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Electrocoagulation: Promising Technology for Removal of Fluoride from Drinking Water - A Review

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ABSTRACT: Electrocoagulation has a long history as a water treatment technology having been employed to remove a wide range of pollutants. Inspite of its manifold applications the technique has never been accepted as a mainstream water treatment technology due to lack of a systematic approach to electrocoagulation reactor design, operation and the issue related to electrode dissolution over period of time. However recent technical improvements made in the field of EC has increased its popularity. Recently, electrocoagulation (EC) has been playing more prominent role in the drinking water treatment because it provides some significant advantages such as quite compact, easy operation, automation, no chemical additives, high velocities and reduced amount of sludge. In this paper various electrocoagulation studies conducted for the efficient removal of fluoride from water has been compiled and presented as available in the literature.

Key words: Electrocoagulation, Drinking Water, Removal of Fluoride

INTRODUCTION

Fluoride is a naturally occurring element in environment and accounts for 0.06-0.09% of earth`s crust present in the form of minerals like topaz, fluorite, fluorapatite, cryolite etc. It also occurs in natural water systems (Environment Canada 1976; Singh and Maheshwari, 2001).

Fluorine and its compounds are valuable and extensively used in industry such as fertilisers, production of high purity graphite, semiconductors, toothpaste, ceramics and electrolysis of alumina, etc. Fluoride is released into atmosphere by natural sources such as volcanoes and by number of anthropogenic sources. It enters food chains through either drinking water or eating plants and cereals. Fluorosilicic acid, sodium hexafluorosilicate and sodium fluoride are used in municipal water fluoridation schemes (IARC, 1982; IPCS, 2002).

High fluoride concentration in groundwater has been reported worldwide. Countries with significant groundwater fluoride contamination include India, Pakistan, China, Southern Africa, Iraq, Iran, Sudan, Uganda, Kenya, Ethiopia and Argentina (WHO, 2006; Nayak *et. al.*, 2009; Paouloni *et. al.*, 2003, Kumar *et al.*, 2009). Fluoride levels in regions of Ethiopia have been found to be as high as 33 mg/L (Shimelis *et.al*, 2006) and levels of up to 2800 mg/L have been measured in soda lakes in Kenya and Tanzania (Nair et.al, 1985). In Mexico alone, an estimated five million people are impacted by fluorosis, representing 6% of the population (López Valdivieso *et.al*, 2006). In India ninteen states - Andhra Pradesh, Bihar, Delhi, Assam, Gujarat, Haryana, Jammu & Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Manipur, Orissa, Punjab, Rajasthan, Tamil Nadu, West Bengal, Jharkhand, Chhattisgarh and Uttar Pradesh have already been identified endemic to fluorosis (Mariappan *et al.*, 2000).

In central and western China, incidences of high fluoride intake is caused not only by drinking fluoride in groundwater but also by breathing airborne fluoride released from the burning of fluoride-laden coal. Worldwide, such instances of industrial fluorosis are on the rise.

In groundwater, the natural concentration of fluoride depends on the geological settings and type of rocks, type and duration of host rock and water interactions, the porosity and acidity of the soil and rocks, temperature, pH, depth of aquifers and the action of other chemicals present in the aquifers. The deep aquifers usually have high fluoride concentration than shallow aquifers. It is due to their long residence time with the host rocks minerals and slow groundwater movement.

Climatic conditions also affect the amount of fluoride in water. Usually the arid regions are more prone to high fluoride concentrations due to evaporation whereas the humid tropical regions have incidences of low fluoride concentration because of high rainfall inputs and diluting effect on chemical composition of water ((Frencken *et al*, 1992). It has also been established that fluoride concentration is positively related to Na, K, HCO_3^-, CO_3^{2-} and PO_4^{3-} and are best obtained for fluoride concentration 1, 0-3, 4 mg/L (Rao, 1997).

A. Toxicity and Health effects

Fluoride is an essential element good for the teeth enamel and helps to prevent dental caries but when consumed in excessive doses, it leads to chronic fluoride poisoning which affects every organ, tissue and cells in the body and results in health complaints having overlapping manifestations with several other diseases like gouts and osteoporosis. World Health Organization (WHO) and ICMR have set 1.5 mg/L as maximum contaminant limit of fluoride in drinking water. At low concentrations fluoride can reduce the risk of dental cavities. WHO noted that mottling of teeth (i.e. dental fluorosis) is sometimes associated with fluoride levels in drinking-water above 1.5 mg/L and crippling skeletal fluorosis can ensue when fluoride levels exceed 10 mg/L. Exposure to somewhat higher amounts of fluoride can cause dental fluorosis. In its mildest form this results in discolouration of teeth, while severe dental fluorosis includes pitting and alteration of tooth enamel. Even higher intakes of fluoride taken over a long period of time can result in changes to bone, a condition known as skeletal fluorosis. This can cause deformities in joints and spinal cord, ligamentous calcifications, restriction of mobility and possibly increase the risk of some bone fractures (Nayak et. al., 2009). Fluoride damages the Pineal Gland, which secretes melatonin hormone in the brain. It also affects the reproductive systems and intelligence (Susheela, 2001). List of biological manifestations associated with high fluoride concentration is shown in Table 1.

Table 1: Relationship between fluoride dosage, route of entry and biological effects.

Fluoride concentration (mg/L)	Exposure medium	Duration of exposure	Biological manifestation
0.002 - 1.00	Air and Water		Injury to vegetation Reduction in dental caries
1.0 mg/L	Water	Long term	Dental fluorosis
2 or more	Water	Long term	Mottled enamel
3-7	Water	Long term	Skeletal fluorosis
7-8	Water	7 years	Osteosclerosis (10%)
Upto 50	Food and water	Long term	Thyroid changes
60-100	Food and water	Long term	Growth retardation
100-120	Food and water	Long term	Kidney changes

Source: Smith *et al.,* (1959) and Felsenfeld and Roberts (1991)

Due to high toxicity of fluoride to mankind, extensive research has been done on various methods for removal of fluoride from water and wastewater. These methods are based on the principle of precipitation-coagulation (Saha, 1993; Singh *et al.,* 1999; Reardon *et al.,* 2001), adsorption (Raichur and Basu, 2001; Srimurali *et al.,* 1998; Reardon et al., 2001; Raichur et al., 2001; Karthikeyan *et al*., 2008), ion-exchange (Singh *et al*., 1999; Vaaramaa *et al*., 2003; Kir *et al*., 2006; Meenakshi *et al*., 2007), membrane processes such as (Dieye *et al*., 1998), Donnan dialysis, electrodialysis (Hichour *et al*., 1999), reverse osmosis (Sourirajan *et al*., 1972) and nanofiltration (Simons, 1993) (Tor, 2006) etc.

B. Electrocoagulation

Electro-coagulation is an electrochemical water treatment technology that is experiencing increased popularity and technical improvements. Recently, electrocoagulation (EC) has been playing more prominent role in the drinking water treatment because it provides some significant advantages such as quite compact and easy operation and automation, no chemical additives, high velocities and reduced amount of sludge (Holt *et al*., 2002). Generally, the Fe and Al plates are used as anode materials and stainless steel is used as cathode material (Holt *et al*., 2002. Some researchers have demonstrated that electrocoagulation using aluminum anodes is effective in defluoridation. (Mameri *et al*., 1998; Hu *et al*., 2003).

GENERAL MECHANISM

In this process, electro-dissolution of the sacrificial anode to the wastewater leads to the formation of hydrolysis products (hydroxo-metal species) that are effective in the destabilization of pollutants and/or in the formation of particles with reduced solubility that entrap the pollutants. As well, the electrochemical reduction of water in the cathode produces the formation of hydrogen bubbles that promotes a soft turbulence in the system and bond with the pollutants decreasing their relative specific weight. Consequently, they enhance the flocculation process (Canizares, P. *et al*.,2009 and Emamjomeh, M.M. *et al*., 2009). The main cathodic and anodic reactions for fluoride removal using aluminum electrodes are as follows:

At the anode

$$Al \rightarrow Al^{+3} + 3e \qquad (1)$$

At the cathode

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad (2)$$

When the anode potential is sufficiently high, secondary reactions may occur, especially oxygen evolution

$$2H_2O \rightarrow O_2 + 4H^+ + 4e$$

Aluminum ions (Al^{3+}) produced by electrolytic dissolution of the anode (Eq.(1)) immediately undergo spontaneous hydrolysis reactions which generate various monomeric species according to the following sequence:

$$Al^{3+} + H_2O\text{----------------}Al(OH)^{2+} + H^+ \qquad (3)$$

$$Al(OH)^{2+} + H_2O\text{---------------}Al(OH)_2^+ + H^+ \qquad (4)$$

$$Al(OH)_2^+ + H_2O\text{--------------------}Al(OH)_{3(s)} + H^+ \qquad (5)$$

$$Al(OH)_3 + xF^- \text{-<---------}\rightarrow Al(OH)_{3-x}Fx + xOH^- \qquad (6)$$

These hydrolysis reactions make the anodic vicinity acidic. Conversely, hydrogen evolution at the cathode (Eq. 2) makes the electrode vicinity alkali. Cationic hydrolysis products of aluminium may react with OH^- ions to transform finally in the bulk solution into amorphous $Al(OH)_{3(s)}$ according to complex precipitation kinetics. Furthermore, this $Al(OH)_3$ complex is believed to have strong fluoride adsorption capacity (Ghosh *et al*., 2008 and Mouedhen *et al*., 2008). The EC process is highly dependent on pH of the solution (Mameri *et al*. 1998, Ming *et al*. 1983). 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. Mohammad *et al*., 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 (Mameri *et al*. 1998 and Mohammad *et al*, 2009).

A. Aluminium Electrodes

Electrocoagulation with aluminium electrodes has proved to be effective in reducing fluoride concentrations found in water resources to drinking water standards of 0.5–1.5 mg/L. The process has also been applied to fluoride bearing wastewaters.

Cook and Uhrich reported the use of electrocoagulation with aluminium electrodes for the treatment of semiconductor wastewaters pre-treated with lime precipitation. The continuous pilot testing of the system was successful in bringing down the fluoride concentrations 1.8 mg/L, but severe passivation problems occurred.

Shen *et al*. used synthetically prepared wastewater to assess the treatability of fluoride using electrocoagulation with bipolar aluminium electrodes. In their study, 15mg/L influent fluoride concentration was reduced lower than 2mg/L at initial pH 6, charge loading 4.97 F/m, and a residence time of 20 min. Lower fluoride concentrations were obtained by adding 50 mg/L of Fe^{3+} or Mg^{2+} into the coagulation unit.

Hu *et al*. effectively removed dissolved fluoride and CaF_2 particles from the semiconductor wastewater pre-treated with CaF_2 precipitation, using electrocoagulation and flotation. Sodium dodecyl sulphate was used to improve flotation performance in their work. They reported that the fluoride treatment efficiency was optimal when the initial acidity was very close to the initial fluoride concentration ($[H^+]_o \approx [F^-]_o$ = 27.8 mg/L) and the final pH was around 7. They also compared batch and continuous systems, and found that fluoride removal was the same for both systems for charge loading of about 1000C/L.

Drouiche *et al*. prepared a synthetic fluoride solution to represent photovoltaic wastewater and assessed the performance of electrocoagulation with bipolar aluminium electrodes using this sample. An initial fluoride concentration of 25 mg/L was reduced to 9.5 mg/L with 30Vapplied potential and at initial pH 6–8. Addition of NaCl up to 100 mg/L further decreased the fluoride concentration.

Khatibikamal *et al*. applied the electrocoagulation process with aluminium electrodes to steel industry wastewater containing 5mg/L F^- 219 mg/L Cl− and 180 mg/L SO_4^{2-}.

Ninety percent (90%) fluoride removal efficiency was obtained under 30V fixed potential in 5 min in the monopolar reactor. The performance was further enhanced by adding extra aluminium plates, turning the system to bipolar. The pH changed from 7 to 4.68 in the first 15 min, and then increased to 9.48 at the end of 40 min. The effect of voltage was also tested between 5–30V; fluoride was reduced to under 1mg/L at an initial 10V for which the current was 0.49 A. The adsorption kinetics was represented by the second-order model.

Beyza *et al*. investigated the treatability of aluminium surface treatment effluent by electrocoagulation using aluminium electrodes. The wastewater was strong, containing over 6000 mg/L fluoride, almost 5000 mg/L aluminium as well as 340–370 mg/L COD. High fluoride removals of over 90% were obtained by electrocoagulation. The final fluoride concentrations were affected by initial fluoride levels. For 1500 mg/L chloride concentration as electrolyte, optimum fluoride removals were obtained with current densities between 22.3 and 29.8mA/cm^2. The process required close control of variables to keep the residual aluminium and COD concentrations at a minimum.

Sinha *et al*. investigated the efficacy of EC process for both simulated and groundwater samples obtained from Shivdaspura, Rajasthan (India). The authors performed continuous flow experiments using aluminium electrodes under varying operational conditions of flow rate, current density, fluoride uptake capacity per unit area anode sacrificed and double stage treatment. The optimum results for control samples were obtained at current density of 25 A/m^2 and flow rate of 150 ml/min. Results of groundwater sample showed the similar trend. Fluoride uptake capacity/g of Al used at 25 A/m^2 was higher when compared with fluoride uptake capacity/g of Al at 37.5A/m^2 current density suggested that increase in current density upto 25 A/m^2 leads to considerable increase in treatment efficiency. Further increase in current density must be avoided to limit aluminium dissolution and to save energy. For continuous flow reactor, defluoridation efficiency of 79% is achieved with control samples and 68 % with groundwater samples. The authors also reported that double stage treatment involving two reactors of same size in series with two pairs of aluminium electrodes of same size and properties further improves the defluoridation efficiency by 30-60% than single treatment process. The amount of residual aluminium in the effluent was also within the permissible limits. (Sinha *et al*., 2014)

B. Iron Electrodes

Fewer studies have been conducted for the evaluation of fluoride removal from wastewaters by electrocoagulation using iron electrodes.

Drouiche *et al*. studied fluoride removal by electrocoagulation using iron electrodes with a synthetically prepared wastewater to simulate the characteristics of photovoltaic wastewater after calcium precipitation. A fluoride concentration of 25 mg/L could be reduced to below 15 mg/L F^-, which was the discharge standard value, in 40 min under 30V potential. When actual wastewater with the same fluoride concentration was used the discharge standard could still be achieved, but longer treatment times were needed. The cost of the process was calculated to be 0.059 US$ per litre of wastewater treated.

Drouiche *et al*. used simulated photovoltaic wastewater after precipitation with lime to evaluate the performance of electrocoagulation with iron electrodes. The optimum pH for the process was found as 6. The initial concentration of 25 mg/L F^- was reduced to below 15 mg/L in 40 min and with 30V potential.

Zhu, J. *et al*. investigated the fluoride removal process mechanism with a new approach by comparing the defluoridation efficiency of electrocoagulation and chemical coagulation under various Al^{3+} dosages and pH values at an initial F^- concentration of 5 mg/L. The results showed that EC process significantly outperformed CC process for fluoride removal for all the Al^{3+} concentrations tested in the pH range of 6.0–7.0, especially for low Al^{3+} dosages. For example, 80% reduction of fluoride was achieved by EC process at an Al^{3+} dosage of 10–20 mg/L, whereas the same reduction achieved by CC process required Al^{3+} dosage of 30–40 mg/L. As a result of electro-condensation that made EC outperform CC in the low coagulant dosage, which was essentially absent in the CC process. With the help of EDX and XPS analysis the authors confirmed the existence of fluoride on the surface of electrodes. (Zhu J. *et al*. 2007)

Zhao *et al*. employed the integrated approach of electro-oxidation and EC for the simultaneous removal of arsenic and fluoride in water using dimensionally stable electrodes (DS), iron electrodes and aluminium electrodes in an EC cell. In this system, the DS electrodes were fitted outside the Al and Fe electrodes and were directly connected to the power supply. The removal of arsenic ions and fluoride ions were attributed to the iron hydroxides and aluminium oxides respectively, formed as a result of electro induced process. Regarding Fe/Al ratio, single Fe plate electrode and three Al plate electrode were effective to reduce As(III) conc. 1mg/L and F^- conc. 45mg/L to below their permissible limits i.e 10 µg/L and 1.0 mg/L. (Zhao *et al*., 2011).

Sailaja *et al*., carried out study with both aluminium and iron electrodes under variable conditions of parameters such as initial fluoride concentration, pH, applied voltage and reaction time, distance between electrodes, electrode reactive area and effect of Co-existing. The authors reported that maximum removal capacities were obtained at 30V electrical potential with reactive surface area of $40cm^2$ and inter electrode distance 1cm. The author further reported that neutral pH and aluminium electrode was the best suitable for EC process. (Sailaja *et al*., 2014).

Regarding design of reactor, very few studies have been performed to investigate the effect of configuration of EC reactor. Mollah *et al*. (2001) and Mollah *et al*. (2004) described six typical configurations for industrial EC cells, and report their respective advantages and drawbacks. Bennajah *et al*. (2009) demonstrated that airlift reactors are suitable units to carry out EC with complained flotation, using only electrochemically generated bubbles, to achieve an overall liquid circulation and good mixing conditions. Mounir Bennajah *et al*. 2010 compared the two different types of reactors the stirred tank reactor and the air-lift reactor having same capacity EC cells with two aluminium electrodes. The comparison of energy consumption demonstrated that the (ALR) was advantageous for carrying out the defluoridation removal process.

Sinha *et al*. performed the continuous flow experiments to investigate the effects of different operational parameters and observed that increase in current density upto 25 A/m^2 led to considerable increase in treatment efficiency. This effect was observed because lower current density caused low coagulant (aluminium) dosage and thus reduced the efficiency of the treatment process. When current density is increased, ion production on electrodes also increases. This leads to production of $Al(OH)_3$ flocs in the solution and hence efficiency 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 efficiency of the treatment process. (Sinha R. *et al*. 2012)

Umran Tezcan Un *et al*. assessed the performance of specially designed electrochemical reactor with a unique design having rotating impeller aluminium cathode and a cylindrical aluminium anode for the fluoride removal. The effect of various investigated parameters such as the electrode material (aluminium and iron), the current density (0.5–2 mA/cm2), the duration of electrolysis, the supporting electrolyte dosage (0.01–0.03 M Na_2SO_4), the initial pH (4–8) and the interference of competing ions ($Ca^{2+,}$ Mg^{2+}, PO_4^{3-} , SO_4^{2-}), were examined to achieve optimal performance of the process. The maximum removal efficiency (97.6%) was observed after 30 minutes at the current density of 2 mA/cm^2, pH of 6 and presence of 0.01 M Na_2SO^4 supporting electrolyte. The presence of Ca^{2+} and Mg^{2+} ions also enhanced the removal efficiency while PO_4^{3-} , SO_4^{2-} ions affected adversely. The required electrocoagulation time to reach the WHO-recommended fluoride limit of 1.2 mg/L at 0.5 mA/cm^2 was 5 min, with an energy consumption of 0.47 kW h/m3. (Umran Tezcan Un *et al*., 2013)

CONCLUSION

Electrocoagulation technology has achieved a level of applicability and hence examined as potential defluoridation technology. Compared with traditional flocculation–coagulation, electrocoagulation has the advantage of removing the smallest colloidal particles and relatively low amount of residue generation.

In spite of having numerous advantages, EC has some drawbacks such as the periodic replacement of sacrificial anodes. Also it requires a minimum conductivity depending on reactor design that limits its use with water containing low dissolved solids.

In addition the control of residual aluminium, technical and economical optimization of the process according to the quality of water being treated needs to be taken into considerations.

Although large numbers of studies are available in literature further studies are required to elucidate the capability and limitations of the process. In order to scale up the method, the future work should be focused on investigating the influence of various operational parameters including residence time, energy consumption and initial fluoride concentration as well as interference from factors such as calcium ions in effluents.

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REFERENCES

Battula, S.K., Cheukuri, J., Raman. N. V. V. S., Himabindu and Bhagawan, D. (2014). Effective Removal of Fluoride from Ground Water Using ElectroCoagulation. *Int. Journal of Engineering Research and Applications.* **4**(2), 439-445.

Bennajah, M. Gourich, B. Essadki, A.H., Vial, C. Delmas, H. (2009). Defluoridation of Morocco drinking water by electrocoagulation/electroflotation in an electrochemical external-loop airlift reactor. *Chem. Eng. J*. **148**, 122–131.

Bennajah, M., Darmane, Y., Touhami, M. E., Maalmi. M., (2010). A variable order kinetic model to predict defluoridation of drinking water by electrocoagulation-electroflotation, *International Journal of Engineering, Science and Technology*, **2**(12): 42-52.

B. Samuk, I. Kabda ˈSlı, O. Tunay, and M. Karpuzcu, Fluoride abatement from aluminium surface treatment effluents by electrocoagulation, *Fresenious Environ. Bullet*. (2012).

Canizares, P., Jimenez, C., Martinez, F., Rodrigo, M.A., Saez, C. (2009). The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters. *J. Hazard. Mater*. **163**, 158–164.

Cook, S.L. and Uhrich, K.D. (1990). Electrochemical fluoride removal in semiconductor wastewater, 44th Purdue University Industrial Waste Conference Proceedings, (1990), Lewis Publishers, Imc., Chelsea, Michigan, pp. 373–383.

Dieye, A., Larchet, C., Auclair, B., Diop, C.M. (1998). Elimination des fluorures parla dialyse ionique croisee. EUl: Polym. **34**, 67-75.

Drouiche, N., Aoudj, S., Lounici, H., Drouiche, M., Ouslimane, T. and Ghaffour, N. (2012). Fluoride removal from pretreated photovoltaic wastewater by electrocoagulation: An investigation of the effect of operational parameters, Procedia Engineering. **33**, 385–391.

Drouiche, N., Aoudj, S., Hecini, M., Ghaffour, N., Lounici, H. and Mameri, N. (2009). Study on the treatment of photovoltaic wastewater using electrocoagulation: Fluoride removal with aluminium electrodes –Characteristics of products. *J. Hazard. Mater*. **169**, 65–69.

Emamjomeh, M.M., Sivakumar, M. (2009). Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. *J. Environ. Manage*. **90**, 1663–1679.

Environment Canada (1976) National inventory of sources and emissions of fluorides; Internal Report APCD 75-7; Air Pollution Directorate, Canada, 1972.

Frencken, J.E. Endemic Fluorosis in Developing Countries, Cause, Effects and Possible Solutions, Publication No. 91.082, NIPG-TNO, Leiden, The Netherlands, 1992.

Felsenfeld, A.J., Roberts, M.A. (1991). A Report of Fluorosis in the United States Secondary to Drinking Well Water. *J. Amer. Med. Assoc.* **265**(4), 486-488.

Ghosh, D., Medhi, C.R., Purkait, M.K. (2008). Treatment of fluoride containing drinking water by electrocoagulation using monopolar and bipolar electrode connections. *Chemosphere*. **73**, 1393–1400.

Hichour, M., Persin, F., Molenat, J., Sandeaux, J., Gavach, C. (1999). Fluoride removal from diluted solutions by Donnan dialysis with anion-exchange membranes. *Desalination*. **122**, 53–62.

Holt, P.K., Barton, G.W., Wark, M., Mitchell, C.A. (2002). A quantitative comparison between chemical dosing and electrocoagulation. *Colloids Surf*. **211**, 233-248.

Hu, C.Y., Lo, S.L., Kuan , W.H. (2003). Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes. *Water Res*. **37**, 4513–4523.

Hu, C.Y., Lo, S.L., Kuan, W.H. and Lee, Y.D. (2005). Removal of fluoride from semiconductor wastewater by electrocoagulation-flotation. *Water Res.* **39**, 895–901.

Hu, C.Y., Lo, S.L., Kuan, W.H. and Lee, Y.D. (2008). Treatment of high fluoride-content wastewater by continuous electrocoagulation-flotation system with bipolar aluminium electrodes. *Sep. Purif. Technol.* **60**, 1–5.

IARC (1982). Some aromatic amines, anthraquinones and nitroso compounds, and inorganic fluorides used in drinking-water and dental preparations. In IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Lyon, International Agency for Research on Cancer, Vol. **27**, 237–303.

IPCS (2002). Fluorides. World Health Organization. International Programme on Chemical Safety (Environmental Health Criteria 227), Geneva.

Khatibikamal, V., Torabian, A., Janpoor, F. and Hoshyaripour, G. (2010). Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics. *J. Hazard. Mater.* 179, 276–280.

Karthikeyan, M., Elango, K.P. (2008). Removal of fluoride from aqueous solution using graphite: A kinetic and thermodynamic study. *Indian journal of chemical Technology*. **15**, 525-532.

Kir, E., Alkan, E. (2006). Fluoride removal by donnan dialysis with plasma-modified and unmodified anion. *Desalination*. **197**, 1217-224.

Kumar, E., Bhatnagar, A., Ji, M., Jung, W., Lee, S.H., Kim, S.J., Lee, G., Song, H., Choi, J.Y., Yang, J.S., Jeon, B.H. (2009). Defluoridation from aqueous solutions by granular ferric hydroxide (GFH). *Water Res*. **43**, 490-498.

Nayak, B. et.al., 2009, Health effects of groundwater fluoride contamination., Clinical toxicology (Phila.), **47**(4), pp 292-295.

Nair, K.R, Manji, F. and Gitonga, J.N. (1984). The occurrence and distribution of fluoride in groundwaters of Kenya. In: Challenges in African Hydrology and Water Resources, Proceedings of the Harare Symposium, IAHS Publ. **144**, 75–86.

López Valdivieso A, Reyes Bahena JL, Song S, Herrera Urbina R. 2006, Temperature effect on the zeta potential and fluoride adsorption at the α-Al_2O_3/aqueous solution interface. *Journal of Colloid and Interface Science*, **298**(1), 1-5.

Mariappan, P., Yegnaraman, V., Vasudevan, T. (2000). Occurrence and removal possibilities of fluoride in ground waters of India. *Pollut. Res*. **19**(2), 165–177.

Mollah, M.Y.A., Morkovsky, P., Gomes, J.A.G., Kesmez, M., Parga, J., Cocke, D.L. (2004). Fundamentals, present and future perspectives of electrocoagulation. *J. Hazard. Mater*. **114**, 199–210.

Mameri N, Yeddou AR, Lounici H, Belhocine D, Grib H, Bariou B. (1998). Defluoridation of Septentrional Sahara Water of North Africa by electro-coagulation process using bipolar aluminium electrode. *Water Res*. **32**, 604–12.

Meenakshi, S., Viswanathan, N. (2007). Identification of selective ion-exchange resin for fluoride sorption. *Journal of colloid and interface science*. **308**(2), 438-450.

Mouedhen, G., Feki, M., De Petris Wery, M., Ayedi, H.F. (2008). Behavior of aluminum electrodes in electrocoagulation process. *J. Hazard. Mater.* **150**, 124–135.

Mohammad M.E., Muttucumaru S. (2009). Fluoride removal by a continuous flow electrocoagulation reactor. *Journal of Environmental Management.* **90**, 1204–1212.

Paoloni, J.D., Fioerentino, C.E., Sequeira, M.E. (2003). Fluoride contamination of aquifers in the southeast sub-humid pampas, Argentina. *Environ. Toxicol.* **18**, 317-320.

Rao, N. S. (1997). The occurrence and behaviour of fluoride in the groundwater of the lower Vamsadhara River basin, India. *Journal of Hydrological Sciences*. **42**, 877 –891.

Reardon, E.J. Wang, Y. (2001). Activation and regeneration of a soil sorbent for defluoridation of drinking water. *Appl. Geochem*. **16**, 531–539.

Raichur, A.M., Basu, M.J. (2001). Adsorption of fluoride onto mixed rare earth oxides. *Sep. Purif. Tech.* **24**, 121–127.

Srimurali, M., Pragati, A., Karthikeyan, J. (1998). A study on removal of fluorides from drinking water by adsorption on to low cost materials. *Environ. Poll.* **99**, 285–289.

Singh, G., Kumar, B., Sen, P.K., Majumdar, J. (1999). Removal of fluoride from spent pot liner leachate using ion exchange. *Wat. Environ. Res.* **71**(1), 36-42.

Sourirajan, S., Matsurra, T. (1972). Studies on reverse osmosis for water pollution control. *Wat. Res*. **6**, 1073-1086.

Simons, R. (1993). Trace element removal from ash dam waters by nanofiltration and diffusion dialysis. *Desalination*. **89**, 325–341.Susheela, A.K. (2001). Fluorosis - Early detection and Management: Importance of practising interventions with focus on consuming safe water and essential nutrients. In Heinz Nutrition Foundation India Publication, “In-Touch", Vol. **3**, No. 3, 2001.

Smith, F.A., Hodge, H.C: (1959). In: Fluorine and dental Health, (Muhler, T.C. and Hne, M.K., eds.) Bloomington, Indian University Press, pp. 11-37.

Saha, S. (1993). Treatment of aqueous effluent for fluoride removal. *Wat. Res.* **27**(8), 1347–1350.

Singh, G., Kumar, B., Sen, P.K., Majumdar, J. (1999). Removal of fluoride from spent pot liner leachate using ion exchange. *Wat. Environ. Res.* **71**(1), 36-42.

Shen, F., Chen, X.M., Gao, P. and Chen, G.H. (2003). Electrochemical removal of fluoride ions from industrial wastewater. *Chem. Eng. Sci*. **58**, 987–993.

Singh, R., Maheshwari, R.C. (2001). Defluoridation of drinking water–A review. *Ind. J. Environ. Prot.* **21**(11), 983–991.

Shimelis, B., Zewge, F., Chandravanshi, B.S. (2006). Removal of excess fluoride from water by aluminium hydroxide. *Bull. Chem. Soc. Ethiop*. **20**, 17–34.

Sinha R, Khazanchi I, Mathur S. (2012). Fluoride removal by a continuous flow Electrocoagulation Reactor from Groundwater of Shivdaspura. *International Journal of Engineering Research and Applications.* **2**(5), 1336-1341.

Tor, A. (2006). Removal of fluoride from an aqueous solution by using montmorillonite. *Desalination*. **201**, 267–276.

Umran Tezcan Un., A. Savas Koparal, Ulker Bakir Ogutveren. (2013). Fluoride removal from water and wastewater with a bach cylindrical electrode using electrocoagulation. *Chemical Engineering Journal*. **223**, 110–115.

Vaaramaa, K. Lehto, J. (2003). Removal of metals and anions from drinking water by ion exchange, *Desalination*. **155**, 157–170.

World Health Organization, Fluoride in drinking water, 2006.

Zhu, J., Zhao, H., Ni, J. (2007). Fluoride distribution in electrocoagulation defluoridation process. *Separation and Purification Technology.* **56**, 184–191.

Zhao, X., Zhang, B., Liu, H., Qu, J. (2011). Simultaneous removal of arsenite and fluoride via an integrated electro-oxidation and electrocoagulation process. *Chemosphere.* **83**, 726–729.