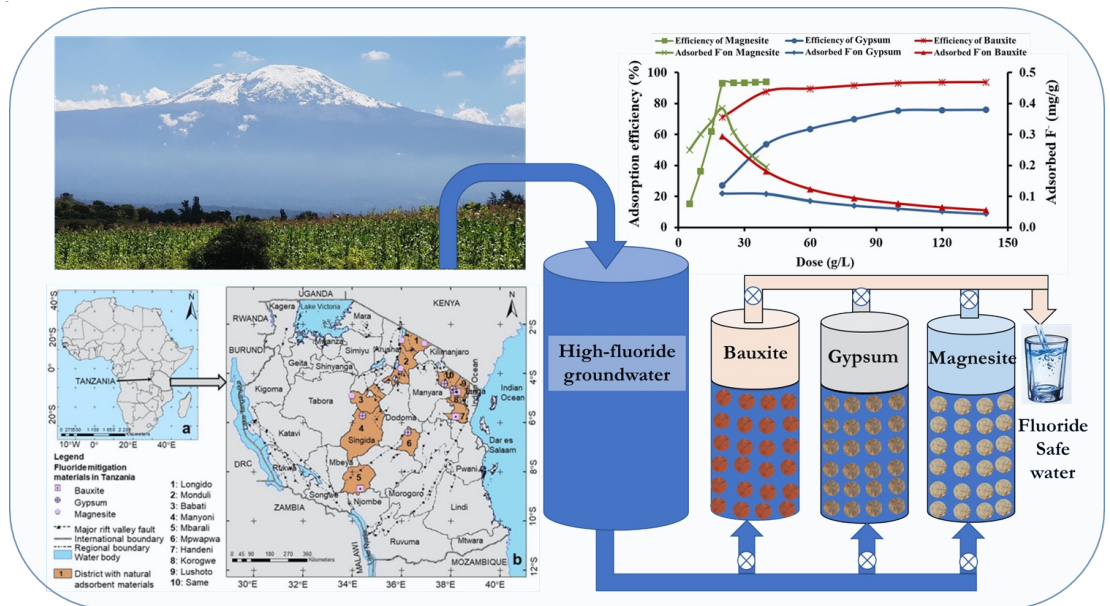


Doctoral Thesis in Land and Water Resources Engineering

# Groundwater defluoridation by natural minerals

Understanding the process of fluoride removal from drinking water sources in Tanzania

VIVIAN KIMAMBO



# Groundwater defluoridation by natural minerals

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VIVIAN KIMAMBO

Academic Dissertation which, with due permission of the KTH Royal Institute of Technology, is submitted for public defence for the Degree of Doctor of Philosophy on Wednesday the 14th of June 2023, at 1.00 pm at Room Sahara, Teknikringen 10B, KTH Royal Institute of Technology, Stockholm and on zoom (<https://kth-se.zoom.us/j/64600615013>).

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Cover page photo and illustration:

The view of the highest peak of the volcanic mountain Mount Kilimanjaro in the East African Rift Valley. The inset maps of Africa and the locations of the occurrence of the natural minerals bauxite, gypsum and magnesite in northern Tanzania. The right panel is the setup of the column experiments and the performance of each of these natural minerals for fluoride removal.

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## DEDICATION

*To  
My Parents  
and  
My Siblings*



*“Safe and readily available water is important for public health, whether it is used for drinking, domestic use, food production or recreational purposes.” (WHO, 2022)*



## SAMMANFATTNING

Förhöjda koncentrationer av fluorid ( $F^-$ ) i grundvattnet är en av vattenkvalitetsparametrarna som utgör en betydande utmaning för säker dricksvattenförsörjning i flera länder globalt. Naturliga mineraler har visat avsevärd effektivitet för att avlägsna fluor. I denna studie har prestandan hos de lokalt tillgängliga naturliga mineralerna, såsom bauxit, magnesit och gips, undersökts i laboratorieskala genom modellering av fluoridavlägsnande från grundvattenkällor i Tanzania. Batchförsök utfördes för att undersöka de optimala förhållandena för  $F^-$  borttagning av den kalcinerade bauxiten, magnesiten och gipsen. Röntgenfluorescens (XRF) spektroskopisk karakterisering visade att  $Al_2O_3$ ,  $MgO$  och  $SO_3$  var de viktigaste oxiderna i bauxit, magnesit respektive gips. Experimentell data för de tre behandlade adsorbenterna följde väl med Freundlich-adsorptionsisotermer och pseudo-andra ordningens kinetik. Värdena för  $\Delta G^\circ$  och  $\Delta H^\circ$  indikerar att  $F^-$  adsorptionen på bauxit- och magnesitytor var spontan och endoterm. Slumpmässigheten, som beskrivs av  $\Delta S^\circ$  vid gränssytan mellan fasta fasen och vätskan, ökade under adsorptionsprocesserna. Medan för gips var reaktionen spontan och exoterm, där slumpmässigheten vid gränssytan mellan fasta fasen och vätskan minskade under adsorptionsprocesserna. Vid optimala förhållanden, sänkte kalcinerad bauxit (400 °C), magnesit (650 °C) och gips (350 °C)  $F^-$  koncentrationen från 8,27 mg/L till 1,02, 0,233 respektive 1,99 mg/L. Bauxit och gips sänkte vattnets pH från 9,38 till 6,74 respektive 7,41. Magnesit höjde pH-värdet från 9,38 till 10,12 vilket är över pH-intervallet mellan 6,5 - 8,5 och 6,5 - 9,2 som rekommenderats av Världshälsoorganisationens (WHO) riktlinjer för dricksvatten och Tanzania Bureau of Standards (TBS). Därför justering av pH behövs innan det behandlade vattnet kan användas för dricksändamål. Designmodellen för bädd djupsservicetid (BDST) användes för att karakterisera genombrottsprocesserna. De högre doserna har högre  $F^-$  borttagningseffektivitet och genombrottsstider. Genombrottsstiderna för adsorbentdoserna 3000, 4000, 5000 och 6000 g visade sig vara 14, 28, 95 och 217 minuter för bauxit respektive 6, 22, 70 och 197 minuter för magnesit. De kritiska bädddjupen ( $Z_0$ ) för erhållna bauxit och magnesit var 7,21 respektive 8,28 cm. Bädddjupsservicetid (BDST)-plotten visade att servicetiderna för  $F^-$  adsorption på den kalcinerade bauxit- och magnesitytan ökade med bädddjupet. Det lägre värdet på kinetisk hastighetsparameter ( $K\alpha$ ) för bauxit ( $1,43E-5$  L/mg s) och magnesit ( $1,50E-5$  L/mg s) visade att genombrottet sker i korta bäddar; därför krävs djupare bäddar för att undvika genombrott. De experimentella resultaten och prediktionsmodellerna har hjälpt till att jämföra adsorptionsprocesserna samt kontrastera deras prestanda och hållbarhet för avlägsnande av fluor med hjälp av bauxit, magnesit och gips i dricksvattenresurserna i Tanzania. Adsorptionsresultaten och den övergripande kostnadsanalysen visar att kostnaden för kalcinerad bauxit och magnesit är låg jämfört med andra tillgängliga adsorbenter; därför kan de användas vid  $F^-$  borttagning från grundvatten.

**Nyckelord:** Fluoridavlägsnande; Grundvatten; Naturliga mineraler; Batch- och kolonnförsök; Adsorptionsisotermer; Kinetik och termodynamik; Dricksvattenkvalitet; Hållbarhet.



## IKISIRI

Mkusanyiko wa floridi ( $F^-$ ) katika maji ya kunywa ni mojawapo ya vigezo vya ubora wa maji katika nchi zilizo na ukolezi mkubwa wa  $F^-$  katika vyanzo vya maji. Madini ya asili yameonyesha ufanisi mkubwa kwa kuondolewa kwa  $F^-$ . Katika utafiti huu, utendaji wa madini asilia yanayopatikana humu nchini kama vile bauxite, magnesite na jasi umechunguzwa katika mizani ya maabara na kutoa mfano wa kuondolewa kwa  $F^-$  kutoka vyanzo vya maji ya chini ya ardhi nchini Tanzania. Majaribio ya kundi yalifanywa ili kuchunguza hali bora za uondoaji wa  $F^-$  kwa bauxite iliyokatwa, magnesite na jasi. Tabia ya uchunguzi wa uchunguzi wa X-ray fluorescence (XRF) ilionyesha kuwa  $Al_2O_3$ ,  $MgO$  na  $SO_3$  zilikuwa oksidi kuu katika bauxite, magnesite na jasi, kwa mtiririko huo. Data ya majaribio ya adsorbenti tatu zilizotibiwa ililingana vyema na isotherm ya Freundlich ya adsorption na kinetiki ya mpangilio wa pili wa uwongo. Thamani za  $\Delta G^\circ$ ,  $\Delta H^\circ$  zinaonyesha utepetevu wa  $F^-$  kwenye uso wa bauxite na magnesite ulikuwa wa pekee na wa mwisho wa joto. Nasibu iliyoelezewa na  $\Delta S^\circ$  kwenye kiolesura kigumu-kioevu iliongezwa wakati wa michakato ya utangazaji. Ilhali kwa jasi majibu yalikuwa ya hiari na ya kupita kiasi ambapo unasahi kwenye kiolesura kigumu-kioevu ulipungua wakati wa michakato ya utangazaji. Katika hali bora zaidi, bauxite iliyokaushwa ( $400^\circ C$ ), magnesite ( $650^\circ C$ ), na jasi ( $350^\circ C$ ) ilipunguza mkusanyiko wa  $F^-$  kutoka 8.27 mg/L hadi 1.02, 0.233 na 1.99 mg/L, kwa mtiririko huo. Bauxite na jasi zilipunguza pH ya maji kutoka 9.38 hadi 6.74 na 7.41, kwa mtiririko huo. Magnesite ilipandisha pH kutoka 9.38 hadi 10.12 ambayo ni juu ya Shirika la Afya Duniani (WHO) (6.5 - 8.5) na Shirika la Viwango Tanzania (IBS) (6.5 - 9.2) kiwango cha maji ya kunywa, kwa hiyo marekebisho ya pH yanahitajika kabla ya maji kuongezwa. kutumika kwa kunywa. Mpango wa Muda wa Huduma ya Kina cha Kitanda (BDST) ulionyesha kuwa nyakati za huduma za  $F^-$  adsorption kwenye uso wa bauxite iliyokaushwa na magnesite ziliongezeka kwa kina cha vitanda. Kina muhimu cha kitanda ( $Z_o$ ) kwa bauxite na magnesite zilizopatikana zilikuwa 7.21 na 8.28 cm, kwa mtiririko huo. Thamani ya chini ya kiwango cha mmenyuko mara kwa mara ( $K_d$ ) kwa bauxite ( $1.43E-5 L/mg\ s$ ) na magnesite ( $1.50E-5 L/mg\ s$ ) iliyoangazia mafanikio yatatokea katika vitanda vifupi; kwa hiyo, vitanda vya kina vinahitajika ili kuepuka mafanikio. Matokeo ya majaribio na utabiri wa modeli umesaidia kulinganisha michakato ya utangazaji pamoja na utofauti wa utendaji na uendeleu wa kuondolewa kwa  $F^-$  kwa kutumia bauxite, magnesite na jasi katika rasilimali za maji ya kunywa nchini Tanzania. Bauxite iliyokaushwa na magnesite iliboresha uondoaji wa  $F^-$ .

**Istilahi muhimu:** Kuondolewa kwa fluoride; Maji ya chini ya ardhi; Madini ya asili; isotherms za majaribio ya adsorbenti; Majaribio ya Kundi-na Safu; Kinetics na thermodynamics; ubora wa maji ya kunywa; Uendeleu.



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This thesis was compiled from research articles, which were developed in collaboration with other partners. I, therefore, extend my heartfelt appreciation to the following partners for their time, commitment, and timely feedback on the draft manuscripts sent to them for review: Dr. Arslan Ahmad of SIBELCO Ankerpoort NV, the Netherlands and fellow doctoral students Dr. Fanuel Ligate, Dr. Julian Ijumulana and Regina Irunde of the KTH-International Groundwater Arsenic Research Group at the Department of Sustainable Development, Environmental Science and Engineering, KTH Royal Institute of Technology, Stockholm, Sweden. To you all, I say “Thank you so much”.

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Vivian Kimambo  
Stockholm, June 2023



**LIST OF SYMBOLS**

$\Delta G^\circ$	Gibbs free energy change for the reaction (kJ/mol)
$\Delta H^\circ$	Enthalpy change for the reaction (kJ/mol)
$\Delta S^\circ$	Entropy change for the reaction (kJ/mol K)
1/n	Adsorption intensity (-)
AER	Adsorbent exhaustion rate (g/L)
b	Langmuir isotherm constant that relates to the energy of adsorption (L/mg)
BD	Bed depth (cm)
BDS <sub>T</sub>	Bed depth service time (s)
BV	Bed volume (cm <sup>3</sup> )
C	Thickness of the boundary layer
C <sub>b</sub>	Breakthrough fluoride concentration (mg/L)
C <sub>e</sub>	Equilibrium fluoride concentration (mg/L)
C <sub>o</sub>	Initial fluoride concentration (mg/L)
EBRT	Empty bed residence time (min)
h	Initial adsorption rate (mg/g min)
k	Pseudo-second-order rate constant (g/mg min)
K <sub>x</sub>	Kinetic rate parameter (L/mg s)
k <sub>ad</sub>	Equilibrium rate constant for pseudo-first-order adsorption (min <sup>-1</sup> )
K <sub>c</sub>	Adsorption equilibrium constant
k <sub>F</sub>	Measure of adsorption capacity
k <sub>int</sub>	Intra-particle rate constant (mg/g min <sup>0.5</sup> )
k <sub>p</sub>	Particle rate constant (min <sup>-1</sup> )
m	Mass of adsorbent (g)
N <sub>o</sub>	Adsorption capacity of bed (mg/L)
q <sub>e</sub>	Amount of fluoride adsorbed by one gram of the adsorbent at equilibrium (mg/g)
Q <sup>o</sup>	Amount of adsorbate at complete monolayer coverage (mg/g)
q <sub>t</sub>	Amount of fluoride adsorbed on the surface of the adsorbent at time t (mg/g)
R	Universal gas constant (8.314 J/mol K)
R <sub>L</sub>	Langmuir equilibrium factor
STBP	Service time at breakthrough point (h)
T	Temperature (K)
t	Time (min)
V	Volume of the F <sup>-</sup> solution (L)
VWTB	Volume of water treated at breakthrough (L)
WA	Weight of adsorbent (g)
Z	Depth of column bed (cm)
Z <sub>o</sub>	Critical bed depths (cm)
v	Water flow rate through the bed (mL/h)



## LIST OF APPENDED PAPERS

This dissertation was developed based on the following four papers:

- I. **Kimambo, V.**, Bhattacharya, P., Mtalo, F, Mtamba, J. & Ahmad, A. (2019). Fluoride occurrence in groundwater systems at global scale and status of defluoridation – State of the art. *Groundwater for Sustainable Development* 9, 100223. <https://doi.org/10.1016/j.gsd.2019.100223>
- II. **Kimambo, V.**, Ligate, F., Ijumulana, J, Maity, J.P., Jong, R, Ahmad, A, Hamisi, R, Mtamba, J. Mtalo, F, Bhattacharya, P. (2023). Optimization of fluoride removal using calcined bauxite: Adsorption isotherms and kinetics. *Groundwater for Sustainable Development* 21: 100922. <https://doi.org/10.1016/j.gsd.2023.100922>
- III. **Kimambo, V.**, Ijumulana, J., Ligate, Jong, R., Mtalo, F., Kumar, R., Maity, J.P., & Bhattacharya, P. (2023) Fluoridated groundwater treatment using natural and calcined magnesite and gypsum: System optimization based on laboratory studies on adsorption kinetics and thermodynamic considerations. *Applied Water Science* (AWSC-D-23-00173, Manuscript under review).
- IV. **Kimambo, V.**, Ijumulana, J., Mtalo, F, Ligate, F., Kumar, R., Jong, R., Maity, J.P., Hamisi, R., & Bhattacharya, P. (2023) Pilot column studies on defluoridation of groundwater using calcined bauxite, gypsum and magnesite. *Groundwater for Sustainable Development* (Manuscript under submission, May, 2023).

### Author's contribution to papers

The authors contributions to the papers included and appended in the thesis are as follows:

- I. Conceptualization of the manuscript by formulating the scientific review objectives, literature search strategy, secondary data collection, writing the original draft, and addressing comments and suggestions from other co-authors and reviewers during the preparation and peer-review process.
- II. Conceptualization of the study, field visits, data collection, data analysis, interpretation of the results, and writing of the first draft of the manuscript. Furthermore, the author was responsible for addressing comments and suggestions from the co-authors and peer reviewers of this manuscript.
- III. Formulating the study objectives, sample collection, data collection, data analysis, and interpretation of the results. The author was also responsible for the design and writing of the first draft of the manuscript and for addressing comments and suggestions from the co-authors and peer reviewers of this manuscript.
- IV. Conceptualization, fieldwork sampling campaign, data collection, data analysis, interpretation of the results, design, and writing of the first draft of the manuscript. Furthermore, the author was responsible for addressing comments and suggestions from the co-authors of this manuscript and managed the review process.

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**LIST OF OTHER RELEVANT PAPERS NOT APPENDED TO THIS THESIS**

- I. Ligate, F.J., Ijumulana, J., Ahmad, A., **Kimambo, V.**, Irunde, R., Mtamba, J.O., Mtalo, F. & Bhattacharya, P. 2021. Groundwater resources in the East African Rift Valley: Understanding the geogenic contamination and water quality challenges in Tanzania. *Scientific African* 13: e00831, <https://doi.org/10.1016/j.sciaf.2021.e00831>
- II. Ligate, F., Lucca, E., Ijumulana, J. Irunde, R., **Kimambo, V.**, Bhattacharya, P., Mtalo, F., Ahmad, A., Hamisi, R. & Maity, J.P. 2022. Geogenic contaminants and groundwater quality around Lake Victoria goldfields of Northwestern Tanzania. *Chemosphere* 307: 135732. <https://doi.org/10.1016/j.chemosphere.2022.135732>
- III. Ligate, F.J., Ijumulana, J., Irunde, R., **Kimambo, V.**, Hamisi R., Maity J.P., Mtamba J.O., Mtalo F. & Bhattacharya, P. 2023. Hydrogeochemistry and spatial variability of arsenic and fluoride co-occurrence in groundwater from Geita district in Lake Victoria Basin, northwest Tanzania. *Groundwater for Sustainable Development* (GSD-23-00042, Manuscript in revision)
- IV. Ligate, F.J., Kumar, R., Ijumulana, J., Irunde, R., **Kimambo, V.**, Hamisi, R., Maity, J.P., Mtamba, J.O., Mtalo, F. & Bhattacharya, P. 2023. Health risk evaluation of arsenic and fluoride in groundwater from Geita district in Lake Victoria Basin, northwest Tanzania. (Manuscript, under preparation)

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## ABSTRACT

Fluoride (F<sup>-</sup>) concentration in drinking water is one of the water quality parameters in countries with high concentrations in groundwater sources. Natural minerals have shown considerable effectiveness in F<sup>-</sup> removal. In this study, the performance of the locally available natural minerals, such as bauxite, magnesites, and gypsum, have been investigated at the laboratory scales and through modelling for F<sup>-</sup> removal from drinking groundwater sources in Tanzania. Batch experiments were carried out to examine the optimum conditions for F<sup>-</sup> removal by the calcined bauxite, magnesite, and gypsum. X-ray fluorescence spectroscopy (XRF) characterization showed that Al<sub>2</sub>O<sub>3</sub>, MgO, and SO<sub>3</sub> were the major oxides in bauxite, magnesite, and gypsum, respectively. The experimental data for the three treated adsorbents fitted well with the Freundlich adsorption isotherm and the pseudo-second-order kinetics. The values of  $\Delta G^\circ$  and  $\Delta H^\circ$  indicate that the F<sup>-</sup> adsorption on bauxite and magnesite surfaces was spontaneous and endothermic. The randomness described by  $\Delta S^\circ$  at the solid–liquid interface was increased during the adsorption processes. While for gypsum, the reaction was spontaneous and exothermic, where the randomness at the solid–liquid interface decreased during the adsorption processes. At optimum conditions, calcined bauxite (400 °C), magnesite (650 °C), and gypsum (350 °C) lowered the F<sup>-</sup> concentration from 8.27 mg/L to 1.02, 0.233 and 1.99 mg/L, respectively. Bauxite and gypsum lowered the pH of water from 9.38 to 6.74 and 7.41, respectively. Magnesite raised the pH from 9.38 to 10.12, which is above the World Health Organization (WHO) (6.5 - 8.5) and Tanzania Bureau of Standards (TBS) (6.5 – 9.2) drinking water standard; therefore, pH adjustments are needed before water can be used for drinking. The Bed Depth Service Time (BDST) plot showed that the service times for F<sup>-</sup> adsorption on the calcined bauxite and magnesite surface increased with bed depth. The critical bed depths ( $Z_o$ ) for bauxite and magnesite obtained were 7.21 and 8.28 cm, respectively. The lower value of the kinetic rate parameter ( $K_a$ ) for bauxite (1.43E-5 L/mg s) and magnesite (1.50E-5 L/mg s) highlighted that the breakthrough occurs in short beds; therefore, deeper beds are required to avoid breakthroughs. The experimental results and model predictions have helped to compare the adsorption processes as well as contrast their performance and sustainability for F<sup>-</sup> removal using the bauxite, magnesite, and gypsum in the drinking water resources in Tanzania. The adsorption results and the overall cost analysis show that the cost of calcined bauxite and magnesite is low compared to other available adsorbents; therefore, they can be used in F<sup>-</sup> removal from water.

**Keywords:** Fluoride removal; Groundwater; Natural minerals; Adsorption isotherms; Batch- and Column Experiments; Kinetics and thermodynamics; Drinking water quality; Sustainability.

## 1. INTRODUCTION

### 1.1. BACKGROUND

Fluoride (F<sup>-</sup>) is an essential element for the human body that can be beneficial or detrimental depending on its concentration (Murutu *et al.*, 2012; Nie *et al.*, 2012; Srimurali *et al.*, 1998) and duration of continuous consumption (Bhatnagar *et al.*, 2011). The F<sup>-</sup> intake to humans is necessary, as long as it does not exceed the recommended limits, as it prevents dental caries and helps bone formation (Grynpas *et al.*, 2000; Mandal & Mayadevi, 2009).

The beneficial effects of F<sup>-</sup> are mainly attributed to its ability to stimulate osteoblast activity and reinforce tooth enamel when incorporated into hydroxyapatite structures (Caverzasio *et al.*, 1998). However, if consumed in excess, it can lead to the development of dental and skeletal fluorosis (Barbier *et al.*, 2010; Gazzano *et al.*, 2010; Jamode *et al.*, 2004; Xu *et al.*, 2011). Dental fluorosis is the decay of dental pulp cells, which results in discolouration and unusual deformation of the enamel structure (Kashyap *et al.*, 2021). On the other hand, skeletal fluorosis leads to muscle weakness, bone structure change, back stiffness, unusual deposition of ligaments, and tingling sensation in the limbs (Kashyap *et al.*, 2021).

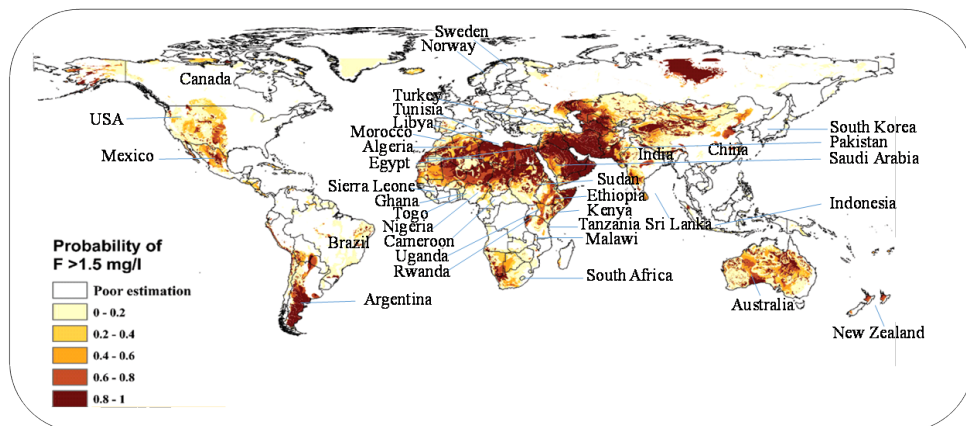
The main principal route of exposure to F<sup>-</sup> is drinking water (Kimambo *et al.*, 2019; Manji *et al.*, 1986). The permissible World Health Organization (WHO) guideline limits F<sup>-</sup> concentration in drinking water is 0.5 – 1.5 mg/L (WHO, 2011). Although drinking water is typically considered the largest single contributor to daily F<sup>-</sup> intake (Zhu *et al.*, 2016), this is not necessarily true in every case (Kheradpisheh *et al.*, 2018). The symptoms of fluorosis have been reported in many parts of the world where F<sup>-</sup> concentration was below the WHO upper limit in drinking water sources means that F<sup>-</sup> from other sources contributes to excessive fluorosis in these areas (Kaseva, 2006a). This is because, the intake of F<sup>-</sup> comes not only from drinking water sources (Harrison, 2005), but also from food (Sujana & Anand, 2011), beverages (Pendry, 2001), use of F<sup>-</sup> rich trona in food

preparation (Kaseva, 2006a; Nielsen & Dahi, 2002) dental products, (e.g., mouthwash and toothpaste), F<sup>-</sup> supplements (such as F<sup>-</sup> tablets), professionally applied F<sup>-</sup> gel and inhalation of aerosol fluoride compounds (Brindha & Elango, 2011).

Fluoride occurs in almost all groundwater, at different concentrations ranging from trace ( $\leq 1$  mg/L) to high concentrations ( $\geq 35$  mg/L) (Ozsvath, 2009; Sivasankar *et al.*, 2016). For example, the Akwira spring in Arusha-Tanzania has F<sup>-</sup> concentrations ranging from 35 - 37 mg/L (Kaseva, 2006a). The elevated concentration of F<sup>-</sup> in groundwater comes from natural and/or anthropogenic sources (Kagne *et al.*, 2009; Kamble *et al.*, 2010; Ku & Chiou, 2002).

The elevated F<sup>-</sup> concentration in groundwater sources and soil is mainly from natural sources, and the majority of F<sup>-</sup> related health problems occur as a result of ingesting F<sup>-</sup> water from natural sources (Ozsvath, 2009). The interaction of water with fluoride-bearing minerals in sediments and rocks is considered to be the main cause of F<sup>-</sup> dissolution into groundwater and soil (Kumar *et al.*, 2016; Saxena & Ahmed, 2003). Cryolite (Na<sub>3</sub>AlF<sub>6</sub>), Fluorite (CaF<sub>2</sub>), micas, fluoroapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F), amphiboles, topaz (Al<sub>2</sub>(SiO<sub>4</sub>)F<sub>2</sub>), villiamite (NaF), sellaite (MgF<sub>2</sub>) and bastnaesite [(Ce, La)(CO<sub>3</sub>)F] are examples of fluoride-rich minerals which occur in rocks and sediments (Apambire *et al.*, 1997; Nagendra Rao, 2003; Ozsvath, 2009). The high F<sup>-</sup> concentration in groundwater is likely in those areas where fluoride-bearing minerals are abundant in the rocks (Msonda *et al.*, 2007) (Vithanage & Bhattacharya, 2015a, 2015b).

Geogenic occurrence of F<sup>-</sup> is often from volcanic activity, the presence of geothermal waters, and fumarolic gases (Thole, 2013). Gases containing HF, SiF<sub>4</sub>, NaSiF<sub>6</sub>, K<sub>2</sub>SiF<sub>6</sub>, (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>, KBF<sub>4</sub>, and NH<sub>4</sub>F can be emitted during volcanic activities (Cronin *et al.*, 2003; D'Alessandro, 2006; García & Borgnino, 2015; Witham *et al.*, 2005) and when the fresh-erupted tephra is in contact with water, significant amounts of soluble elements, e.g.,



**Figure 1.** Map showing the occurrence of fluoride in groundwater in different parts of the world and the probability of fluoride concentration in the groundwater exceeding the WHO guideline of 1.5 mg/L for drinking water (adopted from Amini *et al.*, 2008).

$F^-$  and  $K^+$  can be released (Ayriss & Delmelle, 2012).

The annual estimated global emissions of gaseous F<sup>-</sup> compounds from volcanic sources range from 60 000 to 6 million tons (García & Borgnino, 2015). When these emitted gases interact with the ash particles of the volcanic plume, they form fluorine compounds, such as  $CaF_2$ ,  $AlF_3$ , and  $Ca_5(PO_4)_3F$  (Cronin *et al.*, 2003; Delmelle *et al.*, 2007). During the rainfall, the formed volcanic ash reaches the surface by falling out from the particulate fluorides and F<sup>-</sup> that percolate easily along with rainwater from the surface to the groundwater zone (Brindha & Elango, 2011). As a result, the water which comes into contact with volcanic ash deposits usually contains high concentrations of F<sup>-</sup> (Wolff-Boenisch *et al.*, 2004).

The anthropogenic activities that cause F<sup>-</sup> contamination in groundwater are mainly agricultural (Saxena & Ahmed, 2003) and industrial (Rao & Metre, 2014). The effluents from industries involved with the manufacturing of wood preservatives, fertilizers, electroplating, semiconductor, textile dyeing, glass, plastics, ceramic, bricks, pesticides, TV picture tubes, and disinfectants industries can release fluorine into the environment (Çengelöglu *et al.*, 2002; Mann & Mandal, 2014; Sujana *et al.*, 2009)

either as gaseous (e.g., HF,  $SiF_4$ ,  $F_2$ , and  $H_2SiF_4$ ) or particulate (e.g.,  $CaF_2$ , NaF, and  $Na_2SiF_6$ ) species (Ozsvath, 2009).

The application of fluoride-containing fertilizers and pesticides contributes to F<sup>-</sup> content in the soil and groundwater (Farooqi, 2015). Phosphatic fertilizers, especially the super-phosphates, are the most important source of F<sup>-</sup> contamination from agricultural lands to the groundwater (Jha *et al.*, 2011). Fluoride, often contained as an impurity in phosphatic fertilizers (Dar *et al.*, 2011), leached down to the saturated zone by return irrigation flows. During interaction with water, F<sup>-</sup> eventually precipitates as fluorite (Saxena & Ahmed, 2003), which can result in an elevated F<sup>-</sup> concentration in agricultural fields compared to the domestic wells (Sivasankar *et al.*, 2016).

## 1.2. FLUORIDE OCCURRENCE

In recent times, groundwater has become a large source of freshwater readily available for supporting society and ecosystem services (Mukherjee *et al.*, 2021). Most people use groundwater for irrigation and drinking purposes (Kimambo *et al.*, 2019). There are more than 25 countries in the world with high F<sup>-</sup> concentrations in their groundwater sources, and about 200 million people are at risk of having serious health consequences due to the consumption of drinking

**Table 1. Water sources with high F<sup>-</sup> concentration in Tanzania**

Location	Water source	F <sup>-</sup> concentration (mg/L)	References
Abdi dug well- Ngurdoto	Dug well	9.50-9.60	(Kaseva, 2006a)
Akwira spring- Kitefu Village	Spring	35.00-37.60	(Kaseva, 2006a)
Arumeru District	Lakes	149.1-528.0	(Ghiglieri <i>et al.</i> , 2010)
Arumeru District	Rivers	1.90-29.40	(Ghiglieri <i>et al.</i> , 2010)
Arumeru District	Springs	0.70-60.00	(Ghiglieri <i>et al.</i> , 2010)
Embaseni Village	Usa river piped water	2.80-3.00	(Kaseva, 2006a)
Ibrahimu Mbise well- Ngurdoto	Dug well	9.00-9.20	(Kaseva, 2006a)
Kibola spring- Nkoanekoli Village	Spring	1.70-1.80	(Kaseva, 2006a)
Lake Magadi-Kitefu Village	Lake	89.00-92.00	(Kaseva, 2006a)
Manyamaa dug well- Ngurdoto	Dug well	4.00-4.50	(Kaseva, 2006a)
Maseini spring- Kitefu Village	Spring	40.00-42.50	(Kaseva, 2006a)
Moses Spring- Embaseni Village	Spring	8.00-9.30	(Kaseva, 2006a)
Piter Onel's well- Ngurdoto	Shallow well	6.60-9.50	(Kaseva, 2006a)
Shinyanga Region	Groundwater	110.0-250.0	(Msonda <i>et al.</i> , 2007)
Singida	Boreholes	0.82-4.64	(Titus <i>et al.</i> , 2009)
Singida	Dug out	1.36-14.33	(Titus <i>et al.</i> , 2009)
Singida	Shallow wells	0.21-8.73	(Titus <i>et al.</i> , 2009)

groundwater contaminated with excessive F<sup>-</sup> (Ayooob & Gupta, 2006; Vithanage & Bhattacharya, 2015a, 2015b). Fig. 1 shows that excess fluoride in groundwater is not a common problem in European countries. Argentina, Libya, Egypt, New Zealand, and Australia are some of the countries with high F<sup>-</sup> concentration in their groundwaters.

The East African Rift Valley is one of the natural high F<sup>-</sup> zones (Jacks, 2016; Kut *et al.*, 2016), and the highest groundwater F<sup>-</sup> levels have been reported in alkaline volcanic areas of the Rift Valley (Ijumulana *et al.*, 2020). This occurred due to geochemical processes that take place in volcanic areas (Ijumulana *et al.*, 2021). As a result, more than 80 million

people living in the East African Rift show varying degrees of fluorosis symptoms (Kut *et al.*, 2016). Groundwaters with F<sup>-</sup> concentrations between 15 - 63 mg/L have been reported especially around the northern zone of Tanzania (Ijumulana *et al.*, 2020). About 41% of the total population (2 million) in Hai, Siha, Hanang', Arusha City, Arusha, Meru, and Simanjiro districts have developed dental, skeletal, and crippling fluorosis (Ijumulana *et al.*, 2021). The high concentration in groundwater is a result of geogenic activities (dissolution of fluoride-bearing minerals, weathering of fluoride-bearing volcanic rocks, and geothermal water mixing), and anthropogenic activities (industrial and agricultural activities). Table 1

**Table 2. Comparison of the technologies for fluoride removal and driving processes (Bhatnagar et al., 2011; Habuda-Stanić et al., 2014; Lavecchia et al., 2012).**

Processes	Advantages	Limitations
Adsorption processes	Greater accessibility, low cost, simple operation, availability of wide range of adsorbents, produce high quality water, environmentally friendly	Achieving high efficiency often required adjustment and readjustment of pH, some common water ions can interfere F <sup>-</sup> adsorption, regeneration is difficult for some adsorbents, some adsorbents have low adsorption efficiency under high F <sup>-</sup> concentration
Coagulation/precipitation processes	High efficiency; commercially available chemicals	Can be expensive, efficiency depends on pH and presence of co-existing ions in water, adjustment and readjustment of pH is required, elevated residual aluminum concentration, formation of sludge with high amount of toxic aluminum fluoride complex and high amount of retained water (sludge dewatering is required prior to disposal).
Electrochemical processes	High efficiency; high selectivity	High cost of installation and maintenance
Ion-exchange processes	High efficiency	Expensive, vulnerable to interfering ions (sulfate, phosphate, chloride, bicarbonate, etc.), replacement of media after multiple regenerations, used media present toxic solid waste, regeneration creates toxic liquid waste, efficiency highly pH-dependent
Membrane-based processes	High efficiency; remove other contaminants	High capital, high operation and maintenance costs, toxic concentrate generated

shows F<sup>-</sup> concentration in some water sources in Tanzania (Kimambo et al., 2019).

### 1.3. WATER DEFLUORIDATION

The mitigation measures to control fluorosis where F<sup>-</sup> levels of potable water are consistently beyond permissible levels have been necessary to prevent the adverse effects on human health. This can be done through several methods such as source substitution: searching for the safe water source locally and transported from a distant safe source, blending of high F<sup>-</sup> with low F<sup>-</sup> concentration water; dual water sources where the water source with low F<sup>-</sup> concentration is used for drinking and cooking while the one with high F<sup>-</sup> concentration is used for other domestic activities (MacDonald & Kavanaugh, 1994).

The harvesting of rainwater has also been used as a corrective measure to control fluorosis (Jacks et al., 2005). For areas where other options are not possible, defluoridation is left as the only option (Alagumuthu & Rajan, 2010; Bansawal et al., 2010; Peter, 2009). Up to now, the scientific community in this field has already developed various defluoridation methods. However, their applicability has been complicated because of the high investment, maintenance, operational cost, and low F<sup>-</sup> removal efficiency. Some of the requirements for standard defluoridation methods are low maintenance cost, modest investment, ease of operation, simple design, ingredients maintainable for the acceptable period, improved water quality in general, and the

**Table 3. The countries with largest bauxite, gypsum and magnesite reserves in the world (USGS 2020, 2021, 2022).**

Country	Bauxite		Gypsum		Magnesite	
	Reserves (thousand metric tons)	Percentage (%)	Reserves (thousand metric tons)	Percentage (%)	Reserves (thousand metric tons)	Percentage (%)
Australia	5,100,000	20.58	NA	NA	320,000	6.56
Austria	NA	NA	NA	NA	49,000	1
Brazil	2,700,000	10.8959	450,000	20.51	200,000	4.1
Canada	NA	NA	450,000	20.51	NA	NA
China	1,000,000	4.03551	NA	NA	1,000,000	20.51
France	NA	NA	350,000	15.95	NA	NA
Guinea	7,400,000	29.8628	NA	NA	NA	NA
Greece	NA	NA	NA	NA	280,000	5.74
India	660,000	2.66344	36,000	1.64	82,000	1.68
Indonesia	1,200,000	4.84262	NA	NA	NA	NA
Jamaica	2,000,000	8.07103	NA	NA	NA	NA
Kazakhstan	160,000	0.64568	NA	NA	NA	NA
Malaysia	170,000	0.68604	NA	NA	NA	NA
Pakistan	NA	NA	6,000	0.27	NA	NA
Russia	500,000	2.01776	NA	NA	2,300,000	47.17
Saudi Arabia	190,000	0.76675	NA	NA	NA	NA
Slovakia	NA	NA	NA	NA	370,000	7.59
Spain	NA	NA	NA	NA	35,000	0.72
Thailand	NA	NA	1,700	0.08	NA	NA
Turkey	NA	NA	200,000	9.12	205,000	4.2
United States	NA	NA	700,000	31.91	35,000	0.72
Vietnam	3,700,000	14.9314	NA	NA	NA	NA
<b>Total</b>	<b>24,780,000</b>	<b>100</b>	<b>2,193,700</b>	<b>100</b>	<b>4,876,000</b>	<b>100</b>

ability to reduce F<sup>-</sup> content to standard level (Bjorvatn & Bårdsen, 1995).

The defluoridation techniques include electrochemical techniques (e.g., electro-dialysis, electro-coagulation), precipitation/coagulation techniques (e.g., Nalgonda technique, calcium hydroxide, aluminium hydroxide), membrane techniques (e.g., reverse osmosis, nanofiltration), ion exchange techniques (e.g., strong basic anion-

exchange resin with quaternary ammonium functional groups) and adsorption techniques (e.g., activated alumina; activated carbons; other natural and synthetic adsorbents) (Al-Rawajfeh *et al.*, 2013; Habuda-Stanić *et al.*, 2014; Islam & Patel, 2007). Each technique has its own advantages and limitations (Table 2).

Adsorption is generally considered to be an appropriate defluoridation technique for

scale-up access to drinking water in the community compared to other techniques due to the wide range of available adsorbents, simplicity of design and operation, and reasonable investment and running cost (Bhatnagar *et al.*, 2011; Habuda-Stanić *et al.*, 2014; Lavecchia *et al.*, 2012). The selection criteria of the adsorbents for F<sup>-</sup> removal have been based on the local availability of natural materials, by-products during the treatment, removal capacity, investment, and running cost, operation and design simplicity, user preference, acceptance by the community and users (Mehari *et al.*, 2014a; Mehari *et al.*, 2014b; Miretzky & Cirelli, 2011). Nevertheless, some of the adsorbent materials for defluoridation currently available are not cost-effective and technically not feasible in rural areas (Ghorai & Pant, 2005). Therefore, it is still essential to identify materials that are both applicable in low-income communities and effective (Kebede *et al.*, 2014).

Bauxite, gypsum, and magnesite are industrial minerals that are naturally abundant in the world (Table 3). The estimated resources of global bauxite range between 55 - 75 billion tons (USGS, 2021). The composition of these minerals differs as a result of differences in the production and formation process (Alhassan *et al.*, 2020). Although, these natural minerals have shown considerable effectiveness for fluoride removal, however, they have not been commonly used for fluoride removal. About 70% of the bauxite mined in 2020 was used in the production of alumina or aluminum hydroxide. The remaining percent went to the production of cement, abrasives, proppants, refractories chemicals, and as a slag adjuster in steel mills (USGS, 2020, 2021).

The United States is the largest gypsum producer in the world. The large quantity of gypsum produced in the United States is used in cement production, agriculture, and manufacturers of plaster and wall board products. On the other hand, the small amount of high-purity gypsum is produced in various forms for industrial processes (USGS, 2021). The magnesite mined is

mainly used to manufacture basic refractories in the steel industry (GI, 2022; USGS, 2021).

In this study, the performance of the locally available natural minerals such as bauxite, magnesite, and gypsum have been investigated for F<sup>-</sup> removal from drinking groundwater sources in Tanzania. According to literature, raw bauxite, gypsum, and magnesite have shown a low ability for F<sup>-</sup> removal from water (Thole *et al.*, 2012a). This can be due to the presence of impurities that interfere with the coverage of active sites for F<sup>-</sup> adsorption (Alhassan *et al.*, 2020; Sajidu *et al.*, 2012). However, these materials can be modified by changing their surface chemistry and/or functional properties in order to improve their adsorption efficiency, ability to regenerate adsorbent, and the pH range in which it can adsorb F<sup>-</sup>. The modification can be done by metal impregnation, heating, acidifying, and crushing (Alhassan *et al.*, 2020). Also, the F<sup>-</sup> adsorption capacity of the adsorbent can be affected by changing the adsorption conditions like pH, water temperature, initial fluoride concentration, particle size, adsorbent dose, and contact time (Kimambo *et al.*, 2019).

## 2. RESEARCH IDENTIFICATION

### 2.1. RATIONALE

The prevention of fluorosis in areas with high F<sup>-</sup> concentration can be done by using dual water sources, source substitution, blending, rainwater harvesting, and defluoridation (Kimambo *et al.*, 2019). The ion exchange, membrane separation, electrochemical separation, coagulation/precipitation, and adsorption are the techniques that can be used in F<sup>-</sup> removal. The first four techniques have high F<sup>-</sup> removal efficiency; however, these methods are not recommended in developing countries due to their high installation and running cost (Kimambo *et al.*, 2019).

On the other hand, adsorption is considered to be the best method because of its reasonable installation and running cost, simple design and operation, and availability of a wide range of materials that can be used as adsorbents (Habuda-Stanić *et al.*, 2014; Lavecchia *et al.*, 2012). However, the

applicability of low-cost adsorbents is limited due to the lower efficiency of fluoride removal from fluoride-contaminated water as well as low public acceptance. For example, bone char has shown great F<sup>-</sup> removal ability, but until now, it is not effectively used in large-scale or household applications because of a lack of public acceptance (Leyva-Ramos *et al.*, 2010).

Groundwaters with F<sup>-</sup> concentration between 15 - 63 mg/L have been reported, in the northern zone of Tanzania (Ijumulana *et al.*, 2020). Bauxite, magnesite, and gypsum are naturally available in Tanzania. However, until now, these materials are not used for F<sup>-</sup> removal at the household or community level due to a lack of sufficient studies on their applicability in defluoridation. The F<sup>-</sup> removal capacity of any adsorbent depends on several factors, i.e., initial F<sup>-</sup> concentration, pH, adsorbent dose, water temperature, particle size, shaking speed, contact time, and any other contents in the water (Kimambo *et al.*, 2019), and the properties of adsorbent material (Bhatnagar *et al.*, 2011). The present study involved an investigation of the suitability of Tanzanian bauxite, magnesite, and gypsum in F<sup>-</sup> removal from Ngongongare spring groundwater.

## 2.2. OBJECTIVES AND RESEARCH QUESTIONS

### 2.2.1. General objective

The overall objective of this thesis is to develop a simple and cost-effective method for removing F<sup>-</sup> in groundwater sources using locally available materials.

### 2.2.2. Specific objectives

The specific objectives were to:

- Review the occurrence of F<sup>-</sup>, potential sources in different environmental matrices and defluoridation techniques (*Paper I*)
- Determination of chemical and mineralogical compositions of raw and calcined bauxite, gypsum, and magnesite (*Papers II & III*)
- Determination of optimum conditions and suitable models to explain F<sup>-</sup> removal using calcined bauxite, gypsum, and magnesite (*Papers II & III*)
- Comprehensive evaluation of the results of optimal removal of F<sup>-</sup> by calcined bauxite, gypsum, and magnesite for pilot-scale application (*Paper IV*)

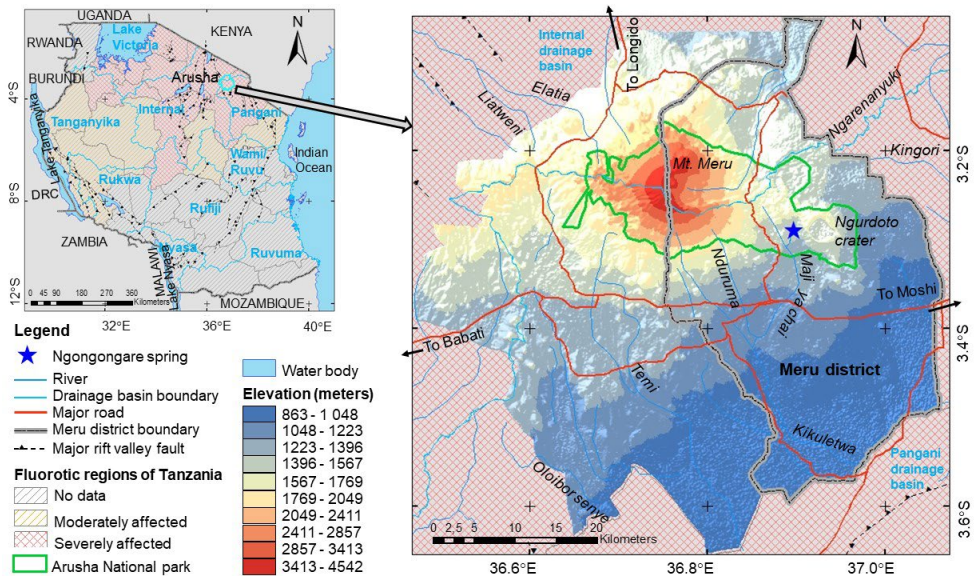
### 2.2.3. Research questions

The specific objectives were achieved through the following research questions:

- i. What is the global F<sup>-</sup> occurrence and defluoridation status? (*Paper I*)
- ii. What are the chemical and mineralogical compositions of raw and calcined bauxite, magnesite, and gypsum from Tanzania? (*Papers II & III*)
- iii. What are the optimum conditions and suitable models to explain F<sup>-</sup> removal using calcined bauxite, magnesite, and gypsum? (*Papers II & III*)
- iv. What adsorption isotherms model fits well with adsorption data from F<sup>-</sup> removal using calcined bauxite, magnesite, and gypsum? (*Papers II & III*)
- v. Can calcined bauxite, magnesite, and gypsum be used for F<sup>-</sup> removal in a pilot-scale? (*Paper IV*)

## 2.3. SCOPE OF THE STUDY

This study is limited to fluoride removal from drinking water by using locally available adsorbent materials with a focus on bauxite, gypsum, and magnesite. The water sample was collected from a source that was used for drinking, irrigation, and other household activities. The characterization of the adsorbent materials, defluoridation experiments, and measurements of inorganic constituents in water samples were done in laboratory conditions.



**Figure 2.** Location of Ngongongare Spring in Tanzania

## 2.4. THESIS STRUCTURE

This thesis is divided into six main sections. Section 1 gives the general introduction and the background of the research problem. Section 2 explains the research problem and states the objectives and scope of the study. Section 3 describes the study area in terms of its geographical location. Section 4 describes the materials and methodology. Section 5 highlights the results and discussions, while Section 6 discusses the cost analysis and policy implications for sustainable application in Tanzania. Section 7 gives conclusions and recommendations for future study.

## 3. STUDY AREA

The water sample used in this study was collected from Ngongongare Springs, located in the Arusha region in northern Tanzania (Fig. 2). This is a hot and semi-arid area with an average annual rainfall and temperature between 600 and 800 mm and 20 – 26 °C, respectively. The area is characterized by high F<sup>-</sup> concentration due to the volcanic activities of Mount Kilimanjaro and Meru (Ijumulana *et al.*, 2020).

About 70% of the groundwater sources in this area have F<sup>-</sup> concentration above the

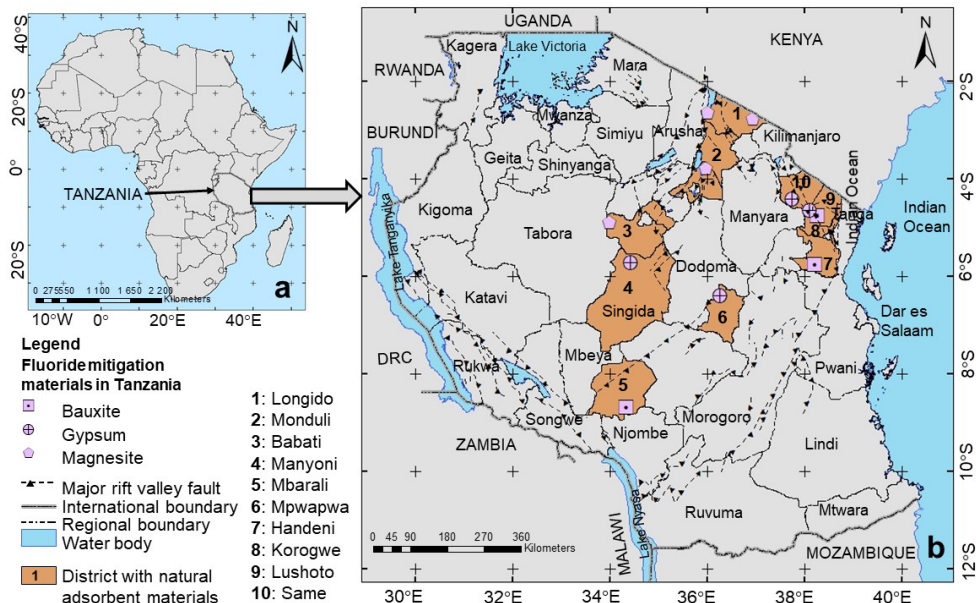
WHO permitted level. Due to this, the majority of community members in this region have been affected by dental, skeletal, and crippling fluorosis (Ijumulana *et al.*, 2021). Ngongongare spring has F<sup>-</sup> concentration of around 8 mg/L, which is used as the source of water for drinking and other domestic activities.

The adsorbent materials were collected from Tanga and Kilimanjaro Region in northern Tanzania (Fig. 3). The bauxite was mined from Lushoto District in Tanga Region. The gypsum and magnesite were mined from the local deposits located at Makanya and Chambogo villages, respectively, in Same District, Kilimanjaro Region.

## 4. METHODS

### 4.1. FLUORIDE OCCURRENCE AND DEFLUORIDATION

A comprehensive review was carried out to establish the global occurrences of F<sup>-</sup> exposure and defluoridation methods in water sources. The literature review included peer-reviewed articles, scientific reports, and books. These materials were accessed from Google Scholar, PubMed, Scopus, Web of



**Figure 3.** Map showing the a) location of Tanzania in the Africa continent, b) Locations of bauxite, magnesite, and gypsum deposits in Tanzania.

Science, and websites. The key terminologies included but were not limited to:  $F^-$ , defluoridation, adsorption, adsorbent materials, adsorption isotherms, groundwater, and drinking water were used. The secondary data from the literature were used for this analysis to expand the understanding of the global fluoride problem in groundwater.

#### 4.2. EXPERIMENTAL STUDIES

The water sample was collected in October 2017 from the spring and packed in three 20 L polyethylene containers. The location of the sampling site was recorded by using the GPS receiver Mobile Mapper 20. The sampling guidance by EPA for unknown contaminants in drinking water was followed (EPA, 2017). The pH and  $F^-$  concentrations were measured using Hach® potable water quality multimeter (HQ40D). The samples were then transported to the Water Quality Laboratory of the University of Dar es Salaam and stored at 14 °C.

##### 4.2.1. Preparation and characterization of adsorbent material

Bauxite, gypsum, and magnesite were ground and sieved to obtain powders of <0.075 mm in diameter. The identification of mineral phases was done by BTX II X-ray Diffraction Analyzer (inXitu Inc, United States) over a range of 5 to 55° using  $Co\ K\alpha_1$  radiation at a wavelength of 1.78897 Å. ARL OPTIM'X XRF spectrometer (Thermo Fisher Scientific Inc, Sweden) was used to determine the chemical compositions of the materials.

##### 4.2.2. Water analysis

The concentrations of anions ( $Cl^-$ ,  $HCO_3^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$ ) were determined by using Dionex DX-120 Ion Chromatography (IC). The concentration of cations ( $Al^{3+}$ ,  $As^{3+}$ ,  $B^{3+}$ ,  $Ba^{2+}$ ,  $Ca^{2+}$ ,  $Cd^{2+}$ ,  $Cr^{3+}$ ,  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Na^+$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Se^{2+}$ ,  $V^{5+}$ , and  $Zn^{2+}$ ) were analyzed by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

##### 4.2.3. Batch experiments

Before the solution was mixed with the adsorbent, the pH and  $F^-$  concentrations were measured using Hach® potable water quality

multimeter (HQ40D). The pH calibration standards (4, 7, and 10) and ion concentration calibration standard solution of F<sup>-</sup> (1, 5, and 10 mg/L) were applied (accuracy  $\pm$  0.5%). Bauxite, magnesite, and gypsum with particle size 0.075 mm were calcined in Muffle furnace LE 1/11 (Nabertherm, Germany) at temperatures between 250 to 800 °C for 2 h. Batch experiments using 50 mL of 8 mg L<sup>-1</sup> F<sup>-</sup> raw water, mixed with 2 g of adsorbent with a shaker speed of 200 rpm at room temperature, were designed to study the effect of calcination temperature for each adsorbent. The pH and F<sup>-</sup> remained in the water after each adsorption was measured (Mndolwa & Mtaló, 2020). All the F<sup>-</sup> adsorption experiments were carried out in duplicate.

The calcination temperature, which gave the highest removal efficiency, was used in subsequent experiments performed at different conditions in order to determine the optimum conditions for adsorption. The adsorption conditions tested in all adsorbents were particle size (0.075 – 1.0 mm) and temperature (30 - 50 °C). The contact time ranging between 1 – 10 min, 4 - 40 min, and 8 – 48 min were used to study the effect of contact time on F<sup>-</sup> adsorption for bauxite, magnesite, and gypsum, respectively. On the other hand, the adsorbent doses of 20 – 120 g/L, 5 – 40 g/L, and 20-140 g/L were studied in bauxite, magnesite, and gypsum, respectively.

The percent F<sup>-</sup> removal from aqueous media was calculated using equation 1 (Izuagie *et al.*, 2015):

$$\% \text{ F}^- \text{ removal} = \left( \frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)$$

The amount of adsorption at time (t), q<sub>t</sub> (mg/g) was calculated by equation 2 (Zhao *et al.*, 2015):

$$q_t = \left( \frac{C_o - C_t}{m} \right) \times V \quad (2)$$

The adsorption loading of the adsorbent was calculated using equation 3 (Maiti *et al.*, 2011):

$$q_e = \left( \frac{C_o - C_e}{m} \right) \times V \quad (3)$$

#### 4.2.4. Thermodynamic parameters of the adsorption process

The thermodynamic feasibilities of calcined adsorbents were studied by changing the temperature in the thermostat-controlled shaker in a range of 303 – 323 K. The thermodynamic parameter Gibbs free energy change ( $\Delta G^\circ$ ), entropy change ( $\Delta S^\circ$ ), and enthalpy change ( $\Delta H^\circ$ ) associated with the adsorption of F<sup>-</sup> were calculated in order to determine the nature of the F<sup>-</sup> adsorption process.

The Gibbs free energy change of the adsorption process is calculated from equation 4:

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

According to its function,  $\Delta G^\circ$  can be expressed in terms of  $\Delta H^\circ$  and  $\Delta S^\circ$  by using equation 5:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

The value of  $\Delta G^\circ$  for the reaction predicts whether the reaction can take place spontaneously ( $\Delta G^\circ < 0$ ) or it is necessary to apply energy to promote the reaction ( $\Delta G^\circ > 0$ ).

The distribution coefficient for adsorption was expressed by using  $\Delta S^\circ$  and  $\Delta H^\circ$  as a function of temperature T (equation 6):

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

The plot of  $\ln K_c$  against  $1/T$  gives the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  from the slope and intercept (Sujana & Anand, 2011). The positive and negative  $\Delta H^\circ$  indicates endothermic and exothermic reactions, respectively. The value of  $\Delta S^\circ > 0$  means the reaction is irreversible and stable (Viswanathan & Meenakshi, 2008a).

#### 4.2.5. Adsorption isotherms

The natural groundwater sample was diluted with deionized water to concentrations ranging between 2 – 8 mg/L. The adsorption mechanism and maximum adsorption capacity for F<sup>-</sup> on the adsorbents surface were determined by using Freundlich and Langmuir adsorption isotherm models.

Freundlich isotherm model which was proposed by Freundlich in 1906 (Maity *et al.*, 2018), assumes that multilayer adsorption occurs on heterogeneous surfaces and the maximum adsorption occurs when the adsorbent surface is covered by adsorbate (Sujana & Anand, 2011). Freundlich adsorption isotherm is given by equation 7:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (7)$$

The plot of  $\log q_e$  against  $\log C_e$  gave the values of  $1/n$  and  $k_F$  from the slope and intercept (Chen *et al.*, 2010). The value of  $1/n$  between 0 and 1 means favourable adsorption (Gogoi & Dutta, 2015).

Langmuir isotherm model was developed by Langmuir in 1916 (Maity *et al.*, 2018) to describe gas-solid phase adsorption and quantify the adsorption capacity of various adsorbents. It accounts for the dynamic equilibrium between the surface coverage during adsorption and desorption. The model assumes that adsorption is proportional to the fraction of the surface of the adsorbent that is open, while desorption is proportional to the fraction of the adsorbent surface that is covered by the adsorbent (Ayawei *et al.*, 2017). The graph of  $C_e/q_e$  against  $C_e$  obtained from Langmuir (equation 8) was used to calculate the value of  $Q^o$  and  $b$  from the slope and intercept (Meenakshi & Viswanathan, 2007)

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \quad (8)$$

The Langmuir isotherm was also expressed in terms of a dimensionless constant equilibrium parameter or separation factor ( $R_L$ ), in order to find out the feasibility of the isotherm by using equation 9

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

The value of  $R_L$  can fall into one of the four probabilities:  $R_L = 0$  (irreversible adsorption),  $0 < R_L < 1$  (favorable adsorption),  $R_L = 1$  (linear adsorption) and  $R_L > 1$  (unfavorable adsorption) (Ayawei *et al.*, 2017; Kebede *et al.*, 2014).

#### 4.2.6. Adsorption kinetics

Adsorption kinetics is one of the essential characteristics of adsorbents which indicates the type and rate of adsorption (Haddad *et al.*, 2019). The two main types of models, which are reaction-based and diffusion-based models (Viswanathan *et al.*, 2009), were adopted in this study.

Reaction-based models are used to determine the rate of reaction (kinetic adsorption constant) for F adsorption on the surface of an adsorbents, which is important in performing accurate modeling and drawing valid conclusions (Hosseini-Bandegharai & Chao, 2017).

The pseudo-first-order and pseudo-second-order were used to study the adsorption of solutes from a liquid solution. The pseudo-first-order basic is on the concept that the rate of reaction is proportional to the concentration of the reactants (Maity *et al.*, 2018). The pseudo-first-order kinetic model is given by equation 10:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (10)$$

The value  $k_{ad}$  was obtained from the slope of the plot of  $\log(q_e - q_t)$  against  $t$  (Viswanathan & Meenakshi, 2008a, 2009).

The basic concept for pseudo-second-order, based on the rate of the reaction is proportional to the square of reactant concentrations (Maity *et al.*, 2018). The most popular linear pseudo-second order is given by equation 11:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (11)$$

The plot  $t/q_t$  against  $t$  gives straight line, and  $k$  was obtained from the slope and intercept as  $k = \text{slope}^2 / \text{intercept}$  (Suneetha *et al.*, 2014).

The solute transfer in a solid/liquid adsorption process is normally characterized by either particle diffusion or intra-particle diffusion control (Hosseini-Bandegharai & Chao, 2017).

The likelihood of particle diffusion resistance affecting the adsorption behaviour was

investigated by using the particle diffusion kinetic model given by equation 12:

$$\ln\left(1 - \frac{C_t}{C_e}\right) = -k_p t \quad (12)$$

The plot of  $\ln(1 - C_t/C_e)$  against  $t$  gives the straight line with the value of particle rate constant as the slope (Sundaram *et al.*, 2008; Viswanathan & Meenakshi, 2008b).

The influence of intra-particle diffusion on the adsorption behaviour was determined using the intra-particle diffusion kinetic model, which is given by equation 13:

$$q_t = k_{int} t^{1/2} + C \quad (13)$$

The plot of  $q_t$  against  $t^{1/2}$  gives the straight line with value of intra-particle diffusion coefficient as a slope (Haddad *et al.*, 2019).

#### 4.2.7. Regeneration of the adsorbents

The used bauxite and magnesite were regenerated by shaking them separately for 2 hours in 0.015 M NaOH solution. The solution was then filtered, and the filtrate was washed using distilled water in order to remove excessive NaOH from adsorbents. The material was dried for 24h at room temperature before oven dried at 105 °C for 3 h (Das *et al.*, 2005). The regenerated adsorbents were then used for  $F^-$  removal under optimum conditions.

#### 4.2.8. Column experiments

The column experiments were performed at room temperature. The column with a diameter of 20 cm and 200 cm length was packed with 2000 - 6000 g of 1-2 mm particle size adsorbent. The height of the adsorbent in the column was measured and recorded. Water with 7 mg/L  $F^-$  concentration with a pH of 8.9 was allowed to pass the through column by up-flow mode to avoid channelling due to gravity and to ensure a uniform distribution of the effluent throughout the column (Damte, 2006).

The flow rate of 390 mL/min was maintained during each experiment by ensuring that the depth of water in the supply reserve tank was kept constant throughout the experiment. Water samples were collected at the effluent at a fixed time interval, and pH and concentration of  $F^-$  remained in water

were measured using Hach® potable water quality multimeter (HQ40D) until the adsorbent became saturated.

#### 4.2.9. Bed depth service time (BDST) model

The bed depth service time (BDST) model is a type of model based on physically measuring the capacity of the bed at various percentage breakthrough values. It is used to predict the column performance for any bed length, if data for some depths are known without further experimentation.

The model states that the bed depth,  $Z$ , and service time,  $t$ , of a column, bears a linear relationship. The service time represents the service time, that is time period through which the bed continues to remove fluoride to within the target concentration before replacement or regeneration of the bed is required. The rate of adsorption is controlled by the surface reaction between the adsorbate and the unused capacity of the adsorbent. The BDST equation can be expressed by equation 14 (Thole *et al.*, 2012b):

$$t = N_o Z / C_o v - 1 / K_x C_o \ln[(C_o / C_b) - 1] \quad (14)$$

The values of  $N_o$  and  $K_x$  were evaluated from the slope and intercept of the BDST plot. The slope ( $N_o / C_o v$ ) represents the time required for the adsorption zone to travel a unit length through the adsorbent under the selected experimental conditions at a given concentration. This is used to predict the performance of the bed, if there is a change in the initial solute concentration,  $C_o$  to a new value. The y-intercept ( $1 / K_x C_o \ln[(C_o / C_b) - 1]$ ) is the time taken for an adsorption wavefront to pass through the critical bed depth.

The critical bed depth ( $Z_o$ ) which is the minimum bed depth that can be used in a sorption column without resulting in instant breakthrough concentrations that is, exit solute concentration ( $C_{exit}$ ) being equal to inlet solute concentration ( $C_{inlet}$ ) at time zero. The critical bed depth which guides the minimum bed depth choice available in fixed bed column design (Ghorai & Pant, 2005; Thole *et al.*, 2012) is given by equation 15 (Ghorai & Pant, 2005)

$$Z_o = \frac{v}{K_x N_o} \ln \left[ \frac{C_o}{C_b} - 1 \right] \quad (15)$$

#### 4.2.10. Empty bed residence time design model

The empty bed residence time (EBRT) model is a design procedure used to determine the optimum adsorbent usage in the fixed-bed adsorption column. The EBRT is the time required for the liquid to fill the column, on the basis that the column contains no adsorbent packing, and is a direct function of liquid flow rate and column bed volume. It is a design tool used to determine the optimum adsorbent usage in the fixed-bed adsorption column. The EBRT is basically hydraulic retention time and can be expressed using the following equation 16 (Damte, 2006).

$$\text{EBRT} = \frac{\text{Bed volume}}{\text{Volume flow rate of the liquid}} \quad (16)$$

In this case, it is also important to find the rate of exhaustion of the adsorbent before the breakthrough time occurs. The adsorbent exhaustion rate (AER), which is the weight of adsorbent used in the column per volume of liquid treated at the time breakthrough occurs equation 17 (Damte, 2006).

$$\text{AER} = \frac{\text{Mass of adsorbent used}}{\text{Volume treated at breakthrough}} \quad (17)$$

## 5. RESULTS AND DISCUSSION

### 5.1. CHARACTERIZATION

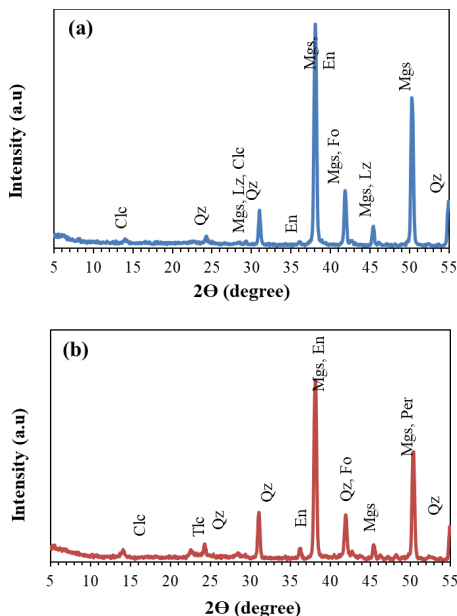
#### 5.1.1. Chemical composition

The oxides  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_3$  were the major oxides in raw and calcined bauxite, while  $\text{MgO}$ , and  $\text{SiO}_2$  were present in large quantities in raw and calcined magnesite (Table 4). On the other hand, raw and calcined gypsum contained large amounts of  $\text{SO}_3$ ,  $\text{CaO}$  and  $\text{SiO}_2$  than any other oxide.

**Table 4. Percentages of oxides present in calcined bauxite, magnesite and gypsum**

Oxide	Raw bauxite	Bauxite calcined at 400 °C	Raw gypsum	Gypsum calcined at 350 °C	Raw magnesite	Magnesite calcined at 650 °C	at
$\text{Al}_2\text{O}_3$	57.67	66.98	2.84	4.76	<0.01	0.33	
$\text{Fe}_2\text{O}_3$	7.39	7.48	0.56	0.67	1.01	1.52	
$\text{SiO}_2$	5.79	6.47	11.85	14.29	5.12	9.10	
$\text{TiO}_2$	0.86	0.85	<0.01	0.1	<0.01	<0.01	
$\text{P}_2\text{O}_5$	0.17	0.14	<0.01	0.19	<0.01	<0.01	
$\text{V}_2\text{O}_5$	0.07	<0.01	<0.01	<0.01	<0.01	<0.01	
$\text{SO}_3$	0.17	0.19	36.07	37.05	<0.01	0.10	
$\text{ZrO}_2$	<0.01	<0.01	0.08	<0.01	<0.01	<0.01	
$\text{NiO}$	<0.01	<0.01	<0.01	<0.01	0.13	<0.01	
$\text{Cr}_2\text{O}_3$	<0.01	<0.01	<0.01	<0.01	0.09	0.10	
$\text{K}_2\text{O}$	<0.01	<0.01	0.28	0.38	<0.01	<0.01	
$\text{Na}_2\text{O}$	<0.01	<0.01	<0.01	0.33	<0.01	<0.01	
$\text{CaO}$	0.28	0.65	21.81	23.92	0.63	1.21	
$\text{MgO}$	<0.01	<0.01	1.06	1.75	44.83	60.21	
$\text{SrO}$	<0.01	<0.01	0.32	0.26	<0.01	<0.01	
$\text{Cl}$	<0.01	<0.01	0.08	<0.01	<0.01	<0.01	
LOI	27.59	17.24	25.05	16.3	48.19	27.43	



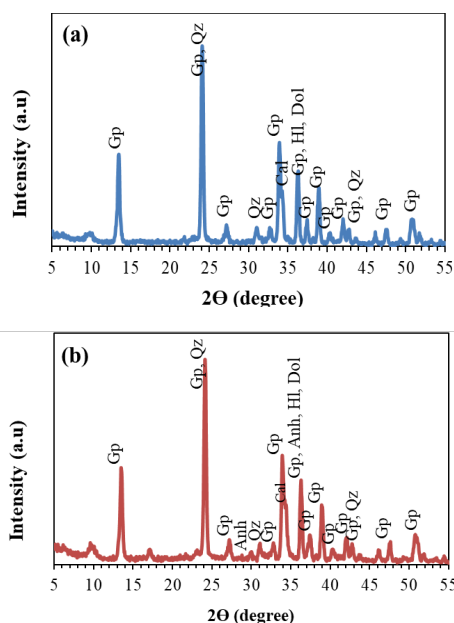


**Figure 5. XRD pattern for a) raw magnesite and b) magnesite calcined at 650 °C. Abbreviations: Clc: Clinoclone ( $Mg_5Al_2Si_3O_{10}(OH)_2$ ); En: Enstatite ( $MgSiO_3$ ); Fo: Forsterite ( $Mg_2SiO_4$ ); Lz: Lizardite ( $Mg_{5.5}Al_{1.0}Si_{3.5}O_{10}(OH)_2$ ); Mgs: Magnesite ( $MgCO_3$ ); Per: Periclase ( $MgO$ ); Qz: Quartz ( $SiO_2$ ); Tlc: Talc ( $Mg_3Si_4O_{10}(OH)_2$ ).**

adsorbed started to decrease due to the sintering of materials and blockage of available pore spaces (Das *et al.*, 2005). The magnesite had the highest optimum calcination temperature (650 °C) (Table 5).

### 5.2.2. Effect of contact time

The amount of F<sup>-</sup> adsorbed increased with an increase in contact time until it reached the equilibrium (Fig. 7b). This was caused by the availability of a large number of vacant adsorbent sites and a high concentration gradient between the water and the adsorbent (Kebede *et al.*, 2016; Sarkar *et al.*, 2006). Bauxite had the lowest optimum contact time compared to other adsorbents (Table 5). This indicates that the F<sup>-</sup> adsorption reaction occurred faster on bauxite, and a short period of time is required to treat water.



**Figure 6. XRD pattern for a) raw gypsum and b) gypsum calcined at 350 °C. Abbreviations: Anh: Anhydrite ( $CaSO_4$ ); Cal: Calcite ( $CaCO_3$ ); Dol: Dolomite ( $CaMg(CO_3)_2$ ); Gp: Gypsum ( $CaSO_4 \cdot 2H_2O$ ); Hl: Halite ( $NaCl$ ); Qz: Quartz ( $SiO_2$ ).**

### 5.2.3. Effect of adsorbent dose

Figure 8 shows the adsorption efficiency increased with an increase in adsorbent dose until optimum. This can be due to the increase in the number of available active sites for F<sup>-</sup> adsorption (Singh *et al.*, 2018). There was no significant increase in the adsorption efficiency after the optimum dose. This is because of a decrease in the ratio of F<sup>-</sup> to the available active sites with an increase in the amount of the adsorbent (Fufa *et al.*, 2014).

On the other hand, the amount of F<sup>-</sup> adsorbed by bauxite increased when the adsorbent dose was increased but started to decrease after the adsorbent dose of 20 g/L. This can be due to the overlapping of active

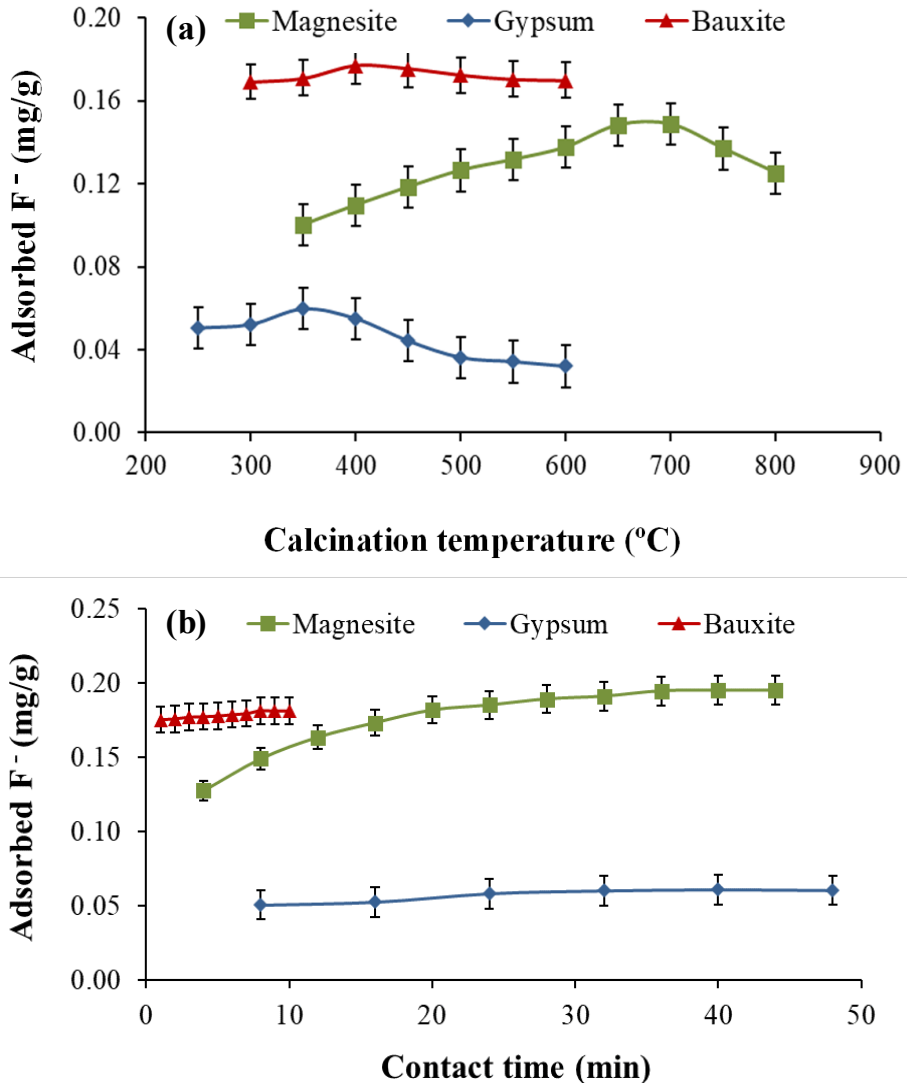


Figure 7. Effect of a) calcination temperature and b) contact time on F<sup>-</sup> adsorption on calcined bauxite, magnesite, and gypsum.

sites as the amount of adsorbent increased per unit volume (Kumar *et al.*, 2007; Rajkumar *et al.*, 2019). For magnesite and gypsum, the amount of F<sup>-</sup> adsorbed decreased when the adsorbent dose was increased. Magnesite had the smallest optimum adsorbent dose (Table 5). This means a small amount of magnesite can be used in the treatment of water compared to when bauxite and gypsum were used.

#### 5.2.4. Effect of particle size

The amount of F<sup>-</sup> adsorbed decreased with the increase in particle size (Fig. 9a). A smaller particle size increases the F<sup>-</sup> adsorption uptake due to increasing the availability of reactive surface areas on the adsorbent surface (Malakootian *et al.*, 2017; Thole *et al.*, 2012a).

**Table 6. The quality of water before and after defluoridation as compared to WHO drinking water guideline (WHO, 2011) and TBS (TBS, 2009)**

Parameter	Raw water	Bauxite	Magnesite	Gypsum	WHO	TBS
Al <sup>3+</sup>	<0.001	0.062	<0.001	<0.001	-	n.m
As <sup>3+</sup>	<0.001	<0.001	<0.001	<0.001	0.01	≤0.05
B <sup>3+</sup>	<0.001	0.03	0.185	0.252	2.4	n.m
Ba <sup>2+</sup>	0.007	0.003	0.116	0.031	0.7	≤1.0
Ca <sup>2+</sup>	297.56	305.36	311.29	451.26	75-200	75-300
Cd <sup>2+</sup>	<0.001	<0.001	<0.001	<0.001	0.003	≤0.05
Cr <sup>3+</sup>	0.008	0.299	0.005	<0.001	0.05	≤0.05
Cu <sup>2+</sup>	<0.001	0.001	0.004	0.007	0.05-1.5	1.0-3.0
Fe <sup>2+</sup>	0.019	0.007	<0.001	<0.001	0.1-1.0	0.3-1.0
Na <sup>+</sup>	33.402	33.172	40.942	74.882	50	n.m
Ni <sup>2+</sup>	0.447	<0.001	0.730	<0.001	0.07	n.m
Pb <sup>2+</sup>	0.028	<0.001	0.068	0.005	0.01	≤0.1
Se <sup>2+</sup>	<0.001	<0.001	<0.001	<0.001	0.04	≤0.05
V <sup>5+</sup>	<0.001	<0.001	<0.001	<0.001	50	10-75
Zn <sup>2+</sup>	<0.001	<0.001	<0.001	<0.001	5.0-15	5-15
Cl <sup>-</sup>	81.54	38.78	92.17	92.17	200-600	200-800
F <sup>-</sup>	8.27	1.02	0.233	1.99	0.5-1.5	1.5-4.0
HCO <sub>3</sub> <sup>-</sup>	520	440	276.2	640	-	n.m
NO <sub>3</sub> <sup>-</sup>	0.2	0.9	0.5	0.4	50	10-75
SO <sub>4</sub> <sup>2-</sup>	4	51	1	119	200-400	200-600
pH	9.38	6.74	10.12	7.41	6.5-8.5	6.5-9.2

### 5.2.5. Effect of water temperature

Fig. 9b shows that the amount of F<sup>-</sup> adsorbed decreased with the increase in temperature when gypsum was used as an adsorbent. This can be caused by the tendency of escaping the water molecules from the interface with increasing temperature. This caused a reduction in the amount of uptake and increase in the desorption of F<sup>-</sup> due to the increase in the thermal energy of the adsorbate (Sujana *et al.*, 1998). Also, the decrease in the solubility of calcite (CaCO<sub>3</sub>) when the temperature rise caused the amount of F<sup>-</sup> removed by precipitation to decrease (Tripathi & Sharma, 2014). The decrease in adsorption uptake with the increase in water temperature indicated that the F<sup>-</sup> adsorption on calcined gypsum was exothermic in nature (Abe *et al.*, 2004).

In the case of bauxite and magnesite, the amount of F<sup>-</sup> adsorbed increased when the

temperature was also increased. This can be due to a decrease in the thickness of the outer surface of the adsorbent, which increased the external boundary layer and rate of diffusion of F<sup>-</sup> across the internal pores of the heated adsorbent (Suneetha *et al.*, 2014). In addition to this reason, the raise in temperature increased the kinetic energy of F<sup>-</sup> that improved the F<sup>-</sup> uptake (Kundu *et al.*, 2017). This indicated that the F<sup>-</sup> adsorption on calcined bauxite and magnesite was an endothermic reaction (Abe *et al.*, 2004).

### 5.3. WATER QUALITY

The pH (9.38) and concentration of F<sup>-</sup> in raw water (8.27 mg/L) were higher than the WHO guidelines (Table 6). The calcined bauxite was able to lower the pH from 9.38 to 6.74) and the F<sup>-</sup> concentration of water from 8.27 mg/L to 1.02 mg/L to reach the WHO drinking water guideline and TBS

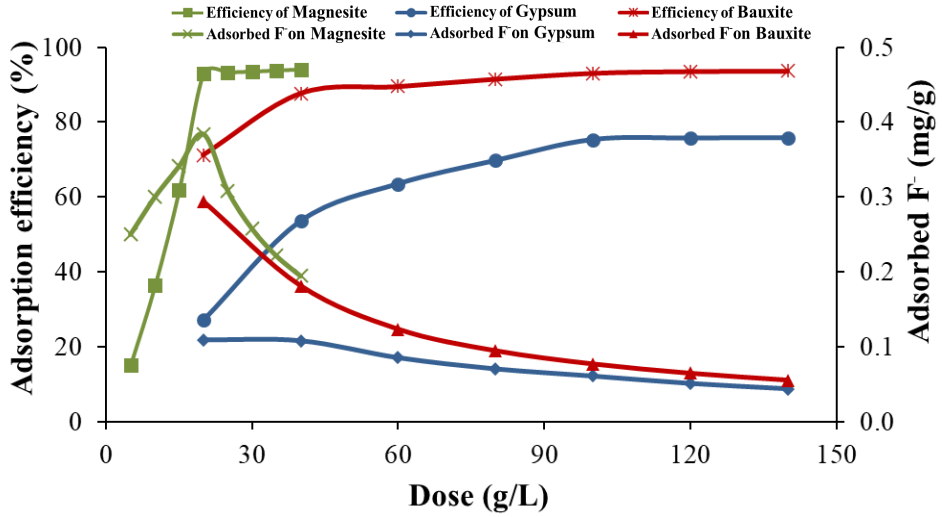
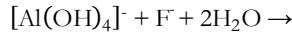
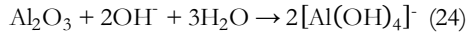


Figure 8. Effect of adsorbent dose on  $F^-$  adsorption on calcined bauxite, magnesite, and gypsum.

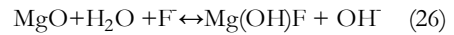
guideline. The pH decreases because bauxite contains a

large amount of  $Al_2O_3$ . Since  $Al_2O_3$  is amphoteric in nature during the adsorption it reacts as acid in the basic water and release  $H^+$  (equation 24 & 25).



During defluoridation, magnesite was able to reduce the initial  $F^-$  concentration of 8.27 mg/L to levels as low as 0.233 mg/L, however, the pH of treated water increased from 9.38 to 10.12 after treatment. This

occurs because the  $MgO$ , which is highly basic was present in large amount in calcined magnesite, and during the adsorption  $MgO$  reacted with  $F^-$  water to produce  $OH^-$ , hence, increasing the pH of water equation 26 (Thole *et al.*, 2013).

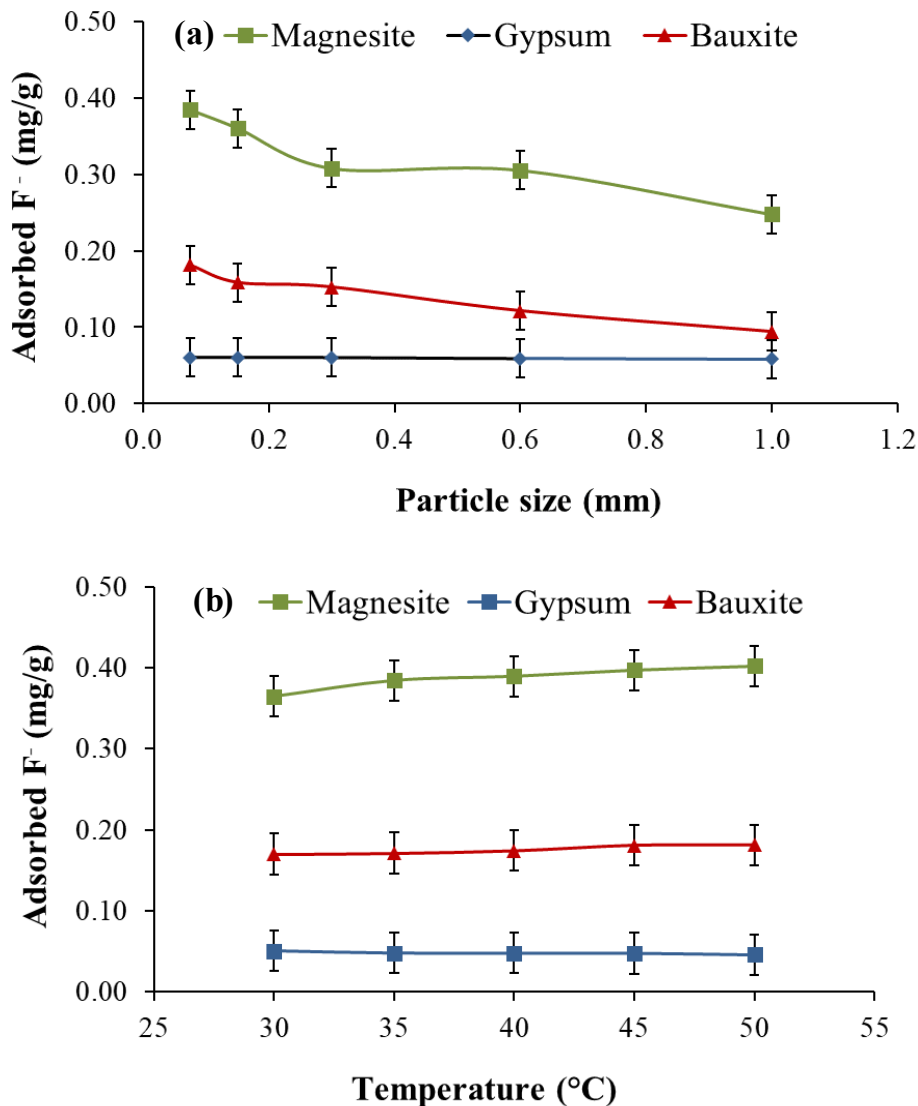


Since the pH after treatment is above the WHO guideline, the pH needs to be adjusted before water can be used for drinking.

Gypsum reduced the concentration of  $F^-$  in raw water to 1.99 mg/L which is slightly higher than the WHO guideline. After adsorption, the pH of the water was lowered from 9.38 to 7.41 because of the presence of

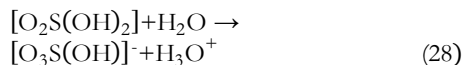
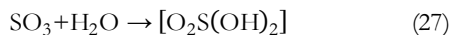
Table 7. The thermodynamic parameters for calcined bauxite, magnesite and gypsum.

Adsorbent	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol K)	$\Delta G^\circ$ (kJ/mol)				
			303 K	308 K	313 K	318 K	323 K
Bauxite	19.892	0.078	-3.75	-4.14	-4.53	-4.92	-5.31
Magnesite	59.703	0.214	-5.22	-6.30	-7.37	-8.44	-9.51
Gypsum	-12.02	-0.031	-2.69	-2.53	-2.38	-2.22	-2.07

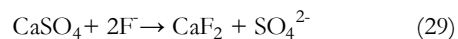


**Figure 9. Effect of a) particle size and b) temperature on  $F^-$  adsorption on calcined bauxite, magnesite, and gypsum.**

a high concentration of sulphur trioxide. Being highly acidic, sulphite binds water molecules and discharges protons to the surrounding medium during dissolution (Thole *et al.*, 2013) (equation 27 & 28)



Water treated with gypsum was found to have a higher amount of sulphate (119 mg/L) than raw water (4 mg/L). This is because, during the adsorption process, sulphate is released to the aqueous media (equation 29) (Masamba *et al.*, 2005).



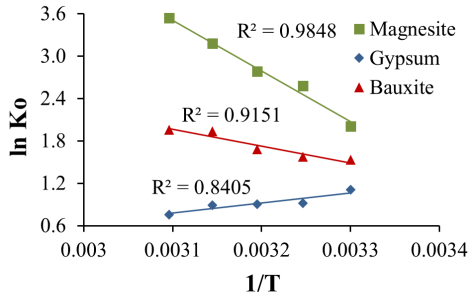


Figure 10. Plot of  $\ln K_o$  against  $1/T$  for  $F^-$  adsorption on calcined bauxite, magnesite, and gypsum.

#### 5.4. THERMODYNAMIC PARAMETERS (PAPERS II & III)

The negative values of  $\Delta G^\circ$  obtained from Figure 10 confirmed the spontaneous nature

of  $F^-$  adsorption on all three adsorbents (Table 7). The values of  $\Delta G^\circ$  are between 0 and -20 kJ/mol, which indicates the  $F^-$  adsorption on all adsorbents was physisorption (Salifu *et al.*, 2016). For bauxite and magnesite, the removal process was favoured by an increase in temperature, which is why the value of  $\Delta G^\circ$  became more negative as the temperature increased (Mourabet *et al.*, 2011).

The positive values of  $\Delta H^\circ$  and  $\Delta S^\circ$  indicate that the  $F^-$  adsorption on bauxite and magnesite was endothermic, and the randomness at the solid-liquid interface increased during the adsorption processes (Chen *et al.*, 2011; Kemer *et al.*, 2009).

In the case of gypsum, the removal process was not favoured with an increase in temperature, and showed a decrease in adsorption, as the value of  $\Delta G^\circ$  became less

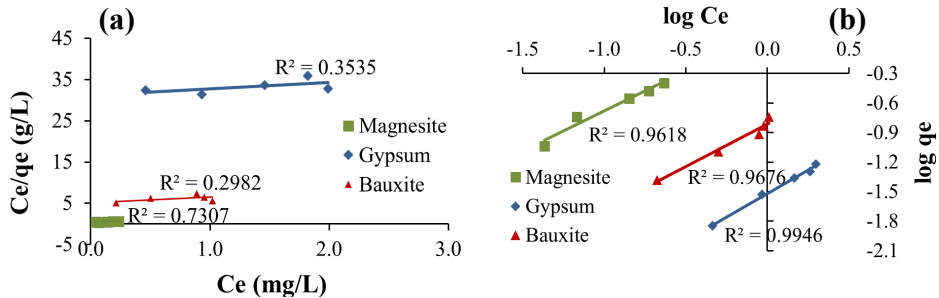


Figure 11. a) Langmuir and b) Freundlich adsorption isotherm for  $F^-$  adsorption on calcined bauxite, magnesite and gypsum.

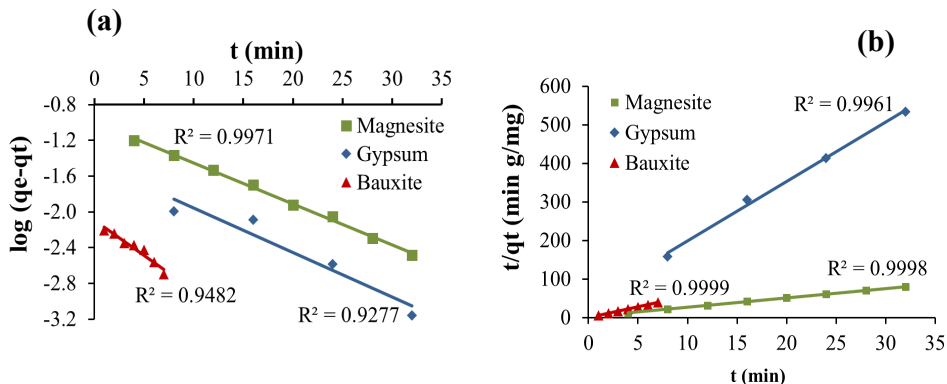
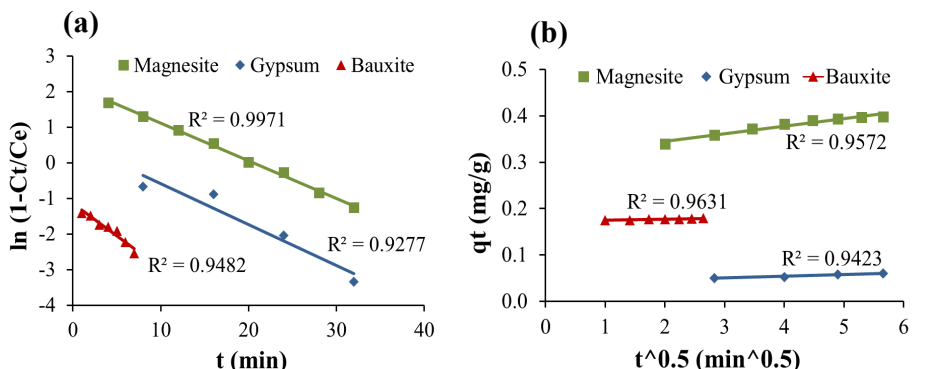


Figure 12. a) Pseudo-first-order and b) Pseudo-second-order for  $F^-$  adsorption on calcined bauxite, magnesite, and gypsum.



**Figure 13. a) Particle diffusion-controlled adsorption and b) Intra-particle diffusion-controlled adsorption for  $F^-$  adsorption on calcined bauxite, magnesite, and gypsum.**

negative as the temperature increased (Mourabet *et al.*, 2011). The negative values of  $\Delta S^\circ$  suggest the decrease in randomness at the solid-liquid interface during adsorption. The exothermic nature of the adsorption process was indicated by the negative values of  $\Delta H^\circ$  (Kamble *et al.*, 2010).

### 5.5. ADSORPTION ISOTHERM

The adsorption data for all adsorbent media exhibited a linear fit with a correlation coefficient close to unity in the Langmuir (Fig. 11a) and Freundlich isotherm models (Fig. 11b). This indicates multilayer adsorption occurred on heterogeneous surfaces on both adsorbents, and magnesite has the highest adsorption capacity ( $k_F$ )

followed by bauxite. The values of  $1/n$  and  $R_L$  for bauxite, gypsum, and magnesite were found to be between 0 and 1 (Table 8), indicating favorable adsorption (Masindi *et al.*, 2015).

### 5.6. ADSORPTION KINETICS

#### 5.6.1. Reaction based model (Paper II & III)

The pseudo-second-order model had a higher correlation coefficient ( $R^2$ ) than the pseudo-first-order model in all adsorbents (Fig. 12a,b). This indicates the applicability of the pseudo-second-order model in all adsorbents (Masindi *et al.*, 2015). All the adsorbents had the highest second-order rate constant than the first-order rate constant. Bauxite had the highest rate constant followed by gypsum (Table 9), which confirms  $F^-$  adsorption

**Table 8. The adsorption isotherm parameters for calcined bauxite, magnesite and gypsum.**

Isotherm	Parameter	Unit	Bauxite	Magnesite	Gypsum
Langmuir	$Q^\circ$	mg/g	0.7416	1.1297	0.0834
	$b$	L/mg	0.2608	2.3412	0.1523
	$R_L$	-	0.3168	0.0491	0.4493
	$R^2$	-	0.2982	0.7307	0.9401
Freundlich	$k_F$	mg/g	0.1537	1.3505	0.0133
	$1/n$	-	0.8607	0.8123	1.5545
	$R^2$	-	0.9676	0.9618	0.9978

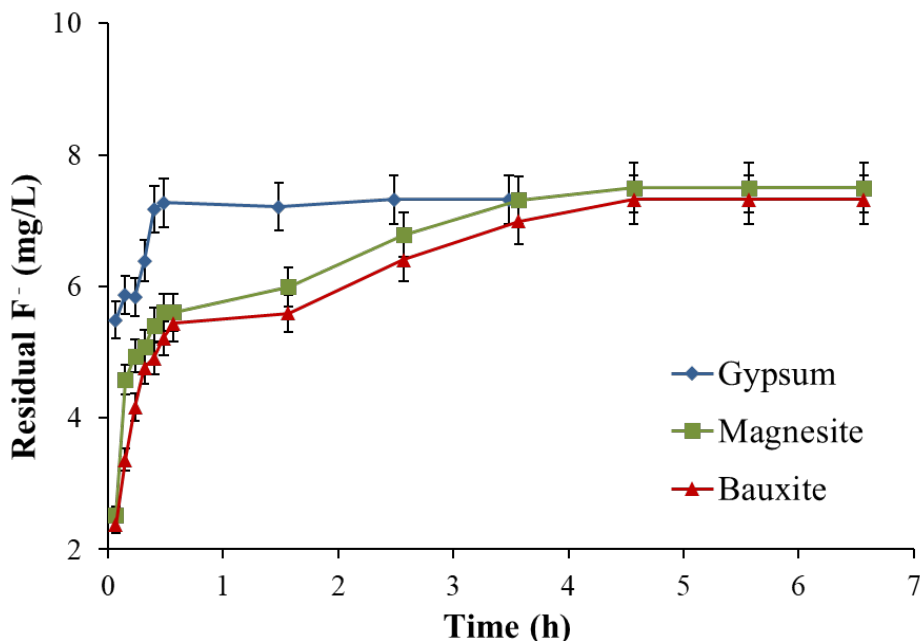


Figure 14. Effect of contact time on  $F^-$  removal from water using calcined bauxite, magnesite, and gypsum (bed depth 5 cm, initial  $F^-$  concentration 7.32 mg/L, initial pH 8.9, and flow rate 390 mL/min).

reaction was fastest in bauxite. The second-order adsorption capacity for magnesite was higher than that of bauxite and gypsum.

#### 5.6.2. Diffusion based model

The adsorption data for bauxite and gypsum fit well with the intra-particle diffusion model, while the particle diffusion model fit well with experimental data for  $F^-$  adsorption on magnesite (Fig. 13a,b). Both adsorbents have the highest rate of particle diffusion model compared to the intra-particle diffusion model (Table 9).

### 5.7. REGENERATION OF THE ADSORBENTS AND $F^-$ REMOVAL

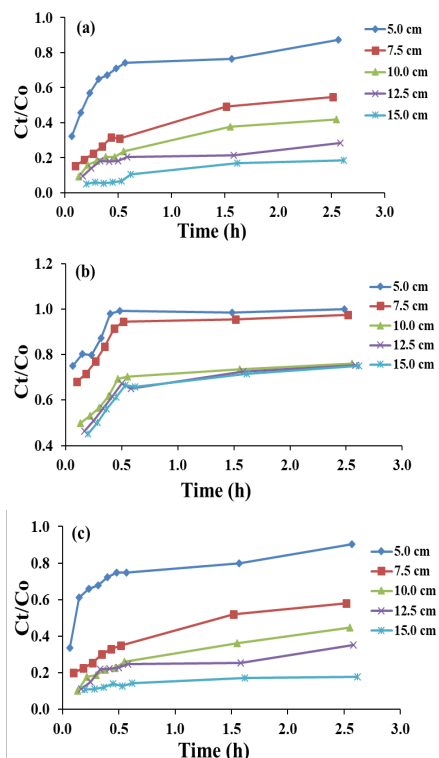
The  $F^-$  adsorption efficiency of the adsorbents decreased after regeneration because of the chemical reactions which take place on the adsorbent surface during adsorption caused the collapse of some of the pores (Li *et al.*, 2020). The  $F^-$  adsorption efficiency of calcined bauxite decreased from 87.67 to 78.23% after the regeneration, and

the 1.8 mg/L of  $F^-$  remained in water when the regenerated bauxite was used (Paper II). This concentration is slightly above the WHO guideline (1.5 mg/L). Magnesite can only be regenerated two times (Paper III), because of the levels of the residual  $F^-$  in the treated water after regeneration for the third time with concentrations of 2.3 mg/L, which is higher than the WHO drinking water guideline (1.5 mg/L).

### 5.8. COLUMN EXPERIMENTS (PAPER IV)

#### 5.8.1. Effect of contact time

Initially, the residual  $F^-$  in water increased with time until no further  $F^-$  removal was observed (Fig. 14). This is because the continuous flow of influent through the column caused the exhaustion of the active sites on the surface of the adsorbents; as a result the  $F^-$  concentration in the effluents increased (Chen *et al.*, 2011).



**Figure 15.** Effect of bed height on  $F^-$  adsorption using calcined a) bauxite, b) gypsum, and c) magnesite at different bed depths (initial  $F^-$  concentration 7.32 mg/L, initial pH 8.9 and flow rate 390 mL/min).



**Figure 16.** The bed depth service time plot for bauxite and magnesite ( $C_o = 7.32$  mg/L).

### 5.8.2. Effect of bed height

Figure 15 shows an increase in the bed height from 5 to 25 cm caused the amount of  $F^-$  adsorption to increase. This can be due to an increase in the surface area of the adsorbent, which proved more binding sites for the adsorption (Murutu *et al.*, 2012). Also, the residence time of  $F^-$  solution inside the column increased with an increase in bed depth, which gives the  $F^-$  enough time to diffuse deeper into the surface of the adsorbents (Chen *et al.*, 2011; Kamble *et al.*, 2010).

### 5.8.3. Bed depth service time (BDST) model

Fig. 16 shows that the service times for  $F^-$  adsorption on the calcined bauxite and magnesite surface at a flow rate of 390 mL/min increased with bed depth. This can

**Table 9.** Kinetics adsorption parameters for calcined bauxite, magnesite and gypsum

Isotherm	Parameter	Bauxite	Magnesite	Gypsum
Pseudo first order	Rate constant ( $\text{min}^{-1}$ )	0.1812	0.1055	0.1149
	$q_c$ (mg/g)	0.0081	0.1010	0.0349
	$R^2$	0.9482	0.9969	0.9277
Pseudo second order	Rate constant (g/mg min)	115.4245	2.2164	5.3805
	$q_c$ (mg/g)	0.1799	0.4113	0.0648
	$R^2$	0.9999	0.9992	0.9961
Particle diffusion model	Rate constant ( $\text{min}^{-1}$ )	0.1813	0.1054	0.1148
	$R^2$	0.9482	0.9969	0.9277
Intra-particle diffusion model	Rate constant ( $\text{mg/g min}^{0.5}$ )	0.0025	0.0163	0.0036
	$R^2$	0.9631	0.9569	0.9423

**Table 10. Parameters obtained from the BDST plot**

Parameter	Unit	Bauxite	Magnesite
$K_x$	L/mg s	1.43E-5	1.50E-5
$N_o$	mg/L	77668.83	71349.62
$Z_o$	cm	7.21	8.28
$\frac{N_o}{C_{ov}}$	s/cm	1622.40	1490.40
-	s	12942	12342
$1/K_x C_o \ln[(C_o/C_b) - 1]$			
$R^2$		0.89	0.86

be due to the increase in the mass of adsorption media with the increase in bed depth which provides a larger surface for fluoride adsorption resulting in longer service times (Thole *et al.*, 2012b). The small values for  $k$  (Table 10) indicate that the breakthrough will occur in a short bed; therefore, a deeper bed is required to avoid a breakthrough (Chen *et al.*, 2011).

#### 5.8.4. Empty bed residence time design model

The results show that the volume of water treated and service time at the breakthrough point increased with increasing bed depth; meanwhile, the adsorbent exhaustion rate decreased (Table 11).

## 6. COST ANALYSIS OF ADSORBENT MATERIALS

The cost analysis is a very important parameter during the selection of adsorbent to be used in water treatment. In the existing study, bauxite, gypsum, and magnesite were suggested as low-cost adsorbents for fluoride removal. The preparation cost of these materials is highly needed in order to determine the overall cost for economic feasibility and large-scale applicability of

these materials in water treatment (Turkey *et al.*, 2018). The production cost of a unit of calcined adsorbent depends on the collection cost and the cost of electricity used in the oven, crusher, sieve, and muffle furnace, which was found to be 8334.58 TSh ( $\approx$  3.55 USD/kg as of 30<sup>th</sup> June 2022) at lab scale (Table 12). The electricity cost can be lowered by drying the materials in sunlight. This will increase the time used to dry the adsorbents but lower the production cost from 3.55 USD/kg to 1.08 USD/kg, which is very low compared to the production cost of the other adsorbents available in the market, e.g., the production of activated carbon is 8.40 USD/kg (Sharma *et al.*, 2021).

## 7. IMPLICATION OF FLUORIDE REMOVAL AND FUTURE OUTLOOK

Significant efforts have been made on the application of naturally occurring minerals in defluoridation. Some of the expected consequences of utilizing bauxite, gypsum, and magnesite in defluoridation include:

#### Public Health Benefits

The use of naturally available minerals in defluoridation can provide clean and safe

**Table 11. Empty bed residence time and adsorption exhaustion rate for bauxite and magnesite at different dose**

WA (g)	BD (cm)	BV (cm <sup>3</sup> )	EBRT (min)	Bauxite			Magnesite		
				VWTB (L)	STBP (h)	AER (g/L)	VWTB (L)	STBP (h)	AER (g/L)
3000	7.5	2355	6	5.495	0.233	545.951	2.355	0.100	1273.89
4000	10	3140	8	10.99	0.467	363.967	8.635	0.367	463.23
5000	12.5	3925	10	37.288	1.583	134.093	27.475	1.167	181.98
6000	15	4710	12	85.173	3.617	70.445	77.323	3.283	77.597

**Table 12. Cost estimation of calcined bauxite, gypsum and magnesite per kg.**

S/ No	Item	Unit Cost (Tsh)	Consumption	Price (Tsh)	Price (\$) (As on 30th June 2022)
1	Bauxite/magnesite/gypsum Collection	1315.60	-	1315.60	0.56
2	Grinder	292.74 per kWh	0.25 kWh for 0.5 h	36.59	0.02
3	Sieving	292.74 per kWh	0.25 kWh for 0.25 h	18.30	0.01
4	Calcining	292.74 per kWh	1.6 kWh for 2 h	936.77	0.40
5	Net Cost	-	-	2307.26	0.98
6	Other Overhead Cost (10% of Net Cost)	-	-	230.73	0.10
<b>Total Cost</b>		-	-	<b>2537.99</b>	<b>1.08</b>

drinking and cooking water and prevent fluoride-related health problems such as dental and skeletal fluorosis. This can lower the healthcare expenditures and higher quality of life for afflicted communities.

#### ***Socio-economic Implications***

Defluoridation can lead to job development and economic growth by establishing small businesses that make and distribute defluoridation products. Also, the decrease in healthcare expenditures connected with fluoride-related health problems can minimize the economic burden on impacted populations.

#### ***Environmental Sustainability***

Natural minerals such as bauxite, magnesite, and gypsum can provide sustainable and eco-friendly alternatives to chemical-based adsorbents for defluoridation. This can aid in decreasing the environmental impact of the chemical-based defluoridation process and encouraging the use of locally available and renewable materials.

#### ***Policy Implementation***

Development and implementation of policies that encourage the study, creation, and spread of inexpensive and efficient defluoridation technologies can stimulate governments to significantly contribute to defluoridation. This may lead to launching public awareness campaigns, offering grants for defluoridation initiatives, and establishing legal structures to oversee and uphold water quality regulations.

#### ***International Cooperation and Knowledge Sharing***

The cooperation between nations and international organizations may assist in the exchange of best practices, technological know-how, and financial resources in order to fight fluorosis on a worldwide scale.

## **8. CONCLUSIONS**

Calcined bauxite, gypsum, and magnesite have higher F<sup>-</sup> removal capacity compared to their raw forms. Magnesite and bauxite lower the F<sup>-</sup> concentration of water to WHO and TBS drinking water guidelines. The F<sup>-</sup> concentration in water treated by gypsum was slightly above WHO but within the TBS standard (4.0 mg/L). The concentration of other inorganic ions in treated water complies with the WHO and TBS drinking water standards. Bauxite and gypsum lowered the pH of the water to WHO and TBS standards. Magnesite raised the pH from 9.38 to 10.12, which is above the standards; therefore, pH adjustment is needed before water can be used for drinking. The adsorption capacities for all adsorbents were lower than that reported in other literature. This can be caused by the higher pH of water, which caused F<sup>-</sup> to compete with OH<sup>-</sup> for the active site on the surface of bauxite, gypsum, and magnesite surface. The adsorption experiments data for both adsorbents fitted well with Freundlich adsorption isotherm and the pseudo-second-order kinetic. Bauxite and gypsum followed the intra-particle diffusion

model, while magnesite followed the particle diffusion model. The values of  $\Delta G^\circ$  indicate that the  $F^-$  adsorptions on all adsorbents surfaces were spontaneous. The value of  $\Delta H^\circ$  and  $\Delta S^\circ$  for bauxite and magnesite show that the adsorption was endothermic, and the randomness at the solid–liquid interface increased during the adsorption processes. For the gypsum, the adsorption was exothermic in nature, and there was a decrease in the randomness at the solid–liquid interface during the adsorption processes. The effectiveness of adsorbent for  $F^-$  removal is reduced after each regeneration due to the collapsing of some pores during the adsorption process. The Bed Depth Service Time (BDST) plot showed that the increase in bed depth caused the service times for  $F^-$  adsorption on the surface of calcined bauxite to increase. The critical bed depths ( $Z_0$ ) obtained were 7.21 and 8.28 cm for bauxite and magnesite, respectively. The small values of the kinetic rate parameter ( $K_2$ ) for bauxite (1.43E-5 L/mg s) and magnesite (1.50E-5 L/mg s) indicate that the deeper beds are required in order to avoid the breakthrough. The adsorption results and the overall cost analysis shows that the cost of calcined bauxite and magnesite is low as compared to other available adsorbents, and

therefore, they can be used in  $F^-$  removal from water.

To prevent fluoride-related health problem, corrective measures to control fluorosis where fluoride levels of potable water are consistently beyond permissible levels is necessary. Defluoridation must be used to remove excess fluoride in drinking and cooking water in areas with no available water source alternatives. Despite the availability of a wide range of techniques developed for removing fluoride from potable water, fluorosis is still a serious and widespread health problem, particularly in rural communities which depend on untreated water supplies. The applications of the existing technologies require some research at the local level because communities differ in socio-economic status.

Further research is therefore required to establish the suitability and sustainability of the existing research results in pilot and full-scale plants. This thesis proved the baseline on the applicability of locally available bauxite, magnesite, and gypsum in fluoride removal from groundwater. In this study, the effects of only a few parameters were investigated. Further investigation is required to study the effect of other parameters, e.g., pH, co-occurrence ions, and flow rate.

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