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## PHYSICAL CHEMISTRY OF WATER TREATMENT PROCESSES

# Fluoride Removal from Groundwater Using Hybrid Cylindrical Electrocoagulation Reactor[1]

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**Abstract**—Long-term consumption of water containing excessive fluoride can lead to fluorosis of the teeth and bones. Electrocoagulation is an electrochemical technique, in which a variety of unwanted dissolved particles and suspended matter can be effectively removed from an aqueous solution by electrolysis. Semi continuous flow experiments for fluoride removal were undertaken to investigate the effects of the different parameters such as: applied voltage (10–20 V), flow rate (150–450 mL/min), initial pH (6–8), and initial fluoride concentration (2–10 mg/L) at lowest cost with novel rector. The maximum of 8 mg/L fluoride treated up to World Health Organization drinking limits within 30 min residual time at a flow rate of 300 mL/min, with an applied voltage of 15 V at influent pH 7. The results obtained, showed that this novel semi continuous flow electrocoagulation reactor is an effective for defluoridation of ground water supplies at lower cost.

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*Keywords:* defluoridation, coagulant, ground water, flocs, sludge.

## INTRODUCTION

Fluoride is an essential element to the human body. But at higher levels above than 1.5 mg/L consumption causes fluorosis. The main source of fluoride intake to the human being is drinking water. Groundwater is an important source of drinking water in widely ranged arid and semi-arid area [1]. Fluoride pollution in environment occurs through two different channels: natural sources and anthropogenic sources. Geochemical reactions in sub surface and erosion of fluoride bearing rocks contribute fluoride to ground water. The discharge of industrial wastewater, such as semiconductor industries, aluminum industries and glass manufacturing industries, also contributes fluoride into water reserves, especially to groundwater [2]. Because of this the concentration of fluoride ion in groundwater is high. This high-dose fluoride (>1.5 mg/L) by consumption, will accumulate in the human body and lead to fluorosis [3]. The water-mineral interaction in aquifer lead the fluoride ion concentration in groundwater is very difficult to decrease in nature condition [1].

Defluoridation of drinking water has long been a focus of studies. This has led to the application of numerous techniques and methods to remove fluoride from drinking water using waste residue, wheat straw, adsorption onto La(III)–Al(III) loaded scoria adsorbent, granular red mud Tamarind (Tamarindus indica) fruit shell carbon, bentonite clay, activated alumina, graphene oxide, nanofiltration, $Fe_3O_4/Al_2O_3$ nanoparticles, zirconium oxide [4–8]. But these techniques operation is complex, poor selectivity and unavoidable operational cost [5]. Therefore the electrocoagulation method might be suitable for fluoride removal.

In the recent years, there is an increasing interest in electrocoagulation (EC) for water treatment. The EC is the process where the sacrificed anodes generate insitu active coagulants. While aluminum and iron are used as electrodes, release of $Al^{3+}$ or $Fe^{2+}$ ions is known to be produced according to [6]. It is reported to be effective in water treatment such as to treat such as petroleum refinery wastewater [7], textile wastewater [8], winery wastewater [9], bio diesel wastewater [10], laundry wastewater [11], dairy effluent and dye containing effluent, Cd from simulated wastewater, and Cr from wastewaters. Recently some studies have been reported in the literature [12–14] on the use of EC for the treatment of fluoride removal from synthetic solutions:

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[1] The text was submitted by the authors in English.

anode

$$Al(s) \rightarrow Al^{3+} + 3e^-, \qquad (1)$$

$$Fe \rightarrow Fe^{2+} + 2e^-; \qquad (2)$$

cathode

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-. \qquad (3)$$

The previous studies represents the square type reactors for the treatment [3, 8], the cylindrical model may increase the pollutant removal efficiency. In the present study, the efficiency of electrocoagulation in the removal of fluoride from ground water is evaluated using cylindrical reactor. The operational parameters like effect of reaction time, applied voltage, initial pH, inlet flow rate, fluoride concentration are studied.

## EXPERIMENTAL

### *Chemicals*

Sodium fluoride (NaF) and HCl purchased from S.D Fine Chemical Limited, NaOH provided by Merck.

### *Electrocoagulation Reactor and Methodology*

A 3 L capacity semi continues mode batch reactor with working volume of 2.5 L cylindrical reactor used for fluoride removal studies. Four aluminum and four iron electrodes were used as anodes while stainless steel electrode was used as the cathode (Fig. 1). Before each test, impurities on electrode surfaces were removed by washing with tap water followed by HCl solution (10 wt %). The electrodes were placed at a distance of 20 mm. The current density has been maintained constant by using a potentiostat mode. The adjustment of pH is made with 0.1 M/1.0 M solution of HCl or 0.1 M/1.0 M NaOH. Working electrodes were connected to a direct current (DC) power supply (APLAB regulated DC power supply L6403) unit with 0 to 84V voltage supply capacity. The samples were collected at 10 min time interval for analyzing residual fluoride content. Fluoride content is determined by "Standard Methods for Examination of the Water and Waste Water" [15] with Shimadzu UV 2450 UV-Vis spectrophotometer.

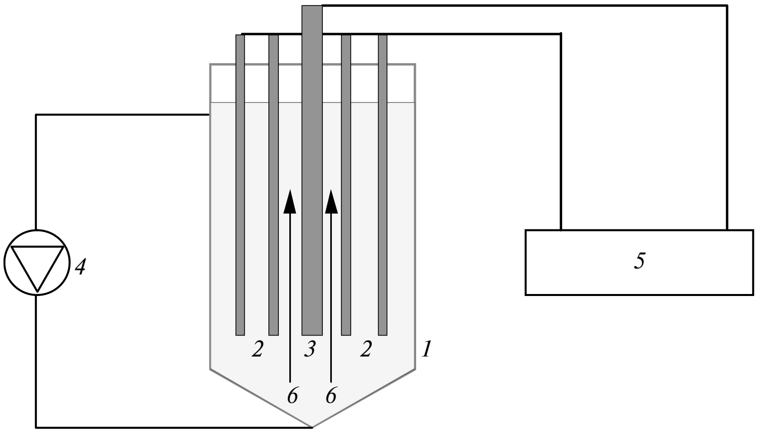

**Fig. 1.** Schematic representation of the electrocoagulation reactor: *1*—reactor; *2*—anode; *3*—cathode; *4*—peristaltic pump; *5*—power supply unit; *6*—liquid flow direction.

The initial characterization of the sample given in the Table 1.

### *Operational Cost (OC) Evaluation*

One of the most important parameter affecting the treatment method of fluoride water is the operating cost. The OC of the EC is calculated by including the material cost (mainly electrodes), and utility cost (mainly electrical energy) [16]:

$$OC = aC_{energy} + bC_{electrode}, \qquad (4)$$

where $a$ is the electricity consumed, kWh/m$^3$, $b$ is the electrode material consumed, kg/m$^3$ of the fluoride treated. The cost values ($) of $a$ and $b$ calculated according to the Indian market. It is the energy price as 0.1 $/kWh (6.40 Rs/kWh) and electrodes price as Fe—1.61 $/kg; Al—3.27 $/kg (97 and 197 Rs/kg).

**Table 1.** Initial characterization of the influent

| Parameter | Initial characters of water sample |
|---|---|
| pH | 7 |
| Electrical conductivity, μs/cm | 715 |
| $F^-$, mg/L | 2 |
| TDS, mg/L | 457 |
| $Ca^{2+}$, mg/L | 80 |
| $Mg^{2+}$, mg/L | 22 |
| Alkalinity, mg/L | 230 |
| $Na^+$, mg/L | 104 |
| $K^+$, mg/L | 5.3 |
| $NO_3^-$, mg/L | 14 |
| $SO_4^{2-}$, mg/L | 60 |
| $Cl^-$, mg/L | 120 |

The electrode and energy consumption were calculated using the following equations:

$$C_{\text{energy}} = \frac{UIt_{\text{EC}}}{V}; \tag{5}$$

$$C_{\text{electrode}} = \frac{It_{\text{EC}}\text{M}}{Z\text{F}V}, \tag{6}$$

where $U$—cell voltage, V; $I$—the current, A; $t_{\text{EC}}$—the operating time, h; $V$—volume of the sample, $m^3$; M—the molecular weight of electrode (for Fe—55.84, Al—26.98 g/mol); $Z$—number of electrons transferred ($Z = 3$ for Al and 2 for Fe); F—the Faraday constant (96487 C/mol).

## RESULTS AND DISCUSSION

### *Effect of Reaction Time on Fluoride Removal*

The effect of residence time on the defluoridation during electrocoagulation was conducted. Fluoride removal (%) up to 30 min reaction time increases and after which, it remains constant. This might be due to the formation of passivation layer on the cathodes which reduces the removal capacity [13]. Finally 30 min reaction time is set to be the optimum for further studies, where 45% of the fluoride removal was observed. Long reaction time (>30 min) might be unnecessary, because excess residual aluminium, iron is unsafe for drinking water and also high current is uneconomic in terms of energy consumption [3, 13].

### *Effect of Applied Voltage on Fluoride Removal*

The amount of fluoride removed from the test solution depends upon the quantity of adsorbent generated during the electrocoagulation, which is directly related to the applied voltage. To investigate the effect of applied voltage on fluoride removal, a series of experiments were carried out on solutions containing a constant fluoride loading of 2 mg/L. The voltage varied at 10; 15 and 20 V. The defluoridation efficiency observed to be increased along with applied voltage up to 15 V (Fig. 2a), above than where the defluoridation efficiency was remained constant. So, further studies were carried out at 15 V, where 45% of the fluoride removal was reported. This shows that there is probably a transition between a domain of voltage in which the kinetics of coagulant electrolysis is the limiting step [12, 17].

The effects of applied voltage on the fluoride removal efficiency from ground water investigated at voltages of 10; 15 and 20 V and corresponding average current drawn is of 1.36; 2.14 and 2.4 A was observed respectively. With increasing the reaction time the change in current flow occurs, hence the average value was calculated.

During the treatment process, the pH of the solution increased to different levels at different applied voltages. Whereas at 10; 15 and 20 V final pH observed to be 7.6; 7.9 and 8.2, respectively. This variation might be due to the release of $OH^-$ [9, 12, 13].

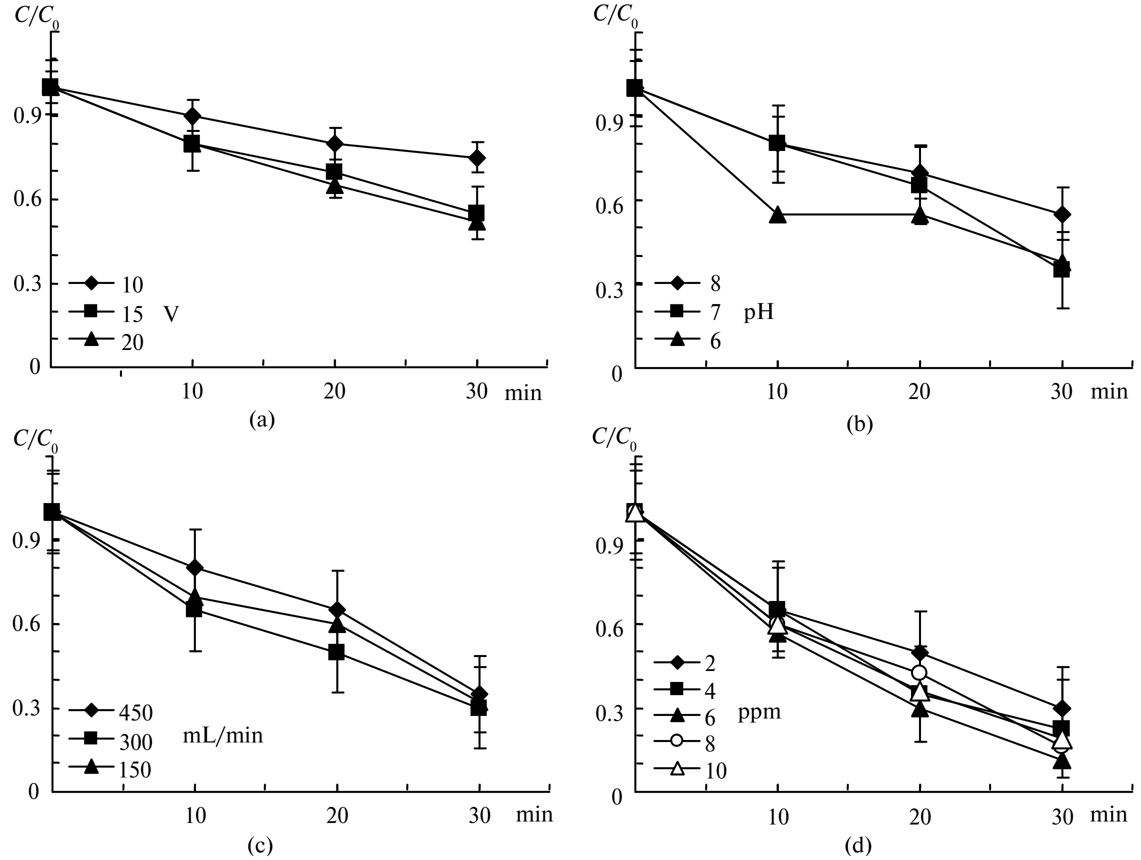

**Fig. 2.** Effect of applied voltage (a), initial pH (b), influent flow rate (c) and initial fluoride concentration (d) on fluoride removal. Experimental conditions: current voltage, V—10, 15, 20 (a), 15 (b–d); pH—6, 7, 8 (b), 7 (a, c, d); flow rate, mL/min—450 (a, b), 150, 300, 450 (c), 300 (d); initial fluoride concentration, ppm—2 (a–c), 2, 4, 6, 8, 10 (d). Other conditions (a–d): 8 iron and 4 aluminum anodes; 1 stainless steel cathode; electrodes distance—2 cm; surface area of electrodes—0.081 $m^2$; sample volume—2.5 L.

### *Effect of Initial pH on Fluoride Removal*

EC is reported to be strongly dependent on pH [2, 9], since flocs are mainly influenced by the pH of the reactor solution. Controlling pH of the solution, however, is very difficult during the electrocoagulation process because increase of pH occurs due to hydrogen and hydroxide generated at the EC cathode [12, 13]. From Fig. 2b, it was observed that maximum fluoride removal (65%) was achieved at neutral pH. Variation trend was observed for defluoridation with the variation of solution pH. When the initial pH value was increased from 6 to 7, the removal rate of fluoride also increased. However, with further increase in pH from 7 to 8, the fluoride removal rate decreased slightly. This decrease in defluoridation might be due to ion exchange of fluoride with $OH^-$ in $Al(OH)_3$ and the solubility of total Al increases as pH increases [18].

### *Effect of Influent Flow Rate on Fluoride Removal*

The effect of flow rate on defluoridation efficiency was studied by varying the flow rate of the solution at 150; 300 and 450 mL/min. As seems in Fig. 2c, at flow rate 150 mL/min fluoride removal rate of 58% was observed, at 300 mL/min removal rate was increased to 71% and at 450 mL/min flow rate removal rate decreased to 65%. It can be seen that when the flow rates are increased (>300 mL/min), the fluoride removal efficiency decreased because the residual time at reaction zone gets effected which is playing a key role in the defluoridation process. At 300 mL/min flow rate defluoridation equilibrium was observed. So, further more decrease in flow rate observed to be not beneficial [3, 13, 18].

### *Effect of Initial Fluoride Concentration*

In the ground water the fluoride concentrations appears up to 8 mg/L. So in this study the defluoridation carried up 10 mg/L of fluoride concentration. The defluoridation increased with increase in reaction time and remained almost constant after 30 min. Hence the equilibrium time of 30 min was chosen for all the concentrations studied. Defluoridation (%) increased with increase of $F^-$ concentration, where 71% for 2 mg/L and 88% for 6 mg/L (see Fig. 2d). The fluoride concentration above than 8 mg/L was shown (Table 2) slight decrease in defluoridation. This might be due to the formation of insufficient amount of coagulant complexes [30], to overcome this imbalance increase of reaction time is necessary, but this increases the operational cost of the treatment process [13, 18, 19].

**Table. 2.** Final characterization of the deflouridated water

| Parameter | Final characters of water sample | | | | |
|---|---|---|---|---|---|
| | 2 | 4 | 6 | 8 | 10 |
| | ppm | | | | |
| pH | 7.9 | 7.5 | 6.9 | 7.3 | 7.2 |
| Electrical conductivity, μs/cm | 476 | 519 | 564 | 543 | 538 |
| $F^-$, mg/L | 0.6 | 0.9 | 0.7 | 1.3 | 1.9 |
| TDS, mg/L | 304 | 332 | 360 | 347 | 344 |
| $Ca^{2+}$, mg/L | 40 | 44 | 44 | 44 | 44 |
| $Mg^{2+}$, mg/L | 9.6 | 12 | 16 | 12 | 7.2 |
| Alkalinity, mg/L | 185 | 205 | 170 | 190 | 180 |
| $Na^+$, mg/L | 95 | 132 | 131 | 122 | 118 |
| $K^+$, mg/L | 4.3 | 4 | 3.9 | 4.0 | 4.0 |
| $NO_3^-$, mg/L | 6 | 8.6 | 8.1 | 8.3 | 8.0 |
| $SO_4^{2-}$, mg/L | 36 | 45 | 46 | 54 | 44 |
| $Cl^-$, mg/L | 74 | 104 | 94 | 108 | 94 |

### *Cost Analysis*

The semi continuous flow EC reactor's operational costs were estimated from sum of the specific costs of electrode material and energy consumption. From the Table 3, it was observed that the total operating cost increased when the current density and concentration of fluoride in influent increases. The variation of voltage has been considered to be between 10 to 20 V, where the operational cost varied between 0.28 and 0.98 US $/m$^3$ of treated water when initial fluoride concentration is 2 mg/L. The maximum total operational cost for defluoridation by amorphous alumina, Nalgonda process was reported to be 1.17 US $/m$^3$ [39], 0.82 US $/m$^3$ [20], respectively. Authors [21] reported that the EC cost for defluoridation is 0.77 US $/m$^3$, but in this study we achieved the maximum removal with the operational cost of 0.70 US $/m$^3$.

**Table 3.** Cost sheet for the fluoride removal process

| Parameter | | Total cost | |
|---|---|---|---|
| | | Rs/m$^3$ | US $/m$^3$ |
| Voltage, V | 10 | 17.41 | 0.28 |
| | 15 | 40.33 | 0.64 |
| | 20 | 61.45 | 0.98 |
| pH | 6 | 51.85 | 0.82 |
| | 7 | 40.33 | 0.64 |
| | 8 | 46.09 | 0.73 |
| Flow rate Fe–Fe, mL/min | 150 | 40.33 | 0.64 |
| | 300 | 40.33 | 0.64 |
| | 450 | 46.09 | 0.73 |

**Table 3.** (Contd.)

| | | | |
|---|---|---|---|
| Concentration fluoride Fe–Fe, ppm | 2 | 40.33 | 0.64 |
| | 4 | 42.25 | 0.67 |
| | 6 | 44.17 | 0.70 |
| | 8 | 45.13 | 0.72 |
| | 10 | 46.09 | 0.73 |

## CONCLUSIONS

The treatment time required for fluoride removal from ground water in semi continuous electrocoagulation method is 30 min with applied voltage of 15 V. Neutral pH is suitable for defluoridation of ground water by EC method at 300 mL/min flow rate. The results showed that electrocoagulation process with iron, aluminum as anodes and stainless steel as cathode successfully removed fluoride from the ground aqueous environments. Cost of this process also is low, while comparing the other treatment methods.

## ACKNOWLEDGEMENTS

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