RESEARCH ARTICLE OPEN ACCESS

Effective Removal of Fluoride from Ground Water Using Electro-Coagulation

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Abstract
Exceeding the level of fluoride (F^-) in drinking water is responsible for skeletal fluorosis in human beings. The present study was carried out to assess the ability of electro coagulation process with iron and aluminum electrodes in order to removal of fluoride from aqueous solutions. Several working parameters, such as concentration of fluoride, pH, applied voltage and reaction time, distance between electrodes, electrode reactive area and effect of Co-existing ions were studied to achieve a higher removal capacity. Variable concentrations (1, 5 and 10 mg L-1) of fluoride solutions were prepared by mixing proper amount of sodium fluoride with tap water. The varying pH of the initial solution (5, 7 and 9) was also studied to measure their effects on the fluoride removal efficiency. Results obtained with synthetic solution revealed that the most effective removal capacities of fluoride could be achieved at 40V electrical potential. In addition, the increase of electrical potential, in the range of 10-40 V, enhanced the treatment rate. The effective reactive surface area found to be $40cm^2$ where as inter electrode distance was 1cm.

I. Introduction

Fluoride pollution in environment occurs through two different channels: natural sources and anthropogenic sources. Fluoride is frequently encountered in minerals and in geochemical deposits. Because of the erosion and weathering of fluoride-bearing minerals, it becomes a surface species. The discharge of industrial wastewater, such as semiconductor industries, aluminum industries, and glass manufacturing industries, also contributes fluoride in water pollution, especially in groundwater. Fluoride is recognized as an essential constituent in the human diet. Low fluoride concentration (<1 mg/L) could prevent dental problem, but higher fluoride concentration (>1.5 mg/L) will cause dental and skeletal fluorosis. Many countries, such as China, Egypt, India, Kenya, etc., have areas where fluorosis is endemic (1).

Many methods have been developed to remove excessive fluoride from drinking water. These methods can be categorized into four categories: adsorption (2), chemical precipitation [3], membrane separation and electrodialysis(4). A number of these techniques suffer from disadvantages; for example the adsorption process is highly pH selective, has a low adsorption capacity, poor physical integrity, and requires acidification and pretreatment and its effectiveness for fluoride removal reduces after each regeneration. In the case of ion-exchange, fluoride can be removed from water with a strongly basic anion exchange resin containing quaternary ammonium functional groups, but limitations such as the cost of resin, regeneration and waste disposal prevent the process being economical. In the coagulation–precipitation method lime and alum are the most commonly used coagulants; addition of lime leads to precipitation of fluoride as insoluble metal fluorides and raises the pH value of water to 11–12. The limitations are very high maintenance cost, large space requirement and high residual aluminum in the treated water. In recent years, membrane processes have emerged as a preferred alternative for drinking water treatment; however disadvantages such as the high cost of membranes, brine disposal and post-treatment of water tend to make the process uneconomical(6).

Recent research has demonstrated that electrochemistry offers an attractive alternative to the above traditional methods for treating waste-waters. One of these techniques, electrocoagulation, based on the electrochemical production of destabilization agents that remove pollutants by charge neutralization, has been used for treatment of water or waste-waters. The advantages of electrocoagulation include highly efficient particulate removal, compact treatment facility and the possibilityof complete automation of the process(7-12).

Electro-coagulation is a simple and efficient method to remove the flocculating agent generated by electro-oxidation of a sacrificial anode and generally made of iron or aluminum. In this process, the treatment is performed without adding any chemical coagulant or flocculants. Thus, reducing the amount of sludge which must be disposed (5). On the other hand, electrocoagulation is based on the in situ formation of the coagulant as the sacrificial anode corrodes due to an applied current, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation. This technique combines three main interdependent processes, operating synergistically to remove pollutants: electrochemistry, coagulation and hydrodynamics. An examination of the chemical reactions occurring in the electrocoagulation process shows that the main reactions occurring at the electrodes (aluminum and iron electrodes) are:

$$Al \longrightarrow Al_3^+ + 3e^- \text{ (anode)} \quad (1)$$

$$3H_2O + 3e^- \longrightarrow 3/2H_2 + 3OH^- \text{ (cathode} \quad (2)$$

In addition, Al_3^+ and OH^- ions generated at electrode surfaces react in the bulk wastewater to form aluminum hydroxide:

$$Al_3^+ + 3OH^- \longrightarrow Al(OH)_3 \quad (3)$$

Also the same chemical reactions occurring in the electrocoagulation process using iron electrodes:

$$Fe\ (s) \longrightarrow Fe^{+3} + 3e^- \text{ (anode)} \quad (4)$$

$$3H_2O + 3e^- \longrightarrow 3/2\ H_2 + 3OH^- \text{ (cathode)} \quad (5)$$

$$Fe^{+3} + 3OH^- \longrightarrow Fe(OH)_3 \quad (6)$$

The aluminum and iron hydroxide flocs normally act as adsorbents. Therefore, they would eliminate fluoride from the solution. (5) The main purpose of this research was to investigate of the efficiency of electrocoagulation process for fluoride removal from aqueous environments with iron and aluminum electrodes and determination of the effects of voltage, pH, initial concentration of fluoride and reaction time on the removal efficiency.

II. Material and Methods:

At present study all chemicals including sodium fluoride (NaF), were used as analytical grade. Variable concentrations (1-10 mg L^{-1}) of fluoride solutions were prepared by mixing proper amount of sodium fluoride with tap water. The pH of initial solution was adjusted (5, 7 and 9) by using sulfuric acid solution (1N) and sodium hydroxide (1N). Experiments were performed in a batch reactor (figure 1). The internal size of the cell was 5 Cm × 10 Cm (width × length) with an effective volume of 200ml. The active area of each electrode was 4× 5 Cm. The distance between electrodes was 4 Cm. Power supply pack having an input of 220V and variable output of 0–40V (10, 20, 30 and 40 V for this study). At different time intervals (10min) 25ml of treated sample was collected and filtered before being analyzed to determine the residual fluoride. The residual fluoride concentration was determined using spectrophoto metric method according to the standard method (APHA, 21st Edition).

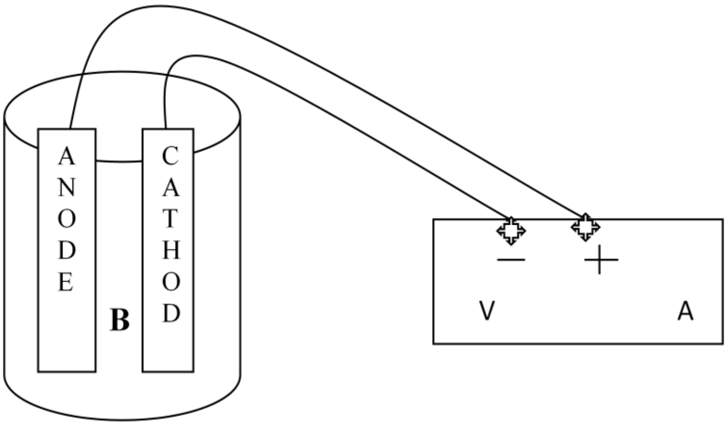

Figure 1 Batch Reactor
A-Amperes display, V- Voltage display, B- reaction beaker

III. Results and Discussions

The electrocoagulation process is quite complex and may be affected by several operating parameters, such as pollutants concentrations, initial pH, electrical potential (voltage). In the present study, electrocoagulation process has been evaluated as a treatment technology for fluoride removal from synthetic solutions and fluoride removal efficiency at different conditions (pH, electrical potential and various initial concentrations) in various reaction times was evaluated.

3.1 Effect of reaction time

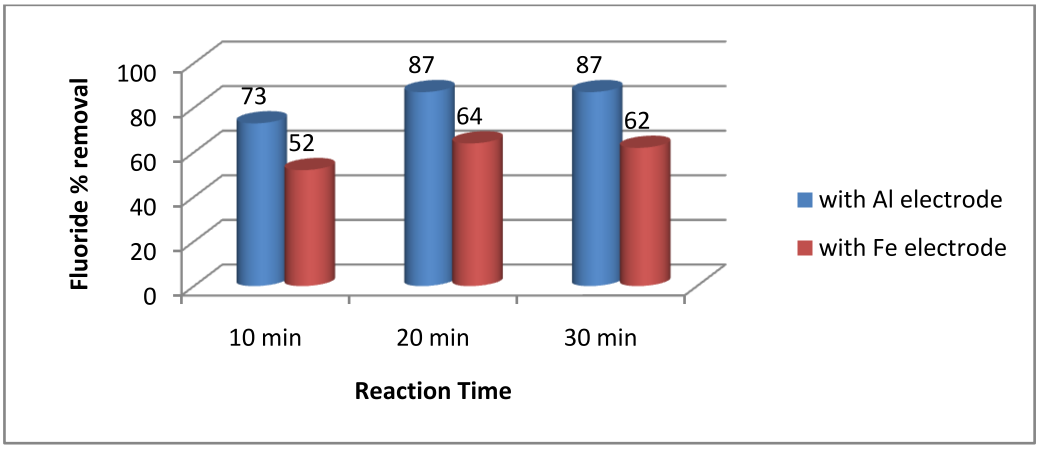

Figure 2 Effect of reaction time on fluoride removal

The time dependence of fluoride removal by electrocoagulation process at different electrodes was shown in figures 1. It can be seen from the figures that up to 50-87 %(figure 2) of the initial concentration of fluoride decreased within 10-30 min of electro coagulation processing for both electrodes. The optimum time for fluoride removal was observed to be 20min and above that contact time the fluoride desorbing from the flocs.

3.2 Effect of the Concentration:

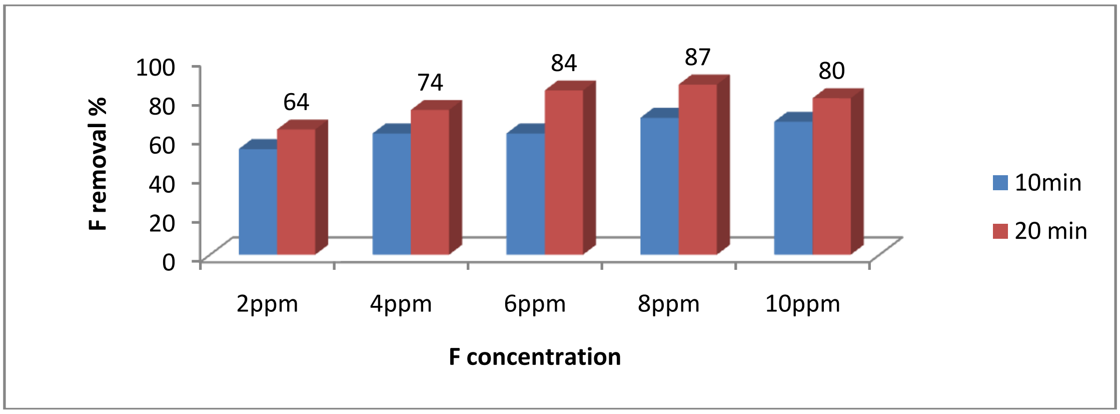

Figure 3 Effect of initial concentration of fluoride

A set of experiments was performed with different initial concentrations of fluoride to determine the concentration effectively removed under various conditions of electrocoagulation process. With increase in concentration the removal rate also increased up to 8ppm of fluoride in ground water at these particular conditions. Above 8ppm of F^- initial concentrationshown the removal 80%(figure 3) only. This can be explained by the theory of dilute solution. In dilute solution, formation of the diffusion layer at the vicinity of the electrode causes a slower reaction rate, but in concentrated solution the diffusion layer has no effect on the rate of diffusion or migration of metal ions to the electrode surface (5,7).

3.3 Effect of applied voltage

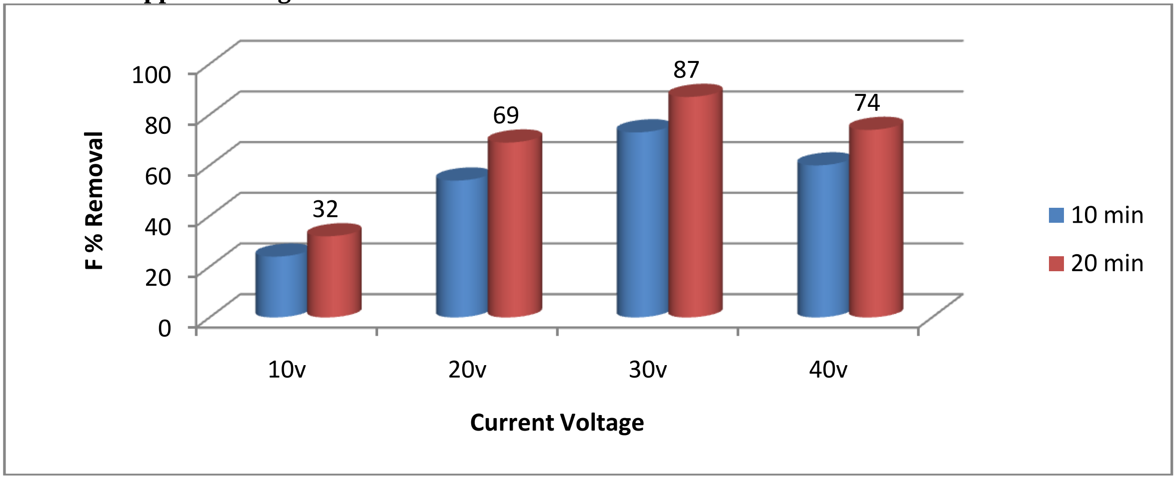

Figure 4 Effect of applied voltage on fluoride removal

It is well-known that electrical current not only determines the coagulant dosage rate but also the bubble production rate and size and the floc growth, (17, 18) which can influence the treatment efficiency of the electrocoagulation. Therefore, the effect of current density or applied voltage (electrical potential) on the fluoride removal was investigated. As expected, it appears that for a given time, the removal efficiency increased significantly with the increase in current density. This is ascribed to the fact that at higher voltage the amount of Al oxidized increased, resulting in a greater amount of precipitate for the removal of pollutants, but it not reacting effectively with fluoride. The maximum removal observed at 30v (figure 4) the lowest fluoride removal efficiency occurred in the lowest electrical potential (10V). In addition, it was demonstrated that bubbles density increases and their size decreases with increasing current density (19). Above than the 30v, there is no considerable increase in defluoridation efficiency. So it is advisable not to exceed the limit of current voltage beyond 30v. This also avoids excess energy consumption. This effect is possibly due to the reason that at lower current density, coagulant (aluminium) dosage also decreases thereby decreasing the efficiency of the treatment process. When current density increases, ion production on electrodes also increases. This leads to production of $Al(OH)_3$ flocs in the solution and hence efficiency of the EC process is improved. But after a certain extent increase in current density leads to increase in pH of the solution as more OH^- enter into the solution. This increase in pH results in lowering the efficiency of the treatment process.

3.4 Effect of initial pH

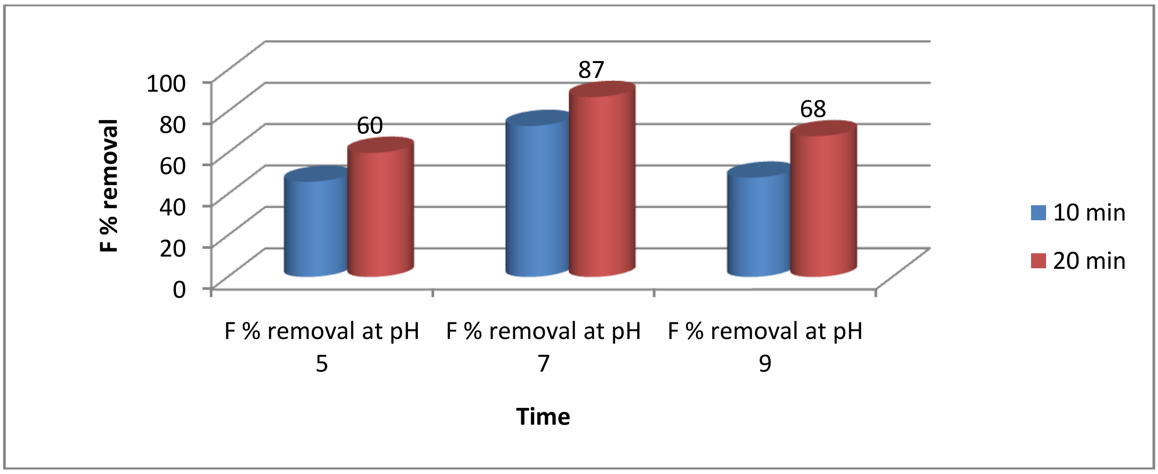

Figure 5 Effect of pH on fluoride removal

It has been established in previous studies (13, 14) that initial pH has a considerable effect on the efficiency of the electrocoagulation process. Also, as observed by other investigators the pH of the medium changed during the process depending on initial pH. The results of this research showed that fluoride removal efficiency in neutral conditions (pH=7) is better than acidic and basic conditions.

In this study, the pH was varied in the range 5–9 in an attempt to investigate the influence of this parameter on the removal of fluoride. Removal efficiencies of fluoride as a function of initial pH are presented in figure 3. As observed by other investigators, (15) pH increase occurs when the initial pH is low (< 7). Vik et al. (16) ascribed this increase to hydrogen evolution at cathodes. The maximum fluoride removal was observed at neutral ph it is of 87% (figure 5).

3.5 Effect of Co-existing ions:

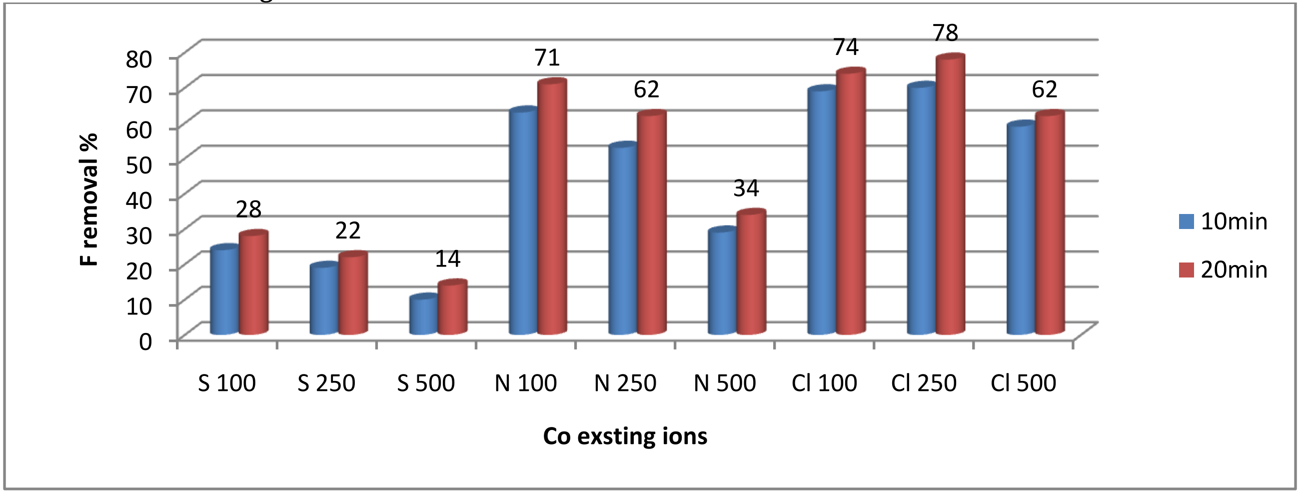

Figure 6 Effect of Co-existing ions on fluoride removal

The above figure explains the effect of the co-existing ions present in the ground water. It shows F^- removal decreased as the concentration of SO_4^{2-} increased. Some of the current flowed though the solution, bypassing the bipolar electrodes and decreasing EC because the kinetic over potential of anodes in the solutions that contained both F^- and SO_4^{2-} ions was very high(figure 6). The concentrations of Cl^- and NO_3^- seemed not to influence the defluoridation process but the concentration of SO_4^{2-} did. It might be due to the competition effect stated by Hao et al. the F removal at Cl 250ppm observed to be 78 % and at 500ppm it decrease to 62% (8, 14).

3.6 Effect of the reactive surface area:

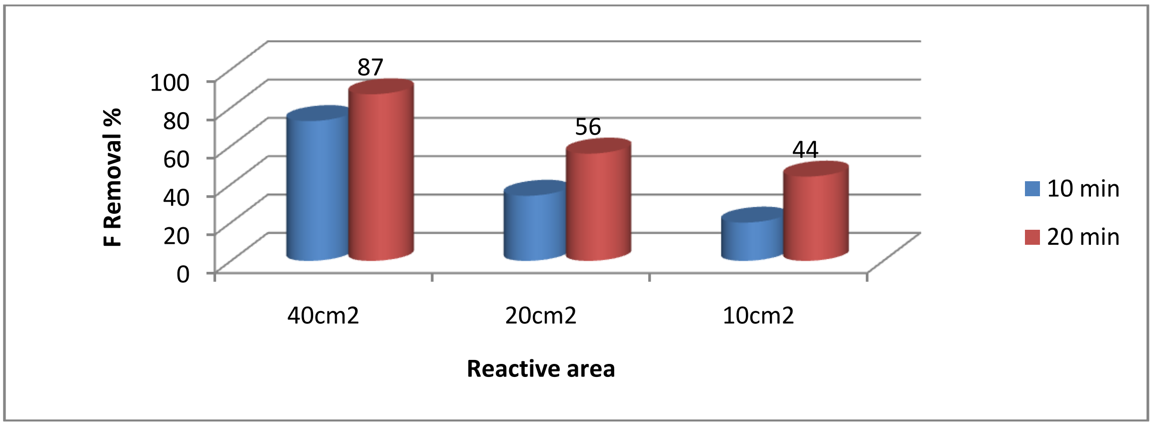

Figure 7 Effect of reactive surface area on fluoride removal

The fluoride removal efficiency was decreased with decrease in electrode surface area from 40cm^2 to 10cm^2. At 40cm^2, 20cm^2 and 10cm^2 the F removal was observed to be 87, 56 and 42 %.

This can be attributed to a greater electrode area that produced larger amounts of anions and cations from the anode and cathode. The greater the electrode is increased the rate of flock's formation, which in turn influenced the removal efficiency (1, 17).

3.7 Effect of the inter electrode distance:

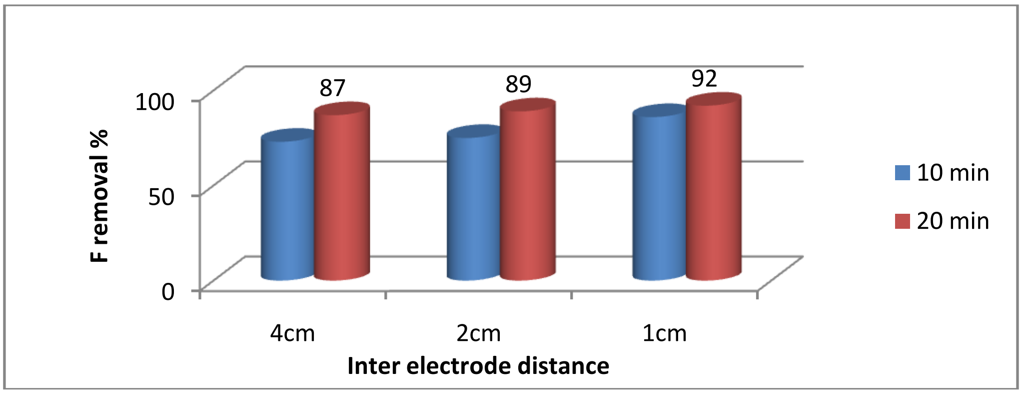

Figure 8 Effect of inter electrode distance on fluoride removal

Inter-electrode distance was observed to be an effective factor in the electrolytic treatment of fluoride removal from ground water. The removal percentage of F$^-$ increased progressively with decrease in inter-electrode distance from 4.0 to 1cm. At 4cm, 2cm and 1cm were observed to be 87, 89 and 92 % of F from ground water. That removal increased might be due to speeds up the anion discharge on the anode and improves the oxidation. It also reduces resistance, the electricity consumption and the cost of the water treatment (18, 19, 14).

IV. Conclusions

- The Al electrode material was observed to be suitable for fluoride removal.
- The optimum fluoride dosage was observed to be 8ppm.
- At 30V the maximum fluoride removal was observed.
- Neutral pH is the suitable for fluoride removal.
- Increasing the reactive surface the F removal increased.
- F removals increased with decrease in inter electrode distance.

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