# STUDY ON DEFLUORIDATION BY THE APPLICATION OF ADSORPTION AND ION-EXCHANGE PROCESS

*A thesis submitted towards partial fulfilment of the*
*requirements for the degree of*

**Master of Engineering in**
**Water Resources and Hydraulic Engineering**
Course affiliated to Faculty of Engineering & Technology
Jadavpur University

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## CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled **"STUDY ON DEFLUORIDATION BY THE APPLICATION OF ADSORPTION AND ION-EXCHANGE PROCESS"** is bonafide work carried out by **DEBDAS CHOWDHURY** under our supervision and guidance for partial fulfilment of the requirement for Post Graduate Degree of Master of Engineering in Water Resources & Hydraulic Engineering during the academic session 2018-2019.

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# CERTIFICATE OF APPROVAL **

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All information in this document has been obtained and presented in accordance with academic rules and ethical conduct.

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# ACKNOWLEDGEMENT

I express my sincere gratitude to my Thesis Advisors **Prof. (Dr.) Arunabha Majumder** and **Prof. (Dr.) Pankaj Kumar Roy** under whose valuable guidance this work has been carried out. It would have been impossible to carry out this thesis work with confidence without their wholehearted involvement, advice, support and constant encouragement throughout. They have not only helped me to complete my thesis work but also have given valuable advice to proceed further in my life.

I also express my sincere gratitude to all the faculty members **Prof. (Dr.) Asis Mazumdar, Director, Dr. Subhasis Das** Assistant Professor and **Dr. Gourab Banerjee** Assistant Professor of School of Water Resources Engineering for their valuable suggestion.

I also express my thankfulness to PhD Scholars, specially Sri Nil Sadhan Mondal, Sritama Chatterjee, Saurabh Kumar Basak, Swetashree Nag, Sudipa Halder of School of Water Resources Engineering, Jadavpur University for their support throughout the study and also thanks to all my classmates of School of Water Resources Engineering, Jadavpur University, specially, Priyabrata Mondal, Anirban Ghosh, Subhankar Giri, Bishwajit Lenka for their helps during thesis work.

Thanks are also due to all staff of School of Water Resources Engineering and the Regional Centre, NAEB, Jadavpur University for their help and support.

Last but not the least; I am also grateful to my family and my friends for their earnest support.

**Date: May, 2019**

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*This thesis work is dedicated to fluorosis affected people…*

# ABSTRACT

The distribution of ionic form of fluoride is uneven in the environment. Fluorides can be present as sedimentary formations in minerals, rock, soil, clay, and anthropogenic activities. Due to high toxicity of fluoride to mankind, there is an urgent need to treat fluoride contaminated drinking water to make it safe for consumption. The allowable drinking water standard for fluoride is 1.5mg/L as per Indian standard. Concentrations of fluoride higher than this level affect both teeth and bone, resulting in dental or skeletal fluorosis. Most of the arid and semi arid zones of the Indian subcontinent are seriously affected by the fluorosis problem due to high concentration of the fluoride in ground water. In developing countries like India, lack of awareness, constraint of fund and scarcity of research work make this challenge of providing hygieninc drinking water to commons harder, that's why extensive research work has to be carried out to counter the situation.

This study depicts that the fluoride removal from drinking water can be accomplished by Ion Exchange process using cationic & anionic resins and Adsorption method using activated alumina.

Cationic and Anionic resins are investigated to assess their sorptive removal capacity of fluoride from water. It is found that when cation-anion exchange resins bed is used as filter media then the removal capacity of fluoride is high but pH of the treated water decrease promptly. But when only anionic resins bed is used as filter media removal capacity of fluoride remains high as well as pH and general parameters of the treated water is in the range of drinking water standards. The maximum sorption of the cation-anion exchange resins and anionic resins are 521.25mg/kg and 509.5mg/kg respectively.

Activated alumina has been investigated as an adsorbent for defluoridation and it is found to have a good affinity for uptaking fluoride ions from water. It is a granular form of aluminum oxide ($Al_2O_3$) and has a very high surface area, which provides a large area for adsorption that makes its removal capacity is more than satisfactory. The adsorption capacity is found to be around 1996.28 mg/kg. The pH values are slightly increased after treatment of water but it still are in the range of drinking water standard. Among the isotherm models of Langmuir and Freundlich, Freundlich model is found to show better means to describe fluoride adsorption at equilibrium.

# List of Abbreviations

| | |
|---|---|
| cm$^2$ | square centimeter |
| Gm | Gram |
| Hr | Hour |
| Kg | Kilogram |
| l/sec | Liters per second |
| m$^2$ | square meter |
| m$^3$ | cubic meter |
| Mg | Milligram |
| min. | Minute |
| L | Liter |
| m$^3$/day | cubic meters per day |
| mg/L | milligram per Liter |
| Mm | Millimeter |
| Ml | Milliliters |
| AA | Activated Alumina |
| pH | pH |
| DD/W | Double Distilled water |
| NEERI | National Environmental Engineering Research Institute |
| RO | Reverse Osmosis |
| IE | Ion Exchange |
| WHO | World Health Organization |
| DDU | Domestic De-fluoridation Unit |
| MOE | Moringa Oleifera seed extract |
| EC | Electro coagulation |
| μS/cm | Micro Siemens/centimeter |
| TDS | Total dissolved solids |
| mA | Milliampere |
| V | Volts |

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# Introduction

## CHAPTER 1

Water pollution and its treatment to avail safe drinking water is a serious concern regarding health prospective of common people. Fluoride is one of the major contaminants in water. Fluoride is one such pollutant that undermines living life forms, specifically people. Fluoride is an vital in little amount for mineralization of bone and assurance against dental caries, higher intake reasons decay of teeth enmel called fluorosis. Fluoride enters aqueous environment by weathering of fluoride rich minerals and as through anthropogenic actions, for example, industrial drains. In the tropical countries where water consumption is more because of the prevailing climate and there is fluoride bearing minerals underground, for example, Ethiopia, Tanzania, South Africa, Jordon, Egypt, Libya, Algeria, Sudan, Malawi, Mexico, Kenya, Pakistan, Brazil, Afghanistan, Sri Lanka, Korea, Syria, Northern Thailand, Indonesia, and India many people are affected by fluorosis. In many parts of Japan, Iran, Germany, China, Norway, Turkey, Southern Algeria, Italy, Canada and the United State of America, fluoride is also found above permissible limits. The best way to pypass this issue is defluoridation. Various methods are accessible for the removal of fluoride from water, for example, precipitation-coagulation, membrane-based processes, ion–exchange and adsorption process.

It is estimated that around 260 million people worldwide (in 30 countries) are drinking water with fluoride content more than 1.0 mg/L. In India, 25 million people in 19 states and union territories have already been affected, and another 66 million are at risk including 6 million children below the age of 14 years.

## 1.1 Fluoride in Environment:

Fluorine is a ubiquitous and the 13th most abundant naturally occurring element in the Earth's crust, one of the most reactive and electronegative of all the elements. Fluorides are found in a wide variety of minerals, including fluorspar [$CaF_2$], sellaite [$MgF_2$], rock phosphate/fluoroapatite [$Ca_5(PO_4)_3F$], cryolite [$Na_3AlF_6$], mica, hornblende and others. Fluorite ($CaF_2$) is a common bearer of fluoride and is found in granite, granite gneisses and pegmatite and as cryolite in igneous rocks. Fluoride also associated with mono valent cations such as NaF and KF which are water soluble.

Fluorine is the lightest halogen and extremely reactive of all chemical elements which has atomic weight of 18.998 and atomic number 9. It is the most electronegative of all the elements (Hem[42], 1989) which means that it has a strong tendency to acquire a negative charge, and in solution forms $F^-$ ions, rarely found outside of its ionic form, fluoride.

### 1.1.1 Fluoride in Water:

Fluoride is found in all natural waters at some concentration. Seawater typically contains about 1mg/l while rivers and lakes generally exhibit concentrations of less than 0.5 mg/L. In ground waters, however, low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride-bearing minerals. Concentrations in water are limited by fluorite solubility, so that in the presence of 40 mg/L calcium it should be limited to 3.1 mg/L (Hem[42], 1989). It is the absence of calcium in solution which allows higher concentrations to be stable (Edmunds[44], 1996). High fluoride concentrations may therefore be expected in ground waters from calcium-poor aquifers and in areas where fluoride-bearing minerals are common.

### 1.1.2 Fluoride in Air:

Due to dust, industrial production of phosphate fertilizers, coal ash from the burning of coal and volcanic activity, fluorides are widely distributed in the atmosphere. However, air is typically responsible for only a small fraction of total fluoride exposure (USNRC[51], 1993). In non-industrial areas, the fluoride concentration in air is typically quite low (0.05–1.90 µg m–3 fluoride) (Murray[45], 1986). In areas where fluoride-containing coal is burned or phosphate fertilizers are produced and used, the fluoride concentration in air is elevated leading to increased exposure by the inhalation route.

### 1.1.3 Fluoride Dental products:

A number of products administered to, or used by, children to reduce dental decay contain fluoride. This includes toothpaste (1.0–1.5 g/ kg fluoride), fluoride solutions and gels for topical treatment (0.25–24.0 g/ kg fluoride) and fluoride tablets (0.25, 0.50 or 1.00 mg fluoride per tablet), among others. These products contribute to total fluoride exposure, albeit to different degrees. It is estimated that the swallowing of toothpaste by some children may contribute about 0.50 or 0.75 mg fluoride per child per day (Murray[45], 1986).

### 1.1.4 Fluoride in Foods & Bevarages:

Vegetables and fruits normally have low levels of fluoride (e.g. 0.1–0.4 mg/ kg) and thus typically contribute little to exposure. However, higher levels of fluoride have been found in barley and rice (e.g. about 2 mg/ kg). However, fluoride accumulates in bone and the bones of canned fish, such as salmon and sardines, which are also eaten. Fish protein concentrates may contain up to 370 mg/ kg fluoride.

**Table 1.1: The fluoride content from some common sources**

| Sources | Fluoride (ppm) |
|---|---|
| Cereals | |
| Wheat | 4.6 |
| Rice | 5.9 |
| Maize | |
| Pulses and legumes | 5.6 |
| Green gram dal | 2.5 |
| Red gram dal | 3.7 |
| Soyabean | 4.0 |
| Vegetables | |
| Cabbage | 3.3 |
| Tomato | 3.4 |
| Cucumber | 4.1 |
| Lady finger | 4.0 |
| Spinach | 2.0 |
| Lettuce | 5.7 |
| Mint | 4.8 |
| Potato | 2.8 |
| Carrot | 4.1 |
| Fruits | |
| Mango | 3.7 |
| Apple | 5.7 |
| Guava | 5.1 |
| Nuts and oil seeds | |
| Almond | 4.0 |
| Coconut | 4.4 |
| Mustard seeds | 5.7 |
| Groundnut | 5.1 |
| Beverage | |
| Tea | 60-112 |
| Aerated drinks | 0.77-1.44 |
| Spices and condiments | |
| Corriander | 2.3 |
| Garlic | 5.0 |
| Turmeric | 3.3 |
| Food from animal sources | |
| Mutton | 3.0-3.5 |
| Beef | 4.0-5.0 |
| Pork | 3.0-4.5 |
| Fishes | 1.0-6.5 |
| Others | |
| Rock salts | 200.0-250.0 |
| Areca but (supari) | 3.8-12.0 |
| Beetle leaf (pan) | 7.8-12.0 |
| Tobacco | 3.2-38 |

Source: Meenakshi and Maheswari[27] (2006)

## 1.2 Impact of Fluoride on Human Health:

Fluoride has beneficial effects on teeth at low concentrations in drinking-water, but excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the world.

**Table 1.2: Effect of fluoride in water on human health**

| Fluoride Concentration (mg/L) | Effects |
|---|---|
| <1.0 | Safe limit |
| 1.0-3.0 | Dental fluorosis (discoloration, mottling and pitting of teeth) |
| 3.0-4.0 | Stiffened and brittle bones and joints |
| 4.0-6.0 and above | Deformities in knee and hip bones and finally paralysis making the person unable to walk or stand in straight posture, crippling fluorosis |

Source: Meenakshi and Maheswari[62] (2006)

### 1.2.1 Effects of Excess Fluoride in Human Health:

Fluoride – a disease caused by ingestion of fluoride in excess through water, food and air and is a serious health problem. Fluoride ingested with water goes on accumulating in bones up to age of 55 years. At high doses fluoride can interfere with carbohydrates, lipid protein, vitamin, enzyme3 and mineral metabolism.

### 1.2.1.1 Dental Fluorosis:

Long term consumption of water containing 1mg $F^-$/L leads to dental fluorosis. Fluoride causes dental fluorosis by poisoning the enamel forming cells, called ameloblasts. The damage of these cell results in an irregular mineralization of the enamel, known as hypo-mineralization.

Fig 1.1: Dental Fluorosis

**Table 1.3: Various stages of dental Fluorosis**

| Sl.No | Type of Dental Fluorosis | Description |
|---|---|---|
| 1. | Very mild Fluorosis | Small opaque, paper white area scattered irregularly over the tooth but not involving as much as approximately 25% of the tooth surface. |
| 2. | Mild Fluorosis | The white opaque area in the enamel of the teeth is more extensive, but do not involve as much 50% of tooth surface. |
| 3. | Moderate Fluorosis | All enamel surface of the teeth are effected and the surface subjected to attrition show market wear. Brown stain is a disfiguring feature. |
| 4. | Moderate Severe Fluorosis | Pitting is marked and generally observed on all teeth surface and brown stain. |
| 5. | Severe Fluorosis | All enamel surface are effected and hyperplasic is so marked that the general from of teeth may be effected the major discrete or confluent pitting. Brown stains are widespread and teeth often [resent a corroded like appearance. |

Source: H.T. Dean[63] (1942)

### 1.2.1.2 Skeletal Fluorosis:

This has been observed in persons when contains more than 3-6 mg/L of fluoride. Skeletal fluorosis is a bone disease caused by excessive consumption of fluoride. In this disease fluoride replaces hydroxides in bones causing chronic effects. Skeletal fluorosis has a number of stages. The first two stages are-

- **Preclinical Stage –**

  Where the patient fells no symptoms but changes have taken place in the body.The First preclinical stage, biochemical abnormalities occur in the blood & bone composition.

  In the second preclinical stage histological changes can be observed in bone in biopsies.
- **Clinical Stage –**

  In the early clinical stage of skeletal fluorosis, symptoms includes pain in the bone and joints, sensation of burning, pricking and tingling in the limp, muscles weakness, chronic fatigue, gastrointestinal disorder and reduces appetite.

  In the second clinical stages pain in bones become constant and some of the ligaments being to calcify.

In the advance skeletal fluorosis, the extremities become weak and moving of joints is difficult. The vertebrae partially fuse together, crippling the patient hence this stage of fluorosis is also called as crippling skeletal fluorosis.

Fig 1.2: Skeletal Fluorosis

Other Diseases on human health by consuming excess fluoride are-

Osteosarcoma (Bone Cancer), Neurological Manifestations, Muscular Manifestations, Allergic Manifestations, Gastro intestinal problems, Head-ache, Loss of teeth (edentate) at an early age, Premature aging.

**Table 1.4: Concentrations of fluoride & biological effects**

| **Concentration of fluoride in ppm *** | **Medium** | **Effect** |
|---|---|---|
| 0.002 | Air | Injury to Vegetation. |
| 1 | Water | Dental caries reduction |
| 2 or more | Water | Mottled enamel |
| 8 | Water | 10% osteoscerosis |
| 50 | Food & water | Thyroid Changes |
| 100 | Food & water | Growth retardation |
| 120 | Food & water | Kidney changes |

*In water medium, ppm can be taken equivalent to mg/L.

Source WHO, 1970

## 1.3 Extent of Fluoride Contamination:

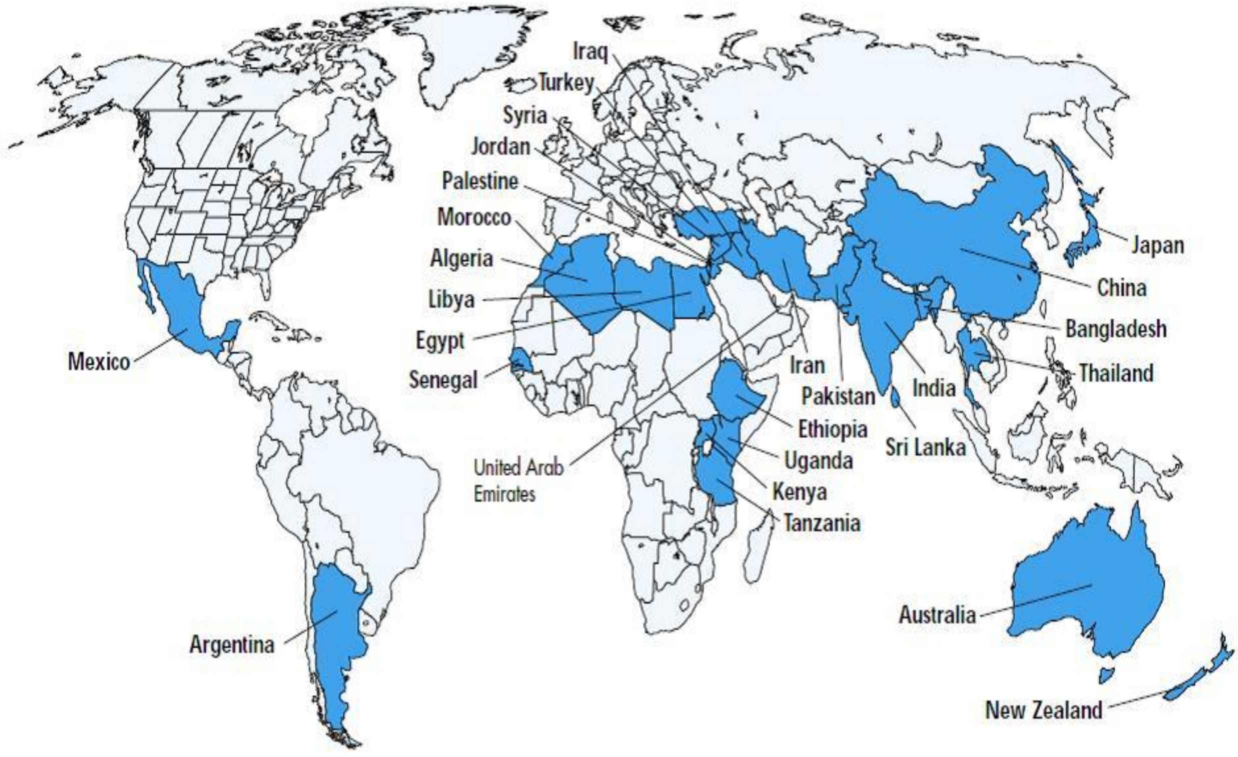
The guidelines followed for fluoride content in drinking water in most of the countries are based on the WHO norms. Optimum fluoride concentration in drinking water may be defined as a one that arrest the prevalence of dental carries sans causing a significant amount of fluorosis. The drinking water standards for fluoride ion stipulated by various authorities are tabulated (Table-1.5):

**Table 1.5 : Drinking water standards for fluoride prescribed by various authorities**

| **Sl No.** | **Authority** | **Fluoride as $F^-$ in mg/L** | |
|---|---|---|---|
| | | **Acceptable limit** | **Maximum Permissible Limit** |
| 1. | WHO (Guideline value) | - | 1.5 |
| 2. | BIS (IS-10500) | 1.0 | 1.5 |
| 3. | CPHEEO (Ministry of urban development, Gov. of India) standard. | 1.0 | 1.5 |

### 1.3.1 Global Scenario of Fluoride Contamination:

The problem of intake high fluoride in drinking water has engulfed several continents- Australia, Asia, Africa, North America & South America. There are more than 20 developed and developing nations that are endemic for fluorosis. The guideline followed for fluoride content in drinking water in most of the nations is based on WHO norms/ guidelines. The WHO guideline is 1.5 mg/L of fluoride is the “desirable” upper limit in drinking water. Ground waters with high fluoride concentrations occur in many areas of the world including large parts of Africa, China, the Eastern Mediterranean and southern Asia (India, Sri Lanka). One of the best-known high fluoride belts on land extends along the East African Rift from Eritrea to Malawi. There is another belt from Turkey through Iraq, Iran, Afghanistan, India, northern Thailand and China. The Americas and Japan have similar belts.



*Countries with endemic fluorosis due to excess fluoride in drinking water*

Fig 1.3: Excess fluoride affected countries around the Globe

### 1.3.2 Indian Scinario of Fluoride Contamination:

In India, it was first detected in Nellore district of Andhra Pradesh in 1937. At present, many parts of India with an estimated 66.62 million people being exposed to fluorosis in various endemic region with more than half a million people already crippled by it. The number of states, where endemicity is known to occur, has increased to 19 out of the 32.

**Table 1.6: Fluoride concentrations reported in ground waters of India**

| Region/State | Fluoride concentration severity of (mg /L) | Maximum fluorosis observed |
|---|---|---|
| North-West India | 0.4 – 19 | Severe |
| Central India | 0.2 – 10 | Moderate |
| South India | 0.2 – 20 | Severe |
| Deccan Province | 0.4 – 8 | Moderate |

Sources: Agarwal et al. (1997); Yadav et al. (1999)

#### 1.3.2.1 State wise details of distribution of Fluoride in Ground Water:

85 % of rural population of the country uses ground water for drinking and domestic purposes. High concentration of fluoride in ground water beyond the permissible limit of 1.5 mg/L poses the health problem. Nearly the occurrence of fluoride beyond permissible limit (> 1.5 mg /litre) has been observed based on the chemical analysis of water samples collected from the groundwater observation wells. The name of the districts having spot values of >1.5 mg/L are given in following table no. 1.7.

**Table 1.7: State wise details of distribution of fluoride in Ground Water above permissible limit**

| Sl. No. | State | Fluoride | |
|---|---|---|---|
| | | No. of districts affected | Districts (in parts) |
| 1. | Andhra Pradesh | 19 | Adilabad, Anantpur, Chitoor, Guntur, Hyderabad, Karimnagar, Khammam, Krishna, Kurnool, Mehboobnagar, Medak, Nalgonda, Nellore, Prakasham, Rangareddy, Vishakhapatnam, Viziangaram, Warangal, West Godawari |
| 2. | Assam | 4 | Goalpara, Kamrup, Karbi Anglong, Naugaon |
| 3 | Bihar | 9 | Aurangabad, Banka, Buxar, Jamui, Kaimur, Munger, Nawada, Rohtas, Supaul |
| 4. | Chhattisgarh | 12 | Bastar, Bilaspur, Dantewara, Janjgir-Champa, Jashpur, Kanker, Korba, Koriya, Mahasamund, Raipur, Rajnandgaon, Suguja |
| 5. | Delhi | 6 | East Delhi, New Delhi, Northwest Delhi, South Delhi, Southwest Delhi, West Delhi |

| **Sl. No.** | **State** | **Fluoride** | |
|---|---|---|---|
| | | **No. of districts affected** | **Districts (in parts)** |
| 6. | Gujarat | 18 | Ahmedabad, Amreli, Anand, Banaskantha, Bharuch, Bhavnagar, Dahod, Junagarh, Kachchh, Mahesana, Narmada, Panchmahals, Patan, Rajkot, Sabarkantha, Surat, Surendranagar, Vadodara |
| 7. | Haryana | 14 | Bhiwani, Faridabad, Gurgaon, Hissar, Jhajjar, Jind, Kaithal, Kurkshetra, Mahendragarh, Panipat, Rewari, Rohtak, Sirsa, Sonepat |
| 8. | Jammu & Kashmir | 2 | Rajauri, Udhampur |
| 9. | Jharkhand | 6 | Bokaro, Giridih, Godda, Gumla, Palamau, Ranchi |
| 10.. | Karnataka | 20 | Bagalkot, Bangalore, Bellary, Belgaum, Bidar, Bijapur, Chamarajnagar, Chikmagalur, Chitradurga, Devangere, Dharwar, Gadag, Gulbarga, Haveri, Kolar, Koppala, Mandya, Mysore, Raichur, Tumkur. |
| 11. | Kerala | 1 | Palakkad |
| 12. | Madhya Pradesh | 19 | Bhind, Chhatarpur, Chhindwara, Datia, Dewas, Dhar, Guna, Gwalior, Harda, Jabalpur, Jhabua, Khargone, Mandsaur, Rajgarh, Satna, Seoni, Shajapur, Sheopur, Sidhi. |
| 13. | Maharashtra | 8 | Amrawati, Chandrapur, Dhule, Gadchiroli, Gondia, Jalna, Nagpur, Nanded, |
| 14. | Orissa | 11 | Angul, Balasore, Bargarh, Bhadrak, Boudh, Cuttack, Deogarh, Dhenkanal, Jajpur, Keonjhar, Suvarnapur |
| 15. | Punjab | 11 | Amritsar, Bhatinda, Faridkot, Fatehgarh-Saheb, Firozpur, Gurdaspur, Mansa, Moga, Muktsar, Patiala, Sangrur, |
| 16. | Rajasthan | 30 | Ajmer, Alwar, Banswara, Barmer, Bharatpur, Bhilwara, Bikaner, Bundi, Chhittorgarh, Churu, Dausa, Dholpur, Dungarpur, Ganganagar, Hanumangarh, Jaipur, Jaisalmer, Jalore, Jhunjhunu, Jodhpur, Karauli, Kota, Nagaur, Pali, Rajasamand, SawaiMadhopur, Sikar, Sirohi, Tonk, Udaipur |
| 17. | Tamil Nadu | 16 | Coimbatore, Dharmapuri, Dindigul, Erode, Karur, Krishnagiri, Namakkal, Perambalur, Puddukotai, Ramnathpuram, Salem, Shivaganga, Theni, Thiruvannamalai, Vellore, Virudunagar |
| 18. | Uttar Pradseh | 10 | Agra, Aligarh, Etah, Firozabad, Jaunpur, Kannauj, Mahamayanagar, Mainpuri, Mathura, Maunathbhanjan, |
| 19. | West Bengal | 8 | Bankura, Bardhhman, Birbhum, Dakhin Dinajpur, Malda, Nadia, Purulia, Uttar Dinajpur |

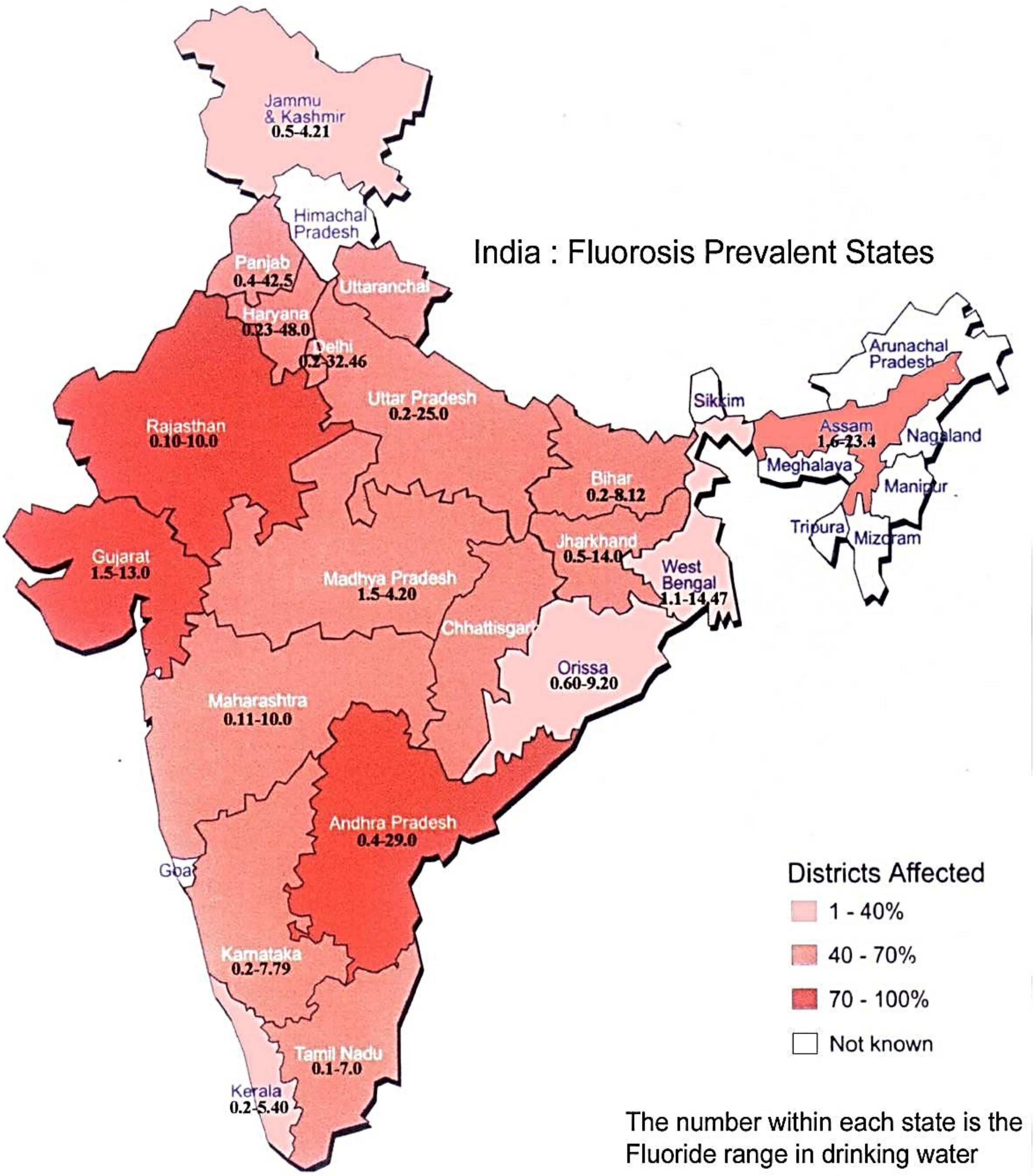
Source: Central Ground Water board[41]

**Table 1.8: Districts known to be endemic for fluoride in various states of India**

| State | Districts | Range of fluoride concentration (mg/L) |
|---|---|---|
| Assam | Karbianglong, Nagaon | 0.2–18.1 |
| Andhra Pradesh | All districts except Adilabad, Nizamabad, West Godhavari, Visakhapattnam, Vijzianagaram, Srikakulam | 0.11–20.0 |
| Bihar | Palamu, Daltonganj, Gridh, Gaya, Rohtas, Gopalganj, Paschim, Champaran | 0.6–8.0 |
| Delhi | Kanjhwala, Najafgarh, Alipur | 0.4–10.0 |
| Gujarat | All districts except Dang | 1.58–31.0 |
| Haryana | Rewari, Faridabad, Karnal, Sonipat, Jind, Gurgaon, Mohindergarh, Rohtak, Kurukshetra, Kaithal, Bhiwani, Sirsa, Hisar | 0.17–24.7 |
| Jammu and Kashmir | Doda | 0.05–4.21 |
| Karnataka | Dharwad, Gadag, Bellary, Belgam, Raichur, Bijapur, Gulbarga, Chitradurga, Tumkur, Chikmagalur, Manya, Banglore, Mysore | 0.2–18.0 |
| Kerala | Palghat, Allepy, Vamanapuram, Alappuzha | 0.2–2.5 |
| Maharasatra | Chandrapur, Bhandara, Nagpur, Jalgaon, Bulduna, Amravati, Akola, Yavatmal, Nanded, Sholapur | 0.11–10.2 |
| Madhya Pradesh | Shivpuri, Jabua, Mandla, Dindori, Chhindwara, Dhar, Vidhisha, Seoni, Sehore, Raisen and Bhopal | 0.08–4.2 |
| Orrissa | Phulbani, Koraput, Dhenkanal | 0.6–5.7 |
| Punjab | Mansa, Faridcot, Bhatinda, Muktsar, Moga, Sangrur, Ferozpur, Ludhiana, Amritsar, Patila, Ropar, Jallandhar, Fatehgarh sahib | 0.44–6.0 |
| Rajasthan | All the 32 districts | 0.2–37.0 |
| Tamil Nadu | Salem, Periyar, Dharampuri, Coimbatore, Tiruchirapalli, Vellore, Madurai, Virudunagar | 1.5–5.0 |
| Uttar Pradesh | Unnao, Agra, Meerut, Mathura, Aligarh, Raibareli, Allahabad | 0.12–8.9 |
| West Bengal | Birbhum, Bardhaman, Bankura | 1.5–13.0 |

Source: Meenakshi and Maheshwari[62] (2006)

In the map of India (Fig 1.4) reveals the states which are presently non-endemic, unless proved otherwise



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

Fig 1.4: Map Depicting fluoride affected areas in India

### 1.3.3 West Bengal Scinario of Fluoride Contamination:

Ground water of 43 blocks of 7 districts in West Bengal is contaminated by fluoride. Fluoride content in ground water was first reported in 1997 around Nasipur village in Nalhati-I block of Birbhum district. Its presence has been suspected in 11 other districts of the state. In 1998, Birbhum district of West Bengal was found to be fluoride affected as reported by School on Environment Studies, Jadavpur University, Kolkata. Extents of fluoride contamination in West Bengal are given in table 1.9

**Table 1.9: Extent of Fluoride Contamination in West Bengal**

| District | Fluoride affected blocks | No. of blocks |
|---|---|---|
| Maldah | Bamongola, Ratua-II | 2 |
| Bankura | Gangajal ghati, Raipur, Indpur, Bankura-II, Chatna, Taldanga, Saltora, Simlapal, Hirabandh Barjora | 10 |
| South 24 Parganas | Baruipur | 1 |
| Purulia | Raghunathpur- I&II, Puncha,Joypur,Neturla,Santuri, Baghmundi, Purulia I &II, Kashipur, Jhalda-I, Arsha, Barabazar,Manbazar-I, Hura, Para, Balrampur | 17 |
| Birbhum | Naalhati-I, Rampurhat-I, Mayureswar-I, Saintha, Suri-II, Rajnagar, Khoirasol | 7 |
| Dakshin Dinajpur | Gangarampur,Kumarganj, Bansihari, Kushmandi, Tapan | 5 |
| Uttar Dinajpur | Itahar | 1 |
| **7 Districts** | | **43 Blocks** |

Source: Public Health Engineering West Bengal[39]

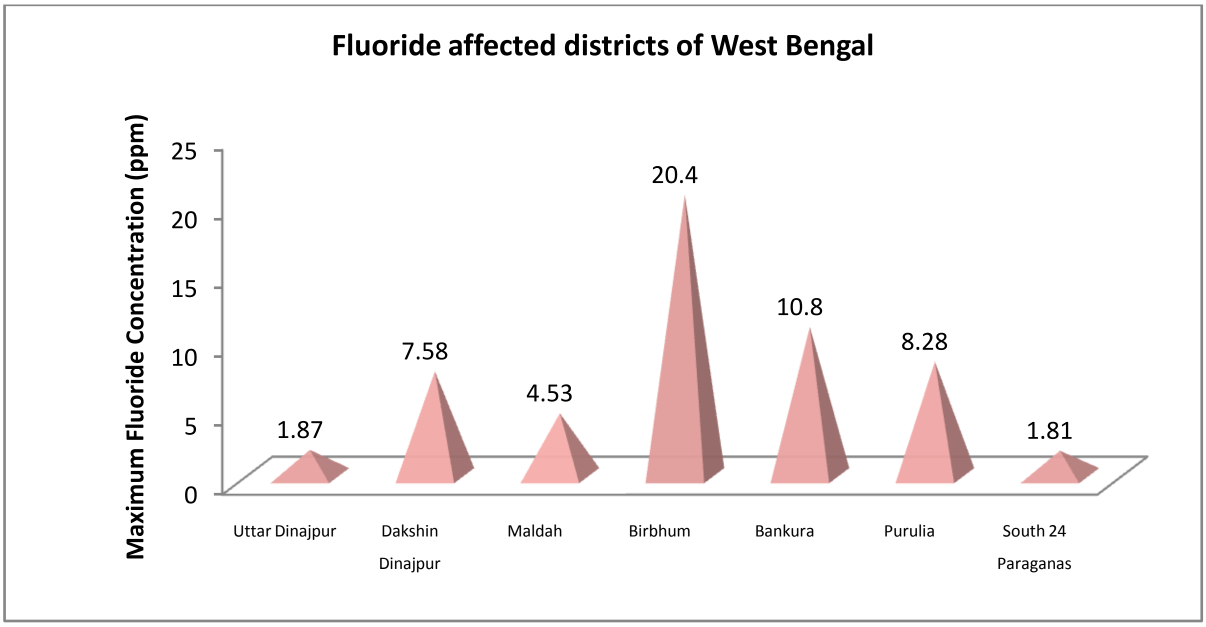


Fig 1.5: Fluoride affected districts of West Bengal with Maximum fluoride concentration (ppm)

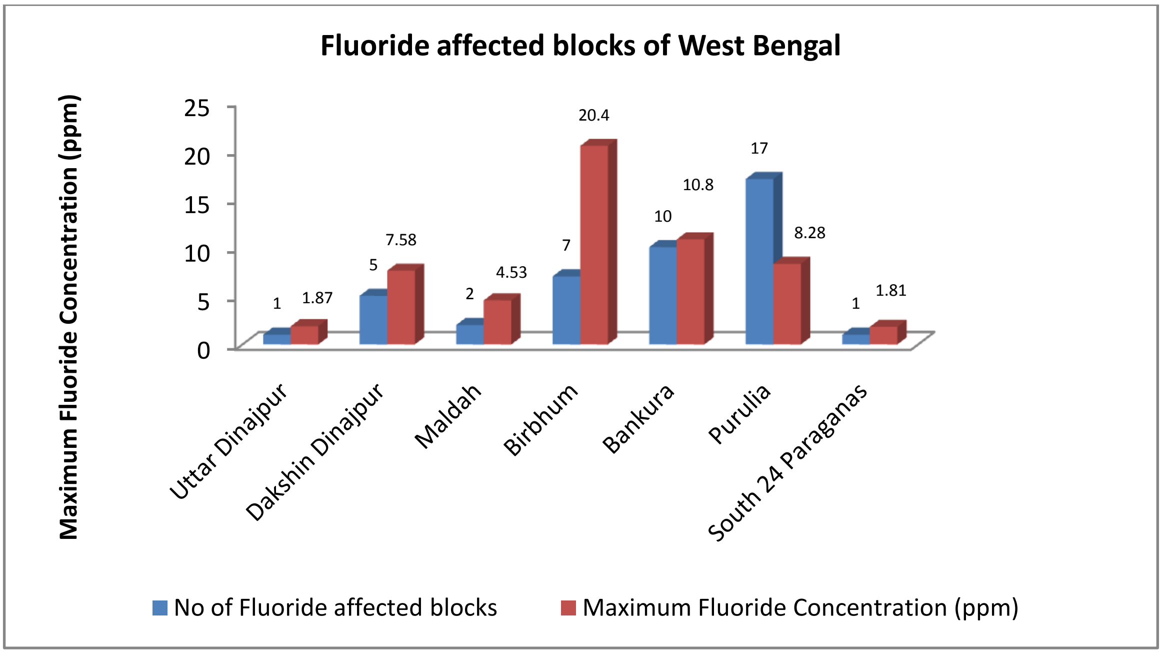


Fig 1.6: Fluoride affected blocks of West Bengal with Maximum fluoride concentration (ppm)

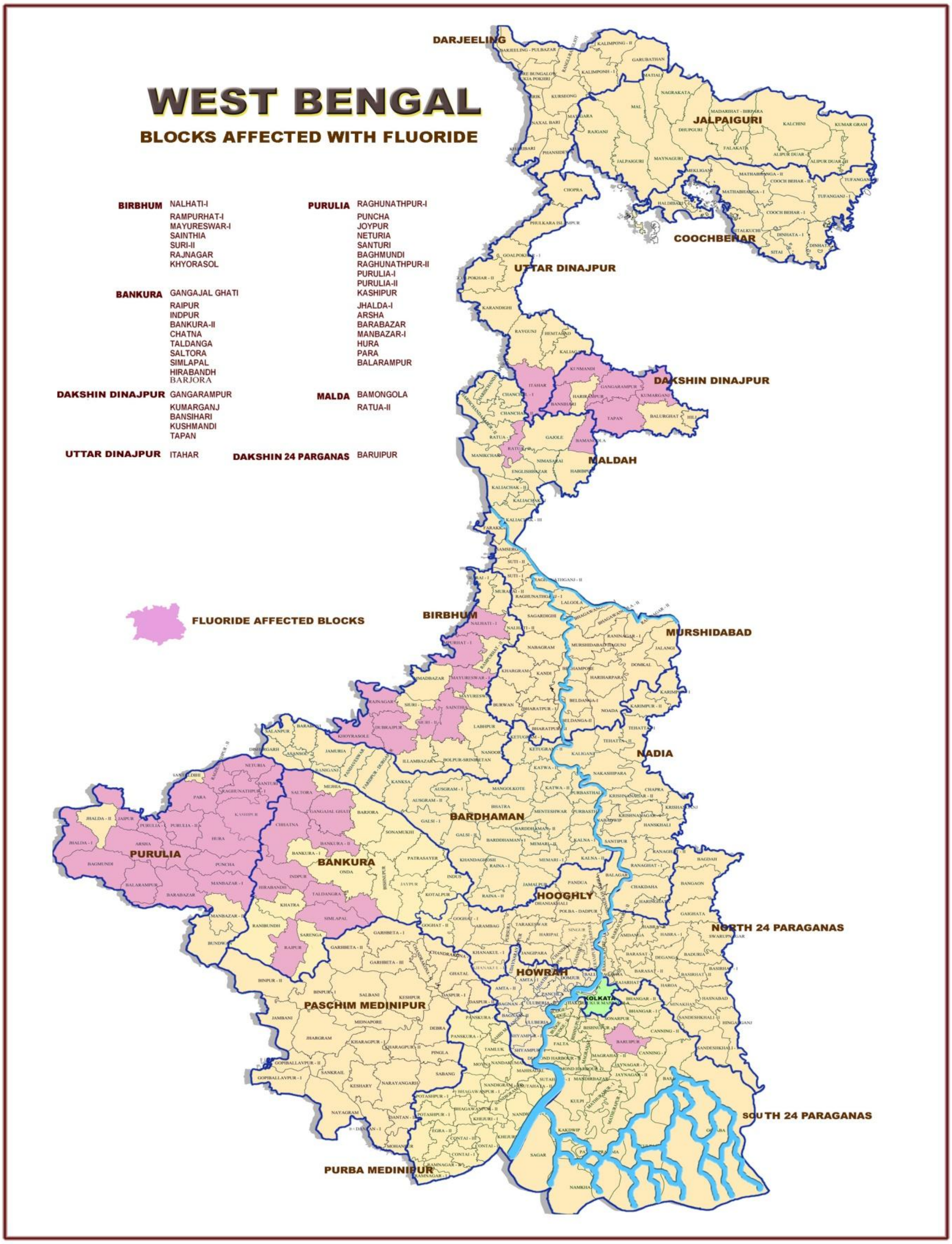


Fig 1.7: Extent of Fluorosis in West Bengal

# Objective

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## CHAPTER 2

## 2.1 Objective of the study:

Objective of this study is to delineate the different techniques for removing of fluoride for drinking purpose and explore ion exchange process (using cationic & anionic resin) and adsorption method (using activated alumina) for defluoridation of fluoride contaminated water. The specific objectives are as follows-

- Study the contamination of fluoride in drinking water.
- Consequences of excess fluoride contamination on human health.
- Exploration of ion exchange process using both cation-anion exchange resin and only anionic resin alone for removal of fluoride of fluoride contaminated water.
- Exploration of adsorption process using activated alumina to analyze defluridation efficiency of the unit.
- To develop an efficient lab scale defluoridation model using easily available low cost material.
- Evaluate technical feasibility and economical viability of above techniques for defluoridarion of fluoride contaminated water.

## 2.2 Scope of work:

- To study defluoridation by application of ion exchange process by using cationic-anionic resin and only anionic resin alone in burette filter
- To study defluoridation by application of adsorption process by using activated alumina in lab scale filter.
- To analyze the various water quality parameters like concentration of fluoride, pH, TDS, EC, Total Hardness, Total Alkalinity, Chloride and Turbidity of trated water.
- To evaluate the isotherm models of adsorption of fluoride.

## 2.3 Deliverables:

- To asses of pros. & cons. of applied defluoridation techniques.
- Make the defluoridation techniques economically vaible, technically efficient and easy to operate.

# Literature Review

## CHAPTER 3

**Kaur I et al. (2019)**[1] stated defluoridation of water using an economic method is important to combat the issue of excessive fluoride content (>1.5 mg/L), which is very detrimental to human health, in drinking water. In the present work, micelle templated mesoporous material, MCM-41, was synthesized and explored as an adsorbent for adsorption of fluoride ions from aqueous media and the process of adsorption was optimized through three levels of Box–Behnken design (BBD) of response surface methodology (RSM). The data obtained were found to be best fitted for Langmuir adsorption isotherm suggesting monolayer adsorption of fluoride ions on the surface of micelle templated MCM-41; Langmuir maximum adsorption capacity was found to be 52.91 mg/g. Optimization through BBD involves approximation of selected input of independent variables, i.e., initial fluoride concentration, solution pH and adsorbent dose with percentage removal of fluoride as the response variable. The quadratic model was suggested to predict the percentage removal of fluoride ions. As per the prediction, maximum removal of 82% can be achieved at initial concentration up to 21 ppm in pH range of 5.4–5.8 and adsorbent dose of 1–1.3 g/L. Experimental and model predicted values of adsorption were found to be in good agreement with each other.

**Gupta *et al.* (2019)**[2]explored heavily doped cationic nano-composites of hydroxyapatite (HA) given its surface chemistry for adsorption of the specific anion. It was synthesized and extensively characterized HA nano-rods (HA-NR), Al/Mg-HA nanocomposites and amorphous aluminum hydroxide, and optimized their efficient defluoridation. The kinetics and thermodynamics of adsorption were further evaluated to establish the mechanistic rationale and its spontaneity. It is reported the optimized ideal adsorbents for the near-total removal of fluoride that demonstrated 99.99% and 99.98% efficiency with adsorption capacities of 83.3 and 81.3mg/g respectively. The adsorbent composites were (Mg-HA)-$Al(OH)_3$ and (HA-NR)-$Al(OH)_3$ in 1:1 ratio. The optimal conditions for defluoridation were 25mg of adsorbent in 25ml (10mg/L) fluoride solution at room temperature agitated for 10h in the pH range of 4.88–7.20.

**Tang et al.(2018)**[3] investigated the potential of a novel hydroxyapatite decorated with carbon nanotube composite (CNT-HAP) for fluoride removal. The synthesized CNT-HAP composite was systematically characterized by X-ray diffraction(XRD), Fourier Transform infrared spectroscopy(FTIR), scanning electron microscope (SEM) and Brunauer–Emmett–Teller(BET). Batch adsorption experiments were conducted to investigate the defluorination capacity of CNT-HAP. The CNT-HAP composite has a maximum adsorption capacity of 11.05 $mg{\cdot}g^{-1}$ for fluoride, and the isothermal adsorption data were fitted by the Freundlich model to calculate the thermodynamic parameters. Thermodynamic analysis implies that the adsorption of fluoride on CNT-HAP is a spontaneous process. Furthermore, the adsorption of fluoride follows pseudo-second-order model. The effects of solution pH, co-existing anions and reaction temperature on defluorination efficiency were examined to optimize the operation conditions for fluoride adsorption. It is found that the optimized pH-value for fluoride removal by CNT-HAP composite is 6. In addition, among five common anions studied in this work, the presence of $HCO_3^-$ and $PO_4^{3-}$ could considerably affect the fluoride removal by CNT-HPA in aqueous media. Finally, the underlying mechanism for the fluoride removal by CNT-HAP is analyzed, and an anion exchange process is proposed.

**Cai H. *et al.* (2016)**[4] described a low-cost and highly efficient biosorbent for fluoride removal. It was prepared by loading zirconium (IV) onto ball-milled, ultrafine tea powder (UTP-Zr). To evaluate the fluoride adsorption capacity of UTP-Zr over a wide range of conditions, the biosorbent dosage, contact time, initial pH, initial fluoride concentration and presence of other ions were varied. UTP-Zr performed well over the considerably wide pH range of 3-10. The residual concentration of Zr in the treated water was below the limit of detection (0.01 mg/L). Fluoride adsorption by the UTP-Zr biosorbent followed the Langmuir model, with a maximum adsorption capacity of 12.43 mg$F^-$/g at room temperature. The fluoride adsorption kinetics fit the pseudo-second-order kinetic model. Results from this study demonstrated that UTP-based biosorbents will be useful and safe for the removal of fluoride from drinking water.

**Zhang K. *et al.*(2016)**[5] discussed about development of a nanosphere adsorbent for the removal of fluoride from water. A new uniform-sized $CeCO_3OH$ nanosphere adsorbent was developed, and tested to establish its efficiency, using kinetic and thermodynamic studies, for fluoride removal. The results demonstrated that the $CeCO_3OH$ nanospheres exhibited much high adsorption capacities for fluoride anions due to electrostatic interactions and exchange of the carbonate and hydroxyl groups on the adsorbent surface with fluoride anions. Adsorption kinetics was fitted well by the pseudo-second-order model as compared to a pseudo-first-order rate expression, and adsorption isotherm data were well described by Langmuir model with max adsorption capacity of 45 mg/g at pH 7.0. Thermodynamic examination demonstrated that fluoride adsorption on the $CeCO_3OH$ nanospheres was reasonably endothermic and spontaneous. Moreover, the $CeCO_3OH$ nanospheres have less influence on adsorption of fluotide by pH and co-exiting ions, such as $NO_3^-$, $SO_4^{2-}$ ,$Cl^-$, $HCO_3^-$, $CO_3^{2-}$ and $PO_4^{3-}$, and the adsorption efficiency is very high at the low initial fluoride concentrations in the basis of the equilibrium adsorption capacities. This study indicated that the $CeCO_3OH$ nanospheres could be developed into a very viable technology for highly effective removal of fluoride from drinking water.

**Wu S. *et al.*(2016)**[6] stated a novel adsorbent, hydroxyl aluminum oxalate (HAO), for the high efficient removal of fluoride from aqueous solution was successfully synthesized. The adsorbent was characterized and its performance in fluoride ($F^-$) removal was evaluated for the first time. Kinetic data reveal that the $F^-$ adsorption is rapid in the beginning followed by a slower adsorption process; 75.9% adsorption can be achieved within 1 min and only 16% additional removal occurred in the following 239 min. The $F^-$ adsorption kinetics was well described by the pseudo second-order kinetic model. The calculated adsorption capacity of this adsorbent for $F^-$ by Langmuir model was 400 mg/g at pH 6.5, which is one of the highest capabilities of today's materials. The thermodynamic parameters calculated from the temperature-dependent isotherms indicate that the adsorption reaction of $F^-$ on the HAO is a spontaneous process.

**Jin *et al.* (2015)**[7] used alumina-modified expanded graphite ($Al_2O_3$/EG) composite via facile solution method at 450°C for 2 hours for the defluoridation of water. The fluoride removal at pH range between 3 and 7 was not readily affected by the pH of aqueous solution. The fluoride removal of 94.4% and adsorption capacity of 1.18 mg/g was observed by $Al_2O_3$/EG composite adsorbent. This adsorbent was quite efficient enough for removing lower concentration of fluoride ions present in water below permissible standard. Therefore, the adsorption was a multi-molecular layer adsorption between the adsorbed molecules where the process was spontaneous and endothermic in nature.

**Mariappan R. *et al.* (2015)**[8] described the use of chemically activated cotton nut (*Gossipium hirsutum*) shell carbon for the removal of fluoride from contaminated drinking water. 100 g of cotton nut shell (CTNS) was treated separately with 40 g of $ZnCl_2$, $K_2CO_3$ and $H_3PO_4$ at room temperature. The raw CTNSC and chemically activated CTNSCs were classified as R-CTNSC, Z-CTNSC, K-CTNSC, and P-CTNSC represent ZnCl2, K2CO3 and H3PO4 impregnated CTNSCs, respectively. Effects of adsorption time, adsorbent dose, pH of the solution, initial concentration of fluoride, and temperature of the solution were studied with equilibrium, thermodynamics and kinetics of the adsorption process by various CTNSC adsorbents. It showed that the chemically activated CTNSCs can effectively remove fluoride from the solution. The adsorption equilibrium data correlate well with the Freundlich isotherm model. The adsorption of fluoride by the chemically activated CTNSC is spontaneous and endothermic in nature. The pseudo first order, pseudo second order and intra particle diffusion kinetic models were applied to test the experimental data. The method is simple and has shown great potential for the removal of fluoride ions. The removal increased with the increase in the adsorbent concentration. The 83.67% salt rejection has been identified in 3mg/L of 100ml fluoride using 1.75 mg dosage of P-CTNSC adsorbent.

**Rajkumar S. *et al.* (2015)**[9] investigated for low cost fluoride adsorbents prepared from renewable bio waste. The preparation of composite adsorbents for fluoride anion was performed from natural cow dung and cow dung impregnated by a solution of calcium and iron salts. These starting materials were dried and carbonized at 300, 500 or 700ºC for 2 hrs leading to Cow Dung Carbon (CDC) or Ca-Fe Impregnated Cow Dung Carbon (ICDC). All these carbons were used as adsorbent in fluoride removal studies. Batch mode experiments using CDC and ICDC were conducted in which the fluoride removal varied linearly as a function of contact time, pH, adsorbent dose, initial fluoride concentration, temperature, interfering anionic species. The most efficient carbon was CDC which was prepared at 500ºC. It showed a defluoridation capacity of 15 mg/g.

**Samadi *et al.*(2014)**[10] investigated on strong-base anion to assess their sorptive removal capacity of fluoride from water. It was found that at natural pH (7) the removal of fluoride was effective and was improved for increasing contact time and adsorbent dosage. According to the Langmuir model the maximum sorption of the resin was 13.7 mg/g. Among the Langmuir, Freundlich and Temkin isotherm models tested, it was found that the Freundlich model was the most appropriate to describe fluoride sorption at equilibrium (r2>0.99); It was also shown that the rate-limiting step was the film diffusion rather than the intra-particle diffusion. A simple and efficient statistical method, based on factorial design analysis using linear regression model, was applied for the determination of the optimal removal conditions deduced from 3D plots and contour plots. To approach real conditions, the effect of co-existing ions showed slightly reverse effect of hardness and chloride ions while a higher reverse effect for nitrate. Contrarily, sulfate had no significant effect on fluoride removal.

**Tomar *et al.* (2014)**[11] examined a novel, cheap, easily available and eco-friendly adsorbent obtained from treated Citrus limonum (lemon) leaf with the aim of fluoride ion removal from aqueous environment. Batch experiments were performed to study the influence of various experimental variables such as pH of aqueous solution from 2 to 8, adsorbent dose of 1 to 10 g/50 mL fluoride solution, contact time 5 to 145 min, initial fluoride concentration from 2 to 15 mg/L and the presence of few competing anions on the adsorption of fluoride on citrus lemon leaf adsorbent. The authors reported that the most efficient fluoride removal was at pH 2, and that the tested adsorbent showed the maximum defluoridation capacity of 70% of 2 mg/L fluoride ion. The experimental data reveals that Freundlich isotherm model fitted better than Langmuir isotherm with Citrus limonum for fluoride removal.

**Nazari *et al.* (2014)**[12] has studied that nanomagnesia alumina adsorbent by dopping γ-Al2O3 with MgO nanoparticle through sonochemical approach for defluoridation of water. The optimum removal up to 85% and its adsorption capacity 5.6 mg/g was attained at neutral pH range of 6.3-7.3 in 140 min and adsorbent dose of 0.5 g/l. The presence of phosphate ions highly responsible for affecting adsorption capacity whereas presence of other ions such as $Cl^-$, $SO_4^{2-}$ and $HCO_3^-$ had the slight effect of the defluoridation capacity. The experimental data fitted well with Langmuir adsorption isotherm and adsorption process followed the pseudo-second-order kinetic model.

**Chai *et al.* (2013)**[13] applied sulfate-doped $Fe_3O_4/Al_2O_3$ nano particles with magnetic separability for fluoride removal from drinking water. Then authors conducted the experiments with 100 mL fluoride solution with initial fluoride concentrations ranging from 2 mg/L to 160 mg/L and 0.1 g of adsorbent during 7 hours. Adsorption experiments were conducted at 25°C and initial pH value of used fluoride solutions were from 2 to 12. The effects of anions like chloride, nitrate, sulfate and phosphate on fluoride adsorption under a fixed initial competing anions concentration (2 m mol $L^{-1}$), and initial fluoride concentrations of 5 mg/L and 20 mg/L at pH 7 was experimented. The Langmuir isotherm model was found to be the best fit, in which the calculated adsorption capacity for fluoride on sulfate-doped $Fe_3O_4/Al_2O_3$ was 70.4 mg/g at pH 7. The optimum pH range for fluoride removal was from 4.0 to 10.0 which make the tested adsorbent appropriate for the applicability in all natural water treatments. The sorption process was purely ion exchange of sulfate by fluoride and formations of inner-sphere fluoride complex .The competing anions, except phosphate, did not inhibit fluoride removal which suggest that used nano adsorbent had a high selectivity for fluoride removal.

**Mondal *et al*.(2012)**[14] conducted a comparative study for removal of fluoride using activated silica gel (ASiG) and activated rice husk ash (ARHA) as adsorbents through batch studies. The authors reported that both adsorbents were efficient for the uptake of fluoride at pH 2.0 and contact time 100 min. ASiG was found to be more efficient than ARHA with an initial fluoride concentration of 5 mg/L; percentage removal efficiency was 88.30 and 96.7 for ARHA and ASiG, respectively. The study on equilibrium sorption revealed that Langmuir isotherm model give best fit to experimental data.

**Ghorban *et al.* (2012)**[15] used pumice stone for fluoride removal. Pumice stone was immersed in 1 M NaCl solution at room temperature, and afterwards it was washed with distilled water to remove acids from the sorbent and dried out at 80 °C. It was then mixed with the specified amount of hexadecyltrimethyl ammoniumbromide (HDTMA) in 1 L of distilled Water. The effect of fluoride removal was studied from pH 3 to 10, contact time from 5 min to 60 min and the adsorbent dosage from 0.15 to 2.5 g/L. 96% of fluoride ion was removed under dosage of 0.5 g/L, pH 6 and fluoride ion concentration of 10 mg/L. Langmuir isotherm fits well and it also follows pseudo-second-order reaction. Thermodynamic study shows that the reaction is spontaneous and endothermic.

**Pandey *et al.* (2012)**[16] took the natural plant Tinospora cordifolia to check the defluoridation capacity. The authors found a good adsorbing capacity for fluoride ion with Tinospora cordifolia, highlighting its potential for the drinking water treatment process. pH had a strong effect on sorption capacity and the optimum pH was found to be 7 and equilibrium time was achieved within 120 min. The uptake capacity of fluoride was found to be 25 mg g-1. The data obtained fits well with Langmuir and Freundlich isotherms. FTIR spectral analysis showed adsorption of fluoride on the functional groups. The biomass was found to be very efficient, instantaneous and economical for removing fluoride from drinking water at neutral pH.

**Ramesh *et al*.(2012)**[17] studied "batch and column operations for the removal of fluoride from aqueous solution using bottom ash." A batch and column studies will be carried out for the removal of fluoride from aqueous solution using bottom ash as adsorbent. The bottom ash is a waste material obtained by thermal power generation plants after combusting solid fuels. It is an undesired collected material, which is transported and dumped near the surrounding land. The equilibrium time decreases with the temperature without much increase in fluoride ion uptake. The time to reach equilibrium was slightly affected by the temperature of fluoride solution. Maximum adsorption by the bottom ash was observed at pH 6.0.

**Gandhi *et al*.(2012)**[18] conducted a study on adsorbents such as concrete, ragi seed powder, red soil, horse gram seed powder, orange peel powder, chalk powder, pineapple peel powder (PPP), and multani mitti. The experimental setup was bath studies. Result indicated fluoride removal efficiency of 86% for chalk powder and pineapple peel powder. 79% and 75% for orange peel powder and horse gram seed powder respectively. Percentage removal for ragi seed and red mud was found to be 65% and 71%. Removal efficiency was recorded less for multani mitti and concrete which was 56% and 53%.

**Vivek and Kalyan (2011)**[19] examined The fluoride removal capacity of aluminium hydroxide coated rice husk ash (RHA). Coating of rice husk was done using aluminium salt solution of 0.6 N and sodium hydroxide solution (five times concentrated than aluminium salt solution). Once the reaction mixture reached the desired value of pH 5-7, the sodium hydroxide addition was stopped. Aluminium hydroxide (AH) coated RHA was dried in an oven at 100°C for 3-4 hours. Batch and column studies were performed using particle size of 425µm. BET surface area results showed 62.8m$^2$/g for RHA and 50.4m$^2$/g for AH coated RHA. Maximum removal of fluoride by AH coated RHA was observed at pH=5.0±0.5. The study was conducted with fluoride ion concentration of 5 mg/L. Batch studies showed an equilibrium time as 10 min and adsorption capacity as 15.08 mg/g with initial fluoride ion concentration from 2 to 20 mg/L and column studies has an adsorption capacity as 9.5 mg/g with fluoride concentration of 5 mg/L. This study shows a best fit to Freundlich isotherm, confirming multilayer adsorption. It also follows a pseudo second order kinetics. AH coated RHA has good adsorption capacity than uncoated RHA.

**Ma *et al.* (2009)**[20] studied with granular activated carbon (GAC) of particle size 0.45 – 0.9 mm. Granular activated carbon was then immersed in 37.5 % HCl for 12 hours to reduce ash content. It was then washed to reach neutrality and dried to remove water from an oven at 105°C for 24 hours. When 5g of GAC was immersed in $MnCl_2$ and stirred strongly for 6 hours at room temperature, the pH was found to be 3.3 + 0.1 for the suspension. $KMnO_4$ is then added and given a constant stirring to oxidate $Mn^{2+}$ solution, on time when the suspension turns dark brown it indicates the formation of $MnO_2$ precipitation. The precipitate was then filtered and washed several times with distilled water and dried at 105°C. SEM image shows uniform surface with small cracks and micro pores surface area of 917.17 $m^2$/g. EDAX shows the presence of Mn and O as the major elements in the absorbent. FTIR and XPS show the existence of hydroxyl and carbonyl groups on activated carbon. Batch studies were performed with 10, 20, 30 mg/L of fluoride ion solution which revealed the optimum contact time 180minutes and maximum removal of fluoride at pH 3.0. Equilibrium data well fitted with Freundlich isotherm and sorption process follows the pseudo second order.

**McKee and Jhonston (2008)**[21] discussed the defluoridation from drinking water using activated carbon prepared from various raw materials like rice husk and wheat husk exhibits good fluoride uptake capacity. The adsorption process depends highly on pH. Removal of fluoride is effective at pH <3.0 and there is little removal at neutral pH of 7.0. Rice husk could accomplished the removal of 83% nearly and attains almost an equilibrium condition in nearly 180 min (3 h). As pH was increased from 2.0 to 12.0, removal of fluoride by rice husk decreased continuously. Decrease in the removal of fluoride in pH range of 2.0–10.0 was low, i.e. 12.8%, whereas from pH 10.0 to 12.0 removal of fluoride decreased significantly. The amount of fluoride adsorbed increased with increase in dose and maximum 84% removal was accomplished at a dosage of 6 g/L.

**Singh *et al*.(2008)**[22] studied "the defluoridation of drinking water using brick powder as an adsorbent, freshly fired brick pieces are used for the removal of fluoride in domestic defluoridation units." The brick bed in the unit is layered on the top with charred coconut shells and pebbles. Water is passed through the unit in an up- flow mode. It is reported that efficiency depends on the quality of the freshly burnt bricks. The unit could be used for 2540 days, when withdrawal of defluoridated water per day was around 8 L and raw water fluoride concentration was 5 mg/L.

**Kamble *et al.* (2007)**[23] studied the performance of removing fluoride ion from aqueous solution by chitin, chitosan and lanthanum incorporated chitosan, which was prepared by adding 1g of chitosan with LaNO3.6H2O with continuous stirring for 6 hours. After stirring, the contents were filtered and washed with deionized water and dried at 75°C in an oven. Batch adsorption studies were performed with chitin, chitosan and lanthanum incorporated chitosan. The maximum adsorption was observed for 20% La-Chitoson proportion than chitin and chitosan. Hence further experiments were conducted with La-Chitoson proportion. Presence of anion in the solution reduces the adsorption capacity. Maximum loading capacity was 3.1 mg/g La-Chitoson proportion at adsorbent dose of 1.5g/g and contact time of 24 hour, pH 6.7.

**Wu *et al*. (2007)**[24] developed a trimetal oxide for fluoride ion removal which was prepared by coprecipitation of Fe(II), Al(III) and Ce(IV) salt solutions with a molar ratio of 1:4:1 under alkaline condition. Batch and column studies were performed. The optimum pH range for fluoride adsorption was 6.0–6.5 and the adsorbent showed high defluoridation ability around pH 5.5–7.0. A high adsorption capacity of 178 mg/g was observed at pH 7, under an equilibrium fluoride concentration of 84.5 mg/L and adsorbent dose of 150 mg/L. The adsorption isotherm was fit better by the two-site (two active sites for monolayer sorption) Langmuir model than the one-site model (single active site for monolayer sorption). While studying the interference of co-ions, presence of sulfate and chloride did not affect fluoride adsorption, but nitrate influenced it only when the concentration of nitrate exceeded 50mg/L.

**Cengeloglu *et al*. (2002)**[25] used alkaline red mud obtained from aluminium plant, which was thoroughly washed with water until neutralisation and subjected to acid treatment with 20% concentrated HCL for acid activation. Then the acid treated alkaline red mud was thoroughly washed with water and allowed for drying. The surface area of red mud was $20.7 m^2/g$. The experiments were carried out in batch mode. The maximum removal of 82% was obtained at pH 5.5, equilibrium time of 2 hrs. Langmuir isotherm showed a best fit for alkaline red mud.

# Methods of Defluoridation

## CHAPTER 4

Defluoridation is “adjustment of level of fluoride in drinking water to the optimal level”.To conquer the hazardous wellbeing impact of fluorosis, different approaches for defluoridations are exists like-

I. Co-precipitation Techniques;
II. Absorption;
III. Ion-exchange Process;
IV. Electrocoagulation Process;
V. Membrane Filtration Technique;
VI. Herbal Coagulation, Flocculation adsorbent Method

## 4.1 Co-precipitation Techniques:

Co-precipitation Technique is effective in removing a broad range of impurities from water, including colloidal particles and dissolved organic substances.

Two mechanisms essentially operate: charge neutralization of negatively charged colloids by cationic hydrolysis products, and incorporation of impurities in an amorphous precipitate of metal hydroxide, generally known as “sweep flocculation.”

The relative importance of these two mechanisms depends on many factors, especially pH and coagulant dosage. Charge neutralization is a simple mechanism for destabilization of negatively charged particles by the adsorption of cations from solution. This adsorption of positively charged species on negative surfaces may occur for simple electrostatic reasons or by formation of some types of surface complexes. Optimum destabilization of colloids generally occurs in the presence of small amounts of hydrolyzing coagulants and corresponds with the neutralization of particle charge, which can be determined by electrophoresis mobility measurements. Large amounts of coagulants cause charge reversal so that the particles become restabilized and show a net positive charge. Destabilization and restabilization typically occur with just micromolar concentrations of coagulant for relatively low particle concentrations. Hence for optimum destabilization by charge neutralization, precise control of the coagulant dosage is essential. If charge neutralization dominates the co-precipitation process, then a relationship should exist between particle concentration and the optimum coagulant dosage.

In many cases it is observed that higher coagulant dosages are much more effective in coagulation contrary to expectations based on the charge neutralization theory. This is attributed to rapid and extensive hydroxide precipitation and sweep flocculation, which occurs at higher coagulant dosages. Thus the term “sweep flocculation” refers to the “sweeping out” of particles from water by the hydroxide precipitate and generally gives improved particle removal compared with when particles are destabilized just by charge neutralization alone. It is known that hydroxide precipitates have an “open” structure so that even a small mass can give a large effective volume concentration and hence a high probability of capturing other particles. Therefore, in sweep flocculation, the rate of aggregation is vastly improved due to increased solids concentration, and it is also possible that the binding of particles by the precipitated hydroxides may give stronger aggregates. Thus, co-precipitation by hydrolyzing coagulants may involve both charge neutralization and sweep flocculation as essential steps in particle removal. Defluoridation processes by co-precipitation are of two types:

1. Precipitation of fluoride by a suitable reagent through a chemical reaction.
2. Co precipitation of fluoride, which involves its simultaneous precipitation with a macro-component from the same solution through the formation of mixed crystals, by adsorption, occlusion, or mechanical entrapment.

### 4.1.1 Nalgonda Technique:

The Nalgonda Technique was developed by the National Environment Engineering Research Institute (NEERI) in Nagpur (India) in the 1960 and has since mainly been implemented in India and Nalgonda technique (named after village in India where the method was pioneered) employs flocculation principle. Nalgonda technique is a combination of several unit operations and process involves – rapid missing, chemical interaction, flocculation, sedimentation, filtration, disinfection and sludge concentration to recover waters and aluminum salt. The process involves adding aluminum sulphate ($Al_2(SO_4)_3$), lime ($Ca(OH)_2$) and Bleaching power($Ca(OCl)Cl$). Alum (hydrated aluminum salts) - a coagulant commonly used for water treatment is used to flocculate fluoride ions in the water. Since the process is best carried out under alkaline condition, lime is added. For disinfection purpose Bleaching powder is added. After through stirring the chemical elements coagulate into flocs and settle down in the bottom. The reaction occurs through the following equations,

$$2Al_2(SO_4)_3 ,18H_2O+NAF+9Na_2Co_3 \rightarrow [5Al(OH_3), Al(OH)_2F]+NaHCO_3+8CO_2+45\ H_2O$$

$$3Al_2(SO_4)_3,18H_2O+NAF+17NaHCO_3 \rightarrow [5Al(OH_3), Al(OH)_2F]+9Na_2SO_4+17CO_2+18H_2O$$

The Nalgonda technique has been successfully used at both individual and community levels and it can be implemented at a household level in India and other developing countries like China and Tanzania. Based on the availability and low cost, the Nalgonda Technique is mostly used in household level.

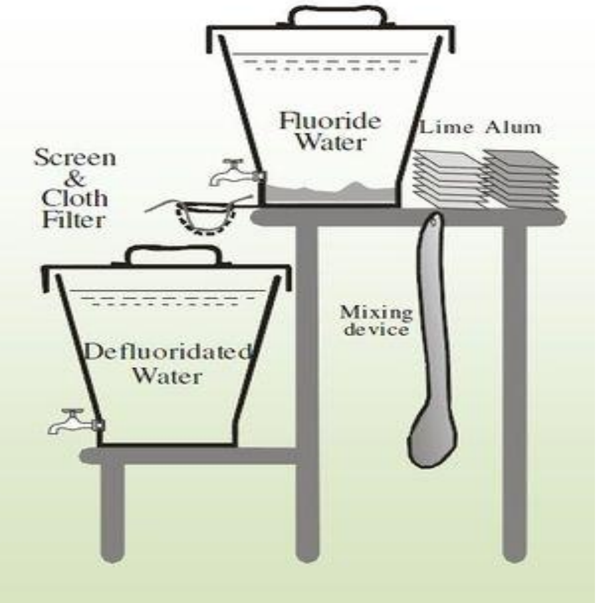

Fig 4.1: Household level coagulation (Nalgonda Technique) Technique

#### 4.1.1.1 Salient feature of Nalgonda Technique:

- No regeneration of media
- No handling of caustic acid and alkalis
- Readily available chemicals used in conventional municipal water treatment are only required
- Adaptable to domestic use
- Flexible up to several thousand $m^3$/d
- Applicable in batch as well as in continuous operation to suit needs simplicity of design, construction, operation and maintenance
- Local skills could be readily employed
- High efficient removal of fluorides from 1.5 to 20 mg/L to desirable levels
- Simultaneous removal of color, odor, turbidity, bacteria and organic contaminants.
- Normally associated alkalinity ensures fluoride removal efficiency
- Sludge generated is convertible to alum for use elsewhere.
- Little wastage of water and least disposal problem
- Needs minimum of mechanical and electrical equipment
- No energy except muscle power for domestic equipment
- Economical- annual cost of de-fluoridation is very low
- Provides de-fluoridated water of uniform acceptable quality

#### 4.1.1.2 Advantages:

- Materials are cheap and locally available
- annual cost is very low
- No need of high skills.
- Treatment is well accepted.
- Fluoride removal capacity is high.
- No need of electrical energy.

#### 4.1.1.3 Disadvantages:

- Fluoride elimination rate is low (80-90%) compare to activated alum.
- The right amounts of chemicals need to be added.
- Proper mixing of chemical in the water.
- Rapid & Slow mixing will be properly.
- Residual aluminum in the water is a constant danger.
- High sulphate concentrations in the water make it taste salty.
- Sludge disposal.

## 4.2 Adsorption:

Adsorption is the process of accumulating substances that are in solution on a suitable interface. The adsorbate is the substance that is being removed from the liquid to the solid phase at the interface. The adsorbent is the solid, liquid, or gas phase onto which the adsorbate accumulates. Although adsorption is used at the air-liquid interface in the flotation process, only the case of Activated Carbon treatment is usually through of as a polishing process for water. In the adsorption method, raw water is passed through a bed containing de-fluoridation material. The adsorbent gets saturated after a period of operation and requires regeneration. Fluoride uptake capacity can be increased by certain pre-treatments like acid washing, calcinations, etc. None of the mentioned materials generally exhibits high fluoride uptake capacities. Processed materials like Activated Alumina, Bone Char etc have been extensively evaluated for de-fluoridation of water. Among these materials, bone char, activated alumina have been successfully used in the field.

Because of the limited applications of treatment techniques like coagulation, adsorption/ion exchange, the adsorption is the most frequently used method of fluoride removal. The fluoride-rich water is passed through a column packed with a strong adsorbent and when saturated with fluoride ions, the filter material has to be backwashed to clean and regenerate it. The criteria for selection of suitable adsorbents include adsorption capacity, cost of the medium, ease of operation, potential for reuse, and possibility of regeneration. The mechanisms of fluoride removal and applications of some of the most frequently encountered adsorbents are shows in this section.

Adsorption process includes several bone formulations, synthetic tricalcium, phosphate and hydroxyl apatite and a variety of adsorbent materials. Some of them are provided below.

### 4.2.1 Activated Alumina:

Activated alumina (AA) is a granular, highly porous material consisting essentially of aluminium oxide, $Al_2O_3$. The surface area per unit weight is quite high, normally in the range of 200– 300 $m^2/g$. The chemical and physical properties of typical activated alumina are shown in Table no 13. The application of AA in the removal of fluoride from drinking water is regarded as one of the best available technologies worldwide. Designing an alumina adsorption system with optimal performance and good regeneration capability depends on an understanding of the mechanisms of fluoride adsorption. The major factors affecting fluoride removal are pH, surface loading (the ratio of total fluoride concentration to the alumina dosage), and presence of other interfering ions. Some researchers have reported an optimal pH of 5 for fluoride removal, though no explanation was offered on the removal mechanism.The hydration, amphoteric hydroxo groups develop on the alumina surface as shown in Eqs. 1-2:

$$AlOH^{+2} = AlOH + H^{+} \qquad (1)$$

$$AlOH = AlO^{-} + H^{+} \qquad (2)$$

Where, $AlOH^{+2}$ , AlOH, and $AlO^{-}$ are positive, neutral, and negative surfacehydroxo and oxo groups, respectively.The adsorption model of fluoride can be described by the followingEqs. 3-4:

$$AlOH + F^{-} = AlF + OH^{-} \ (pH > 7) \qquad (3)$$

This equation implies that $OH^{-}$is released from the AA surface into the bulk phase. The rise in pH is related to fluoride adsorption and is more prominent at high initial fluoride concentrations. The extent of $OH^{-}$release is most pronounced at pH >6–7 and diminishes at pH <7. The reduction in $OH^{-}$ release at lower pH suggests that a different adsorption mechanism may be in operation under these conditions, which may be represented as:

$$AlOH^{+2} + F^{-} = AlF + H_2O \ (pH < 6) \qquad (4)$$

The mechanism operates in the pH range of 3–5. In many cases at high initial fluoride concentrations and low pH, the amount of fluoride adsorbed exceeded the total available surface sites. Instead of considering this phenomenon as a multilayer adsorption, polynuclear surface complex formation is suggested:

$$AlOH + 2F^{-} = AlF^{-2} + OH^{-} \qquad (5)$$

Alumina–fluoro complexes $AlF_x^{3-x}$ ($x$ = 1–6) are stable in the low pH region.In the presence of fluoride, AAis rendered soluble by forming alumina–fluoro complexes, which are stablein acidic pH and become unstable as pH increases. It has been suggestedthat alumina adsorption systems for fluoride removal should be operated atpH values where alumina–fluoro complexes are unstable to prevent aluminafrom dissolving. The regeneration of AA is usually done with a caustic solution (usually 1% sodium hydroxide) followed by a dilute acid (usually 0.05 N sulfuric acid) and water rinse. The following reactions take place in the regeneration/ reactivation cycle:

$$AlF(s) + OH^{-} \rightarrow AlOH(s) + F^{-} \qquad (6)$$

$$AlOH(s) + H_2SO_4 \rightarrow AlHSO_4(s) + H_2O \qquad (7)$$

The specific affinity of AA for fluoride coupled with excellent exchange capacity makes it an ideal candidate for defluoridation. The uptake capacity and reuse potential are considered important parameters for the application of AA for de-fluoridation in the field. Packed beds of granular activated alumina have been traditionally used for de-fluoridation of public water supplies, and their reported capacity is in the range 6750–11,760 $g/m^3$in a continuous-flow system.

The Department of Science and Technology, Government of India, has supported the public health engineering departments of many state governments of fluoride-endemic areas in the development of hand-pump-attached de-fluoridation units quite recently in 2001–2003. A cylindrical de-fluoridation unit was fabricated and field tested in Makkur, Unnao district of the state of Uttar Pradesh, in 1993. It is a mild steel cylindrical drum 0.5 m in diameter and 1.5 m height. The unit was designed to operate in the up-flow mode using a bed of 110 kg alumina in 55 cm height with a particle size range 0.3–0.9 mm. The installation required rising of hand pump discharge level and construction of an elevated platform as shown in Figure 13. Users are to go up few steps to operate the hand pump. A bypass line was provided to draw water directly from the hand pump for washing and bathing. Raw water fluoride concentration was in the range of 6–7 mg/L. Regeneration of exhausted AA was carried out within the column itself in a time span of 8–10h and the average yield per cycle was 25 $m^3$. Within 4 years, 17 de-fluoridation cycles were completed. During this period, the UNICEF approach changed from community-based systems to DDUs.

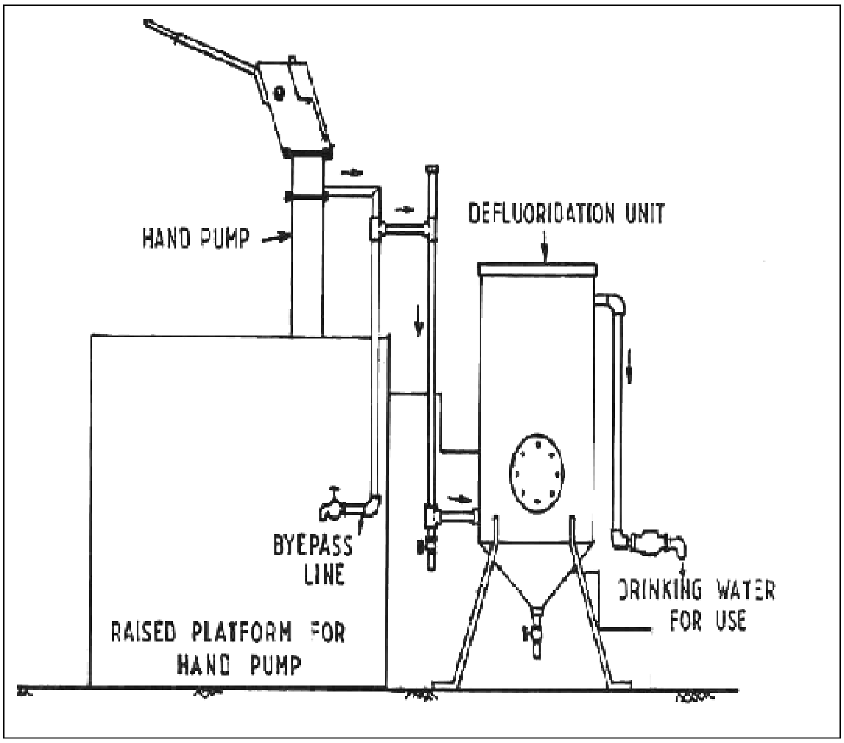

Fig 4.2: Defluoridation unit using Activated alumina

De-fluoridation of water by activated alumina is the method of choice in developed countries. Its affinity for fluoride is very high. It is a porous material with the surface comprised largely of active sites. It is prepared by dehydration of $Al(OH)_3$ in the temperature of 300-600°C. Activated alumina is regarded as an excellent material for fluoride removal. However, pH and alkalinity are the factors which affect the sorption capacity. The exhausted material can be regenerated by washing with alkali following by acid and finally with distilled water.

**Table 4.1: Typical Properties of Activated Alumina**

| Sl.No | Physical characteristics | Value |
|---|---|---|
| 1. | Particle form | Spheres |
| 2. | Particle size (mm) | 2-5 |
| 3. | Water adsorption capacity at 30◦C by weight | 21 |
| 4. | Minimum surface area (m2/g) | 250 |
| 5. | Pore volume (cm3/g) | 0.42 |
| 6. | Bulk density (mg/ cm3) | 800 |
| 7. | Bed crushing strength (wt.%) (minimum) | 92 |
| 8. | Loss of attrition (wt.%) (maximum) | 0.3 |
| 9. | Loss of ignition (250–1000◦C) | 7.5 |
| **Chemical characteristics** | | |
| 10. | Al2O3 (by difference) (minimum) | 92 |
| 11. | Fe2O3 (maximum) | 0.05 |
| 12. | SiO2(maximum) | 0.20 |
| 13. | Na2O (maximum) | 0.30 |

### 4.2.1.1 Advantages:

- High adsorption capacity
- Implementation experience from many different countries.
- Well accepted amongst users.
- It requires minimum contact time for maximum de-fluoridation.
- Percentage of regeneration is considerably high
- There is very little attrition loss (to a negligible extent) during the regeneration at the initial stage of operation.
- It is indigenous available and cheep.
- De-fluoridation capacity at neutral pH is appreciable, although it has greater de-fluoridation efficiency at low pH.
- Its de-fluoridation capacity is independent of temperature.

### 4.2.1.2 Disadvantages:

- Fluoride removal efficiency decreases with increasing pH.
- Potentially expensive if chemicals/filter material are not locally available and have to be imported.
- Regular maintenance needed to regenerate or replace filter material.
- Adsorption capacity deteriorates with each regeneration cycle.
- Acidic/alkaline waste needs disposing.

### 4.2.2 Bone Charcoal:

Bone Charcoal has fluoride-scavenging potential, caustic-and-acid treated bone material could effectively reduce fluoride concentration from 3.5 to less than 0.2 mg/L. The suggested removal mechanism was of ion exchange in which the carbonate radical of the apatite ($Ca_9(PO_4)_6 \cdot CaCO_3$) comprising bone was replaced by fluoride to form an insoluble fluorapatite, as:

$Ca_9(PO_4)_6 \cdot CaCO_3 + 2F^- \rightarrow Ca_9(PO^4)_6 \cdot CaF_2 + CO_3^{2-}$

But the high cost of bone, became an inhibiting factor for its wider use. However, soon it was recognized that bone char, produced by carbonizing bone at temperatures of 1100–1600$^0$C, had superior scavenging potential to unprocessed bone. Thereafter, bone char replaced bone as a de-fluoridation Bone char is ground animal bones charred to remove all organics, and essentially consists of tricalcium phosphate and carbon.It was suggested that adsorption mechanism of fluoride ion onto bone char is ion exchange where the phosphate in bone char was exchanged for fluoride ion. Explained the uptake of fluoride on hydroxyapatite as:

$Ca_{10}(PO_4)_6(OH)_2 + nF^- = Ca_{10}(PO_4)_6(OH)_{2-n} F_n + nOH^-$

It has also been suggested that removal of fluoride is endothermic.The Amount of fluoride ion adsorbed onto bone char increases with decreasing pH. At lower pH, the phosphate ions in bone char are more dissociated and easily cede to fluoride ions. The amount of fluoride ion adsorbed is found to increase in the presence of sodium chloride in solution due to a “salting out” effect. Typical properties of bone char are presented in Table no 11, observed that black grade bone char is better in the de-fluoridation of drinking water than white or gray bone char, though it increases the pH of the treated water. Fluoride removal by bone char from water seeded with brushite and calcium hydroxide. The addition of brushite and calcium hydroxide resulted in high concentrations of calcium and phosphate, making the solutions highly supersaturated with respect to fluorapatite, leading to a 20-fold increase in fluoride removal. Bone charcoal is the oldest known water de-fluoridation agent, and was in use in the United States in the 1940s to 1960s due to its wide commercial availability because of its large-scale use in sugar industry.

**Table 4.2: Typical Properties of Bone Char**

| Constituent | Content |
|---|---|
| $Ca_3(PO_4)_2$ | 73.5% |
| $CaCO_3$ | 8.5% |
| Iron and aluminum oxide | 0.4% |
| Magnesia | 0.2% |
| Acid insoluble ash | 0.3% |
| Total volatile | 16.5% |
| Apparent density (g/cc) | 0.64–0.74 |

Bone Char (28–48 mesh size) has been successfully used in many full-scale installations for de-fluoridation of drinking water.

#### 4.2.2.1 Advantages:

- Locally available, cheap raw material (animal bone).
- High sorption capacity.
- Fast reaction time (less than 30 min).
- No additional chemicals are needed for the treatment process.
- Filtered water is neutral in test and color.

#### 4.2.2.2 Disadvantages:

- Limited acceptability of animal bones as filter material for drinking water.
- Initial investment and experienced needed to set up bone char process.
- Maintenance and regular monitoring necessary – if filter is saturated it needs to be regenerated or replaced.
- May impart taste and odour and result in organic leaching if not prepared properly.
- Affected by high alkalinity.
- May not be acceptable in some countries

### 4.2.3 Processed Bone:

Bone contains calcium phosphate and has a great affinity for fluoride. The bone is degreased, dried and powered. The powder can be used as a contact bed for removal of fluoride in water. The exhausted bed is regenerated with sodium hydroxide solution.

### 4.2.4 Tricalcium Phosphate:

Tricalcium phosphates natural or prepared synthetically by reacting milk of lime and phosphoric acid have been used for de-fluoridation.

### 4.2.5 Activated Carbons:

Activated Carbons prepared from paddy husk has a high de-fluoridation capacity. Similarly activated carbon prepared from cotton waste, coffee waste and coconut waste were tried for de-fluoridation but all these materials are academic interest only.

### 4.2.6 Activated magnesia:

Activated Magnesia is a good adsorbent among several substances. Activated magnesia has been better fluoride removal capacities at high temperature.

### 4.2.7 Tamarind Gel:

The concentration of fluoride from solution of sodium fluoride of 10 mg/l could be brought down to 2 mg/l by the addition of tamarind gel alone and to 0.05mg/l by addition of tamarind gel alone to 0.05 mg/l by the addition of small quantity of chloride with the tamarind gel.

### 4.2.8 Serpentine:

It is the name which applies to the material containing one or both the minerals chrysolite and antigorite. The medium could not be regenerated and had to be discarded after the use. The yellow variety was found to have better fluoride removal capacity than the green mineral.

### 4.2.9 Plant materials:

The plant materials such as barks of Moringa Olifera and Emblica Officinalis, the roots of Vetiveria Zizanoides and the leaves of Cyanondon tactylon were found to be good de-fluoridation agent.

### 4.2.10 Burnt Clay:

Burnt clay obtained from brick Chula; prepared by burning a mixture of 70% clay and 30% red soil was observed to possess commendable de-fluoridation property. Clay with particle size 500 microns exhibited maximum de-fluoridation efficiency. At low pH range the de-fluoridation efficiency was more compared to that at high pH range 6.

### 4.2.11 Clays and Soils:

The potential of clay and soil-based systems for de-fluoridation is under investigation in many fluoride-endemic regions of the world, especially in Developing countries. Thereafter, fluoride adsorption onto soils and clays both in natural and modified activated forms has been studied extensively. Research in this area includes Illinois soils in the United States, sodic soils, clay pottery, fly ash in India, Ando soils in Kenya, Alberta soil, soils and fired clay chips in Africa and Sri Lanka, activated clay, bentonite and kaolinite, and illite– goethite soils in China.

**Table 4.3: A Comparison of the Fluoride Adsorption Capacity of Major Clay Types**

| Sorbent Type | Place description | pH | Initial Fluoride Concentration (mg/L) | Maximum adsorption (mg/g) |
|---|---|---|---|---|
| Gibbsite | Australia | 5-7 | 10.0 | 0.40 |
| | South Africa | 5-7 | 10.0 | 0.25-0.40 |
| Goethite<br>Goethite/kaolinite<br>Goethite/illite<br>Goethite/kaolinite | South Africa<br>China<br>Sri Lanka | 5-7<br>5-7<br>5-7 | 10.0<br>10.0<br>10.0 | 0.20<br>0.23<br>0.35 |
| Palygorskite<br>Palygorskite/ dolomite | South Africa | 5-7 | 10.0 | 0.21-0.29 |
| Bentonite | Stockfeed bentonite | 6-7 | 16-660 | 63.30 |
| Smectite | South Africa | 5-7 | 10.0 | 0.10 |
| | USA | 5-7 | 10.0 | Trace |
| | Alkaline soil,USA | 5-7 | 10.0 | 0.40-0.08 |
| Kaolinite | South Africa | 5-7 | 10.0 | 0.03 |
| Kaolinite | Acidic soils, USA | 5-7 | 10.0 | 0.17-0.25 |
| | Acid soils, Illinois | 5-7 | 10.0 | 0.130 |
| | Pottery clay | 5-7 | 10.0 | 0.12 |
| | Clay pots, Ethiopia | 5-7 | 10.0 | 0.07 |
| | South Carolina, Australia | 6-7 | 16-660 | 4.05 |
| | Kaolin clay | 6 | 10-250 | 3.48 |

## 4.3 Ion Exchange Resins:

Ion exchange process are used to remove inorganic contaminates if they cannot be removed adequately by filtration or sedimentation. Ion exchange can be used to treat hard water. It can also be used to remove arsenic, chromium, excess fluoride, nitrates, radium, and uranium.

Fluoride can be removed from water supplies with a strongly basic anion-exchange resin containing quarternary ammonium functional groups. The removal takes place according to the following reaction:

Matrix-$NR_3^+Cl^- + F^- \rightarrow$ Matrix-$NR_3^+F^- + Cl^-$

The fluoride ions replace the chloride ions of the resin. This process continues until all the sites on the resin are occupied. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt. New chloride ions then replace the fluoride ions leading to recharge of the resin and starting the process again. The driving force for the replacement of chloride ions from the resin is the stronger electronegativity of the fluoride ions. Generally two types of ion exchange resins are used.

### 4.3.1 Anion exchange resins:

These are found to removal fluorides either by hydroxyl cycle or chloride cycle along with other anions. Polystyrene anion exchange resin and basic quaternary ammonium type are used to remove fluoride along resin and basic quaternary ammonium types are used to remove fluoride along with other anions. Ply anion exchange resin, Tlsion A – 27, Deacodite FF (IP), Lawatit MIH – 59, Ambelite IRA 400 are the few examples.

### 4.3.2 Cation exchange resins:

Cation exchange resins impregnable with alum solution have found to act as defluoridating agents. "Bark" based cation exchange resin works effectively I removing fluoride from water. Bhakuni 13 compared the performance of defluoron-1 and 2, Carnion, Wasoresin- 14 and polystyrene cation exchange resin.

### 4.3.3 Advantages

- Removes fluoride up to 90–95%.
- Retains the taste and colour of water intact.

### 4.3.4 Disadvantages

- Efficiency is reduced in presence of other ions like sulfate, carbonate, phosphate and alkalinity.
- Regeneration of resin is a problem because it leads to fluoride rich waste, which has to be treated separately before final disposal.
- The technique is expensive because of the cost of resin, pretreatment required to maintain the pH, regeneration and waste disposal.
- Treated water has a very low pH and high levels of chloride.

## 4.4 Elecctrocoagulation Process:

Electrocoagulation (EC) utilizes an electrolytic process to generate a coagulant in situ by oxidation of an appropriate anodic material. The coagulant ions then react with the target pollutant ions, initiating normal coagulation. Aluminum and iron are most commonly used as additional sacrificial electrodes, which continuously produce ions in the system. The sacrificial electrodes protect the normal anode by lowering its dissolution potential and the cathode by passivation. When an electric current passes through the aluminum electrodes, an anodic reaction releases Al(III) ions, which then react with hydroxide ions produced at the cathode and with fluoride ions in solution. The de-fluoridation efficiency of the EC system may exceed that of the traditional coagulation process because of electrocondensation. Since fluoride ions are attracted to the anode, fluoride concentration near the anode exceeds that in the bulk solution, which may lead to higher efficiency (condensation effect) for the EC process (Figure 4.3).

### 4.4.1 Advantages:

- The process is highly effective for fluoride removal.
- No chemical required.
- It works under wide pH range.

### 4.4.2 Disadvantages:

- The process is expensive in comparison to other options.
- Electrodes have to clean regularly
- Sludge management is a big issue

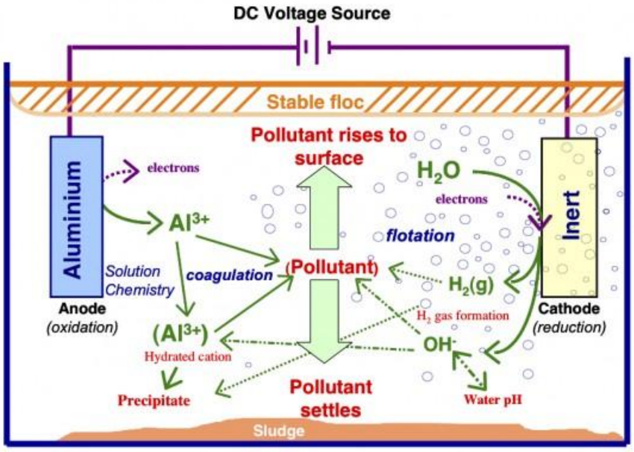

Fig 4.3: Diagram representing the electro-condensation process

## 4.5 Membrane Filtration Process:

Membrane filtration is used to remove particles that are too small for ordinary filters to remove. Most membrane filtration systems use cross flow filtration where the feed stream flows across the membrane rather than through it, as inconventional filtration. This helps prevent clogging of the membrane by retained particles. Membrane filtration systems also can be used to recover valuable materials from a waste stream. For example, As shown in the diagram below, wastewater from a chemical process can be separated throughmembrane filtration into two parts: concentrated chemicals and nearly pure water. The concentrated chemicals and the water then can be returned to the process, thereby reducing both raw material costs and disposal costs. If the recovered materials cannot be reused, membrane filtration stillcan be used to reduce the volume of hazardous waste nee-disposal. The basic types ofmembrane filtration systems are: microfiltration, ultra filtration, nano filtration and reverse osmosis. These types differ mostly in the size of particles they remove. Listed below are descriptions of these Filtration systems:

### 4.5.1 Microfiltration Process:

This type of filtration retains particles in the range of 0.1 to 10 Particles in this size range, suchas paint pigments and bacteria, are retained and concentrated by the membrane. Microfiltration can be used to remove bacteria and small suspended solids.

### 4.5.2 Ultrafiitration and Nanofiltration Process:

These filtration types retain particles in the range Protein and sugar molecules are in this size range. Ultra filtration or nanofiltration can be used to reduce the biochemical oxygen demand (BOD) of wastewater by removing substances such as sugars. Both systems also can be used to separate oil from wastewater so that the oil may be recycled.

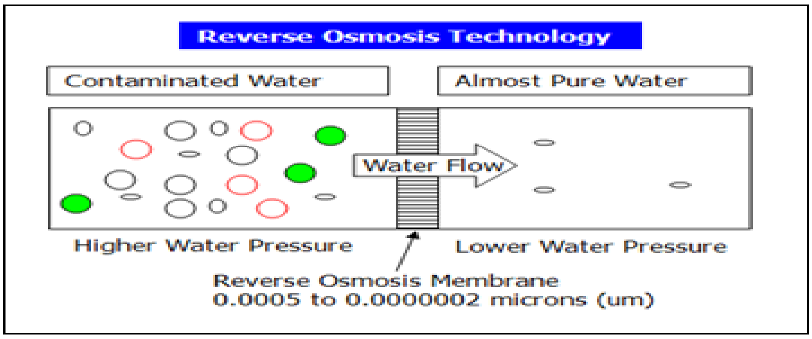

Fig 4.4: Diagram of Reverse Osmosis Technique

### 4.5.3 Advantages

- The process is highly effective for fluoride removal. Membranes also provide an effective barrier to suspended solids, all inorganic pollutants, organic micropollutants, pesticides and microorganisms, etc.

- The process permits the treatment and disinfection of water in one step.
- It ensures constant water quality.
- No chemicals are required and very little maintenance is needed.
- Life of membrane is sufficiently long, so problem of regeneration or replacement is encountered less frequently.
- It works under wide pH range.
- No interference by other ions is observed.
- The process works in a simple, reliable automated operating regime with minimal manpower using compact modular model.

**4.5.4 Disadvantages:**

- It removes all the ions present in water, though some minerals are essential for proper growth, remineralisation is required after treatment.
- The process is expensive in comparison to other options.
- The water becomes acidic and needs pH correction.
- Lot of water gets wasted as brine.
- Disposal of brine is a problem.
- The performance of all the above processes has been tested in the laboratory.

## 4.6 Herbal Coagulation Flocculation Adsorption Process:

Naturally available herbs are used as fluoride removing media .The defluoridation capacities of the following plant materials like Rama- cham (Vetiveria zizanioides), Tamarind seed (Tamarindus indica), Clove (Eugenia carryophyllata), Neem (Azadira- chta indica), Acacia (Acacia catechu willd), Nutmeg (Myristica fragarns), and coffee husk (Coffea arabica), Rice husk, Drum stick seed (Moringa Oleifera) is high. And they are naturally occurring and easily available low cost materials. Rice husk was obtained from a local mill. The fluoride removal capacity depends on some factor like, Effect of important controlling factors, viz pH, dose of adsorbent, contact time, particle size and initial fluoride ion concentration on water.

## Table 4.4: An Overview of the Defluoridation Techniques

| Defluoridation technique | Defluoridation capacity/dose | State of development/strengths | Limitations |
|---|---|---|---|
| Precipitation by calcium oxide | ~30 mg/mg F | Coagulation Cheapest, established, and most commonly used technology. | Quantity of sludge production and pH of treated water are high. Poor settling characteristics of the precipitate. High effluent fluoride concentration |
| Precipitation by magnesium oxide | 0.8 g/L (for fluoride concentrations of 1.8–3.5 mg/L) | Established technology. Affordable cost. | Quantity of sludge production and pH of treated water are high |
| Precipitation by calcium chloride and monosodium phosphate | 0.28 g/L and 0.17g/L<br>for domestic use | Emerging technology at reliable operating cost. No health risk in the case of misuse or overdosage of chemicals as in conventional precipitation techniques. | Too short contact times increase the escape of chemicals in the treated water. Long contact time may result in precipitation of calcium phosphates in the upper parts of the filter bed. Both<br>these actions will reduce the removal efficiency |
| Coprecipitation by alum | ~0.15 g/mg F | Well-known and established technique. Widely practiced in fluoride-endemic areas. | Low pH of treated water. High dose requirements for higher fluoride concentrations. Expected presence of sulfate and aluminium concentrations in treated water especially at high pHs. |
| Coprecipitation by alum and lime<br>(Nalgonda) | 12.8 g alum and 6.4 g<br>lime reduces F from<br>8.8–12.5 mg/L to<br>2.1± 0.7mg/L. | Well known, widely practiced and established technology for individual household, and community level pilot scale applications. Chemicals readily available. Easy operation and maintenance. | Difficult to control dosages for different sources of raw water with varying alkalinity and fluoride concentration. Hardness, pH, and residual aluminium of the treated water are high. |
| Adsorption/ion exchange Bone | ~ 0.9mg F/g | Long established technique for local applications | Impart taste to water. Limited social acceptance. |

| Defluoridation technique | Defluoridation capacity/dose | State of development/strengths | Limitations |
|---|---|---|---|
| Bone char | 2–4 mg F/g | Well known and established technique. Good potential. Local availability and processing facilities aids local applications. Ability to remove fluoride to very low levels | Capacity reduces drastically after successive regenerations. More expensive than coagulation techniques. The use is constrained by the religious beliefs in many societies and communities. Limited social acceptance. |
| Clays | 0.03–0.35 mg F/g | Economical. Very limited local applications. | Dfluoridation potential is generally low. Regeneration is very difficult. |
| Activated alumina | 1.0 mg/g | Very well established technique. Regarded as one of the best available technologies worldwide. Best performance at pH ~5. Minimum interference from counter-ions with consistent potential. Versatile applications | Costly compared to coagulation<br>Processes and bone char. High pH reduces potential. Regeneration result in a reduction of about 5–10% in material, and 30–40% in capacity with increased presence of aluminum (>0.2 mg/L). |
| Electrochemical methods Electrocoagulation | Efficiency ~100% | Emerging technique. Efficiency of EC system is very high compared to the traditional coagulation process. | Interference from other anions like sulphate. Need for regular replacement of sacrificial electrodes. Costly due to high consumption of electric power. |
| Electrosorption | Highly efficient | Emerging technique. Capacity of<br>adsorbent enhanced by more than 50%.Excellent regeneration potential | Costly due to high consumption of electric power. |
| Reverse osmosis | Highly efficient | Well-studied and established technology. Immense commercial applications. | Sensitive to polarization phenomenon. Chances of biological and mineral fouling. Treated water may lack the right balance of minerals. Poor water recoveries. High cost. |

# Analytical Procedure for testing Different Water Quality Parameters

## CHAPTER 5

These under listed parameters were tested in laboratory during the experimental studies

1. Fluoride
2. Total Alkalinity
3. Total Hardness
4. Chloride
5. pH
6. TDS and Electrical Conductivity
7. Turbidity

Test procedures are described below-

## 5.1 Fluoride Test:

### 5.1.1 Ion Selective Electrode Method:

The fluoride ion selective electrode can be used to measure the activity or concentration of fluoride in aqueous sample by use of an appropriate calibration curve. However, fluoride activity depends on the total ionic strength of the sample. The electrode does not respond to bound or complexed fluoride. Addition of a buffer solution of high total ionic strength containing a chelate to complex aluminium preferentially overcomes these difficulties.

### 5.1.2 Interference:

Polyvalent cations such as Al (III), Fe (III) and Si (IV) will complex fluoride ions. However, the additions of CDTA (Cyclohexylene diamine tetra acetic acid) preferentially will complex concentrations of aluminium up to 5 mg/l. Hydrogen ion forms complex with fluoride while hydroxide ion interferes with electrode response. By adjusting the pH in between 5 to 8 no interference occurs.

Fig5.1: inoLab pH/ION 735 meter and TISAB & NaF Solution.

### 5.1.3 Apparatus

- Ion meter
- Fluoride sensitive electrode
- Thermally Isolated Magnetic Stirrer
- Poly tetra fluoro ethylene (PTFE) coated stir bar

- Plastic labwares (Samples and standards should always be stored in plastic containers as fluoride reacts with glass)

### 5.1.4 Reagents

- **Standard fluoride solution**
  Prepared by dissolving 22.1gm anhydrous Sodium Fluoride (NaF) in 1 liter double distilled water and making 1000ml in volumetric flask then 1 liter stock solution will be produced. To make NaF anhydrous it should be kept in hot air oven for 4 hrs at 120ºC. Then it has to cool to room temperature in a decicator. So, in 1L $F^-$ Stock solution, Fluoride concentration is 1000mg/L or 1 mg/ ml.

- **Total Ionic Strength Adjustment Buffer (TISAB)**
  Place approximately 500 ml distilled water in 1 L beaker; add 57 ml glacial acetic acid, 58gm NaCI and 4.0 gm 1,2 cyclohexylene diamine tetra acetic acid. Stir to dissolve. Place beaker in a cool water bath and add slowly 6N NaOH (About 125 ml) with stirring, until pH is in between 5 and 5.5 transfer to a 1 L volumetric flask and make up the volume to the mark.

### 5.1.5 Procedure

- For connecting the electrode to meter and for further operation of the instrument follow the instruction manual supplied by the manufacturer
- Check the electrode slope with the ion meter (59.16 mV for monovalent ions and 29.58 mV for divalent ions at 25°C)
- Take 50 ml of each 1 ppm and 10 ppm fluoride standard. Add 50 ml TISAB (or 5 ml if conc. TISAB is used) and calibrate the instrument.
- Transfer 50 ml of sample to a 150 ml plastic beaker. Add TISAB as mentioned in step above.
- Rinse electrode, blot to dry and place in the sample. Stir thoroughly and note down the steady reading on the meter.
- Recalibrate every 2 hours.
- Direct measurement is a simple procedure for measuring a large number of samples. The temperature of samples and standards should be the same and the ionic strength of standards and samples should be made the same by addition of TISAB to all solutions.

Fig 5.2: Testing in ion meter to determine concentration of fluoride

### 5.2 Total Alkalinity:

Alkalinity of water is its acid neutralizing capacity. It is the sum of all titratable bases. The measured value may vary significantly with the end point pH or the type of indicator used. Water samples are titrated with standard acid using an acid-base indicator. Total alkalinity (T-value) is the quantity measured by titration using mixed bromocresol green- methyl red indicator.

#### 5.2.1 Reagents:

**Standard $H_2S0_4$ (0.02 N) :**
Prepare 0.1N $H_2S0_4$ by diluting 3.0 ml conc. $H_2S0_4$ to 1000 ml. standardise it against standard 0.1N $Na_2C0_3$. Dilute appropriate volume of $H_2S0_4$ (approx. 0.1N) to 1000 ml to obtain standard 0.02N $H_2S0_4$.

**Mixed bromocresol green – methyl red indicator:**
100mg bromocresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.

#### 5.2.2 Procedure

- Take an aliquot of sample (50-250 mL) in a conical flask
- add 2-3 drops of mixed indicator
- Titrate with 0.02 N $H_2S0_4$ until colour changes from green to red.

Calculation:

$$\text{Alkalinity, mg/I as CaCO3} = \frac{\text{AxNx50x1000}}{\text{ml of sample}}$$

Where,
N =Normality of $H_2S0_4$ used and
A = ml standard acid used to reach colour changes**.**

Fig 5.3: Titration for determination of Total Alkalinity

**5.3 Total Hardness:**

Total Hardness is defined as the sum of the calcium and magnesium concentrations, expressed as calcium carbonate in mg/litre.

All natural waters have salts dissolved in them and these salts are helped to produce a unique taste in water. Sometimes the water can contain too much of these salts and can cause problems when the water is used for drinking or washing. These problems are caused mainly by the presence of calcium and magnesium ions in the water.
Sodium salt of EDTA forms chelating soluble complex with calcium and magnesium ions. If small amount of Erichrome Black T (EBT) indicator is added to water samples at pH 10, the solution becomes wine red. If the solution is titrated with EDTA, the calcium and magnesium ions will be complexed with EDTA and when all the ions have composited the solution turns from wine to red.

### 5.3.1 Reagents:

**Buffer Solution**

Dissolve 16.9 gm Ammonium Chloride ($NH_4Cl$) in 143 ml conc. Ammonium hydroxide ($NH_4OH$) and dilute to 250 ml with distilled water.

**Erichrome Black T (EBT) Indicator Solution**

Dissolve 0.5 gm EBT dye in 100gm of triethanolamine or prepare dry mixture of this dye with an inert salt like sodium chloride.

**Standard EDTA Titrant (0.01 N)**

Weigh accurately 3.723 gm analytical grade disodium EDTA, dissolved in distilled water and dilute to 1000 ml with metal ion free distilled water.

### 5.3.2 Procedure:

- Take 25 ml of Sample
- Add (1-2) ml buffer solution.
- Add (1-2) drops of indicator solution.
- Add the standard EDTA titrant slowly with continuous stirring, until the wine reddish colour changes to blue.

Calculation:

$$\text{Hardness (EDTA) as mg CaCO3 mg/ L} = \frac{\text{Ax1000}}{\text{ml of sample}}$$

where, A = ml of EDTA used in titration

### 5.4 Chloride:

Chloride is determined in a neutral or slightly alkaline solution by titration with standard silver nitrate, using potassium chromate as an indicator. Silver chloride is quantitatively precipitated before red silver chromate is formed.

### 5.4.1 Interference:

If the sample is too coloured or turbid to allow the end point to be readily detected, this interference may be reduced by alum flocculation followed by filtration prior to the estimation of chloride.

### 5.4.2 Reagents

- **Potassium chromate Indicator:**
  Dissolve 50 g $K_2CrO_4$ in distilled water. Add $AgNO_3$ till definite red precipitate is formed Allow to stand for 12 hrs. Filter and dilute to 1000 ml.

- **Silver nitrate (O.0141N:**
  Dissolve 2.395 gm $AgNO_3$ and dilute to 1000 ml. Standardise against 0.0141N NaCl. 1 ml of 0.0141 N $AgNO_3$= 0.5 mg Cl.

- **Sodium Chloride 0.0141 N:**
  Dissolve 824.1 mg NaCI dried at 140°C and diluteBto 1000 ml. 1 ml = 0.5 mg Cl.

- **Special reagent to remove colour and turbidity:**
  Dissolve 125 gm $[K_2AI_2 (SO_4)_4.12\ H_20]$ or $[(NH_4)_2AI_2(S0_4)_4.\ 24H_20]$ and dilute to 1000 ml warm to 60°C and add 55 ml conc. $NH_4OH$ slowly. Allow to stand for 1 hr. Solution should be free from Cl.

### 5.4.3 Procedure

- Take 100 ml sample and adjust the pH between 7.0 and 8.0
- Take 50 ml well mixed sample adjusted to pH 7.0 - 8.0 and add 1.0 ml $K_2\,Cr0_4$
- Titrate with standard $AgNO_3$ solution till $AgCrO_4$ starts precipitating
- Standardize $AgNO_3$ against standard NaCl.
- For better accuracy titrate distilled water (50 ml) in the same way to establish reagent blank.

Calculate as follows:

$$\text{Chloride, Mg/L} = \frac{(\text{A} - \text{B})\text{xNx}35.45\text{x}1000}{\text{ml of smple}}$$

Where A = ml $AgNO_3$ required for sample
B = ml $AgNO_3$ required for blank
N = Normality of $AgNO_3$ used

## 5.5 pH:

The basic principle of the pH meter is to measure the concentration of hydrogen ions. A pH meter provides a value as to how acidic or alkaline a liquid is. The pH varies with temperature.

### 5.5.1 Procedure

Electromagnetic Method:

- At first switch on the pH meter and given it 15mins for warm up.
- Then for calibration press CAL button.
- Dip electrode into pH buffer solution 1 (pH 10.01), press AR & then run ENTER
- Rinse electrode with distilled water & wipe clean, display shows insert Buffer 2 (pH 7.00)
- Dip electrode into pH Buffer 2 (pH 7.00), press AR & then run ENTER
- Again, display shows insert Buffer 3 (pH 4.01), rinse electrode with distilled water & wipe clean with tissues.
- Calibration is done.
- Immerse electrode into experimental sample and press MEAS For measurement
- Wait for the stable reading in display of pH meter.
- Rinse electrode with distilled water & wipe clean with tissues

Fig5.4: pH Meter

### 5.6 TDS and EC:

A TDS displayed the concentration of total dissolved solids in a solution.

#### 5.6.1 Procedure

Ion selective Electrode method
Immerse the conductivity electrode in water sample and measure electrical conductivity (E.C) as well as total dissolved solid (TDS) concentration.

1. At first switch on the conductivity meter.
2. Take 25-50 ml of water sample in a clean and dry beaker(100 ml)
3. Immerse the electrode into sample for measurement
4. Press MEAS button for measuring the TDS, waits for the stable reading in display.
5. TDS result shows in mg/l
6. Then press MODE button for measuring the EC of the sample.
7. Wait for a second until the reading is stabled in screen.
8. EC results shows in µS/cm

Fig 5.5: Electrical Conductivity Meter

### 5.7 Turbidity

The main principle of turbidity meter is based on the comparison of the intensity of light a sample with the intensity of light scattered by a standard suspension. The intensity of scattered light is sensed by a photocell kept at 90° to the beam.

### 5.7.1 Procedure

Nephelometric Method:

1. Switch on the Turbidity Meter
2. Press CAL for calibrate it, insert 800 NTU, 100 NTU, 20.0 NTU, 0.02 NTU standard bottles and press READ respectively for each.
3. Turbidity meter shows the exact value for each standard sample, that means the calibration is done correctly.
4. For sample analysis, shake the sample bottle, fill the sample vial till the mark and clean it with dry tissue and kept it in the photocell.
5. Press READ and wait for the stable result is shown in screen.
6. Turbidity results shows in NTU
7. Wash the sample vial with distilled water & wipe with a clean tissue before filling the next sample.

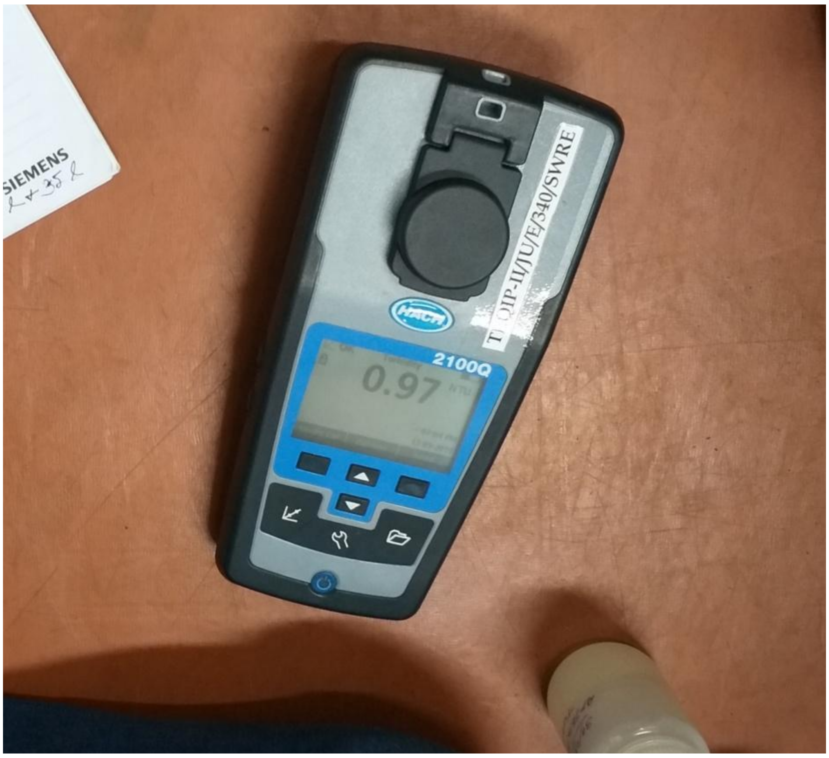

Fig 5.6: Turbidity Meter

# Experimental study on removal of excess Fluoride from drinking water: Result & Discussion

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CHAPTER 6

## 6.0 Introduction:

Pollution and treatment of water to avail safe drinking water is a serious concern regarding health prospective of people. Fluoride is one of the major pollutants in water. The issue of fluoride in water bodies is serious for some developing countries. To bypass this issue, various methods are accessible for defluoridation from drinking water. Ion-exchange and Adsorption are two of them.

## 6.1. Experimental Methodology:

### 6.1.1. Sampling

All chemicals used were AR/GR grade and were used without any added purification. All the solutions were prepared with doubled distilled water in the laboratory of School of Water Resources Engineering. Plastic container & apparatuses were cleaned by acid-wash before use. All concentrations of Fluoride solution are freshly prepared by using concentrated primary stock solutions for each experiment. 100ppm & 1000 ppm of primary stock solutions of Fluoride were prepared. Water samples were collected by 20 litres plastic container. All used containers were washed with 1% nitric acid. Before collecting the sample, container was rinsed three to five times with the water to be used.

### 6.1.2. Analytics

Total Fluoride contents of each test are measured by **inoLab pH/ION 735** meter along with Thermally Isolated Magnetic Stirrer and Poly tetra fluoro ethylene (PTFE) coated stir bar. inoLab pH/ION 735 meter has following modes:

1. Measuring
2. Calibration
3. Storage
4. Transmitting Data
5. Settings

An electrode sensor is attached with inoLab pH/ION 735 meter. TISAB (Total Ionic Strength Adjuster Buffer) is used as buffer solution. Only polyethylene containers are used for Fluoride solutions.

Fig 6.1: Magnetic Stirrer, inoLab 735 pH/ION meter and TISAB

## 6.2 Ion-Exchange Process:

Ion exchange is a process used extensively to control the purity and pH of water by removing undesirable ions and replacing them with acceptable ones, which means the process whereby impurities present in the incoming fluid (water) are removed by exchanging impure ions with H and OH ions.
The ion exchanger is of complex nature and is in fact polymeric. An ion-exchange resin or ion-exchange polymer is an insoluble matrix normally in the form of small (0.25-0.5 mm radius) micro beads.
Anionic resins and Cationic resins are the two most common resins used in the ion-exchange process. While negatively charged ions are attracted by anionic resin and positively charged ions are attracted by cationic resin.

Four main types of ion-exchange resins differ in their functional group:

- **Strongly acidic**, typically featuring sulfonic acid groups.e.g. sodium polystyrene sulfonate.
- **Strongly basic**, typically featuring quaternary amino groups.
  e.g. trimethylammonium groups
- **Weakly acidic**, typically featuring carboxylik acid groups.
- **Weakly basic**, typically featuring primary, secondary, and/or tertiary amino groups.
  e.g. polyethylene amine

## 6.2.1 Mechanism:

### Cation exchange Resin:

Cation exchange resins contain free cations which can be exchanged for cationsin solution.

Reaction:

$R–H + M^+ = R^-M^+ + H^+$ where, R→ Cation exchange Resin

M→ Positive charged Ion

A typical example is the displacement of sodium ions in a sulfonate resin by calcium ions:

$2(Res.SO_3^-)Na^+ + Ca^{2+} =(Res.SO_3^-)_2^-Ca_2^+ +2Na^+$

### Anion exchange Resin:

Formula: $NR_4^+OH^-$

Often these are styrene–divinylbenzene copolymer resins that have quaternary ammonium functional group as an integral part of the resin matrix.

Reaction:

$NR_4^+OH^- + HF = NR_4^+F^- + H_2O$

Fig 6.2: Anion Exchange resin

Fig 6.3: Cation Exchange Resin

## 6.2.2 Material required:

### 6.2.2.1 Apparatus required:

- Burette
- Stand with clamp
- Gravels and sand
- Cationic Resin(10 gm)& Anionic Resin(10 gm) as a filter media
- Polyethylene lab ware
- WTW InoLab pH/ION 735 meter
- pH meter
- Conductivity meter

### 6.2.2.2 Reagents required:

1. Primary stock solution of Fluoride. Concentration of 100 mg/L Fluoride stock solution was prepared.

2. Stock solution of Fluoride was spiked in concentrations of 5.5, 7.98 & 10.6 mg/L with water of Garden reach water supply from JU.

3. TISAB (Total Ionic Strength Adjuster Buffer), a buffer solution is required for fluoride electrode when test is conducted.

### 6.2.2.3 Preparation of Fluoride Stock Solution:

To make 100mg/L fluoride stock solution of 1000ml, 2.21gm pure sodium fluoride (NaF) salts is dissolved in 1000ml doubled distilled water and take it in a 1000ml bottle. Primary Stock solution of 1litre of 100mg/L fluoride concentration is prepared.

### 6.2.3 Method of using Cation-Anion Exchange Resin Filter:

1. Description of Burette filter unit:
   A polyethylene burette of 750mm height ×10mm dia. was taken. Cross section are of the burette is 78.5398mm$^2$.A stopcock valve was fixed at the bottom of the burette to maintain the flow rate. Hydraulic flow rate of that burette filter was fixed at 496.81 l/hr/m$^2$. Filtered water was collected on a plastic container for testing the fluoride conc. as well as general parameters.

2. Arrangement of filter bed:
   Filter bed was arranged of 20mm of gravels (smaller dia.) at bottom, then 130mm of coarse sand, above that 125mm of anionic resin (10gm) then again 5mm of sand layer, cationic resin of 125mm (10gm) was above that thin sand layer. Sand bed of 20mm was at the top.

3. Filtration:
   After arrangement of filter media, burette was clamped on its stand. Then raw water made of Garden reach supply water spiked with fluoride stock solution was passed through this filter media. After filtration, treated water was collected.

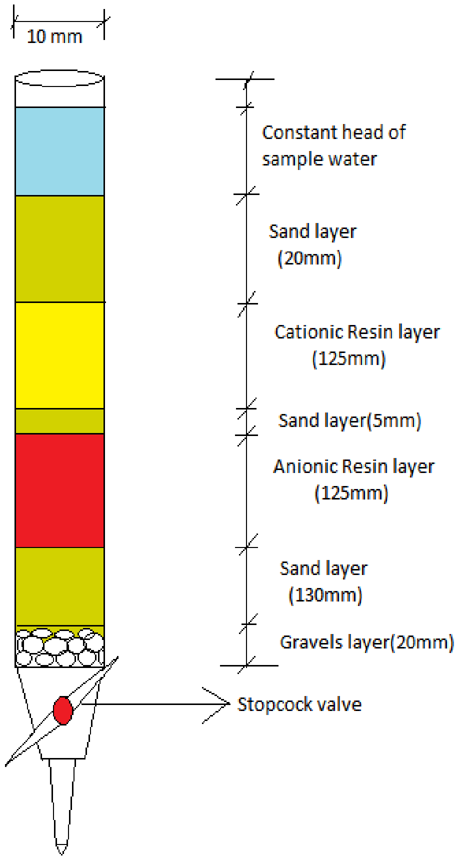


Fig 6.4: Typical Model of Burette filter using Cation-Anion Exchange Resin

### 6.2.4 Procedure:

1. First of all coarse sand and smaller size gravels are collected.
2. Sieve the sand by 600µ sieve size. Retained sand on that sieve and gravels are cleaned thoroughly by water.
3. Clean wet sand& gravels are dried in air for 24 hours.
4. After completion of air dry, those sand and gravels are kept in oven for 24hours.
5. Clean the polyethylene burette with doubled distilled water. Then mark the heights of various beds of filter media.

6. From bottom of this burette fill 20mm of smaller size gravels, then 130mm of sand above it, after that take 10 gm of Anionic Resin which is 125mm in burette. Make a 5mm thin layer of sand above anionic resin. Then take 10 gm of Cationic Resin which is also 125mm in burette. Lastly take 20mm of sand layer at the top. Arrangement of filter media is done.

7. Stand this burette filter with the help of clamp.

8. Take a plastic biker of volume 500ml, firstly wash it with acid then wash it with doubled distilled water. Keep it below of outlet of burette filter so as to collect the treated water.

9. Stock solution of Fluoride is spiked in concentrations of fluoride 5.5, 7.98 & 10.6 mg/L with water of Garden reach water supply from JU and uses it as raw water.

10. Pour the raw water on the burette filter. Try to keep 135mm of head of water above the filter media.

11. Fixed the hydraulic flow rate at 496.81 l/hr/m$^2$ by fixed the stopcock valve on burette.

12. Collect treated water and analyze the concentration of fluoride with Inolab pH/ion 735 meter and TISAB.

13. Analyze pH, TDS, EC of treated water by using pH meter and Conductivity meter.

### 6.2.5 Observation:

Raw water passes through burette filter. Filtered water comes out with the hydraulic flow rate of 496.81 l/hr/m$^2$. Filter media has to be submerged with water always.

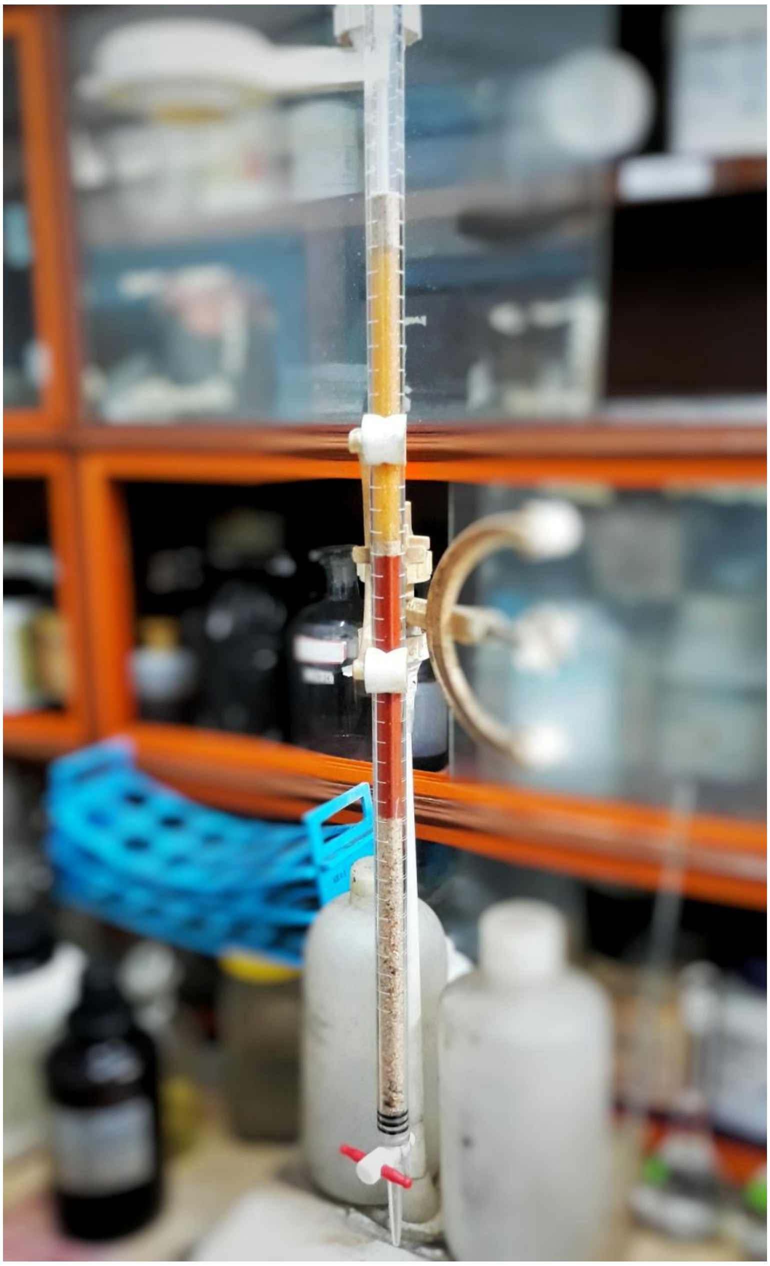


Fig 6.5: Experimental set up of Cation-Anion exchange resin filter process

## 6.2.6 Results:

**Table 6.1: Results of various parameters of Raw and Filtered Water using Cation-Anion Exchange Resin**

| | **Trial 1**<br>Hydraulic Flow Rate: 496.81 L/h/$m^2$<br>Water Consumption: 500ml | | **Trial 2**<br>Hydraulic Flow Rate: 496.81 L/h/$m^2$<br>Water Consumption: 500ml | | **Trial 3**<br>Hydraulic Flow Rate: 496.81 L/h/$m^2$<br>Water Consumption: 500ml | |
|---|---|---|---|---|---|---|
| **Parameters** | **Raw Water** | **Filtered Water** | **Raw Water** | **Filtered Water** | **Raw Water** | **Filtered Water** |
| **Fluoride** (mg/L) | 5.5 | 0 | 7.98 | 0.67 | 10.6 | 2.56 |
| **pH** | 7.94 | 3.34 | 6.87 | 3.26 | 6.58 | 3.19 |
| **TDS** (mg/L) | 330 | 653 | 386 | 668 | 357 | 782 |
| **EC** (µS/cm) | 552 | 1087 | 645 | 1116 | 544 | 1294 |

Above table shows Fluoride, pH, TDS, EC of raw and filtered water by using Ion-exchange process (Cation-Anion exchange resin) in burette filter. It shows that pH value is decreasing in all trials and it’s not in the range of drinking water according to upper guidelines.

**Table 6.2: Percentage Removal efficiency of Fluoride Concentration using Cation-Anion exchange Resin Filter**

| | **Raw Water** | **Filtered Water** | **Percentage Removal** |
|---|---|---|---|
| **Trial 1** | 5.5 | 0 | 100% |
| **Trial 2** | 7.98 | 0.67 | 91.60% |
| **Trial 3** | 10.6 | 2.56 | 75.85% |

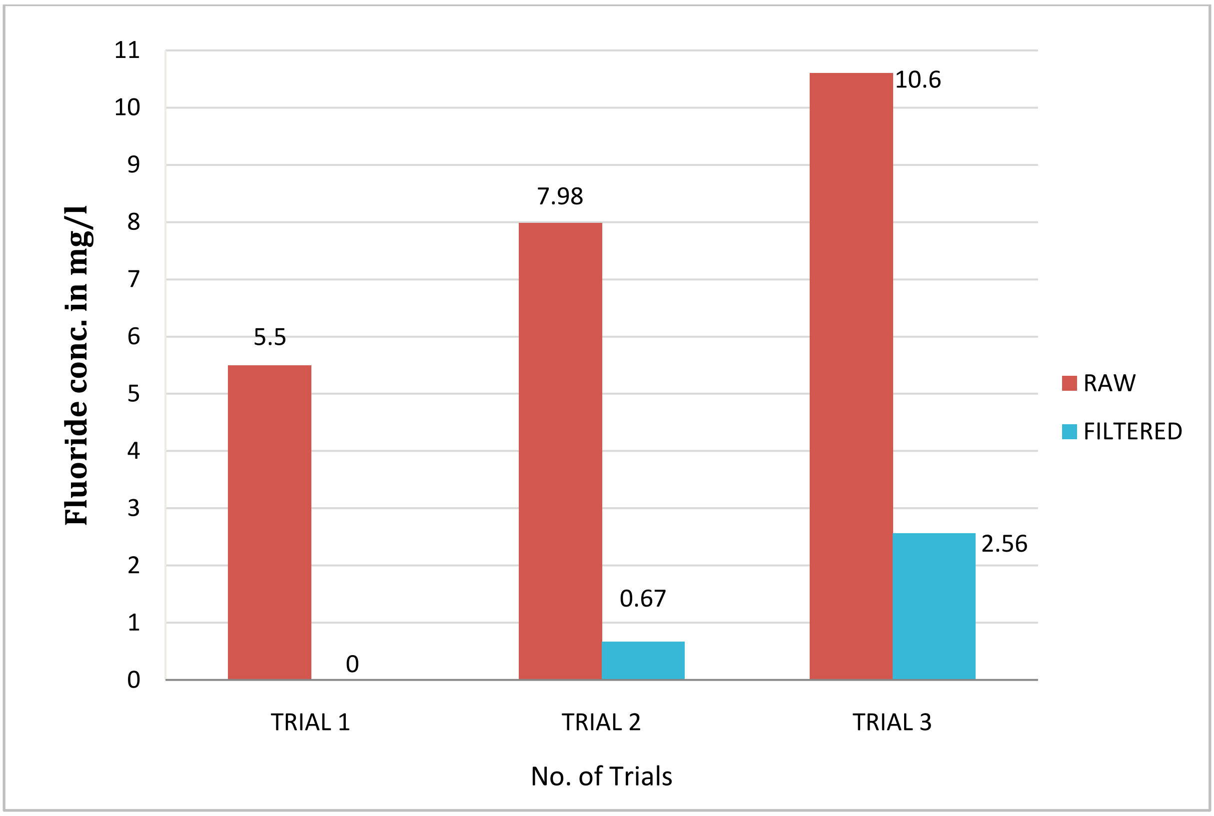
### 6.2.6.1 Sorption Capacity of Cation-Anion Exchange Resin:

- Amount of water passed in each trial = 500 ml
- Total amount of Fluoride present in raw water = (5.5+7.98+10.6)x (500/1000) mg

  = 12.04 mg
- Total amount of Fluoride present in treated water = (0+0.67+2.56)x (500/1000) mg
  = 1.615 mg
- Amount of Fluoride adsorbed = (12.04 – 1.615) mg
  = 10.425 mg
- Total amount of Cation-Anion Exchange resin used = 20gm
- Sorption Capacity of Cation-Anion Exchange resin = (10.425/20) x 1000

  = 521.25 mg/kg

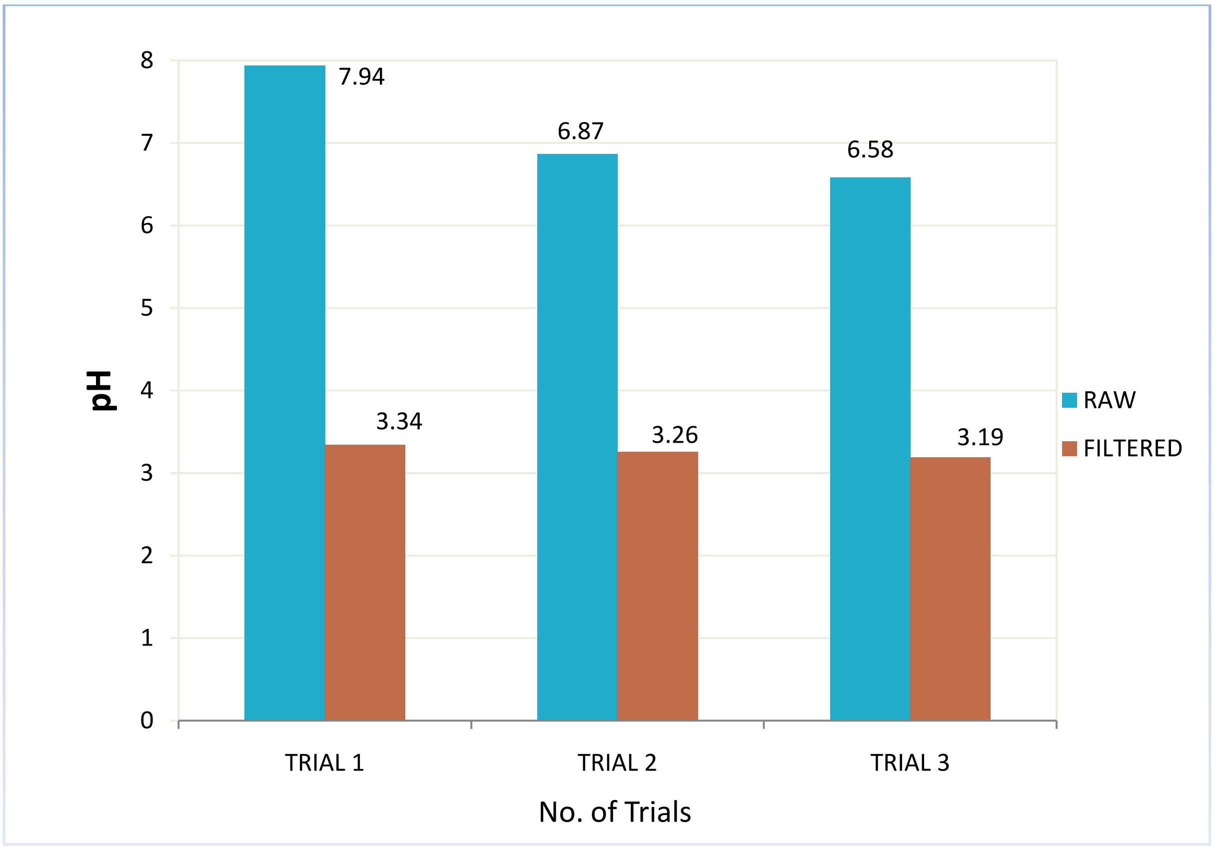
**Chart 6.1: Concentration of Fluoride in Raw and Filtered water**



**Discussion:**

Above figure shows that column chart of concentration of Fluoride in Raw water and Treated water. At the time of Trial-2 filtered water has 0.67mg/L fluoride conc. after 1000ml of raw water passed through burette filter which is in the desirable limit but at Trial-3 filtered water exceed permissible limit of fluoride conc. according to IS 10500:2012 after 1500ml of water passed through Cation-Anion Exchange Resin of 10 gm each.

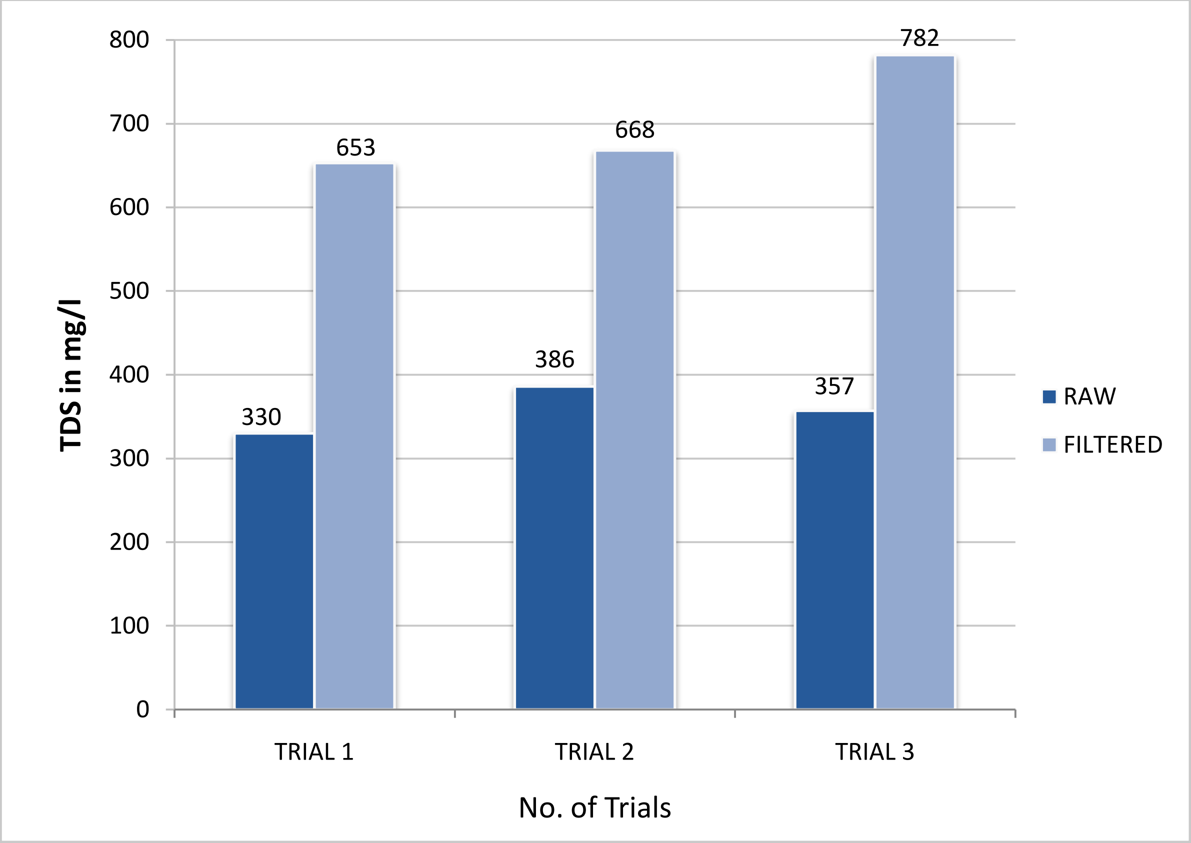
**Chart 6.2: pH of raw and filtered water**



**Discussion:**

Above figure shows that pH of raw water is in the limit of drinking water but when it is passed through Cation-Anion exchange Resin beds, pH of treated water is decreased which is not in the range of potable water according to is 10500:2012.

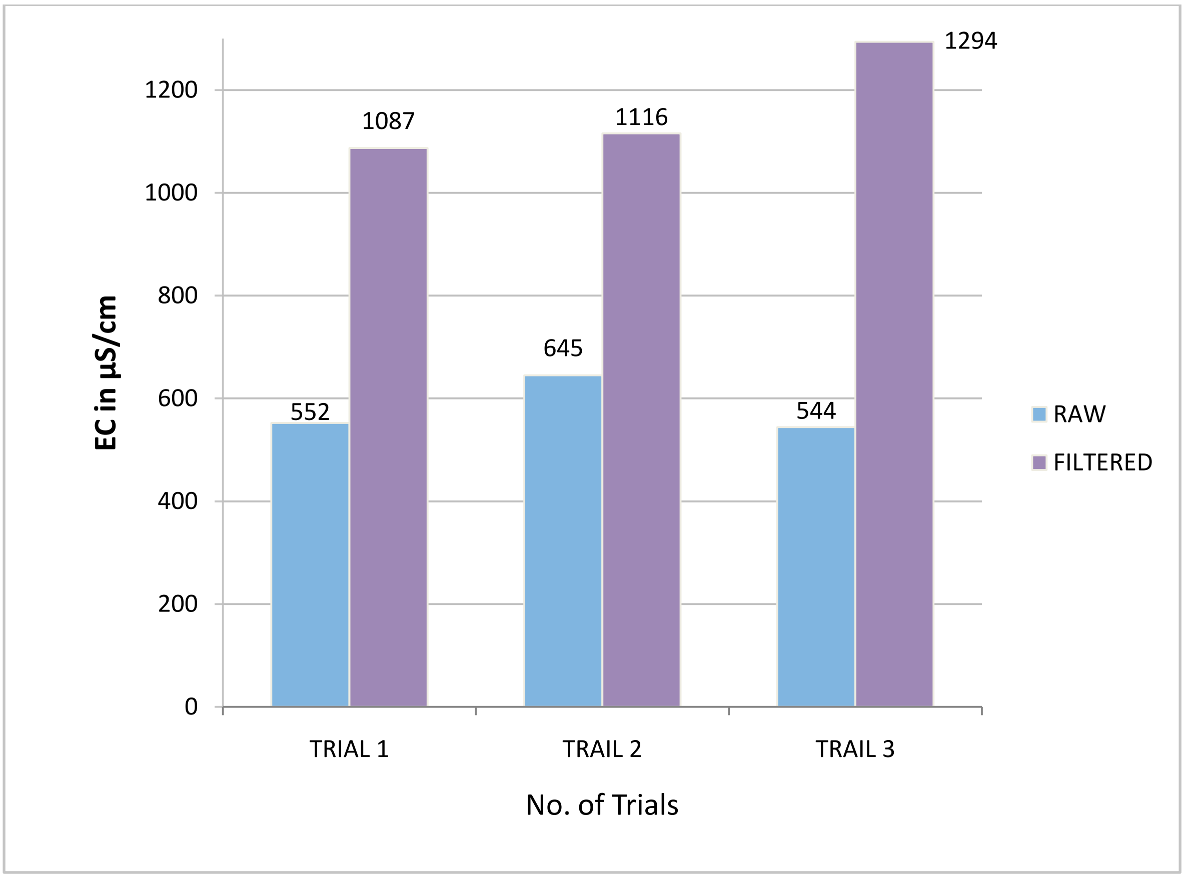
**Chart 6.3: TDS of Raw and Filtered Water**



**Discussion:**

TDS (Total Dissolved Solid) is used to express salinity level of water. Above figure shows that TDS variation of various trials of raw and filtered water. It shows that TDS of Raw water is in the range of desirable limit which is 500mg/L while Filtered water is in the range of permissible limit according to IS 10500:2012 which is 2000mg/L for drinking purpose.

**Chart 6.4: Electrical Conductivity (EC) of Raw and Filtered Water**



**Discussion:**

Electrical Conductivity is also used to describe salinity level of water. Above figure shows variation of EC in various trials of raw and filtered water.

## 6.2.7 Overall Discussion:

From the experiment and results of Ion-Exchange Process of Cation-Anion exchange Resin, it shows that in raw water of Trial 1 & Trial 2, concentrations of Fluoride (5.5mg/L & 7.98mg/L) are removed up to the desirable limit of Fluoride by Cation-Anion Exchange Resin of 10 gm each but at the time of high concentration (10.6mg/L), these filter media are unable to remove up to the permissible limit of Fluoride which is 1.5mg/L. Another significant thing of this filter media is pH value of filtered water decreased promptly which is not in the range of drinking water (6.5-8.5) according to IS 10500:2012. It is concluded that pretreatment is needed to use Cation-Anion exchange Resin bed as filter media for drinking purpose.

## 6.3 Ion-exchange process for Defluoridation using Anion Exchange Resin:

### 6.3.1 Materials Required:

#### 6.3.1.1 Apparatus required:

- Burette
- Stand with clamp
- Gravels and sand
- Anionic Resin(20gm) as a filter media
- Polyethylene lab ware
- WTW InoLab pH/ION 735 meter
- pH meter
- Conductivity meter

#### 6.3.1.2 Reagents required:

1. Primary stock solution of Fluoride. Concentration of 100 mg/L Fluoride stock solution was prepared.

2. Stock solution of Fluoride was spiked in concentrations of 4.1, 6.2, 6.5 & 8.5 mg/L with Ground Water of JU.

3. TISAB (Total Ionic Strength Adjuster Buffer), a buffer solution is required for fluoride electrode when test is conducted.

4. 0.02N $H_2SO_4$ and Mixed bromocresol green-methyl red indicator are needed for conducting the test of Total Alkalinity

5. Ammonium Buffer Solution, EBT indicator solution and standard 0.01N EDTA are required to test Total Hardness of water.

6. $K_2Cr_2O_4$ indicator and Standard $AgNO_3$ are required to check the presence of Chloride in water.

#### Preparation of Fluoride Stock Solution:

To make 100mg/L fluoride stock solution of 1000ml, 2.21gm pure sodium fluoride (NaF) salts is dissolved in 1000ml doubled distilled water and take it in a 1000ml bottle. Primary Stock solution of 1litre of 100mg $F^-$/L concentration is prepared.

### 6.3.2 Method of using Anion Exchange Resin Filter:

1. Description of Burette filter unit:
   A polyethylene burette of 750mm height × 10mm dia. was taken. Cross section are of the burette is 78.5398mm$^2$. A stopcock valve was fixed at the bottom of the burette to maintain the flow rate. Hydraulic flow rate of that burette filter was fixed at 496.81 L/hr/m$^2$. Filtered water was collected on a plastic container for testing the fluoride conc. as well as general parameters.

2. Arrangement of filter bed:
   Filter bed was arranged in 20mm of gravels (smaller dia.) at bottom, then 180mm of coarse sand, above that 250mm of anionic resin (20gm) then again 100mm of Sand bed was at the top.

3. Filtration:
   After arrangement of filter media, burette was clamped on its stand. Then raw water prepared from Ground water of JU spiked with fluoride stock solution. Raw water was passed through this filter media. After filtration, treated water was collected.

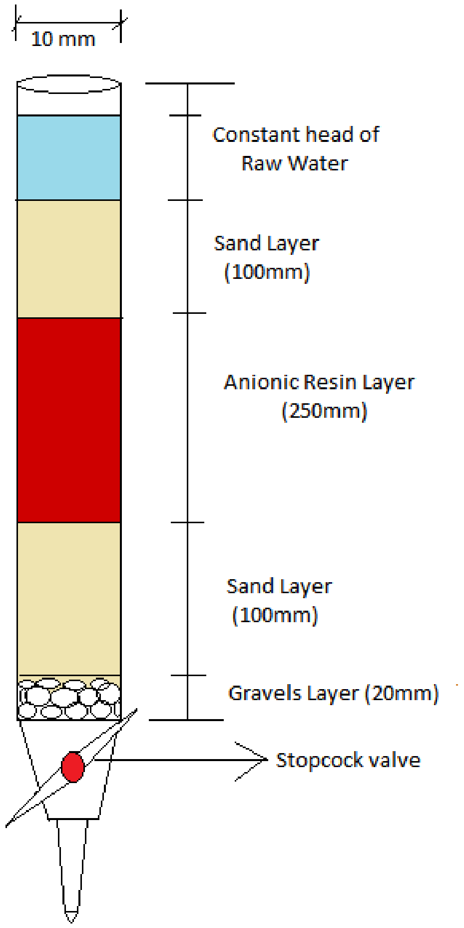


Fig 6.6: Typical Model of Burette filter using Anionic Resin

## 6.3.3 Procedure:

1. First of all coarse sand and smaller size gravels are collected.
2. Sieve the sand by 600µ sieve size. Retained sand on that sieve and gravels are cleaned thoroughly by water.
3. Cleaned wet sand & gravels are dried in air for 24 hours.
4. After completion of air dry, those sand and gravels are kept in oven for 24 hours.
5. Clean the polyethylene burette with doubled distilled water. Then mark the heights of various beds of filter media.
6. From bottom of this burette, fill 20mm of smaller size gravels, then 180mm of sand above it, after that take 20gm of Anionic Resin which is 250mm in burette. Lastly 100mm of sand layer at the top. Arrangement of filter media is done.
7. Stand this burette filter with the help of clamp.
8. Take a plastic biker of volume 500ml, firstly wash it with acid then wash it with doubled distilled water. Keep it below of outlet of burette filter so as to collect the treated water.
9. Stock solution of Fluoride is spiked in concentrations of 4.1, 6.2, 6.5 & 8.5 mg $F^-$/l with ground water of JU and uses it as raw water.
10. Pour the raw water on the burette filter. Try to keep 100mm of constant head of water above the filter media.
11. Fixed the hydraulic flow rate at 496.81 l/hr/$m^2$ by fixed the stopcock valve on burette.
12. Collect treated water and analyze the concentration of fluoride with Inolab pH/ion 735 meter with TISAB & Magnetic Stirrer
13. Other general parameters like pH, TDS, EC, Total Alkalinity, Total Hardness and Chloride are also tested to analyze treated water.

### 6.3.4 Observation:

Raw water passes through burette filter. Filtered water comes out with the hydraulic flow rate of 496.81 L/hr/m$^2$. Filter media has to be submerged with water always.

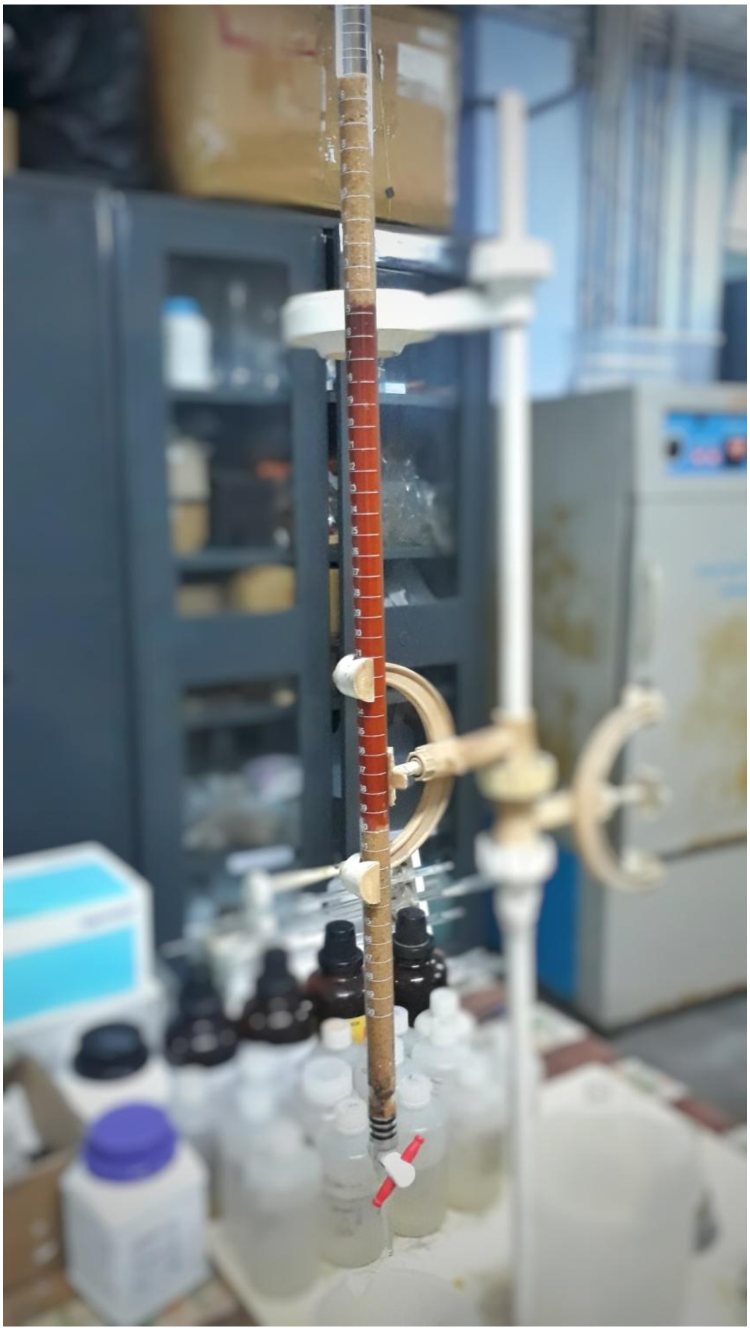


Fig 6.7: Experimental set up of burette filter using Anion exchange resin

### 6.3.5 Result:

**Table 6.3: Results of various parameters of Raw and Filtered water using Anionic Resin**

|  | **Trial 1**<br>Hydraulic Flow Rate: 496.81 L/h/$m^2$<br>Water Consumption: 500ml |  | **Trial 2**<br>Hydraulic Flow Rate: 496.81 L/h/$m^2$<br>Water Consumption: 500ml |  | **Trial 3**<br>Hydraulic Flow Rate: 496.81 L/h/$m^2$<br>Water Consumption: 500ml |  | **Trial 4**<br>Hydraulic Flow Rate: 496.81 L/h/$m^2$<br>Water Consumption: 500ml |  |
|---|---|---|---|---|---|---|---|---|
| **Parameters** | **Raw Water** | **Filtered Water** | **Raw Water** | **Filtered Water** | **Raw Water** | **Filtered Water** | **Raw Water** | **Filtered Water** |
| **Fluoride** (mg/L) | 4.1 | 0 | 6.2 | 1.1 | 6.5 | 1.2 | 8.5 | 2.6 |
| **pH** | 7.34 | 6.68 | 7.28 | 6.85 | 7.5 | 7.33 | 7.56 | 7.23 |
| **TDS** (mg/L) | 1636 | 1808 | 1597 | 1688 | 1654 | 1730 | 1640 | 1700 |
| **EC** (µS/cm) | 2750 | 3000 | 2680 | 2790 | 2760 | 2850 | 2720 | 2830 |
| **Total Alkalinity as $CaCO_3$** (mg/L) | 316 | Nil | 304 | 16 | 315 | 190 | 310 | 205 |
| **Total Hardness as $CaCO_3$** (mg/L) | 664 | 380 | 704 | 580 | 695 | 560 | 710 | 585 |
| **Chloride** (mg/L) | 961.7 | 1097.65 | 1023.67 | 1285.59 | 1054.67 | 1307.09 | 1094.66 | 1329.58 |

Above table shows that removing fluoride up to 3rd Trial is in the Permissible limit (1.5mg $F^-$/L) according to IS 10500:2012. But at 4th trial when concentration of fluoride in raw water is 8.5 mg $F^-$/L passed through Anionic Resin Filter of 25gm, it removed fluoride concentration but not in the range of permissible limit. According to IS 10500:2012, pH, TDS, EC, Total Alkalinity and Total Hardness are in the permissible limit of drinking water. But range of Chloride is crossed the permissible limit.

**Table 6.4: Percentage removal efficiency of Fluoride concentration using Anionic Resin Filter**

| | Raw Water | Filtered Water | Percentage Removal |
|---|---|---|---|
| **Trial 1** | 4.1 | 0 | 100% |
| **Trial 2** | 6.2 | 1.1 | 82.25% |
| **Trial 3** | 6.5 | 1.2 | 81.54% |
| **Trial 4** | 8.5 | 2.6 | 69.41% |

### 6.3.5.1 Sorption Capacity of Anion Exchange Resin:

- Amount of water passed in each trial = 500 ml
- Total amount of Fluoride present in raw water = (4.1+6.2+6.5+8.5)x (500/1000)mg

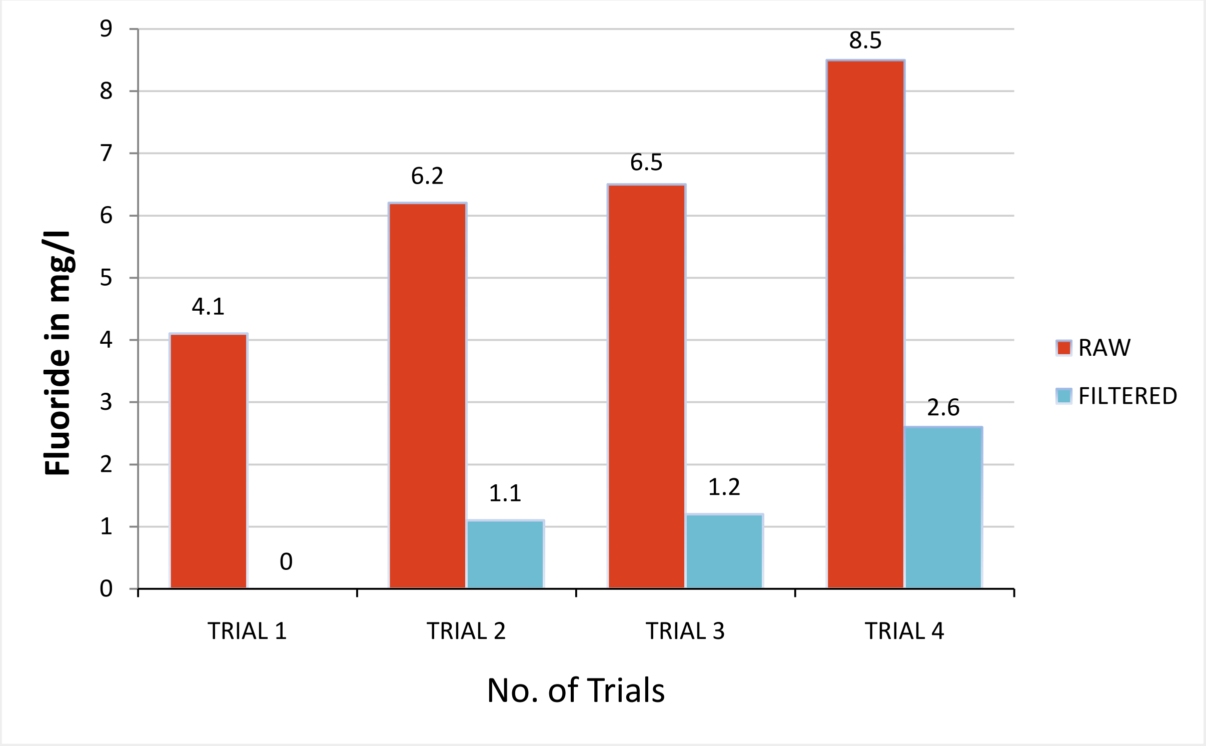
  = 12.64 mg
- Total amount of Fluoride present in treated water mg = (0+1.1+1.2+2.6)x (500/1000)

  = 2.45 mg
- Amount of Fluoride adsorbed = (12.64 – 2.45) mg

  = 10.19 mg
- Total amount of Anion Exchange resin used = 20gm
- Sorption Capacity of Anion Exchange resin = (10.19/20) x1000

  = 509.5 mg/kg

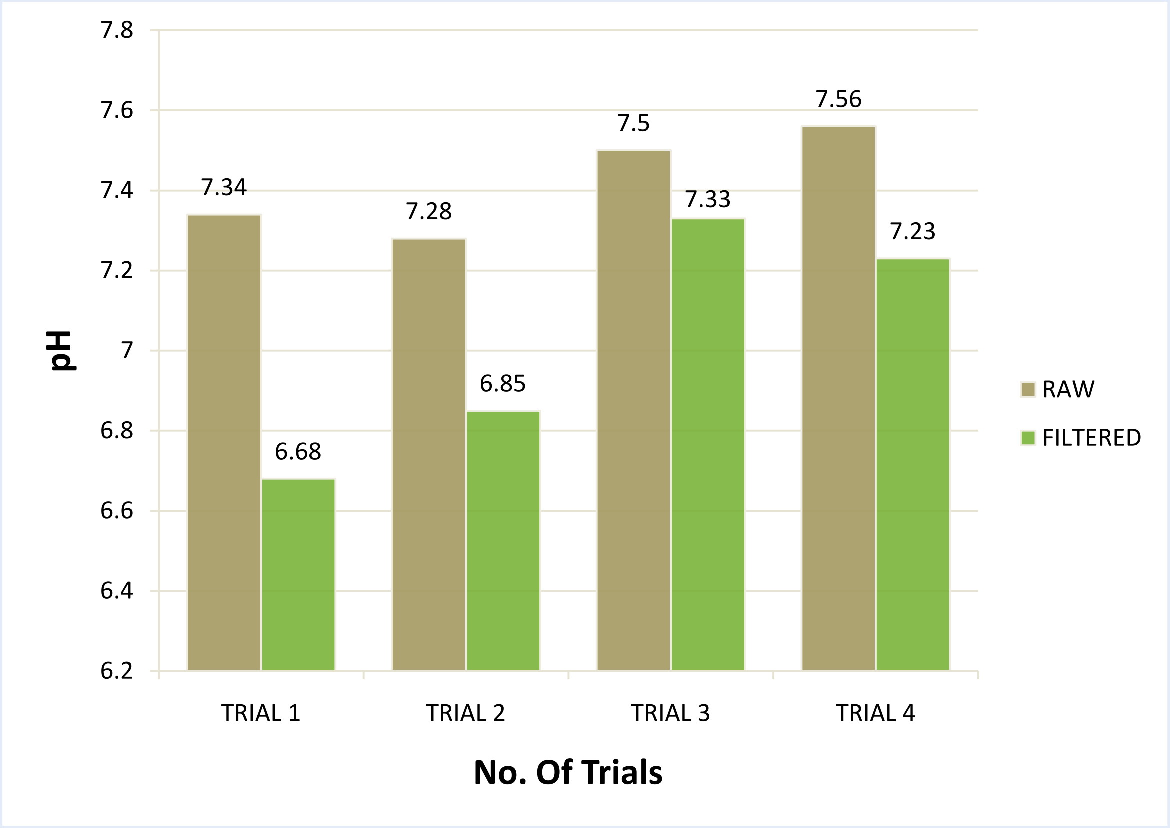
**Chart 6.5: Concentration of Fluoride in mg/L in Raw and Filtered Water**



**Discussion:**

Above figure shows that column chart of concentration of Fluoride in Raw water and Treated water. In Trial-1, 4.1mg/L conc. of Fluoride in Raw water is totally removed by Anionic Resin bed of 25gm. At the time of Trial-2 & Trial-3 filtered water have 1.1mg/L & 1.2mg/L fluoride conc. respectively which are in the desirable limit but at Trial-3 filtered water, conc. of Fluoride 2.6mg/L which exceed permissible limit of fluoride conc. in drinking water according to IS 10500:2012.

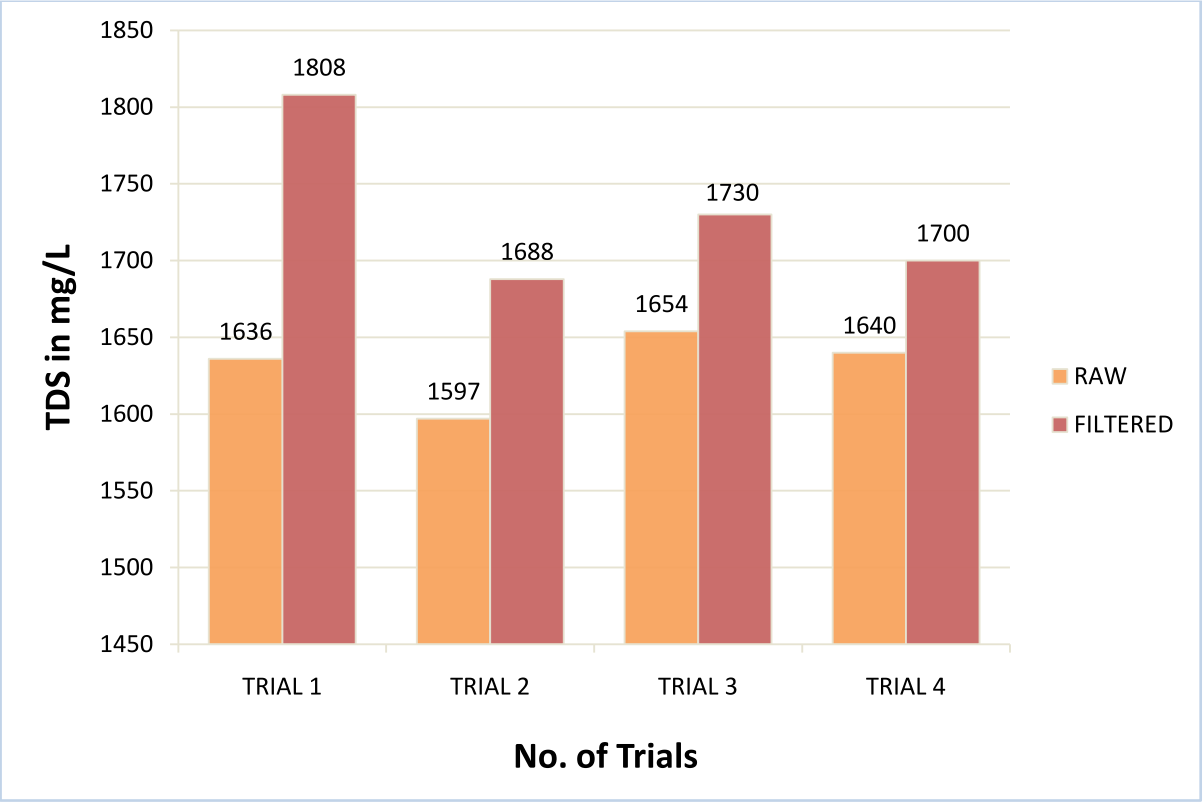
**Chart 6.6: pH of raw and filtered water**



**Discussion:**

Above chart shows that pH of raw and filtered water. According to IS 10500:2012, pH of raw water in every trials is in the limit of drinking water and when it is filtered using Ion exchange process( Anionic resin bed), the pH of filtered water slightly decreased but it is in the range of drinking water(6.5-8.5).

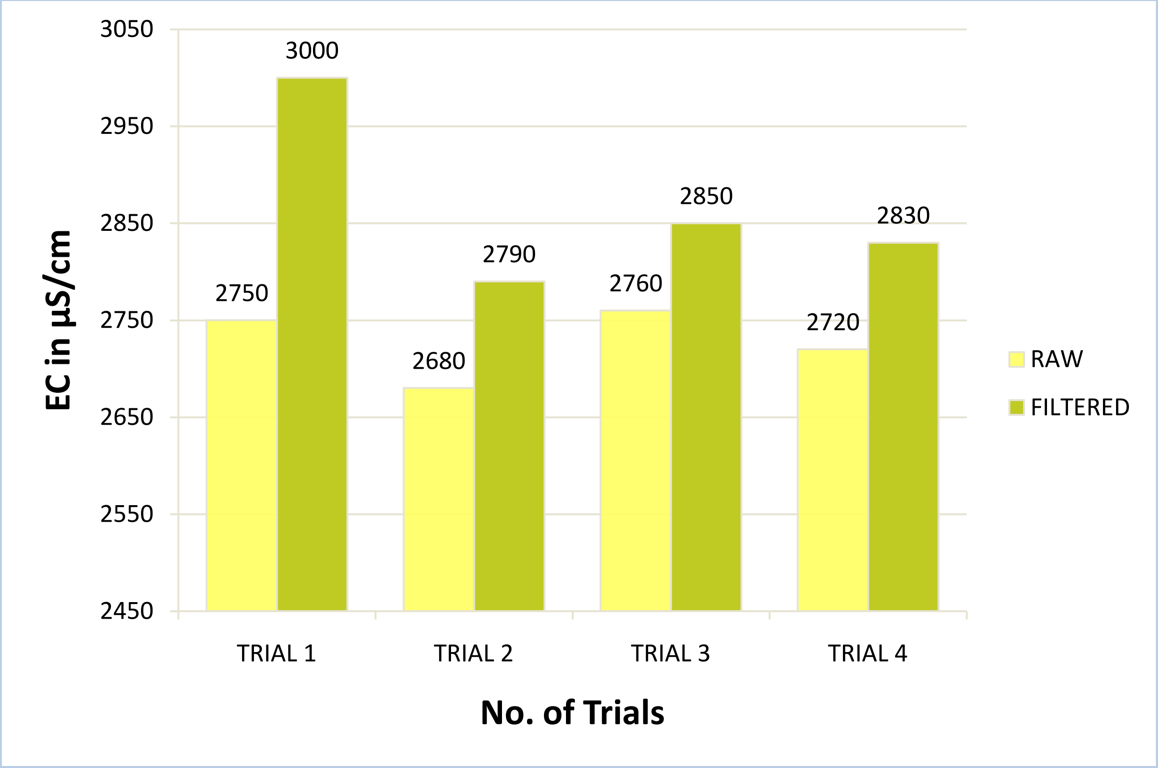
**Chart 6.7: TDS of Raw and Filtered Water**



**Discussion:**

TDS (Total Dissolved Solid) is used to express salinity level of water. Above figure shows that TDS variation of various trials of raw and filtered water. It shows that TDS of Raw and Filtered water is not in the range of desirable limit (500mg/L) but it is within the permissible limit (2000mg/L) according to IS 10500:2012 for drinking purpose.

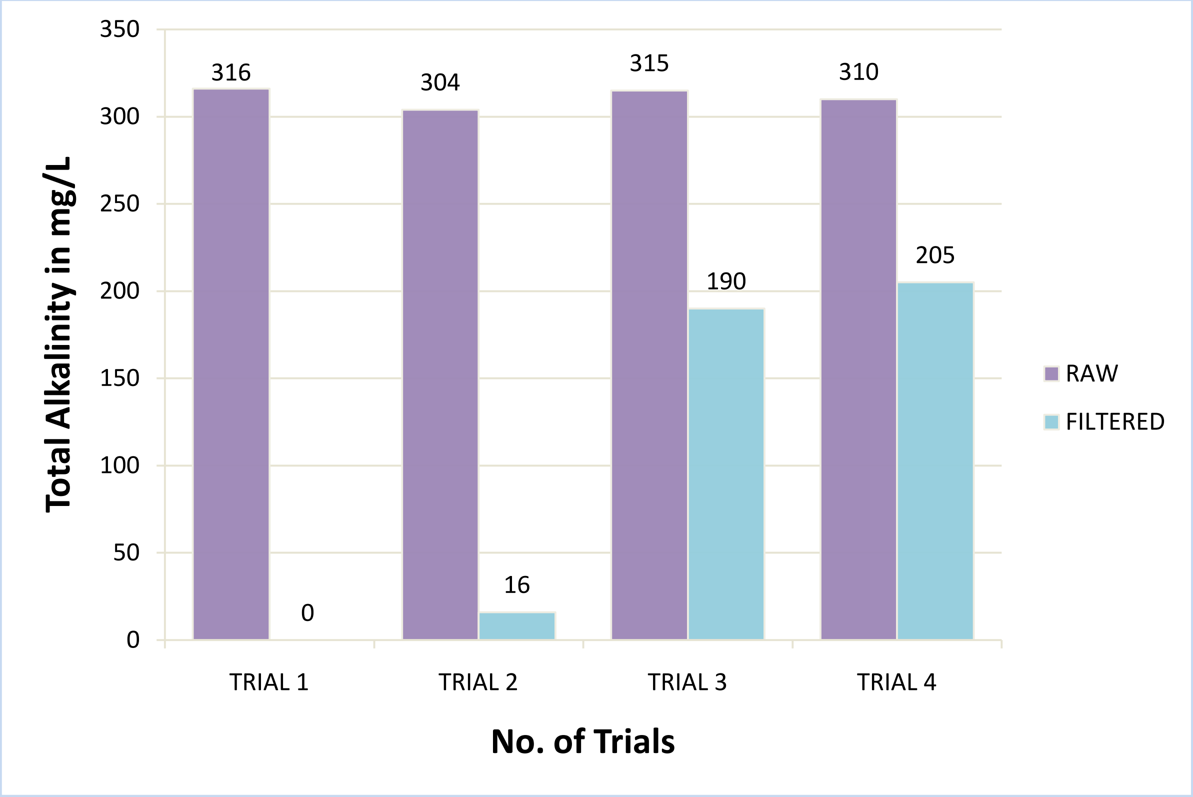
**Chart 6.8: Electrical Conductivity (EC) of Raw and Filtered Water**



**Discussion:**

Electrical Conductivity is also used to describe salinity level of water. Above figure shows variation of EC in various trials of raw and filtered water.

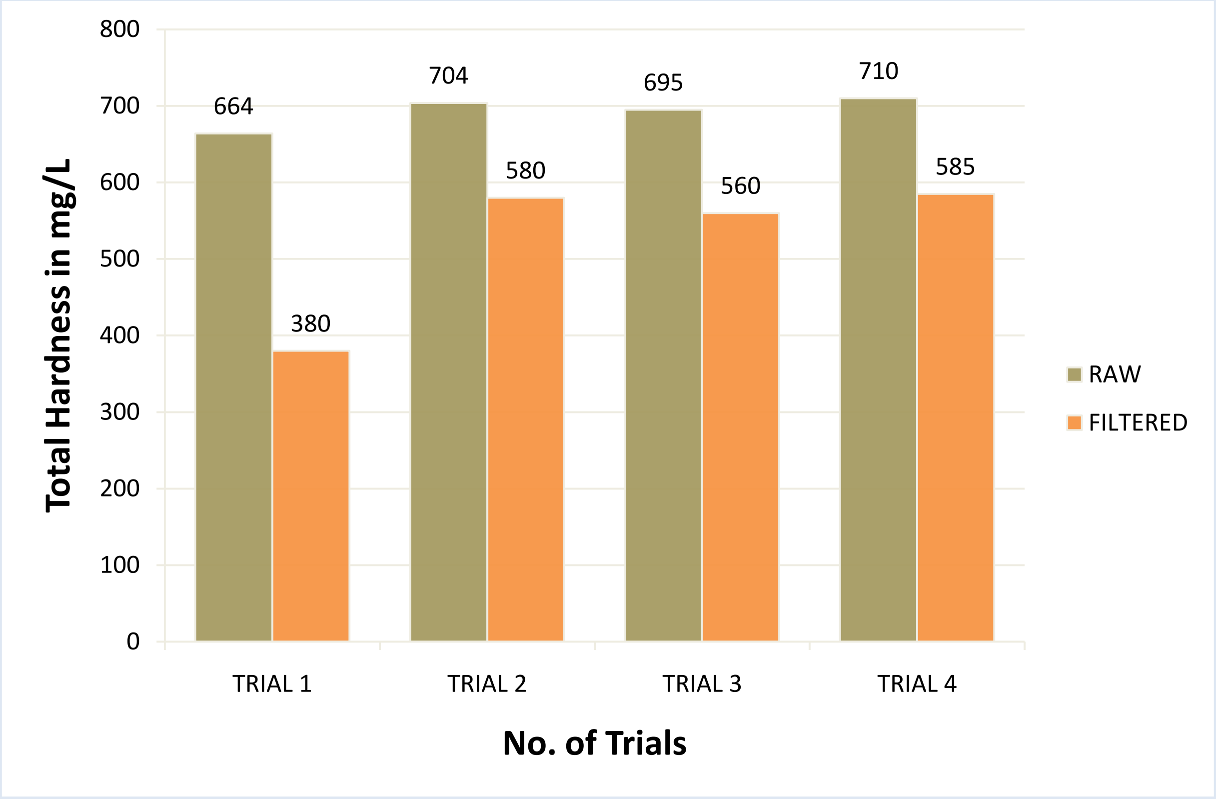
**Chart 6.9: Total Alkalinity as $CaCO_3$ of Raw & Filtered water**



**Discussion:**

Alkalinity of water is its acid neutralizing capacity. It is the sum of all titratable bases. Here the chart shows that Total Alkalinity as $CaCO_3$ of raw and filtered water of various trials. According to IS 10500:2012, Total Alkalinity of raw water is not in the range of acceptable limit(200mg/L) but it is within the permissible limit(600mg/L). Total Alkalinity of Filtered water is in the acceptable limit of drinking water.

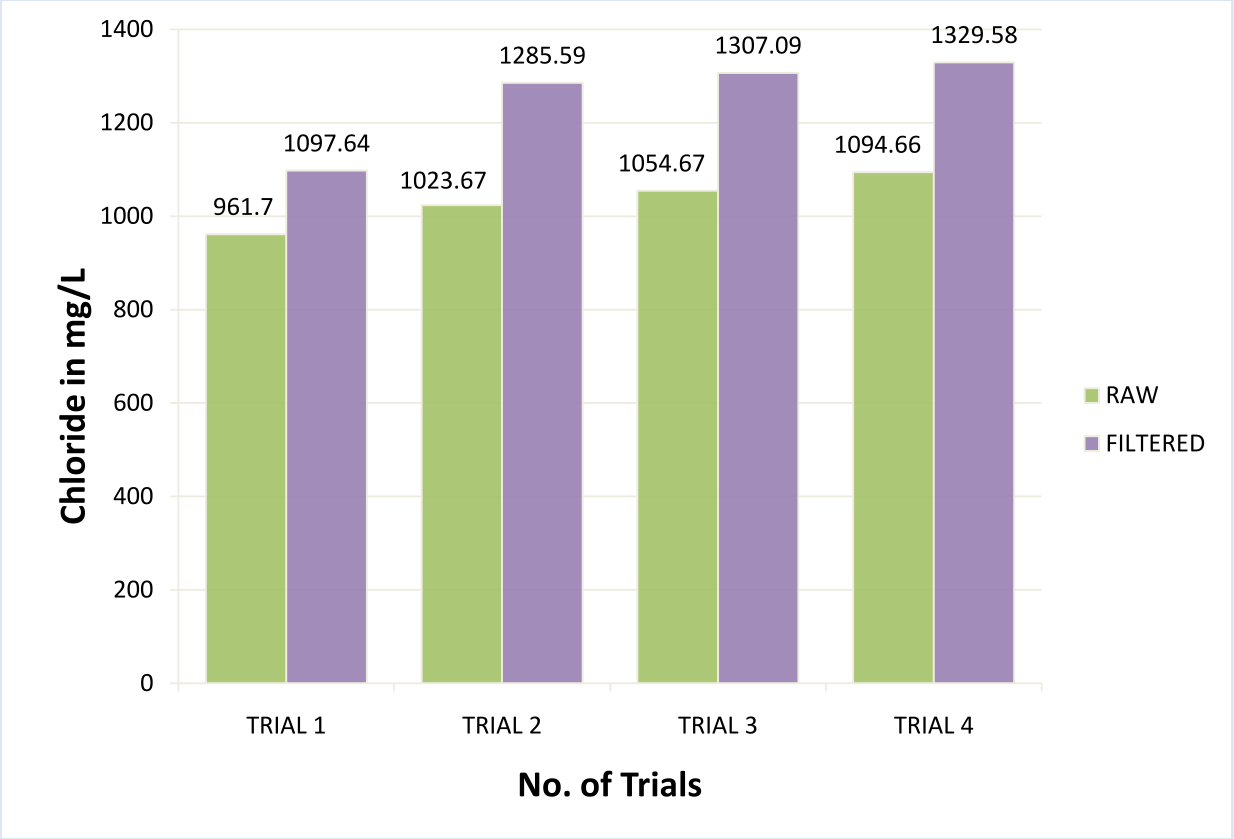
**Chart 6.10: Total Hardness as CaCO3 of Raw & Filtered Water**



## Discussion:

Total Hardness as $CaCO_3$ is defined as sum of all calcium and magnesium concentrations expressed as calcium carbonate in mg/L. Above chart shows that Total Hardness as $CaCO_3$ of Raw and Filtered water. According to IS 10500:2012, Total Hardness of raw water exceeds the permissible limit (600mg/L) and when it is filtered Total Hardness come to its range of permissible limit of drinking water.

**Chart 6.11: Presence of Chloride in Raw and Filtered Water**



**Discussion:**

Chloride is one of the major anions present in water and wastewater. In the above chart presence of Chloride is increasing in filtered water which exceeds the range of permissible limit (1000mg/L) of drinking water according to IS 10500:2012.

### 6.3.6 Overall Discussion:

From the experiment and results of Ion-Exchange Process by Anionic Resin bed, it shows that raw water of Trial 1, Trial 2 and Trial 3, concentrations of Fluoride (4.1mg/L, 6.2mg/L & 6.5mg/L) are removed up to the desirable limit of Fluoride in drinking water according to IS 10500:2012 by Anionic Resin of 20 gm and 496.81 L/h/$m^2$ hydraulic flow rate but after 1500ml of raw water passed through anionic resin bed in burette filter , high concentration of Fluoride in raw water which is 8.5mg/L removed up to 2.6mg/L after filtration which exceeds the permissible limit of fluoride (1.5mg/L) in drinking water. According to IS 10500:2012, other general parameters like pH, TDS, EC, Total Alkalinity and Total Hardness of Filtered water are in the range of permissible limit of drinking water but presence of Chloride in filtered water increase slightly which can be remained in the range of permissible limit by applying pretreatment process. It is concluded that for removing the concentration of Fluoride to its desirable limit, Ion exchange Process by using Anionic Resin is effective method.

## 6.4 Adsorption:

### 6.4.1 Activated Alumina:

Activated Alumina was commonly used as adsorbents. Activated alumina is a granular, highly porous material consisting essentially of aluminum trihydrate. It is widely used as a commercial desiccant in many gas drying processes. Studies employing activated alumina for fluoride removal were conducted by many workers and all these works confirmed the ability of activated alumina for higher uptake of fluoride from water.

### 6.4.2 Mechanism:

Activated alumina has high affinity for fluoride because in aqueous environment at pH values below its $pH_{pzc(\text{the point of zero charge})}$ it forms protonated ($=Al\text{-}OH_2^+$) and neutral (=Al-OH) aluminol sites, which are responsible for binding fluoride ions by formation of inner-sphere complexes. The fluoride uptake by Activate Alumina usually decreases with a decrease in pH due to the fact that HF is weakly ionized (pH<3.2), and soluble alumino–fluoro complexes are formed resulting in the presence of aluminum ions in the treated water and lowering of the active sites. At near neutral pHs, the uptake of fluoride is maximum. The interaction between fluoride and the protonated aluminol sites leads to the formation of inner-sphere complexes and elimination of water. The reaction can be represented by

$Al\text{-}OH_2^+ + F^- \leftrightarrow AlF + H2O$

$Al\text{-}OH + F^- \leftrightarrow Al\text{-}F + OH^-$

The use of Activated Alumina in water de-fluoridation has been limited to certain extent to countries with well-established economies.

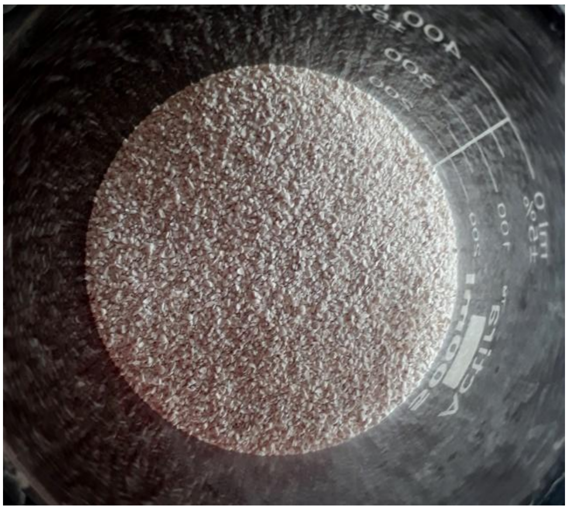


Fig 6.8: Activated Alumina granules

## 6.4.3 Material Required:

### 6.4.3.1 Apparatus Required:

1. Filter setup
2. A large plastic bucket of 20L with a tap attached at the bottom
3. Two pipes
4. Stand with clamp
5. Gravels (large, medium and small)
6. Sand
7. Activated Alumina as a filter media (100 gm)
8. Plastic container for collecting the treated water
9. Inolab pH/ION 735 Meter, pH meter, Conductivity meter & Turbidity meter

### 6.4.3.2 Reagents required:

1. Primary stock solution of Fluoride. Concentration of 1000 mg/L Fluoride stock solution was prepared.

2. Stock solution of Fluoride was spiked in concentration of 7.6 mg/L with Garden reach supply water of JU.

3. TISAB (Total Ionic Strength Adjuster Buffer), a buffer solution is required for fluoride electrode when test is conducted.

4. 0.02N $H_2SO_4$ and Mixed bromocresol green-methyl red indicator are needed for conducting the test of Total Alkalinity

5. Ammonium Buffer Solution, EBT indicator solution and standard 0.01N EDTA are required to test Total Hardness of water.

6. $K_2Cr_2O_4$ indicator and Standard $AgNO_3$ are required to check the presence of Chloride in water.

- **Preparation of Fluoride Stock Solution:**
  To make 1000mg/L fluoride stock solution of 1000ml, 22.1gm pure sodium fluoride (NaF) salts is dissolved in 1000ml doubled distilled water and take it in a 1000ml bottle. Primary Stock solution of 1litre of 1000mg $F^-$/L concentration is prepared.

### 6.4.4 Method of using Activated Alumina Filter:

1. <u>Development of De-fluoridation filters Unit</u>

   De-fluoridation Filter unit fabricated in the laboratory consisted of a chambers, fabricated from PVC pipes. 100 gm of Activated Alumina was taken in the upper portion of gravel-sand bed of 25 mm dia. x 600 mm height filter, which gave a Activated Alumina bed depth of 240 mm. A flow control device was fixed at the bottom of the filter so as to have a flow rate of 300ml/h and collect the treated water at a plastic container. Size of the containers is decided based on the volume of water.

2. <u>Preparation of the filter bed</u>

   The filter bed is prepared by gravels (large, medium and small diameter) at the bottom, 60 mm length from bottom of the filter, then sand of 120mm above the gravels bed to arrest the iron present in the raw water & 100 gm of Activated Alumina at the top as a medium for adsorbing fluoride at 240 mm above sand bed. Rest 180 mm at the top is kept for water head.

3. <u>Filtration</u>

   After prepared the filter media, the raw water passed through the filter. And after filtration the filtered water is collected.

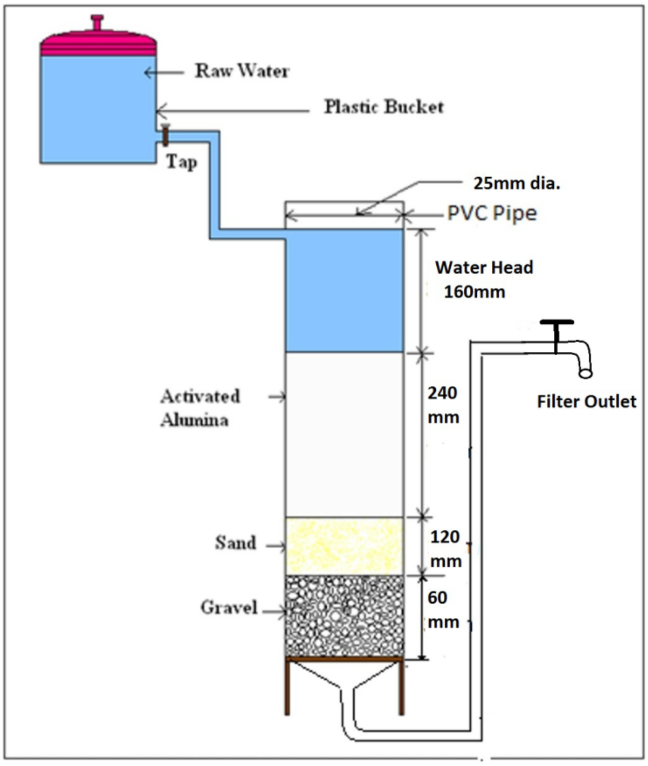


Fig 6.9: Typical filter model for defluoridation by adsorption process using Activated Alumina

### 6.4.5 Procedure:

An experimental set up was prepared which is described below.

1. First of all coarse sand and smaller size gravels are collected.
2. Sand and gravels are cleaned thoroughly by water.
3. Cleaned wet sand & gravels are dried in air for 24 hours
4. After completion of air dry, those sand and gravels are kept in oven for 24 hours.
5. Fluoride concentrated raw water is taken in a plastic bucket & kept over a certain height and filter is kept below the height of bucket to provide it the necessary pressure head.
6. A filter is kept on a wooden stand with the help of clamp.
7. The fluoride concentrated raw water is passed through the pipe attached at the filter in an up flow manner.
8. The filter bed is prepared by gravels (large, medium and small diameter) at the bottom, 60 mm length from bottom of the filter, then sand of 120mm above the gravels bed to arrest the iron present in the raw water & 100 gm of Activated Alumina at the top as a medium for adsorbing fluoride at 240 mm above sand bed. Rest 180 mm at the top is kept for water head.
9. There is an outlet at the bottom of the filter extended by plastic pipe attached a tap at the end to collect the treated water.
10. Treated water is analyzed using Inolab pH/ION 735 meter to obtain the fluoride concentration.
11. pH, TDS, EC and Turbidity are analyzed using pH meter, Conductivity meter & Turbidity meter.
12. Total hardness and Total Alkalinity are analyzed by titration.

### 6.4.6 Observation:

From the bucket fluoride concentrated raw water is flowing through the pipe attached with filter and raw water passes through the filter media. Treated water comes out from the filter with a flow rate of 300ml/h. Filter media should be kept saturated.

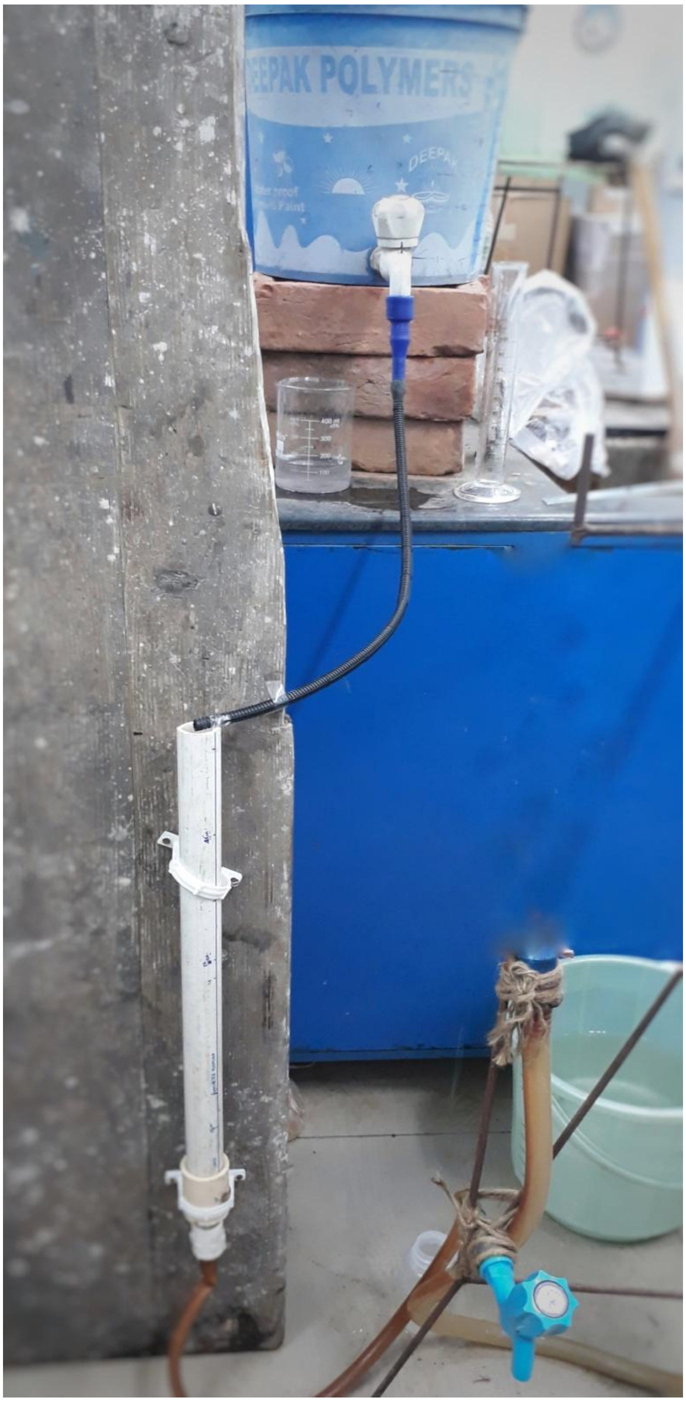


Fig 6.10: Experimental Set-up for adsorption method using Activated Alumina

## 6.4.7 Result:

**Extent of Fluoride removal by Activated Alumina adsorbent of fluoride spiked Garden reach supply water in JU**

Initial Fluoride concentration of Raw Water (Garden reach Supply Water) = 7.6 mg/L
Filter Flow Rate = 300 ml/h
Weight of Activated Alumina = 100 gm
Total Water Consumption = 27.1 Liters

**Table 6.5: Tested results of various parameters of Raw & Filtered water by Adsorption Process using Activated Alumina**

| Sl. No. | Cumulative Vol. of Water in Liters | Specification of Water | PARAMETERS | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Fluoride (mg/L) | pH | TDS (mg/L) | EC (µS/cm) | Total Hardness (mg/L) | Total Alkalinity (mg/L) | Turbidity (NTU) |
| 1 | 3 | Raw | 7.6 | 7.46 | 394 | 656 | 75 | 105 | 15.3 |
| | | Filtered | 0 | 7.83 | 374 | 621 | 30 | 90 | 0.45 |
| 2 | 5.5 | Raw | 7.6 | 7.66 | 394 | 656 | 75 | 105 | 15.3 |
| | | Filtered | 0 | 7.47 | 363 | 602 | 25 | 85 | 0.52 |
| 3 | 7.5 | Raw | 7.6 | 7.3 | 387 | 648 | 85 | 95 | 7.59 |
| | | Filtered | 0 | 7.41 | 367 | 628 | 45 | 85 | 0.57 |
| 4 | 9 | Raw | 7.6 | 7.73 | 387 | 648 | 85 | 95 | 7.59 |
| | | Filtered | 0 | 6.93 | 371 | 632 | 40 | 110 | 0.69 |
| 5 | 11.5 | Raw | 7.6 | 7.43 | 412 | 655 | 85 | 95 | 7.59 |
| | | Filtered | 0 | 6.87 | 396 | 663 | 40 | 95 | 0.6 |
| 6 | 13.5 | Raw | 7.6 | 7.43 | 388 | 648 | 75 | 115 | 15.8 |
| | | Filtered | 0 | 7.12 | 371 | 622 | 25 | 85 | 1.01 |
| 7 | 16.5 | Raw | 7.6 | 7.68 | 382 | 641 | 75 | 115 | 15.8 |
| | | Filtered | 0 | 7.46 | 391 | 652 | 25 | 95 | 0.97 |
| 8 | 18.5 | Raw | 7.6 | 7.22 | 396 | 660 | 75 | 105 | 21.1 |
| | | Filtered | 0 | 7.34 | 368 | 612 | 20 | 95 | 2.1 |
| 9 | 20.5 | Raw | 7.6 | 7.22 | 396 | 660 | 75 | 105 | 21.1 |
| | | Filtered | 0 | 7.83 | 367 | 611 | 20 | 100 | 1.09 |
| 10 | 22.5 | Raw | 7.6 | 7.22 | 396 | 660 | 75 | 105 | 21.1 |
| | | Filtered | 0.225 | 7.69 | 384 | 641 | 20 | 125 | 0.79 |
| 11 | 25.1 | Raw | 7.6 | 7.56 | 398 | 664 | 60 | 120 | 8.58 |
| | | Filtered | 1.08 | 7.69 | 363 | 607 | 30 | 135 | 0.67 |
| 12 | 27.1 | Raw | 7.6 | 7.56 | 398 | 664 | 60 | 120 | 8.58 |
| | | Filtered | 1.51 | 7.82 | 372 | 621 | 30 | 135 | 0.4 |

**Table 6.6: Determination of percentage removal of Fluoride and water consumption**

| Sl. No. | Water Consumption (L) | Cumulative Consumption of Water (L) | Fluoride influent (mg/L) | Fluoride effluent (mg/L) | Fluoride Removal (%) |
|---|---|---|---|---|---|
| 1 | 3 | 3 | 7.6 | 0.0 | 100 |
| 2 | 2.5 | 5.5 | 7.6 | 0.0 | 100 |
| 3 | 2 | 7.5 | 7.6 | 0.0 | 100 |
| 4 | 1.5 | 9 | 7.6 | 0.0 | 100 |
| 5 | 2.5 | 11.5 | 7.6 | 0.0 | 100 |
| 6 | 2 | 13.5 | 7.6 | 0.0 | 100 |
| 7 | 3 | 16.5 | 7.6 | 0.0 | 100 |
| 8 | 2 | 18.5 | 7.6 | 0.0 | 100 |
| 9 | 2 | 20.5 | 7.6 | 0.0 | 100 |
| 10 | 2 | 22.5 | 7.6 | 0.225 | 97.04 |
| 11 | 2.6 | 25.1 | 7.6 | 1.08 | 85.79 |
| 12 | 2 | 27.1 | 7.6 | 1.51 | 80.13 |

### 6.4.7.1 Calculation:

From the above experiment the adsorption capacity of the activated alumina can also be calculated from the total amount of water passed through the filter which is as follows:

- Total amount of water passed through the filter = 27.1 lit.
- Total amount of fluoride present in 27.1 lit. of raw water = (27.1 x 7.6) mg
  = 205.96 mg
- Total amount of fluoride present in treated water = 6.278 mg
- Amount of fluoride removed from 27.1lit of water passed through filter media
  = (205.96 - 6.278) mg
  = 199.628 mg

Therefore, 100 gm of activated alumina can remove 199.628 mg of fluoride.

Adsorption capacity of 1 kg of activated alumina = (199.628/100)*1000 = 1996.28 mg

Adsorption capacity of the activated alumina used is 1996.28 mg/kg

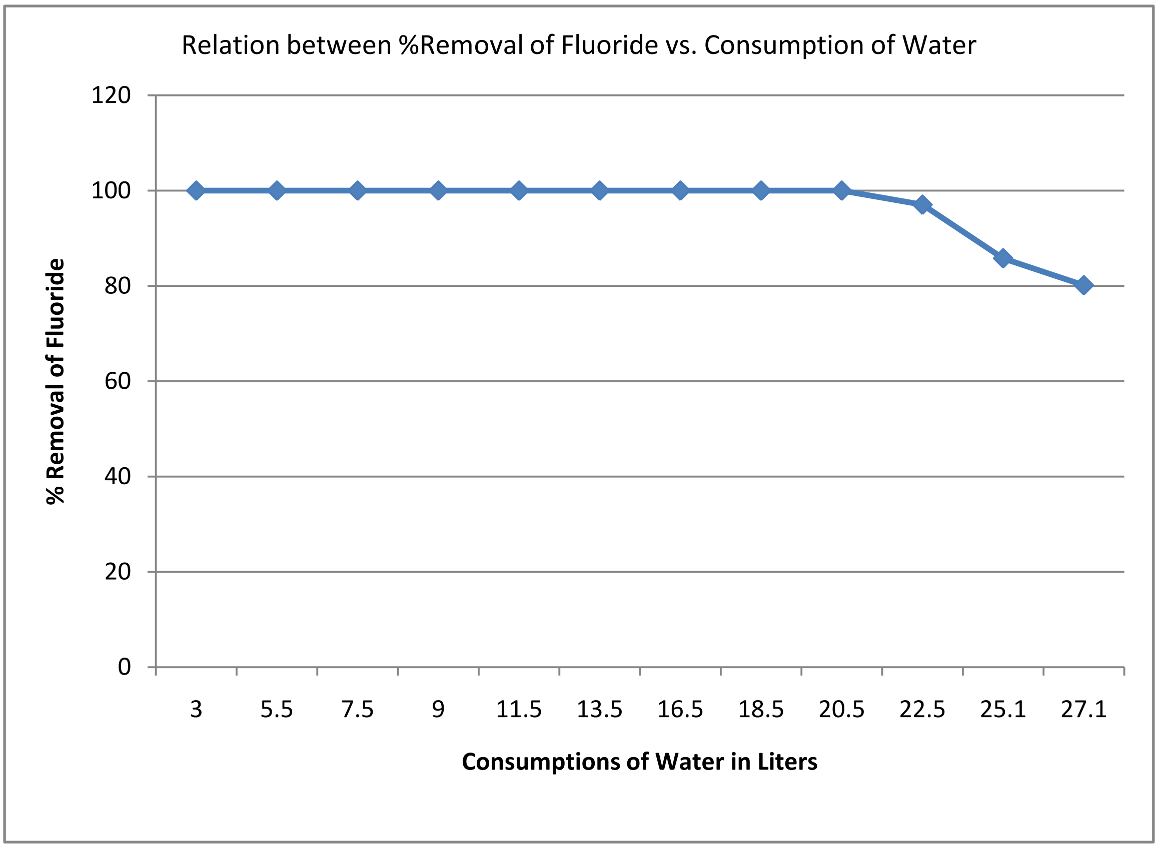


Fig 6.11: Percentage of removal of $F^-$ with respect to vol. of water treated

From the above graph it is shown, the optimum percentage of Fluoride removal was 100%. And percentage of fluoride removal was decreased with increasing of volume of water passed through the filter. Treatment upto 20.5L of water, fluoride was below detection level. After treatment of 27.1L of water, the percentage of fluoride removal decreased from 100 % to 80.13%.

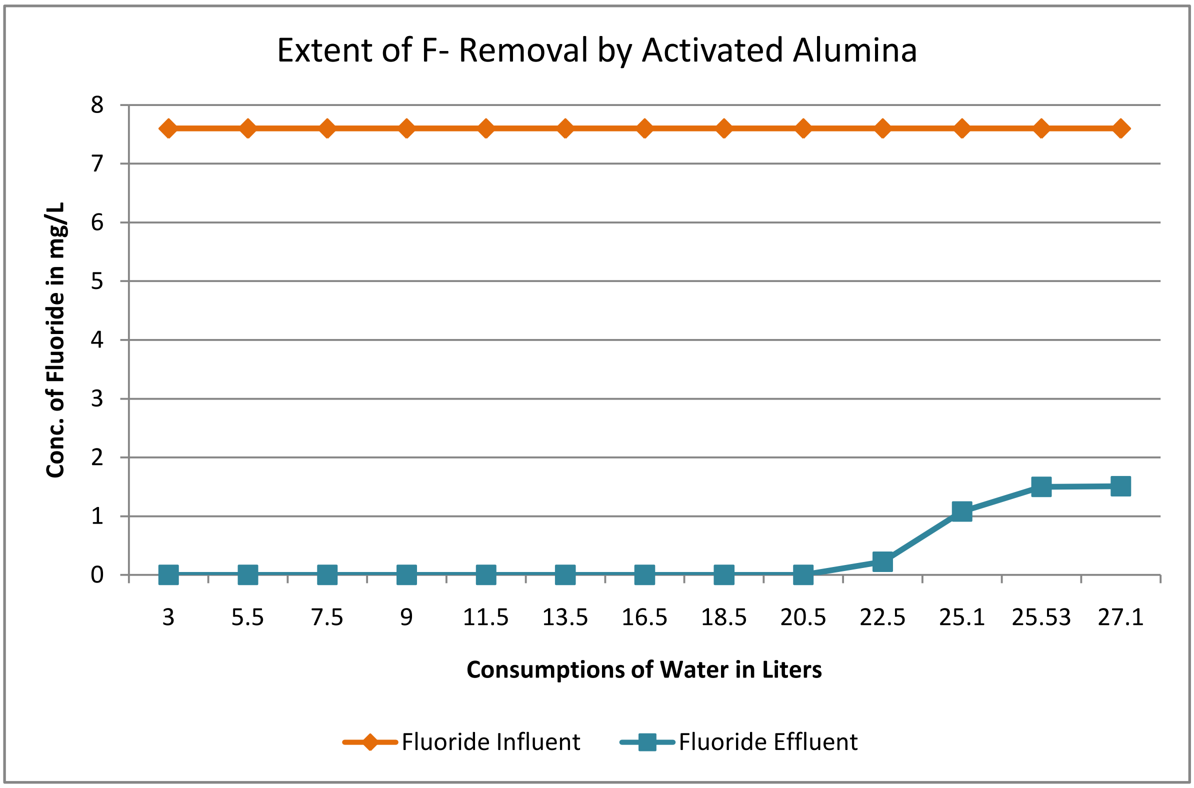


Fig 6.12: Variation of concentrations of $F^-$ in raw & treated water

Above graph shows that concentrations of fluoride in raw water and removal of concentrations of fluoride by activated alumina of filtration of 27.1 liters of water passed through the filter media. Here it is shown that treatment upto 22.5 liters of water, fluoride was in the range of desirable limit but at 27.1 liters, fluoride conc. reach the value of permissible limit of drinking water.

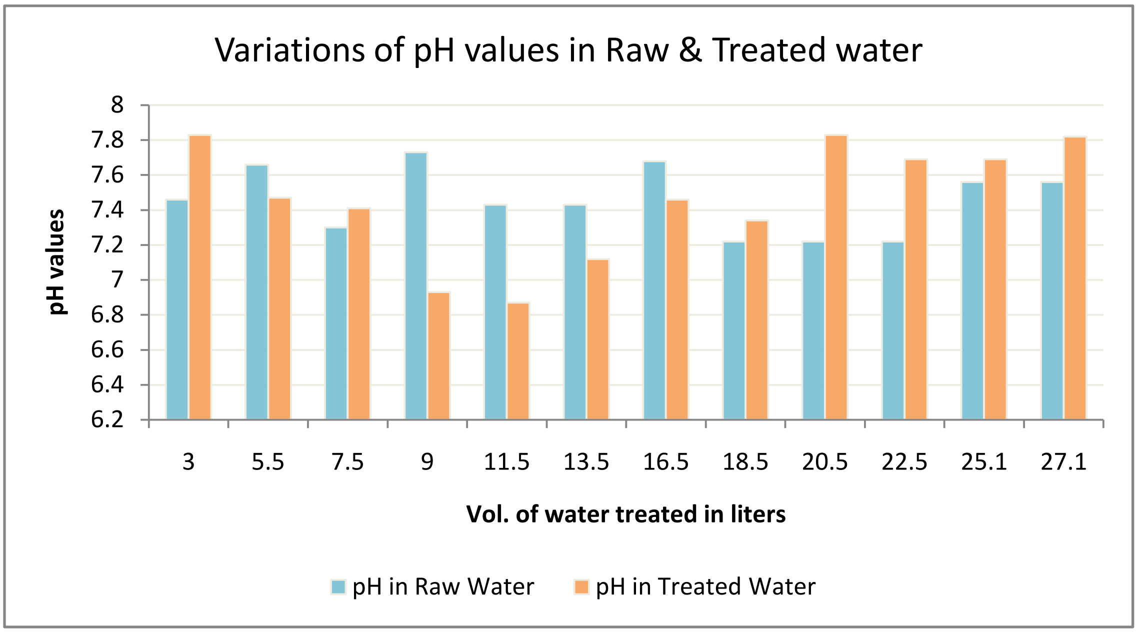


Fig 6.13: Variations of pH values in raw & treated water

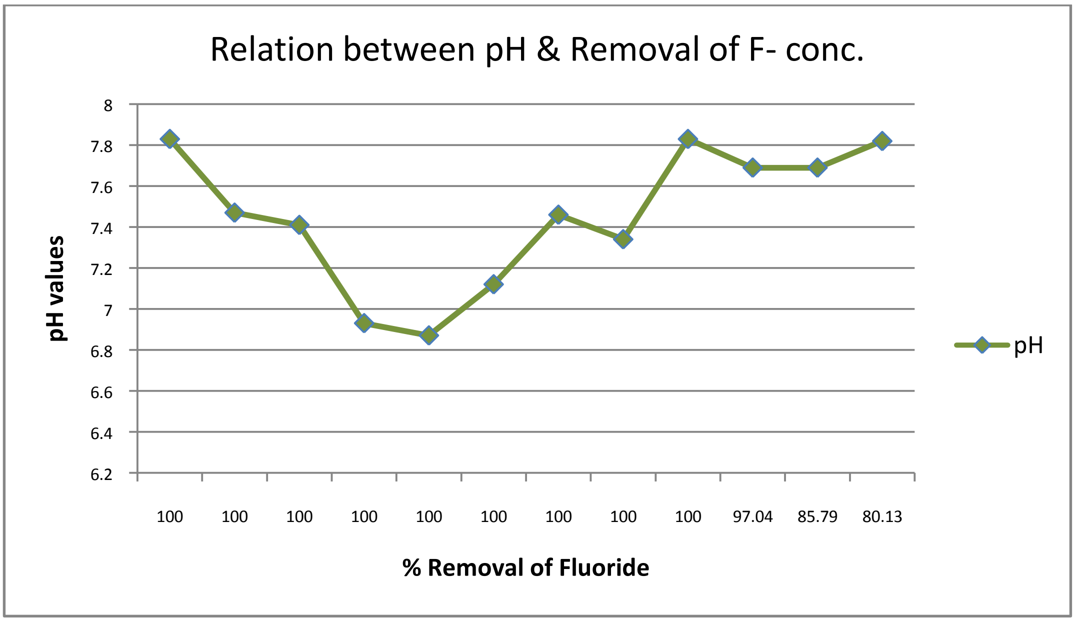


Fig 6.14: Variations of pH values with respect to Percentage removal of $F^-$ conc.

From the graph, it is shown that pH values are changing with respect to percentage removal of fluoride concentrations. Here pH values are increasing with decreasing percentage removal of fluoride concentrations.

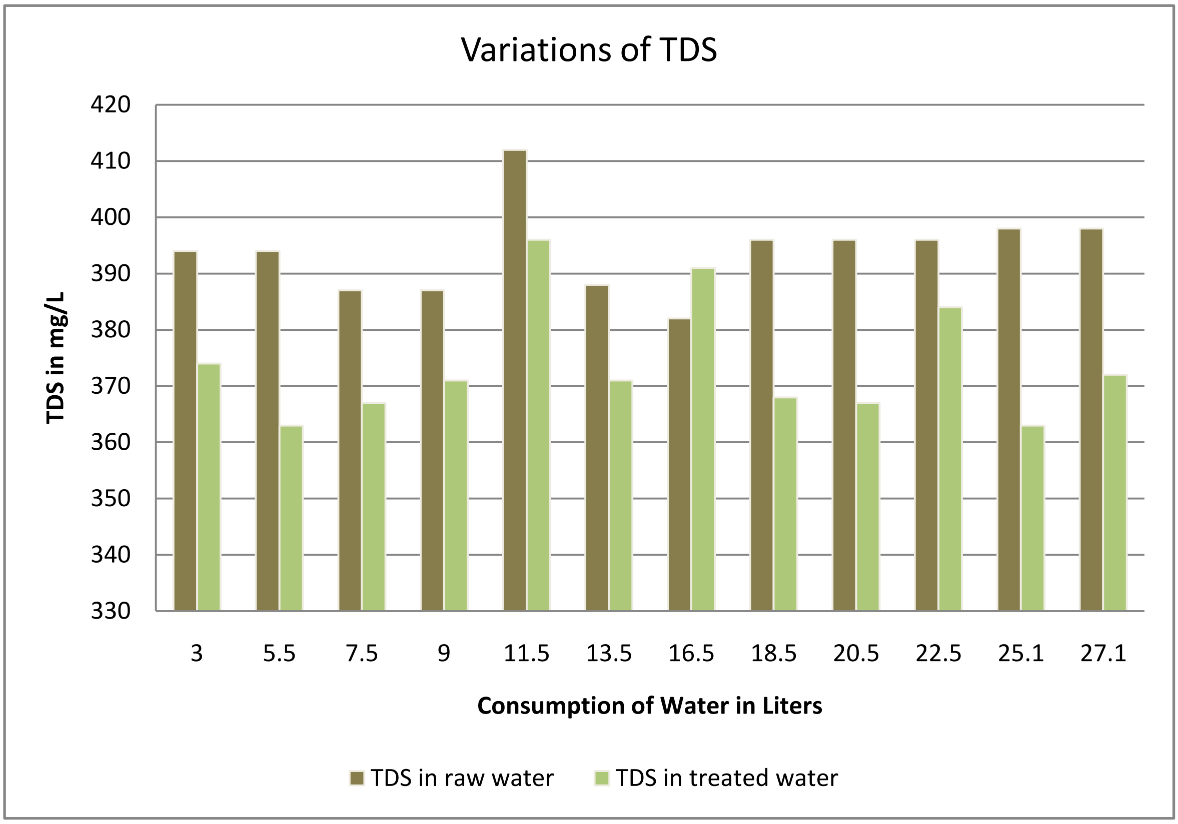


Fig 6.15: Variations of TDS in raw and treated water used

TDS (Total Dissolved Solid) values are decreasing in treated water and it is in the range of acceptable limit of drinking purpose according to IS 10500:2012.

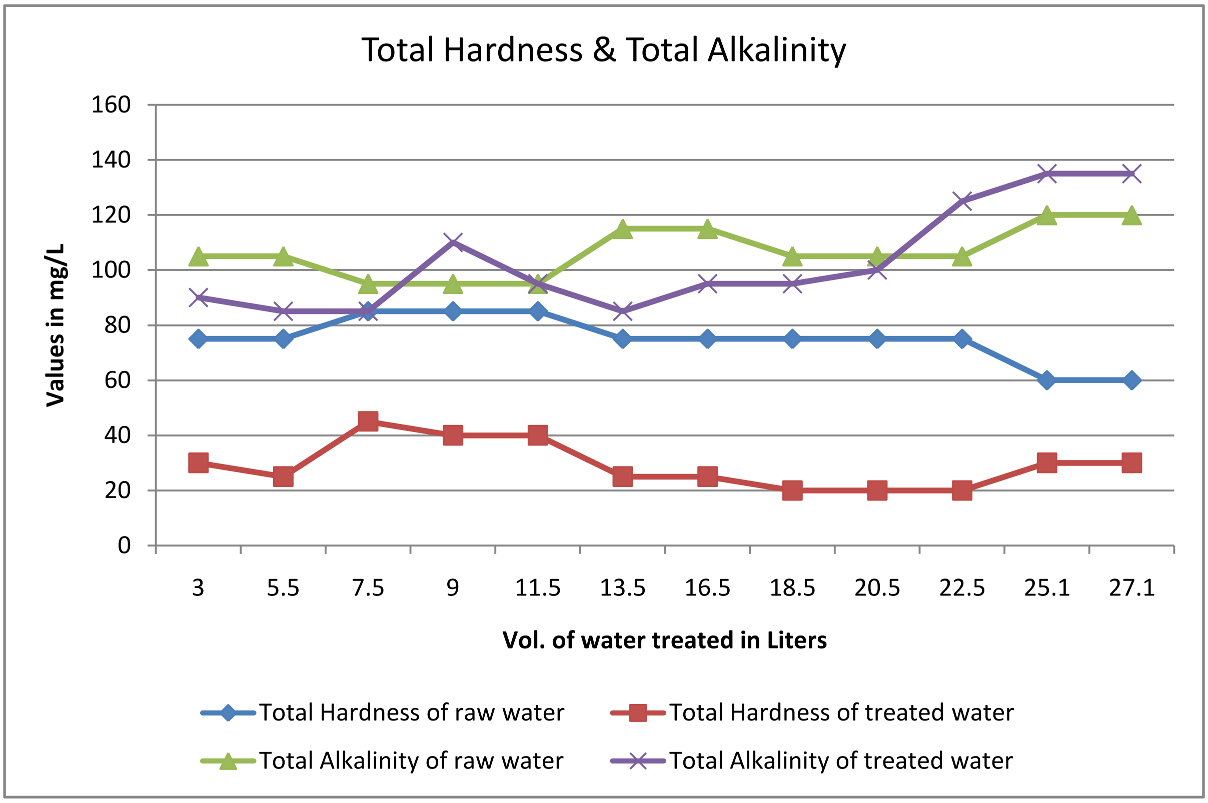


Fig 6.16: Variations of Total Hardness & Total Alkalinity in Raw & Treated Water

Here Total hardness and Total Alkalinity of raw and treated water are shown. Total Hardness of treated water decreases and it is within acceptable limit of drinking water. Total alkalinity of treated water is increasing with decrease in percentage removal of fluoride concentrations.

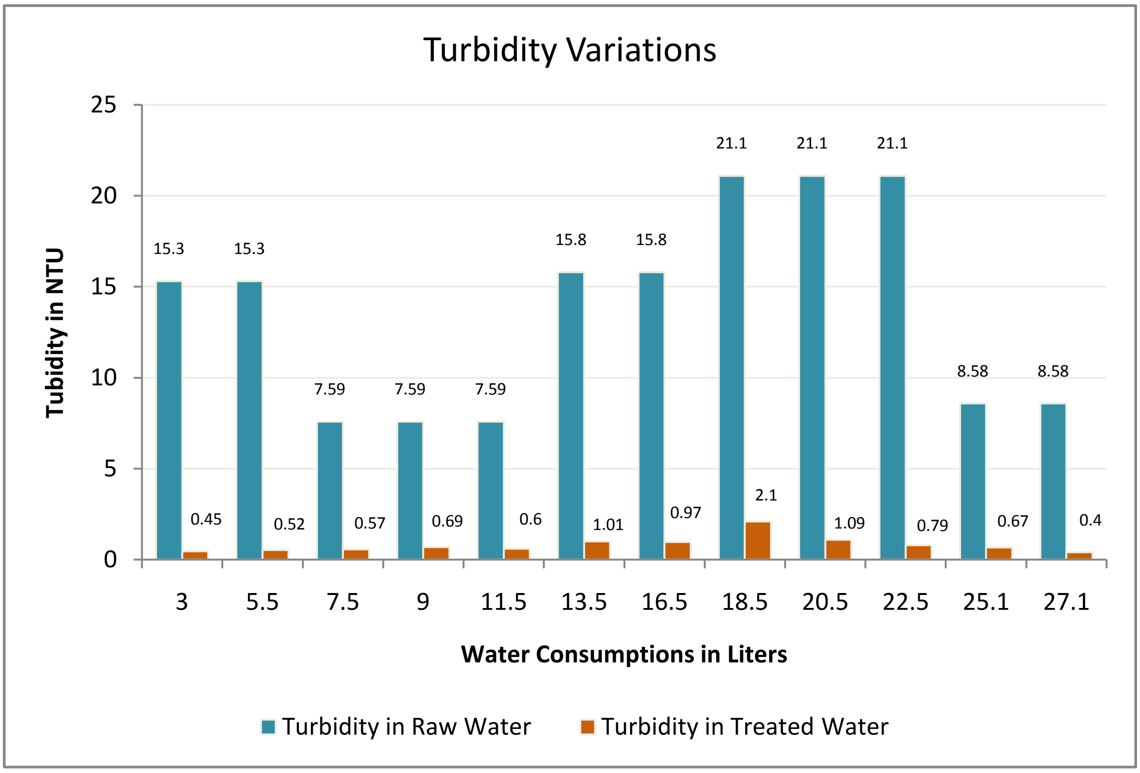


Fig 6.17: Turbidity values varying in Raw and Filtered Water consumptions

In above graph Turbidity is decreasing after filter of raw water. At the time of 18.5L & 20.5L of water consumption turbidity values are decreasing but not within the range of acceptable limit of drinking purpose (1NTU) but in the range of permissible limit (5NTU).

## 6.5 Fluoride Adsorption Isotherm:

Table 6.7: Experimental data of Fluoride adsorption using Activated Alumina

| Cumulative Consumptions of Water, **V in Liters** | Weight of adsorbent(AA), **m in gm** | Fluoride influent conc., **$C_0$ in mg/L** | Equilibrium Concentration, **$C_e$ in mg/L** | Amount of adsorbate adsorbed by AA **X= [($C_0$-$C_e$)/m] in mg** | Adsorbate to Adsorbent ratio, **q=(X/m) in mg/g** |
|---|---|---|---|---|---|
| 3 | 100 | 7.6 | 0.0001 | 22.7997 | 0.227997 |
| 5.5 | 100 | 7.6 | 0.0001 | 41.79945 | 0.417995 |
| 7.5 | 100 | 7.6 | 0.0001 | 56.99925 | 0.569993 |
| 9 | 100 | 7.6 | 0.0001 | 68.3991 | 0.683991 |
| 11.5 | 100 | 7.6 | 0.0001 | 87.39885 | 0.873989 |
| 13.5 | 100 | 7.6 | 0.0001 | 102.5987 | 1.025987 |
| 16.5 | 100 | 7.6 | 0.0001 | 125.3984 | 1.253984 |
| 18.5 | 100 | 7.6 | 0.0001 | 140.5982 | 1.405982 |
| 20.5 | 100 | 7.6 | 0.0001 | 155.798 | 1.55798 |
| 22.5 | 100 | 7.6 | 0.225 | 165.9375 | 1.659375 |
| 25.1 | 100 | 7.6 | 1.08 | 163.652 | 1.63652 |
| 27.1 | 100 | 7.6 | 1.51 | 165.039 | 1.65039 |

## 6.5.1. Compare the experimental data with Langmuir and Freundlich Isotherm model

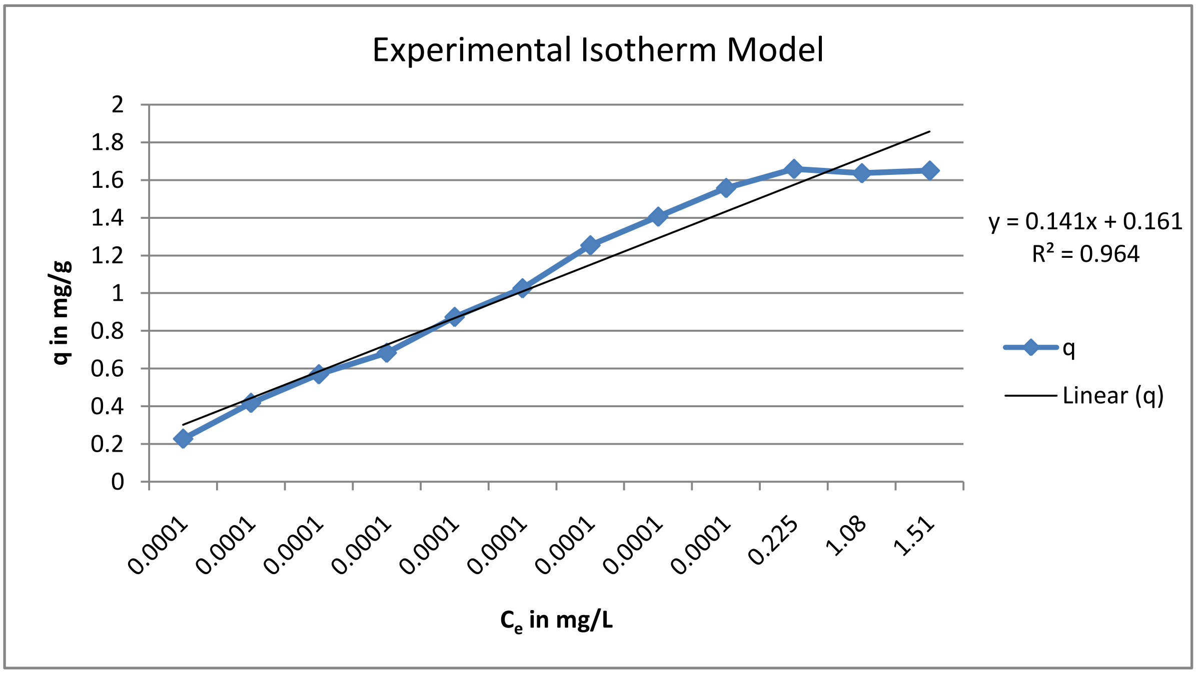


Fig 6.18: Experimental graph of Fluoride adsorption isotherm

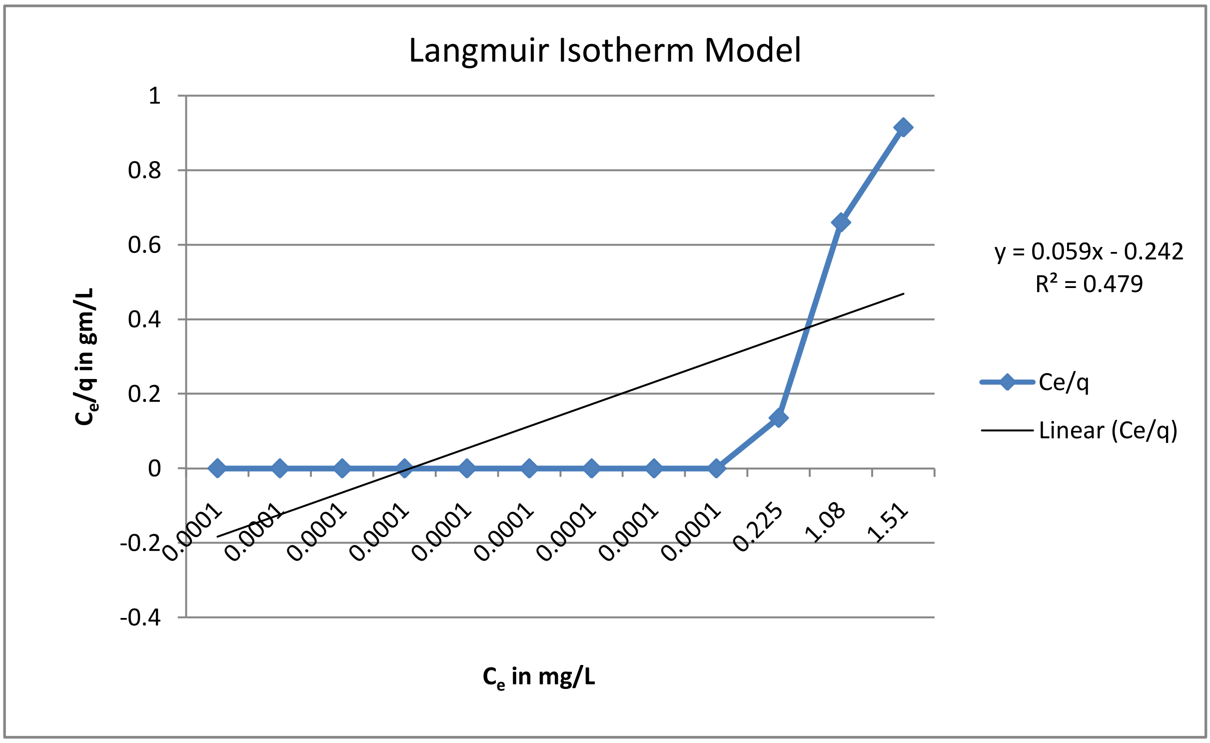


Fig 6.19: Langmuir Isotherm Model from experimental data

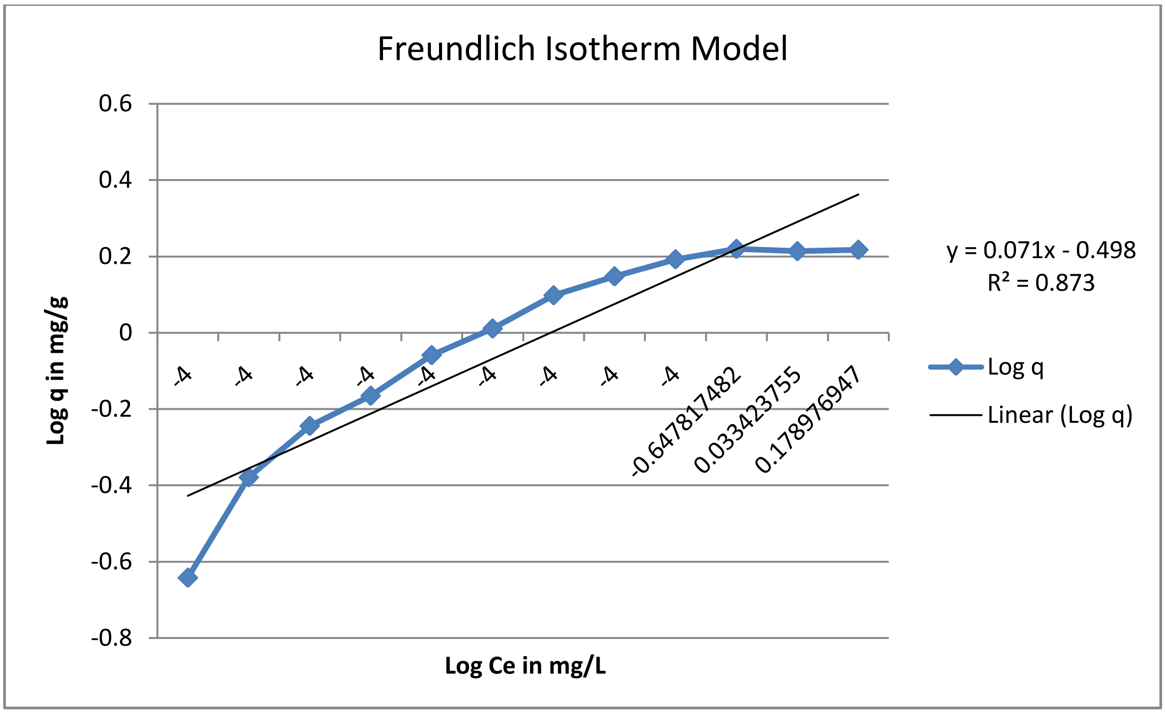


Fig 6.20: Freundlich Isotherm Model from experimental data

Table 6.8: Isotherm Models with Correlation Coefficient

| **Adsorption Isotherm Model** | **X** | **Y** | **Linear Equations** | **Correlation Coefficient $R^2$** |
|---|---|---|---|---|
| Experimental | $C_e$ | q | y= 0.141x + 0.161 | 0.964 |
| Langmuir | $C_e$ | $C_e/q$ | y= 0.059x - 0.242 | 0.479 |
| Freundlich | Log $C_e$ | Log q | y= 0.071x - 0.498 | 0.873 |

In the above study of adsorption Isotherm, the equations of Langmuir and Freundlich are calculated with the help of experimental data to analyze adsorption isotherm of fluoride removal. Comparing the experimental model with Langmuir model and Freundich model, it is presumed that experimental isotherm model is nearly similar to Freundlich isotherm model and above table shows that fluoride adsorption is best described by Freundlich equation for the study of adsorption of fluoride by activated alumina.

# Conclusion

## CHAPTER 7

Ion Exchange process to remove fluoride from fluoride contaminated water is found to be one of the efficient methods. From the experiment and results of Ion-Exchange Process of Cation-Anion exchange Resins, it is concluded that in raw water of Trial 1 & Trial 2, concentrations of Fluoride (5.5mg/L and 7.98mg/L) are removed up to the desirable limit by using 20 gms of Cation-Anion Exchange Resin and 496.81 L/h/m$^2$ hydraulic flow rate but at the time of high concentration (10.6mg/L), these filter media are unable to remove up to the permissible limit of Fluoride in drinking water(1.5mg/L) standard. Fluoride sorption capacity of cation-anion exchange resins is found to be 521.25 mg/kg. TDS values are increasing after filter of each trial but it is in the range of permissible limit of drinking water standard. Disadvantage of this filter media is pH value of filtered water decrease promptly which lies in the range between 3 and 4, which makes it slightly acidic and it fails to reach in the range of drinking water (6.5-8.5) standard according to IS 10500:2012. A Pretreatment may used to address this issue of lower pH value of treated water.

From the experiment and results of Ion-Exchange Process by Anionic Resin bed, it shows that raw water of Trial 1, Trial 2 and Trial 3, concentrations of Fluoride (4.1mg/L, 6.2mg/L & 6.5mg/L) are removed up to the desirable limit of Fluoride in drinking water according to IS 10500:2012 by Anionic Resin of 20 gm and 496.81 L/h/m$^2$ hydraulic flow rate but after passing 1500ml of raw water through anionic resin bed in burette filter , high concentration of Fluoride in raw water which is 8.5mg/L removed up to 2.6mg/L after filtration which doesn't meet the permissible limit of fluoride (1.5mg/L) in drinking water standard. Fluoride sorption capacity of Anionic Resins is 509.5 mg/kg. According to IS 10500:2012, other general parameters like pH, TDS, EC, Total Alkalinity and Total Hardness of filtered water are in the range of permissible limit of drinking water but presence of Chloride in filtered water increases slightly which can be retained in the range of permissible limit by applying pretreatment process. It is concluded that for removing the concentration of Fluoride to its desirable limit, Ion exchange process by using Anionic Resin is found to be a satisfactory solution.

Studies show that the adsorption capacity of the activated alumina was found to be 1996.28 mg/kg at flow rate of 300 ml/hour and using initial fluoride concentration was 7.6mg/L. The optimal percentage of fluoride removal was found to be 100%. Activated alumina amounting 100 gm removed 100 % fluoride from 20.5 L of raw water. The volume of treated water was 27.1 liters. The pH values are found to be changing with respect to percentage removal of fluoride concentrations. Here it is found that pH values are kept increasing with a decrease in percentage removal of fluoride concentrations. Total Hardness of treated water decreases and it is within the acceptable limit of drinking water standard. Total alkalinity of treated water is found to be increasing with a decrease in percentage removal of fluoride concentrations. Comparing the experimental model with Langmuir model and Freundich model, it is presumed that experimental isotherm model is nearly similar to Freundlich isotherm model and fluoride adsorption is best described by Freundlich equation for the study of adsorption isotherm of fluoride by activated alumina. Another advantage of this media is that it can be regenerated and reused, which makes this unit sustainable, eco-friendly and economically viable.

**Following action plans are suggested for mitigation of fluoride problem in drinking water:**

- Extensive research work has to be carried out in this field to find a sustainable solution for all the people belonging from rural to urban areas. As this problem predominates in rural areas so instruments which are available at low cost preferably used.
- Surface water usually does not contain excess fluoride. So, surface water (River) after proper treatment can be supplied in fluoride affected areas.
- Roof top rain water harvesting can be popularized. If rain water is collected and used for drinking and cooking then it can be give some relief to affected region.
- Deep bore well may be an alternative to supply fluoride free water but due to its high price it is restricted to few hands.
- Nutritional supplements can be extended to the people residing in excess fluoride affected areas.
- Health care services may be extended for proper and low cost diagnosis and treatment.

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## CHAPTER 8

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