

Synthesis of Ce/Al/Fe Tri-Metal Oxide Modified Diatomaceous Earth /Chitosan Composite Films for Fluoride Removal from Groundwater

By

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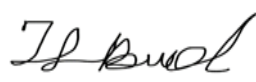
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Declaration

I, Tshilidzi Lloyd Budeli, hereby declare that the dissertation for the master's degree project titled **“Synthesis of Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films for fluoride removal from groundwater”** at the University of Venda, is submitted by me, has not been submitted previously for a degree this or any other university, that it is my own work in design and in execution, and that all reference material contained therein has been duly acknowledged.

Signature: 

Date: 21/02/2025

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I want to thank my Lord and Savior, Jesus Christ, for the strength and good health which enabled me to complete this milestone.

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Abstract

Sustainable Development Goal 6.1 calls for developing technologies to improve water quality for human consumption to ensure clean drinking water for everyone by 2030. This study aims to contribute to the goal by synthesizing Ce/Al/Fe metal oxides modified diatomaceous earth and the fabrication of Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films for the adsorption of fluoride from drinking water. The results were presented in two chapters i.e. Enhancing the fluoride adsorption efficiency of diatomaceous earth through modification by Ce/Al/Fe metal oxides and Synthesis of Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films for fluoride removal from groundwater.

The first chapter of results focused on enhancing the fluoride adsorption efficiency of diatomaceous earth through modification by Ce/Al/Fe metal oxides. Adsorption experiments were performed to determine the efficiency of the Ce/Al/Fe metal oxides modified diatomaceous earth in fluoride removal. About 98% fluoride removal efficiency was obtained from an initial fluoride concentration of 5 mg/L using 0.6 g/100 mL adsorbent dosage at an initial pH range of 7 after 50 mins' agitation time. The adsorption kinetics models revealed that fluoride adsorption occurred via chemisorption, while the isotherm models confirmed both monolayer and multi-layer adsorption. Thermodynamic studies showed that the adsorption process was spontaneous, endothermic, and random, as denoted by the negative ΔG° , positive ΔH° , and positive ΔS° , respectively. Regeneration studies showed that Ce/Al/Fe metal oxides modified diatomaceous earth can be reused for 8 successive regeneration-reuse cycles. This study revealed that modification of diatomaceous earth with Ce/Al/Fe metal oxides enhances the adsorption of fluoride and the material has the potential for use in defluoridation of groundwater.

The synthesized adsorbent in the first chapter had low permeability due to its fine particle size which limits its applicability in a column set-up. Therefore, there was a need to further modify the synthesized adsorbent. The second chapter of results aimed to synthesize the Ce/Al/Fe tri-metal oxide modified diatomaceous earth-chitosan composite films for removal of fluoride from drinking water. The modified DE/chitosan films were developed using the casting method. The functional groups, elemental composition and morphology of the synthesized material were characterized using Fourier Transform Infrared (FTIR) and scanning electron microscopy-energy dispersion X-ray (SEM-EDX), respectively. Batch experiments were conducted to evaluate the effectiveness of

the material in fluoride removal. The results showed 7.89 mg/g adsorption capacity towards fluoride from 5 mg/L initial fluoride concentration, when adsorbent dosage of 0.3 g/100 mL was used at initial pH range of 7 after 50 mins agitation time at shaking speed of 200 rpm. The data for adsorption kinetics showed a better fit to pseudo-second order which indicates that the adsorption mechanism was chemisorption. The adsorption isotherm model data best fitted to Langmuir isotherm model which suggests that the adsorption took place on a monolayer surface. The presence of co-existing anions such as Cl^- , SO_4^{2-} , CO_3^{2-} and NO_3^{2-} reduces the fluoride removal efficiency of the material. The Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films showed lower adsorption capacity relative to Ce/Al/Fe tri-metal oxide modified DE. Based on the results obtained, the synthesized Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films can be used for Groundwater defluoridation. It is therefore recommended that future studies further modify Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films to enhance their fluoride affinity. Furthermore, future studies should evaluate Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films performance in a column set-up and further evaluate their anti-microbial potency.

Keywords: Fluoride; Adsorption; Drinking water; Diatomaceous earth; Metal oxides

Academic Outputs

- Budeli, T.L., Gitari, W.M. and Mudzielwana, R., 2018. Evaluation of groundwater defluoridation potential of Mg/Ce/Mn-diatomaceous earth in a fixed bed using gravity flow mode. In *Conference in Sustainable Management of Natural Resources* (p. 262)
- Budeli, T.L., Gitari, W.M. and Mudzielwana, R., 2025. Enhancing the Fluoride Adsorption Efficiency of Diatomaceous Earth Through Modification with Ce/Al/Fe Metal Oxides. *Water*, 17(1), p.129.

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Chapter 1: Introduction

1.1 Background

Fluoride is a negatively charged non-metallic halogen which is found in natural environments such as the atmosphere in a form of fluorine, geosphere and the hydrosphere in both organic and inorganic forms (Huyen *et al.*, 2023). Mtavangu *et al.*, (2022) reported that fluoride normally occurs as fluorite (CaF_2), fluorapatite ($3\text{Ca}_3\text{P}_2\text{C}_8\text{CaF}_2$), cryolite (Na_3AlF_6), apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). High concentrations of fluoride in groundwater are mainly due to leaching of fluoride from fluoride bearing rocks such as fluorspar, cryolite, fluorapatite and hydroxyapatite (Cruz-Briano *et al.*, 2024).

The consumption of water with fluoride concentration within permissible limits of 1.5 mg/L as prescribed by the World Health Organization (WHO) is vital for the development of bones and dental caries (Mudzielwana *et al.*, 2017). Huyen *et al.*, (2023) reported that the consumption of water with fluoride concentration above 1.5 mg/L may cause dental and skeletal fluorosis. Dental fluorosis is characterized by mottling of teeth whereas skeletal fluorosis is characterized by structural changes in human skeleton (Guissouma *et al.*, 2017; Kut *et al.*, 2016; Ono *et al.*, 2023). The severity depends on the concentration and period of exposure. Other health effects associated with exposure to fluoride includes interference of fluoride with carbohydrates, protein, lipid and mineral metabolism (Izuagie *et al.*, 2015).

At least 28 countries from South Asia, Africa, the Middle East, North, Central and South America, and Europe were reported to be affected by fluorosis due to excessive concentration of fluoride in groundwater (Bailey *et al.*, 2006). Moreover, India was reported to be the most affected country with 56.2 million people affected by fluorosis (Loganathan *et al.*, 2013). Four areas have been reported to be affected by the high prevalence of fluoride in groundwater in South Africa which are Limpopo, Northern Cape, North-West and Kwa-Zulu-Natal Provinces (Ncube & Schutte, 2005; Elumalai *et al.*, 2019). Moreover, Odiyo and Makungo (2012) conducted a survey in Siloam Village in Limpopo province and reveal that 87% of households rely on groundwater. Among these households, 85% reported cases of mottled teeth among members. Additionally, 50% of school-aged learners (11–14 years) were found to have mottled teeth. Izuagie *et al.*, (2015)

indicated that it is therefore of paramount importance to remove excess fluoride to an acceptable level for human consumption from drinking water due to the impacts it poses on human health.

There are different methods that have been employed to reduce fluoride concentrations from water such as adsorption, ion exchange, precipitation/coagulation, and membrane processes (Gao & Liu, 2022). Amongst the available techniques adsorption technique is the most affordable and effective of all defluoridation techniques due to factors such as cost efficiency, socio-cultural acceptance, environmental benignity and simplicity (Behera & Sahu, 2023). On the other hand, water treated by ion exchange is characterised by low pH and high chloride content (Meenakshi & Maheshwari, 2006). Precipitation/coagulation process is most likely to contaminate drinking water owing to unwanted chemicals (Kahu *et al.*, 2017). Membrane process is costly because of the constant maintenance needed (Mtavangu *et al.*, 2022). Several adsorbents such as activated carbon, activated alumina, natural and modified biotite, kaolinite, diatomaceous earth and chitosan have been used for defluoridation of groundwater (Gitari *et al.*, 2015). Izuagie *et al.*, (2015) reported that diatomaceous earth (DE) is a good and interesting candidate for research as an adsorbent since it is naturally abundant, non-toxic and finally because of its bonded hydroxyl groups which could be exchangeable with anions. DE is an alumino-silicate material that typically consists of 87–91% silicon dioxide (SiO_2), 2% to 4% of alumina (Al_2O_3) and 0.5% to 2% of hematite (Tsai *et al.*, 2006).

Izuagie *et al.*, (2016) reported that binary metal Al/Fe oxide-modified DE is more effective sorbent than either Al or Fe oxide-modified DE for groundwater defluoridation. It was found that the maximum fluoride removal capacity of raw DE was 26.52% (Izuagie *et al.*, 2015) whereas Al/Fe oxide-modified DE's maximum fluoride removal capacity was 93.1% (Izuagie *et al.*, 2016). Furthermore, a tri-metal oxide-modified DE of magnesium (Mg), Cerium (Ce) and Manganese (Mn) was also evaluated for fluoride removal using a batch experiment. Gitari *et al.*, (2017) recorded the sorption capacity of approximately 97.1% while using a solid/liquid ratio of 0.6 g/100 mL. It can be concluded that increasing the number of modifying oxides increases the effectiveness of DE. However, the physical properties of modified DE make it hard for it to be used for rural household level setup which requires the use of a column on gravity flow mode, such as very low permeability which suggests that the material requires further modification.

Chitosan is a potent amino polysaccharide and it has unique characteristics such as chemical stability, high reactivity, chelation behaviour (Salih & Ghosh, 2018) and it consists of amino and hydroxyl groups which make it to be exchangeable with fluoride ions which can also be used for making its derivatives through crosslinking and impregnation technique (Afshin *et al.*, 2019). These qualities make chitosan a good candidate to modify DE or to be used as a modified DE carrier in order to combat high pressure drop and to improve hydraulic properties by forming beads or films for column application (Qi *et al.*, 2015; de Freitas *et al.*, 2021). This study aims to synthesize Ce/Al/Fe-modified DE for application in groundwater defluoridation. The study further aims to convert the powdery Ce/Al/Fe-modified DE into films by modifying the adsorbent with chitosan.

1.2 Problem statement

The excessive ingestion of water with fluoride concentration above the recommended limit of 1.5 mg/L causes dental and skeletal fluorosis (Huyen *et al.*, 2023). Dental fluorosis is commonly shown by staining of teeth's enamel (Guissouma *et al.*, 2017) and calcification of teeth whereas in skeletal fluorosis the defects are shown by structural changes on the human skeleton (Ono *et al.*, 2023). It is estimated that 200 million people are at risk of fluorosis worldwide, which is an alarming number (Johnson & Bretzler, 2015). Izuagie *et al.*, (2015) revealed that fluorosis mostly affects rural community dwellers who depend on fluoride rich groundwater for drinking due to the absence of piped borne water. Furthermore, fluorosis is an incurable disease and thus there is a need for prevention.

In previous studies Mg/Ce/Mn tri-metal oxide modified DE was developed (Gitari *et al.*, 2017) and it showed high fluoride affinity, however it was not applicable in household set up due to its low permeability due to the fine particles of the adsorbent. Therefore, in this study Ce/Al/Fe tri-metal oxide modified DE will be modified with chitosan to form a composite which will be further converted into films. Chitosan beads and films are reported to have high surface area and they also have a low pressure drop effect as compared to flake or powder chitosan (de Freitas *et al.*, 2021).

1.3.1 Main Objective

The main objective of the study is to synthesize Ce/Al/Fe tri-metal oxide modified diatomaceous earth/chitosan composite films and further evaluate its applicability for fluoride removal in groundwater.

1.3.2 Specific objectives

- To synthesize and optimize conditions of Ce/Al/Fe tri-metal modified diatomaceous earth for fluoride removal.
- To synthesize and optimize conditions of Ce/Al/Fe tri-metal modified diatomaceous earth/chitosan films for fluoride removal.
- To elucidate the adsorption mechanism using adsorption kinetics and isotherm data for both synthesized adsorbents.

1.4 Research questions

- What are the optimum conditions for the synthesis of Ce/Al/Fe tri-metal oxide modified-diatomaceous earth for fluoride removal?
- What are the optimum conditions for the synthesis of Ce/Al/Fe tri-metal oxide modified-diatomaceous earth/chitosan films for fluoride removal?
- What are the fluoride adsorption mechanisms by Ce/Al/Fe tri-metal oxide modified-diatomaceous earth and Ce/Al/Fe-tri-metal oxide modified-diatomaceous earth/chitosan films, respectively?

1.5 Hypothesis

The synthesized Ce/Al/Fe tri-metal diatomaceous/chitosan composite films can effectively remove fluoride from groundwater.

1.6 Assumption

It is assumed that:

- Ce/Al/Fe tri-metal diatomaceous earth/chitosan composite films will effectively remove fluoride ions from drinking water.

1.7 Motivation

Groundwater remains the main source of water in many parts of developing countries due to its affordability and accessibility. However, most of the groundwater resources have high fluoride concentration which can be detrimental to human health (Huyen *et al.*, 2023). There are techniques that have been developed to remove fluoride species from drinking water, but they are not

economically viable in most developing countries including South Africa such as ion exchange, electro coagulation, precipitation, and membrane separation (Medellín-Castillo *et al.*, 2020; Gao & Liu, 2022). Therefore, there is a need to develop cost effective, household-based and user-friendly approaches to reduce fluoride concentration to acceptable levels in drinking water. Diatomaceous earth is a good candidate to be used as an adsorbent because it is locally sourced, abundant, affordable and contains hydroxyl groups that could be exchangeable with fluoride and other anions (Qi *et al.*, 2015; Izuagie *et al.*, 2016).

In the previous study Al/Fe-DE was used in a column study which showed high fluoride affinity, however, the column had high pressure drop. This study will make use of fixed bed column which depicts the applicability of the technology in the field, and it can also be up scaled. Therefore, Ce/Al/Fe tri-metal oxide modified diatomaceous earth will be synthesized and modified physically by chitosan and converted into films in order to enhance the permeability of the material, improve its total surface area and its mechanical strength thus enhancing the adsorption capacity of the adsorbent. The physical modification will help to preserve the active amine groups for anti-microbial activity instead of immobilizing them through cross-linking. Chitosan has qualities such as stability in water, biodegradable, good chelation behaviour and nontoxic to humans and the environment (Salih & Ghosh, 2018; Ayinde *et al.*, 2020).

The study will benefit the South African rural communities by reducing poverty and improving human health through the eradication of waterborne diseases such as those associated with fluoride by developing a sustainable, economically viable and user-friendly technology which can be applicable in a rural household setup. This is in line with the Sustainable Development Goals, specifically goal 6 which encourages and supports the development of water treatment technologies to ensure safe and affordable drinking water in developing countries (FIPP, 2015).

1.8 Chapter outline

Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Enhancing the fluoride adsorption efficiency of diatomaceous earth through modification by Ce/Al/Fe metal oxides

Chapter 4: Synthesis of Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films for fluoride removal from groundwater

Chapter 5: Conclusion and recommendations

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Chapter 2: Literature review

2.1 Introduction

This chapter reviews the literature related to fluoride. It further reviews health implications associated with it when it is in high quantity in water and finally, techniques and materials that have been used to reduce it to acceptable limits as prescribed by the World Health Organization (WHO).

2.2 Fluoride

Fluoride is an inorganic, monatomic anion of fluorine with the chemical formula F^- and it is one of the halogens found in group 7 of the periodic table of elements. Furthermore, Fluorine is one of the most common elements on the earth's crust and has the highest electronegativity (Huyen *et al.*, 2023). Fluorides are used for different industrial purposes such as aluminium, ceramic, glass, steel and pharmaceutical production (Weerasooriyagedara *et al.*, 2020; Ono *et al.*, 2023).

The source of fluoride is commonly of hydrogeochemical origin. The enrichment of fluoride in water occurs by rock alteration, evaporation and geothermal mixing (Olaka *et al.*, 2016; Elumalai *et al.*, 2019). Areas with higher concentrations are characterized by recent or past pyroclastic activities of geological uplift. Furthermore, fluoride concentrations are more often related to geologic sources such as the primary magmatic minerals, biotite and muscovite which are known to contain about 1 wt% of fluoride, while, the fluoride content is higher in accessory minerals such as fluorapatite (~3.8 wt%), topaz (~11.5 wt%), and fluorite (~48 wt%) (Shaji *et al.*, 2024; Cruz-Briano *et al.*, 2024). On the other hand, minerals such as cryolite may contain up to 54 wt% fluoride (García & Borgnino, 2015). However, excess fluoride is sometimes caused by anthropogenic activities such as mining and drilling (Brindha & Elango, 2011).

Figure 2.1 below is the map showing areas in South Africa with fluoride concentration above 1.5 mg/L. What is common about these areas with high fluoride content is that they are associated with low calcium and a high bicarbonate alkalinity (Ali *et al.*, 2023). Consequently, water with a high concentration of fluoride is normally soft, contains a large amount of silica and has high pH. In groundwater, the concentration of fluoride mainly depends on the geological, chemical and physical characteristics of the aquifer, the porosity and the pH of the soil and rocks, temperature

and the depth of wells (Kazapoe *et al.*, 2024). Hence, the variation of fluoride concentration is dependent on these variables in groundwater.

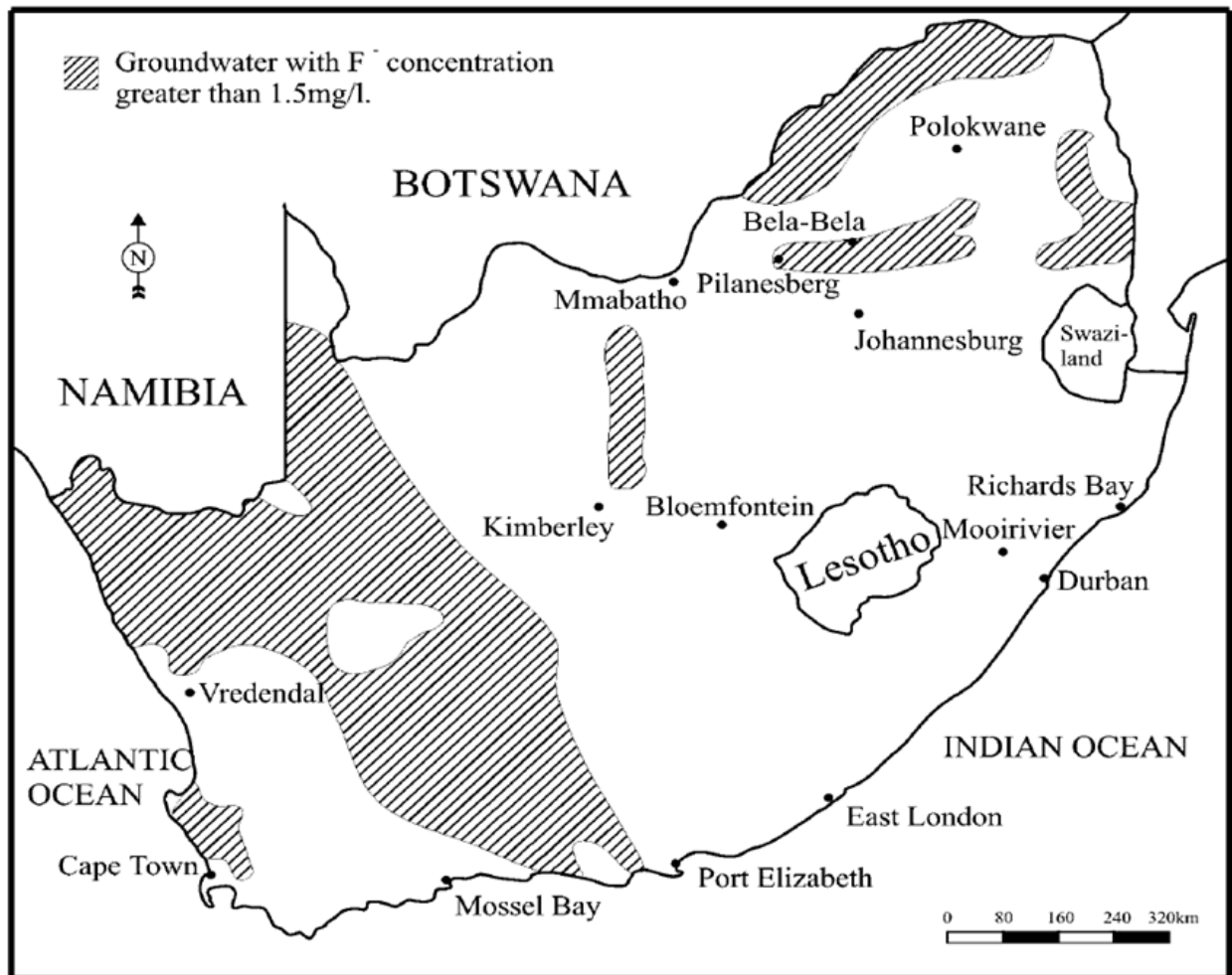


Figure 2.1: Groundwater in South Africa with fluoride concentrations > 1.5 mg/L (McCaffery & Willis, 2001)

2.2.1 Factors affecting the occurrence of fluoride

The occurrence of high fluoride in groundwater is mainly influenced by the bedrock chemistry, groundwater age, well depth, and geologic structure. Granites contain fluorine-rich biotite and amphibole grains (about 1.40 and 1.58 wt% in F contents), about 1% in fluorite (CaF₂) (Ali *et al.*, 2023). These minerals cause the high fluoride levels in groundwater. Sedimentary and volcanic rocks are likely to be related to the underlying fluoride-rich granites as a batholith (Sunkari & Abu, 2019; Kazapoe *et al.*, 2024). This suggests that the distribution of high F⁻ groundwater is closely related to the location of granite.

Residence time of groundwater is one of the controlling factors of the fluoride concentration (Ali *et al.*, 2023). Fluoride concentration of the old groundwater increases because of the precipitation of calcite even though the water is saturated with respect to fluorite (Huyen *et al.*, 2023). Well depth is also a controlling factor for fluoride concentration. Deeper wells are associated with very high F^- levels.

Geological structures such as faults influence high F^- levels in groundwater since fluoride concentrations are commonly higher in the fault zone groundwater than the non-fault zone groundwater (Kim & Jeong, 2005). This is due to enhanced weathering of the in-situ granite fragments generated during the fault displacements and the upward flowing of F^- enriched deep groundwater (Kesari *et al.*, 2021).

2.3 Problems associated with high fluoride in groundwater

Fluorine element has the highest electronegativity. Consequently, it has strong affinity to positively charged ions such as calcium. According to Kazapoe *et al.*, (2024) the result of fluoride on mineralized tissues such as bones and teeth leads to the development of alterations which are of clinical significance as they have highest amount of calcium and thus attract excessive fluoride that gets deposited as calcium–fluorapatite crystals. The effect of prolonged exposure to drinking-water with varying concentrations of fluoride are tabulated below. Table 2.1 below is showing the effects of prolonged use of drinking water on human health.

Table 2.1: Effects of prolonged use of drinking water on human health, related to fluoride content (Dissanayake, 1991)

F ⁻ CONCENTRATION (mg/L)	HEALTH OUTCOMES
<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	Crippling fluorosis

According to WHO (2011) guidelines on drinking water, the optimum dental health at fluoride concentration ranges from 1.0 -1.5 mg/L. Any concentration level less than 1.0 mg/L is reported to cause dental caries due to deficiency. In contrast, levels above 1.5 mg/L cause dental and skeletal

fluorosis which may get to an advanced stage which is called crippling the severity depending on the concentration of fluoride in drinking water (Zango *et al.*, 2021). Zerbo *et al.* (2020) reported that cases of fluoride health impacts mostly exist mostly in rural areas of the country due to the intense dependence on ground water with high fluoride content.

2.3.1 Fluorosis

Ncube and Schutte (2005) defined fluorosis as a condition which is caused by the ingestion of water with high concentration of fluoride and which affects the calcification of teeth and bones. It is called dental fluorosis when the calcification has affected the teeth (Zango *et al.*, 2021). In contrast, it is referred as skeletal fluorosis when the calcification has affected the bones (Yousefi *et al.*, 2018). Furthermore, it is referred as crippling fluorosis when the skeletal fluorosis has reached an advanced stage (Ali *et al.*, 2023).

2.3.1.1 Dental fluorosis

Dental fluorosis is a condition whereby the dental enamel is disturbed, and it loses its lustre as result (Yousefi *et al.*, 2018). It is caused by excessive ingestion of fluoride higher than the recommended limit by WHO of 1.5 mg/L during tooth development, leading to enamel with lower mineral content and increased porosity (Alvarez *et al.*, 2009). Dental fluorosis is characterized by white opaque areas on the tooth surface its mild state and characterized by yellowish brown to black stains at its server state (Zango *et al.*, 2021; He *et al.*, 2021). Furthermore, dental fluorosis mainly targets children whose teeth are still developing (Ono *et al.*, 2023; Kazapoe *et al.*, 2024). Alvarez *et al.*, (2009) pointed out that the severity of dental fluorosis depends on the period of overexposure to fluoride, the individual susceptibility and tolerance and finally nutritional factors. Ncube and Schutte (2005) investigated the morbidity of fluoride and pointed out many cases of dental fluorosis in North West province, Limpopo province and Kwa-Zulu Natal province, South Africa. Odiyo and Makungo (2012) conducted a study in Limpopo, Siloam village and found that 87% of households that depend on groundwater and 85% of these households have their members with mottled teeth. Furthermore, 50% of school learners between the ages of 11 and 14 also have mottled teeth. The figure 2.2 is a map showing the % morbidity of dental fluorosis in South Africa.

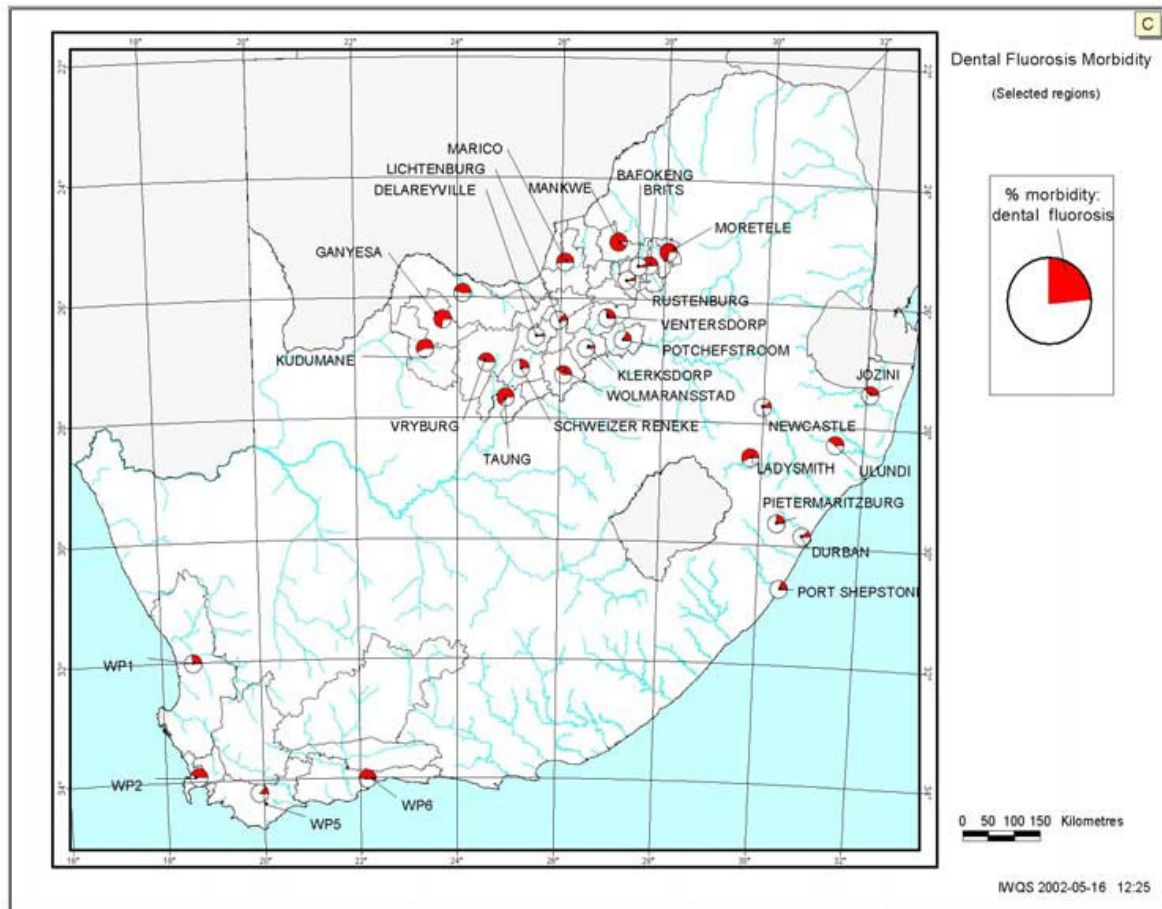


Figure 2.2: The % morbidity of dental fluorosis in South Africa (Ncube & Schutte, 2005).

2.3.1.2 Skeletal fluorosis

The uptake of water with fluoride concentration greater than 4 mg/L causes skeletal fluorosis (Bretzler & Johnson, 2015; Zhao *et al.*, 2023). Skeletal fluorosis is non-discriminant meaning that it affects both children as well as adults, contrary to dental fluorosis (Kazapoe *et al.*, 2024). Meenakshi and Maheshwari (2006) reported that skeletal fluorosis is caused by the deposition of fluoride in the joints of the neck, pelvic, knee and shoulder bones which result in the difficulty to move or walk. Its symptoms include sporadic pain, back stiffness, pricking and tingling in the limbs, muscle weakness, chronic fatigue, abnormal calcium deposits in bones and ligaments. Gao and Liu (2022) pointed out that at an advanced stage which normally induced by fluoride concentration above 10 mg/L may cause crippling which is chronic condition.

2.3.1.3 Other health problems

Besides dental and skeletal fluorosis there are other health problems associated with the ingestion of water with high fluoride concentration. Ingestion of high fluoride concentration may lead to

muscle fibre degeneration, low haemoglobin levels, abnormal thirst, skin rashes, neurological disorders, depression, gastrointestinal problems, urinary tract malfunctioning, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, male sterility (Wasana *et al.*, 2015). Furthermore, it also affects functional mechanisms of liver, kidney, digestive system, respiratory system, excretory system, central nervous system and reproductive systems (Alarcón-Herrera *et al.*, 2020). Having mentioned the health effects caused by excess fluoride in drinking water Izuagie *et al.* (2015) emphasized that it is important to remove excess fluoride to a reasonable level for human consumption.

2.4 Defluoridation

Defluoridation is a process of removing or lowering fluoride concentration in water to a level which is permissible as recommended by WHO which is 1.5 mg/L (Hiremath, 2006). According to Meenakshi and Maheshwari (2006) defluoridation is the only practical solution to combat the problem of excessive fluoride in water. There are different defluoridation methods or techniques that can be employed in the process of defluoridation include adsorption (Budeli *et al.*, 2025), ion-exchange (Ojekunle *et al.*, 2016), precipitation/coagulation (Dhillon *et al.*, 2017), electrocoagulation (Bhatnagar *et al.*, 2011) and membrane processes (Al-Asheh *et al.*, 2021). There are factor that influence the choice of a technique to use and they include cost effectiveness, availability, the ease of operation, maintenance and safety during operation.

2.5 Defluoridation techniques

2.5.1 Adsorption

Adsorption is a process in which a gas, liquid, or solid adheres to the surface of a solid or a liquid but does not penetrate it. According to Kwai *et al.* (2016), adsorption is an attractive method for the removal of aqueous fluoride. Hence, adsorption technique operates by the binding or adhesion of fluoride ions onto the surface of an adsorbent. The technique removes fluoride from water with the aid of adsorbents such as activated alumina, activated carbon, activated alumina coated silica gel, calcite, activated saw dust, activated coconut shell carbon and activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, serpentine, tricalcium phosphate, bone charcoal, activated soil sorbent and modified clay soil (Meenakshi & Maheshwari, 2006).

The most commonly used adsorbents for fluoride removal are activated alumina and activated carbon. Mtavangu *et al.* (2022) reported that activated alumina was found to be a good adsorbent,

however it forms sludge which is related to health implications such as Alzheimer disease. Generally, fluoride adsorption from water is governed by pH, temperature, co-existing ions, sorption kinetics, sorbent particle size, sorbent/sorbate concentrations and adsorbent surface area (Loganathan *et al.*, 2013). Furthermore, during ion exchange, fluoride anion is covalently bonded to metallic cation at the sorbent surface which result in the release of an ion previously bonded to metallic ion (Kwai *et al.*, 2016). Therefore, it is necessary to impregnate an adsorbent constituted by negatively charged ions or weakly electropositive ions by positively charged multivalent cations so to enhance the electro positivity and adsorption capacity of the adsorbent (Munzhelele *et al.*, 2022). Adsorption is considered to be superior to other techniques for defluoridation due to its cost effectiveness, flexibility simplicity of design, ease of operation and maintenance (Huyen *et al.*, 2023). Hence, it has great relevance on rural application due to its properties.

Adsorption process advantages and limitations (Loganathan *et al.*, 2013)

Advantages

- Simplicity and flexibility of design
- Effective at low fluoride concentration
- The process is cost effective
- The process has high fluoride removal capacity

Limitations

- The process has narrow pH range
- The process requires frequent regeneration of adsorbent
- Ionic competition

2.5.2 Ion exchange

According to Loganathan *et al.* (2013), ion exchange is a stoichiometric process where any counter ion leaving the ion exchanger surface is replaced by an equivalent number of moles of another counter ion to maintain electro-neutrality of the ion exchanger. Furthermore, the process is rapid and reversible. Fluoride can be removed from aqueous solution supplies with a strongly basic anion-exchange resin containing quaternary ammonium functional groups (Meenakshi & Maheshwari, 2006). The process has a tendency of preferring counter ions of higher valency, higher concentration and ions of hydrated equivalent volume (Loganathan *et al.*, 2013).

The removal takes place according to the Equation 2.1 (Meenakshi & Maheshwari, 2006):



The chloride ions of the resin are replaced by fluoride ions. This is a continuous process until all the sites on the resin are occupied. Thereafter, the resin is backwashed with water that is supersaturated with dissolved sodium chloride salt. Finally, fluoride ions are replaced by new chloride ions leading to the recharge of the resin and starting the process again.

Ion exchange process advantages and disadvantages (Meenakshi & Maheshwari, 2006)

Advantages

- Fluoride removal is up to 90-95%
- Taste and colour the water is retained

Limitations

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

2.5.3 Precipitation/coagulation

Precipitation methods are based on the addition of chemicals (coagulants and coagulant aids) and the subsequent precipitation of a sparingly soluble fluoride salt as insoluble fluorapatite. There are two chemicals that are mainly used as coagulants, which are lime and alum. According to Meenakshi and Maheshwari (2006) the addition of lime result in precipitation of fluoride as insoluble calcium fluoride and raises the pH value of the water to 11-12.

Equation 2.2 depicts the coagulation process (Meenakshi & Maheshwari, 2006):



As lime leaves a residue of 8.0 mg/L fluoride, to ensure proper removal of fluoride it is used only in conjunction with alum treatment (Culp & Stolenberg, 1958). During the first step, precipitation occurs by lime dosing followed by the second step in which alum is added to cause coagulation. Furthermore, there are two reactions that occur when alum is added in water. In the first reaction, alum reacts with some of the alkalinity to produce insoluble aluminium hydroxide $[\text{Al}(\text{OH})_3]$. In the second reaction, alum reacts with fluoride ions present in the water. The best defluoridation results are accomplished at pH range of 5.5-7.5 (Potgeiter, 1990). The most popular example of this technique is Nalgonda technique.

The Nalgonda technique of defluoridation is based on combined use of alum and lime in a two-step process. In the Nalgonda Technique two chemicals, alum (aluminium sulphate or kalium aluminium sulphate) and lime are added to the and rapidly mixed, with the fluoride contaminated water, the process also includes flocculation, sedimentation, filtration and disinfection (Dahi *et al.*, 1996). Nalgonda technique includes rapid mixing, coagulation/flocculation, sedimentation, filtration, disinfection and sludge concentration to recover potable water and aluminium salts (Kwai *et al.*, 2016). Disinfection is achieved using bleaching powder. The process is induced by a subsequent gentle stirring, consequently, cotton wool-like flocs develop which are aluminium hydroxides and are removed by simple settling. Furthermore, the main contents of the fluoride are removed along with the flocs, this result from the combination of sorption and ion exchange with some of the hydroxide groups.

Precipitation/coagulation process advantages and disadvantages (Meenakshi & Maheshwari, 2006) and (Loganathan *et al.*, 2013)

Advantages

- The Nalgonda technique of defluoridation is based on combined use of alum and lime in a two-step process and has been claimed as the most effective technique for fluoride removal
- Several fill and draw (F&D) type and handpump attached (HPA) plants based on Nalgonda technique have come up in rural areas for which design and technology has been developed by NEERI, Nagpur.
- Most widely use

Disadvantages

- Low effectiveness; cannot remove F^- below 5 mg/L because of high solubility product of CaF_2 ; need secondary treatment
- Large amounts of chemicals required
- Costs of chemicals, chemical storage and feeding system
- Toxic chemicals left in treated water (AlF complexes, SO_4)
- Large volumes of waste sludge; disposal problem

2.5.4 Membrane process

(Rathi *et al.*, 2024) defined a membrane as a perm-selective barrier between two homogeneous fluid phases. Membrane separation processes used for water treatment and purification include reverse osmosis, nanofiltration and electrodialysis (Lacson *et al.*, 2021). In recent decades, improvements in membrane processing for water recovery and increasing water quality have made membrane filtration the most widely preferred operation in water treatment and re-cycling processes since it was previously considered as uneconomical due to the design and materials that were used before the technical improvements (Wu *et al.*, 2017). The efficiency of membrane process is governed by raw water characteristics, pressure, temperature, regular monitoring and maintenance. According to Jagtap *et al.* (2012) reverse osmosis is a physical process used to remove aqueous contaminants such as fluoride ions by applying high pressure on the feed water to direct it through a semi-permeable membrane. Reverse osmosis is the most preferred alternative to provide safe drinking water without posing the problems associated with other conventional methods (Meenakshi & Maheshwari, 2006). Furthermore, this process is the opposite of natural

osmosis because of the applied pressure to the concentrated side of the membrane, moreover, the process rejects ions based on size and electrical charge. Contrary nanofiltration is a low-pressure process that removes higher concentrations of large molecules from a solvent compared to reverse osmosis (Jagtap *et al.*, 2012). The process uses nanometre sized cylindrical pores that pass through the membrane. Ali *et al.*, (2024) reported that the normal pore size of nanofiltration membranes are $\sim 0.001 \mu\text{m}$. Furthermore, most of these membranes are commonly made up of polymer thin films with polyethylene terephthalate (Baker & Martin, 2007). In electrodialysis, the membranes allow the ions to pass but not the water. In this process is governed by electric current which carries the ions through the membranes. The removal of fluoride in the reverse osmosis process has been reported to vary from 45 to 90% as the pH of the water was raised from 5.5 to 7 (Meenakshi & Maheshwari, 2006).

Membrane process advantages and disadvantages (Meenakshi & Maheshwari, 2006)

Advantages

- The process is highly effective for fluoride removal.
- The process permits the treatment and disinfection of water in one step
- No chemicals are required, and very little maintenance is needed.
- It works under wide pH range.
- No interference by other ions is observed

Disadvantages

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

2.6 Diatomaceous earth

Diatomaceous earth (often shortened to “D.E.”) is the unconsolidated or less lithified sediment of diatomite (Izevbekhai *et al.*, 2021). DE is silicate material typically consists of 87–91% silicon

dioxide (SiO_2), 2% to 4% of alumina (Al_2O_3) and 0.5% to 2% of hematite (Tsai *et al.*, 2006). Antonides (1998) reported that the deposits of DE result from an accumulation in oceans or fresh waters of the amorphous silica cell walls of dead diatoms that are microscopic single-cell aquatic plants (algae). Owing to some of its advantageous physical and chemical properties which include high porosity (80–90% void), large surface area, high liquid absorption capacity, low thermal conductivity and chemical inertness, DE has found variety of uses industrially such as filter aid, adsorbent, insulating material and natural insecticide (Gitari *et al.*, 2017; Kumar & Gupta, 2021). However, due to its chemical inertness DE requires activation by strong alkali for the activation of silica and acid to enhance its adsorption capacity, furthermore it requires chemical modification of the surface chemistry of the solid for it to be a good adsorbent (Tsai *et al.*, 2006). Izuagie *et al.*, (2015) reported that the structure of DE contains bonded hydroxyl groups which could be exchangeable with electronegative fluoride. Scholars such as (Gitari *et al.*, 2017) and (Izuagie *et al.*, 2015) investigated the defluoridation potential of a tri-metal Mg/Ce/Mn oxide-modified DE and binary metal Al/Fe oxide-modified DE and it was found that they are good fluoride adsorbents.

2.7 Chitosan

Chitosan an amino polysaccharide material which is derived by partial or total deacetylation of chitin and it is obtained from the hard-outer skeleton of shellfish, including crab, lobster, and shrimp (Kahu *et al.*, 2017; Izevbekhai *et al.*, 2021). It is reported to be biocompatible, biodegradable, hydrophilic, and nontoxic to human and environment (Salih & Ghosh, 2018). Due to its qualities such as chemical stability, high reactivity, binding groups (amino and hydroxyl groups which can be used for making its derivatives by cross-linking and impragnation method) chitosan has been used for metal and fluoride removal from water. However, it has drawbacks such as low specific surface area, swelling properties and a tendency to agglomerate which limits its application in defluoridation as in form of a powder (Salih & Ghosh, 2018). Consequently, scholars have devoted their efforts in modifying chitosan chemically or physically. Moreover, Zhang *et al.*, (2014) and de Freitas, *et al.*, (2021) reported that chitosan beads and films have desirable stability, surface area and regeneration potential as compared to the natural flakes or powder chitosan. As a result scholars such as (Zhang *et al.*, 2014; Jagtap *et al.*, 2011; Salih & Ghosh, 2018; de Freitas *et al.*, 2021) developed modified chitosan beads and chitosan films and

evaluated them for fluoride, zinc, dye, lead and nickel removal from groundwater and showed to be effective.

2.8 Defluoridation in South Africa

Defluoridation in South Africa was introduced after intensive studies, engagements, and discussions on whether to fluoridate or defluoridate drinking water around the country (Louw & Chickte, 1997). Defluoridation was recommended after studies revealed that there are health impacts related to ingestion of water with high levels of fluoride such as dental and skeletal fluorosis depending on the content range in drinking water. Current studies focusing on South Africa's fluoride health impacts and treatment suggests different methods to solve the problem of high fluoride concentration in groundwater such as adsorption methods, membrane techniques, ion exchange and precipitation methods (Kwai *et al.*, 2016). However, the use Activated alumina as an adsorbent and reverse osmosis which is a membrane method is disadvantageous due to costs and operational issues. Nevertheless, scholars have and still review natural clay soils as potential adsorbents of fluoride ions. Coetzee *et al.*, (2003) assessed 25 clay samples from around 50 areas in Northern parts of South Africa for their capacity to remove fluoride in water. According to the findings, only few South Africa's clay soils can remove fluoride ions. This is the reason scholars are now modifying clay soils in South Africa prior to use in defluoridation. Mudzielwana *et al.*, (2017) investigated the defluoridation potential of MnO₂ coated Na-bentonite clay and it was found to have above 91% F⁻ removal at all evaluated pH levels (2-12). Furthermore, Gitari *et al.*, (2017) modified diatomaceous earth with Mg/Ce/Mn tri-metal oxides groundwater defluoridation and it fielded F⁻ removal percentage of 97.1%. Moreover, Mudzielwana *et al.*, (2016) characterised smectite-rich clay soil for groundwater defluoridation and F⁻ removal at optimum conditions was found to be ≈92%.

2.9 Defluoridation at household and community level

According to Gwala *et al.*, (2014) and (Oladoja *et al.*, (2015) defluoridation system at household setup and community level must be cost effective, efficient and sustainable, it should furthermore provide drinking water with fluoride concentrations <1 mg/L with a potential of field implementation in fluoride affected rural areas. However, in poor rural settings, most technologies such as the use Activated alumina and ion exchange have failed in the field due to high costs, non-availability of skilled operators, unpalatable taste of treated water and impractical operational

requirements (Meenakshi & Maheshwari, 2006). In most of the rural areas hand pump and tube wells are the major source of water, water source substitution may be impossible due to non-availability of alternate sources and therefore removal of excess fluoride is the only feasible solution.

Nalgonda process is the most widely used defluoridation method particularly at community level (Nawlakhe *et al.*, 1975). The bucket defluoridation system based on Nalgonda technique has also been developed for domestic use (Mjengera & Mkongo, 2002). Bucket defluoridation process is suitable for a daily routine, where one bucket of water is treated for one day's water supply of about 20 L. The process produces water with residual fluoride between 1 and 1.5 mg/L. Yang & Dluhy (2002) reported that calcium salts are also used in the process of precipitation. When calcium salt is reacted with fluoride it gets removed by forming insoluble CaF_2 in a wide range of pH 4.0–10.4. However, generation of a large amount of sludge is a major limitation associated with precipitation and therefore from environmental point of view it is not acceptable in cases where fluoride concentration is considerably high.

2.10 Conclusion

Fluoride concentration in drinking water whether higher or lower than recommended levels have negative effects on human health. Therefore, it is of paramount importance to remedy the effects, various methods have been proposed and it is advisable to practice those that are cost effective, sustainable, accessible and effective. The use of clay as an adsorbent is highly recommended by scholars especially in a case of South Africa since it is an abundant resource, cost effective and due to its high fluoride binding affinity. Moreover, clays can be chemically modified by metal oxide, acid and base to improve their adsorption capacity. Clays can also be physically modified by materials such as chitosan to enhance their physical properties, particularly, stability and permeability. This study proposes the synthesis of Ce/Al/Fe-modified diatomaceous earth/chitosan and based on the previous studies highlighted in this chapter, it can be stated that Ce/Al/Fe-modified diatomaceous earth/chitosan is the most probable adsorbent for defluoridation at household and community level.

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Chapter 3: Enhancing the Fluoride Adsorption Efficiency of Diatomaceous Earth Through Modification by Ce/Al/Fe Metal Oxides

Abstract

Sustainable Development Goal 6.1 calls for developing technologies to improve water quality for human consumption to ensure clean drinking water for everyone by 2030. This chapter aims to contribute to the goal by synthesizing Ce/Al/Fe metal oxides modified diatomaceous earth for adsorption of fluoride from drinking water. Adsorption experiments were performed to determine the efficiency of the Ce/Al/Fe metal oxides modified diatomaceous earth in fluoride removal. About 98% fluoride removal efficiency was obtained from an initial fluoride concentration of 5 mg/L using 0.6 g/100 mL adsorbent dosage at an initial pH range of 4 to 10 after 50 mins' agitation time. The adsorption kinetics models revealed that fluoride adsorption occurred via chemisorption, while the isotherm models confirmed both monolayer and multi-layer adsorption. Thermodynamic studies showed that the adsorption process was spontaneous, endothermic, and random, as denoted by the negative ΔG° , positive ΔH° , and positive ΔS° , respectively. Regeneration studies showed that Ce/Al/Fe metal oxides modified diatomaceous earth can be reused for 8 successive regeneration-reuse cycles. This chapter revealed that modification of diatomaceous earth with Ce/Al/Fe metal oxides enhances the adsorption of fluoride and the material has the potential for use in defluoridation of groundwater.

Keywords: Adsorption; Adsorption mechanisms; Diatomaceous earth; Fluoride; Metal oxides

3.1 Introduction

Drinking water with fluoride concentration below 1.5 mg/L, as prescribed by the World Health Organization (WHO), is vital for the development of bones and the prevention of dental caries (Mudzielwana *et al.*, 2017; Girkar *et al.*, 2024). Conversely, long-term consumption of water with fluoride concentration above 1.5 mg/L leads to fluorosis (Guissouma *et al.*, 2017; Patil *et al.*, 2018; He *et al.*, 2020; Murambasvina & Mahamadi, 2020; Wang *et al.*, 2024). Fluorosis is common in numerous countries worldwide, including Kenya, Tanzania, India, Bangladesh, Pakistan, and the United States (Bailey *et al.*, 2006; Loganathan *et al.*, 2013; Kazapoe *et al.*, 2024).

In South Africa, the prevalence of fluorosis has been reported in provinces such as Limpopo, Northern Cape, North West, and Kwa-Zulu Natal, where groundwater contains excessive fluoride levels (Ncube and Schutte, 2005). Elumalai *et al.* (2019) reported that 51% of boreholes in the Jozini area within Kwa-Zulu Natal Province have an average fluoride concentration of 2.8 mg/L. Makubalo and Diamond (2020) reported fluoride concentrations as high as 5 mg/L in the Northern Cape Province. Owing to the lack of alternative sources of fluoride-free water, it is paramount to develop flexible and sustainable systems for water defluoridation.

Adsorbents like activated alumina (Rafique *et al.*, 2013), diatomaceous earth (Gitari *et al.*, 2017), natural and modified bentonite (Mudzielwana *et al.*, 2017), activated carbon (Fito *et al.*, 2019), kaolinite (Ayalew, 2020), chitosan (Viswanathana *et al.*, 2009) and aluminium furmarate metal-organic framework and hydroxyapatite composite (Kumari *et al.*, 2024) have been tested for groundwater defluoridation. Izuagie *et al.* (2015) evaluated the performance of raw diatomaceous earth (DE) in fluoride adsorption and recorded 25.62% removal efficiency with 0.65 mg/g adsorption capacity. The introduction of metal oxides into the diatomaceous earth has been observed to enhance its efficiency due to their ability to bind fluoride ions (Oladoja & Helmreich, 2014).

This chapter aims to synthesize Ce/Al/Fe metal oxides modified diatomaceous earth and evaluate its applicability in the adsorption of fluoride from groundwater. The specific objectives are i) to evaluate the optimum conditions for modification of diatomaceous earth using Ce/Al/Fe metal oxides modified and further evaluate its physicochemical characteristics ii) to assess the fluoride adsorption efficiency of the prepared material, iii) to establish the adsorption mechanisms for

fluoride by Ce/Al/Fe metal oxides modified diatomaceous earth and lastly, v) to assess the reusability potential the synthesized adsorbent.

3.2 Material and method

3.2.1 Materials

Diatomaceous earth (DE) was purchased from Eco-Earth Traders, South Africa. All chemicals and reagents used in this study, including sodium hydroxide (NaOH), hydrochloric acid (HCl), cerium(III) chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium fluoride (NaF), and total ionic strength adjustment buffer (TISAB III) were of analytical grade purchased from Merck Life Sciences company.

3.2.2 Adsorbent preparation

Diatomaceous earth (DE) was pre-cleaned to remove silt and excess organic matter using Milli-Q water (18.2 MΩ/cm). Thereafter, cleaned DE was dried for 12 hours in an oven at a temperature of 110°C and then milled to pass through a 75 μm sieve. Solutions containing 0.25 M of Ce^{2+} , Al^{3+} , and Fe^{2+} were prepared by dissolving 4.68 g of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, 8.33 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 2.485 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, respectively in 100 mL of Milli Q water. Solutions of Ce^{2+} , Al^{3+} , and Fe^{2+} were added into 250 mL bottles to make up a final volume ratio of 1:1:1. 3 g of clean DE was then added to keep the S/L ratio of 20 mL to 3 g and the mixtures were shaken for 20 mins at 100 rpm for proper soaking. This was followed by the dropwise addition of 2 M NaOH solution till the pH reached 8.2 with continuous agitation for 60 mins to precipitate Ce^{2+} , Al^{3+} , and Fe^{2+} into their respective oxides. Thereafter, mixtures were centrifuged for 30 mins, and the recovered solid residues were exposed to air for 10 hours to ensure further oxidation of Fe^{2+} to Fe^{3+} . The pH of the residues was adjusted to near neutral through continuous washing using Milli-Q water. This was followed by oven drying at 110 °C for 12 hours and subsequent milling to pass through <75 μm sieve. Adsorbent was then stored in a plastic bottle for further use.

3.2.3 Material characterisation

The surface chemistry of the material was determined using Fourier Transform Infrared (FTIR) (Bruker Alpha Platinum-ATR). The chemical composition and the crystalline structure were determined using X-ray fluorescence (XRF) (Bruker SI Titan/Tracer Handheld XRF) and D8

Advance X-ray diffractometer (XRD) (Bruker, Germany), respectively. Barrett Joyner Halenda (BJH) and the Brunauer-Emmett-Teller (BET) (Autosorb-iQ & Quadrasorb SI, USA) techniques were used to determine the surface area and pore properties. Surface morphology was determined using Scanning electron microscopy (Leo1450 SEM, at 5 kV, working distance of 10 mm).

3.2.4 Batch fluoride removal experiments

Parameters such as contact time, initial concentration, adsorbent dosage and pH were varied to establish their influence on fluoride removal. The influence of contact time and adsorption kinetics were determined by varying time from 1 to 120 mins. The effect of initial fluoride concentration and adsorption isotherms were determined by varying the concentration from 3 to 50 mg/L at temperatures of 298, 323 and 348 K. For the effect of pH; the initial pH was adjusted to the ranges of 4 to 10 using 0.1 M NaOH and 0.1 M HCl solutions. The effect of competing ions was evaluated by using 5 mg/L of Cl^- , SO_4^{2-} , CO_3^{2-} , Ca^{2+} , and Mg^{2+} , respectively, at the initial concentration of 5 mg/L of F^- , with the adsorbent dosage of 0.6 g and agitation time of 50 mins. The regeneration study was performed using 0.001 M HCl as a regenerant. All experiments were performed in triplicate for validity and quality control. The residual fluoride concentration was analysed using an ion-selective electrode (9609BNWP) attached to the Orion StarTM A211 Benchtop Meter. The electrode was calibrated with four standards i.e. 0.1, 1, 10 and 100 mg/L of F^- . TISAB III was added for ion decomplexation at a ratio of 1:10 in both standards and samples prior to analysis.

3.3 Results and discussion

3.3.1 Adsorbent characterization

3.3.1.1 Bulk chemical composition

Table 3.1 presents the elemental composition of raw and metal oxide-modified DE. The raw DE contains SiO_2 (82.98%) as the major oxide and traces of Al_2O_3 (0.98%) and Fe_2O_3 (0.45%). After modification, Al_2O_3 and Fe_2O_3 contents increased to 5.38% and 1.9%, respectively. Ce was only observed in the modified diatomaceous earth with a %w/w of 3.99%. The increase observed shows that the modification or the introduction of the metal oxides was successful.

Table 3.1: Chemical composition of the raw and modified diatomaceous earth

Oxides	Raw DE (%w/w)	Modified DE (%w/w)
SiO ₂	82.98	61.29
Al ₂ O ₃	0.97	5.38
MgO	0.96	1.36
Fe ₂ O ₃	0.459	1.9
K ₂ O	0.31	0.19
P ₂ O ₅	0.112	0.064
Ce	<LOD	3.99

*LOD= Limit of detection

3.3.1.2 Functional groups analysis

The FTIR spectra showing the functional groups of raw and modified DE is presented in Figure 3.1. Clear absorption bands attributed to vibration of Al-O, Si-O-Si, -OH bonds are observed at wavelength regions of 800 cm⁻¹, 1052 cm⁻¹, 1440 cm⁻¹ and between 3100 cm⁻¹ and 3600 cm⁻¹, respectively. The vibration and stretching of Al-O and Si-O-Si bonds is attributed to the aluminosilicate nature of the material. The vibration of -OH bond at 1300 - 1600 cm⁻¹ could be attributed to the adsorbed water molecules in the interlayers of the diatomaceous earth. On the Ce/Al/Fe-modified DE there is a noticeable decrease in the intensity of the Si-O-Si band this could be attributed dissolution of silica due to the use of NaOH in the cause of the modification process or dilution of the SiO₂ component on addition of the metal oxides. The -OH band is not observed which could be attributed to removal of adsorbed water molecules during the oven drying process.

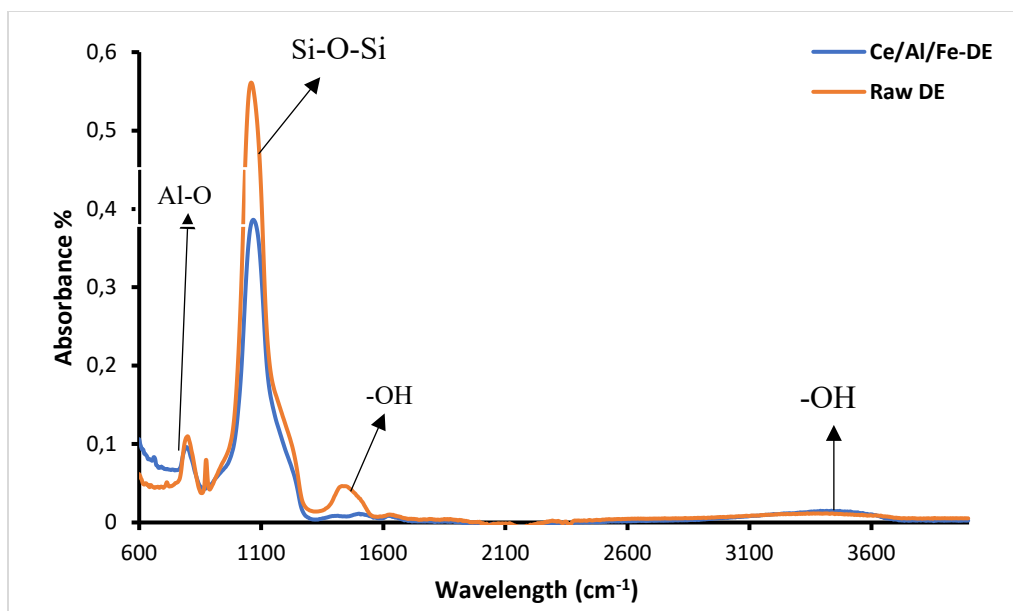


Figure 3.1: Spectrum of raw metal oxides modified DE

3.3.1.3 Crystallinity analysis

Figure 3.2 shows the composition-ray diffractogram of raw DE and metal oxide-modified DE. It is observed that DE is largely amorphous in nature with crystalline peaks of quartz and calcite noted. After modification, the material appears to be largely amorphous with more peaks of quartz disappearing. This could be due to the dissolution of silica during the alkaline treatment of the material. It is confirmed by the FTIR and the XRF results. The absence of calcite peaks is complemented by the SEM-EDX results and could be due to the ion exchange during the process of modification.

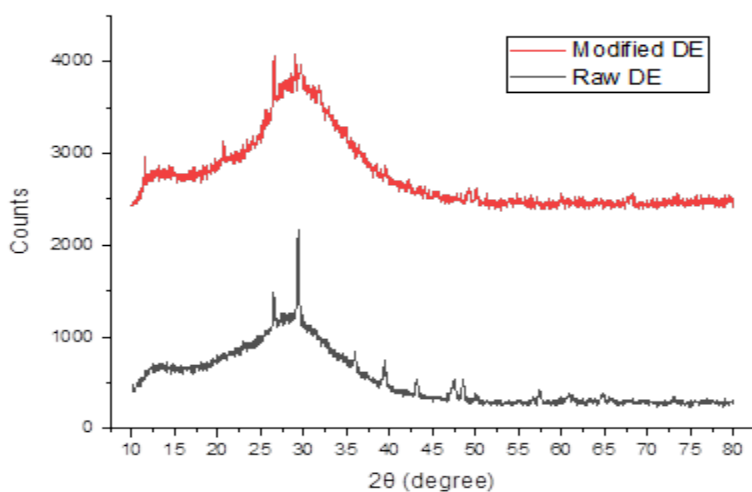


Figure3.2: X-ray diffractogram of raw DE and modified DE.

3.3.1.4 Morphological analysis

The surface micrographs of raw and metal oxide-modified DE and their respective energy dispersion spectrums (EDS) are presented in Figure 3.3a-d. The morphology of the raw DE (a) is characterised by the slightly crystalline and porous surface. In contrast, the morphology of the Ce/Al/Fe-modified DE (c), appears to be amorphous with fewer pores and fine clustered particles which could be attributed to the precipitates of metal oxides on the surface of the material. The results correlate with XRD analysis, which depicted slightly crystalline raw DE and essentially amorphous as compared to modified DE. Elemental composition given by the EDX spectra in Figure 3 (b) shows the presence of exchangeable cations Ca, Si, and Al, while the EDX spectra of modified DE show the presence of Ce, Fe, and Al.

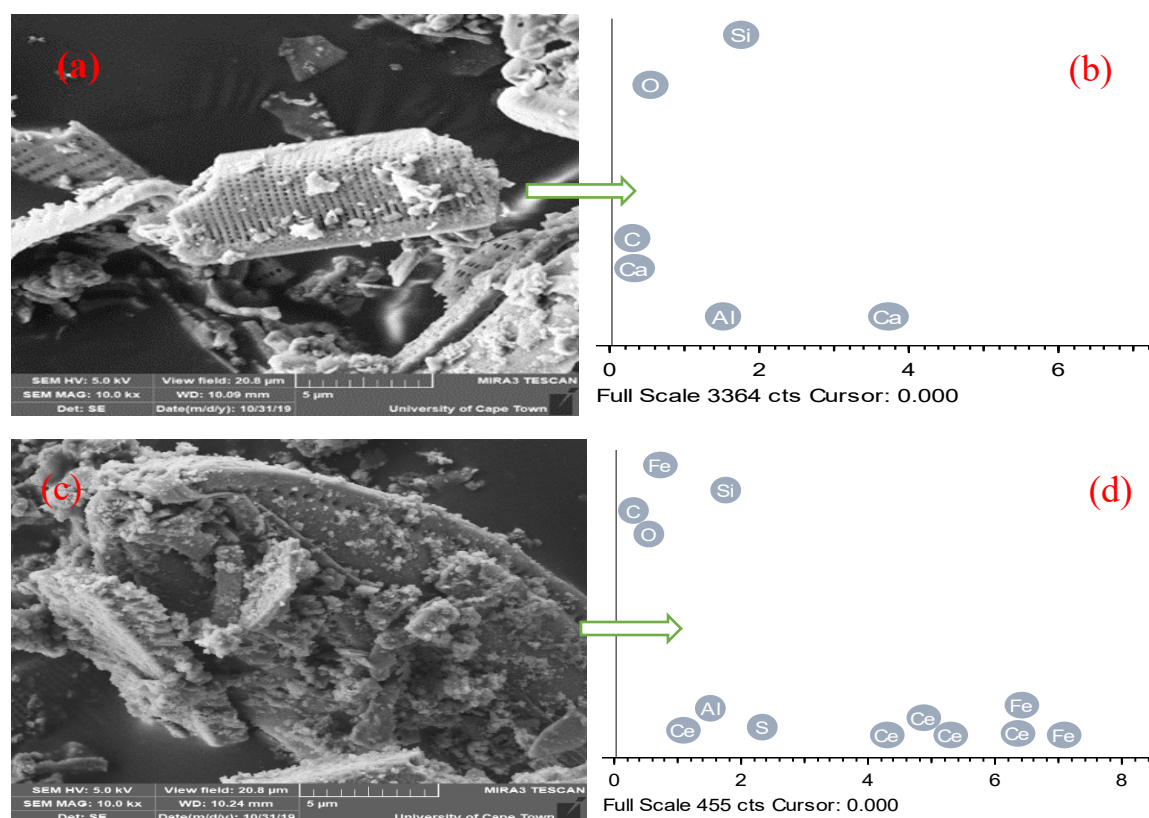


Figure 3.3: Micrographs of (a) raw DE and (c) modified DE; EDX spectra of (b) raw DE and (d) modified DE

3.3.1.5 Surface area and pore properties

Table 3.2 depicts the BET surface area and pore properties of the raw and metal oxides modified diatomaceous earth. The surface area of the material increased from 17.95 m²/g to 28.61 m²/g in metal oxides modified DE. This could be attributed to the fact that modified DE is highly amorphous than raw DE. Increasing surface area often corresponds to increasing sorption sites; as such, metal oxides modified DE might have higher adsorption capacity compared to raw DE. The pore diameter slightly increased from 15.39 nm to 15.45 nm, which will enhance percolation during the defluoridation process. From Figure 3.4, it can be deduced that a vast number of pores range between 20 nm pore diameter, which implies that the adsorbent is mesoporous.

Table 3.2: Surface area and pore properties of raw and metal oxides modified diatomaceous earth.

Samples	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	BJH pore volume (nm)
Raw diatomaceous earth	17.96	0.000916	15.39	14.58
Modified diatomaceous earth	28.61	0.000835	15.45	15.78

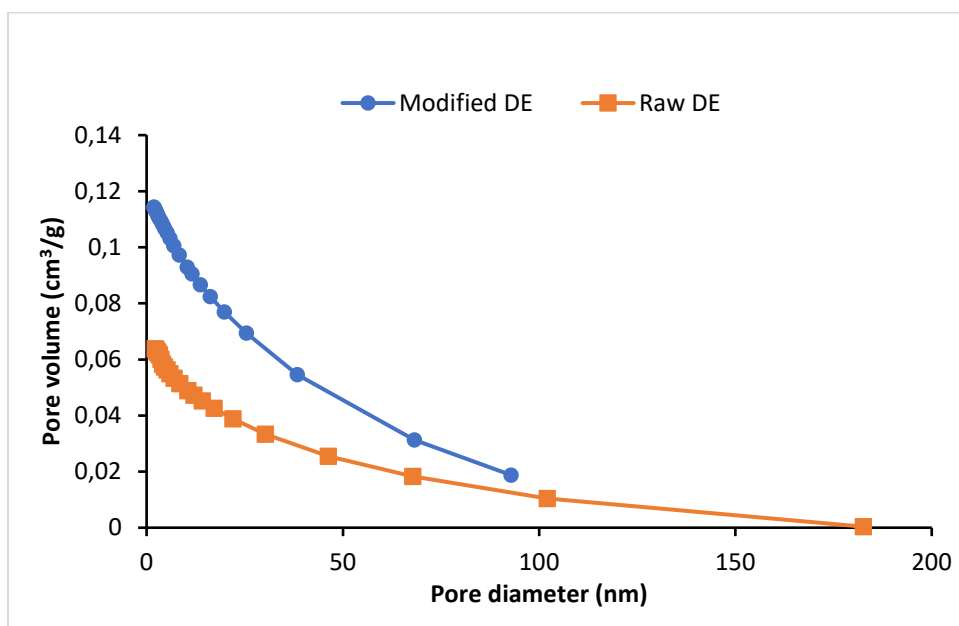


Figure 3.4: Pore distribution plot for raw and modified diatomaceous earth.

3.3.2 Fluoride removal efficiency

3.3.2.1 Variation of contact time and adsorption kinetics.

Figure 3.5 shows variation of contact time with fluoride efficiency. The removal efficiency was observed to be $\approx 75\%$ within the first 10 mins of the reaction. Thereafter, it declines from 75% to 70% 40 mins. After 40 mins, there was a rapid increase to 78% up to 50 mins which was followed by slight increase of 2% at 90 min as reaction continues to 120 mins indicating that the adsorbent has reached saturation. The adsorption within the first 10 mins could be attributed to boundary layer sorption in which the fluoride ions may easily migrate into the active sites via electrostatic attraction. The decrease in fluoride removal observed between 10 and 40 mins could be attributed to the intra-particle diffusion of fluoride ions through the tiny pores of the material into the internal structures of the particles hence reduced adsorption rate. The increase beyond 40 min could be attributed to adsorption within the pores of the material where fluoride ions interact with atoms within the pores of the adsorbent which is subsequently followed by equilibrium as indicated by slight change in percentage fluoride removal as time increases to 120 mins. Contact time of 50 mins was there for selected as the optimum contact time and was used for subsequent experiments.

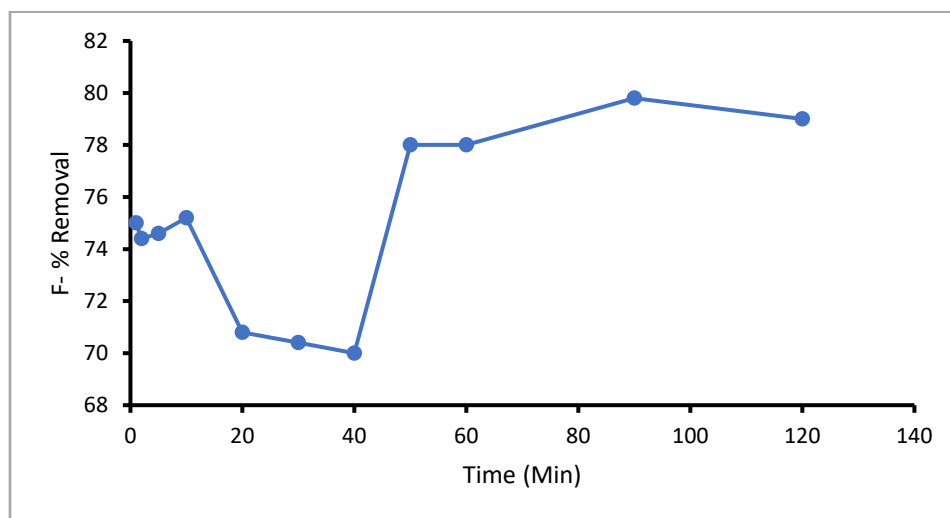


Figure 3.5: Variation of % F^- removal by Ce/Al/Fe modified DE with contact time (Adsorbent dosage 0.15g/100 ml; C_i 5 mg/L F^- ; pH 7; shaking speed 200 rpm).

To define the rate-limiting steps and the adsorption mechanisms of fluoride by the metal oxide modified DE, the adsorption data obtained at different contact times was fitted to the pseudo-first and pseudo-second order reaction-based kinetic and intra-particle diffusion models. The Lagergren

pseudo-first order assumes that the process signifies reversible interaction and that adsorption occurs via physisorption (Lagergren, 1898; Oladoja *et al.*, 2015). The pseudo-second order assumes that the adsorption is limited to chemisorption, in which the chemical interaction leads to the binding of the adsorbate ions to the surface by bonding as strong as covalent bonding (Ding *et al.*, 2007; Gupta & Bhattacharyya, 2011). Equations 3.1 and 3.2 were used to fit the adsorption data to pseudo-first order and pseudo-second order, respectively.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_{ad}t}{2.303} \quad (3.1)$$

$$\frac{t}{q_t} = \frac{1}{K_{2ads}q_e^2} + \frac{1}{q_e}t \quad (3.2)$$

Where q_t (mg/g) is the quantity of fluoride ions adsorbed by the absorbent at a given time t (min), q_e is the quantity of fluoride adsorbed at equilibrium. K_{ad} and K_{2ads} (g.mg⁻¹/min) are the reaction rate constants of pseudo first-order and pseudo second-order adsorption, respectively. The value of K_{ad} is computed from the slope and intercepts of $\log(q_e - q_t)$ versus time while K_{2ads} is computed from the slope and intercepts of t/q_t vs time. The linear plots of pseudo first and second order models are presented in Figure 6(a) and (b), respectively and their constant values are shown in Figure 3.6 and Table 3.3. The correlation co-efficient value for pseudo second order ($R^2=0.99$) was found to be higher than that of pseudo first order ($R^2=0.57$) which suggest the dominance of chemisorption. This is also supported by high values of K_{2ads} and q_e for pseudo second order model (Table 3.3).

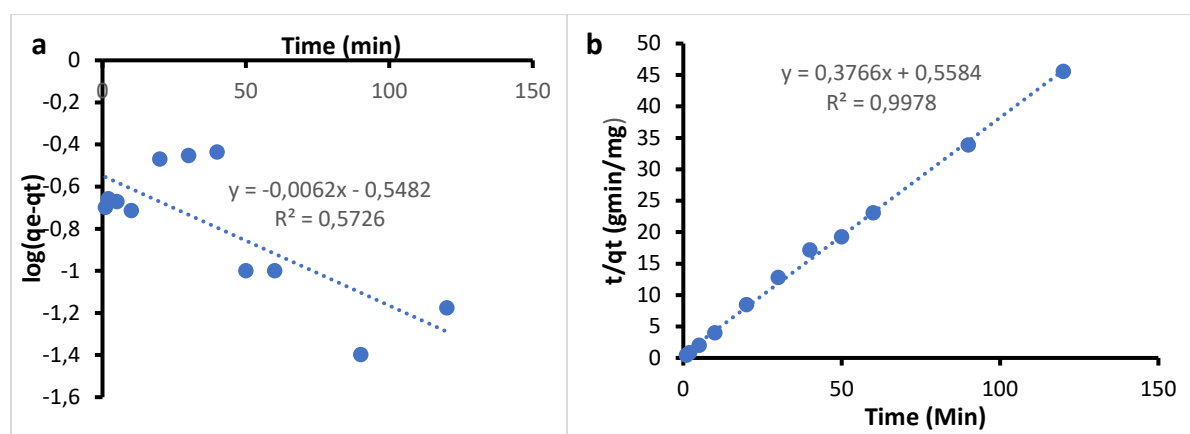


Figure 3.6: linear plot for pseudo first order (a) and pseudo second order models of reaction kinetics for adsorption of fluoride by metal oxide modified DE.

Table 3.3: Constant parameters of pseudo first order and pseudo second order reaction kinetics model

	$q_{e(exp)} \text{ (mg/g)}$	$K_{ad}/K_{2ad} \text{ (g mg}^{-1} \text{ min}^{-1})$	$q_{e(cal)} \text{ (mg/g)}$	R^2
Pseudo first order	2.7	0.01	0.28	0.57
Pseudo second order	2.7	0.25	2.66	0.99

Equation 3.3 of Weber-Morris intra-particle diffusion model was used to determine the rate limiting steps for fluoride adsorption by metal oxides modified diatomaceous earth (Chen *et al.*, 2010).

$$q_t = K_i t^{0.5} + C \quad (3.3)$$

Where q_t is the quantity of fluoride adsorbed (mg/g) at a given time t (mins), K_i (mg/g/mins) is the rate constant of intra-particle diffusion which is determined from the slope of $t^{0.5}$ vs q_t . C intercept constant is associated to the thickness of the boundary layer. The intra-particle diffusion plot depicted in Figure 7 yielded 3 clear phases indicating that the adsorption process involved more than one process. The first phase is linked to physical attraction of fluoride ions onto the boundary layer of the adsorbent. The second phase represents inter-particle diffusion in the micro-pores and mesopores. The fluoride ions are diffusing through the tiny pores of the material into the internal structures of the particles leading to chemisorption. Lastly, the third phase could be attributed to sorption of fluoride ions to the internal surface of sorbent through chemisorption. The rate constant for phase 1, phase 2, and phase 3 were represented by the values of K_{i1} , K_{i2} and K_{i3} , respectively, as shown in Table 3.4. Adsorption in the boundary layer was faster than the intra-particle diffusion and chemisorption within the pores as depicted by the higher K_{i1} value compared to K_{i2} and K_{i3} .

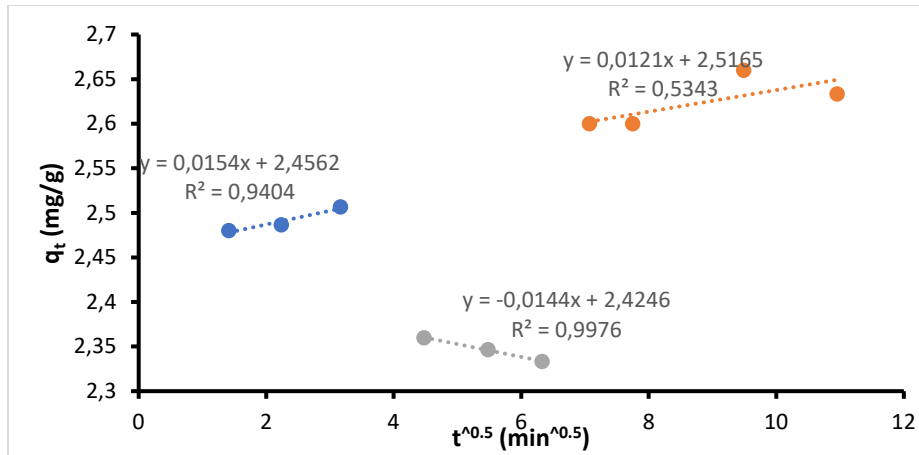


Figure 3.7: Plot for intra-particle diffusion at various concentrations (0.15 g/100 mL adsorbent dosage, pH 7.11 and shaking speed of 200 rpm).

Table 3.4: Constant values of intra-particle diffusion model.

K_{i1} (mg/g/mins)	C_1 (mg/g)	K_{i2} (mg/g/mins)	C_2 (mg/g)	K_{i3} (mg/g/mins)	C_3 (mg/g)
0.02	2.46	0.014	2.42	0.012	2.52

3.3.2.3 Effect of initial concentration and adsorption isotherms

The variation of adsorption capacity with equilibrium adsorbate concentration is depicted in Figure 3.8. It is noted that adsorption capacity increased with the increasing equilibrium concentration. The same trend was noted at all temperatures. Langmuir and Freundlich's adsorption isotherm models were used to elucidate the dynamic relationship between the adsorbate ions and the adsorbent (Mudzielwana *et al.*, 2019).

Langmuir isotherm model assumes that the adsorption occurred on a monolayered surface (Al-Ghouti & Da'ana, 2020). On the contrary, the Freundlich adsorption model assumes that the adsorption occurred on a multi-layered surface (Mudzielwana *et al.*, 2017). The Langmuir and Freundlich adsorption isotherm models are expressed by non-linear equations 3.4 and 3.5, respectively.

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (3.4)$$

$$q_e = K_f C_e^{1/n} \quad (3.5)$$

Where, C_e correspond to the fluoride concentration at equilibrium (mg/L), q_e quantity adsorbed at equilibrium per unit mass (mg/g), q_m is maximum theoretical adsorption capacity (mg/g) and b is the Langmuir constant related to enthalpy of adsorption (L/mg). K_f and $1/n$ are empirical constants based on Freundlich isotherm models, indicating the adsorption capacity and adsorption intensity, respectively. Figure 3.8 depicts Langmuir and Freundlich isotherms at different temperatures i.e. 298 K, 323K and 348K.

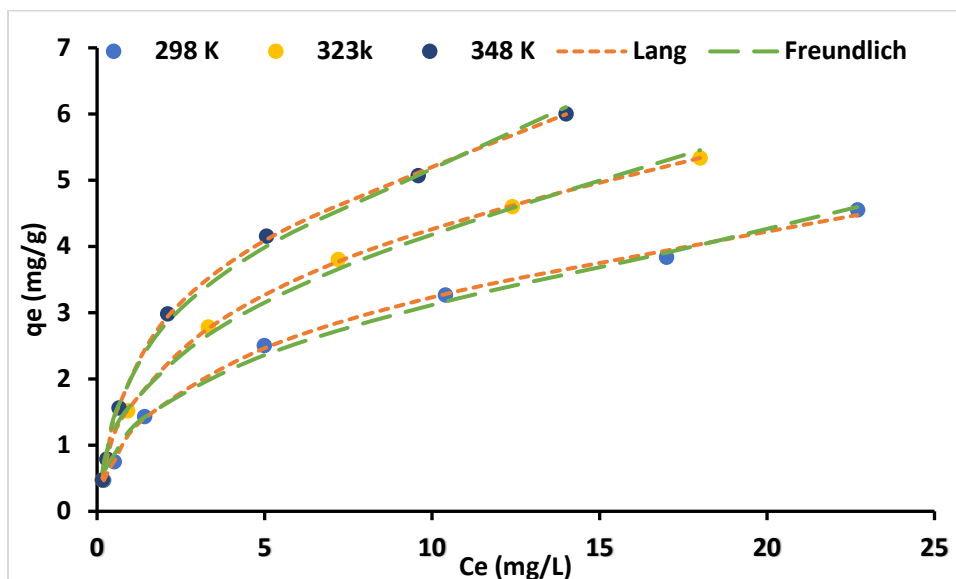


Figure 3.8: Adsorption isotherms of F^- onto Ce/Al/Fe-tri-metal modified DE (contact time 50 min; adsorbent dosage 0.6 g/100 mL; temperature: 298 K, 323 K and 348 K; and shaking speed of 200 rpm).

Based on the regression coefficient values, the data fits best with both Langmuir and Freundlich isotherm models, at all temperatures, as shown in Table 3.5. This suggests that F^- adsorption favoured homogeneous and heterogeneous adsorption on Ce/Al/Fe-tri-metal modified DE. However, the Langmuir isotherm maximum adsorption capacity (q_{max}) is higher than the Freundlich isotherm adsorption capacity (K_f) at all temperatures. This shows that the adsorption favoured Langmuir isotherm more. It is observed that as the temperature increases, the maximum adsorption capacity (q_{max}) also increases on Langmuir isotherm.

Table 3.5: Values of Langmuir and Freundlich isotherm models (contact time 50 mins, adsorbent dosage 0.6 g/100 mL, temperature: 298 K, 323 K and 348 K; and shaking speed of 200 rpm).

	Langmuir isotherm			Freundlich isotherm		
Temperature	$Q_{\max}$ (mg/g)	b (L/mg)	R^2	K_f (mg/g)	1/n	R^2
298 K	9.86	0.01	0.99	0.27	0.73	0.99
323 K	14.12	0.01	0.99	0.26	0.78	0.99
348 K	19.44	0.009	0.99	0.24	0.83	0.99

3.3.2.4 Thermodynamics study

Thermodynamics study is essential in determining the type and mechanism of the adsorption process at different temperatures and in determining the spontaneity and the randomness of the adsorption process (Tran *et al.*, 2016). It comprises three parameters, the Gibbs energy change, which determines the degree of spontaneity of the adsorption process. A higher negative value of ΔG° indicates more energetically favourable adsorption. Secondly, the standard enthalpy (ΔH°) determines if the adsorption process is either endothermic or exothermic. If the adsorption process is endothermic, the process is attributable to chemisorption unequivocally (Tran *et al.*, 2016). Lastly, the entropy (ΔS°) which reveals if the adsorption process is less random ($\Delta S^\circ < 0$) or more random ($\Delta S^\circ > 0$). Positive ΔS° corresponds to a dissociative mechanism that is favourable for adsorption.

The Gibbs energy change is expressed by equation 3.6:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3.6)$$

In sorption equilibria, the Langmuir's constant K_L is related to the Gibbs free energy change by equation 3.7:

$$\Delta G^\circ = -RT \ln K_L \quad (3.7)$$

Where R is the molar gas constant, $8.314 \text{ J mol}^{-1}\text{K}^{-1}$ and T is the absolute temperature in Kelvin (K).

The van't Hoff equation 3.8 is expressed as follows:

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3.8)$$

Equation (3.9) was used to determine the standard enthalpy change from the slope of the linear plot of $\ln K_L$ against $1/T$:

$$\ln K_L = -\frac{\Delta H}{RT} + R \quad (3.9)$$

Table 3.6 depicts the adsorption thermodynamic parameters. The Gibbs energy change was found to be negative at all temperatures, which indicates that the adsorption process was favourable and spontaneous. Furthermore, the enthalpy was found to be endothermic, given the positive value, and the adsorption mechanism can be attributed to chemisorption. Moreover, the positive entropy value suggests that the process was random and dissociative, which favours the adsorption process because of a high degree of freedom of F^- ion in a solution. The standard enthalpy change for the adsorption process was obtained from the slope of the linear plot of $\ln K_L$ against $1/T$ (Figure 3.9).

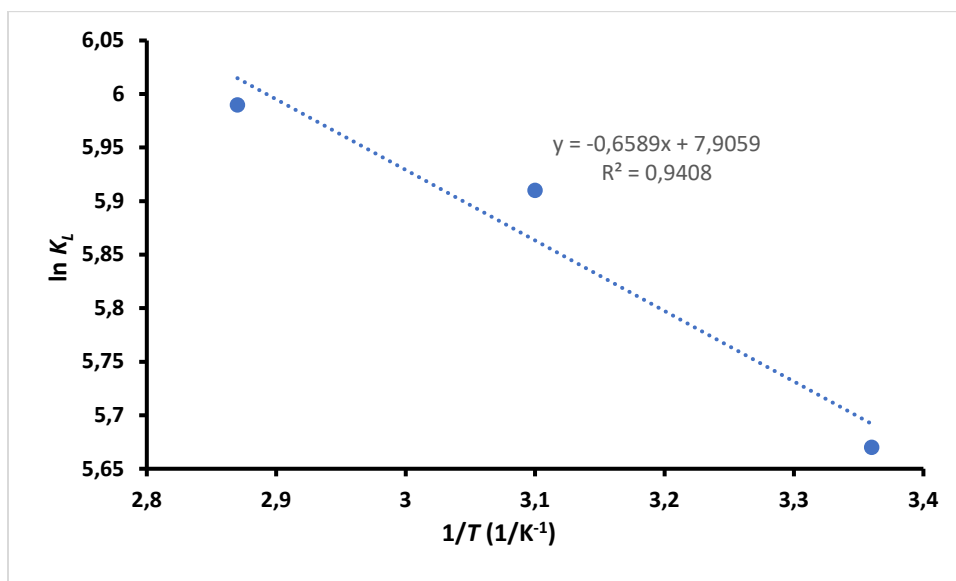


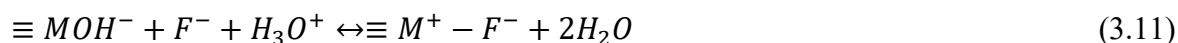
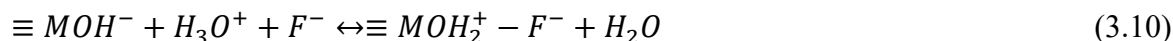
Figure 3.9: $\ln K_L$ as a function of reciprocal of adsorption temperatures.

Table 3.6: Adsorption thermodynamic parameters.

T (K)	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (Kj/mol)
298	-140478	5.48	65.72
323	-15870.8		
348	-17330.7		

3.2.5 Effect of pH

Figure 3.10 depicts the effect of pH on adsorption of fluoride by Ce/Al/Fe tri-metal oxides modified DE. The fluoride removal across all the evaluated pH levels was found to be above 98% which suggests that Ce/Al/Fe modified DE is suitable for practical defluoridation in the field since it would not require prior solution pH adjustment. The highest fluoride % removal of 99.5% at a pH of 4 could be attributed to the positive charges on the surface of the material. The point of zero charge (pHpzc) of the synthesized material was found to be 6, as depicted in Figure 3.11. This means that at pH 6, the surface of the material is neutrally charged. While at pH below 6, the surface is positively charged, and at pH above 6, the surface is negatively charged. Therefore, at pH below 6, defluoridation was found to be high because the surface of the adsorbent is positively charged. The mechanism responsible for the adsorption is electrostatic interaction and the protonation of hydroxyl groups, as shown in equations (3.10) and (3.11). At pH above the point of zero charge (pzc), a decrease in fluoride uptake could be due to electrostatic repulsion between F^- ions and the negatively charged surface, as shown in equations (3.12) and (3.13). It could also be attributed to increased competition for adsorbent sites between F^- and increased OH^- species at high pH. The fluoride adsorption mechanism at pH beyond pzc could be attributed to the ion exchange between F^- and OH^- .



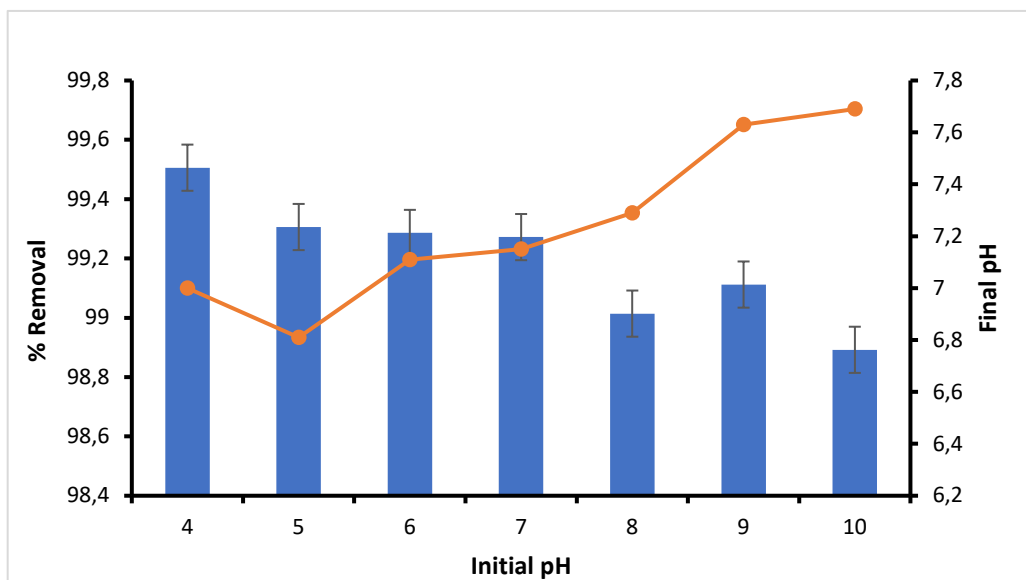


Figure 3.10: Variation of % F^- removal by Ce/Al/Fe modified DE as a function of pH (Ci 5 mg/L F^- ; Contact time 50 min; dosage 0.6 g/100 mL; shaking speed 200 rpm)

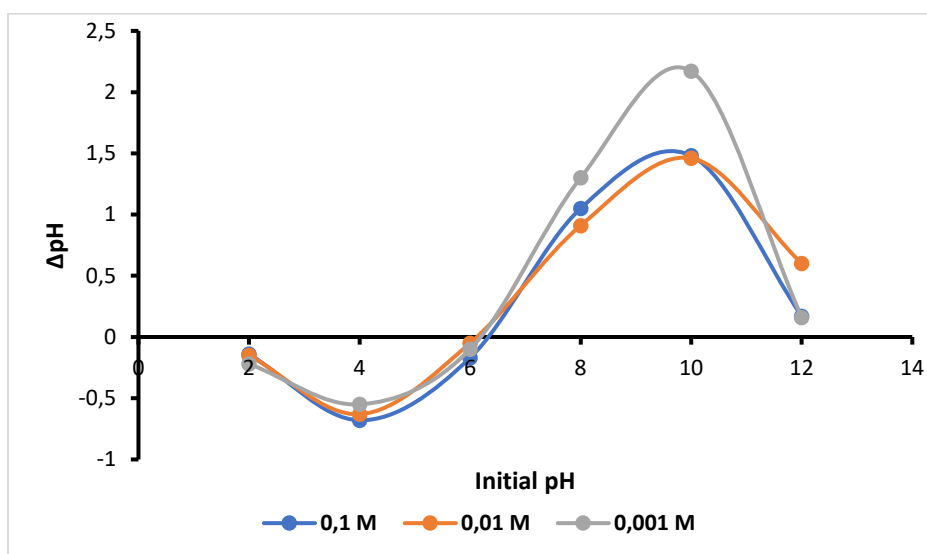


Figure 3.11: pH at a point-of-zero charge of Ce/Al/Fe oxide-modified DE using 0.1, 0.01 and 0.001 M KCl.

3.3.2.6 Effect of co-existing ions

Coexisting ions in water could either enhance or inhibit fluoride removal. Figure 3.12 shows the effect of co-existing ions on fluoride adsorption. To evaluate the influence of co-existing ions in fluoride removal by Ce/Al/Fe modified DE, the experiments were conducted in the presence of 5 mg/L of Cl^- , SO_4^{2-} , CO_3^{2-} , Ca^{2+} and Mg^{2+} . The results are presented in Figure 3.12. It is observed

that the presence of Cl^- , SO_4^{2-} , CO_3^{2-} , Ca^{2+} and Mg^{2+} enhanced fluoride removal since they showed slightly higher fluoride removal as compared to ion-free solution. There was a slight decrease of fluoride up take in the presence of Ca^{2+} and Mg^{2+} , respectively. This could be attributed to the possible repulsion between the positively charged surface of the adsorbent and positively charged ions. This suggests that the performance of Ce/Al/Fe metal oxides modified DE in the field may not be limited by co-existing ions.

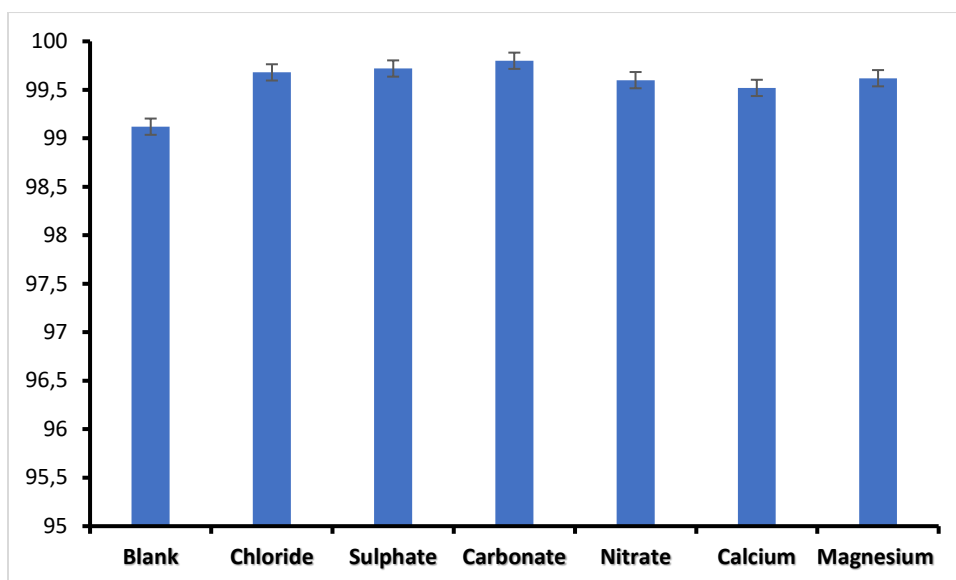


Figure 3.12: Effect of co-existing ions on fluoride removal by Ce/Al/Fe oxide-modified DE (C_i 5 mg/L F^- ; 5 mg/L of co-existing ions Contact time 50 mins; dosage 0.6 g/100 mL; pH 7.2; shaking speed 200 rpm)

3.3.2.7 Regeneration-reuse studies

The reusability of the material was evaluated using 0.001 M HCl as the regenerant, and the results are presented in Figure 3.13. The first and second cycles yielded a percentage removal of 99.69%, which is very close to the percentage removal of the fresh adsorbent. Thereafter, a gradual decrease of up to 93% was observed as the regeneration-reuse cycle continued to cycle 8. The good performance of the adsorbent in reusability could be attributed to the protonation of the surface of the adsorbent in the process of releasing F^- by 0.001 M HCl. This promotes electrostatic attraction forces between the surface of the adsorbent and F^- . The Ce/Al/Fe modified DE could be

economically viable due to its reusability. The Ce/Al/Fe modified DE's reusability indicates that it can be used over a longer period in the field.

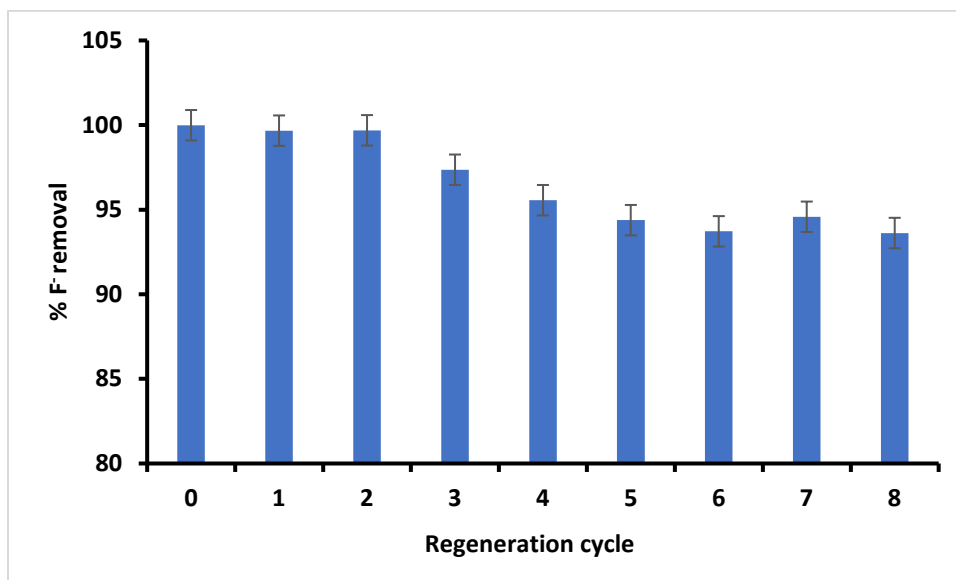


Figure 3.13: Percent fluoride removal as a function of defluoridation cycle using 0.001 M HCl as a regenerant (Ci 5 mg/L F⁻; 5 mg/L; Contact time 50 min; dosage 1.5 g/100 mL; shaking speed 200 rpm)

3.4 Comparison with other adsorbents

Table 3.7 depicts the maximum adsorption capacities of different adsorbents for defluoridation. It is important to compare the adsorbent synthesized to determine its competitiveness. It can be noted that the Ce/Al/Fe tri-metal oxide modified is a competitive adsorbent relative to other adsorbents reported in the literature. Therefore, the developed adsorbent in the current study has the potential to be used for the removal of fluoride in groundwater.

Table 3.7: Comparison of maximum adsorption capacities with other adsorbents

Adsorbent	Experimental conditions	Defluoridation capacity	Reference
Fish scales derived biochar	Concentration 0.6 mg/L, pH 6, adsorbent dosage 0.3 g/100 mL	6.3 mg/g	(Kumari <i>et al.</i> , 2024)
Hydrothermally treated aluminosilicate clay	Concentration 6 mg/L, pH 6, adsorbent dosage 0.8 g/40 mL	2.75 mg/g	(Obijole <i>et al.</i> , 2021)
Hydroxyapatite modified Corbula trigona shell powder	Concentration 2.20 mg/L, pH 7.5, adsorbent dosage 0.8 g/L	4.52 mg/g	(Aw <i>et al.</i> , 2022)
Ce/Al/Fe tri-metal oxide modified DE	Concentration 5 mg/L, pH 4-10, adsorbent dosage 0.6 g/100 mL	9.8 mg/g	Present study

3.5 Chapter summary

In this study, Ce/Al/Fe tri-metal oxide modified DE was successfully synthesized and further evaluated for the removal of F^- from groundwater. The optimum metal oxides ratio was 1:1:1. The modified DE yielded 9.8 mg/g adsorption capacity at optimum conditions of 5 mg/L initial concentration, dosage of 0.6 g/100 ml, 50 mins optimum time, pH 7.5, and shaking speed of 200 rpm. The adsorption kinetics data fit better in pseudo-second order, which implies that the adsorption mechanism is chemisorption. The isotherm data showed a better fit for the Freundlich adsorption isotherm model, indicating that adsorption occurred on a multilayer surface. Thermodynamic studies showed that the adsorption was spontaneous, endothermic, and random, given by the negative value of the ΔG° change, positive ΔH° value, and a positive ΔS° value, respectively. The presence of co-existing ions increased the percentage of fluoride removal. Regeneration studies showed that the material can be used for up to 8 successive regeneration-reuse cycles using 0.001 M HCl as an adsorbent. This study concludes that the synthesized adsorbent is suitable for the removal of F^- from groundwater for drinking water.

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Chapter 4: Synthesis of Ce/Al/Fe Tri-Metal Oxide Modified DE/Chitosan Composite Films for Fluoride Removal from Groundwater

Abstract

In the previous chapter Ce/Al/Fe tri-metal oxide modified diatomaceous earth was synthesized and evaluated for F^- removal. However, due to its low permeability, it could not be applied in a column set-up. Therefore, to improve its physical characteristics, this chapter aims to synthesize the Ce/Al/Fe tri-metal oxide modified diatomaceous earth-chitosan composite films for the removal of fluoride from drinking water. The chitosan films were formed by dissolving 2.5 g chitosan in 100 mL of 2% acetic acid and was stirred until it formed a gel. 1 g of Ce/Al/Fe tri-metal oxides modified DE was introduced gradually into the gel. The Ce/Al/Fe tri-metal oxides modified DE-chitosan gel was transferred into petri dishes then oven dried and the films were formed. 1 M NaOH was poured over the formed films for the precipitation of metal oxides and were left to rest. The excess NaOH was washed, then the films were oven dried. Finally, the Ce/Al/Fe tri-metal oxides modified DE-chitosan films were hand-crushed and used for subsequent experiments. The functional groups, elemental composition and morphology of the synthesized material were characterised using Fourier Transform Infrared (FTIR) and scanning electron microscopy-energy dispersion X-ray (SEM-EDX), respectively. Batch experiments were conducted to evaluate the effectiveness of the material in fluoride removal. The results showed 7.89 mg/g adsorption capacity towards fluoride from 5 mg/L initial fluoride concentration, when adsorbent dosage of 0.3 g/100 mL was used at initial pH of 7.17 after 50 mins agitation time at shaking speed of 200 rpm. The data for adsorption kinetics showed a better fit to pseudo-second order which indicates that the adsorption mechanism was chemisorption. The adsorption isotherm model data best fitted to Langmuir isotherm model which suggests that the adsorption took place on a monolayer surface. The co-existing anions showed a significant effect which indicates a competition of active adsorption sites with F^- . Whereas the co-existing cations showed no significant effect. The Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films have shown potential for application in the removal of fluoride from drinking water.

Keywords: Fluoride; drinking water; diatomaceous earth; adsorption

4.1 Introduction

Groundwater remains the most utilised source of water globally for different uses (Igibah *et al.*, 2022). The utilisation proportionally increases in rural areas, where it is the primary source of drinking water (Toolabi *et al.*, 2021). However, the state of groundwater is in decline due to contamination emanating from anthropogenic activities and natural processes (Makubalo & Diamond, 2020; Munzhelele *et al.*, 2022). It has been reported that prolonged exposure of humans to contaminated drinking water results in health issues (Adimalla *et al.*, 2020). One of the pollutants that affect the quality of groundwater is fluoride (F^-) (Maity *et al.*, 2021). Fluoride is released into the groundwater system through geochemical processes and ion exchange (Mtavangu *et al.*, 2022). Fluoride bearing rocks such as fluoroapatite ($Ca_5(PO_4)_3F$), fluorite (CaF_2) and cryolite (Na_3AlF_6), are the source of fluoride that leaches in the groundwater system (Kom *et al.*, 2023).

Fluoride concentration between 0.5 mg/L and 1 mg/L in drinking water has health benefits such as development of dental caries, bone mineralisation and teeth enamel (Murambasvina & Mahamadi, 2020; Ali *et al.*, 2023). However, the prolonged consumption of water with fluoride concentration of 1.5-4.0 mg/L, 4.0-10.0 mg/L, and >10.0 mg/L has adverse health effects which are, dental, skeletal, and crippling fluorosis, respectively (Mtavangu *et al.*, 2022; Ali *et al.*, 2023). In addition to fluorosis, other adverse health conditions are postpartum paralysis in pregnant women (Sawangjang *et al.*, 2019), cancer, stomach corrosion, kidney and liver damage and miscarriage (Hossain & Patra, 2020; Kom *et al.*, 2023). As a result, the World Health Organization (WHO) has set the permissible limit for fluoride concentration in drinking water at 1.5 mg/L (WHO, 2011) to eliminate the health risk.

Mulaudzi *et al.*, (2024) assessed the quality of groundwater in Lephalale Municipality, Limpopo Province, South Africa. A total of 71 samples were collected from 15 boreholes in 15 different villages, through April, July and October. It was reported that the F^- concentrations ranged from 0.3 mg/L to 7.4 mg/L. 9 villages had F^- concentration above 1.5 mg/L with Matladi Village having 7.4 mg/L F^- concentration which is higher than the recommended limit by the World Health Organization. Odiyo and Makungo (2012), conducted a survey in Siloam village, Limpopo province and reported that 87% of the households depend on groundwater and consequently, 85%

of the residence with 50% of children between the ages of 11 and 14 have mottled teeth. Furthermore, in the Northern part of KwaZulu Natal, 51% of wells were found to have fluoride concentrations higher than 1.5 mg/L which is above the recommended limits set by WHO (Elumalai *et al.*, 2019). Moreover, in the Namakwaland region of the Northern Cape Province, the highest groundwater fluoride concentration reported is 5 mg/L, which is hazardous for drinking (Makubalo & Diamond, 2020). Owing to the prevalence of fluoride in groundwater, there is a need to develop materials for groundwater defluoridation.

In the previous chapter Ce/Al/Fe modified DE was prepared and tested for its efficiency towards fluoride removal. An adsorption capacity of 9.86 mg/g was achieved. However, the adsorbent could not be applicable in a household gravity flow-mode filtration set-up due to the pressure drop caused by the low permeability of the adsorbent. Izuagie and Gitari (2025), evaluated the fluoride Removal Capability of Al-Fe Oxide-Infused Diatomaceous Earth in a Fixed-Bed Column. Peristaltic pump was used to compensate for the low permeability of the material.

To combat pressure drop, de Freitas *et al.*, (2021), activated carbon with chitosan and convert the composite into films. Chitosan is a polysaccharide chitin derived from the desacetylation of chitin which is found in crustacean shells and fungal biomass (Jaafari *et al.*, 2004; Viswanathan *et al.*, 2009). It consists of amine and hydroxyl functional groups in its structure, due to free amine groups it has multiple active sites and consequently, chitosan is a good adsorbent. This chapter aims to prepare Ce/Al/Fe tri-metal modified DE-chitosan composite films for groundwater defluoridation. The prepared material was characterised using Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM) and batch experiments were used to evaluate its effectiveness towards fluoride removal.

4.2 Materials and methods

4.2.1 Materials

Diatomaceous earth was acquired from Eco-Earth Traders, South Africa. High molecular weight chitosan (>700 kDa) was purchased from Sigma-Aldrich, South Africa. All analytical grade chemicals and reagents were purchased from Rochelle chemicals in Johannesburg, South Africa. This includes sodium hydroxide (NaOH), hydrochloric acid (HCl), cerium(III) chloride

heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium fluoride (NaF), and total ionic strength adjustment buffer (TISAB III).

4.2.3 Synthesis of Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films

The Ce/Al/Fe tri-metal oxides- chitosan composite films were prepared following the method developed by Freitas *et al.*, (2021) with slight modification. Briefly, 2.5 g of chitosan was dissolved in 100 mL of 2% acetic acid solution under continuous stirring of 200 rpm at the temperature of 60 °C until viscous chitosan gel was formed. Thereafter, 1 g of Ce/Al/Fe tri-metal oxides modified DE prepared as per section 3.2.2 was slowly added into the chitosan gel and continued to be stirred for 3 h to obtain the homogeneous mixture. The modified DE-Chitosan gel was poured into petri dishes, enough to cover the base of the petri dishes and oven-dried at the temperature of 60 °C for 8 h and the films were formed. 1 M NaOH solution was poured onto the films and covered them for 30 min for the precipitation of metal oxides. The films were then washed with deionized water to wash off excess NaOH and oven-dried for 8 h and 60 °C temperature. The synthesized films were then hand-crushed and stored in corked plastic bottles to prevent moisture. The procedure was repeated several times until the desired amount of the adsorbent was acquired.

4.2.4 Characterisation of the adsorbent

Fourier Transform Infrared (FTIR) (Bruker Alpha Platinum-ATR) was used to determine the functional groups of the Ce/Al/Fe tri-metal oxide modified DE, chitosan and Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films. Surface morphology was determined using SEM (Leo1450 SEM, at 10 kV, working distance 14 mm). The pH_{pzc} was evaluated using the titration method.

4.2.5 Batch experiments

Stock solution containing 1000 mg/L was prepared by dissolving 2.21 g NaF in a 1000 mL volumetric flask using deionized water (18.2 MΩ/cm). Working solution and standards were prepared by appropriate dilutions from the stock solution. Batch experiments were used to determine the optimum operating parameters such as contact time, adsorbent dosage, pH, and the initial fluoride conditions. The contact time was evaluated by varying contact time from 1 to 120

min maintaining the adsorbent dosage and adsorbate concentration of 0.3 g/100 mL and 5 mg/L, respectively. The obtained data was also used for adsorption kinetics studies. The effect of adsorbate concentration and adsorption isotherms were evaluated by varying the initial fluoride concentration 3 to 50 mg/L maintaining adsorbent dosage of 0.3 g/100 mL and contact time of 50 min and solution pH of 7.17. The effect of initial pH was evaluated using the initial F^- concentration of 5 mg/L, adsorbent dosage of 0.3 g/100 mL and contact time of 50 min. The initial solution pH was adjusted from 4 to 10 using 0.1 M NaOH and 0.1 M HCl. The effect of co-existing ions was evaluated by agitating solution of 5 mg/L F^- in the presence of 5 mg/L of NO_3^{2-} , Cl^- , SO_4^{2-} , CO_3^{2-} , Ca^{2+} and Mg^{2+} , respectively. The adsorbent dosage of 0.3 g/100 mL and a contact time of 50 min were used. All the experiments were performed in duplicate and mean values were reported. To calculate the adsorption capacity and fluoride percentage removal, equation 4.1 and 4.2 were used, respectively.

$$Q = \left(\frac{C_i - C_e}{m} \right) \times V \quad (4.1)$$

Where: C_i is the initial fluoride (mg/L), C_e is the fluoride concentration at equilibrium (mg/L), V is volume of the solution (L), and m is the weight of the adsorbent (g)

$$\% \text{ removal} = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \quad (4.2)$$

Where: C_i is the initial fluoride concentration (mg/L), and C_e is the equilibrium fluoride concentration (mg/L).

4.3 Results and discussion

4.3.1 Characterisation

4.3.1.1 Fourier Transform Infra-Red (FTIR) spectroscopy

Figure 4.1 presents the FTIR spectrums of Ce/Al/Fe tri-metal modified DE, chitosan, modified DE/chitosan films and F^- reacted films. In the spectra of chitosan, the absorption band between 3040 and 3550 cm^{-1} , the bands at 2890 cm^{-1} , 1658 cm^{-1} , 1550 cm^{-1} and 1062 cm^{-1} represent the –OH stretching vibration due to absorbed water or alcohols; the bending vibration of –CH in the –CH and –CH₂; vibration of C=O in the acetyl group; vibration of the amine group –NH₂; the

symmetric bending vibration of the -CH in the -CHOH ; the stretching vibration of the -CO band. The spectra of the Ce/Al/Fe tri-metal modified DE shows a noticeably high intensity of the Si-O-Si band. This could be attributed to high content of silica in the composition of DE. The -OH band is observed which could be attributed to absorbed water. There is a notable decrease in intensity and disappearance of bands on the modified DE/chitosan films relative to chitosan, which could be attributed to the covering of chitosan by Ce/Al/Fe tri-metal modified DE. de Freitas *et al.*, (2021), reported similar results after modifying chitosan with activated carbon. F^- reacted films showed a slight increase in the intensity of bands relative to modified DE/chitosan films. This can be attributed to the defluorination process they went through.

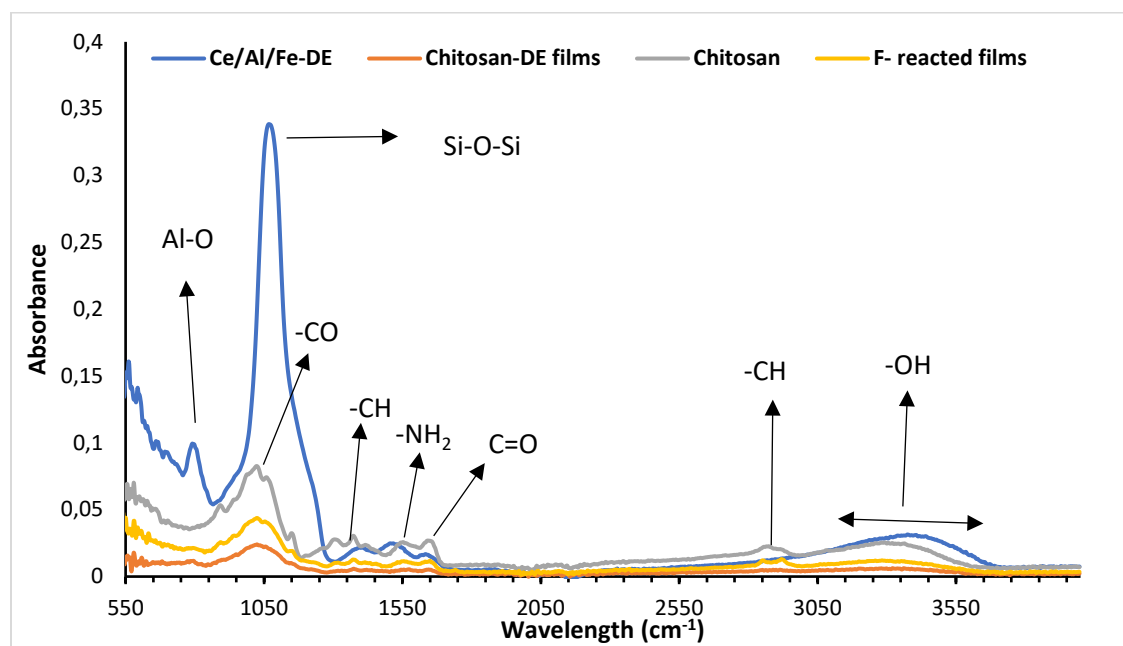


Figure 4.1: FTIR spectrums of Ce/Al/Fe oxide-modified DE, chitosan, chitosan-DE films and F^- reacted films

4.3.1.2 Scanning electron microscopy-energy dispersion X-ray analysis (SEM-EDX)

Figure 4.2 shows the SEM micrographs for surface morphology of (a) raw chitosan, (c) Ce/Al/Fe-modified DE and (e) Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films. The raw chitosan surface morphology is observed to have a smooth layered structure with no pores. Whereas the surface of the Ce/Al/Fe-modified DE has an irregular shape morphology and visible

pores. Finally, the (e) Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films' morphology is relatively smooth due to the presence of chitosan with cubic and porous objects on its surface which could be the Ce/Al/Fe-modified DE. Furthermore, the EDX spectra presented by Figure 4.2 (b), (d) and (f) show the elemental composition of the adsorbents. The EDX spectrum of (c) Ce/Al/Fe-modified DE confirms the successful modification of the DE by Ce:Al:Fe metal oxides. The EDX spectrum of (f) Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films also confirms a successful synthesis with the presence of Ce and Fe. However, the absence of Al is observed. This could be due to the exchange of the Al and Ca^{2+} in the matrix of the adsorbent.

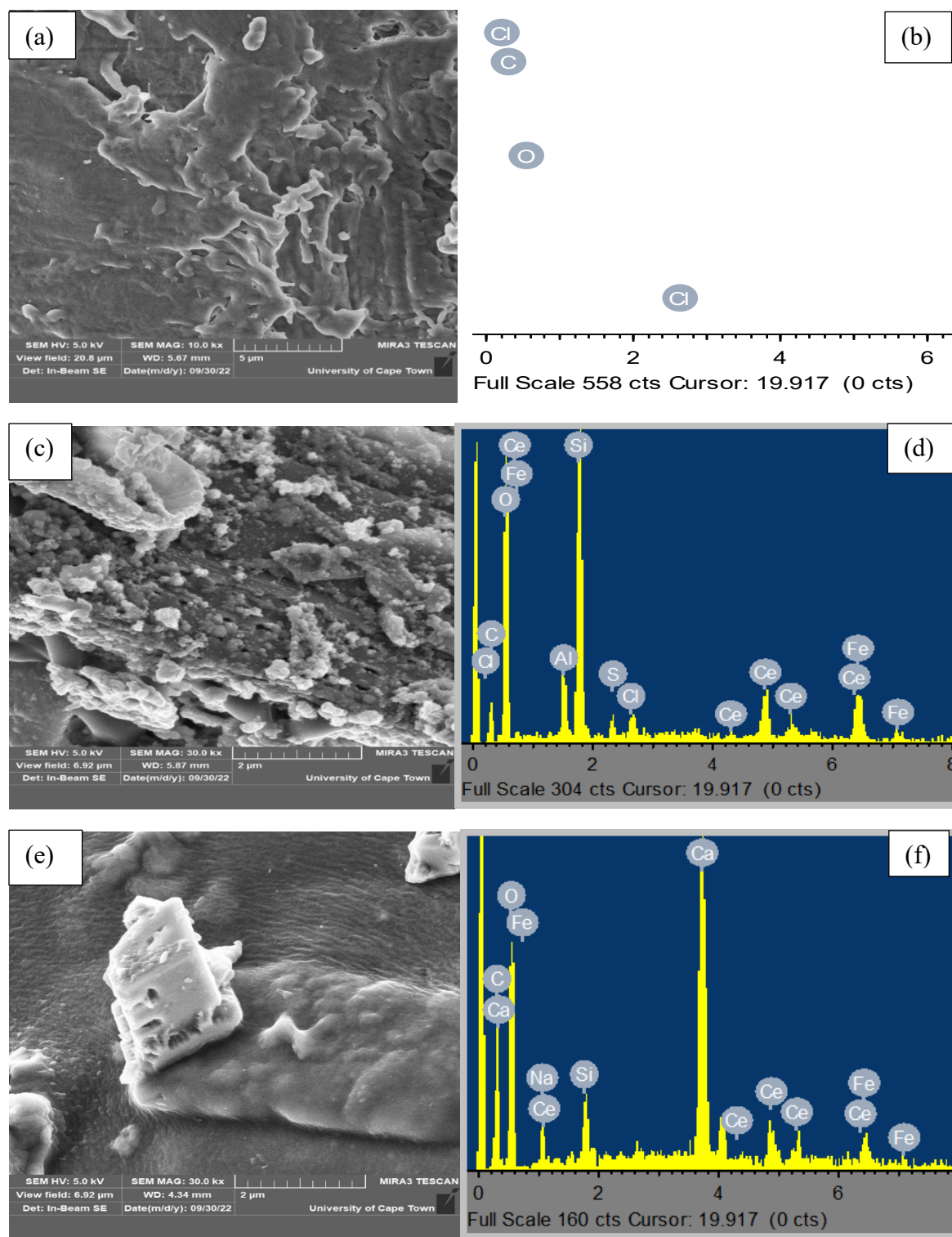


Figure 4.2: Surface morphology of (a) raw chitosan, (c) Ce/Al/Fe-modified DE and (e) Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films; EDX spectra of (b) raw chitosan, (d) Ce/Al/Fe-modified DE and (f) Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films

4.3.2 Batch experiments

4.3.2.1 Effect of contact time and adsorption kinetics.

Figure 4.3 depicts the effect of contact time on the fluoride adsorption percentage. The percentage fluoride removal was observed to be increasing with increasing contact time reaching maximum of 75% after 50 mins. No further increase was observed beyond 60 mins indicating that the system has reached equilibrium. The increase in fluoride adsorption could be attributed to available active sorption sites for F^- ions. Therefore, 50 mins was selected as optimum contact time for further experiments.

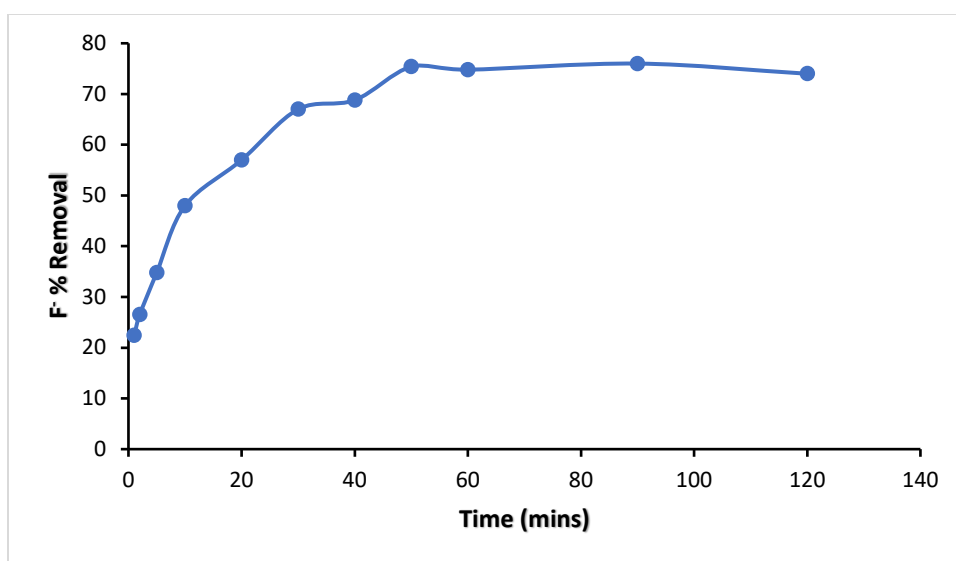


Figure 4.3: Variation of % F^- removal by Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films with contact time (Adsorbent dosage 0.3g/100 ml; C_i 5 mg/L F^- ; pH 7.17; shaking speed 200 rpm).

To determine the adsorption mechanism, reaction pathway and the rate limiting steps of F^- , the pseudo first order, the pseudo second order reaction kinetics and intra-particle diffusion models were used. The Lagergren pseudo-first order represents reversible interactions and physisorption adsorption (Gupta & Bhattacharyya, 2011; Oladoja & Helmreich, 2014). Whereas the pseudo-second order assumes that the rate-limiting step is chemisorption and it is facilitated by the binding of the adsorbate's ions on the adsorbent surface by covalent bonding (Ding *et al.*, 2007). Equations

4.3 and 4.5 represents the linear equation for pseudo first order and pseudo second order, respectively.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_{ad}t}{2.303} \quad (4.3)$$

$$\frac{t}{q_t} = \frac{1}{K_{2ads}q_e^2} + \frac{1}{q_e}t \quad (4.4)$$

Where q_t (mg/g) is the amount of fluoride adsorbed by the adsorbent at time t (min), q_e is the amount of fluoride adsorbed at equilibrium and K_{ad} and K_{2ads} (g.mg⁻¹/min) are the equilibrium rate constant of pseudo-first order and pseudo-second-order adsorption respectively. The value of K_{ad} is calculated from the slope and intercepts of $\log(q_e - q_t)$ versus time t for plots in which straight lines were obtained. K_{2ads} is determined from the slope and intercepts of t/q_t vs t . Figure 4.4 (a) and (b) represent pseudo-first order and pseudo-second order plots, respectively. Table 4.1 shows the calculated parameters for pseudo first order and pseudo second order kinetics models. Based on the correlation co-efficient, the data fitted best to pseudo-second order ($R^2=0.97$) than pseudo first order ($R^2=0.74$). This was further supported by the value of K_{2ads} and q_e that are higher, which are the equilibrium rate constant and the amount of fluoride adsorbed at equilibrium, respectively on pseudo-second order. This suggests that the adsorption was chemisorption.

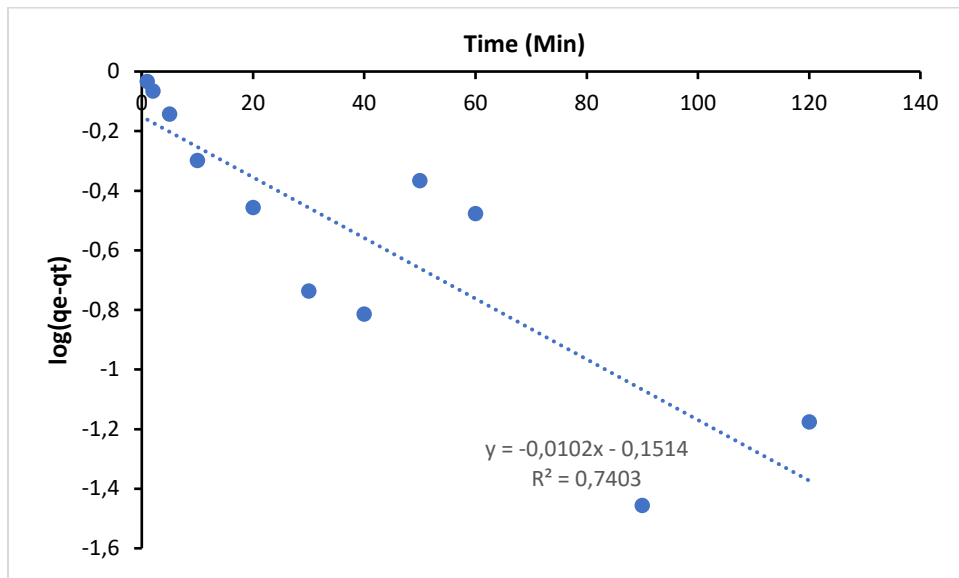


Figure 4.4a: Pseudo-first order model of fluoride adsorption on the Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films.

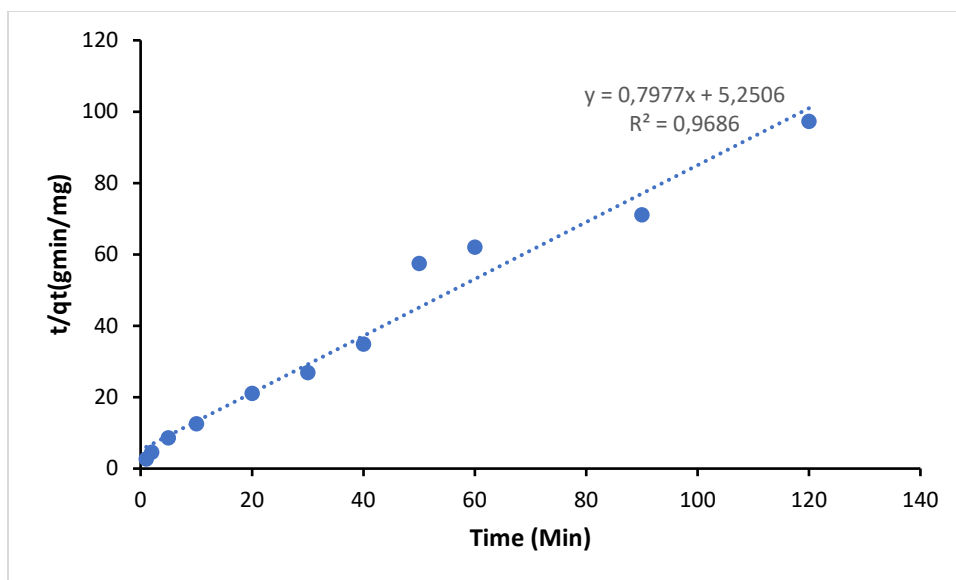


Figure 4.4b: (Pseudo-second order model of fluoride adsorption on the Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films.

Table 4.1: Calculated parameters for pseudo first order and pseudo second order reaction kinetics model

	$q_{e(exp)} \text{ (mg/g)}$	$K_{ad}/K_{2ad} \text{ (g mg}^{-1} \text{ min}^{-1})$	$q_{e(cal)} \text{ (mg/g)}$	R^2
Pseudo first order	1.3	0.02	1	0.74
Pseudo second order	1.3	3.36	1.25	0.97

The Weber-Morris intra-particle diffusion model expressed by equation 4.5 was used to determine the rate of limiting steps for fluoride adsorption using the synthesized adsorbent (Tran *et al.*, 2017).

$$q_t = K_i t^{0.5} + C \quad (4.5)$$

Where q_t is the amount adsorbed (mg/g) at a given time t (mins), K_i (mg/g/mins) is the intra-particle diffusion rate constant determined from the slope of $t^{0.5}$ vs q_t . C (mg/g) is the intercept constant is associated to the thickness of the boundary layer. The higher the C value, the greater the effect on the limiting boundary layer. If the adsorption of a solute is controlled by the intra-particle diffusion process, a plot of $t^{0.5}$ vs q_t should give a straight line passing through the origin. The intra-particle

diffusion plot is presented in Figure 4.5. From the plot, two clear phases can be observed indicating that adsorption of fluoride by Ce/Al/Fe tri-metal modified DE/chitosan films involves two processes. The first phase represents boundary layer adsorption occurring on the surface of the material within the first 10 mins of the reaction followed by intra-particle diffusion into the pores of the adsorbent and subsequent adsorption within the pores in phase two taking place beyond 50 mins. The rate constant for phase 1 and phase 2 were represented by the values of K_{i1} and K_{i2} , respectively as shown in Table 4. K_{i1} is higher than the value of K_{i2} which indicates that adsorption on the boundary layer was faster than the inter-particle diffusion. This indicates that the rate of mass transfer on the first phase was higher than of the second phase of adsorption. Furthermore, the higher C_2 indicates that the boundary layer of the intra-particle diffusion is thicker.

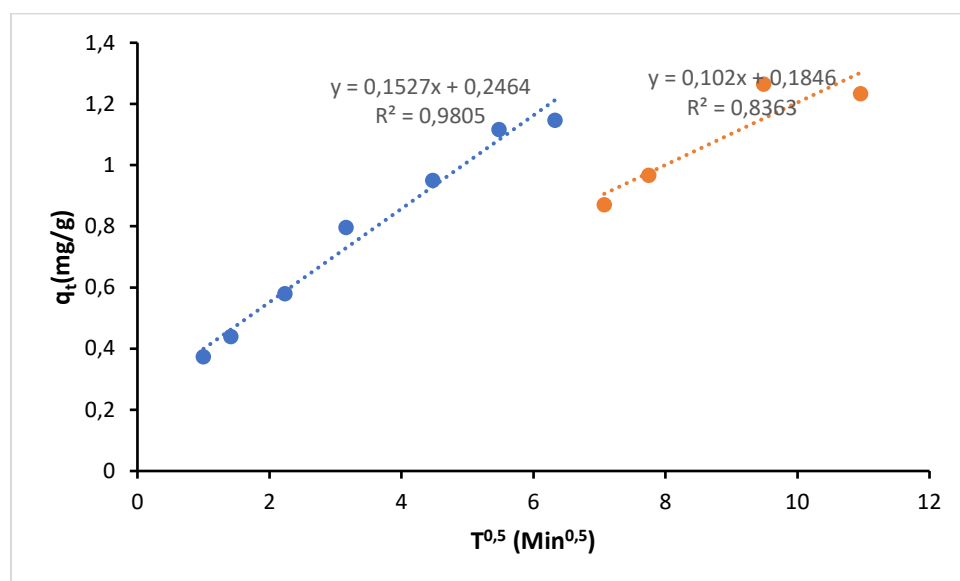


Figure 4.5: Plot for intra-particle diffusion at various concentrations (0.3 g/100 mL, pH 7.17 and shaking speed of 200 rpm).

Table 4.2: Constant values of intra-particle diffusion model.

K_{i1} (mg/g/mins)	C_1 (mg/g)	K_{i2} (mg/g/mins)	C_2 (mg/g)
1.5	0.25	0.1	0.18

3.2.2 Effect of initial concentration and adsorption isotherms

Figure 4.6 shows the variation of equilibrium fluoride concentration against adsorption capacity. A gradual and steady increase of adsorption capacity between initial concentration of 1 mg/L and 19 mg/L is observed. Furthermore, a sharp increase is also observed between 20 mg/L and 25 mg/L initial concentration. The equilibrium is reached. This trend shows that adsorption capacity increases with initial adsorbate concentration. To further illustrate the relationship between adsorbent and adsorbate, the Langmuir and Freundlich adsorption isotherm models were applied. Langmuir isotherm model entails an adsorption process that takes place on a monolayer and homogenous surface (Mtavangu *et al.*, 2022). Meaning that, the adsorption takes place at localized identical and equivalent sites (Al-Ghouti & Da'ana, 2020). Whereas, Freundlich isotherm model describes a reversible, multilayer adsorption system (Mudzielwana *et al.*, 2017). It is characterized by heterogeneous surface whereby the active sites and their energies are distributed exponentially (Al-Ghouti & Da'ana, 2020).

The Langmuir and Freundlich non-linear equations (4.6 and 4.7) were used to model the data. Where, C_e is the equilibrium concentration (mg/L), q_e is the adsorption capacity (mg/L), q_m is theoretical maximum adsorption capacity (mg/g) and b is the Langmuir constant related to enthalpy of adsorption (L/mg). K_f and $1/n$ are empirical constants, indicating the adsorption capacity and adsorption intensity, respectively. When $1/n$ is greater than zero ($0 < 1/n < 1$) the adsorption is favourable, when $1/n$ is greater than 1, the adsorption process is unfavourable, and it is irreversible when $1/n = 1$.

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (4.6)$$

$$q_e = K_f C_e^{1/n} \quad (4.7)$$

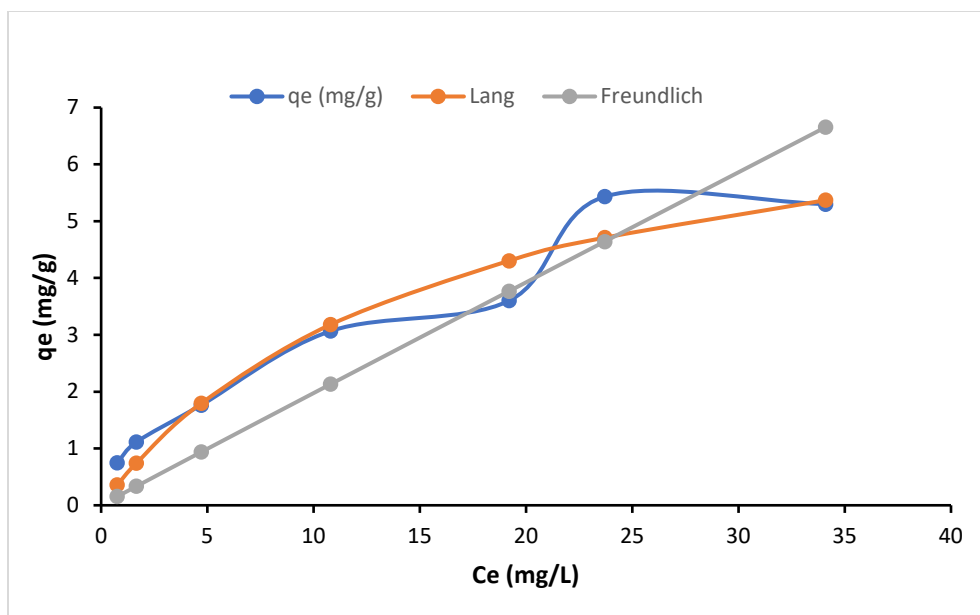


Figure 4.6: Adsorption isotherms plot for F^- adsorption onto Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films (contact time 50 min; adsorbent dosage 0.3 g/100 mL and agitation speed of 200 rpm).

Table 4.3 depicts the constant values of Langmuir and Freundlich adsorption isotherms. Based on the R^2 value, F^- adsorption fitted to Langmuir isotherm model ($R^2=0.94$). This suggests that the adsorption took place on monolayer surface of the Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films. It further suggests that after one F^- ion occupied and adsorption active site, no other ion occupied it (Al-Othman *et al.*, 2012). Furthermore, the Langmuir maximum adsorption capacity ($Q_{\max}$) is significantly higher than the Freundlich adsorption capacity (K_f) which further affirms that the adsorption favoured Langmuir adsorption isotherm. The favourability of the adsorption for Langmuir adsorption isotherm is expressed by R_L which is a dimensionless constant. R_L is expressed by equation 4.8.

$$R_L = \frac{1}{1+bC_0} \quad (4.8)$$

Where R_L is dimensionless constant and C_0 is the initial concentration of F^- (mg/L). When R_L is greater than zero and less than 1 ($0 < R_L < 1$) the adsorption is favourable, when R_L is greater than 1, the adsorption process is unfavourable, and it is irreversible when $R_L = 1$. Figure 7 shows the dimensionless constant plot (R_L). From the plot it is deduced that the adsorption was favourable

since the R_L value lies between 0 and 1. The favourability of the adsorption was also confirmed by the value of $1/n$ which also lies between 0 and 1 depicted on Table 4.2.

Table 4.3: Constant values of Langmuir and Freundlich isotherm models

Langmuir isotherm			Freundlich isotherm		
$Q_{\max}$ (mg/g)	b (L/mg)	R^2	K_f (mg/g)	$1/n$	R^2
7.89	0.06	0.94	0.2	0.99	0.77

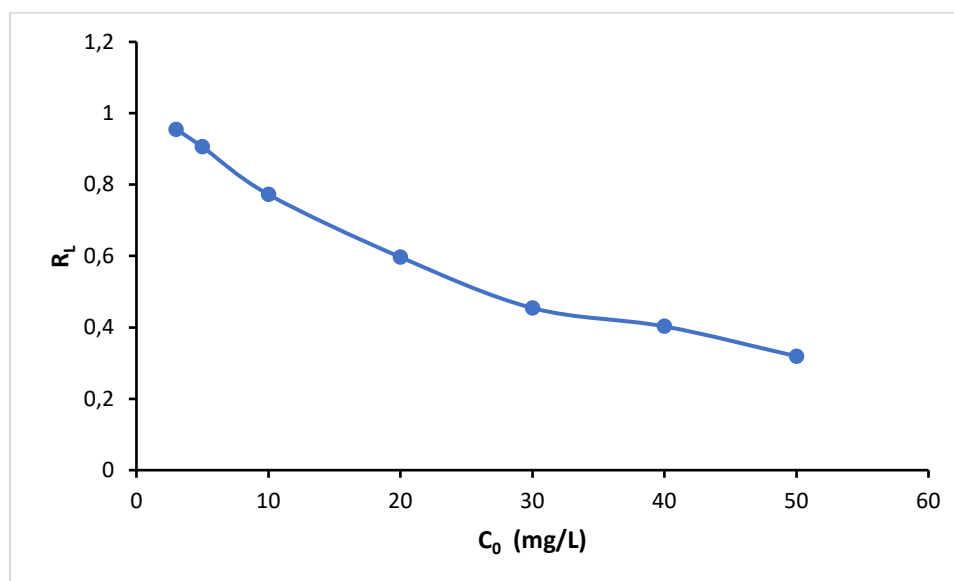
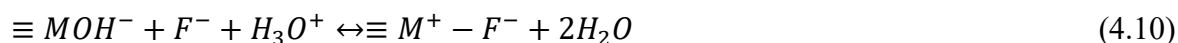
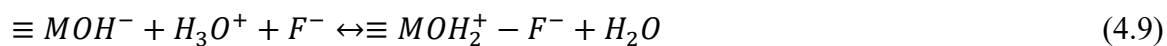


Figure 4.7: Dimensionless constant plot (R_L) for F^- adsorption onto Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films.

4.3.2.3 Effect of pH

Figure 4.8 presents the effect of pH on the adsorption of F^- by Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films. The highest fluoride removal was observed at pH 4 which is $\approx 74\%$ which could be due to the positively charged surface. A dip was observed at pH 6 which had $\approx 54\%$ F^- removal which could be due to the competition between positive and negative F^- ion on the surface of the material. The optimum pH is determined to be pH 7 because there is no significant

difference in F^- removal between pH 4 ($\approx 74\%$) and pH 7 ($\approx 72\%$). This suggests that Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films is suitable for practical defluoridation in the field since it would not require prior pH adjustment. Figure 4.9 depicts the point of zero charge (pH_{pzc}) of the material determined using titration method. The pH_{pzc} was found to be at $pH \approx 9$. At this pH, the surface of the material is neutrally charge. The material is positively charged at pH below pH_{pzc} and negatively charged at pH above pH_{pzc} . Therefore, the mechanism responsible for high adsorption below pH_{pzc} , is the electrostatic interaction between the F^- ions and the positively charged surface of the adsorbent as well as the protonation of the OH^- molecules as shown in equation 4.9 and 4.10. Furthermore, the mechanism responsible for the reduction in the uptake of F^- ions at pH above the pH_{pzc} , is the repulsion between the F^- and the negatively charged surface as shown in equation (4.11) and (4.12). However, the adsorption at pH above the pH_{pzc} is due to the ion-exchange between F^- and OH^- ions.



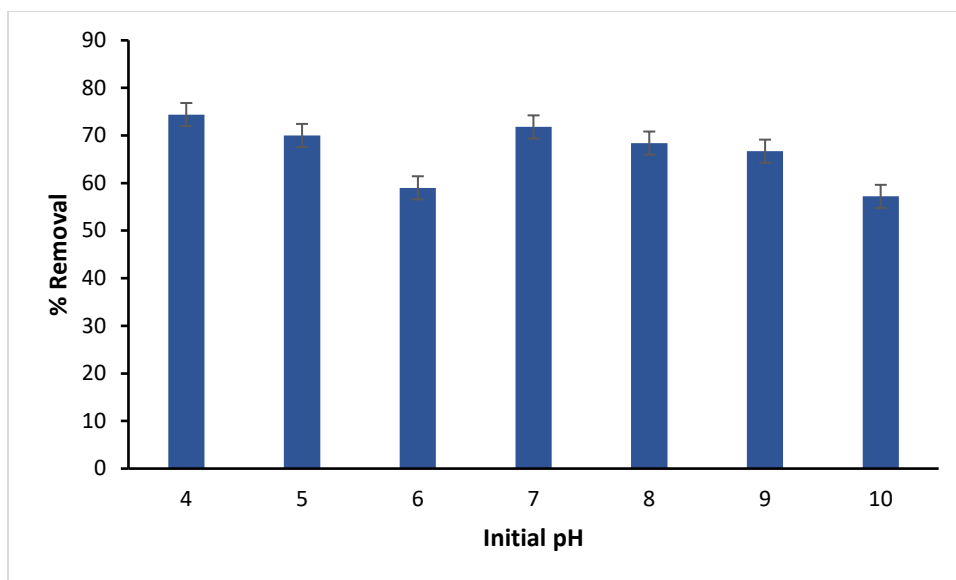


Figure 4.8: Effect of pH on F^- percentage removal (Ci 5 mg/L F^- ; Contact time 50 min⁻¹; dosage 0.3 g/100 mL; shaking speed 200 rpm)

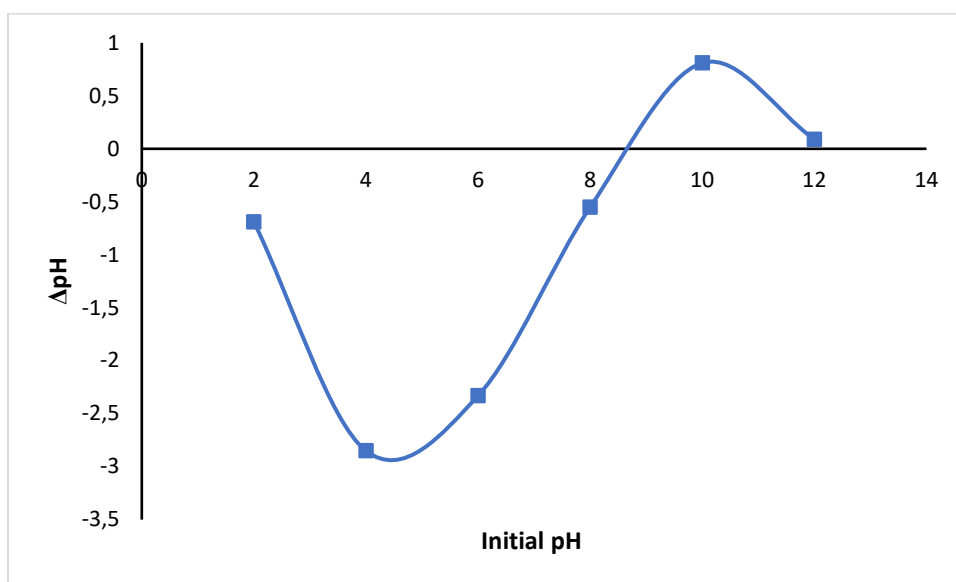


Figure 4.9: Point-of-zero charge of Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films 0.1 M KCl

4.3.2.4 Effect of co-existing ions

Naturally, groundwater contains other ions in addition to F^- which may limit the adsorption process due to the completion of adsorption active sites. To evaluate the effect of co-existing ions,

F⁻ adsorption was performed in the presence of 5 mg/L of Cl⁻, SO₄²⁻, CO₃²⁻, NO₃²⁻, Ca²⁺, and Mg²⁺ as shown in figure 4.10. It was observed that all the co-existing ions had an effect on F⁻ adsorption. However, a severe effect was observed Cl⁻, SO₄²⁻, CO₃²⁻ and NO₃²⁻ due to the notable decrease in F⁻ adsorption. This suggests that, these ions compete with F⁻ ions for the available active sites, which consequently limits the F⁻ uptake. It is also observed that Ca²⁺ and Mg²⁺ had a negligible effect on the inhibition of F⁻ adsorption. This is because the positive charges create more adsorption sites which encourages the adsorption process (Mudzielwana *et al.*, 2019; Budeli *et al.*, 2025).

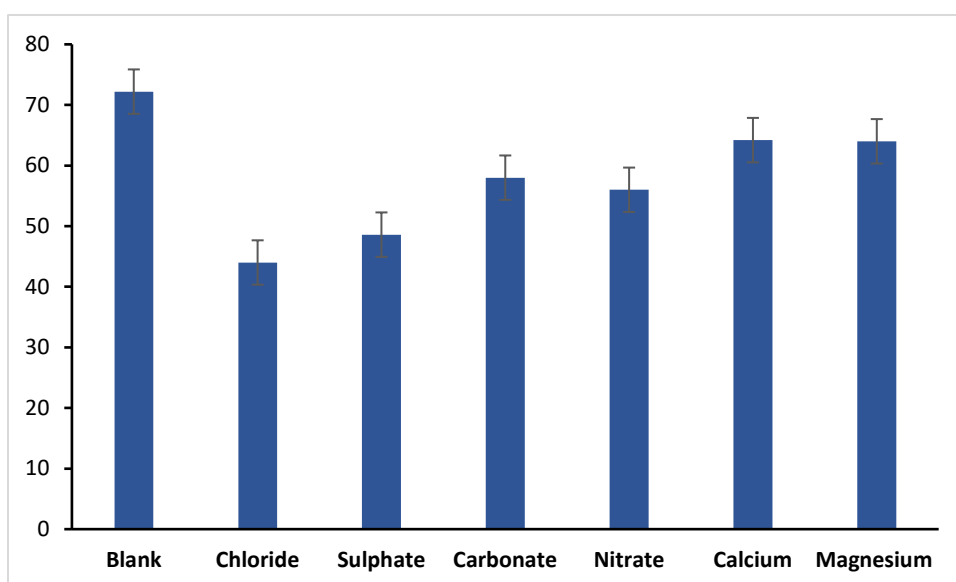


Figure 4.10: The effect of co-existing ions during F⁻ adsorption by Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films (Ci 5 mg/L F⁻; 5 mg/L of co-existing ions; contact time 50 mins; dosage 0.3 g/100 mL; shaking speed 200 rpm)

4.3.2.5 Comparison with other adsorbents

The competitiveness of Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films was evaluated by comparing its adsorption capacity to adsorption capacities reported in literature. Table 4.4 depicts the maximum adsorption capacities of different adsorbents for defluoridation. It can be noted that the developed adsorbent in this chapter is competitive relative to other adsorbents reported in the literature. This implies that the developed adsorbent in this chapter has the potential

to be used for the removal of fluoride in groundwater. It is however observed that Ce/Al/Fe tri-metal oxide modified DE synthesized in the previous chapter had higher adsorption capacity.

Table 4.4: Comparison of maximum adsorption capacities with other adsorbents

Adsorbent	Experimental conditions	Defluoridation capacity	Reference
AgMgOnHaP nanoparticles supported on chitosan matrix	Concentration 10 mg/L, pH 7, adsorbent dosage 2,25 g/50 mL	6.86 mg/g	(Ayinde <i>et al.</i> , 2020)
Mesoporous magnetic malachite nanocomposites	Concentration 10 mg/L, pH 7, adsorbent dosage 0,5 mg/mL	6.57 mg/g	(Sarwar <i>et al.</i> , 2024)
Aluminum based chitosan/zeolite molecular sieve composite	Concentration 10 mg/L, pH 7, adsorbent dosage 2 g/100 mL	2.848 mg/g	(Gao & Liu, 2022)
Ce/Al/Fe tri-metal oxide modified DE	Concentration 5 mg/L, pH 4-10, adsorbent dosage 0.6 g/100 mL	9.8 mg/g	Previous chapter
Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films	Concentration 5 mg/L, pH 4-10, adsorbent dosage 0.3 g/100 mL	7.86 mg/g	Present study

4.4 Summary of the chapter

In this chapter, Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films were successfully synthesized for drinking water defluoridation. The maximum adsorption capacity of 7.89 mg/g was achieved from 5 mg/L, using when adsorbent dosage of 0.6 g/100 mL was used at initial pH range of 4 to 10 after 50 mins agitation time at shaking speed of 200 rpm. The data for adsorption kinetics showed a better fit to pseudo-second order which indicates that the adsorption mechanism was chemisorption. The adsorption isotherm model data best fitted to Langmuir isotherm model which suggests that the adsorption took place on a monolayer surface. The co-existing anions showed a significant effect which indicates a competition of active adsorption sites with F⁻. Whereas the co-existing cations showed no significant effect. The Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films have shown potential for application in the removal of

fluoride from drinking water. Therefore, the application of the developed films in the column set-up is recommended for future studies.

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Chapter 5. Conclusions and recommendations

5.1 Conclusions

The first objective aimed to synthesize and optimize conditions of Ce/Al/Fe tri-metal modified diatomaceous earth for fluoride removal. Ce/Al/Fe tri-metal oxide modified DE was successfully synthesized. The optimum metal oxides ratio was 1:1:1. The adsorbent was further and further evaluated for the removal of F^- from groundwater. The developed adsorbent achieved 9.8 mg/g adsorption capacity at optimum conditions of 5 mg/L initial concentration, dosage of 0.6 g/100 ml, 50 mins optimum time, pH 7.5, and shaking speed of 200 rpm. The presence of co-existing ions increased the percentage of fluoride removal. Regeneration studies showed that the material can be used for up to 8 successive regeneration-reuse cycles using 0.001 M HCl as an adsorbent. Based on the obtained results, it could be concluded that the synthesized adsorbent is suitable for the removal of F^- from groundwater for drinking water.

The second objective aimed to synthesize and optimize conditions of Ce/Al/Fe tri-metal modified diatomaceous earth/chitosan films for fluoride removal. Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films were successfully synthesized and optimized for groundwater defluoridation. The fabricated adsorbent showed maximum adsorption capacity of 7,89 mg/g was achieved from 5 mg/L, when adsorbent dosage of 0.6 g/100 mL was used an initial pH range of 4 to 10 after 50 mins agitation time at shaking speed of 200 rpm. The co-existing anions showed a significant effect which indicates a competition of active adsorption sites with F^- . Whereas the co-existing cations showed no significant effect. The Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films have shown potential for application in the removal of fluoride from groundwater.

The third and final objective aimed to elucidate the adsorption mechanism using adsorption kinetics and isotherm data for both Ce/Al/Fe tri-metal modified diatomaceous earth and Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films. The adsorption kinetics data for Ce/Al/Fe tri-metal modified diatomaceous earth fitted better in pseudo-second order, which implies that the adsorption mechanism is chemisorption. The isotherm data for the same, showed a better fit for the Freundlich adsorption isotherm model, indicating that adsorption occurred on a multilayer surface. Thermodynamic studies showed that the adsorption by Ce/Al/Fe tri-metal modified

diatomaceous earth was spontaneous, endothermic, and random, given by the negative value of the ΔG° change, positive ΔH° value, and a positive ΔS° value, respectively.

On the other hand, the data for adsorption kinetics for Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films showed a better fit to pseudo-second order which indicates that the adsorption mechanism was chemisorption. The adsorption isotherm model data best fitted to Langmuir isotherm model which suggests that the adsorption took place on a monolayer surface.

5.2 Recommendations

Based on the findings, the following recommendations were made:

- The Ce^{3+} in the Ce/Al/Fe tri-metal oxide modified DE adsorbent is reported to have antimicrobial activity, therefore, it is recommended that future studies evaluate the antimicrobial potency of Ce/Al/Fe tri-metal oxide modified DE.
- The Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films showed lower adsorption capacity relative to Ce/Al/Fe tri-metal oxide modified DE. It is therefore recommended that future studies further modify the Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films to enhance it improves its fluoride removal potency.
- For household set-up application, column studies for Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films are recommended for future studies.
- Chitosan is reported to have antimicrobial activity. Therefore, it is recommended that future studies test antimicrobial potency of Ce/Al/Fe tri-metal oxide modified DE/chitosan composite films.