AFRICA CENTER OF EXCELLENCE FOR WATER MANAGEMENT

ADDIS ABABA UNIVERSITY

FLUORIDE REMOVAL FROM WATER USING ALUMINIUM MODIFIED ACTIVATED CARBON PREPARED FROM KHAT (*CATHA EDULIS*) STEM.

By

Hyacinthe Niyitegeka

A thesis submitted to the African Centre of Excellence for Water Management (ACEWM) in partial fulfillment of the requirement for a Master's Degree in Water Management (Water and Wastewater Technology) of Addis Ababa University

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Thesis Approval Form

APPROVED BY BOARD OF EXAMINERS

This is to certify that we the undersigned, have examined this MSc thesis entitled **"Fluoride Removal from Aqueous Solution Using Aluminium Modified Activated Carbon Prepared from Khat (*Catha edulis*) stem"** and that in our opinion; it is fully adequate, in scope and quality, as an MSc thesis for the degree of Master of Science in Water Management (Water and Wastewater Technology).

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Statement of the author

I, **Hyacinthe Niyitegeka,** declare that this research report is my original effort and work and to the best of my knowledge, the findings have never been previously presented to the Addis Ababa University or elsewhere for the award of any academic qualification. Where assistance was sought, it has been accordingly acknowledged. The findings, interpretations and conclusions expressed in this study neither reflect the views of the Addis Ababa, African Centre of Excellence for Water Management (ACEWM), nor those of the individual members of the MSc Examination Committee.

Signature..... Date: 13/07/2021

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Abbreviations

ABC: Activated bamboo charcoal

AC: Activated Carbon

AIAABC: Aluminium-iron-amended activated bamboo charcoal

ASTM: American Society for Testing and Materials

BBD: Box-Behnken design

BET: Brunauer–Emmett–Teller

CAC: *Catha edulis* activated carbon

CCD: Central Composite Design

DNA: Deoxyribonucleic acid

EC: Electro Coagulation

ED: Electrodialysis

ERV: Ethiopia Rift Valley

F^-: Fluoride Ion

FTIR: Fourier-transform infrared spectroscopy

MAC: Macroporous Activated Carbon

RO: Reverse Osmosis

RSM: Response Surface Methodology

SEM: Scanning Electron Microscopy

SSA: Specific surface area

WHO: World Health Organization

XRD: X-Ray Diffraction

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Abstract

Fluoride is one of the most abundant elements found in Ethiopian groundwater and in many other parts of the world, posing a significant threat to the regions' groundwater supply. The presence of fluoride above the set limit of 1.5 mg/L in drinking water consumed by humans has resulted in a variety of physical health issues such as dental and skeletal fluorosis. In the Ethiopian Rift Valley, nearly 8 million people drink fluoride-contaminated water. The same problem has been seen in other regions such as the Kenyan and Tanzanian Rift Valleys. The current study describes the preparation of a low-cost adsorbent using aluminium-modified activated carbon prepared from Khat (*Catha edulis*) stem as well as its adsorption effectiveness for fluoride ion removal from aqueous solution. The fluoride adsorption capacity of the resulting modified adsorbent was experimentally evaluated with batch adsorption experiments in numerous operating conditions, which include pH, adsorbent dose, and fluoride initial concentration. The results showed that the modified activated carbon retained good fluoride performance; with an adsorbent dose of 2.47 g/L, 87.9 % of 2.1 mg/L initial fluoride concentration could be reduced from aqueous solution containing at pH 6.08 in 60 minutes. The adsorbent was applied to real drinking water samples collected from Tube, Wadesha, Dollessa, and Tejitu, and it was discovered that the concentrations of ground water collected from Tube and Wadesha were reduced from 3.67 mg/L and 4.33 mg/L to 1.0 mg/L and 1.28 mg/L, respectively, and are within WHO permissible drinking water limits. The scanning electron microscopy (SEM) and Fourier transform-infrared spectroscopy (FTIR) were used to describe modified activated carbon and investigate the possible adsorption mechanism. The results show that aluminium-modified activated carbon derived from khat (*Catha edulis*) has a reasonable defluoridating capacity and could be used as an appropriate and effective adsorbent for a long-term solution to the fluoride problem in drinking water with lower fluoride concentrations.

Keywords: Fluoride removal, fluorosis, Khat (*Catha edulis)* stem, adsorption.

1. Introduction

1.1. Background of the study

Water is very important for sustaining life, development (Mulugeta & Weijun, 2016), and the environment (Meenakshi and R. C. Maheshwari, 2006). It has a broad impact on human life's aspects including but not limited to health, food, energy as well as the economy (M. T. Amin, A. A. Alazba, 2014). The freshwater is considered as surface water and groundwater where the groundwater is the main source of water in many different areas (Ramya Araga, Suresh Kali, and Chandra S. Sharma, 2019), especially in developing countries (Meenakshi and R. C. Maheshwari, 2006). Sufficient and reliable freshwater supply is essential in the protection of human health, supporting food production, ecosystem preservation, sustaining economic development, and providing the essential goods and services (The GWP and the INBO, 2009). Water is essential for life and health; the human right to water is obligatory for a better life in human self-regard. It is a pre-requisite to other human rights (Zemenu Awoke, 2012), it is a public good (The GWP and the INBO, 2009). Even though the sources of water may seem to be in abundance (consider the oceans and seas), only less than one per cent of the world's water is usable for basic human needs (Jean-Pierre Sandwidi & Stein Alexander J., 2003).

Today, there is an ever-increasing population growth worldwide which leads to the increased freshwater consumption (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019). The ever increasing industries, rapid infrastructure development and land-use alterations, ineffective use of water, and over-abstraction have been reported as the main threats to the deterioration of freshwater quality (M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, 2009; Meenakshi and R. C. Maheshwari, 2006; Nathanial Matthews, 2016). Fluoride is one of the pollutants that impact water quality (G.R. Kiran Kumar, M. Shambavi Kamath, and Praveen S Mallapur, 2016). Fluoride in drinking water has a great impact on teeth and bones; when its level is within the allowable limit, it prevents the caries of teeth and strengthens the enamel; it increases the mineralization of teeth and demineralizes the enamel (Amit B., Eva K., Mika S., 2011; M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, 2009; Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018), in animals and humans (Mekala Suneetha, Bethanabhatla Syama Sundar, and Kunta Ravindhranath, 2015).

It was highlighted that the fluoride concentration of about 0.7 mg/L is desirable for teeth and bones (Kalpana Singh, Dilip H. Lataye, 2016; M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, 2009) while according to Ayu Haslija Abu Bakar et al. (2019), it is the fluoride levels ranging from 0.8 to 1.0 mg/L (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019) and this is mostly beneficial in children (Amit B., Eva K., Mika S., 2011) whose age is below 8 years old (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019).

Fluoride contamination of drinking water is so common, especially in the regions where the main source of water supply is the groundwater (AL Ramanathan, S Chidambaram, 2003; Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019; World Health Organization, 2004). The groundwater is considered as the second main source of fresh water on Earth after polar ice caps, as it holds more than a hundred times the volume of freshwater lakes and streams. It is approximately equal to 30% of the global freshwater. It provides fresh water to people for various activities. Unfortunately, it is being overexploited and contaminated due to the population growing at an alarming rate which is associated with the increased human activities (Edwin Brands, Raj Rajagopal, Usha Eleswarapu and Peter Li, 1993). It was stressed that a freshwater reserve of about 97% is retained in the aquifers that is the source of drinking water for more than 1.5 billion people worldwide. It has many pros over the surface water like it is pathogenic bacteria and viruses free as well as having less concentration of organic matter. But unfortunately, the various inorganic and organic pollutants which are very harmful to animals and humans have been revealed (Jan Hoinkis, Sara Valero-Freitag, Martin P. Caporgno & Christian Pätzold, 2011).

It was mentioned that groundwater is the main source of fluoride intake. An estimated population of more than 200 million is suffering from pollution caused by fluoride that exceeds the concentrations limit allowed by the WHO (Amit B., Eva K., Mika S., 2011; Jagvir Singh, Prashant Singh, Anuradha Singh, 2014; Tao Wu, Lili Maoa, Haizeng Wang, 2017; Vivek Ganvir and Kalyan Das Tata, 2011), all these people are from more than 25 nations worldwide (Teshome L. Yami, Jim F. Chamberlain, Feleke Z. Beshah, David A. Sabatini, 2018). The fluoride tolerance in drinking water allowed by WHO is 1.5 mg/L (World Health Organization, 2004). Fluoride is mainly found in mineral rocks (Ayu Haslija Abu Bakar, Luqman Chuah

Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019) such as Sellaite (MgF_2), Fluorspar (CaF_2), cryolite (Na_3AlF), and fluorapatite ($3Ca_3(PO_4)_2Ca(FCl_2)$) (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019; M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, 2009). Cryolite is found in igneous rocks while Fluorspar is found in sedimentary rocks. These minerals of fluoride are almost insoluble in water. Therefore, for the fluorides to be present in groundwater, this only happens when the conditions favour the dissolution of fluorides or when the industrial effluents discharged to the water bodies contain a high content of Fluoride (M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, 2009).

It was noted that in order of magnitude, fluorapatite is less soluble than hydroxyapatite, and after prolonged exposure to a high concentration of fluoride, the conversion of a large amount of hydroxyapatite into fluorapatite makes teeth and the bones denser, harder, and more brittle. This causes fluorosis of the teeth; their mottling and embrittlement. The dental fluorosis progresses to skeletal fluorosis when the exposure to a higher fluoride concentration is prolonged (Kalpana Singh, Dilip H. Lataye, 2016; M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, 2009; Vivek Ganvir and Kalyan Das Tata, 2011). Ayu Haslija Abu Bakar et al. (2019) noted that the fluoride levels that cause the fluorosis of teeth range from 1.5 to 2.0 mg/L while the concentration greater than 3.0 mg/L causes skeletal fluorosis (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019). WHO classifies fluoride as one of the water pollutants consumed by human, besides nitrate and arsenic that cause adverse health problems such as restraining DNA synthesis, carbohydrates, lipids, proteins, vitamins, and metabolism (Amit B., Eva K., Mika S., 2011; Habiba Lebrahimi, Mohammed Fekhaoui and Abdelkabir Bellaouchou, 2020)

1.2. Problem statement

Excess fluoride consumption above 1.5 mg/L in drinking water can cause a variety of health problems, including dental and skeletal fluorosis, cancer, lower birth rates, neurological disorders, thyroid gland injury, and lower intelligence quotient (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019; Soumaya Gmar, Ilhem Ben Salah Sayadi, Nawel Helali, Mohamed Tlili, and Mohamed Ben Amor, 2015; Teshome L. Yami, Jim F. Chamberlain, Feleke Z. Beshah, David A. Sabatini, 2018); in extreme cases, it can even result in death (Mekala Suneetha, Bethanabhatla Syama Sundar, and Kunta Ravindhranath, 2015). Fluoride affects the intestinal mucosa, which produces hydrofluoric acid, which causes corrosive effects in the stomach. Their high concentrations aggravate kidney disease by interfering with various enzymes, disrupting various processes in the body such as coagulation, oxidative phosphorylation, neurotransmission, and glycolysis. Fluoride has also been shown to interfere with the functioning of the pineal gland and brain (Amit B., Eva K., Mika S., 2011).

Globally, fluoride contamination in the groundwater has been acknowledged as one of the serious issues of water pollution (Amit B., Eva K., Mika S., 2011; Vivek Ganvir and Kalyan Das Tata, 2011). Fluoride levels in groundwater have been found to be high in several developing and developed countries, including various regions of the United States, Asia, and Africa. Fluoride levels in groundwater greater than 30 mg/L have been found in a number of Asian, African, and American regions (Ramya Araga, Shantanu Soni, Chandra S. Sharma, 2017; Vaishali Tomar and Dinesh Kumar, 2013). According to Shikha Modi and Ranjeeta Soni (2013), India is one of the countries where fluoridated groundwater has a significant impact on the population. Groundwater is the primary source of drinking water in this country's rural areas, and it is heavily contaminated by fluoride, with fluoride concentrations ranging from 1 to 48 mg/L in 17 regions. Fluorosis affects over 62 million Indians, 6 million of whom are children (Dr. Shikha Modi and Ranjeeta Soni, 2013). The same issue was discovered in groundwater from several wells in Morocco's Khouribga region; residents of this region are suffering from endemic illnesses, particularly dental fluorosis, as a result of their consumption of fluoridated underground waters (Habiba Lebrahimi, Mohammed Fekhaoui and Abdelkabir Bellaouchou, 2020).

Groundwater fluoride concentrations are high in East African Rift Valley countries such as Tanzania, Kenya, and Ethiopia. The highest fluoride concentration recorded was 2800 mg/l in Kenya's Lake Nakuru. Fluoride, like in other African countries located in the Rift Valley, is a major health concern for communities in the Ethiopian Rift Valley area that rely on ground water sources. In the Ethiopian Rift Valley, nearly 8 million people drink fluoride-contaminated water. (Habtamu Demelash, Abebe Beyene, Zewdu Abebe, and Addisu Melese, 2019). It was mentioned that Ethiopia is one of 23 countries where the drinking water is contaminated with a high concentration of fluoride, nearly 33 mg/L. This is very common in many Ethiopian Rift Valleys towns and has been reported since the 1970s (T. Getachew, A. Hussen, V. M. Rao, 2014). An example of people from the ERV, approximately 11-14 million, rely on fluoride-polluted groundwater with average levels ranging from 5 to 26 mg/L (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019). Fluoride concentrations of 11 mg/L and 4.6 mg/L were found in the Kenyan and Tanzanian Rift Valleys, respectively (Habtamu Demelash, Abebe Beyene, Zewdu Abebe, and Addisu Melese, 2019).

Ethiopian cities such as Addis Ababa, Bahir Dar, Debre Birhan, Debre Markos, Dire Dawa, Harar town, and Shambu town have been identified as producing large amounts of solid waste. The majority of it is khat waste that users and exporters have discarded. Ethiopia's capital city, Addis Ababa, generates 0.5 kg of solid waste per capita per day, and managing these wastes is difficult. It was noted that the young leaves of khat are chewed as a social activity, while the older leaves and twigs are discarded. This constitutes the majority of municipal solid waste, which is dumped in large quantities (H. Y. Rameshwar and A. Argaw, 2016). The Khat (*Catha edulis*) stems are discarded all over Ethiopia, particularly in open market areas, on streets, and at dumpsites. As a result, they are regarded as the primary source of a large amount of solid waste in many Ethiopian cities, posing a threat to the environment. Therefore, preparing the activated carbon from the Khat (*Catha edulis*) and applying it as an adsorbent in removing the fluoride from water can be an environment-friendly method as it reduces the high quantity of stems disposed to the environment (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019).

There are several alternative treatments for removing fluoride ion from water; however, the majority of these technologies are characterized by ineffectiveness, operational difficulty, higher operational costs, sludge generation, and, most importantly, they cannot be applied on a small

scale. Therefore, this research aims to develop and investigate for an alternative cost-effective defluoridation treatment adsorbent prepared from khat *(Catha edulus)* which is locally available.

1.3. Research questions

1. What are the characteristics of the synthesized activated carbon derived from khat *(Catha edulus*)?
2. What are the major operating parameters that affect prepared aluminium modified activated carbon derived from khat *(Catha edulus*)?
3. To what extent can, aluminium modified activated carbon derived from khat *(Catha edulus*) remove the fluoride from the aqueous solution?
4. Is the use of aluminium-modified activated carbon a promising technique for the removal of fluoride from drinking water?

1.4. Research objectives

1.4.1. Main objective

The main objective of this study was to synthesize, characterize and investigate the fluoride removal efficiency of aluminium modified Khat (*Catha edulis)* based activated carbon from aqueous solution.

1.4.2. Specific objectives

1. To synthesize and characterize activated carbon from Khat (*Catha edulis)* stems with different Temperatures.
2. To synthesize and characterize Aluminium modified activated carbon with impregnation techniques.
3. To evaluate the performance of the prepared Aluminium modified activated carbon on the removal of fluoride from aqueous solution.
4. To statistically optimize the best adsorption operational parameters for higher fluoride removal efficiency.
5. To investigate adsorption isotherms and kinetics of Aluminium modified activated carbon prepared under optimum conditions.

1.5. Significance of the study

The findings of this research will help to propose an alternative fluoride removal treatment method using the locally available raw material such as Khat (*Catha edulis*) stem that is already considered as solid waste. By using such material, we can get the advantage not only preparing adsorbent material to remove the fluoride contaminant from water, but also lessen environmental impact through conversion of solid waste to useful material. This is therefore enhancing the use of cost-effective local materials to for the sustainable development. Furthermore, the data, which obtained from this study, will help the other researchers to investigate the material for a similar purpose and serve as the baseline information on the fluoride removal from water using Aluminium-modified activated carbon prepared from Khat (*Catha edulis)* stem for further investigation.

1.6. Scope and limitation of the study

This research is limited to preparation, modification, and characterization of unmodified and modified activated carbon using aluminum oxide through impregnation techniques. It also focused on the study and optimization of operational parameters for the removal of fluoride from synthetic fluoridated water under controlled laboratory conditions and the real drinking ground water samples collected from Tube, Wadesha, Dollessa and Tejitu sites, Ethiopia. Furthermore, it includes the investigation of adsorption isotherms and kinetics of the prepared modified activated carbon material.

2 Literature review

2.1.History and effects of Khat (*Catha edulis*)

Khat (*Catha edulis*) is a plant known as a dicotyledonous evergreen shrub that belongs to the family of Celastraceae and is cultivated for its soothing impact in its leaves (Ezar N. Al-Hebshi and Nils Skaug, 2005; Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019; Siddig Ibrahim Abdelwahab, Rashad Alsanosy, Manal Mohamed Elhassan Taha, and Syam Mohan, 2018). Khat is known to be cultivated mainly in Africa and the Arabian Peninsula (Siddig Ibrahim Abdelwahab, Rashad Alsanosy, Manal Mohamed Elhassan Taha, and Syam Mohan, 2018). Since the practice of chewing Khat (*Catha edulis*) deems to be acceptable in Ethiopia, it is believed to originate in Ethiopia, and is mainly cultivated and produced in Ethiopia, Kenya, Yamen (Eden Yitna et al., 2018; Nilesh B. Patel, 2019; Siddig Ibrahim Abdelwahab, Rashad Alsanosy, Manal Mohamed Elhassan Taha, and Syam Mohan, 2018; Workineh Getahun, Teferi Gedif, 2010), and Indonesia (Nilesh B. Patel, 2019). It is also grown in a few other countries, particularly in mountainous areas. If properly cared for, Khat is resistant to various diseases and can live for up to 100 years (Ezar N. Al-Hebshi and Nils Skaug, 2005).

The extensive use of Khat can cause adverse negative effects on an individual, family, society, economy, public health (Nilesh B. Patel, 2019), and environment (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019). It was claimed that Khat chewing has adverse health effects such as hypertension (Workineh Getahun, Teferi Gedif, 2010), malnutrition, insomnia, and many others (Siddig Ibrahim Abdelwahab, Rashad Alsanosy, Manal Mohamed Elhassan Taha, and Syam Mohan, 2018). Consumption of the khat also was reported to affect the activities of the enzymes in the body (Worku Bedada, Fernando de Andrés, Ephrem Engidawork, Jemal Hussein, Adrián LLerena, 2018).

Ethiopia is the world's leading producer of khat, with production steadily increasing. The total amount produced has increased at a faster rate, increasing by 246 percent, amounting to hundreds of millions of kilograms of khat per year. From a few thousand hectares in the 1950s, khat is now grown by millions of farmers on a quarter million hectares of land in Ethiopia (L. Cochrane and D. O'Regan, 2016). The increased production of khat is associated with an increase in solid waste, as older leaves and stems are discarded by export packagers and chewers in many Ethiopian cities (H. Y. Rameshwar and A. Argaw, 2016).

2.2.The source of Fluoride

A fluoride is an ionic form of the element fluorine. Fluorine is a corrosive gas that appears pale yellow-green (Mirna Habuda-Stanić, 2014); it is rare in the natural environment (AL Ramanathan, S Chidambaram, 2003; Mirna Habuda-Stanić, 2014); the lightest among other halogens (Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018), and it is an element with the highest electronegativity hence high reactivity; thus, it does not exist in an elemental form instead it occurs in the ionic form. It can form complexes when present in aquatic environments with a lower pH and it exists as a single fluoride ion F^- at higher pH (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019; Malago et al., 2017; Mirna Habuda-Stanić, 2014). Fluoride ion has the characterizations such as small radius hence high tendency of forming different many organic as well as inorganic compounds (Mirna Habuda-Stanić, 2014). Tao Wu et al. (2017) mentioned that Fluorine is a very important element for the human body (Tao Wu, Lili Maoa, Haizeng Wang, 2017).

Fluoride presence in drinking water happens either naturally or by the addition of salts containing a certain amount of fluoride to drinking water (Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018). The presence of fluoride can be in the surface and groundwater (Mirna Habuda-Stanić, 2014), where its main source is groundwater. It is widely present in different mineral rocks then released gradually into the groundwater after the slow dissolution of the rocks occurs (Amit B., Eva K., Mika S., 2011; G.R. Kiran Kumar, M. Shambavi Kamath, and Praveen S Mallapur, 2016). In addition to the groundwater enrichment of natural sources for fluoride, natural sources of fluoride such as volcanic eruption as they release hydrogen fluoride gases; and the marine aerosols (Kalpana Singh, Dilip H. Lataye, 2016). The anthropogenic activities predominantly the use of pesticides as well as industrial activities (Lucía I. Moran Ayala, Marie Paquet, Katarzyna Janowska, Paul Jamard, Cejna A. Quist-Jensen, Gabriela N. Bosio, Daniel O. Mártire, Debora Fabbri, 2018). The industrial effluents discharged into the natural watercourses without prior treatments are the other sources of fluoride; for some specific industries whose wastewaters contain higher concentrations of fluoride than the natural waters which range from ten to thousands of milligrams per litre including semiconductor, electroplating, ceramic and glass

industries, etc. (Amit B., Eva K., Mika S., 2011; G.R. Kiran Kumar, M. Shambavi Kamath, and Praveen S Mallapur, 2016; Mirna Habuda-Stanić, 2014); the industries that use the $HF_{(aq)}$ acid as agents for cleaning/etchant. An example is one Fluorine Chemical industry from Zhejiang Juhua whose effluent was reported to have more than 100 mg/L of fluoride concentration at pH ranging from 5 to 7 (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019).

2.3.Activated carbon

2.3.1. The source and importance of activated carbon

Activated carbon is referred to as a final product of the activation operation of materials with greater carbon content (> 60%) (O. F. Olorundare,T. A. M. Msagati, R. W. M. Krause, J. O. Okonkwo, and B. B. Mamba, 2014; S. Khedr, Mona S., Nady Fathy, and A. Attia, 2014). Due to its unique qualities, the activated carbon is predominantly applied in desalination, water and wastewater treatment as well as the air purification. Globally, the annual production of AC is estimated to be approximately 100,000 tonnes (Mohammad Hadi Dehghani, 2020). John C. Crittenden et al. (2012) noted that activated carbon is one of three types of adsorbents commercially available that considered in water treatment (John C. Crittenden, 2012). It is a cost-effective adsorbent (S. Khedr, Mona S., Nady Fathy, and A. Attia, 2014). There are three major forms of carbon, they include; granular, powder and pellet (M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016); amongst the above-mentioned forms, granular and powdered activated carbons are mostly used (John C. Crittenden, 2012; M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016), their mean sizes range from 20 to 50 micrometres for powdered activated carbon and 0.5 to 3 mm for granular activated carbon (John C. Crittenden, 2012). In the research conducted by Ademiluyi F. T. et al. (2009), they revealed that using granular activated carbon made from agricultural waste materials is so effective in removing different kinds of pollutants from water (Ademiluyi, F. T.; Amadi, S. A.; Amakama, 2009).

Activated carbon is greatly known as activated charcoal, and it is diversely used for different applications due to its reliability (M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016). It can be prepared from many

carbonaceous source materials. Choosing an appropriate precursor depends on different factors such as its cost, purity, manufacturing process as well as the intended use of the final product (Devarly Prahas, Y. Kartika, N. Indraswati and S. Ismadji, 2008). Furthermore, the availability and transportation of carbon materials and raw materials, as well as seasonal changes in quality and accessibility must be considered (Mohammad Hadi Dehghani, 2020). AC can be produced from diverse raw and waste materials of both agricultural and forestry wastes (C. Namasivayam & K. Kadirvelu, 1997; D. D. Do and A. Ahmadpour, 1996; M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016). It can also be developed from non-agricultural products such as automobile tires wastes (M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016).

The application of waste materials from agricultural activities seem to be an appropriate option for the treatment of water as they are renewable, cost-effective, environmental friendly (Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018), non-toxic, and adequately obtainable (Ramya Araga, Suresh Kali, and Chandra S. Sharma, 2019). ACs prepared from agricultural wastes/residues would minimize the pressure on forests by the reason of wood is widely applied for the same purpose (Devarly Prahas, Y. Kartika, N. Indraswati and S. Ismadji, 2008).

Many residues rich in carbon have been used; they include, the coir fibre industries by-product, coir pith (C. Namasivayam & K. Kadirvelu, 1997), jamun (*Syzygium cumini*) seed (Ramya Araga, Shantanu Soni, Chandra S. Sharma, 2017), peels of Citrus fruits (Ch. Chakrapani, Ch. Suresh Babu, K.N.K. Vani, K. Somasekhara Rao, 2010), olive stones (S.M. Yakout and G. Sharaf El-Deen, 2016), lemon peels (G.R. Kiran Kumar, M. Shambavi Kamath, and Praveen S Mallapur, 2016), Saffron (*Crocus sativus*) leaves (Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018), coconut shell, palm kernel and cocoa pod husks (John. Bentil and William Kwame Buah, 2016),banana (*Musa paradisiaca*) peel and coffee (*Coffea arabica*) husk (T. Getachew, A. Hussen, V. M. Rao, 2014), bamboo waste (Gizachew Wendimu, Feleke Zewge, Eyobel Mulugeta, 2017), tomato processing waste (Hasan Saygılı and Fuat Güzel, 2016), jackfruit peel waste (Devarly Prahas, Y. Kartika, N. Indraswati and S. Ismadji, 2008), cotton stalks-biomass waste (Nady A. Fathy, Badie S Girgis,

Lila B. Khalil, and Joseph Y. Farah, 2010), barks of *Vitex negundo* plant (Mekala Suneetha, Bethanabhatla Syama Sundar, and Kunta Ravindhranath, 2015), *Chamaecyparis obtusa, Q. phillyraeoides, Q. mongolica, and Q. pubescens* (I. Abe and Seiki Tanada, 2004), cashew nut shell (*Anacardium occidentale*) (G. Alagumuthu and M. Rajan, 2010), rice husk and corn cob (B. D. Gebrewolda, K. Pimluck , E. R. Rene, 2019; Vivek Ganvir and Kalyan Das Tata, 2011), *Morringa Indica* bark (G. Karthikeyan and S. Siva Ilango, 2007), Hazelnut Shells (Aziz Sencan and Mehmet KJlJç, 2015), plantain peel and coconut shell (V.E. Efeovbokhan, E.E Alagbe, B. Odika, R. Babalola, T.E. Oladimeji, 2019), aloe vera green wastes (Yusef Omidi-Khaniabadi, Ali Jafari, Heshmatollah Nourmoradi, 2015), Peanut Husk (Abdisa Gebisa Jebessa, 2018), and *Tamarindus indica* fruit shells (TIFSs) (V. Sivasankar, S. Rajkumar, S. Murugesh, A. Darchen, 2012).

In various industrial fields, activated carbon is applied in adsorption processes (Eric Mutegoa, Isaac Onoka, 2014), because it is known to be having high adsorption capacity, a higher degree of porosity and internal surface area (O. F. Olorundare,T. A. M. Msagati, R. W. M. Krause, J. O. Okonkwo, and B. B. Mamba, 2014; Paul T. Williams and Anton R. Reed, 2006; S. Khedr, Mona S., Nady Fathy, and A. Attia, 2014), the internal area of pores is greater than 1000 m^2/g (M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016). M.A. Tadda et al. (2016) outlined the factors that affect the production of activated carbon, they include; raw materials, temperature, and activated time (M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016); O. F. Olorundare et al. (2009) noted that the parameters such as activating agents, activation temperature, dynamic process in the films, high density of the precursor, the low ash content of the precursor and high adsorption capacity greatly affects the production of activated carbon and its structure (O. F. Olorundare,T. A. M. Msagati, R. W. M. Krause, J. O. Okonkwo, and B. B. Mamba, 2014), while Eric Mutegoa et al. (2014) mentioned that well-developed structure of pores, higher surface area, low content of ash, and the higher capacity of adsorption are the needed properties that characterize the activated carbon. Based on its pore radius, the activated carbon's pores are mainly classified into micropores, mesopores, and macropores which have a radius of 1 nanometer, 1 to 25 nanometers, and 25 nanometers respectively (Eric Mutegoa, Isaac Onoka, 2014).

AC plays an important role in controlling different kinds of pollutions including water pollution and the conservation of the environment (Eric Mutegoa, Isaac Onoka, 2014), it removes different kinds of pollutants from both potable water and wastewater (M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016). The activated carbons are greatly used in the treatment of industrial effluents and are adversely known in the chemical recovery processes (Paul T. Williams and Anton R. Reed, 2006). They are extensively applied in the removal of odorous dissolved compounds from the industrial effluents by the process of adsorption (Ademiluyi, F. T.; Amadi, S. A.; Amakama, 2009).

2.3.2. Methods of activated carbon production

The production of activated carbon can typically be achieved through two ways, physical and chemical activation (Devarly Prahas, Y. Kartika, N. Indraswati and S. Ismadji, 2008).

AC physical activation method

The physical activation is best described as a two-step operation (M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016; Mohammad Hadi Dehghani, 2020). In this kind of activation, the precursors are carbonized at higher temperatures in combination with the activating agents which are mostly used (carbon dioxide and water (steam) (John C. Crittenden, 2012; O. F. Olorundare,T. A. M. Msagati, R. W. M. Krause, J. O. Okonkwo, and B. B. Mamba, 2014; Paul T. Williams and Anton R. Reed, 2006). Activating with the steam impacts the specific surface, pore size distributions as well as pore volumes (Henrik Romar, Davide Bergna, Toni Varila, 2018). This method includes the carbonizing the precursor contains the significant amount of carbon; then the char produced undergoes the process of activation by adding the activators. It is very important to remove a high amount of internal mass for carbon in order to produce a well-developed carbon structure. Higher temperatures are applied for the production of activated carbon using the physical method than the ones applied during the chemical activation (D. D. Do and A. Ahmadpour, 1996; Qinyan Yue, Jiaojiao Kong, Lihui Huang, Yuan Gao, Yuanyuan Sun, Baoyu Gao, 2013). The activation gas that is mostly applied in activation operation is carbon dioxide; it is easier to handle, clean and its reaction rate at a high temperature of about 800°C is slow which alleviates the activation process regulation. The carbonization temperature ranges from 400°C to 850°C, however it might sometimes arise to 1000°C. The activated carbon generated by the physical

activation method is impaired to some extent, hence this makes it unsuitable to be applied as adsorbents or filters (M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016).

Temperature and activation time were reported to have the main effects on the yield. Long-activation time and greater temperature lower the total yield. This is due to the fact that at the higher temperatures, volatile constituents escape from the system which results in less yield of AC. Increasing the activation time burns the carbon away due to the presence of oxygen in the steam, thus lowers the yield (Henrik Romar, Davide Bergna, Toni Varila, 2018). This approach is capable of producing the AC of porous structure and excellent physical power; it is cost-effective and environmental friendly since it is chemical-free. Despite the advantages, it also has disadvantages such as it takes a long time to activate the carbon, the produced AC possesses low adsorption capacity and high energy consumption (Mohammad Hadi Dehghani, 2020).

AC chemical activation method

The chemical activation process, the multiple one-step processes happens with impregnation of the precursor by the use of an acid or alkali (John C. Crittenden, 2012; M.A. Tadda, A. Ahsan, A. Shitu, M. ElSergany, T. Arunkumar, Bipin Jose, M. Abdur Razzaque and N.N. Nik Daud, 2016; O. F. Olorundare,T. A. M. Msagati, R. W. M. Krause, J. O. Okonkwo, and B. B. Mamba, 2014; Paul T. Williams and Anton R. Reed, 2006), such as Potassium Hydroxide (KOH), potassium carbonate (K_2CO_3), Phosphoric acid (H_3PO_4), Sodium hydroxide (NaOH). Sodium carbonate (Na_2CO_3), Aluminium Chloride ($AlCl_3$), Zinc Chloride ($ZnCl_2$), and Magnesium Chloride ($MgCl_2$) (D. D. Do and A. Ahmadpour, 1996; Henrik Romar, Davide Bergna, Toni Varila, 2018; Mohammad Hadi Dehghani, 2020), and phosphoric acid (H_3PO_4) is mostly used due to the fact that it doesn't greatly affect the environment (Devarly Prahas, Y. Kartika, N. Indraswati and S. Ismadji, 2008; Qinyan Yue, Jiaojiao Kong, Lihui Huang, Yuan Gao, Yuanyuan Sun, Baoyu Gao, 2013) and it produces significant mesopores and substantial macropores (Avinash V. Palodkar, Kumar Anupam, Soumya Banerjee, and Gopinath Haldera, 2017).

In this case, the raw materials are soaked within the chemical activation agent (Qinyan Yue, Jiaojiao Kong, Lihui Huang, Yuan Gao, Yuanyuan Sun, Baoyu Gao, 2013). For this approach, firstly, the raw material surface is saturated with the chemical activation agent. After the impregnation process, the suspension is dehydrated and the remained mixture undergoes the

process of heating for a certain moment ranges from 1 to 4 hours under the inert atmosphere. The dilute mineral acid is added to reflux away the chemical activators then the filtration and drying processes follow. The chemical activation temperatures are in the range of 400 and 600°C depending on the activating material and the final product needed (Henrik Romar, Davide Bergna, Toni Varila, 2018). The chemical agents are used for carbonizing the precursor. All the chemical agents that are used are dehydrating agents which induce pyrolysis and hinder the tar formation, hence reinforcing the carbon yield. Due to the production of AC by chemical process requires fewer temperatures, consequently, the pores structure is much better compared to that of physical activation which uses higher temperatures (D. D. Do and A. Ahmadpour, 1996).

S. Ismadji et al. (2008) stressed that chemical activation is more advantageous than physical activation due to its cost-effectiveness; since chemical activation occurs at a lower temperature than that utilized by physical one and produces a higher yield. It develops a better porous structure (Devarly Prahas, Y. Kartika, N. Indraswati and S. Ismadji, 2008). It requires less processing time (Mohammad Hadi Dehghani, 2020), and it's easier to adjust the porosity. Its disadvantages include not being environmentally friendly, corrosive to the used equipment and the inclusion of acid washing step which removes the chemical activators (Henrik Romar, Davide Bergna, Toni Varila, 2018).

2.4.The techniques for water defluoridation

Many defluoridation techniques have been used in the past, including chemical oxidation, foam floatation (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019), bone char (I. Abe and Seiki Tanada, 2004), chemical precipitation, nanofiltration, ion exchange, reverse osmosis (RO), electrocoagulation (EC), electrodialysis (ED), and Electro defluoridation. They were discovered to be capable of absorbing a large amount of fluoride from industrial wastewaters (Ch. Chakrapani, Ch. Suresh Babu, K.N.K. Vani, K. Somasekhara Rao, 2010; Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019; Mirna Habuda-Stanić, 2014; Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018; S N A Jalil, N Amri, A A Ajien, N F Ismail, and B Ballinger, 2019; Teshome L. Yami, Jim F. Chamberlain, Feleke Z. Beshah, David A. Sabatini, 2018) such as from semiconductor industries effluents (S N A Jalil, N Amri, A A Ajien, N F Ismail, and B Ballinger, 2019). Some of the methods mentioned above have been

shown to be effective, but they have some drawbacks, such as requiring a large amount of energy and chemicals, high costs for operational activities, and capital advanced technologies, making them not cost-effective (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019; G.R. Kiran Kumar, M. Shambavi Kamath, and Praveen S Mallapur, 2016; Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019; Mirna Habuda-Stanić, 2014); some of them are not efficacious at lower F^- concentration (Ramya Araga, Suresh Kali, and Chandra S. Sharma, 2019). For example, Ramya Araga et al. (2017) stated that the membrane and ion exchange processes need a high cost for operation and maintenance, they generate the harmful sludge, and the procedures for treating the fluoridated water are complicated (Ramya Araga, Shantanu Soni, Chandra S. Sharma, 2017). Hence, cost-effective alternative defluoridation techniques are required (Ramya Araga, Suresh Kali, and Chandra S. Sharma, 2019; Vaishali Tomar and Dinesh Kumar, 2013).

Nalgonda technique is also one of the liked methods for removing F^- from water for drinking in the developing world such as Senegal, Tanzania, Kenya (Amit B., Eva K., Mika S., 2011; Vaishali Tomar and Dinesh Kumar, 2013), Ethiopia (Teshome L. Yami, Jim F. Chamberlain, Feleke Z. Beshah, David A. Sabatini, 2018), and India (G.R. Kiran Kumar, M. Shambavi Kamath, and Praveen S Mallapur, 2016). Unfortunately, it has also shown some limitations such as the generation of alkaline or acidic water, residues of aluminium and soluble complexes of aluminium fluoride, production of the higher quantity of sludge and increased amount of fluoride concentration residues (Kalpana Singh, Dilip H. Lataye, 2016; Teshome L. Yami, Jim F. Chamberlain, Feleke Z. Beshah, David A. Sabatini, 2018). The aluminium level resulted from the Nalgonda technique ranges from 2 mg/L to 7 mg/L (Ramya Araga, Shantanu Soni, Chandra S. Sharma, 2017), where the aluminium level allowed by WHO is 0.2 mg/L (Vaishali Tomar and Dinesh Kumar, 2013).

So far, adsorption of fluoride removal from drinking water was reported to be the most appropriate alternative treatment technique because it is flexible, simple in design, easier in operation, cost-effectiveness, environment friendly and it produces a high water quality after treatment. (G.R. Kiran Kumar, M. Shambavi Kamath, and Praveen S Mallapur, 2016; Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019; Lin Chen, Bo-Yang He, Shuai He, Ting-Jie Wang, Chao-Li Su, 2012; M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, 2009; Mirna

Habuda-Stanić, 2014; Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018; Ramya Araga, Shantanu Soni, Chandra S. Sharma, 2017) the end treated water containing the lowest dissolved organic matter (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019).

Table 1: The advantages and disadvantages of some of the fluoride removal techniques

Technique	**Advantages**	**Disadvantages**	**References**
Nalgonda	• It is suitable for the domestic as well as community level; • It is simple to design, construct, operate and maintain; • High fluoride removal efficiency; • It removes other contaminants such as odour, colour, pesticides, turbidity and organic substances.	• It generates the alkaline/acidic water, residues of aluminium and soluble complexes of aluminium fluoride; the aluminium residues range from 2 to 7 mg/L which exceed the WHO allowed limit of 0.2 mg/L; • It produces a higher quantity of sludge which is toxic due to the high concentration of fluoride hence poses serious environmental health problems; • It needs high maintenance cost, • The users don't like the taste of treated water; • Greater chemical dosage is required.	(Amit B., Eva K., Mika S., 2011; Dr. Shikha Modi and Ranjeeta Soni, 2013; Kalpana Singh, Dilip H. Lataye, 2016; Teshome L. Yami, Jim F. Chamberlain, Feleke Z. Beshah, David A. Sabatini, 2018)
Electro defluoridation	• It removes excess fluoride levels from drinking water; • The process requires a small space; • It doesn't require chemical storage, pH adjustment as well as the chemical storage; • It doesn't require considerable investment; • It produces less amount of sludge	• It is suitable for a small or medium community.	(Teshome L. Yami, Jim F. Chamberlain, Feleke Z. Beshah, David A. Sabatini, 2018)

Reverse Osmosis	• RO consumes the lowest energy as its operation relies on the pressure as a driving force; • It can be implemented at room temperature hence no change in phase; • It scarcely affects the environment as it doesn't discharge chemically polluted waste due to the fact that the chemical reagents are not applied during the treatment process; • Its simple design, operate and occupies small space; • It likely eliminates other ions.	• RO's operation and management are not strict; • The pressure must be in the proper range while the system is running; • The water loses all its mineral content leaving the water with an acidic pH which is very harmful to human health; • It takes a lot of time to filter the water; • It is very costly to run the system as whole units including installation costs a lot of money; • The membrane fouling is an issue faced during the process; • Its products may generate bacteria; • It needs skilled workers; • It involves the high wastage of raw water.	(Ahamefula A. Ahuchaogu and John Bull Onyekachi Echeme, 2018; Bhausaheb L. Pangarkar, 2011; Dr. Shikha Modi and Ranjeeta Soni, 2013; Haixiang Li, Lei Jiang, Yue Tu, 2018)
Nanofiltration	• It operates under low pressure hence it consumes less energy; • Higher permeability; • It can remove other ions especially bivalent, thus suited for hardness removal.	• The produced water quality is impaired by the fluoride level present in the feed; • The technique is so expensive and too complicated; • The fouling of the membrane; • Membranes' lifetime is limited; • The concentration polarization phenomena reduce productivity.	(Jan Hoinkis, Sara Valero-Freitag, Martin P. Caporgno & Christian Pätzold, 2011; K. Ravindhranath, M. Suneetha, 2015; Krishna Kumar Yadav & , Neha Gupta, Vinit Kumar, Shakeel Ahmad Khan, 2018; Lucía I. Moran Ayala, Marie Paquet, Katarzyna Janowska, Paul Jamard, Cejna A. Quist-Jensen, Gabriela N. Bosio, Daniel O. Mártire, Debora Fabbri, 2018; M. Tahaikt and A. Elmidaoui, 2007)
Electrodialysis	• It is flexible respectfully to the seasonal change of fluoride content; • It doesn't require a high amount of chemicals; • It is simple and eco-friendly; • High defluoridation efficiency; • The average cost for installation is required.	• The technique is expensive to process and too complicated; • A high amount of water is lost as brine; • The membrane gets fouled; • It removes all-important ions hence the re-mineralization operation to regain them; • It consumes high energy.	(K. Ravindhranath, M. Suneetha, 2015; Krishna Kumar Yadav & , Neha Gupta, Vinit Kumar, Shakeel Ahmad Khan, 2018; M. Grzegorzek & K. Majewska-Nowak, 2016; M. Tahaikt and A. Elmidaoui, 2006)

Activated Alumina	• It removes maximum fluoride in a a short contact time; • It is effective for defluoridation; • A high percentage of regeneration.	• It is expensive to process; • It has the logistical constraints of operation and maintenance; • It requires skilled labour; • It can generate the aluminium residues in the output water which are toxic; • It regenerates periodically which can lead to exhaustion of activated alumina; • The process depends on a specific pH range and thus water pre and post pH water adjusted is needed; • During regeneration, the higher F^- concentrated solution is produced hence hard to dispose of.	(Dr. Shikha Modi and Ranjeeta Soni, 2013; K. Ravindhranath, M. Suneetha, 2015; Teshome L. Yami, Jim F. Chamberlain, Feleke Z. Beshah, David A. Sabatini, 2018)
Bone char	• The technology is economical; • It shows high fluoride removal capacity as much as 1000 mg/L; • The media is available at the local level.	• Bone char can sometimes be undesirable due to religious and cultural beliefs, hence it may not be permitted in some regions; • When it's not well prepared, it may contribute the odour to the treated water; • It hides the bacteria and thus unclean; • It extremely affected by high alkalinity.	(Dr. Shikha Modi and Ranjeeta Soni, 2013; Gizachew Wendimu, Feleke Zewge, Eyobel Mulugeta, 2017; K. Ravindhranath, M. Suneetha, 2015)
Activated carbons	• Operation and maintenance of low cost; • Simple operation; • Lack of sludge generation; • Readily available raw materials and higher accessibility; • They are environmental-friendly; • Effective and efficiency adsorption capacity.	• Once there are the interfering ions such as bicarbonate, sulphate, etc.; they can reduce the fluoride removal efficiency; • They lack in terms of pilot scale.	(Avinash V. Palodkar, Kumar Anupam, Soumya Banerjee, and Gopinath Haldera, 2017; Habiba Lebrahimi, Mohammed Fekhaoui and Abdelkabir Bellaouchou, 2020; K. Ravindhranath, M. Suneetha, 2015; Mirna Habuda-Stanić, 2014; Ramya Araga, Shantanu Soni, Chandra S. Sharma, 2017; Vaishali Tomar and Dinesh Kumar, 2013)

2.5.Fluoride removal by activated carbons adsorbents

2.5.1. Adsorption Process

Adsorption is defined as the transfer process where the solid phase substance is put in the liquid hence adsorb or accumulate, and then remove the solid phase substances that are present in that liquid (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019). The substance which undertakes the adsorption operation is named an adsorbate while the solid substance which adsorbs/accumulates the other substances such as organic and inorganic is known as an adsorbent. Adsorption operation involves the dissolved substances that are transferred into the solid adsorbent granule' pores by the diffusion process and they are then accumulated on to an adsorbent's extensive inner surface by either chemical or physical reaction (John C. Crittenden, 2012; Mirna Habuda-Stanić, 2014). The physical adsorption (physisorption) barely alters the nature of the adsorbed molecules; it is known to be a reversible process. It involves the comparably weak intermolecular forces of attraction such as Van der Waals forces, dipolar or dispersion interactions among the adsorbate and adsorbent's surface. Chemical adsorption (chemisorption) also known as an irreversible process on solid materials is achieved by the chemical bonds, sharing of electrons between the adsorbent and adsorbate to form an ionic or covalent bond. Hence the chemisorption could involve the high need for energy for regeneration (Habiba Lebrahimi, Mohammed Fekhaoui and Abdelkabir Bellaouchou, 2020; Soonchul Kwon, 2011).

2.5.2. Main factors affecting the fluoride removal by ACs adsorption

The effective removal of fluoride from water by the adsorption process is affected by different factors such as contact time, agitation speed, pH, and the initial fluoride concentration (Habiba Lebrahimi, Mohammed Fekhaoui and Abdelkabir Bellaouchou, 2020). Temperature, adsorbent dose, particle size, surface area, and the existence and the nature of interfering ions are the other main factors that influence the defluoridation by activated carbons (Vaishali Tomar and Dinesh Kumar, 2013).

2.5.3. Properties that describe the activated carbon as an effective adsorbent

The adsorption processes are known to remove different pollutants from drinking water such as some inorganic and organic pollutants (Devarly Prahas, J. C. Liu, Suryadi Ismadji, 2012; John C. Crittenden, 2012; Qinyan Yue, Jiaojiao Kong, Lihui Huang, Yuan Gao, Yuanyuan Sun, Baoyu Gao, 2013). The physical and chemical properties of the raw materials, as well as the condition

and activation process, greatly affect the properties of adsorption for AC (O. F. Olorundare,T. A. M. Msagati, R. W. M. Krause, J. O. Okonkwo, and B. B. Mamba, 2014). Adsorbent dosage, contact time, temperature, initial concentration of fluoride in the solution and pH are the factors that play a big role in the efficient removal of fluoride, with the adsorbent's selectivity for the fluoride ion as the main factor (Mirna Habuda-Stanić, 2014). Qinyan Yue et al. (2013) discussed that AC with the thermostability, high adsorptive effect, higher performance, substantial specific area as well as the properties of the well-structured pore has been demonstrated as a perfect adsorbent for different inorganic or organic contaminants (Qinyan Yue, Jiaojiao Kong, Lihui Huang, Yuan Gao, Yuanyuan Sun, Baoyu Gao, 2013) while other researchers noted that the activated carbon's characteristics such as high porosity, large surface area as well as the great catalytic activities used to define it as a very useful adsorbent especially for the removal of different pollutants from drinking water (Aziz Sencan and Mehmet KJlJç, 2015; Gizachew Wendimu, Feleke Zewge, Eyobel Mulugeta, 2017).

2.5.4. Some of studies conducted on the adsorption capacity of different ACs

According to Jemal Fito et al. (2019), the maximum fluoride ions removed from aqueous solution is 73%. They used sulfuric acid-activated C.edulis stems in their study, and variables such as adsorbent dose, solution pH, and contact time were used in a factorial experimental design. The maximum removal capacity was recorded under an adsorbent dose of 1.5 g into 100 mL; 60 minutes contact time and pH of 2 as the optimum conditions. The model-based predicted value under the experimental conditions was 69%. The *Catha Edulis* derived activated carbon showed a high adsorption capacity hence a promising adsorbent, where it was found that the 33.3 mg/g was the maximum adsorptive capacity, yet the predicted value was 18 mg/g under the Langmuir isotherm model. The Freundlich isotherm of R^2=0.98 was found to better fit the experimental data and showed that the process was multilayer and cooperative (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019).

Ramya Araga et al. (2017) studied the defluoridation of drinking water using activated carbon prepared from Jamun seed. The seed was activated by the addition of KOH and the temperature of 900^{o}C for pyrolisis was applied. The parameters such as temperature, initial fluoride concentration, contact time, adsorbent dosage, and pH were used. The maximum fluoride removal was obtained at the contact time of 120 min and pH of 2.5; the maximum adsorptive

capacity of fluoride on AC for initial concentration for fluoride of 10 mg/L and the adsorbent dosage of 0.4 g/L was found to be 3.65 mg/g. More importantly, the results obtained were compared to other ACs prepared from other biomass and the adsorbent's performance was reported to be efficient based on its capacity of adsorbing the fluoride (Ramya Araga, Shantanu Soni, Chandra S. Sharma, 2017).

Feleke Zewge et al. (2017) investigated F^- removal from aqueous solutions using AIAABC derived from bamboo waste. To prepare the adsorbent (AIAABC), the Activated Bamboo Charcoal was impregnated in an Aluminium Chloride/Iron (III) Chloride solution and then treated at 400^oC, resulting in a higher F^- adsorptive capacity. The batch experiments were used while characterizing and testing the samples. Carbon, aluminium, sodium, oxygen, iron, and sulfur are the main elements that were found in AIAABC. After adsorption, the F^- was associated with the AO particles in the spaces of the pore of the Activated Bamboo Charcoal; and when the AO was impregnated to AO, it demonstrated that the AO particles could cover the spaces of the surface or pore found in the Activated Bamboo Charcoal. The SSA was reduced from 80.5 to 3.7 m^2g^-. The higher adsorption capability of fluoride was reported to be 21.1 mg/g and was obtained in 3 hours contact time, at pH ranging from 5-9, and the adsorption capacity decreased as the pH increased. The results were well fitted by the Langmuir adsorption isotherm and obeyed a pseudo-second-order rate equation. It was deduced that the AIAABC adsorbent was a low-cost adsorbent that was effective for removing F^- from drinking water in areas with high fluoride levels in water (Gizachew Wendimu, Feleke Zewge, Eyobel Mulugeta, 2017).

G.R.Kiran Kumar et al. (2016) investigated fluoride removal from water using a low-cost activated carbon derived from lemon peels. The adsorption parameters were pH, adsorbent dosage, rotation speed, and contact time; they discovered that lemon peel activated carbon can remove fluoride from water and can be used as a cost-effective defluoridation technique. The high fluoride adsorptive capacity was obtained at a pH of 4, the contact time of 120 minutes, the rotation speed of 225 rpm, and 10 g/L of adsorbent dosage (G.R. Kiran Kumar, M. Shambavi Kamath, and Praveen S Mallapur, 2016).

Chakrapani et al. (2010) investigated the adsorption kinetics for the fluoride removal from the aqueous solution by the activated carbon adsorbents derived from the peels of selected citrus fruits. The ACs were derived from *Citrus documana* (NCDC), *Citrus medica* (NCMC), and

Citrus aurantifolia (NCAC) fruits peels. The pseudo-second-order equation is the one that represented the fluoride adsorption onto adsorbents. The *Citrus documana* fruits peels showed the highest adsorptive capacity followed by *Citrus medica* fruits peels, and *Citrus aurantifolia* fruits peels, i.e 0.4503, 0.4214, and 0.4098 at the contact time of 30, 35 and 35 min respectively. 5 mg/L fluoride concentration was used throughout the processes (Ch. Chakrapani, Ch. Suresh Babu, K.N.K. Vani, K. Somasekhara Rao, 2010).

The AC derived from calcium chloride modified Saffron (*Crocus sativus*) leaves; AC-CMCSL was applied for the uptake of fluoride from water. The adsorption parameters investigated during the process are pH, initial concentration of fluoride, adsorbent dosage, and contact time. The analysis of data and optimization process were investigated using CCD in RSM. The maximum removal of fluoride was 85.43% and was obtained at the optimal conditions; initial concentration of fluoride of 6.5 mg/L, pH of 4.5, adsorbent dose of 15 g/L, and contact time of 70 minutes. The highest adsorptive capacity (q_{max}) from the Langmuir model was 2.01mg/g. The results from the study revealed that the use of AC derived from calcium chloride modified *Crocus sativus* leaves is a promising alternative adsorbent for the removal of fluoride from aqueous solution (Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018).

John. Bentil & William Kwame Buah (2016) conducted a research on the removal of fluoride using the activated carbons prepared from three different selected agricultural wastes; palm kernel shell, coconut shells and cocoa pod husks. The water samples used for the test were both raw and distilled water. In order to obtain the chars, 900^0C was applied by the use of steam as an activating agent. By considering the average values of adsorptive capacities; It was found that palm kernel shell had the greatest adsorptive capacity among all the three followed by coconut shells and cocoa pod husks. All the three adsorbents showed the high potential for the removal of the fluoride from the water with the palm kernel shell being the best amongst the rest (John. Bentil and William Kwame Buah, 2016).

In the study conducted by Ayu Haslija Abu Bakar et al. (2019), they prepared the quaternized palm kernel shell for the removal of F^- from aqueous solution by the use of the fixed bed adsorption column. The $C_6H_{15}Cl_2NO$ (Dextrosil) was added to the waste of raw palm kernel shell for modifying the surface charge. The maximum adsorption capacity achieved was 0.99 mg/g

and the adsorption was best fitted to Thomas and Yoon-Nelson models. The optimum conditions for the maximum fluoride removal were 6 cm bed height, initial fluoride concentration of 6mg/L, and a pH of 3. Hence, based on the adsorption capacity and the performance, a quaternized palm kernel shell was reported to be more suitable for the removal of fluoride from both drinking water as well as wastewater (Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019).

T. Getachew et al. (2014) investigated the removal of F^- from the aqueous solution by using the banana *(Musa paradisiaca)* peel and coffee *(Coffea arabica)* husk prepared activated biosorbents. To determine and monitor the fluoride ion levels, the fluoride ion-selective electrode was used. The experiments, the batch were conducted in order to optimize different factors; pH, adsorbent dosage and contact time. The real water samples determined concentrations were collected from flour factory, poultry and Hawassa lake sites and they were 12.54 mg/L, 11.02 mg/L, and 6.72 mg/L, respectively. For the banana *(Musa paradisiaca)* peel, the optimal conditions were pH 2, the contact time of 13 h, an adsorbent dosage of 24 g into 250 mL, and the initial fluoride concentration of 10 mg/L. The maximum adsorptive capacity obtained was 0.3950 mg/g, 85% (for aqueous solution), and it was well fitted to the Langmuir adsorption model, and 80%-83% for the real water samples. Then for the coffee *(Coffea arabica)* husk, the optimal conditions were pH 2, a contact time of 3 h, an adsorbent dosage of 18g in 250 mL. The maximum adsorptive capacity obtained was 0.4260, 86% (for aqueous solution) and it was well fitted to the Langmuir adsorption model and 81%-84% for the real water samples. Based on the time and dose of the adsorbent, the coffee *(Coffea arabica)* husk was noticed to be a lot better than the banana *(Musa paradisiaca)* peel (T. Getachew, A. Hussen, V. M. Rao, 2014).

Suneetha et al. (2015) studied the fluoride removal from contaminated water using the activated carbon prepared from the barks of the Vitex Negundo plant. The real groundwater samples were used for defluoridation. FTIR and SEM-EDX approaches were used in characterizing physicochemical properties and surface morphologies of the AC. Several parameters were considered; including adsorbent dose, pH, fluoride initial concentration, particle size, agitation time and the presence of the interfering ions; the study was conducted using the batch experiments. The isotherms models such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich were applied to analyze the adsorption process; the adsorption kinetics was also

examined. The maximum fluoride adsorption was achieved at agitation time of 50 min, the adsorbent dosage of 4.0 g/L, the temperature of 30±1 ° C, pH of 7.0 and a particle size of 45µm. The adsorption was well fitted with the Langmuir model with the value of 0.998 and it showed monolayer adsorption. Adsorption kinetics was found to obey the pseudo-second-order equation with the value of 0.994. They concluded by emphasizing that barks of *Vitex negundo* plant-derived activated carbon is effective for adsorption of fluoride from waters as it showed a successful removal of fluoride from the real groundwater samples (Mekala Suneetha, Bethanabhatla Syama Sundar, and Kunta Ravindhranath, 2015).

G. Alagumuthu & M. Rajan (2010) utilized Zirconium impregnated cashew nutshell carbon (ZICNSC) in defluoridation of water; the aqueous solutions were first used then real samples from the field. The contact time ranging from 60 to 210 minutes at ambient temperature was applied. Various cashew nutshell carbon (CNSC) particle sizes were tried out to define the best size for the maximum removal of F^-. pH was also another parameter that was studied to obtain an optimum pH. The isotherms models such as Langmuir, Freundlich, and Redlich–Peterson were applied to analyze the adsorption process. The fluoride adsorption rate and constants were described and calculated by using pseudo-first and second equations. The optimum conditions for the maximum defluoridation were found to be a pH of 7.0, a particle size of 53 µm, and a contact time of 180 min. at room temperature. The percentage removal for fluoride was recorded as 80.33% by the zirconium impregnated cashew nutshell carbon and 72.67% by cashew nut shell carbon; this was detected in 3 mg/L of 100 mL fluoride utilizing a 1.5 mg adsorbent dose. The highest defluoridation capacity was well suited to the Langmuir isotherm model. The sorption process obeyed the pseudo-second-order equation. The ZICNSC was reported to have the potential in removing fluoride from waters. (G. Alagumuthu and M. Rajan, 2010).

The researchers from India investigated the defluoridation of water by using *morringa indica* derived activated carbon. They first removed the F^- ions from synthetic aqueous solution and then used the real samples collected from 5 regions of India. The effects of adsorbent dose, pH and ions (cations and anions) were studied. The adsorption kinetics and isotherms of adsorption were also studied. Batch experiments were applied using 3 g of the adsorbent in 50 mL of the solution containing fluoride ions. The initial fluoride level used was 3 mg/L at pH ranging from 2 to 12. The maximum removal of fluoride from the aqueous solution was found to be 71%; it

occurred at a pH of 7. The adsorption rate for maximum removal was reported as 3g/50mL. The anions such as bicarbonate, sulphate, chloride and nitrate were experimentally confirmed where the bicarbonate interfered greatly and reduced the adsorption rate of fluoride. The percentage removal of fluoride from real samples ranged from 31 to 50%. The samples from two villages had the fluoride concentration from 2.6 to 2.8 mg/L and their removal ranged from 47 to 50% while the fluoride levels of the other 3 villages were in the range of 1.6 and 1.8 mg/L and the removal percentage was 31 to 35 %. The adsorption of fluoride followed both Langmuir and Freundlich isotherms models as well as the pseudo-first-order kinetic equation (G. Karthikeyan and S. Siva Ilango, 2007).

B. D. Gebrewolda et al. (2019) investigated the possibility of chemically modified activated carbons derived from rice husk and corn cob to uptake the fluoride ions from groundwater. They examined the impacts of contact time, pH, adsorbent dose and initial concentration of fluoride on the F^- removal efficiency. The analysis of Variance was utilized to analyze the results of batch experiments. The maximum adsorptive capacities for the rice husks and corn cob are 7.7 and 5.8 mg/g and 91% and 89% removal efficiency respectively. It was revealed that the adsorption results well fitted to Langmuir isotherm and the kinetic model obeyed the pseudo-second-order equation. They concluded that activated carbons derived from rice husks and corn cob have the potential to uptake the fluoride (B. D. Gebrewolda, K. Pimluck , E. R. Rene, 2019).

Table 2: Comparison of adsorption capacity by different activated carbons on fluoride removal.

No.	Adsorbent Precursor	Activation Temp. (^{0}C)	Optimum conditions for max. F^- removal	Adsorption capacity/removal efficiency (mg g^-)/ %	References
1.	*Catha edulis* stems	600	Contact time=60 min, adsorbent dosage=1.5 g in 100 mL, and pH 2	33.3 (73%)	(Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019)
2.	jamun seed	900	Contact time=120 min, adsorbent dosage= 0.4 g/L, initial F^- concentration= 10 mg/L and pH 3	3.65	(Ramya Araga, Shantanu Soni, Chandra S. Sharma, 2017)
3.	Bamboo waste	400	pH of 5-9, agitation time=48 h, initial fluoride	21.1	(Gizachew Wendimu, Feleke Zewge,

			concentration of 10 mg/L		Eyobel Mulugeta, 2017)
4.	Peels of *Citrus documana* fruits (NCDC)	500	**(The best adsorption capacities were obtained under pseudo-second-order model)** Fluoride concentration = 5 mg/L, contact time for NCDC, NCMC and NCAC is 30, 35 and 35 min respectively	0.4503	(Ch. Chakrapani, Ch. Suresh Babu, K.N.K. Vani, K. Somasekhara Rao, 2010)
	Peels of *Citrus medica* fruits (NCMC)			0.4214	
	Peels of *Citrus aurantifolia* fruits (NCAC)			0.4098	
5.	lemon peel	500± 5	Fluoride concentration = 10 mg/L, **pH 4.0,** adsorbent dose of 10 g/l, contact time= 100 min and at rotation speed of 125 rpm	83%	(G.R. Kiran Kumar, M. Shambavi Kamath, and Praveen S Mallapur, 2016)
			Fluoride concentration = 10 mg/L, contact time= 100 min, pH 7.0 **adsorbent dose of 10 g/l**, and at rotation speed of 125 rpm	58.5%	
			Contact time= 120 min, adsorbent dose of 10 g/l	70.6%	
			Fluoride concentration = 10 mg/L, contact time= 100 min, pH 7.0 adsorbent dose of 10 g/l, and **at rotation speed of 225 rpm**	82%	
6.	*Crocus sativus* leaves	800	Initial fluoride concentration= 6.5 mg/L, pH of 4.5, adsorbent dose of 15 g/L, and contact time of 70 minutes.	2.01 (from the Langmuir model) 85.43%	(Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018)
7.	Quaternized palm kernel shell	-	Bed height = 6 cm, initial fluoride concentration= 6 mg/L, and optimum pH= 3	0.99 (based on Thomas and Yoon–Nelson models)	(Ayu Haslija Abu Bakar, Luqman Chuah Abdullah, Nur Amirah Mohd Zahri, and Ma'an Alkhatib, 2019)
8.	banana (*Musa paradisiaca*) peel	400	Contact time=13 h, adsorbent dosage=24 g in 250 mL, initial fluoride concentration= 10 mg/L and pH 2	0.3950 (Langmuir model), 85% (for aqueous solution), 80%-83% (for real	(T. Getachew, A. Hussen, V. M. Rao, 2014)

				water samples)	
	coffee (*Coffea arabica*) husk	150	Contact time=3 h, adsorbent dosage=18 g in 250 mL, initial fluoride concentration= 10 mg/L and pH 2	0.4260 (Langmuir model), 86% (for aqueous solution), 81%-84% (for real water samples)	
9.	barks of *Vitex negundo* plant	500	Agitation time= 50 min, adsorbent dosage= 4.0 g/L, Temperature of 30±1, pH 7.0 , particle size of 45 µm and initial F^- concentration of 1-12 mg/L	1.150 (at fluoride initial concentration of 12mg/L); 92%	(Mekala Suneetha, Bethanabhatla Syama Sundar, and Kunta Ravindhranath, 2015)
10.	Cashew nut shell	300-400	Contact time = 180 min, particle size of 53 µm, pH = 7.0 at room temperature.	**80.33%** by the zirconium impregnated cashew nutshell carbon & **72.67%** by cashew nut shell carbon	(G. Alagumuthu and M. Rajan, 2010)
11.	*Morringa Indica* bark	400	Contact time of 30 min, the initial F^- concentration= 3 mg/L, and the pH 7	**71%** (from aqueous solution); **47-50%** (from the real samples with the F^- conc. of 2.6-2.8 mg/L); **31-35%** (from the real samples with the F^- conc. of 1.6-1.8 mg/L.	(G. Karthikeyan and S. Siva Ilango, 2007)
12.	Rice husks	350	A pH of 4.0, the contact time of 3h, adsorbent dose of 5 g/L, and initial fluoride conc. of 18 mg/L.	7.9 (91%)	(B. D. Gebrewolda, K. Pimluck , E. R. Rene, 2019)
	Corn cob		A pH of 6.0, the contact time of 5 h, adsorbent dose of 4 g/L, and initial fluoride conc. of 18 mg/L.	5.8 (89%)	
13.	Coconut Shell	900	Contact time= 3 h, initial F^- conc. = 4.4 mg/L, adsorbent dosage of 10 g/L, pH of 2, and temperature of 323 K (50°C).	71.14%	(Ramya Araga, Suresh Kali, and Chandra S. Sharma,

					2019)
14.	Rice straw (using KMnO4-modified activated carbon derived from steam pyrolysis of rice straw)	750	pH of 2, a temperature of 45°C, adsorbate conc. of 18 mg/L, and adsorbent dosage of 1.5 g/L.	18.9	(A.A.M. Daifullah, 2007)

3. Materials and Methods

3.1.Reagents

The main chemicals used for this study included Phosphoric acid (H_3PO_4), Aluminium Sulfate ($Al_2(SO_4)_3$), Sodium hydroxide (NaOH), Nitric acid (HNO_3), Sodium Fluoride (NaF), sodium citrate ($Na_3C_6H_5O_7$), sodium chloride (NaCl), acetic acid (CH_3CHOOH) and hydrochloric acid (HCl). All chemicals were purchased from RANCHEM INDUSTRY &TRADING, Addis Ababa and were used without further purification.

3.2. Preparation of Activated Carbon Powder

Khat (*Catha edulis*) stem samples were collected from the roadside in Amist Kilo, Addis Ababa, Ethiopia. The gathered Khat stems were cut into small pieces and then thoroughly cleaned with water to remove contaminants and they were totally dried in direct day sunlight for 5 days to remove the moisture. The dried samples were then ground in a Retsch processor (Model RETSCH GmhH, 5657 HAAN, Germany). Lastly, the squashed samples were sieved through a cross-section size ranging from 1.8 mm - 1.0 mm.

Figure 1: The raw dried khat stem (a) and the mechanical grinder (b)

Figure 2: The sample sizes (in mm) after being ground and sieved.

To chemically activate the sample, 195 mL of 40% H_3PO_4 solution was added to 50 g of ground sample (pan fine particles), mixed uniformly and left to soak for 5 h at room temperature. The resulting activated samples were then dried in the oven at 105 °C for 21 h to attain a complete charring (Luo et al., 2019).

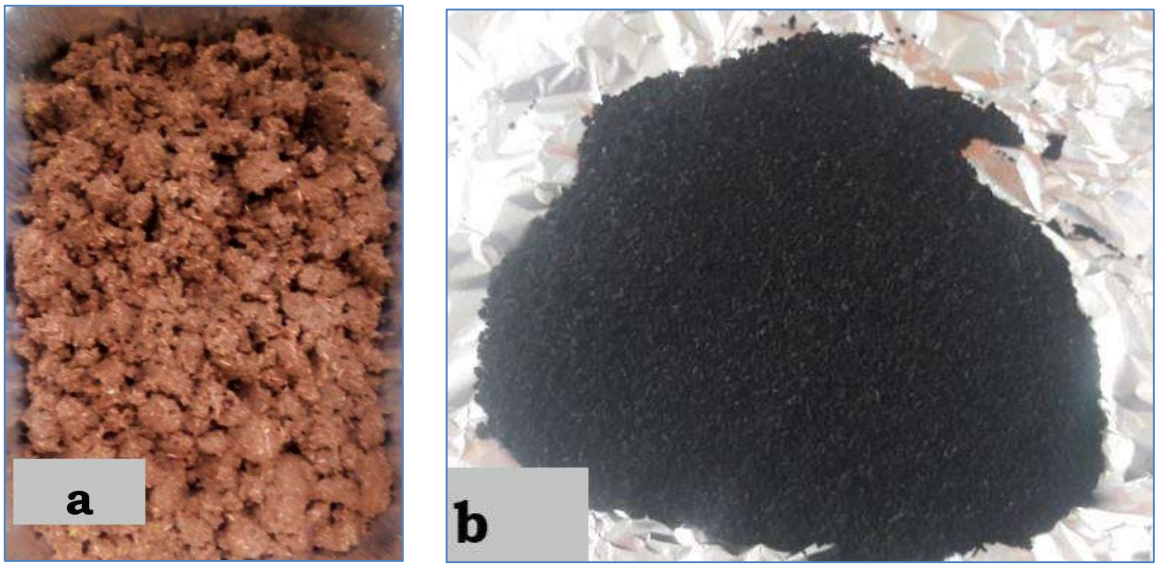

Figure 3: The soaking sample in 40% H_3PO_4, (a) and a washed & dried activated sample (b).

Following several washes, the char was thermally carbonized in the furnace (Model VF2, UK) at temperatures of 400, 500, and 600 °C in the absence of oxygen for 1 hour.

Finally, the activated carbon was subjected to proximate analysis such as moisture content, ash content, volatile matter, and fixed carbon; and physico-chemical characterization using Fourier Transform Infra-Red Spectroscopy and Scanning electron microscope analysis.

3.3. Modification of *Catha edulis* Activated Carbon

The modification process of *Catha edulis* activated carbon was performed based on the method used by Vivek Ganvir & Kalyan Das Tata (2011) with minor modifications. 25 mL of 0.6 M aluminium salt solution was first added to a reactor tank (a 200 mL beaker), then 5 g of *Catha edulis* activated carbon was slowly added to the reactor under the stirring condition at 150 rpm. This condition to ensure the thorough soaking of CAC in $Al_2(SO_4)_3$ solution. Afterwards, 3 M NaOH was slowly added to the solution in order to facilitate the deposition of aluminium hydroxide precipitate on the *Catha edulis* activated carbon's surface. The addition of sodium hydroxide was done until the pH reaches 7. Thereafter, the filtration of the slurry was done and oven dried at 105 ^{o}C for 4 hours. The activated carbon with and without modification was designated as MAC and AC respectively (Vivek Ganvir and Kalyan Das Tata, 2011).

3.4. Characterization of CAC

3.4.1. Proximate Analysis

The carbon moisture content, volatile matter, ash content, and fixed carbon of the activated *Catha edulis* were then determined using the methods described below.

Moisture content

To determine the moisture content of the adsorbent, three clean glass petri dishes were premeasured and then preheated in an oven for 30 minutes at 105 ^{o}C. This operation was done to remove the moisture content from them. After drying, they were put in a desiccator to cool down. 1 g from each adsorbent samples carbonized at 400, 500 and 600 ^{o}C was weighed and dried in the oven at the temperature of 105 ^{o}C for 2 h (O.A. Ekpete,A.C.Marcus,and V. Osi, 2017).

The general formula for calculating the moisture content is given by;

$$\text{Moisture content } \% = \frac{W1-W2}{W1} * 100 \quad (1)$$

Where; w_1 and w_2 in g are the weight of the sample before and after drying

Ash content

The amount of inorganic residue in activated carbon is represented by its ash constituents. To determine the ash content of the adsorbent, three crucibles were preheated in an oven for 25 minutes at 100 ^{o}C. This process was done to remove the moisture from them. After drying, they were put in a desiccator to cool down for 20 minutes at room temperature. The 1 g mass was taken from the adsorbent samples carbonized at 400, 500 and 600 ^{o}C and dried in a muffle furnace at the temperature of 550 ^{o}C for 4 h. then, the mass of each sample and crucible was measured after heating and was denoted as w_2 (Zulkania et al., 2018).

The general formula for determining the ash content is given by;

$$\text{Ash content } \% = \frac{W2-W1}{Ws} * 100 \quad (2)$$

Where; w_1 is the weight of the crucible, w_2 is the weight of the sample and crucible after drying and w_s is the weight of a sample in g.

Volatile matter

For determining the volatile matter of the adsorbent, three clean crucibles were preheated in an oven for 25 minutes at 100 ^{o}C. This process was done to remove the moisture from them. After drying, they were put in a desiccator to cool down for 20 minutes, at an ambient temperature. 1 g mass from each adsorbent sample carbonized at 400, 500 and 600 ^{o}C was weighed and heated in the muffle furnace at the temperature of 900 ^{o}C for 7 minutes (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019).

The general formula for determining the volatile matter is given by;

$$\text{Volatile matter, } v_m \% = \frac{W1-W2}{W1} * 100 \quad (3)$$

Where; w_1 is the weight of the adsorbent sample before heating, w_2 is the weight of the adsorbent sample after heating.

Fixed carbon

The fixed carbon of the adsorbent carbonized at 400, 500, and 600 ^{o}C was calculated by using the following general formula;

Fixed carbon content (%) = 100% - (moisture content % + volatile content % + Ash content %)

3.4.2. FT-IR and SEM analyses

The Fourier Transform Infra-Red spectroscopy (FT-IR) and scanning electron microscope (SEM) were performed to determine surface functional group and surface morphology of the prepared activated carbon. The FT-IR was measured in the wavenumber range of 4000-400 cm^{-1} (resolution: 4 cm^{-1}, the number of scans: 4) by using KBr pellets using spectrum 65 FT-IR (PerkinElmer). Surface morphology also observed by scanning electron microscopes (SEM-Inspect F50).

3.5. Preparation of stock fluoride solution and adjustment buffer

A stock solution with a concentration of 100 milligrams per liter was prepared by dissolving 0.221 g of anhydrous sodium fluoride (98.0 percent NaF, Guanghua Chemical, China) in 1 liter of deionized water. The initial stock solution was made by diluting NaF with deionized water to the desired concentrations, while the pH of the aqueous solutions was adjusted to the preferred initial value using by either 0.1 M NaOH or HCl. The pH values were determined using a pH/ISE meter (ISTE, Korea). pH calibration buffers were used to regularly calibrate the pH meter (M. E. Ravančić & M. Habuda-Stanić, 2015). To synthesize the fluoride solution for adsorption, the appropriate aliquot of the stock solution in distilled water.

The TISAB, total ionic strength adjustment buffer was then prepared. The 57 ml of A.R. grade glacial acetic acid, 58 grams of Analytical Reagent grade Sodium Chloride, and 0.30 g of sodium citrate were measured and mixed, then after 500 mL of deionized water was added. 5 M Sodium hydroxide solution was slowly added to the prepared solution until the pH reached 5.42 (as the range is 5 to 5.5). The solution was then cooled down and more deionized water was added to make a one liter solution. The procedure used was derived from the research conducted by

(Martin S. Frant and James W. Ross, 1968). TISAB is important in reducing interference from elements such as aluminum, iron, and silicon. The addition of TISAB to samples is intended to bring the sample and standards to the same ionic strength and pH, as well as to de-complex F ions from certain interfering elements. Because F-ISE only detects free fluoride ions, samples containing free or ionisable fluoride ions should be analyzed immediately after adding total ionic adjustment buffer (TISAB) (Patel et al., 2018).

3.6. Selection of Activated Carbon

In order to evaluate the removal efficiency of both modified and unmodified activated carbon prepared at 400 ^{o}C, 500 ^{o}C and 600 ^{o}C, batch adsorption experiment was performed by agitating 1 g/L of the adsorbent from each sample for 40 minutes, 60 minutes and 80 minutes in 5 mg/L fluoride standard solutions at pH 7.0 in a 250 mL beaker. At the end of each experiment, a 15 mL solution was then withdrawn and fluoride ion concentration was determined using a pH/ISE meter equipped with a combination fluoride selective electrode (ISTE, Korea). The concentration was measured immediately using direct potentiometry. Prior to each experiment, the fluoride ion selective electrode was calibrated, and all experiments were carried out at room temperature. Finally, the activated carbon with best fluoride removal efficiency further investigated using statistical experimental design.

3.7. Statistical Experimental Design

A statistical experimental design is an effective approach for determining interaction effects among study parameters, to investigate and optimize the most influential study parameters as well as to get a mathematical relationship with prediction capability. It is also important to obtain maximum information within limited resources, time, cost and labour. In the present study, the optimization of operation factors; initial fluoride concentration, solution pH and adsorbent dose for the fluoride removal by the MAC was done using the Box–Behnken design (BBD) of the Response surface method (RSM). Accordingly, 15 runs were used in an experiment, which calculated with the following formula:

$$N=k^2 + k + Cp \quad (4)$$

Where k is a number of experimental factors, and Cp is a central replication point. The factors with levels and experimental runs are given in Table 3 and Table 4.

Table 3: Selected experimental factors with study levels

Factor	Name	Unit	Study Level		
			Lower Level	Middle Level	High Level
A	Initial Fluoride Concentration	mg/L	2.00	5.50	9.00
B	Dose	g/L	1.00	1.50	3.00
C	pH	---	3.00	6.00	9.00

Table 4: Number of experimental runs arranged according to BBD

	Factor 1	Factor 2	Factor 3	Response 1
Run	A:Intial Fluoride Concentration	B:Dose	C:pH	Removal efficiency
	mg/L	g/ L of solution		%
1	2	2	3	
2	9	1	6	
3	5.5	2	6	
4	5.5	2	6	
5	2	3	6	
6	2	2	9	
7	5.5	2	6	
8	2	1	6	
9	5.5	1	9	
10	9	2	3	
11	9	2	9	
12	5.5	1	3	
13	5.5	3	9	
14	5.5	3	3	
15	9	3	6	

3.8.Adsorption Experiment for Fluoride removal Using BBD- RSM

The adsorption of modified activated carbon was investigated using fluoride ion as a model chemical in a batch process. A 250 mL beaker was used as a reactor for all experiments. At this process, the adsorbent dose, initial fluoride concentration and solution pH were varied in the experimental level listed in Table 3. The solution was continuously mixed by using a magnetic stirrer to ensure homogenous mixing for 60 minutes adsorption contact time. As listed in Table 4, at the end of each experiment performed, 5 - 10 mL of the solution was withdrawn from the reactor and filtered through a 45μm diameter syringe filter. The remaining concentration of the

supernatant was then analyzed with a pH/ISE meter with a fluoride electrode. The fluoride removal efficiency (E) was then calculated using the following equation:

$$E = \frac{C_i - C_f}{C_i} * 100\% \quad (5)$$

Where C_i and C_f are the concentrations of fluoride (mg/L) before and after a given adsorption contact time. The resulting efficiency from each experiment was used as an experimental response (Table 4).

The relationship between study factor and response was evaluated with a second-order polynomial equation using the following relationship.

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j} \sum \beta_{ij} X_i X_j + \varepsilon \quad (6)$$

Where Y is an experimental response, X_i and X_j are experimental variables or factors, β_o is a constant, β_i, β_{ii} and β_{ij} are the regression coefficients for linear interaction effect, quadratic interaction effects, and cross-products interaction effects, respectively and ε is the random error. The regression analysis and estimation of these coefficients were performed by a statistical software package Design-Expert version 10.0.0.1 (Stat–Ease, Inc.). The model equations sufficiency was also evaluated using analysis of variance (ANOVA). Quality of fit of the model equations and their statistical significances were expressed using F-test and p-value, coefficient of determination (R^2), prediction coefficients of determination (Pred R^2), adjusted coefficients of determination (adj-R^2), and coefficients of variation (CV).

According to the Box–Behnken design, combined with the numerical optimization technique, the optimal conditions to obtain maximal removal efficiency were calculated by Derringer's desire function methodology. The optimum conditions were then evaluated by composite desirability, which had a value from 0 to 1, to determine to what degree the optimum conditions satisfy the ultimate goal of response.

Once the optimum conditions were obtained, the sample was prepared and verified by the model equation. Then the amount of fluoride adsorbed per unit mass of the adsorbent at any time t (qt, mg/g) from the sample prepared at optimum conditions was calculated using the following equation:

$$q_t = \frac{C_i - C_f}{m} * V \quad (7)$$

Where C_i and C_f are the fluoride concentrations in solution (mg/L) initially and at a given contact time (t), respectively, m the mass of the adsorbent (g) and V is the volume (L) of the solution.

Adsorption Equilibrium Isotherms; Langmuir and Freundlich and kinetics; pseudo first and second order were also investigated on the optimized operational conditions.

3.9. The real water samples

Real groundwater samples with higher fluoride concentrations were collected using a convenience sampling technique from different sites such as Tube, Wadesha, Dollessa, and Tejitu, and their concentrations determined were 3.67 mg/L, 4.33 mg/L, 5.55 mg/L, and 9.63 mg/L, respectively, and their pHs were 7.55, 7.10, 8.19, and 8.10, respectively. Water samples were collected in 2-L plastic bottles that had been cleaned with deionized water. Under optimal conditions, the efficiency of the chosen adsorbent was tested.

4. Results and Discussions

4.1.Characterization of CAC

4.1.1. Proximate analysis

The proximate analysis results of moisture content, ash content, and volatile matter are summarized in the following table. (For detailed calculations, see Annex)

Table 5: The proximate analysis results

Sample	Moisture content (%)	Ash content (%)	Volatile matter (%)	Fixed Carbon (%)
AC at 400^{o}C	4.3	5.78	32.79	57.16
AC at 500^{o}C	1.6	9.84	29.42	59.14
AC at 600^{o}C	5.5	18.63	35.21	40.66

As indicated in the table 5, the results show that the amount of generated fixed carbon content varies as the pyrolysis temperatures change. It was reported that increasing the temperature reduces the moisture content of the samples while increasing the value of rehydration (Abasi et al., 2009). In this study, the moisture content decreased of AC carbonized at 400 and 500 ^{o}C and then increased at higher carbonizing temperature, 600 ^{o}C); this might have been caused by the immediate rehydration. It was reported that the fixed carbon content is influenced by the amount of lignin and cellulose, which can be transformed into carbon atoms. At 600 °C, there is a decrease in fixed carbon due to the breaking of AC structures at elevated temperatures or carbon burning. A decline in carbon content could also be influenced by the reaction between both the carbon and the activator at elevated doses, which can affect the micropore upon on carbon surface (S Maulina and M Iriansyah, 2018). The low moisture content, ash, and volatile matter imply that the particle density is considerably lower, and the biomaterial should be a great raw material for adsorbents utilized in section or batch reactors (O.A. Ekpete,A.C.Marcus,and V. Osi, 2017).

In this study, an adsorbent carbonized at 500 ^{o}C showed a good content of fixed carbon, which was 59.14%, a substantial amount for locally prepared activated carbon. In general, the produced activated carbon was a much more carbonaceous substance and a great precursor for adsorbent formation. It was close to 60 % which is considered as the minimum amount of carbon content of

an AC (O. F. Olorundare,T. A. M. Msagati, R. W. M. Krause, J. O. Okonkwo, and B. B. Mamba, 2014)

Other research of affordably produced AC revealed moisture content of 4.0 %, ash content of 18.0 %, volatile substances of 25.0 % and fixed carbon content of 53.0 %, and, this was consistent with the current study (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019).

4.1.2. Fourier Transform Infra-Red Spectroscopy (FTIR)

FTIR analysis is utilized to describe the functional group of AC's surface (S Maulina and M Iriansyah, 2018). The prepared AC and MAC carbonized at 400 °C, 500 °C and 600 °C respectively were presented in figure 4 as analyzed by Fourier Transform Infra-Red Spectroscopy.

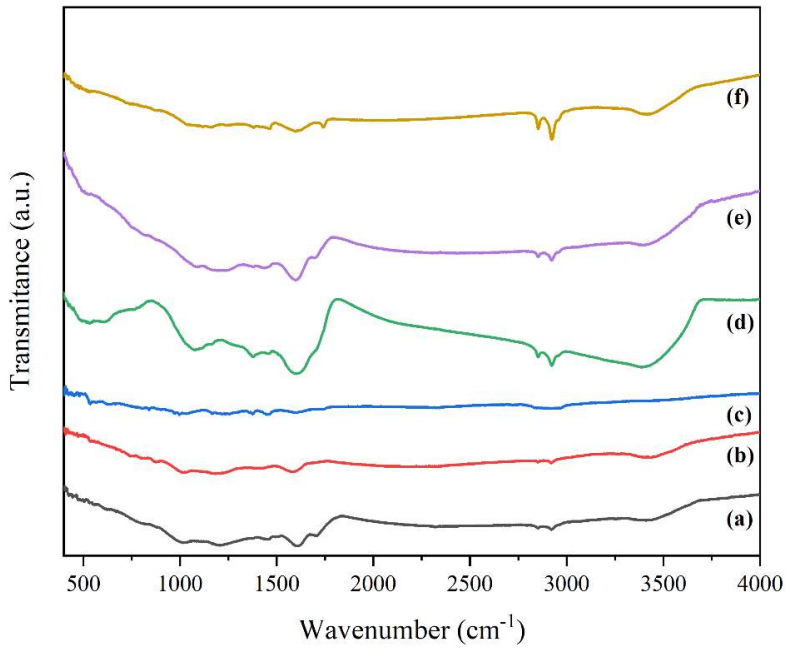

Figure 4: FT-IR spectra of (a) AC at 400°C, (b) AC at 500°C, (c) AC at 600°C, (d) MAC at 400°C, (e) MAC at 500°C and (f) MAC at 600°C

The broaden band peaks at about 3420 cm^{-1} is assigned for the vibration of water molecules hydroxyl group (-OH) of alcohols (≡C–O–H) or phenols (C_6H_5–OH). Furthermore, the peaks at 1622 cm^{-1} indicate the presence of the water molecules adsorbing and C=O stretching of

carboxylic acids on the surface of activated carbon. These major peaks demonstrated significantly decreasing trend as the calcination temperature increases from 400 ^{o}C to 600 ^{o}C for both modified and unmodified activated carbon. This may be due to temperature has direct effect on surface O-H group. In general, these functional groups are helpful to improve the fluoride absorption on the surface of activated carbon because it can bring about surface charge upon hydration. Similarly, other peaks, at 2947 cm^{-1} and 2843 cm^{-1} attributed to aliphatic C–H stretch of CH, CH_2 and CH_3 groups. Furthermore, the peak at 1000 cm^{-1} is related to the C–O group.

4.1.3. Scanning electron microscope (SEM)

SEM investigation is utilized to envision the surface morphology of the product which has been carbonized and actuated (S Maulina and M Iriansyah, 2018). In this study, SEM analysis of both AC and MAC prepared from *Catha edulis* stem was detected by utilizing a Scanning Electron Microscope. Figures 5 and 6 show SEM images for AC and MAC carbonized at 400, 500 and 600 °C respectively.

Figures 5 and 6 (a, b and c) show SEM micrographs of activated carbon modified activated carbon at numerous activation temperatures; at 400, 500, and 600 degrees Celsius. All of the activated carbon samples were found to have varying surface morphologies and pore sizes. This is due to the thermal treatment, which ejected volatile substances during the activation and carbonization stages. As the calcination temperature increased from 400^{o}C to 500^{o}C, the pore development on the sample is increased, however it decreases as the temperature further increased to 600 ^{o}C. This may be due to a higher temperature there is expected pore collapse. As indicated from figure 5b and 6b the sample prepared at 500^{o}C demonstrated a good pore distribution on the surface of the activated carbon allowing them to adsorb a large amount of fluoride ions. Furthermore, the presence of micropores, as seen in the AC and MAC samples, is responsible for chemically activated carbons' high adsorptive capacity.

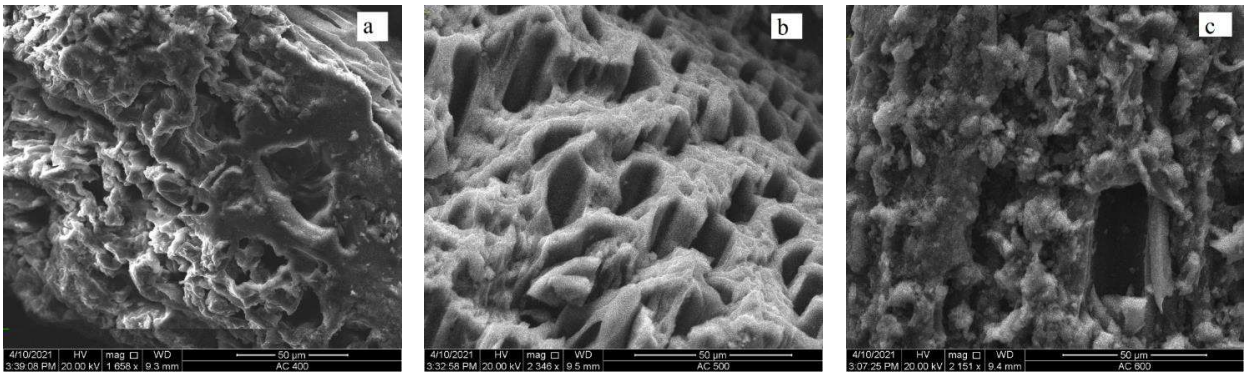

Figure 5: SEM images (a, b, and c) of prepared AC carbonized at 400, 500, and 600 °C, respectively.

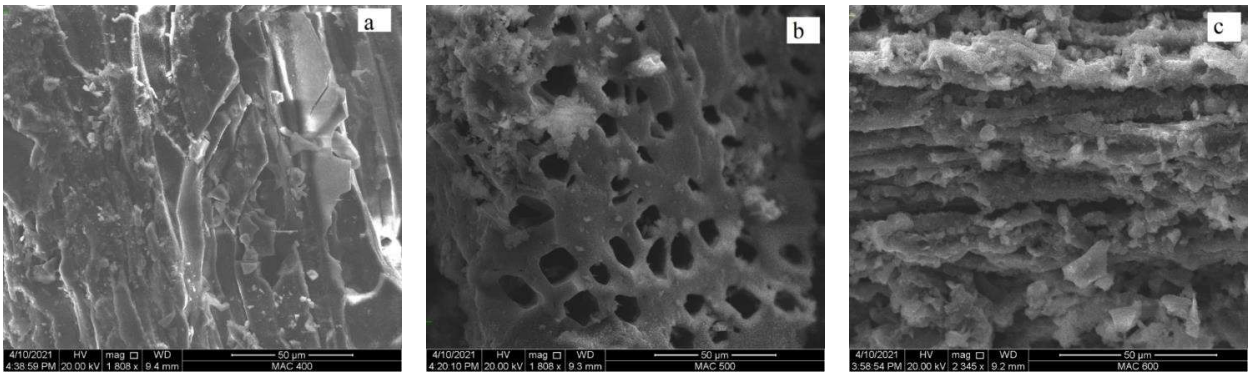

Figure 6: SEM images (a, b, and c) of prepared MAC carbonized at 400, 500, and 600 °C, respectively.

4.2. Data Analysis and optimization

4.2.1. Selection of Activated Carbon

In order to select the best activated carbon for further investigation, fluoride efficiency by the prepared modified and unmodified activated carbons was evaluated under similar operational conditions, such as initial fluoride concentration of 5 mg/L and adsorbent dose of 1 g/L and pH at 7. Accordingly, the sample prepared at 500 ^{o}C demonstrated higher fluoride removal efficiency of 81.8%, for modified sample (Table 6). They confirm that, surface modification has significant effect on the adsorption capacity of the activated carbon. These may be due to the fact that the sample prepared at 500^{o}C has very good adsorption capacity in relation to higher surface

area, pore distribution and surface functional group as it discussed in sections 4.1.2 and 4.1.3. However, the modified activated carbon exhibited much better efficiency than unmodified sample. Therefore, the modified activated carbon prepared at 500 ^{o}C (MAC at 500 ^{o}C) further investigated and optimized under different operational parameter using statistical experimental design.

Table 6: The preliminary fluoride removal efficiency of both AC and MAC

Adsorbents types	**Activation temp./ ℃**	**Initial F^- conc./ mg/L**	**Final F^- conc./ mg/L**	**F^- removal efficiency/ %**
AC	400	5	4.88	51.2
	500	5	2.88	71.2
	600	5	6.34	36.6
MAC	400	5	3.15	68.5
	500	5	2.98	81.8
	600	5	3.41	65.9

4.3. Adsorption Experiment for Fluoride removal

The selected modified activated carbon's efficiency is expressed as the percentage of fluoride removed from various fluoride initial concentrations, adsorbent dose, and pH for 60 minutes contact time. As a result, 15 experiments were carried out in accordance with surface response methodology statistical experimental design (Table 7).

As presented in the table, the removal efficiency ranged from 38.2 to 87.1 %. The highest fluoride removal was observed at the following conditions: initial concentration of 5.5 mg/L, pH 3, and adsorbent dose of 3 g/ L under uniform magnetic mixing at 120 rpm.

Table 7: Fluoride removal efficiency

	Factor 1	Factor 2	Factor 3	Response 1	
Run	A:Intial Fluoride Concentration	B:Dose	C:pH	Removal efficiency (%)	
	mg/L	g/ L of solution		Actual value	Predicted Value
1	2	2	3	72.8	72.84
2	9	1	6	44.5	43.75
3	5.5	2	6	65.9	64.57
4	5.5	2	6	64.5	64.57
5	2	3	6	87.1	87.85
6	2	2	9	77.4	76.74
7	5.5	2	6	63.3	64.57
8	2	1	6	80	79.87
9	5.5	1	9	47.8	48.59
10	9	2	3	38.2	38.86
11	9	2	9	40.3	40.26
12	5.5	1	3	37.9	37.99
13	5.5	3	9	49.6	49.51
14	5.5	3	3	55.6	54.81
15	9	3	6	53.4	53.52

4.4.Application to real water samples

Fluoride removal efficiency of the adsorbent prepared from khat samples activated at 500 °C and modified has been tested on the real water samples under optimized conditions for each sample. The concentrations of fluoride in all the water samples collected are observed to be higher than the permissible level. The concentrations of fluoride in the water sample of Tube, Wadesha, Dollessa and Tejitu are 3.67 mg/L, 4.33 mg/L, 5.55 mg/L and 9.63 mg/L and these concentrations were reduced to 1.0 mg/L, 1.28 mg/L, 2.32 mg/L and 5.22 mg/L respectively after treatment with MAC prepared at 500°C, respectively. The concentrations of the ground water collected from Tube and Wadesha are within the permissible limits set by WHO for drinking water. The fluoride concentrations in the ground water samples collected from Dollessa and Tejitu were reduced to lower concentrations but not to the permissible limits of but not to World health organization concentrations. Table 8 shows the real water samples concentrations before and after treatment and fluoride removal efficiencies on MAC.

Table 8: Real drinking water samples concentrations and fluoride removal efficiencies on MAC

Sites	Untreated water F^- conc. (mg/L)	Treated water F^- conc. (mg/L)	pH	Efficiency (%)
Tube	3.67	2.67	1.00	72.84
Wadesha	4.33	3.05	1.28	70.37
Dollessa	5.55	3.23	2.32	58.25
Tejitu	9.63	4.41	5.22	45.77

4.5.Analysis of variance

Analysis of variance is a statistical method that divides the variability in a data set into component parts related to specific sources of variation for the aim of testing hypotheses on the model's parameters (K. S. K. Reddy, A. Al Shoaibi, C. Srinivasakannan, 2015). The table 9 depicts the analysis of variance (ANOVA) for the fluoride removal, the models were significant ($P<0.0001$). The model F-value of 294.51 indicates that the model is significant for fluoride removal. There is only a 0.01% chance that an F-value this large could occur due to noise. In the ANOVA table, a p-value less than 0.05 implies that the model terms are significant, and vice versa. As a result, the model terms for fluoride removal A, B, C, AB, AC, BC, A^2, B^2, C^2 were significant.

The lack of fit test assesses the model's failure to represent data in the experimental domain at points that are not included in regression (Birhan Gebregziabher, Shimelis Kebede Kassahun, and Zebene Kiflie, 2021). As illustrated in table 10, the F and p values of the lack of fit test for fluoride removal were 0.6481 and 0.6539, respectively. It indicated that the lack of fit was not significant and that the quadratic equation for predicting the removal efficiency of modified activated carbon adsorbent. There is a 65.39 percent chance that a large Lack of Fit F-value could occur due to noise in the experiment.

Table 9: Variance analysis of the modified quadratic model for fluoride removal.

Source	Sum of Squares	Degree of freedom	Mean Square	F-value	p-value	
Model	3540.80	9	393.42	294.51	< 0.0001	significant
A-Initial Fluoride Concentration	2481.60	1	2481.60	1857.72	< 0.0001	
B-Dose	157.53	1	157.53	117.93	0.0001	
C-pH	14.05	1	14.05	10.51	0.0229	
AB	0.8100	1	0.8100	0.6064	0.4714	
AC	1.56	1	1.56	1.17	0.3288	
BC	63.20	1	63.20	47.31	0.0010	
A^2	114.42	1	114.42	85.65	0.0002	
B^2	55.68	1	55.68	41.68	0.0013	
C^2	620.01	1	620.01	464.13	< 0.0001	
Residual	6.68	5	1.34			
Lack of Fit	3.29	3	1.10	0.6481	0.6539	not significant
Pure Error	3.39	2	1.69			
Cor Total	3547.48	14				

A quadratic equation was used to determine the empirical relationship between response and input variables. A positive sign in the model terms indicated a synergistic influence, while a negative sign indicated an antagonistic influence. After the insignificant model terms were removed from the RSM model, the final equation obtained in terms of actual factors was as follows (Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018).

$$\text{Removal efficiency (\%)} = 10.65 - 9.93A + 27.21B + 20.697C + 0.13AB - 0.0595AC - 1.325BC + 0.454A^2 - 3.88B^2 - 1.44C^2 \quad (8)$$

4.6.Summary of model fit

The sequential model fitting results in Table 10 show that a quadratic model was suggested by the design expert for the experimental response. According to the lack of fit test, the second-order quadratic model was appropriate, prob>F is 0.0013. It is preferable for a model to have a minor lack of fit in order to properly fit the given experimental data. Tables 11 and 12 show that the coefficient of determination R^2 for the regression model of removal efficiency was 0.9981,

implying that the models attributed for 99.81 percent of the variability within the experimental range. Furthermore, the "pred R^2" value of 0.9830 agrees with the "Adj R^2" value of 0.9947 i.e. the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 52.838 indicates an adequate signal. This model can be used to navigate the design space. The model equations can also predict the response of removal efficiency with pred R^2 of 98.30% variability while the study factors are out of the experimental range. In general, for a good model, the values of R^2 and prediction R^2 should be close to 1.

Table 10: Sequential Model Fitting for removal efficiency

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	51427.39	1	51427.39			
Linear vs Mean	2653.18	3	884.39	10.88	0.0013	
2FI vs Linear	65.57	3	21.86	0.2110	0.8860	
Quadratic vs 2FI	**822.05**	**3**	**274.02**	**205.13**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	3.29	3	1.10	0.6481	0.6539	Aliased
Residual	3.39	2	1.69			
Total	54974.87	15	3664.99			

Table 11: Model statistical summary for removal efficiency

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	9.02	0.7479	0.6792	0.4915	1804.06	
2FI	10.18	0.7664	0.5912	-0.1123	3946.00	
Quadratic	**1.16**	**0.9981**	**0.9947**	**0.9830**	**60.30**	**Suggested**
Cubic	1.30	0.9990	0.9933		*	Aliased

Table 12: Fit Statistics

Std. Dev.	1.16	**R^2**	0.9981
Mean	58.55	**Adjusted R^2**	0.9947
C.V. %	1.97	**Predicted R^2**	0.9830
		Adeq Precision	52.8377

4.7.Diagnostic plots

The internally studentized residuals plot, which was created to represent the satisfactory fit of the developed model, reveals that each of the data points fall within the range of -3 to +3 (Figure 7). The models' adequacy was further tested by creating various diagnostic plots to determine whether the model equation would provide adequate approximations to the actual values. Figure 8 depicts the normal percent probability plot of residuals for the responses, which are normally

distributed because the data are reasonably close to the straight line and show no variance deviation. The results indicate that the models can be used to predict the best conditions for producing removal efficiency. Figure 9 depicts the predicted vs. actual fluoride removal efficiency values. The figure indicates that there is a strong correlation between the actual and predicted fluoride sorption values.

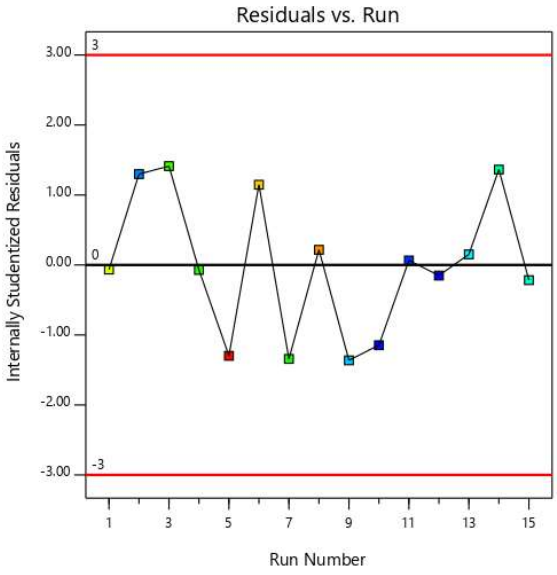

Figure 7: Residual vs. run plot for removal efficiency.

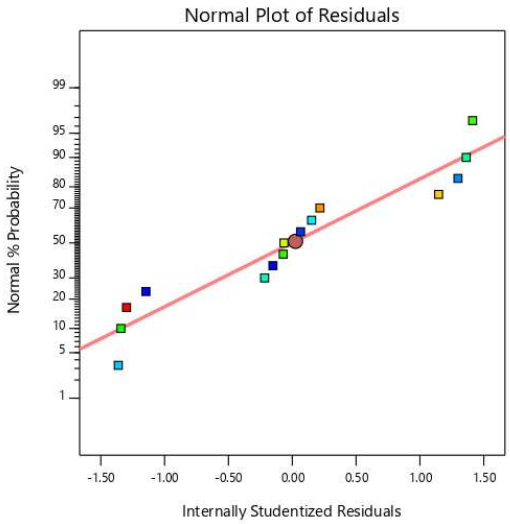

Figure 8: Normal Plot of residual for removal efficiency

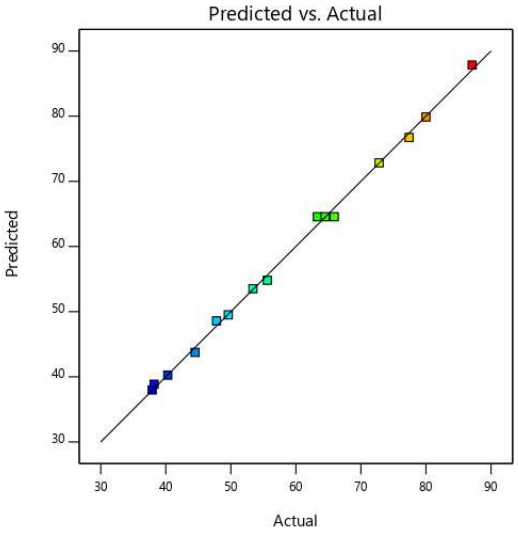

Figure 9: Predicted vs. Actual values of F^- removal efficiency

4.8.The effects and optimization of adsorption parameters on the removal of fluoride

Optimization is used for improving the performance of some parameters by varying one parameter while holding the others constant (T. Getachew, A. Hussen, V. M. Rao, 2014). For a batch adsorption experiment, the influence of adsorption factors namely initial fluoride concentration, pH, and adsorbent dose on adsorptive removal of fluoride from aqueous solution was investigated and optimized. The following section discusses the findings and observations.

4.8.1. The influence of initial fluoride concentration on fluoride removal

Figure 10 depicts the trend of the effect of various initial fluoride concentrations on fluoride removal from aqueous solution. It shows that as the initial fluoride concentration of fluoride increased from 2 to 9 mg/L, the removal efficiency of fluoride decreased from 87.74% to 52.52%. Therefore, the maximum fluoride removal percentage was obtained at the lowest initial concentration of 2 mg/L. This occurrence can be attributed to the availability of fewer active adsorption sites on the adsorbent surface for higher pollutant concentrations (Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018).

4.8.2. The influence of adsorbent dose on fluoride removal

The quantity of adsorbent is a critical parameter in determining an adsorbent's adsorptive capacity under given operating conditions. The effect of the amount of MAC on the adsorption of fluoride from aqueous solution was studied for 60 minutes at a stirrer speed of 120 rpm. It was discovered that increasing the adsorbent dose from 1 to 3 g/L resulted in a greater removal of fluoride. Fluoride adsorption increases with increasing adsorbent dose because there are more adsorption sites and surface area. Figure 11 shows that the amount of adsorbent used in the adsorption process had a strong influence on fluoride removal. Fluoride removal was observed to be 56.25 percent for 1 g of modified activated carbon, increasing to 65.12 percent for 3 g MAC.

4.8.3. The influence of pH on fluoride removal

The pH of the solution is an essential variable in the adsorption mechanism. In many cases, the removal of fluoride ions from aqueous solutions was highly dependent on solution pH, as it changes the surface charge on the adsorbents (V. Sivasankar, S. Rajkumar, S. Murugesh, A. Darchen, 2012). The effect of pH on fluoride removal uptake was investigated by changing the

solution pH from 2 to 9 using 0.1 M Sodium Hydroxide and Hydrochloric acid while holding other parameters constant; initial fluoride concentration 5.5 mg/L and MAC dose of 2g/L at 120 rpm mixing speed for 60 minutes. Figure 12 shows that at pH 6, 64.5 percent fluoride removal is possible, but as pH decreases towards the acidity and increases towards basicity regions, the fluoride capacity decreases to 50.28 percent at pH 3 and 52.93 percent at pH 9, respectively. This can be due to the production of poorly ionized hydrofluoric acid in acidic conditions (M. Malakootian, M. Moosazadeh, N. Yousefi, A. Fatehizadeh, 2011). Fluoride adsorption was found to reduce at higher pH due to an increase in electrostatic repulsion for fluoride ions caused by an abundance of negative adsorption surface sites (Avinash V. Palodkar, Kumar Anupam, Soumya Banerjee, and Gopinath Haldera, 2017). According to Mohammad et al. (2018), the decrease in fluoride adsorbed in alkaline pH is most likely due to competition between hydroxyl ions and fluoride ions on active sites (Mohammad Hadi Dehghani, Mansoureh Farhang, Mahmood Alimohammadi, Mojtaba Afsharnia & Gordon Mckay, 2018).

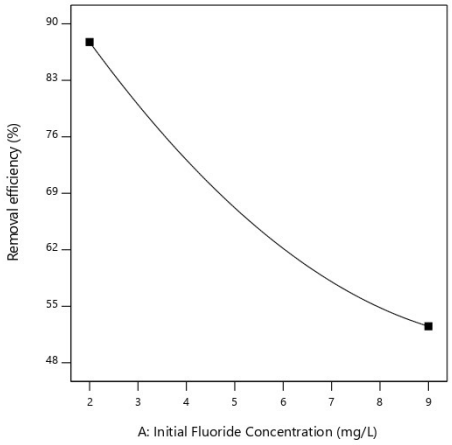

Figure 10: The effect of initial fluoride concentration on fluoride ion adsorption onto MAC

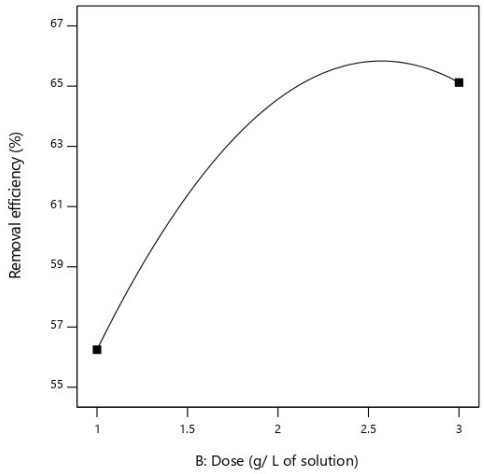

Figure 11: Effect of MAC dose on fluoride removal efficiency.

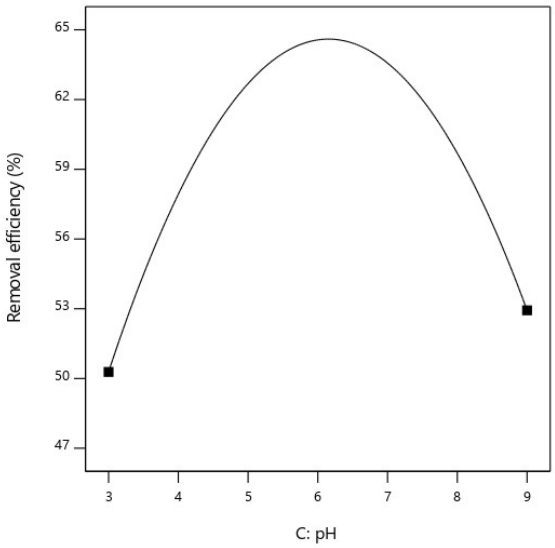

Figure 12: The effect of pH on fluoride ion adsorption onto MAC

Figures 13, 14, and 15 depict 3D surface plots of the effects of initial fluoride concentration and adsorbent dose, initial fluoride concentration and pH, and MAC dose and pH on fluoride removal by modified activated carbon, respectively. Figure 13 shows that as the MAC dose increases and the initial fluoride concentration decreases, fluoride removal increases. Figure 14 shows that F^- removal increases as the initial fluoride concentration increases and the pH approaches neutral, whereas the fluoride removal decreases as the MAC dose increases and the pH approaches neutral as depicted in figure 15.

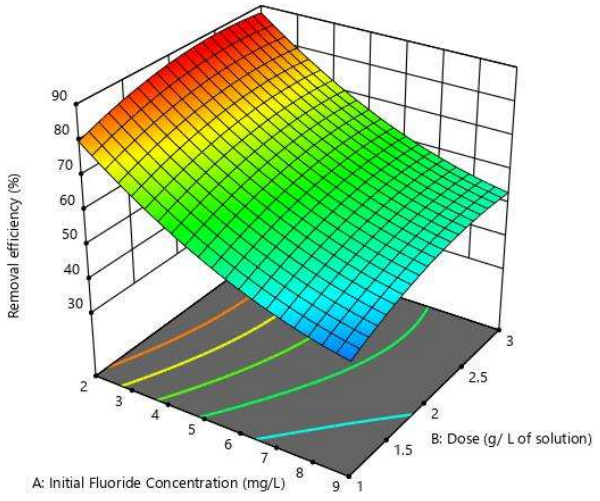

Figure 13: Effect of both initial fluoride concentration and dose on fluoride removal.

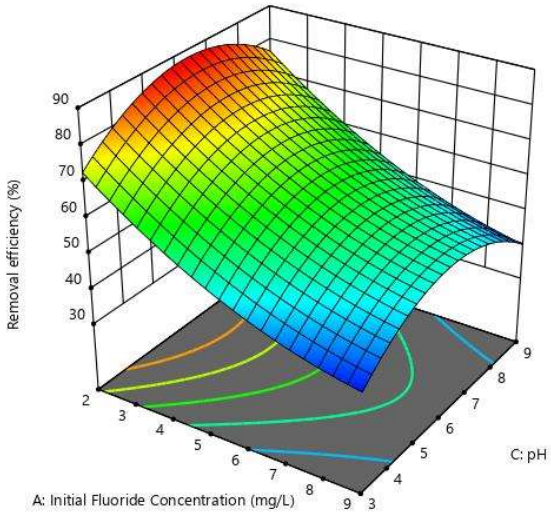

Figure 14: Effects of Initial fluoride concentration and pH on fluoride removal.

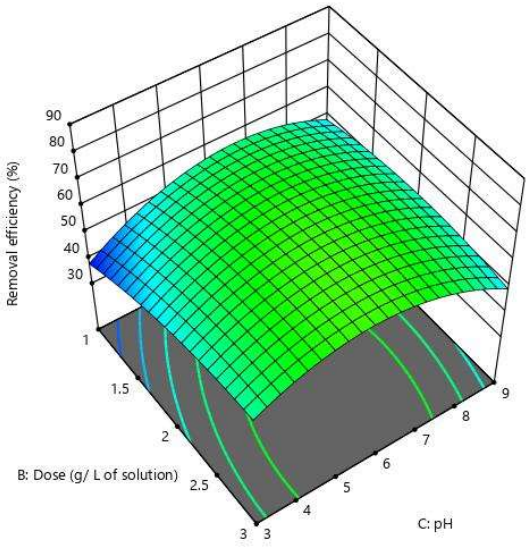

Figure 15: Effects of both MAC dose and pH on fluoride removal.

4.7. Operating parameters optimization and verification

The optimum fluoride removal process conditions were determined using a numerical optimization technique based on BBD-RSM. The primary objective was to calculate the maximum fluoride removal efficiencies. BBD-RSM optimum conditions were evaluated using Derringer's desired function methodology, which has values ranging from 0 to 1, to determine how well the optimum conditions satisfy the ultimate goal of response. To achieve the highest fluoride removal efficiency, the initial fluoride concentration, solution pH, and modified activated carbon dose were all kept within the study ranges of 3 to 9, 2 to 9 mg/L, and 1 to 3 g/L, respectively. As a result, an optimum fluoride removal of 87.9 % was forecasted at the optimum operating parameters of initial fluoride concentration of 2.1 mg/l, the solution pH of 6.08 and the MAC dose of 2.47 g/L at 60 minutes contact time with desirability of 1 (figure 17). The optimum operational parameter also verified and obtained 85.66 ± 1.03 % removal efficiency, which is very close to the predicted value.

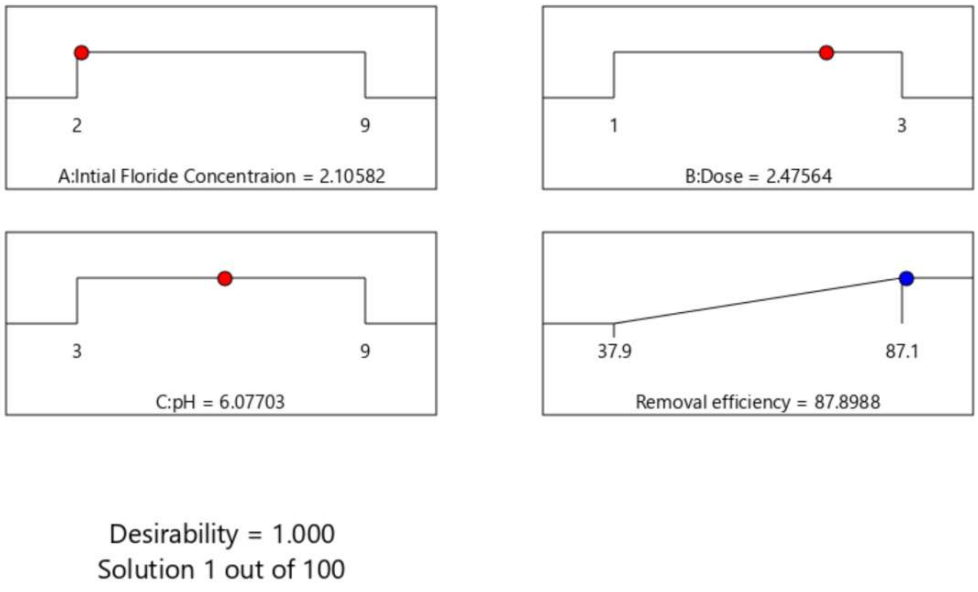

Figure 16: Numerical optimization solutions

4.9.Isotherms of equilibrium adsorption

Adsorption isotherms are amongst the most important methods for representing the adsorbent's adsorption capacity and the mechanism of the adsorption system. An adsorption model is used to determine the connection between the fluoride concentrations remaining in the bulk solution and the total value of fluoride adsorbed at the solid/solution interface (Mekala Suneetha,

Bethanabhatla Syama Sundar, and Kunta Ravindhranath, 2015). In this study, the obtained data from sorption experiments were analyzed in this study using two conventional isotherm models, namely the Langmuir and Freundlich. The Langmuir isotherm model is applied to explain the surface-solution equilibrium as a reversible chemical equilibrium between species while the Freundlich adsorption isotherm, which was first proposed as an empirical equation, is used to describe the data for heterogeneous adsorbent materials like activated carbon (John C. Crittenden, 2012). The Langmuir isotherm is predicated on adsorbate monolayer adsorption onto an adsorbent surface with the scarcity of binding sites. The Freundlich equation is applicable to adsorption on adsorbents with a heterogeneous adsorbing surface, including multilayer adsorption.

The Langmuir and Freundlich equations are written as; $q_e = \frac{q_{max} K_L C_e}{1+K_L C_e}$ and $q_e = K_F C_e^{1/n}$ respectively.

The following equations (9 & 10) represent the models' linear format:

$$\text{Langmuir} : \frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{max}} C_e \quad (9)$$

$$\text{Freundlich} : \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (10)$$

$$R_L = \frac{1}{1+K_L C_o} \quad (11)$$

Ce in is the concentration of fluoride at equilibrium in the aqueous (mg/L), q_e is the adsorbed amount of adsorbate per unit mass of the adsorbent at equilibrium (mg/g), q_{max} is the maximum adsorption capacity for Langmuir isotherm (mg/g), q_{max} and K_L in Equation (1) are calculated from the slope and intercept of the plot of C_e/q_e versus C_e, respectively. K_L (L/mg) is a Langmuir constant. K_F and 1/n are Freundlich constants for the adsorption capacity and adsorption intensity, respectively. K_F and 1/n values can be calculated from a plot of ln q_e versus ln C_e (John. Bentil and William Kwame Buah, 2016).

The equation 11 shows the separation factor (R_L) which is a dimensionless constant that can be used to express the important characteristics of the Langmuir isotherm; K_L and C_o are the Langmuir adsorption constant of adsorbate (L/mg) and initial concentration of the adsorbate in mg/g, respectively. R_L values indicate the adsorption to be unfavourable, linear, favourable and irreversible when $R_L>1$, $R_L=1$ $0<R_L<1$ and $R_L=0$, respectively (Nimibofa Ayawei, Augustus

Newton Ebelegi, and Donbebe Wankasi, 2017). The values of Langmuir and Freundlich constants are given in Table 14. From the data calculated in table 14, the R_L (0.087) is greater than 0 but less than 1 indicating that Langmuir isotherm is favourable. The value n=1 demonstrates that the equilibrium distribution between the solid and liquid phases is independent of concentration, while $\frac{1}{n} > 1$ indicates cooperative adsorption and $\frac{1}{n} < 1$ indicates normal adsorption (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019).

The isotherm study was carried out with initial fluoride concentration of mg/L and an adsorbent dosage of 3 g/L with solution pH 6 under room temperature. As shown in Table 14, the Langmuir isotherm model fit the experimental data better, as demonstrated by the higher correlation coefficient (R^2) of 0.972.

Table 13: Experimental data of adsorption for Langmuir and Freundlich Isotherms

Time (minutes)	Final F^- conc. (Ce/mg/L)	Fluoride removal (%)	q_e (mg/g)	c_e/q_e	ln c_e	ln q_e
15	1.1213	43.94	0.2929	3.828269	0.114489	-1.22792
30	0.8014	59.93	0.3995	2.00584	-0.2214	-0.91746
45	0.4121	79.40	0.5293	0.778575	-0.88649	-0.6362
60	0.2698	86.51	0.5767	0.467807	-1.31007	-0.55038
75	0.2376	88.12	0.5875	0.404448	-1.43717	-0.53194
90	0.228	88.60	0.5907	0.386005	-1.47841	-0.5265
105	0.2019	89.91	0.5994	0.336856	-1.59998	-0.51188

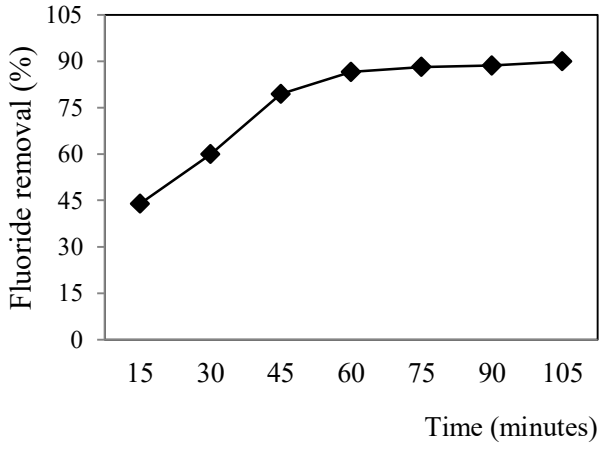

Figure 17: Graph of the fluoride removal efficiency vs time.

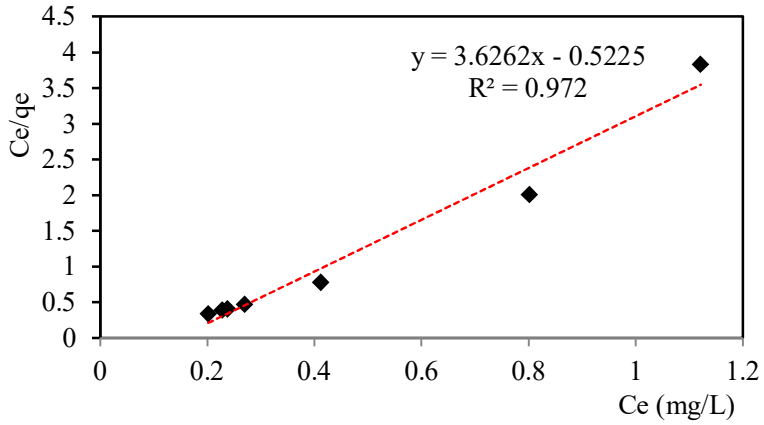

Figure 18: The Langmuir plot for fluoride adsorption on MAC.

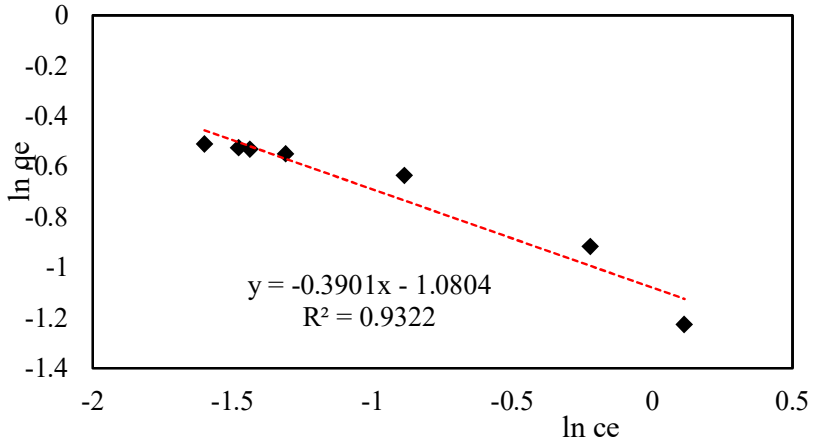

Figure 19: The Freundlich plot for fluoride adsorption on MAC.

Table 14: Isotherms of fluoride adsorption on MAC

Isotherm models	**Constant Parameters**						**Corr. Coeff.**
	Slope	Intercept	q_m	R_L	K_F	n	R^2
Langmuir	3.26262	-0.5225	0.3065	0.087	--	--	0.972
Freundlich	-0.3901	`-1.0804	--	--	0.3395	-2.5634	0.9322

4.10. The Kinetics of Fluoride Adsorption

Using reaction kinetics, the mechanism of fluoride removal on modified activated carbon prepared from khat stem was investigated. Lagergren's rate equation is a widely known rate

equation for describing adsorbate adsorption from the liquid phase (Ch. Chakrapani, Ch. Suresh Babu, K.N.K. Vani, K. Somasekhara Rao, 2010). The general pseudo-first-order and pseudo-second-order equations are written as; $\frac{dq_t}{dt} = K_1(q_e - q_t)$ and $\frac{dq_t}{dt} = K_2(q_e - q_t)^2$ respectively. Equation 12 depicts the linear form of Lagergren's pseudo first-order rate expression. The pseudo-first-order plot is log(qe-qt) vs. t, while the pseudo-second-order plot is t/qt vs. t (equation 13) (G. Alagumuthu and M. Rajan, 2010).

$$\log(q_e - q_t) = log\, q_e - \frac{K_1}{2.303} t \tag{12}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{13}$$

Where q_e and q_t are the amounts of fluoride adsorbed on the adsorbent (mg/g) at equilibrium and time t (min), respectively, and k_1 and k_2 are the pseudo first-order kinetics rate and the pseudo second-order kinetics rate constants. Linearization of the pseudo-first and pseudo-second order models was performed, and qe and k_1 or k_2 values were determined (Jin Hee Park, Girish Choppala, Seul Ji Lee, Nanthi Bolan, Jae Woo Chung and Mansour Edraki, 2013).

Adsorption experimental data for pseudo-first-order and pseudo-second-order kinetics are shown in Table 15. The pseudo-first order and pseudo-second order kinetic models for the adsorption of fluoride from aqueous solutions by modified activated carbon obtained from khat (*catha edulis*) stem are shown in Figures 20 and 21. The higher liner correlation coefficient (R^2= 0.9895) of the pseudo-second order kinetic model demonstrated that it fit the experimental data better than the pseudo-first-order kinetic model.

Table 15: Adsorption experimental data for pseudo-first-order and pseudo-second-order kinetics

Time (minutes)	c_f (mg/L)	q_t (mg/g)	q_e (mg/g)	q_e-q_t (mg/g)	log (q_e-q_t)	t/q_t
15	1.1213	0.2929	0.5994	0.3065	-0.51357	51.21202
30	0.8014	0.3995	0.5994	0.1999	-0.69926	75.0876
45	0.4121	0.5293	0.5994	0.0701	-1.15428	85.01795
60	0.2698	0.5767	0.5994	0.0227	-1.64461	104.0342
75	0.2376	0.5875	0.5994	0.0119	-1.92324	127.6668
90	0.228	0.5907	0.5994	0.0087	-2.05882	152.3702
105	0.2019	0.5994	0.5994	0.0000	-4.47712	175.1849

Table 16: Pseudo-first-order and pseudo-second-order kinetic models' parameters

Kinetics Model	Parameter	Values
Pseudo-first-order	**K_1**	0.0843
	q_e (mg/g)	2.6026
	R^2	0.8003
Pseudo-second-order	**K_2**	0.0638
	q_e (mg/g)	0.7380
	R^2	0.9895

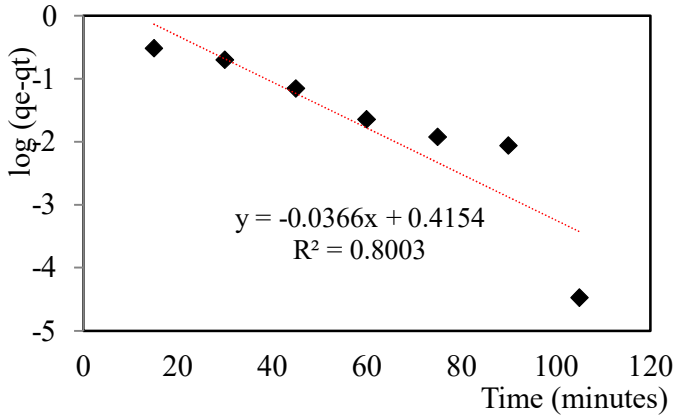

Figure 20: Plot of pseudo-first-order kinetic fit for fluoride adsorption onto MAC

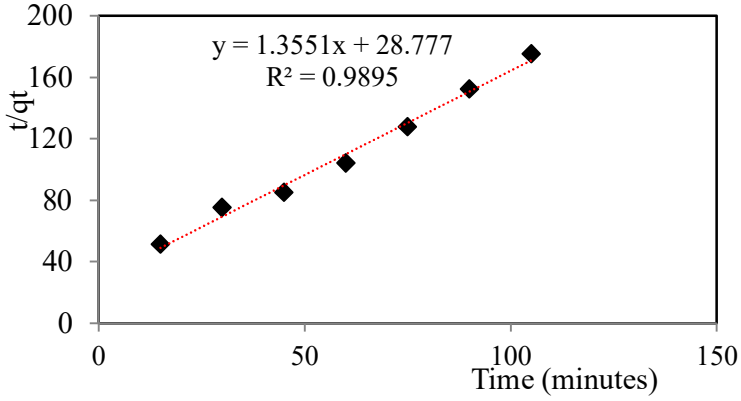

Figure 21: Plot of pseudo-second-order kinetic fit for fluoride adsorption onto MAC

5. Conclusion and Recommendations

5.1.Conclusion

In this batch experiment, khat (*Catha edulus*) stem waste activated carbon was used as an adsorbent for fluoride uptake from aqueous solutions. Fluoride removal increases as the adsorbent dose increases, the initial fluoride concentration decreases, and the pH approaches neutral (7). The activated carbon and modified activated carbon produced at 500^{o}C had better adsorptive capacity compared to those produced at 400 and 600^{o}C. The maximum fluoride removal was 87.1 % at the optimal conditions of initial fluoride concentration, pH, and adsorbent dose (MAC) of 2 mg/L, 6 mg/L, and 3 g/L, respectively, whilst model-based predicted value of fluoride removal under the same experimental condition was 87.9 %. The concentrations of fluoride in the water sample of Tube, Wadesha, Dollessa and Tejitu sites are 3.67 mg/L, 4.33 mg/L, 5.55 mg/L and 9.63 mg/L and these concentrations were reduced to 1.0 mg/L, 1.28 mg/L, 2.32 mg/L and 5.22 mg/L respectively after treatment with MAC prepared at 500°C, respectively. The concentrations of the ground water collected from Tube and Wadesha are within the permissible limits set by WHO for drinking water. The fluoride concentrations in the ground water samples collected from Dollessa and Tejitu were reduced to lower concentrations but not to the permissible limits of but not to WHO. The data were better described by the Langmuir isotherm model and the pseudo-second order kinetic model than by other isotherm and kinetic models. According to the adsorption study, activated carbon samples obtained from the khat stem were effective at removing fluoride from its solution. It is concluded that the modified activated carbon derived from khat can be used as a low-cost adsorbent for fluoride removal from solutions.

5.2.Recommendation

In general, the performance of modified activated carbon derived from khat stems for the removal of fluoride from water is a good potential defluoridation technique that could be used in water treatment. However, more research into this treatment technology is expected in terms of removing fluoride from highly fluoride polluted water as well as the effects of other ions in polluted water.

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Annex

Moisture content

Moisture content (for adsorbent carbonized at 400 ^{o}C) % = $\frac{1-0.957}{1}$*100= 4.3%

Moisture content (for adsorbent carbonized at 500 ^{o}C) % = $\frac{1-0.984}{1}$*100= 1.6%

Moisture content (for adsorbent carbonized at 600 ^{o}C) % = $\frac{1-0.945}{1}$*100= 5.5%

The *Catha edulis* char carbonized at 500 ^{o}C showed the lowest moisture content of 1.6%. The lowest moisture content indicates the good quality of the activated carbon (Jemal Fito, Hanan Said, Sisay Feleke, and Abebe Worku, 2019).

Ash content

Ash content (for adsorbent carbonized at 400 ^{o}C) % = $\frac{W2-W1}{Ws}$*100

- The weight of the crucible, w_1 = 23.1803 g
- The weight of the sample, w_s = 1 g
- The weight of crucible and sample after drying, w_2 = 23.2381 g

Then, Ash content (for adsorbent carbonized at 400 ^{o}C) % = $\frac{23.2381-23.1803}{1}$*100= 5.78%

Ash content (for adsorbent carbonized at 500 ^{o}C) % = $\frac{W2-W1}{Ws}$*100

- The weight of the crucible, w_1 = 30.2724 g
- The weight of the sample, w_s = 1 g
- The weight of crucible and sample after drying, w_2 = 30.3708 g

Then, Ash content (for adsorbent carbonized at 500 ^{o}C) % = $\frac{30.3708-30.2724}{1}$*100= 9.84%

Ash content (for adsorbent carbonized at 600 ^{o}C) % = $\frac{W2-W1}{Ws}$*100

- The weight of the crucible, w_1 = 22.0698 g
- The weight of the sample, w_s = 1 g
- The weight of crucible and sample after drying, w_2 = 22.2561 g

Then, Ash content (for adsorbent carbonized at 600 ^{o}C) % = $\frac{22.2561 - 22.0698}{1}$*100=18.63%

Volatile matter

The volatile matter of the activated carbon carbonized at three different temperatures was calculated and the results are as follows;

Volatile matter (for 400 ^{o}C sample) % = $\frac{1-0.6724}{1}$*100= 32.76 %

Volatile matter (for 500 ^{o}C sample) % = $\frac{1-0.7058}{1}$*100= 29.42 %

Volatile matter (for 600 ^{o}C sample) % = $\frac{1-0.6479}{1}$*100= 35.21 %

Fixed Carbon

The fixed carbon content of adsorbent carbonized at 400 ^{o}C, 500 ^{o}C, and 600 ^{o}C was calculated as follows;

Fixed Carbon Content (for 400 ^{o}C sample) % = 100% - (4.3% + 5.78% + 32.76%) = 57.16%

Fixed Carbon Content (for 500 ^{o}C sample) % = 100 % – (1.6% + 9.84% + 29.42%) = 59.14%

Fixed Carbon Content (for 500 ^{o}C sample) % = 100 % – (5.5%+ 18.63%+ 35.21%)= 40.66%