REMOVAL OF FLUORIDE FROM GROUNDWATER USING SUITABLE ADSORBENTS AND MANAGEMENT OF GENERATED WASTE

IZAZ AHAMED

Roll Number: 002130904013

Exam Roll Number: M4EBT23009

MASTER OF TECHNOLOGY

IN

ENVIRONMENTAL BIOTECHNOLOGY

SCHOOL OF ENVIRONMENTAL STUDIES

FACULTY OF INTERDISCIPLINARY STUDIES, LAW AND MANAGEMENT (F.I.S.L.M)

JADAVPUR UNIVERSITY

JADAVPUR, KOLKATA-700032

Removal of Fluoride from Groundwater Using Suitable Adsorbents and Management of Generated Waste

A thesis

Submitted in partial fulfilment of the requirements for the award of the degree of

M. Tech in Environmental Biotechnology

Jadavpur University

by

Izaz Ahamed

Environmental Biotechnology

Roll Number: 002130904013

Exam Roll Number: M4EBT23009

Under the supervision of

Dr. Tarit Roychowdhury

School of Environmental Studies

Faculty of Interdisciplinary Studies, Law and Management

Jadavpur University

Jadavpur, Kolkata-700032

DECLARATION

I hereby declare that the work presented in this thesis report title **“Removal of Fluoride from Groundwater Using Suitable Adsorbents and Management of Generated Waste”** submitted to Jadavpur University, Kolkata in partial fulfilment of the requirements for the award of the degree of Master of Technology in Environmental Biotechnology is a bonafide record of the research work carried out under the supervision of Dr. Tarit Roychowdhury. The contents of Thesis report in parts, have not been submitted to and will not be submitted by me to any other Institute or University in India or abroad for the award of any degree or diploma.

Izaz Ahamed

Izaz Ahamed

Roll number: 002130904013
Exam Roll number: M4EBT23009
Registration number: 139567 of 2017-2018
Environmental Biotechnology
School of Environmental Studies
Jadavpur University, Kolkata

CERTIFICATE

This is to certify that the Thesis Report titled "**Removal of Fluoride from Groundwater Using Suitable Adsorbents and Management of Generated Waste**", submitted by Izaz Ahamed (002130904013) to Jadavpur University, Kolkata for the award of the degree of Master of Technology in Environmental Biotechnology is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the constituents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Tarit Roychowdhury Ph.D.
Associate Professor
School of Environmental Studies
Jadavpur University
Kolkata-700 032 INDIA

(Signature with Seal) 28/07/2023

Dr. Tarit Roychowdhury

Thesis Supervisor

School of Environmental Studies

Jadavpur University, Kolkata-700032

TO WHOM IT MAY CONCERN

It is hereby notified that this thesis titled "**Removal of Fluoride from Groundwater Using Suitable Adsorbents and Management of Generated Waste**", is prepared and submitted for the partial fulfilment of the continuous assessment of Master of Technology in Environmental Biotechnology course of Jadavpur University by Izaz Ahamed (002130904013), a student of the said course for session 2021-2023. It is also declared that no part of this thesis has been presented or published elsewhere.

Tushar Jash 28/7/2023
(Signature with Seal)

(Signature with Seal)

Director

Prof. Tushar Jash

School of Environmental Studies

Jadavpur University, Kolkata-700032

Director
School of Environmental Studies
JADAVPUR UNIVERSITY
Kolkata - 700 032

Tarit Roychowdhury 28/7/2023
Tarit Roychowdhury, Ph.D.
Associate Professor
School of Environmental Studies
Jadavpur University
Kolkata-700 032 INDIA
(Signature with Seal)

(Signature with Seal)

Thesis Supervisor

Dr. Tarit Roychowdhury

School of Environmental Studies

Jadavpur University, Kolkata-700032

Tushar Jash 28/7/2023
(Signature with Seal)

(Signature with Seal)

Dean
Faculty of Interdisciplinary Studies, Law & Management
Jadavpur University, Kolkata-700032

Dean, Faculty of Interdisciplinary Studies Law and Management

Prof. Tushar Jash

Jadavpur University, Kolkata-700032

CERTIFICATE OF APPROVAL

This foregoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner satisfactorily to warranty its acceptance as a prerequisite to degree for which it has been submitted. It is understood that by this approval the undersigned do not endorse or approve any statement made or opinion expressed or conclusion drawn therein but approve the thesis only for purpose for which it has been submitted.

Final examination for evaluation of thesis

Signature of the Examiner

ACKNOWLEDGEMENT

I would like to sincerely express my heartfelt gratitude to Dr. Tarit Roychowdhury, Associate Professor, School of Environmental Studies, Jadavpur University for guiding, encouraging and providing me all necessary facilities to carry out my project work. I would like to express my sincere gratitude to Dr. Joydeep Mukherjee, Associate Professor, School of Environmental studies, Jadavpur University for all his guidance and support during my project work. I am thankful to Dr. Subarna Bhattacharya, Assistant Professor, School of Environmental Studies, Jadavpur University and Dr. Reshmi Das, Assistant Professor, School of Environmental Studies, Jadavpur University for their constant support during my work. I am especially thankful to Ayan De, Dipajan Mridha, Swetajana Ghosh, Sharmistha Majumder, Urvashi Lama, Archita Dey (research scholars) of the respective department for helping and supporting me throughout the duration of my project work. I am especially grateful to my dear friends Mantu Mandal, Debangshi Das, Jyoti Saha, Divyangana Lahiri, Shreyasee Tudu, Saptaparni Ghosh, Utpal Sinha, Pritam Lakra for their esteem help and assistance. I am also grateful to Aziz Ahamed and Soyel Rana for their esteem help during my project work. Finally, this research project would not have been possible without the confidence, encouragement and support of my parents.

Izaz Ahamed

Date: 28.07.2023

Place: Jadavpur, Kolkata-700032

ABSTRACT

The presence of excessive fluoride in groundwater poses a serious threat to human health and has become a pressing global concern. In regions where fluoride-contaminated groundwater is prevalent, developing cost-effective and sustainable methods for its removal is imperative. This study focuses on the utilization of suitable adsorbents for the removal of fluoride from groundwater, coupled with an innovative waste management approach by incorporating the generated waste into brick manufacturing. The research begins with an extensive review of existing adsorbents and their capacity to adsorb fluoride ions from water. The potential adsorbents include activated alumina, activated carbon, and various modified clays, among others. Their efficiency is evaluated through laboratory experiments, considering factors such as pH, contact time, initial fluoride concentration, and adsorption isotherms. Results demonstrate that certain adsorbents exhibit promising fluoride removal capabilities, highlighting their potential for application in real-world scenarios. Subsequently, attention is directed towards the management of the adsorbent waste generated during the fluoride removal process. Traditionally, the disposal of spent adsorbents contributes to environmental pollution. However, this study proposes an eco-friendly solution by incorporating the waste into brick manufacturing. The bricks are fabricated through a controlled blending process, ensuring that the final product meets quality standards while effectively immobilizing the fluoride-rich waste within the bricks. The engineering properties of the produced bricks are examined, including compressive strength, water absorption, and durability, to ascertain their feasibility for construction purposes. Additionally, leaching tests are conducted to evaluate the potential release of fluoride from the bricks, ensuring compliance with safety guidelines. The proposed approach not only addresses the issue of fluoride contamination in groundwater but also introduces a sustainable method for waste management. By converting waste into value-added building materials, the environmental burden is reduced, and communities' benefit from improved water quality and affordable, eco-friendly bricks.

Keyword: Fluoride, Groundwater, Adsorbents, Waste Management, Brick Manufacturing.

TABLE OF CONTENTS

Index

LIST OF FIGURES

LIST OF TABLES

TABLE OF GRAPHS

TABLE OF CHARTS

CHAPTER-I

1 INTRODUCTION

Only 1% of the world's total water is available as freshwater, which includes sources such as lakes, streams, ponds, reserves, and groundwater. The scarcity of drinking water is a significant issue not only in India but also worldwide. While 70% of the earth's surface is covered in water, the majority of it is in the form of oceans (96.5%) and frozen states (1.74%). Only a small percentage is available as freshwater, with lakes, swamp water, and rivers holding 0.014%, soil moisture accounting for 0.001%, vapor in the air at 0.001%, and groundwater in aquifers at 1.7% (Gleick, 1996).

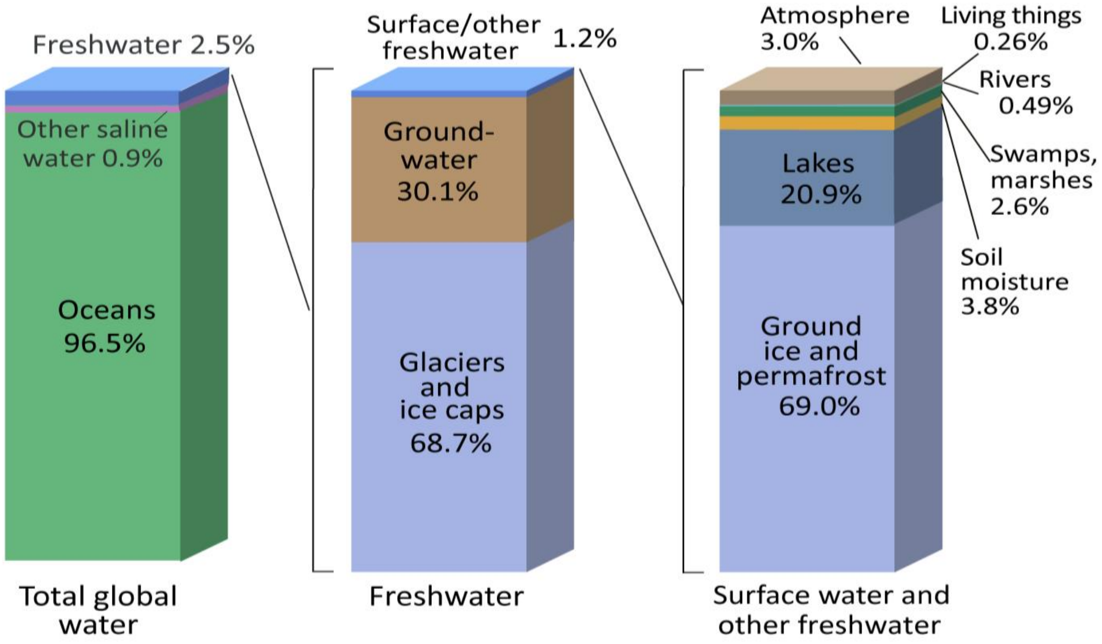


Figure 1-1:Distribution of water
(Source: U.S Geological Survey, Water Science School, https://water.usgs.gov/edu/gallery/watercyclekids/earth-water-distribution.html)

Surface water is found in rivers, lakes, or fresh water wetlands, and is naturally replenished by precipitation and lost through evaporation, evapotranspiration, groundwater recharge, and discharge to the oceans. On the other hand, groundwater is freshwater situated in the subsurface pore space of soil and rocks, which can flow within aquifers below the groundwater table. It is sometimes helpful to differentiate between groundwater that is closely associated with surface water and deep groundwater in an aquifer.

1.1 Water usage

Approximately 70% of the world's water is utilized for irrigation purposes, with 15-35% of irrigation withdrawals being unsustainable. It takes roughly 2,000-3,000 liters of water to produce enough food to fulfill the daily dietary requirements of one person (UN Water, 2007). This is a significant amount compared to the 2-5 liters required for drinking. Meeting the food demands of the current population of over 7 billion individuals necessitates a considerable amount of water. The industry consumes roughly 22% of the world's water, with major industrial users including hydroelectric dams, thermoelectric power plants (which utilize water for cooling), ore and crude oil refineries (which use water in chemical processes), and manufacturing plants (which use water as a solvent). While water withdrawal rates are high for certain industries, consumption is generally much lower than that of agriculture. Domestic use accounts for an estimated 8% of worldwide water usage, encompassing drinking water, bathing, cooking, toilet flushing, cleaning, laundry, and gardening. Basic domestic water requirements have been estimated to be around 50 liters per person per day, excluding water for gardens, by Peter Gleick. As global populations increase and demand for food rises in a world with a fixed water supply, efforts are being made to find ways to produce more food with less water through improvements in irrigation methods and technologies, agricultural water management, crop types, and water monitoring.

1.2 Water stress

Water stress occurs when there is insufficient water to meet all needs, including agricultural, industrial, and domestic. The World Business Council for Sustainable Development defines water stress as a situation where there is not enough water for all uses. Defining thresholds for water stress in terms of available water per capita is complex. The global population was 6.2 billion in 2000, and the UN predicts that by 2050, there will be an additional 3.5 billion people. Therefore, unless there are corresponding increases in water conservation and recycling efforts, water demand will increase. The trend towards urbanization is accelerating, which requires significant investment in water infrastructure to deliver water to individuals and process wastewater from both individuals and industries. Climate change is expected to have significant impacts on water resources around the world. Rising temperatures will lead to increased evaporation and precipitation, but there will be regional variations in rainfall, and droughts and floods may become more frequent in different regions at different times. Water pollution is also a major concern worldwide.

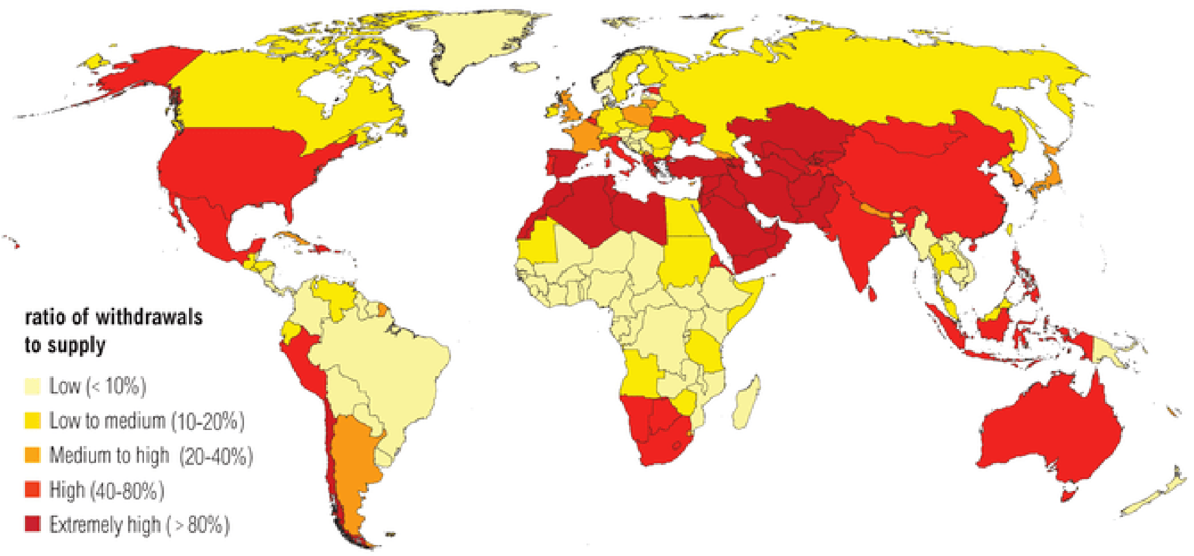


Figure 1-2: Water stress 2040 (World Resources Institute)

1.3 Groundwater Contamination

Water can become contaminated either naturally or as a result of human activities. Heavy metals such as lead, mercury, chromium, and cadmium, toxic metalloids like arsenic, and inorganic ions such as fluoride, nitrate, chloride, perchlorate, and sulphate, as well as various colorants from dye, textile, and paper industries, are the major contaminants. All of these pollutants have severe health effects on humans and animals. Among these, fluoride is considered one of the most harmful and toxic pollutants found in water. Fluorine is a common element that does not exist in nature in its elemental state due to its high reactivity. Fluoride is generally present in many waters, but high concentrations of fluoride are mainly associated with groundwater. Consuming water contaminated with high levels of fluoride leads to severe health effects such as dental fluorosis, skeletal fluorosis, and crippling fluorosis. Fluoride is one of the ions that cause health problems in people living in more than 25 countries worldwide. The WHO (World Health Organization) guideline value for fluoride in drinking water is 1.5 mg/l. As per the Bureau of Indian Standards, the acceptable limit of fluoride is 1.0 mg/l and the permissible limit in the absence of an alternate source is 1.5 mg/l. Since fluorosis is an irreversible condition with no cure, prevention is the only solution to this problem. Providing water with an optimal fluoride concentration is the only way to protect future generations from this disease. All defluoridation techniques are divided into two main categories: physical processes and chemical processes. Adsorption, ion exchange, and membrane separation techniques are physical processes, while chemical coagulation-precipitation and electro-coagulation techniques are chemical processes. Therefore, it is necessary to keep fluoride concentrations within permissible limits to provide safe drinking water, particularly in rural areas where people mostly rely on groundwater for their drinking water.

1.4 Groundwater Fluoride Contamination & Remedial Technique

The harmful effects of fluoride in groundwater on human health have been well-documented by researchers worldwide. Further research is needed to identify areas with high concentrations of fluoride, including testing human blood and urine samples to determine consumption levels. Consumption of elevated levels of fluoride-contaminated water can lead to various diseases such as dental fluorosis, skeletal fluorosis, and crippling fluorosis. Previous studies have identified several fluoride-affected areas in West Bengal, with variations in fluoride concentrations evident seasonally and at different depths. The presence of various anions and cations can also affect fluoride concentrations. Defluoridation techniques are necessary to remove excess fluoride from drinking water, including adsorption, ion exchange, coagulation and precipitation, reverse osmosis, and electrodialysis. Adsorption using various types of low-cost adsorbent materials has been proven effective in environmental remediation. The integration of nanostructured materials in environmental science is a promising area of current and future research, with nano sorbents and bio sorbents contributing to solving major environmental remediation problems more efficiently.

CHAPTER-II

2 FLUORIDE CONTAMINATION IN GROUNDWATER: a brief review

2.1 Background

Fluoride is a well-known substance that can effectively prevent dental caries and strengthen bones. However, excessive intake of fluoride can cause pathological changes in teeth and bones, leading to permanent disability. Fluorosis can occur when the fluoride content in drinking water is more than 1.5 mg/l, particularly in rural areas of developing countries like India where millions of people lack awareness of this issue and are affected by fluorosis due to drinking water containing poisonous amounts of fluoride.

2.2 Literature Review

The literature review below will provide information on the chemical properties of fluoride, its sources and occurrence in the environment, as well as its presence in groundwater. It will also examine fluoride contamination in groundwater, with a focus on the situation in World, India, and West Bengal.

2.2.1 Fluoride

Fluorine is a poisonous, pale yellow-green, univalent gaseous halogen. It is the most chemically reactive and electronegative of all elements, readily forming compounds with most other elements, including noble gases. Its atomic mass is 18.998403 $g.mol^{-1}$ and its atomic number is 9. According to Pauling, its electronegativity is 4. Fluorine exists as a diatomic gas in its elemental form and has a valence number of 1 (Greenwood & Earnshaw, 1984). It makes up approximately 0.3 g/kg of the Earth's crust and exists in the form of fluorides in several minerals, with fluorspar, cryolite, and fluorapatite being the most common. The fluoride ion has an oxidation state of -1 and does not exhibit any color, taste, or smell when dissolved in water, making it difficult to detect through physical examination. Only a chemical analysis of groundwater samples can determine the concentration of this ion (WHO, 2011).

2.2.2 Source of Fluoride in the Environment

There are mainly two sources of Fluoride in the environment, that are the geogenic and anthropogenic sources.

2.2.2.1 Geogenic Sources

The fluoride content of groundwater varies greatly depending on geological settings and types of rocks. Fluorite, apatite, and micas are the most common fluorine-bearing minerals, and fluoride problems tend to occur in areas where these minerals are most abundant in the host rocks. Fluorine can be leached out and dissolved in groundwater during weathering and circulation of water in rocks and soils. Naturally occurring fluoride is present as a natural constituent of rocks in the form of fluorite, fluorspar, calcium fluoride (CaF_2), apatite or rock phosphate [$Ca_3F(PO_4)$], cryolite (Na_3AlF_6), and magnesium fluoride (MgF_2) (De et al., 2023). Igneous and volcanic rock has a fluoride concentration ranging from 100 mg/kg up to over 1000 mg/kg. Fluorine accumulates during magmatic crystallization and differentiation processes of the magma. As a result, the residual magma is often enriched in fluorine. Groundwater from crystalline rocks, especially granite, is particularly sensitive to relatively high fluoride concentrations. Sedimentary rocks have a fluoride concentration ranging from 200 mg/kg (limestone) to 1000 mg/kg (shales). In carbonate sedimentary rocks, fluorine is present as fluorite. The concentration of fluoride in groundwater largely depends on the time of contact. A high concentration of fluoride can occur when groundwater is present in an aquifer for a long time or the groundwater flow is slow, as is the case with deep aquifers. Shallow aquifers contain only recently infiltrated rainwater and have a relatively low concentration of fluoride, but there can be exceptions. The solubility of fluorite increases with increasing temperature. Arid regions are prone to high fluoride concentrations. Here, groundwater flow is slow, and the reaction times with rocks are therefore long. Fluoride concentrations are lower in humid regions because of their high rainfall and diluting effect (Brunt & Griffioen, 2004).

2.2.2.1.1 Primary Source: Fluorine bearing minerals & Volcanic gases

There are approximately 150 minerals that contain fluorine that have been identified to date. Among these minerals, fluorite (CaF_2) is the most significant one containing fluorine in the chemical bond. In minerals such as amphiboles, micas, and apatite, hydroxyl ions can be replaced by fluoride. Fluorine is also present in volcanic gases produced by magma, such as HF, SiF_2, or H_2SiF_6. Although the total volume of HF in volcanic gases accounts for only 1 to 2 percent, the concentration of fluorine can reach several thousands of parts per million.

Table 2-1: Fluorine bearing minerals

Group	Number	Examples
Silicates	63	Amphiboles, Micas
Halides	34	Fluorite, Villiaumite
Phosphates	22	Apatite
Other	30	Aragonite

2.2.2.1.2 Fluorine in Different Geological Environment

According to the origin of the rocks, geological environments can be divided into igneous, sedimentary, and metamorphic categories. In igneous rocks, fluorine is primarily bound in micas and amphiboles, comprising up to 80% of the fluorine content, with a smaller proportion found in apatite, up to 20%. In basalt, all fluorine can be contained in apatite. In general, alkalic rocks contain higher amounts of fluorine compared to ultramafic rocks. In carbonate sedimentary rocks, fluorine is present as fluorite but in low concentrations. Fluorine is concentrated in micas and illites, resulting in higher fluorine concentrations in clastic sediments (Allmann & Koritnig, 1974). Sedimentary phosphate beds of volcanic ash layers may also contain high concentrations of fluorine. In metamorphic rocks, the highest concentrations of fluorine are found in rocks formed through contact metamorphism. In these rocks, the original minerals are enriched with fluorine through metasomatic processes.

Table 2-2: Ranges of Concentration of fluorine in major Rock groups

Type of Rock	Fluorine Concentration
Igneous Rock	100 mg/kg (Ultramafic) – 1000 mg/kg (Alkalic)
Sedimentary Rock	200 mg/kg (Limestone) – 1000 mg/kg (Shale)
Metamorphic Rock	100 mg/kg (Regional) – 5000 mg/kg (Contact)

2.2.2.1.3 Interaction Between Rock & Water

The concentration of fluoride in water is influenced by the presence of minerals and gases containing fluorine, with the specific levels determined by the local climate and geochemical conditions. Griffioen (1986) extensively examined the formation of fluoride-rich waters, providing a detailed explanation of the process, as illustrated in the accompanying chart 2-1. The pH of water can be reduced and the weathering of fluorine-bearing minerals can be enhanced by the addition of CO_2. In cases where calcium ions (Ca^{2+}) are not readily available for leaching, the fluoride concentration can be high, as it is primarily influenced by the solubility of fluorite. The decrease in Ca^{2+} concentration can be attributed to the precipitation of calcite or the exchange of sodium ions (Na^{+}) with calcium ions (Ca^{2+}). When water undergoes evaporation, the fluoride content of the fluid increases if two conditions are satisfied: the solution remains in equilibrium with calcite, and the alkalinity exceeds the hardness.

The interaction between rock and water is a fundamental geological process that shapes the Earth's surface over time. Water plays a crucial role in various processes such as weathering, erosion, and sedimentation. Through physical weathering, water can freeze and expand in cracks, breaking rocks apart. Chemically, water can react with minerals, dissolving them or altering their composition. Biological weathering occurs when plants and organisms physically break down rocks or secrete chemicals that dissolve minerals. Water erosion wears away rock surfaces and transports eroded material downstream, leading to the formation of valleys and canyons. Additionally, sedimentation occurs as eroded particles settle and accumulate, forming sedimentary rocks. These interactions create diverse and dynamic landscapes across the Earth.

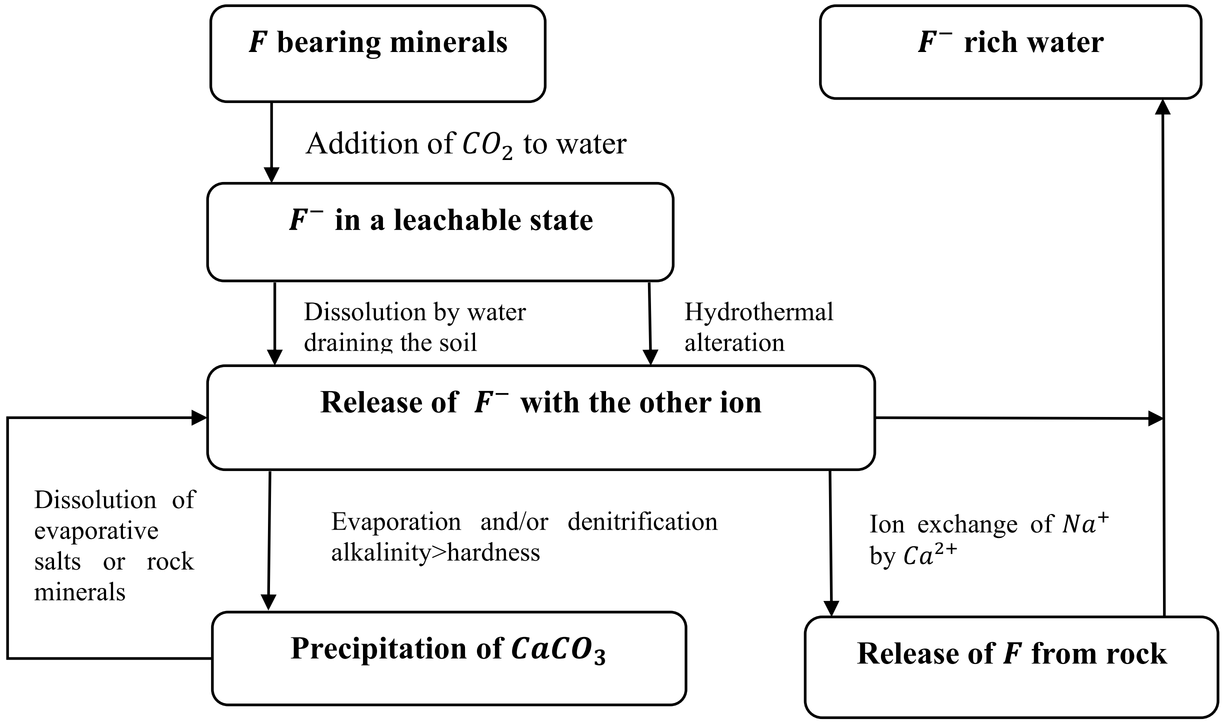


Chart 2-1: Rock water Interaction

2.2.2.2 Anthropogenic Sources

Industrial effluents are a major source of fluoride in human activities, with inorganic fluorine compounds being extensively used for various industrial purposes. These compounds find applications in industries such as aluminum production, steel and glass fiber manufacturing, as well as in the production of phosphate fertilizers, bricks, tiles, and ceramics. Municipal water fluoridation schemes utilize substances like fluorosilicic acid, sodium hexafluorosilicate, and sodium fluoride. Fluoride contamination in groundwater is prevalent in areas associated with aluminum industries, as well as due to the heavy use of fluoride-containing fertilizers and pesticides. Power plant boiler cleaning wastes can also contribute to fluoride discharge. The burning of coal in power plants leads to the production of significant amounts of fly ash, which, when used for landfill, can contaminate groundwater through leaching. Geological surveys have identified widespread availability of fluoride-rich minerals like apatite, rock phosphate, fluorite, topaz, phosphatic nodules, and phosphorites, which contribute to groundwater and soil contamination. Fluoride is also present in crops and edible items, and variations in fluoride concentration exist across different regions. Additionally, fluoride is found in cosmetics, drugs, and toothpaste, with concerns regarding its accumulation in the body over time.

2.2.2.2.1 Fluoride in Rocks & Soil

Fluoride naturally occurs in rock and soil formations, as mentioned earlier, but human activities also play a substantial role in increasing fluoride concentrations in soils. This is primarily attributed to the use of fluoride-containing phosphate fertilizers, pesticides, irrigation water, and the deposition of industrial emissions. Although the direct impact of these sources on human health is relatively minor, their indirect significance is significant as high fluoride levels in rocks and soils can significantly affect the quality of surface and groundwater.

2.2.2.2.2 Fluoride in Atmosphere

Airborne fluoride can be found in trace amounts as a result of both natural phenomena and human activities. Volcanic regions often contain dust containing fluoride, and aerosols from seawater also contribute to the presence of fluoride. However, human activities play a prominent role in the generation of airborne fluoride, with significant levels observed in urban industrial areas. Industries such as steel and aluminum production plants, superphosphate plants, ceramic factories, brickworks, glassworks, oil refineries, and coal-burning power plants are major sources of airborne fluoride, particularly in urban industrial areas.

2.2.2.2.3 Fluoride in Food & Drinks

Under normal circumstances, the fluoride concentration in food is typically low, ranging from 0.2 to 0.3 mg/kg. However, elevated levels of fluoride can be found in fresh vegetables due to pesticide pollution, with concentrations reaching up to 7 mg/kg. Various processed drinks also contain fluoride, such as tea leaves which can have high fluoride content ranging from 3.2 to 400 mg/kg in dry weight. Most of the fluoride in tea leaves dissolves in water during brewing. Depending on the fluoride content of the tea leaves and the amount consumed, this source can contribute approximately 2.5 to 3.0 mg of fluoride to the daily intake (De et al., 2021).

2.2.3 Fluoride in Drinking Water

In regions where fluoride-rich geological formations are present, groundwater typically contains higher levels of fluoride compared to nearby surface water sources. The fluoride content in groundwater from boreholes, wells, and springs can range from 0.1 to over 100 mg/l, depending on various factors. During rainy seasons, shallow groundwater tends to have lower fluoride concentrations due to dilution from rainwater infiltration, while deep groundwater maintains a relatively consistent fluoride concentration. Surface waters, such as rivers, streams, and lakes, generally have low fluoride levels unless they are contaminated by the discharge of fluoride-containing waste products. Adults typically consume an average of 2 to 5 liters per capita per day (lpcd) of drinking water, and in some cases, even up to 10 lpcd. When the drinking water has a high or very high fluoride content, and alternative water sources or treatment methods are limited, drinking water becomes the primary source of fluoride exposure, posing a greater health risk.

2.2.4 Permissible Limit of Fluoride in Drinking Water

The World Health Organization (WHO) has established a guideline value of 1.5 mg/l for fluoride in drinking water (WHO, 2004). Concentrations exceeding this value pose an elevated risk of dental fluorosis, while significantly higher concentrations can lead to skeletal fluorosis. According to the Bureau of Indian Standards (BIS), the acceptable limit for fluoride in drinking water is 1.0 mg/l, with a permissible limit of 1.5 mg/l in cases where alternative sources of water are not available (BIS, 2012).

Table 2-3:Permissible limit of fluoride in drinking water

Name of the Organization	Permissible Limit (mg/l)
Bureau of Indian Standards (IS 10500: 2012)	1.0 - 1.5
Indian Council of Medical Research	1.0
The Committee on Public Health Engineering Manual and Code of Practice, Government of India	1.0
World Health Organization (WHO)	1.5

2.2.5 Health Effect of Fluoride

Researchers from various disciplines have conducted studies on the relationship between environmental fluoride and human health for over a century. It is widely acknowledged that small amounts of dietary fluoride can help prevent dental cavities and promote bone strength. However, chronic ingestion of high doses of fluoride can have several adverse effects on human health, including dental fluorosis, skeletal fluorosis, increased rates of bone fractures, decreased birth rates, and increased rates of urolithiasis (kidney stones). Dental fluorosis, characterized by discolored, mottled, or chalky white teeth, indicates excessive fluoride exposure during childhood when the teeth were developing. Skeletal fluorosis manifests as increased bone mass and density, accompanied by various skeletal and joint symptoms. The threshold level of fluoride ingestion required to cause skeletal fluorosis varies depending on water intake, water quality, and other dietary factors. Studies on the relationship between fluoride ingestion and reproductive structure or function have mostly been conducted on animals exposed to high daily doses for short durations, making the applicability to typical human exposure uncertain. Non-skeletal fluorosis affects soft tissues, organs, and systems of the body and includes symptoms such as swollen joints, rheumatism-like pain, stiffness, and impaired movement.

Table 2-4:Beneficial and adverse effects of fluoride on physiological health (Dey & Giri,2016)

Fluoride concentrations	Exposure	Physiological effects
Greater than 1 mg/l	Chronic	Impaired glucose metabolism in both animals and humans
Greater than 4 mg/l	Chronic	Skeletal fluorosis, dental fluorosis hypo-mineralization of tooth enamel
Sub-acute exposure to fluoride at a dose of 20 mg/l/day (orally to rat)	Chronic	Induces thyroidal dysfunction including suppressed synthetic machinery of the thyroid gland to produce thyroid hormones, mainly T_3 and T_4. Alteration of

		$Na^+ - K^+$ -ATPase, thyroid peroxidase, and 5,5'-deiodinase
100-200 mg/l	Chronic	Changes in the thyroid hormone status, the histopathology of discrete brain regions, the acetylcholine esterase activity, and the learning and memory abilities in multi generation rats.
High fluoride	Chronic	Increases risk of Alzheimer’s disease. Increased levels of FSH and LH Decreased estrogen levels, decreased testosterone levels and changes in its conversion into its potent metabolites, Reduced thyroid hormones, Disturbed androgen to estrogen ratios (A/E) and estrogen receptor to androgen receptor ratios (ER/AR).
1000-1500 mg/l (toothpastes)	Chronic	Prevent caries in permanent teeth
Greater than 1000-1500 mg/l (in toothpastes)	Chronic	Enamel fluorosis of the front permanent incisors
1.5mg/l or above (through water)	Daily intake	Produces insulin resistance
0.05-0.07 mg/kg body weight (should not from all sources)	Daily	To minimize the risk of dental fluorosis (Canadian Dental Association 2012)

Figure 2-1Dental Fluorosis

Figure 2-2Crippling Fluorosis

Table 2-5:Fluoride contents in drinking water and possible effects (WHO, 1984a)

Concentration of Fluoride (mg/l)	Possible effects
0.5 - 1.5	Fluoride in water has no adverse effects, the incidence of caries decreases
Above 1.5	Mottling of teeth may occur to an objectionable degree results dental fluorosis incidence of caries decreases
3 - 6	Association with skeletal fluorosis
Above 10	Crippling skeletal fluorosis

2.2.6 Status of Groundwater Fluoride Contamination in World

Groundwater often contains hazardous substances that can pose risks to human health, including fluoride. A study conducted in 1993 reported the prevalence of fluorosis in various states across the United States, such as Arizona, Arkansas, California, Colorado, Idaho, Illinois, Iowa, Kansas, Minnesota, Nevada, New Mexico, North Carolina, North Dakota, Oklahoma, Oregon, South Carolina, South Dakota, Texas, Utah, and Virginia (Brindha & Elango, 2011). In South Carolina, where 40% of the population relies on groundwater, a high concentration of fluoride (>3.5 mg/l) was observed (South Carolina Ambient Groundwater Quality Report, 2003).

In southern Brazil, the emission from a phosphate fertilizer production factory led to high fluoride levels in groundwater. Interestingly, the vegetation cover influenced the fluoride levels, with areas covered by grasslands having higher fluoride concentrations compared to those with eucalyptus plantations (Mirlean & Roisenberg, 2007). A similar influence of vegetation cover was observed in a different study conducted in southern Brazil (Oral Health Strategy for Northern Ireland, 2007). In Norway, high fluoride concentrations (up to 8.26 mg/l) were found in groundwater due to fluoride-rich rocks. The presence of dental fluorosis in certain parts of Norway was linked to the fluoride content in the bedrock (Banks et al., 1998). In Estonia, over 90% of the population consumed water with fluoride concentrations below 1.5 mg/l. However, naturally occurring fluoride levels of approximately 7 mg/l were detected in western Estonia, attributed to the Silurian

Ordovician aquifer system (Indermitte, Saava, & Karro, 2009). In Algeria, dental decay was found to increase, with groundwater containing fluoride concentrations of up to 2.3 mg/l. Approximately 70% of the fluoride intake in this region was attributed to drinking groundwater (Messaïtfa, 2008). Tanzania exhibited high fluoride contents in rivers (12-26 mg/l), springs (15-63 mg/l), alkaline ponds, and lakes (60-690 mg/l) (Nanyaro, 1984). Studies on groundwater fluoride levels in South Korea indicated that the concentration of fluoride depends on the residence time (Kim & Jeong, 2005).

Japan, known for its numerous volcanoes, faces the potential contamination of fluoride through volcanic ash. A volcanic explosion of Sakurajima volcano in Japan yielded an average fluoride concentration of 788.1 mg/l in the ash (Nogami et al., 2006). In China, more than 30 million people suffer from chronic fluorosis, with dental fluorosis affecting 26 million individuals due to high fluoride consumption through water and 16.5 million individuals due to coal smoke pollution (Liang, Ji & Cao, 1997). Fluoride issues in China arise from drinking water, indoor coal combustion, and brick tea, particularly in the Taiyuan basin (Guo et al., 2007). In east Punjab, Pakistan, groundwater pollution with high fluoride levels is caused by fertilizer containing leachable fluoride (ranging from 53 to 255 mg/l) and coal (containing fluoride ranging from 5 to 20 mg/l) (Farooqi et al., 2007). Nagar Parkar area in Pakistan contains granitic rocks with an average fluoride concentration of 1939 mg/l, kaolin deposits with fluoride ranging from 468 to 1722 mg/kg, and secondary kaolin deposits with 270 mg/l, contributing to fluoride levels up to 7.85 mg/l in the groundwater of this area (Naseem et al., 2010). Studies on groundwater fluoride levels in Sri Lanka indicate concentrations exceeding 4 mg/l. High fluoride areas were found in low plains, while low fluoride areas were typically in highland regions (Dissanayake, 1991).

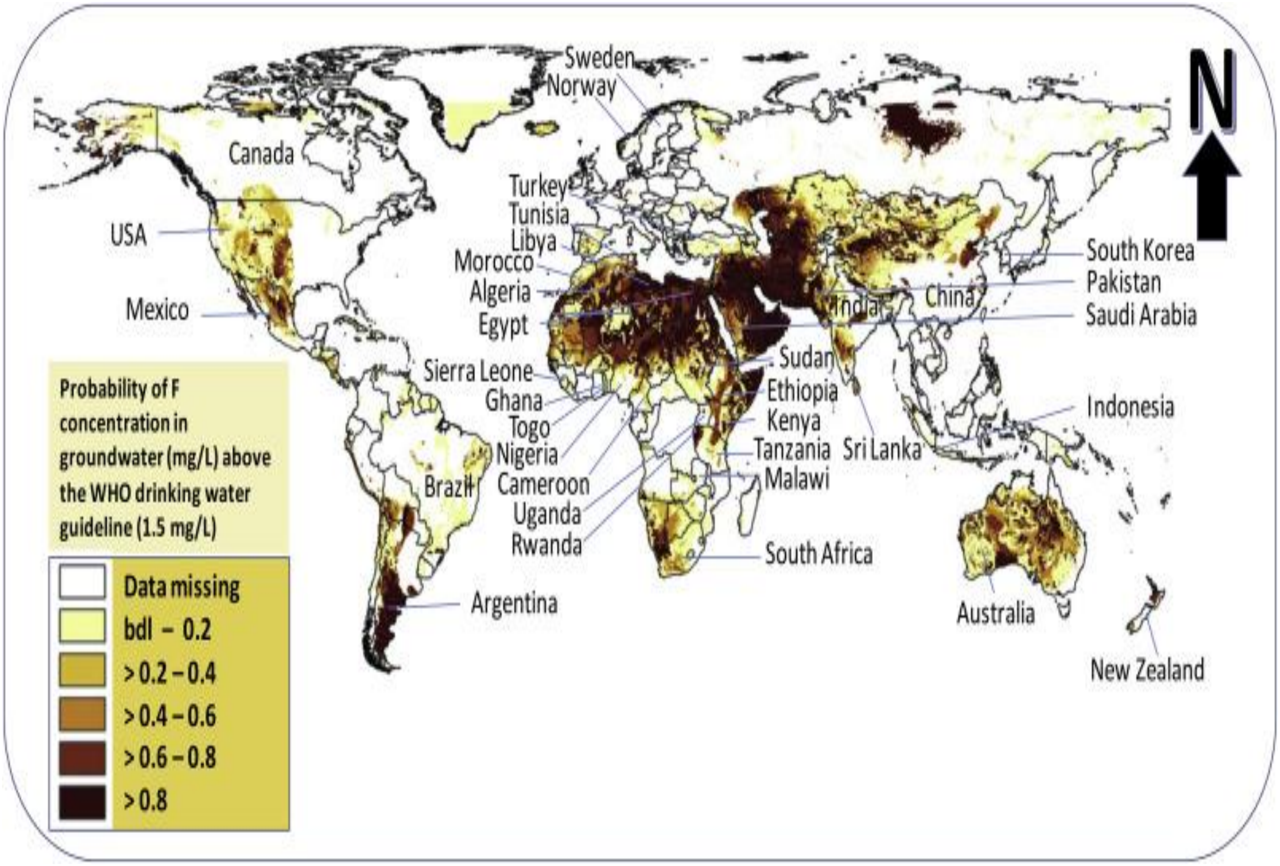


Figure 2-3:Occurrence of fluoride in groundwater in various parts of the world (Source:ScienceDirect, Creator: TNQ Graphics)

Table 2-6:Concentration of fluoride in groundwater and its sources in various parts of the world based on literature (Brindha & Elango, 2011)

Country	Source	General range of fluoride concentration in groundwater
Algeria	Fluorinated minerals	0.4 to 2.3 mg/l
Australia	Atmospheric	Up to 0.69 mg/l
Brazil	Phosphate fertilizer production emission	0.1 to 4.79 mg/l

Canada	Fluoride rich rock	Up to15.1 mg/l
China, Taiyuan basin	Dissolution of the fluorine minerals and evaporation	>2 mg/1
China	Fluorine rich minerals and rocks	2.5 to 10.3 mg/l
China, Mongolia	Fluorite from Holocene sediments	2.3 to 9.8 mg/l
China, Taiyuan basin	Limestone	Up to 6.20 mg/l
Estonia	Silurian-Ordovician carbonaceous aquifer	0.01 to 7.2 mg/l
Ethiopia	Geochemical characteristics	0.01 to 13 mg/l
Ghana, Keta basin	Mineral weathering	0 to 282.29 mg/l
Ghana	Fluorine enriched Bongo coarse-grained hornblende granite and syenite suite	0.11 to 4.60 mg/l
Iran	Dolomite and limestone along with gypsum	0.7 to 6.6 mg/l
Iran, Maku	Basaltic rocks	0.30 to 5.96 mg/l
Jordan	Fluorite and calcite solubility	0.009 to0.055 mg/l
Kenya	Volcanic activity and chemical weathering	0.1 to 25 mg/l
Korea, Gimcheon	Pegmatite	Up to 2.15 mg/l
Korea	Granitic rocks	> 5 mg/l
Korea	Geological	0 to 40.8 mg/l
Malawi	Geological, chemical and physical characteristics of the aquifer	1.65 to 7.5 mg/l

Malawi, Lilongwe	Weathering of rocks containing biotite, dissolution of hornblende, fluorite, and amphibole	0.5 to 6.98 mg/l
Mexico, Sonora	Deep regional flows, heating processes and fluorite dissolutions in granitic rocks	0.53 to 7.59 mg/l
Mexico, San LuisPotosí basin	Fluorite	2.10 to 3.65 mg/l
Norway	Lithological	Up to 8.26 mg/l
Pakistan, Punjab	Phosphate fertilizers and coal combustion	0.11 to 22.8 mg/l
Pakistan, Thar desert	Granitic rocks	1.13 to 7.85 mg/l
Poland	Anthropogenic	0.3 to 2.45 mg/l
Saudi Arabia	-----	0.42 to 1.8 mg/l
Sri Lanka	Granitic gneiss	0.01 to 4.34 mg/l
Sri Lanka	Fluoride in rocks	> 5 mg/l
Tanzania	Fluoride rich nephelinite and carbonatitic rocks	15 to 63 mg/l
Turkey	Fluorite in limestone	1.5 to 13.7 mg/l
USA, Wisconsin	Felsic igneous and equivalent metamorphic rocks	0.01 to 7.60 mg/l
USA, Texas	Volcanic ash deposits	0.3 to 6.27 mg/l
USA, South Carolina	Cryptocrystalline fluorapatite	> 3.5 mg/l
USA, Utah	Fluorite rich rocks	0.01 to 0.6 mg/l
USA, Ohio	Bedrock	0.2 to 2.8 mg/l

2.2.7 Distribution of Fluoride in Groundwater in India

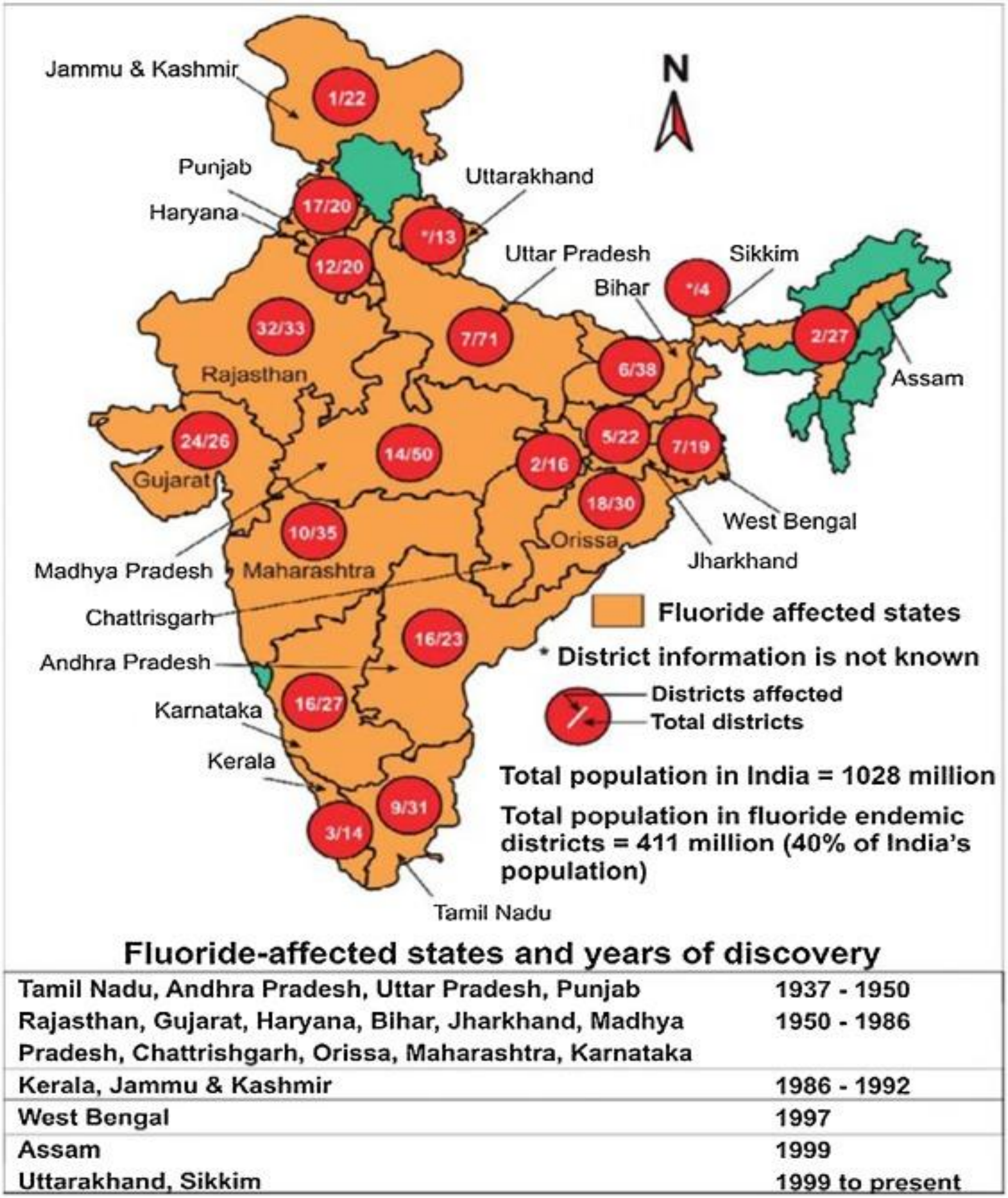
In India, a significant number of people, approximately 62 million, are at risk of developing fluorosis due to the consumption of water with high fluoride levels. The problem is particularly prominent in states such as Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu, and Uttar Pradesh (Pillai & Stanley, 2002). Among the global fluoride reserves of 85 million tons, India alone accounts for approximately 12 million tons (Teotia & Teotia, 1994). Regions in northwestern and southern India are heavily affected by fluorosis (Agarwal, Vaish & Vaish, 1997; Yadav et al., 1999). In Delhi, around 50% of the groundwater exceeds the maximum permissible limit for fluoride in drinking water (Datta, Deb & Tayagi, 1996).

The primary reason for high fluoride levels in groundwater is the evapotranspiration of residual alkaline groundwater (Jacks et al., 2005). Deeper aquifers in Maharashtra have higher fluoride content compared to shallow groundwater due to longer residence times (Madhnure et al., 2007). The presence of fluoride-rich rocks in southern India is a significant contributor to groundwater contamination. Inherent fluoride-rich granitic rocks in Nalgonda district, Andhra Pradesh, are well-known sources of high fluoride levels in groundwater. Currently, fluorosis is prevalent in 17 out of 29 states and 7 union territories in India. States such as Andhra Pradesh, Assam, Bihar, Delhi, Gujarat, Haryana, Jammu and Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh, and West Bengal experience fluoride-related issues (Rwenyonyi et al., 2000).

Table 2-7:Concentration of fluoride in groundwater in India and its sources based on literature (Brindha & Elango, 2011)

State, district/place	**Source**	**General range of fluoride concentration in groundwater**
Andhra Pradesh, Kurmapalli watershed	Fluoride rich rocks	Up to 21.0 mg/l
Andhra Pradesh, Nalgonda	Fluoride rich granitic rocks	0.4 to 20 mg/1

Andhra Pradesh, part of Nalgonda district	Fluoride rich granitic Rocks	0.1 to 8.8 mg/l
Andhra Pradesh, Vamsadhara river basin	Pyroxene amphiboles and pegmatites	Up to 3.4 mg/1
Andhra Pradesh, Visakhapatnam	Granitic rocks	0.6 to 2.1 mg/l
Andhra Pradesh, Wailapally watershed	Fluorite bearing rocks	0.97 to 5.83 mg/l
Andhra Pradesh and Jharkhand	Coal ash	0.1 to >4 mg/l
Assam, Guwahati	Granite	0.18 to 6.88 mg/l
Delhi	Irrigation water and brick industries	0.1-16.5 mg/l
Gujarat, Mehsana	Granite, gneiss and pegmatite	0.94 to 2.81 mg/l
Gujarat, Mehsana	Calcite and dissolution of dolomite	1.5 to 5.6 mg /l
Haryana, Bhiwani	Rock	0.14 to 86 mg/l
Karnataka, Bellary	Apatite, hornblende and biotite	0.33 to 7.8 mg/l
Kerala, Palghat	Hornblende and biotite Gneiss	0.2 to 5.75 mg/l
Maharashtra, Yavatmal	Amphibole, biotite and fluorapatite	0.30 to 13.41 mg/l
Rajasthan, Hanumangarh	Fluoride bearing host rocks	1.01 to 4.42 mg/l
West Bengal, Hooghly	Super phosphate fertilizer	0.01to 1.18 mg/l



Fluoride-affected states and years of discovery

Tamil Nadu, Andhra Pradesh, Uttar Pradesh, Punjab	1937 - 1950
Rajasthan, Gujarat, Haryana, Bihar, Jharkhand, Madhya Pradesh, Chattrishgarh, Orissa, Maharashtra, Karnataka	1950 - 1986
Kerala, Jammu & Kashmir	1986 - 1992
West Bengal	1997
Assam	1999
Uttarakhand, Sikkim	1999 to present

Figure 2-4:Contamination of Fluoride in various states in India (Chakraborti et al., 2016)

2.2.8 Fluoride Affected Zones in West Bengal

Figure 2-5: Affected areas in West Bengal according to the Public Health Engineering Department, Government of West Bengal

2.2.9 Fluoride Toxicity in Human – Study of Urine as Biomarker

Biological markers or biomarkers are defined as indicators that signal events in biological systems (human body) or samples. A biomarker is not used as a diagnostic test, but as an indicator of a disease or biological alteration. The biomarkers are classified into three types:

1. Exposure - plasma, bone, teeth, urine, saliva, dental plaque, plaque fluid, hair, nails;
2. Susceptibility - genetic factors, acid-base disturbances, renal disturbances, bone growth, and nutritional state;
3. Biomarkers of effect - reduction in the activity and severity of dental caries, dental fluorosis, and skeletal fluorosis.

As urine is the main excretion route for ingested fluoride, analysis of the fluoride concentration in urine is a useful way to estimate the overall fluoride intake of a population. A proportion of ingested fluoride is excreted in the urine. The concentrations in urine reflect the fluoride concentrations during the recent hours. Urinary fluoride excretions and concentrations are variable because of variations in urinary flow and pH.

CHAPTER-III

3 MITIGATION TECHNIQUE

Because fluorosis is an irreversible condition and has no cure, prevention is the only solution for this menace. Providing water, with optimal fluoride concentration is the only way by which the generation yet to be born can be protected against the disease (Susheela, 1984). It can be achieved by the following methods (Piddennavar, Renuka, & krishnappa Pushpanjali, 2013):

- Removal of fluoride from water (defluoridation), using suitable techniques.
- Locating alternative sources of safe water.
- Bringing in water from a distant, safe source.
- Prevention of industrial fluorosis by rigorous enforcement of procedures for minimizing industrial fluoride pollution.

Defluoridation is a widely tested method for supplying safe water to the fluorosis affected communities (Piddennavar, Renuka, & krishnappa Pushpanjali, 2013). Defluoridation is defined as, ‘‘the downward adjustment of the level of fluoride in drinking water to the optimal level’’ (Hiremath, 2006). To solve the hazardous impact of fluorosis, different approaches for defluoridations are existed like, (Waghmare & Afrin, 2015).

- Adsorption Technique
- Ion-exchange technique
- Coagulation-Precipitation technique
- Membrane separation

Now various materials used as defluoridation agent in these above-discussed techniques are discussed below,

3.1 Adsorption Technique

Adsorption is the process by which molecules or species from a bulk solution bond to the surface of a solid through physical or chemical forces. Adsorption procedures are commonly used for removing fluoride from water, either through ion exchange or surface chemical reactions with the solid bed matrix. Compared to other defluoridation methods, adsorption is favored due to its simplicity and the availability of a wide range of adsorbents. Several adsorbent materials have been tested in the past to assess their potential and techno-economic feasibility as defluoridating agents. These include activated alumina, activated carbon, activated alumina coated silica gel, calcite, activated sawdust, activated coconut shell powder, activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, serpentine, tricalcium phosphate, bone charcoal, activated soil sorbent, defluoron-1, defluoron-2, and others (Waghmare & Afrin, 2015).

The application of domestic defluoridation plants based on activated alumina was launched by UNICEF in rural India (Mariappan & Vasudevan, 2011). Industrial-grade aluminum hydroxide that does not meet certain specifications and is considered a spoiled batch can be procured and used in this technique (P. Mariappan, Yegnaraman & Vasudevan, 2002). However, activated alumina has some drawbacks. Fluoride adsorption is only possible within a specific pH range, necessitating pre- and post-pH adjustment of water. Frequent reactivation of alumina is required, making the technique expensive (Central Electrochemical Research Institute). Additionally, the adsorption efficiency of activated alumina decreases with an increasing number of usage-regeneration cycles (Piddennavar, Renuka, & Krishnappa Pushpanjali, 2013).

Another adsorbent commonly used is bone char. It has been found that bone char can adsorb maximum amounts of fluoride per gram of surface at temperatures of 250°C, 350°C, and 450°C, which are approximately 21.1 μmol, 22.4 μmol, and 25.7 μmol, respectively. The optimal time for saturation adsorption is 9 hours, and the optimal pH range for the fluoride solution is between 7.00 and 7.50. Particle size has a negligible effect on fluoride adsorption. Various natural adsorbents derived from different trees have also been tested as defluoridation agents, including drumstick tree seeds, vetiver grass roots, and tamarind seeds (Piddennavar, Renuka, & Krishnappa Pushpanjali, 2013).

3.2 Ion-exchange Technique

The ion-exchange technique is a widely used method in chemistry and related fields for separating and purifying ions from a solution. It involves the exchange of ions between a solid material, known as an ion-exchange resin, and the ions present in the solution. Ion-exchange resins are typically made of small polymer beads containing fixed ionic groups (e.g., $-COOH$, $-SO_3H$, $-NH_2$) that can attract and bind ions of opposite charge from the surrounding solution. When the solution containing various ions comes into contact with the resin, the ions of interest are attracted and adhere to the resin, displacing other ions previously attached to the resin.

The ion-exchange process can be classified into two main types:

1. **Cation Exchange:** In cation exchange, the resin has negatively charged functional groups, and it selectively binds and removes positively charged ions (cations) from the solution. Common cations include sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}). This process is often used in water softening to remove hardness-causing ions like calcium and magnesium.
2. **Anion Exchange:** In anion exchange, the resin has positively charged functional groups, and it selectively binds and removes negatively charged ions (anions) from the solution. Common anions include chloride (Cl^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-). Anion exchange is employed in applications such as water purification and the removal of harmful anions from solutions.

The ion-exchange technique finds applications in various industries and processes, including:

- **Water Treatment:** Ion exchange is used to remove unwanted ions, such as hardness ions or contaminants, from water, making it suitable for consumption or specific industrial applications.
- **Chemical Separations:** It can be used to separate and purify specific ions from complex mixtures, facilitating the isolation of desired compounds.
- **Pharmaceutical Industry:** Ion exchange is employed to purify drugs and separate different components in pharmaceutical products.
- **Nuclear Industry:** In nuclear processes, ion exchange is used for the separation and recovery of specific radioactive ions.
- **Sugar Refining:** It is used in the purification of sugar solutions to remove impurities.

One of the significant advantages of the ion-exchange technique is its ability to be regenerated and reused. Once the ion-exchange resin becomes saturated with ions, it can be treated with a regenerating agent to release the bound ions and restore the resin's original ion-binding capacity. Overall, the ion-exchange technique is a valuable tool for selective ion separation and purification, playing a vital role in a wide range of scientific, industrial, and environmental applications.

3.3 Coagulation-Precipitation Technique

Lime and alum are commonly used coagulants in the Nalgonda technique for defluoridation of water. After extensive testing of various materials and processes, including activated alumina, since 1961, the CSIR-National Environmental Engineering Research Institute (NEERI) in Nagpur has developed an economical and simple method known as the "Nalgonda Technique" for fluoride removal. This technique involves the addition of aluminum salts, lime, and bleaching powder to the water, followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection. Aluminum salts can be added as aluminum sulfate (alum), aluminum chloride, or a combination of both, and they are responsible for removing fluoride from the water. The dosage of aluminum salt increases with higher levels of fluoride and alkalinity in the raw water (Piddennavar, Renuka, & Krishnappa Pushpanjali, 2013).

The Nalgonda Technique achieves the best fluoride removal at a pH range of 5.5 to 7.5 (Razbe et al., 2013). It is a versatile technique that can be applied to various scenarios, such as large communities, small communities using the fill-and-draw technique, rural water supply using fill-and-draw defluoridation plants, and domestic defluoridation (Piddennavar, Renuka, & Krishnappa Pushpanjali, 2013). A bucket defluoridation system based on the Nalgonda Technique has also been developed for household use (Mjengera & Mkongo, 2002). The advantages of the Nalgonda Technique include its practicality compared to other defluoridation techniques and its ease of implementation. However, there are limitations to this technique. It requires high chemical dosages, with aluminum hydroxide ($Al(OH)_3$) doses ranging from 700 to 1200 mg/l. It may not achieve satisfactory fluoride removal limits, and there are challenges related to sludge disposal and the need for skilled labor. The release of aluminum in treated water is a concern as it may be associated with Alzheimer's syndrome. The final concentration of fluoride in treated water depends significantly on the solubility of precipitated fluoride, calcium, and aluminum salts. Additionally, the use of aluminum sulfate as a coagulant significantly increases the sulfate ion concentration, which can have laxative effects in humans (Waghmare and Afrin, 2015).

3.4 Membrane Separation

The membrane separation process is widely recognized in the industrial context for defluoridation of groundwater, wastewater treatment, and seawater desalination (Maheswari & Hoelzel, 2002). In this process, particles are separated based on their molecular size and shape using specially designed semi-permeable membranes. These membranes can be thin, nonporous or porous films made of polymeric, ceramic, or metallic materials, as well as liquid or gas membranes. It is crucial that the membranes do not dissolve, deteriorate, or rupture during operation (Seader & Heneley, 2005). Membrane techniques used for defluoridation include reverse osmosis (RO), nanofiltration, dialysis, and electrodialysis.

Reverse osmosis (RO) is a physical process in which pressure is applied to the feed water to force it through a semi-permeable membrane, effectively removing anions. RO operates at higher pressures and achieves greater rejection of dissolved solids (Waghmare & Afrin, 2015). RO produces water of exceptionally high purity, with fluoride ion rejection typically exceeding 98% when the RO membrane is fully regenerated (Mohapatra et al., 2009). The advantages of RO include its effective fluoride removal capabilities, complete recovery of the RO membrane after each cycle of operation, the ability to remove fluoride by over 90% regardless of the initial concentration, simultaneous removal of other dissolved solids, effectiveness over a wide pH range, no chemical requirements, minimal labor requirements, low operational costs, and assurance of consistent water quality. However, limitations of RO include its infeasibility for rural areas, high cost, removal of valuable minerals necessary for proper growth (requiring remineralization after treatment), significant water wastage as brine, challenges in disposing of the saltwater waste, and the water becoming acidic and requiring pH adjustment (Waghmare & Afrin, 2015).

Nanofiltration (NF) operates on the same principles as reverse osmosis but with membranes that have slightly larger pores and offer less resistance to solvent and solute passage. This leads to lower required pressures, reduced energy requirements, less thorough solute removal, and faster flow rates (Mohapatra et al., 2009).

Dialysis and electrodialysis are other membrane processes used for defluoridation. Dialysis involves the transport of solutes through a membrane, while electrodialysis uses an applied electric field to drive solutes through the membrane. Donnan dialysis, also known as diffusion dialysis, relies on a concentration difference as the driving force for ion transport (Waghmare & Afrin, 2015). Electrodialysis uses an electric current to separate ionic components from aqueous solutions. However, electro-dialysis is not suitable for rural areas due to its electricity consumption (Waghmare & Afrin, 2015).

Table 3-1: Different defluoridation techniques and the materials used (Mariappan et al.,2002)

Adsorption	Ion-exchange	Precipitation	Others
Carbon materials, Activated Alumina, Magnesia, Tricalcium phosphate, Calcite, Hydroxy apatite, Wood, Lignite, activated char coal, fish bone char, Processed bone, Nut shells, Avaram bark, Paddy husk, Coffee husk, Tea waste, Jute waste, Coir pitch, Fly ash, Bauxite, Serpentine	**Anion exchange resins:** NCL poly anion resin, Tulsion A27, Lewatit-MIH 59, Amberlite IRA 400, Deacedodite FF-IP, Waso resin 14, Polystyrene. **Cation exchange resins:** Defluoron-1, Defluoron-2, Carbion.	Lime, Alum, Lime & Alum (Nalgonda technique), Alum flock blanket method, Poly Aluminium Chloride (PAC), Poly Aluminium Hydroxy Sulphate (PAHS), Brushite.	Electrochemical method (Aluminium electrode), Electro dialysis, Electrolysis, Reverse Osmosis.

Table 3-2: Advantages & limitations of various technique (Waghmare & Afrin, 2015)

Technique	**Advantages**	**Limitations**
Adsorption	1. Ease of operation. 2. Adsorption procedure is worthwhile 3. High productivity for fluoride removal and can remove up to 90% fluoride. 4. Produce high quality water. 5. Regeneration is conceivable	1. Disposal of depleted adsorbents and concentrated regenerated makes issue. 2. Interference because of the vicinity of different anions may bring about competition for active sites on adsorbent. 3. Drop in removal effectiveness after regeneration step. 4. Highly pH subordinate. 5. High concentration of total dissolved salts (TDS) can brings about fouling of the alumina bed.
Ion-Exchange	1. High productivity (90 95 % fluoride removal). 2. Retains the superiority of water.	1. Technique is exceptionally costly. 2. pH of treated water is low and contains high concentration of chloride.

		3. Interference because of the presence of other anions like sulphate, carbonate, phosphate and alkalinity. 4. Regeneration of resin is an issue on the grounds that it prompts fluoride rich waste, which must deal with before last disposal. 5. It requires longer reaction period.
Coagulation Precipitation technique	1. Generally utilized technique. 2. Technique is more practical when contrasted with other defluoridation technique. 3. Technique is easy to understand.	1. Required chemical dosages are high (Al (OH)3 up to 700 - 1200 mg/l). 2. Sludge transfer issue. 3. Cannot accomplish the passable furthest reaches of fluoride. 4. Prerequisite of talented labor. 5. Release of aluminum in treated water which may bring about

		Alzheimer's syndrome. 6. Final concentration of fluoride in the treated water significantly relies on upon dissolvability of precipitated fluoride and calcium and aluminum salt. 7. The utilization of aluminum sulphate as coagulant expands the sulphate ion concentration greatly which prompting cathartic impacts in human.
RO membrane separation	1. Technique is profoundly compelling for fluoride removal. 2. RO membrane was completely recovered after every arrangement of examination. 3. This strategy can remove fluoride more	1. Non-attainable for rural regions. 2. Expensive technique. 3. Remove valuable minerals which are basically require for fitting development, remineralization is require after treatment. 4. Lot of water get squandered as saline

	than 90% regardless of initial concentration. 4. This strategy gives the synchronous removal of other dissolved solids. 5. Its efforts under wide pH range. 6. No obstruction by different ions. 7. No chemical obliges, least labor prerequisite and least operational expense. 8. The process allows the treatment and purification of water in one stage. 9. It guarantees steady water quality.	solution and expendable of salt water is an issue. 5. The water gets to be acidic and need pH improvement.
Nano Filtration membrane process	1. High productivity. 2. No chemicals are needed. 3. It lives up to expectations under wide pH range. 4. Interference because of the presence of	1. Highly expensive technique when contrasted with other defluoridation techniques. 2. Prone to fouling, scaling or membrane degradation.

	another ion is not observed. 5. This process gives an effective barrier to suspended solids, all inorganic toxin, organic micro pollutants, pesticides and microorganism.	3. It removes all the ions present in water some of which are key for the ordinary development and henceforth remineralization of treated water is needed.
Electro-dialysis	1. Inexpensive pre and post treatment. 2. Flexible (seasonal operation). 3. Low chemical request 4. High water recovery	1. Only separation of Ionic components. 2. Potential formation of H2 in the electrode rinse. 3. Specific power consumption for Pumping. 4. Necessity of concentrate treatment.
Electrocoagulation	1. EC obliges basic equipment, simple to handle and less support cost. 2. EC treated water is consumable, colorless and odorless. 3. EC produces low sludge that is	1. The ‘sacrificial electrodes’ are dissolved into wastewater streams as an after effect of oxidation, and should be consistently supplanted.

	promptly settable and simple to de water since it essentially content metallic oxides or hydroxides. 4. EC produces steadier and effectively separated by filtration.	2. The utilization of electricity may be lavish in numerous spots. 3. An impermeable oxide film may be framed on the cathode prompting loss of productivity of the EC unit. 4. High conductivity of the wastewater suspension is needed. 5. Gelatinous hydroxide may tend to solubilize now and again.

CHAPTER-IV

4 ADSORPTION: A MITIGATION TECHNIQUE

4.1 Literature Review

Adsorption and absorption are distinct processes. Adsorption refers to the adhesion of atoms, ions, or molecules to a surface, while absorption involves the diffusion of a substance into a liquid or solid to form a solution. Sorption is a general term that encompasses both adsorption and absorption, while desorption is the reverse process of releasing the adsorbed or absorbed substance. During adsorption, a film of the adsorbate forms on the surface of the adsorbent material.

The removal of excess fluoride from water by adsorption involves physical, chemical, or ion exchange interactions within the adsorbent material. This typically occurs in a fixed bed packed with resin or mineral particles. It is important to differentiate between adsorption of a single compound and adsorption in the presence of multiple compounds. In a multi-component system, different adsorbates may compete for adsorption sites, leading to different adsorption equilibria and isotherms compared to adsorption without competition. The initial concentration of the target adsorbate also influences the resulting isotherm in a multi-component system.

Several factors influence the adsorption process, including the surface area of the adsorbent material, particle size (smaller particles reduce diffusion limitations), affinity of the solute for the adsorbent, degree of ionization of the adsorbate molecule (more highly ionized molecules are adsorbed to a lesser extent than neutral molecules), and pH of the solution. Adsorption remains one of the most widely used methods due to its simplicity and the availability of a wide range of adsorbent materials (Mohapatra et al., 1984).

It is important to distinguish between physical adsorption, which involves relatively weak intermolecular forces, and chemisorption, which entails the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent. The table below, adapted from Douglas (1984), compares the two techniques (Mohapatra et al., 1984).

Table 4-1: Comparison of Physical Adsorption and Chemisorption

Property	Physical Adsorption	Chemisorption
Heat of adsorption	Low	High
Specificity	Low	High
Reversibility	Easily reversible	Irreversible or reversible with difficulty
Coverage	Monolayer	Multilayer or monolayer
Bonding mechanism	Weak van der Waals forces	Covalent or ionic bonding

Table 4-2: Difference between Physical Adsorption and Chemisorption (Mohapatra et al.,1984)

Physical Adsorption	Chemisorption
The forces operating are weak Vander Waal's forces	The forces are similar to chemical bond
Form nonspecific multi molecular layers	Form specific unimolecular layers
No dissociation of adsorbed species	May involve in dissociation
The heat of adsorption is low, that is about $20 - 40\ KJ\ mol^{-}$.	The heat of adsorption is high, that is about $40 - 400\ KJ\ mol^{-}$.
This process is reversible	This process is irreversible
This type of adsorption decreases with increase of temperature	This type of adsorption increases with increase of temperature

4.2 Importance of Adsorption

1. Low cost installation & maintenance.
2. High efficiency, high productivity of removal.
3. Easy post-treatment after adsorption & High selectivity of adsorbents.
4. Simple in the operation and design.
5. Eco-friendly nature & Lack of sludge production.
6. Removal of fluoride even at low concentration.
7. Wide range of availability of adsorbents.

Table 4-3: Various low-cost adsorbent of removal of fluoride

Name of adsorbent	pH	Dosage (g/l)	Contact time (hr)	Removal Percentage (%)	Reference
Clay material	2	5-10	3	40-50	Ravikumar and Nazeebkhan (2015)
Granular activated carbon & sewage sludge	neutral	GAC-4 SS-3	3	60-70	Poundyl and Sandhya (2015)
Tea Ash	6	0.8	1	51.3-77.6	Mondal.et.al. (2011)
Pumic	7	20	3	74.64	Malakootianet.al., (2011)
Neem leaves	2	10	1	90	Goswami et al., (2015)
Rice Husk	2-10	10	2	75	Deshmukh et.al., (2009)
Eggshell powder	2-6	5	2	94	R. Bhavnik & N.K. Mondal,2015
Neem stem charcoal	5	0.1 - 0.6	3	94	Chakrabarty & Sharma (2012)
Citrus limonum (lemon)leaf	2-8	1-10	2.4	70	V.Jomae.et.al (2014)
Devadaru leaf powder	7	7-8	3	77	Bharali and Bhattachary (2011)
Banana peel and coffee husk	2	72	12	80-84	Getechew et al.,2014
Wheat straw and sawdust	6	4	1	42 & 50	Yadav et al., 2013

Table 4-4: Comparison with reported methods for the removal of fluoride using different low-cost materials

Material	**Removal Capacity**	**Contact time**	**Initial fluoride concentration**	**Reference**
Heat activated dolomite	1.74-227.18	5 min	5 – 500	Chaudhary & Prasad, 2015
Calcium oxide modified activated aluminium	101.01	48 h	1 – 1000	Camacho et al., 2010
Quick lime	16.67	75 min	0 – 50	Islam & Patel, 2007
Granular ferric hydroxide	7.0	24 h	1 – 100	Kumar et al., 2009
Fe–Al–Ce oxide	178	24 h	2 – 110	Xu et al., 2007
Various graphite	0.16-3.13	60 min	2 – 10	Kartikeyan & Elango, 2008
Modified attapulgite	41.5	48 h	20 – 200	Zhanng et al., 2009
Modified chitosan	22.380	24 h	10 – 100	Yao et al., 2009
Magnetic chitosan	22.49	150 min	5 – 140	Ma et al., 2007
Cross-linked calcium alginate	73.6	90-150 min	10 – 25	Viyaya et al., 2011
Waste carbon slurry	4.306	1 h	1 – 11	Gupta et al., 2007
Carbon nano-tubes	4.5	180 min	15	Li et al., 2003
Nano-magnesia	267.82	90-120 min	5 – 200	Maliyekkal et al., 2010

CHAPTER-V

5 AIM & OBJECTIVE

Groundwater serves as the primary source of drinking and agricultural water for rural communities in India. Unfortunately, a significant number of people face the challenge of excessive fluoride content in their groundwater, which poses health risks. Defluoridation, the process of removing excess fluoride from water, is crucial to address this issue. To effectively combat this problem, it is essential to develop cost-effective and efficient technologies for quick fluoride removal.

Numerous defluoridation technologies exist, but the key challenge lies in identifying and implementing methods that are both economical and swift in removing fluoride from water. Ensuring the availability of safe drinking water is a fundamental requirement for public health and agricultural development.By investing in research and development, it becomes possible to create innovative and affordable defluoridation solutions that cater to the specific needs of rural communities in India. These technologies should be capable of delivering results quickly to meet the immediate demand for safe drinking water. The main objective of this study is to develop a treatment for drinking water containing fluoride by carrying out experimental investigation on the removal of fluoride from aqueous solution using suitable adsorbents.

Objectives are specified as follows:

1. To identify an effective technique for the removal of fluoride from groundwater.
2. Adsorbent Characterization
3. Batch study of an adsorbent for percentage removal of fluoride with variation of
    a. Effective pH
    b. Effective contact time
    c. Effective adsorbent dose
    d. Effective activated temperature
    e. Effective initial fluoride concentration
4. Management of the generated waste.

CHAPTER-VI

6 METHODOLOGY

My current work is structured around seven distinct stages, each carefully designed to fulfill the project's objectives. These stages form a well-defined process that will lead us to achieve our ultimate goal. Below, I have provided an outline outlining the project's scheme for better understanding and visualization.

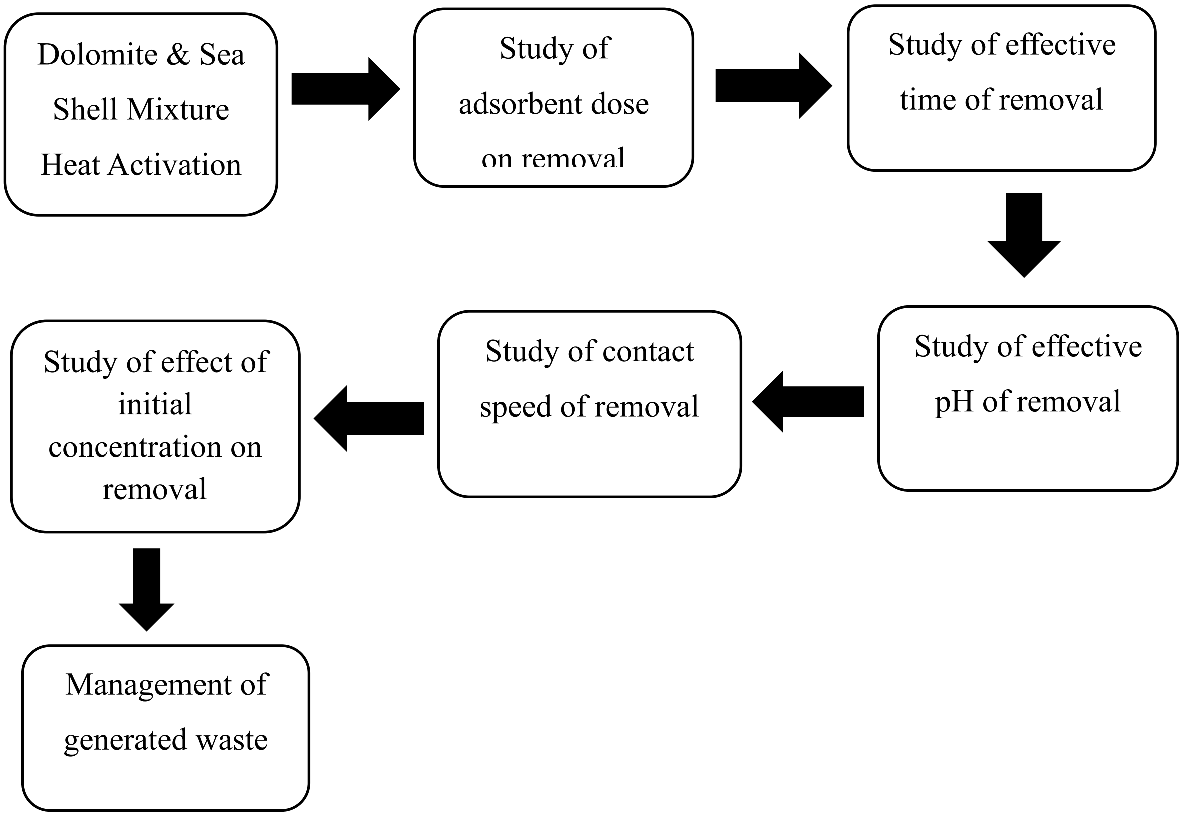


Chart 6-1: Schematic diagram of the project

6.1 Chemicals & Instruments Required

i. Dolomite (Disha Aggrotech, Paschim Midnapore).
ii. Sea Shell (Disha Aggrotech, Paschim Midnapore).
iii. Mettler AE240 Fine Balance.
iv. Rotary Shaker (Remi).
v. Fluoride Standard 100 mg/l [or mg/l] (Thermo Scientific).
vi. TISAB III [Total Ionic Strength Adjustment Buffer] (Thermo Scientific).
vii. Orion Star A214 pH / ISE Meter.
viii. pH Meter CL 46+ (Toshcon Industries).
ix. Whatman Filter paper 42.
x. Muffle Furnace.

6.2 Adsorbent Materials

Dolomite $[CaMg(CO_3)_2]$ is a common rock-forming mineral, constituting layer of carbonate ion (CO_3^{2-}) separated by an alternating layer of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions. It is an anhydrous carbonate mineral. Dolomite is also known as dolostone. This a sedimentary rock and found in the sedimentary rock basin worldwide. Color of dolomite is white to grey. Thermal treatment of dolomite at 800°C led to changes in its chemical composition. In this change Calcite, Calcium Oxide & Magnesium Oxide are formed (Staszczuk et al., 1997).

$$2CaCO_3MgCO_3 \rightarrow 2MgO + CaCO_3 + CaO + 3CO_2$$

Figure 6-1: Dolomite (Source: Learning Geology)

The change in chemical composition increases the BET (Brunaur, Emmet & Teller Method) surface area of dolomite in many folds which increase the adsorption properties (Walker et al., 2003).A seashell is usually the exoskeleton of an invertebrate (an animal without a backbone) and is typically composed of calcium carbonate or chitin. Most shells that are found on beaches are the shells of marine mollusks, partly because these shells are usually made of calcium carbonate, and endure better than shells made of chitin. Seashells are composed of an outer layer of protein followed by an intermediate layer of calcite and a smooth inner layer of platy calcium carbonate crystal (Narayanan et al. 2006). It has important functional groups like $-CH_2$, OH,$-CO_2$ and $-PO_4$ which make its more effective adsorbent for removal both organic and inorganic pollutants (Chowdhury & Saha 2010).

Figure 6-2: Sea shell (Source: Pinterest)

6.3 Pre-treatment of Dolomite & Seashell

The dolomite & seashell are needed to be activated before use as an adsorbent. This activation is called thermally activated dolomite & seashell. Pre-treatment procedure for activation is explained below.

50 mg Dolomite & Seashells are taken separately then 12.5 ml of HCl (1:5) is added and mixed thoroughly

↓

Acid mixed dolomite & seashell are placed inside the muffle furnace at 600°C for 30 minutes.

↓

Then the heated dolomite & seashells are grounded into fine particles and collected after sieving with 150 µ sieve

Chart 6-2: Pre-treatment process of Dolomite & Seashell

6.4 Defluoridation Procedure

Thermally treated dolomite and seashell are used for defluoridation procedure as adsorbent. Defluoridation procedure is described below.

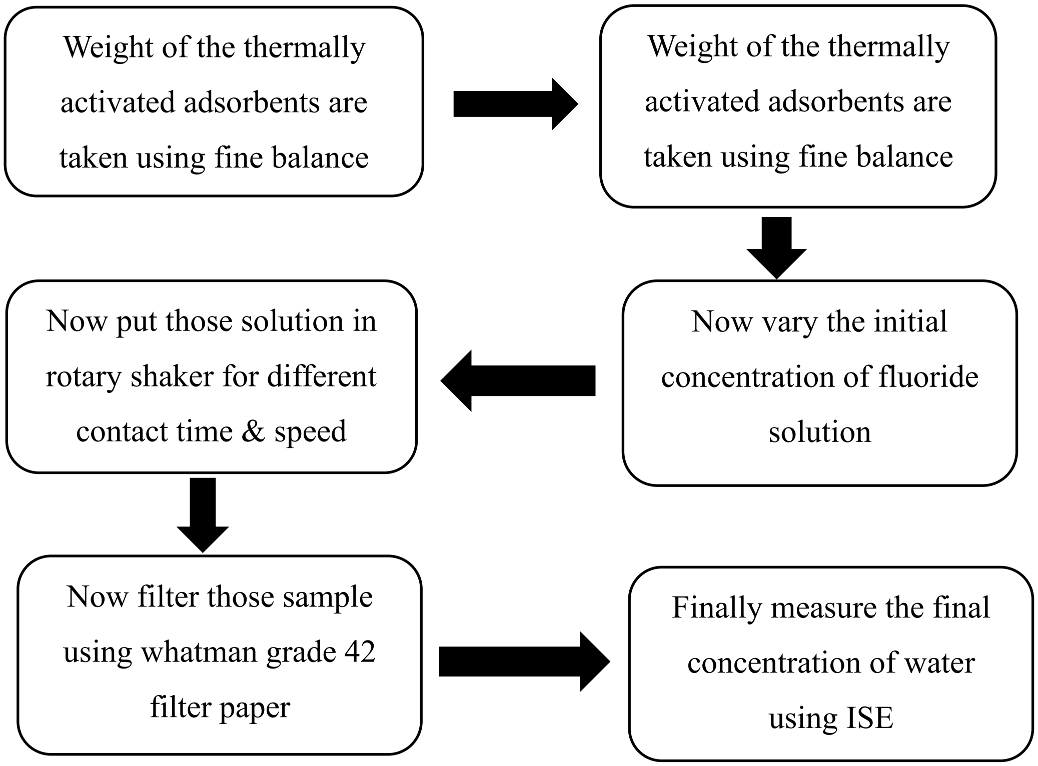


Chart 6-3: Process of Defluoridation

CHAPTER-VII

7 RESULT & DISCUSSION

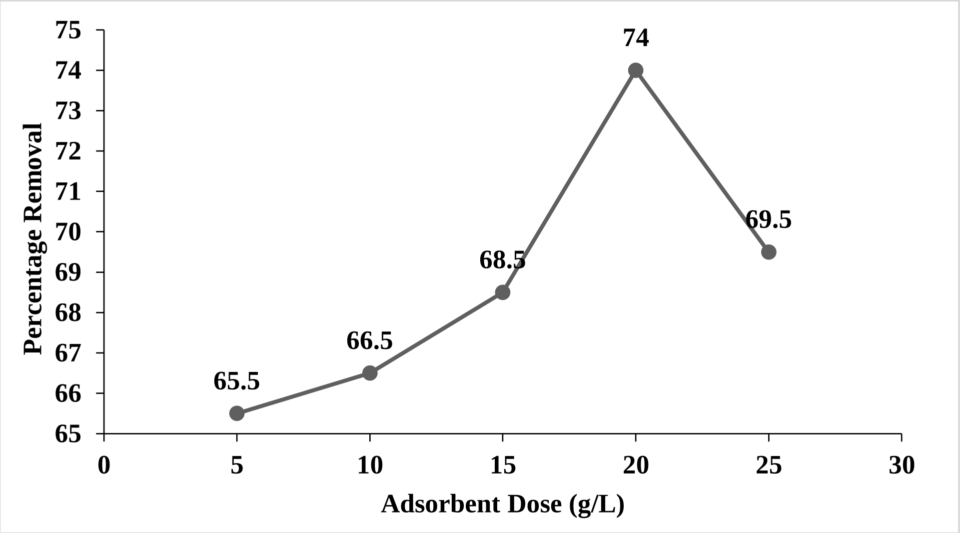
7.1 Effect of Adsorbent Dose

Experiment: Dolomite as Adsorbent:

Contact Time: 30 min, pH: 7-8, Temperature: 600°C

Adsorbent Dose (g/l)	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
5	20	6.9	13.1	65.5
10	20	6.7	13.3	66.5
15	20	6.3	13.7	68.5
20	20	5.2	14.8	74
25	20	6.1	13.9	69.5

Experiment shows percentage of fluoride removed at different adsorbent dosage range from 5 g/l to 25 g/l. It is observed that fluoride removal by the adsorbent increases from 65.5% to 69.5% at 5 g/l to 25 g/l of Dolomite. The maximum removal of fluoride ions can be obtained by using 20 g/l of dolomite.



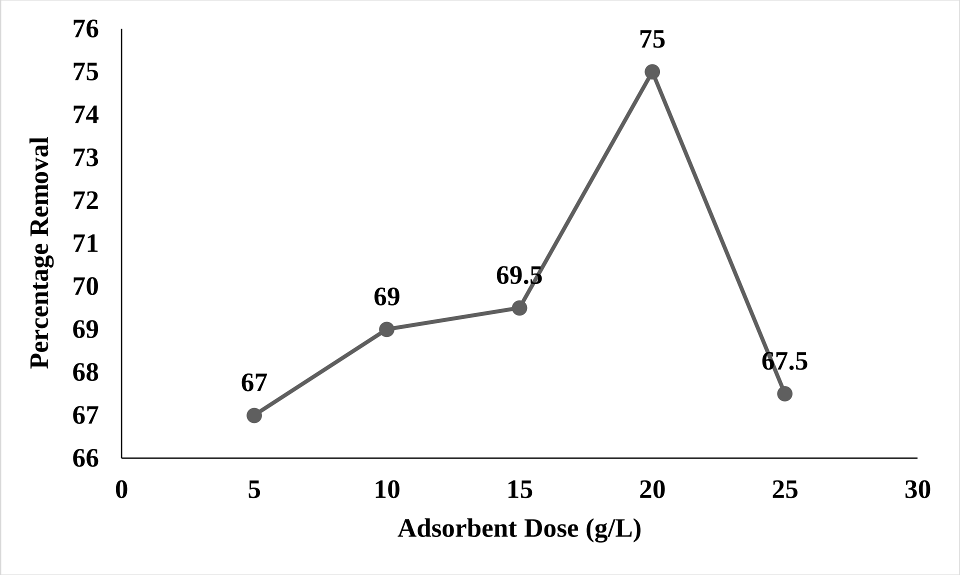
Graph 7-1: Percentage Removal VS dolomite Adsorbent Dose

Experiment: Seashell as Adsorbent

Contact Time: 30 min, pH: 7-8, Temperature: 600°C

Adsorbent Dose (g/l)	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
5	20	6.6	13.4	67
10	20	6.2	13.8	69
15	20	6.1	13.9	69.5
20	20	5	15	75
25	20	6.5	13.5	67.5

Experiment shows percentage of fluoride removed at different adsorbent dosage range from 5 g/l to 25 g/l. It is observed that fluoride removal by the adsorbent increases from 67% to 67.5% at 5 g/l to 25 g/l of Dolomite. The maximum removal of fluoride ions can be obtained by using 20 g/l of Seashell.



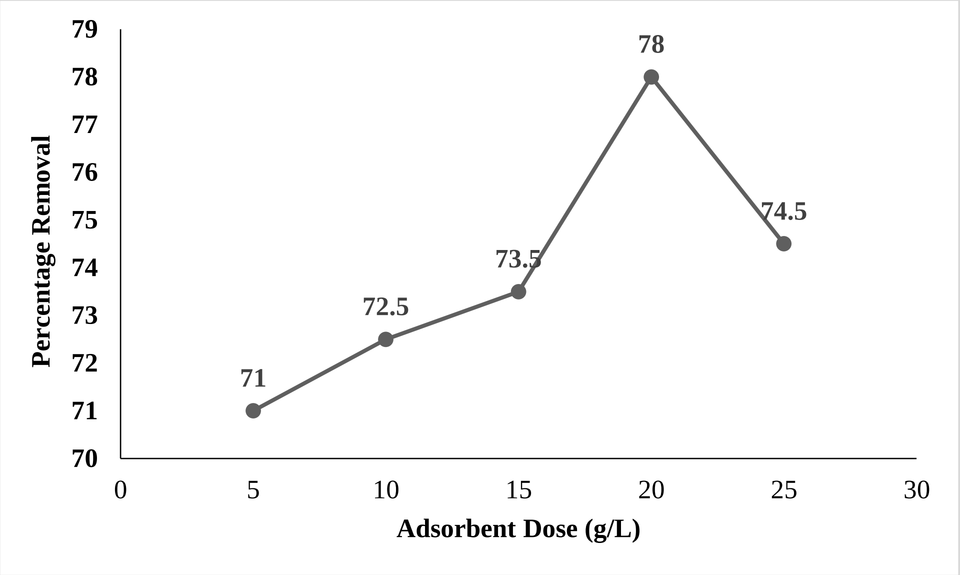
Graph 7-2:Percentage Removal VS seashell Adsorbent Dose

Experiment: Dolomite & Seashell mixture (1:1) as Adsorbent

Contact Time: 30 min, pH: 7-8, Temperature: 600°C

Adsorbent Dose (g/l)	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
5	20	5.8	14.2	71
10	20	5.5	14.5	72.5
15	20	5.3	14.7	73.5
20	20	4.4	15.6	78
25	20	5.1	14.9	74.5

Experiment shows percentage of fluoride removed at different adsorbent dosage range from 5 g/l to 25 g/l. It is observed that fluoride removal by the adsorbent increases from 71% to 74.5% at 5 g/l to 25 g/l of Dolomite. The maximum removal of fluoride ions can be obtained by using 20 g/l of dolomite & Seashell mixture.



Graph 7-3:Percentage Removal VS Dolomite & Seashell mixture (1:1) Adsorbent Dose

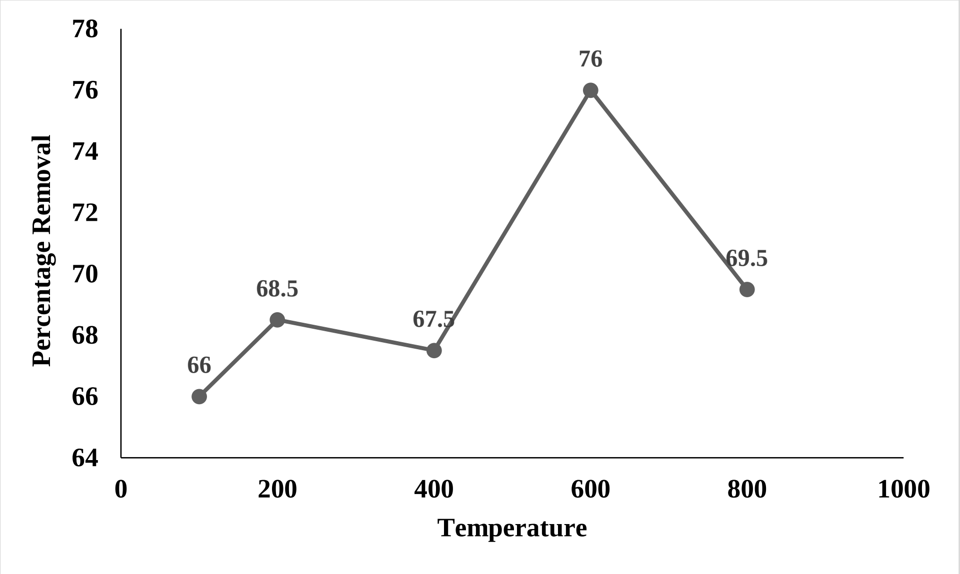
7.2 Effect of Temperature

Experiment: Dolomite as Adsorbent

Adsorbent Dose: 20 g/l, pH: 7-8, Contact time: 30 min

Temperature	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
100	20	6.8	13.2	66
200	20	6.3	13.7	68.5
400	20	6.5	13.5	67.5
600	20	4.8	15.2	76
800	20	6.1	13.9	69.5

Experiment shows percentage of fluoride removed at different adsorbent activation temperature range from 100°C to 800°C. It is observed that fluoride removal by the adsorbent increases from 66% to 69.5% at 100°C to 800°C of Dolomite activation temperature. The maximum removal of fluoride ions can be obtained by using 600°C of temperature.



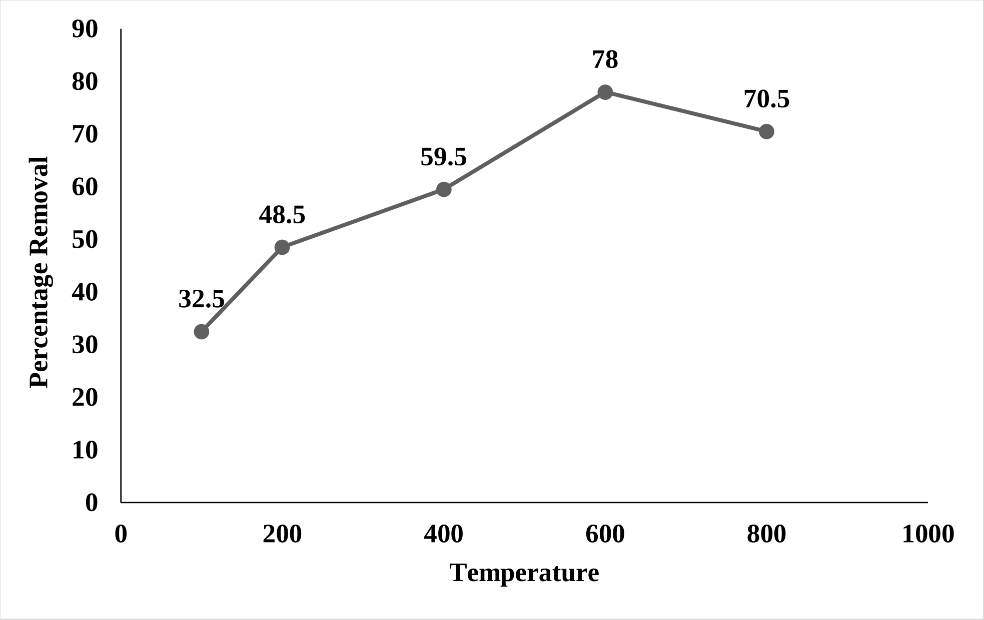
Graph 7-4:Percentage Removal VS Dolomite Activation Temperature

Experiment: Seashell as Adsorbent

Adsorbent Dose: 20 g/l, pH: 7-8, Contact time: 30 min

Temperature	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
100	20	13.5	6.5	32.5
200	20	10.3	9.7	48.5
400	20	8.1	11.9	59.5
600	20	4.4	15.6	78
800	20	5.9	14.1	70.5

Experiment shows percentage of fluoride removed at different adsorbent activation temperature range from 100°C to 800°C. It is observed that fluoride removal by the adsorbent increases from 32.5% to 70.5% at 100°C to 800°C of Seashell activation temperature. The maximum removal of fluoride ions can be obtained by using 600°C of temperature.



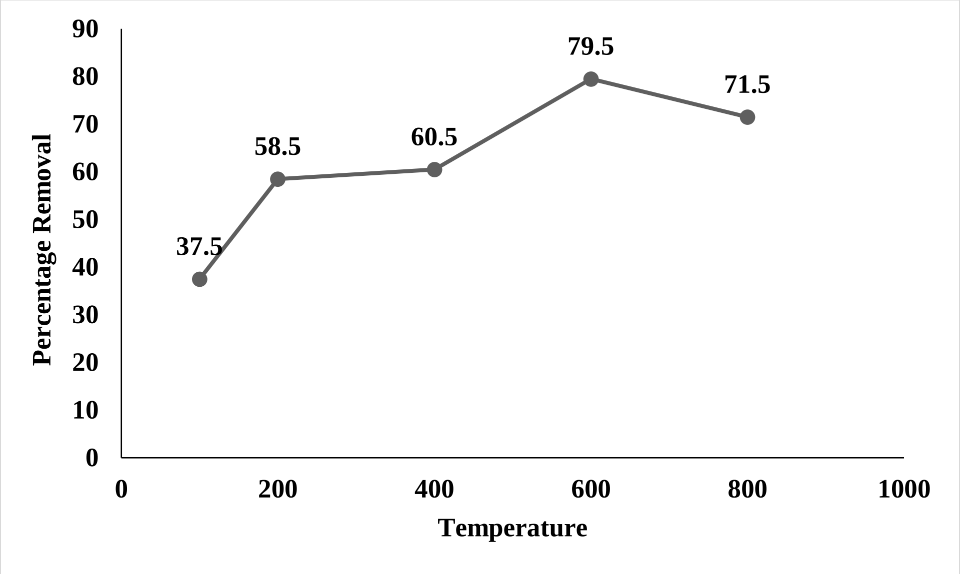
Graph 7-5:Percentage Removal VS Seashell Activation Temperature

Experiment: Dolomite & Seashell mixture (1:1) as Adsorbent

Adsorbent Dose: 20 g/l, pH: 7-8, Contact time: 30 min

Temperature	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
100	20	12.5	7.5	37.5
200	20	8.3	11.7	58.5
400	20	7.9	12.1	60.5
600	20	4.1	15.9	79.5
800	20	5.7	14.3	71.5

Experiment shows percentage of fluoride removed at different adsorbent activation temperature range from 100°C to 800°C. It is observed that fluoride removal by the adsorbent increases from 37.5% to 71.5% at 100°C to 800°C of mixture activation temperature. The maximum removal of fluoride ions can be obtained by using 600°C of temperature.



Graph 7-6:Percentage Removal VS Mixture Activation Temperature

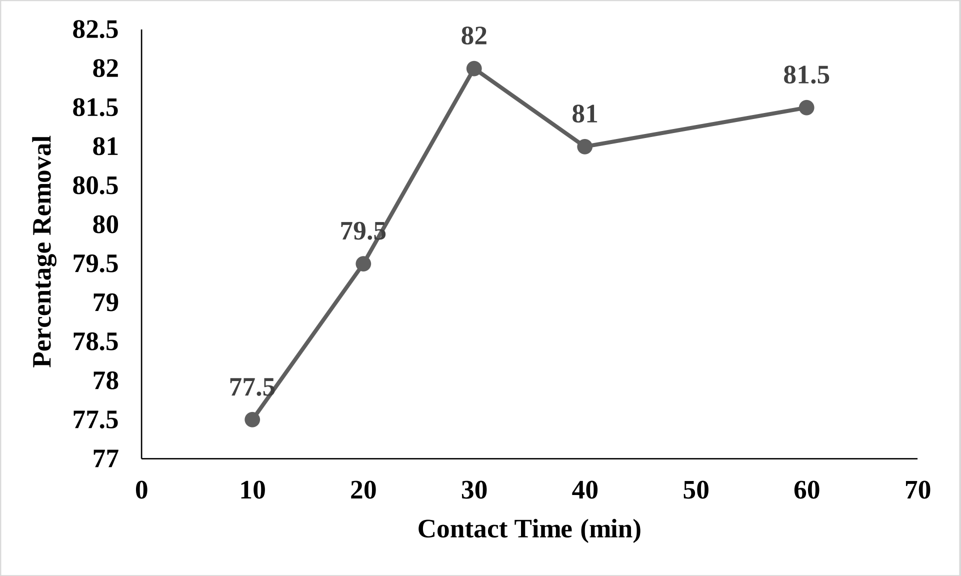
7.3 Effect of Contact Time

Experiment: Dolomite as Adsorbent

Adsorbent Dose: 20 g/l, pH: 7-8, Temperature: 600°C, Contact Time: 30 min

Contact Time (min)	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
10	20	4.5	15.5	77.5
20	20	4.1	15.9	79.5
30	20	3.6	16.4	82
40	20	3.8	16.2	81
60	20	3.7	16.3	81.5

Experiment shows percentage of fluoride removed at different contact time range from 10 min to 60 min. It is observed that fluoride removal by the adsorbent increases from 77.5% to 81.5% at 10 min to 60 min of contact time. The maximum removal of fluoride ions can be obtained by using 30 min of contact time of dolomite.



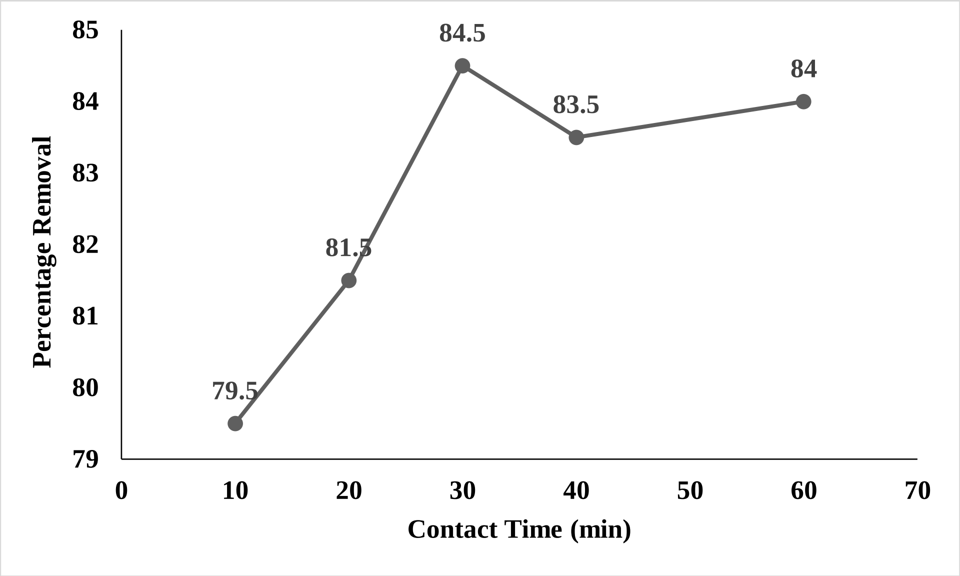
Graph 7-7:Percentage Removal VS Dolomite contact time

Experiment: Seashell as Adsorbent

Adsorbent Dose: 20 g/l, pH: 7-8, Temperature: 600°C, Contact Time: 30 min

Contact Time (min)	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
10	20	4.1	15.9	79.5
20	20	3.7	16.3	81.5
30	20	3.1	16.9	84.5
40	20	3.3	16.7	83.5
60	20	3.2	16.8	84

Experiment shows percentage of fluoride removed at different contact time range from 10 min to 60 min. It is observed that fluoride removal by the adsorbent increases from 79.5% to 84% at 10 min to 60 min of contact time. The maximum removal of fluoride ions can be obtained by using 30 min of contact time of seashell.



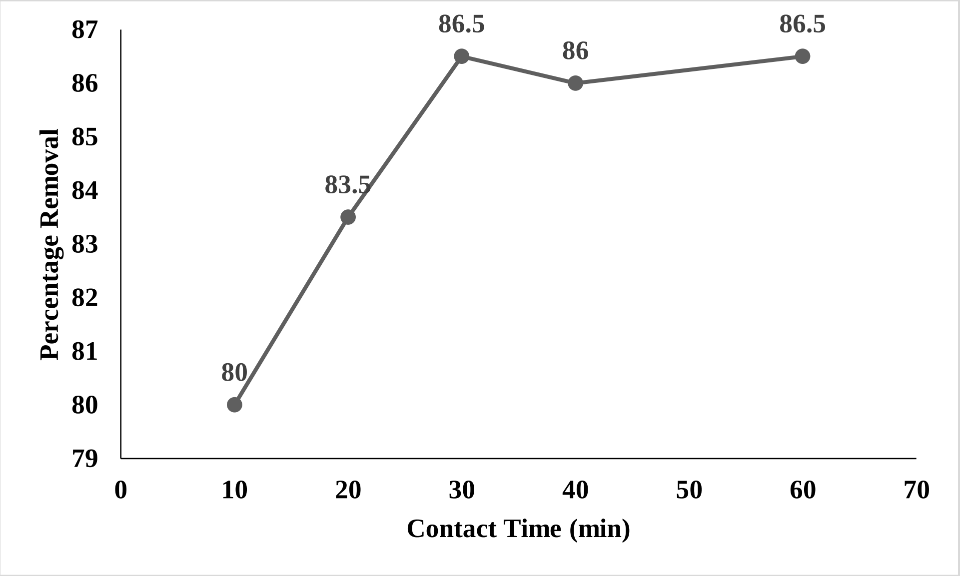
Graph 7-8:Percentage Removal VS Seashell contact time

Experiment: Dolomite & Seashell Mixture (1:1) as Adsorbent

Adsorbent Dose: 20 g/l, pH: 7-8, Temperature: 600°C, Contact Time: 30 min

Contact Time (min)	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
10	20	4	16	80
20	20	3.3	16.7	83.5
30	20	2.7	17.3	86.5
40	20	2.8	17.2	86
60	20	2.7	17.3	86.5

Experiment shows percentage of fluoride removed at different contact time range from 10 min to 60 min. It is observed that fluoride removal by the adsorbent increases from 80% to 86.5% at 10 min to 60 min of contact time. The maximum removal of fluoride ions can be obtained by using 30 min of contact time of dolomite & seashell mixture.



Graph 7-9:Percentage Removal VS Mixture (1:1) contact time

7.4 Effect of Adsorbent on Synthetic & Actual water Sample

Experiment: Adsorbent on Synthetic water sample

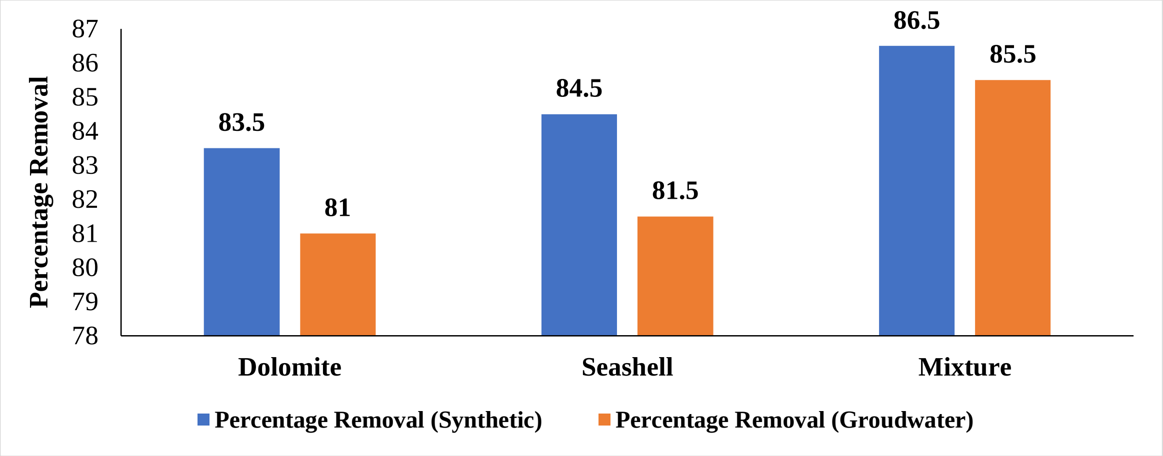
Adsorbent Dose: 20 g/l, pH: 7-8, Temperature: 600°C, Time: 30 min

Adsorbent	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
Dolomite	20	3.3	16.7	83.5
Seashell	20	3.1	16.9	84.5
Mixture	20	2.7	17.3	86.5

Experiment: Adsorbent on Groundwater sample

Adsorbent Dose: 20 g/l, pH: 7-8, Temperature: 600°C, Time: 30 min

Adsorbent	Initial Concentration (mg/l)	Final Concentration (mg/l)	Removal	Percentage Removal
Dolomite	20	3.8	16.2	81
Seashell	20	3.7	16.3	81.5
Mixture	20	2.9	17.1	85.5



Graph 7-10: Percentage Removal on Synthetic & Actual water sample

CHAPTER-VIII

8 WATER QUALITY

8.1 Introduction

Water is one of the most essential resources on our planet, vital for sustaining life and supporting ecosystems. Whether for drinking, agriculture, industry, or recreational purposes, the quality of water plays a critical role in human health and the overall well-being of our environment. Water quality refers to the chemical, physical, biological, and radiological characteristics of water that determine its suitability for specific uses. Maintaining good water quality is of paramount importance to ensure a safe and sustainable water supply. However, various natural and anthropogenic factors can impact water quality, leading to potential hazards and challenges. Natural processes like weathering of rocks, soil erosion, and microbial activity can introduce various substances into water bodies. Additionally, human activities, such as industrial discharge, agricultural runoff, and improper waste disposal, can introduce pollutants that degrade water quality. Contaminants in water can range from naturally occurring substances like dissolved minerals and metals to synthetic chemicals, pathogens, and microorganisms. High concentrations of pollutants can make water unsafe for consumption, detrimental to aquatic life, and unsuitable for agricultural or industrial uses. Hence, monitoring and managing water quality have become critical responsibilities to protect public health and preserve ecosystems. The measurement and assessment of water quality parameters are done through a series of physical, chemical, and biological tests. These parameters include pH, temperature, dissolved oxygen, turbidity, total dissolved solids (TDS), nutrient levels (nitrogen and phosphorus), heavy metals, coliform bacteria, and various other indicators of water health. Analyzing these factors helps scientists, water authorities, and environmental agencies determine if water bodies meet regulatory standards and identify potential sources of contamination. One of the major concerns in water quality management is the presence of harmful pollutants, such as pesticides, heavy metals, and organic chemicals, which may have long-lasting effects on human health and aquatic ecosystems. Industrial discharges, agricultural runoff, and untreated sewage are among the primary sources of these pollutants. Additionally, emerging contaminants, like pharmaceuticals and microplastics, have raised new challenges in monitoring and safeguarding water quality. Addressing water quality issues requires a multi-faceted approach that involves scientific research, policy development, public awareness, and active participation from communities, industries, and governments. Implementing effective water quality management strategies, such as water treatment, watershed protection, and pollution prevention, is essential to safeguard freshwater resources for future generations.

8.2 Literature Review

Water quality is a crucial aspect of environmental health, and its assessment is essential to ensure the sustainability of surface water resources. In this study conducted by P. J. Puri, M. K. N. Yenkie, and their team, the focus was on evaluating the water quality of lakes in Nagpur city, Maharashtra, India, during three seasons: monsoon, winter, and summer. The Water Quality Index (WQI) was employed as a numerical indicator to assess and compare the overall water quality of different lakes. The study aimed to identify seasonal variations and potential factors affecting water quality.

8.2.1 Methods:

The researchers utilized the Water Quality Index (WQI), a comprehensive numerical tool that integrates various water parameters to provide an overall indication of water quality. The WQI calculator provided by the National Sanitation Foundation (NSF) information system was used for the calculations. By employing this index, the researchers were able to make comparative assessments of water quality across the studied lakes during the different seasons.

8.2.2 Findings:

1. **Monsoon Season**: During the monsoon season, the water quality of the studied lakes was rated as fair. The influx of monsoon rainfall likely contributed to the dilution of pollutants, leading to an improvement in water quality during this period.
2. **Winter Season:** The water quality of the lakes deteriorated during the winter season, with a medium water quality rating observed. Factors such as reduced water flow and stagnation potentially contributed to the accumulation of pollutants, negatively impacting water quality.

3. **Summer Season:** The summer season exhibited the poorest water quality among the three seasons studied. High temperatures and lower water levels likely exacerbated the concentration of pollutants, resulting in declining water quality.

8.2.3 Specific Lake Observations:

1. **Gorewada Lake:** Gorewada lake consistently showed a medium water quality rating across all seasons, except during the monsoon season. Further investigation is required to determine the reasons behind this specific pattern.
2. **Aquatic Weed Invasion:** Futala, Ambazari, and Gandhisagar lakes experienced a decline in aesthetic water quality over the past decade due to the invasion of aquatic weeds, such as hydrilla and water primrose. Aquatic weed growth negatively impacts water quality by reducing dissolved oxygen levels and interfering with natural ecosystems.

The findings of this study underscore the importance of implementing effective measures for surface water quality management in Nagpur city. Addressing challenges such as aquatic weed invasion, monitoring and regulating pollutant discharges, and maintaining water flow to prevent stagnation are crucial steps in preserving and improving water quality. The Water Quality Index serves as a valuable tool to communicate water quality status, identify areas for improvement, and promote the adoption of protective practices for sustainable water resources.

Lakes serve as vital sources of drinking and domestic water for both rural and urban populations in India. In this study conducted by S. Chandra, A. Singh, and P. K. Tomar, the drinking water quality of three lakes, namely Porur Lake in Chennai, Hussain Sagar in Hyderabad, and Vihar Lake in Mumbai, was assessed. Water samples were collected from six different sites in each lake, and various water quality parameters, including pH, turbidity, TDS, BOD, COD, NO_3, Cl^-, and heavy metals, were analyzed. The findings revealed variations in water quality parameters at different sites, with some parameters exceeding the recommended limits set by WHO and BIS standards, indicating potential water pollution. Effective measures to control contamination and continuous water quality monitoring are essential to ensure access to safe drinking water and safeguard public health in these cities.

8.3 Analysis of Water Quality Parameters

Various water quality parameters such as Fluoride, Arsenic, Iron, Total Calcium, Total Sodium, Total Potassium, pH, Total & calcium hardness was analyzed of the collected samples. (After removal)

8.3.1 Fluoride Estimation

Chemicals Used: Fluoride Standard 100 mg/l (Thermo Scientific) TISAB III [Total Ionic Strength Adjustment Buffer] (Thermo Scientific)

Reagents: 10 mg/l, 1 mg/l & 0.1 mg/l of standard fluoride solution is prepared from the 100 mg/l Fluoride Standard solution using serial dilution method.

Instruments Used: Orion Star A214 pH / ISE Meter.

Calibration: Calibration curve is prepared using 0.1, 1 & 10 mg/l Fluoride Solution.

Preparation of Samples: To every water sample 10% of TISAB III is added.

Figure 8-1: Orion Star A214 pH/ISE Meter

8.3.2 Iron Estimation

Chemicals Used: Iron Standard Solution 1000 mg/l (Merck Life Science Pvt. Ltd.), Acetic Acid Glacial 100% [CH_3COOH] (Merck Life Science Pvt. Ltd.), Sodium Acetate Anhydrous extra pure AR [$C_2H_3NaO_2$] (Sisco Research Laboratories Pvt. Ltd.), Hydroxyl Ammonium Chloride [$(NH_2OH).HCL$] (Merck Life Science Pvt. Ltd.) & 1,10 – Phenanthroline monohydrate [$C_{12}H_8N_2.H_2O$] (Merck Life Science Pvt. Ltd.).

Figure 8-2: Orion Aquamate 8000 UV – VIS Spectrophotometer at 510 nm Wavelength

Reagents: From the Iron Standard Stock solution 10 mg/l was prepared, from that 0.25, 0.50 and 1.0 mg/l was prepared. Iron Buffer per 1000 ml – 3.8 gm Sodium Acetate + 48 ml Acetic Acid then the volume was made up to the mark with dd H_2O. Hydroxyl Ammonium Hydrochloride – 10% of total volume Ortho-phenanthroline – 0.25% of total volume.

Calibration: Calibration curve was prepared using Blank, 0.25, 0.50 & 1.0 mg/l Iron standard solution.

Figure 8-3: Chemical used for iron estimation

Preparation of Samples: In a 25 ml volumetric flask for every 5 ml of water sample add 10 ml of Iron Buffer, 2.5 ml of Hydroxyl Ammonium Hydrochloride and 2 ml of Ortho- phenanthroline then the volume was made up to the mark with dd H_2O.

Instrument Used: Orion Aquamate 8000 UV – VIS Spectrophotometer at 510 nm Wavelength.

8.3.3 Total Calcium Estimation

Chemicals Used: Calcium Carbonate Precipitated [$CaCO_3$] (Merck Life Science Pvt. Ltd.), and Hydrochloric Acid about 35% (Merck Life Science Pvt. Ltd.).

Reagents: For the preparation of 250 ml 1000 mg/l Calcium Carbonate Standard Solution – 0.625 gm $CaCO_3$ + 1:1 HCl (dropwise) in a volumetric flask, then volume made up to the mark by dd H_2O.

Instrument Used: HPG Systems Microcontroller Flame Photometer G- 301.

Calibration: From 1000 mg/l Standard Solution 10, 20, 50, 80, 100 mg/l is prepared. Then Calibration Curve is prepared using Blank, 10, 20, 50, 80 & 100 mg/l Calcium Standard Solution.

Preparation of Samples: Filter the sample water using a filter paper before measuring.

8.3.4 Total Sodium Estimation

Chemicals Used: Sodium Chloride Precipitated [$NaCl$] (Merck Life Science Pvt. Ltd.)

Reagents: For the preparation of 250 ml 1000 mg/l Sodium Chloride Standard Solution – 0.625 gm $NaCl$ is added in a volumetric flask, then volume make up to the mark by dd H_2O.

Instrument Used: HPG Systems Microcontroller Flame Photometer G-301

Calibration: From 1000 mg/l Standard Solution 10, 20, 50, 80, 100 mg/l is prepared. Then Calibration Curve is prepared using Blank, 10, 20, 50, 80 & 100 mg/l Sodium Standard Solution.

Figure 8-4: HPG Systems Microcontroller Flame Photometer G- 301

Preparation of Samples: Filter the sample water using a filter paper before measuring.

8.3.5 Total Potassium Estimation

Chemicals Used: Potassium Chloride Precipitated [KCl] (Merck Life Science Pvt. Ltd).

Reagents: For the preparation of 250 ml 1000 mg/l Potassium Chloride Standard Solution – 0.625 gm KCl is added in a volumetric flask, then volume made up to the mark by dd H_2O.

Instruments Used: HPG Systems Microcontroller Flame Photometer G- 301.

Calibration: From 1000 mg/l Standard Solution 10, 20, 50, 80, 100 mg/l is prepared. Then Calibration Curve is prepared using Blank, 10, 20, 50, 80 & 100 mg/l Potassium Standard Solution.

Preparation of Samples: Filter the sample water using a filter paper before measuring.

8.3.6 pH Estimation

Chemicals Used: Diluted Hydrochloric Acid (HCl)

Instrument Used: pH metre with temperature & pH probe.

Calibration: Three solutions having a known pH value of 4.0, 7.0 & 10.0 are taken as a standard to calibrate the pH metre.

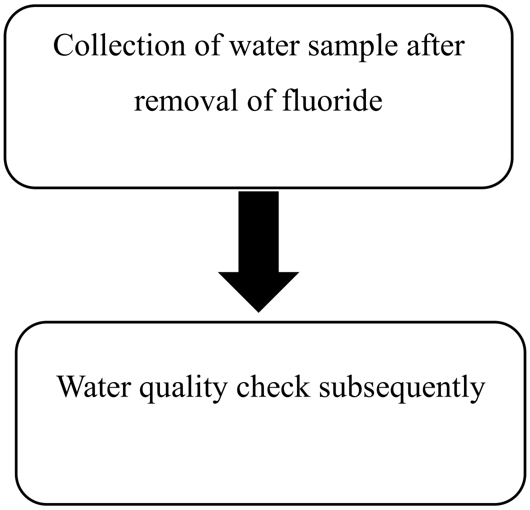
Figure 8-5: pH metre

Table 8-1: Physical and chemical properties of tube well water as per BIS 10500-2012

Sl.No.	Parameter	Unit	Acceptable Limit	Permissible Limit
1	Colour	Hazen Unit	5	15
2	Odour		Agreeable	Agreeable
3	pH		6.5-8.5	No relaxation
4	Turbidity	NTU	1	5
5	Total Dissolved Solids	mg/l	500	2000
6	Ammonia	mg/l	0.5	No relaxation
7	Boron	mg/l	0.5	1
8	Calcium	mg/l	75	200
9	Chloride	mg/l	250	1000
10	Fluoride	mg/l	1	1.5
11	Magnesium	mg/l	30	100
12	Nitrate	mg/l	45	No relaxation
15	Total Alkalinity	mg/l	200	600
16	Sulphate	mg/l	200	400
17	Total Hardness	mg/l	200	600
18	Temperature	Degree C	-	
19	Sodium	mg/l	-	
21	Iron	mg/l	0.3	No relaxation
22	Cadmium	mg/l	0.003	No relaxation
23	Chromium	mg/l	0.05	No relaxation

8.4 Result and Discussion

The water sample was collected after removing fluoride, and its water quality was subsequently checked.



After analyzing the water samples and removing all the above-mentioned water quality parameters, it was found that all the parameters were within the permissible limits.

CHAPTER-IX

9 Waste Management

Fluoride contamination in water sources is a growing environmental concern in many regions worldwide. High fluoride levels in water can have detrimental effects on human health, leading to dental and skeletal fluorosis. The presence of fluoride in water also affects agricultural practices, as it can accumulate in crops and negatively impact plant growth. Proper waste management of fluoride-contaminated flocks is crucial to prevent further environmental contamination and health risks. In recent years, a sustainable approach to manage fluoride-contaminated flocks has emerged, involving their reuse through brick encapsulation, which not only helps in waste disposal but also offers a potential solution for constructing low-cost, eco-friendly bricks.

9.1 Waste Management of Fluoride-Contaminated Flocks:

Fluoride-contaminated flocks refer to the sludge or precipitates that form when water with high fluoride levels is treated using coagulants such as aluminum sulfate or lime. These flocks contain significant amounts of fluoride and other pollutants removed from the water, making their proper disposal essential to prevent secondary contamination. Inadequate waste management of these flocks can lead to their leaching into the soil and groundwater, perpetuating the fluoride contamination cycle.

Traditionally, fluoride-contaminated flocks have been disposed of in landfills, which poses a considerable environmental burden. Landfilling is not a sustainable solution as it can lead to leachate generation, potentially contaminating nearby water bodies and posing health risks. To address these issues, innovative techniques, such as brick encapsulation, have been explored to manage fluoride-contaminated flocks effectively.

9.2 Reuse of Fluoride-Contaminated Flocks through Brick Encapsulation:

Brick encapsulation is a promising approach that involves incorporating fluoride-contaminated flocks into the manufacturing process of bricks. The technique not only aids in waste management but also offers an ingenious way to recycle the flocks and produce low-cost, durable, and eco-friendly bricks. The process typically involves the following steps:

1. Collection and Dewatering: The fluoride-contaminated flocks are first collected from the water treatment plants and dewatered to remove excess moisture.
2. Brick Formation: The dewatered flocks are mixed with traditional brick-making materials such as clay, sand, and water to form a homogenous mixture.
3. Molding and Drying: The mixture is then molded into brick shapes and allowed to dry naturally or through kiln firing.
4. Quality Testing: The finished bricks are subjected to quality tests to ensure their strength, durability, and compliance with construction standards.

9.3 Bricks Making Procedure:

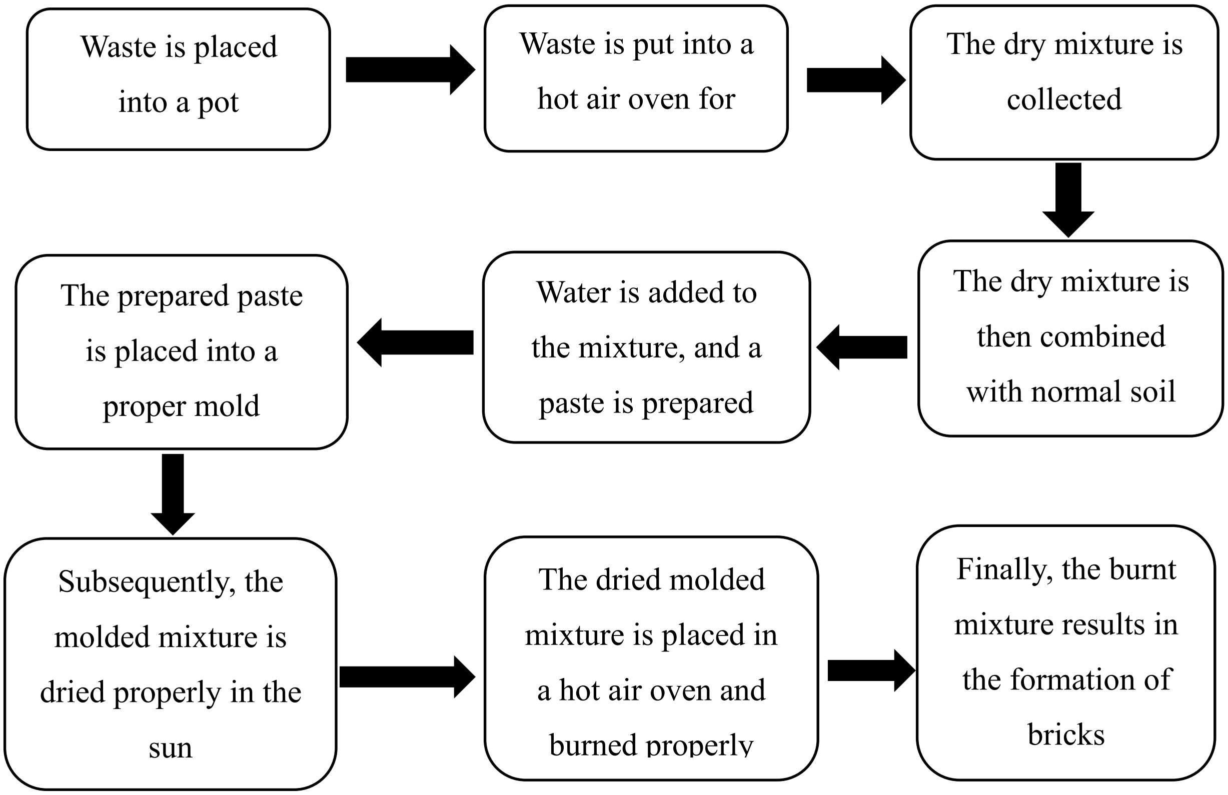


Chart 9-1: Bricks making procedure

9.4 Compressive Strength of bricks:

he compressive strength of bricks refers to the maximum amount of compressive load that a brick can withstand before it fails or breaks. It is an essential property to consider in construction and engineering, as it indicates the brick's ability to support heavy loads without undergoing deformation or crumbling.

The compressive strength of bricks can vary depending on their composition, manufacturing process, and specific use. Generally, bricks are classified into different classes based on their compressive strength as per IS-3495:1976 (Part-1). The most common classes of bricks include:

1. First-class bricks: These bricks have a high compressive strength and are used for load-bearing structures. Their compressive strength can range from 7 to 14 N/mm² (Newtons per square millimeter) or higher.
2. Second-class bricks: These bricks have a lower compressive strength than first-class bricks and are used for non-load-bearing walls. Their compressive strength can range from 3.5 to 7 N/mm².
3. Third-class bricks: These bricks have the lowest compressive strength and are used for temporary and unimportant structures. Their compressive strength can range from 2.5 to 3.5 N/mm².

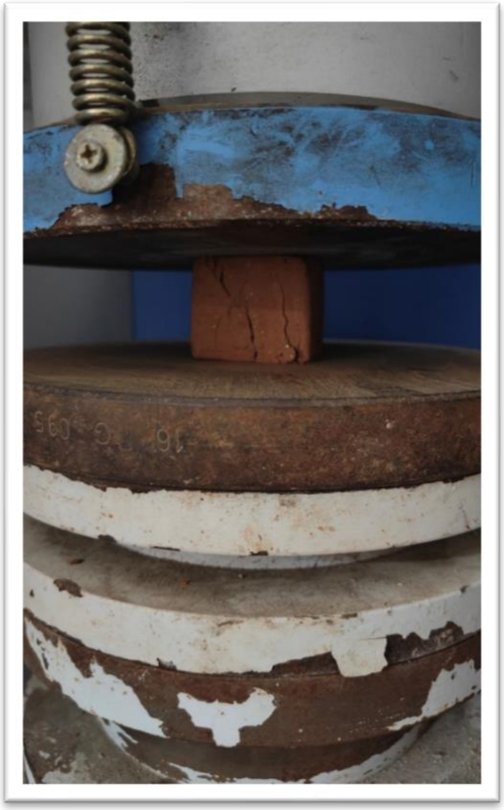


Figure 9-1: Compressive Strength Test

It's important to note that the compressive strength of bricks is typically measured in a laboratory under controlled conditions. The bricks are subjected to a compressive force until they break, and the maximum force applied before failure is recorded as the compressive strength. Additionally, some specialized bricks, such as engineering bricks or high-strength bricks, may have even higher compressive strength, reaching values of 40 N/mm² or more. When using bricks for construction, it is crucial to consider their compressive strength and choose the appropriate class based on the specific requirements of the structure. Proper selection ensures the safety and durability of the construction project. Compressive strength has been measured by the given equation below.

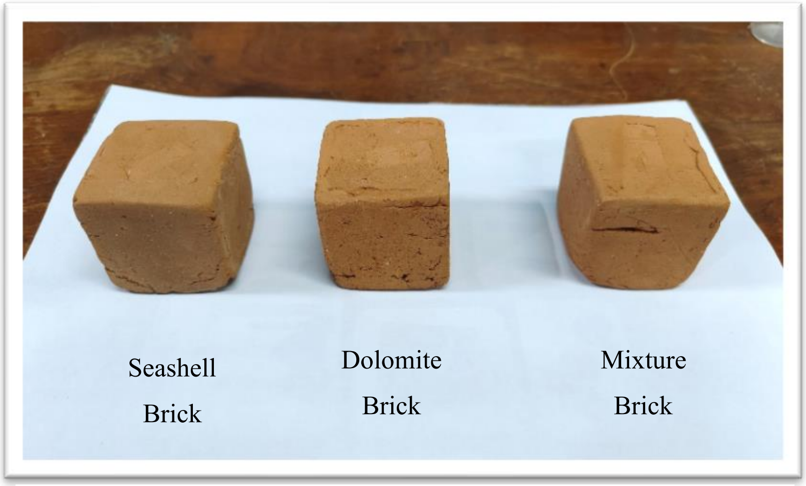


Figure 9-2: Bricks using waste materials

$$Compressive\ Strength \left(\frac{N}{mm^2}\right) = \frac{Applied\ Force}{Area}$$

Table 9-1: Compressive strength of bricks

Bricks (Waste Materials)	Weight (gm)	Strength Reading (kN)	Compressive Strength (N/mm^2)	Brick Class
Seashell	160	18	7.2	First Class
Dolomite	155	14.2	5.68	Second Class
Mixture	155	15.6	6.24	Second Class

*Note: All the bricks are 5mm×5mm size.

The process of heating clay bricks at a high temperature is known as "firing" or "burning." This process transforms the raw clay into a durable and hardened brick. The temperature and duration of firing can significantly influence the properties of the bricks, including their strength and porosity.

Firing temperature: The firing temperature for clay bricks typically ranges between 800 to 1000 degrees Celsius (1472 to 1832 degrees Fahrenheit). At this temperature range, the clay undergoes a process called vitrification, where the particles fuse together, resulting in a solid, dense structure.

Firing duration: The firing duration depends on various factors, such as the type of clay used, the size of the bricks, the kiln design, and the desired properties of the final product. Generally, bricks are fired for several hours, ranging from 24 to 48 hours or more. For common clay bricks, firing for 24 hours is quite common.

During the firing process, the bricks are placed inside a kiln, and the temperature is gradually raised to the desired firing temperature. After reaching the target temperature, the bricks are held at that temperature for the required duration to ensure even firing and proper vitrification of the clay.

9.5 Benefits of Brick Encapsulation for Fluoride-Contaminated Flocks:

Brick encapsulation offers numerous benefits for managing fluoride-contaminated flocks, some of which are listed below:

1. Waste Diversion: Brick encapsulation diverts fluoride-contaminated flocks from landfills, reducing the environmental impact and promoting a more sustainable waste management approach.
2. Reduced Environmental Contamination: By encapsulating the fluoride-contaminated flocks within bricks, the risk of leaching and secondary contamination is minimized, safeguarding soil and water quality.
3. Eco-Friendly Construction Material: The brick encapsulation process yields bricks with enhanced properties, making them suitable for various construction applications. These eco-friendly bricks reduce the demand for traditional clay bricks, conserving natural resources.
4. Cost-Effective: The use of fluoride-contaminated flocks in brick manufacturing lowers the production cost, resulting in a cost-effective building material option.

5. Community Development: Brick encapsulation projects can contribute to community development by creating employment opportunities and supporting local industries.
6. Contribution to Circular Economy: By converting waste into a valuable resource, brick encapsulation aligns with the principles of the circular economy, where materials are recycled and repurposed, minimizing waste and maximizing resource efficiency.

9.6 Challenges and Considerations:

While brick encapsulation offers a promising solution for managing fluoride-contaminated flocks, several challenges and considerations should be addressed. One of the primary concerns is ensuring that the encapsulated fluoride remains stable within the bricks and does not leach out over time. Rigorous testing and quality control measures are necessary to ascertain the long-term stability of the bricks and their compliance with construction standards. Additionally, community acceptance and awareness of the benefits of using these bricks may influence their widespread adoption in construction practices.

9.7 Conclusion:

Waste management of fluoride-contaminated flocks is a critical environmental issue, and brick encapsulation presents a sustainable and innovative solution to tackle this problem effectively. By reusing the flocks in brick production, we can mitigate the environmental impact, conserve natural resources, and create a cost-effective and eco-friendly construction material. Further research and development in this area are essential to optimize the encapsulation process, ensure the long-term stability of the bricks, and promote their integration into mainstream construction practices, contributing to a more sustainable future.

CHAPTER-X

10 CONCLUSION AND FUTURE SCOPE

The present study has proven that thermally activated adsorbents like dolomite, sea shell and their mixture has the excellent removal efficiency for fluoride. The removal capacity found 83.5% for dolomite at initial fluoride concentration of 20 mg/l and dose of 20 g/l. Whereas the removal capacity found 84.5% for sea shell at initial concentration of 20 mg/l & for mixture of dolomite & seashell the removal capacity is 86.5% at initial concentration of 20 mg/l. For both case dose is 20 g/l, activation temperature of 600°C & contact time of 30 min. But in all above cases if the activation temperature is increased to 800°C or the contact time increases to 1hour then there is a negligible increase in removal percentage. But at 600°C of activation temperature and in 30 min of contact time desirable amount of removal of fluoride can be achieved which is more than 80%. Moreover, it helps the method to be cost effective.

Effective waste management of fluoride-contaminated flocks is of utmost importance to address environmental concerns. Brick encapsulation emerges as a sustainable and innovative solution, offering numerous benefits in tackling this issue. By incorporating the flocks into brick production, we not only reduce environmental impact but also conserve precious natural resources. The resulting bricks are cost-effective, eco-friendly, and durable, making them a viable construction material. Continued research and development efforts are crucial to enhance the encapsulation process, ensuring the long-term stability of the bricks and promoting their widespread adoption in construction practices. This proactive approach contributes significantly to building a more sustainable and greener future for our planet.

CHAPTER-XI

11 REFERENCES

Allmann, R., & Koritnig, S. (1974). Fluorine. Handbook of Geochemistry, 2, 1.

Banks, D., Frengstad, B., Midtgård, A. K., Krog, J. R., & Strand, T. (1998). The chemistry of Norwegian groundwaters: I. The distribution of radon, major and minor elements in 1604 crystalline bedrock groundwaters. Science of the Total environment, 222(1-2), 71-91.

Brindha, K., & Elango, L. (2011). Fluoride in groundwater: causes, implications and mitigation measures. Fluoride properties, applications and environmental management, 1, 111-136.

Brunt, R., Vasak, L., & Griffioen, J. (2004). Fluoride in groundwater: Probability of occurrence of excessive. Netherlands Institute of Applied Geoscience TNO National Geological Survey, Utrecht, The Netherlands.

Chakraborti, D., Rahman, M. M., Ahamed, S., Dutta, R. N., Pati, S., & Mukherjee, S. C. (2016). Arsenic groundwater contamination and its health effects in Patna district (capital of Bihar) in the middle Ganga plain, India. Chemosphere, 152, 520-529.

Datta, P. S., Deb, D. L., & Tyagi, S. K. (1996). Stable isotope (18O) investigations on the processes controlling fluoride contamination of groundwater. Journal of contaminant hydrology, 24(1), 85-96.

De, A., Mridha, D., Ray, I., Joardar, M., Das, A., Chowdhury, N. R., & Roychowdhury, T. (2021). Fluoride exposure and probabilistic health risk assessment through different agricultural food crops from fluoride endemic Bankura and Purulia districts of West Bengal, India. Frontiers in environmental science, 9, 713148.

De, A., Mridha, D., Joardar, M., Das, A., Chowdhury, N. R., & Roychowdhury, T. (2022). Distribution, prevalence and health risk assessment of fluoride and arsenic in groundwater from lower Gangetic plain in West Bengal, India. Groundwater for Sustainable Development, 16, 100722.

De, A., Das, A., Joardar, M., Mridha, D., Majumdar, A., Das, J., & Roychowdhury, T. (2023). Investigating spatial distribution of fluoride in groundwater with respect to hydro-geochemical characteristics and associated probabilistic health risk in Baruipur block of West Bengal, India. Science of The Total Environment, 886, 163877.

Deshmukh, W. S., Attar, S. J., & Waghmare, M. D. (2009). Investigation on sorption of fluoride in water using rice husk as an adsorbent. Nature, Environment and Pollution Technology, 8(2), 217-223.

Dey, S., & Giri, B. (2016). Fluoride fact on human health and health problems: a review. Medical & Clinical Reviews, 2(01).

Dissanayake, C. B. (1991). The fluoride problem in the ground water of Sri Lanka-environmental management and health. International Journal of Environmental Studies, 38(2-3), 137-155.

Farooqi, A., Masuda, H., Kusakabe, M., Naseem, M., & Firdous, N. (2007). Distribution of highly arsenic and fluoride contaminated groundwater from east Punjab, Pakistan, and the controlling role of anthropogenic pollutants in the natural hydrological cycle. Geochemical journal, 41(4), 213-234.

Greenwood, N. N., & Earnshaw, A. (1984). Chemistry of the Elements. Pergamon Press, Toronto.

Guo, Q., Wang, Y., Ma, T., & Ma, R. (2007). Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China. Journal of Geochemical Exploration, 93(1), 1-12.

Indermitte, E., Saava, A., & Karro, E. (2009). Exposure to high fluoride drinking water and risk of dental fluorosis in Estonia. International journal of environmental research and public health, 6(2), 710-721.

Jacks, G., Bhattacharya, P., Chaudhary, V., & Singh, K. P. (2005). Controls on the genesis of some high-fluoride groundwaters in India. Applied geochemistry, 20(2), 221-228.

Kim, K., & Jeong, G. Y. (2005). Factors influencing natural occurrence of fluoride-rich groundwaters: a case study in the southeastern part of the Korean Peninsula. Chemosphere, 58(10), 1399-1408.

Maddocks, A., Young, R. S., & Reig, P. (2015). Ranking the world's most water-stressed countries in 2040.

Madhnure, P., Sirsikar, D. Y., Tiwari, A. N., Ranjan, B., & Malpe, D. B. (2007). Occurrence of fluoride in the groundwaters of Pandharkawada area, Yavatmal district, Maharashtra, India. Current Science, 675-679.

Maheshwari, R. C., & Hoelzel, G. (2002, January). Potential of membrane separation technology for fluoride removal from underground water. In Industrial Wastes (IW) Conference 2002 (pp. 620-636). Water Environment Federation.

Mandal, N., Doloi, B., Mondal, B., & Das, R. (2011). Optimization of flank wear using Zirconia Toughened Alumina (ZTA) cutting tool: Taguchi method and Regression analysis. Measurement, 44(10), 2149-2155.

Mariappan, P., Yegnaraman, V., & Vasudevan, T. (2002). Defluoridation of water using PAHS. JOURNAL-INDIAN WATERWORKS ASSOCIATION, 34(3), 217-224.

Mariappan, P. and Vasudevan, T. (2011). Domestic defluoridation techniques and sector approach for fluorosis mitigation. Pages 1-11.

Mariappan, R., Vairamuthu, R., & Ganapathy, A. (2015). Use of chemically activated cotton nut shell carbon for the removal of fluoride contaminated drinking water: kinetics evaluation. Chinese Journal of Chemical Engineering, 23(4), 710-721.

Messaïtfa, A. (2008). Fluoride contents in groundwaters and the main consumed foods (dates and tea) in Southern Algeria region. Environmental geology, 55(2), 377-383.

Mirlean, N., & Roisenberg, A. (2007). Fluoride distribution in the environment along the gradient of a phosphate-fertilizer production emission (southern Brazil). Environmental geochemistry and health, 29, 179-187.

Mjengera, H., & Mkongo, G. (2002). Appropriate Deflouridation Technology for Use in Flourotic Areas in Tanzania 1. 3rdWaterNet/Warfsa Symposium 'Water Demand Management for Sustainable Development. Ministry of Water and Livestock Development. Dar Es Salaam, Tanzania.

Naseem, S., Rafique, T., Bashir, E., Bhanger, M. I., Laghari, A., & Usmani, T. H. (2010). Lithological influences on occurrence of high-fluoride groundwater in Nagar Parkar area, Thar Desert, Pakistan. Chemosphere, 78(11), 1313-1321.

Nogami, K., Iguchi, M., Ishihara, K., Hirabayashi, J. I., & Miki, D. (2006). Behavior of fluorine and chlorine in volcanic ash of Sakurajima volcano, Japan in the sequence of its eruptive activity. Earth, planets and space, 58(5), 595-600.

Pillai, K. S., & Stanley, V. A. (2002). Implications of fluoride--an endless uncertainty. Journal of Environmental Biology, 23(1), 81-87.

Pushpanjali, K., Mohan, M., & Renuka, P. (2013). Assessing impact of oral diseases on oral health related quality of life of institutionalized elderly using OHIP-14 in Bengaluru: A cross sectional study. Journal of Dental and Medical Science, 6(6), 57-64.

Ravikumar, A., & MMN, K. (2015). Mitigation of Fluoride from Groundwater by Natural Clay as an Adsorbent. Iranian (Iranica) Journal of Energy & Environment, 6(4).

Razbe, N. R. N. (2013). Various options for removal of fluoride from drinking water. IOSR Journal of Applied Physics, 3(2), 40-47.

Rwenyonyi, C. M., Birkeland, J. M., Haugejorden, O., & Bjorvatn, K. (2000). Age as a determinant of severity of dental fluorosis in children residing in areas with 0.5 and 2.5 mg fluoride per liter in drinking water. Clinical Oral Investigations, 4, 157-161.

Susheela, A. K. (1984). Epidemiology and control of fluorosis in India. J Nutr Found India, 1-3.

Waghmare, S. S., & Arfin, T. (2015). Fluoride removal from water by various techniques. Int. J. Innov. Sci. Eng. Technol, 2(3), 560-571.

WHO, G. (2011). Guidelines for drinking-water quality. World health organization, 216, 303-304.