FACULTY OF SCIENCE, ENGINEERING AND AGRICULTURE

DEPARTMENT OF EARTH SCIENCES

DEFLUORIDATION USING MODIFIED MUCILAGE FROM INDIGENOUS PLANT MATERIAL IN VHEMBE DISTRICT, LIMPOPO PROVINCE, SOUTH AFRICA

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A research dissertation submitted to the Department of Earth Sciences in fulfilment of the requirement for a Master in Hydrology and Water Resources at the University of Venda

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DECLARATION

I, Mannzhi Mukhethwa Patience hereby declare that this dissertation - DEFLUORIDATION USING MODIFIED MUCILAGE FROM INDIGENOUS PLANT MATERIAL IN VHEMBE DISTRICT, LIMPOPO PROVINCE, SOUTH AFRICA - submitted to the Department of Earth Sciences for the award of a Master's degree in Hydrology and Water Resources at the University of Venda is my concept in design and implementation. This study has not been previously submitted to this or other institutions. All references cited have been fully acknowledged and are in the list of references.

17/02/2022

Mannzhi M.P **Date**

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ABSTRACT

Access to clean and safe water is one of the Sustainable Development Goals. Unfortunately, it has been reported that groundwater, as another source of water has elevated fluoride levels exceeding the World Health Organisation permissible limit of 1.5 mg/L in some regions around the world. This study aims to apply aluminium (AlDE) and magnesium modified (MgDE) *Dicerocaryum eriocarpum* (DE) leaves mucilage as adsorbents for fluoride sequestration from aqueous solution. AlDE and MgDE are characterized by Fourier transform infrared spectrometer (FTIR), scanning electron microscopy and energy-dispersive X-ray (SEM-EDX), X-ray fluorescence (XRF), X-ray diffraction (XRD), Thermo-gravimetric analysis (TGA), elemental composition and proximate analysis. Batch adsorption studies as the effects of dosage, pH, time, temperature and change in water chemistry were investigated. The modification process introduced alkanes in AlDE and MgDE while other functional groups such as hydroxyl and carboxyl were improved. Enhancement of sorbent surface was observed in AlDE and MgDE SEM graphs when compared to unmodified DE. Functionalization also increased the chemical composition and elemental composition in both sorbents which were confirmed by EDX data. AlDE and MgDE also displayed good thermal stability. The adsorption studies recorded 84.23% removal by applying 0.25 g dosage of AlDE for 2 hours to 100 mL aqueous solution with 10 mgF^-/L at 200 rpm. Change in water chemistry from deionized fluoride water to groundwater recorded an increase of fluoride sorption by the AlDE and MgDE. The increase in temperature led to a decrease in the adsorption capacity when applying both sorbents. Langmuir isotherm best describes the equilibrium sorption based on regression coefficient (R^2) ranging from 0.89 to 0.91 (AlDE) and 0.96 to 0.98 (MgDE). A higher fluoride adsorption capacity was recorded at 69.65 mg/g using AlDE and 41.84 mg/g using MgDE. Kinetics studies favoured pseudo-second-order model based on 0.98 - 0.99 regression coefficient (R^2) from linear plots of AlDE and MgDE. The sorption process was feasible and exothermic. The adsorbents can be best regenerated using deionized water as a desorbing agent.

Keywords: Fluoride concentration, DE modification, *Dicerocaryum eriocarpum*, deflouridation, adsorption capacity

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LIST OF ABBREVIATIONS

AlDE	Aluminium modified *Dicerocaryum eriocarpum*
CDTA	Cyclohexylene diamine tetraacetic
CHNS	Carbon hydrogen nitrogen sulphur
Cps	Counts per second
DE	*Dicerocaryum eriocarpum*
DTG	Derivative thermo-gravimetric
DSC	Differential scanning calorimetry
DW	Deionised water
FT-IR	Fourier Transform Infrared spectrometer
HCl	Hydrochloric acid
ISE	Ion-selective electrode
IPM	Indigenous plant mucilage
MgDE	Magnesium modified *Dicerocaryum eriocarpum*
NaOH	Sodium hydroxide
NH_4^+	Ammonium
NO_3^-	Nitrate
Pty (Ltd)	Propriety limited
RDE	Raw *Dicerocaryum eriocarpum*
RSA	Republic of South Africa
SEM-EDX	Scanning Electron Microscope- Energy Dispersive X-ray spectroscopy
TG	Thermal degradation
TGA	Thermo-gravimetric analysis
TISAB	Total Ion Strength Adjuster Buffer
UK	United Kingdom
UNICEF	United Nations Children's Fund
USA	United States of America
WHO	World Health Organisation
XRF	X-ray Fluorescence
XRD	X-ray Diffractometer

LIST OF PUBLICATION

1. Mannzhi and Edokpayi (2022). Fluoride sorption using Al and Mg modified *Dicerocaryum eriocarpum* leaves mucilage (**In Draft to be submitted to Journal of Environmental Management).**

CHAPTER 1: INTRODUCTION

1.1. BACKGROUND

Portable water is a limited resource worldwide and one of the basic needs for every human being which is one of the main global issue mentioned in the Sustainable Development Goals (Kooy et al., 2018). Due to the limited supply of this resource, millions of people have insufficient water for their day-to-day use and what is available is mostly not of a good quality (Jadhav et al., 2015). As a result of increasing awareness of surface water contamination, exploiting of groundwater has been observed as a major and quick alternative source of water (Alhassan et al., 2020).

In some communities, the groundwater which they rely on is contaminated and quality analysis of such water must be conducted often to apply relevant water treatment methods (Arslan & Akün, 2019). In Ghana, it has been reported that groundwater is mostly consumed without any form of treatment exposing people to health risks (Ganyaglo et al., 2019). In countries such as China, groundwater which is mostly polluted, is often used for domestic, industrial and agricultural purposes (Jia et al., 2019).

Fluoride is one of the pollutants that have been reported to be present in groundwater in many remote areas (Barathi et al., 2019). Excess fluoride in the human body has impacts relative to the amount and period of exposure to the element (Adimalla et al., 2019). WHO approved a range of 0.5 to 1 mg/L or a maximum of 1.5 mg/L of fluoride in drinking water for bones and teeth improvement (WHO, 2011; Zhang & Huang, 2019a). When fluoride enters the human body, it is absorbed in food nutrients uptake after digestion into the blood; this then ends up being stored in the high calcium parts of the body, such as bones and teeth (Yadav et al., 2018).

Throughout the years, reports on fluoride determination in groundwater have been conducted to inform the public, as the effects of such water may be unknown (Ganyaglo et al., 2019). Methods of deflouridation have been developed and many are applied daily to supply potable water to people. From the current established and operating deflouridation methods, scientists and researchers have observed some benefits and limitations (Singh et al., 2016). The use of indigenous plants as an adsorbent of fluoride in water has not widely experimented with, hence, usually not applied nor recommended. In the current study, the ability of aluminium and magnesium modified *Dicerocaryum eriocarpum* (DE) leaves was exploited for the

adsorption of fluoride in water. The findings will be useful for water treatment authorities, researchers and households with low income.

1.2. PROBLEM STATEMENT

Water is a basic need for every human globally but with the rapid increase in population, water has become a limited resource (Rasool et al., 2018). Both in the rural and urban areas the problem of potable water scarcity seems to be growing, however, with no solution in sight. The increase of human population and climate change have had an impact on natural resources, such as water sources (Odiyo & Makungo, 2018). The use of surface water in its raw form is minimal due to its exposure to direct pollution that is toxic to human health (Jadhav et al., 2015). These toxic water pollutants occur naturally while majority are also introduced via human activities.

Fluoride in water has been reported to be higher than the recommended limit in many parts of the world (Vaddi et al., 2021). Worldwide, there are more than 200 million patients suffering from health conditions linked to the consumption of water with high fluoride concentration (Tiwari et al., 2017). Most of the affected countries, therefore, depend on groundwater as a source of their water supply for daily use. In most remote areas, people have no other alternative but to use groundwater without quality tests being performed or treatment (Fito et al., 2019).

Some parts of the world, such as India and China are marked as fluoride-hazard areas due to extreme fluoride concentration in their groundwater; this has resulted in majority of the population suffering from fluorosis (Ali et al., 2016; Sahu et al., 2020). A high concentration of fluoride in water has been reported in the largest state in India, Rajasthan, recorded F^- above 1.5 mg/L - the maximum limit recommended by WHO (Amarasooriya & Kawakami, 2019). Majority of the rural population in India depends on groundwater for their daily living (Nanjundan & Ramalingam, 2018); this situation has led to more than 62 million people, including infants, teenagers and adults, being diagnosed with effects of high fluoride concentration in their bodies (Collivignarelli et al., 2020).

In Africa, the problem of diseases, such as dental fluorosis caused by intake of fluoride-rich water was reported at the Bongo District in Ghana where fluoride concentrations above 4 mg/L in groundwater were recorded (Annan et al., 2021). Boreholes in Tororo District in Uganda recorded a range of 0.4 to 3 mg/L of fluoride in the hills of Sukulu (Egor & Birungi, 2020). In southern Africa, a range of 5 to 10 mg/L of fluoride has been reported in Zimbabwe

(Murambasvina & Mahamadi, 2020). These reports raise a concern about the quality of groundwater in Africa.

The Republic of South Africa (RSA) is one of the countries that has reported fluorosis as an effect of excess fluoride in drinking water (Tan et al., 2020). A study by Masindi and Foteinis (2021) reported fluoride levels up to 8.6 mg/L in boreholes used for domestic purposes in Northwest Province, RSA, while in Limpopo Province Durowoju et al. (2018) reported 7.28 mg/L of fluoride in Tshipise. The geological factor of Limpopo Province has been found to contribute high fluoride amounts in groundwater in Siloam village (Vhembe District) up to 6.74 mgF^-/L, causing tooth decay and skeletal damage (Odiyo & Makungo, 2018). A study by Onipe et al. (2021) also confirmed excess fluoride in groundwater in Vhembe District. This is a clear indication that the treatment of fluoride water in the region is needed.

1.3. MOTIVATION

Domestic water consumed by most people in remote areas of developing countries is untreated groundwater from boreholes. Water from boreholes is likely to have pathogens and harmful metals or non-metals which pose health risks to the people.

The northern, eastern and western parts of the Republic of South Africa, mainly the rural locations, have been reported to be fluoride-hazard areas; due to this and with most of the population in Limpopo residing in rural areas and relying on groundwater, the issue of fluoride in such water is a concern (Malago et al., 2017). The process of deflouridation has been a challenge to most developing countries, especially in rural areas. With fluorosis threats that humans face due to the increasing medical cases reported after consuming fluoride-rich water. The reduction of fluoride in water is essential for the improvement of health of people located in fluoride-rich water areas.

The application of modified DE leaves for fluoride removal will add to the methods of natural materials (bio-sorbent) used for the deflouridation process. The use of DE as an adsorbent of fluoride has advantages - it is readily available in the environment, has no cultural or religious restrictions, is edible and livestock farmers use it (Bishayee et al., 2020). In addition, the use of DE has been reported to be effective in removing lead (II) ions in aqueous solutions (Edokpayi et al., 2015), therefore, there is a probability for its usage for fluoride adsorption since preliminary work has shown the potential of fluoride sorption by DE deflouridation.

1.4. OBJECTIVES

1.4.1. Main objective

The main objective of this study was to evaluate the potential of 0.1 M Al modified DE (AlDE) and 0.1 M Mg modified DE (MgDE) for fluoride removal in water.

1.4.2. Specific objectives

1. Modification of mucilage from Dicerocaryum eriocarpum using aluminium and magnesium and characterization of the modified DE.
2. To investigate fluoride sorption removal efficiency.
3. To investigate the kinetics, equilibrium and thermodynamics of the sorption process.

1.5. RESEARCH QUESTIONS

1. How did modification with AlDE and MgDE affected the functional groups, morphology, chemical composition, surface crystallinity, mass weight loss, elemental composition and proximate of *Dicerocaryum eriocarpum*?
2. How can utilizing modified *Dicerocaryum eriocarpum* for deflouridation process have an impact on fluoride sorption efficiency?
3. How can kinetic, equilibrium and thermodynamics models best describe the sorption process of modified *Dicerocaryum eriocarpum*?

1.6. STUDY AREA

Vhembe District is situated in the northern part of Limpopo, South Africa (Figure 1.1) and covers a surface area of 21 407 km^2. The District shares a border with Zimbabwe through Beitbridge at Musina and is divided into four municipalities - Makhado, Thulamela, Musina and Collins Chabane (Onipe et al., 2021) with an estimated population of 537.454 (Edokpayi et al., 2018). Vhembe District is rich with various indigenous plants which are beneficial to people. The DE used in this study is a prostrate perennial herb with sharp stud, commonly seen as a free-growing plant in the grasslands fields of the District. Traditionally, the leaves of this plant have been used - as a vegetable side-dish called *delele* by the Vhavenḓa tribe; as bath soap and wound treatment (Muyambo et al., 2019); as lubricate during infant and livestock birth (Tshikalange et al., 2016); for teeth development in toddlers (Constant & Tshisikhawe, 2018); to treat blood diseases in cattle (Chakale et al., 2021) and hair shampoo

(Kunatsa & Katerere, 2021). Scientifically, DE has been utilized as a sorbent for cadmium (II) (Jones et al., 2016) and lead (II) (Edokpayi et al., 2015).

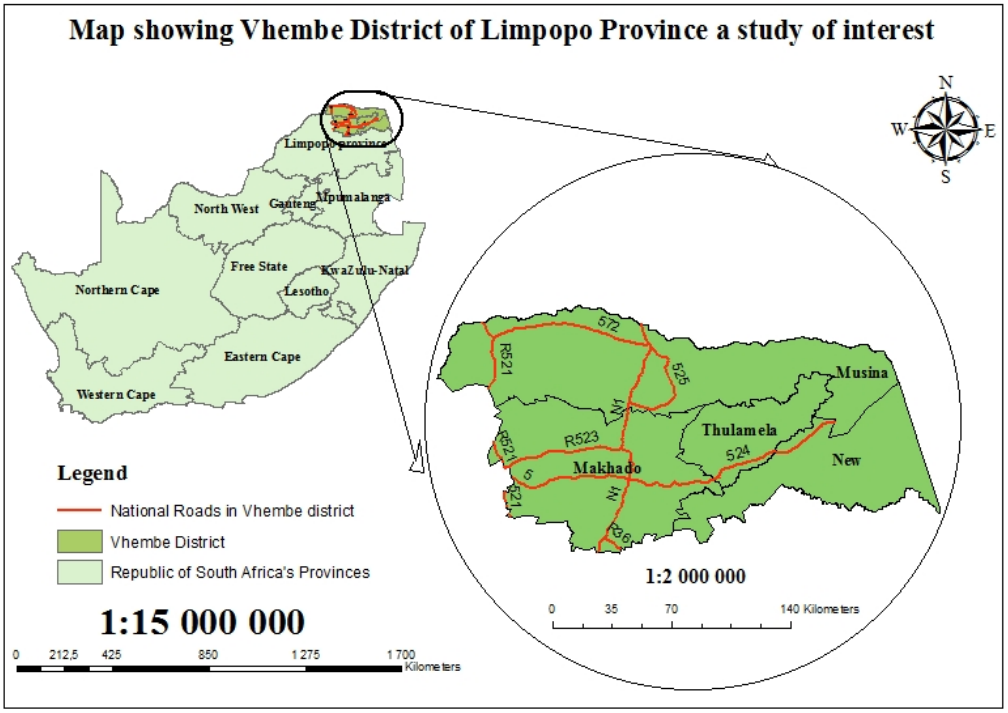

Figure 1.1. Map of the study area (Drawn using Arc GIS software)

CHAPTER 2: LITERATURE REVIEW

2.1. WATER SUPPLY

Water is a basic need for the life of every living organism on earth (Yousefi et al., 2019). Adequate and safe potable water should be supplied to populations worldwide, however, there are billions of people in need of clean and safe water (Corral-Capulin et al., 2019). The delivery of potable water to people has been a major challenge for many years, hence, is on the list of Sustainable Development Goal initiated by Unites Nations to be achieved in many parts of the world (Barathi et al., 2019). The increase of population and industrial activities require great quantity and quality of this limited natural resource which result in competition for and unfair distribution of water (Mukherjee & Singh, 2018).

Developing and developed countries with arid and semi-arid climate are the most challenged when it comes to water supply, due to high temperatures and low recharge of groundwater (Onipe et al., 2020). Most rural areas in developing countries are disadvantaged when it comes to adequate water supply and they rely both on surface water resources (rivers, springs, canals, reservoirs and streams) and groundwater sources (Choubisa, 2018). Most surface water sources are now regarded as unacceptable for human consumption due to high level of pollution caused by human activities (Alhassan et al., 2020); for example, the citizens of Cape Town in South Africa experienced surface-water drought threat (Foster et al., 2018). In places around the globe, most of the water supplied for household purposes does not comply with the World Health Organization (WHO) drinking-water standards since it is not treated from the source; this results in various human health ill-effects (Gitis & Hankins, 2018). In most parts of the world, the supply of water is inadequate when compared to the demand; this is due to the rapid increase of the population and lack of maintenance of water infrastructure (Masindi & Foteinis, 2021).

2.2. GROUNDWATER SUPPLY

Groundwater is water that is located under surface in a deep or shallow aquifer (Argade & Narayanan, 2019). For ages, groundwater has been the major solution when surface water quality and quantity is unreliable (Grönwall & Danert, 2020). Due to the shortage of water supply in many areas by the government by the pipeline system, millions of private and public boreholes are providing water to different end-users worldwide. The extraction of groundwater has escalated due to the rapid increase in population and the daily water required per day per

person as well as climate change (Foster et al., 2020). Regions with high water table access groundwater through hand-dug wells and hand pump wells (Addison et al., 2020).

The water needs of domestic, agricultural and industrial activities in most developing countries around the world are often met via augmentation with groundwater. Like most countries, India depend largely on groundwater for domestic and drinking purposes, however, this water source has been questioned for its water quality, recently (Maurya, 2017). Similarly, in Africa there are millions of people relying on groundwater for their daily needs (Elumalai et al., 2019).

2.3. CONTAMINATION OF GROUNDWATER

Groundwater seems to be clean due to its low turbidity, however, physicochemical parameters and microbiological tests need to be conducted for scientific confirmation of whether it is of the consumption standard recommended by WHO. The world is facing challenges of accessing potable water and groundwater data is limited in most parts of the world where they depend on groundwater (Burri et al., 2019). Common groundwater contaminants reported are magnesium, nitrate, iron, fluoride, sodium, mercury, calcium, pesticides, pharmaceutical products, phosphate and arsenic (Anim-Gyampo et al., 2019). Overuse of soil fertilizers in agriculture, saline intrusion, fuel linkage, mining, industrial and residential effluents as well as underground minerals has greatly contributed to groundwater contamination (Baghdadi et al., 2019). For instance, China has reported that its groundwater is mostly contaminated by anthropologic activities (Han et al., 2016).

In rural communities, inspection and land survey before drilling a borehole are not routinely conducted and most boreholes are drilled close to pit latrine toilets (Grönwall & Danert, 2020). This increases faecal contamination of groundwater with unconfined aquifers being most vulnerable to accumulating such pollutants than confined aquifers (Chuah et al., 2016). Many water-related diseases are linked to groundwater consumption without treatment and this affects mostly those of low socio-economic status (Onipe et al., 2020).

Unfortunately, water from most private-owned boreholes, in residential areas are contaminated or contains excess minerals exceeding the permissible limits of various countries (Ganyaglo et al., 2019). Many municipalities, in most developing countries supply groundwater that is contaminated to users for drinking and other domestic purposes (Healy et al., 2017). Water quality analysis of groundwater, therefore, must be performed regularly to prevent the use of contaminated water which results in acute and chronic health effects (Ndé-Tchoupé et al., 2015). In addition, the increase in groundwater contamination has resulted in

governments and private owners incurring some financial losses, since the drilled boreholes are no longer in use, due to contamination (Kimambo et al., 2019).

2.4. FLUORIDE ION

The earth's crust is known to contain fluorine in abundance, naturally as gas at room temperature with the atomic number of nine, atomic mass 18.998 g/mol and light halogen in the periodic table of elements (Narsimha & Sudarshan, 2017). Fluorine is recorded as number 13 of the abundant minerals on the earth's crust weighing 300 mg/kg (Bishayee et al., 2020; Yousefi et al., 2019). In nature, the fluorine atom does not exist in a free and unmixed state (Strunecka & Strunecky, 2020) as fluorine anion is converted into fluoride element when it attracts positively-charged elements such as metals, non-metals and hydrogen due to its high electronegativity (Barathi et al., 2019). Fluoride is the most reactive element (Malago et al., 2017) and analysis have confirmed that fluoride can dissolve, react in acidic pH while it stabilizes in basic pH (Suneetha et al., 2015). Researchers found that besides its presence in food, air, water and manufactured products, fluoride is also rich underground in rocks (Addison et al., 2020; Bakar et al., 2019; Yadav et al., 2019). In the environment, fluoride is known to be inorganic pollutant, although, it is also known to be essential micronutrient in human beings depending on the quantity consumed (Corral-Capulin et al., 2019). In humans and animals, fluoride is attracted by calcium in the bones and teeth (Keshavarz et al., 2015).

2.5. SOURCES OF FLUORIDE

2.5.1. Natural sources

Naturally, fluoride is found in sedimentary phosphate rocks and minerals (Malago et al., 2017). When fluorspar, sellaite, cryolite, fluorapatite and mica minerals underground dissolve, leach or precipitate, they catalyse the solubility of fluoride rock into the aquifer (Wan et al., 2021). The presence of calcium and bicarbonate ion promote the availability of fluoride (Kaur et al., 2017). The science of these natural sources is known to be complicated when compared to anthropogenic sources (Li et al., 2015). Volcanic, sedimentary, igneous and metamorphic rocks contain high concentrated fluoride which finds its way to the environment during a volcanic eruption, weathering and marine aerosols (Haji et al., 2018; Kanduti et al., 2016; Mukherjee & Singh, 2018). Table 2.1 shows different types of rocks with various range of fluoride concentration (Onipe et al., 2020).

Natural resources such as water, soil and air also contain fluoride element (Bharti et al., 2017). Water sources that contain high fluoride concentrations are freshwater, groundwater, saltwater and rainwater (Keshavarz et al., 2015). Water consumption is the major source of fluoride in humans (Kimambo et al., 2019), although, the consumption of vegetables, crops

and fruits irrigated with fluoride-rich water also play a role in the accumulation of fluoride in humans (Bhattacharya & Samal, 2018). Fish from high fluoride concentrated water bodies are also likely to accumulate fluoride in their fillets through gills (Mannzhi et al., 2021). In many case studies and reports, natural sources of fluoride are mostly related to endemic fluorosis which is classified under dreadful diseases (Ali et al., 2016; Choubisa, 2018).

Table 2.1. Fluoride concentration in various rock types (Onipe et al., 2020).

Rock	Fluoride concentration (mg/L)
1. Ultramafic igneous and volcanic rocks	~100
2. Alkaline igneous rocks	>1000
3. Sedimentary rocks - Limestone - Shales	 >200 <1000
4. Metamorphic rocks - Regional metamorphism - Contact metamorphism	 100 5000

2.5.2. Anthropogenic sources

Fluoride can enter the body through cosmetics, dental products, pharmaceutical drugs (Tiwari et al., 2017), and inhaling smoke from charcoal combustion (Zhang & Huang, 2019a). Industries that manufacture aluminium, bricks, melt iron, copper and nickel (Rasool et al., 2018), electroplating, glasses, burn coal, phosphate fertilizers, steel wastes (Gandhi & Sirisha, 2019), refrigerators and pesticides discharge wastewater with excess fluoride, which is mainly directed to the surface water bodies (Yadav et al., 2018). Some of this fluoride-rich effluent infiltrate into the soil making its way to groundwater (Unde et al., 2018). A study by Colombani et al., (2018) highlighted that preparation and production of food, for instance, tea and alcohol, with water rich in fluoride contributes a significant percentage of fluoride to consumers of those products.

2.6. DISTRIBUTION OF FLUORIDE

2.6.1. Global picture of fluoride occurrence and distribution

Fluoride contamination is a global problem that affects people every day. Countries around the world with excess concentration of fluoride in water are displayed in Figure 2.1. Geological reports show that there is a fluoride belt discovered that connects Jordan, Egypt, Libya, Algeria, Sudan, and Kenya to Syria; another belt connects Turkey via Iraq, Iran, Afghanistan,

India, northern Thailand, and China (Khairnar et al., 2015); some belts have been discovered in America and Republic of South Africa (O'Mullane et al., 2016).

Sweden and Moldova also reported having high concentration of fluoride in their water due to natural abundance of this element in these countries (Omarova et al., 2017). Globally, India and China have been identified as the most fluoride-polluted countries and this has been confirmed by the high rate of fluorosis cases reported in these countries (Narsimha & Sudarshan, 2017).

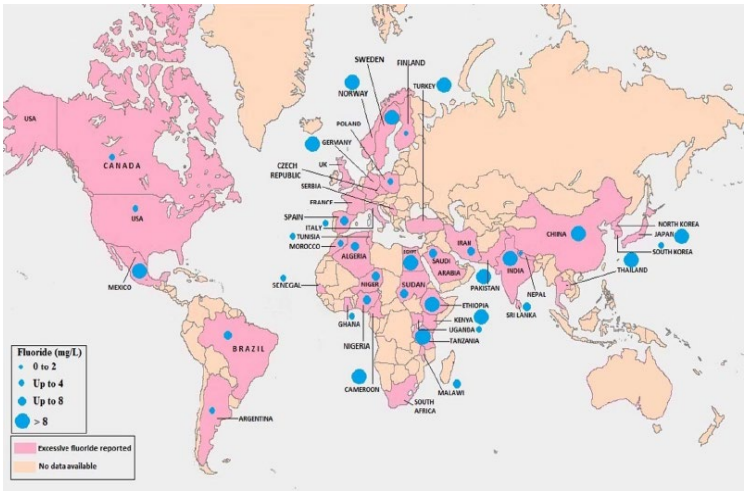

Figure 2.1.Countries with various fluoride concentrations (Yadav et al., 2018).

India is one of the countries that rely on groundwater, however, most of the districts have been contaminated with fluoride due to granite and other fluoride-related rocks (Adimalla et al., 2019). In India, more than 65 million patients were reported to be suffering from fluorosis due to excess fluoride intake (Sreekanth et al., 2018). A report by UNICEF declared that India has many districts which are regarded with endemic levels of fluoride, therefore, many fluorosis and fluoride-linked health implications are expected due to this high distribution and consumption (Kaur et al., 2017). The study by Mukherjee et al. (2019) confirmed that many assessments and reports have been published about fluoride in India.

2.6.2. Fluoride occurrence and distribution in Africa

In the African continent, there are two fluoride belts reported, the East African Rift Valley and Ethiopian Rift Valley (Kimambo et al., 2019), but the highest concentration has been reported from the East African Rift belt which connects Malawi and Eritrea (Karmakar et al., 2016). Even though Africa is a tropical continent, some countries record high fluoride concentrations (Waghmare & Arfin, 2015). Figure 2.2 displays groundwater fluoride concentration across African countries. Countries such as Mauritania, Libya, Niger, Sudan, Ethiopia, Kenya,

Tanzania and South Africa have recorded the highest occurrence of fluoride (Kut et al., 2016; Malago et al., 2017). Countries that have published concentration of fluoride above WHO standard in their groundwater in Africa includes Malawi (7.0 mg/L) and Uganda (3 mg/L) (Addison et al., 2020; Egor & Birungi, 2020) although, most African regions report fluoride distribution that is in the endemic phase (Onipe et al., 2020).

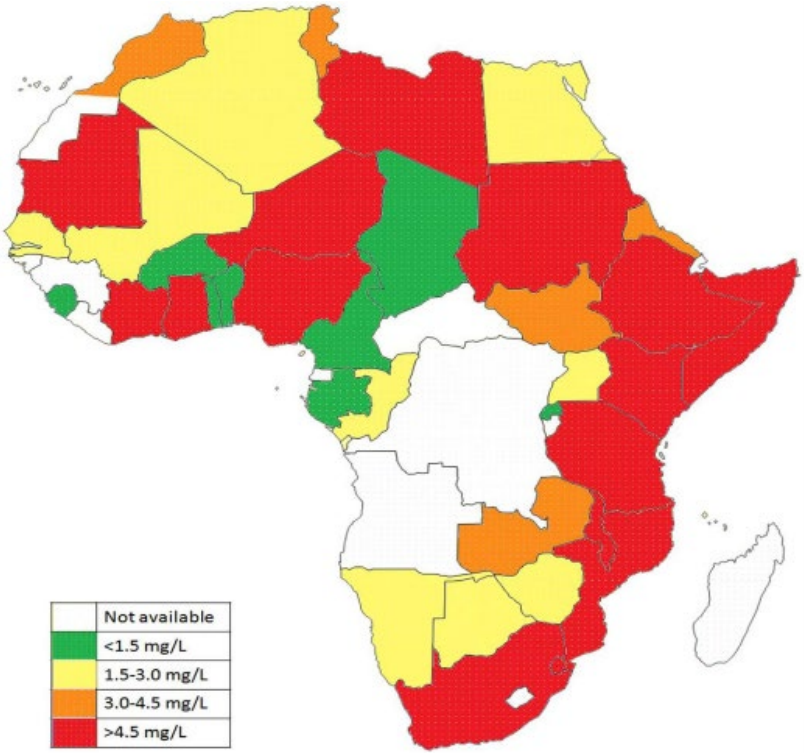

Figure 2.2. Fluoride levels across the African continent (Kut et al., 2016).

Western Cape, Kwa-Zulu Natal and Northwest have been found to have higher fluoride concentrations in groundwater than the permissible limit; this is linked to sedimentary and igneous rocks located in these areas (Figure 2.3). Fluoride levels of less than 1.5 mg/L have been reported in several regions across Limpopo Province, however, other areas such as Siloam and Tshipise have recorded high levels of fluoride in groundwater and thermal springs (Elumalai et al., 2019). According to a preliminary study at Siloam and Tshipise which are located in Soutpansberg region, the geothermal springs recorded 5.97 – 7.28 mgF^-/L which is associated with mica and clay minerals particularly montmorillonite, kaolinite, muscovite and chlorite have been found in the sedimentary terrain in the area (Durowoju et al., 2018; Onipe et al., 2021).

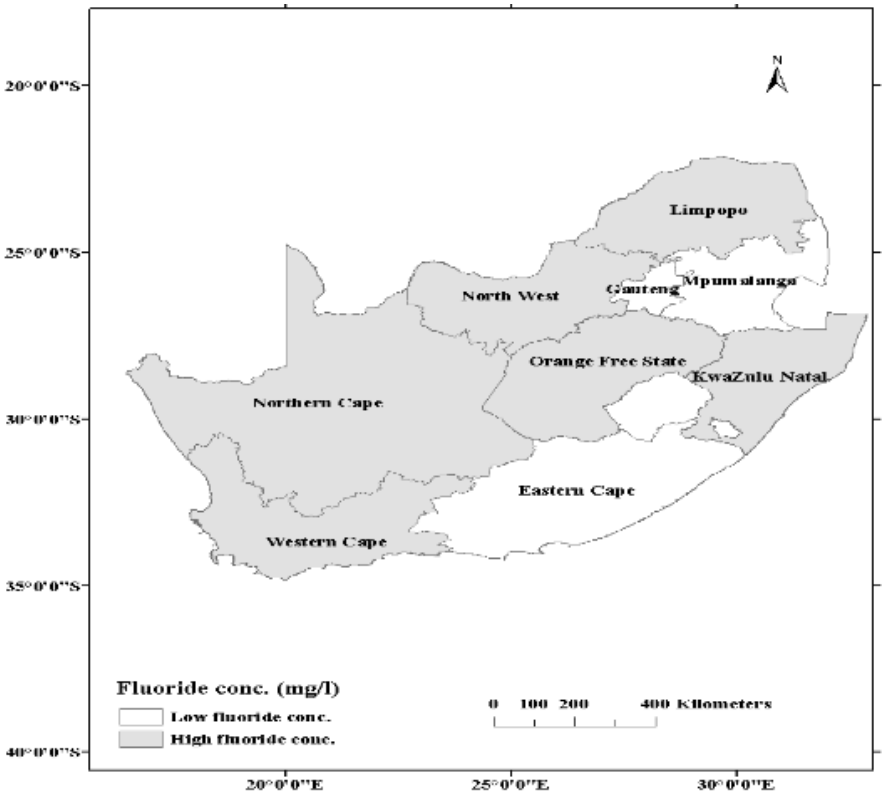

Figure 2.3. Fluoride distribution map in South Africa (Malago et al., 2017).

2.7. FLUORIDE IN WATER SOURCES

2.7.1. Groundwater fluoride

Groundwater is mostly used as a source of drinking water in most parts of the world, both in rural and urban communities. It is mostly regarded as safe for human consumption and pre-treatment is not needed (Yousefi et al., 2019). Deep extraction of groundwater is a solution to water scarcity in most parts of the globe. With the over-extraction of groundwater, population increase and environmental changes, some challenges have arisen with regard to water quality and its effect on human wellbeing. Unfortunately, there are pollutants, such as fluoride that are found in groundwater causing health implications (Sandoval et al., 2019). The source of fluoride in groundwater is bedrock mineralogy and the presence of igneous rock (Dehbandi et al., 2018), however, human activities and geochemical factors have been shown to have an impact in increasing fluoride concentration in groundwater (Li et al., 2015). Table 2.2 shows a list of countries with their reported associated levels of fluoride.

Table 2.2. Fluoride occurrence in some countries of the world

Location	F^- (mg/L)	Reference
1. Bahabad, Iran	2.35	Dehbandi et al., (2018)
2. Showt city, Iran	5.50	Yousefi et al., (2019)
3. Kassena Nankana, Ghana	4.27	Ganyaglo et al., (2019)
4. Birbhum District, India	18.08	Mondal et al., (2015)
5. Yuncheng Basin, China	14.10	Li et al., (2015)
6. Lamphun Thailand	14.12	Chuah et al., (2016)
7. Chihuahua, Mexico	11.80	Gonzalez-Horta et al., (2015)
8. Kalmar, Sweden	15.00	Augustsson & Berger (2014)
9. Tharparkar, Pakistan	49.30	Rahman et al., (2018)
10. Liwonde, Malawi	6.17	Kayira et al., (2014)
13. Mayo Tsanga, Cameroon	15.02	Kimambo et al., (2019)
14. Rajnandgaon district, India	27.00	Mukherjee & Singh (2018)
15. Tororo District, Uganda	3.00	Egor and Birungi (2020)
16. Dassa-Zoume´, Benin	7.19	Tossou et al., (2017)
17. Siloam, South Africa	4.95	Onipe et al., (2021)
18. Kalalan Wala, Pakistan	21.30	Yasar et al., (2021)
19. Mokopane, South Africa	3.39	Molekoa et al., (2019)
20. Namaqualand, South Africa	38.00	Abiye et al., (2018)
21. Turkana, Kenya	5.87	Rusiniak et al., (2021)
22. South Carolina, United States	3.50	Brindha and Elango (2011)
23. Kasteel, South Africa	40.49	Onipe et al., (2020)
24. South Carolina, United States	5.50	Nordstrom & Smedley (2022)
25. Medawachchiya, Sri Lanka	3.70	McDonough et al., (2021)
26. Ungheni District, Maldova	9.20	Pînzaru et al., (2020)
27. Gombe State, Nigeria	3.46	Giwa et al., (2021)
28. La Pampa, Argentina	25.70	Ali et al., (2016)
29. São Paulo, Brazil	10.00	Martins et al., (2018)
30. Calabria, Italy	30.00	Fuoco et al., (2021)

Most rural areas in semi-arid and arid countries when compared to tropical areas have the challenge of fluoride in their groundwater used for domestic purposes (Mukherjee et al., 2019). Factors such as climate change, pH, ion exchange, solubility, water quality parameters, well

depth, water flow and geological formation are significant to the concentration of fluoride in groundwater (Bhattacharya & Samal, 2018; Sreekanth et al., 2018). A study by Choubisa (2018) revealed less fluoride concentration in groundwater from areas that receive high rainfall and are composed of slope landscapes.

2.7.2. Occurrence of fluoride in surface water

Excess fluoride in surface water is not often reported when compared to groundwater. Fluoride concentrations in surface water differ according to the geological formation of the area causing either a high or low concentrations, than groundwater (Hayes et al., 2017; Onipe et al., 2020). Surface water in the Yuncheng basin in China recorded fluoride concentration ranging from 0.32 to 15.36 mg/L (Luo et al., 2018). The lowest fluoride content was measured in the mountains resulting in less contamination while the highest was recorded from reservoirs and lakes; this situation is believed to be the effects of anthropogenic activities such as fluorine mineral dissolution and leaching of fertilizers with fluorine minerals during irrigation (Liu et al., 2020; Luo et al., 2018). The Kärrsvik stream in Sweden recorded 4.2 mgF^-/L where the source of the fluoride is suspected to be granite rock which dissolves in the soil fluxes into the stream during rainfall runoff (Berger, 2016; Colombani et al., 2018).

Countries located in the East African Rift Valley are likely to have excess fluoride concentration in their surface water resources above the standard set by WHO (Onipe et al., 2020). Lake Nakuru located in Kenya recorded 2 800 mgF^-/L, while Lake Momella in Tanzania recorded 690 mgF^-/L due to contact with volcanic rocks ashes which contain excess fluoride (Malago et al., 2017; Mbabaye et al., 2018). The Ethiopian hot springs and the Bilate River basin which are associated with the southern Ethiopian Main Rift measured concentration levels of 57.4 and 112 mgF^-/L, respectively. The source of fluoride in this surface water is suspected to be the discharge of volcanic elements from volcanic aquifers from northern Ethiopia during rock-water interaction (Haji et al., 2018). Kumadugu-Yobe River in Yobe State, Nigeria recorded 2.07 mgF^-/L levels; the river is also a source of raw water to a treatment plant. The source of fluoride content in this downstream river could be the sedimentary rock formation and fluoride pollution from upstream Hadejia and Jama'are Rivers (Waziri et al., 2012). A study of the Nzhelele River which surrounds Siloam village in South Africa recorded fluoride concentration below 1 mg/L which is the result of syn-rift sequence of sedimentary rock and basaltic lava volcanic deposition (Edokpayi et al., 2018; Onipe et al., 2021). The geothermal springs at Tshipise and Siloam in South Africa recorded fluoride levels ranging from 6.72 – 7.28 mg/L and 5.97 – 6.66 mg/L, respectively; the geology factors of Tshipise and Siloam responsible for

this high fluoride level are the volcanic rock of the Letaba formation and basalt formation, respectively (Durowoju et al., 2018).

2.8. BENEFITS OF FLUORIDE

Like most of the elements, fluoride can either be beneficial or harmful to human health depending on the levels at which it occurs (Gudipudi et al., 2019). In literature, fluoride has been stated as a micro-nutrient that is essential for human health (Barathi et al., 2019; Hussein & Vegi, 2020; Kaur et al., 2017; Mohammadi et al., 2017; Murambasvina & Mahamadi, 2020). Fluoride is essential in low quantities (0.5 – 1.5 mg/L) for healthy development and demineralises skeletal system and teeth; this results in dental caries prevention (Valentukeviciene et al., 2019). In some countries, with water containing low fluoride levels, it is added through the process of fluoridation (Malin & Till, 2015). Children under the age of 8 require fluoride during their bones, teeth and enamel developmental stage but only within the acceptable limit (Sreekanth et al., 2018). Besides health benefits such as pharmaceutical products' production, fluoride is used in the manufacturing industries for the production of aluminium, steel, glass, paint and refrigerator (Hayes et al., 2017).

2.9. FLUORIDE HEALTH EFFECTS

Fluoride is a complicated nutrient since it has impacts on human health either in very low or excess amounts (Kaur et al., 2017). Malago et al. (2017) listed various countries that are providing drinking water to households that contain fluoride concentration above the acceptable limit set by WHO. Besides water intake, fluoride content can be accumulated via food, gas from industries and over-use of toothpaste (Bhattacharya & Samal, 2018). Approximately 50% of fluoride intake by an individual is stored in the teeth and bones while the remaining is flashed from the body with urine, however, this process takes time to occur (Valentukeviciene et al., 2019). Diagnosis of fluoride concentration can be done through saliva, bone, urine, teeth, plasma, hair and nail examination (Lavalle-Carrasco et al., 2021).

Patients who are diagnosed with kidney failure are at high risk of fluorosis due to their difficulties in excretion of fluoride (Yadav et al., 2018). Fluoride becomes harmful in large quantities (>1.5 mg/L), therefore, moderation of its intake is essential and the effects differ between children and adults, exposure time and diet choices (De et al., 2021). If the human body system has low or excess content of fluoride, there are health implications that can be manifested as presented in Table 2.3 (Zhang & Huang, 2019b).

Table 2.3. Fluoride implications with the level of consumption

F^- level (mg/L)	Implications	Reference
<0.5	Dental caries (teeth changing colour and rotting)	Irigoyen-Camacho et al., (2016)
0.5 – 1.5	Optimum dental health (no effects)	Keshavarz et al., (2015)
1.5 – 4.0	Dental fluorosis (teeth cracking and breaking)	Sreekanth et al., (2018)
4.0 - 10	Dental and skeletal fluorosis (fracture risk)	Guth et al., (2020)
>10	Crippling fluorosis and neurological damage	Kashyap et al., (2021)

Children are more vulnerable to excess fluoride consumption, although, Bhattacharya and Samal (2018) reported that the accumulation of fluoride in children decreases as they get older. A study in Brazil was conducted with children (2 - 5 age) which revealed less dental fluorosis due to parental assistance during teeth brushing and usage of toothpaste (Oliveira et al., 2018). Another study from Pakistan reported that children face high health implications from consuming ground water rich in fluoride, when compared to adults (Rahman et al., 2018).

A high concentration of fluoride in the human body commonly results in dental and skeletal fluorosis, however, diagnosis has also showed that patient can suffer from poor development and functioning of the brain (Jiang et al., 2019); red blood cell deformation, muscle fibre degeneration, headache, stomach pain (Malago et al., 2017); decreased sperm count, mouth sores, toes tingling (Mumtaz, 2017); female infertility, brain damage, cancer (Murambasvina & Mahamadi, 2020); constipation, severe thirst, ligaments calcification, nausea, appetite loss, depression and dysfunction of the urinary tract after a long-term intake of the element (Mukherjee et al., 2019). Ingestion of high fluoride-concentrated water disturbs the metabolism of phosphorus and calcium in human beings (Sharma et al., 2017). Fluoride is expected to be excreted with urine and sweat, but kidney patients suffer more fluorosis effects, even when their fluoride intake is within the acceptable range (Yadav et al., 2018).

In India, studies showed that dental fluorosis (Figure 2.4A) is more common in school children aged 8 to 10 during their developmental stage (Nakornchai et al., 2016). At this young age, the intelligence of these children may also be affected due to their neurological system damage caused by the excess of fluoride in their body system (Ganyaglo et al., 2019). Ageing quicker, cracking of teeth and crippling of limbs (Figure 2.4B) are symptoms of a high concentration of fluoride, after a long-term exposure (Srivastava & Flora, 2020). Human Immune Virus and tuberculosis patients are in danger of their immune system being further suppressed if they continue drinking water rich in fluoride (Elumalai et al., 2019).

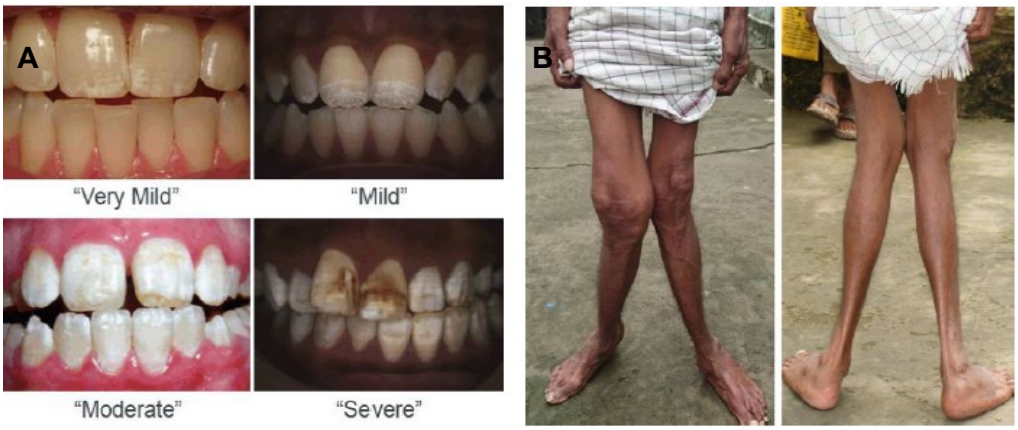

Figure 2.4. Stages of dental fluorosis condition (A) (https://fluoridealert.org/issues/fluorosis/). Skeletal fluorosis condition (B) (Choubisa & Choubisa, 2018).

2.10. METHODS OF FLUORIDE REMOVAL

2.10.1. Technological methods

The use of innovative techniques has reduced the time spent on water defluoridation. Defluoridation can be done at the water-treatment plants for mega water supply and households or communities which will cater to a number of water users (Shakya et al., 2020). For ages, scientists and water-users (non-scientist) have been coming up with methods to remove excess fluoride in water - adsorption, coagulation, precipitation, membrane filtration, electro-chemical, ion-exchange, natural rock, bone char, Nalgonda technique and osmosis - (Ranjan et al., 2016). Washed fly-ash has been used for defluoridation purposes with the intention of moderating pH to achieve acceptable fluoride concentration in drinking water (Waghmare & Arfin, 2015). These defluoridation methods that have been experimented worldwide, have disadvantages and advantages that must be considered before the actual selection of any one of them (Table 2.4) (Mukherjee & Singh, 2018).

In most defluoridation processes, fluoride-rich water passes through a designed surface bed which adsorbs fluoride ions, reducing the fluoride concentration before human use (Sharma et al., 2017). Factors such as contact time, adsorbent size and type, initial fluoride concentration and pH of the water, determine the effectiveness of the fluoride adsorber (An, 2020). Various methods of deflouridation have been tested at the municipal level which are expensive, hence, there is a need for innovative low-cost and eco-friendly methods appropriate for households' levels and, particularly, for poor communities in fluoride-rich areas (Barathi et al., 2019); these deflouridation methods must minimize effluents and the disposal of media that contain fluoride in the environment (Buamah et al., 2016).

Table 2.4. Deflouridation methods.

Method/process	Advantages	Disadvantages	Reference
1. Membrane process 1.1. Ion-exchange	-High fluoride percentage removal -Sorbent is reusable -No electricity power is required -Improves water colour and taste	-Require before and after pH regulation of water -Initial cost is high -Time consuming process	Bakar et al., (2016), Karunanithi et al., (2019), Waghmare and Arfin (2015)
1.2. Osmosis	-High fluoride removal -It can function in different pH -Disinfection is done during the purification process	-High installation and running costs -Removes essential elements too -High waste-water after treatment -Requires training -Low permeability	Ayala et al., (2018), Karunanithi et al., (2019), Kumar et al., (2019), Samrat et al., (2018)
1.3. Electro-dialysis	-No chemicals added	-Initial and operating costs are high -Trained operator needed	Sivarajasekar et al., (2017)
2. Adsorption 2.1. Bone char	-Relatively high fluoride removal -Works better at neutral pH -Reduces turbidity -Improves taste and odour	-Stringent preparation condition -Requires a skilled person to prepare -Harbours bacteria -Possible religious and cultural objections -Frequent filter monitoring	Karunanithi et al., (2019), Mobeen and Kumar (2017), Suneetha et al., (2015)
2.2. Modified natural adsorbents	- Good fluoride removal - Works better at near-neutral pH	- Can introduce organic compounds into the water if it is not prepared well	Nigri et al., (2019), Ramos-Vargas et al., (2018), Waghmare and Arfin (2015), Yadav et al., (2018)

Table 2.4 continues

Method/process	Advantages	Disadvantages	Reference
2.3. Activated alumina	- High porous granular -Easy to use/ less training	-Effective at a specific pH level -Expensive maintenance -Effluent discharge is highly concentrated with F^- -Depends on ions present in the water -Requires low water-flow rate	Jadhav et al. (2015), Kumar et al., (2019), Suneetha et al., (2015)
3. Coagulation-precipitation 3.1. Nalgonda technique	-Uses cheap materials -Good fluoride removal -Widely available fly ash -It can be used at a domestic level -Improves colour and odour -Removes other inorganic and organic substances	-Introduces aluminium in the treated water which can cause Alzheimer -Difficult to treat low fluoride concentration -Lime used elevates the pH of the treated water -Time consuming -Expensive maintenance cost -Excess and toxic effluents discharged	Mobeen and Kumar (2017), Soni (2015), Zhang and Huang (2019a)

2.10.2. Fluoride Bio-sorbent (Indigenous Plant)

Indigenous plants are classified as organic material and researchers have been investigating their capacity in the adsorption processes (Sivarajasekar et al., 2017). Plants have been used as bio-sorbent for the defluoridation process, especially in developing countries due to their cost-effectiveness, being environmentally friendly, availability, ease of use, as well as their mechanical and chemical properties (Gandhi & Sirisha, 2019). Plants' adsorption process is suitable for small community set-ups even households can apply this method for defluoridation (Reddy et al., 2017). Plant parts that are mostly used for the extraction of adsorbent are leaves, roots, seeds and barks. In addition, a huge quantity of agricultural products' residuals which are produced, can be used for fluoride removal from aqueous solution (Waghmare & Arfin, 2015).

Bio-sorbents investigated for defluoridation include the use of neem leaf and bark, lemon peels, guava leaf, tea leaves, maize leaf, *Aloe Vera*, goose grass, banana false, stem, tea ash, maize ash and corn cob (Ndé-Tchoupé et al., 2015; Sivarajasekar et al., 2017; Waghmare & Arfin, 2015). Other researchers have experimented with seeds from *Moringa olifera* and *Pithecellobium Ducle,* fruits of *Passiflora foetida fruits, barks from Emblica officinalis*, *zizanoides,* leaves from *Cyanodon tactylon* and roots from *Vetiveria* (Gandhi & Sirisha, 2019; Ranjan et al., 2016). A study conducted by Karmakar et al., (2016) revealed deflouridation using aquatic plants, such as *Pistia stratiotes, Eichhornia crassipes* and *Spirodela polyrhiza* which are commonly known as - water lettuce, water hyacinth and duckweed, respectively. Calcium, aluminium, zirconium and magnesium have been utilized as modification agents during fluoride adsorbent preparation of plants extracts and residuals (Corral-Capulin et al., 2019; Samrat et al., 2018). Some researchers have experimented with activated rice husk, carbonized tea waste and samarium-modified orange waste as fluoride adsorbents (Alhassan et al., 2020).

Kirthy et al., (2018) recommended the use of indigenous plant mucilage (IPM) due to its ability to thicken, emulsify and stabilize; Sharma et al., (2017) add that IPM is safe and socially acceptable for consumption since the plants used for the extraction are mostly edible. The other great property of IPM is its low toxicity level and the quality of the functional group responsible for adsorption (Edokpayi et al., 2015). Nevertheless, the adjustment of pH, fluoride concentration, contact time and dosage have to be monitored during deflouridation using any type of sorbent (Kaur et al., 2017).

2.10.3. Diet

Diet is the route of many hazardous substances into human health, but it can also be used as the solution to flash some of these substances from the body. The use of selective food intake to correct fluoride concentration in an individual differs according to the source of fluoride in the body (Abouleish, 2016). Consumers of high fluoride water or food can include rich magnesium, calcium and antioxidants (Vitamin A, C and E) food items in their diet to reduce the effects caused by excess fluoride intake, since these items contain positive charge (Kebede et al., 2016a). The intake of dairy products, organic products (fresh vegetables and fruits, tamarind pulp and juice made of black berries) were reported to be useful in preventing fluoride effects (Kaur et al., 2017; Mondal, 2018).

Tobacco, black tea, fish, citrus fruits and beetle nut have been highlighted as prohibited intakes for people consuming high-fluoride water (Soni, 2015; Tiwari et al., 2017). The intake of bottled water (Irigoyen-Camacho et al., 2016) and rain-harvested water (Kebede et al., 2016a) in high-fluoride areas, can be used as a fluoride-reduction method. For example, developed countries such as the United Arab Emirates prefer bottled water for consumption. In the preparation of food, it is advisable to also use the prepared water with a known quantity of fluoride (Casaglia et al., 2021), however, such bottled water or tap water must be tested to ascertain that the minerals and micronutrients contained are within the acceptable limits (Bhattacharya & Samal, 2018).

2.11. MITIGATION OF FLUORIDE EFFECTS

Fluoride effects' mitigation measures in affected areas are essential and consistency is required in such programmes, especially, in developing countries. The government of India, since 1987 has implemented the use of activated alumina, Nalgonda, defluoridation kits and artificial aquifer recharge in most affected areas, intending to supply water with acceptable fluoride levels (Gudipudi et al., 2019; Razbe et al., 2013). In Teresina, Brazil, oral care education was frequently shared with residents, mainly with school children (Oliveira et al., 2018). Countries in the East African Rift valley, such as Ethiopia and Kenya tried to use Nalgonda defluoridation technique, but there were many disadvantages and its process was confusing users at the household level which led to the implementation of bone char and alum methods (Dahi, 2016). In Tanzania, a defluoridation project has been implemented in schools, households and other public facilities. Furthermore, after years of applying a 4 mg/L standard for fluoride concentration in drinking water, in April 2018, the Tanzanian government adopted the WHO standard of 1.5 mgF^-/L (Malago et al., 2017; Marwa et al., 2018).

CHAPTER 3: RESEARCH METHODOLOGY

3.1. SAMPLING

Dicerocaryum eriocarpum (DE) commonly known as “devil’s thorn leaves” was chosen to be the experimental indigenous plant for the process of fluoride adsorption from rich-fluoride solution. DE samples (Figure 3.1) were harvested from the veld and abandoned farms at Muila Village located in Vhembe District, South Africa, during the summer season. The DE was stored in a polyethylene plastic bag with holes for ventilation and some detached DE samples were preserved in a refrigerator (-4˚C) for further use.

Figure 3.1. *Dicerocaryum eriocarpum* sample (Picture taken by the candidate: M.P Mannzhi).

3.2. REAGENTS

Fluoride standards of 1.00, 2.00, 10.00 mg/L, pH buffers of 4.01, 7.00, 10.1 and Total Ionic Strength Adjustment Buffer (TISAB) II with CDTA were purchased from Thermo Scientific (USA). Sodium hydroxide (NaOH) pellets and hydrochloric acid (32%) analytical reagent were purchased from Merck (Germany) and were used to adjust the pH of the solution, respectively. The fluoride salt used in this study was supplied by MINENA (Pty) Ltd chemicals, South Africa.

3.3. PREPARATION OF FLUORIDE STOCK SOLUTION

Fluoride stock solution was prepared using 2.21 g DE dried for 30 minutes at 80˚C in a drying oven (EcoTherm 276, Labotec, RSA). NaF and 500 mL of deionized water were stirred in a 1000 ml volumetric flask for 15 minutes (Figure 3.2). The volumetric flask was then filled to the mark with deionized water and stirring continued for another 15 minutes to make 100 mg/L of

fluoride-concentration stock solution. To get 10 mg/L of fluoride concentration, a standard solution (Figure 3.2.B) was used as the optimum concentration during this study; 20 mL of fluoride stock solution was diluted with 1980 mL of deionized water in a 2000 mL volumetric flask (Nigri et al., 2019). The initial fluoride standard solution was verified using Thermo Scientific ISE 9609 BNWP Orion (USA) probe attached to Thermo Scientific Orion Star A214 ISE/pH meter.

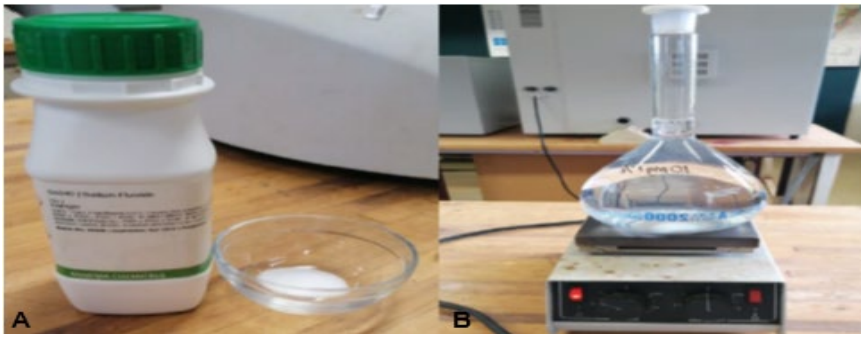

Figure 3.2. Fluoride stock solution (Picture taken by the candidate: M.P Mannzhi).

3.4. PREPARATION OF SORBENT

3.4.1. Unmodified sorbent

DE leaves were detached from the stem. The mucilage extraction method, from Monrroy et al., (2017), with some modifications, was applied for this study. DE leaves (50 g) were dispersed in boiling deionized water (1500 mL) for 30 minutes with constant stirring to produce a viscous slimy solution as displayed in Figure 3.3.A. The resulting solution was cooled for 30 minutes prior filtration of mucilage using a 0.45 µm filtration unit (Sartorius Lab Equipment, Germany) powered by a suction system (VWR vacuum pump VCP 130, USA). Precipitation of the filtered mucilage was achieved using 99% absolute ethanol reagent (Rochelle Chemicals, RSA) in a ratio of 1:3 (mucilage: ethanol). Precipitate extraction (Figure 3.3.B) lasted for 12 hours at room temperature. The supernatant was then centrifuged for a minute at 3000 rpm (Grant-bio laboratory centrifuge LMC-3000, UK). The precipitate was washed twice with analytical acetone supplied by Rochelle Chemicals (RSA) for colour improvement (Otalora et al., 2021). The precipitate was then oven-dried (EcoTherm 276, USA) at 50˚C for 150 minutes. Dried precipitate was pulverized into powder using mortar and pestle, sieved (<75 µm) then stored in the tight container, labelled “RDE” for the raw DE, until further processing (Figure 3.3.C).

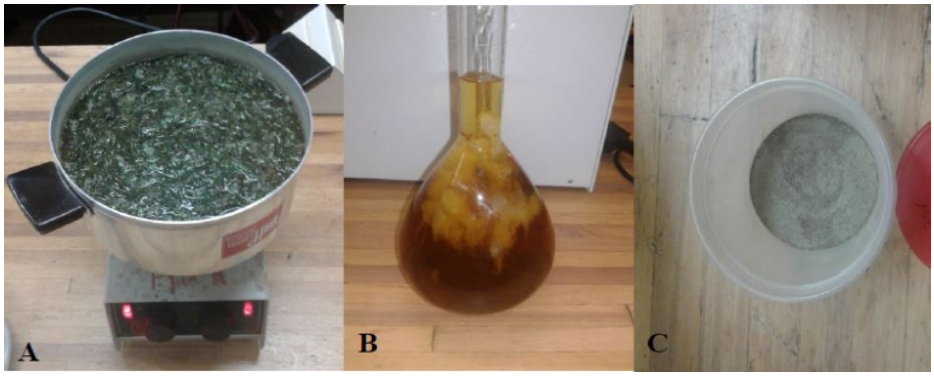

Figure 3.3. DE extraction (Picture taken by the candidate: M.P Mannzhi).

3.4.2. Modified sorbent

Mahmoodi and Javanbakht's (2021) method for the functionalization of mucilage was used with some modification. An amount of 700 mL of deionized water was filled into a 2000 mL conical flask. A dosage of 100 µl of aluminium (Al) and magnesium (Mg) solution standard of 1000 mgL^{-1} (AAS Standard solution, Rochelle Chemicals, RSA), in Figure 3.4.A, were administered into separate conical flasks (2000 mL) with deionized water (700 mL) measured using a micropipette (Series Autoclavable 100-1000 µl, BOECO, Germany). The solutions were left for 1 hour, while being stirred with a magnetic stirring bar. Filtered DE leaves mucilage (300 mL) as prepared in 3.4.1. were added to 0.1M Al and Mg solution prepared while stirring the solution (Figure 3.4.B). The solutions were left for a reaction for another hour, thereafter, ethanol was used to precipitate Al and Mg solution prepared using 1:3 (mucilage-alcohol) ratio (Figure 3.4.C). Precipitation continued for 12 hours before washing the supernatant twice, using acetone. Subsequently, 0.1 M Al and Mg modified precipitate were oven-dried, ground (Figure 3.4.B and 3.4.C) and sieved, as done with the unmodified precipitate. A 0.1M Al precipitate was labelled as 'AlDE', while, the 0.1M Mg precipitate as MgDE', respectively.

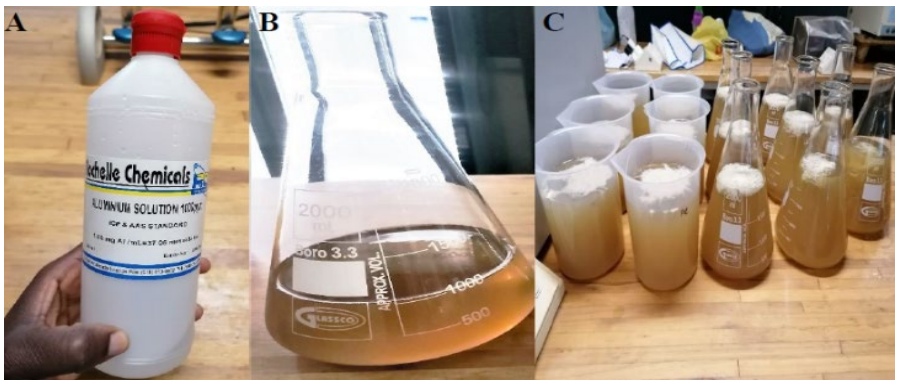

Figure 3.4. DE mucilage modification (Picture taken by the candidate: M.P Mannzhi).

3.5. ADSORBENT CHARACTERIZATION

RDE, AlDE and MgDE fluoride adsorbents were characterized at the accredited University of Johannesburg Extraction Metallurgy Assay laboratory. Plant characterization provides the sample experimented with detailed information regarding the functional group (FT-IR), surface morphology (SEM-EDX), element composition (XRF), crystalline state (XRD), thermal stability (TGA), elemental (CHNS) and proximate analyses.

3.5.1 FT-IR analysis

The functional groups analysis of raw and spent sorbent (RDE, AlDE and MgDE) were analysed using Thermo Scientific Fourier Transform Infrared (FT-IR) spectrometer (Nicolet iS10, USA) equipped with Diamond Attenuated Total Reflectance crystal (Figure 3.5.A) to characterize molecular bonds present on the sample surface (Javanbakht & Shafiei, 2020). Crystal lenses were cleaned, prior to analysis of each sample to prevent contamination. Crystal lenses were covered with sorbent sample prior applying pressure on the sample, using the arm pressure attached to the FT-IR equipment. To identify small particles, the infrared (IR) spectrum of samples were recorded using Thermo Scientific^{TM} OMNIC^{TM} specta software. The spectra were obtained over the range of 4500 to 400 cm^{-1} at a resolution rate of 4 cm^{-1} following 32 scans and the average was displayed (Edokpayi et al., 2015).

3.5.2. SEM-EDX analysis

The structural surface morphology and particle size (Ghomashi et al., 2020) of the RDE, AlDE and MgDE were characterized by a scanning electron microscope (SEM) model called 'Vega 3X MU' (TESCAN, UK) equipped with tungsten filament as a source of electron (Figure 3.5.B). Vega software was utilized to acquire images in various magnifications, while, energy dispersive x-ray (EDX) spectroscopy coupled with SEM Vega 3X MU which provides chemical composition analysis of the samples were performed by installing INCA software Oxford.

3.5.3. XRF analysis

Trace elements analysis and composition in RDE, AlDE and MgDE samples were determined by ZSX Primus II (Rigaku, Japan) X-ray fluorescence (XRF) instrument. A sorbent (0.5 g) in a pellet form was placed on the instrument holder, in a vacuum atmosphere to be scanned for its intensity. Pellets were produced using a presser at a pressure of 100 kN (Zhang & Huang, 2019a).

3.5.4. XRD analysis

With the modified procedure by Rajkumar et al., (2019) crystalline state (chemical components) of RDE, AlDE and MgDE were analysed by x-ray diffractometer (XRD) model using XRD Ultima IV (Rigaku, USA) equipped with x-ray generator CuK (λ=1.54); this is a generator with 3 kW power and Goniometer and with the ability to measure step size of 2-theta angle from 0° to 162° (Figure 3.5.C). The XRD instrument was set to scan the samples at a speed of 1°/min starting from 5° up to 90° 2-theta angles sourced with 40 kV voltage and 30 mA current per run.

3.5.5. TGA analysis

An analysis of thermal degradation (TG) measuring the physical change, focusing on mass loss or gain (mg) of RDE, AlDE and MgDE before sorption at constant temperature (30 to 950°C) and time (93 minutes) was performed by a modified thermo-gravimetric analysis (TGA) method adopted from a study by Gaur et al., (2018) using Hitachi STA 7200RV (Japan) (Figure 3.5.D). Approximately, 10 mg of sample was heated at a rate of 10°C per minute, under nitrogen and synthetic gas environment at a rate of 20 mL per minute. Furthermore, samples were analysed for differential scanning calorimetry (DSC) and derivative thermo-gravimetric (DTG) which determine the heat and temperature differences, respectively.

3.5.6. Elemental analysis

Elemental analysis of RDE, AlDE and MgDE before adsorption of fluoride were determined by the improved method devised by Rajkumar et al., (2019). Thermo Fisher Scientific organic elemental analyser FLASH 2000 (USA), shown in Figure 3.5.E, was used to analyse carbon (C), hydrogen (H), nitrogen (N) and sulphur (S). A sterilised ceramic crucible was used to measure the sample mass before analysis. The temperature of the elemental analyser was increased to 1300°C after the sample was placed inside the instrument. High temperature resulted in sample combustion. At the end of oxidation, generated gases rich with nitrogen, carbon dioxide, water vapour and sulphur dioxide flowed into the chromatographic column to be separated by the elution process. The reactor was then cleaned for excess gases. Eager 300 software, thereafter, determined the percentage composition of CHNS from the eluted product.

Figure 3.5. Equipment used for characterisation analysis includes FT-IR (A), SEM-EDX (B), XRD (C), TGA (D) and elemental analysis (E). (Picture taken by UJ lab technician Ms. N. Baloyi).

3.5.7. Proximate analysis

Proximate analysis of RDE, AlDE and MgDE samples were determined by the modified method outlined by Fito et al., (2019). The proximate analysis determined the ash content, moisture, volatile matter and fixed carbon percentages. Samples were dried and sieved (212 µm). Crucible mass (in grams) was weighed before the sample (~1 g) was measured. The sample was placed in a muffle furnace at 25˚C room temperature; this was increased to 500˚C for 30 minutes. The temperature was increased for the second time to 820˚C for another 30 minutes before the crucible was removed from the furnace. The crucible was cooled for 10 minutes on a cold metal slab prior to placing it in a desiccator for 15 minutes. The crucible was then weighed before it was returned to the muffle furnace, at the same temperature and time range, until the ash mass was < 0.001 g. The crucible was cleaned and weighed (in grams) to calculate the ash percentage obtained using Equation 3.1.

$$\text{Ash}\ (\%) = \frac{M_3 - M_1}{M_2 - M_1} \times 100\% \qquad 3.1$$

where M_1 stands for initial crucible mass, M_2 for crucible and sample mass (before heating) and M_3 for crucible and ash mass (after heating).

The moisture content of the RDE, AlDE and MgDE were also determined. The washed and dried crucible was preheated for 10 minutes at ~110˚C followed by cooling (20 minutes) prior to weighing (in grams). A finely-grounded sample (1 g) with a particle size of <212 µm was spread uniformly on a crucible before weighing the total mass (in grams). For 90 minutes the crucible with the sample uncovered was oven-dried (~110˚), then, for 20 minutes the crucible was cooled in the desiccator prior to weighing (in grams). Moisture content (Equation 3.2) of the sample was obtained by calculating the difference between the initial and final mass which display loss of sample mass due to drying.

$$\text{Moisture (\%)} = \frac{M_2 - M_3}{M_2 - M_1} \times 100\% \qquad 3.2$$

where M_1 stands for empty crucible mass, M_2 for crucible and sample mass (before heating) and M_3 for crucible and ash mass (after heating).

Furthermore, the volatile matter which is a converted heat present in the carbon content of the adsorbents was also analysed. Preheated crucible (910˚C/7 minutes) was cooled (5 minutes) on a metal plate before being placed in a desiccator (10 minutes) prior to weighing (in grams). Weighing of the sample (in grams) then followed. A muffle furnace (910˚C) was then used to heat the sample for 7 minutes. The procedure used for moisture content after heating was followed until the mass (in grams) of the crucible was measured. Fixed carbon and ash were observed on the crucible after heating. Equation 3.3 shows the calculation of the volatile matter of the sorbents.

$$\text{Volatile matter (\%)} = \left(\frac{M_2 - M_3}{M_2 - M_1}\right) \times 100\% - M_o \qquad 3.3$$

where M_1 stands for empty crucible mass, M_2 for crucible and sample mass (before heating), M_3 for crucible and ash mass (after heating) and Mo for moisture content (%).

Lastly, the fixed carbon content of the sorbents was determined by the difference. The sum of percentages obtained from ash content, moisture content and the volatile matter was deducted from one hundred percent (Equation 3.4).

$$\text{Fixed carbon (\%)} = 100\% - (A + M + V) \qquad 3.4$$

where A stands for ash content (%), M for moisture content (%) and V for volatile matter (%).

3.6. BATCH ADSORPTION STUDIES

For batch adsorption studies, effects such as dosage, pH, time and temperature were studied. Sterile polyethylene bottles (250 mL) were filled with 100 mL of 10 mgF^-/L stock solution prepared before sorbents were added (Ye et al., 2019). For the purpose of accuracy, each effect's condition was analysed in triplicate; these occurred at room temperature of 25˚C. Equations 3.5 and 3.6 were utilized to calculate the percentage removal of fluoride and fluoride adsorption capacity, respectively (Edokpayi et al., 2015).

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \quad 3.5$$

$$q_e = \frac{C_o - C_e}{m} \times V \quad 3.6$$

where C_o stands for initial fluoride concentration (mg/L), C_e for fluoride concentration at equilibrium (mg/L), q_e for adsorption capacity (mg/g), m for adsorbent mass (g) and V for volume of solution (*L*).

3.6.1. Effect of dosage

Differences in mass, during adsorption studies, have been known to influence the adsorption capacity of the sorbent (Collivignarelli et al., 2020). The effect of the different dosages was achieved by weighing various masses (0.05, 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 and 2 g) of AlDE and MgDE sorbent using an analytical balance (RADWAG weighing balance AS 220.R2, Poland). Measured sorbents were added to 100 mL of fluoride solution which were immediately agitated in a water-bath shaker (EcoBath 207-ThermoScientific, RSA) at 200 rpm for 2 hours. At the end of the agitation process, the residual solutions were filtered using a 0.45 µm membrane filter (CHMLab, Spain) placed in a filtration unit and transferred into a 50 mL centrifuge tube. TISAB II with CDTA was put into a filtered supernatant to prevent interference of ions in the solution during fluoride ion analysis using the ratio of 1:1. The solution was left for interaction for 10 minutes before measuring the residual fluoride concentration using Thermo Scientific ISE 9609 BNWP Orion (USA) probe, attached to Thermo Scientific Orion Star A214 ISE/pH meter (USA) (Mudzielwana et al., 2018). Percentage removal (Equation 3.5) and adsorption capacity (Equation 3.6) for each sample was calculated and recorded in Microsoft Excel software for future analysis.

3.6.2. Effect of pH

The acidity and the alkalinity of a solution affect fluoride removal from water (Mukherjee & Halder, 2018). Measuring of the pH level was achieved using ROSS sure-flow combination pH 8172 BNWP Orion (USA) installed on Thermo Scientific Orion Star A214 ISE/pH meter (USA). The pH meter was calibrated using 4.01, 7.00 and 10.1 pH buffer from Thermo Scientific (USA) before pH measurements. The effect of pH on fluoride removal was analysed from the range of 2.35 to 12.00. Before the pH adjustment, the fluoride stock solution was measured for the initial pH level. The adjustment of pH was accomplished by dosing 1M of HCl (Figure 3.6.A) and 1M of NaOH (Figure 3.6.B) until the desired pH level was reached (Javanbakht & Shafiei, 2020). The pH adjusted fluoride stock solution was then dosed with AlDE and MgDE adsorbent (0.25 and 0.5 g) and agitated for 2 hours at 200 rpm in a 30˚C water bath-shaker (Figure 3.6.C), thereafter, all the samples followed the procedure mentioned in 3.7.1 for fluoride concentration determination.

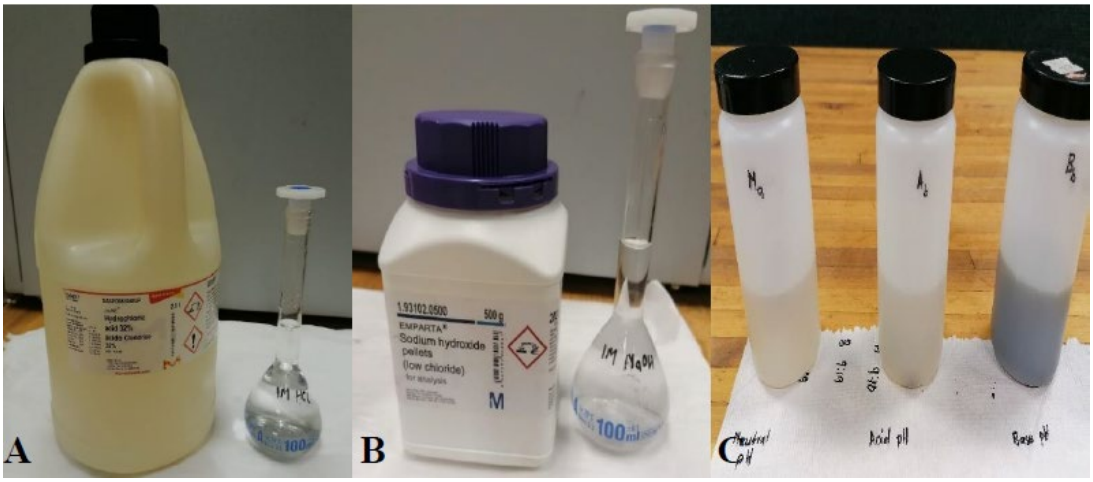

Figure 3.6. Effect of various pH levels during fluoride sorption (Picture taken by M.P Mannzhi)

3.6.3. Effect of time

Time duration of the adsorption process has been observed to be essential regardless of other experimental factors in kinetics (Suneetha et al., 2015). Equilibrium time for optimum adsorption was determined at various time intervals (15, 30, 60, 120, 150 and 180 minutes) at 200 rpm (Jegede et al., 2021). Adsorbent doses (0.25, 0.5 and 1 g) of AlDE and MgDE were varied during batch studies with a fluoride solution of 10 mg/L. Subsequently, at the end of

each time interval, the procedure is mentioned in 3.7.1. for measuring residual fluoride concentration in the solution after agitation was followed.

3.6.4. Effect of temperature

Temperature is known as the catalyst and enhancer for fluoride removal (Ye et al., 2019). For this study, the temperatures that were experimented are 25, 35 and 40˚C in a water bath shaker. Each temperature studied, a dosage of 0.25 and 0.5 g of AlDE and MgDE were added to 10 mg F^-/L solution (100 mL) in polyethylene bottles and agitated in a water-bath shaker for 2 hours at 200 rpm to observe the fluoride removal. Residual fluoride concentration was measured following the procedure discussed in 3.7.1.

3.6.5. Effects of change in water chemistry

To investigate the practical use of AlDE and MgDE adsorbent, natural groundwater rich with fluoride from Siloam Village at Vhembe District (RSA) was tested for defluoridation. Siloam has been reported to have high fluoride concentration from groundwater and health effects such as mottling of teeth have been reported among the community members (Odiyo & Makungo, 2018). Water sample from Siloam Village recorded 4.83 mgF^-/L. Batch adsorption conditions applied were dosage (0.25 and 0.5 g), temperature (30˚C), agitation speed (200 rpm), time (2 hours) and 100 mL of natural water without pH adjustment. Fluoride concentration was analysed at the end of the agitation and its removal efficiency (Equation 3.5) were recorded.

3.7. EQUILIBRIUM STUDIES

3.7.1. Isotherm studies

For the isothermal experiment, Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) isotherm models were used to determine the adsorption capacity of the adsorbent at a constant temperature using Equation 3.7 and Equation 3.8, respectively. Adsorption intensity can be influenced by the chemisorption mechanism which is the involvement of valence strength between the sorbent used and the fluoride ions in the solution (Raghav & Kumar, 2019). A Langmuir graph was achieved by plotting $1/q_e$ against $1/C_e$. Langmuir constant (K_L) which determine the binding strength of the adsorbent was calculated from the slope of the plot, while the Q_{max} was calculated from the intercept.

Freundlich isotherms make assumptions between uneven sorption sites with various energies of sorption on a heterogeneous adsorption surface (Edokpayi et al., 2020). A plot of log q_e against log C_e produced a linear graph of Freundlich; a Freundlich isotherm assumes heterogeneous sorbent surface has multiply sorption sites (Jegede et al., 2021). A Freundlich constant (K_F) determines the adsorption capacity and it is calculated from the intercept of the linear graph. Adsorption intensity (n_f) calculated from the slope and values, within a range of 1 to 10 are known to be favourable for Freundlich adsorption (Chinnakoti et al., 2016). The isotherm model which records the highest linearized coefficient (R^2) reading better describes the sorption process (Meilani et al., 2021). Furthermore, the separation factor (R_L) (Equation 3.9) which is essential to Langmuir isotherm was used to determine if the adsorbent used was favourable or not, during the adsorption experiment. R_L values indicates isotherm and $R_L > 1$, $R_L = 1$, $R_L = 0$ and $R_L = 0 < R_L < 1$ denotes unfavourable, linear, irreversible and favourable, respectively (Hussein & Vegi, 2020).

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{K_L q_e}\right)\frac{1}{c_e} \quad 3.7$$

$$log_{q_e} = log_{k_F} + \frac{1}{n_f} log_{c_e} \quad 3.8$$

$$R_L = \frac{1}{1+K_L\, C_o} \quad 3.9$$

where q_e stand for fluoride adsorption capacity (mg/g), q_{max} for maximum amount adsorbed (mg/g), K_L - Langmuir constant (L/mg), K_F for Freundlich constant (mg/g), R_L for separation factor, n_f for adsorption intensity, C_o for initial fluoride ion in solution (mg/L) and C_e for fluoride ion at equilibrium in solution (mg/L).

3.7.2. Kinetic studies

The pseudo-first-order (Equation 3.10) and pseudo-second-order (Equation 3.11) kinetic models were used for kinetic reaction experiments for this study (Ho & McKay, 1998; Lagergren, 1898). Batch adsorption studies focusing on the effect of time data were used to plot kinetics models and to ascertain the plot which gives linear correlation coefficient (R^2) (Baghdadi et al., 2019; Jegede et al., 2021). Pseudo-first-order plot was obtained by plotting Log ($q_e - q_t$) against time while pseudo-second-order was plotted by t/q_e against time. Constant rates and fluoride ion at equilibrium were calculated from the slope and intercept of the pseudo-first-order linear graph, while, K_2 and q_e were calculated from slope and intercept of

pseudo-second-order plots, respectively. The adsorption mechanism was estimated using the intra-particle diffusion model (Equation 3.12) from a plot of q_t against $t^{0.5}$ (Weber Jr & Morris, 1963). The constant intra-particle diffusion rate and intercept were calculated from the slope and intercept of the linearized plot. It is assumed that intra-particle diffusion is the slowest step which determines the rate-controlling step of the reaction if the linear curve passes through the origin (Akafu et al., 2019).

$$log(q_e - q_t) = log_{q_e} - \frac{K_1}{203.3} \quad 3.10$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e 2} + \frac{t}{q_e} \quad 3.11$$

$$Q_t = K_i\, t^{0.5} + C \quad 3.12$$

Where q_e stands for amount of F^- ions at equilibrium (mg/g), q_t for F^- adsorption capacity at any time (mg/g), t for time (min), k_1 for constant rate for 1st pseudo-order (min^{-1}), k_2 for constant rate for 2nd pseudo-order (mg/g.min), Q_t for F^- absorbed (mg/g), C for intercept (mg/L), and K_i for intra particle diffusion rate constant ($mg/g.min^{0.5}$).

3.8. THERMODYNAMICS STUDIES

The feasibility and spontaneity of the adsorption process were determined by thermodynamics studies where the effect of temperature was the key component of the process (Dehghani et al., 2018). Gibb's free energy (ΔG, kJ/mol) was calculated using Equation 3.13. Recalculation of K_o (Equation 3.14) was obtained by multiplying q_e/C_e with the molar weight of sorbate (18.99 mg/L) and concentration of water (55.55 mol/L) to fit in plotting Van't Hoff (Van't Hoff, 1884). The linear relationship obtained from plotting In K_o against 1/T provided slope and intercept to calculate ΔH^o and ΔS^o parameters in Equation 3.15, respectively.

$$\Delta G = -RT\, ln\, ln\, K_c \quad 3.13$$

$$K_o = \frac{q_e}{C_e} \quad 3.14$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad 3.15$$

where K_c stands for equilibrium constant (L/g), q_e for equilibrium F^- concentration in solution (mg/L), C_e for equilibrium concentration of water (mg/L), R for universal gas constant (8.314 J/mol/K) and T for temperature (k).

3.9. DESORPTION STUDY AND RE-USE

The desorption process refers to the washing and drying of the adsorbent rich with the adsorbate by a desorbing agent after the adsorption experiment. Adsorption occurred under optimum conditions, such as temperature (30˚C), contact time (2 hours), agitation speed (200 rpm), dosage (1 g) and 100 mL standard solution containing 10 mgF^-/L. At the end of the adsorption process, centrifuging and filtrating of adsorbent residual and fluoride solution occurred, respectively and then, the fluoride solution was measured for fluoride concentration (mg/L).

Residual adsorbent obtained after centrifuging was soaked and washed with 40 mL of desorbing agent (deionised water, 0.1M NaOH solution and 0.1M HCl solution) for 1 hour in agitating water-bath shaker at 200 rpm at room temperature. Desorbing agent residuals were filtered and measured fluoride concentration was used in Equation 3.16 to calculate desorption efficiency (Kebede et al., 2016b). The recovered adsorbent was oven-dried and pulverized before re-use (Hussein & Vegi, 2020). Regeneration of the spent adsorbent (AlDE and MgDE) was repeated 3 times while recording percentage removal of fluoride (Equation 3.5) from each adsorbent.

$$\text{Desorption efficiency (\%)} = \frac{\text{Desorbed } F^- \text{ concentration}}{\text{Adsorbed } F^- \text{ concentration}} \times 100\% \qquad 3.16$$

3.10. ETHICAL CONSIDERATION

Ethical clearance for this project (SES/21/HWR/10405) was approved by the University of Venda Research Ethical Committee.

CHAPTER 4: RESULTS AND DISCUSSION

4.1. ADSORBENT CHARACTERIZATION

4.1.1. Fourier transform infrared spectrometer (FT-IR)

Functional groups in the surface of the adsorbent were analysed using FT-IR. The assignment bands and the peaks of RDE, AlDE and MgDE sorbents are recorded in Table 4.1 and Figure 4.1. A broad peak was observed for O-H stretches of alcohol in all the sorbents, while the broad and absorption peaks for N-H stretches of amines were only observed in RDE and MgDE. The N-H and OH wavelengths of the sorbents were too close to each other, however, OH showed strong intensity when compared to NH. Other major absorption peaks observed in RDE, AlDE and MgDE were O-H, C=O and C-O (Dan & Chattree, 2018), while the C-H stretch of alkanes did not appear in RDE. Modified AlDE and MgDE displayed a decrease of the spectrum when compared to the RDE which might be the result of breakage and linkage of intermolecular bonds responsible for absorption during functionalisation process (Jegede et al., 2021). The decrease was more significant in AlDE (Figure 4.1.B) than in MgDE (Figure 4.1.C). The presence of carbon atoms in functional groups, such as esters, saturated aliphatic, amides, amines, aromatic, carboxylic acids and ethers enhanced fluoride removal due to their strong bonding ions (Mukherjee & Halder, 2018). Comparable functional groups were observed in *Moringa oleifera* leaves as reported by Dan and Chattree (2018).

Table 4.1. Bands assignments of the sorbents.

		Band assignment (cm^{-1})		
Peaks	**Functional group**	**RDE**	**AlDE**	**MgDE**
1	O-H stretch of carboxylic acids	2908	2883	3123
2	N-H stretch of 1˚ and 2˚ amines, amides	3399	*	3358
3	O-H stretch of alcohols	3485	3381	3399
4	C-H stretch of alkanes	*	2883	2928
5	C=O stretch of esters, saturated aliphatic	1745	1744	1744
6	C-O stretch of alcohols, carboxylic acids, esters, ethers	1086	1031	1298
7	C-C stretch of aromatic	1401	1423	1421

RDE- raw DE, AlDE- Al modified DE, MgDE- Mg modified DE and * peak not observed

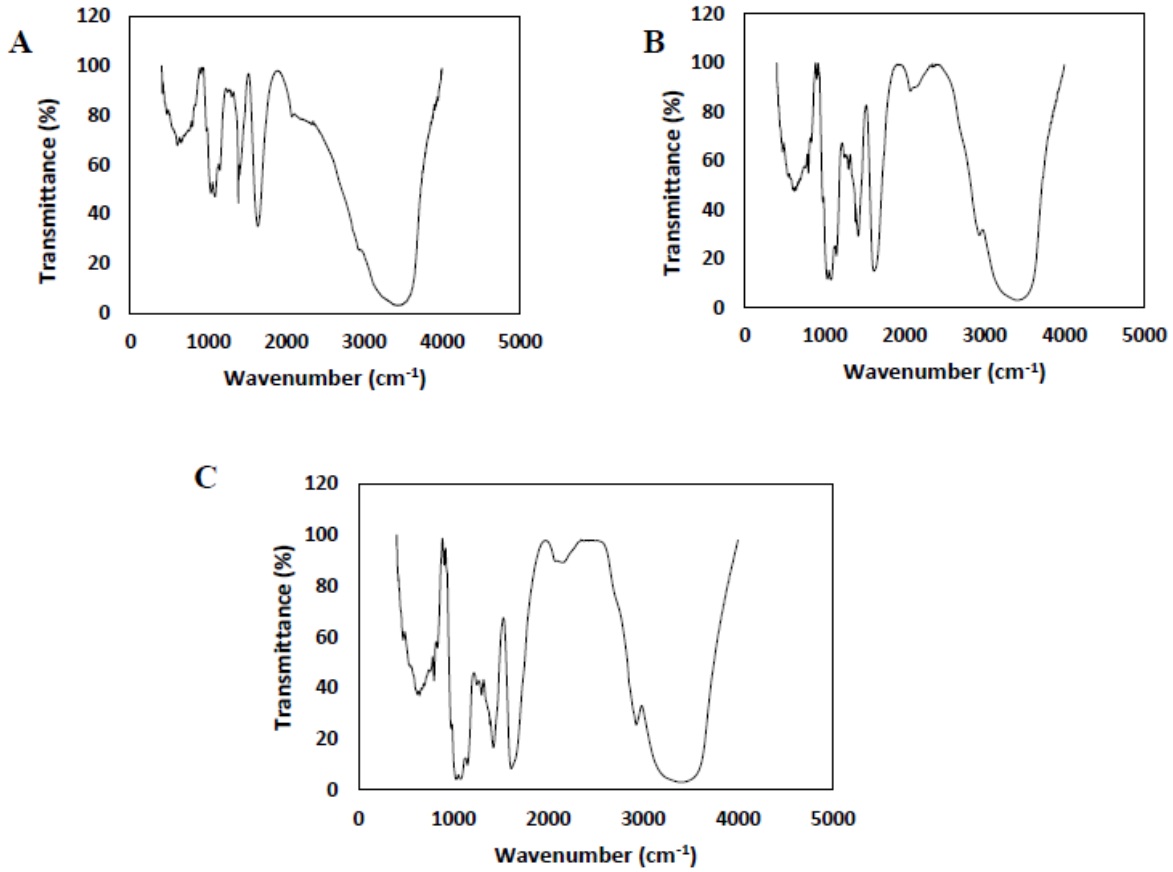

Figure 4.1. FT-IR plots of RDE (A), AlDE (B) and MgDE (C).

4.1.2. Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

The surface morphology and internal structure of the sorbent before and after fluoride sorption are presented in Figure 4.2. SEM images of modified sorbent before fluoride adsorption showed a more porous and flaky surface than the RDE micrograph due to the existence of aluminium and magnesium which improved the sorbent surface capacity for more adsorption (Mukherjee & Halder, 2018). The surface morphology of MgDE (Figure 4.2.E) was more porous showing more active sites for adsorption than AlDE (Figure 4.2.C). The spent sorbent showed a surface more homogeneous as the surface was free in the raw sorbents, although it was occupied by the sorbate in the modified one. In contrast to data recorded in this study, mucilage of *Ocimum basilicum* employed for deflouridation displayed a heterogeneous, irregular and lumpy adsorption surface (Lodhi et al., 2019).

EDX spectrum of raw sorbent (Figure 4.3.A) analysis had Fe, S and Na elements which deformed after F^- adsorption. AlDE also displayed (Figure 4.3.C and D) disappearing and appearing of elements after F^- adsorption. Major elemental composition peaks between RDE,

AlDE and MgDE sorbent recorded were carbon, calcium, potassium, oxygen, magnesium, aluminium, cobalt, silicon and sodium which confirmed the presence of functional groups reported in FT-IR results. As observed in *Abelmoschus esculentus* mucilage, calcium and magnesium were spotted numerous times in Figure 4.3 (Prasad et al., 2019).

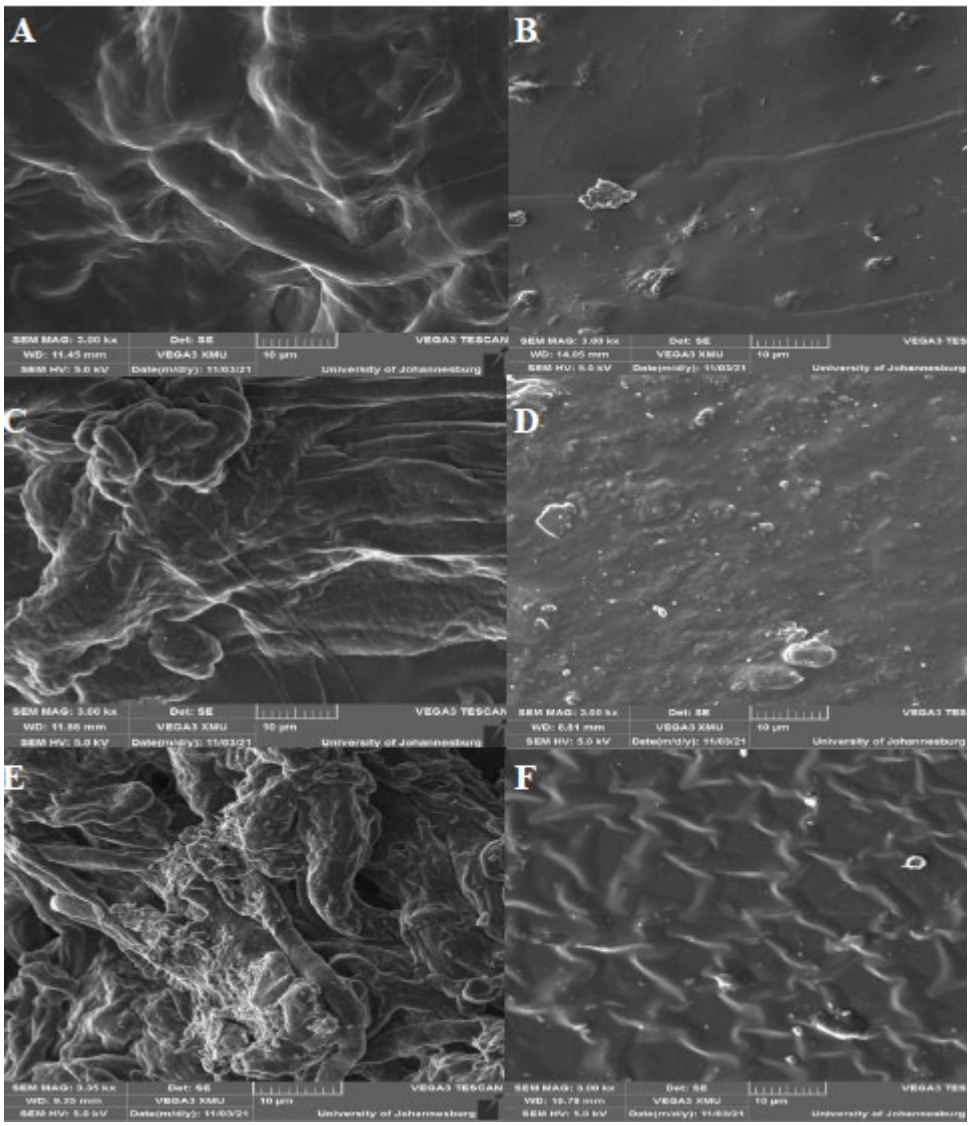

Figure 4.2. SEM images of RDE (A), AlDE(C) and MgDE (E) before fluoride adsorption. RDE (D), AlDE (D) and MgDE (F) images of after fluoride adsorption

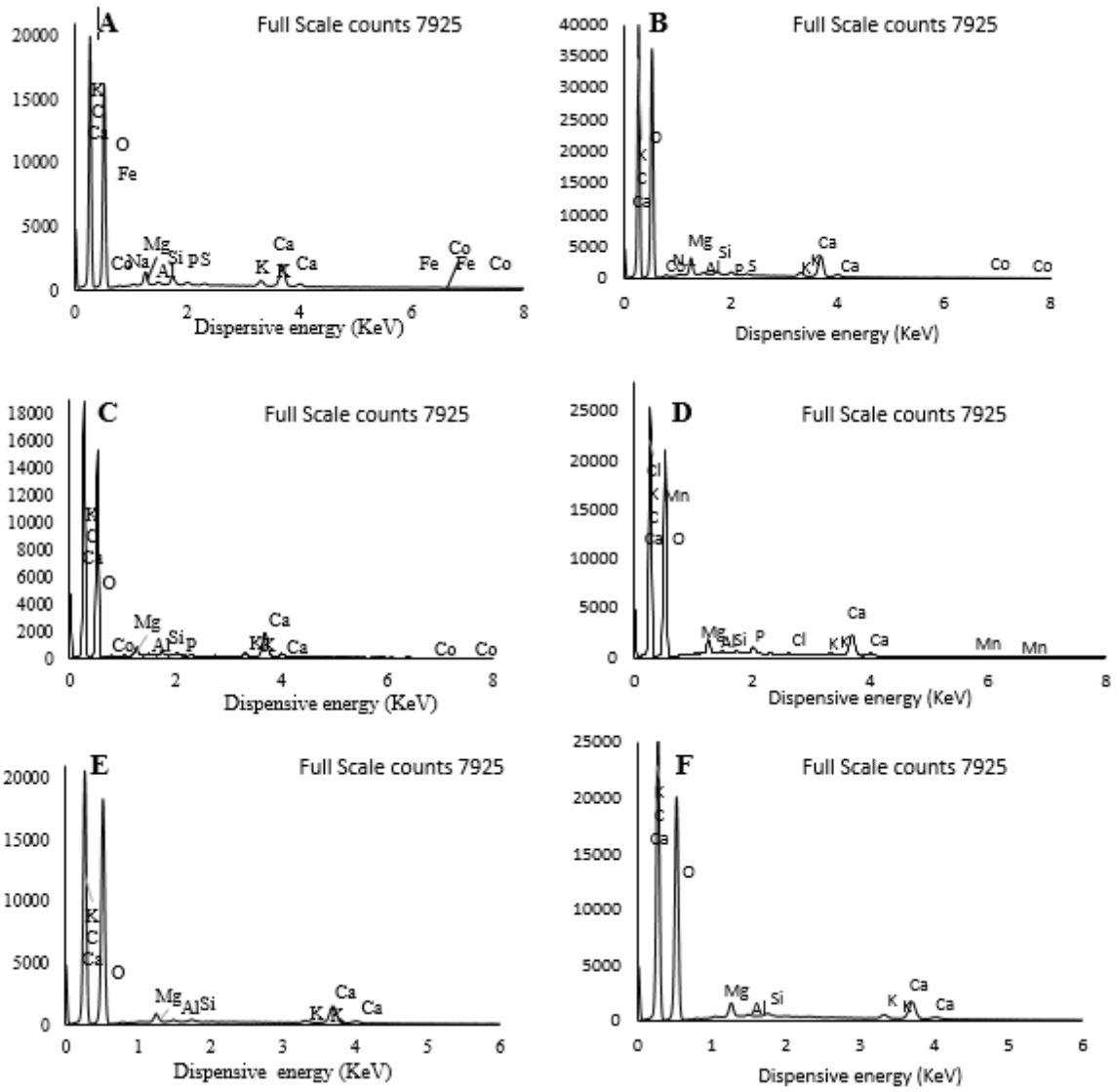

Figure 4.3. EDX plots of RDE (A), AlDE (C), MgDE (E) prior and RDE (B), AlDE (D) and MgDE (F) after fluoride adsorption

4.1.3. X-ray fluorescence (XRF)

Chemical composition in RDE, AlDE and MgDE are listed in Table 4.2. Modification with 0.1M Al and 0.1M Mg enhanced the chemical composition of aluminium and magnesium in the sorbent with 0.76% (AlDE) and 1.62% (MgDE) when compared to RDE, respectively. The chemical composition increased these major elements (Al and Mg) responsible for attracting fluoride ions and enhanced the sorption process as expected. Calcium composition was the highest in AlDE recording 59.36% after modification while MgDE recorded 57.65%. The abundance of calcium in the sorbents confirmed the high removal potential of fluoride due to strong chemical attraction between Ca and F^- which corresponds to the results of EDX

mentioned above (Chinnakoti et al., 2016). Oxides of manganese, aluminium and strontium also increased with modification but with a slight difference when compared to RDE, while, silicon, iron, potassium, sulphur, sodium, titanium and rubidium decreased in percentage composition in AlDE and MgDE modified sorbent. *Malva verticillata* mucilage also recorded similar elemental composition with calcium ranked the highest and the presence of magnesium has been reported to cause sorbent knit-webbed texture (Korir et al., 2018).

Table 4.2. XRF analysis of sorbents.

	RDE (%)	AlDE (%)	MgDE (%)
CaO	52.28	59.36	57.65
SiO_2	9.75	7.09	5.82
Fe_2O_3	8.46	6.63	5.91
MgO	8.33	7.16	9.95
K_2O	7.85	6.21	6.93
P_2O_5	3.96	3.85	4.10
MnO	2.73	3.79	3.28
SO_3	2.14	1.32	1.76
Al_2O_3	1.98	2.74	2.21
SrO	0.81	0.88	1.10
Na_2O	0.73	0.37	0.56
TiO_2	0.70	0.43	0.42
Cl	0.16	0.16	0.24
Rb_2O	0.10	-	0.06
Total	100.00	100.00	100.00

4.1.4. X-ray diffractometer (XRD)

Diffraction patterns that determine the crystalline or amorphous forms of the sorbents are displayed in Figure 4.4 (Chunhui et al., 2018). XRD data displayed a lot of amorphous material with few random crystalline peaks. There was a significant decrease of sharp, intense and high peaks of crystalline at 2-theta angle 26.58˚ noted from RDE after modification (Figure 4.4.B-C) (Lin et al., 2017). AlDE displayed a small peak at an angle of 26.55˚ (Figure 4.4.B). MgDE did not show any sharp nor well-defined peaks, thus, corresponding to an amorphous surface (Figure 4.4.C). A broad peak that was common among RDE, AlDE and MgDE was observed between 20 and 30 theta degrees which shows the existence of carbon content that bonds with silicon (Armynah et al., 2019). The responding crystal structure confirms the presence of quartz, calcium alumosilicate and cordierite in Figure 4.4.A, while in Figure 4.4.B quartz, mullite and orthopyroxene were observed, however, only the quartz displaying the presence of silicon dioxide was observed in modified AlDE and MgDE. A study by Prasad et al. (2019) reported sharp peaks in *Abelmoschus esculentus* mucilage indicating pure

crystallinity, while Sayyad and Sakhare (2018) reported an amorphous nature from *Ocimum basilicum* mucilage.

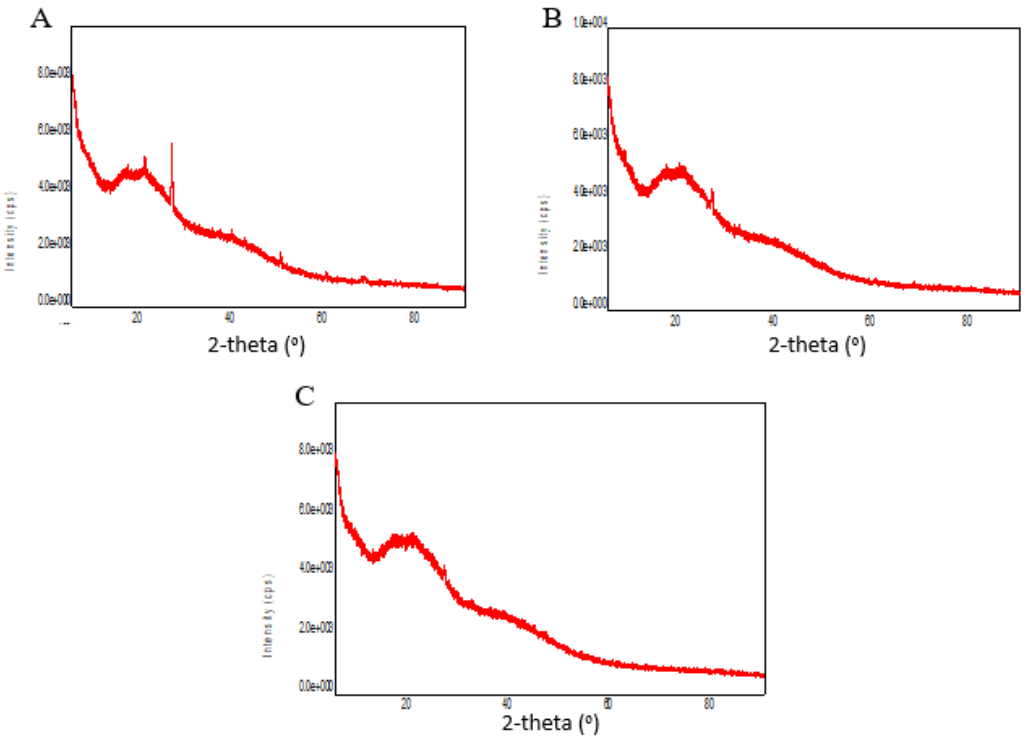

Figure 4.4. XRD peaks for RDE (A), AlDE (B) and MgDE (C) before adsorption of fluoride

4.1.5. Thermo-gravimetric analysis (TGA)

To determine the thermal stability of the sorbents' weight loss, decomposition rate and heat difference were analysed using thermogravimetric (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC), respectively. The results obtained are displayed in Figure 4.5. TGA showed the same trend of mass loss among the samples with the increase in temperature. From the relationship between DTG and TG, three major steps of thermal degradation were observed in all sorbents. The first mass loss occurred in a range of 90 to 100˚C which can be linked to bound water (Burhenne et al., 2013; Zhou et al., 2019). The greatest mass loss was recorded in the second loss stage observed between 200 to 380˚C showing the highest endothermic peak which constitutes about 43% mass loss corresponding to the disintegration of hemicellulose and cellulose on both sorbents (Madera-Santana et al., 2018; Mansor et al., 2019; Waters et al., 2017). The third step of mass loss was observed in a range of 420 to 500˚C which can be assigned to lignin degradation (Andrade et al., 2019; López-Beceiro et al., 2021). Thermal stability of mass between the range of 553 to 689˚C

displayed no significant weight loss which is less than 8% (Javanbakht & Shafiei, 2020). These results show that the RDE, AlDE and MgDE are stable between temperatures 0 and ~210˚C (Janssen Radley et al., 2019). DTA-TG results of biochar impregnated with magnesium oxide usually displayed high thermal stability as compared with this study with only ~25% mass loss between ~10 to 800˚C (Wan et al., 2019). A study by Bessaies et al. (2021) also observed two steps of thermal decomposition displaying endothermic process at ~310 and 490˚C. Three decomposition patterns were observed in Figure 4.5 for differential scanning calorimetry (DSC) analysis. The first ramp had a low heat difference displaying a small endotherm peak (~60˚C) when compared to the second ramp (~400˚C). The third ramp (~485˚C) displayed a high DSC curve showing an exothermic reaction in the sample; this shows high evaporation which is mostly observed in organic compounds (Madera-Santana et al., 2018).

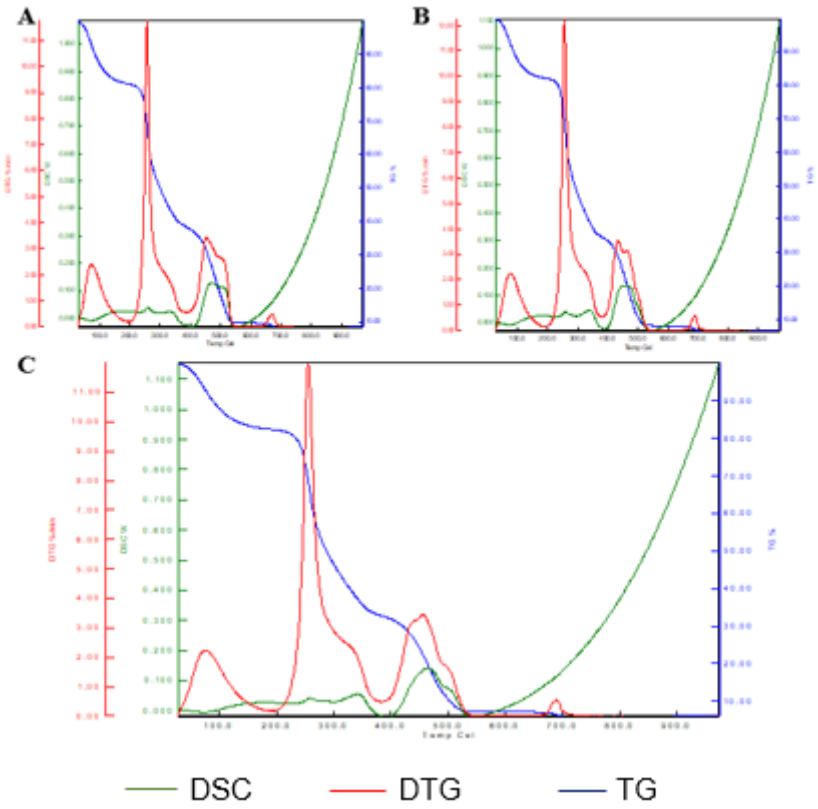

Figure 4.5. TG, DTG and DSC analysis of RDE (A), AlDE (B) and MgDE (C)

4.1.6. Elemental composition

The elemental composition of RDE, AlDE and MgDE adsorbent are listed in Table 4.3. Carbon content ranked the highest percentage composition, then followed by hydrogen and nitrogen was the least. MgDE recorded the highest carbon content when compared to AlDE and RDE. The increase of hydrogen element in MgDE is associated with the potential of the sample to

be a chemical agent responsible for dehydrogenation (Bhomick et al., 2019). Rajkumar et al. (2019) reported a decrease in hydrogen (1.61%) and nitrogen (1.33%) which was higher than the difference found in this study. Sulphur was not detected in the adsorbents analysed.

Table 4.3. Elemental analysis.

	Carbon%	Hydrogen%	Nitrogen%
1. RDE	31.43	6.01	0.67
2. AlDE	32.70	5.96	0.65
3. MgDE	32.96	5.82	0.67

4.1.7. Proximate

Chemical properties of the adsorbents (RDE, AlDE and MgDE) before fluoride adsorption were determined and listed in Table 4.4. RDE recorded the highest ash content and moisture content than AlDE and MgDE. Moisture content below 15% is associated with long shelf life due to the low possibility of microbial growth in the product (Andrade et al., 2019; Pasha et al., 2021; Sheela & Vimala, 2021). Volatile matter recorded by all the adsorbents used was higher than the ash content which showed a high quantity of organic content after heating. The use of activated carbon derived from *Aegle marmelos* shells experimented with by Singh et al. (2017), however, recorded 33.01% and 55.07% of volatile matter and ash content, respectively. MgDE adsorbent recorded high fixed carbon (14.45%) which confirms the improvement of the surface area enhancing the adsorption capacity of the adsorbent when compared to RDE (11.78%). However, activated carbon from the *Catha edulis* stem recorded higher fixed carbon of 53% (Fito et al., 2019), when compared to this study.

Table 4.4. Proximate analysis data.

	Ash (%)	Moisture (%)	Volatile matter (%)	Fixed carbon (%)
1. RDE	8.49	14.99	64.74	11.78
2. AlDE	6.29	12.23	68.64	12.84
3. MgDE	5.67	12.12	67.76	14.45

4.2. ADSORPTION EXPERIMENTS

4.2.1. Effect of Dosage

The sorbent dosage usually influences the amount of sorbate to be adsorbed in a solution (Edokpayi & Makete, 2021). The effect of sorbent dosage was studied in a 10 mg/L fluoride solution. The relationship between sorbent dose and percentage removal of fluoride is

displayed in Figure 4.6. An optimum removal efficiency of 84.23% was recorded using 0.25 g of AlDE, while MgDE recorded 75.95% and RDE 20%, at a maximum dosage of 1 g/100 mL. AlDE reached equilibrium at 0.25 g dosage, thereafter, there was a slight decrease of removal efficiency, even though the sorbent mass was increased; this could be due to overlapping or aggregation of active sites in the sorbent surface, however, RDE and MgDE removal efficiency slowly increased with the increase of sorbent. This observation can be the result of the availability of active sites in the sorbent vacant for sorption (Jegede et al., 2021). Similar results have been reported in palm kernel shells in fluoride removal, reaching an equilibrium efficiency with a 0.4 g sorbent (Collivignarelli et al., 2020).

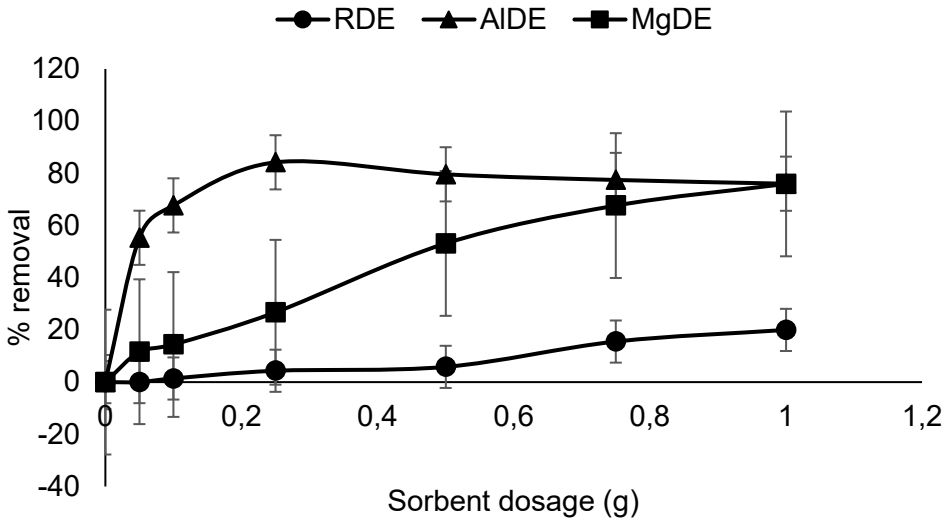

Figure 4.6. Effect of sorbent dosage on percentage removal of fluoride ions in solution

4.2.2. Effect of pH

The pH state (acid, neutral or alkaline) of the solution is essential since it can modify functional groups on the adsorbent surface which, in turn can increase or decrease the removal efficiency of the sorbate (Javanbakht & Shafiei, 2020). Optimum pH was observed at slightly lower pH recording of 76.92% removal of fluoride (Figure 4.7.A). This was due to the availability of positive charges on the adsorbent surface to bind with negative fluoride ions (Mukherjee & Halder, 2018). Defluoridation at pH 5.01 also showed high removal efficiency of 84.23% (Figure 4.7.A) which might be due to excess positive charges from the aluminium in AlDE that bind with negative charges of fluoride ions (Hussein & Vegi, 2020; Marwa et al., 2018). MgDE (Figure 4.7.B) sorption efficiency, however, was higher when compared to AlDE (Figure 4.7.A) in basic fluoride solution. A study by Mereta (2017) also confirmed that removal efficiency of fluoride ions by *Moringa stenopetala* seeds is likely to increase below pH value of 7, while a decrease above pH of 7 is mostly affected by competition between fluoride and

hydroxide ions. It was then concluded that as the initial pH solution was increased, the adsorption of fluoride also reduced with both sorbents due to less active sites and negative hydroxyl ions being available for the adsorption process (Kebede et al., 2016b).

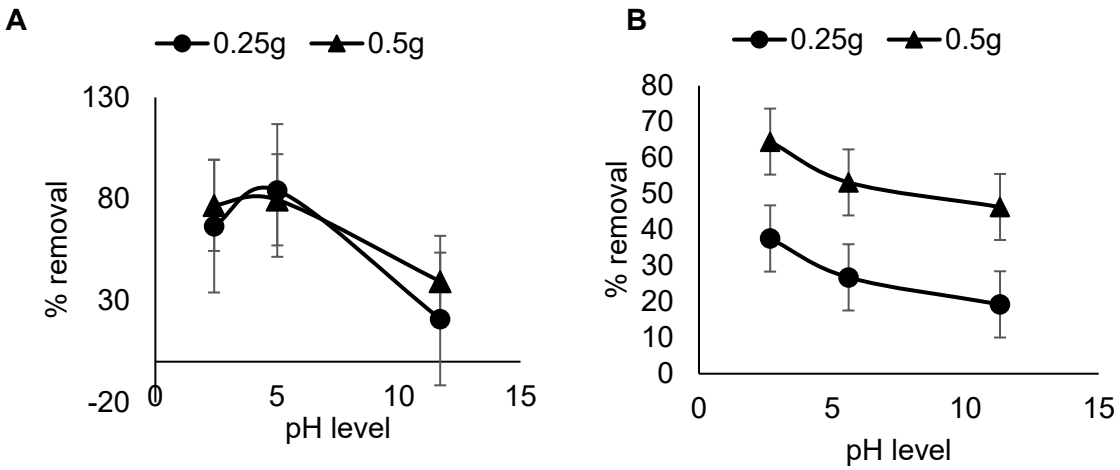

Figure 4.7. Percentage removal for deflouridation study under different pH conditions using AlDE (A) and MgDE (B)

4.2.3. Effect of Time

Contact time of the reaction is essential in determining the sorption equilibrium and it also has a role in kinetics studies (Dessalegne et al., 2018). As shown in Figure 4.8, the increase of contact time during the batch experiment using three masses enhanced the rate of fluoride-ion removal from the solution until equilibrium was reached. It was observed that AlDE attained equilibrium at 120 minutes with the fluoride efficiency ranging from 43.2 to 74.9%. The rapid uptake of fluoride by MgDE was attained within 150 minutes (4.61 to 73.79%). Both the sorbents used showed consistency in reaching equilibrium and beyond equilibrium; there was a decline in fluoride sorption. This could be due to the availability of vacant sites on the sorbents until saturation at equilibrium with fewer sorption sites beyond equilibrium time. Fluoride adsorbent extracted from *Psidium guajava* leaves reached equilibrium at 180 minutes (Shukla et al., 2016), which was higher than equilibriums recorded in this study.

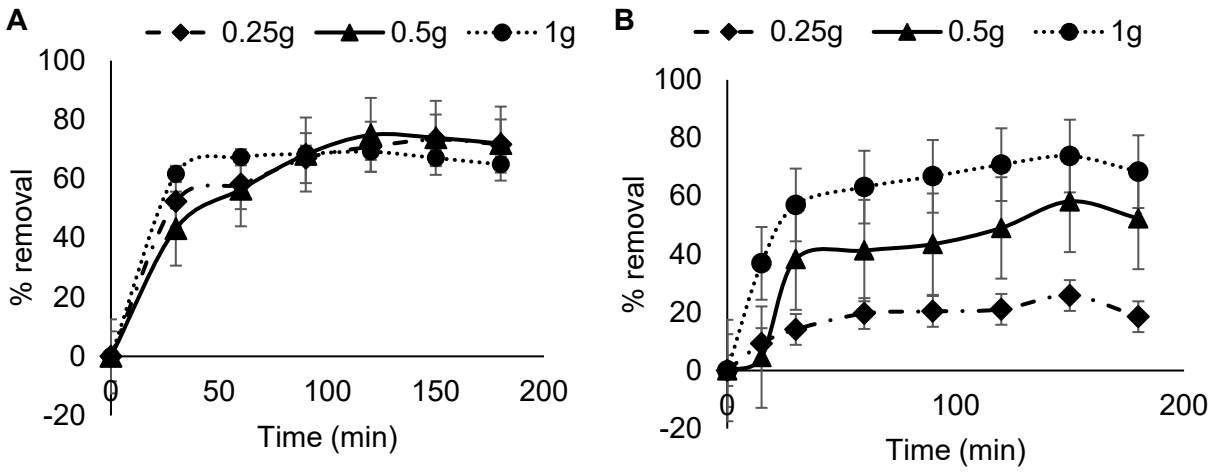

Figure 4.8. Effect of time on deflouridation using AlDE (A) and MgDE (B)

4.2.4. Effect of temperature

Temperature is essential during defluoridation, however, it can bind or alter the physical properties of the sorbent (Yadav et al., 2018). The effect of temperature during fluoride adsorption is displayed in Figure 4.9. An exothermic process was observed and the increase of temperature decreased fluoride adsorption by the sorbents used (Collivignarelli et al., 2020). The results showed MgDE sorbent having higher fluoride sorption in both 0.25 and 0.5 g dosages when compared to AlDE sorbent as the temperature increases. The sorption process was favourable within the range of 20 to 35˚C due to the availability of active sites on the sorbent surface. Temperatures beyond 35˚C reported low percentage removal of fluoride as a result of layer coating of the sorbent which reduced the adsorption capacity and ions interaction between sorbent and fluoride solution (Mukherjee & Halder, 2018). A previous study, Ghomashi et al., (2020) reported a decrease of fluoride adsorption as the temperature increased in modified nano-clinoptilolite, thus, agreeing with the findings of this study.

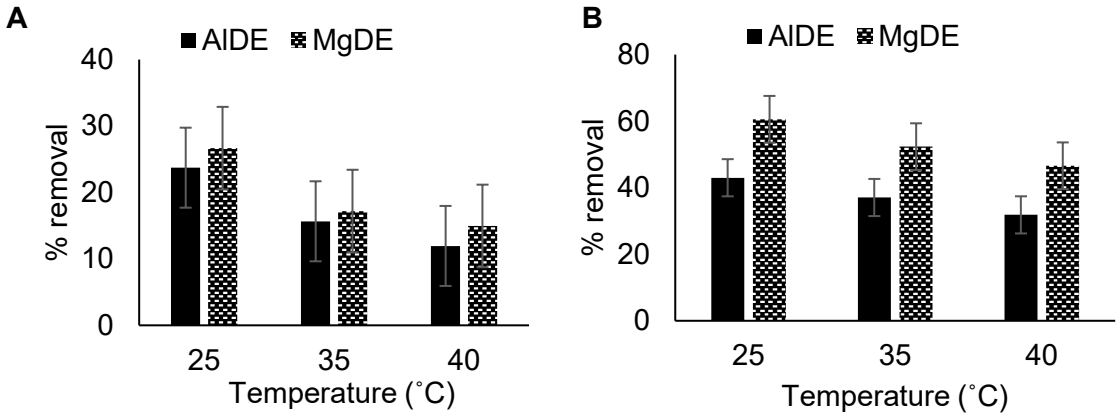

Figure 4.9. Effect of various temperatures during deflouridation process with 0.25 g (A) and 0.5 g (B)

4.2.5. Effects of change in water chemistry

The water source plays a role in its chemistry. AlDE and MgDE were tested on synthetic fluoride solution (4.94 mgF^-/L) and random borehole water (4.83 mgF^-/L) from Siloam, South Africa; the batch adsorption results are displayed in Figure 4.10. The use of 0.5 g of AlDE recorded fluoride removal efficiency of 69.36% with a reduction of fluoride levels in natural water from 4.83 to 1.48 mg/L which complied to the WHO and SANS standards of drinking water (1.50 mg/L). The use of MgDE, although this recorded a removal efficiency of 53.83%, only reduced the initial fluoride levels to 2.23 mg/L which does not comply to regulatory standards. Deflouridation using AlDE and MgDE, as in this study was better on natural water than synthesized fluoride solution. These results confirm the potential of using AlDE on real-life fluoride-rich water from groundwater, however, Wirtu et al., (2021) reported 85.06% removal efficiency and 2.3 mg/L fluoride residual which is above WHO guideline, using aluminium-coated stilbite tuff applied on well water.

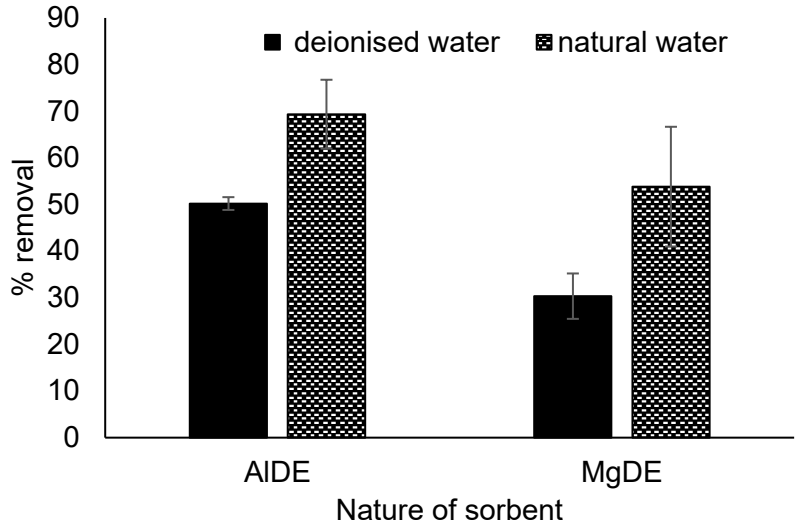

Figure 4.10. Application of sorbents in deionised and natural water

4.3. EQUILIBRIUM STUDIES

4.3.1. Isotherm studies

Linearized plots of Langmuir and Freundlich isotherms obtained from Equations 3.7 and 3.8 are displayed in Figure 4.11, respectively. Slope and intercept from the isotherms equations and adsorption capacity of the sorbents were used to calculate constants presented in Table 4.5. Freundlich isotherm using AlDE recorded the lowest positive coefficients (R^2) ranging from

0.67 to 0.83 when compared to MgDE ranging from 0.95 to 0.99. The overall sorption data best fit the Langmuir model based on R^2 of AlDE (0.89 - 0.91) and MgDE (0.96 – 0.98) (Edokpayi et al., 2020). This study, therefore, confirms the monolayer and homogenous sorption process on sorption sites showing an equal affinity for fluoride ion (Raghav & Kumar, 2019). The separation factor (R_L) of this study were less than one (0.44 – 0.71) which shows that sorbents were favourably confirming the Langmuir adsorption process (Shikuku et al., 2018). AlDE recorded a higher adsorption capacity (69.65 mg/g) than MgDE (41.84 mg/g). Table 4.6 displayed the adsorption capacity (q_e) of AlDE and MgDE when compared with other reported studies.

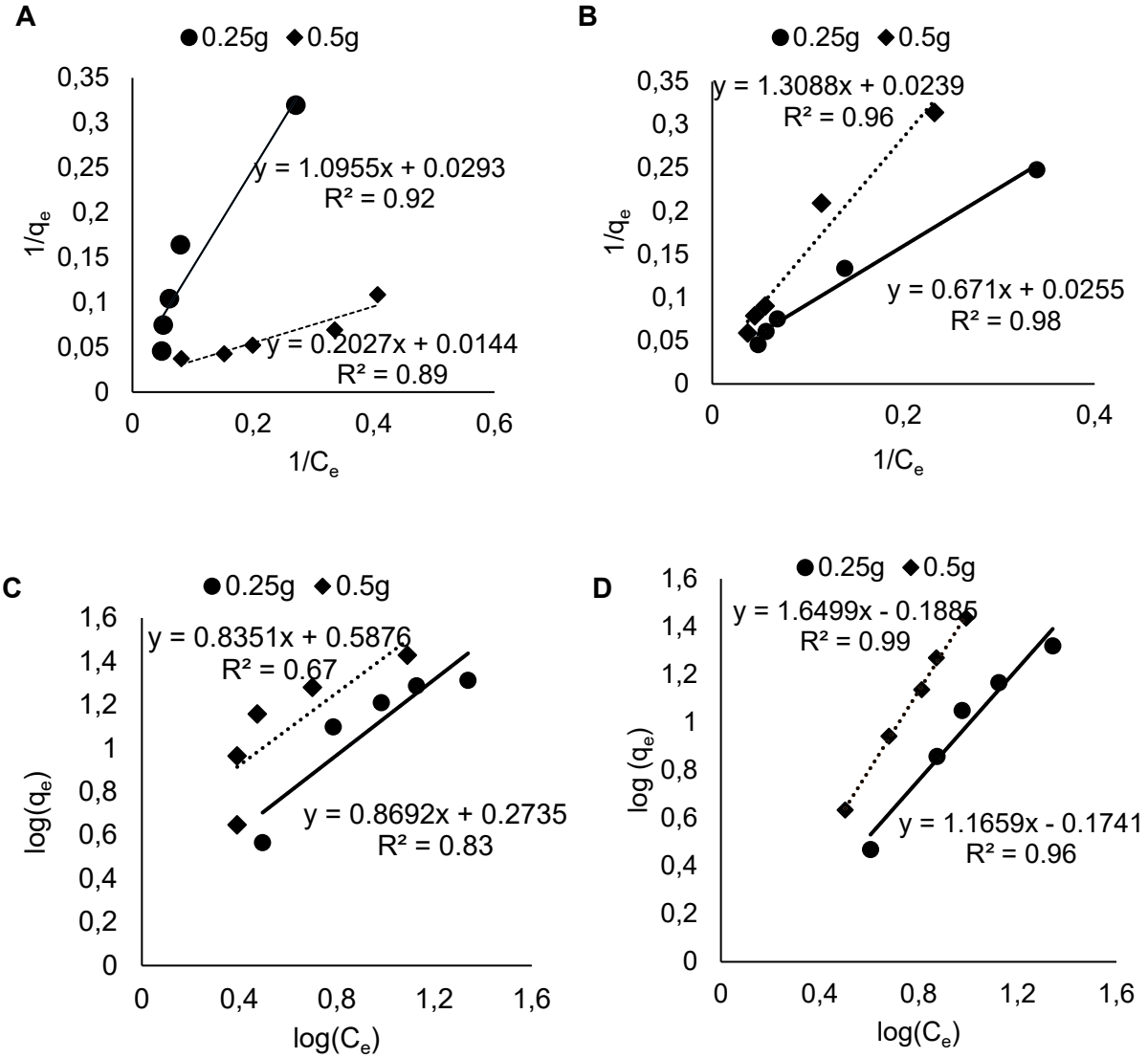

Figure 4.11. Langmuir isotherm plot for AlDE (A) and MgDE (B). Freundlich isotherm plot for AlDE (C) and MgDE (D) sorbent

Table 4.5. Isotherm model Constants

		Langmuir				Freundlich		
Adsorbent	Mass (g)	Q_e (mg/g)	K_L (L/mg)	R^2	R_L	K_F (mg/g)	R^2	n_f
AlDE	0.25	34.13	0.03	0.92	0.68	1.88	0.83	1.15
	0.5	69.65	0.07	0.89	0.44	3.87	0.67	1.20
MgDE	0.25	39.21	0.04	0.98	0.55	0.66	0.96	0.85
	0.5	41.84	0.02	0.96	0.71	0.70	0.99	0.63

Table 4.6. Comparison of different fluoride sorbent applied in groundwater

Sorbent used	**Initial F^- concentration (mg/L)**	**Dosage (g/L)**	**Q_e (mg/m)**	**Reference**
AlDE	4.94	0.5	69.65	This study
MgDE	4.94	0.5	41.84	This study
Aluminium metal embedded *Thuja Occidentalis* leaves carbon	1.2	20	0.625	Vaddi et al., (2021)
Aluminium coated stilbite	15.4	40	0.033	Wirtu et al., (2021)
Aluminium and iron pectin biopolymeric Material	10	5	0.175	Raghav and Kumar (2019)
Nitric acid activated carbon derived from *Vitex negundo* bark	4.27	4	0.088	Suneetha et al., (2015)

4.3.2. Kinetics studies

To determine the kinetics of the sorption process, the pseudo-first and second-order models were plotted (Figure 4.12.A-D). Linearized coefficient (R^2) for kinetics models in Figure 4.12 gave a range of 0.09 – 0.99. Based on the R^2, sorption of fluoride ion on AlDE and MgDE best fits pseudo-second-order recorded with R^2 ranged between 0.98 – 0.99 for both dosages used. Many studies tend to fit in with pseudo-second-order due to the hypothesis which predicts that adsorption rate (K_2) is independent of chemical sorption which involves ions exchange during fluoride adsorption (Meilani et al., 2021). Figure 4.12E-F shows that the intra-particle diffusion plots for AlDE and MgDE did not pass the origin displaying that particle diffusion is not the sole rate-controlling step. Furthermore, it can be confirmed that film diffusion is also involved in the rate-determining step suggesting that the fluoride sorption mechanism for this study is multilinear (Edokpayi et al., 2020). The thickness of the sorbent layer ranged 0.8635 – 0.9555 (AlDE) and 6.0884– 8.4617 (MgDE) which are greater than zero displaying that the boundary layer of MgDE was thicker than that of AlDE (Alhassan et al., 2020). It was also observed that the increase of sorbent dose results in decreasing regression coefficient and intraparticle diffusion rate constant (Table 4.7).

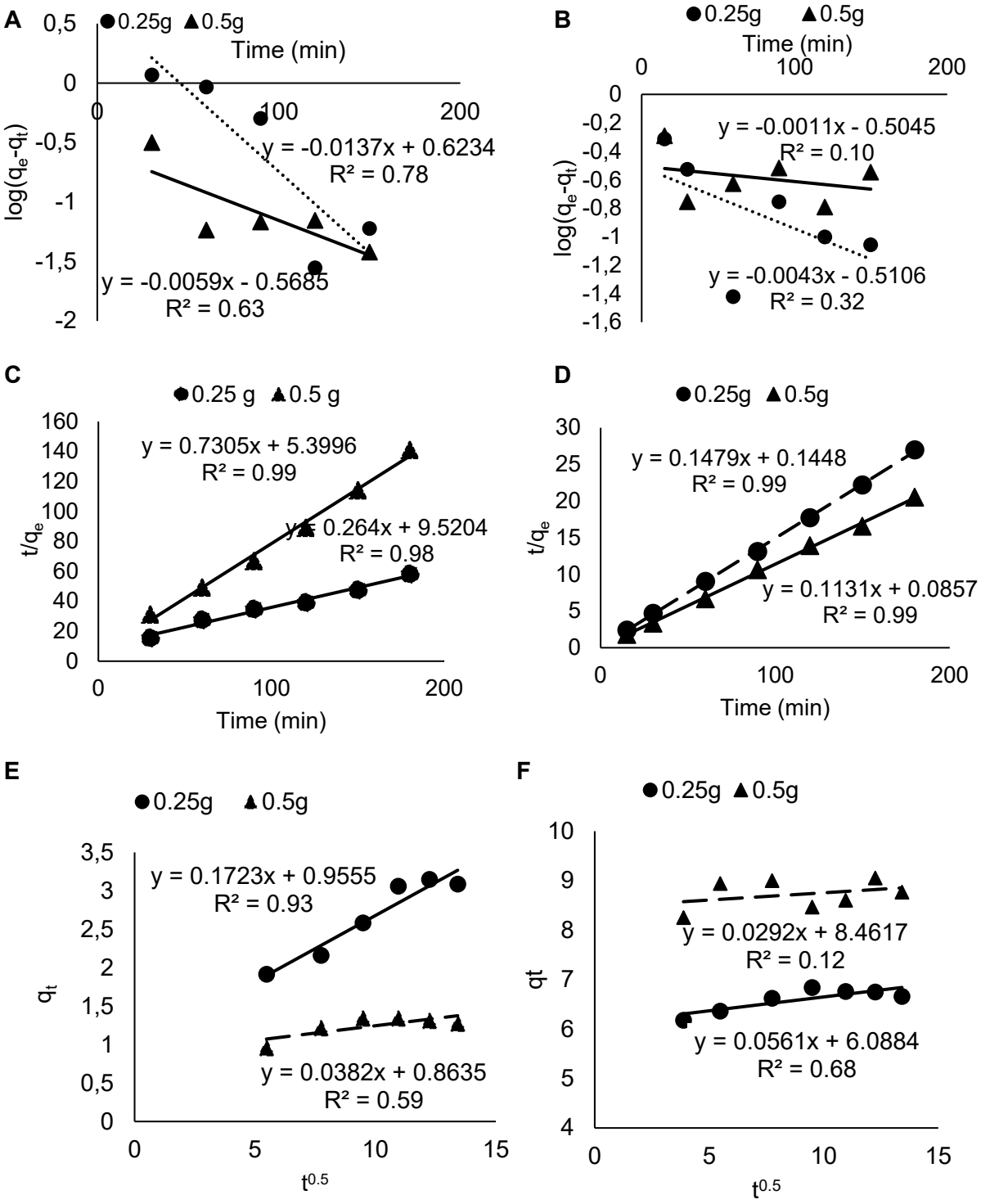

Figure 4.12. Pseudo 1st order for AlDE (A) and MgDE (B). Pseudo 2nd order of AlDE (C) and MgDE (D). Intra-particle diffusion of AlDE (E) and MgDE (F)

Table 4.7. Kinetics constants.

		Pseudo 1st order			Pseudo 2nd order			Intra-particle Diffusion	
Sorbent	Mass (g)	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg min^{-1})	R^2	K_i ($mg/g.min^{0.5}$)	R^2
AlDE	0.25	4.20	2.78	0.78	3.78	0.01	0.98	0.17	0.93
	0.5	0.27	1.19	0.63	1.37	0.10	0.99	0.04	0.59
MgDE	0.25	0.31	0.88	0.32	6.76	0.15	0.99	0.06	0.68
	0.5	0.31	0.22	0.10	8.84	0.15	0.99	0.03	0.12

4.3.3. Thermodynamics

Effect of temperature has an impact during fluoride adsorption process depending on the composition of the adsorbent in use (Mukherjee et al., 2018). Figure 4.13 displays the Van't Hoff plot computed from lnK_o against 1/T for AlDE and MgDE with R^2 ranging from 0.88 to 0.99. The plot provided the slope and intercept for calculating both enthalpy and entropy. Thermodynamics parameters computed are listed in Table 4.8. The exothermic process was confirmed when negative enthalpy (ΔH°) was recorded confirming the exothermic sorption process. There was a decrease of ΔH noted with the increase of sorbent mass. Similar observations in lichen biomass adsorbent were reported by Mondal and Kundu (2016). ΔG recorded negative readings in all the temperatures used for the batch experiment which show that fluoride adsorption by AlDE and MgDE is spontaneous and feasible. The sorption capacity of the sorbents reduces as the temperature increase. Positive entropy recorded indicates a good attraction between the solution and the sorbent surface. Positive entropy also implies that there is a freedom of movement of fluoride ions during the adsorption process. Negative values of entropy were reported on calcium-chloride modified *Crocus sativus* leaves (Dehghani et al., 2018).

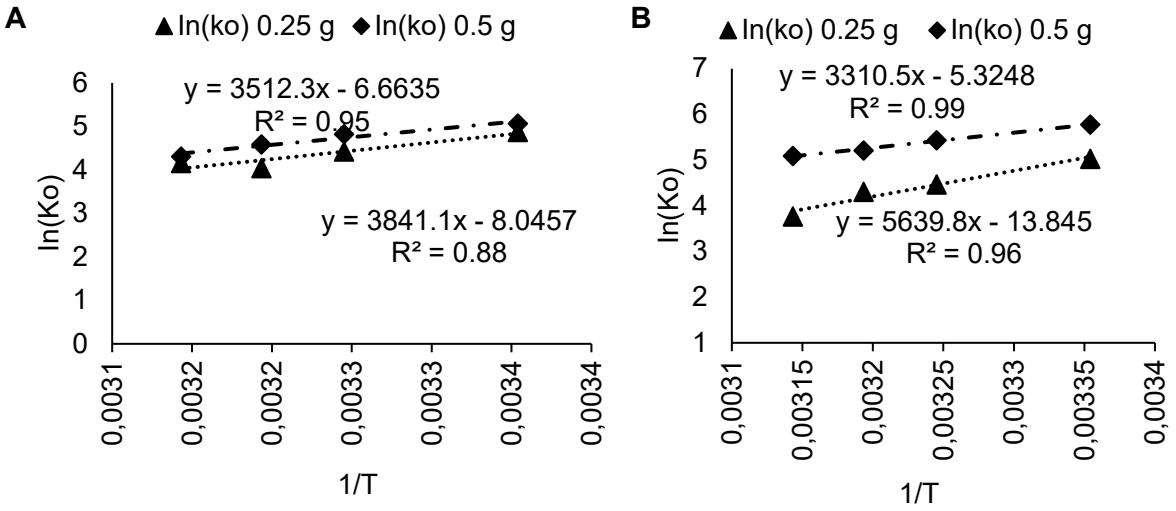

Figure 4.13. Thermodynamics data of AlDE (A) and MgDE (B)

Table 4.8. Thermodynamics parameters

Sorbent	Dosage (g)	-ΔH° (kJ/mol)	ΔS° (J/mol/k)	-ΔG (KJ/mol)			
				298.15K	308.15K	313.15K	318.15K
AlDE	0.25	34.26	0.07	12.08	11.34	10.82	10.70
	0.5	29.20	0.06	12.56	12.35	11.95	11.38
MgDE	0.25	46.89	0.12	12.47	11.46	11.21	9.97
	0.5	27.52	0.04	14.32	13.93	13.58	13.48

ΔH° - enthalpy, ΔS° - entropy, ΔG – Gibb's free energy

4.4. DESORPTION AND REGENERATION

Desorption studies of AlDE and MgDE sorbents after fluoride adsorption data are displayed in Figure 4.14.A. Among the three desorbing agents, deionised water (DW) was more effective and consistent after 3 trials. Moreover, deionised water can be used freely in a household setting with no handling procedures when compared to hydrochloric acid and sodium hydroxide. The hydrogen bonding and electrostatic interaction between desorbing agent and the spent adsorbent played a role in desorption efficiency.

Washing the residual adsorbent surface by DW was performed after each cycle 2 – 3 times before drying. MgDE adsorbent recorded high percentage removal of fluoride from cycle 1 to 3 when compared to AlDE adsorbent (Figure 4.14.B). There was a decrease in fluoride sorption capacity by the adsorbents as the regeneration cycle increased. Depleting of sorbent mass was also observed after each cycle. A column made of *Musa paradisiaca* peels was used for defluoridation for 3 cycles similar to this study when desorbed by 0.1M NaOH (Mondal & Roy, 2018).

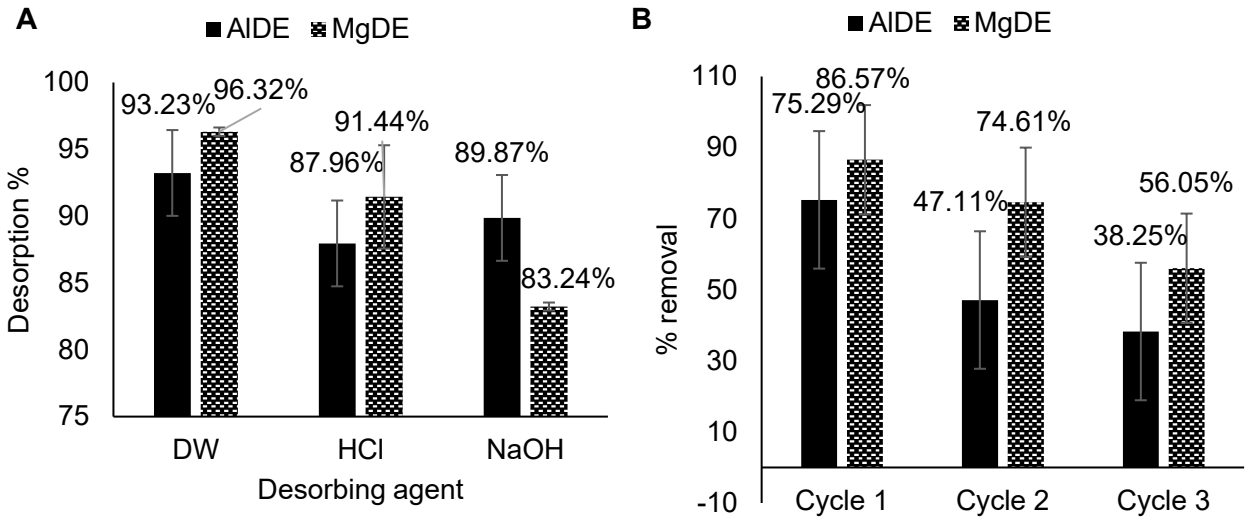

Figure 4.14. Desorption efficiency (A) and regeneration cycle (B)

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1. CONCLUSION

The present study presents findings of deflouridation using modified AlDE and MgDE by adsorption method. The nature of the RDE, AlDE and MgDE was characterised using FT-IR, SEM-EDX, XRF, XRD, TGA, elemental composition, proximate analysis and the optimum adsorption conditions were experimented upon. FTIR analysis revealed the presence of carboxylic acids, esters, alcohol and esters functional groups in the sorbents. Surface morphology with active sites, which were homogenous, together with large and small pores available for adsorption was observed more in the SEM micrographs of MgDE than in AlDE. Major peaks of the EDX spectrum showed the presence of C, Ca, K, Fe, Mg, Si, Al, Mn and Na in AlDE and MgDE which corresponded well with chemical composition from XRF data, however, AlDE displayed higher Ca composition than MgDE which is essential in the fluoride sorption process.

AlDE and MgDE exhibited amorphous nature while RDE showed a single crystalline peak. TGA analysis displayed 3 steps of degradation and mass loss in TG, endothermic reaction in DTG and slow DSC rates between RDE, AlDE and MgDE which confirmed that the adsorbents cannot stand high temperature. Elemental analysis proved that modification had an effect by increasing carbon element 32.70 and 32.96 % in AlDE and MgDE, respectively.

The highest percentage removal recorded was 84.23% from AlDE (0.25 g). Langmuir and Freundlich's models were favoured and applied looking at their high linear correlation. However, the maximum quantity of fluoride adsorbed (Q_e) were 69.65 mg/g (AlDE) and 41.84 mg/g (MgDE). Kinetics studies followed the Pseudo 2nd order kinetic model and the intra-particle diffusion displayed a complex deflouridation reaction mechanism revealing the possibility of other rate-controlling steps involved in the adsorption process. Enthalpy change showed an exothermic process, while the reaction was spontaneous and feasible denoted by the negative free Gibb’s energy change. Deionised water was a suitable and eco-friendly desorbing agent and was used for regeneration studies.

5.2. RECOMMENDATION

This study investigated the development of fluoride adsorbent using *Dicerocaryum eriocarpum* (DE). This provided insight into batch adsorption experiments and characterisation analysis performed; the process showed the potential of AlDE and MgDE to adsorb fluoride ions from the solution, however, there are some recommendations for future studies in line with this work:

- Column studies using sorbents should be investigated.
- There is a need to develop a base for the sorbents.
- There should be further investigation as to whether sorbents regenerations require enhancement to increase the number of cycles, while removing toxic fluoride from the water.

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