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Fluoride Removal By A Continuous Flow Electrocoagulation Reactor From Groundwater Of Shivdaspura.

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ABSTRACT

The present study focuses on the technique of defluoridation by using the process of electrocoagulation (EC). Efficacy of EC process was investigated for laboratory simulated sample called as control sample and groundwater sample collected from Shivdaspura (Rajasthan) under different operating conditions. Continuous flow experiments were conducted for fluoride removal using aluminium electrodes to study the parameters such as: current density, flow rate, number of stages in treatment, fluoride uptake capacity and residual aluminium. The results obtained showed that double stage treatment system gave higher treatment efficiency than single stage system. Residual Aluminium was measured and found in the range of 0.08-0.1 ppm which shows that EC offers better quality of water when compared with other methods of defluoridation like Activated Alumina (AA) process and Nalgonda technique.

Keywords- defluoridation, electrocoagulation, fluoride uptake capacity, residual aluminium

1. INTRODUCTION

Fluorine, the lightest member of the halogen group is the most electronegative and hence chemically reactive. Fluorine is therefore found as fluorides which together represent about 0.06-0.09% of earth's crust [1]. Prevalence of fluorosis in India is mainly due to hydrogeochemical origin. Groundwater fluoride contents in high levels are present in all the 33 districts and have become a serious health related issue in 23 districts of Rajasthan [2]. Presence of fluoride in traces has beneficial effects on teeth but high and continuous exposure can cause mild dental fluorosis to crippling skeletal fluorosis. Desirable limit of fluoride is less than 1 mg/l [3]. The drawback of defluoridation techniques like Nalgonda and AA process includes large sludge generation and high residual aluminium in the effluent. The present research is directed primarily to address this issue. Hence residual aluminium in the effluent was determined for the process of EC. Also a range of operating parameters such as flow rate, current density, fluoride uptake capacity and multistage treatment were developed to study the efficacy of the process. Lui *et al*,[4] reported that the defluoridation efficiency in the EC system exceeded that of the traditional process due to the electrocondensation effect.

In the process of EC, oxidation reaction occurs which causes dissolution of anode and aqueous Al^{3+} species are formed. The electrode reactions are outlined below [5]:

Anodes: $Al(s) \rightarrow Al^{3+} + 3e^-$ (1)

Cathodes: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ (2)

The H_2 bubbles float and hence drive the flotation process. The Al^{3+} ions further react to form a solid $Al(OH)_3$ precipitate:

$Al^{3+} + 3H_2O <-> Al(OH)_3(s) + 3H^+$ (3)

The basic principle of the process is adsorption of fluoride at precipitated Al $Al(OH)_3$ as depicted in reaction (4) [5]:

$Al(OH)_3 + x\ F^- <-> Al(OH)_{3-x}F_x + x\ OH^-$ (4)

The EC process is highly dependent on pH of the solution [6, 7]. Studies revealed that pH plays an important role in the formation of $Al(OH)_3$ flocs. The solid $Al(OH)_3$ is most prevalent between pH 6 and 8, and above pH 9, the soluble species $Al(OH)_4^-$ is the predominant species [8]. Mohammad et *al*, [8] found that the defluoridation efficiency decreases from 90 to 75% when the final pH is more than 8. Researches show that more efficiency is obtained when the pH ranges from 6 – 8 [5, 8]. Hence the pH in present study was kept constant at 6 for all runs.

2. MATERIALS AND METHODS

A continuous flow bench scale EC reactor was designed and constructed for fluoride removal as shown in Figure.1. Aluminium electrodes each having surface area of 0.012 m^2 was used with rectangular reactor of dimensions (25 cm X 10 cm X 8 cm, volume 2 litres). The distance between electrodes was kept constant at 1cm for all the runs. Sample to be treated was placed in an influent tank (polycon) which can hold a sample volume of 110 litres. pH of the sample was maintained 6 by using dilute HCl. Conductivity and pH were measured using a calibrated conductivity meter (Lutron CD 4302) and pH meter (Electronics India, deluxe 101) respectively. Sample was continuously fed into EC reactor at desired flow rate which was set using a peristaltic pump (Miclins PP- 20). Before each run electrodes were cleaned by acetone and HCl solution. Electrolysis was performed and samples

were collected from the outlet of reactor 30 minutes after the pseudo steady state has been achieved. Pseudo steady state was characterized by almost constant fluoride content of effluent. These samples were immediately filtered with Whatman No. 1 filter paper and the fluoride content was measured using fluoride ion meter (Thermo scientific Orion 5-star meter, 9609BNWP fluoride electrode). Digital power display (Testronix, 230 V DC regulated power supply) was used to maintain current. The sacrificial weight of electrode was calculated by measuring its weight before and after the process. The samples for estimating aluminium concentration were collected after pseudo steady state, from desired sets and then filtered with 0.45 µm filter paper. Aluminium concentration in the filtered samples was analyzed by Atomic Adsorption spectrophotometer of PG Instruments (model no. PG990) having graphite furnace at a wavelength of 309.3 nm. All the experiments were conducted at room temperature with water temperature varying in a close range of 25-27^{0}C.

For the present study, two samples were used viz laboratory simulated (control) sample and the groundwater sample. Control sample was prepared by mixing sodium fluoride in distilled water. Sodium chloride (2mM) was added to the aqueous solution to increase the conductivity. Ground water sample with fluoride content of 11.6 mg/l was collected from village Shivdaspura near Jaipur (Rajasthan) (Location: 26°42´26.6”N/ 75°53´45.3”E with elevation of 330 m). Poor efficiency of EC process was observed when study was conducted on this sample probably due to high TDS (Total dissolved Solids). So samples were diluted with distilled water. In the present study results of diluted groundwater sample were taken into consideration. The chemical parameters of control, groundwater and diluted groundwater samples are mentioned in Table 1.

Table1. Description of water quality of samples

Chemical parameters	***Control Sample***	***Groundwater sample***	***Diluted Groundwater Sample***
Alkalinity(total),mg/l	10	840	394
Total dissolved solids, mg/l	48	2230	1120
Conductivity, mS/cm	0.50	2.76	1.90
pH	6.07	8.4	8.35
Fluoride, mg/l	6	11.6	6.2

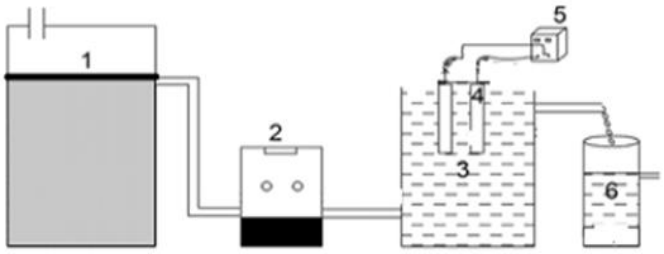


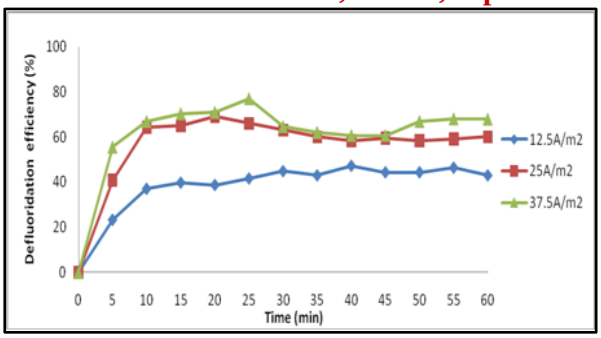
Figure. 1: Experimental setup of continuous EC cell (**1**: Influent tank; **2**: peristaltic pump; **3**: inlet of the first compartment; **4**: electrodes; **5**: DC power supply; **6**: treated effluent outlet)

3. RESULTS AND DISCUSSIONS

3.1 Effect of current density on defluoridation efficiency

Current density directly affects coagulant dosage and bubble generation rate, as well as the mixing intensity and mass transfer near electrodes [9], so increasing current density would accelerate the liberation rate of Al^{3+} and OH^- ions [10]. The effect of current density on defluoridation efficiency in continuous treatment mode was studied at two flow rates (200 ml/min and 150 ml/min). For control sample at the flow rate of 200 ml/min, defluoridation efficiency increases from 42% to 60% when current density increases from 12.5A/m^2 to 25A/m^2. Further increment in removal efficiency to 62% was observed at 37.5A/m^2 as shown in Figure 2(a). Similar trends were observed for a flow rate of 150 ml/min as depicted in Figure 2(c). But there was no significant improvement in defluoridation efficiency when current density increases from 25A/m^2 to 37.5A/m^2. Also for a flow rate of 200 ml/min, the defluoridation efficiency of groundwater sample increases from 24% at 12.5 A/m^2 to 57% at 25 A/m^2. But only 0.7% improvement in defluoridation efficiency was observed when current density was increased from 25 to 37.5A/m^2, as shown in Figure 2(b). Results for 150 ml/min flow rate with groundwater sample are shown in Figure 2(d). It was observed that if current density was increased beyond 25 A/m^2 there is no considerable increase in defluoridation efficiency. So it is advisable not to exceed the limit of current density beyond 25A/m^2. 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 effciency 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 effciency 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 effciency of the treatment process.



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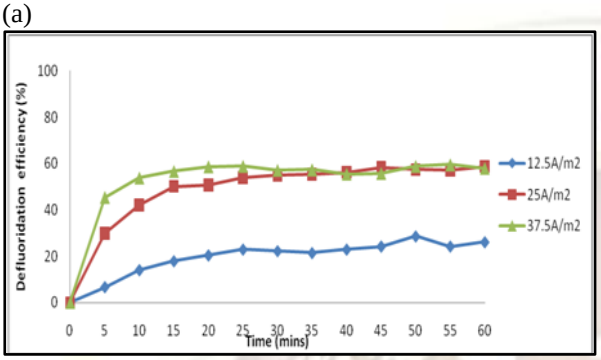

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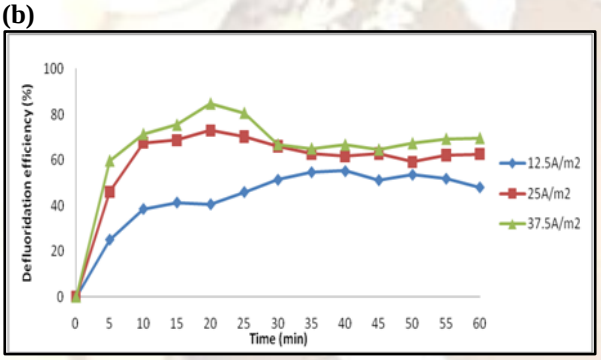

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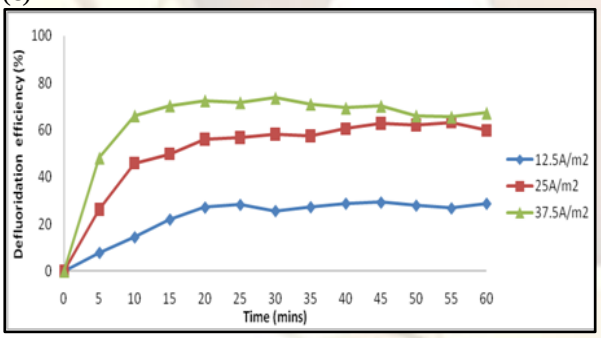
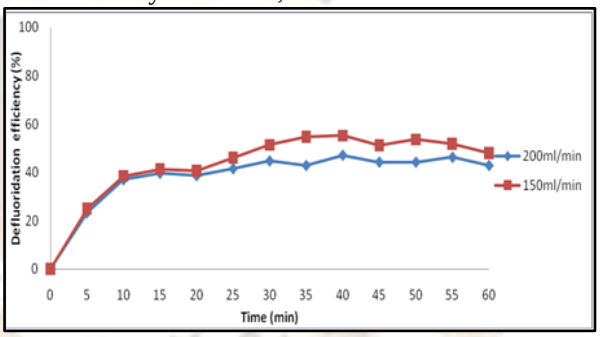


(d)

Figure. 2: (a) Effect of current density on control sample at 200 ml/min. **(b)** Effect of current density on groundwater sample at 200 ml/min. **(c)** Effect of current density on control sample at 150 ml/min. **(d)** Effect of current density on groundwater sample at 150 ml/min.

3.2 Effect of flow rate on Defluoridation efficiency

Flow rate has an inverse relation with defluoridation effciency. With the decrease in flow rate the defluoridation effciency increases because the reaction time is increased in the EC reactor and fluoride gets more time to adsorb to the flocs. The effect of flow rate on defluoridation effciency was studied at three current densities (12.5, 25 and 37.5A/m$^{2)}$ at varying flow rates of 150 ml/min and 200 ml/min. For control sample at 12.5A/m^2, the defluoridation effciency increases from 43% to 57% when flow rate was decreased from 200 ml/min to 150 ml/min as shown in Figure 3(a). As seen in Figure 3(b), at 25A/m^2 the defluoridation effciency increases from 59% to 62% when flow rate was decreased from 200 ml/min to 150 ml/min. Similarly at 37.5 A/m^2 defluoridation efficiency increases from 61% at 200 ml/min to 65% at 150 ml/min as shown in Figure 3(c). Results of groundwater sample are shown in Figure 4 for current density 12.5 A/m^2, 25 A/m^2 and 37.5 A/m^2.



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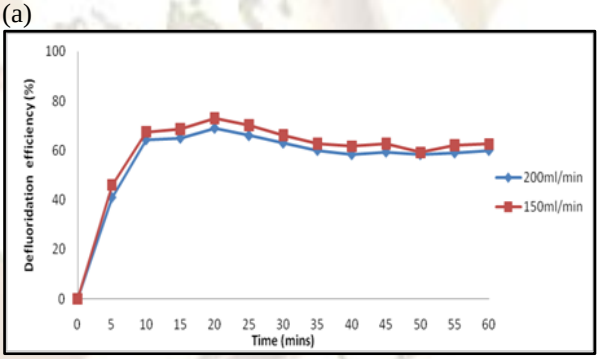

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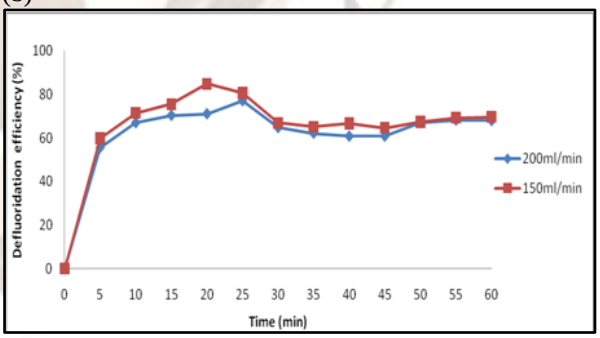

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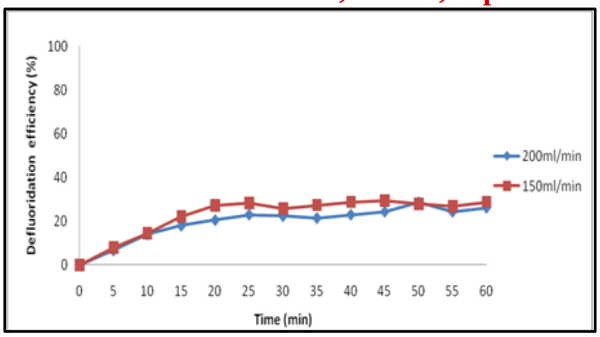
Figure. 3: Effect of flow rate on control sample **(a)** At 12.5A/m^2. **(b)** At 25A/m^2. **(c)** At 37.5A/m^2.



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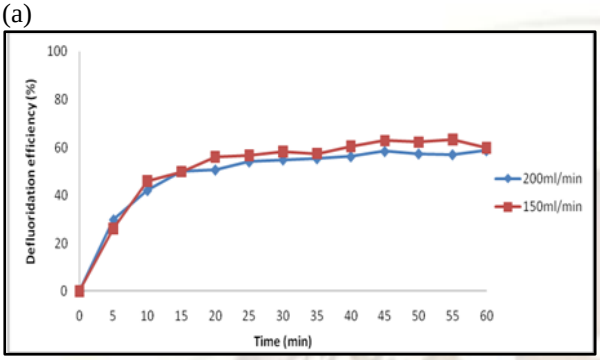

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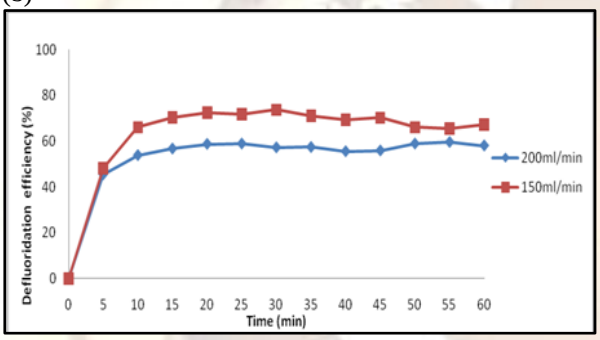
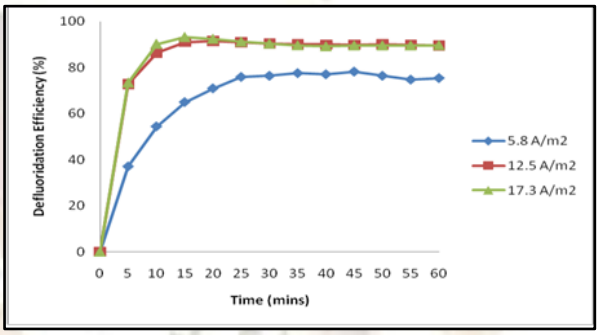


(c)

Fig. 4: Effect of flow rate on groundwater sample **(a)** At 12.5A/m^2. **(b)** At 25A/m^2. **(c)** At 37.5A/m^2.

3.3 Double Stage treatment process

Two rectangular reactors of same size in series along with two pairs of aluminium electrodes of same size and properties were used in continuous flow mode, to study the effect of double stage treatment on defluoridation efficiency. Electrodes were connected in series to complete the electric circuit. Experiments were run using groundwater samples of initial fluoride concentration 6.2 mg/l. The effect of double stage treatment on defluoridation efficiency was studied by varying flow rate (150 ml/min and 200 ml/min) and current density (5.8, 12.5 and 17.3A/m^2). Same current was applied as that of single stage but difference in current density is due to increase in number of electrodes. Results are shown in Figure 5 and Figure 6. Instead of increasing, the defluoridation efficiency decreases slightly for both the flow rates at current density of 37.5A/m^2. This is because at higher current density, a rapid increase in the pH of the sample was observed which limits further improvement in the efficiency. Comparing Figure 5(a) and 2(b) for current density 12.5 A/m^2 and flow rate of 200 ml/min, a considerable improvement in defluoridation efficiency by 52% was observed using double stage over single stage treatment. Similarly at 25 A/m^2 defluoridation efficiency increases from 57% (single stage) to 90% (double stage) and at 37.5 A/m^2 it increases from 58% (single stage) to 89 % (double stage). Results for the effect of flow rate also indicate an increase in defluoridation efficiency when multi stage treatment was used. Referring Figure 6 and Figure 4 at 150 ml/min, an increment of 60% was observed for 12.5A/m^2, 36% for 25 A/m^2 and 25% for 37.5 A/m^2 when double stage was used over single stage. Similar trends were observed for 200 ml/min flow rate.



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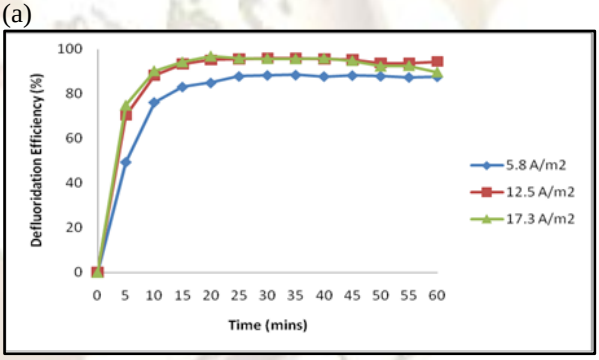

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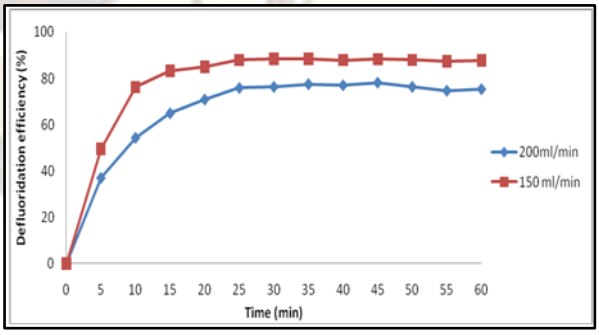
Figure. 5: Effect of current density in double stage treatment **(a)** At flow rate of 200 ml/min. **(b)** At flow rate of 150 ml/min.



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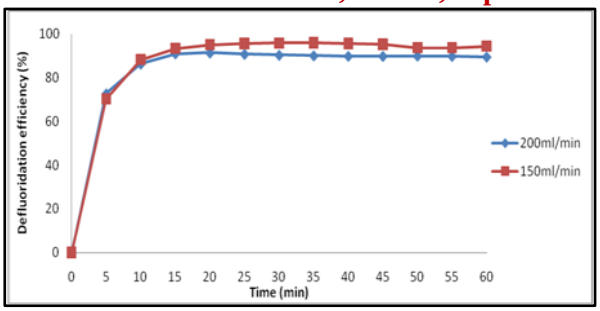

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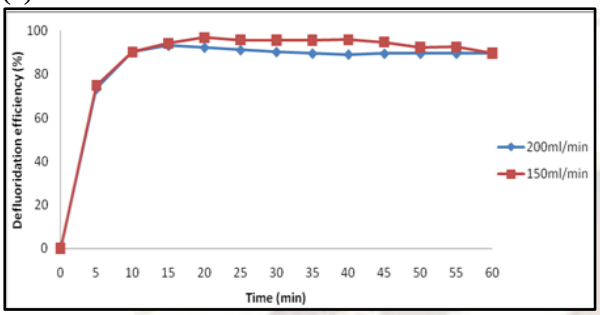

(c)

Figure. 6: Effect of flow rate in double stage treatment **(a)** At current density of 5.8A/m^2. **(b)** At current density of 12.5A/m^2. **(c)** At current density of 17.3A/m^2.

3.4 Fluoride Uptake Capacity per unit anode sacrificed

Total fluoride uptake capacity per unit aluminium consumed was calculated for all set of experiments with both control as well as groundwater samples and results are listed in Table 2 and Table 3 respectively. Aluminium consumed refers to the anode consumption during the run. Researchers [11, 12] have reported the defluoridation capacity of AA to be between 3 mg F/g in alkaline water and 20 mg F/g in acidic water. At pH 7, the defluoridation capacity was found to be 5.6 mgF/g. In Nalgonda technique, coagulant dose required is very high about 150 mg alum along with 7 mg lime/mg F as reported by researchers [12]. In EC process, it was found that there was an effcient use of aluminium and high FUC (214-410.37 mg F/g Al) was observed that may result in low residual aluminium in treated water.

Table 2: Fluoride uptake capacity per unit aluminium consumed in control sample.

Flow rate (ml/min)	Current Density(A/m^2)	Fluoride Removed (mg)	Al Consumed(mg)	FUC (mg/gAl)
200	12.5	30.45	0.064	475.78
200	25	43.72	0.117	373.68
200	37.5	47.59	0.180	264.39
150	12.5	27.50	0.067	410.37
150	25	35.85	0.117	306.41
150	37.5	39.38	0.184	214.46

Table 3: Fluoride uptake capacity per unit aluminium consumed in groundwater sample.

Flow rate (ml/min)	Current Density(A/m^2)	Fluoride Removed (mg)	Al Consumed(mg)	FUC (mg/gAl)
200	12.5	15.64	0.062	252.26
200	25	38.10	0.125	304.80
200	37.5	40.80	0.175	233.14
150	12.5	13.94	0.057	244.56
150	25	31.31	0.121	258.72
150	37.5	37.86	0.171	221.40

3.5 Residual Al in the effluent

Samples collected after achieving pseudo steady state were analyzed for residual aluminium. The results are listed in the Table 4 and it can be observed that the concentration of aluminium in all the samples is not higher than the permissible value of 0.2 mg/l [3]. The reported residual Aluminium concentration in AA process and Nalgonda technique is 0.16-0.45 ppm and 2.01-6.86 ppm respectively, which is a major drawback of these techniques [13]. This can be overcome in EC process by efficient use of aluminium under ideal operational parameters.

Table 4: Residual Al in effluent (initial F^- = 6 mg/l, influent pH=6, flow rate = 200 ml/min)

Sample	Current density(A/m^2)	Residual Al
1	12.5	0.083
2	25	0.058
3	37.5	0.145

4. CONCLUSIONS

Continuous flow experiments were designed to investigate the effects of different parameters including current density, flow rate, FUC, and double stage treatment on defluoridation efficiency by using electrocoagulation. In continuous flow reactor, optimum results for defluoridation of control samples were determined at current density of 25 A/m^2 and flow rate of 150 ml/min. Results of groundwater sample followed the similar trend. FUC/g of Al used at 25 A/m^2 was higher when compared with FUC/g of Al at 37.5A/m^2 current density. This suggests that increase in current density upto 25 A/m^2 leads to considerable increase in treatment efficiency but further increase must be avoided to limit aluminium dissolution and to save energy. Therefore, defluoridation efficiency is not directly proportional to current density. For continuous flow reactor, defluoridation efficiency of 79% is achieved with control samples and 68 % with groundwater samples. The reduction in efficiency of groundwater sample is probably due to difference in TDS

between the two samples. Double stage treatment process further improves the defluoridation efficiency by 30-60% than single stage treatment process. The residual Al in the effluent is also within permissible values, and hence better quality of water is provided.

5. ACKNOWLEDGEMENT

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