), and process time (t_p). The time of electrocoagulation (t_p) was investigated at five levels with run durations of 5, 20, 60, 90, and 120 min. The levels for each parameter and its interval were determined by pre-testing.

A 1.25 L handmade cylindrical glass reactor (diameter 9.5 cm, height 20 cm) was prepared with a 120 rpm magnetic stirrer, a DC power supply (RXN-303D-II, Zhaoxin Electronic Tech. Co.), and two aluminum electrodes (anode and cathode). The electrodes were made of aluminum sheets ($4 \times 10 \times 0.1$ cm) and each had an effective immersed surface area of 40 cm^2 . The electrodes were placed vertically dipping into 1 L of the synthetic solutions with the distance between electrodes fixed at 1 cm (Figure 1).

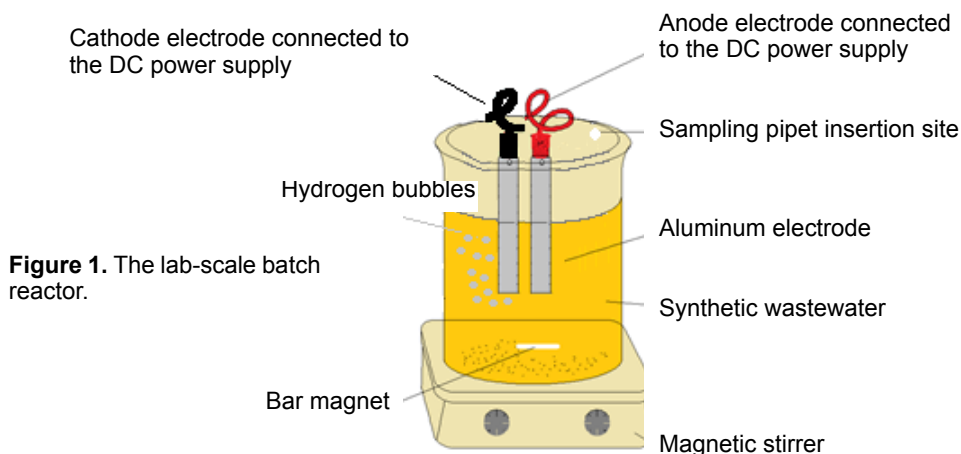


Figure 1. The lab-scale batch reactor.

In each run, 1 L synthetic waste solution was decanted into the reactor. The operational parameters and concentration of coexisting anions were adjusted to the desired values based on the experimental design. Along with an initial sample at zero time, at each of the five desired process times a 10 mL sample was extracted at a specific position in the reactor using a sampling pipet. The samples were filtered with a 42 micron syringe filter and the anions content determined for the filtered solution. The concentration of samples was evaluated by the standard ion chromatographic method using the calibration curve method. Finally, the fluoride removal (FR) (mg) was calculated for the samples using the following equation:

$$FR = \left(1 - \frac{C}{C_0}\right) \times V$$

where, C_0 and C are the F concentrations of the solution before and after the process, respectively and V is the solution volume.

RESULTS AND DISCUSSION

Twenty-four of the total of 27 runs had acceptable results and the parameter levels for these are shown in Table 1.

Table 1. The parameter levels for the 24 runs with acceptable results from the total of 27 runs

Run no.	pH ₀	C _{B_r} (mg/L)	I (amps)	C _F (mg/L)	C _{Cl} (mg/L)	C _{NO₃} (mg/L)	C _{SO₄} (mg/L)	C _{PO₄} (mg/L)
2	4	8	0.05	2	10	50	200	10
3	4	8	0.05	2	10	200	500	50
4	4	8	0.1	10	200	5	10	2
5	4	8	0.1	10	200	50	200	10
6	4	8	0.1	10	200	200	500	50
7	4	8	0.2	50	500	5	10	2
8	4	8	0.2	50	500	50	200	10
9	4	8	0.2	50	500	200	500	50
10	7	0	0.05	10	500	5	200	50
11	7	0	0.05	10	500	50	500	2
12	7	0	0.05	10	500	200	10	10
13	7	0	0.1	50	10	5	200	50
14	7	0	0.1	50	10	50	500	2
15	7	0	0.1	50	10	200	10	10
16	7	0	0.2	2	200	5	200	50
17	7	0	0.2	2	200	50	500	2
18	7	0	0.2	2	200	200	10	10
19	10	0	0.05	50	200	5	500	10
22	10	0	0.1	2	500	5	500	10
23	10	0	0.1	2	500	50	10	50
24	10	0	0.1	2	500	200	200	2
25	10	0	0.2	10	10	5	500	10
26	10	0	0.2	10	10	50	10	50
27	10	0	0.2	10	10	200	200	2

The FR for each sample was determined for different process times (time of reaction, t_p). After the removal of the 3 runs that had missing data, the remaining 131 data for the FR values for the remaining 24 acceptable runs are shown in Figures 2-5.

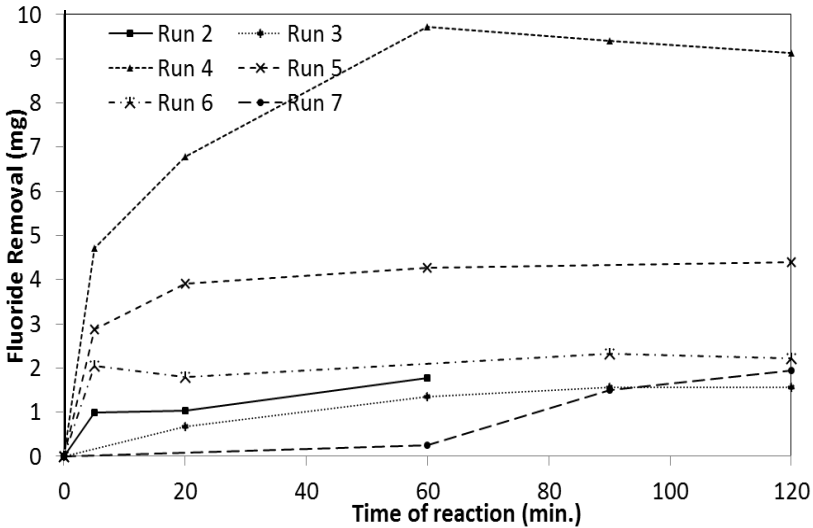


Figure 2. The experimental fluoride removal in runs 2-7.

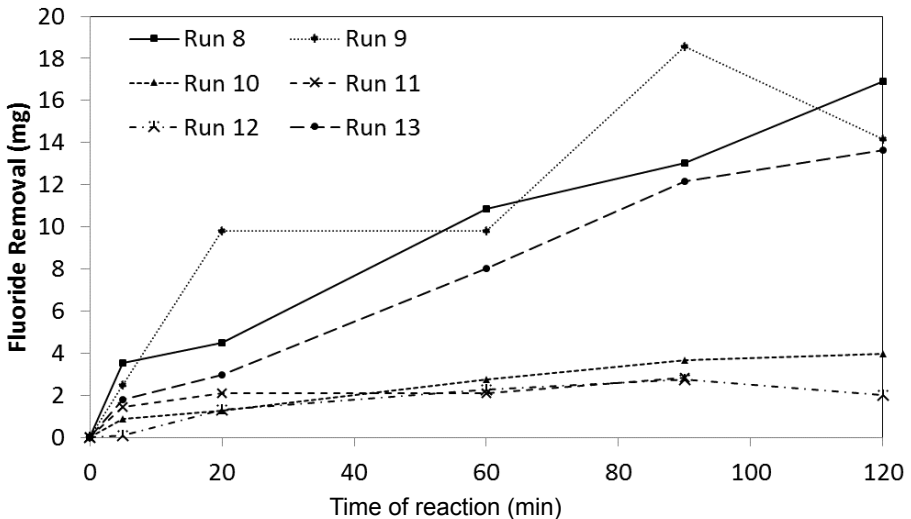


Figure 3. The experimental fluoride removal in runs 8-13.

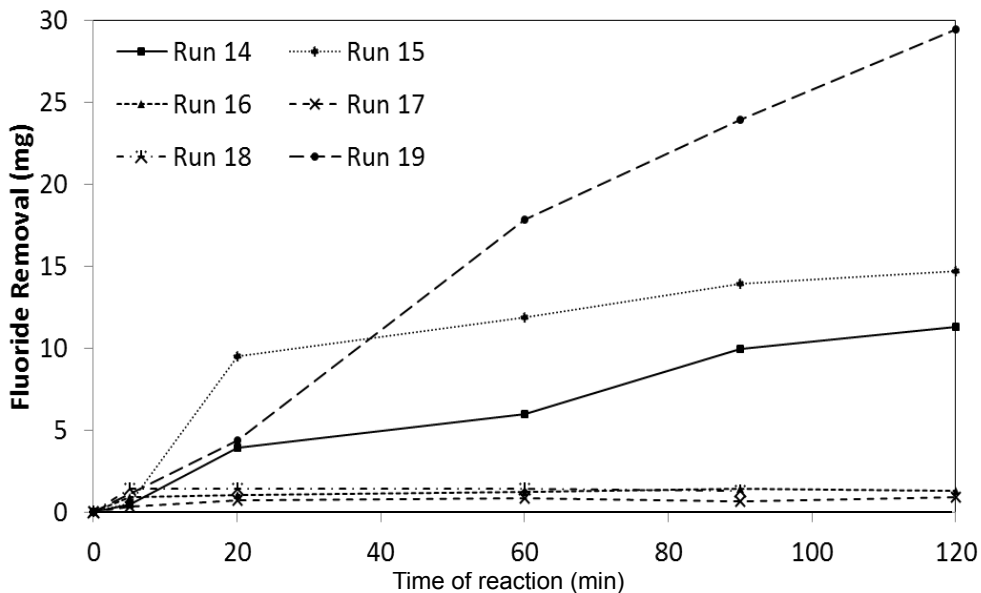


Figure 4. The experimental fluoride removal in runs 14–19.

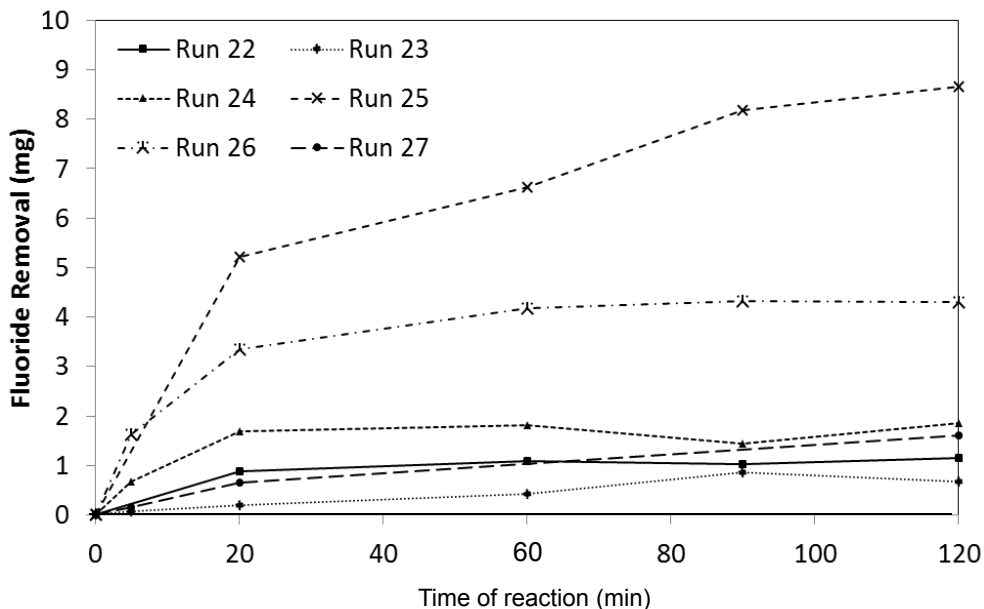


Figure 5. The experimental fluoride removal in runs 22–27.

EC/EF can be very effective in removing F with different operational parameters resulting in FR ranging from less than 1 mg to up to 29 mg (Figures 2–5). In run 19, a FR of 29.4 mg (60%) was achieved during the process (Figure 4). In run 24,

a FR of 93% (1.85 mg) was achieved with an initial F concentration of 2 mg/L. (Figure 5). In run 4, a FR of 91% (9.13 mg) was achieved with an initial F concentration of 10 mg/l (Figure 2).

A glance at Figures 2–5 will clarify the influence of the various operational parameters on FR. Although, as frequently reported, the time of reaction (process time, t_p) has an obvious positive influence, the influence of other seven parameters is less clear (Table 1 and Figures 2–5). Thus, it seems essential to use statistical tools in order to clarify the influence of the various parameters and allow the identification of those parameters which are effective for modeling and optimization.

Linear, interactional, and squared parameters were used in regression and ANOVA analysis to investigate the influence of the various parameters and the statistical results are presented in Table 2.

Table 2. Results of regression and ANOVA analysis with linear, interactional, and squared parameters

Term	Coefficient	p value	Term	Coefficient	p value
*Constant	-8.67	0.10	t_p^2	0.00	0.01
pH	0.80	0.02	pH$\times$$t_p$	0.01	0.01
C_{Br}	0.38	0.04	C _{Br} \times t	0.00	0.08
I	67.3	0.16	I\timesC_{NO3}	-0.85	0.00
C_F	-0.32	0.01	I \times C _{SO4}	-0.12	0.14
C _{Cl}	0.02	0.14	I\timesC_{PO4}	-3.30	0.00
C _{NO3}	0.05	0.12	I$\times$$t_p$	-0.17	0.04
C _{SO4}	-0.01	0.44	C_F\timesC_{NO3}	0.00	0.00
C_{PO4}	0.39	0.00	C_F\timesC_{SO4}	0.00	0.00
t_p	-0.01	0.71	C _F \times C _{PO4}	0.00	0.11
I²	338	0.00	C_F$\times$$t_p$	0.00	0.00
C _F ²	0.00	0.19	C _{Cl} \times C _{NO3}	0.00	0.51
C_{Cl}²	0.00	0.00	C_{Cl}\timesC_{SO4}	0.00	0.00
C _{NO3} ²	0.00	0.40	C _{Cl} \times t_p	0.00	0.48
C_{SO4}²	0.00	0.02	C _{NO3} \times t_p	0.00	0.15
C _{PO4} ²	0.00	0.32	C _{SO4} \times t_p	0.00	0.21

The meaningful parameters are bolded. *Constant of regression

As seen from Table 2, all nine investigated parameters (C_{Br}, C_{Cl}, C_{NO3}, C_{SO4}, C_{PO4}, pH₀, I, C_F, and t_p) had a meaningful result in at least one statistical test when the parameter was used in a linear, interactional, or squared form. Thus, all nine parameters should be considered for modeling and optimization.

Another important issue is the ranking for efficacy of the nine parameters. This was determined, based on additional statistical analysis, and is presented in Table 3.

Table 3. The ranking of the nine parameters investigated

Level	t_p	C_F	C_{PO_4}	pH_0	C_{Cl}	C_{Br}	C_{NO_3}	C_{SO_4}	I
1	-5.73	-0.52	4.84	10.8	9.95	6.01	10.4	5.82	6.22
2	-1.41	8.01	10.6	6.32	8.30	10.8	5.74	7.41	8.31
3	5.94	15.6	6.57	5.56	4.93		6.39	8.92	7.48
4	9.19								
5	11.1								
6	11.8								
Delta	17.5	16.1	5.75	5.27	5.01	4.82	4.73	3.10	2.08
Rank	1	2	3	4	5	6	7	8	9

As presented in Table 3, t_p and C_F , with rankings of 1 and 2 respectively, had more influence on FR than C_{SO_4} and I, with rankings of 8 and 9 respectively. Amongst the co-existing anions C_{PO_4} , with a ranking of 4, had more influence than C_{Cl} , C_{Br} , C_{NO_3} , and C_{SO_4} ranked at 5, 6, 7, and 8 respectively.

A graphical illustration of the influence of each parameter is shown in Figure 6.

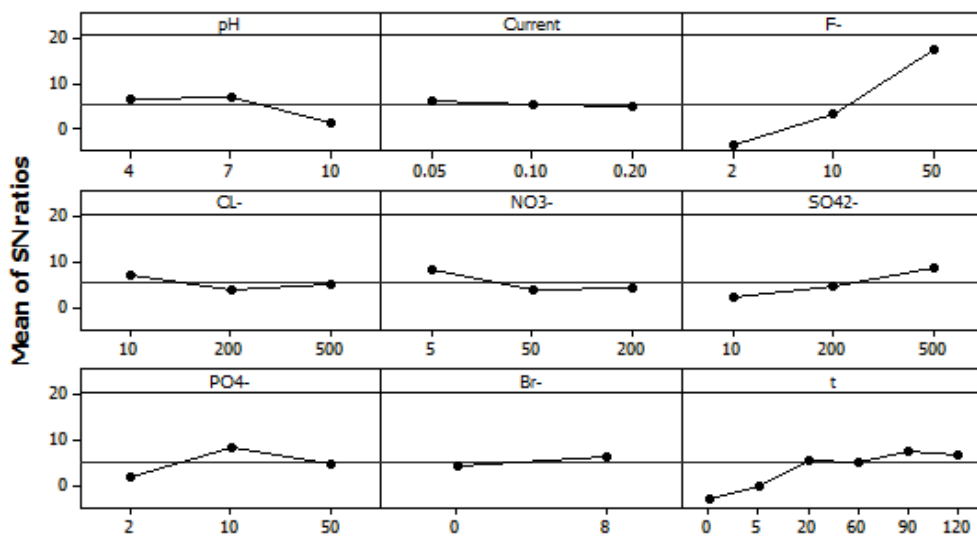


Figure 6. Graphical illustration of the influence of the nine parameters investigated on the mean of the signal-noise ratio. The units for the current are amperes, for the anions mg/L, and for process time min.

As shown in Figure 6, pH_0 , C_{Cl} , C_{NO_3} , and C_{PO_4} had a negative effect on the mean of the serial to noise ratio, with the formula shown below being used to maximize the FR as the response variable.

$$- 10 \log (10 [\Sigma \frac{Y^{-2}}{n}])$$

In contrast, C_F , C_{SO_4} , and t_p had a positive effect while the influence of I and C_{Br} was almost negligible.

Based on Figure 6, it can be said that, more t_p will cause more coagulant (sorber) to be released from the anode and more hydrogen bubbles to form at the cathode resulting in more FR. A lower pH_0 will, on the one hand, increase the concentration of H^+ making it easier to reduce water at the cathode and increase the production of hydrogen bubbles, while, on the other hand, it will result in less competition of OH^- with F^- . Also, based on Figure 6, co-existing anions can have an opposite effect depending on the kind and concentration of each anion. Two other important mechanisms which may affect the complex pattern of each anion's influence on the FR are competition with F and corrosion effects. Hu et al. investigated the influence of coexisting Cl^- , SO_4^{2-} , and NO_3^- in defluoridation by electrocoagulation and focused on the electrodic and corrosion influences of the anions.¹⁸ In his study, he found sulfate exhibited a different pattern of influence to nitrate and chloride, and that nitrate and chloride exhibited a similar pattern of influence. These findings are in good agreement with the results of the present study (Figure 6).

When the presence of an anion causes a direct positive effect on FR, it may be because of electrodic and corrosion influences. The presence of these anions make it easier to release the coagulants from the anodic electrode and hydrogen bubbles from the cathodic electrode. Also, the direct influence of such an anion may be due to a synergistic effect on the coagulation mechanism.

When the presence of an anion causes a negative or inverse effect, this may also be because of electrodic influences. The presence of these anions make harder to release the coagulants from the anodic electrode and hydrogen bubbles from the cathodic electrode. In addition, a negative or inverse effect may result from the influence of such anions on the coagulation mechanism.

The RSM was applied to find the optimum values of the operational parameters to maximize the response variable (FR). The calculation was done based on the obtained multiple linear model that was extracted from RSM basic analysis. The results of the RSM optimization for FR (more than 60) were not in good agreement with the experimental results presented in Figures 2–5 (Table 4). This may be because of the complicated nature of the EC/EF process and the interaction between the parameters. Thus, in this kind of study, more powerful approaches for modeling and optimization are essential.

Table 4. The GA optimization result

	Inputs									Response
	pH ₀	C _{Br}	I	C _F	C _{Cl}	C _{NO3}	C _{SO4}	C _{PO4}	t _P	FR
Lower bound	4	0	0.05	2	10	5	10	2	0	-
Upper bound	10	8	0.2	50	500	200	500	50	120	-
ANN/GA optimum values	4.05	2.64	0.064	49.6	474	57.8	483	45.3	18.2	23.4
RSM optimum values	10	8	0.05	50	376	200	500	50	120	69.1

The artificial neural network (ANN) is a parallel computational procedure consisting highly interconnected processing element groups named neurons. Owing their inherent nature to model and learn ‘complexities’, ANNs have found wide application in various areas of wastewater treatment studies. These facts inspired us to use ANN as a powerful nonlinear modeling approach to get a good predictable model. Therefore, a nine operational parameter set was applied as the input for the ANN models while the FR was considered as the dependent variable. The data set was randomly divided into three parts: 60% (78 data) as the training set, 20% (27 data) as the validation set and the remainder 20% (26 data) as the testing set. The training set was used to adjust the parameters of the models, the testing set to calculate its estimation power, and the validation set to prevent over-train. Back propagation algorithm has been used as it is very fast and user friendly. The number of hidden layers, the number of neurons in each hidden layer, and the learning rate were determined via trial and error.¹⁹⁻²¹

The best ANN model selected a net with one hidden layer with 3 neurons and a 0.17 learning rate (9:3:1 net). The ‘tansig’ transfer function was selected for the input and the hidden layers, and ‘purelin’ for the output layer. Once the networks were trained, the weights and biases of each neuron and layer were saved in the ANN model. They were then used to estimate the test set. Finally, the consistency of the ANN models was revealed by tests quantified with predictive Q^2 and R^2 when the reliability or accuracy of the models was revealed by the root-mean-square error (RMSE). The test results of the ANN model goodness are presented in Table 5. The high quality of the statistical parameters presented in Table 5 clearly confirm that the ANN can model the complicated nonlinear nature of the process.

The golden goal of each modeling study is the optimization of process and the optimized parameters can be used to identify the effective parameters. The genetic algorithm (GA) was used to optimize the experimental parameters using the best obtained models. GA is an adaptive heuristic search algorithm based on the

evolutionary ideas of natural selection and genetics. The GA toolbox in MATLAB was used to generate the optimal solution of FR by using 'ga' function. MATLAB functions using best ANN models written for creating fitness functions for the optimization problem. The FR component to be maximized was negated in the vector valued fitness function since GA minimizes all the objectives. The results of the GA solution are shown in Table 5.¹⁹

Table 5. The test results of the ANN model goodness

Data set	Training set	Validation set	Testing set
R ²	0.96	0.94	0.93
Q ²	0.96	0.93	0.93
RMSE	0.94	1.6	1.4

Based on Table 5, the optimization process proved that the ANN model is more compatible with the experimental results rather than the RSM and it can predict the optimum FR with good accuracy. Also, the obtained optimum values for the experimental parameters were different for these two approaches. The ANN model is a more powerful and accurate model and should give a global optimum with more logical values.

In the present study, pH₀ was investigated between 4 to 10. The optimum values for pH₀ were 4 in ANN and 10 in RSM. An acidic condition is frequently reported as a more desirable condition for this kind of process and there are meaningful differences between results obtained with the ANN and the RSM models. The optimum values for electric current intensity obtained for the two models were similar and near 0.05 ampere. However, although a higher I makes the electrodic process easier it can cause an inversion of the efficiency in the EC process by the production of more coagulant than is needed. In case of the C_F, for both optimization approaches, the maximum available concentration (50 ppm) was selected as the optimum. This is the usual first order kinetic for this kind of process but it may rise also from an improper range selection for the optimization process.

CONCLUSION

The present study clearly shows the power of EC/EF as a fast applicable tool for defluoridation especially as an alternative method for the initial treatment of wastewater with a low or reduced F content. The results confirm that in EC defluoridation operational parameters have an important influence on the efficiency of the method and also show that the types and concentrations of co-existing anions have a significant role. The design of experiments, modeling, and optimization were applied successfully and the determined statistical goals were achieved. The artificial intelligence systems, such as ANN and GA, applied in the

study, gave an acceptable performance in the modeling and optimization of the complicated EC/EF process for the removal of fluoride.

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