

## ELECTROCHEMICAL PROCESS FOR THE TREATMENT OF DRINKING WATER

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### ABSTRACT

In this study removal of fluoride from synthetic water (distilled water + NaF salt + Na<sub>2</sub>SO<sub>4</sub>) by electrocoagulation using iron electrode was examined. Experiments were conducted to evaluate the effects of current density (0.5-3 mA/cm<sup>2</sup>), initial pH (5-9), and supporting electrolyte (Na<sub>2</sub>SO<sub>4</sub>) dosage (0.005-0.03M) on the performance of the system. The influent pH value was found to be a very important variable that affected fluoride removal significantly. The preferable influent pH is 6.0. The highest treatment efficiency was obtained for the largest current density. The initial fluoride concentrations of 5 mg/L was reduced to the 0.70 mg/L with the removal efficiency of 85.9% at 3 mA/cm<sup>2</sup>.

**Keywords:** Defluoridation, Electrocoagulation, Iron, Treatment

### 1. INTRODUCTION

Fluorine is an essential element for human health. However, excess intake of fluoride would lead to various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility in women, brain damage, Alzheimer syndrome, and thyroid disorder [1]. Fluoride concentrations less than 1 mg/L are beneficial to prevent skeletal and dental problems. The 1984 World Health Organization (WHO) guidelines suggest optimum levels of fluoride concentration at 1 and 1.2 mg/L [2]. Health impacts from long-term use of drinking water with a high fluoride concentration have been summarized in Table 1. Fluoride also can be found in industrial wastewaters, such as in semiconductor, metal processing, fertilizers, and glass manufacturing industries. The discharge of such wastewater into the surface water would lead to the contamination of groundwater. Many people in the world are affected by the fluorosis. A study by UNICEF shows that fluorosis is endemic in at least 27 countries across the globe. These countries are: Algeria, Argentina, Australia, Bangladesh, China, Egypt, Ethiopia, India, Iran, Iraq, Japan, Jordan, Kenya, Libya, Mexico, Morocco, New Zealand, Palestine, Pakistan, Senegal, Sri Lanka, Syria, Tanzania, Thailand, Turkey, Uganda, and United Arab Emirates [3].

**Table 1: Health impacts from long term use of high fluoride concentration in drinking water [3].**

Fluoride Concentration (mg/l)	Health effect
<0.5	Dental caries
0.5-1.5.1	Promotes dental health
1.5-4.1	Dental fluorosis
>4	Dental and skeletal fluorosis

Different techniques were used like adsorption [4,5], membrane separation [6], ion-exchange [7], and electrochemical methods [8,9]. Electrocoagulation (EC) is the electrochemical production of destabilization agents that brings about charge neutralization for pollutant removal and it has been used for water or wastewater treatment. Recently, there are numerous electrocoagulation reports using aluminum as the anode for defluorination [10, 11, 12, 13, 14]. There is no report published iron as anode material for the removal of fluoride by electrocoagulation.

In the iron electrode two mechanisms have been proposed for the production of  $Fe(OH)_n$  where  $n=2$  or  $3$  as seen from Table 2. In the EC cell, the iron electrodes sacrifice themselves to form iron ions first. Afterwards, the iron ions are transformed to  $Fe(OH)_n$  before polymerized. The  $Fe(OH)_{n(s)}$  formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [15].

**Table 2: The reactions occurred at iron electrode and in the solution [15].**

Iron Electrode	
<i>Mechanism 1</i>	<i>Mechanism 2</i>
----- Anode -----	
$4Fe_{(s)} \rightarrow 4Fe_{(aq)}^{2+} + 8e^-$	$Fe_{(s)} \rightarrow Fe_{(aq)}^{2+} + 2e^-$
----- In the solution -----	
$4Fe_{(aq)}^{2+} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H_{(aq)}^+$	$Fe_{(aq)}^{2+} + 2OH_{(aq)}^- \rightarrow Fe(OH)_{2(s)}$
----- Cathode -----	
$8H_{(aq)}^+ + 8e^- \rightarrow 4H_{2(g)}$	$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^-$

Unfortunately, up to date, no iron electrode was reported for defluorination. Hence, the influence of iron electrode on the performance of fluoride removal will be the further contribution of the research. This study elucidates the effects of parameters such as: current density initial pH, and supporting electrolyte concentration on the fluoride removal efficiency for a batch EC reactor. Information regarding the electrical energy

consumption (EEC) is also included to provide an estimation of the cost of fluoride removal by the EC system.

## 2. MATERIALS AND METHODS

### 2.1. Solution Chemistry

The influence of the experimental design parameters on the defluoridation process was achieved with “synthetic” water (distilled water + NaF salt + Na<sub>2</sub>SO<sub>4</sub>). Fluoride solutions (5 mg/L as F<sup>-</sup>) were prepared by mixing sodium fluoride in deionized water. Sodium sulfate was added to the aqueous solution to increase conductivity. 1 N Sodium hydroxide and 1N sulphuric acid solutions were added for initial pH adjustment.

### 2.2. Bench scale batch EC apparatus

The electrochemical system consists of a reactor, a mechanical stirrer, and a direct current (DC) power supply (Statron Type 3234.4); its schematic representation and photograph are shown in Fig. 1. The iron cylindrical reactors that operated as anodes had an internal diameter of 10 cm. The mechanical stirrer (Heidolph RZR 2102) consisted of two iron blades and operated as the cathode; it was dipped into the reactor containing wastewater. It was also used to maintain uniform composition and to enable the agglomeration of flocs in the solution by rapidly stirring the mixture at 100 rpm. The performance of the reactor was evaluated in the batch mode.

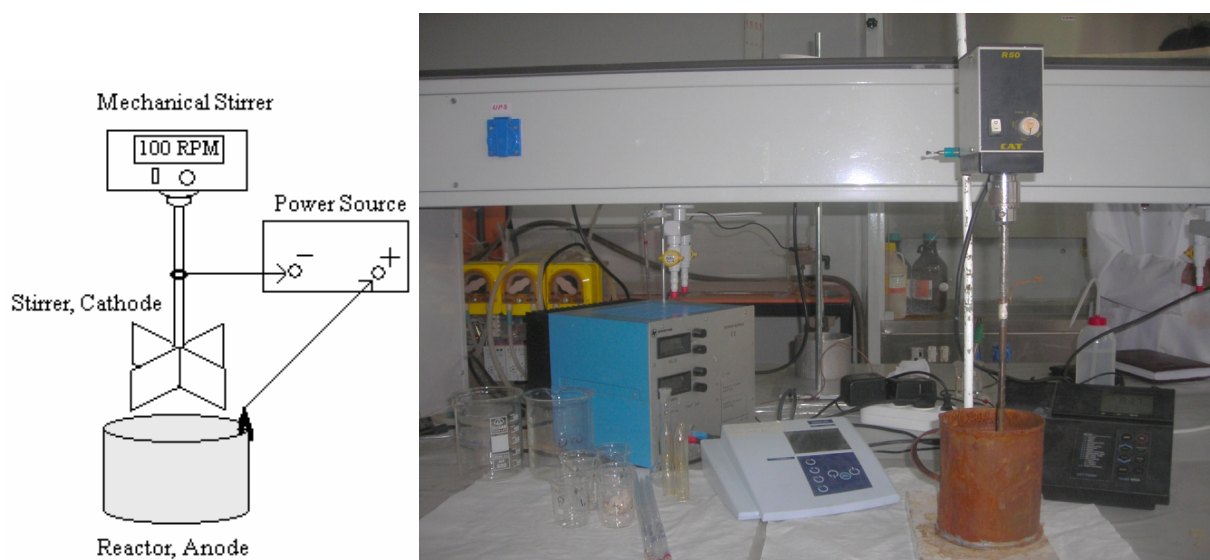


Figure 1: Experimental set up and its photograph.

### 2.3. Experimental Protocol

All experiments were conducted at a room temperature of about 25°C with initial  $F^-$  concentration of 5 mg/L. Current was varied over the range 0.5-3 mA/cm<sup>2</sup>, however, it was held constant for each run. In each run, wastewater (0.5 L) was poured into the electrolytic cell, and the pH, conductivity, and current density were adjusted to the desired value. The reaction was started by switching the DC power supply on. At the end of the run, the stirrer and inside reactor were washed thoroughly with 0.1M HCl and then with distilled water to remove any solid residues on the surfaces and dried. Electrocoagulation experiments were performed for 30 min for each run and samples were taken every 5 min interval from the electrocoagulator and centrifuged. The supernatant liquid was analyzed for fluoride determination. Fluoride concentrations in the sample were determined by SPANDS Method from Standards Methods. Conductivity, and pH were determined in by means of conductimeter (Inolab Cond., Level 1), and pH meter (Orion 420 A), respectively. All the samples were analyzed in duplicate to ensure data reproducibility, and an additional measurement was carried out, if necessary.

## 3. RESULTS AND DISCUSSION

The calculation of removal efficiency ( $RE\%$ ) after EC and the electrical energy consumed per unit volume of treated wastewater (EEC) was calculated using the equation 1 and 2 respectively.

$$RE\% = \frac{C_0 - C}{C_0} \times 100 \quad , \quad (1)$$

where  $C_0$  and  $C$  are the concentrations of fluoride before and after EC, respectively, in mg/L and

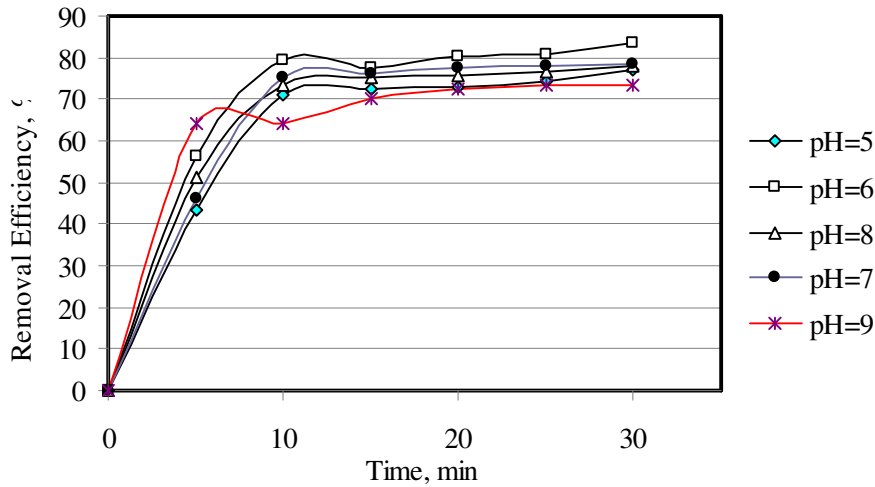
$$EEC = \frac{V \cdot I \cdot t}{v} \quad (2)$$

where  $EEC$  is the electrical energy consumption (kWh/m<sup>3</sup>),  $V$  is the potential (V),  $I$  is the current (A),  $t$  is the time (h), and  $v$  is the volume of solution (m<sup>3</sup>).

### 3.1 Effect of Initial pH

To investigate the effects of the initial pH on the electrocoagulation of wastewater the laboratory experiments was done by modifying the initial pH values of 5.0, 6.0, 7.0, 8.0 and 9.0 pH at 1 mA/cm<sup>2</sup> in the presence of 0.01 M Na<sub>2</sub>SO<sub>4</sub>. In all experiments, pH was not controlled but monitored throughout the electrolysis. A trend observed was seen in Fig. 2. The removal efficiency clearly increased with an increase of pH from 5 pH to 6 and subsequently dropped at pH 9.0. The removal efficiencies of 77.2, 83.6, 78.4, 77.8, and 73.6% were obtained at pH 5.0, 6.0, 7.0, 8.0, and 9.0 respectively. The maximum removal efficiency was observed at pH 6. The drop of removal efficiency

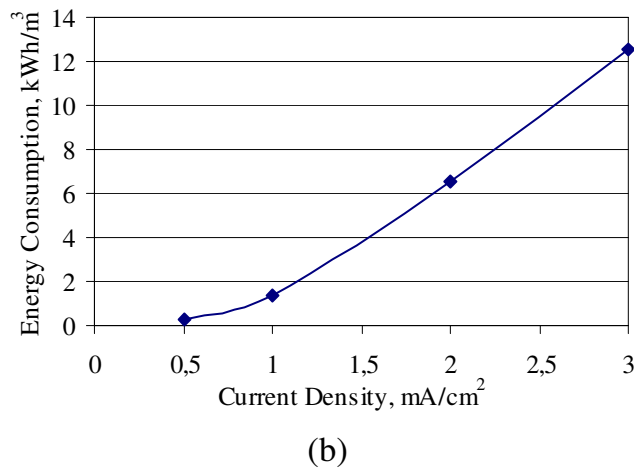
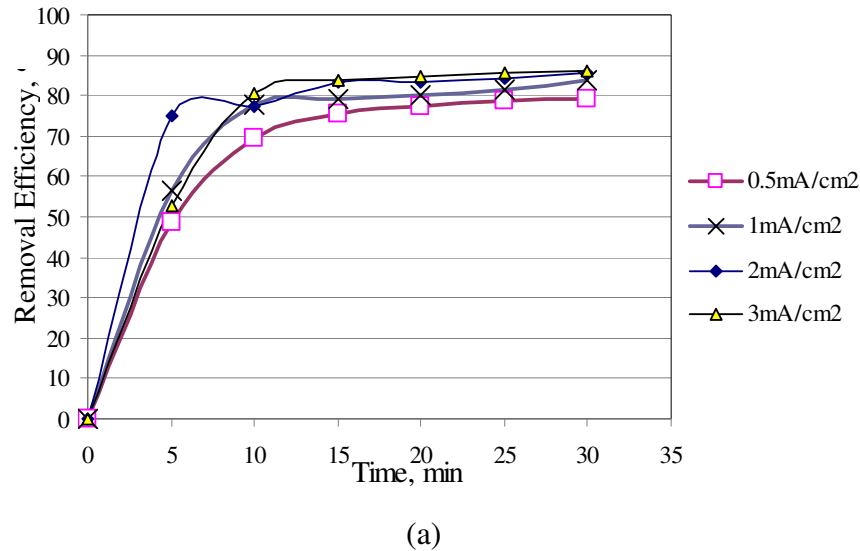
occurred when pH tends towards acid or basic values. Similar results were obtained with an iron electrode by Daneshvar et al. [16].



**Figure 2: Variation of fluoride removal efficiency with time for different initial pH values. Current Density=1 mA/cm<sup>2</sup>, C<sub>Na<sub>2</sub>SO<sub>4</sub></sub>=0.01M**

### 3.2 Effect of Current Density

It is well-known that current not only determines the coagulant dosage rate but also the bubble production rate, size and the floc's growth, which can influence the treatment efficiency of the electrocoagulation, were determined by the current. The influence of current density on the removal rates was investigated at the pH 6 with 0.01 M Na<sub>2</sub>SO<sub>4</sub>. Removal efficiency rapidly increases on increasing the current density during the first 10 minutes; after this time, the removal efficiency scarcely increases (Fig. 3a). Removal efficiencies of 79.4, 83.6, 85.6 and 85.9% corresponding to 1.03, 0.82, 0.72, and 0.70 mg/L fluoride concentrations was achieved at 0.5, 1, 2 and 3 mA/cm<sup>2</sup> respectively. Similar results were obtained by Tezcan Un and coworkers [17, 18] for the electrochemical treatment of olive mill wastewater and Tezcan Un [19] for the electrocoagulation of vegetable-oil refineries wastewater using iron electrode. Thus, the higher the rate of formation of iron hydroxide, the lower the time required for emulsion abatement. However, it is advisable to limit the current density in order to avoid excessive oxygen evolution as well as to eliminate other adverse effect, like heat generation.



**Figure 3: a) Variation of fluoride removal efficiency with time for different current densities, b) Variation of electrical energy consumptions with current densities. Initial pH:6,  $C_{Na_2SO_4}=0.01M$ .**

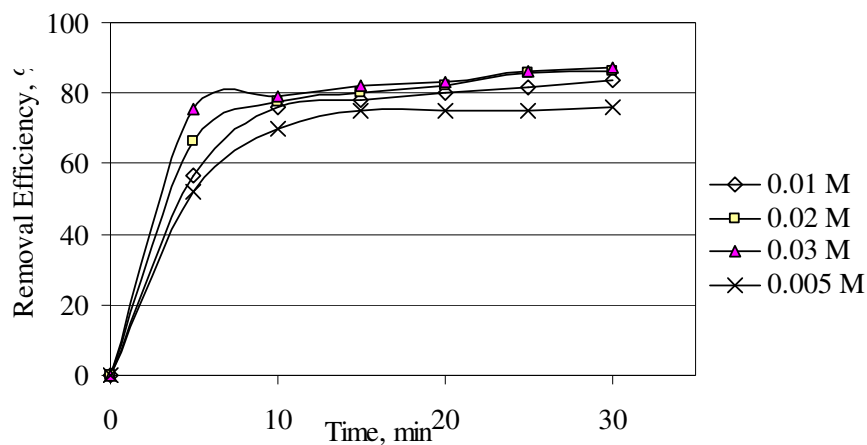
The effect of the current density on the EEC during the EC process is presented in Fig.3b. Electrical energy consumption increased more rapidly as the current density increased. Because the applied potential increased by increasing the current density, EEC also increased. Thus, when the optimal current density and potential have been selected, either higher removal rate or lower energy consumption can be preferred.

### 3.3 Effect of Supporting Electrolyte Concentration

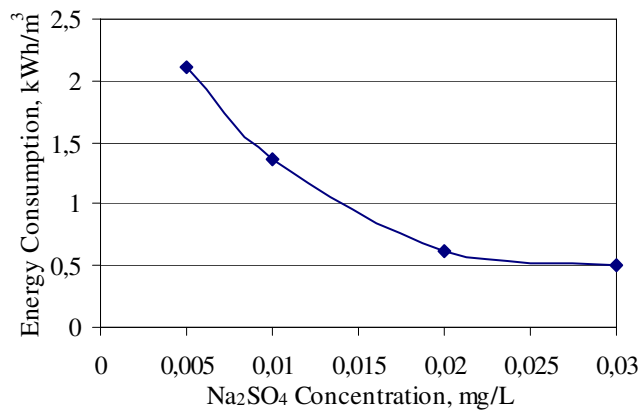
The conductivity of wastewater can influence the electrochemical treatment because it facilitates the passage of current. To evaluate the effect of the supporting electrolyte concentration on removal efficiency at 1 mA/cm<sup>2</sup>, and pH 6, different quantities of Na<sub>2</sub>SO<sub>4</sub> were added. The results are shown in Fig. 4a. As the Na<sub>2</sub>SO<sub>4</sub> concentration increased, the removal efficiency increased. Removal efficiencies of 76.2, 83.6, 86.3,

87.4% were obtained at 0.005, 0.01, 0.02 and 0.03M Na<sub>2</sub>SO<sub>4</sub> concentrations respectively.

The effect of Na<sub>2</sub>SO<sub>4</sub> concentration on EEC is shown in Fig.4b. As shown in Figure 4b with the conductivity increasing, the electrical energy consumption (EEC) was considerably reduced. It is clear that the cell voltage decreased with an increase in the conductivity at constant current density. When the conductivity of solution increases, IR-drop decreases, so the necessary voltage to reach on optimum current density will be diminished, and consequently the consumed electrical energy is decreased. The EEC of 2.10 kWh/m<sup>3</sup> at 0.005 M Na<sub>2</sub>SO<sub>4</sub> decreased to 0.50 kWh/m<sup>3</sup>, with increasing Na<sub>2</sub>SO<sub>4</sub> concentration up to 0.03 M. Similar effects on the EEC with increase in conductivity were previously reported by Tezcan Un et al. [15, 20].



(a)



(b)

**Figure 4: a) Variation of fluoride removal efficiency with time for different Na<sub>2</sub>SO<sub>4</sub> concentrations, b) variation of energy consumption with Na<sub>2</sub>SO<sub>4</sub> concentrations. Initial pH:6, Current density=1mA/cm<sup>2</sup>.**

## 4. CONCLUSIONS

Based on the results of experiments, the following conclusions may be obtained:

1. The results of this study showed that electrocoagulation with iron electrode could be applied for the defluoridation.
2. The use of iron as sacrificial electrode material in the treatment of fluoride by electrocoagulation was found to be pH dependent. The most effective removal capacity was achieved at the pH 6.
3. According to the results obtained from the above experiments, the removal efficiencies increased by increasing the current density. Moreover, the energy consumption increased by increasing the current density. The effluent fluoride concentration of 0.70 mg/L was reached at 3mA/cm<sup>2</sup> with the removal efficiency of 85.9%.
4. Different Na<sub>2</sub>SO<sub>4</sub> concentrations were used to increase the ionic conductivity of the wastewater and to minimize EEC. An increase in conductivity caused a decrease in EEC. On the contrary, it was found that higher concentration of Na<sub>2</sub>SO<sub>4</sub> caused a rises in the removal of fluoride from water.

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