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De-fluoridation of Ground Water by Electro Coagulation Method

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Abstract:
Environmental issues have become serious social concerns of a global scale. Among these issues, the impact of water pollution is getting more serious because it is closely related to the health and lives of human beings. The removal or breakdown of organic compounds from wastewater is an important and integral part of any industrial chemical process. Treatment plants intended for the purification of any industrial wastewater utilize a combination of processing techniques such as Physical treatment, Physicochemical treatment and Biological treatment. Also, recent literature indicates the applicability of electrochemical process as an attractive alternative for application prior to biological methods. Electrochemical (EC) treatments such as electrocoagulation, electroflotation and electrochemical oxidation have been studied extensively because of their several advantages over a typical wastewater treatment plant. Electrochemical treatments generally have lower temperature requirements and require less space, and produce fewer byproducts or sludge.

1. Introduction

Throughout history people around the world have used groundwater as a source of drinking water and even today, more than half of the world’s population depends on it for survival. Ground water quality may be impaired by many natural constituents such as fluoride, arsenic, iron, nitrate and salinity of which fluoride stands as a pollutant of geogenic origin in many countries. Fluoride concentration in groundwater is reported from as many as 40 countries including India.

Fluoride is a normal constituent of natural water samples. Its concentration, though, varies significantly depending on the water source. Although both geological and man-made sources contribute to the occurrence of fluoride in water, the major contribution comes from geological resources. Except in isolated cases, surface waters seldom have fluoride levels exceeding 0.3 mg/l. Examples are streams flowing over granite rich in fluoride minerals and rivers that receive untreated fluoride-rich industrial wastewater. There are several fluoride bearing minerals in the earth's crust. They occur in sedimentary (limestone and sandstone) and igneous (granite) rocks. Weathering of these minerals along with volcanic and fumarolic processes lead to higher fluoride levels in groundwater. Dissolution of these barely soluble minerals depends on the water composition and the time of contact between the source minerals and the water.

Over the year’s groundwater has generally been considered to be a protected and safe source of water, fit for drinking without treatment, as the main focus has been on the bacteriological quality of potable water. Little consideration used to be given to the risks of chemical pollution, particularly to the presence of elevated levels of fluoride, arsenic and nitrate in groundwater. This chapter deals with only fluoride. Consumption of water having excess fluoride over a prolonged period leads to a chronic ailment known as fluorosis. Incidence of high-fluoride groundwater has been reported from 27 nations around the globe. It has led to endemic fluorosis, which has become a major geo- environmental health issue in many developing countries. According to a recent estimate, 62 million people are affected by various degrees of fluorosis in India alone (Susheela, 2001).

1.1. Ground Water

Groundwateris the waterlocated beneath the earth's surface in soil pores spaces and in the fractures of rock formations. The depth at which soil pore spaces or fractures and voids in rock become completely saturated with water is called the water table. Groundwater is recharged from, and eventually flows to, the surface naturally; natural discharge often occurs at springs, seeps and can form oases or wetlands. Groundwater is also often withdrawn for agricultural, municipal and industrial use by constructing and operating extraction wells. The study of the distribution and movement of groundwater is hydrogeology, also called groundwater hydrology.

Ground water contributes to about eighty percent of drinking water requirements in the rural area, fifty percent of the urban water requirements and more than fifty percent of the irrigation requirements of the nation

In the past five decades since independence, the development of water resources in country has increased rapidly in order to meet the demands for diverse users. Ground water has played a significant role in maintenance of India's economy, environment and standard of living. Besides being the primary source of water supply for domestic and many industrial uses, it is the single largest and most productive source of irrigation water. Uncontrolled development of the resource for meeting the increased demands has resulted in declining ground water levels. Further haphazard disposal of domestic, industrial wastes and excessive application of fertilizers, pesticides in agricultural fields have led to deterioration of ground water quality thereby further limiting the availability of fresh ground water resources.

1.1.1. Groundwater Contamination

Groundwater can be contaminated in many ways. If surface water that recharges the aquifer is contaminated, the groundwater will also become contaminated. This in turn, affects the quality of surface water at discharge areas. Groundwater can also be contaminated by liquid hazardous substances (or solids that can dissolve in water) that filter through the soil into groundwater, by saltwater moving in from the ocean, or by minerals that are naturally present in the area.

Groundwater contamination is almost a result of human activity. In areas where population density is high and human use of land is intensive. Ground water is especially vulnerable. Virtually any activity where by chemicals or wastes may be released to the environment either intentionally or accidentally, has the potential to pollute groundwater.

1.2. Fluoride in Groundwater

In ground water the natural concentration of fluoride depends on geological, chemical and physical characteristics of aquifer. Water with high fluoride content is usually found at the foot of high mountains and in areas with geological deposits of marine origin. Due to these variables, the fluoride concentrations in ground water can range from less than 1mg/l to more than 35 mg/l(WHO 2005).

Fluoride is a chemical that occurs naturally with in many types of rocks. Fluoride element is found in the environment and constitute 0.06-0.09% of the earth crust. Fluoride is the important for development of healthy teeth and bones. Lower concentration of fluoride in water (< 0.6 mg/ L) causes dental caries and high Fluoride in water resources cause dental and skeletal fluorosis. Fluoride occurs in combined form because of its high reactiveness. It is present naturally in almost all food and a beverage including water. Fluoride has various uses in many industries including tooth paste, ceramic tiles, bricks etc.

1.3. National and International Status of Ground Water

1.3.1. International Scenario

A study by UNICEF illustrates that presence of higher fluoride in ground water is reported in as many as 27 countries across the globe which include Algeria, Argentina, Australia, Bangladesh, China, Egypt, Ethiopia, India, Iran, Iraq, Japan, Jordan, Kenya, Libya, Mexico, Morocco, New Zealand, Palestine, Pakistan, Senegal, Sri Lanka, Syria, Tanzania, Thailand, Turkey, Uganda and United Arab Emirates. The two most populated countries of the world China and India are considered as the severe fluoride affected regions.

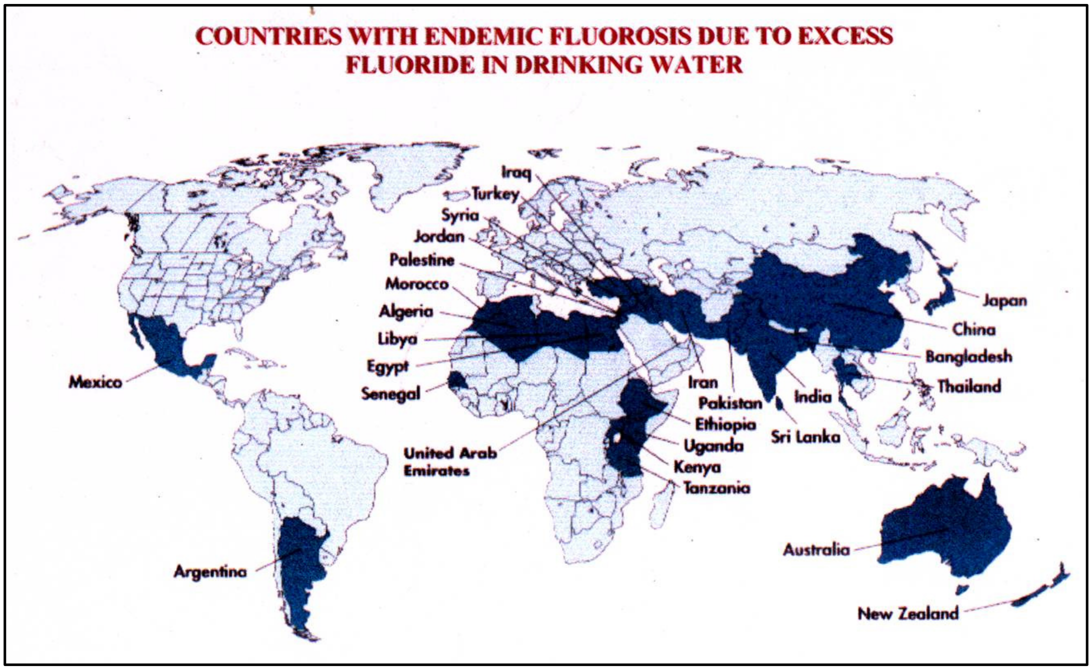


Figure 1: International Status of Ground water

1.3.2. Indian Scenario

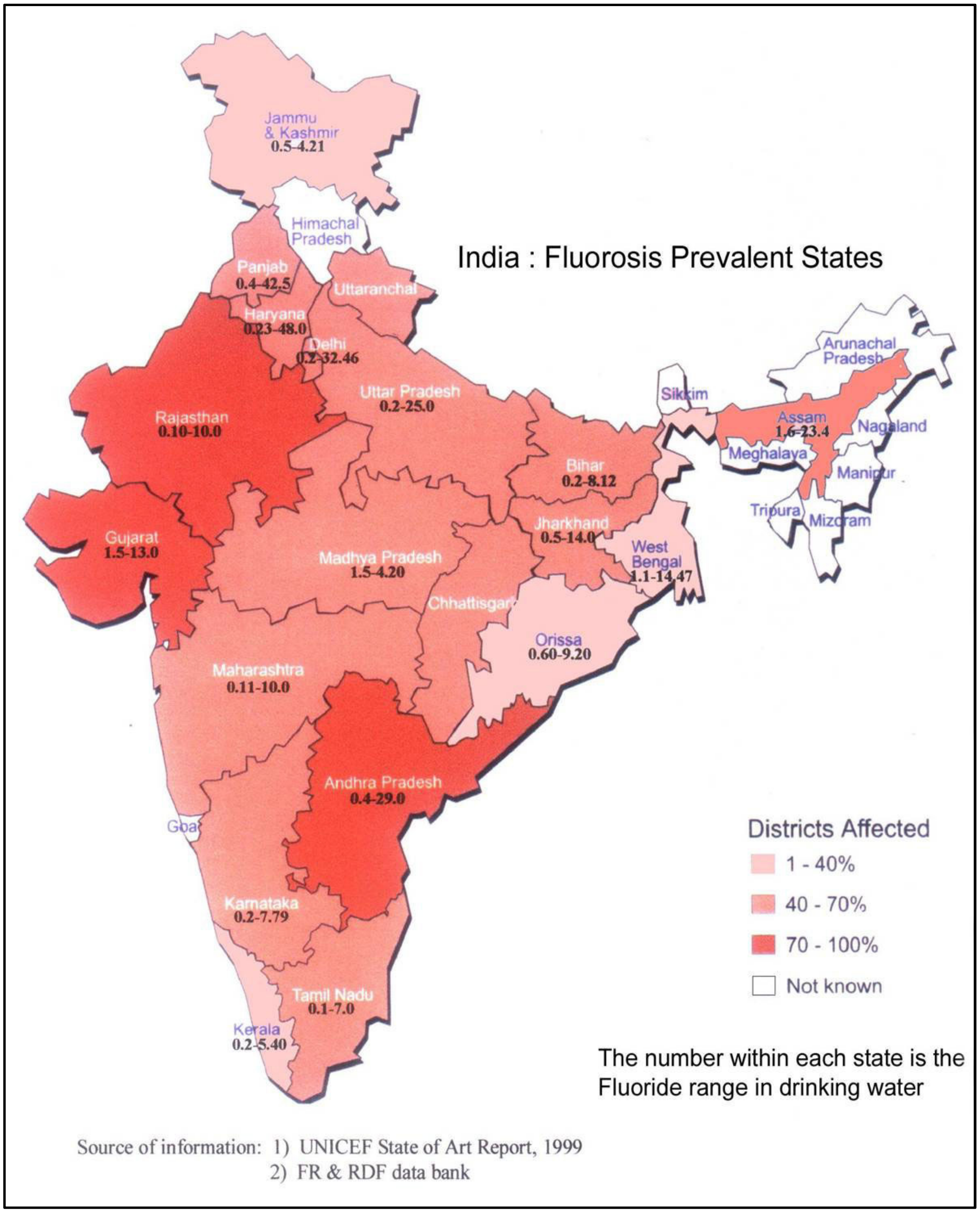
It is estimated that in India, 80% of domestic needs in rural areas and 50% in urban areas are met by ground water and its purity is under threat due to excess fluoride concentration. A recent study conducted by the UNICEF in India on the extent and magnitude of presence of fluoride in ground water indicated that 213 districts with affected 25 million people and 66 million people at risk. The overall concentration of fluoride in ground water varies from 0.2 to 35 mg/l with maximum sources found in the range of 3-5 mg/l.

1.3.2.1. Fluoride affected regions in India

Prevalence of fluorosis in India is mainly due to hydro geochemical origin. Depending on the extent of the fluoride problem, states have been categorized into three groups as following [16]:

- Category I: Less than 30% districts affected. Jammu, Kashmir, Kerala and Orissa.
- Category II: 30-50% districts affected. Bihar, Haryana, Karnataka, Maharashtra, Madhya Pradesh and Punjab.
- Category III: More than 50% districts affected. Andhra Pradesh, Gujarat, Rajasthan, Tamilnadu, Kerala.

Presence of fluoride above the permissible limit in groundwater has become a major toxicological and geo-environmental problem in 19 states of India according to a survey carried out by Ministry of water resource (2008).



The number within each state is the Fluoride range in drinking water

Source of information: 1) UNICEF State of Art Report, 1999
2) FR & RDF data bank

Figure 2: National Status of Ground Water

Maximum permissible limit	Health impact	Parameter	Affected states
1.5 mg/l	• Immediate symptoms include digestive disorders, skin diseases, dental fluorosis • Fluoride in larger quantities (20-80 mg/day) taken over a period of 10-20 years results in crippling and skeletal fluorosis which is severe bone damage	Fluoride	Andhra Pradesh, Assam, Bihar, Chhattisgarh, Gujarat, Haryana, Jharkhand, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Tripura, Uttar Pradesh, West Bengal
.05 mg/l	• Immediate symptoms of acute poisoning typically include vomiting esophageal and abdominal pain, and bloody 'rice water' diarrhea. • Long-term exposure to arsenic causes cancer of the skin, lungs, urinary bladder,	Arsenic	Assam, Bihar, Chhattisgarh, Jharkhand, Tripura, West Bengal, Uttar Pradesh

	and kidney. There can also be skin changes such as lesions, pigmentation changes and thickening (hyperkeratosis		
1mg/l	• A dose of 1500 mg/l has a poisoning effect on a child as it can damage blood tissues • Digestive disorders, skin diseases and dental problems	Iron	Arunachal Pradesh, Assam, Bihar, Chhattisgarh, Jharkhand, Jammu and Kashmir, Karnataka, Kerala, Manipur, Meghalaya, Mizoram, Madhya Pradesh, Maharashtra, Nagaland, Orissa, Punjab, Rajasthan, Sikkim, Tripura, Tamil Nadu, Uttar Pradesh, West Bengal, A&N Islands, Pondicherry
100 mg/l	• Causes Methamoglobinemia (Blue Baby disease) where the skin of infants becomes blue due to decreased efficiency of hemoglobin to combine with oxygen. It may also increase risk of cancer.	Nitrate	Bihar, Gujarat, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh
200 mg/l	• Objectionable taste to water. • May affect osmotic flow and movement of fluids	Salinity	Andhra Pradesh, Chhattisgarh, Gujarat, Haryana, Kerala, Madhya Pradesh, Maharashtra, movement of fluids Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh, West Bengal, Pondicherry
Cadmium – 0.01 mg/ 1 Zinc – 15 mg/ 0.001 mg/ 1	Damage to nervous system, kidney, and other metabolic disruptions	Heavy Metals	Gujarat, Andhra Pradesh, Delhi, Haryana, Kerala

Table 1:States affected by various water quality problems

1.3.2.2. Fluoride affected regions in Karnataka

According to mines and geology department, 2008 study Kolar, Tumkur, Gadag, Bellary, Chitradurga, Bagalkot and Bijapur are the severely fluoride affected regions having fluoride concentrations above 3mg/L in most of the areas.

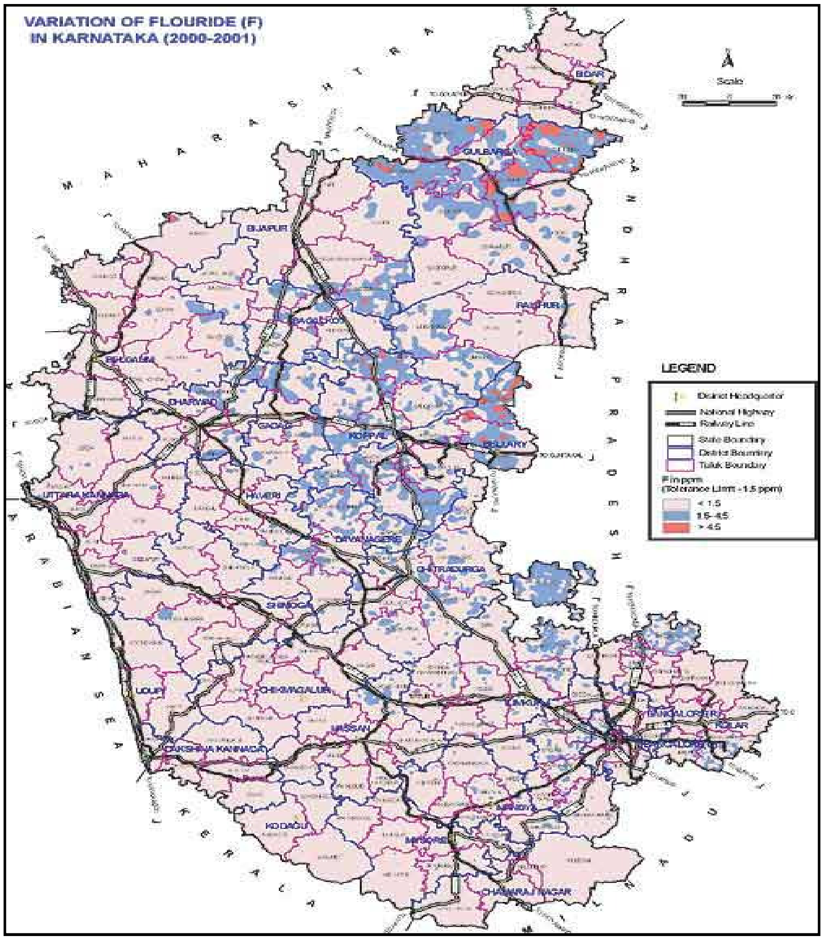


Figure 3: Fluoride affected regions in Karnataka

1.3.2.3. Fluoride affected regions in Gadag District
In Gadag district there are areas, which are severely fluoride affected these include Gojnur, Bannikoppa, Mundargi, Kalkeri etc.In each area, Fluoride affected bore wells are identified and fluoride concentration varied from 0.8 to 6 mg/l. Water at most of the locations is not suitable for drinking purpose as per WHO and IS guidelines.

1.4.Health significance of fluoride

Fluoride is one often called a two edged sword. Fluoride is among the substances for which there are both lower (1.0 mg/l) and upper (1.5 mg/l) limits of concentration in drinking water, with identified health effect and benefits for human beings. Very low doses of Fluoride (<0.6 mg/l) in water promote tooth decay. However, when consumed in higher doses (>1.5 mg/l) leads to dental fluorosis or mottled enamel and excessively high concentration (> 3.0 mg/l) of Fluoride may lead to skeletal fluorosis. Crippling skeletal fluorosis can occur when water supply contains more than 10 mg/l of Fluoride.

1.5. Limiting Fluoride Concentrations and its Health Effects

Sl. No.	Fluoride concentration (mg/l)	Health impacts
1	<0.5	Dental carries
2	0.5-1.5	Promotes dental health
3	1.5-4.0	Dental fluorosis
4	>4.0	Dental and skeletal fluorosis
5	>10	Crippling fluorosis

Table 2: Limiting fluoride concentration and their health impacts

About 95% of the fluoride in the body deposited in hard tissues and it continues to be deposited in calcified structures even after other bone constituents (Ca, P, Mg, CO3 and citrate) have reached a steady state. Age is an important factor in deciding to what extent fluorine is incorporated into the skeletal tissues. Due to all the above mentioned health ailments there is limit for fluoride in drinking water set by various governing bodies as shown in table.

Sl.No.	Authority	Permissible limit (mg/l)
1	WHO	(In Indian context)1.5
2	BIS(IS-10500)	1.0-1.5
3	ICMR	1.0-2.0
4	CPHEEO	1.0-1.5
5	US public-health	0.7-1.2

Table 3: Drinking water quality standards with reference to Fluoride

1.5.1. Dental Fluorosis

Dental fluorosis is prominent in children who are brought up in an endemic area of fluorosis. Dental fluorosis can occur in both milk teeth and the permanent teeth. Discoloration due to excess fluoride intake will be visible to naked eye.Dental fluorosis occurs in human beings consuming water containing 1.5 mg/l or more of Fluorides, particularly during first eight years of child life.

1.5.2. Skeletal Fluorosis

Prevalence of skeletal Fluorosis increases with increase in Fluoride concentration (> 4 mg/L) and age. Following are the symptoms of skeletal fluorosis:

- Severe pain and stiffness in the back bone
- Severe pain and stiffness in joints
- Severe pain and rigidity in hip region
- X-ray: increased girth/thickening and density of bone besides calcification of ligaments.
- Paralysis.

1.5.3. Crippling Fluorosis

This aspect of fluorosis is often overlooked because of the wrong notion prevailing that Fluoride will only affect bone and teeth however when Fluoride is consumed in excess can cause several ailments besides skeletal and dental fluorosis such as crippling of bones which results in permanent physical disability.

1.5.4. Neurological Manifestations of Fluorosis

The neurological complications in fluorosis for the first time in India were reported in 1937; approximately 214 such patients have been reported from India. The neurological complications of fluorosis occur mainly due to compression of spinal cord, nerve roots or peripheral nerves secondary to bone hypertrophy or ligaments calcification or both. Considerable works have been done on treatment of fluorosis but their results have indicated its affects as irreversible.

When the concentration of Fluoride in water source exceeds the permissible level of 1.5 mg/L consistently, it is essential to consider some remedial measures to prevent the incidence of fluorosis. There are two options for preventing the fluorosis incidences. First is to check the aquifer from different depths around the same location for the possible water source having fluoride level with in the permissible levels. Another option is to consider a different water source altogether. Though both the options are possible but are not practical and feasible in real sense. In that case, only feasible practicable option available at large scale is defluoridation of water.

Figure 4: Crippling fluorosis

Normal

Questionable

Very mild

Mild

Moderate

Severe

Source: Fluoridation Forum Report 2002 (Page 126)

Figure 5: Dental fluorosis

2. Theory of Electrolytic Defluoridation

2.1. Defluoridation Process

There are several defluoridation processes that have been tested globally, such as adsorption, chemical precipitation, reverse osmosis, electro dialysisand the electrochemical method. The important defluoridation techniques for drinking water are considered as nalgonda technique (alum and lime) and prasanthi technology (activated alumina) in India. Although use of chemical coagulants is quite popular for water treatment but it’s less acceptable than other processes because it generates large volume of sludge, it’s costly and requires the hazardous waste characterization of metal hydroxides. If a new process can replace conventional chemical coagulation which is efficient and can be installed with little modifications to existing water treatment plants, then many problems caused by chemical coagulation would be solved. Electrocoagulation is a new electrochemical technique explored widely for wastewater treatment has also found application in defluoridation of drinking water and has been suggested as an alternative to conventional coagulation process.Therefore, an attempt can be made for defluoridation of groundwater using electrocoagulation to find feasibility of this treatment process for providing clean drinking water at low cost.

2.1.1. Different Defluoridation Methods

Fluoride in drinking water has been the subject of many publications and studies. Fluoride removal methods can be broadly divided into following categories:

- Chemical addition/precipitation
- Adsorption/ion exchange
- Membrane
- Electro coagulation/Electrochemical

2.2. Significance of the Study

Several methods are globally applied for defluoridation namely adsorption, chemical precipitation, electrodialysis and reverse osmosis which have their own limitations. Evaluating the potential of Electrocoagulation for defluoridation of ground water results in overcoming few drawbacks of conventional process as electrolytic defluoridation is efficient, cost effective, results in lower sludge generation and more importantly no external additive chemicals have to be added to aid coagulation.

Electro coagulation is a low cost process and efficient method for defluoridation which involves electrochemical production of destabilizing agents that bring about charge neutralization for pollutant removal. It was tested successfully for defluoridation using aluminum electrodes. Stainless steel was also successfully used for defluoridation. Based on the literature survey an attempt is made to closely study in detail the fluoride removal process in batch electrocoagulation reactor using different electrodes(Iron & aluminum) which are not attempted so far.

2.3. Objectives of the Study

The main objective of the present study isto evaluate the feasibility of electrocoagulation for defluoridation of ground water.

Specific objectives are as follows:

1. To review the literature for information and data on pollutant removal by electrocoagulationwith specific emphasis on fluoride removal by electrocoagulation.
2. To study and understand the fundamentals of electrocoagulation process
3. To design and construct batchelectrocoagulation reactor for defluoridation.
4. To study the effect of operating parameters such as:
    - Effect of pH
    - Effect of voltage
    - Effect of electrolysis duration
    - Effect of distance between the electrodes.
5. To study the efficiency of different electrodes (aluminum and iron).
6. Treatment of actual groundwater sample by electrocoagulation collected from Gojnur, Kalkeri, Bannikoppa and Mundargi of Gadag district.

2.4. Study Methodology

To begin with literature was reviewed for information and data on pollutant removal by electrocoagulation with specific emphasis on fluoride removal by electrocoagulation. Following study methodology wasadopted as shown in Figure 6

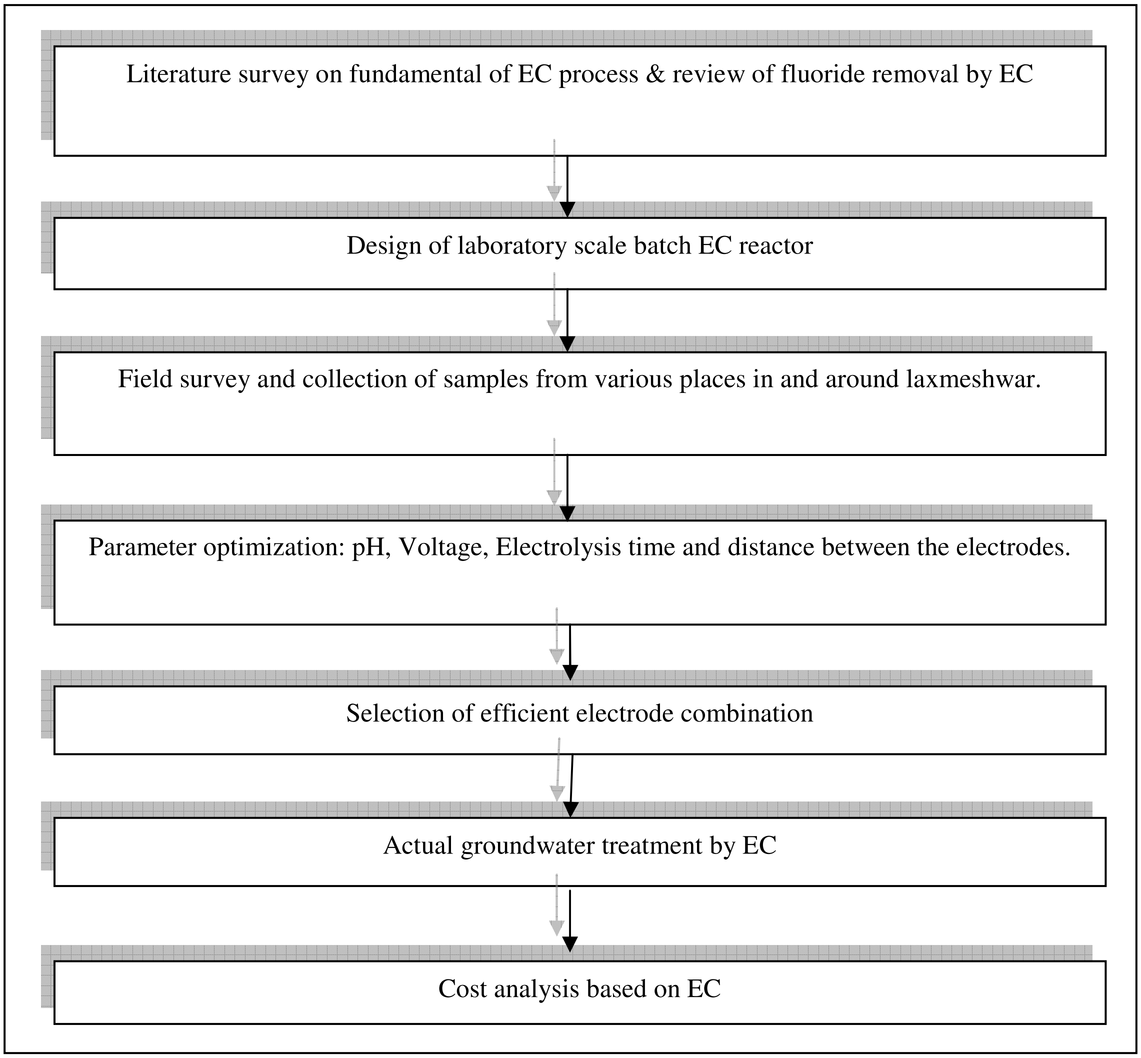


Figure 6: Study methodology

2.5. Electrocoagulation Process

Electro coagulation (EC) is process whereby metallic hydroxide flocs are created within the water/wastewater due to the action of soluble anodes (iron or aluminum). The anode material undergoes oxidation and hence various monomeric and polymeric metal hydrolyzed species are formed. These metal hydroxides remove organics from water by sweep coagulation and/or by aggregating with the colloidal particles present in the water to form bigger size flocs and ultimately get removed by settling. An electrocoagulation reactor consists of anode and cathode like a battery cell; metal plates of specific dimensions are used as electrodes and supplied with adequate direct current using power supply as shown in Figure 7

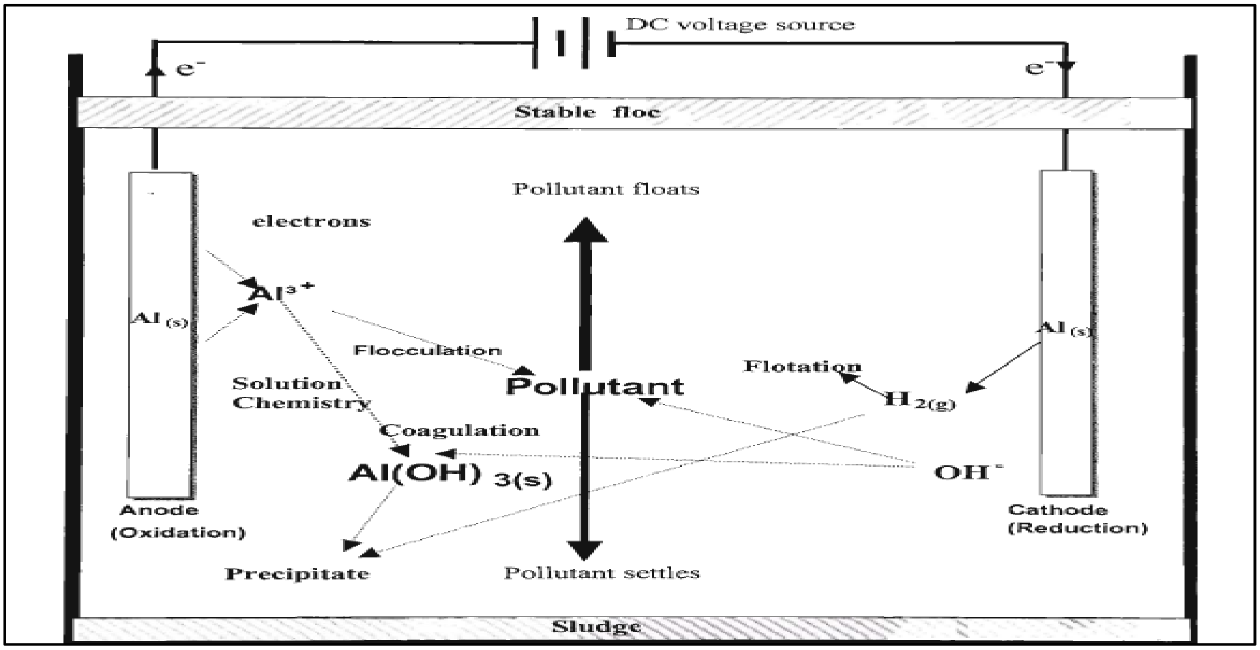


Figure 7: Processes occurring in an EC reactor

The EC technique combines three main interdependent processes; Electrochemistry, coagulation and hydrodynamics. In an EC process, the coagulating ions are produced in situ and it involves three successive stages:

1. Formation of coagulants due to electrical oxidation of anode.
2. Destabilization of pollutants and emulsion breaking. Destabilization mechanisms in this process include electrical double layer compression, adsorption and charge neutralization,and enmeshment in a precipitate and inter-particle bridging.
3. Combining of instable particles to form flocs.

If M is considered as anode, the following reactions will occur:

At the anode:

$M_{(S)} \rightarrow M^{n+}_{(aq)} + ne^-$

$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2\,(g)} + 4e^-$

At the cathode:

$M^{n+}_{(aq)} + ne^- \rightarrow M_{(S)}$

$2H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2OH^-$

Freshly formed amorphous $M(OH)_3$ has large surface areas that are beneficial for rapid adsorption of soluble organic compounds and trapping of colloidal particles. If iron or aluminium electrodes are used, the generated $Fe_{(aq)}^{3+}$ or $Al_{(aq)}^{3+\ ions}$ will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. For example, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric ions, $Fe(OH)_3$ and polymeric hydroxyl complexes, namely: $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$. Al^{3+}ions on hydrolysis may generate $Al(H_2O)_6^{3+}$,$Al(H_2O)_5\,OH^{2+}$, $Al(H_2O)_4\,OH^{2+}$ and the hydrolysis products may form many monomeric and polymeric species such as, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al(OH)^{4-}$, $Al_6(OH)_{15}^{3+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ over a wide pH range. These hydroxides/polyhydroxides/polyhydroxy metallic compounds have strong affinity for dispersed particles as well as counter ions to cause coagulation. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials. The hydroxides/polyhydroxides/polyhydroxy metallic compounds increase the elimination efficiency.

2.6. Set Up

A simple electrocoagulation set up includes only one anode and cathode. A pairs of anode and cathode electrodes are used which are connected to battery. One-liter sample of water is added to cell. Magnetic bar stirrer is placed at bottom of cell undergoes number of revolutions. Magnetic bar stirrer is used for homogenous mix.

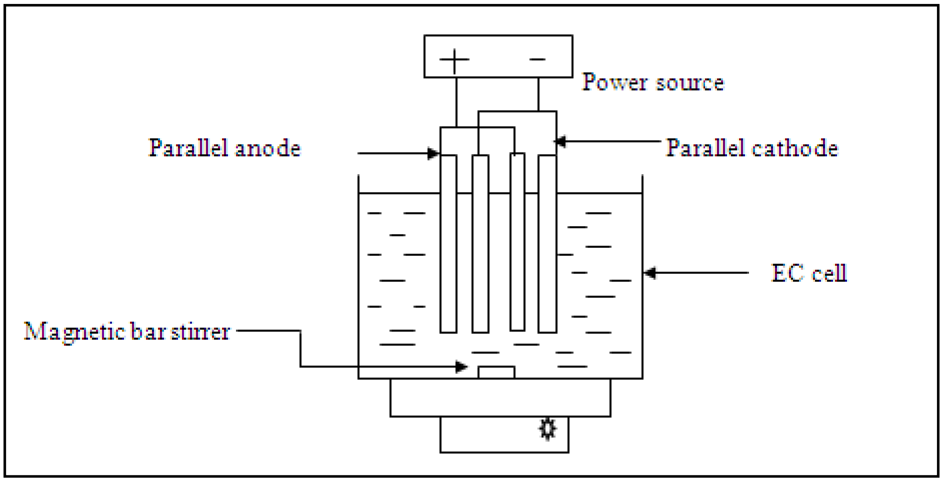


Figure 8: EC reactor

2.7. Electrode Material

Electrode material defines which electrochemical reactions take place in the EC system. Aluminum and iron electrodes have both been used successfully in EC systems. Aluminum dissolves in all cases as Al(III) whereas there is some controversyas to whether iron dissolves as Fe(II) or Fe(III). Most results indicate that iron dissolves as Fe(II) and is oxidized in bulk solution to Fe(III) if there are oxidants, such as oxygen, present in sufficient concentration and pH is alkaline. Fe(II) is a poor coagulant compared toFe(III) due to higher solubility of hydroxides and lower positive charge, which explains some poor results obtained when iron is used as a sacrificial electrode. Optimal material selection depends on the pollutants to be removed and the chemical properties of the electrolyte. In general, aluminum seems to be superior compared to iron in most cases when only the efficiency of the treatment is considered. However, it should be noted that aluminum is more expensive than iron.

Inert electrodes such as metal oxide coated titanium are used as cathodes in some constructions also platinum electrodes have been studies owing to its non- corrosive properties but the cost of such electrodes is very high. When water has significant amounts of calcium or magnesium ions, the inert cathode material is recommended. There are also some studies where combinations of aluminums and copper electrodes have been used and found to reasonably successful.

2.8. Applications of Electro coagulation Process

The Electrocoagulation process is a simple and efficient method for the treatment of water and wastewaters. In recent years, many investigations have been especially focused on the use of EC owing to the increase in environmental restrictions on effluent. The EC has been applied to treat water containing foodstuff waste, oil waste, dyes, suspended particles, chemical and mechanical polishing waste, and organic matters from landfill leachates, defluoridation of water, synthetic detergent effluents, mine wastes and heavy metal containing solution. The advantages of the electro coagulation technique can be listed as follows:

1. No need to add chemicals, thus preventing secondary pollution and reduction of amount of generated sludge needing disposal.
2. Low reaction time and thus small size of reactor.
3. Simple operation and maintenance.
4. Flocs formed settle easily and are readily dewater able.
5. The salt content of the treated water does not increase appreciably as in case of chemical treatment.
6. The EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

There are also various disadvantages of EC process:

1. The use of electricity may be expensive in many places.
2. An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit.
3. High conductivity of the water/ wastewater suspension is required for effective flow of current.

Figure 9: Sample Collection

3. Literature Review

Most commonly employed defluoridation techniques are activated alumina, Nalgonda technique, reverse osmosis and ion exchange. Brief discussion about these processes and relative literature is discussed below.

Sl.No.	Reference	Defluoridation method	Results	Advantages	Disadvantages	Relative cost
1	Solsona (1985)	Nalgonda technique (Alum+lime)	88 % fluoride removal efficiency	Established Process	Higher chemical dose and sludge production	Medium-high
2	Susheela (1992)	Adsorption by activated alumina	More than 90% fluoride removal at pH range 5-8	Effective method and well established	Regeneration of AA by caustic soda and acid solution	Medium – high
3	Toyoda &Taira (2000)	Addition of CaF_2 and Al salt	Up to 85-90% removal efficiency	Low cost	Higher sludge generation	Medium
4	Hiedweiller (2002)	Electrodialysis and Reverse Osmosis	Greater than 98% fluoride ion rejection in both the systems	Higher efficiency	High cost, skilled operators required	High
5	Dzung (2004)	Activated alumina	More than 95% fluoride removal at neutral pH 7	Effective method and well established	Regeneration of AA by caustic soda and acid	Medium – high
6	Dahi (2006)	Contact precipitation with calcium and phosphate	80% fluoride removal with contact period of 3 hours	Relatively cheaper	Higher sludge generation	Medium-low
7	Wei Yaping (2006),	Coconut shell as adsorbent	89 % fluoride removal	Low cost	large amount of adsorbent is needed	Low
8	Maria*et al.*, (2007)	Agricultural refuse as adsorbent	80 % fluoride removal at acidic pH	Economical	Lower fluoride removal efficiency	Low
9	Theodora (2009)	Activated alumina	Greater than 90 % removal efficiency	Effective method and well established	Regeneration of AA by caustic soda and acid solution	Medium – high

Table 4: Summary of different defluoridation methods

3.1. Defluoridation by Electrocoagulation

Owing to the disadvantages of conventional defluoridation processes, researchers have explored various other alternatives one such method is electrocoagulation which is known to be cost effective, less time consuming and results in lesser sludge generation. Both batch and continuous study has been carried out so far by various researchers which are discussed below.

3.1.1. Batch EC Studies

- Ming *et al.,* (1987), “Elimination of excess fluoride in potable water with coacervation by electrolysis using aluminum anode” [30] applied the electrocoagulation process for to remove excess fluoride from potable water. Different parameters were investigated in this study including pH, current density and stirring rate on defluoridation. It was found that fluoride can be reduced from 5 to 1 mg/l at a pH range of 5.5-7. The experimental results showed that when the speed of stirring is increased the defluoridation efficiency decreases. This is because, micro bubble cut off the adsorption layer between the fluoride and colloids and the shearing stress will be produced on the colloidal clots. In summary the results indicated that the electrocoagulation method is an efficient fluoride treatment for potable water. However, the mechanism of fluoride removal was not considered by the authors in the paper.
- Drondia and Drako(1994),“Electrochemical technology of fluorine removal from underground and waste waters” [31] studied the removal of fluorine from groundwater’s using electrochemical technology consisting of two stages. In the first stage calcium and iron solutions were added and the sediment was separated. In the second stage electrocoagulation and electrofloatation process was applied after acidification. Different electrode material like aluminum, insoluble anode (titanium coated with manganese oxide) and soluble anode like stainless steel was used. The experimental results showed that defluoridation is efficient for a pH ranging from 6.35-6.65 where in initial fluoride concentration decreased from 14 to 1 mg/l. In this research effect of important parameters including current density and electrolysis time were not considered.
- Mameri *et al.,*(1998), “Defluoridation of Sahara water of North Africa by Electrocoagulation process using bipolar aluminum electrodes” [32] evaluated the efficiency of Electrocoagulation process for Sahara waters with initial fluoride concentrations 10mg/l. The influence of some experimental parameters including electrolysis time, initial concentration of fluoride, distance between electrodes, current density, electrode area to cell volume ratio. The results showed 90% defluoridation efficiency at pH 6.5-7.0 in bipolar configuration using aluminum electrodes.
- Hu *et al.,* (2003), “Effects of co-existing anions on fluoride removal in Electrocoagulation process using aluminum electrodes” [33] studied defluoridation in a laboratory scale batch EC reactor and investigated the effect of some anions including Cl^-, NO_3^- and SO_4^{2-}. Defluoridation in solutions containing F^-, SO_4^{2-} and Cl^- ions was higher because the lypotropic series of anions for Al^{3+} are $F^- > SO_4^{2-} >> Cl^- > NO_3^-$. The experimental results showed that defluoridation did not change very much with concentrations of Cl^- and NO_3^- but decreased when the concentration of sulphate ions is increased. It may be due to competition effect which increases the concentration of sulphate and other anions which have strong affinity with Al^{3+}. Further research is needed to yield more complete understanding of the mechanism of the EC process. The effect of pH was not considered by the authors.
- Hu *et al.,* (2005), “Removal of fluoride from semiconductor waste water by electrocoagulation-floatation” [34] studied defluoridation in a bipolar batch electrocoagulation reactor. Experiments with were carried out using seven aluminum electrodes. An anodic surfactant SDS (sodium dodecyl sulphate) was applied to improve the flotation performance of the ECF process to remove the dissolved fluoride ions and CaF_2 particles. The raw water sample was first treated by conventional precipitation using calcium salts and the removed by proposed ECF process. The dissolved fluoride ions after calcium precipitation were effectively removed (more than 90%) in EC process.
- Edris *et al*., (2012), “Application of electrocoagulation process using iron and aluminum electrodes for fluoride removal from aqueous environment,”[35] carried out study for defluoridation by electrocoagulation in a batch reactor using aluminum electrodes in bipolar combination with initial fluoride concentration of 1,5 and 10 mg/l. The results obtained with synthetic fluoride samples revealed that most effective fluoride removal was observed at 40 V and pH 7. Further they studied fluoride removal using aluminum and iron in bipolar combination and it was concluded that the fluoride removal efficiency is much higher using aluminum/ aluminum electrodes rather than combination.
- Mine tastaban *et al.,* (2013), “Fluoride removal by electrocoagulation process using aluminum electrodes at acidic pH range,” [36] evaluated the efficiency of EC process for removal of fluoride using aluminum electrodes in bipolar combination. They mainly concentrated on removal of fluoride at acidic pH range of 4 to 5. They also varied the current density in the range of 1-10 A/m^2 and highest removal efficiency was obtained at 10 A/m^2. They concluded that fluoride removal rate increased at acidic pH range and also lower sludge production was observed.
- Umran Tezcan *et. al.,* (2013), “Fluoride removal from water and waste water with a batch cylindrical electrode using electrocoagulation”, [37] developed a unique design for defluoridation of water consisting of a rotating impeller aluminum cathode and a cylindrical aluminum anode. They studied various operating parameters like ph., current density, electrolyte dosage, various electrode materials (Iron and aluminum). Fluoride concentration was reduced from the initial value of 5 to 0.12 mg/l with a removal efficiency of 97.6 % after 30 minutes of treatment at current density 2 mA/cm^2, pH of 6 and in presence of 0.01 M $NaSO_4$.
- Sinha R. (2012), “Fluoride removal by continuous flow electrocoagulation reactor from ground water of shivdaspura,” [38] evaluated efficiency of EC process using a control sample and ground water sample from Rajasthan.They studied fluoride removal in various range of 5-25 ppm at current density of 37.52 A/m^2. They studied various parameters like flow rate, current density and fluoride uptake capacity (FUC). Optimum results were obtained at 25 A/m^2, flow rate of 150 ml/ min. The defluoridation efficiency of 79% and 68 % was achieved for control and groundwater sample respectively.

- Yang and Dluhy(2002), “Electrochemical process for clean technology”, [39] studied electrochemical defluoridation by aluminum sorbent in a parallel plate electrochemical reactor by anodic dissolution of aluminum electrodes in a dilute sodium chloride (NaCl) aqueous solution. A trace amount of chloride ions in the solution is enough to penetrate the oxide film on aluminum electrodes for dissolving to continue. Tap water was used as experimental design parameters for defluoridation. Based on the aluminum hydroxide solubility diagram, the principle soluble specie is the monomeric ion of $Al(OH)^-_4$ when pH>8. At pH<6 the dominant soluble species are cationic monomers such as $Al^{3+.}$ The experimental result indicated that the freshly generated Al-sorbent is able to reduce fluoride from 16 to 12 mg/L in 6 min. However, the effluent from reactor needs pH adjustment. The review showed that measurement of fluoride concentration was done by SPADNS method. A buffer must be added to the samples to prevent the interference of Al^{3+} ions, which was not considered by the authors.
- Shen *et al.*, (2003), “Electrochemical method to remove fluorine from drinking water,” [40] studied the combined electrocoagulation and electrofloatation for defluoridation. In this combined process the EC unit was used to produce aluminum hydroxide flocs. The EF unit was used to separate the flocs formed from water, by floating them to the surface of the cell. The research investigated that aluminum hydroxide floc is believed to strongly adsorb fluoride ions. The experimental results depicted that residual fluoride concentration decreases from 25 mg/l to 1 mg/l with increase in charge loading up to 6 Faradays/m^3at pH 6 with an ET of 32 minutes.
- Khazanchi I *et al.*, (2012), “Effective removal of fluoride from groundwater using electrocoagulation,” [41]studied the defluoridation process in a continuous mode EC reactor in both single and two stage using control sample and ground water sample from Shivadaspura, Rajasthan. The study was carried out using aluminum electrodes to study the effect of current density, flow rate, stages and residual aluminum. 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 (0.08-0.1 ppm), and hence better quality of water is provided. Their experimental results depicted that EC offers better quality of water when compared with other methods of defluoridation like Activated Alumina (AA) process and Nalgonda technique.
- Subhash Andey *et al.*, (2013), “Performance Evaluation of Solar Power Based Electrolytic Defluoridation plants in India”, [42] at NEERI, Nagpur Solar power based electrolytic defluoridation demonstration units were successfully installed at 4 places in India in the fluoride affected villages during the period of 2008 to 2011. Performance evaluation of these plants is being undertaken. It was found that EDF plants produce the treated water with fluoride less than 1 mg/l and 90 - 99% reduction in bacterial load from the raw water with the fluoride in the range 2 – 5 mg/L and total coliform and fecal coliform counts in the range 120–630 CFU/100 ml and 70-100 CFU/100 ml respectively in raw water. Reduction in hardness and nitrate is also observed in treated water. The recurring cost for the treatment worked out for electrolytic defluoridation demonstration plant is $ 0.4 / m3 of treated water which is much more less than the treatment cost by any other defluoridation system available in the market. The capital cost of the plant is about $ 12000 that is 7,80,000 in Indian rupees. Electrolytic defluoridation technique is easy tooperate with least maintenance problem. It increases thepalatability of treated water and thus acceptability of theconsumers for defluoridated water. From the whole year evaluation study, it was observed that the solar electrolytic defluoridation plants are working satisfactorily even in critical rainy season when the sunlight is not bright due to cloudy sky. EDF plants produce the treated water with fluoride less than 1 mg/l and 90-99% reduction in bacterial load.

Sl.No.	Reference	Pollutants	Current density	Cell voltage (V)	Electrode material	Efficiency (%)	Reactor type
1	Ming et al. (1987)	Fluoride	14A/m^2	-	Al/Al monopolar	80-88	Batch
2	Drondia and Drako (1994)	Fluoride	-	-	Al electrodes for EC and stainless steel titanium for EF	85-90	Batch
3	Mameri et al. (1998)	Fluoride	3.12 -289 A/m^2	1-2.4	Al/Al bipolar	70-92	Batch
4	Hu *et al.*, (2003)	Fluoride	0.4 A	-	Al/Al bipolar	-	Batch
5	Hu *et al.*, (2005 a)	Fluoride	0.6 A	35	Al/Al bipolar	20-100	Batch
6	Edris *et al.*, (2012)	Fluoride 1,5 & 10 mg/L	-	10-40	Al/Al bipolar	92	Batch
8	Mine Tastaban *et al.*,	Fluoride 5 mg/L	1-10A/m^2	-	Al/Al bipolar	81	Batch

	(2013)						
9	Umran Tezcan *et al.,* (2013)	Fluoride 5 mg/L	0.5-2 A/m^2	-	Al/Al cylindrical	97.6	Batch
10	Sinha R. (2012)	Fluoride 5-25 mg/L	37.52A/m^2	20	Al/Al monopolar	98	Continuous
11	Yang and Dluhy (2002)	Fluoride	1 A	14	Al/Al monopolar	55-88	Continuous
12	Shen *et al.*, (2003)	Fluoride	0.5 F/m^3	-	Al/Al bipolar	67-90	Continuous
13	Khazanchi I. *et al.,* (2012)	Fluoride	25-37.5 A/m^2	-	Al/Al monopolar	98	Continuous
14	Suhash Andey *et al*., (2013)	Fluoride, Nitrate, Hardness, Total coliform	19.4-20 A	-	Al/Al bipolar	85-90	Continuous

Table 5: Summary of Electrocoagulation processes applied for defluoridation.

4. Materials and Methods

Materials and methodology adopted to carry-out the present study is discussed in depth in this chapter. The issues discussed include:Water samples considered, Electrodes considered, Parameters considered, Variables considered, Analysis of parameters, Experimental set-up, Procedure adopted, Compilation of result.

4.1. Water Samples Considered

Water samples considered for the present study is ground water samples of various locations viz, Gojnur, Bannikoppa, Mundaragi and Kalakeri locations in Gadag district.

4.2. Lab Scale EC Reactor Design

Literature reviewed does not disclose any regular approach to EC reactor design and operation. A laboratory batchEC reactor was designedand constructed for coagulation.

Sl.No.	Reactor Components	Details
1	Number of electrodes	2 pair
2	Electrode used	Aluminium and Iron
3	Working volume	1000 ml
4	Electrode dimensions	10cm×4cm×0.2cm
5	Distance between electrodes	3cm and 6cm

Table 6: Details of reactor and electrode dimension

The schematic and photographic representations of the experimental set up are shown in the Fig. 10 and Fig. 11.

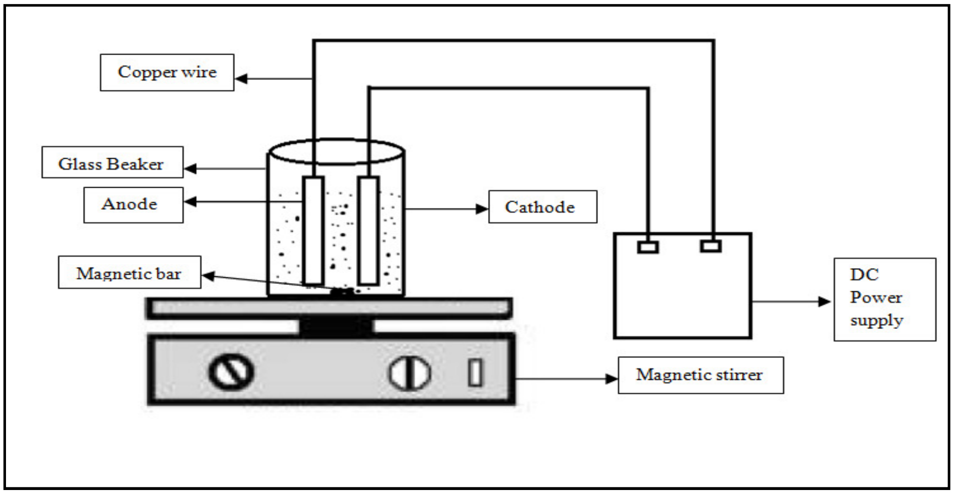


Figure 10: the experimental set up

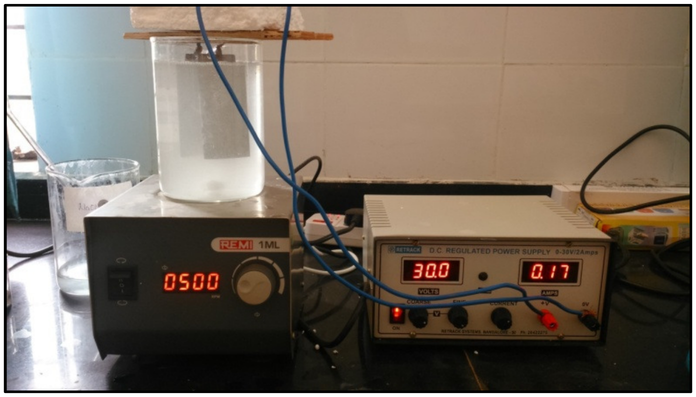


Figure 11: Pictorial View of Experimental Set-Up

4.3.Methodology

Sl.No.	Parameter	Range
1	Initial fluoride concentration	3-7 ppm
2	Electrolysis time(ET),	Up to 10-15minutes
3	pH	4,8
4	Voltage	15-30V
5	Distance between the electrodes	3-6cms

Table 7: Parameter optimization specification

Towards the end of the chapter the optimized parameters are evaluated which will ensure effective and efficient fluoride removal, further the sludge generated at different pH and voltages is quantified along with change in weights of electrodes. Based on the optimized parameters efficiency of EC process in different electrode combinations was studied. Further batch study was carried out using optimum parameters and actual groundwater sample was treated using EC process and finally the economics of the process for treatment of 1000ml of water is evaluated.

The initial study was carried out on samples of varying fluoride range. Initial pH, conductivity, acidity, alkalinity and total hardness of the samples were determined. Experimental studies were conducted to optimize various parameters such as pH, electrolysis duration, voltage and distance between the electrodes.

The space between the electrodes was maintained 3cm and 6cm in all the experiments. In each run the voltage was varied to a desired value of 15V and 30V. The volume of solution in each batch experiment was 1000ml. To ensure homogenous mixing of the reactor content, magnetic stirring at 500 rpm was employed for all run. All the analyses of the water were conducted as per standard analytical techniques. Before and after electrolysis pH was measured using standard pH meter, conductivity by conductivity meter and fluoride by fluoride meter.

Before each run electrodes were washed and cleansed by HCl solution. Electrolysis wereperformed and samples were collected from the reactor at every 10 minutes and 15minutes interval. Post electrolysis these samples were immediately filtered with filter paper and the fluoride content was measured using fluoride meter. The sacrificial weight of electrode was calculated by measuring its weight before and after the process.

4.4.Procedures for the Analysis

The procedure followed for the analysis of various quality parameters were as per 'standard methods' for examination of water.

4.4.1. pH

pH is measured by a pH meter using a glass electrode which generates a potential varying linearly with the pH of the solution in which it is immersed. A calomel or Ag/AgCl/KCl reference electrode was usually located around the glass electrode stem for sample operation

Procedure:

1. Calibrate the electrode with two standard buffer solutions of pH 4.0 and 9.2.
2. The sample temperature is determined at the same time and is entered into the meter to allow for a temperature correction.
3. Rinse the electrode thoroughly with de-ionized distilled water and carefully wipe with a tissue paper.
4. Dip the electrodes into the sample solution, swirl the solution and wait upto one minute for steady reading. A pHmeter reading within ±0.1 pH unit will be adequate for such work.
5. The reading is taken after the indicated value remains constant for about a minute.

4.4.2. Fluoride

Fluoride is a chemical element that has shown to cause significant effects on human health, through drinking water. Different forms of Fluoride exposure are of important and have shown to affect the body's Fluoride content and thus increasing the risk of Fluoride-prone diseases. Fluoride has beneficial effect on teeth at low concentration of 0.5mg/l by preventing and reducing the risk of tooth decay. Concentration less than 0.5 mg/l of Fluoride however has shown to intensify the risk of tooth decay. Fluoride can also be quite detrimental at higher concentration exceeding 1.5 to 2 mg/l of water. High concentration of Fluoride poses a risk of dental fluorosis as well as skeletal fluorosis.

Procedure:
1. Fluoride was tested byfluoride analyser. Set-up the instrument according to the user manual.
2. Calibrate the instrument by using the 2 standard solutions (1 ppm & 10 ppm).
3. Dip the electrode in distilled water & clean it with filter paper.
4. Take 20ml of water sample in a container.
5. Add 20ml of TISAB-II solution shake well & dip the electrode in the solution and read Fluoride concentration directly from the instrument.

4.4.3. Conductivity

Electrolytic conductivity is a measure of the ability of a solution to carry electric current. Specific conductance 'K' is defined as the reciprocal of resistance in ohms.

Procedure:
1. Power on the instrument.
2. Take a clean conductivity cell and connect it to the terminals on the instrument. Take the solution of known standard in a clean beaker, place the cell in the beaker and ensure that the platinum plates of the cell are completely immersed. Ensure there is no air bubble between the plates in the conductivity cell.
3. Select the appropriate conductance range and cell constant.
4. Select 'Cal' position of CAL/MEANS switch.
5. Keep select 25^0 C on the temperature scale and adjust the calibrate knob such that the digital display reads 1000 on the Digital LED panel meter, ignoring the location of the decimal point.
6. Set the temperature of the standard solution on the temperature dial. Select measure position of CAL/MEANS switch.
7. Set the conductivity value of the standard solution by adjusting the cell adjust control at the rear of the instrument with the help of a screw driver.
8. Now thoroughly clean the cell with distilled water and dip the cell in the solution whose conductivity has to be measured and set the temperature of the solution on the temperature scale.
9. Read the conductivity of the solution directly at 25^0 C.
10. If the display reads over range (by displaying 1 on the left hand side of the digital display) select the appropriate higher range and repeat steps 4 and 5.
11. Set the temperature of the solution on the temperature scale. Select measure position of the CAL/MEANS switch and read the conductivity of the solution directly referred at 25^0C.

4.4.4. Total hardness

Hardness of water is not a specific constituent but it is variable complex mixture of cat ions. Principle Hardness causing ions are calcium and magnesium. However, the iron, strontium, barium and manganese also contribute to Hardness. The degree of Hardness of drinking water has been classified in terms of magnesium and equivalent of CaCO3 concentration as follows.
Soft: 0-60 mg/L
Medium: 60- 120 mg/L
Hard: 120- 180 mg/L
Very hard: > 180 mg/L as CaCO3
Magnesium concentrations of less than 50mg/L are desirable in potable waters.Although many public health problems arise if concentration exceeds 50 mg/L. Infact the water is apparently beneficial to the human cardiovascular system.

Procedure:
1. Take 25 ml of sample in a conical flask.
2. Add 0.5 ml of buffer solution (ammonia buffer).
3. Add a pinch of Erichrome Black-T indicator and titrate with standard EDTA solution till wine red color changes to blue note down the reading.

Figure 12: Conducting Initial Tests

Figure 13: Preparation of Samples

Figure 14: Determining Final Fluoride Content in Water

5. Results and Discussion

Results of experimentation carried out under varied conditions of experimentation are tabulated and are represented by graphs and are documented in this chapter. Based on the results inferences have been drawn.

The discussions are made in further sections and subsection emphasizing variables of experimentation on fiuoride removal efficiency.

Results of experimentation are summarized in tables 4.1 to 4.16. Accordingly, the results represented in linear and bar charts (Figure10 to 14).

5.1. Effect of Contact Time

Experiments were carried out to evaluate the influence of contact time on removal efficiency. Three contact times viz,. 10 and15 min were considered for study.

Based on the observations the following inferences have been drawn.

- Linear and direct relationship between the fluoride removal efficiency and contact time has been observed. Maximum removal efficiency for steady contact time of 15 min and minimum removal efficiency for steady contact time of 10 min has been recorded. Same trends have been observed for all conditions of experimentation carried out.

5.2. Effect of Electrode Distance

Two electrode distances viz,. 3 and 6 cm were considered for the experimentation and observe the effect of electrode distance on fluoride removal efficiency. From these observations the following inferences have been drawn.

- The maximum fluoride removal efficiency has been observed at electrode distance of 6 cm compare to electrode distance of 3 cm. In all conditions of experimentation, same trend have been observed. Thus the direct relationship was found to exist between electrode distance and removal efficiency.

5.3. Effect of Voltage

The effect of voltage on fluoride removal efficiency has been studied in the present experiment. 15 and 30 V was considered for the study.

The following inferences were made based on the observation of the experimentation

- The linear increase in fluoride removal efficiency with increase in voltage has been recorded.
- Minimum and maximum removal efficiency has been observed at voltage of 15V and 30V respectively.

- The similar trends have been observed from the observations of all conditions of experimentation.

5.4. Effect of pH

pH viz,. 4 and 8.0 were considered for the study to evaluate the effect of pH on the fluoride removal efficiency.
Based on the observations, the following inferences were drawn.

- pH has the indirect influence on the fluoride removal efficiency.
- The removal efficiency for the pH 4 is significantly more than that of pH 8. Same trend was continued in all the conditions of experimentation.

5.5. Effect of type of electrodes

- To evaluate the influence of type of electrodes on fluoride removal efficiency, the experiments were carried out using two electrodes viz, Iron and aluminium. The relationship between type of electrodes and fluoride removal efficiency has been studied from the observations.

Based on the observation, following inference has been drawn.

- Aluminium electrodes have more significant effect on fluoride removal efficiency and iron electrodes have least effect on fluoride removal efficiency.

Sl No	**Distance between electrodes**	**Contact time (min)**	**Voltage (Volt)**	**Final pH**	**Conductivity (ms)**	**Hardness mg/l**	**Final fluoride**	**Efficiency in %**
1	3	10	15	4.44	2.93	142	0.94	76.44
2	3	15	15	4.03	2.81	147	0.87	78.19
3	3	10	30	4.13	2.88	145	0.79	82.20
4	3	15	30	4.33	2.76	144	0.63	84.21
5	6	10	15	4.12	2.59	132	0.83	79.19
6	6	15	15	4.16	2.63	138	0.69	82.70
7	6	10	30	4.20	2.55	136	0.66	83.45
8	6	15	30	4.38	2.71	135	0.51	87.21

Table 8: Gojnur sample
pH-4, Initial Fluoride-3.99, Electrode Used-Iron

Sl No	**Distance between electrodes**	**Contact time (min)**	**Voltage (Volt)**	**Final pH**	**Conductivity (ms)**	**Hardness mg/l**	**Final fluoride**	**Efficiency in %**
1	3	10	15	4.50	2.59	137	0.85	78.69
2	3	15	15	4.08	2.63	141	0.80	79.94
3	3	10	30	4.16	2.55	142	0.70	82.45
4	3	15	30	4.42	2.71	139	0.63	84.21
5	6	10	15	4.12	2.93	132	0.62	84.46
6	6	15	15	4.18	2.81	136	0.45	88.72
7	6	10	30	4.19	2.88	137	0.42	89.56
8	6	15	30	4.42	2.76	139	0.25	93.73

Table 9: Gojnur sample
pH-4, Initial Fluoride-3.99, Electrode Used-Aluminium.

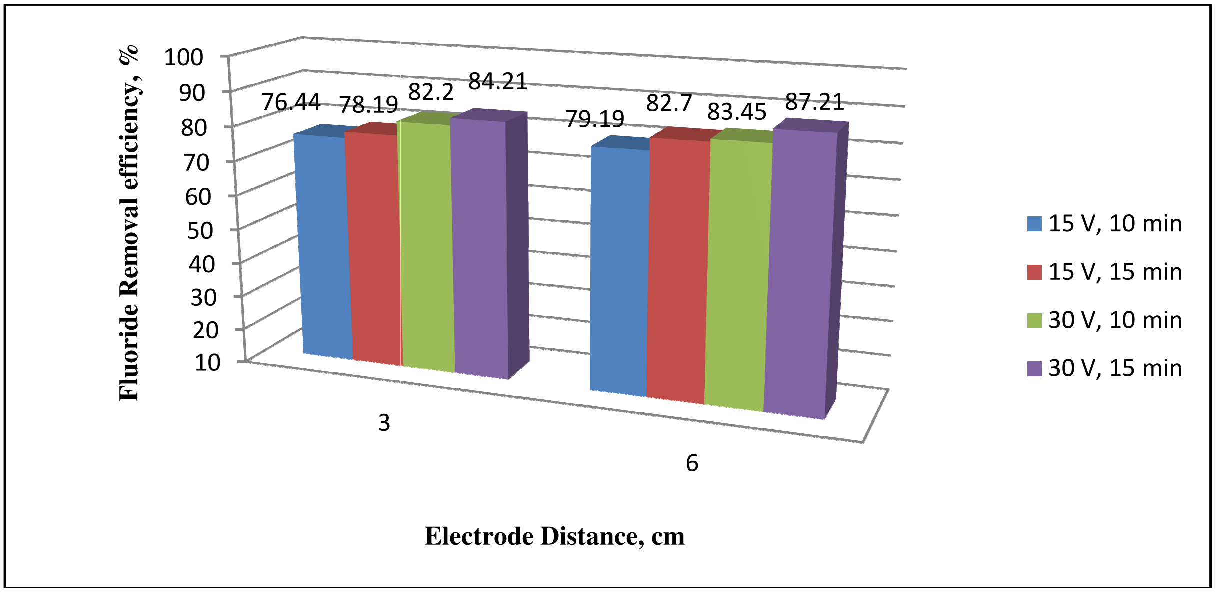


Figure 15: Fluoride Removal Efficiency
(pH-4, Initial Fluoride-3.99, Electrode Used-Iron)

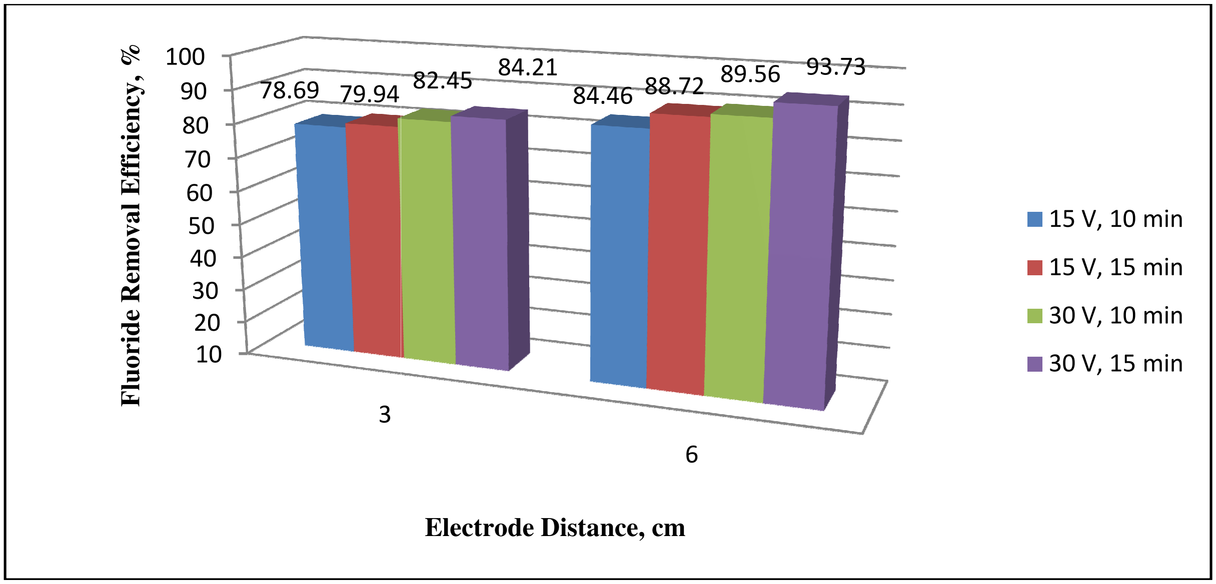


Figure 16:Fluoride Removal Efficiency
(pH-4, Initial Fluoride-3.99, Electrode Used-Aluminium)

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	8.10	1.48	136	1.21	69.66
2	3	15	15	7.90	1.52	137	1.19	70.16
3	3	10	30	8.38	1.39	139	1.07	73.18
4	3	15	30	8.10	1.45	141	0.97	75.61
5	6	10	15	8.29	1.38	142	1.02	74.28
6	6	15	15	8.20	1.41	139	0.87	78.16
7	6	10	30	8.05	1.44	132	0.82	79.28
8	6	15	30	8.31	1.36	137	0.71	82.18

Table 10: Gojnur sample
pH-8, Initial Fluoride-3.99, Electrode Used-Iron

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	8.07	1.48	152	0.83	79.12
2	3	15	15	7.80	1.52	148	0.85	78.69
3	3	10	30	8.48	1.39	153	0.75	81.2
4	3	15	30	8.04	1.45	164	0.70	82.45
5	6	10	15	8.19	1.48	172	0.87	78.19
6	6	15	15	8.18	1.52	164	0.75	81.2
7	6	10	30	8.07	1.39	152	0.63	84.21
8	6	15	30	8.33	1.45	166	0.49	87.71

Table 11: Gojnur sample
pH-8, Initial Fluoride-3.99, Electrode Used-Aluminium

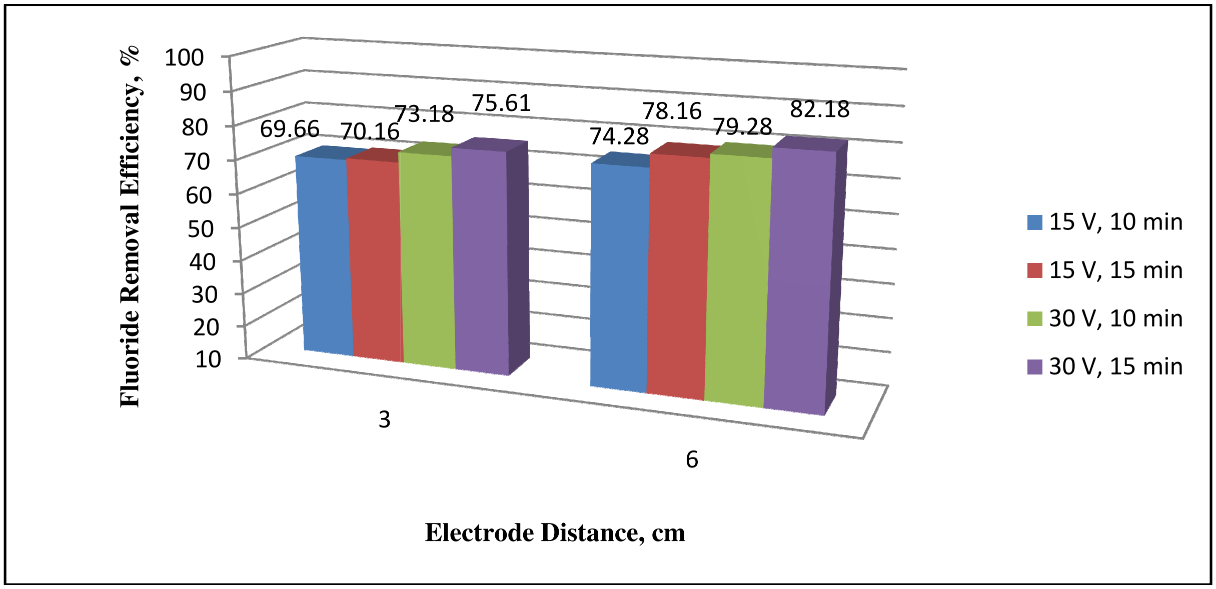


Figure 17: Fluoride Removal Efficiency
(pH-8, Initial Fluoride-3.99, Electrode Used-Iron)

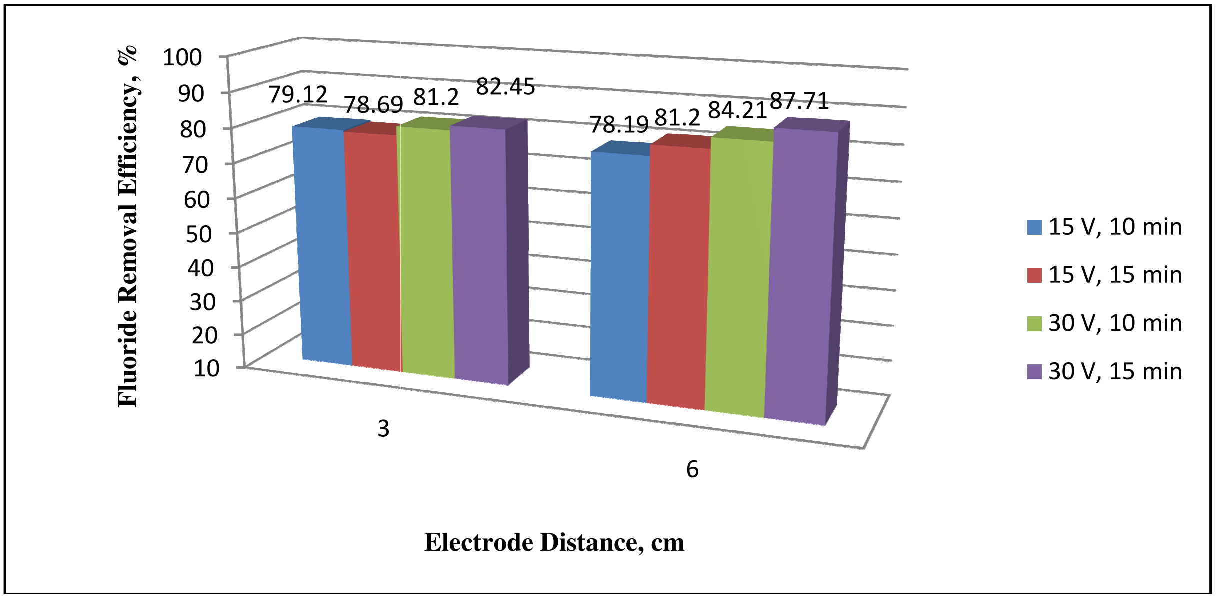


Figure 18: Fluoride Removal Efficiency
(pH-8, Initial Fluoride-3.99, Electrode Used-Aluminium)

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	5.60	3.52	130	1.07	70.33
2	3	15	15	5.02	3.81	137	0.95	73.82
3	3	10	30	5.15	3.66	116	0.87	75.86
4	3	15	30	5.48	3.54	120	0.83	77.13
5	6	10	15	5.05	3.45	134	0.80	77.96
6	6	15	15	5.19	3.66	150	0.74	79.61
7	6	10	30	5.21	3.57	154	0.70	80.71
8	6	15	30	5.52	3.64	145	0.63	82.64

Table 12: Bannikoppa sample
pH-4, Initial Fluoride-3.63, Electrode Used-Iron

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	5.68	3.52	135	0.76	79.06
2	3	15	15	5.01	3.81	143	0.66	81.81
3	3	10	30	5.18	3.66	112	0.61	83.19
4	3	15	30	5.38	3.54	123	0.52	85.67
5	6	10	15	5.10	3.66	145	0.56	84.32
6	6	15	15	5.18	3.57	149	0.50	86.22
7	6	10	30	5.20	3.64	154	0.40	88.98
8	6	15	30	5.42	3.66	132	0.35	90.35

Table 13: Bannikoppa sample
pH-4, Initial Fluoride-3.63, Electrode Used-Aluminium

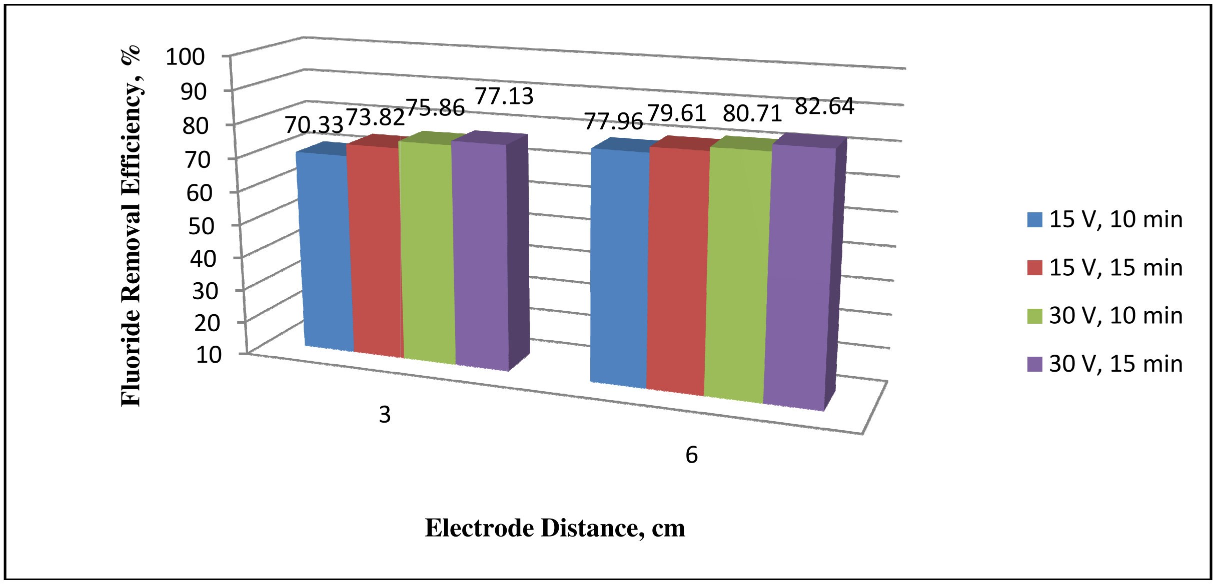


Figure 19: Fluoride Removal Efficiency
(pH-4, Initial Fluoride-3.63, Electrode Used-Iron)

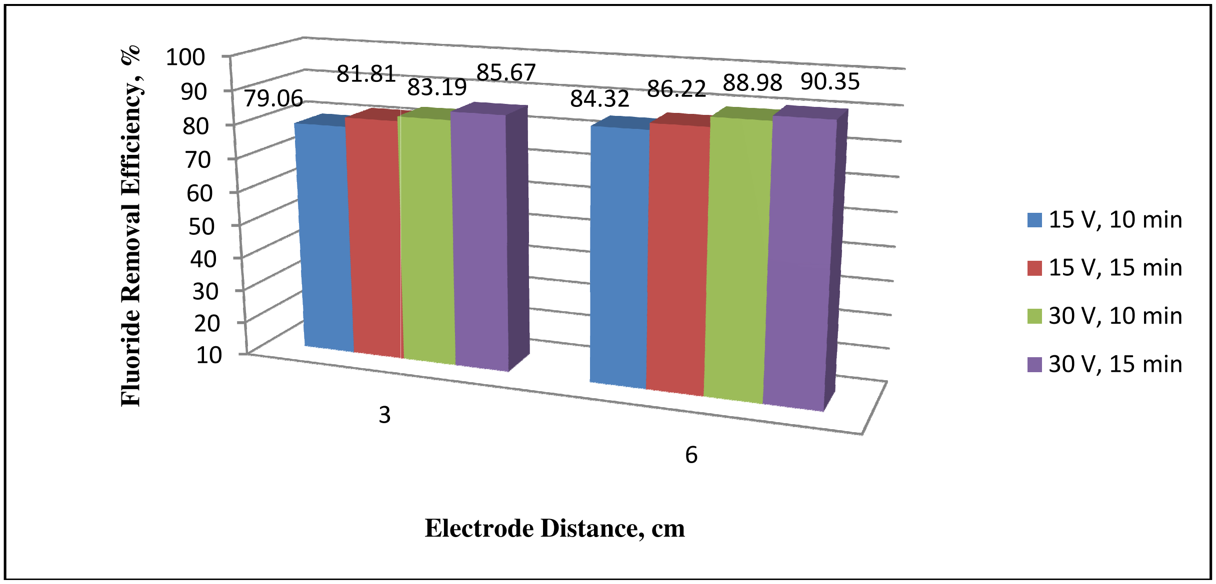


Figure 20:Fluoride Removal Efficiency
(pH-4, Initial Fluoride-3.63, Electrode Used-Aluminium)

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	9.10	2.56	123	1.03	71.62
2	3	15	15	8.60	2.38	114	0.97	73.27
3	3	10	30	9.30	2.55	121	0.93	74.38
4	3	15	30	9.18	2.63	132	0.86	76.30
5	6	10	15	9.22	2.71	142	0.90	75.20
6	6	15	15	9.19	2.56	152	0.81	77.68
7	6	10	30	9.05	2.57	114	0.73	79.88
8	6	15	30	9.45	2.64	134	0.71	80.44

Table 14; Bannikoppa sample
pH-8, Initial Fluoride-3.63, Electrode Used-Iron

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	9.01	2.56	155	0.85	76.58
2	3	15	15	8.80	2.57	145	0.77	78.78
3	3	10	30	9.48	2.64	123	0.73	79.88
4	3	15	30	9.12	2.56	143	0.66	81.81
5	6	10	15	9.19	2.38	132	0.72	80.16
6	6	15	15	9.16	2.55	123	0.64	82.36
7	6	10	30	9.02	2.63	134	0.60	83.47
8	6	15	30	9.30	2.71	123	0.52	85.67

Table 15: Bannikoppa sample
pH-8, Initial Fluoride-3.63, Electrode Used-Aluminium

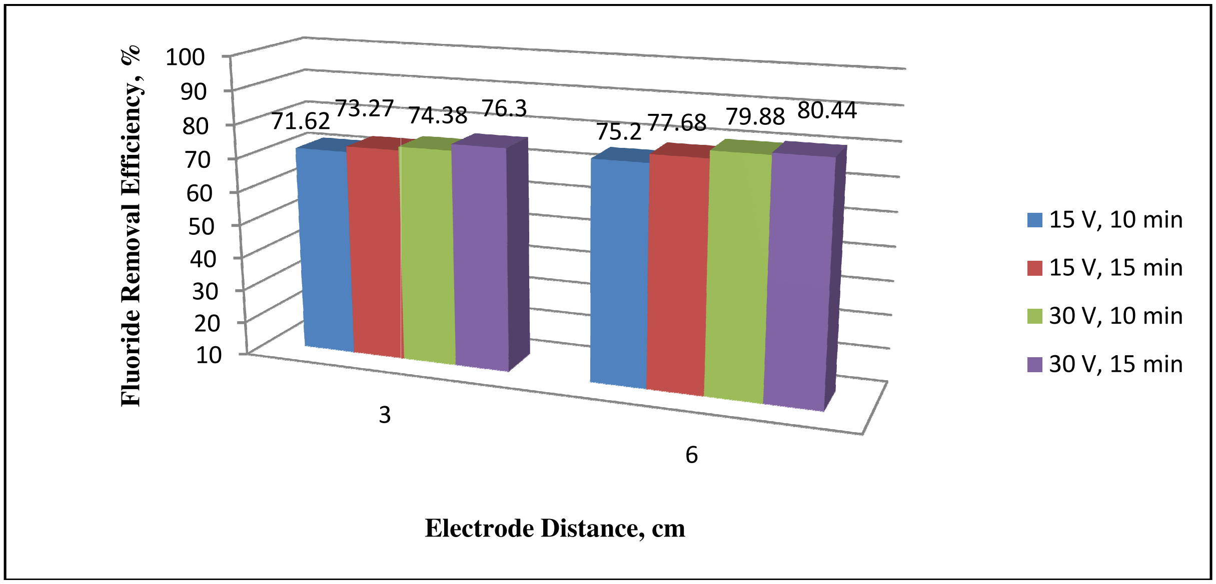


Figure 21: Fluoride Removal Efficiency
(pH-8, Initial Fluoride-3.63, Electrode Used-Iron)

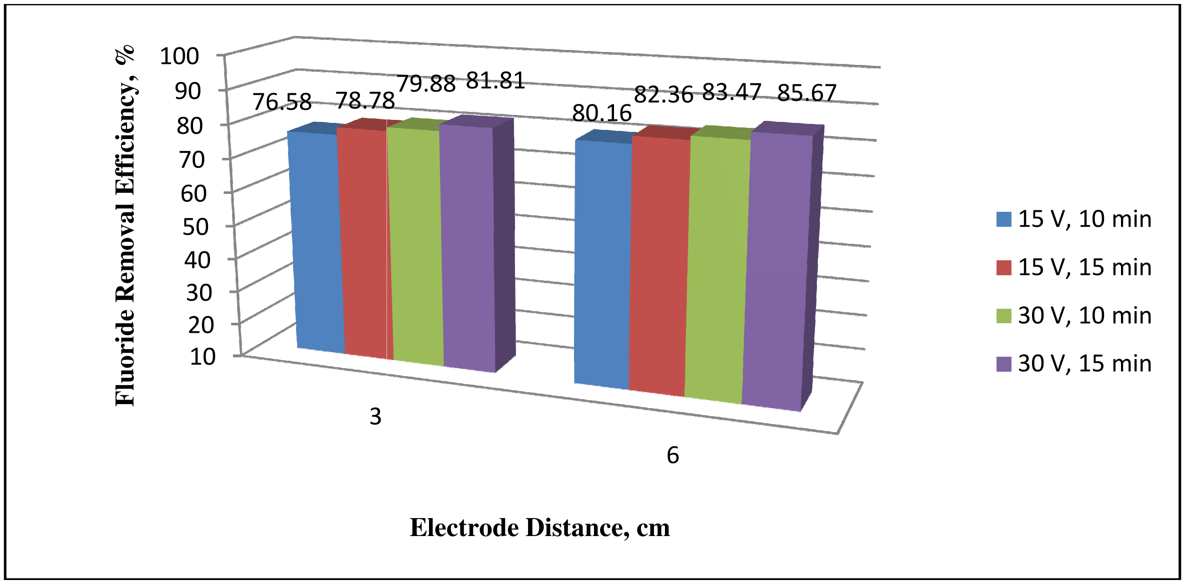


Figure 22: Fluoride Removal Efficiency
(pH-8, Initial Fluoride-3.63, Electrode Used-Aluminium)

Sl No	Distance between electrodes	Contact time (min)	Voltage (Volt)	Final Ph	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	4.70	3.16	132	1.76	74.15
2	3	15	15	4.56	3.28	145	1.62	76.21
3	3	10	30	4.10	3.45	165	1.55	77.23
4	3	15	30	4.55	3.66	154	1.35	80.17
5	6	10	15	4.61	3.51	167	1.38	79.73
6	6	15	15	4.32	3.49	143	1.28	81.20
7	6	10	30	4.17	3.44	123	1.21	82.23
8	6	15	30	4.28	3.28	132	0.97	85.75

Table 16: Mundaragi sample
pH-4, Initial Fluoride-6.81, Electrode Used-Iron

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	4.90	3.51	156	1.35	80.17
2	3	15	15	4.76	3.49	165	1.14	83.25
3	3	10	30	4.20	3.44	176	1.06	84.43
4	3	15	30	4.45	3.28	176	1.84	87.66
5	6	10	15	4.63	3.16	143	1.83	87.81
6	6	15	15	4.22	3.28	154	1.80	88.25
7	6	10	30	4.19	3.45	124	0.70	89.72
8	6	15	30	4.38	3.66	143	0.60	91.18

Table 17: Mundaragi sample
pH-4, Initial Fluoride-6.81, Electrode Used-Aluminium

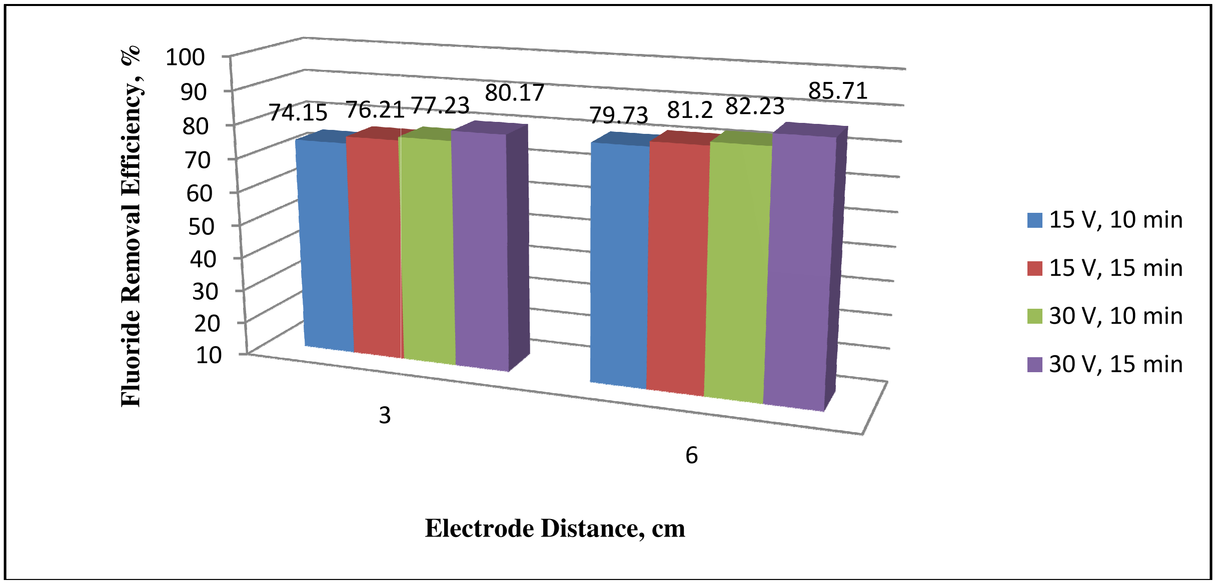


Figure 23: Fluoride Removal Efficiency
(pH-4, Initial Fluoride-6.81, Electrode Used-Iron)

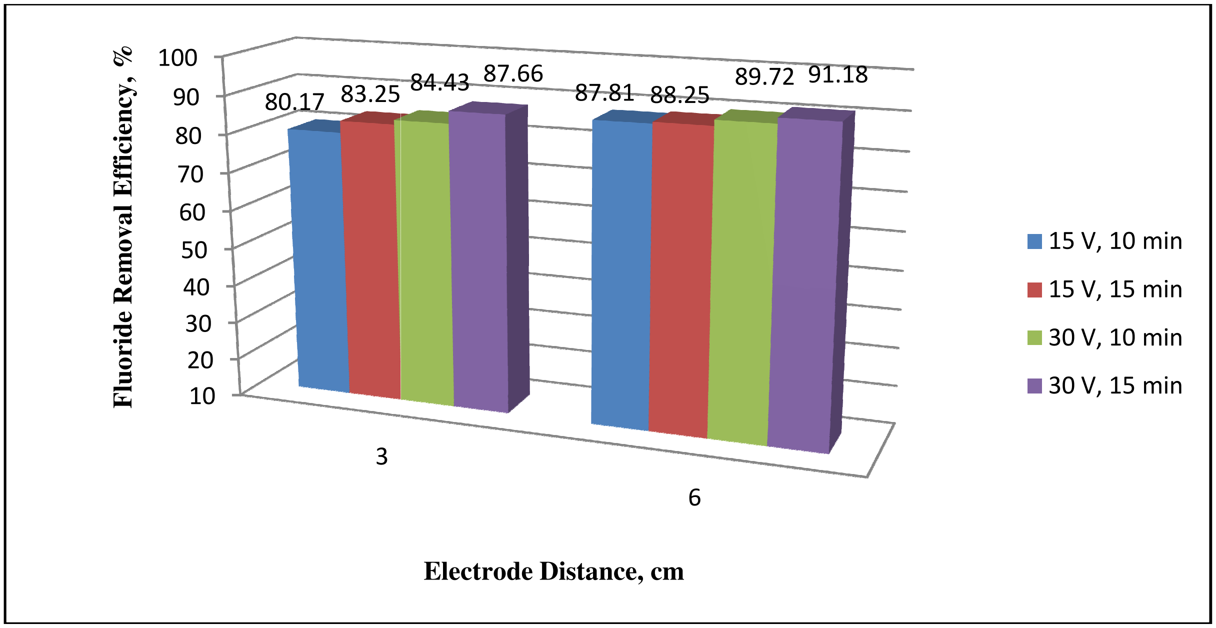


Figure 24: Fluoride Removal Efficiency
(pH-4, Initial Fluoride-6.81, Electrode Used-Aluminium)

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	7.55	2.79	189	1.96	71.21
2	3	15	15	7.15	2.56	187	1.75	74.30
3	3	10	30	7.35	2.48	167	1.61	76.35
4	3	15	30	7.02	2.64	176	1.42	79.14
5	6	10	15	7.32	2.55	185	1.45	78.70
6	6	15	15	7.38	2.48	123	1.38	79.73
7	6	10	30	7.21	2.64	156	1.35	80.17
8	6	15	30	7.42	2.61	178	1.17	82.81

Table 18: Mundaragi sample
pH-8, Initial Fluoride-6.81, Electrode Used-Iron

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	7.45	2.55	145	1.82	73.27
2	3	15	15	7.10	2.48	167	1.76	74.15
3	3	10	30	7.45	2.64	176	1.48	78.18
4	3	15	30	7.08	2.61	156	1.32	80.61
5	6	10	15	7.20	2.79	123	1.42	79.14
6	6	15	15	7.28	2.56	143	1.28	81.20
7	6	10	30	7.14	2.48	154	1.01	83.16
8	6	15	30	7.38	2.64	143	0.93	86.34

Table 19: Mundaragi sample
pH-8, Initial Fluoride-6.81, Electrode Used-Aluminium

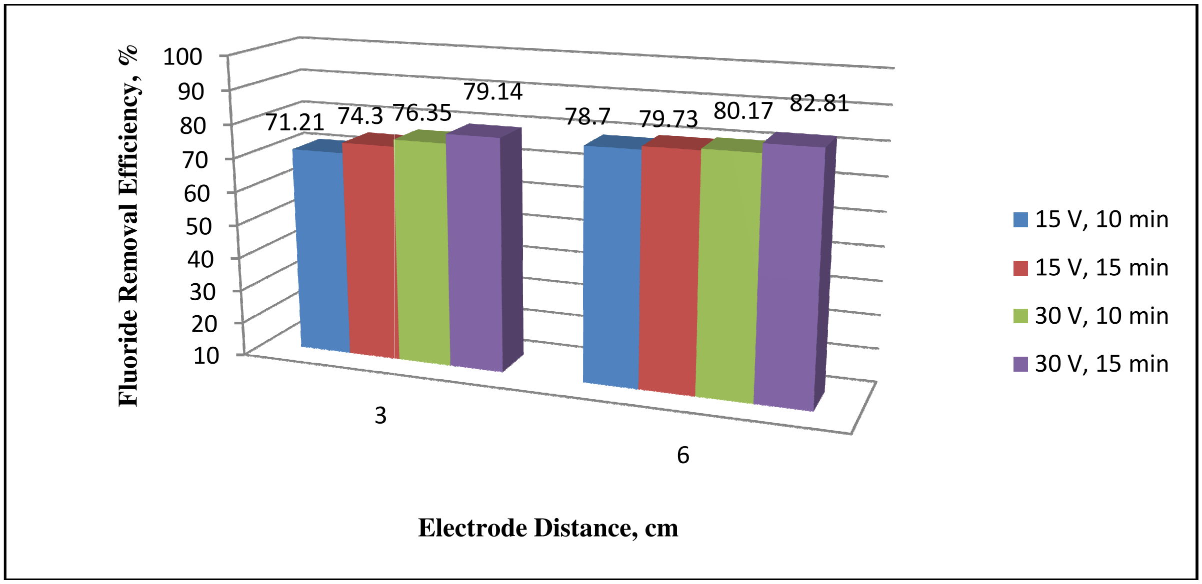


Figure 25: Fluoride Removal Efficiency
(pH-8, Initial Fluoride-6.81, Electrode Used-Iron)

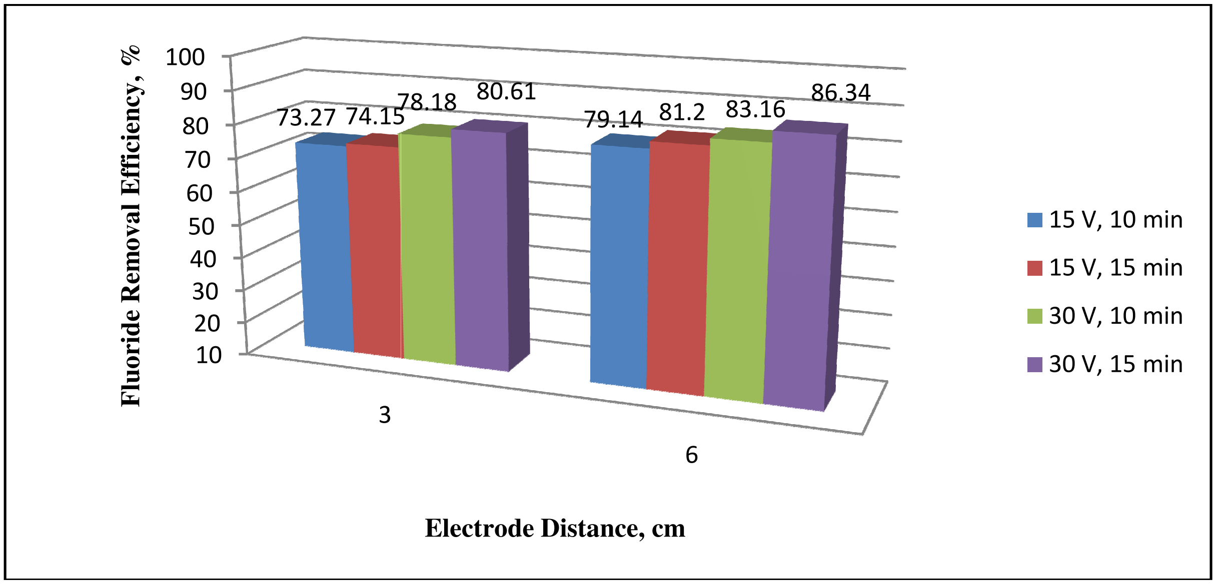


Figure 26: Fluoride Removal Efficiency
(pH-8, Initial Fluoride-6.81, Electrode Used-Aluminium)

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	4.48	1.41	145	1.06	76.49
2	3	15	15	4.02	1.59	154	0.98	78.16
3	3	10	30	4.15	1.39	156	0.89	80.26
4	3	15	30	4.30	1.45	165	0.82	81.81
5	6	10	15	4.11	1.36	176	0.89	80.26
6	6	15	15	4.19	1.45	142	0.75	83.37
7	6	10	30	4.20	1.44	144	0.71	84.25
8	6	15	30	4.33	1.34	155	0.64	85.80

Table 20: Kalakeri sample
pH-4, Initial Fluoride-4.51, Electrode Used-Iron

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	4.52	1.41	176	0.76	83.14
2	3	15	15	4.06	1.52	198	0.71	84.25
3	3	10	30	4.17	1.35	198	0.62	86.25
4	3	15	30	4.27	1.45	167	0.53	88.24
5	6	10	15	4.10	1.38	189	0.52	88.47
6	6	15	15	4.18	1.51	176	0.46	89.80
7	6	10	30	4.22	1.42	188	0.44	90.24
8	6	15	30	4.50	1.38	176	0.28	93.79

Table 21: Kalakeri sample
pH-4, Initial Fluoride-4.51, Electrode Used-Aluminium

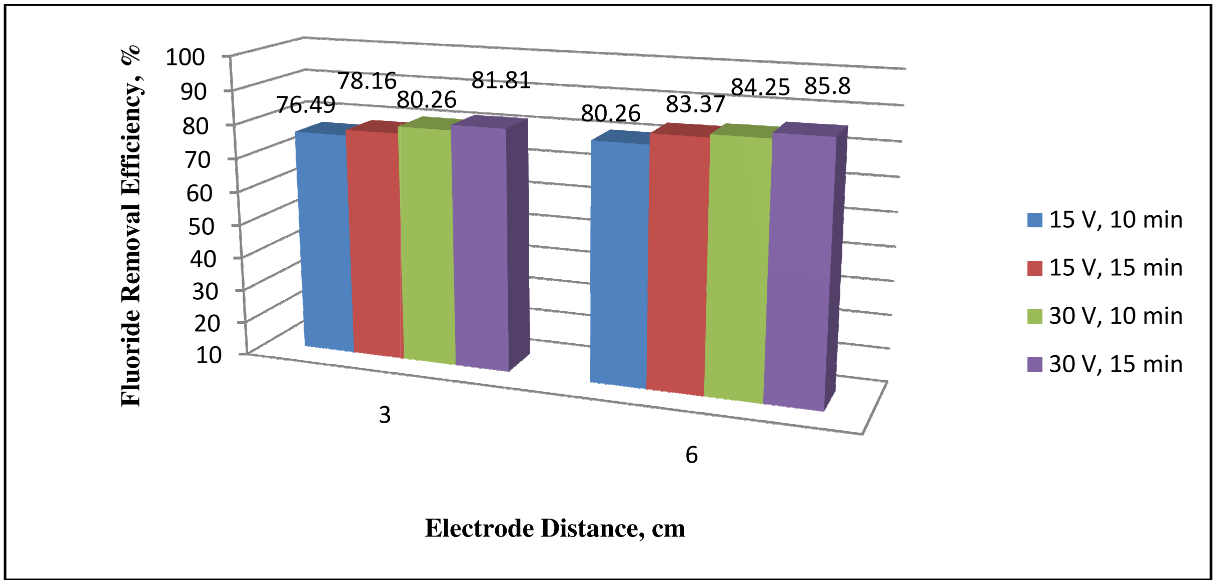


Figure 27: Fluoride Removal Efficiency
(pH-4, Initial Fluoride-4.51, Electrode Used-Iron)

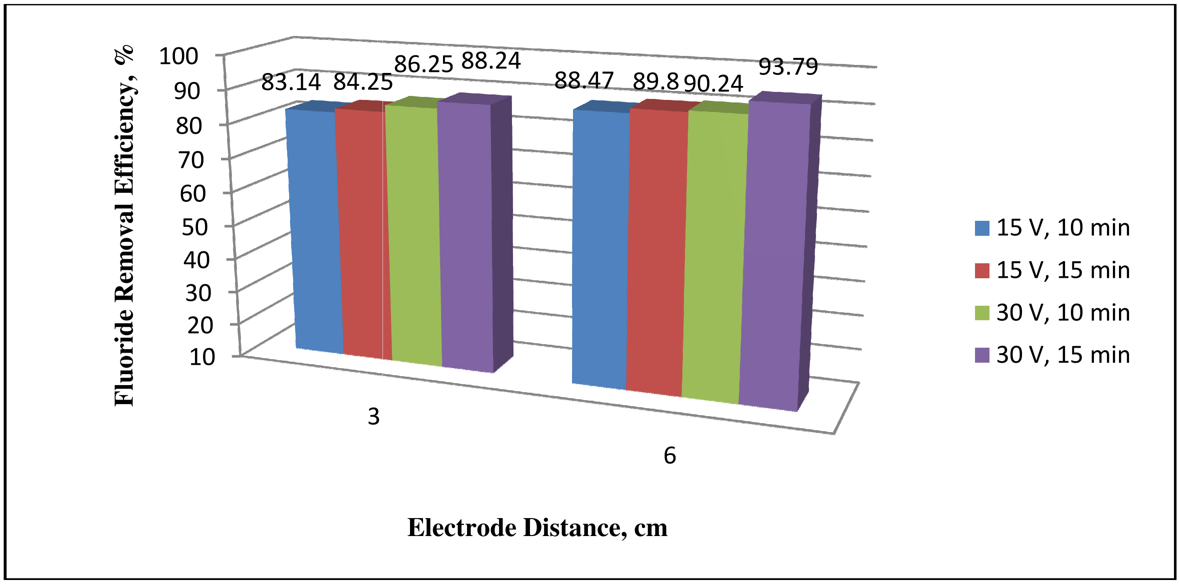


Figure 28: Fluoride Removal Efficiency
(pH-4, Initial Fluoride-4.51, Electrode Used-Aluminium)

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	9.20	1.39	167	1.32	70.73
2	3	15	15	9.02	1.52	165	1.26	72.06
3	3	10	30	9.41	1.36	178	1.20	73.39
4	3	15	30	9.15	1.45	189	1.08	76.05
5	6	10	15	9.21	1.35	188	1.12	75.16
6	6	15	15	9.29	1.41	187	0.96	78.71
7	6	10	30	9.16	1.33	156	0.89	80.26
8	6	15	30	9.38	1.36	187	0.77	82.92

Table 22: Kalakeri sample
pH-8, Initial Fluoride-4.51, Electrode Used-Iron

Sl No	Distance between electrodes	Contact time(min)	Voltage (Volt)	Final pH	Conductivity (ms)	Hardness mg/l	Final fluoride	Efficiency in %
1	3	10	15	9.18	1.38	198	0.79	82.48
2	3	15	15	9.07	1.52	200	0.75	83.37
3	3	10	30	9.40	1.41	234	0.70	84.47
4	3	15	30	9.20	1.45	222	0.63	86.03
5	6	10	15	9.14	1.38	222	0.64	85.80
6	6	15	15	9.29	1.32	223	0.55	87.80
7	6	10	30	9.12	1.49	234	0.49	89.13
8	6	15	30	9.40	1.31	213	0.41	90.91

Table 23: Kalakeri sample
pH-8, Initial Fluoride-4.51, Electrode Used-Aluminium

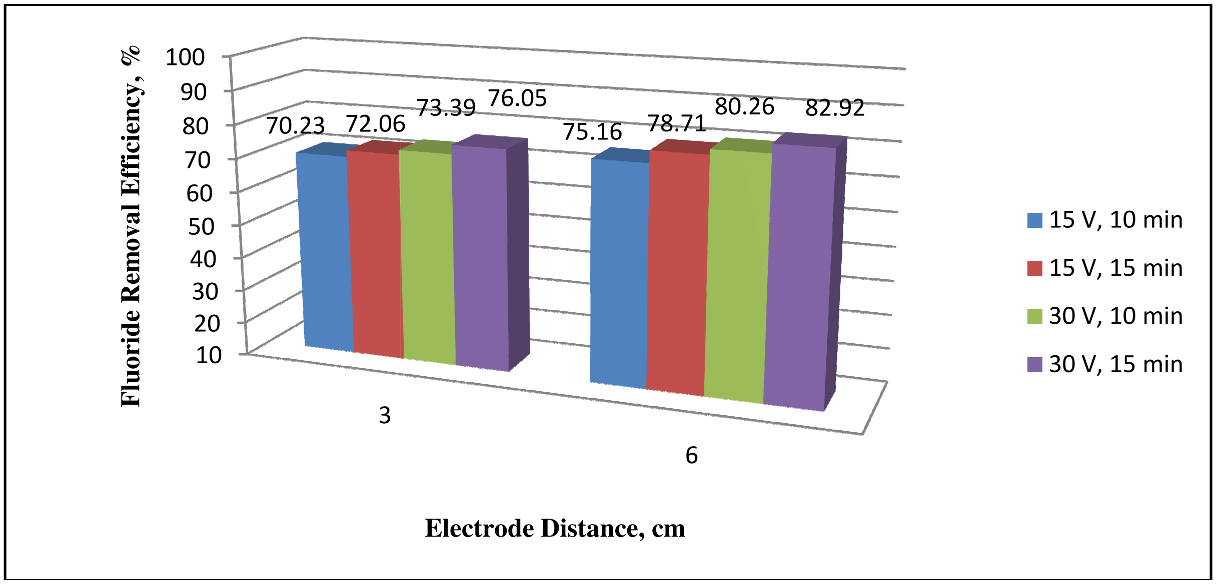


Figure 29: Fluoride Removal Efficiency
(pH-8, Initial Fluoride-4.51, Electrode Used-Iron)

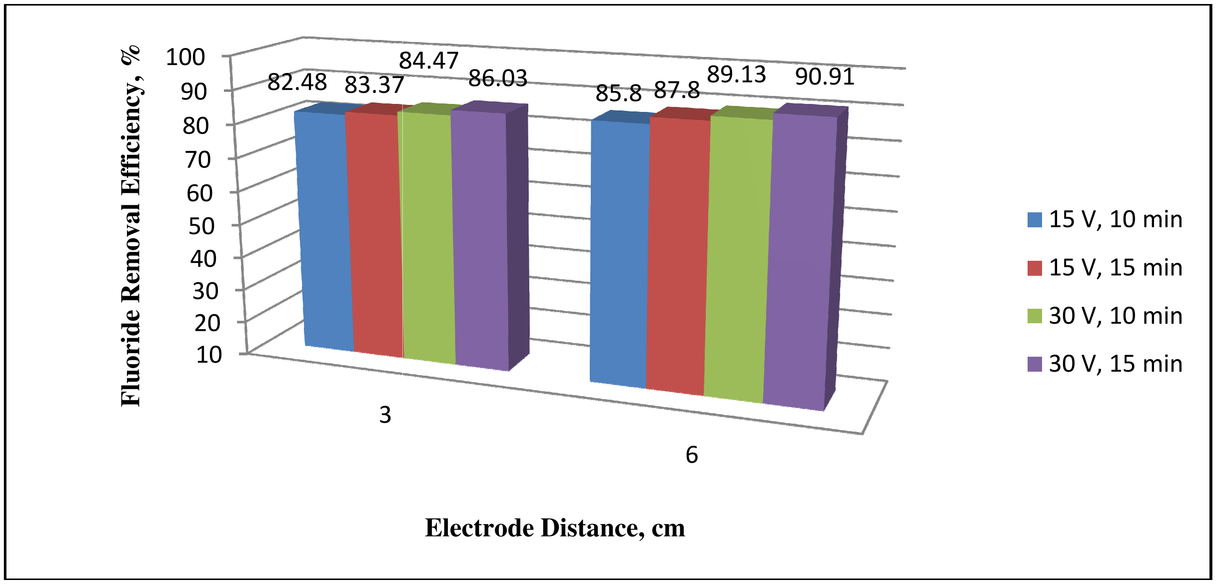


Figure 30: Fluoride Removal Efficiency
(pH-8, Initial Fluoride-4.51, Electrode Used-Aluminium)

6. Conclusions, Limitations and Scope for Further Study

Based on the results of experimentation carried out under varied experimental conditions and the analysis of the same thereby the following conclusions have been drawn.

- It is concluded that the variables tried viz, Distance between electrodes, pH, voltage, electrode material, contact time have good bearing on removal efficiency.
- It is concluded that fluoride removal efficiency is directly proportional to Distance between electrodes, voltage, contact time.
- It is concluded that fluoride removal efficiency is inversely proportional to pH.
- It is concluded that aluminium electrodes are more efficient than iron electrodes.
- The highest removal efficiency of 93.73% for optimum conditions of variables viz, pH=4.0, CT=15 min, D=6 cm, V= 30 V, Electrode= Aluminium have been recorded.
- The lowest removal efficiency of 69.66% for optimum conditions of variables viz, pH=8.0, CT= 10 min, D=3cm, V=15V, Electrode=Iron have been recorded.
- It is concluded that the process tried in the present work with varied experimental conditions is not so efficient compare to the biological treatment processes of wastewater s however the confirmative/ confined conclusion on this parameter can be drawn only after the repetitive experimentations and final optimization of parameters. Such as optimization has not been done in present dissertation work.

6.1. Limitations of Present Study

The following are the limitation of present study and these limitations are attributed to non-availability of data, lack of infrastructure facility, time shortage, not within the preview of objectives of present study etc.

- The experiments have been carried out only for set of variables. Confined conclusions can be drawn based only on the results of wide ranges of variables.
- Investigations to evaluate the leaching of metal into water by iron and electrodes.

6.2. Scope for Further Study

- The limitations listed above can be the subject matters for further study.
- Studies to access the leaching of metals from electrodes into water can be taken up for further study.
- Studies to evaluate the feasibility of electrochemical oxidation and coagulation processes for treating other industrial water and wastewaters.

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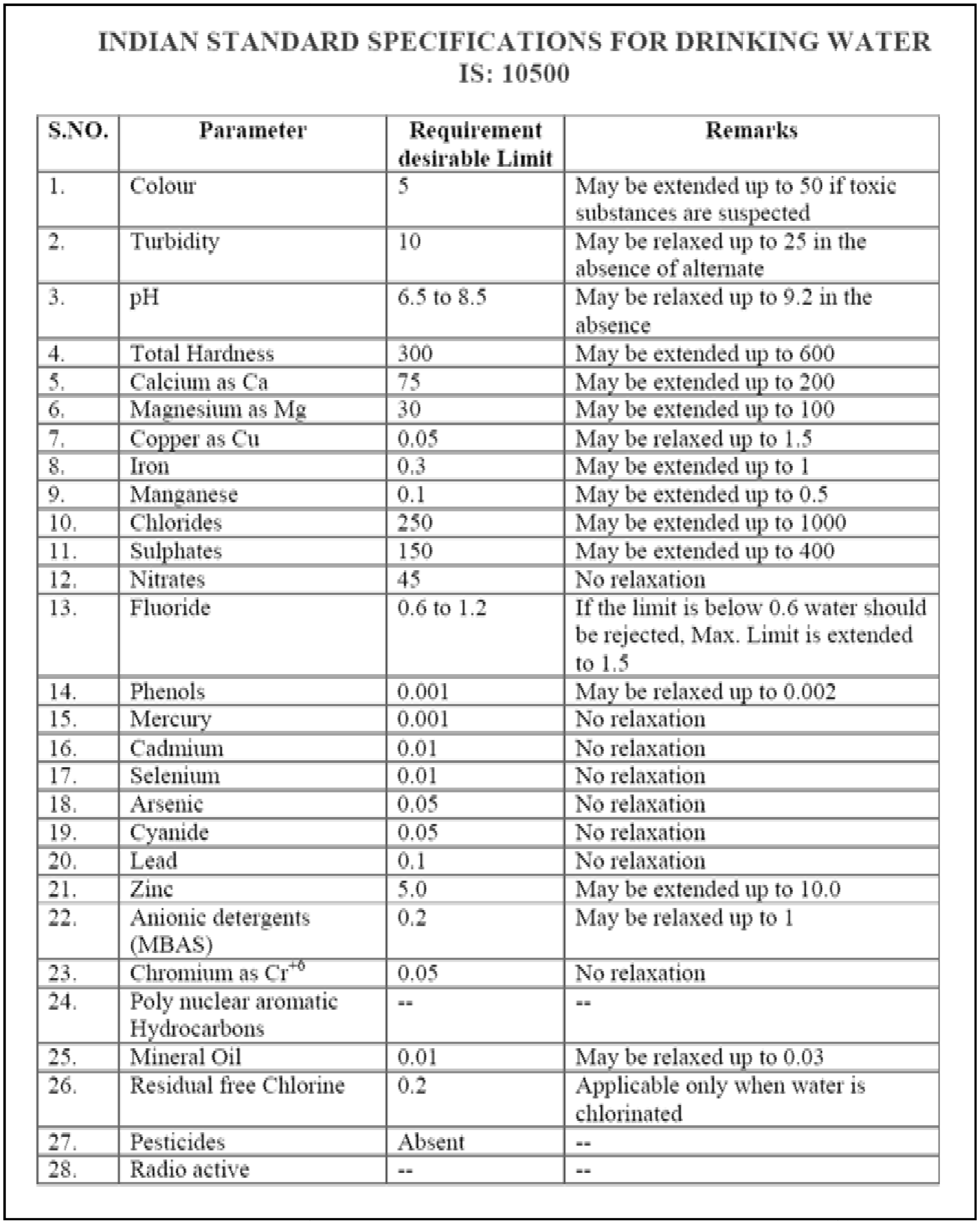
APPENDIX



INDIAN STANDARD SPECIFICATIONS FOR DRINKING WATER
IS: 10500

S.NO.	Parameter	Requirement desirable Limit	Remarks
1.	Colour	5	May be extended up to 50 if toxic substances are suspected
2.	Turbidity	10	May be relaxed up to 25 in the absence of alternate
3.	pH	6.5 to 8.5	May be relaxed up to 9.2 in the absence
4.	Total Hardness	300	May be extended up to 600
5.	Calcium as Ca	75	May be extended up to 200
6.	Magnesium as Mg	30	May be extended up to 100
7.	Copper as Cu	0.05	May be relaxed up to 1.5
8.	Iron	0.3	May be extended up to 1
9.	Manganese	0.1	May be extended up to 0.5
10.	Chlorides	250	May be extended up to 1000
11.	Sulphates	150	May be extended up to 400
12.	Nitrates	45	No relaxation
13.	Fluoride	0.6 to 1.2	If the limit is below 0.6 water should be rejected, Max. Limit is extended to 1.5
14.	Phenols	0.001	May be relaxed up to 0.002
15.	Mercury	0.001	No relaxation
16.	Cadmium	0.01	No relaxation
17.	Selenium	0.01	No relaxation
18.	Arsenic	0.05	No relaxation
19.	Cyanide	0.05	No relaxation
20.	Lead	0.1	No relaxation
21.	Zinc	5.0	May be extended up to 10.0
22.	Anionic detergents (MBAS)	0.2	May be relaxed up to 1
23.	Chromium as Cr^{+6}	0.05	No relaxation
24.	Poly nuclear aromatic Hydrocarbons	--	--
25.	Mineral Oil	0.01	May be relaxed up to 0.03
26.	Residual free Chlorine	0.2	Applicable only when water is chlorinated
27.	Pesticides	Absent	--
28.	Radio active	--	--

Table 1: Indian drinking water standards