Defluoridation of drinking water using a new flow column-electrocoagulation reactor (FCER) - Experimental, statistical, and economic approach

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Abstract

A new batch, flow column electrocoagulation reactor (FCER) that utilises a perforated plate flow column as a mixer has been used to remove fluoride from drinking water. A comprehensive study has been carried out to assess its performance. The efficiency of fluoride removal (R%) as a function of key operational parameters such as initial pH, detention time (t), current density (CD), inter-electrode distance (ID) and initial concentration (C_0) has been examined and an empirical model has been developed. A scanning electron microscopy (SEM) investigation of the influence of the EC process on morphology of the surface of the aluminium electrodes, showed the erosion caused by aluminium loss. A preliminary estimation of the reactor's operating cost is suggested, allowing for the energy from recycling of hydrogen gas hydrogen gas produced amount

The results obtained showed that 98% of fluoride was removed within 25 minutes of electrolysis at pH of 6, ID of 5 mm, and CD of 2 mA/cm^2. The general relationship between fluoride removal and operating parameters could be described by a linear model with R^2 of 0.823. The contribution of the operating parameters to the suggested model followed the order: $t > CD > C_0 > ID > pH$. The SEM images obtained showed that, after the EC process, the surface of the anodes, became non-uniform with a large number of irregularities due to the generation of aluminium hydroxides. It is suggested that these do not materially affect the performance. A provisional estimate of the operating cost was 0.379 US $\$/m^3$. Additionally, it has been found that 0.6 kW/m^3 is potentially recoverable from the H_2 gas.

Keywords: fluoride, electrocoagulation, perforated electrodes, modelling, SEM, operating cost.

1. Introduction

Fluorine is the 13th most abundant element in nature as overall it represents 0.054% of the earth's crust, and it is found in significant amounts in the oceans and atmosphere (Budisa *et al.*, 2014; Smith, 2007). Additionally, it can be found in more concentrated form in mineral deposits such as fluorspar (Meenakshi and Maheshwari, 2006; Gwala *et al.*, 2011). Weathering of these geochemical deposits is the natural source of water pollution by fluoride, whilst industrial wastewaters represent the anthropogenic source; for instance effluents from semiconductor manufacture, high temperature plastics, glass, and aluminium industries contain high fluoride concentrations (Zhu *et al.*, 2007; Emamjomeh and Sivakumar, 2009; Un *et al.*, 2013).

The presence of fluoride in minute quantity in drinking water is essential for mineralization of bones and prevention of tooth cavities (Meenakshi and Maheshwari, 2006). However, an excessive intake of fluoride may cause serious diseases such as skeletal fluorosis, teeth mottling, crippling skeletal fluorosis, infertility in women, and Alzheimer's syndrome (Mameri *et al.*, 1998; Zhu *et al.*, 2007; Zuo *et al.*, 2008; Vasudevan *et al.*, 2009a). Therefore, the WHO has limited the fluoride in drinking water to 1.2 mg/L (Un *et al.*, 2013).

In order to meet this limitation, different techniques have been used to reduce fluoride concentration, such as electrodialysis (Tahaikt *et al.*, 2004), membrane separation (Ndiaye *et al.*, 2005), adsorption (Zuo *et al.*, 2008), coagulation-electroflotation (Aoudj *et al.*, 2016), and electrocoagulation (EC) (Vasudevan and Oturan, 2014; Kim *et al.*, 2016). Recent studies have demonstrated that the EC method is an attractive alternative for water defluoridation (Un *et al.*, 2009; Aoudj *et al.*, 2010; Kim *et al.*, 2016), because the EC method does not require chemical handling, it is easy to perform, and remarkably reduces the sludge volume and the required space (Zhu *et al.*, 2007; Emamjomeh and Sivakumar, 2009). For instance, Vasudevan *et al.* (2009a) used an EC cell supplied with stainless steel as a cathode and magnesium-aluminium-zinc alloy, magnesium, aluminium and mild steel as anodes to remove fluoride from drinking water. The results obtained showed that the maximum fluoride removal efficiency, 96%, was achieved using magnesium as an anode and stainless steel as a cathode. While Un *et al.* (2013) removed 97.6% of fluoride from drinking water using an EC cell supplied with aluminium electrodes. Additionally, the EC technology has recently been integrated with other methods to remove fluoride from water. For instance, Zuo *et al.* (2008) used a combination of electrocoagulation and electroflotation to reduce fluoride in drinking water. The authors integrated an EC cell, which supplied with three aluminium electrodes, with electroflotation chamber (EF) to enhance flocs separation from water. This integrated EC-EF reactor reduced fluoride concentration from 4-6 to 1 mg/L (83% removal efficiency) within 30 minutes of treatment. Aoudj *et al.* (2015) also used an integrated electrocoagulation–flotation cell to remove fluoride from semiconductor wastewater, the results obtained shoed that this EC-EF cell was efficient enough to reduce fluoride from 42 to 4.61 mg/L within 120 min of treatment.

However, the lack of reactor design represents one of the major drawbacks of the EC method (Holt *et al.*, 2005; Un *et al.*, 2013), where the majority of the EC reactors still rely on a parallel arrangement of simple plate electrodes inside a container. In addition, the availability empirical or systematic approaches to design or reproduce the performance of EC units is also limited, which represents another drawback of this treatment method (Kabdaşlı *et al.*, 2012; Kuokkanen, 2016).

The current study therefore; has been devoted to fill a part of the gaps in the literature.

2. Aims and objectives

The current study has been devoted to fill a part of the gaps in the literature. The objectives of this study are:

1. Investigate the applicability of a new flow-column EC reactor (FCER), which utilises a perforated plate flow-column to achieve water mixing and aerating processes, to remove fluoride from drinking water. The influence of key operating parameters, such as electrolysis time (t) (0-30 min), initial pH value (4 to 8), current density (CD) (1, 2, and 3 mA/cm^2), inter-electrode distance (ID) (5, 8, and 11 mm), initial iron concentration (C_0) (10, 15, and 20 mg/L), will be taking into accounts.
2. Development of an empirical model to reproduce the fluoride removal performance of the FCER within the studied values of the operating parameters.
3. Conducting a preliminary economic study to estimate the operating cost of water defluoridation by FCER.
4. Estimate the harvestable amount of hydrogen gas (H_2), during the defluoridation process, and the yieldable energy from recycling this gas.
5. Carry out a SEM (scanning electron microscopy) investigation of the effects of the electrolysing process on the morphology of the surface of the aluminium anodes.

3. Theory of fluoride removal by the EC method

The principle of the electrocoagulation processes is the formation of the coagulating ions as the sacrificial metallic anode dissolves because of the applied current (Essadki *et al.*, 2009). When aluminium (Al) is used as electrodes, the anode releases the Al^{3+} ions, while the cathode generates hydrogen gas (Essadki *et al.*, 2009; Chaturvedi, 2013). The aluminium cations are converted, after dissolution, into $Al\ (OH)_{3(s)}$ and polymeric species such as $Al_{13}O_4(OH)_{24}{}^{7+}$ which readily coagulate to form flocs (Adhoum *et al.*, 2004; Essadki *et al.*, 2009). Pollutants present in the aqueous medium are removed due to chemical precipitation or chemical and physical attachment to the coagulating ions being produced by the erosion of electrodes (Gomes *et al.*, 2007; Chaturvedi, 2013). The electro-chemical reactions at the electrodes are (Essadki *et al.*, 2009; Kamaraj and Vasudevan, 2016):

At the anode: $Al_{(s)} \rightarrow Al^{3+} + 3e^{-}$ **(1)**

At the cathode: $2H_2O + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}$ **(2)**

Thus the highly absorbent aluminium hydroxide gel is formed *in situ*.

Generally, fluoride removal occurs due to three basic mechanisms (Essadki *et al.*, 2009):

1- Adsorption on $Al(OH)_3$ particles:

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

2- Co-precipitation:

$$n.Al + (3n-m)\cdot OH^- + m\cdot F^- \rightarrow Al_nF_m(OH)_{3n-m} \quad \textbf{(4)}$$

3- Fluoride attachment to the electrodes (physical attachment).

4. Materials and methods

4.1. FCER apparatus

The defluoridation process has been carried out using a new cylindrical EC reactor. This new EC reactor (FCER) employs a perforated-plate flow column to enhance water mixing process that increases the collision rate between coagulants and pollutants, which in turn enhances the removal efficiency. FCER consists of a hollow Perspex cylinder 25 cm in height and 10.5 cm in internal diameter, which in turn contains a flow column consists of 6 aluminium perorated discoid plates, 10.4 cm in diameter and 1 mm in thickness, of 99.5% purity provided by LJUM laboratories. Aluminium has been used as electrodes material due to its high affinity for fluoride ions (Aoudj *et al.*, 2013). More details about the whole EC unit are presented by Hashim *et al.* (2017).

4.2. Preparation of synthetic water samples

All chemicals were supplied by Sigma-Aldrich and used as supplied. Fluoride synthetic stock solution was prepared by dissolving the required quantities of NaF in deionised water. The initial fluoride concentration in this stock solution was100 mg/L, 500 mL samples with lower concentrations were diluted from this stock solution. The pH level of the prepared samples was varied in the range of 4 to 8 using 1 M HCl or 1 M NaOH solutions, while their conductivity was kept constant at 0.32 mS/cm using sodium chloride salt (NaCl).

4.3. Experimental procedures

The electrolysing process was carried out by placing a 500 mL synthetic water sample into the FCER, which supplied with two electrodes (284 cm^2 active area), and applying the required magnitude of electrical current using a DC rectifier (HQ Power; Model: PS 3010, 0-10 A, 0–30 V). In order to achieve the best removal efficiency, the influence of different operational parameters such as t (0-30 min), initial pH (4 -8), CD (1 - 3 mA/cm^2), C_0 of fluoride (10 - 20 mg/L), and ID (5 - 11 mm) were investigated.

The progress of fluoride removal, during the course of the experiment, was monitored by collecting 5 mL samples from the reactor at 5-minute intervals. The collected samples were filtered with 0.22 µm filters, supplied by Sigma-Aldrich, to remove unwanted solids, then the residual fluoride concentration in the filtrate was determined using standard Hach-Lange fluoride cuvettes test (LCK-323) (with the required dilution) and a Hach-Lange spectrophotometer (Model: DR 2800).

The removal efficiency (RE %) was determined using the following equation:

$$RE\% = \frac{C_0 - C_t}{Co} \times 100\% \qquad \textbf{(5)}$$

Where, C_0 and C_t are the initial and the residual concentrations of fluoride, in mg/L, respectively.

At the end of the run, the electrodes were abraded with sandpaper and dipped for 5 min in an HCl solution (35%), and then carefully rinsed with deionised water to remove impurities from the surfaces (Sharma, 2014). All experiments were conducted at room temperature (20 ± 1 ^{0}C).

4.4. Statistical analysis and modelling

The efficiency of the EC units is highly affected by serval operating parameters, such as initial pH, CD, C_o, t, and Id (Emamjomeh, 2006; Behbahani *et al.*, 2011). In order to investigate the combined influences of these parameters on fluoride removal using FCER, an empirical model was developed basing on the experimental results.

Mameri *et al.* (1998), and Emamjomeh (2006) indicated that the defluoridation rate of the EC process exhibits first order kinetics with respect to the fluoride concentration, thus:

$$\frac{dC_t}{dt} = -\, C_o . k . \mathrm{t} \qquad \textbf{(6)}$$

Integration of Eq. (6) yields:

$$C_t = \ C_o * \ e^{-(k.t)} \qquad \textbf{(7)}$$

Where k is the first order rate constant (min^{-1}). In order to calculate the value of the experimental rate constant (k_{exp}); Eq. (7) can be simplified by using the natural logarithm form:

$$-\, Ln\left(\frac{C_t}{C_o}\right) = k_{exp} . t \qquad \textbf{(8)}$$

In addition, the experimental value of the first order rate constant is a function of the key operating parameters (Emamjomeh, 2006). Therefore, it can be written as follows:

$$k_{exp} = f(CD, pH, C_0, ID) \qquad \textbf{(9)}$$

Based on these considerations and the obtained experimental data, a statistical model, was developed by applying the principles of multiple regression technique, using Minitab17.2 to reproduce the performance of the new reactor. In addition, the statistical significance of each individual operating parameter and its contribution to the predication of the removal efficiency were calculated.

Development of a reliable multiple regression model must pass through three basic steps (Pallant, 2005). Firstly, the data must be tested to check the normality, linearity, and homoscedasticity of residuals, and to detect the existence of multicollinearity (MC) and outliers within the studied data. More details about these tests are presented by Hashim *et al.* (2017). Additionally, the sample size must checked using the following formula (Tabachnick and Fidell, 2001).

$$N > 50 + 8 * IVs \qquad \textbf{(10)}$$

Where *N* and *IVs* are the sample size and number of independent parameters respectively.

Secondly, the ability of the suggested model to explain the variation in the DV must be checked using a proper statistical tool (Pallant, 2005). The coefficient of determination (R^2) is an efficient tool to achieve this purpose because R^2 shows how much of the experimental data is explained by the model (Tabachnick and Fidell, 2001).

While the last step concerns the contribution of each IV to the constructed model, which can be assessed by determining the statistical significance (*Sig.*). Any IV with a *Sig.* greater than 0.05 can be omitted from the model as it has no significant contribution (Field, 2008; Pallant, 2005). Additionally, Beta value can be used to assess the contribution of each individual IV to the suggested model. Statistically, the higher the absolute beta value is, the stronger the influence of the IV on the outcomes of the suggested model is (Tabachnick and Fidell, 2001; Pallant, 2005; Field, 2008).

4.5. Economic analysis of performance of FCER

The operating cost (OC) of the EC process includes the costs of energy, chemicals, material of electrodes, labour, treatment of sludge, maintenance, and fixed costs such as the basin and pipes (Ghosh *et al.*, 2008b). In this research, a preliminary economic study were conducted taking into account the costs of the energy, electrodes material, and chemicals (HCl and NaCl) according to the following equation (Kobya *et al.*, 2010):

$$OC = \alpha\, C_{energy} + \gamma\, C_{material} + \beta\, C_{chemicals} \qquad \textbf{(11)}$$

Where C_{energy} (kWh/m^3), $C_{material}$ (kg Al/m^3), and $C_{chemical}$ (kg /m^3) are the consumed energy electrode material, and chemicals respectively, α, γ, and β are the unit price of energy, aluminium, and chemicals according to the Iraqi markets 2016 (in US $) respectively. The energy consumption is calculated according to the following equation (Behbahani *et al.*, 2011):

$$C_{energy} = \int_0^{\mho} I * V * dt \qquad \textbf{(12)}$$

Where I is the current (A), V is the potential (V), and t is the treatment time (H). Integration of Eq. (12) yields:

$$C_{energy} = V * I * t \qquad \textbf{(13)}$$

Hence, the consumed energy per volume unit of treated water can be calculated using the following equation:

$$C_{energy} = \frac{I * V * t}{Vol.} \qquad \textbf{(14)}$$

Where *Vol.* is the volume of treated water (m^3). The $C_{material}$ is the weight loss of the electrodes due to the oxidation process, and calculated using Faraday's Second Law:

$$C_{material} = \frac{(I)(t)(m)}{(Z)(F)} \qquad \textbf{(15)}$$

Where I is the applied current in amperes, t is electrolysing time (second), m is the molecular weight (26.98 g/mole), Z the number of the electrons (3 for aluminium), and F is Faraday's constant (96487 C/mole). The cost of chemicals was calculated according to the consumed amounts.

4.6. Estimating the yieldable energy from the harvested hydrogen gas

Hydrogen gas (H_2) represents the main by-product of the EC method (Nasution *et al.*, 2011; Lakshmi *et al.*, 2013), which classified as eco-friendly and high energy fuel (122 kJ/g) (Eker and Kargi, 2010). Hence, harvesting of H_2 gas is one of the most important advantages of the EC technology. For instance, Phalakornkule *et al.* (2010) found that about 5.8 to13% of the required electrical energy to perform the EC cell could be obtained from the produced H_2 gas.

The produced H_2 gas from an EC cell can be determined using the following formula (Phalakornkule *et al.*, 2010):

$$Q_{H_2} = \frac{CD\,.\,A\,.\,t\,.\,H}{F} \qquad \textbf{(16)}$$

Where,Q_{H_2}, *Cd*, *A*, *t*, *H*, and F represent the quantity of the produced H_2 gas (mole), applied current density in (A/m^2), effective surface area of electrodes (m^2), treatment time (sec), number of hydrogen molecules (1/2), and Faraday's constant (96,500), respectively. While the produced energy from the H_2 gas is 0.244 MJ.mole^{-1} (Phalakornkule *et al.*, 2010).

4.7. Scanning electron microscopy characterisation of electrodes

In order to gain more an accurate insight into the influence of EC process on aluminium electrodes, the morphology of the surface of electrodes, before and after defluoridation process, were characterised by scanning electron microscopy (SEM) (Model: Quanta 200).

5. Results and discussion

5.1. Fluoride removal using FCER

5.1.1. Effect of initial pH

According to the literature, the performance of the EC method is greatly dependent on the pH of the solution (Zuo *et al.*, 2008; Emamjomeh and Sivakumar, 2009; Zeboudji *et al.*, 2013). Hence, to explore the influence of the initial pH on the fluoride removal by FCER, the initial pH of water samples containing 10 mg/L of fluoride was adjusted to the required value (from 4 to 8) using sodium hydroxide solution and hydrochloric acid. Then, these water samples were electrolysed for 25 min, in batch flow mode, at CD of 1 mA/cm^2, and ID of 5 mm. The influence of the initial pH on the removal of fluoride is shown in Figure 1. A decrease was observed in fluoride removal as the initial pH increased from 4 to 8 to reach the lowest value at initial pH of 8. This could be primarily attributed to amphoteric characteristics of aluminium hydroxide, where the pH governs the formation of $Al(OH)_3$ flocs (Un *et al.*, 2013). In alkaline conditions, the negatively charged complex ion $[Al(OH)_4]^-$, which has low adsorption capacity, becomes the prevailing hydroxide species, causing an obvious decrease in the removal efficiency.

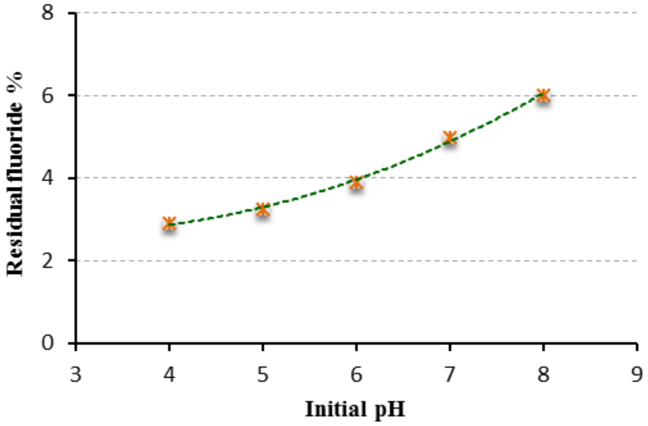


Fig. 1. Fluoride removal at different initial pHs.

In the current project, initial pH of 6. 0 was then used to commence the rest of the experiments due to two reasons; firstly, it is near to the neutral pH level, i.e. no need to add high amounts of chemicals to modify pH of water. Secondly, there was no significant difference in fluoride removal at initial pH of 4 and 6 (less than 2%).

5.1.2. Effect of the inter-electrode distance

Electrodes spacing exerts a significant influence on the energy consumption and the removal efficiency due to its effect on the ohmic resistance (Mameri *et al.*, 1998; Mohora *et al.*, 2012; Kamaraj *et al.*, 2016). To investigate the influence of electrodes spacing on fluoride removal, a series of batch experiments were carried out at different IDs (5, 8, and 11 mm) using a constant CD of 1 mA/cm^2, t of 25 min, and initial pH of 6.

The results obtained, Figure 2-(A), indicated that fluoride removal decreased as the ID is increased, where it can be clearly seen that residual fluoride increased from about 4% to about 15% when the ID increased from 5 mm to 11 mm respectively. In addition, Figure 2-(B) shows that the energy consumption increased from 1.75 to 3.6 kW.h/m^3 as the ID increased from 5 to 11 mm respectively. This could be explained by the fact that if the ID increases then both the resistance and the growth of the passive anodic film will also increase. Therefore the current will decrease, and the amount of floc formed will likewise decrease. Hence the efficiency will change (Ghosh *et al.*, 2008a; Hashim *et al.*, 2017). The effect of this film will be diminished as the inter-electrode distances decreased because the hydrogen gas, which is formed in the vicinity of the cathode, sweeps those fluoroaluminium complexes from the anode surface, and promotes the dissolution of the aluminium anode as a consequence (Mameri *et al.*, 1998; Hashim *et al.*, 2017). However, very short IDs should be avoided because the high electrostatic attraction will increase the collision rate between the formed flocs, which could result in flocs degradation (Daneshvar *et al.*, 2004; Khandegar and Saroha, 2013). Additionally, Hashim *et al.* (2017) indicated that very short ID must be avoided in FCER because it hinders the excluding of the accumulated air bubbles between electrodes, which negatively influences the energy consumption. Thus, in this investigation, the ID will be maintained at 5 mm for the rest of the experiments.

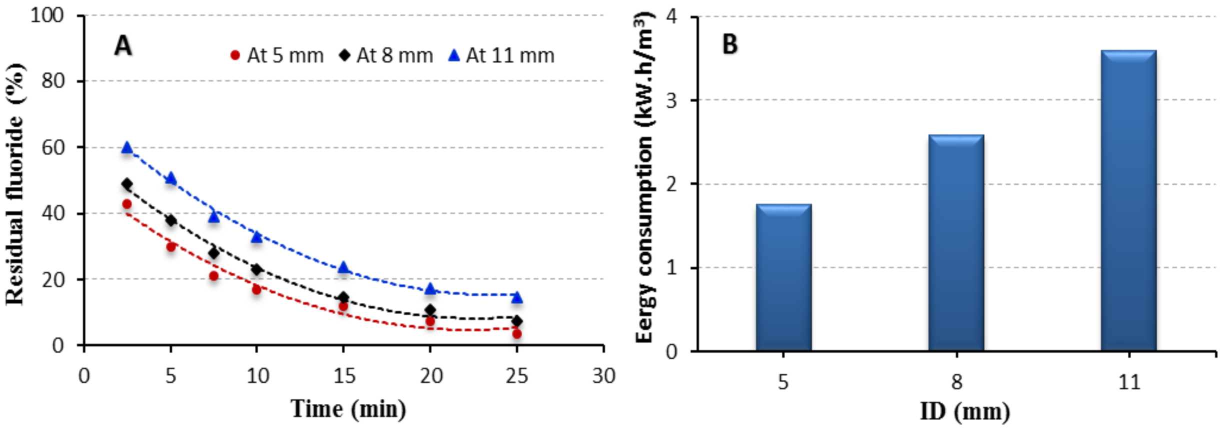


Fig. 2. (A) Fluoride removal at different IDs, (B) influence of Id on energy consumption.

5.1.3. Effect of current density

Current density has a significant influence on the performance and energy consumption of the EC cells as it determines the rate of coagulant dosage, the rate of bubble generation and size and the floc's growth (Un *et al.*, 2009; Vasudevan *et al.*, 2009b; Gao *et al.*, 2010; Boudjema *et al.*, 2014). Therefore, a set of batch experiments, to determine the influence of current density on fluoride removal and energy consumption, were commenced using 10 mg/L of fluoride at different CDs (1, 2, and 3 mA/cm^2). While, the initial pH and ID were kept constant at 6 and 5 mm, respectively. Figure 3-(A) shows that the residual fluoride concentration is reversely proportional to the applied Cd. For instance, increasing the CD from 1 to 3 mA/cm^2 decreased the residual fluoride, after 25 min, from about 4% to 1.1%. This could be explained by the fact that the dissolved aluminium ions from the anode increases as the CD increase, and enhances flocs formation and fluoride removal as a consequence (Un *et al.*, 2013).

Although fluoride removal was enhanced as the CD, increasing the CD also increased the energy consumption, where the results (Figure 3-(B)) showed that when Cd increased from 1 to 3 mA/cm^2, the energy consumption exponentially rose from 1.75 to 12.4 kWh/m^3, respectively. Therefore, in this investigation, it might be reasonable to use the current density of 2 mA/cm^2 to commence the rest of experiments.

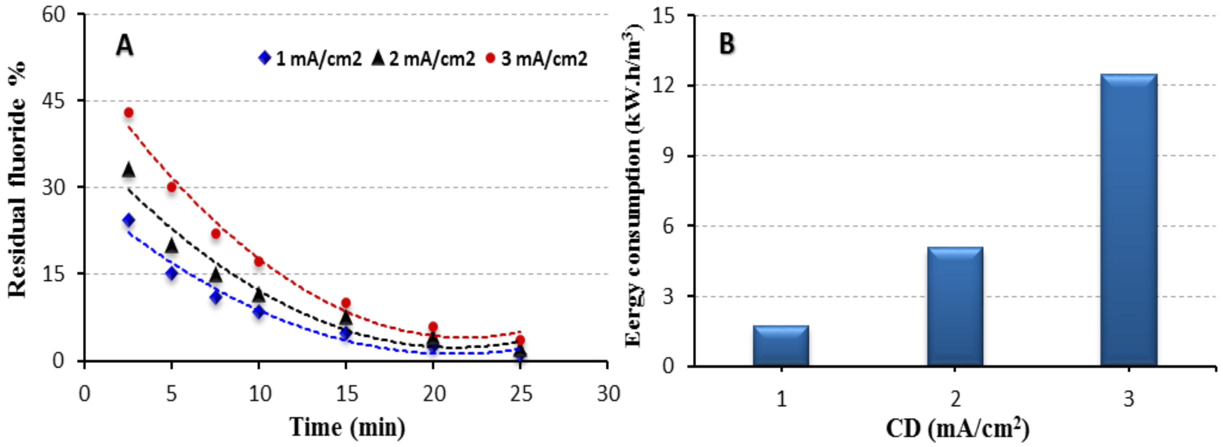


Fig. 3. Influence of CD on (A) Fluoride removal, (B) energy consumption.

5.1.4. Effect of initial fluoride concentration

In order to explore the influence of the initial concentration of fluoride on the defluoridation process, fluoride solutions with different initial concentrations of 10, 15, and 20 mg/L were electrolysed by FCER for 30 min at a constant ID of 5mm, CD of 2 mA/cm^2, and initial pH of 6. The results obtained, Figure 4, indicate that the higher the initial fluoride concentration was, the slower fluoride removal was, i.e., the required electrolysis duration for a permissible residual fluoride concentration increases as the initial concentration increases. For instance, detention time of 11 min was enough to meet the WHO requirements (1.2 mg/L) when the initial fluoride concentration was 10 mg/L, but about 25 min was required when the initial fluoride concentration was 20 mg/L.

One of the predominant pathways of pollutant removal by the EC method is the adsorption of pollutant molecules on the freshly produced metallic hydroxide flocs (Emamjomeh and Sivakumar, 2009; Dalvand *et al.*, 2011). According to Faraday's law (Eq. 15), a constant number of coagulation ions is liberated from the sacrificial anode for the same CD and electrolysing time. Consequently, the same quantity of aluminium hydroxide flocs (coagulants) was produced in the solution. Therefore, the formed flocs, at high fluoride concentrations, were not sufficient to absorb all fluoride ions within the studied treatment period, i.e., FCER needs longer time to remove high fluoride concentrations. Additionally, the results obtained showed that the initial concentration of fluoride did not influence the rate constant (k) value. Therefore, in the present study, 25 min was considered as the best electrolysing time.

It is noteworthy to highlight that the obtained removal efficiency, 98%, is very comparable to those in literature. For instance, Un *et al.* (2013) removed 97.6% of fluoride from drinking water using an aluminium-based EC cell, while Vasudevan *et al.* (2009a) achieved a 96% fluoride removal efficiency using an EC cell supplied with magnesium anode and stainless steel cathode. However, it is noteworthy that the new bench scale reactor FCER reduces the use of mechanical or magnetic stirrers which require extra power to work. Therefore, FCER could be a cost-effective alternative to the traditional lab-scale EC reactors.

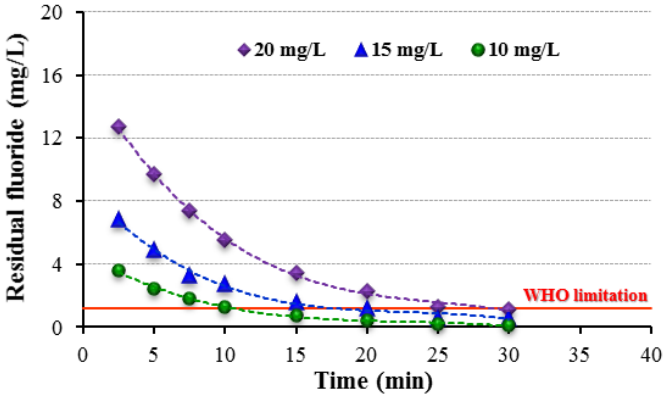


Fig. 4. Fluoride removal at different initial concentrations.

5.2. Statistical analysis of the results and model construction

A multiple regression analysis was performed using the Minitab17.2 package to assess the relationship between the reaction rate constant (*k*) (dependant variable (DV)) and the operating parameters (independent variables (IVs)). Multiple regression was chosen as it suitable to perform a complex investigation of the interrelationship among several variables (Pallant, 2005). The general regression form is (Mustapha and Abdu, 2012):

$$Y = A + B_1 X_1 + B_2 X_2 + \cdots + B_k X_k + \boldsymbol{\varepsilon} \qquad \textbf{(19)}$$

Where Y is the predicted value of the dependant variable, A represents the Y intercept, B_k are the regression coefficients, X_s are the independent variables, and ($\boldsymbol{\varepsilon}$) is the random error coefficient. To construct a model with a reliable reproducibility, as mentioned before, the multiple regression assumptions were tested:

5.2.1. Sample size

According to Eq. (10), the required data points to construct a reliable model is 82 points because 4 IVs were experimentally investigated. In the present investigation, the experimental data points were 92. Thus this condition has been met.

5.2.2. Multicollinearity

The VIF value of each IV has been calculated in order to investigate the existence of multicollinearity. The obtained results (Table 1) shows that the VIF values for the studied IVs were less than 10, which indicates the absence of the multicollinearity in the studied data.

Table 1: Summary of statistical analysis results.

IVs	Beta	Sig.	VIF	Max. MDs	Standardised residual exceeds the range of 3.0 to -3.0	
					No. of cases	Value
Cd	0.42	0.000	1.210	9.39	1	3.01
Co	-0.38	0.000	1.136			
Id	-0.30	0.001	1.098			
pH	-0.18	0.036	1.000			

5.2.3. Outliers

The presence of the outliers in the studied data can be detected by determining the MDs for the studied observations, which must be less than 20.52 (the critical value for five IVs (Pallant, 2005)). The results obtained, Table 1, indicates that the maximum detected MD was 9.39, which indicates the absence of the outliers in the studied data.

5.2.4. Normality, linearity, and homoscedasticity of residuals

It is expected, in normal distribution, that not more than 1% of the standardised residual values of the data points outside the range 3.0 to -3.0. Results of Table 1 show that one observation (out of 92 observations) exceeded the specified range; thus this assumption has not been met.

In such case, it is recommended to calculate the Cook's Distance (COO_1) to check whether these observations are having any influence on the outcomes of the built model as a whole (Tabachnick and Fidell, 2001). Where, any observation with COO_1 greater than 1.0 is a potential problem. Minitab 17.2 package has been used to determine the COO_1 value of this observation. The obtained results showed that the maximum COO_1 value is 0.21, suggesting no potential problems associated with the presence of this observation.

5.2.5. Significance of each IVs

The statistical significance (*Sig.*) and Beta value of each individual IVs have been calculated to check whether this IV makes a statistically significant contribution to the suggested model or not. Results of Table 1 showed that the highest *Sig.* was 0.03 (less than 0.05), which indicates that all the studied operating parameters exert an influence of different magnitudes. According to the Beta values, the electrolysing time made the highest contribution to the outcomes of the suggested model at a Beta value 0.68, followed by Cd at 0.42, C_0 at 0.38, and Id at 0.3. While the initial pH made the lowest contribution to the suggested model at Beta value of 0.18.

After the testing process, the multiple regression analysing was performed to assess the relation between the rest of the operating parameters (CD, C_0, Id, and t) and the reaction rate constant (*k*). The results yield the following formula (with R^2 of 0.823):

$$K_{Pre} = 0.322 + 0.04\,CD - 0.007\,C_0 - 0.01\,Id - 0.012\,pH \qquad \textbf{(20)}$$

Where K_{Pre} represents the predicted reaction constant. Substitution of Eq. (20) in Eq. (7) gives:

$$C_f = C_o * e^{-[0.322+0.04\,CD-0.007\,C_0-0.01\,Id-0.012\,pH]*t} \qquad \textbf{(21)}$$

Hence, the predicted fluoride removal efficiency can be written (the model) as follows:

$$R_{Pre}(\%) = \left\{1 - e^{-[0.322+0.04\,CD-0.007\,C_0-0.01\,Id-0.012\,pH]*t}\right\} * 100 \qquad \textbf{(22)}$$

The suggested model has been used to predict fluoride removal from drinking water, using FCER, at different operating conditions; the obtained results were compared to the experimental removal values. Indeed, this step is to check whether the suggested model has the ability to reproduce the performance of FCER in terms of fluoride removal (within the studied values of the operating parameters) or not. The suggested model has been applied to a set of experimental data consists of 40 experimental observations (at different operating conditions), which were randomly selected from the experimental data.

The results obtained, Figure 5, showed a good agreement between the predicted and experimental fluoride removal. Where R^2 value, for this randomly selected sample, was 0.843. Statistically, these results, indicate that the suggested model is able to describe about 84.3% of the influences of the operating parameters on the removal of fluoride (for the studied sample).

Based on the results obtained from these comparisons, it could be reasonable to consider that the suggested model is reliable enough to reproduce the fluoride removal performance of FCER.

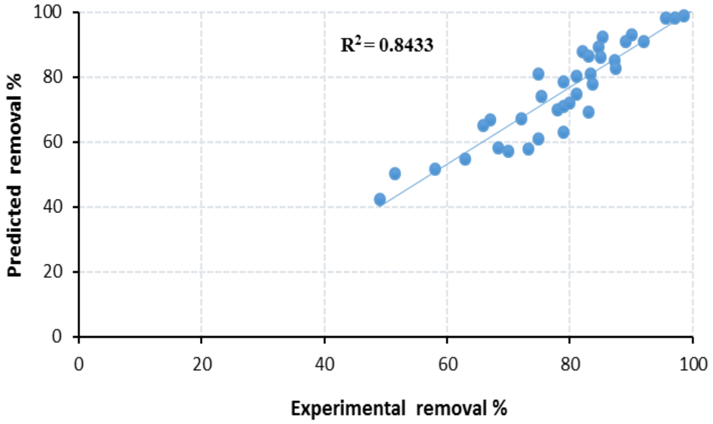


Fig. 5. Relationship between the predicted and experimental fluoride removal efficiencies.

5.3. Economic analysis of performance of FCER

Operating cost, as mentioned before, is an important parameter as it determines the applications of the treatment method. Therefore, in the present study, a preliminary economic study was conducted to estimate the operating cost of defluoridation process by FCER. The cost of energy, materials (aluminium), and chemicals were considered in this economic study. The energy consumption was calculated using Eq. (14), while the consumed electrode material was calculated using Eq. (15). The consumed amounts of chemicals were manually calculated during the experimental work. Unites prices, according to the Iraqi market 2016, were 2.5 pence/kWh of electricity, 1.53 \$/kg of aluminium (minimum purity > 99%), 0.32 \$/L of HCl (35%), and 0.2 \$/kg of NaCl (purity 99.4% min.). Basing on these prices, the operating cost of fluoride removal from drinking water using the FCER is:

$$OC = \left(\frac{2.5}{100}\right)\$ * 5.1\frac{kWh}{m^3} + 1.53\ \$ * 0.15\frac{kg}{m^3} + 0.02\frac{\$}{m^3} = 0.379\ USA\ \$/m^3$$

Emamjomeh and Sivakumar (2009), reported that the fluoride removal from drinking water costs from 0.36 to 0.61 AUD/m^3 (about 0.27 to 0.45 USA\$/m^3) depending on the operating conditions, for instance they reported that fluoride removal at current density of 2.5 mA/cm^2 and initial pH of 6 costs about 0.5 AUD/m^3 (about 0.37 USA\$/m^3). Therefore, it can be said that the cost of defluoridation of drinking water using FCER is very comparable with those of previous studies. But, it is noteworthy that FCER reduces the use of mechanical or magnetic stirrers which require extra power to work; these stirrers until now have been widely used in the EC reactors (especially laboratory scale ones). Thus, FCER could be a cost-effective alternative to the traditional lab-scale EC reactors.

5.4. Estimating the energy yieldable from the harvested hydrogen gas

As it was mentioned before, investment of the produced H_2 gas from the EC units could minimise the operating cost as it is categorised as an eco-friendly and high energy fuel. In this study therefore, the produced amount of H_2 gas from FCER during the defluoridation process has been calculated using Eq.16. While the producible energy from recycling this quantity of H_2 gas was calculated using Eq.17.

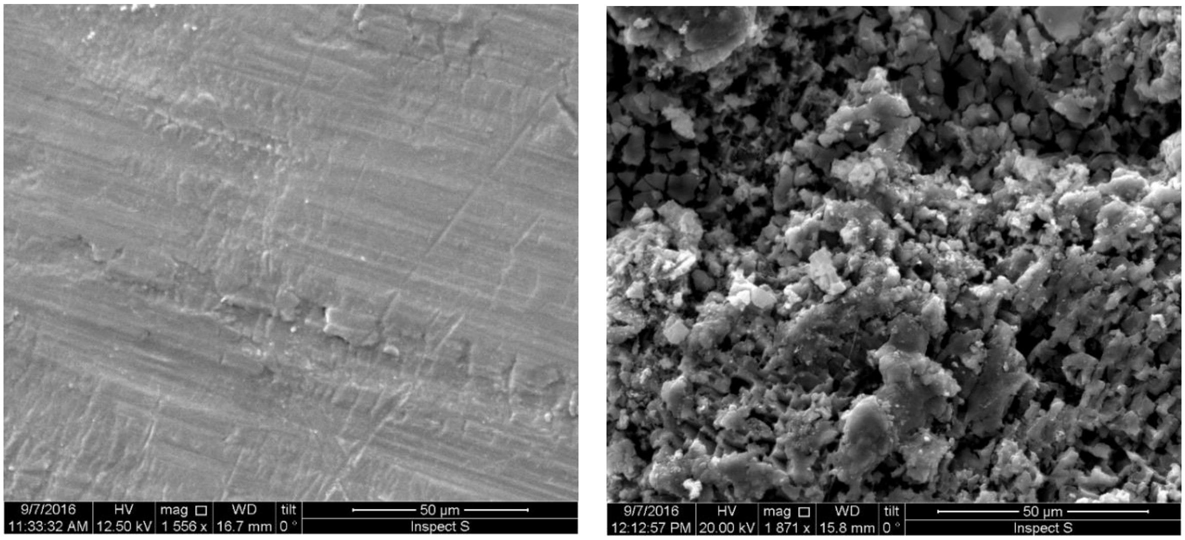
The produced amount of H_2 gas, in the current study, was calculated at the obtained optimum operating conditions for fluoride removal, which were 25 min of electrolysing at CD of 2 mA/cm^2. While the effective surface area of electrodes was 284 cm^2. Hence, the produced amount of H_2 gas from the FCER during the removal of 20 mg/L of fluoride from 500 mL water sample is:

$$Q_{H_2} = \frac{20 \ * 0.0284 * 1500 * \ 0.5}{96500} = 0.0044 \text{ mole}$$

Taking into consideration that each 1.0 kWh = 3.6 MJ (Phalakornkule *et al.*, 2010), then the energy produces from recycling the produced H_2 gas from FCER could be 0.6 kW/m^3 of water. According to these results, the produced amount of H_2 gas from filed scale treatment plants could be used to produce a considerable amount of energy.

5.5. SEM characterisation of electrodes

Magnified SEM images of aluminium anode, before and after, electrocoagulation of fluoride electrolyte was obtained to compare the texture of the electrode's surface. Figure 6-(A) shows the metal surface before the electrocoagulation process. It can be observed from this figure that the surface of the anode was uniform except minor dents, which could have occurred due to the mechanical handling of metal during electrode shaping process. While Figure 6-(B) shows the same anode after a series of EC experiments. The surface of anode became totally non-uniform with a large number of dents. The generation of these dents could be attributed to the consumption of anode material at the active sites where the anode dissolution results in the generation of aluminium hydroxides (coagulation ions) (Ahlawat *et al.*, 2008; Vasudevan *et al.*, 2012).



(A) **(B)**

Fig. 6. SEM images of aluminium anode, (A) before EC process, and (B) After EC process.

6. Conclusion

The performance of the new closed batch EC reactor, FECR, has been investigated in terms of fluoride removal from drinking water and modelled using the multiple regression concepts. Experimentally, the ability of FECR to remove fluoride from drinking water was investigated taking into consideration the effects of different operational parameters, including the detention time, initial pH, current density, inter-electrode distance, and initial fluoride concentration. The experimental results revealed that the fluoride removal could be enhanced by increasing either the current density or the detention time. The initial pH of the water being treated exerts a slight beneficial influence on removal efficiency. Contrarily, the initial concentration of fluoride highly influences the removal efficiency, where it was found that about 11 min was quite enough to meet the WHO requirements when the initial fluoride concentration was 10 mg/L, but it increased to about 25 min when the initial fluoride concentration was 20 mg/L.

Statistically, the suggested model, which has R^2 of 0.823, shows a good reproducibility of the FCER performance and there was a good agreement between the measured and predicted fluoride removal efficiencies. In addition, the statistical results indicated that each single operating parameter made a different contribution to the suggested model (fluoride removal); the significance of the studied operating parameters followed the order: $t > CD > C_0 > ID > pH$.

Economically, the preliminary operating cost of fluoride removal from drinking water using the FCER is 0.379 US $\$/m^3$, which is comparable with those in literature. However, it is noteworthy that the new bench scale reactor FCER reduces the use of mechanical or magnetic stirrers which require extra power to work. Therefore, FCER could be a cost-effective alternative to the traditional lab-scale EC reactors.

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