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Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections

D. Ghosh, C.R. Medhi, M.K. Purkait *

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India

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ABSTRACT

Electrocoagulation was investigated for the effective removal of fluoride from drinking water. Different initial concentrations (2–10 mg L^{-1}) of fluoride were considered for the experiment. Two different electrode connections (monopolar and bipolar) were examined for choosing the better alternative in order to intensify the performance of the process. It was observed that the removal of fluoride was better for bipolar connection than for monopolar connection. The final recommendable limit of fluoride (1 mg L^{-1}) was obtained in 30 min at 625 A m^{-2} using bipolar connection. The corrosion of electrodes as well as the sludge formed during the process was estimated for the bipolar connection. Thickness of film generated on the electrode surfaces in bipolar connection was also estimated at different current densities as well as for different initial fluoride concentrations. By-products obtained from the electrocoagulation bath were analyzed using SEM, EDAX, FTIR and XRD and explained. Comparative cost estimation for both electrode connections was adopted and presented as well. Total operating costs for monopolar and bipolar connections were 0.38 and 0.62 US$ m^{-3}, respectively, for the initial fluoride concentration of 10 mg L^{-1}. These findings might be useful in order to treat the fluoride contaminated water for drinking.

1. Introduction

Groundwater contamination has been a major issue due to the presence of various pollutants such as fluoride, pesticides, heavy metals, etc. Fluoride contamination is a serious problem in several parts of India as well as in different parts of the world associated with its adequate presence (>4 mg L^{-1}) in the ground water causes serious damage to the teeth and bones called fluorosis. The acceptable safe limit of fluoride recommended by World Health Organization is 1 mg L^{-1} (WHO, 1984). Different techniques like adsorption, membrane separation, ion-exchange, hybrid techniques and electrocoagulation (EC) were reported for the removal of fluoride from drinking water. Adsorption process using different adsorbents such as trimetal oxide (Wu et al., 2007), waste carbon slurry (Gupta et al., 2007) and many low-cost materials (Srimurali et al., 1998) were investigated for the removal of fluoride from aqueous medium. Membrane separation techniques were investigated for the effective separation of fluoride using electrodialysis (Amor et al., 2001), Donnan dialysis (Hichour et al., 2000), nanofiltration (Hu and Dickson, 2006) and anion-exchange membrane (Tor, 2007). Garmes et al. (2002) had performed defluoridation of ground water by a hybrid process combining adsorption and Donnan dialysis. Integrated biological and physicochemical treatment process for nitrate and fluoride removal was investigated by Mekonen et al. (2001). Fluoride distribution in electrocoagulation defluoridation process was investigated in order to explore the mechanism involved in fluoride removal process (Zhu et al., 2007). The kinetics was developed empirically in the removal process of fluoride using monopolar electrode connection (Emamjomeh and Sivakumar, 2006; Hu et al., 2007).

All the works mentioned above focussed mainly on few parameters such as current density, conductivity, pH and interelectrode distance for the EC process. There are certain other factors like number of electrodes and electrode connection mode (monopolar and bipolar) that may also play an important role in the EC process. Inadequate information about the influence of electrode connection on the removal of fluoride using EC was encountered. In order to achieve the cost-effective fluoride removal from drinking water a techno-economical comparative analysis is undoubtedly essential. Hence, the influence of monopolar and bipolar electrode connections on the performance of fluoride removal will be the further contribution of the research.

In this work, two different electrode connections (monopolar and bipolar) were investigated for choosing the better alternative in order to intensify the performance of the process. Different initial concentration (4–10 mg L^{-1}) of fluoride was considered for the experiment that had duration of 45 min. Experiments were carried out with different current densities. Corrosion of electrodes as well as the sludge formation during the experiments for both electrode connections were estimated. Variation of film thickness deposited over the electrode surfaces with change in initial

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* Corresponding author. Tel.: +91 361 2582262; fax: +91 361 2582291.
E-mail address: mihir@iitg.ernet.in (M.K. Purkait).

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fluoride concentrations and current densities were determined. By-products obtained from the EC bath were characterized by SEM, EDAX, FTIR and XRD analysis. Operating cost for the removal of fluoride was calculated and presented as well. In the calculation of the operating cost, only material and energy costs were considered. Other cost items such as labour, maintenance and solid/liquid separation costs were not taken into account. A simplified cost equation was used to evaluate the operating cost. The findings of the present study might be useful in order to treat the fluoride contaminated water for the drinking purpose effectively and further advancement in designing an electrocoagulation unit for the treatment of fluoride-rich ground water.

2. Fluoride removal mechanism by electrocoagulation

In electrocoagulation process, an applied potential generates the coagulant species in situ as the sacrificial metal anode (aluminium or iron) dissolves, while hydrogen is simultaneously evolved at the cathode. Coagulant species aggregate the suspended particles or precipitate and adsorb dissolved contaminants. Tiny bubbles of hydrogen and oxygen that are formed during electrolysis of water, collide with air bubbles which compel to float the pollutant particles. Choice of electrode material depends on various criteria such as low-cost, low-oxidation potential, inertness towards the system under consideration, etc. Different electrodes were reported in the literature like carbon (Gallegos and Pletcher, 1999), mild steel (Golder et al., 2005), iron (Yildiz et al., 2007), graphite titanium (Linares-Hernández et al., 2007) and aluminium (Bi et al., 2004). Aluminium was reported to be very effective and successful in pollutant removal at favorable operating conditions. The electrode and bulk reactions for the removal of fluoride are summarized as follows:Anode:

$$Al \rightarrow Al^{3+} + 3e^- \tag{1}$$

Cathode:

$$3H_2O + 3e^- \rightarrow \frac{3}{2}H_2\uparrow + 3OH^- \tag{2}$$

Bulk:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_{3(S)}\downarrow + 3H^+ \tag{3}$$

$$Al(OH)_3 + xF^- \Longleftrightarrow Al(OH)_{3-x}F_x + xOH^- \tag{4}$$

The major interaction mechanism considered in recent years is adsorption followed by precipitation. Al^{3+} and OH^- ions generated by the electrode reactions (1) and (2) react to form various monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$ and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$ and $Al_{13}(OH)_{34}^{5+}$, which are transformed mostly into $Al(OH)_{3(S)}$ according to complex precipitation kinetics (3) (Moudhen et al., 2008). Furthermore, this $Al(OH)_3$ complex is believed to have strong fluoride adsorption capacity (Hu et al., 2003).

3. Experimental

3.1. Experimental set-up

A perspex made tank having dimension of 0.18 m × 0.18 m × 0.18 m with a working volume of about 3 L was used to conduct experiments. Aluminium sheets of 0.15 m × 0.1 m × 0.002 m were used as electrodes for electrocoagulation. Interelectrode distance was maintained at 0.005 m. In bipolar connection, four electrodes were used. Among four such electrodes, only two end electrodes were connected to the DC power source whereas other two electrodes had no connection to the DC source. In such condition, induced polarization took place when voltage was applied to the end electrodes so that the inner electrodes started acting as a secondary cell. Therefore, the total assembly was bipolarized with a primary and a secondary cell acting together. The entire electrode assembly was fitted on non-conducting wedges and hung from the top of the electrocoagulation tank. The effective surface area of each electrode was $4 \times 10^{-3}\ m^2$. The assembly was connected to DC power source (Textronics 36D, Agarwal Electronics, Mumbai, India) to constitute an electrochemical cell with galvanostatic mode for constant current supply. Schematic diagram of monopolar and bipolar electrochemical cell is shown in Fig. 1. The electrode assembly was placed in the cell and the electrodes were connected to the respective terminals of the DC power supply and a constant current was supplied for a given time.

3.2. Materials and methods

Sodium fluoride (NaF, supplied by Aldrich Chemical Company, USA) was used in this study for the preparation of fluoride solution. All the experiments were performed at constant temperature of 25 °C. A measured quantity (1 L) of freshly prepared solution of fluoride using tap water was taken into the electrochemical cell. Initial fluoride concentration varied from 4 to 10 mg L^{-1}. Current density was maintained in the range of 250–625 A m^{-2}. After each experiment, the power was switched off and the electrodes were dismantled. The treated fluoride sample collected at different time interval was filtered before analysis. Electrodes were washed with acetone to remove surface grease, and the aluminium electrode surfaces were dipped for 5 min in acetone solution followed by rubbing with an abrasive paper (C220) in order to ensure the complete removal of impurities before every experiment. After each experiment the used anode and cathode plate were interchanged for effective electrode utilization. In connection with the usefulness of the treated water for the drinking purpose conductivity was measured (using a digital conductivity meter make: Electronics Pvt. Ltd., India, Model: VS1) before and after the treatment to match with the recommendable limit of 0.2 mmhos (Weber, 1972). Fluoride ion meter (Make: Eutech Instrument, Singapore, Model: ECFOO301BEU) was used to determine the fluoride concentration after calibrating the sample using TISAB (Total Ionic Strength Adjuster Buffer). This is a solution containing CH_3COOH (acetic acid), NaCl (sodium chloride), CDTA (*trans* 1,2-diaminocyclohexane–*N*,*N*,*N*′,*N*′ tetra acetic acid monohydrate) and NaOH (sodium hydroxide). Microscopic observation of by-products from the electrocoagulation unit was carried out by a scanning electron microscope (SEM, Make: LEO 1430VP, UK), which directly provided the visual information of morphology of electrocoagulation by-product. Energy dispersive X-ray analysis (EDAX) was an integrated feature of a scanning electron microscope (SEM). This

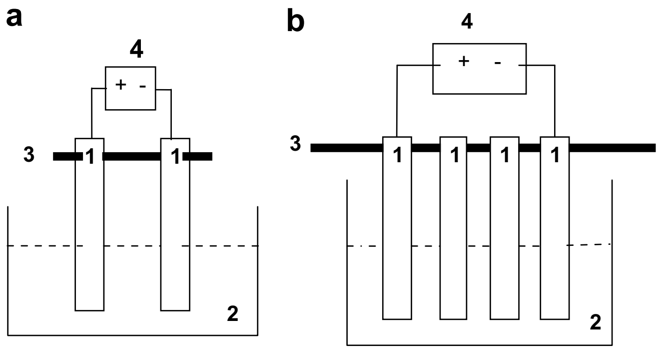

Fig. 1. Schematic diagram of electrochemical cell for the removal of fluoride. (a) Monopolar connection; and (b) bipolar connection. (1) electrodes; (2) fluoride contaminated drinking water; (3) electrode support; and (4) DC power source.

analysis was performed to identify the elemental composition of the by-products obtained from the electrochemical unit. X-ray diffractometer (XRD, Make: Bruker, Germany, Model: AXS D8 Advance) as well as Fourier transform infrared spectroscopy (FTIR, Make: Perkin Elmer, USA, Model: LR 64912C) analysis were carried out to confirm the nature (crystalline or amorphous) as well as the bond stretching of the sludge formed during the electrocoagulation, respectively.

4. Results and discussion

4.1. Fluoride removal efficiency

4.1.1. Effect of initial fluoride concentration

In the fluoride removal process by electrocoagulation, initial fluoride concentration is an important parameter for a particular mode of electrode connection. Fig. 2a reveals the variation of fluoride concentration in the EC bath during the experiment using monopolar electrode connection. It was observed that after the treatment, final fluoride concentration was not dropped below the recommendable limit suggested by WHO. It was also observed from Fig. 2a that around 35 min was required to attain final fluoride concentration of 1 mg L^{-1} for the initial fluoride concentration of 4 mg L^{-1} and current density of 250 A m^{-2}. Again, for an initial fluoride concentration of 6 mg L^{-1} with monopolar connection, 45 min was needed for the final fluoride concentration to be of 1.4 mg L^{-1}. It was very much clear that with an increase in initial fluoride concentration the treatment time increases to attain the final fluoride concentration at its recommendable limit (1 mg L^{-1}). In EC, initially aluminium cations contribute to charge neutralization of the pollutant particles as the isoelectric point is attained. Here a sorption coagulation mechanism occurs resulting in the formation of loose aggregates. As time progresses, further aluminium cation addition results in amorphous aluminium hydroxide precipitation that promotes pollutant aggregation. As the current density was kept constant so the production of the aluminium cation remained fixed and therefore with an increase in initial fluoride concentration, the complex formation process between the amorphous aluminium hydroxide and fluoride was insufficient at the applied current density mentioned above. This could be the reason so that the drinking water with an initial fluoride concentration of 8 and 10 mg L^{-1} had a final fluoride concentration of 1.8 and 2.2 mg L^{-1} at the end of 45 min treatment by EC with monopolar electrode connection.

4.1.2. Effect of bipolar connection of electrodes with prolonging time

In order to improve the fluoride removal from the contaminated drinking water with higher initial fluoride concentration efficiently, electrode connection can have a justified effect on the sludge formation as well as on the corrosion of the electrode. Effect of electrode connections (monopolar and bipolar) for the fluoride removal by EC is shown in the inset of Fig. 2b. Investigation was performed for the treatment of drinking water with initial fluoride concentration of 10 mg L^{-1}. Other parameters like current density, interelectrode distance and duration of the experiment were maintained at 250 A m^{-2}, 0.005 m and 45 min, respectively. It was observed that with the passage of time fluoride concentration inside the EC bath was decreased for both electrode connections. It is also seen from Fig. 2b that at the end of 45 min in bipolar connection, final fluoride concentration was 1.7 mg L^{-1}, whereas for monopolar connection, the fluoride concentration dropped down to a value of 2.2 mg L^{-1} which was far away from the recommendable limit. It is necessary to mention that in the bipolar connection, two pair of electrodes were used of which only the end electrodes were connected to respective anode and cathode connection of the DC source. In bipolar connection, two electrochemical cells acted together (Fig. 1) for which higher surface area compared to that of monopolar connection favored the adequate anodic oxidation. As a result, with the same current density applied for both kind of connection, the intensity is higher in the bipolar connection. Therefore, final fluoride concentration in the solution was found lower than that was observed in monopolar electrode connection. However, in the bipolar connection, final fluoride concentration could not attain the satisfactory level so that the treated water would be permissible for drinking purpose under the above mentioned operating conditions. Finally, it remained clear that with the bipolar connection mode, fluoride removal process would be beneficial by changing current density.

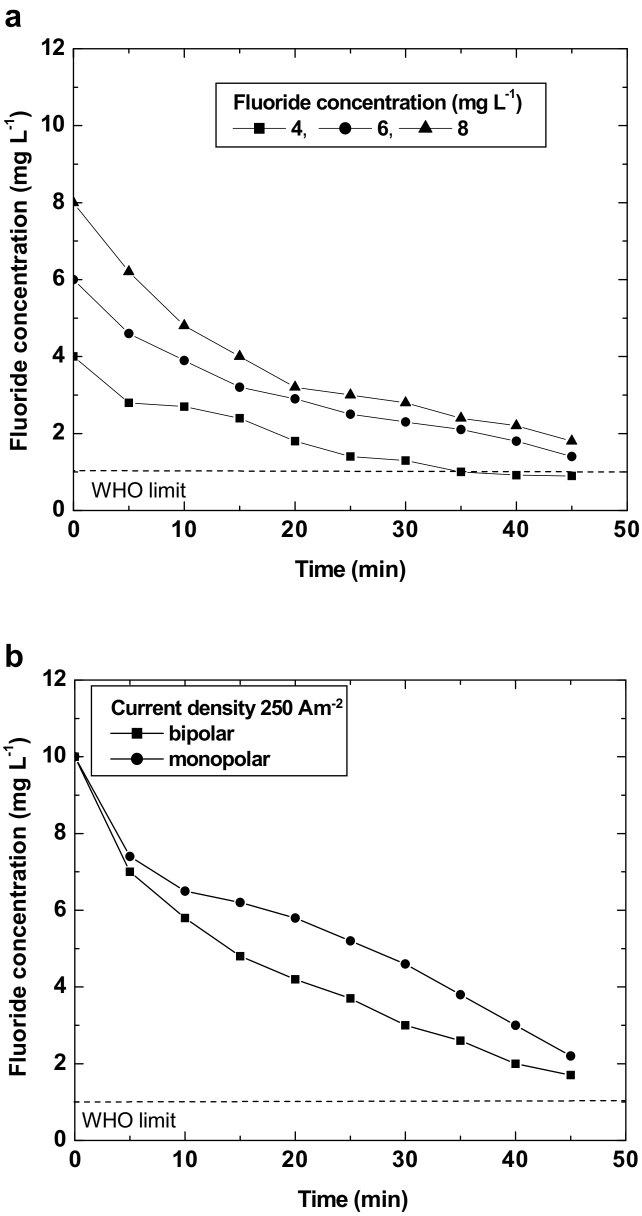

Fig. 2. Variation of fluoride concentration in the EC bath with time. Interelectrode distance: 0.005 m; current density: 250 A m^{-2}; temperature: 25 °C. (a) Monopolar connection; and (b) bipolar and monopolar connections. Initial fluoride concentration: 10 mg L^{-1}.

4.1.3. Effect of current density

Fig. 3 represents the effect of current density on the fluoride concentration in the EC bath during the experiment. Current

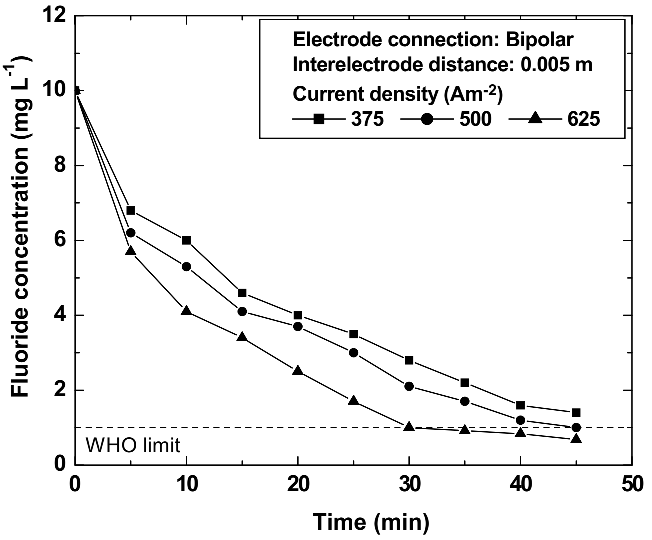

Fig. 3. Effect of current density on the fluoride concentration in the EC bath with time. Initial fluoride concentration: 10 mg L^{-1}; interelectrode distance: 0.005 m; electrode connection: bipolar; temperature: 25 °C.

density varied from 375 to 625 A m^{-2} using bipolar electrode connection. It was seen from Fig. 3 that with an increase in current density, defluoridation was improved. Generally an increase in current density causes the anodic oxidation to take place more readily, which in turn favors the formation of amorphous aluminium hydroxides species adequately in the vicinity of the electrode as well as in the bulk. This generally occurs at the vicinity of the anode–water interface and thus forms a fine gelatinous film on the electrode surface. It was seen that in the system with co-existing anions, the defluoridation occurs in the bulk of the solution and without co-existing anions it happens on the surface of the anode. Therefore, fluoride ions present in the solution could get the allowance to interact at the vicinity of anode and form complex as described in Section 2. It was found that the final fluoride concentration of 1 mg L^{-1} was achieved at the end of 30 min of the EC using bipolar connection with an application of 625 A m^{-2}. Furthermore, this was also supported by the fact that with an increase in current density and initial fluoride concentration, the corrosion of the electrodes as well as the sludge formation also increased.

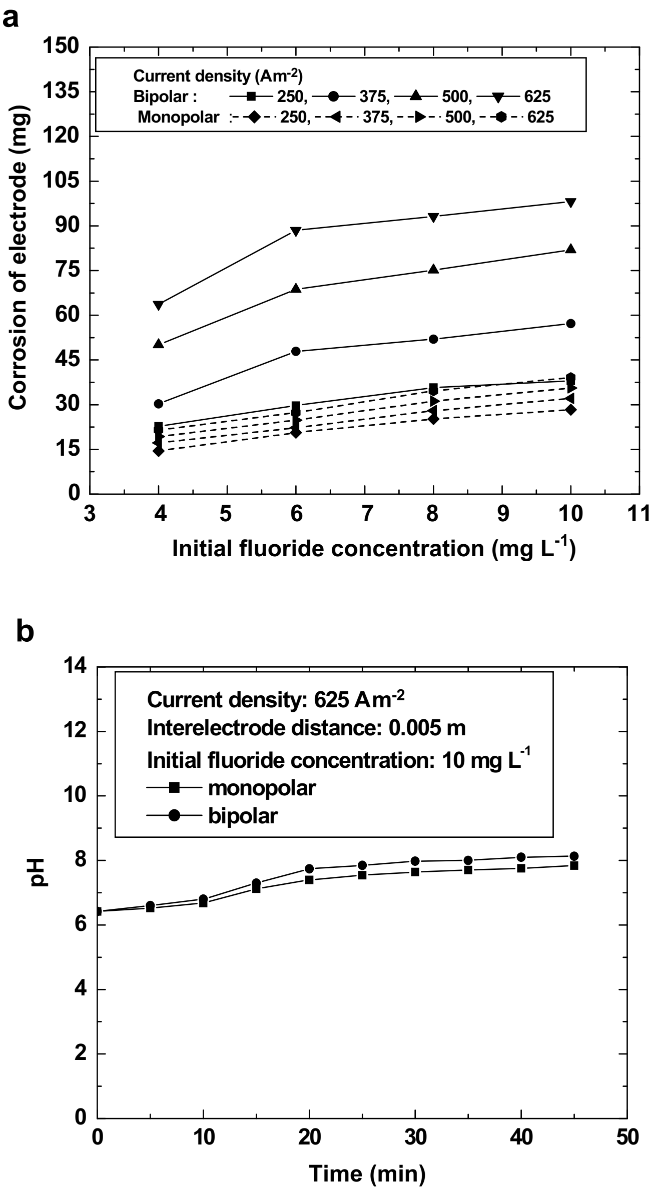

Fig. 4. (a) Variation of electrode corrosion with bipolar and monopolar connections at different current densities. Interelectrode distance: 0.005 m; duration of the experiment: 45 min; temperature: 25 °C. (b) Variation of pH with time in the EC bath for bipolar and monopolar connections. Initial fluoride concentration: 10 mg L^{-1}; interelectrode distance: 0.005 m; duration of the experiment: 45 min; temperature: 25 °C.

4.1.4. Variation of electrodes corrosion and sludge formation

Anodic oxidation gives rise to the corrosion of electrode material (aluminium in the present case) by means of aluminium hydroxide formation during EC. The corrosion of electrodes gives an over-view of the life time as well as the experimental cost of the electrode material. Therefore, electrode corrosion during EC can be considered as an important parameter that reflects the viability of the process. Corrosion of the electrodes can be defined as the weight loss (mg) of the electrodes due to anodic oxidation. This loss was calculated by subtracting the weight of the electrodes taken at the end of the experiment from the weight taken before the experiment of the same electrodes. Fig. 4a describes the extent of electrode corrosion at different current densities with bipolar as well as monopolar electrode connection. The investigation was performed using different initial fluoride concentrations. Parameters like interelectrode distance and duration of the experiment were kept constant at the values mentioned in Fig. 2a. It was observed that with an increase in initial fluoride concentration and current density, the electrode corrosion increased due to the increased dissolution of electrodes. In addition to this it was seen that electrode corrosion was greater for bipolar connection. It can be seen from Fig. 4a that the electrode corrosion was 14.5 mg with monopolar connection whereas with bipolar connection the corrosion was 22.8 mg at an applied current density of 250 A m^{-2} for the initial fluoride concentration of 4 mg L^{-1}. This was an obvious situation since anodic oxidation in bipolar connection was higher compared to monopolar connection.

Sludge generated in the EC bath was estimated for bipolar and monopolar electrode connections. It was found more sludge formation for the bipolar connection, whereas for both cases it increased with increasing current density. In the treatment of drinking water with initial fluoride concentration of 4 mg L^{-1} by EC at a current density of 250 A m^{-2}, the amount of sludge produced was 68.6 and 42 mg for bipolar and monopolar connections, respectively. It was noticed that the removal of fluoride from the drinking water having initial fluoride concentration of 4 mg L^{-1} using bipolar connection, the amount of sludge generated was equal to 90.2, 148.5 and 190.3 mg at 375, 500 and 625 A m^{-2}, respectively. It was also observed that with an increase in initial fluoride concentration, more sludge was produced. Fig. 4b represents the pH variation with time in the EC bath during the experiment using bipolar and monopolar connections. The pH increased with time in both cases (varied from 6.4 to 8.1). It was also observed that for bipolar connection, the pH of the solution was marginally higher than the monopolar connection. For example, at a current density of 625 A m^{-2} and an initial fluoride concentration of 10 mg L^{-1}, the solution pH was always around 8 at the end of all trials. According to the complex precipitation kinetics, most of the charged aluminium species transformed into $Al(OH)_3$ which exist in equilibrium with some of the soluble species (Duan and Gregory, 2003). It can be also seen from Fig. 4b that after attaining the pH close to 8, it does not increase significantly irrespective of the connection mode. This is probably because of an equilibrium between the $Al(OH)_3$ and the soluble aluminium species at pH about 8 for both electrode connections. This observation also supported the reason behind the electrode dissolution which was above discussed.

4.1.5. Variation of film thickness

In EC process, anodic oxidation favors the formation of gelatinous hydroxide species with an interaction between positive metal ions and negative OH^- ions. This gelatinous behavior allows such hydroxide to stick with the electrode surface growing like a film with the progress of the process. Therefore an extra resistance is created, which in turn affects the performance of the process. Hence, it is very much clear that the film generated during the electrocoagulation process plays a major role in order to operate the technique for the removal of pollutants. The film thickness was calculated using the following simple mass balance equation:

$$\delta \cong \frac{(m_1 - m_2) \times 10^{-6}}{\rho \times A} \tag{5}$$

where δ is the film-thickness (nm), m_1 is the weight of the electrodes (mg) after the experiment without cleaning, m_2 is the weight of the electrodes (mg) after the experiment after cleaning, ρ is the density of the film (g L^{-1}) and A is the area of the electrodes (m_2).

Fig. 5 depicts the variation of film-thickness over electrode surface with different current densities and initial concentrations of fluoride. It was seen that with an increase in current density and initial fluoride concentration of the drinking water, film-thickness increased for both monopolar (Fig. 5) and bipolar connections. It can be observed from Fig. 5 that the film-thickness increased from around 131 to 470 nm when the initial fluoride concentration increased from 4 to 10 mg L^{-1} at an applied current density of 375 A m^{-2} for bipolar connection. This parameter also increased from 147 to 180 nm when current density increases from 500 to 625 A m^{-2}. Variation of film-thickness using monopolar connection has been estimated at the same condition as that of bipolar connection and shown in the inset of Fig. 5. It was observed that film formation followed the same trend but it was much lower than in the case of bipolar connection. For example, the film-thickness increased from 23.5 to 57 nm when the initial fluoride concentration varied from 4 to 10 mg L^{-1} at an applied current density of 375 A m^{-2} for 45 min of operation. Furthermore, it was also found that with the increase in current density from 500 to 625 A m^{-2}, the film-thickness increased from 69 to 76.4 nm for an initial fluoride concentration of 10 mg L^{-1}. An enhancement in the current density favored the anodic oxidation and hence, it increased the possibility of the formation of more metal ions as well as the interactions between the metal hydroxides and the fluoride ions. Therefore, the generation of the film formed during the experiment became thicker.

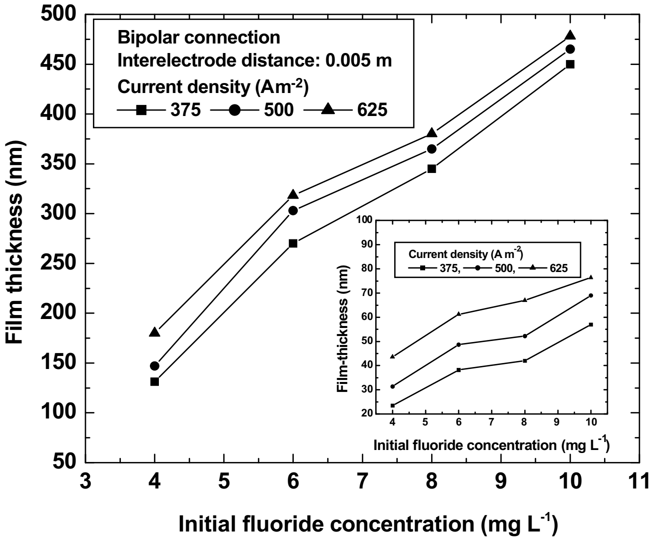

Fig. 5. Variation of film-thickness over electrode surface with different current densities and initial fluoride ion concentrations. Current density: 375 A m^{-2}; interelectrode distance: 0.005 m; duration of the experiment: 45 min; electrode connection: bipolar; temperature: 25 °C. Inset: film-thickness variation over electrode surface with different current densities and initial fluoride ion concentrations for monopolar electrode connection.

4.2. Conductivity measurement

In order to examine the treated water quality by electrocoagulation, conductivity measurement was made so that it could be permissible for the drinking purpose. Before each experiment using bipolar electrode connection, the conductivity of the contaminated water was measured as 0.4, 0.6 and 0.9 mmhos for the initial fluoride concentration of 6, 8 and 10 mg L^{-1}, respectively. After the treatment, the sludge was filtered out and the clear solution was collected. The conductivity of treated water was around 0.2 mmhos for all cases, that is, in the range of permissible limit of drinking water (Weber, 1972).

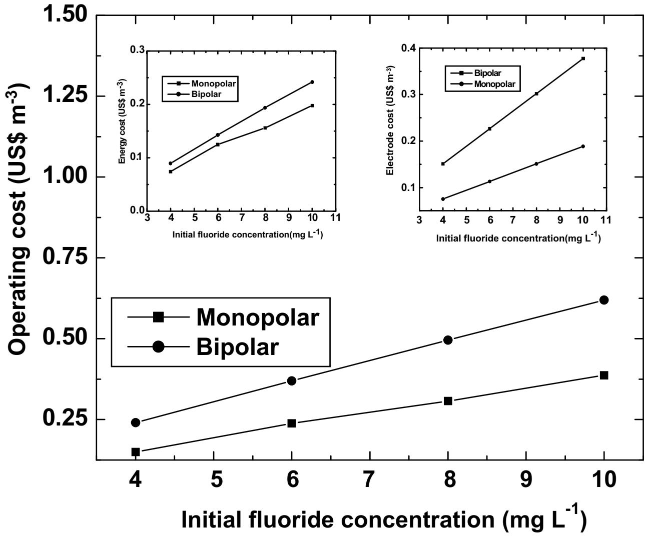

Fig. 6. Cost for the treatment of drinking water containing different concentration of fluoride. Current density: 625 A m^{-2}; interelectrode distance 0.005 m; duration of the experiment: 45 min; temperature: 25 °C. Inset: cost for electrode and energy required for monopolar and bipolar connections.

4.3. Estimation of energy consumption and operation cost

In any electrical process, cost is incurred due to electrical energy demand, which affects the operating cost. For EC process the operating cost includes material, mainly electrodes, and electrical energy costs, as well as labour, maintenance, sludge dewatering and disposal, and fixed costs. In this preliminary economic investigation, energy and electrode material costs were taken into account as major cost items in the calculation of the operating cost (US$ m^{-3} of fluoride solution) in the form:

$$\text{Operating cost} = a\,C_{\text{energy}} + b\,C_{\text{electrode}} \tag{6}$$

where C_{energy} and $C_{\text{electrode}}$ (kg Al m^{-3} of fluoride solution) are consumption quantities for the fluoride removal, which are obtained experimentally. “*a*” and “*b*” given for Indian market in February 2008, are as follows: “*a*” electrical energy price 0.0065 US$ kW h^{-1}; “*b*” electrode material price 0.3 US$ kg Al^{-1}. Cost due to electrical energy was calculated from the expression:

$$C_{\text{energy}} = \frac{U \times I \times t_{\text{EC}}}{V} \tag{7}$$

where *U* is the cell voltage (V), I is the current (A), t_{EC} is the time of electrolysis (s) and *V* is the volume (m^3) of fluoride solution. Cost for electrode was calculated from the Faraday’s law:

$$C_{\text{electrode}} = \frac{I \times t \times M_{\text{w}}}{z \times F \times V} \tag{8}$$

where *I* is the current (A), t is the time of electrolysis (s), M_{W} is the molecular mass of aluminium (26.98 g mol^{-1}), z is the number of electron transferred ($z = 3$), *F* is the Faraday’s constant (96487 C mol^{-1}) and *V* is the volume (m^3) of fluoride solution (Daneshvar et al., 2006). Total operating costs for the treatment of different initial fluoride concentration using monopolar and bipolar electrode connections were calculated and shown in Fig. 6. It was seen from Fig. 6 that operating cost was increased with initial fluoride concentration. This is due to the increase in electrode cost as dissolution of electrodes increases with initial fluoride concentration as described in Section 4.1.4. Fig. 6 shows that theoretical electrode cost varied from 0.075 to 0.12 US$ m^{-3} and from 0.15 to 0.38 US$ m^{-3} for monopolar and bipolar electrode connections, respectively. Similarly, energy cost increased from 0.07 to 0.19 US$ m^{-3} and from 0.09 to

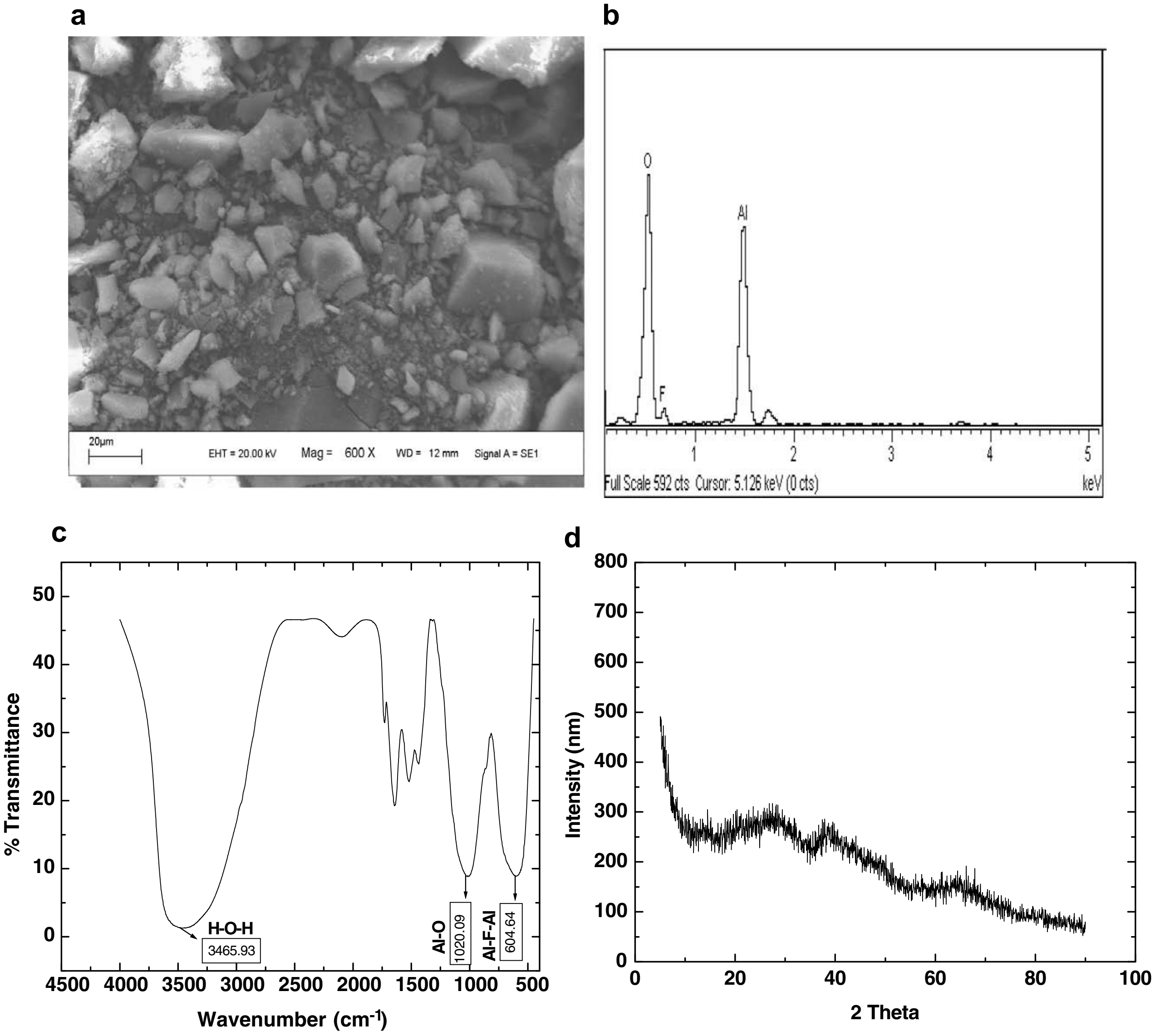

Fig. 7. Characterization of by-products obtained from EC bath. Current density: 625 A m^{-2}, initial fluoride concentration: 10 mg L^{-1}; duration of the experiment: 45 min; temperature: 25 °C; electrode connection: bipolar. (a) SEM image; (b) elemental analysis; (c) FTIR analysis; and (d) XRD analysis.

0.24 US$ m^{-3} for monopolar and bipolar connections, respectively, while initial fluoride concentration varied from 4 to 10 mg L^{-1}. In addition to this, it would be necessary to mention that though energy cost was 21% higher for bipolar connection but electrode cost dominates more over the energy cost due to the higher dissolution of electrodes compared to the monopolar connection. Fig. 6 also evidences that the operating cost for the treatment of drinking water containing initial fluoride concentration 10 mg L^{-1} in bipolar and monopolar connections under the same operating conditions (current density of 625 A m^{-2}, interelectrode distance of 0.005 m, 45 min of operation, 25 °C and pH $\sim$ 8) were 0.62 and 0.38 US$ m^{-3}, respectively. The highest operation cost for the bipolar connection could be related to its greater surface area compared to the monopolar one.

4.4. Characterization of the by-products obtained from the EC bath

A whitish precipitate was formed at the bottom of the electrocoagulation bath at the end of EC process. The precipitate was taken out after the filtration using a filter paper (HM2, Indiachem, India) and dried inside a hot-air oven for 3–4 h. It was then grinded to a fine powder and prepared for SEM, EDAX, FTIR and XRD analysis in order to characterize the by-product obtained from the EC bath.

4.4.1. Scanning electron microscopy and energy dispersive X-ray

The morphology of the by-products obtained from the EC bath using bipolar connection was shown in Fig. 7a. It might be seen from the figure that the by-products formed during the process were whitish and the amount of aluminium hydroxides and dissolved electrode were much higher than that of fluoride present in the EC bath. It was seen from Fig. 7b that the by-products formed during electrocoagulation were composed of elements like Al, O and F. This analysis confirmed that fluoride was entrapped within the aluminium hydroxide complex and formed sludge.

4.4.2. Fourier transform infrared spectroscopy (FTIR)

FTIR was performed using potassium bromide pellets and the result was shown in Fig. 7c. The wave numbers ranged from 4000 to 450 cm^{-1}. Peaks at 3466, 1020 and 605 cm^{-1} corresponding to H–O–H, Al–O and Al–F–Al bond stretching, respectively, can be observed in Fig. 7c. Al–F–Al bond stretching was matched with the analysis made by Gross et al. (2007) for various amorphous trifluoride complexes. From this analysis, it was confirmed that fluoride was linked with aluminium hydroxide complexes and precipitated at the bottom of EC bath.

4.4.3. Powder X-ray diffraction

The X-ray diffraction of the by-product was recorded by a diffractometer operating with a Cu Kα radiation source and nanobragg mode. The XRD analysis result is shown in Fig. 7d. The 2θ scans were recorded from 5° to 90°. The spectrum of the analyzed by-products showed broad and diffuse peaks. Therefore, the identification of peaks with such broad humps is a well known confirmed characteristic of phases which are amorphous or poorly crystalline in nature (Gomes et al., 2007).

5. Conclusions

Electrocoagulation technique was investigated for the removal of fluoride from drinking water using monopolar and bipolar electrode connections. Effects of initial fluoride concentration and current density on the extent of fluoride removal were studied in detail and explained as well. The results showed that the removal efficiency increases with the increase in current density. The results also confirmed that the bipolar connection can serve better fluoride removal than the monopolar connection. The corrosion of the electrodes and sludge formation were greater for bipolar connection. Operating costs for the treatment of drinking water using EC were evaluated for different initial fluoride concentrations up to 10 mg L^{-1}. The operating costs for monopolar and bipolar connections were 0.38 and 0.62 US$ m^{-3}, respectively, for the initial fluoride concentration of 10 mg L^{-1}. The total operating cost thus estimated was seen to be cost-effective although slightly higher operating cost was found in the case of bipolar connection. It must be recalled that using bipolar connection the treatment time was shorten which may lead the process to be studied in detail for designing a economical batch electro-coagulator in future. Finally, EC was found to be a very effective treatment technology for the removal of fluoride. In addition, it must be remembered that an EC process comprises also other equipments than the electrolysis unit.

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