# Electrochemical Removal and Kinetics in the Removal of Fluoride from Underground Water in Kenya

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## Abstract

The geology of Kenya makes it one of the countries in the World where Fluoride (F) occurs in high concentrations, in rocks, soil, surface and groundwater. Fluoride levels above 1.5 mg/L leads to skeletal and dental fluorosis which is evident in Rift Valley and Central Kenya. Electrochemical batch tests were conducted using standard NaF solution and aluminium anode to study the effects of; inter-electrode distance, supporting electrolyte, solution pH and Initial F concentration. The optimum inter electrode distance was 12 mm - 25 mm. Increasing surface area reduced F removal and current density with 20 $cm^2$ being optimum. Optimum pH ranged between 4 and 6 and was related to the amphoteric character of $Al\ (OH)_3$. Addition of NaCl supporting electrolyte increased F removal by 43.3 % and reduced specific energy by 44.6%. Adsorption process followed a second order reaction with the Lagegren model confirming that the rate constant increased with increasing fluoride concentration. The optimum results will be used to fabricate a prototype flow reactor that uses renewable solar energy.

**Key words:** Electrocoagulation, Kinetics, Lagegren, Amphoteric, Aluminium

## Introduction

Fluoride occurs commonly in drinking water. Whilst fluoride was artificially added to drinking water for 210 million people [WHO, 1994) in industrial countries (Peterson 2004) to prevent caries, the fluoride concentration is exceeded to an unhealthy extent in at least 27 (Takdastan *et al.* 2014) developing countries. The concentration of fluoride between 0.8 mg/L and 1.0 mg/L is considered as healthy and as an effective prevention of caries. The WHO recommended limit of fluoride in drinking water is 1.5 mg/L. Long-term intake of water with higher concentration causes dental and skeletal fluorosis (WHO, 2018). Whereas dental fluorosis has only esthetical effect skeletal fluorosis leads to weakening of the bone frame due to accumulation over several years and finally to deformation of the whole skeleton. Furthermore, the damaged skeleton causes stiffness and pain in connecting joints.

Sources of exceeding fluoride concentration can be natural, e.g. volcanic (WHO 1994) as well as anthropogenic. The latter is caused by releasing untreated wastewater from industries like glass manufacturing, semiconductor production (Emamjomeh *et al.* 2011) and mining of fluorspar.

There are several conventional methods for treating wastewater to remove pollutants. However, the methods may not remove F to the desired levels. Electrocoagulation method that uses Aluminium anode will be investigated under different conditions in an electrolytic cell in a batch reactor to come up with optimum conditions

## Methodology

The electrocoagulation reaction was carried out as batch tests in 250 mL polypropylene vessels. During the process, the treatment

*Figure 1* *system of two and four electrodes*

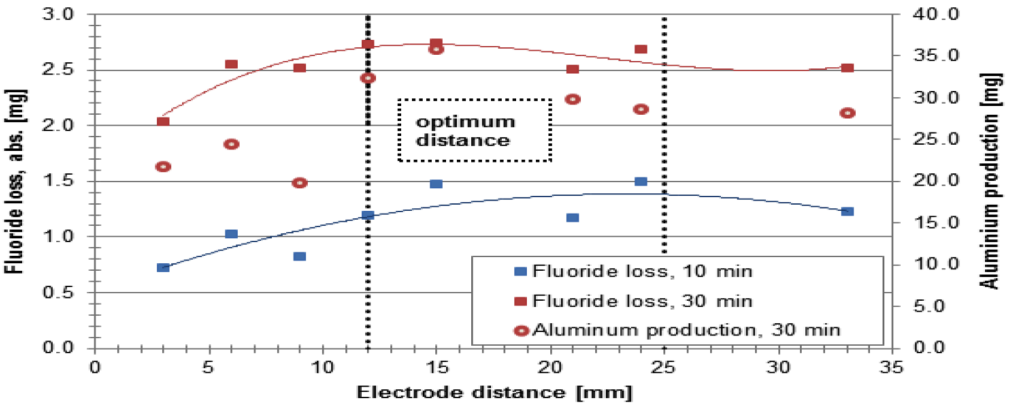

*Figure 2* *Fluoride removal and aluminium production at different electrode distances*

solutions were stirred by a magnetic stirrer at 200 rpm. The treatment was carried out by a system of two or four electrodes provided with direct current. After the treatment the solution was filtered through cellulose round filters and analyzed.

During the experimental part the number of electrodes was increased from two to four which increases the active cell volume by three.

The parameters measured in raw and treated samples included; fluoride, aluminium ion concentration, conductivity and pH. Voltage was recorded in 10-min intervals.

Electrode distance was varied to 3 mm, 6 mm, 9 mm, 12 mm, 15 mm, 21 mm, 24 mm and 33 mm using an insulator. Initial fluoride concentration was varied to 4.5 mg/L, 11.3 mg/L, 17.1 mg/L, and 44 mg/L. Sodium Chloride Supporting electrolyte was varied to give 0,10,20,30 and 50 mg/L NaCl. The initial pH of the solution was varied to 4,5,6,7.8 and 9 using dilute solutions of either 0.1M NaOH or 0.1M HCl. Fluoride concentration was varied to 4.5 mg/L, 11.3 mg/L, 17.1 mg/L and 44 mg/L.

Conductivity and pH were determined by Fluorides were analyzed by the SPADNS spectrometric method using spectrometer MD 600

## Results and Discussion

### *(a) Electrode distance*

The amount of removed fluoride and produced aluminium ions at different times and same conditions except for the electrode distance was determined. The results are shown in Figure 2.

The fluoride removal efficiency along with the aluminium production increases at both treatment times with increasing electrode distance up to an optimum between approximately 12 mm and 25 mm. Non-conductive hydrogen bubbles cover the surface of the cathode and hence reduce the active area. Because of the small distance between the electrode plates there is only little mixing within the cell.

Therefore, hydrogen bubbles as well as formed aluminium hydroxide covering the plates cannot be removed. Also the change of already treated electrolyte between the

*Table 2* *Fluoride removal and aluminium production at different NaCl concentrations*

| Supporting Electrolyte NaCl [mg/L] | Initial conductivity [µS/cm] | Fluoride loss [mg] | Aluminium production [mg] |
|---|---|---|---|
| **0.00** | **646** | 1.50 | 13.8 |
| **10.00** | **654** | 1.88 | 15.0 |
| **20.00** | **666** | 1.90 | 15.6 |
| **30.00** | **684** | 2.08 | 17.1 |
| **50.00** | **716** | 2.15 | 18.1 |
| **Max. efficiency increase** | -- | **43.3%** | **31.2%** |

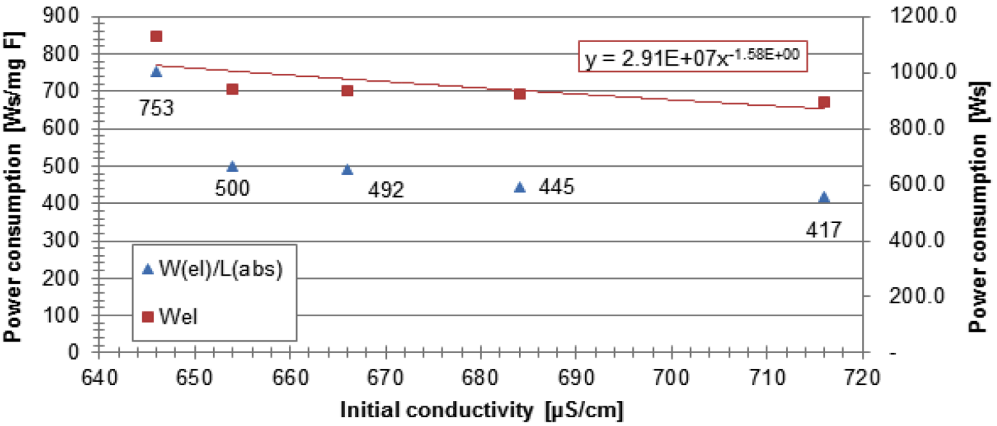

***Figure 3*** *Power Consumption per Removed Amount of Fluoride at different Initial Conductivities*

electrodes is more difficult with less mixing. After passing the optimum the EC process is complicated because of the larger way the charge carriers have to cover. Takdastan (2014) also confirmed this correlation in his studies of influence of electrode distance on the EC of fluoride which confirmed less removal efficiency with increasing distance.

### *b) Supporting electrolyte*

The amounts of removed fluoride and produced aluminium ions at different initial conductivities caused by addition of sodium chloride were determined. The results are shown in Table 2 and Figure 3.

Increased conductivity caused by a strong supporting electrolyte like sodium chloride increased the fluoride removal efficiency in a linear correlation. However, addition of 50 mg/L NaCl led to to 43.3% fluoride removal and 44.6 % power reduction.

The results show that the addition of a supporting electrolyte decreases the power consumption of the process in an inverse relationship. The power consumption per removed amount of fluoride is decreased by 44.6 % at 50 mg/L added NaCl respectively 716 µS/cm. Hence addition of a strong electrolyte supports fluoride removal efficiency as well as energy consumption.

### *c) Initial pH*

The amounts of removed fluoride and produced aluminium ions as well as the final pH at different initial pH were determined and the results are shown in Figure 4. The results show that the fluoride removal efficiency decreases with increasing initial pH. This behaviour is explained by the amphoteric character of aluminium hydroxide which reacts to tetra hydroxy aluminate beginning at pH above 6 (Eqn. 5).

According to Pearson the aluminium ion is a hard acid (trivalent, ionic radius 50 pm) and therefor has a tendency to react with hydroxide ions as a hard base. The hydrolysis

$$pH\ 3 - 7: [Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(H_2O)_5OH]^{2+} + H^+ \qquad \text{Eqn. 2}$$
$$pH\ 4 - 8: [Al(H_2O)_5OH]^{2+} + H_2O \rightarrow [Al(H_2O)_4(OH)_2]^{+} + H^+ \qquad \text{Eqn. 3}$$
$$pH\ 4 - 9: [Al(H_2O)_4(OH)_2]^{+} + H_2O \rightarrow [Al(H_2O)_3(OH)_3]_{(s)} + H^+ \qquad \text{Eqn. 4}$$
$$pH > 6: [Al(H_2O)_3(OH)_3]_{(s)} + H_2O \rightarrow [Al(H_2O)_2(OH)_4]^{-} + H^+ \qquad \text{Eqn. 5}$$

$$\text{Cathode reaction: } 3H_2O + 3e^- \longrightarrow 3/2\ H_{2\,(g)} + 3OH^- \qquad E^0 = 0V\ (pH\ 0) \quad E^0 = -0.83V\ (pH\ 14) \qquad \text{Eqn. 6}$$

of the aluminium ion depends on pH of the aqueous environment. Aluminium complexes are octahedral and hence have six ligands. At pH < 4 the dominant species is $[Al(H_2O)_6]^{3+}$ while at pH > 3 hydroxide ions begin to join the complex. The pH-dependent reactions whose describe the amphoteric character of aluminium hydroxide are listed in Eqns. 2 -4.

This ion cannot act as coagulant thus fluoride remains in the treatment solution. Furthermore, the pH is raised during the EC process due to its consumption of hydrogen ions respectively the formation of hydroxyl ions at the cathode (Equ. 6).

In case of a high initial reaction, Eqn. 4 seems to be dominant and the consumption of hydrogen ions occurs hence pH drops. To ensure comparability between the different pH series the initial conductivity was maintained to the same value using NaCl. This step was necessary because the initial pH was adjusted using HCl.

### *d) Initial fluoride concentration*

The amount of removed fluoride at different initial fluoride concentrations during the treatment process was determined. Therefore samples from the treatment solution were taken at different time intervals. The results are shown in Figure 5.

The fluoride loss is not linear to the reaction time because the complexation of aluminium fluoride hydroxide obeys a second order Lagegren model (Vasuderan et al. 2011; Zegwe 2017) (Eqn. 6) featuring time t, mass concentration of fluoride $\beta(F^-)$, rate constant $K_2$ and equilibrium mass concentration $\beta e(F^-)$

$$t/\beta(F^-) = 1/k_2\ \beta e(F^-)^2 + 1/\beta e(F^-) \qquad 6$$

Therefore, the half-life period of fluoride depends on the initial concentration. This is shown in Figure 5 using the dotted 50 %-line for the relative fluoride loss. Noticeably the half-life period between the initial fluoride concentrations from 4.5 mg/L to 44.0 mg/L increased from about 7 min to 16 min. The applied Lagegren model for all four concentrations is shown in Figure 7.

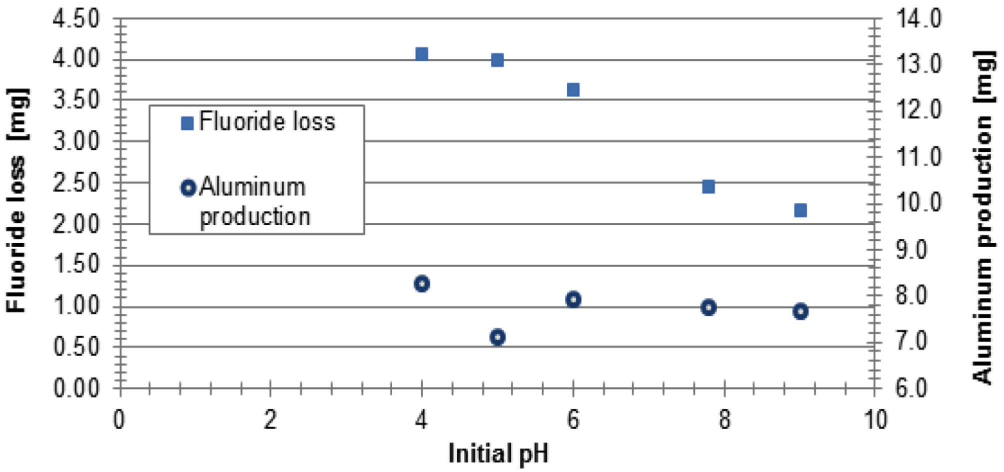

*Figure 4* *Fluoride removal and aluminium production at different initial pH values*

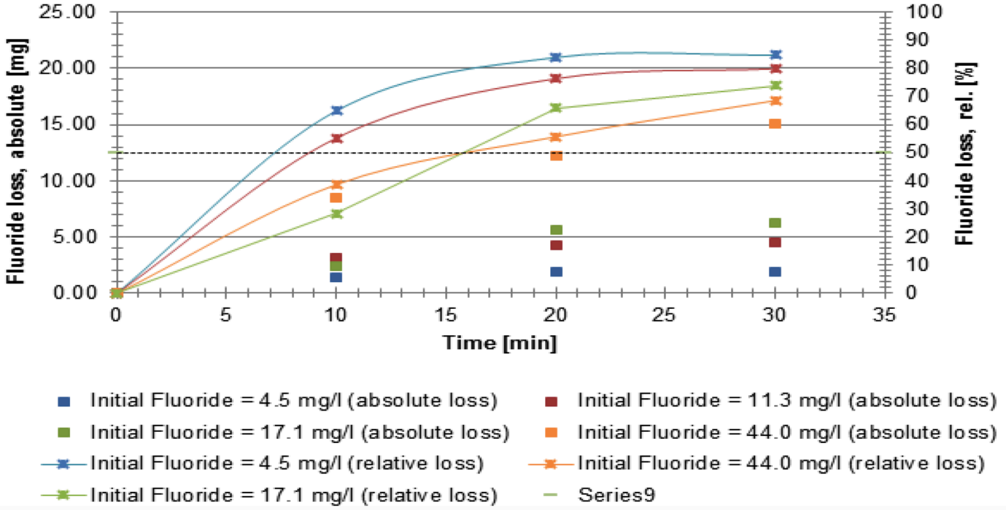

***Figure 5** Absolute (abs.) and relative (rel.) Fluoride removal at different initial fluoride concentrations with ongoing treatment time.*

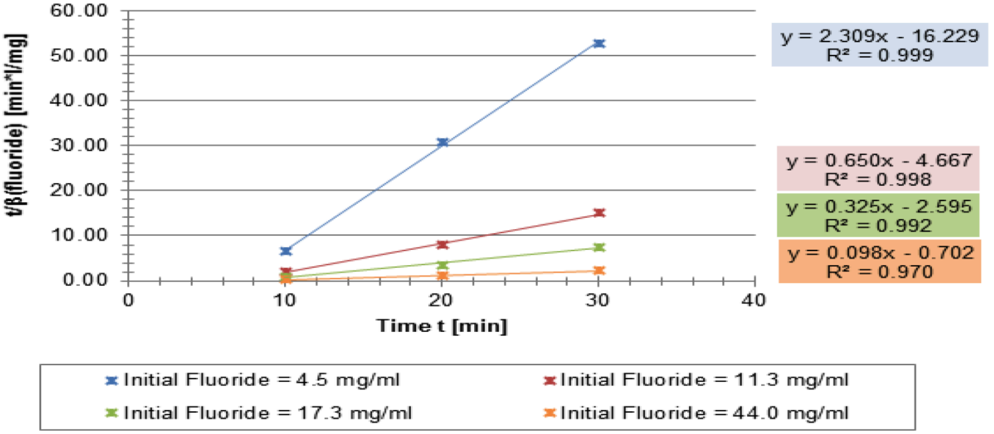

***Figure 6** Applied Lagegren model for different initial fluoride concentrations*

This includes equilibrium concentration of fluoride $\beta_e$ (F), rate constant $k_2$ and all second order terms t/β(F-).

Figure 6 shows that the slope of the Lagegren function decreases with increasing initial fluoride concentration. As a result the rate constant increases with increasing initial fluoride concentration as well as the equilibrium concentration of fluoride. Between 4.5 mg/L and 44.0 mg/L initial concentration, which is about tenfold higher, the slope decreased by 24 and the rate constant as well as equilibrium concentration increased by same margin. These results can be applied only for the treatment time of 30 min.

The functions of fluoride loss in Figure 22 assume that the reactions are not finished within this time interval. Vasudevan (2011) and Zewge (2017) determined the rate constants within 300 min and 1400 min respectively. Therefore, our resulting rate constants and equilibrium concentrations can only give a tendency about the influence of the initial fluoride concentration. To determine the exact parameters within our applied conditions, a longer treatment time has to be used.

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