Indian Journal of Chemical Technology
Vol. 29, September 2022, pp. 554-559
DOI: 10.56042/ijct.v29i5.62186

Defluoridation of water by electrocoagulation using aluminium electrode

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Received 18 April 2022; accepted 28 July 2022

Fluoride (F^-) has been removed successfully removal from laboratory prepared fluoride water solution through electrocoagulation using Aluminium (Al) electrode. Consequence of parameters such as *p*H, current density (CD), initial mass of F^- and treatment hour are analyzed over F^- removal. The maximum defluoridation of 85.2% occurred at *p*H 6.5, CD 34.72 A/m^2 (1A) and contact time of 50 min for starting F^- concentration of 50 mg/L in the solution. The kinetic study has been performed to explore the mechanism of electrocoagulation technique, disclosed that the order of the reaction was in the span 2.0-2.07 and 0.05 for fluoride concentration and current density, respectively. This study shows that electrocoagulation using Al electrode has good potential for fluoride removal.

Keywords: Current density, Electrocoagulation, Fluoride reduction, Kinetic, Synthetic water study

In several parts of India the ground water still serves as a main source for drinking water need. However, surplus concentration of fluoride is a common concern in many of these sources. While, moderate mass of F^- (0.5–1.5 mg/L) in potable water acts as nutrient for the healthy teeth and bone formation, overdosing of fluoride in human body generates serious illness on teeth and bones. Fluoride occurs in ground water basically due to the sellaite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$CaF_2{\cdot}3Ca_3(PO_4)_2$] that are present in sedimentary rocks and igneous rocks. F^- contaminations occurs due to earthly processes (like volcanic eruption) also. Additionally, some industries also discharge fluoride bearing waste water that is added to the ground water through penetration[1]. Therefore, its proper treatment is required.

Several physicochemical techniques such as coagulation, precipitation[2], membrane separation[1], electrocoagulation[3], ion-exchange[4,5] and adsorption [6,7]are accessible to treat fluoride containing water/waste water. However, these processes have several limitations. Contamination of water due to insertion of chemicals and considerable quantity of sludge formation are prime drawbacks of coagulation technique. Chemical precipitation produces low-density sludge hence, cleaning of the remaining heavy metal pollutants present in sludge possess serious issues. Membrane separation requires high pressure that enhances cost of the process. Furthermore, accumulation of deposits in membrane is another problem associated with these processes[6]. The need of acidic environment is a major drawback of ion-exchange process. Selection of good adsorbent and their regeneration limits the application of adsorption process. Differently electrocoagulation technique is a better choice for treatment of water/wastewater due to the small volume of sludge generation, easier maintenance and low operating cost. Thus it has ability to overcome the complications of other remedies and prove to be a very effective and economic approach for clarification of water and wastewater from fluoride.

The electrocoagulation treatment method is based on the generation of metallic ions (M^{n+}) through the DC power supply in submerged metal electrode (generally Fe or Al). These metallic ions attaches with colloids which results in increasing of particle size and causing them to settle down due to gravitational force, in the form of hydroxide. While using aluminium electrodes following reactions takes place[8]:

At cathode

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad \ldots(1)$$

At anode

$$Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^- \qquad \ldots(2)$$

$$Al^{3+}{}_{(aq)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3H^+{}_{(aq)} \qquad \ldots(3)$$

Fluoride by adsorption:

$$Al_n(OH)_{3n(s)} + mF^-_{(aq)} \rightarrow Al_nF_m(OH)_{(3n-m)(s)} + m(OH)^-_{(aq)} \quad \ldots(4)$$

Fluoride by co-precipitation:

$$nAl^{3+}_{(aq)} + 3n\text{-}mOH^-_{(aq)} + mF^-_{(aq)} \rightarrow Al_nFm(OH)_{3n-m(s)} \quad \ldots(5)$$

Consequently, monomeric and polymeric species forms as $Al(OH)^+$, $Al\ OH^{2+}$, $Al\ _2(OH)_2^{4+}$, $Al\ (OH)_4^{5+}$, $Al\ (OH)_2^0(s)$ and $Al\ (OH)_4^-$, etc[9].

In the present study the aluminium electrode was selected for defluoridation of laboratory prepared fluoride water solution. Defluoridation by electrocoagulation using aluminium as a sacrificial electrode is because of the sweep coagulation or entrapment of F^- ions by unsolvable aluminium hydroxide precipitates ($Al(OH)_3$) in synthetic solution. The result of several variables such as pH, current density and treatment hour on the defluoridation were evaluated. The mechanism of defluoridation was examined through kinetic study.

Experimental Section

Materials

Fluoride water solution was made in laboratory by adding measured quantity of NaF in tap water. Although, tap water may contain other coexisting ions that ions either present in the same form or combined with other cations[10]. Desired quality of chemicals (Analytical grade like NaF) were supplied by Merk India Ltd, Mumbai.

The concentration of F^- was estimated by making use of colorometery technique as suggested by APHA, and manual provided by Merck, Germany.

Process

Electrochemical reactor (ECR) was made of Pyrex glass and it was constructed in the workshop of NIT, Raipur. The capacity of the reactor was 1.5 L with dimensions of L × W × H=110 mm × 110 mm × 120 mm (Fig. 1). The ECR was placed over a magnetic stirrer setup where the solution was agitated. The speed of agitator was fixed at 200 RPM. A gap of 2 cm was adjusted between metal (electrode) surface and base of the ECR for well mixing of solution. Four Al electrodes included equal quantity of anodes and cathodes were employed in the electrocoagulation treatment. The inter electrode gap (i.e. A gap adjusted between the two electrodes) was set at 20mm. Now, direct current was supplied to the submerged plates by using DC power supply (5 A × 30 V). Current was maintained by a regulator. The samples were taken at a fixed time interval to analyse the fluoride concentration. To avoid any error in fluoride measurement, these sample were let to settle for approximately 2 h. The details of electrode and reactor used in the process are presented in Table 1.

Results and Discussion

Consequence of initial *p*H

The initial *p*H of synthetic water is a major factor during the practice of electro coagulation. Hence, the impact of *p*H on removal efficiency of fluoride was observed at different *p*H and presented in Fig. 2. It was shown in Fig. 2 that the F^- decreased to 9.2, 8.2, 7.4, 10.2 and 11.2 mg/L at *p*H 4, 6, 6.5, 8 and 10 respectively, from the starting mass of F^-=50 mg/L. It is clear that optimum defluoridation is achieved at *p*H 6.5. Further change in *p*H of solution decreased the removal efficiency of F^- from the F^- contaminated water. This may be due to reason that

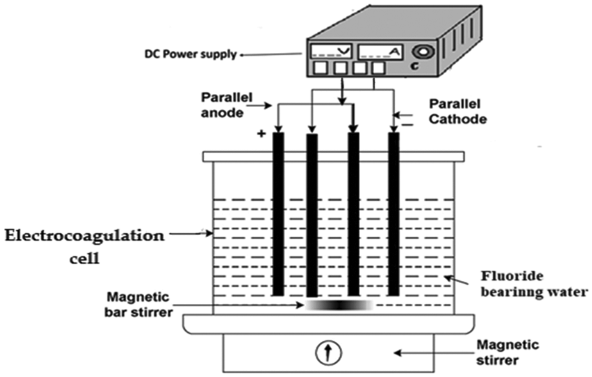

Fig. 1 — Experimental setup of the electrocoagulation treatment.

Table 1 — Properties of electrode and reactor

Electrodes	
Material (Anode and Cathode)	Aluminium
Shape	Rectangular plate
Size of each plate (mm)	90x80
Thickness (mm)	2
Effective area (mm^2)	7200
Plate arrangement	Parallel
Submergence	Full
Reactor	
Make	Perspex glass
Dimensions (L x W x H) (mm)	110 x 110 x 120
Volume (L)	1.5
Electrode gap (cm)	2
Type	Up flow
Mode of operation	Batch

the defluoridation efficiency at various *p*H based on varieties of metal hydroxide formation and presence of other coexisting ions in F^- contaminated water. Possibly, majority of aluminium complex, commonly known as electro-coagulants, may have occurred at *p*H 6.5due to the equilibrium between H^+ ions and the metallic ions[11]. It was also observed that at *p*H 6.4, after polymerization and decomposition amorphous flocs of $Al(OH)_3$ were formed[12].

Consequence of current density

CD is also an significant parameter during the electrocoagulation treatment. In this work, the effect of the CD on the F^- reduction was examined with initial *p*H of 6.5 and varying CD (17.36-69.44 A/m^2). It is clear from Fig. 3 that CD of 34.72 A/m^2provided better fluoride removal as compared to higher CD. The F^- concentration was reduced to 10.2, 7.4, 8.6 and 11.6 mg/L in 50 min for CD of 17.36, 34.72, 52.08 and 69.44 A/m^2 respectively. The passing of electricity causes positive metal ions to be discharged from the submerged electrode (anode) which react with F^- to produce a neutral mass that settles down because of gravitational force. The fluoride concentration decreases with increase in CD up to a definite extent then increased due to increase in metal ion concentration with raise in CD. The excess amount of metal ions results in the destabilization of the particle[11].

The influence of CD on defluoridation in terms of power expenditure and power expenditure per unit mass of F^- removed are given in Fig. 4 (a-c).The result of increase in CD on defluoridation is given in Fig. 4 (a). Fig. 4(b) and Fig. 4 (c) shows that when CD was increased the power expenditure and power expenditure per unit mass of F^- removed both increased. Hence, the calculation of energy consumption and specific energy consumption (SEC) are required that given by equations[11];

$$Energy\ consumption\ \left(\frac{Wh}{L}\right) = \frac{VIt}{Treated\ volume} \ldots \quad \ldots (6)$$

It should be noted that V represents the cell voltage with unit of volt (V), I represent the current intensity with unit of ampere (A) and t leads the value of the treatment time in hour (h). When the value of CD enhances, it promotes the more consumption of voltage of the system simultaneously consequently electrical power expenditure rises. Table 2 shows the mean voltage with respect to the current densities used.

$$Specific\ Energy\ consumption\ \left(\frac{Wh}{dm^3.gm}\right) = \frac{Energy\ consumption}{(Mass\ of\ flouride\ removed)} \quad \ldots (7)$$

Consequence of starting concentration of F^-

The influence of F^- concentration on defluoridation efficiency during the electrocoagulation treatment is presented in Fig. 5. It can be observed that the concentration of F^- reduced to 1.5, 3.2, 5.2, 6.8 and 7.4 from starting concentrations range of 10-50 mg/L respectively. It may be noted that starting

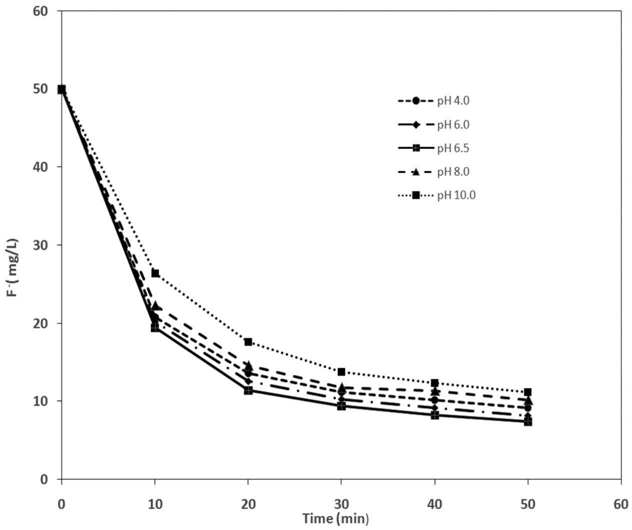

Fig. 2 — Consequence of *p*H on electrocoagulation of F^- contaminated water (current=1 A).

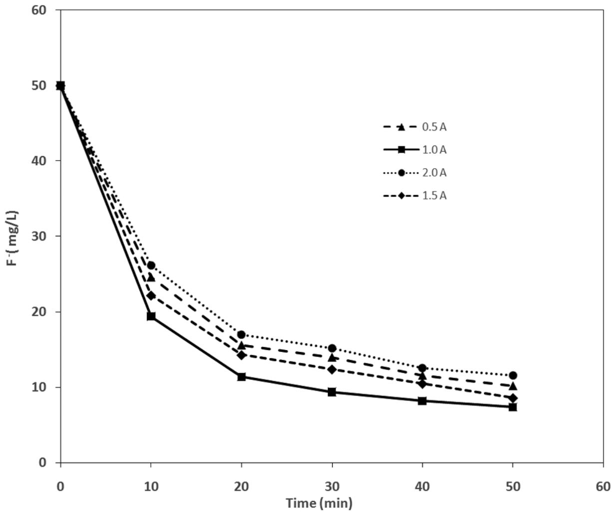

Fig. 3 — Consequence of current density on electrocoagulation of F^- contaminated water.

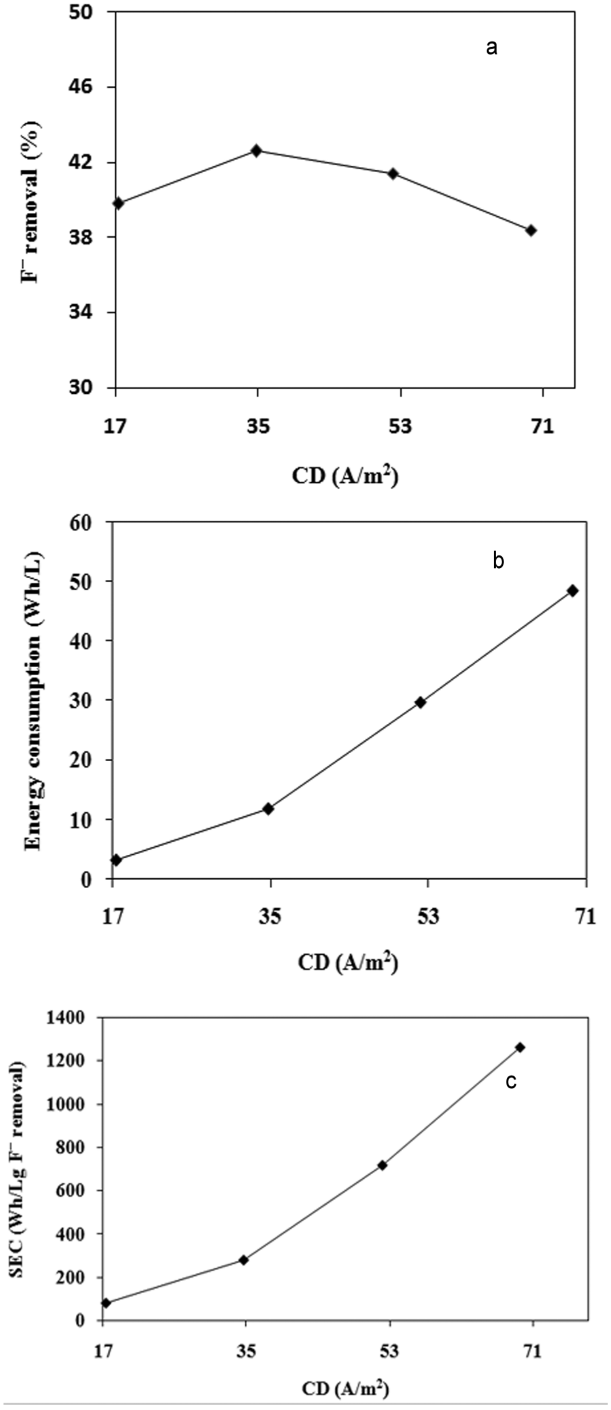

Fig. 4 — Consequence of CD on (a) % F^- reduction, (b) energy consumption and (c) specific energy consumption.

F^- concentration of 10 mg/L was reduced to 1.5 mg/L an acceptable range of fluoride in water as per WHO norms. Other higher concentration may require some addition treatment to reduce the fluoride concentration to that WHO standard. Maximum percentage removal (85.2%) takes place at maximum initial fluoride concentration i.e. for 50 mg/L.

Kinetics of electrocoagulation process

To understand the mechanism of EC process kinetic study has been also performed. When the current passes in aluminium electrode, metal cations (aluminium cations) are released in the water sample because of the dissolution of electrode material. The fluoride removal rate is analysed by kinetic study and a universal equation of kinetic analysis for defluoridation can be given by;

$$\frac{dF^-}{dt} = -k\mathrm{CD}^{\mathrm{m}}(\mathrm{F}^-)^n \quad \ldots (8)$$

In the above equation n represent order of reaction for fluoride variation while m represent for CD and k represents the constant of F^- removal rate. For more clarification, values of n, m, and k are given in Table 3. Gondudey *et al.*[13] also used similar type of

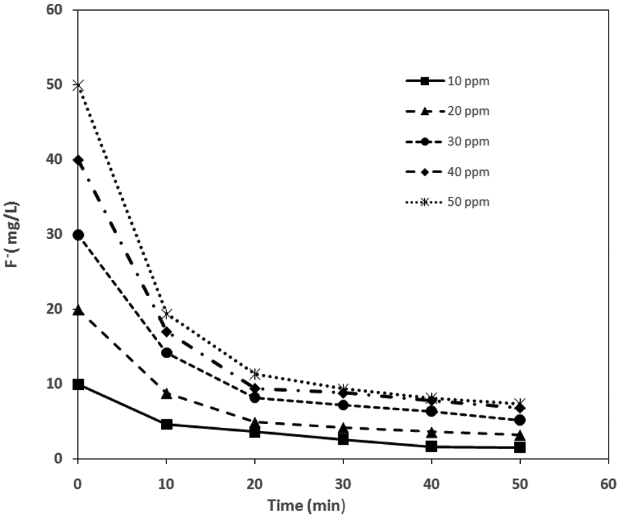

Fig. 5 — Consequence of starting concentration of F^- on its removal. $pH_i = 6.5$, CD = 34.72 A/m^2.

Table 2 — Data for electrocoagulation using Al electrode. $pH_i = 6.5$, EG = 2.0 cm, $t_R = 50$ min, Starting mass of F^-= 50 mg/L, Total F^- contaminated water taken = 1.0 L.

	Electrode material Al			
Current, A	0.5	1.0	1.5	2.0
Current density, A/m^2	17.36	34.72	52.08	69.44
Voltage (average), V	7.8	14.3	23.8	29.1

Table 3 — Value of kinetic parameters for Al electrode.

Current density (A/m^2)	K × 10^5 $\left(\left(\frac{m^2}{A}\right)^m \left(\frac{L}{mg}\right)^{n-1}\right) min^{-1}$	m	n
17.36	1.00	0.05	2.05
34.72	1.20	0.05	2.07
52.08	1.32	0.05	2.03
69.44	1.41	0.05	2.00

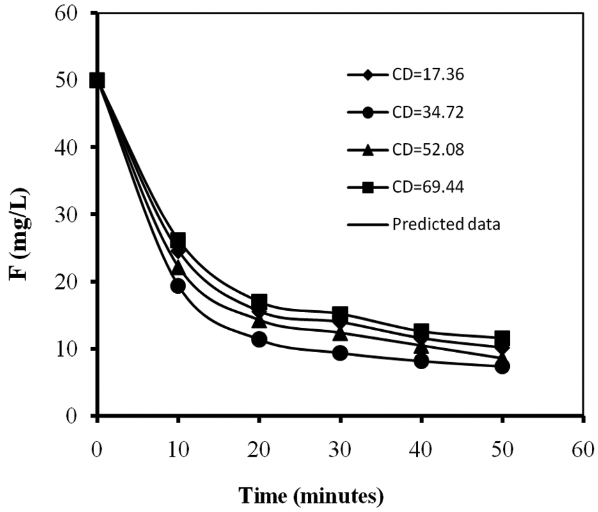

Fig. 6 — Kinetics plot of F^- removal. Starting value of F^-= 50 mg/L and pH= 6.5.

kinetic equation for COD reduction from water utilizing electrocoagulation technique. It can be seen from Fig. 2 and Fig. 3 that the fluoride removal rate enhanced quickly up to initial 40 min of treatment time after that it is nearly in equilibrium. This can be attributed to the reason that in the initial 40 minutes of experiment the concentration of aluminium ion (Al^{3+}) and fluoride were balanced. Later on the fluoride ion concentration decreased causing the defluoridation process to reach to equilibrium. It is clear from the kinetic plot that order of reaction is not one hence, kinetic data are evaluated by changing reaction order. The values of the kinetic variables k, n and m are calculated with the help of MATLAB toolbox. To achieve the values of different parameter, an optimization function was established by the summation of the square of errors between the model estimated and experimental fluoride concentration for whole data points of a CD. The kinetic data given in Fig. 6 might be potentially modelled by the following equation:

$$\frac{dF^-}{dt} = -k\mathrm{CD}^{0.05}(\mathrm{F}^-)^n \qquad \text{... (9)}$$

It can be seen from Table 3 that, value of k, for CD (17.36–69.44) are obtained in the range of 1.00 × 10^{-5} to $1.41\mathrm{x}10^{-5}\left(\left(\frac{m^2}{A}\right)^{0.05}\left(\frac{L}{mg}\right)^{n-1}\right) min^{-1}$ and the value of n lied from 2.00 to 2.07.It is found that the model (Eq. 9) the experimental values and predicted values of F^- concentration for all CDs fitted well as shown in Fig. 6.

Conclusion

The usage of aluminium as a self sacrificing electrode and its consequence on defluoridation during electrocoagulation treatment has been investigated. The EC technique is found quite fruitful and useful for the defluoridation of the laboratory prepared fluoride solution. The result of various operating parameters such as *p*H 6.5, CD 34.72 A/m^2 and treatment time 50 min are found optimum. Maximum F^- removal 85.2% is achieved for starting F^- concentration of 50 mg/L. The F^- concentration can be decreased from its starting concentration of 10 mg/L to 1.5 mg/L, which is acceptable as per WHO norms. Other higher concentrations are not reduced to such limit which entails further treatment. The process could be effective in treating low concentration of fluoride in the water to get it reduced to WHO acceptable limits.

Acknowledgement

Authors are thankful to NIT, Raipur and Guru Ghasidas Vishwavidyalya for providing facilities for carry out the work.

Conflict of interest

Authors of manuscript entitled, “Defluoridation of water by electrocoagulation using Aluminium electrode,” reveal that there are no clash of interest for this work.

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