



Original Research Article

Assessment of electrolytic process for water defluoridation

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Excessive intake of fluoride causes fluorosis, a disease affecting the multiple tissues, organs and systems in the body. Higher concentrations of fluoride in groundwater are a global problem, occurring in at least 25 countries across the globe and affecting millions of people. It is a threat to millions in the country as it ultimately leads to crippled and vegetative life. National Environmental Engineering research Institute (CSIR-NEERI), India has developed Electrolytic Defluoridation (EDF) technique for the treatment of excessive fluoride in water sources. The process is based on the principle of electrolysis by passing Direct Current (DC) through aluminium plate electrodes placed in fluoride containing water. During the process, aluminium plate connected to anode dissolves and form polyhydroxy aluminium species that remove fluoride in water by complex formation followed by adsorption and removal by settling. The effects of operational parameters such as initial pH, current intensity, influent fluoride concentration, flow rate and residual aluminium were considered. The pH value was found to be an important variable that affected fluoride removal significantly. The optimal influent pH range is 6.0–7.0 at which effective defluoridation was achieved and optimum value was adopted as 6.5. It was found that EDF plants produce the treated water with fluoride less than 1 mg/L. It is revealed that current intensity has little effect on fluoride removal and the residence time requirement increases with the rise in initial fluoride concentration.

Key words: Aluminium electrodes; electrolytic defluoridation; operational parameters

INTRODUCTION

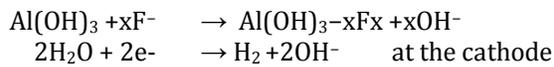
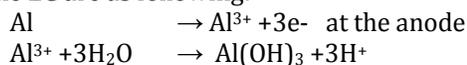
The global need for clean water is particularly critical in increased resource demand scenario. One of the major challenges faced globally is to provide safe drinking water to a vast population around the world. Drinking water containing high fluoride content for longer time can result in fluorosis characterized by mottling of teeth, softening of bones and ossification of tendons and ligaments. According to the guidelines of World Health Organization (2011) issued in the guideline value is 1.5 mg/l for drinking water quality. Almost 25 nations and 200 million people globally

are affected by fluorosis. People across the globe face issues of excess fluoride in drinking water, the intensity and severity of which varies with the environmental settings in terms of their geographical and economical status. According to the report of Ministry of Environment and Forest, India (2009), it has been estimated that fluorosis is prevalent in 19 states of India affecting a population of 65 million approximately. Excessive fluoride concentrations have been reported in groundwater of more than 20 developed and developing countries including India where

19 states are facing acute fluorosis problems. As per Indian drinking water quality standards (BIS 10500-1991) the desirable and permissible limit of fluoride is 1 mg/L and 1.5 mg/L respectively. Fluorides are released into the environment naturally through weathering and dissolution of rock minerals, in emissions of volcanoes, and in marine aerosols. The two most populated countries of the world, China and India, stand at the top in the list of worst hit nations in groundwater contamination with fluoride. In both these countries, the major source of fluoride pollution is the natural weathering process. Drinking water containing high fluoride content for longer time can result in mottling of teeth, softening of bones and ossification of tendons and ligaments. The burden of disease associated with fluoride, therefore, arises from the adverse effects of both excess and insufficient fluoride (Ayoob et al., 2008). Emamjomeh et al. (2009) enunciated that fluoride concentrations in groundwater in the world range from 0.01 up to 48mg/L.

There are several defluoridation processes tested or employed globally, such as adsorption (Azbar and Turkman, 2000), chemical precipitation (Azbar and Turkman, 2000), and electrochemical method (Shen et al., 2003). Currently, some of the popular processes for drinking water defluoridation are the adsorption using activated alumina (Ghorai and Pant, 2005, Tripathy et al., 2006, Chauhan et al., 2007), bone char (Mjengeru and Mkongo, 2003; Hernandez-Montoya, 2007), activated carbon (Daifullah et al., 2007, Kumar et al., 2007), other adsorbents (Biswas et al., 2007) and the coagulation using aluminum salts (Pinon - Miramontes et al., 2003). Other major processes for defluoridation include electro-dialysis (Tahaikt et al., 2006), reverse osmosis (Arora et al., 2004) and nanofiltration (Hu and Dickson, 2006). According to Zuoa et al. (2008), the membrane processes are known to be effective means for defluoridation but this not only removes the beneficial contents present in water during defluoridation, but also increases the operational cost.

Currently, there is a growing interest in Electrocoagulation (EC) process or electrolytic defluoridation. The technique is used to treat restaurant wastewater (Chen et al., 2000), textile wastewater (Bayramoglu et al., 2004), and fluoride-containing wastewater effectively. Electrocoagulation process (EC) using sacrificial aluminum electrodes has been demonstrated to be an effective process since it does not require a substantial investment, presents similar advantages as chemical coagulation and reduces disadvantages, (Hu et al., 2005) and less waste slurry production (Essadki et al., 2009). Defluoridation efficiency by electrocoagulation process depends on applied current intensity, initial fluoride concentration, initial pH, raw water quality and flow rate. The main reactions involved in the EC are as following:



Reduction in pH definitely has positive impact on other parameters of the process such as aluminium-fluoride ratio, energy consumption and residence time, but also increased residual aluminium levels (permit value, 0.2 mg/L WHO, 2011) were observed.

METHODOLOGY

In India, most of the work on defluoridation process is done using batch mode. Here, in the present study the main focus is on electrolytic defluoridation by continuous process which is more efficient and less time consuming in comparison to the batch process. The methodology applied in the present study has been illustrated here.

Analytical techniques

The experiments were performed in the laboratory at ambient temperatures ranging from 26° to 28°C. The chemicals were analytical reagent grade and were used without any further purification. Stock solution of 1000 mg/L of fluoride was prepared by dissolving 2.21 gm oven dried sodium fluoride (NaF) in 1 litre distilled water. The solutions of various concentrations of fluoride used in the experiments were prepared by diluting the measured quantity of stock solution in tap water. Fluoride concentration was determined by Specific Ion Meter (Orion 720A, USA). Standard procedure for determining the fluoride was followed. To prevent the interference from other ions (Al^{3+} , Fe^{3+} , etc.), Total ionic strength adjustment (TISAB) buffer was added to the samples. This solution forms complex with interfering cations and release fluoride ions. The pH value was determined as per standard method by portable pH meter (APHA, 2005)

Experimental protocol

In its simplest form, an electro-coagulating reactor is made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material electrochemically corrodes due to oxidation, while the cathode is subjected to passivation. A feed tank of 200 L (A nestable tank) capacity was filled with raw water of initial fluoride concentrations of 5, 8, 6 and 10 mg/L. The initial pH of raw water was adjusted around 6.5-6.9 by adding concentrated HCl.

A peristaltic pump was used to maintain the flow rate accordingly for a continuous process up to maximum of 1L/min. The flow rate was adjusted by setting the rpm (rotation per minute) on the digital display. Experiments were performed in a reactor consisting of plastic bucket of 19 L capacity. A direct current (DC) by stabilized power supply (TESTRONIX 34C, Volt and Ampere Digital Display)

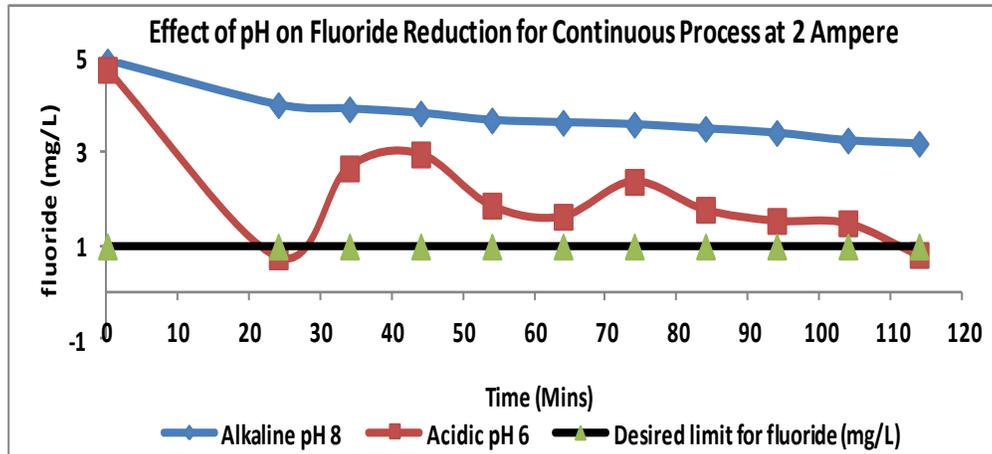


Figure 1. Effect of pH ($C_0=5$ mg/L)

was applied to the terminal electrodes in which electrical current was controlled by a variable transformer. Current was varied from 2.0A to 3.0A, however, it was held constant for each run by appropriately adjusting the impressed cell voltage from a regulated DC power supply. A bucket of 52 cm height and diameter of 44 cm was used as a settling tank in the lab scale experiment for electrolytic defluoridation by continuous process. Treated water residual aluminium estimation was carried out by Eriochrome cyanine R method (WHO, 1997).

Electrode configurations

Aluminium plates were cut from a commercial grade Aluminium sheet (99% purity) of 2 mm thickness each with a dimension of 100 mm×180 mm and an effective area of 180 cm² on each side. Distance between the electrodes was 5 mm. Monopolar configurations with three aluminium plate electrodes were used. Central plate was connected to anode and two end plates were connected to cathode. The electrodes were designed with a surface area to volume ratio of 7.2 m²/m³ which is within cited range of 6.9 - 43 m²/m³ [0]. Raw water of various fluoride concentrations was prepared by diluting the stock solution in tap water. The experimental procedure was divided into two major steps i.e. start up batch process and Continuous treatment process. Each run was conducted using 19 litre of raw water in the reactor for start-up batch process and rendering it up to the desired limit of 1 mg/L by providing proper detention time. Detention time (t) is calculated by using Eq. 1 based on *Faraday's law*:

$$m = K \cdot i \cdot t \quad (1)$$

Where, m = Weight of aluminium dissolved (g)

K = Electro-chemical constant

i = Current (Ampere)

t = Time of electrolysis

Value of m can be calculated by; $m = (C_0 - C_f) \times \text{volume}$ (2)

$\times (Al / F)$

Where, C_0 = Initial fluoride concentration = 5 mg/L

C_f = Fluoride conc. in treated water = 1 mg/L

Volume = Volume of treated water

RESULTS AND DISCUSSION

In the study, experiments were conducted to ascertain the feasibility of electrolytic defluoridation process and the effects of operational parameters on electrolytic defluoridation process are discussed here.

Effect of initial pH on fluoride removal

The experiment was conducted to study the effect of initial pH on the efficiency of electrolytic defluoridation process. The influent pH was found to be one of the important factors affecting the performance. The optimal pH range was 6–7, at which higher fluoride removal efficiency could be reached, but the fluoride removal efficiency varied with variation in pH. Lower pH was favorable for early fluoride removal in the EC process. The pH could be increased not only because of the hydrogen generation at the EC cathodes, but also the liberation of hydroxide ions from Aluminium hydroxide due to the substitution of fluoride ions. Therefore, further increase of the influent pH would decrease the defluoridation capability. Since Aluminium hydroxide is an amphoteric hydroxide, high pH lead to the formation of $Al(OH)_4^-$ which was soluble. Effect of pH on fluoride reduction for batch and continuous processes are shown in Figure. 1.

The experiments were conducted to determine the effect of pH variation on fluoride removal efficiency, keeping other parameters constant and the optimum fluoride reduction was observed between pH 6 and 7 for influent fluoride concentration 5 mg/l. With this in view, the

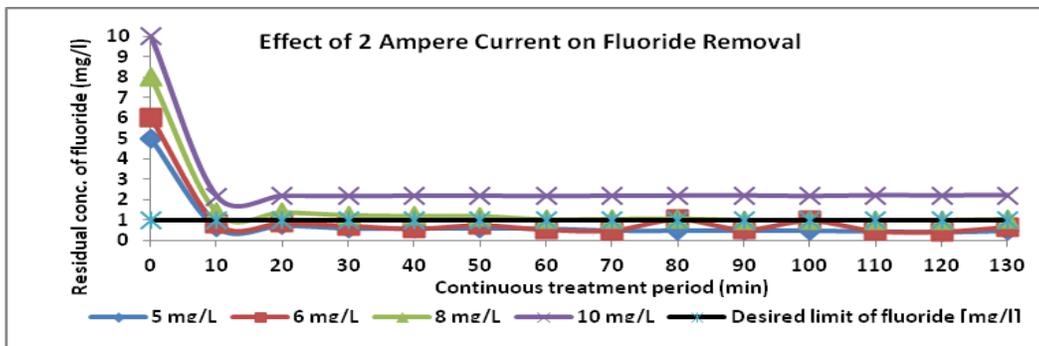


Figure 2. Effect of Current on Fluoride Removal

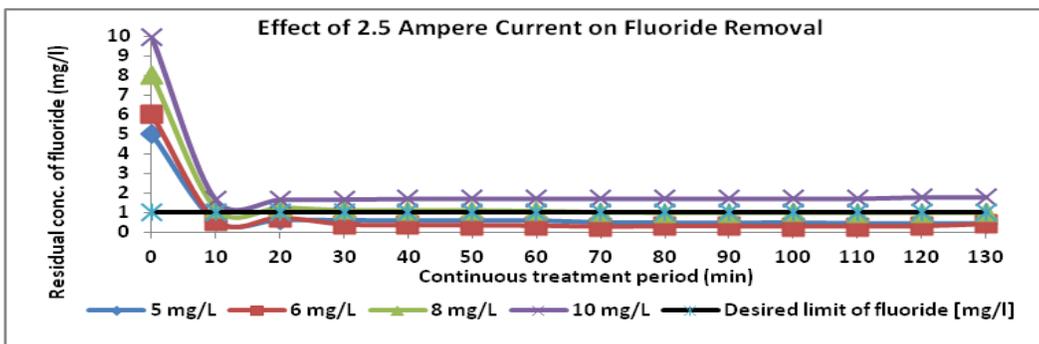


Figure 3. Effect of 2.5 Ampere Current on Fluoride Removal

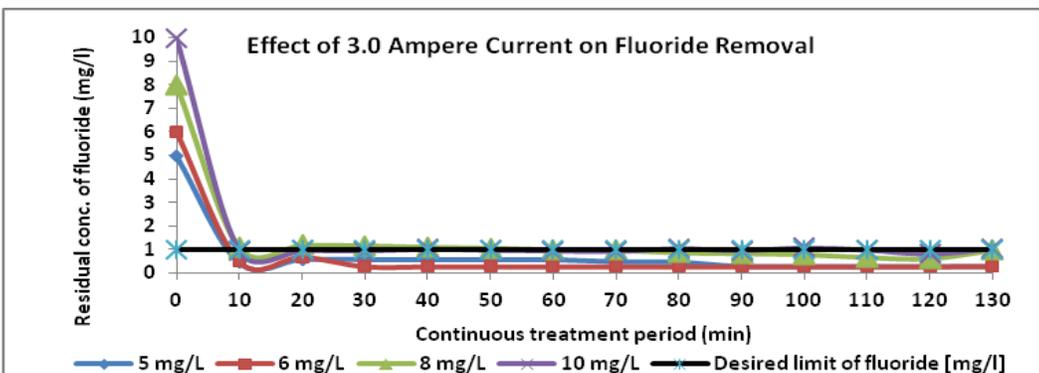


Figure 4. Effect of 3 Ampere Current on Fluoride Removal

working pH in the optimum range of 6-7 was adopted as 6.5, which yielded the best.

Effect of current intensity on fluoride removal

It was found that current intensity has little effect on defluoridation because the principal factor influencing adsorption of fluoride by flocs is the pH of the solution. Consequently, an increase in current intensity lead to an increase in power requirement. Infact, there should be an optimal current applied for the electrolytic defluoridation

system. Increasing current intensity would accelerate the liberation rate of Al³⁺ and OH⁻ ions. The rapid liberation of Al³⁺ and OH⁻ ions from the surface of the electrode would make the solution around the anode and cathode extremely acidic or basic respectively, which would decrease the removal efficiency of electrodes as depicted in Figure. 2, 3 and 4.

Effect of influent fluoride removal

The experiments were conducted by varying initial fluoride

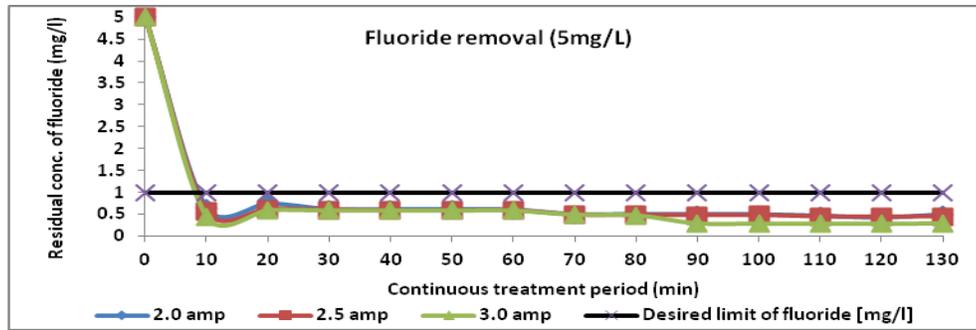


Figure 5. Effect of Current Intensity on Removal of Fluoride (Concentration: 5 mg/L)

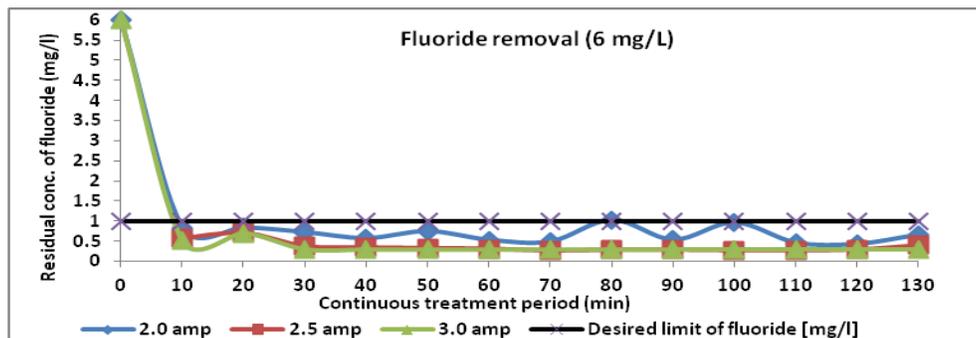


Figure 6. Effect of Current Intensity on Removal of Fluoride (Concentration: 6 mg/L)

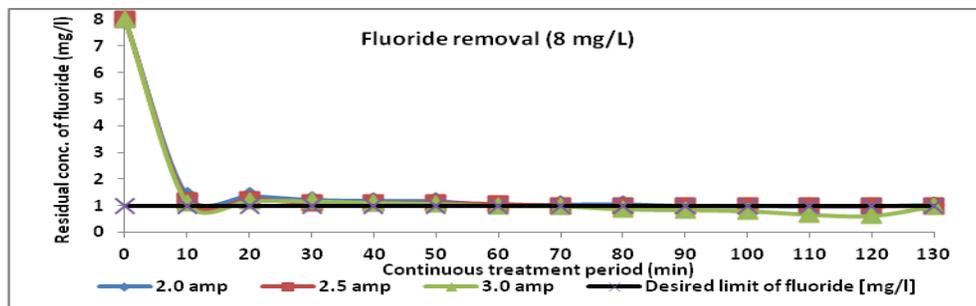


Figure 7. Effect of Current Intensity on Removal of Fluoride (Concentration: 8 mg/L)

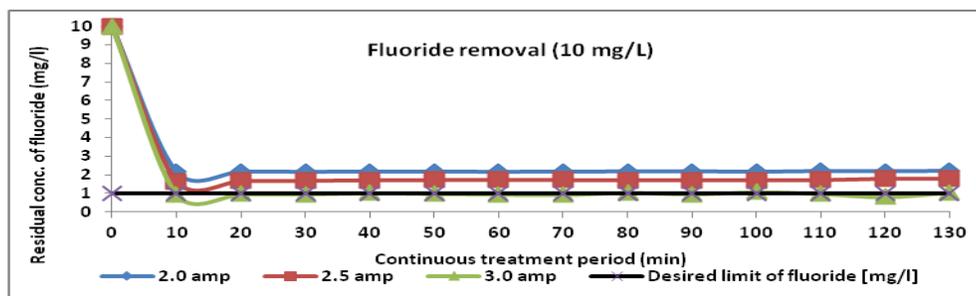


Figure 8. Effect of Current Intensity on Removal of Fluoride (Concentration: 10 mg/L)

concentrations 5, 6, 8, 10 mg/L, keeping all other experimental conditions identical. Figures 5, 6, 7, 8 and 9

illustrate fluoride reduction below 1 mg/l for pH 6.5 and current intensity 2, 2.5 and 3 amperes.

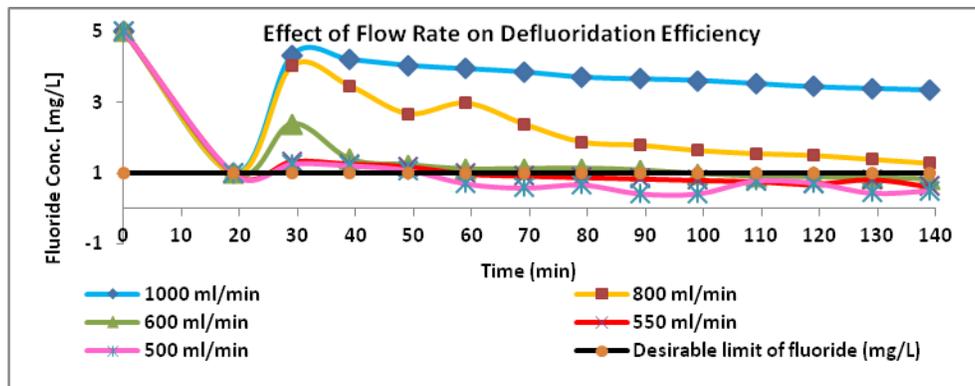


Figure 9. Effect of Various Flow Rates on Defluoridation Efficiency Residual Aluminium in Treated Water

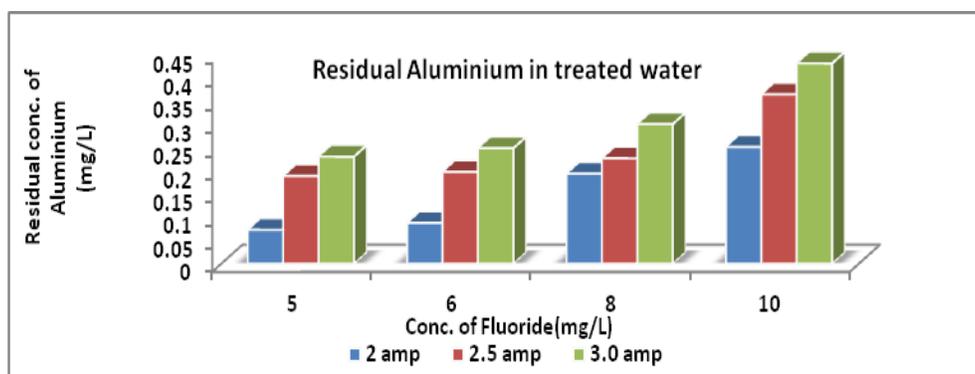


Figure 10. Effect of Current Intensity on Residual Aluminium Concentration

These figures reflect that the retention time required for an acceptable residual fluoride concentration, which is <1mg/l of fluoride, increased when the initial concentration was increased. Maximum fluoride removal efficiency was observed at current intensity of 3 A. The defluoridation efficiency of electrodes tended to decrease since they required longer time with the initial F⁻ concentration rising.

Effect of flow rate on defluoridation efficiency

In the study, a continuous stirred tank reactor was utilized and a peristaltic pump was used to maintain the desired flow rate. To study the effect of flow rate on defluoridation efficiency, operating experimental parameters such as fluoride concentration 5 mg/l, 3-ampere current and pH 6.5 were kept constant for various flow rates. The study of the effect of flow rates on the removal efficiency of a continuous type of electrolytic process, which is given in Figure 10, revealed that the flow rate of 550 ml/min gave the optimum results with residual fluoride concentration within the desirable limit

Residual Aluminium in treated water

The residual aluminium found in treated water is one of the

important factors, because leaching of the same was demonstrated in the experiments conducted. Aluminium found above 0.2 mg/L in drinking water, is a risk cause of Alzheimer disease (AD) in humans (WHO, 2011). Effect of different current intensities on the concentration of residual aluminium is shown in Figure. 10.

Higher residual aluminium was found at optimum removal efficiency with current intensity 3 ampere and pH 6.5, but it is not beyond permissible limit in drinking water for the current intensities 2 and 2.5 ampere for lower fluoride concentrations. The optimum current intensity of 2 ampere with optimum pH of 6.5 gives better results in comparison to higher current intensities.

Conclusions

In the present work, the laboratory scale study has focussed on the feasibility of electrolytic defluoridation as a viable methodology of water defluoridation. The overall defluoridation efficiency varies with initial fluoride concentration that is altered by operating parameters such as pH, current intensity initial fluoride concentration and flow rate. With the rise in initial fluoride concentration, the time required for the desired removal efficiency was found to be increased. Current intensity has little influence on

fluoride removal and optimum removal was found at 3 A for fluoride removal. Acidic pH has more fluoride removal efficiency with higher residual aluminium concentration in treated water. Therefore, it is recommended to maintain pH in the range 6-7 for maximum fluoride removal and the optimum pH is taken as 6.5. The study of the effect of flow rates on the removal efficiency of a continuous type of electrolytic process reveals that the flow rate of 550 ml/min has the optimum results with residual fluoride concentration within the desirable limit. Considering aluminium leaching, optimum conditions are observed to be at current intensity 2 A and pH 6.5. The approach proposed in this study could provide not only a useful insight into optimization of EC process but also more detailed information on residual aluminium in the process.

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