Removal of Fluoride from Drinking Water by Electro-coagulation

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Abstract: Prolonged consumption of fluoride contaminated water can lead to fluorosis of the teeth and bones. Electro-coagulation(EC) is a electrochemical technique, in which a variety of unwanted dissolved contaminants like fluoride, iron, arsenic and suspended matter can be effectively removed from an aqueous solution by electrolysis. EC, in this work, was investigated for the effective removal of fluoride from drinking water. Different initial fluoride concentrations (5 -25) mg/L were considered. The electrode selected was aluminium and electrode connection was considered as monopolar. Experiments was carried out at different current intensities (40-190) mA and at different initial pH levels (5 -9). Operating parameters like conductivity, resistivity, salinity, TDS, turbidity were studied. The final recommendable limit of fluoride (1mg/l) was obtained at about 20 minutes of EC at initial pH of (5-7). The highest treatment efficiency was obtained for the largest current and the removal efficiency was found to be dependent on the current density (CD), initial fluoride concentration and final pH that ranged from 6 to 8.The corrosion of the electrodes as well as the sludge formed during the process was estimated for the monopolar connection. These findings could be useful to treat the fluoride contaminated drinking water.

Keywords: *Electro-coagulation, Fluoride removal, Analysis, corrosion, Drinking water*

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 world because of its significant presence (> 4 mg/ L) in the ground water causes serious damage to the teeth and bones. The disease is known as fluorosis. Fluorine is highly reactive and is found naturally as CaF_2. It is an essential constituent in minerals like topaz, fluorite, fluorapatite, cryolite, phosphorite, theorapatite, etc. [1]. The fluoride is found in the atmosphere, soil and water. It enters the soil through weathering of rocks, precipitation or waste run off. Surface waters generally do not contain more than 0.3 mg/ L of fluoride unless they are polluted from external sources. Though drinking water is the major contributor (75–90% of daily intake), other sources of fluoride poisoning are food, industrial exposure, drugs, cosmetics, etc. [2].With the development of industries, establishment of townships and with growing urbanization

environmental pollution has become significant in recent years. A major feature of this pollution is contamination of drinking water. This calls for innovative effort to supply healthy drinking water in each and every locality. Industry has to pro-actively reduce the amount of pollutants discharged into the environment. Treatment of drinking water for fluoride removal will help in the supply of water in and around the industrially developed areas. Details on effects of fluoride on human health are summarized in Table 1.

Table 1: Effects of fluoride in water on human health

Fluoride concentration (mg/L)	Effects
<1.5	Safe limit
1.5 – 3.0	Dental fluorosis (discoloration, mottling and pitting of teeth)
3.0 – 4.0	Stiffened and brittle bones and joints
4.0 – 6.0 and above	Deformities in knee and hip bones and finally paralysis making the person unable to walk or stand in straight posture, crippling fluorosis

1.2 Existing processes for the separation of fluoride from drinking water

De-fluoridation is the process of removal of fluoride ion from drinking water. The different methods tried so far for the removal of excess fluoride from water can be broadly be classified into four categories. A) Adsorption methods: Activated alumina, activated carbon, calcite, activated saw dust, activated coconut shell carbon and activated fly ash, groundnut shell, coffee husk, rice husk, bone charcoal, activated soil sorbent, etc. The process can remove fluoride up to 90%. Treatment is cost-effective. The process is highly dependent on pH. Presence of sulfate, phosphate or carbonate results in ionic competition. B) Ion exchange methods: Strongly basic anion-exchange resin containing quaternary ammonium functional groups is used. The process can remove fluoride up to 90–95%. It retains the taste and color of water intact. Efficiency is reduced in presence of other ions. The technique is expensive because of the cost of resin. C) Precipitation methods-Nalgonda technique-In first step, precipitation occurs by lime dosing which is followed by a second step in which alum is added to cause coagulation. The two-step process has been claimed as the most effective technique by NEERI under Rajiv Gandhi Drinking Water Mission, several fill and draw (F&D) type and hand pump attached (HPA) plants based on Nalgonda technique have come up in rural areas for which design and technology has been developed by NEERI. The process removes only a small portion of fluoride (18–33%) in the form of precipitates and converts a greater portion of ionic fluoride (67–82%) into soluble aluminum fluoride complex ion, and therefore this technology appears to be erroneous. Silicates have adverse effect on de-fluoridation by Nalgonda Technique. D) Membrane

separation (reverse osmosis) - NF and RO are generally used for fluoride removal. The process is highly effective. Membranes also provide an effective barrier to suspended solids, all inorganic pollutants, organic micro pollutants, pesticides etc. This process has the advantages of no chemicals addition and of being applicable in wider pH range. However the process is expensive in comparison to other options and it removes all the ions present in water, though some minerals are essential for proper growth, therefore re-mineralization is required.

2. Electro-coagulation (EC)

2.1 Applications of electro-coagulation

Electro-coagulation uses an electrochemical cell to treat polluted water. Sacrificial anodes corrode to release active coagulant (cation) usually aluminum or iron, to solution. Accompanying electrochemical reactions are dependent on species present and usually evolve electrolytic gases. The coagulant's delivery and its nature influence the coagulation and separation processes. In recent years, however, smaller scale electro-coagulation processes have made advances to the point where they are seen as a reliable and effective technology. Numerous examples of water treatment systems have been reported in the recent literatures.

2.2 Removal Mechanism by EC

The EC process operates on the principle that the cations produced electrolytically from iron and/or aluminum anodes enhance the coagulation of contaminants from an aqueous medium. Electrophoretic motion tends to concentrate negatively charged particles in the region of the anode and positively charged ions in the region of the cathode. The consumable, or sacrificial, metal anodes are used to continuously produce polyvalent metal cations in the vicinity of the anode. These cations neutralize the negative charge of the particles carried toward the anodes by electrophoretic motion, thereby facilitating coagulation. In the EC techniques presented hereafter, the production of polyvalent cations from the oxidation of the sacrificial anodes (Fe and Al) and the electrolysis gases (H_2 and O_2) works in combination to flocculate the coagulant materials. Even inert electrodes, such as titanium and the passage of an alternating current have also been observed to remove metal ions from solutions and to initiate the coagulation of suspended solids. Gas bubbles produced by the electrolysis carry the pollutant to the top of the solution where it is concentrated, collected and removed. The removal mechanisms in EC may involve oxidation, reduction, decomposition, deposition, coagulation, absorption, adsorption, precipitation and flotation.

Different electrodes have been reported in the literature such as carbon, mild steel, graphite, titanium, iron and Aluminum. Iron and Aluminum have however been reported to be very effective and successful in pollutant removal at favorable operating conditions. The electrode reactions are summarized as follows:

Anode: $Al \longrightarrow Al^{3+} + 3e$ (1)

Cathode: $3H_2O + 3e^- \rightarrow \dfrac{3}{2}H_2 + 3OH^-$ (2)

During the final stages, coagulated aggregates interact with bubbles and float to the surface or settle to the bottom of the EC bath. Flotation is the dominant pollutant removal path for high operating currents, while sedimentation is dominant at lower currents. The shift is due to the fact that bubble number concentration at low currents is insufficient to remove the aggregated material, allowing sedimentation to dominate. Al (III) and OH⁻ ions generated by 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 $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)^{7+}_{24}$, $Al_{13}(OH)_{34}^{5+}$, which transform finally into Al $(OH)_{3(S)}$ according to complex precipitation kinetics

$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$ (3)

Freshly formed amorphous Al $(OH)_{3(S)}$ occurs as "sweep flocks" having large surface areas. These flocks are active in rapid adsorption of soluble organic compounds and trapping of colloidal particles and are easily separated from aqueous medium by sedimentation or H_2 flotation. These flocks polymerize as: $n\,Al(OH)_3 \rightarrow Al_n(OH)_{3n}$

This Al(OH)₃ complex is believed to have strong fluoride adsorption capacity

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

Precipitation depends on the size and shape of the particle which is formed after coagulation followed by the adsorption on the active surfaces of the coagulants formed during the electro-coagulation process.

3. Experimental

A 5000 ml beaker was used to conduct the experiment with working volume of 3000ml. Aluminum sheets of dimension (20×10×0.1) cm³ were used as electrode for EC with an effective area of 0.0116m² in monopolar connection. Inter electrode distance and RPM were maintained at 1cm and 500, respectively. The two electrode ends were connected to the DC power source and a constant current was supplied for a given time. Sodium fluoride (NaF) was used in this study for the preparation of fluoride solution. Initial concentration of 0.5g NaCl was added in the EC bath in order to resist the resistance created in the EC bath and to maintain constant current. All the experiments were performed at a constant temperature of 25ºC. A measured quantity (3L) of freshly prepared solution of fluoride using tap water was taken into the EC cell. Initial fluoride concentration varied from 5 to 25ppm. Current intensity was maintained at the rate of 40-190mA. After each experiment, the power was switched off and the electrodes were dismantled. Sample of the treated water was collected at a frequency of 5minutes and it was filtered for further analysis. The electrodes were washed and cleaned using acetone for further use. In assess the usefulness of the treated water for drinking purpose conductivity, TDS and turbidity were measured using digital multi-meter. Fluoride

ISE electrode was used to determine the fluoride concentration after calibrating the sample using fluoride ISA (TISAB).

4. Results and Discussion

4.1 Fluoride removal efficiency

4.1.1 Effect of initial fluoride concentration

In this particular EC process, initial fluoride concentration plays an important role for fluoride removal at particular mode of connection. Fig.1 shows the variation of fluoride removal with time at CD: 43.20A/m² and at IED: 1cm, RPM: 500, initial salt concentration: 0.5g and pH: 7. It was seen that for initial concentration of 5mg/L fluoride, it took 15 minutes to attain 1 mg/L of final fluoride concentration. Similarly for initial fluoride concentration of 10mg/L, it took about 30 minutes to reach final concentration of 1mg/L. But for 15mg/L, 20mg/Land 25mg/L, after 60min of EC it reached final concentration of 3.33mg/L, 3.66mg/L and 6.04mg/L, respectively. Thus it clearly shows that with increase in initial fluoride concentration the removal rate decreases and the current intensity should be higher.
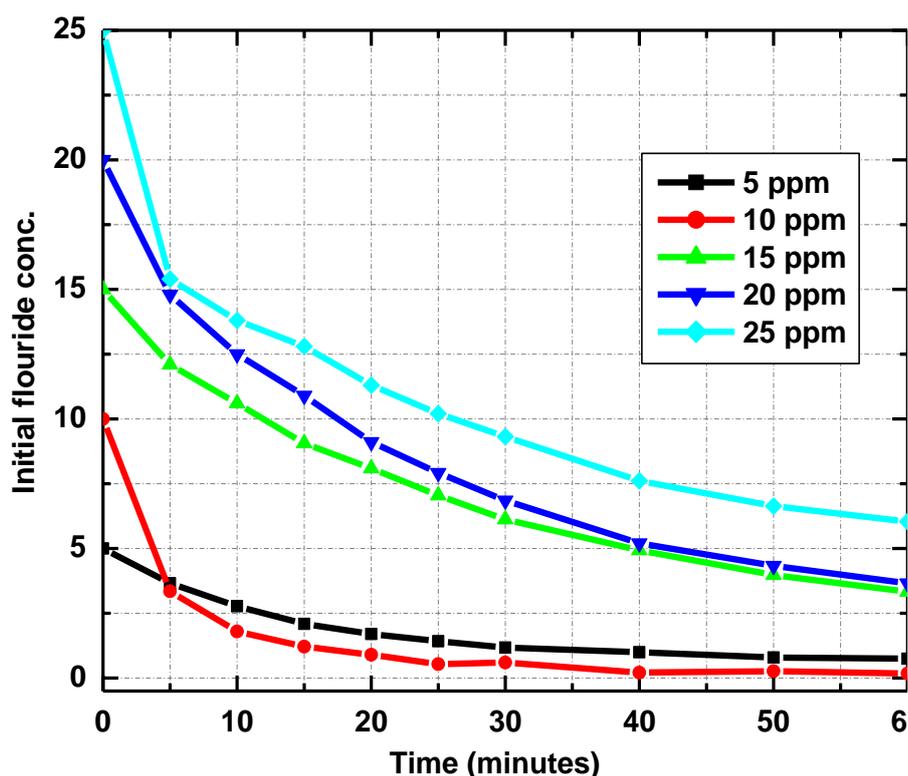

Figure 1. Variation of fluoride concentration in the EC bath with time; Inter-electrode distance:1 cm, current density: 43.20A/m², temperature: 25ºC, Connection: monopolar

4.1.2 Effect of initial pH

It was observed that the initial pH increases up to a certain range as the EC reaction proceeded. Fig 2 shows the trends of increase of pH with time. For initial pH level of 5 to 7, the final pH was 6 to 8. After increasing the initial pH level to 7.5-9, the final pH became 8 to 9. It was observed that after attaining final pH of around 9, it did not increase further irrespective of current intensity.
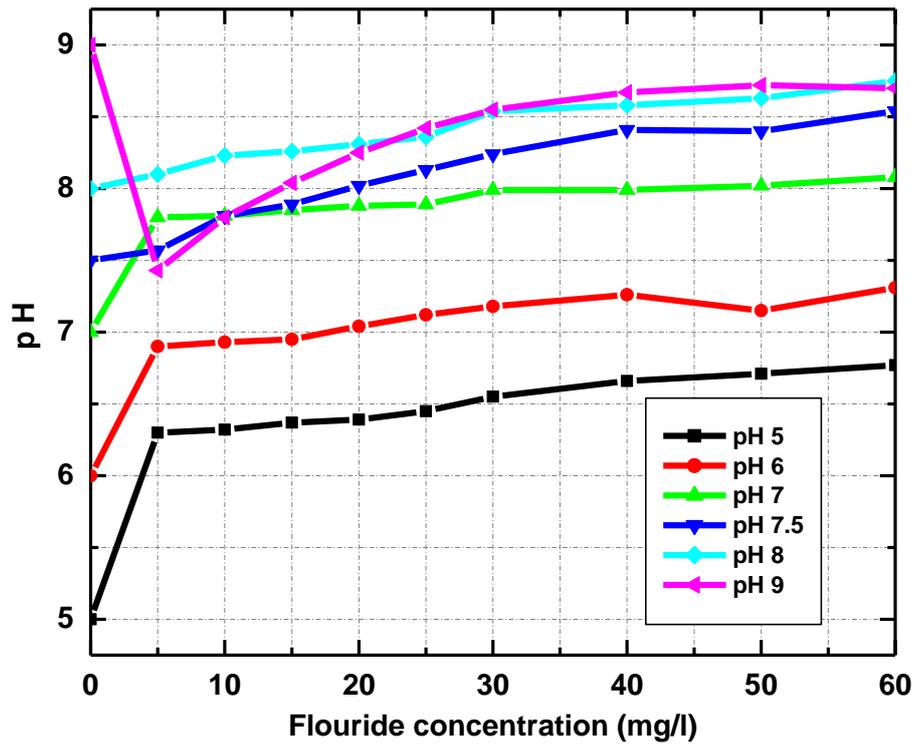
Figure 2. Variation of pH with time in EC bath; Initial fluoride concentration: 10 mg/L, IED:1cm, CD:43.20A/m²

4.1.3 Effect of pH on removal percentage

It was observed that at initial pH level of 5-7, the removal percentage was almost about 95 or above after 60minutes at CD: 43.20A/m². With the increase in initial pH to 7.5-9, the removal decreased to 85-80%. Therefore the initial pH was maintained at 7 for highest removal for the further experiments.
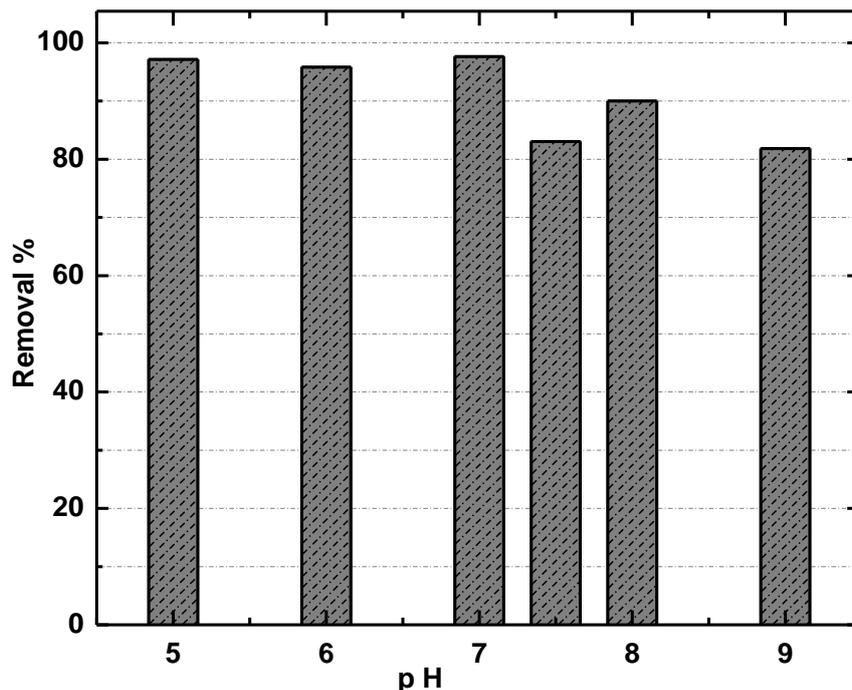

Figure 3. Variation of percentage removal of fluoride at different pH; CD-43.20 A/m², IED: 1cm, initial fluoride con; 10mg/L

4.1.4 Corrosion of electrode at different initial concentrations

Figure 4 shows the corrosion of aluminum electrode at different initial fluoride concentrations. It was observed that with the increase in initial fluoride concentration, the corrosion was not effected much though with the increase in CD, the corrosion rate would also increase.
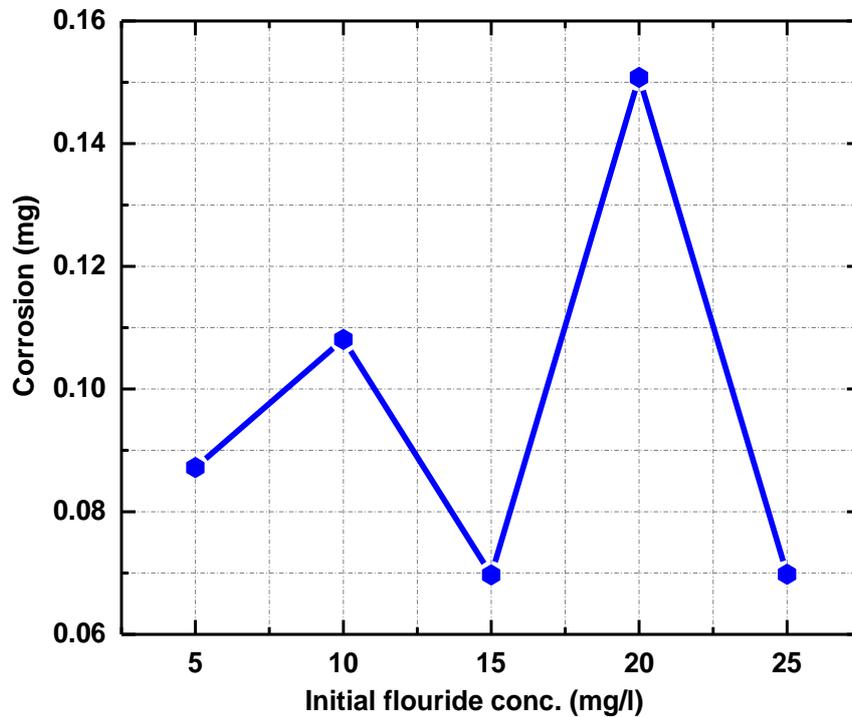

Figure 4. Corrosion of electrode in mg at different initial concentrations of fluoride; IED:1cm, pH:7 Duration: 60 minutes

4.1.5 Effect of current intensity on removal percentage

Current intensity plays an important role in de-fluoridation. Figure 5 shows the removal percentage with different current intensities. It was seen that with the increase in current intensity, the removal percentage also increased. The removal percentage was highest at current intensity of 190 mA.
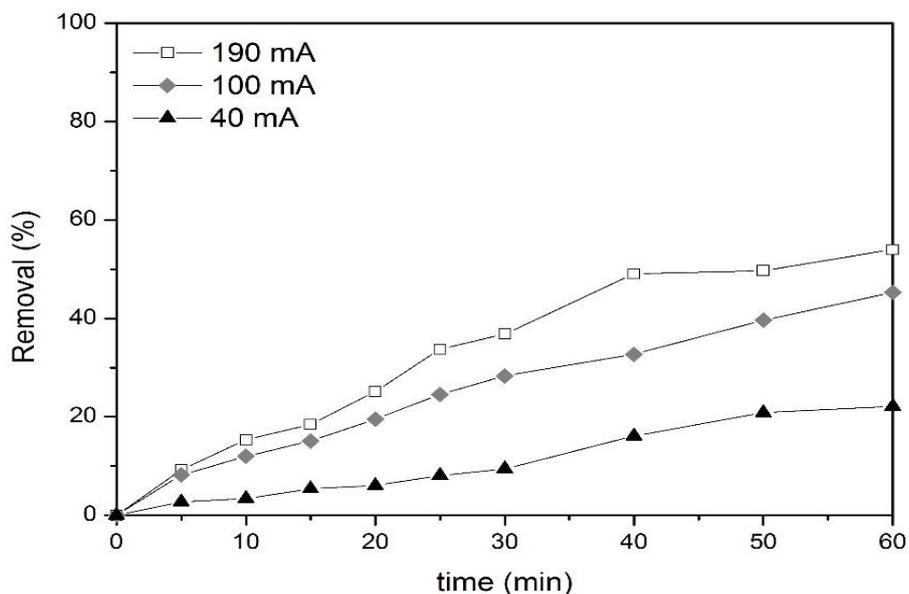

Figure 5. Variation of removal percentage of fluoride at different current intensities; IED: 1cm, pH:7

Generally increase in current density causes the anodic oxidation to take place more readily and as a result de-fluoridation increases.

4.2 Measurement of operating parameters for fluoride removal

Table 2: The different operating parameters in the experimental work like conductivity, TDS, turbidity, resistivity, salinity, pH

Initial conc.(ppm)	pH		Conductivity(µs)		TDS(ppm)		Turbidity(NTU)		Salinity(ppm)		Resistivity(kΩ)	
	Initial	Final	Initial	Final	Initial	Final	initial	Final	Initial	Final	Initial	Final
5	7	8.02	1993	911.20	1003	459	1.51	0.26	814	447	0.610	1.099
10	7	8.02	1200	1080.00	598	544	0.74	0.35	588	532	0.836	0.925
15	7	8.61	1419	496.20	716	250	1.18	0.78	706	239	0.704	2.010
20	7	8.76	1301	775.30	660	390	1.16	0.67	648	376	0.766	1.291
25	7	8.68	930	563.00	468	284	2.52	0.65	455	273	1.078	1.783

Table 2 shows the operating parameters of conductivity, TDS, turbidity, resistivity, salinity and pH for fluoride removal. The same were measured for all the samples collected after every 5 minutes and the trend has been analyzed. It is observed that as the concentration was increased from 5ppm to 25ppm, the pH value was incremented from initial constant pH at 7 to 8.02 at 5ppm, and to 8.60 at 25ppm. Similarly for conductivity there was non-linear variation in the final and initial conductivity from 5ppm concentration to 25ppm concentration. For TDS there was decrease in the final TDS (ppm) of 459 at 5ppm concentration to initial TDS 1003 and similarly at 25ppm concentration the final TDS got reduced to 284ppm from 468ppm. There was decrease in final turbidity at 0.26 NTU from initial 1.51 NTU at 5ppm concentration to final turbidity of 0.65 NTU from 2.52 NTU at 25ppm concentration. Similarly, as the resistivity value (kΩ) was increased from 0.610 at 5ppm concentration to 1.078 at 25ppm concentration the final resistivity also increased for 5ppm and 15ppm concentrations with respect to initial resistivity and decreased for 20ppm to 1.291kΩ and then again increased for 25ppm at 1.783kΩ.

5. Conclusion

Electro-coagulation technique was investigated for the removal of fluoride from drinking water using monopolar connections. Effects of initial fluoride concentration and current density, removal efficiency with different pH were studied. The results showed that the removal efficiency increases with current intensity and at initial pH level of 5 to 7. Corrosion of the electrodes was also observed. Simultaneously, the operating parameters like TDS, turbidity, salinity were also observed to get decreased from initial values. EC was found to be an effective treatment technology for fluoride removal from drinking water.

6. References

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7. Acknowledgement

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