Treated and Regenerated Deactivated Alumina Solid Waste for Fluoride Removal from Ground Water as an Adsorbent.

By:Habtamu Tadesse Eba

A Thesis Submitted to

Department of Applied Chemistry

College of Applied Natural Science

In Partial Fulfillment of the Requirements for the Degree of

Master of Science in Chemistry (Industrial Chemistry)

Office of Graduate Studies

Adama Science and Technology University

March, 2025

Adama, Ethiopia

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APPROVAL PAGE

I, the advisors of the thesis entitled "**Treated and Regenerated Deactivated Alumina Solid Waste as an Adsorbent for Fluoride Removal from Ground Water**" and developed by **Habtamu Tadesse Eba**, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Major Advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by **Habtamu Tadesse Eba** have read and evaluated the thesis entitled "**Treated and Regenerated Deactivated Alumina Solid Waste as an Adsorbent for Fluoride Removal from Ground Water**" and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemistry (Industrial Chemistry).

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Finally, approval and acceptance of the thesis are contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

Department Head	Signature	Date
School Dean	Signature	Date
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DECLARATION

I hereby declare that this Master Thesis entitled "**Treated and Regenerated Deactivated Alumina Solid Waste as an Adsorbent for Fluoride Removal from Ground Water**" been carried out by me under the supervision of Dr.Bedasa Abdisa , during the year 2024/2025 as part of Master of Science Program in Industrial Chemistry. I further declare that this work has not been submitted to any other Universities or institution for the award of any degree. All quotations and their sources were specially acknowledged by means of references.

Name: Habtamu Tadese

Signature _____

This M.Sc thesis has been submitted for examination with my approval as thesis advisor.

Advisor Name: Bedasa Abdisa (PhD)

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Date of Submission -------/-------/--------

ACKNOWLEDGEMENTS

Firstly, I am sincerely thankful to my almighty GOD for his blessing that giving me strength and wisdom to successfully complete this study .To Him alone, I give all the glory.

Although this thesis work ultimately represents my accomplishments, I have benefited significantly from multiple peoples that I would like to acknowledge. First, I am grateful to goes to my hard working advisor: Dr. Bedasa Abdisa for his excellent supervision and scientific input in this research work. It is a great privilege and honor for me to be advised by him. I special thanks him, whose unique scientific passion and extensive knowledge. I strongly admire and will always aspire to achieve; his patience, daily guidance and support have kept me on the right track all the way to the end. His positive influence will always be a guide as I venture out on my own to tackle challenging scientific problems. I am lucky to be guided and advised by him and in general, his brotherly and humble approach makes me successful. Then I would like to express my sincere gratitude to Awash Melkassa Chemical Factory for providing all the necessary assistance and facilities to conduct my research work. I also express my genuine heartfelt gratitude to all workers of the factory, especially to Quality Control Laboratory staff members for their help on my work. I never forgot your great contribution. I greatly acknowledge Mr Demeke from ASTU, School of Material Sciences and Engineering for his assistance in XRD, SEM, and UV-VIS characterization. Again, I would like to give the greatest thanks to OSHO staff members, specially, Mr. Getachew and Mr. Temam to share their knowledge and permit me ISE for the determination of Fluoride Content in ground water. Finally, I would like to thank greatly Adama Science and Technology University for giving me the opportunity to join this postgraduate.

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LIST OF ABBREVIATIONS AND ACRONYMS

AA	Activated Alumina
Al-HAP	Aluminum modified hydroxyapatite
AMCF	Awash Melkasa Chemical Factory
ASTU	Adama Science and Technology University
DA-SW	Deactivated Alumina Solid Waste
EPA	Environmental Protection Agency
FISE	Fluoride Ion Selective Electrode
FT-IR	Fourier transforms infrared spectroscopy
IQ	Intelligence Quotient
ISE	Ion Selective Electrode
IUPAC	International Union of Pure and Applied Chemistry
OSHO	Oromia Self Health Organization
PFO	Pseudo-First-Order
PSO	Pseudo-Second-Order
RAA	Regenerated Activated Alumina
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
TISAB	Total Ionic Strength Adjustment Buffer
TSS	Total Suspended Solid
UNESCO	United Nations Educational, Scientific and Cultural Organization
UV-VIS	Ultraviolet Spectrophotometer spectroscopy
WHO	World Health Organization
XRD	X-ray Diffraction

ABSTRACT

Fluorine is among the prioritized contaminant of water that causes for fata problem if taken above recommended levels. Hence, the design and development of effective management is very crucial. One of the removal techniques of fluoride is implementing a cost effective, locally accessible, not time consuming and at the same time, environmentally friendly technology has been widely studied by many scholars. The objective of this study was to use treated deactivated Alumina solid waste disposed from the hydrogen peroxide plant as an adsorbent for the effective removal of fluoride from Fluoride attacked ground water at optimized contact time, adsorbent dose, and initial concentration by using response surface methodology (RSM). All batch scale experiments were carried out according to the statistical-design order. Central composite design (CCD) was applied to ascertain the effect of adsorbent dose, initial fluoride con centration and contact time on fluoride adsorption. The original deactivated alumina solid waste disposed from hydrogen peroxide plant; the sample were treated with Soxhlet extraction with a mixture of methanol and ethyl acetate, caustic soda treatment followed by thermal treatment at a temperature of 500 ^{0}C. The prepared deactivated alumina was characterized using XRD, SEM, FTIR and UV-DRS techniques. The characterization result confirms that the prepared adsorbent found to be crystalline, absorbs light in the visible and UV-DRS region. The FTIR results show the presence of various functional groups such as carboxylic acids, ketones, aldehydes and related. The SEM images and XRD patterns of the adsorbent were recorded to get a better insight into the adsorption process. The effects of experimental parameters such as contact time, dosage of adsorbent and initial concentration of fluoride were thoroughly investigated. The maximum fluoride removal efficiency (92.61%) was obtained at adsorbent dose of 2 g, contact time 90 min, and initial fluoride concentration of 5 mg/L. The adsorption result fitted well with pseudo-second order kinetic and Freundlich model. The current study reveals that the prepared deactivated alumina waste was found to be highly effective in removing fluoride ion from flouring containing ground water sources.

Keywords: *Adsorption, activated alumina and Fluoride removal.*

1. INTRODUCTION

1.1. Background of the study

A crucial physicochemical component that needs to be taken into account when evaluating the quality of water is the amount of fluoride present in drinking water. The World Health Organization states that 1.5 mg/L is the maximum amount of fluoride ions that can be present in drinking water(WHO, 2008). While dental caries is thought to be prevented by a low daily intake of fluoride (0.6 mg/L), a larger daily dose has been connected to persistent dental and skeletal fluorosis (Guo & Guo, 2013). Fluoride is present in several part of Ethiopian water sources at high levels of up to 33 mg/L (Kloos & Tekle Haimanot, 1999).The Ethiopian Ministry of Water Resources estimated that more than 14 million people in the Ethiopian Rift Valley still rely on fluoride-contaminated drinking water(Moreno & Moreno, 2018).

When consumed within the allowed limits, fluoride ion (F^-) helps calcify dental enamel and protects strong, healthy bones, especially in youth. Excessive fluoride ion intake from a variety of sources can cause dental fluorosis (discoloration and pitting of teeth), skeletal fluorosis (pain and stiffness in the backbone and joints) and non-skeletal fluorosis (skin rashes, anxiety, weaker muscles, etc.).The most severely impacted areas of the human body are the teeth and bones, which are particularly negatively impacted when fluoride intake reaches or surpasses 3.18 mg/L. In addition to lowering children's IQ, it affects infants' brain development and results in abnormal behaviors (IQ)(Dhawane et al., 2017).In addition, osteosclerosis (brittle bones), arthritis, brain impairment, infertility, and terminal cancer have all been linked to fluoridation(Ahmad et al., 2022). Due to this fact, the effective management and control of fluoride removal has been current world-wide issue that attracts the attentions of researchers around the globe.

Fluoride has previously been removed from drinking water using a variety of methods, including adsorption, ion exchange, electrolysis, electrocoagulation, and precipitation procedures. Majority of those mentioned methods have numerous limitations and challenges such as time consume, requires advanced protocol, advanced techniques, and not easy for handing and managing. Instead, adsorption has been the most commonly adopted removal of fluoride ions that involves the use of various adsorbents such as activated alumina, activated charcoal,

zeolites, nanomaterial and others. Of the various types of adsorbents, activated alumina prepared from waste materials has been the most cost effective and environmentally friendly adsorbents as compared to other materials due to its suitable physic-chemical properties such as simple, versatile, and appropriate process for treating a drinking water system, especially for small communities. Adsorption can remove ions over a wide pH range and to residual concentrations lower than precipitation, and it is an economical technique(Ram et al., 2016).

The application of adsorption has grown significantly on a large scale for local community water, despite the fact that it is widely acknowledged to be the most ideal and suitable process when compared to other methods. This is because adsorption is very cost-effective in getting rid of most contaminants, yields high-quality water, and can withstand larger flow rates. In past few years, many researchers have developed low cost and efficient adsorbents for treatment of pollutants from contaminated water. Many adsorbents have been used for defluoridation viz. activated carbon , amorphous alumina , activated alumina , and low-priced adsorbent like calcite, clay, charcoal, red mud, rice husk, and zeolites(Dhawane et al., 2017).

Alumina is the most widely utilized de-fluoridating material because of its high availability, enhanced surface porosity, mechanical robustness, and significant affinity for the selective capture of fluoride ions with appropriate surface shape. Its crystalline structure determines its capacity to extract fluoride from drinking water (Ahmad & Singh, 2022).

Fluoride ions have a strong attraction to multivalent metal ions, which makes alumina (Al_2O_3) a preferred metal oxide for use as an adsorbent material in wastewater fluoride removal. Alumina exhibits a high degree of fluoride affinity and selectivity. This characteristic has long drawn the attention of researchers (Pillai et al., 2021). Furthermore, alumina's widespread use in de-fluoridation is attributed to its inexpensive price, easy accessibility, and amphoteric character. Alumina, in the form of commercially available activated alumina, is commonly used for de-fluoridation. However, there aren't many studies on the use of acid activated alumina (AAA), a low-cost and practical high surface area adsorbent, to remove fluoride ions from aqueous solutions (P. S. Kumar et al., 2019).

In this thesis work, the method of treatment and regeneration of used alumina produced during hydrogen peroxide process was employed as adsorbent for fluoride removal from ground water.

1.2. Statement of the Problem

Fluoride contamination in groundwater is a significant environmental and public health concern, particularly in regions where natural geological processes or industrial activities contribute to elevated fluoride levels. In Ethiopia, the main supply of drinking water is usually groundwater. Reports of fluoride concentrations over 1.5 mg/L have been made in many parts of Ethiopia. However, fluoride levels in the Rift Valley settlements, which get their fluoride from boreholes, are said to range from 1 to 33 mg/L(Kloos & Tekle Haimanot, 1999). High temperatures, low calcium content, high subsurface carbon dioxide pressure, and volcanoes have all been linked to this high fluoride ion concentration content. Dental and skeletal fluorosis has become a major medical issue in the Rift Valley of Ethiopia after many years of consuming water from drilled wells. Due to their limited fluoride absorption ability and cultural differences, commercially available adsorption technologies like activated alumina and bone char are not cost-effective in the Ethiopian Rift Valley, where groundwater is significantly loaded in fluoride (Gizachew,2022)

Fluorine from drinking water has also been removed using various adsorbents. Adsorbents with a high removal capacity, low cost, and convenient accessibility, however, are unquestionably the best option for treating groundwater contaminated by fluoride. Deactivated alumina solid waste discarded from a reversion bed of hydrogen peroxide plant, after treated and regenerated has shown potential as an adsorbent for fluoride removal due to its high surface area and porous structure. However, the disposal of deactivated alumina poses environmental challenges, contributing to solid waste management issues. The regeneration of deactivated alumina not only offers a sustainable solution for waste management but also enhances its adsorption capacity for fluoride ions.

The study aims to investigate the feasibility of utilizing regenerated alumina from deactivated alumina solid waste (DAl-SW) disposed from hydrogen peroxide plant, as an adsorbent for fluoride removal from groundwater. By focusing on the regeneration of deactivated alumina and its subsequent application in water treatment processes, the research seeks to address the challenges associated with fluoride contamination and contribute to the development of sustainable remediation technologies

To the best of our knowledge, there is a limited research on the effectiveness of treated and

regeneration process of deactivated alumina discarded as waste material from the hydrogen peroxide plant as an adsorbent and evaluate its performance in removing fluoride from contaminated groundwater. Therefore, the focus of the current report was on the preparation and modification of activated alumina, released as waste, characterization using different techniques for the removal of fluoride ion from fluorine-sourced ground water at different adsorption parameters.

1.3. Objective of the study

1.3.1. General Objective

The general objective of the study was to investigate the adsorption removal efficiency of regenerated deactivated alumina solid waste obtained from reversion bed of hydrogen peroxide plant for fluoride ion removal from ground water.

1.3.2. Specific Objectives

- Treatment and reactivation of deactivated alumina solid waste as adsorbent by soxhlet extraction, caustic treatment and thermal reactivation.
- Characterization of the formed re-generated alumina using FTIR, SEM, UV-DRS and XRD analysis.
- Investigating the removal efficiency of treated alumina solid waste with respect to fluoride ion removal from contaminated ground water at optimized conditions.
- To study the effects of different variables on adsorption of fluoride ion using treated activated alumina solid waste.
- To determine the adsorption isotherm and kinetics models.

1.4. Significance of the study

The increasing prevalence of fluoride contamination in groundwater poses serious health risks, particularly in developing regions where access to clean drinking water is limited. This study on treated and regenerated deactivated alumina solid waste, as an adsorbent for fluoride removal is significant for public health improvement, sustainable waste management and cost effective.

The work aims to develop a method for treatment and regeneration of used alumina produced in the hydrogen peroxide process by using different methods and reusing of treated alumina in the fluoride removal process as a high porous surface area adsorbent. The focus is to treat the solid alumina waste as an effective regeneration method hence the solid alumina waste disposed to the environment without effective treatment can have different impurities. The effective treatment and regeneration of the solid waste was important for fluoride ion removal from fluorine containing ground. This work contributes a significant role for the local community and health centers as well as for the government on governmental organization.

1.5. Scope of the Study

The scope of the study involves the pretreatment and regeneration of deactivated alumina solid waste discarded from the hydrogen peroxide plant, in Awash Melkasa chemical factory as adsorbent for the removal of fluoride ion from ground water.

The work also focuses on the characterization of the prepared re-generated alumina using XRD, SEM, FTIR and UV-DRS techniques. Application of response surface analysis techniques to develop predictive models such us adsorption isotherm and kinetics model, optimize process parameters, and enhance the fluoride adsorption capacity of regenerated alumina.

2. LITERATURE REVIEW

2.1. Water Contamination

Water contamination is a widespread issue worldwide, and elevated environmental and drinking water pollutant levels can have detrimental health impacts and raise environmental concerns (Gandhi et al., 2015). These pollutants may originate from both non-point and point sources. The geological materials that the groundwater passes through as well as the recharge water's quality determine the kinds of natural contaminants and their quantity. Groundwater moving through sedimentary rocks and soils may pick up a wide range of compounds, such as Magnesium, Calcium, Chloride, Arsenate, Fluoride, Nitrate, and Iron ions. Those metal ions may affect the quality of groundwater depends on their types and concentrations. Moreover, naturally occurring elements present at unacceptable levels can contaminate water (Sitompul, 2017). Other contaminants are man-made such as by-products of industry, and agriculture, including heavy metals, hazardous chemicals, and oxygen demanding pollutants, dyes and nutrients.

Among the water contaminants that are commonly found in the majority of ground and surface water at greater levels, fluorine has major negative health impacts and degrades the overall quality of the ecosystem (Jayashree et al., 2020). Fluoride can come from both natural and man-made sources. The earth's crust contains fluoride-bearing minerals such fluorite, fluorspar crystallite, fluor apatite, ralstonite, and others. Because of weathering, fluoride levels in groundwater are frequently elevated. Their consequences are particularly detrimental to older adults and children. Dental and skeletal fluorosis were known to be caused by fluoride. Additionally, it was linked to dementia in general and Alzheimer's disease in particular. The removal and efficient treatment of these harmful pollutants from wastewater has been a concern for various academics in the field.

2.2. Fluoride Contamination in Ground Water

According to the periodic table, fluorine (F_2) belongs to the halogen group. This gas has a distinctive pale yellow-green appearance and is corrosive. Both reactivity and electronegativity are high. As with other halides, fluoride is a reduced form of fluorine, a monovalent ion with a charge of -1. Compared to other halides, it has unique compound-level characteristics. It shares

structural and chemical similarities with hydroxide ions. Inorganic fluoride in water produces the fluoride ion (F^-) and the bi-fluoride ion (HF_2^-) (Ahmad & Singh, 2022). One of the biggest worldwide concerns is the poisoning of groundwater by fluoride ions (F^-). The World Health Organization (WHO) considers fluoride, nitrate, and arsenic to be major health hazards, and they are found in drinking water. Drinking fluoridated water is a serious health risk in several regions (Dhawane et al., 2017).

The fluoride content of the water is one important physicochemical factor that must be considered when determining if it is suitable for human consumption. According to the World Health Organization, the maximum concentration of fluoride ions that can be found in drinking water is 1.5 mg/L(WHO, 2008). Although a low daily fluoride dose is believed to be responsible for avoiding dental caries, a larger daily fluoride dosage has been linked to persistent dental and skeletal fluorosis. In large geographic bands, volcanic rocks, marine-derived sediments in hilly areas, and granitic and gneissic rocks are linked to high fluoride concentrations in water.

2.3. Sources of Fluoride

In vast geographic swaths, volcanic rocks, sediments from marine sources in mountainous areas, and granitic and gneissic rocks are linked to high fluoride concentrations in ground water. Geogenic and anthropogenic sources are the two primary causes of this contamination, according to reports (Ahmad et al., 2022). The average fluoride concentration in the various rocks that make up the Earth's crust is 625 mg kg-1. The increased fluoride content in groundwater, which has a major detrimental impact on both human health and the environment, is caused by a variety of geological processes. Weathering, tectonic movements, volcanic eruptions, geothermal springs, and other geological processes are the main ways that rocks and water contaminate fluoride (Kimambo et al., 2019).

Fluoride levels in water had a negative correlation with calcium ions but a positive correlation with ions such as phosphate and chloride. After a thorough research, it was concluded that geogenic sources of groundwater pollution were the main source of fluoride exposure in the population. Numerous minerals, such as topaz, fluorite, and their parent rocks, basalt, granite, and shale, emit fluoride into groundwater(Ahmad & Singh, 2022). Evaporating water, holding water between rocks and soil for a long time, and using irrigation systems for extended periods of time are all indirect ways to contaminate groundwater.

Anthropogenic influences, such as the usage of phosphate fertilizers containing fluoride, rodenticides, fumigants, herbicides, and insecticides, may increase the amount of fluoride in groundwater. Additional sources of fluoride pollution include fly ash, coal combustion, and fluoride particle emissions from the glass, tile, steel, and aluminum sectors. Comparing these industrial effluents to natural water, the fluoride concentrations are incredibly high, ranging from 10 to 1000 parts per million. It has been discovered that incorrect usage of fertilizers, such as phosphate, is one of the primary human-caused sources of fluoride contamination in groundwater(Ahmad & Singh, 2022). In superphosphate fertilizers, which are used to increase agricultural productivity, fluoride levels are close to 0.34 parts per million. Higher quantities of fluoride are seen in groundwater around brick kiln facilities.

2.4. Occurrence of Fluoride in Groundwater

Fluoride is present in trace amounts in many natural fluids, with ground waters frequently having higher levels that come from a variety of sources. Fluoride is released into groundwater through a chemical and physical interaction between the groundwater and its geological environment. Fluorite is the primary mineral that controls the concentration of dissolved fluoride in groundwater (CaF_2). Therefore, fluoride-rich ground fluids are frequently associated with high pH conditions where sodium bicarbonate predominates and calcium precipitates as calcite, or low calcium concentrations associated with rocks with low calcium content ($CaCO_3$). Hydrological features (like residency time), climatic factors (like evapotranspiration and precipitation), and soil parameters like (pH and soil type) all affect fluoride content in addition to groundwater chemistry (Ayoob et al., 2008).

High fluoride levels are significantly associated with high alkalinity (HCO_3^-) and high warmth in Ethiopian groundwater. Consequently, these measurements could be helpful as potential indicators of fluoride-related issues in groundwater while looking for new groundwater sources. For many people, especially in areas with high amounts of fluoride in surface and/or groundwater, drinking water is the main source of fluoride intake. Some foods, especially tea, may have high fluoride contents (0.1 mg/g)(Zerabruk et al., 2010). Furthermore, the daily consumption of fluoride may be significantly impacted by indoor air pollution brought on by the burning of coal. Anthropogenic operations that use phosphate-containing fertilizers or

aluminum smelting have the potential to contribute significant levels of fluoride to the environment at a local level (Saxena & Ahmed, 2003) .

2.5. Health Effects of Fluoride

The overall amount of fluoride that is consumed over time will determine whether fluoride is good or bad for human health. Fluoride concentrations below 0.5 mg/L cause dental cavities and weaken bones; concentrations exceeding 1.5 mg/L cause fluorosis. Drinking water with high fluoride levels can cause dental fluorosis, which shows up as tooth discolouration and pitting, skeletal fluorosis, which shows up as back discomfort and stiff joints, and non-skeletal fluorosis, which shows up as skin rashes, anxiety, and weak muscles(Kabir et al., 2020). Fluoride ingestion has a very negative impact on human health when it approaches or surpasses 3.18 mg/L. Infants who have it exhibit abnormal behaviors, have their brains develop more slowly, and have lower IQs (IQ). Fluoridation has also been connected to infertility, arthritis, terminal cancer, brain damage, and osteosclerosis (brittle bones)(Dhawane et al., 2017). Fluoride doesn't have an immediate effect on a person; it accumulates in the brain and gradually deteriorates the various parts of the body over time(Ahmad & Singh, 2022).

The effects of fluoride upon human health have been studied since the early 20^{th} century. Both the benefits of minimal exposure and the risks of high fluoride doses have been established (Hichour,et al, 2000). A higher daily dose of the fluoride ion has been linked to permanent dental and skeletal fluorosis (Mahramanlioglu,et al, 2002). It was estimated that more than 200 million people worldwide (UNESCO) rely on drinking water with Fluoride concentrations exceeding the present WHO guideline of 1.5 mg/L (WHO, 2004). The incidence of fluorosis has been reported in some parts of Ethiopia, where fluoride concentrations in drinking water exceed the WHO guideline value of 1.5 mg/L. Many water sources in Ethiopia contain Fluoride in elevated concentrations up to 26 mg/L. According to estimates of the Ethiopian Ministry of Water Resources, more than 11 million people in the Ethiopian Rift Valley rely on drinking water contaminated by Fluoride. Over 40% of deep and shallow wells are contaminated and over 80% of children suffer from different degrees of dental fluorosis and skeletal fluorosis is increasing, mainly among older people (Kloos and Tekle-Haimanot, 1999).

Excess fluoride may occasionally harm the parathyroid gland. Hyperparathyroidism, which is characterized by an unchecked release of parathyroid hormones, may arise from this. This may

lead to a greater than usual calcium concentration in the blood and a decrease in calcium in bone structures. Bones that have lower concentrations are more prone to breaking (Brazier, 2018). In 2017, a research report was proves that exposure to fluoride before birth could lead to poorer cognitive outcomes in the future. The researchers measure fluoride levels in 299 women during pregnancy and in their children between the ages of 6 and 12 years. They tested thinking ability at the ages of 4 years and between 6 and 12 years. Higher levels of fluoride were associated with lower scores on IQ tests (Salifu, 2017).

Table 1: Effect of prolonged use of drinking water on human health, related to fluoride content (Gizachew, 2015).

F - concentration, mg/L	Health outcome
< 0.5	Dental caries
0.5-1.5	Optimum dental health
1.5-4.0	Dental fluorosis
4.0-10	Dental and skeletal fluorosis
> 10.0	Crippling fluorosis

2.6. Available Technologies for Fluoride Removal

Reducing the fluoride content of tainted water to safe levels is the goal of fluoride removal. Fluoride ions can be eliminated from tainted water through the noteworthy process of defluoridation. The several fluoride removal processes-adsorption, ion exchange, membrane filtration, and electrocoagulation that are employed to extract fluoride from fluid media are the subject of numerous ongoing studies. However, by employing other methods such as layer filtration, electrocoagulation, and ion exchange, evacuation productivity was raised to 90–95 percent, 99 percent, and 85.5 percent, respectively. Due to its ease of use, low effort requirements, need for basic tools and procedures, and reasonable efficiency, adsorption has been extensively studied as an environmentally benign strategy that is highly feasible and an emerging methodology (Sunitha, 2021).

2.6.1. Membrane Process

The membrane separation method is more well-known in the industrial sector for defluoridating groundwater, desalinating saltwater, and treating wastewater. In a membrane separation process, particles are separated according to the size and shape of their molecules using a highly well-composed semi-permeable membrane. A semi-permeable barrier can frequently be made of a thin, porous or nonporous polymeric sheet, ceramic, metal, or even a liquid or gas. The membrane must not break down, disintegrate, or dissolve (Waghmare & Arfin, 2015). The most common membrane separation methods for removing fluoride include reverse osmosis, electrodialysis, nanofiltration, and Donnan dialysis. Immature technologies, high energy consumption, and poor selectivity are the primary drawbacks of these techniques, which restrict their widespread adoption (Pillai et al., 2021).

2.6.2. Ion-Exchange Process

Ion exchange occurs when a solid adsorbent removes charged fluoride ions from a solution and returns an equivalent amount of another ion to the solution. An excess of positive or negative charge facilitates ion exchange in the matrix. The excess charge that arises from the adsorbent absorbing charge species that are localized in specific sites or functional groups is offset by the counter ions in a solution(Bhatnagar et al., 2011). Anion and cation exchange resins are examples of synthetic compounds that have been employed to remove fluoride ion from polluted water source. Among them are Amberlite IRA 400, Lewatit MIH-59, Polyanion (NCL), Tulsion A-27, Deacedite FF (IP), and Amberlite XE-75. Both the chloride and hydroxyl forms of these resins have been applied. The ratio of fluoride to total anions in water determines these resins' ability to exchange fluoride (Ingle et al., 2014). A strongly fundamental anion-exchange resin with quaternary ammonium functional groups can be used to remove fluoride from water supplies. Fluoride ions were added to the resin to replace the chloride ions. This process keeps going until every spot in the resin was filled. The resin is then backwashed using supersaturated water that has sodium chloride salt dissolved in it. A fresh chloride ion then replaces the fluoride ions, causing the resin to recharge and restarting the process. The reason fluoride ions are replacing chloride ions in the resin is because of their stronger electro negativity(P. S. Kumar et al., 2019). This process has generally decreased operational expenses and the quantity of

garbage that must be disposed of. The pH of the water is a limitation on the method's effectiveness.

2.6.3. Precipitation and Coagulation

The precipitation method uses solid-liquid separation to extract fluoride from water. To do this, chemical agents, coagulants, and flocculants are added to wastewater in order to produce flocculation or fluoride precipitation. The main factors influencing the effectiveness of precipitation treatment are agents, reaction conditions, and the effect of solid-liquid separation. Coagulation precipitation and chemical precipitation are the two fundamental categories of precipitation techniques. Often used for high-concentration fluoride-containing industrial effluent, the chemical precipitation method involves adding lime, calcium carbide slag, calcium chloride, and other modified chemicals to the wastewater(Pillai et al., 2021). Fluoride is eventually separated from calcium by the precipitation process, which is the result of a chemical reaction between the two ions. This is the major treatment method used currently for industrial wastewater with high fluoride levels. Unfortunately, since the fluoride level of wastewater is typically not less than 20–30 mg/L, the effects of treatment by this method are not practicable. Furthermore, the precipitated particle that results (CaF_2) typically exhibits weeny characteristics and does not settle down soon (C. C. Liu & Liu, 2016).

The main disadvantage of the precipitation method was flocculants like poly aluminum chloride added during the flocculation process was to enhance solid-phase separation. Therefore, the characteristics and processes of colloidal, dissolved, and precipitated AlF complexes and other Al related species were investigated in order to manage the quantity of residual aluminum in defluorinated water(Dubey et al., 2018). The flocculation mechanism of PACl is determined to be particle bridging. In comparison to alum, the particle effect in PACl is significantly better, indicating that it performs better at eliminating fluoride. When the complexation role in coagulation is investigated using an aluminum salt coagulant, it is discovered that the AlF complex reacted with less OH- to produce a new Al-F-OH precipitate (Gong et al., 2012). By coprecipitation, Al-F-OH and AlF complex can remove fluoride more effectively. The following is the primary reaction formula. In order to study the process of fluoride ion removal, Gan et al. suggested using $ZrCl_4$ as a coagulant. They were able to demonstrate that electrostatic contact, ion-exchange, and hydrogen bonding between flocs and fluoride ions were the main methods of fluoride ion removal(Gan et al., 2019) .

2.6.4. Adsorption

Adsorption is the process via which atoms, molecules, or ions of a liquid or gas adhere to the surface of a solid object. As an alternative, it describes how material molecules will physically or chemically bond with surface effective sites through the weak Vander Waals force or by forming chemical bonds with those sites(Crini et al., 2019). Adsorption is the process by which molecular species from bulk solution adhere to a solid surface by physical or chemical means. Due to its simpler design, availability of a range of adsorbents, easier operation, and relatively low setup costs, adsorption is thought to be the most efficient de-fluoridation technique for small populations(Waghmare & Arfin, 2015). However, some adsorbents are very expensive, while some of them for de-fluoridation were not fit technically in rural areas. In addition, the use of some adsorbents is limited due to their inadequate removal capacity.

The extent to which an adsorbent is efficient in removing fluoride depends on factors such as the initial concentration of fluoride, the type of adsorbent used, pH of the water, the existence of interfering ions, and the time of contact. Activated alumina (AA) has been used as adsorbent of interest and extensively studied for fluoride removal from drinking water. It has a high affinity and selectivity for fluoride ion adsorption from the source of pollution. De-fluoridation processes based on AA have been used at both community and domestic levels(Ghorai & Pant, 2004). The term ‘‘activation’’ is used to indicate a change in properties resulting from heating. In general, as a hydrous alumina precursor is heated, water is driven off leaving a porous solid structure of activated alumina. (Farrah et al., 1987) studied the interaction of fluoride ion with amorphous Al $(OH)_3$, gibbsite and alumina (Al_2O_3) over a wide pH range (3-8) and F^- concentrations (0.1-1.0 mM). It was found that at pH < 6 and total F: Al ratios > 2.5, most of the amorphous Al $(OH)_3$ gel dissolved through the formation of AlFx complexes. At lower F: Al ratios, some solid persisted in the pH 4-7 region and strongly adsorbed F^- from solution. It was also observed that maximum uptake of F^- occurs in the pH range of 5.5-6.5 (up to 9 mol/kg). At lower pH, fluoride uptake decreased due to the preferential formation of AlFx soluble species; at higher pH, OH^- displaced F^- from the solid and the amount of F^- adsorbed or converted to complexes declined rapidly towards zero between pH 6 and 8. At a fixed pH (between 5 and 7.5), fluoride uptake varied in accordance with Langmuir model (maximum

capacity ~ 1 mol/kg). The amount of substrate converted into AlFx complexes in acid media increased with decreasing pH and increasing initial fluoride concentration.

(Ghorai & Pant, 2004) concluded that removal of fluoride was the result of ion- exchange as well as adsorption, which follows both Freundlich and Langmuir isotherms. AA has a great capacity for fluoride adsorption, which is dependent upon the crystalline form, activation process, solution pH, and alkalinity.(Mulugeta et al., 2015) also showed the importance of activation by comparing untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) obtained from hydrolysis of locally manufactured aluminum sulfate.

The use of activated alumina in a continuous-flow system was reported to be an economical and efficient method for defluoridating water supplies and an adsorption capacity of 1.45 mg/g at pH 7 can be achieved(Ghorai & Pant, 2004). The greatest disadvantage of fluoride removal by activated alumina is that the optimum fluoride removal capacity occurs only at a pH value of the solution below 6.0, which strongly limits the practical applications of the AA. The authors observed that adsorption of fluoride was retarded in acidic solutions because of the electrostatic repulsion and when equilibrium solution pH was greater than 7, the fluoride adsorption by alumina decreased due to the electrostatic repulsion of fluoride ions by the negatively charged surface of alumina and the competition for active sites by excessive amounts of hydroxide ions. In addition interference due to the presence of other anions/cations has been reported to affect fluoride removal capacities of AA (Zou et al., 2011).

(Ghorai & Pant, 2004) investigated the removal of fluoride using activated alumina (AA) in batch and continuous experiments. An adsorption capacity of 1.45 mg/g was obtained at pH 7. The percentage of fluoride removal increased in the pH range from 4 to 7 and subsequently decreased. At pH > 7 silicates and hydroxyl ions were well-thought-out to compete strongly with F - ions for alumina exchange sites, whereas, at pH < 7, the soluble alumino-fluoro complexes were formed which in return accounts for the presence of aluminum ions in the treated water. Early saturation and lower percentage fluoride removal was observed at higher flow rates and at higher concentrations. There was a minimal decrease in the adsorption capacity after each regeneration cycle. Regeneration procedure resulted in 85 % efficiency with the grade of AA studied. A loss of 5 % in adsorption capacity of AA was observed after five cycles.

2.7. Commonly Used Adsorbents for Fluoride Removal

Among all the de-fluoridation methods, the adsorption technique is perhaps the most adaptable because of its affordability, variety of end applications, sociocultural acceptability, regulatory compliance, environmental friendliness, and ease of use. Additionally, due to its affordability and easy access of supplies, it is the method of choice in rural areas. Many naturally occurring materials have been utilized as adsorbents for the removal of fluoride, including activated alumina, aluminum hydroxide, aluminum oxide, activated carbon, activated bone char, industrial wastes, bauxite, kaolinite, and different kinds of clay.

2.7.1. Activated Alumina

The primary component of activated alumina is made up of spherical beads of aluminum oxide (Al_2O_3), which are extremely porous and have a large surface area. 345-415 m^2/g is the surface area of activated alumina. When submerged in water, it doesn't sag, expand, soften, or dissolve. There are three different types of it: activated alumina desiccant, activated alumina sorbent, and activated alumina catalyst carrier. The internal active surface of the granulated alumina is present. In this procedure, tainted water is run through an activated alumina cartridge or canister. The impurity adheres to the alumina surface(A. S. C. Chen & Snoeyink, 1987).

The most extensively studied adsorbent for removing fluoride from water was activated alumina (AA). The study examined the relationship between the amount of adsorbent dosage, concentration, flow rate, and pH and the removal performance. Freundlich and Langmuir isotherms have been connected with sorption data (Ghorai & Pant, 2004). Major anions, on the other hand, decreased fluoride adsorption on activated alumina in the following order: HPO_4^{2-} $>HCO_3^-$ $>SO_4^{2-}$ $>Cl^-$. Through competing for the same surface locations, other hazardous elements like arsenic and selenium that may coexist with fluoride in groundwater also decreased fluoride adsorption(Tang et al., 2009). The ability of alumina particles treated with acids and bases to adsorb fluoride from aqueous solutions was investigated. The surface of the alumina particle was mostly where the fluoride adsorption occurred superficially. At a pH of 7, the adsorption capacity of base-treated alumina was only roughly half that of alumina, but the capacity of acid-treated alumina was approximately double that of alumina (Gandhi et al., 2015). It was discovered that at 25°C, nano-alumina had a maximum sorption capacity of 14.0 mg/g

for the elimination of fluoride. pH 6.15 was the point at which maximum fluoride elimination was achieved(E. Kumar et al., 2011).

The adsorptive capacity of freshly synthesized aluminum hydroxide, or in-situ $Al_2O_3 \cdot xH_2O$, towards fluoride was examined by Liu et al. (2011). pH ranges from 5.0 to 7.2 were shown to have the greatest adsorption of more than 110 mg F^-/g Al (R. Liu et al., 2011). Using the biopolymer chitosan as a template, mesoporous alumina (MA450) was created and is used to de-fluoridate water. MA450 was found to function well across a broad pH range and to have a maximum 26-adsorption capacity of 8.26 mg/g at a starting fluoride concentration of 5.0 mg/L, which is significantly superior to that of standard alumina. The experimental results obeyed pseudo-second order kinetics and suited the Langmuir isotherm satisfactorily. In field water, MA450 revealed a noticeably high fluoride removal rate. MA450 proved successful in eliminating fluoride and seems to be a cost-effective solution(Jagtap et al., 2011).

Acidic alumina has an ideal pH of 4.4 and a maximum fluoride adsorption capability of 8.4 mg/g, according to research by Goswami et al. (2012). They also found that, depending on the process settings, acidic alumina could be able to adsorb fluoride. The endothermic character of the process implies that fluoride was adsorbed physically onto acidic alumina.

Aluminum modified hydroxyapatite (Al-HAP) with a fluoride adsorption capacity of 16.8 mg/g was produced by for the defluoridation of aqueous solution(Nie et al., 2012). They deduced that the surface of AlHAP had a large number of hydroxyl groups, or adsorption sites. created a novel carbon composite supported by alumina using eggshell waste, intended for the selective adsorption of fluoride. With an adsorption capacity of 37 mg/g, this calcium-containing eggshell composite efficiently removed fluoride from wastewater and the ground (Lunge et al., 2012).

2.7.2. Clay Adsorbent

Naturally occurring clay materials such as kaolinite, bentonite, charfines and lignite were examined for fluoride adsorption (Dianti, 2017). Low-cost bentonite clay was chemically modified using magnesium chloride in order to enhance its fluoride removal capacity by Thakre et al. The adsorbing efficiency of the natural and modified clay in the purification of drinking water, when compared to existing technologies, materials, and methods was found to be significantly higher or comparable(Srinivasan, 2011).

For the purpose of removing fluoride from aqueous solutions, diatomaceous earth (diatomite), which is readily available in Ethiopia, was altered by treating it with an aluminum hydroxide solution (Akafu et al., 2019). Samples of soil had relatively low adsorption capabilities that might be used in the field. Fe (III) modified bentonite clay was employed by Gitari et al. (2015) to defluoridate water. Over the broad pH range of 2–10, In order to overcome the drawback associated with the release of fluoride ions, the modified bentonite could completely remove fluoride. Furthermore, heavy metals and other contaminants that could be harmful and need to be removed by pretreatment may be present in the clay, depending on where it came from (WAghmare & Arfin, 2015).

2.7.3. Zeolite

Many forms of zeolites are employed in filtration, ion exchange, adsorption, photocatalytic degradation, and membrane separation technologies in the treatment of water and tertiary wastewater. Zeolites are a well-known class of minerals. Zeolite has garnered a lot of interest from researchers looking to use it as an adsorbent for the treatment of water and waste water due to its vast surface area and capacity to exchange weakly bound cations with those in solution. Natural zeolite is an alumina silicate mineral that exhibits a wide surface area, excellent ion exchange capabilities, and adsorption for its unique tetrahedral pore architecture(Zou et al., 2011).

Zeolite media are silicon, aluminum, and oxygen-based microporeous crystalline solid formations that create a framework with channels and cavities for adsorption operations. Natural zeolite modified with cationic surfactants are hydrated alumino silicate minerals with excellent ion-exchange and adsorption capabilities that are used to clean waste water or drinking water. They are also economically and environmentally acceptable(Rahmani et al., 2018).

2.8. Low-Cost Adsorbents

Since there are many readily available materials locally, such as natural materials, agricultural wastes, and industrial byproducts, that can be used as inexpensive adsorbents, the removal of heavy metals by the use of inexpensive adsorbents is found to be more encouraging over the long run (Abas et al., 2013). In order to be economically feasible, an adsorbent needs to possess the following qualities: low solubility in the liquid it comes into contact with, resistance to fouling, favorable transport and kinetic properties, mechanical strength, thermal and chemical

stability, and high selectivity for speedy separations. The adsorption approach is superior to traditional heavy metal removal techniques in a number of ways. A few benefits of the adsorption process are: economical; metal selectivity; regenerative; lack of production of hazardous sludge; and, most significantly, effectiveness. Several affordable adsorbents, sourced from both natural and man-made sources, have been used to detoxify heavy metal-contaminated wastewater. The most common adsorbents are natural materials, modified biopolymers, industrial wastes, and agricultural waste.

2.8.1. Industrial Wastes as Low-Cost Adsorbent

As byproducts of widespread industrial activity, enormous amounts of solid waste materials were produced. Using these wastes to create low-cost adsorbents for water treatment is one of their advantageous applications. Fluoride removal from water has been investigated with and without modifications using a variety of industrial wastes. According to research (Chaturvedi et al., 1990), fly ash, a waste product of thermal power plants, may effectively remove fluoride from water and wastewaters, especially when the concentration is low, the temperature is high, and the pH is acidic. Fly ash has a Langmuir maximum fluoride adsorption capacity of 20.0–20.3 mg/g.

2.9. Factors Influencing Adsorption Process

The following variables influence the adsorption process of defluoridation and other adsorption-based water treatment:pH, temperature, adsorbent dose, initial adsorbate concentration, coexisting ions, contact time, adsorption kinetics, isotherm, and thermodynamics, among others (Iftekhar et al., 2018).

2.9.1. Initial Concentration Effect

The main concentration of the adsorbate material has an impact on the adsorption process because at high concentrations, the maximum numbers of ions or absorbable molecules are exposed to the adsorbent's active sites, increasing both the rate of adsorption and its percentage. Experiments were carried out at various fluoride concentrations as researchers looked into the impact of the initial fluoride concentration(Getachew et al., 2015).

Since a given mass of sorbent material can only adsorb a set amount of ions, the initial concentration of the contaminant is crucial to the adsorption process. Adsorbents removal ability

often decreases as initial pollutant concentration rises. This is true because the amount of ions that can be adsorbed was fixed for a given mass of adsorbent material. The higher the concentration of the contaminant, the smaller the volume it can remove. There will be empty active sites on the adsorbent surface at low concentrations, and when the initial concentration rises, there will not be enough active sites for the ions to adsorb. However, when the concentration of contaminants increased, so did the real amount of contaminants absorbed per unit mass of adsorbent. The strong driving force for mass transfer at a high initial ion concentration could be the cause of this (Thacker, 2019).

2.9.2. Contact Time

In the adsorption process, one of the determining factors is contact time. Every waste treatment method ought to be financially viable (Tangjuank and Udeye, 2009). It is crucial to examine the impact of time in order to determine the pace and efficacy of any wastewater treatment procedure. The kinetics and equilibrium of the adsorption process are determined by the duration of the contact between the adsorbent and adsorbate. As a result, research into how contact time affects adsorption experiments is crucial for their practical uses (Lebrahimi et al., 2020).

2.9.3. Dose of Adsorbent

Increased adsorbent volume will result in an increase in the number of active sites that can bind more metal contaminants (Padmavathy et al., 2016). The adsorption process will be negatively impacted by a subsequent increasing the amount of adsorbent. Because of a screening action blocking the adsorption active site, the metal adsorption either declines or becomes stable.

2.9.4. Co-existing Anions

Natural water contains multiple anions that can compete with F for removal by adsorbents. These anions include PO_4^{3-}, Cl^-, $SO4^{2-}$, Br^-, and NO_3^-. The ion concentrations' relative amounts and their affinity for the adsorbent determine how fierce the competition is. An anion exchange resin adsorbs anions by an ion exchange mechanism.(Meenakshi & Viswanathan, 2007), found that increased concentrations of Cl^-, $SO4^{2-}$, Br^-, NO_3^-, and HCO_3^- decreased F adsorption by this resin. On the other hand, these anions had no effect on F adsorption by a chelating resin, which adsorbed F selectively by an H-bonding mechanism. It was reported that $F^- > Cl^- > NO_3^- > SO_4^{2-}$ is the preferred order in which the chelating resin adsorbs anions.

The unique adsorption mechanism of ligand exchange is responsible for the selective adsorption of F by multivalent metal oxides. When SO_4^{2-} and NO_3^- were present, an alum sludge with a high concentration of Al, Ti, and Fe oxides absorbed F selectively. The F adsorption from a solution containing 20 mg F/L was reduced by SO_4^{2-} and NO_3^- at 50 mg/L, from 85% to 40% and 62%, respectively. Comparatively, F^- adsorption was reduced to 25% of F in solution by PO_4^{-3} and selenate concentrations at 20 mg/L. The findings of Sujana et al. suggested that $PO_4^{3-} \geq$selenate > SO_4^{2-} > NO_3^- represents the reduced order of competition of anions for F adsorption.

Studied the adsorption characteristic of fluoride on activated alumina. The fluoride adsorption study was carried out on a wide range of pH be-tween 5 and 10.5. They observed that the fluoride uptake decreases for an increase in pH. The major anions reduce fluoride in the sequence following the order of HPO_4^{2-} > HCO_3^- > SO_4^{2-} > Cl^-. Arsenic and selenium present in water are comparatively reducing fluoride adsorption showing competition for the same surface sites. A speciation-based model was developed for pH 5-10.5 and a wide surface loading range of 1–10 mgF^-/g adsorbent was observed(Tang et al., 2009).

(George et al., 2010)investigated the modeling and simulation of remaining aluminum in water defluoridated using activated alumina adsorbent. An Activated Alumina de-fluoridation Model Simulator (AAD) that has to be developed predicted that the dissolution of aluminum fluoride and aluminum complexes is more favorable to high fluoride concentration with low alumina dosage in pH range of 6.5-7.5, which may lead to increase in residual aluminum in treated water. Thus, regeneration is essentially required before the complete exhaust of alumina to minimize residual aluminum concentration in treated water within a permissible limits.

2.9.5. pH Effect

Different researchers investigated the effect of pH on defluoridation process by using different adsorbents. Since the aqueous solution's pH plays a significant role in the adsorption process, the role of hydrogen ion concentration is investigated at various pH values (Waghmare & Arfin, 2015b). (Farrah et al., 1987)investigated the interaction of fluoride ion with amorphous aluminium hydroxide, gibbsite which is naturally-occurring aluminium hydroxide and aluminium oxide over a wide range of pH values from 3 to 8 and fluoride concentrations from 0.1 - 1 mM (1.9-19 mg/l). It was remarkable that most of the aluminium hydroxide formed AlF complexes and dissolves at pH<6 and total F-Al ratio >2.5. Maximum fluoride uptake occurred

within the pH range of 5.5 - 6.5. The fluoride uptake varied in accordance with the Langmuir model at fixed pH between 5 and 7.5. The Gibbsite removal capacity was less as compared to other compounds by same reaction.

(Ku & Chiou, 2002) studied about the maximum fluoride at a pH range of 5-7, which was 16.3 mg/g by using activated alumina as an adsorbent. They observed that adsorption of fluoride considerately retarded in acidic solutions because of the electrostatic repulsion between them. If the equilibrium solution pH was greater than 7.0, the fluoride adsorption was reduced by alumina. It was attributed to the electrostatic repulsion of fluoride ions to the negatively charged surface of alumina and it competes for active sites through excessive amounts of hydroxide ions. For neutral, the adsorption capacity of alumina for fluoride was found to be interfered due to the presence of sulphate.

(Ghorai & Pant, 2004)investigated the removal of fluoride using activated alumina (Grade OA - 25) in batch and continuous operation and observed the adsorption capacity to be as 1450 mg/kg at pH 7. It was noticed that there was a marginal decrease in the uptake capacity after each regeneration cycle. The regeneration procedure resulted in 85% efficiency with the grade of AA studied. However, later on, a loss of 5% in uptake capacity of AA was observed after five cycles.

2.9.6. Temperature Effect

Adsorption is an exothermic (heat-generating) process, whereas absorption is a heat-absorbing process, as was previously mentioned (endothermic). Many researchers, both domestically and abroad, have studied the impact of temperature on fluoride adsorption.(Girma et al., 2020), studied the impact of temperature on the defluoridation process using adsorption technology in Ethiopia. Lower values of protonation constants result from either hydroxide sorption to the surface or from protons being desorb able from the surface due to the higher temperatures. The physical processes that bind fluoride to a sorbent can be affected by temperature.

It is clear that as temperature rose, more desorption occurred, which reduced adsorption. It was discovered that as the temperature rose, the modified biomass adsorbent's fluoride adsorption potential decreased the adsorption capacity (Telkapalliwar, 2020). The efficacy of removing fluoride as a function of temperature demonstrates that adsorption declines as temperature rises (Yilmaz et al., 2015).

2.10. Adsorbent Characterization Techniques

The process of characterizing an adsorbent usually yields details on its structure and morphology, chemical makeup, capacity to adsorb and hold onto molecules, and capacity to chemically transform these molecules. Information on the structural, chemical, and catalytic characteristics of the adsorbent is crucial for establishing a relationship between its chemical and physicochemical qualities and its adsorptive and catalytic properties. These relationships are extremely important because they make it possible to build improved structural materials, catalysts, and adsorbents in a sensible manner (Hayashi et al., 2011).

The adsorbent phases have been characterized using a variety of approaches such as X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR),are among the most often utilized methods (Barberi & Spriano, 2021).

2.10.1. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a crucial and conclusive characterization technique that is frequently used to explain the crystalline structure of samples and other synthetic materials. It explains the formation of the prepared sample in references to the standard sample. The purpose of the test is to validate the synthetic specimen's structural properties. The X-ray Diffraction (XRD) technique was employed to ascertain the crystalline phases found in both natural and synthetic materials. Additionally, the nucleation and growth processes during the synthesis of various materials intended for use as adsorbents, ion exchangers, and catalysts were investigated (Achparaki et al., 2012).

2.10.2. Fourier Transforms Infrared Spectroscopy (FTIR)

A physicochemical method known as Fourier transform infrared (FT-IR) spectroscopy is based on the vibrations of a molecule excited by infrared radiation within a particular wavelength range. The surfaces functional groups of the adsorbent are ascertained by Fourier transform infrared spectroscopy, or FTIR. The many functional groups present in the sorbent material are essential to comprehending the mechanism of the fluoride-binding process on the adsorbent(Santos et al., 2019). (Erdoğan & Ülkü, 2011) states that the FTIR approach can be helpful in obtaining crucial information on the structure, channel size, and cation exchange in the tetrahedral sites of the adsorbents. The characterization technique significantly deals with the role of the adsorbent, its chemical composition in terms of functional groups.

2.10.3. Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) deals with the surface area and surface morphology of materials (Vernon-Parry, 2000). The operation of a scanning electron microscope is identical to that of an optical microscope, with the exception that instead of using light to "image" the object and determine its composition and structure, they employ a concentrated electron beam. A fundamental method for examining the microstructural properties of solid materials, such as kaolin, charcoal, and zeolite membranes, is scanning electron microscopy (SEM) (Subramanian et al., 2022).

2.10.4. Ultraviolet-diffuse reflectance (UV-DRS) analysis

DRS is an analytical technique used to study the optical property of materials, particularly solids and powders. It involves measuring the light that scattered and reflected off sample when it was illuminated by a light source.

2.11. Modeling of Adsorption

Adsorption occurs when a solid and a liquid or gas come into contact, transferring mass to the solid. A solid's ability to concentrate specific liquid substances onto its surface is exploited in this procedure. Adsorbent is a solid, while adsorbate is a substance that has been adsorbed(Ye et al., 2016) Molecules are drawn from one phase (the liquid phase) and concentrated at the surface of a second phase (the solid phase, the adsorbent) during the adsorption process due to an attractive force between the adsorbent surface and the adsorbate molecules. Consequently, in a removal process, certain molecules are drawn to the surface of an adsorbent particle either chemically or physically. Three consecutive steps make up the adsorption process(Muhi Mohammed, 2011). Materials first adsorb to the adsorbents outside, then they go into its pores and adsorb to the internal walls of the adsorbent.

2.11.1. Adsorption Isotherm

The adsorption isotherm is a crucial calculation for forecasting and examining the diverse mechanisms that may arise during the adsorption process (Ragadhita & Nandiyanto, 2021). Adsorption isotherms are helpful for determining the adsorbent's capacity at the equilibrium state of the adsorption process and for elucidating the interaction between the adsorbent and the adsorbate. The parameters of the isotherm model offer crucial information about the adsorption

processes, the adsorbent's surface properties, and its effectiveness(Moughaoui et al., 2017). The ten most widely used adsorption isotherms, including Florry-Huggins, Fowler-Guggenheim, Hill-Deboer, Jovanovich, Harkin-Jura, Halsey, Freundlich, Temkin, Dubinin-Radushkevich, and Langmuir(Ayawei et al., 2017).

Langmuir Adsorption Isotherm

This model explains how monolayer adsorbate forms on the adsorbent's exterior. The underlying premise is that maximal adsorption happens when there is no adsorbate molecule migration in the surface plane, a saturated monolayer of solute molecules is present on the adsorbent surface, and the energy of adsorption is constant (Heraldy et al., 2016).

While there are other empirical adsorption models, the Langmuir adsorption isotherm model is the most often used. Of all the isotherms used to characterize saturated monolayer adsorption in solid/liquid systems, the Langmuir adsorption isotherm is arguably the most well-known. It can be shown like this:

$$qe = \frac{qmkaCe}{1 + KaCe} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 1$$

Where Ce is the equilibrium concentration (mg/L);

qe is the amount ion adsorbed per adsorbent at equilibrium (mg/g);

qm is a monolayer adsorption capacity per adsorbent (mg/g);

Ka is adsorption equilibrium constant (L/mg).

To evaluate the adsorption capacity for a particular range of adsorbate concentration, aforementioned equation (Eq. (1)) can be used as a linear form as follows:

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{KLqm} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2$$

The constants qm and K_l can be determined from a linearized form of the above equation by the slope of the linear plot of Ce/qe versus Ce.

Freundlich Adsorption Isotherm

The Freundlich model describes the adsorbent's surface heterogeneity, while the Langmuir model presupposes uniform adsorption energies onto the surface and no adsorbate transmigration in the surface's plane (Getachew et al., 2015).

The earliest known relationship explaining the adsorption equilibrium is provided by the model, which is based on adsorption on a heterogeneous surface.

$$Qe = \mathrm{KfCe}^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

The linear form of Freundlich equation is expressed as;

$$\text{Log (qe)} = \log (k) + \frac{\mathbf{1}}{\mathbf{n}} \log (Ce) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where qe is the amount of fluoride adsorbed (mg/g);

Ce is the equilibrium concentration (mg/L);

Kf and 1/n are empirical constants, indicating the adsorption capacity and adsorption intensity, respectively.

2.11.2. Adsorption Kinetics

Adsorption kinetics is among the most crucial concepts to understand before deciding if an adsorbent is appropriate. Both linear and non-linear kinetics studies can be useful for any adsorption process. The pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, and intra-particle (IP) models are some of the kinetics that predict the adsorbent-adsorbate interaction(Achparaki et al., 2012). The most popular kinetic models, known as pseudo-first order and pseudo-second order reaction models, are used extensively in practically all sorption processes (Inyinbor et al., 2016).

- **Pseudo-first-order equation is given by equation (Johnson & Chandravanshi, 2014):**

$$(\log(qe - qt) = \log qe - \frac{k1t}{2.303} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

Where qe (mg/g) and qt (mg/g) are the amounts of fluoride adsorbed at equilibrium and at time t respectively, and k_1 (min^{-1}) is the adsorption rate constant and can be obtained from the slope of plot ln (qe-qt) versus time t.

- **Pseudo-second-order equation is expressed by:**

$$\frac{1}{qt} = \frac{1}{k_2 qe^2} + \frac{1}{qe} t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

Where K_2 is the pseudo-second-order rate constant (g/mg*min), the slope of the plot between t/qt versus t gives the value of K_2, and qe

- **Intra particle diffusion**

To realize the exact diffusion mechanism, the adsorption kinetic data were further analyzed by an intra-particle diffusion model.

$$qt = kdt^{\frac{1}{2}} + I \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 7$$

Where kd is the intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$), and

I is a constant that gives idea about the boundary layer thickness (mg g^{-1})

This model states that intra-particle diffusion controls the adsorption process if the plot of qt vs $t^{1/2}$ results in a straight line(Doke & Khan, 2017).

In this study adsorption technology was applied for defluoridation process that is most preferable method because of easy of operation, cost effectiveness, use of raw materials are locally available i.e. adsorbent. It can be used on house hold and community level, and Highly effective technique. Langmuir and Freundlich adsorption isotherm are the most common and easily used models in solid- liquid adsorption with independent of temperature, so it was applied in this study to determine the interaction between adsorbate and the produced adsorbent in adsorption process. Pseudo first order and pseudo second order adsorption kinetic reaction model was applied in this experimental study.

2.12. Regeneration of used Alumina (Deactivated Alumina)

Large amounts of activated gamma alumina are required as an adsorbent to regenerate the working solution in the anthraquinone process, which produces hydrogen peroxide. Hydrogenation, oxidation, extraction, and regeneration of the working solution are the four main stages of the whole reaction, which is cyclic.

In the anthraquinone process, regeneration of the working solution is an important phase. Since undesirable side effects result in the production of degraded molecules, such as inactive

quinones. If regeneration was not carried out, the active quinone balance was also altered. The working solution is passed over an alumina adsorbent to regenerate it, converting inactive anthraquinones into desired ones(Q. Chen, 2008). Alumina also eliminates certain undesirable byproducts from the working solution by depositing them onto its surface. These inerts were eliminated via adsorption onto the alumina surface. Alumina is well-adhered to by a number of highly polar inerts through the hydroxyl groups and acid sites. The alumina is deactivated by the organics' adsorption (fouling) on it, and activated alumina loses its capacity to regenerate anthraquinones. Due to the deactivation of the activated form used in the process, it would be desirable to regenerate the gamma alumina to its active state once more by the following methods.

Washing Deactivated Alumina Solid Waste Sample with Deionized Water

The collected deactivated alumina was washed several times with deionized water to remove dusts and hydrogen peroxide from its surface and dry to remove moisture at 110^{o}C in an oven dryer for about 2 hours.

Soxhlet Extraction of Alumina Solid Waste

The conventional Soxhlet extraction was used for the removal of desired organic compounds from a heterogeneous material with the help of an appropriate solvent. The advantage of this method is that the heterogeneous material is washed with a pure solvent without using large amounts of solvent. Thus, the Soxhlet extraction is therefore interesting to use for the washing of used alumina. Evaporation of an appropriate organic solvent is the method used in the Soxhlet process of solid-liquid extraction of alumina. In a parallel pipe, the solvent flows past the alumina before condensing on top of it. At that point, the condensed solvent was dripping over the alumina. The unit's construction includes a swan neck that completely submerges the alumina before returning the solvent to the distillation flask at the bottom. Soluble organic compounds are removed from the alumina surface by the solvent's interaction with it. Mostly big molecules, the extracted organics will remain in the distillation flask because of their high boiling point (assuming the solvent having low boiling point)(Balasubramanian, 2020). The beginning of the solvent's evaporation and its return to the distillation flask, along with the extract, constitute the full cycle of this operation, which is repeated in a cyclic motion. This ongoing procedure is continued until the whole extraction is achieved. (Zygler et al., 2012).

Caustic Treatment of Alumina Solid Waste

Caustic is known to dissolve organic materials, and it may also dissolve alumina, which means that it is unstable in environments that are too caustic. Alumina should be treated with an aqueous sodium hydroxide solution that has a concentration of 0.5–5 %, according to Browning et al. For caustic treatments, a concentration of 1.5 % of the sodium hydroxide solution temperature (25°C) is typically the best method. Being able to determine the concentration range is crucial since it will impact the solid crystalline structure of γ alumina and may even cause the structure to fail. Since there would be less sodium hydroxide in the drained solution than in the fresh alumina solution, it is anticipated that the sodium hydroxide will either be adsorbed onto or react with the γ-alumina during the contact time(Browning, 1974).

Thermal Treatment of Alumina Solid Waste

The process of thermal regeneration uses high temperatures to replenish depleted adsorbents. It typically consists of three steps: adsorbent drying at about 105˚C, high-temperature desorption and decomposition (500-900˚C) in an inert atmosphere, and residual organic gasification by an oxidizing gas (CO_2 or steam) at an elevated temperature of 800˚C. It is frequently used in a variety of industrial processes in columns. The thermal stability and thermal history of an adsorbent must be thoroughly studied in order to perform thermal regeneration. When adsorbents are exposed to temperatures that are too high for them to withstand, they will melt(Suri et al., 1999).

There are two methods for thermally regenerating wasted adsorbents in practice: onsite and offsite. In situations where a significant quantity of spent adsorbent needs to be recycled, the offshore approach is utilized. Here, the adsorbent is brought to a designated location and regenerated in a furnace or kiln. When adsorbents loaded with various contaminants from various sources are combined for regeneration, the process becomes more complex and this technology has the drawback of being less effective than the onsite mode. The onsite regeneration method is thought to be highly costly and unsuitable for small establishments. When the concentration of adsorbate is high and the adsorbent is regarded as hazardous waste, the onsite approach is employed. Offsite regeneration is taken into consideration if the wasted adsorbent generation rate is between 225 and 700 kg/d, whereas onsite regeneration is not cost-effective unless the regeneration rate is more than 910 kg/d(Taylor et al.,2014). In this thesis

regeneration of treated alumina with both soxhlet and caustic is calcined at 500°C for 2hr until organic matter is removed (the black color were removed and it becomes white in color) and the alumina retrieves its active sites(Browning, 1974).

3. MATERIALS AND METHODS

3.1. Apparatus and Equipments

The apparatus used during this research were sieve mesh, digital electronic balance (FA2104, made in China), round bottom flask, oven, Soxhlet and their apparatus, thermometer, beaker, crucible, Muffle furnace (Ambassador F-07, Made in India), dissector, mortar and pestle, gravimeter sieves for the raw material pretreatment. Others like magnetic stirrer, test tube, conical flask, volumetric flask, funnel, filter paper(What man 125mm), pH meter(AD8000,Made in Romania), pipettes, glass rod, spatulas, and Fluoride Ion selective Electrode (Metrohm 826 pH mobile made in Germany), buckets, and plastic bottles were used in the application process and for sample collection. In addition to this, different characterization techniques such as UV-Vis, XRD, SEM, and FTIR were used to deal with the physicochemical characteristics of the adsorbent.

3.2. Chemicals and Reagents

The chemicals and solvents employed during the study were supplied from Fine Chemical Supplier except TISAB from OSHO, and De ionized water from AMCF quality control laboratory includes sodium fluoride, sodium hydro oxide pellet, TISAB methanol, ethyl acetate, distilled water and sulphuric acid. The chemicals and solvents were of analytical grades and used without any further modification and purification.

3.3. Methodology

3.3.1. Fluoride Containing Real Water Sample Collection and Preparation

Fluoride attacked ground water was collected from a deep well found around Wonji, which is located in the Rift Valley region of the country. Samples were collected from three different sampling sites with a total sample volume of 6 L using plastic bottles. The bottles used for collecting fluoride attacked ground water samples were washed carefully with detergent and 1 M H_2SO_4 and rinsed with water samples at the point of collection. Care was taken to avoid introducing errors during sampling and storage as contamination resulted from improperly cleaned sampling devices and sample containers. The loss of metals or precipitation in the sample containers was avoided by properly acidifying the sample using HNO_3 to pH < 2. The

collected samples were then refrigerated at 4°C. Prior to treatment, the samples were warmed to room temperature (25°C). Sample collection, preservation and storage were performed according to the standard procedures recommended by the USEPA guideline for drinking water sample collection.

3.3.2. Preparation of Standard Stock Solutions and Working Solutions

Fluoride stock solution (1000 mg/L) was prepared by dissolving 2.21g anhydrous sodium fluoride in 1L deionized water. Standard F^- sample at 5, 10 and 15mg/L concentration were prepared using appropriate dilution of the stock solution. Standard working solutions of fluoride with different concentrations were prepared by pipetting 5, 10, 15 ml of 1000 ppm NaF solution into different 1000 mL volumetric flasks and deionized water was added up to 1000 mL. The pH of the solution was controlled by adding 0.1 mol/L HCl or NaOH solution. The pH values were periodically measured and readjusted until they were constant or reach pH 7.

3.3.3. Collection and Pretreatment Adsorbent Material

Deactivated Alumina Solid Waste (DA-SW) was collected from Awash Melkassa Chemical Factory, Oromia regional state, Ethiopia. 500 g, freshly generated one batch drained from solid reversion beds were taken. The solid waste was washed with demineralized water to remove any impurities or remaining hydrogen peroxide.

Washing Deactivated Alumina Solid Waste Sample with Deionized Water

The collected deactivated alumina was washed three times with deionized water to remove dusts and hydrogen peroxide from its surface and dry to remove moisture at 110^{o}C in an oven dryer for about 2 hours.

Procedures of the Soxhlet Extraction

The heating bath was filled with 1.5 dm3 of Polyethylene Glycol (PEG) to warm the distillation flask. PEG was chosen as the heat transfer medium due to its elevated boiling point (exceeding 250 °C) and minimal vapor pressure (below 0.01 mm of Hg at 20°C), making it ideal for extended studies. The PEG bath temperature was set according to the boiling point (BP) of the extraction solvent.

The solid sample for extraction consisted of approximately 100 g of alumina, with 200 mL of solvent utilized per sample. The initial heating set point was set at 100°C, slightly above the

boiling point of the solvent, to trigger evaporation and condensation. The PEG bath temperature set point was modified according to the duration of the first cycle. Upon contact with aluminum oxide, organic substances, including carbon deposits and the working solution, were extracted and transported to the distillation flask alongside the solvent. The extraction of the organic material was evident from the reddish-brown coloration of the solvent surrounding the thimble. The experiment concluded that no further color change was observed around the thimble. To ensure the most thorough extraction of alumina, the process was continued for 4 h.

Procedures for Caustic Treatment

The used alumina sample treated with a mixture of methanol and ethyl acetate (the Soxhlet treated alumina samples) then treated with caustic. Approximately 100 g of alumina were immersed in 1.5wt % concentration of sodium hydroxide solution. The caustic solution was formed by 15.46 g of NaOH diluted in 500 mL of H2O. During the treatment, which took place for approximately 2 h, it was essential to maintain the temperature at 70°C, and a stirrer was added to ensure that the reaction between sodium hydroxide and alumina took place uniformly(Balasubramanian, 2020). The filtered alumina was separated and washed with 200 ml of demineralized water through a filter funnel. The filtered alumina was then placed in a porcelain dish and kept inside the dryer at approximately 110°C for approximately 2 h.

Thermal Treatment of Alumina Solid Waste

This thesis investigates the restoration of processed alumina utilizing both Soxhlet and caustic techniques. The procedure-involved calcination at 500°C for 2 hours, which removed organic material, changing the black substance to white and reactivating the alumina's active site(Balasubramanian, 2020). The refined activated alumina was then allowed to cool in a desiccator, ground, and passed through a gravimetric sieve to produce particles as small as 0.2 mm. These specimens were subsequently stored for later use and analysis. The spent alumina solid waste underwent graphical processing at the locations shown in Figure 1.

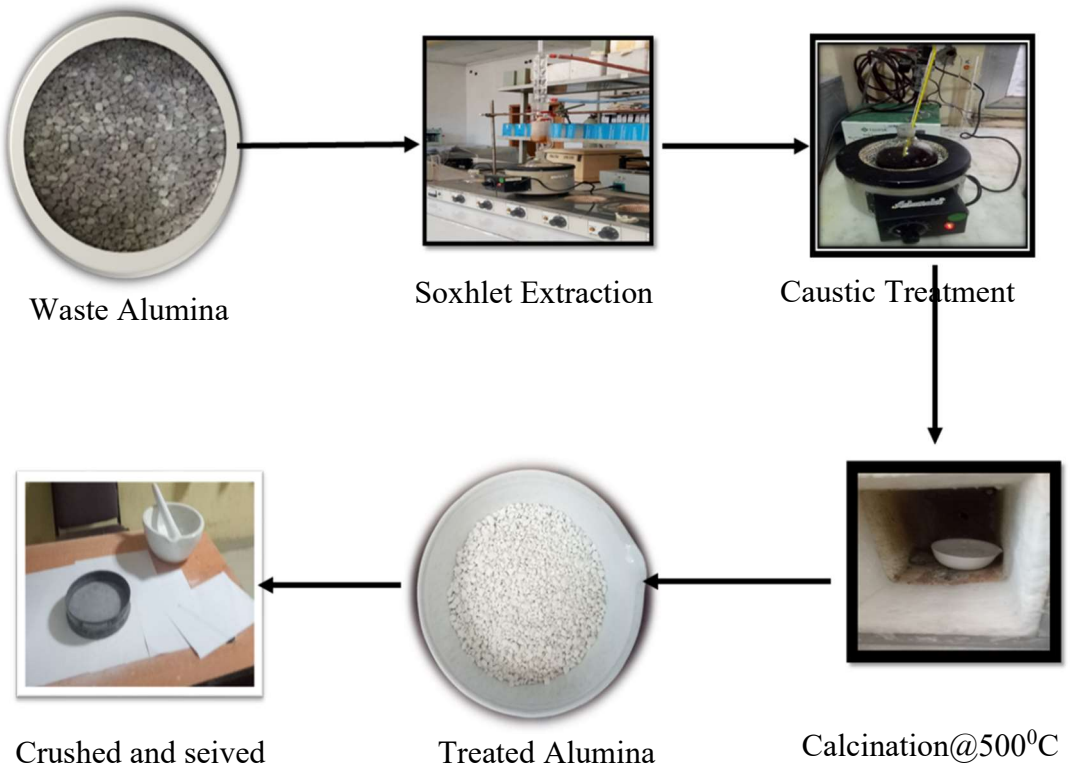


Figure 1: Methods of threating deactivated alumina solid waste.

3.4. Physio-chemical Characterization of Regenerated Activated Alumina Adsorbent

FTIR analysis

Regenerated activated alumina was characterized using Fourier transform infrared spectroscopy (FTIR). This was designed to determine the availability of the functional groups on the surface of the re-generated solid activated alumina using FTIR, Perkin Elmer 65 within the range of 4000-400 cm^{-1}.

XRD analysis

The X-ray diffraction method was used to characterize the formation of re-generated alumina and to deal its crystallinity as well phase formation. The XRD analysis of the prepared sample was done using x-ray diffractometer (XRD-7000S South Korea) was recorded from 10^o- 80^o with 2θ angles operated at 40 kV and 30 mA.

SEM analysis

SEM is a power-full and popular technique for the surface morphology and structural analysis. The surface morphology of the prepared re-generated solid waste alumina was characterized using SEM (JCM-6000Plus, JEOL/EO, and Japan) before and after the adsorption process were carried out.

UV-DRS analysis

DRS is an analytical technique used to study the optical property of materials, particularly solids and powders. It involves measuring the light that scattered and reflected off sample when it was illuminated by a light source. The light absorption behavior of the prepared re-generated alumina was also characterized via the UV-DRS technique.

3.5. Experimental Design

Response surface methodology (RSM), which is an effective statistical technique for experimental multiple parameter optimization, was used in this study to obtain a series of experiments designed to obtain an optimal response (Mihayo et al., 2021). Contact time, initial concentration, and adsorbent dose were some of the experimental parameters included. With the assistance of the Design-Expert (version 13) statistical tool, the experimental design was carried out. To evaluate the effect of the operating parameters on adsorption performance, the Central Composite Design (CCD) was used. To test multiple parameters and their interactions, CCD reduces the number of experimental trials needed. It is useful because it generates tremendous data by carrying out a limited number of experiments. It also offers the possibility to analyze the effects of a single variable on the response and their mixture of interactions. For all the adsorbents, the results of CCD were used to study the mutual effects of the parameters and optimum parameters according to RSM. The ranges analyzed were 30-120 min, 5-15 mg/L, and 1-2 g, respectively, for initial concentration, contact time, and adsorbent dose. To obtain the number of experiments and the set of parameters under consideration, these levels were introduced into the Design-Expert statistical program.

The experiment was designed using the design expert software package (Design expert 13), which was used to evaluate the coefficients of the regression model equation as well as their statistical significance. Three factors and three levels with runs of duplicate accomplished the experimental design.

Table 2: Factors and their level for removal of fluoride using full factorial experimental design with duplicate.

Factor	Code	Minimum	Intermediate	Maximum
Adsorbent dose (gram)	A	1	1.5	2
Initial concentration (mg/L)	B	5	10	15
Contact time (min.)	C	30	60	90

Table 3: Factorial design

	Factor 1	Factor 2	Factor 3
Std	A:Adsorbent Dosage (g)	B:Initial concentration (mg/L)	C:Contact time (min)
1	1.5	10	60
2	2	15	60
3	1.5	10	90
4	2	10	60
5	1.5	5	60
6	1	10	30
7	1	10	90
8	1	15	30
9	1.5	5	90
10	2	15	90
11	2	10	30
12	1	5	90
13	1	5	60
14	1.5	15	60

15	1.5	15	30
16	2	5	60
17	2	10	90
18	1	15	60
19	2	5	30
20	1	5	30
21	1.5	15	90
22	1.5	5	30
23	2	15	30
24	1	15	90
25	2	5	90
26	1.5	10	30
27	1	10	60

3.6. Batch Adsorption Experiment on De-fluoridation Process

During the investigation, the F^- concentration was measured using a fluoride ion-selective electrode (FISE). Because the batch mode is simple and reliable, it was used in all adsorption studies (Curkovic et al., 2001). The batch adsorption tests were conducted using the method reported by Aynekugnemn et al. (2015)

Tests of batch adsorption were used to evaluate the regenerated activated alumina's efficacy in removing fluoride. At neutral pH and constant temperature, the effects of process variables such initial concentration, dosage, and contact duration on fluoride uptake were examined. The fluoride solutions (5, 10, and 15 mg/L) were placed in beakers with the appropriate masses of treated alumina (1, 1.5, and 2 g) and continuously swirled for approximately 15 minutes using a magnetic stirrer set to 150 rpm. The setup was run for 1-2 hours and the analyzed samples were sampled into test tubes at pre-determined time intervals (i.e. 30, 60, and 90 minutes). All

solutions were adjusted to the required pH using 0.1 N NaOH and 0.1M HCl by adding the drop wisely. Finally, the concentration of fluoride and the corresponding potential of the analyzed samples (collected in the test tubes) were measured with a Fluoride Ion selective Electrode (FISE). During the batch experiments, 250 mL beakers were filled with 100 mL fluoridated aqueous solutions having an initial concentration of 5, 10 and 15 mg fluoride /L.

Equilibrium of the experiment was studied using Langmuir and Freundlich isotherm models. Pseudo- first order and Pseudo-second order models also studied the kinetics. Satisfactory conformity between experimental data and the model-predicted values was expressed by the correlation coefficient (R^2). Adsorption efficiency in percent and milligram of F^- adsorbed per gram of adsorbent were calculated using the equations 8 and 9 respectively.

The specific amount of fluoride uptake, qt (mg/g) at time t (min), was determined using the mass balance relationship:

$$Q_t = \frac{V\,(C_o - C_t)}{W} \quad \ldots\ldots 8$$

And the fluoride removal efficiency (% adsorption) was calculated using the equation:

$$\%\ \text{adsorption} = 100 * \left(\frac{C_o - C_t}{C_o}\right) \quad \ldots\ldots 9$$

Where Co and Ct (mg/L) are initial fluoride concentration and the concentrations at time t (h), respectively, V is volume of solution (L), and W (g) is mass of adsorbent used.

3.7. Fluoride determination

The fluoride determination procedure followed the methodology employed by the OSHO Fluoride Removal Centre. The total ionic strength adjustment buffer (TISAB) was prepared using Agarwal's technique. This involved combining 57 milliliters of glacial acetic acid, 58 grams of sodium chloride, 7 grams of sodium citrate, and 2 grams of EDTA with 500 milliliters of double-distilled water. Once dissolved, the solution's pH was adjusted to 7 using 6 M NaOH. The mixture was then diluted to 1,000 mL with double-distilled water in a volumetric flask. Standard solutions of 5, 10, and 15 mg/L were created from a stock solution (1000 mg/L of fluoride) by dissolving 2.210 gm of anhydrous sodium fluoride in fluoride-free double distilled water and diluting to 1 L through serial dilution. For each parameter, a calibration graph was

constructed, plotting potential against the logarithm of fluoride ion concentration. The resulting slope and intercept were utilized to convert the measured potential into fluoride concentration. To measure the liquid phase fluoride concentration, 15 mL of distilled water, 20 mL of sample, and 3 mL of TISAB were combined in a 100 mL volumetric flask and uniformly stirred using a magnetic stirrer. This sample volume remained constant throughout the experiment. The adsorption performance of the prepared adsorbent was then determined in mV using the Fluoride ISE.

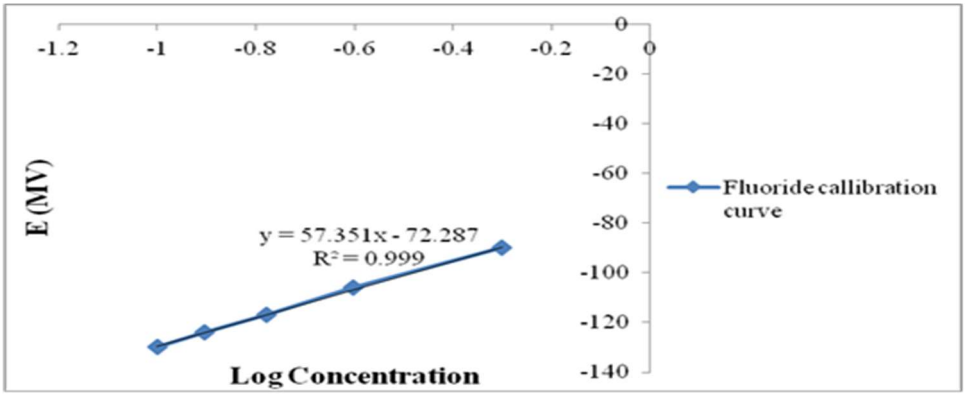


Figure 2: Calibration line for determination of F-.

3.8. Adsorption Isotherm

The most often used technique for depicting the equilibrium states of an adsorption system is the adsorption isotherm, which can be used to correlate the quantity of adsorbed pollutant at the solid/solution interface with the concentration of adsorbate in the bulk solution (Subasri et al., 2015). The two most widely used models, the Freundlich and Langmuir adsorption isotherm models, served as the foundation for the adsorption isotherm model used in this investigation. An adsorbent dosage of 2 g/l00 mL and different starting fluoride concentrations ranging from 5 to 15 mg/L were used in the adsorption isotherm tests. The contact time was 90 minutes, the solution was at room temperature, and the pH was seven. Using a magnetic stirrer, agitation was accomplished while stirring continuously at 150 rpm.

3.9. Adsorption Kinetics

Kinetic models were employed to examine the mechanisms that govern the sorption process, including mass transfer, diffusion control, and chemical reactions (Meena Soni et al., 2012). Understanding the rate at which the process occurs and the variables influencing that rate is

crucial; for this reason, the kinetics of the process were assessed. Based on the reaction kinetics of pseudo-first-order and pseudo-second-order reaction mechanisms, the adsorption data's kinetic analysis is conducted. Using optimum parameters, such as a constant surface loading of 10 mg/g (1, 1.5, and 2 g/L adsorbents for the corresponding fluoride content of 5, 10, and 15 mg/L, respectively), the adsorption kinetics were ascertained in this investigation.

3.10. Data Analyses

Batch adsorption experiment and the analysis of variables were presented using tables, and graphs, Microsoft excel, Origin, design expert software was used for data analysis.

3.11. Experimental Framework

The overall experimental frame works are described as follow:

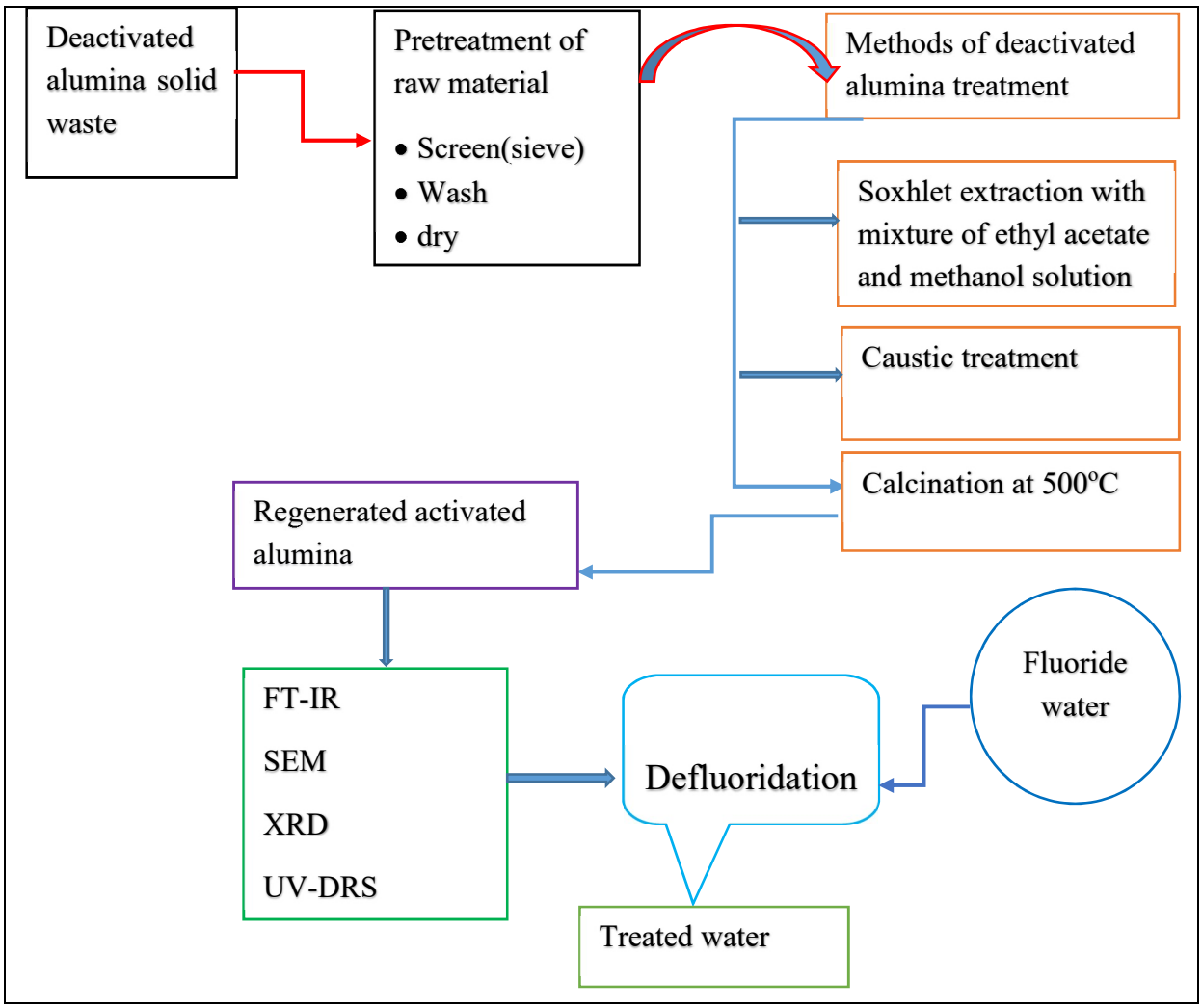


Figure 3: The overall experimental frame works.

4. RESULT AND DISCUSSION

4.1. Characterization Technique of Treated Alumina

The formations of regenerated solid alumina adsorbent were confirmed via characterization a technique includes Fourier transferred infrared radiation (FT-IR), scanning electron microscopy (SEM) UV- DRS and X- ray diffraction (XRD) analysis method.

4.1.1. Scanning electron microscope (SEM) analysis

The surface structure of the prepared re-generated active alumina obtained via caustic treatment and calcination at 500^{o}C was characterized via SEM both before and after adsorption of the fluoride ion (Figure 4a and 4b). The surface structure of an activated alumina particle was fractured, rough and porous. The particles presented a compacted morphology and some particles had a spheroidal shape. The morphology possessed spongy like porous rough surface, which are the crucial characteristics of an effective adsorbent. Figure 4a presents the morphology of re-generated active alumina adsorbent. The dominant surface morphology was found to be spherical with some aggregation and agglomerations. Both aggregation and agglomeration might be attributed due to the surface modifiers and the calcination temperature. Figure 4b depicts the SEM image of the re-generated activated alumina after the adsorption of the fluoride ion. The primary surface structure has been found to be spherical with high surface roughness, with particle size lies in the range of 1-10 μm, similar to SEM of regenerated active alumina before adsorption (Figure 4a). However, the degree of aggregation and agglomeration for the SEM of activated alumina after adsorption of fluoride ions has been dominantly observed. This might be due to the presence of the certain ions adsorbed on the surface of the re-generated alumina.

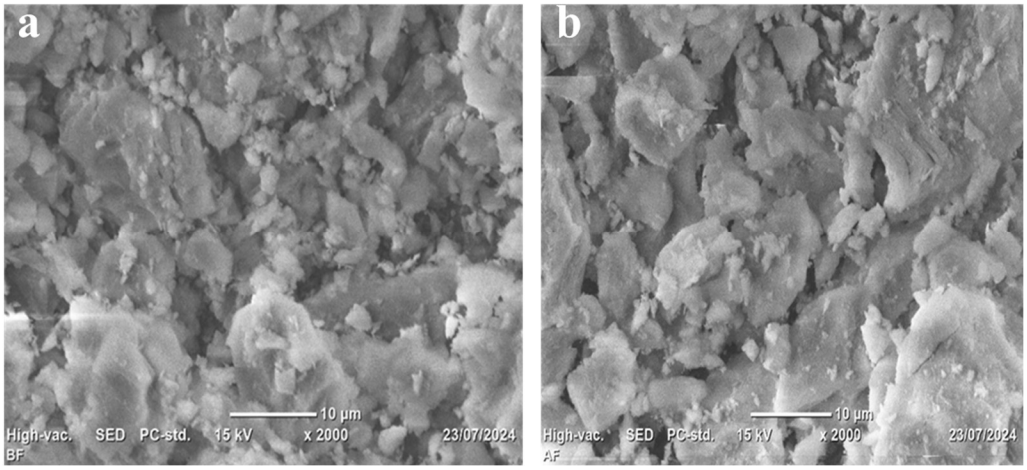


Figure 4: SEM image of treated activated alumina before (a) and after adsorption (b) of fluoride ion.

The SEM image shows that both samples have similar surface morphology, which was a heterogeneous mixture with irregular packed of flake like particles shape.(Flanagan & Road, 2014) have reported similar observations. The micrographs also clearly show that the surface of regenerated activated alumina before and after adsorption were rough and porous, therefore it is good candidate as an effective adsorbent.

4.1.2. X ray diffraction (XRD) analysis

The formation and degree of crystallinity of re-generated alumina was characterized using XRD technique. The XRD was done in the range of 10-80^0, it shows very broad, and sharp peaks were observed (Figure 5). The XRD analysis of regenerated activated alumina shows the formation of broad peaks with high degree of crystallinity, which confirms the smaller average crystalline size and the high degree of crystallinity, respectively. The formed peaks of the re-generated alumina adsorbent directly match with the JCPDS card number of 00-004-0880.It is known that amorphous materials have good adsorbent properties due to their high specific surface area and more active available sites on their surfaces (Wan et al., 2021). The surface sites associated with functional groups represent a small proportion of the total surface area. However, small variations in the chemical nature of an adsorbent may produce important changes in its adsorption capacity (Moughaoui et al., 2017).

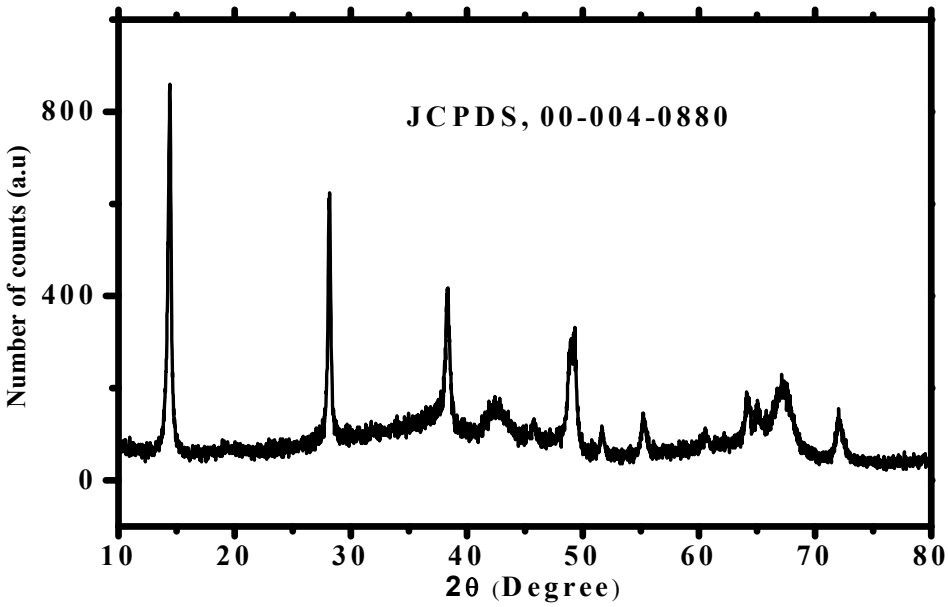


Figure 5: XRD image of regenerated activated alumina (γ) alumina.

The relative average crystalline size of the prepared re-generated active alumina oxide was calculated using the Debye Scherer's equation and the value were found to be 24.87 nm. The result directly confirms that the size of the prepared alumina oxide was found to be in nano-range. Due to its enhanced surface area, high adsorption efficiency was record.

4.1.3. Fourier Transform Infrared Spectroscopy (FT-IR) analysis

The possible functional groups and the formation of re-generated alumina were characterized via FT-IR characterization in the range of 4000-400 cm-1 (Figure 6). The FT-IR result of re-generated alumina oxide shows peaks at 3015, 1740, 1368, 1216 and 520 cm^{-1}. The strong intense broad peak located at around 3015 cm^{-1} assigned for -OH stretching vibrations mode in the prepared active alumina oxide, which might be attributed surface adsorbed moisture. While the next broad peak at 1740 cm^{-1} due to the stretching of asymmetric COO mode of vibration. The band peak at 1368 and 1216 cm^{-1} might have occurred due to the stretching vibrations of Al=O bond. The main peaks at 520 cm^{-1} are assigned for Al-O stretching mode in a tetrahedron with symmetric bending of Al-O-H in the alumina(R. Kumar et al., 2020). This peak directly reveals the formation of pure alumina oxide, as confirmed via the XRD result. These functional groups play a vital role in the adsorption of fluoride ion on the surface of the active re-generated alumina.

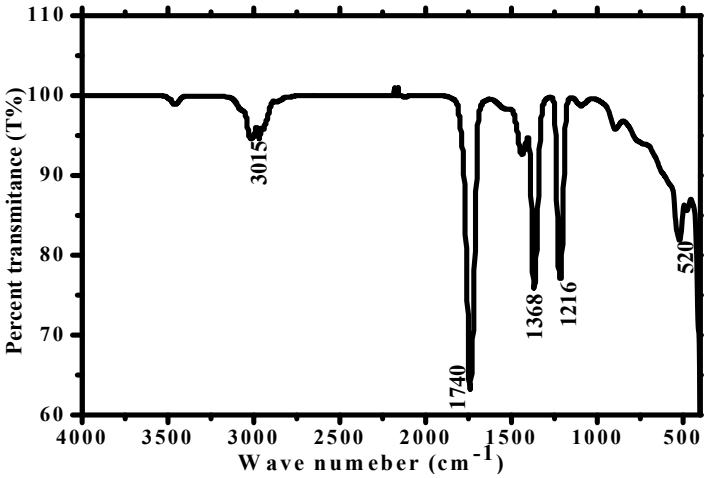


Figure 6: FT-IR spectra of regenerated activated alumina.

The FT-IR analysis in side with the XRD and SEM result, confirms the formation of highly crystalline with large porous surface morphology and diverse functional groups contained re-generated alumina. These properties plays essential role for the adsorption of fluoride ion on the surface of re-generated alumina.

4.1.4. Ultraviolet-diffuse reflectance (UV-DRS) analysis

The light absorption behavior of the prepared re-generated alumina was also characterized via the UV-DRS technique (Figure 7). A sample of the regenerated alumina is prepared, typically in powder form and exposed to UV-Vis light, and the absorption was recorded as a function of wavelength. The alumina was found to absorb light source in both the UV and visible region. The maximum light absorption peak was absorbed at around 379 nm wavelength. The band gap energy (Eg) can be estimated from the absorption edge using the equation (Eg = hc/lambda)and the calculated result become 8.4 eV, which is in good agreement with the previously reported works of the study(French, 1985).

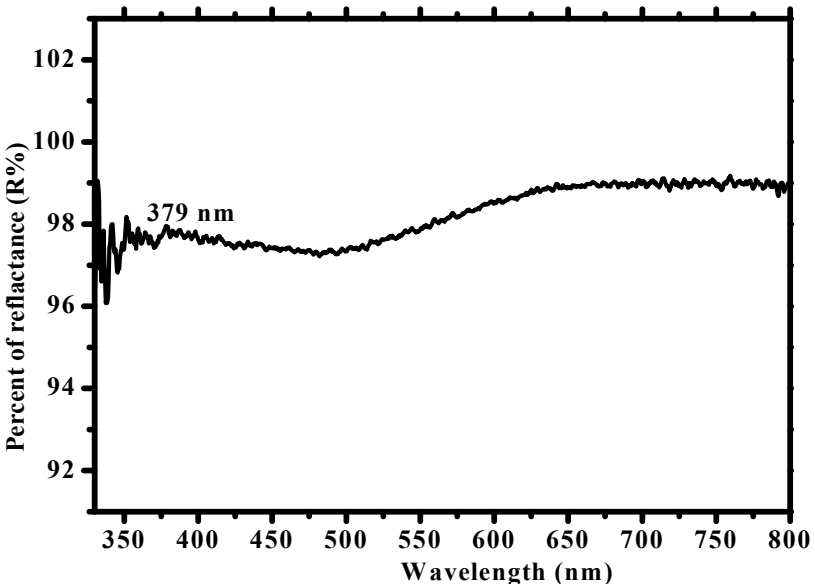


Figure 7: UV-DRS of re-generated alumina.

To improve light absorption behavior of the re-generated solid alumina attributes from its high surface area and improved degree of crystallinity. Such property is very essential for the effectiveness of an adsorbent.

4.2. Experimental Design Result

The experimental design was accomplished by full factorial in Design Expert 13 and the result was shown in appendix B.

Effects of factors on percent of fluoride removal in the desired factorial model were explained in terms of the P-values less than 0.05 indicate model terms are significant as it has been presented in Table 4. In this case, factors A, B, C and AC are significant model terms. P-Values greater than 0.001 indicates the model terms are no significant. In this case, AB, BC and ABC are case, so modify the model by neglect the interaction effect of AB, BC and ABC.

Table 4: Effects of factors on percent of fluoride removal in the desired factorial model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1380.52	18	76.70	359.88	< 0.0001	significant
A-Adsorbent Dosage	504.12	2	252.06	1182.74	< 0.0001	
B-Initial Concentration	205.35	2	102.68	481.79	< 0.0001	

C-Contact Time	634.36	2	317.18	1488.30	< 0.0001	
AB	0.0547	4	0.0137	0.0641	0.9909	
BC	0.4533	4	0.1133	0.5318	0.7166	
AC	14.85	4	3.71	17.42	0.0005	
Residual	1.70	8	0.2131			
Lack of Fit	1.70	7	0.2436			
Pure Error	0.0000	1	0.0000			
Cor Total	1382.22	26				

After the model reductions that improve the model or the modified model is followed by ANOVA (Table 5) for selected factorial model.

Table 5: ANOVA for selected factorial model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1380.00	10	138.00	992.79	< 0.0001	significant
A-Adsorbent Dosage	504.12	2	252.06	1813.35	< 0.0001	
B-Initial Concentration	205.20	2	102.60	738.13	< 0.0001	
C-Contact Time	641.77	2	320.89	2308.50	< 0.0001	
AC	15.38	4	3.85	27.67	< 0.0001	
Residual	2.22	16	0.1390			
Lack of Fit	2.22	15	0.1483			
Pure Error	0.0000	1	0.0000			
Cor Total	1382.22	26				

The Model F-value of 992.79 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AC was significant model terms. P-Values greater than 0.1000 indicate the model terms are not significant.

Table 6:Model Acceptability Measures for percent fluoride removal efficiency

Std. Dev.	1.10	R^2	0.9939
Mean	73.81	Adjusted R^2	0.9901
C.V. %	1.49	Predicted R^2	0.9827
		Adeq Precision	56.1404

The Predicted R^2 of 0.9827 is in reasonable agreement with the Adjusted R^2 of 0.9901; i.e. the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 56.140 indicates an adequate signal. This model can be used to navigate the design space. Experiments were performed according design given by software, 27 runs performed to have responses (%) adsorption and final Equation in Terms of Coded Factors are given below:

Percent of fluoride removal = 77.66 + 5.19A[1] -0.1513 A[2] -3.35 B[1] +0.1554 B[2] +5.66C[1] +0.6310C[2] + 1.08A[1]C[1] + 0.0322A[2]C[1] +0.0466A[1]C[2] -0.0504 A[2]C[2]

Where: A is adsorbent dose in gram

B is initial fluoride concentration in mg/L and

C is contact time in minutes

The equation in terms of coded factors can be used to make predictions about the response to given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. A report for actual and predicted data in the experimental design was shown in appendix C, and the actual versus predicted graph was shown below in the Figure 8.

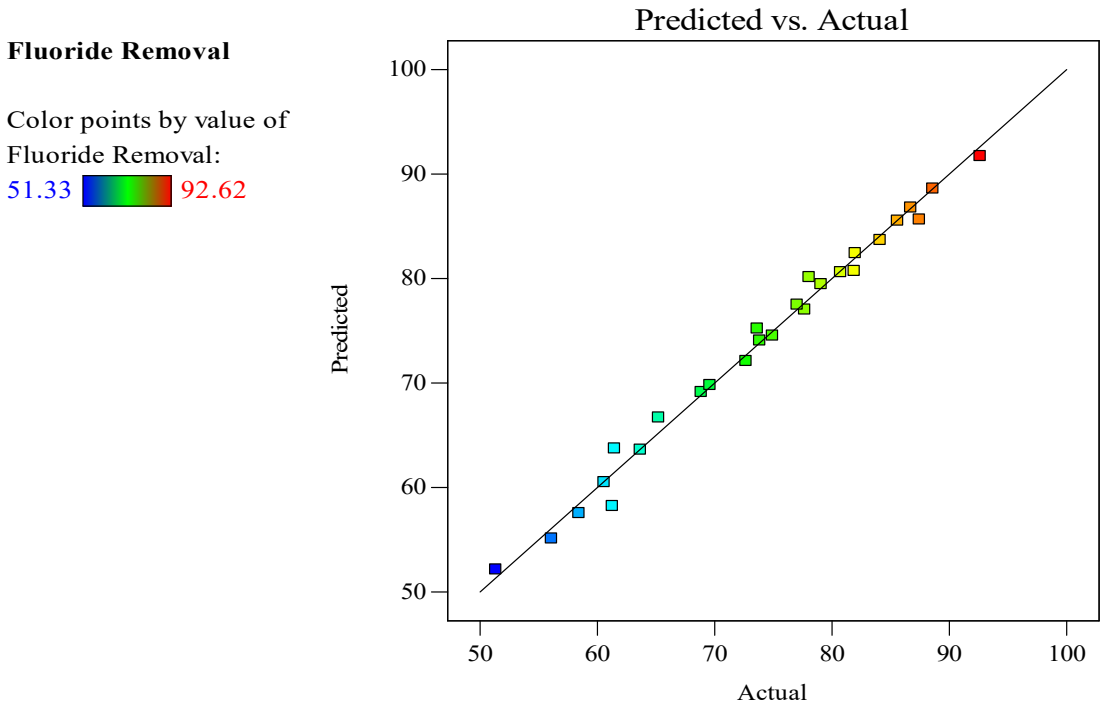


Figure 8: Actual versus predicted graph of de-fluoridation by regenerated activated alumina.

From the above Figure 8, shows the two values that are the experimental prediction value and the actual value lie on the same line. This shows that the experiment was performed properly and the adsorption parameters (adsorbent dose, initial fluoride concentration, and contact time) are fit to the experimental prediction value. The purpose is to identify a value, or group of values, that are not easily predicted by the model and easily compare to the actual value.

4.2.1. Interaction factors effect on defluoridation

The interaction factors that affect the adsorption performance of the re-generated solid alumina includes initial concentrations of 5 mg/L, contact time of 90 min, and adsorbent dosage of 2 g at neutral PH.

A. Effect of adsorbent (dose) with initial fluoride concentration

The amount of contact surface between an adsorbent and adsorbate solution plays an important role in the adsorption process system. The effect of adsorbent dose and initial fluoride concentration were investigated by varying the adsorbent dose in the range between 1-2 g in a 100 mL desired solution with the range of 5-15 mg/L initial fluoride concentration at 90 min contact time and pH 7. The highest fluoride removal was achieved at a higher dose and at a low fluoride concentration and minimal removal of fluoride was recorded at low adsorbent dose and

a higher initial fluoride concentration. When the initial fluoride concentration increased, the removal effectiveness decreased sharply because there was not enough surface area with an improved porous adsorption site to hold additional fluoride ions on its active surface regions(Getachew et al., 2015).

The existence of an enormously large number of porous active sites available for fluoride ion binding was credited with the increase in fluoride adsorption effectiveness with increasing adsorbate dosage. On the other hand, the adsorption capacity decreases with increasing dose.

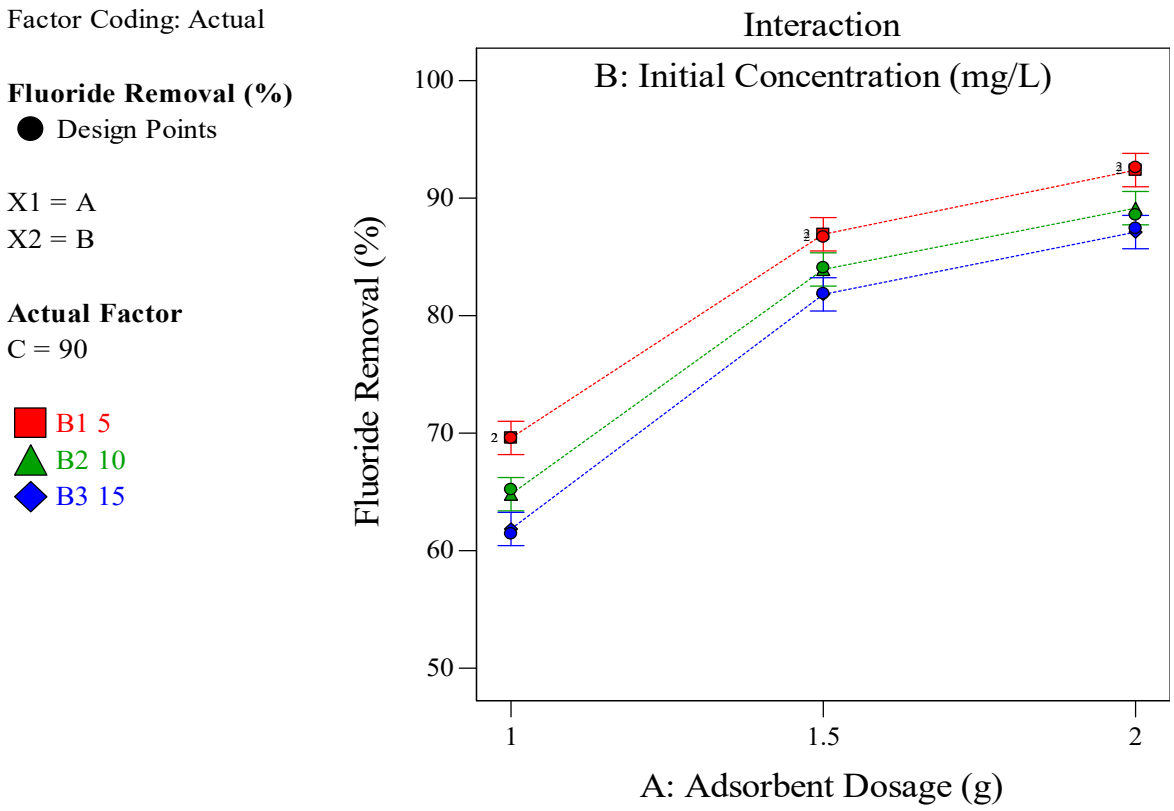


Figure 9: Interaction effect of dosage and initial concentration in fluoride removal efficiency.

B. Effect of adsorbent dose with contact time

The removal efficiency of the adsorbent was increased with the increment of the adsorbent dose and contact time until they reached the equilibrium point of time and dose. The analysis was conducted at seven pH and 5 mg/L of initial fluoride concentration. The fluoride removal efficiency increased sharply from 51.33 to 92.62 %, when the adsorbent dose and contact time increase correspondingly. The maximum fluoride removal efficiency (92.62%) was recorded at a lower initial fluoride concentration (5 mg/L) with a contact time of 90 min and 2 g of adsorbent

dose with 7pH value. This indicates higher removal efficiencies obtained at high adsorbent dose with high contact time, at lower initial fluoride concentrations are due to higher ratio of active surface area to total fluoride ions, which leads to the utilization of more accessible energetically active sites on the adsorbent surface. Figure 10 below shown indicates the increase of removal efficiency of re-generated solid alumina adsorbent at high adsorbent by increasing the contact time of adsorption.

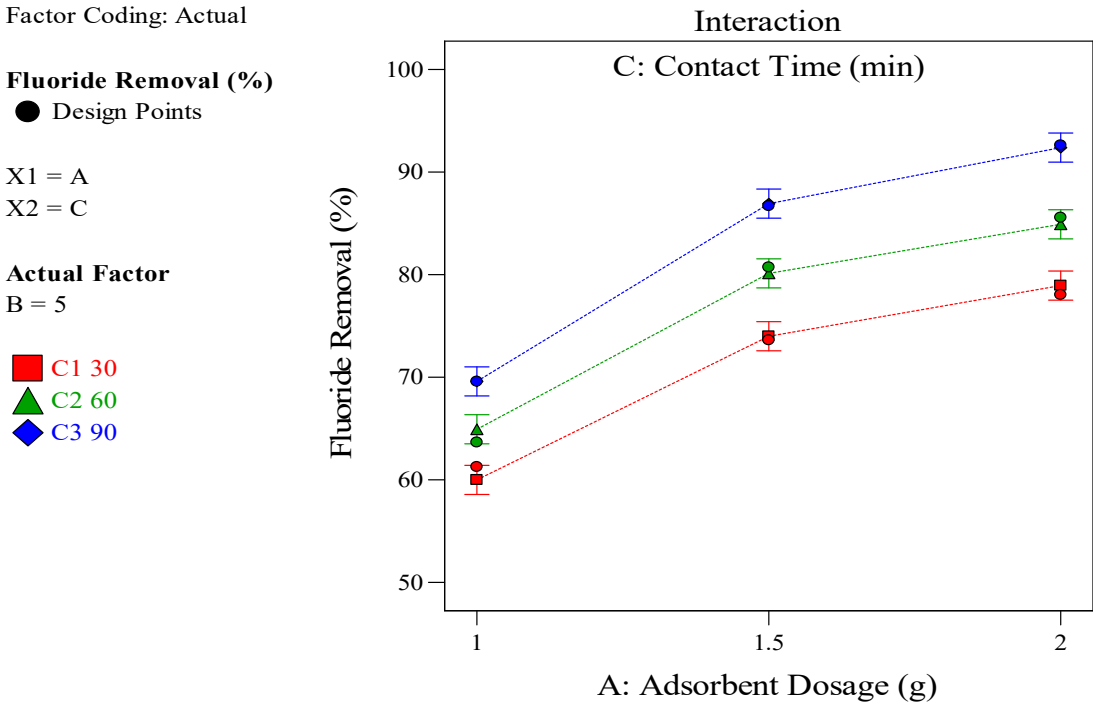


Figure 10: Interaction effect of dosage and contact time in fluoride removal efficiency.

4.2.2. Effect of contact time

Adsorption experiments were performed to investigate the impact of contact time on the kinetics of fluoride ion removal adsorption using regenerated solid alumina adsorbent. The degree of fluoride ion removal was determined by varying the contact time from 30 to 90 minutes, with a fluoride ion concentration of 5 mg/L, at neutral pH, and with an adsorbent dosage of 2 g. Figure 11 below illustrates the results, which were represented as the proportion of the fluoride ion removed vs contact time.

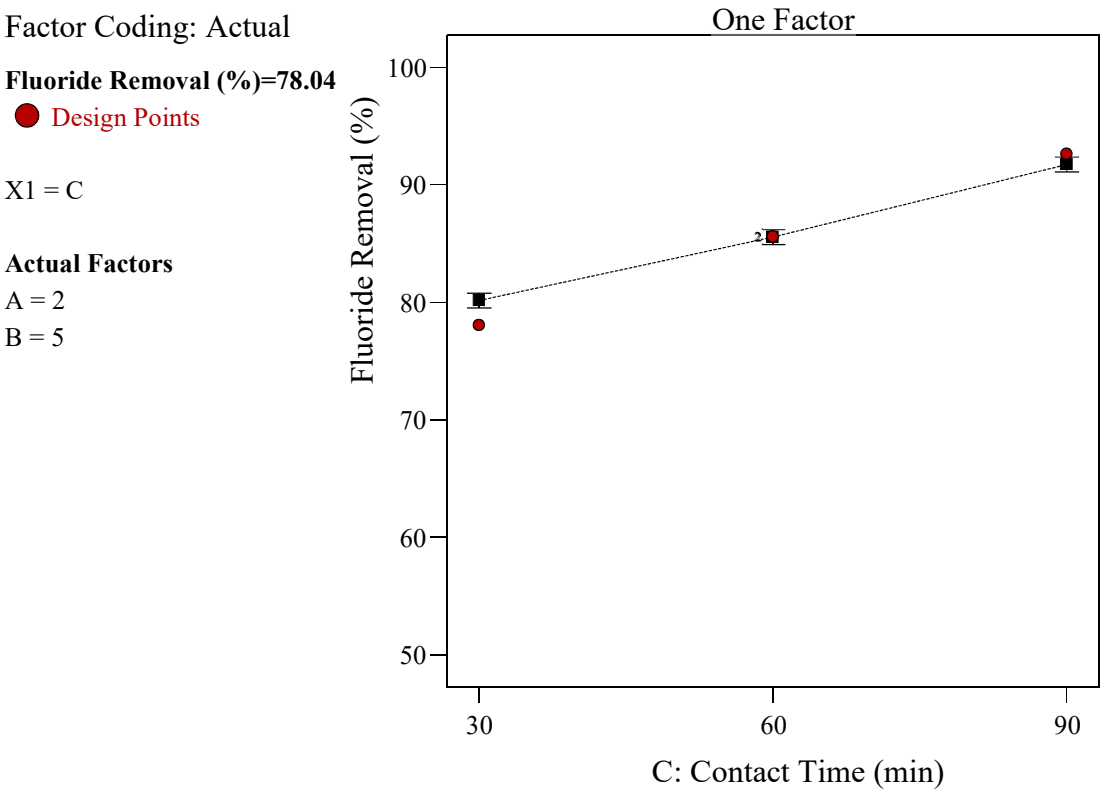


Figure 11: The effect of contact time on the fluoride removal efficiency.

As can be seen in Figure 11, the fluoride removal efficiency of prepared re-generated activated alumina was increased as the contact time increased. The maximum fluoride removal of 92.62 % was recorded at 90 min and the minimum fluoride removal was 78.04 % at 30 min of contact time with the high adsorbent dose (2 g.) and fluoride concentration of 5 mg/L. The variation in the adsorption performance might be attributed because initially all adsorbent sites were free and the solute concentration gradient was high. Later, the fluoride uptake rate by the adsorbent had decreased significantly, due to the decrease in the number of adsorption sites, which means the adsorption capacity of the adsorbent had become low.

4.2.3. Effect of initial fluoride concentration

The effect of the initial concentration of the fluoride ion on to the adsorption of the prepared adsorbent surface was studied by varying the initial concentration of the fluoride ion solution from 5 to 15 mg/L under pH of 7, contact time of 90 min, and a dose of 2 g. The results obtained were plotted as percentage removal of the fluoride ion versus initial concentration of the fluoride ion solution as shown in Figure 12. With an increase in the initial concentration of the fluoride

ion solution, the percentage removal of the fluoride ion has been decreased due to an insufficient number of active sites that are available on the regenerated activated alumina adsorbents to adsorb the fluoride ions from the highly concentrated solution of the fluoride ions. As a result, the majority of fluoride ions interact with the active sites on the activated alumina adsorbent, resulting in a higher fluoride removal percentage. With an increase in the initial concentration of the fluoride ion solution from 5 to 15 mg/L, the percentage removal (% R) of the fluoride ion is decreased from 92.62% to 87.44% at maximum contact time and adsorbent dose. Thus, the initial fluoride concentration has an influence on sorption. Hence, it is necessary to determine initial fluoride concentration before attempting removal. The adsorbent dosage and contact time required to reduce fluoride concentration to an acceptable level are determined by the sample's initial fluoride .If the fluoride concentration in the real water sample is high, then the dosage as well as the contact time required to bring the fluoride concentration to permissible level will also be high.

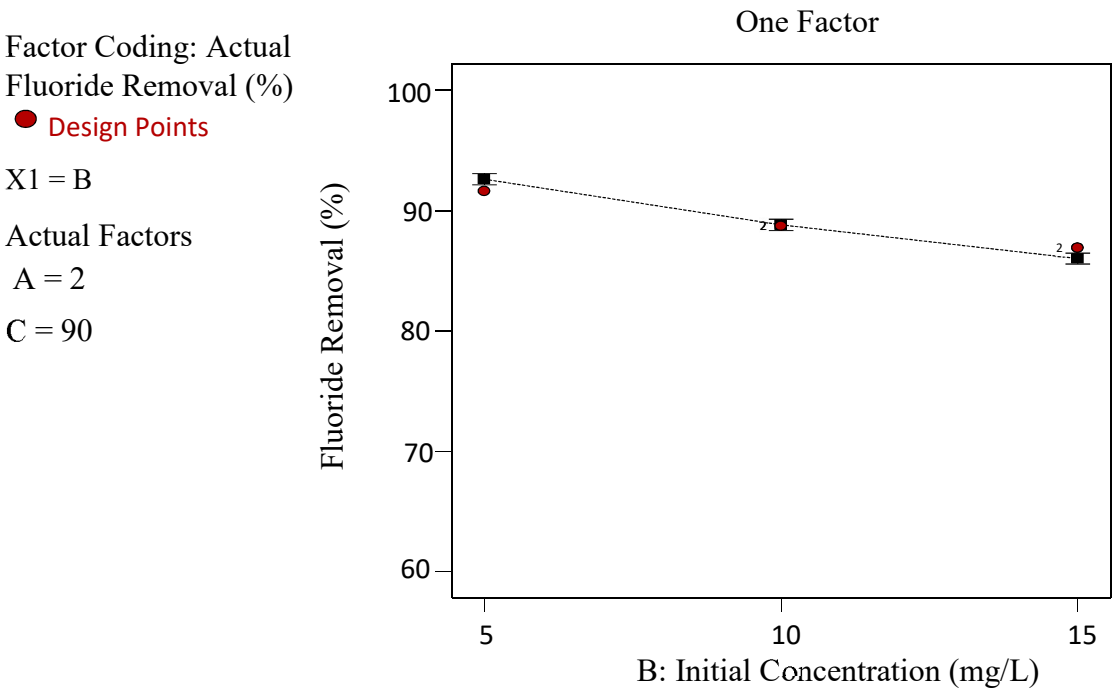


Figure 12: The Effect of initial concentration on fluoride removal efficiency.

4.2.4. Effect of adsorbent dose

It was found that the fluoride removal efficiency increased from 69.59% to 92.62% when the amount of the adsorbent dose was increased from 1 to 2 g as can be presented in Figure 13. This is likely due to the greater availability of active surface sites for F- binding as a result of increased adsorbent dose. The response of the adsorbent dose at a fixed fluoride concentration of 5 mg/L and a contact time of 90 min is presented in the Figure 9, below. The maximum fluoride removal efficiency (92.62%) was obtained at 2 gm. of adsorbent dose with a 5 mg/L initial fluoride concentration and 90 min contact time. The change in the given adsorbent level was decreased; this can be indicating the maximum point. In this study the maximum adsorbent dosage was found to be 2 g. However, it has been found that above 2 g dosage, the removal efficiency can be either constant or increased by small amount.

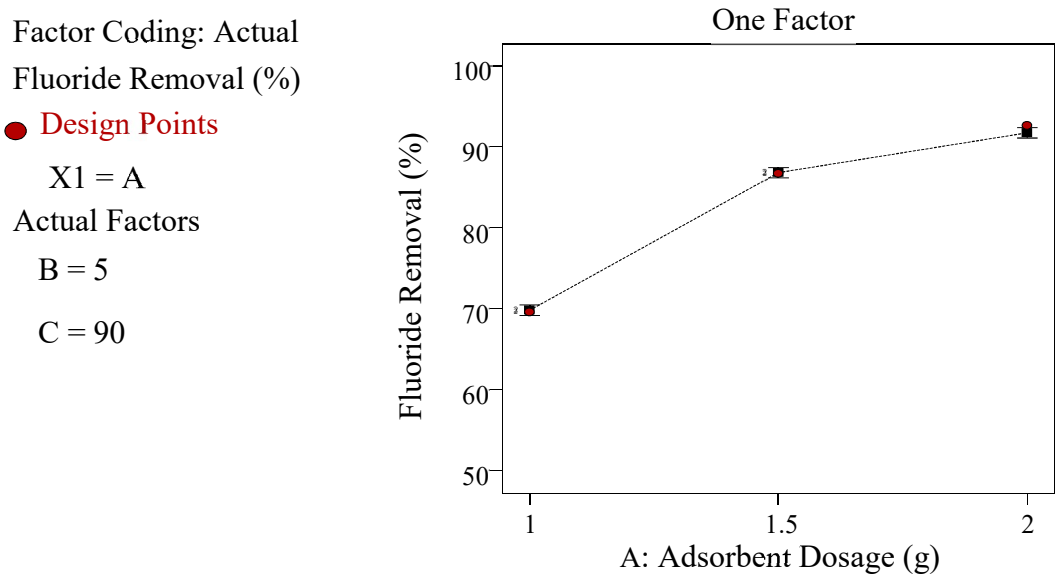


Figure 13: The effect of adsorbent dosage on fluoride removal efficiency.

4.3. Adsorption Isotherm

The adsorption isotherm is useful for determining the feasibility of removing ions from the bulk of solutions. Langmuir and Freundlich isotherm models were used in this study to investigate the adsorption equilibrium between the fluoride solutions and the regenerated activated alumina. Table 7 shows the experimental data collected to determine the adsorption isotherm in the

fluoride removal process by regenerated activated alumina at neutral pH, initial fluoride concentration of 5, 10 and 15 mg/l , 90 min contact time and at 2 grams of adsorbent dose.

Table 7: Data for the determination of adsorption isotherm

Initial fluoride concentration(Co) (mg/l)	Ce(mg/l)	1/Ce	Log (Ce)	qe (mg/g)	1/qe	Log(qe)
5	0.369	2.710	-0.433	2.316	0.432	0.365
10	1.141	0.876	0.057	4.430	0.226	0.646
15	1.884	0.531	0.275	6.558	0.152	0.817

Langmuir isotherm

In Patiha et al., (2016), they presented a simple technique for the determination of the isotherm equation based on the main assumption so called the monolayer assumption. The linearization form of the Langmuir equation becomes;

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{kLqm} * \frac{1}{Ce} \quad \text{.....10}$$

The Langmuir isotherm was determined by plotting (Ce/qe) versus (Ce). The maximum adsorption capacity (qm), the Langmuir isotherm constant KL and R^2 were determined from the graph.

The effect of isotherm shape can be used to predict whether an adsorption system is ‘‘favorable” or ‘’unfavorable”, used the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter RL, which is defined by the following relationship (Pillai et al., 2021).

$$RL = \frac{1}{1+Co*RL} \quad \text{.....11}$$

Where RL is the dimensionless separation factor, Co is the initial fluoride concentration mg/l and KL is the Langmuir constant L/mg. When the value of RL =1, the adsorption isotherm system is linear, RL>1 is unfavorable, 0<RL<1 is favorable and RL=0 irreversible.

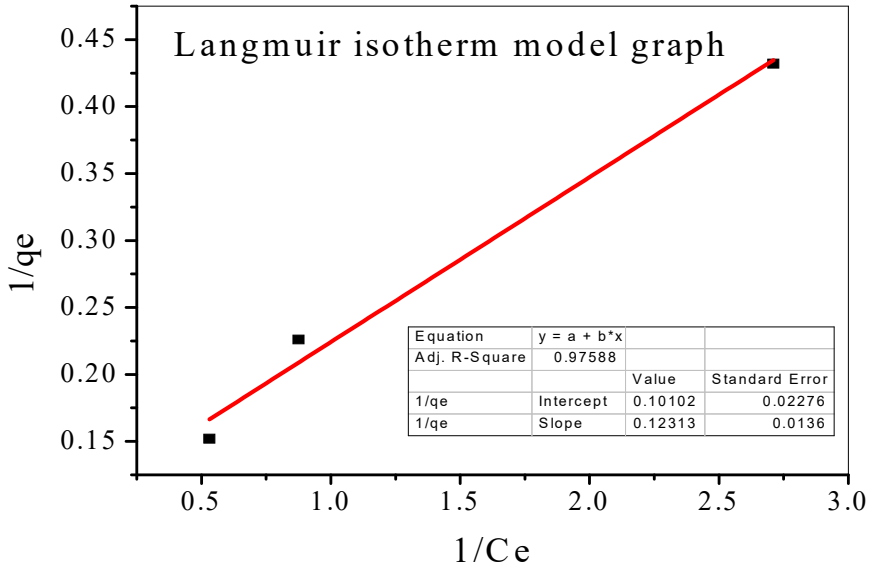


Figure 14: Langmuir isotherm model of de-fluoridation by regenerated activated alumina.

Table 8: Summary table for the line fit graph of Langmuir Isotherm model parameters for the adsorption of fluoride onto regenerated activated alumina.

Isotherm model	Equation	Plot	Parameters		
Langmuir	$\frac{\mathbf{1}}{\mathbf{qe}} = \frac{\mathbf{1}}{\mathbf{KLqmax}} \cdot \frac{\mathbf{1}}{\mathbf{Ce}} \cdot \frac{\mathbf{1}}{\mathbf{qmax}}$	$\frac{1}{ce}\ vs\ \frac{1}{qe}$	1/qm=intercept = 0.10102 qm=1/intercept =9.889mg/g	1/(qmKL)=slope =0.12313 KL=1/(qm*slope) =0.8213L/mg	R^2 = 0.97588

Freundlich adsorption isotherm

The model is based on adsorption on a heterogeneous surface. The earliest known relationship describing the adsorption equilibrium is given by(Getachew et al., 2015).

$$qe = Kf Ce^{1/n}$$

The linear form of Freundlich equation is expressed as;

$$\log(qe) = \log(kf) + \frac{1}{n}\log(Ce)$$

Where qe is the amount of ion adsorbed (mg/g), Ce is the equilibrium concentration (mg/L), Kf and 1/n are empirical constants, indicating the adsorption capacity and adsorption intensity, respectively. The values of Kf and 1/n can be calculated from the slopes and the intercepts of the plot of log qe versus log Ce.

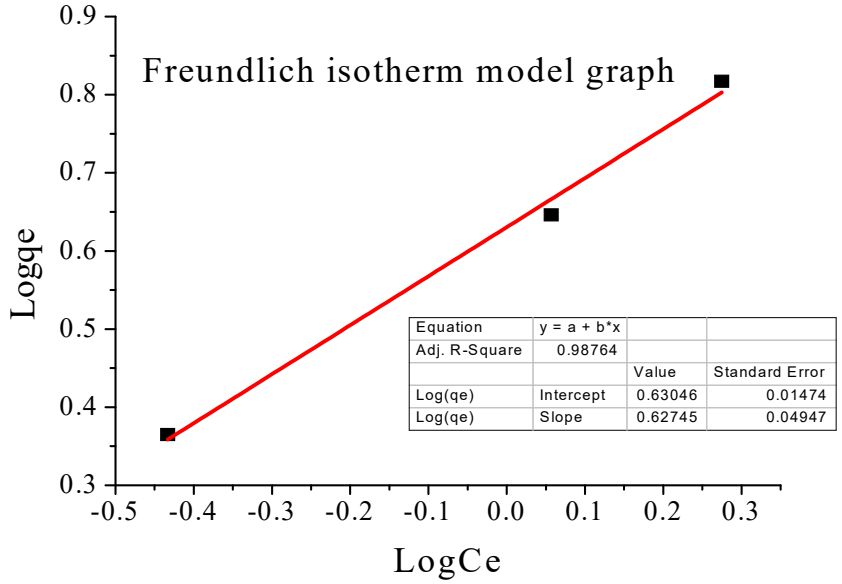


Figure 15: Freundlich isotherm model of regenerated activated alumina.

Table 9: Summary of Freundlich isotherm model parameters for the adsorption of fluoride onto regenerated activated alumina.

Isotherm model	Equation	Plot	Parameters		
Freundlich	$Logqe=\frac{1}{n}*Logc+Logkf$	$LogC_e$ Vs Logqe	Logkf=intercept = 0.63046 kf= 4.2703	1/n=slope, = 0.6274 n= 1/slope =1.594	R^2= 0.9876

Therefore, from the above Table 8 and 9, it was observed that the correlation coefficient value for the linear form of Freundlich (R^2=0.98764) is higher than the Langmuir (R^2 =0.97588)

isotherms. Thus, from the values' of correlation coefficient, the Freundlich isotherm model was found to be the best representative of the adsorption of fluoride by regenerated activated alumina. The Freundlich model equation was preferred for the estimation of maximum adsorption capacity; Kf and 1/n were 4.2703 g and 0.6304 respectively. The slope ranges between 0 and 1 and it is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below 1 implies chemisorption process where 1/n above 1is an indicative of cooperative adsorption.

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes (Santhi and Smitha.2010)

During the study, both pseudo first order and pseudo second order kinetic model were investigated. The experimental data that used to evaluate the adsorption pseudo-first order and pseudo-second order kinetic model were shown below in the Table 10, and the graph was plotted by using Microsoft excel software to obtain the correlation coefficient and the rate constant of the model equation.

Table 10: Data to determine the rate equation of pseudo first order and d second order model.

Dosage (g)	Initial concentration (mg/L)	Contact time t(min)	qt (mg/g)	qe,exp	t/qt	log(qe-qt)
1	5	30	3.063	3.482	9.793	-0.378
		60	3.192	3.482	18.794	-0.538
		90	3.479	3.482	25.866	-2.602
1.5	10	30	4.844	5.61	6.193	-0.116
		60	5.135	5.61	11.684	-0.323
		90	5.606	5.61	16.054	-2.398
2	15	30	5.534	6.562	5.421	0.012
		60	5.929	6.562	10.119	-0.198
		90	6.558	6.562	13.724	-2.347

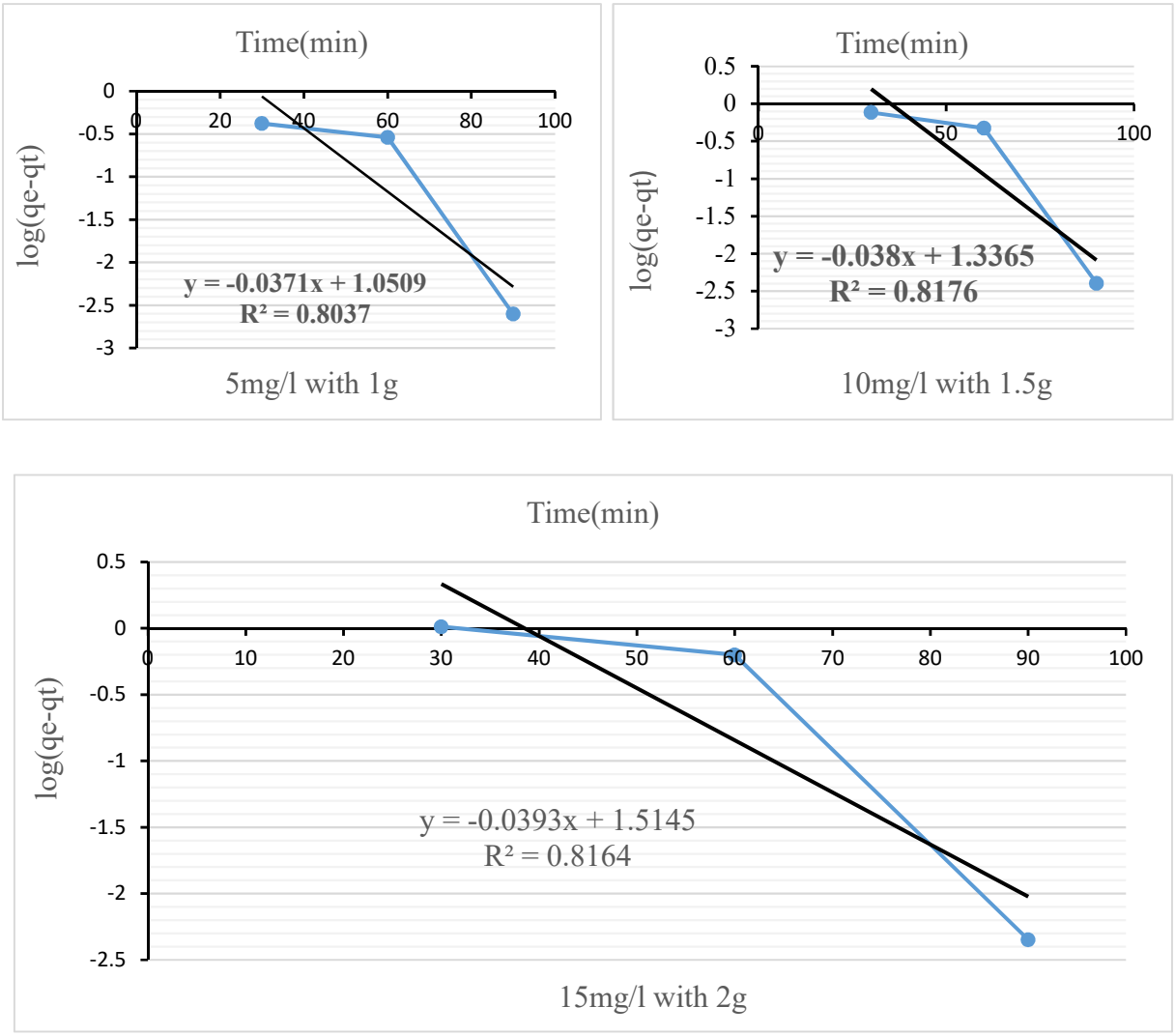
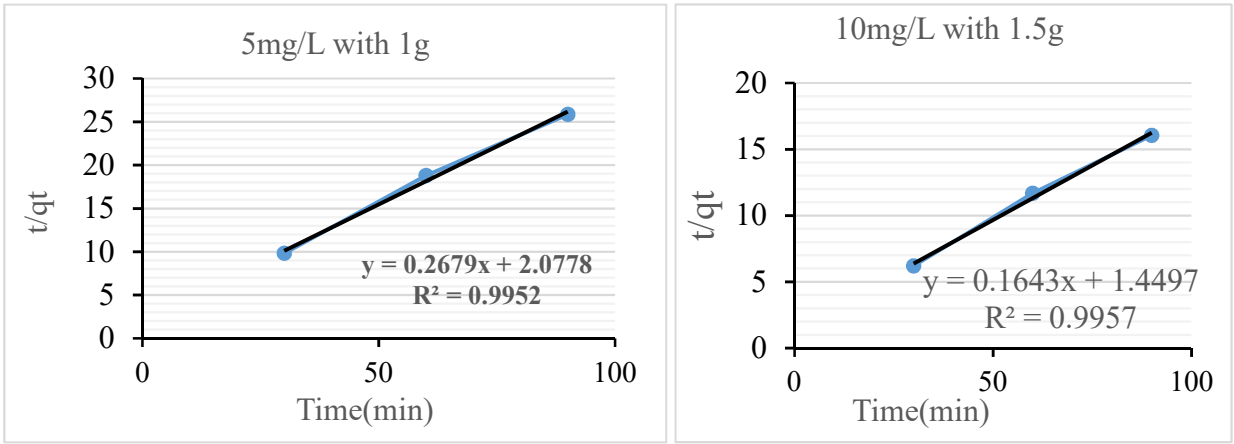


Figure 16: Adsorption kinetics of pseudo first order model graph.



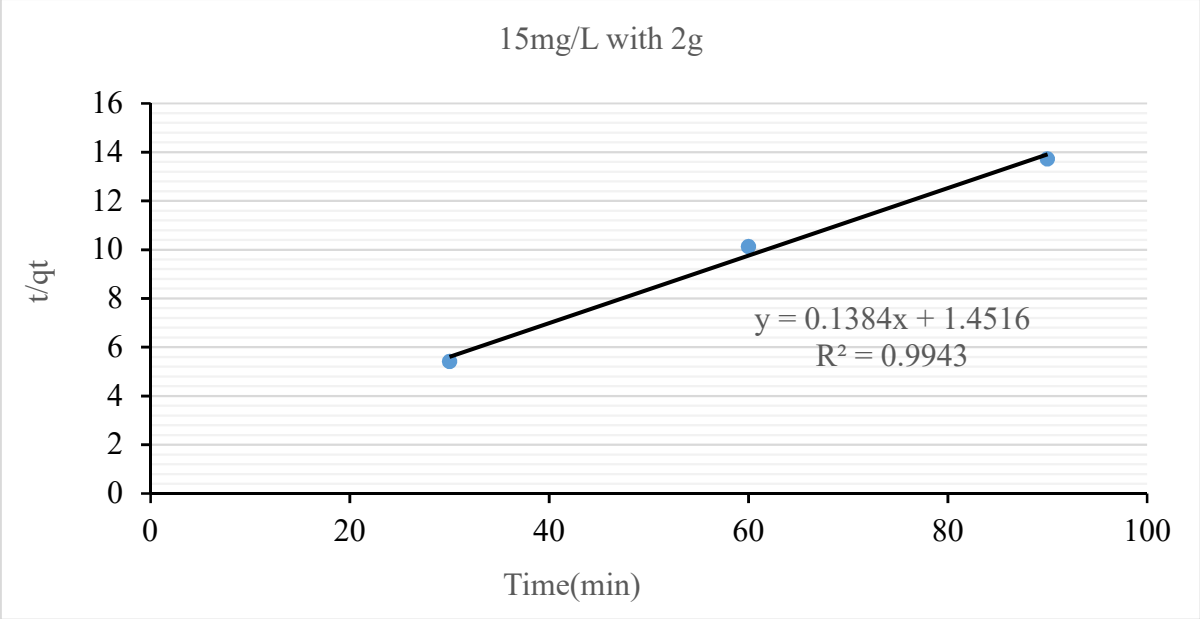


Figure 17: Adsorption kinetics of pseudo second order model graph.

Adsorption kinetics model graph for the adsorption of fluoride ion on the active high porous re-generated activated alumina with initial fluoride concentrations of 5, 10, and 15 mg/L using an adsorbent dosage of 1, 1.5 and 2 g, respectively at pH = 7 and contact time of 90 min. The calculated values of K_1, K_2, qe and their corresponding regression coefficient values (R^2) presented in Table 11. The correlation coefficients are found to be closer to unity for pseudo-second-order kinetics model than for pseudo- first order kinetics model. This suggests that the adsorption system can be better represented by pseudo-second- order kinetics model.

Table 11: Data for pseudo first and pseudo second order kinetic model.

Pseudo first order model	Parameters			Rate equation	Correlation coefficient
Fluoride concentration and adsorbent dose	qe,exp (mg/g)	qe,cal (mg/g)	K_1	$\log qe - qt = \log qe - \frac{K1t}{2.303}$	R^2
5mg/l with 1 g	3.482	2.860	0.0371	$\log qe - qt = -0.037x + 1.0509$	0.8037
10mg/l with 1.5g	5.61	3.8057	0.038	$\log qe - qt = 0.038x + 1.3365$	0.8176

15mg/l with 2 g	6.5625	4.547	0.8164	$\log qe - qt = -0.039x + 1.5145$	0.8164
Pseudo second order model	Parameters			Rate equation	Correlation coefficient
Fluoride concentration and adsorbent dose	qe,cal (mg/g)	K_2		$\frac{1}{qt} = \frac{1}{K2qe^2} + \frac{1}{qe}t$	R^2
5mg/l with 1 g	3.733	0.034542		$\frac{1}{qt} = 0.2679x + 2.0778$	0.9952
10mg/l with 1.5g	6.0864	0.018621		$\frac{1}{qt} = 0.1643x + 1.4497$	0.9957
15mg/l with 2 g	7.2254	0.013195		$\frac{1}{qt} = 0.1384x + 1.4516$	0.9943

In Table 11, the average correlation coefficients of pseudo first and second order kinetics model were 0.8126 and 0.995, respectively. Hence, the higher correlation coefficient of the pseudo second order adsorption kinetic model was indicate preferable than pseudo first order kinetic model.

4.4. Treatment of Contaminated real water sample

Fluoride attacked ground water was collected from deep well found around Wonji shoa, which is located in the Rift valley region of the country and its initial fluoride concentration and others physiochemical characterization was analyzed in laboratory as shown in Table 12 below.

Table 12: The concentration of various ions and others physiochemical characterization of the ground water real sample analyzed in laboratory

Parameter Test	Test Result	Units	Test method
Fluoride	11.87	Mg/L	spectrophotometry
Bicarbonate	829.60	mg/L	Titrimetric
Carbonate	96.0	mg/L	Titrimetric

Chloride	30	mg/L	Titrimetric
Sulphate	20	mg/L	Titrimetric
Phosphate	0.4	mg/L	Spectrophotometry
Nitrate	0	mg/L	spectrophotometry
TDS	645	ppm	Potentiometry
PH	7.14	-	Potentiometry

The real sample initial fluoride concentration (11.87mg/L) was diluted to 5ppm, hence its concentration is above permissible level as well as very high it consume or needs high adsorbent dose to remove fluoride ion. Then, the sample was analyzed at room temperature and shaker speed of 150 rpm with treated activated alumina using the optimized values of other parameters (adsorbent dose 2gm/l, pH 7, contact time 90 min.

Table 13 shows the removal efficiency of treated alumina adsorbent for diluted fluoride contaminated real water sample .

Table 13: Fluoride contaminated real water sample data after diluting to 5 mg/L

Contaminated water samples	Contaminant Concentration Before Adsorption (ppm)	Adsorbent dose(gm/L)	Contact time (min)	Concentration after adsorption (ppm)	% Removal
Fluoride attacked water	5	2	90	0.65	87

Treated activated alumina effectively removed the contaminant as it can be seen on Table 13. But the percentage removal of real water samples were low compared to standard solutions (used for optimization process).This is because of the real water samples have different ions which may affect the adsorption of the adsorbent as shown in Table 12 above.

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In the present study, high surface area crystalline alumina was treated and regenerated from deactivated alumina solid waste disposed from the hydrogen oxide plant of Awash Melkasa Chemical factory via physico-chemical modifications and regeneration techniques followed by various characterization techniques. The result of XRD confirms as the calculated average crystalline size was estimated to be 24.78 nm with highly degree of crystallinity. The SEM micrograph conveys that the morphology was dominantly found to be spherical with certain surface aggregation and agglomeration. FTIR analysis confirms presence of immense functional groups such as saturated and unsaturated hydrocarbons, carboxylic acids, ketones and aldehydes. During the adsorption of fluoride ion the three key factors (dose, initial fluoride concentration, and contact time) were conducted with the regenerated activated alumina at different level of dose (1.0, 1.5, and 2 g/ 100 mL), initial concentration (5, 10, and 15 mg/L), and contact time (30, 60, and 90 min) in a batch process. The maximum percent fluoride removal and adsorption capacity were 92.62% and 9.87mg/g, respectively for 5 mg/L fluoride water under optimum adsorption conditions. The adsorption data fitted well with the Freundlich adsorption isotherm with correlation coefficient (R^2=0.98765) value, which indicates adsorption intensity or surface heterogeneity, becoming more heterogeneous on adsorbent surface. The adsorption of the fluoride ion found to be fit with pseudo second order kinetic model with a value of (R^2=0. 995).

Fluoride contaminated real water samples that were collected from wonji shoa were treated using treated and regenerated activated alumina with optimized parameters. The adsorbent removes fluoride ion from Fluoride attacked water 87.00% after diluting its concentration from 11.87mg/L to 5mg/L. These and the above results indicate that treated and regenerated activated alumina solid waste can be used for the removal of fluoride from fluoride-attacked ground water.

5.2. Recommendation

During this study, the adsorption of fluoride on the active surface area of re-generated alumina was carried out at optimized adsorption parameters. Based on the result of the current study, the following recommendations should be considered for future researchers. To improve and achieve high removal efficiency of fluoride ion, the combination of the re-generated alumina with other conductive polymers and metals could improve the surface morphology and so the adsorption efficiency. Furthermore, in order to recorded highest possible adsorption applications, the preparation of re-generated alumina from solid waste at various modifiers are very crucial. In addition to this, to get a small average crystalline re-generated alumina, further modification via green templating agent.

All of the experiments used a fixed pH for the solution. Thus, more research on the defluoridation process using regenerated activated alumina at various solution pHs should be conducted. In order for this to be applied to ground water after more research.

The carbonization process effect of regenerated activated alumina was not considered in the present study, so if it is necessary, further investigation can be conducted by using different carbonization temperature

The influence of coexisting ions in groundwater on the adsorption of fluoride on regenerated activated alumina was not taken into account in this work, but it can have an impact on the defluoridation process, so more research is required to take coexisting ions in drinking ground water into account. Lastly, it is also very crucial to recommend the concerned governmental body to apply for real life wastewater applications sourced by different factors.

REFFERENCES

Abas, S. N. A., Ismail, M. H. S., Kamal, M. L., & Izhar, S. (2013). Adsorption process of heavy metals by low-cost adsorbent: A review. World Applied Sciences Journal, 28(11), 1518–1530. https://doi.org/10.5829/idosi.wasj.2013.28.11.1874

Achparaki, M., Thessalonikeos, E., Tsoukali, H., Mastrogianni, O., Zaggelidou, E., Chatzinikolaou, F., Vasilliades, N., Raikos, N., Isabirye, M., & Raju, D. V. (n.d.). J. Poesen Additional.(2012). We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists TOP 1%. Intech, 13. Intech.

Ahmad, S., & Singh, R. (2022). removal techniques in water : a review †. 620–661. https://doi.org/10.1039/d1va00039j

Ahmad, S., Singh, R., Arfin, T., & Neeti, K. (2022). Fluoride contamination, consequences and removal techniques in water: a review. Environmental Science: Advances, 1(5), 620–661. https://doi.org/10.1039/d1va00039j

Akafu, T., Chimdi, A., & Gomoro, K. (2019). Removal of Fluoride from Drinking Water by Sorption Using Diatomite Modified with Aluminum Hydroxide. Journal of Analytical Methods in Chemistry, 2019. https://doi.org/10.1155/2019/4831926

Gizachew Wendimu Kifle A Thesis Submitted to Center for Environmental Science Presented in Partial Fulfillment of the Requirements for the Degree of Master of Science in Environmental Science Addis Ababa Uni. (2015).

Ayawei, N., Ebelegi, A. N., & Wankasi, D. (2017). Modelling and Interpretation of Adsorption Isotherms. Journal of Chemistry, 2017. https://doi.org/10.1155/2017/3039817

Ayoob, S., Gupta, A. K., Bhakat, P. B., & Bhat, V. T. (2008). Investigations on the kinetics and mechanisms of sorptive removal of fluoride from water using alumina cement granules. Chemical Engineering Journal, 140(1–3), 6–14. https://doi.org/10.1016/j.cej.2007.08.029

Balasubramanian, G. R. (2020). Regeneration method development for used alumina in the hydrogen peroxide process.

Barberi, J., & Spriano, S. (2021). Titanium and protein adsorption: An overview of mechanisms and effects of surface features. Materials, 14(7). https://doi.org/10.3390/ma14071590

Bhatnagar, A., Kumar, E., & Sillanpää, M. (2011). Fluoride removal from water by adsorption-A review. Chemical Engineering Journal, 171(3), 811–840.

https://doi.org/10.1016/j.cej.2011.05.028

Browning, J. (1974). Regeneration of spent alumina. Google Patents.

Chen, A. S. C., & Snoeyink, V. L. (1987). Activated Alumina Adsorption of Dissolved Organic Compounds before and after Ozonation. 21(1), 83–90.

Chen, Q. (2008). Development of an anthraquinone process for the production of hydrogen peroxide in a trickle bed reactor-From bench scale to industrial scale. Chemical Engineering and Processing: Process Intensification, 47(5), 787–792. https://doi.org/10.1016/j.cep.2006.12.012

Crini, G., Lichtfouse, E., Wilson, L., Morin-crini, N., Crini, G., Lichtfouse, E., Wilson, L., & Conventional, N. M. (2019). Conventional and non-conventional adsorbents for wastewater treatment To cite this version : HAL Id : hal-02082916 Conventional and non - conventional adsorbents for wastewater treatment. Environmental Chemistry Letters, 17(1), 195–213. https://doi.org/10.1007/s10311-018-0786-8

Dhawane, S. H., Khan, A. A., Singh, K., Tripathi, A., & Hasda, R. (2017). Insight into Optimization , Isotherm , Kinetics , and Thermodynamics of Fluoride Adsorption onto Activated Alumina. 00(00). https://doi.org/10.1002/ep.12814

Doke, K. M., & Khan, E. M. (2017). Equilibrium, kinetic and diffusion mechanism of Cr(VI) adsorption onto activated carbon derived from wood apple shell. Arabian Journal of Chemistry, 10, S252–S260. https://doi.org/10.1016/j.arabjc.2012.07.031

Dubey, S., Agarwal, M., & Gupta, A. B. (2018). Experimental investigation of Al-F species formation and transformation during coagulation for fluoride removal using alum and PACl. Journal of Molecular Liquids, 266, 349–360. https://doi.org/10.1016/j.molliq.2018.06.080

Erdoğan, B. C., & Ülkü, S. (2011). Ammonium sorption by Gördes clinoptilolite rich mineral specimen. Applied Clay Science, 54(3–4), 217–225.

Farrah, H., Slavek, J., & Pickering, W. F. (1987). Fluoride interactions with hydrous aluminium oxides and alumina. Australian Journal of Soil Research, 25(1), 55–69. https://doi.org/10.1071/SR9870055

Flanagan, A., & Road, S. Q. (2014). A Review on Adsorption of Fluoride from Aqueous Solution. 6317–6366. https://doi.org/10.3390/ma7096317

French, R. H. (1985). by.

Gan, Y., Wang, X., Zhang, L., Wu, B., Zhang, G., & Zhang, S. (2019). Coagulation removal of fluoride by zirconium tetrachloride: Performance evaluation and mechanism analysis. Chemosphere, 218, 860–868. https://doi.org/10.1016/j.chemosphere.2018.11.192

Gandhi, I., For, C., & Philosophy, D. O. F. (2015). ARSENIC AND FLUORIDE REMOVAL FROM DRINKING By. Engg 02200904010.

George, S., Pandit, P., & Gupta, A. B. (2010). Residual aluminium in water defluoridated using activated alumina adsorption – Modeling and simulation studies. Water Research, 44(10), 3055–3064. https://doi.org/10.1016/j.watres.2010.02.028

Getachew, T., Hussen, A., & Rao, V. M. (2015). Defluoridation of water by activated carbon prepared from banana (Musa paradisiaca) peel and coffee (Coffea arabica) husk. International Journal of Environmental Science and Technology, 12(6), 1857–1866. https://doi.org/10.1007/s13762-014-0545-8

Ghorai, S., & Pant, K. K. (2004). Investigations on the column performance of fluoride adsorption by activated alumina in a fixed-bed. Chemical Engineering Journal, 98(1–2), 165–173. https://doi.org/10.1016/j.cej.2003.07.003

Girma, M., Zewge, F., & Chandravanshi, B. S. (2020). Fluoride removal from water using magnetic Iron Oxide/Aluminium hydroxide composite. SINET: Ethiopian Journal of Science, 43(1), 32–45.

Gong, W. X., Qu, J. H., Liu, R. P., & Lan, H. C. (2012). Effect of aluminum fluoride complexation on fluoride removal by coagulation. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 395, 88–93. https://doi.org/10.1016/j.colsurfa.2011.12.010

Guo, Q., & Guo, Q. (2013). Water defluoridation by hydrotalcite and takovite and subsequent formation of new fluoride-bearing phases. Environmental Technology (United Kingdom), 34(8), 1053–1062. https://doi.org/10.1080/09593330.2012.733502

Hayashi, S. I., Kimura, M., Tanaka, K., Ikematsu, Y., & Mizukami, K. (2011). Development of materials characterization techniques and their future prospects. Nippon Steel Technical Report, 100, 2–7.

Heraldy, E., Hidayat, Y., & Firdaus, M. (2016). The langmuir isotherm adsorption equation: the monolayer approach. IOP Conference Series: Materials Science and Engineering, 107(1), 12067.

Iftekhar, S., Ramasamy, D. L., Srivastava, V., Asif, M. B., & Sillanpää, M. (2018). Understanding the factors affecting the adsorption of Lanthanum using different adsorbents: A critical review. Chemosphere, 204, 413–430. https://doi.org/10.1016/j.chemosphere.2018.04.053

Ingle, N., Dubey, H., Kaur, N., & Sharma, I. (2014). Defluoridation techniques: Which one to choose. Journal of Health Research and Reviews, 1(1), 1. https://doi.org/10.4103/2394-2010.143315

Inyinbor, A. A., Adekola, F. A., & Olatunji, G. A. (2016). Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto Raphia hookerie fruit epicarp. Water Resources and Industry, 15, 14–27. https://doi.org/10.1016/j.wri.2016.06.001

Jagtap, S., Yenkie, M. K. N., Labhsetwar, N., & Rayalu, S. (2011). Defluoridation of drinking water using chitosan based mesoporous alumina. Microporous and Mesoporous Materials, 142(2–3), 454–463. https://doi.org/10.1016/j.micromeso.2010.12.028

Jayashree, D. E., Pooja, G., Kumar, P. S., & Prasannamedha, G. (2020). A review on fluoride : treatment strategies and scope for further research. 200, 167–186. https://doi.org/10.5004/dwt.2020.26010

Johnson, C. A., & Chandravanshi, B. S. (2014). Synthesis, characterization and development of aluminium hydroxide–based adsorbents for defluoridation of drinking water.

Kabir, H., Gupta, A. K., & Tripathy, S. (2020). Fluoride and human health: Systematic appraisal of sources, exposures, metabolism, and toxicity. Critical Reviews in Environmental Science and Technology, 50(11), 1116–1193. https://doi.org/10.1080/10643389.2019.1647028

Kimambo, V., Bhattacharya, P., Mtalo, F., Mtamba, J., & Ahmad, A. (2019). Fluoride occurrence in groundwater systems at global scale and status of defluoridation – State of the art. Groundwater for Sustainable Development, 9(August 2018), 100223. https://doi.org/10.1016/j.gsd.2019.100223

Kloos, H., & Tekle Haimanot, R. (1999). Distribution of fluoride and fluorosis in Ethiopia and prospects for control. Tropical Medicine and International Health, 4(5), 355–364. https://doi.org/10.1046/j.1365-3156.1999.00405.x

Ku, Y., & Chiou, H. M. (2002). The adsorption of fluoride ion from aqueous solution by

activated alumina. Water, Air, and Soil Pollution, 133(1–4), 349–361. https://doi.org/10.1023/A:1012929900113

Kumar, E., Bhatnagar, A., Kumar, U., & Sillanpää, M. (2011). Defluoridation from aqueous solutions by nano-alumina: Characterization and sorption studies. Journal of Hazardous Materials, 186(2–3), 1042–1049. https://doi.org/10.1016/j.jhazmat.2010.11.102

Kumar, P. S., Suganya, S., Srinivas, S., Priyadharshini, S., Karthika, M., Sri, K., Swetha, V., Naushad, M., Lichtfouse, E., Kumar, P. S., Suganya, S., Srinivas, S., Priyadharshini, S., & Karthika, M. (2019). Treatment of fluoride-contaminated water . A review To cite this version : HAL Id : hal-02403012. Environmental Chemistry Letters, 17(4), 1707–1726. https://doi.org/10.1007/s10311-019-00906-9

Kumar, R., Sharma, P., Kumar, A., & Kumar, R. (2020). Equilibrium sorption of fluoride on the activated alumina in aqueous solution. 197, 224–236. https://doi.org/10.5004/dwt.2020.26002

Lebrahimi, H., Fekhaoui, M., & Bellaouchou, A. (2020). Removal of Fluoride Ions from Drinking Water by Activated Alumina and Activated Charcoal. October.

Liu, C. C., & Liu, J. C. (2016). Coupled precipitation-ultrafiltration for treatment of high fluoride-content wastewater. Journal of the Taiwan Institute of Chemical Engineers, 58, 259–263. https://doi.org/10.1016/j.jtice.2015.05.038

Liu, R., Gong, W., Lan, H., Gao, Y., Liu, H., & Qu, J. (2011). Defluoridation by freshly prepared aluminum hydroxides. Chemical Engineering Journal, 175(1), 144–149. https://doi.org/10.1016/j.cej.2011.09.083

Lunge, S., Thakre, D., Kamble, S., Labhsetwar, N., & Rayalu, S. (2012). Alumina supported carbon composite material with exceptionally high defluoridation property from eggshell waste. Journal of Hazardous Materials, 237–238, 161–169. https://doi.org/10.1016/j.jhazmat.2012.08.023

Meenakshi, S., & Viswanathan, N. (2007). Identification of selective ion-exchange resin for fluoride sorption. Journal of Colloid and Interface Science, 308(2), 438–450.

Mihayo, D., Vegi, M. R., Ali, S., & Vuai, H. (2021). Defluoridation of Aqueous Solution Using Thermally Activated Biosorbents Prepared from Adansonia digitata Fruit Pericarp. 2021.

Moreno, A. G., & Moreno, A. G. (2018). Renewables-driven membrane distillation for drinking water purification : Main Ethiopian Rift Valley case study.

Moughaoui, F., Ouaket, A., Eddebbagh, M., Bennamara, A., Abourriche, A., Anbaoui, Z., & Berrada, M. (2017). Study of Adsorption Isotherms and Kinetic Models of Methylene Blue Adsorption on Moroccan Bagasse Waste. 7th International Conference on Innovation in Chemical, Agricultural, Biological and Environmental Sciences (ICABES-2017), 59–65.

Muhi Mohammed, F. (2011). Modeling and design of water treatment processes using adsorption and electrochemical regeneration. Msc. thesis, University of Manchester.

Mulugeta, E., Zewge, F., Johnson, C. A., & Chandravanshi, B. S. (2015). Aluminium hydro (oxide)– based (AO) adsorbent for defluoridation of drinking water : Optimisation , performance comparison , and field testing. 41(1), 121–128.

Nie, Y., Hu, C., & Kong, C. (2012). Enhanced fluoride adsorption using Al (III) modified calcium hydroxyapatite. Journal of Hazardous Materials, 233–234, 194–199. https://doi.org/10.1016/j.jhazmat.2012.07.020

Padmavathy, K. S., Madhu, G., & Haseena, P. V. (2016). A study on Effects of pH, Adsorbent Dosage, Time, Initial Concentration and Adsorption Isotherm Study for the Removal of Hexavalent Chromium (Cr (VI)) from Wastewater by Magnetite Nanoparticles. Procedia Technology, 24, 585–594. https://doi.org/10.1016/j.protcy.2016.05.127

Pillai, P., Dharaskar, S., Pandian, S., & Panchal, H. (2021). Overview of fluoride removal from water using separation techniques. Environmental Technology and Innovation, 21(xxxx), 101246. https://doi.org/10.1016/j.eti.2020.101246

Ragadhita, R., & Nandiyanto, A. B. D. (2021). How to calculate adsorption isotherms of particles using two-parameter monolayer adsorption models and equations. Indonesian Journal of Science and Technology, 6(1), 205–234. https://doi.org/10.17509/ijost.v6i1.32354

Rahmani, K., Rahmani, H., Moeinian, K., Sarafraz, M., & Rahmani, A. (2018). Water Defluoridation Using Modify Zeolite by Al + 3 Ions and Nanoscale Zero- Valent Iron (nZVI) in a Fixed Bed Column. 6(2), 1226–1232.

Ram, N., Mart, M., & Seraf, A. H. (2016). Synthesis and characterization of gamma alumina and compared with an activated charcoal on the fluoride removal from potable well water. 26(77), 30–35. https://doi.org/10.15174/au.2016.878

Santos, D. I., Correia, M. J. N., Mateus, M. M., Saraiva, J. A., Vicente, A. A., & Moldão, M. (2019). Fourier transform infrared (FT-IR) spectroscopy as a possible rapid tool to evaluate

abiotic stress effects on pineapple by-products. Applied Sciences (Switzerland), 9(19). https://doi.org/10.3390/app9194141

Saxena, V. K., & Ahmed, S. (2003). Inferring the chemical parameters for the dissolution of fluoride in groundwater. Environmental Geology, 43(6), 731–736. https://doi.org/10.1007/s00254-002-0672-2

Sitompul, D. N. (2017). Development and application of iron / alumina nanocomposites for household level water treatment. April.

Srinivasan, R. (2011). Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. Advances in Materials Science and Engineering, 2011. https://doi.org/10.1155/2011/872531

Subramanian, K. S., Janavi, G. J., Marimuthu, S., Kannan, M., Raja, K., Haripriya, S., Sharmila, D., & Moorthy, P. S. (2022). A textbook on fundamentals and applications of nanotechnology. ASTRAL INTERNATIONAL PVT.

Tang, Y., Guan, X., Su, T., Gao, N., & Wang, J. (2009). Fluoride adsorption onto activated alumina: Modeling the effects of pH and some competing ions. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 337(1–3), 33–38. https://doi.org/10.1016/j.colsurfa.2008.11.027

Taylor, P., Omorogie, M. O., Babalola, J. O., & Unuabonah, E. I. (n.d.). Desalination and Water Treatment Regeneration strategies for spent solid matrices used in adsorption of organic pollutants from surface water : a critical review. November 2014, 37–41. https://doi.org/10.1080/19443994.2014.967726

Telkapalliwar, N. G. (2020). Defluoridation of Water by Using Modified Material Developed from Ficus benghalensis Leaf: Characterization, Kinetic and Thermodynamic Study. IOP Conference Series: Materials Science and Engineering, 983(1). https://doi.org/10.1088/1757-899X/983/1/012008

Thacker, H. (2019). Dye Removal from Aqueous Solution using Low Cost Bioadsorbents Derived from Agricultural Waste: A Review. International Journal for Research in Applied Science and Engineering Technology, 7(7), 135–144. https://doi.org/10.22214/ijraset.2019.7021

Vernon-Parry, K. D. (2000). Scanning electron microscopy: an introduction. III-Vs Review, 13(4), 40–44.

Waghmare, S. S., & Arfin, T. (2015a). Fluoride removal by clays, geomaterials, minerals, low cost materials and zeolites by adsorption: a review. International Journal of Science, Engineering and Technology Research, 4(11), 3663–3676.

Waghmare, S. S., & Arfin, T. (2015b). Fluoride Removal from Water by Aluminium Based Adsorption : A Review. 2(1), 1–11.

Wan, K., Huang, L., Yan, J., Ma, B., Huang, X., Luo, Z., Zhang, H., & Xiao, T. (2021). Science of the Total Environment Removal of fl uoride from industrial wastewater by using different adsorbents : A review. Science of the Total Environment, 773, 145535. https://doi.org/10.1016/j.scitotenv.2021.145535

WHO (2008). Guidelines for Drinking-water Quality: Second addendum. World Health OrganizationPress,1,17–19. http://www.who.int/water_sanitation_health/dwq/secondaddendum20081119.pdf

Ye, J., Cong, X., Zhang, P., Zeng, G., Hoffmann, E., Wu, Y., Zhang, H., & Fang, W. (2016). Operational parameter impact and back propagation artificial neural network modeling for phosphate adsorption onto acid-activated neutralized red mud. Journal of Molecular Liquids, 216, 35–41.

Yilmaz, A. E., Fil, B. A., Bayar, S., & Karcioğlu Karakaş, Z. (2015). A new adsorbent for fluoride removal: The utilization of sludge waste from electrocoagulation as adsorbent. Global Nest Journal, 17(1), 186–197. https://doi.org/10.30955/gnj.001472

Zerabruk, S., Chandravanshi, B. S., & Zewge, F. (2010). Fluoride in black and green tea (Camellia sinensis) infusions in Ethiopia: Measurement and safety evaluation. Bulletin of theChemicalSocietyof Ethiopia, 24(3), 327–338. https://doi.org/10.4314/bcse.v24i3.60662

Zou, W., Bai, H., Zhao, L., Li, K., & Han, R. (2011). Characterization and properties of zeolite as adsorbent for removal of uranium(VI) from solution in fixed bed column. Journal of Radioanalytical and Nuclear Chemistry, 288(3), 779–788. https://doi.org/10.1007/s10967-011-1026-x

Zygler, A., Słomińska, M., & Namieśnik, J. (2012). Soxhlet extraction and new developments such as soxtec.

APPENDIXES

APPENDIX A: The desired initial fluoride concentration was calculated by dilution method.

The dilution formula used is given as;

$$C_1V_1 = C_2V_2$$

$$V_1 = C_2V_2/C_1$$

Where C_2= (5, 10 and 15mg/L) = initial fluoride concentration

C_1= 1000mg/L= concentration of stock solution

V_2=100ml = volume of initial solution used in batch

V_1= volume of stock solution taken and filled with distilled water to 100 ml mark

Initial concentration(mg/L) C_2	Concentration of stock solution C_1(mg/L)	Volume of desired solution V_2 (ml)	Volume of stock solution taken and filled to 100ml mark (V_1) (ml)
5	1000	100	0.5
10	1000	100	1
15	1000	100	1.5

APPENDEX B: Table for full factorial experimental matrix for fluoride removal in percent and removal capacity of adsorbent

Run	Dosage (g)	Co (ppm)	Contact time (min)	Residual fluoride in mg/L			% of fluoride removal efficiency			Removal capacity in mg/g		
				Tr. 1	Tr. 2	Aver	Tr. 1	Tr. 2	Aver	Tr. 1	Tr. 2	Aver
1	1	5	30	1.925	1.948	1.936	61.5	61.04	61.27	3.075	3.052	3.063
2	1.5	5	30	1.271	1.367	1.319	74.58	72.66	73.62	37.29	2.422	19.856
3	2	5	30	1.065	1.131	1.098	78.7	77.38	78.04	1.967	1.934	1.951
4	1	10	30	4.421	4.363	4.392	55.79	56.37	56.08	5.579	5.637	5.608

5	1.5	10	30	2.728	2.74	2.723	72.72	72.6	72.66	4.848	4.84	4.844
6	2	10	30	2.253	2.215	2.265	77.47	77.85	77.66	3.873	3.892	3.883
7	1	15	30	7.317	7.284	7.301	51.22	51.44	51.33	7.683	7.716	7.699
8	1.5	15	30	4.731	4.617	4.674	68.46	69.22	68.84	6.846	6.884	6.865
9	2	15	30	3.921	3.942	3.931	73.86	73.79	73.83	5.539	5.529	5.534
10	1	5	60	1.826	1.789	1.807	63.48	63.85	63.66	3.174	3.211	3.192
11	1.5	5	60	0.959	0.968	0.963	80.82	80.64	80.73	2.694	2.688	2.691
12	2	5	60	0.725	0.717	0.721	85.5	85.66	85.58	2.137	2.141	2.139
13	1	10	60	3.935	3.952	3.943	60.65	60.48	60.56	6.065	6.056	6.061
14	1.5	10	60	2.317	2.278	2.297	76.83	77.22	77.02	5.122	5.148	5.135
15	2	10	60	1.813	1.792	1.802	81.87	82.08	81.97	4.093	4.104	4.099
16	1	15	60	6.243	6.231	6.237	58.38	58.46	58.42	8.757	8.769	8.763
17	1.5	15	60	3.768	3.756	3.762	74.88	74.96	74.92	7.488	7.496	7.492
18	2	15	60	3.147	3.135	3.141	79.02	79.1	79.06	5.926	5.932	5.929
19	1	5	90	1.523	1.518	1.521	69.54	69.64	69.59	3.477	3.482	3.479
20	1.5	5	90	0.671	0.659	0.665	86.58	86.82	86.7	2.886	2.894	2.890
21	2	5	90	0.366	0.372	0.369	92.68	92.56	92.62	2.317	2.314	2.315
22	1	10	90	3.483	3.475	3.479	65.17	65.25	65.21	6.517	6.525	6.521
23	1.5	10	90	1.585	1.597	1.591	84.15	84.03	84.09	5.61	5.602	5.606
24	2	10	90	1.144	1.138	1.141	88.56	88.62	88.59	4.428	4.431	4.429
25	1	15	90	5.772	5.793	5.782	61.52	61.38	61.45	9.228	9.207	9.217
26	1.5	15	90	2.724	2.712	2.718	81.84	81.92	81.88	8.184	8.192	8.188
27	2	15	90	1.893	1.875	1.884	87.38	87.5	87.44	6.553	6.562	6.558

APPENDEX C: Coefficients in Terms of Coded Factors (Sum Contrasts)

Term	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	77.66	1	0.0732	77.50	77.81
A[1]	5.19	1	0.0861	5.00	5.37
A[2]	-0.1513	1	0.0534	-0.2645	-0.0380
B[1]	-3.35	1	0.0861	-3.53	-3.16
B[2]	0.1554	1	0.0534	0.0422	0.2686
C[1]	5.66	1	0.0861	5.48	5.84
C[2]	0.6310	1	0.0534	0.5177	0.7442
A[1]C[1]	1.08	1	0.1044	0.8603	1.30
A[2]C[1]	0.0322	1	0.0615	-0.0982	0.1626
A[1]C[2]	0.0466	1	0.0615	-0.0838	0.1771
A[2]C[2]	-0.0504	1	0.0401	-0.1353	0.0345