ADSORPTION OF FLUORIDE FROM SOLUTION USING RAW AND MODIFIED EDIBLE CLAY

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A THESIS WRITTEN IN THE DEPARTMENT OF CHEMISTRY FACULTY OF PHYSICAL SCIENCES UNIVERSITY OF BENIN, BENIN CITY IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF BACHELOR OF SCIENCE (B.Sc) DEGREE IN INDUSTRIAL CHEMISTRY

JULY, 2021

CERTIFICATION

This is to certify that this project work was carried out by Egbon Akpevwe Dickson with matriculation number PSC1607116 in the Department of Chemistry, Faculty of Physical Sciences, University of Benin, in partial fulfilment of the award of BSc degree in Industrial Chemistry.

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DEDICATION

This research work is dedicated to God Almighty and to my family for their love and care all through my studies at the University of Benin.

ACKNOWLEDGEMENTS

First of all, I appreciate God almighty who strengthened and furnished me with all I needed to make my project a success.

I also acknowledge my supervisor, Dr. (Mrs.) S. I. Omonmhenle for her care, concern and love in dealing with me throughout the course of this research work.

My gratitude also goes to my parents for their guidance they gave all through my stay at the University of Benin.

I am also using this medium to thank Abel Jessah, Egbon A. Dickson, Ogala O. Christopher, Iyonmana I. Grace, Uboh V. Oluchi, and family who made sure my success during my stay at the University of Benin was guaranteed.

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ABSTRACT

Cases of dental and skeletal fluorosis have been reported in children especially in low income earning countries and this has been a major problem as documented in recent studies.

Clay is an adsorbent material that is cheap and readily available relative to other industrially synthesized adsorbents and its properties has been explored by recent researchers.

This study aims at assessing the adsorptive properties of raw and modified edible clay on fluoride from solution. The effect of concentration, adsorbent dosage, and time and isotherm studies were conducted using standard procedures documented in literatures.

From the result, activated edible clay had the highest percentage removal at 15 minutes with a value of 95.37%, 96.74% at a concentration of 50mg/L of fluoride, and 96.92% at an adsorbent dosage of 1.3g. The raw edible clay showed maximum adsorption at 25 minutes, at maximum concentration of 30mg/L fluoride, and at a dosage of 1.3g with values of 93.98%, 96.63%, and 96.34% respectively. The adsorption does not follow a monolayer coverage as the data could not fit into the Langmuir and Freundlich's isotherms. These values indicate that the raw and oxalic acid modified clay are good adsorbents for the removal of fluoride from solution.

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Adsorption has been a major industrial separation technique for the purification of effluents. For one reason, it employs the use of low-cost materials as the adsorbing specie with ease of maintenance. Most of the materials used for adsorption are sourced internationally from manufacturers and may be costly depending on the manufacturer and the nature of the material *(Adeyemo et al., 2015)*.

It involves the separation of the specie to be adsorbed via mass transfer mechanism where the material adsorbed is removed from the medium (solution) by attracting the dissolved solute to the surface of the solid material. This has led to various studies using different materials to treat effluents either naturally or modified to suit the intended use depending on the nature of the material to be removed from the solution *(Adeyemo et al., 2015)*.

It is s separation technique that has found wide application in the removal of dye from aqueous media, specifically in the textile, leather, paper, dyeing, plastics, and cosmetics industry where recovery is very essential *(Adeyemo et al., 2015)*.

1.1.1 Background of Study

Activated carbon and clay have been classified among many different adsorbents used in the adsorption of solutes from solutions and studies has given more attention to activated carbon. For example, Chen et al. (2001) and Markovska et al. (2001) have reported the use of activated carbon in removing coloured organic materials and is the most widely used due to its high capacity adsorption of organic species.

It has been reported that the practice of eating clay known as Geophagy has been an ancient practice *(Gomes, 2018).* The clay eaten is usually referred to as the edible clay majorly consumed by pregnant women, a practice common in West Africa. The adsorptive capacity of clay for many organic and inorganic species thus could also cause a reduction in the content of some major minerals present in the human body although, consideration has not been given to this from various studies in vivo.

Reports has shown that clay can remove approximately 70 % of wastes in water removal systems and the remaining 30 % can be removed using activated carbon *(Zakaria et al. 2009).* The wyrd and movement of adsorbates is greatly influenced by their strong interaction with natural clay and oxides of minerals that are widely present in the natural environment *(Sheng et al. 2013; Miller et al. 2010).*

1.1.2 Statement of Problem(s)

In addition to heavy metal, fluoride has been classified as one of the contaminants of water for human consumption by the World Health Organization (WHO) (*Grim et al., 1998)*. The World Health Organization has recommended that the maximum fluoride dosage permissible in drinking water for a day shouldn't exceed 1.5mg/L for a 2L of water to be consumed (World Health Organization, 2011; World Health Organization, 2017). Irrespective of this, series of cases of fluorosis has been reported in recent studies, an indication that fluoride is being consumed beyond the maximum dosage as specified by the World Health Organization. A report documented by Amini et al. (2008) has shown that fluorosis, associated with elevated fluoride concentrations in drinking water, has been recorded in various countries around the world such as India, China, Tanzania, Mexico, Argentina, and South Africa. According to recent studies, more than 200 million people worldwide consume more than the recommended amount of fluoride *(Kumar et al., 2020).* Only in India, more than 62 million people suffer from dental, skeletal and non-skeletal fluorosis *(Chaudhry et al., 2017)*. Dental fluorosis has been reported to occur in 10% of children exposed to 4 mg L^{-1} fluoride in their drinking water, where skeletal fluorosis occurred when the fluoride concentration is greater than 10 mg L^{-1} *(Tan et al., 2020).* A study published in Environmental Health Perspectives in 2012 also found that a high level of fluoride in drinking water has potential in lowering IQ levels in children *(Tan et al., 2020).* In Malaysia, the recommended level of fluoride in the public water supply is 0.4 to 0.6 mg L^{-1}. It was however, found that 7% of the population in Malaysia are exposed to a public water supply which exceeded the upper limit of the recommended fluoride level which is more than 0.6 mgL^{-1} *(Zhang et al., 2019).*

It should be noted that the aforementioned countries that are greatly affected by fluorosis are Low-Medium Income Countries and are readily affected by this health condition based on their inability to acquire and maintain water treatment technologies that have been advanced by High Income Countries. Thus, the treatment of water so as to avert fluorosis remains a major problem.

1.1.3 Justification of Study

In low- and medium-income countries, the treatment of water from drinking sources and effluents from industries poses a challenge which majorly is the procurement and maintenance of technologies that has been advanced for removal of contaminants. Activated carbon has been a major adsorbent for the treatment and removal of organic and inorganic contaminants from water. However, due to it being a limited natural resource, slow adsorption kinetics and low adsorption capacity of bulky adsorbate because of its microporous nature, disposal problems and also the high cost and difficulty of regeneration, a search for cheap, effective adsorbents such as clay or its derivatives has become important *(Joo et al., 2009).*

1.1.4 Scope of Work

This project covers the use of the natural and oxalic acid modified edible clay as an adsorbent for adsorption studies of fluorides from solution. It encompasses the study of the effect of contact time, adsorbent dosage, and effect of fluorides initial concentrations on the sorption properties of the clay material.

1.1.5 Aim and Objectives

This study aims at assessing the adsorptive properties of raw and modified edible clay as a low-cost material for the adsorption of fluoride from a solution.

The Objectives of this study are;

- Crushing of the edible clay material to fine particles to increase its surface area and modification using oxalic acid
- Batch adsorption using the raw and modified edible clay material on the effect of adsorbate’s concentration, contact time, and adsorbent’s dosage.

1.2 LITERATURE REVIEW

Several studies have shown that clay has the capacity to adsorb heavy metals, dyestuffs, and anions *(El-Maaghrabi and Mikail, 2014; Adeyemo et al., 2015).* In solutions, metals or non-metals can either exist as cations and anions while dyes could either be cationic or anionic and the choice of adsorbent will be determined by the nature of the material to be adsorbed. The study of clay as an adsorbent has been embarked on by interested researchers owing to the fact that is readily in nature and is cheap.

1.2.1 Clay

Clays are defined as fine grained minerals, which may be plastic in nature, that can be hardened when dried or fired and they contain appropriate water contents. Clays generally contain phyllosilicates however, the other contents present may impart either plasticity or harden when fried or dried *(Adeyemo et al., 2015)*. It should however be noted that there are other fine soil particles but clay can be differentiated from these by their minerology and size. Clays generally are good adsorbing species. This is evidenced from the fact that water from underground is usually clean as a result of the removal of organic materials and other inorganic species from water deposited on the oil surface while leaching takes place gradually through the different soil profiles.

Adeyemo et al (2019), described the various types of clay and their chemical constituents. According to their research, he reported that the main class of clay are montmorillonite- sematic, kaolinite, Illite, bentonite and chlorite.

Kaolinite group includes the mineral kaolinite, dickite, halloysite and nacrite. The smectite group includes pyrophyllite, talc, vermiculite, sauconite, saponite, nontronite and montmorillonite. The illite comprises of the clay micas. Illite is the only mineral common to these class of clays *(Kloprogge et al., 1999)*.

Although chlorites are not always considered clay however, they are sometimes classified as a separate group within the phyllosilicates. There are approximately 30 different types of pure clays in these categories, but most natural clays are mixtures of these different types, along with other weathered minerals.

The composition of raw clay was further validated by El-Maghrabi and Mikhail (2014) when they studied its chemical composition via chemical analytical techniques from where they obtained the results

Compound	Weight (%)
SiO_2	53.25
Al_2O_3	18.15
Fe_2O_3	6.65
Na_2O	4.97
MgO	1.42
K_2O	1.05
Cl^-	0.62
Ignition Loss	13.85
SiO_2/ Al_2O_3 molar ratio	~ 5

Table 1.0 Components of natural clay

The ignition loss was determined by ashing one gram of the sample at 1000°C till constant weight.

1.2.1.1 Structure of Clay

Clay minerals are hydrous aluminosilicates with fine particle size; they are composed of two basic building blocks: silicon–oxygen tetrahedron $(Si_2O_5)^{2-}$ and aluminium octahedron (gibbsite sheet). Tetrahedral sheets are composed of individual tetrahedrons which share every three out of four oxygens. They are arranged in a hexagonal pattern with the basal oxygens linked and the apical oxygen atoms pointing up/down. Octahedral sheets are composed of individual octahedrons that share edges composed of oxygen and hydroxyl anion groups with Al3, Mg2 and Fe2 typically serving as the coordinating cation. These octahedrons are arranged in a hexagonal pattern (Guggenheim and Martin 1995; Zakaria et al. 2009).

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1.2.1.2 Types of Clay

Clays have been grouped into types depending on the academic source and they are montmorillonite, kaolinite, smectite, illite, and chlorite *(Kausar et al., 2018; Adeyemo et al., 2015).* Some other literatures would give other classes which possess the structures of these types along with other chemical components making the impure such as bentonite.

- *Kaolinite Clay:* this is a white and soft plastic clay comprising of hydrated aluminium silicate, a mineral kaolinite. This group possess silicate sheets (Si_2O_5) bonded to aluminium oxide or hydroxide layers which are the gibbsite layers. It is a layered silicate mineral with one of its octahedral sheets linked to an alumina octahedra via one of its oxygen atoms. It has been reported to contain trioctahedral minerals like cronstedite, antigorite, chamosite, and dioctahedral minerals like nacrite, dickite, and kaolinite (*Kausar et al., 2018)*. This group is made up of primary structural unit of a layer composed of one octahedral sheet packed with one tetrahedral sheet. The octahedral sites are occupied by aluminium in dioctahedral minerals, while in the trioctahedral minerals, these sites are occupied by magnesium and iron. Kaolinite and halloysite are monolayered layer structures. Kaolinite, dickite and nacrite occur as plates; halloysite, which can have a monolayer of water between its sheets, occurring in a tubular form. It is formed by the alteration of feldspar and muscovite *(Moore and Reynolds, 1989; Liu and Zhang, 2007).*

A well-known fact is that kaolinite clay contains heterogeneous surface charge. It assumed that its basal surface possesses a constant structural charge which is ascribed to isomorphs substitutions of Si^{4+} by Al^{3+}. The charge on the edges is due to protonation of surface or abstraction of proton from hydroxyl groups thus causing a dependence on the pH of a solution. Adsorption can occur on flat exposed planes of silica and alumina sheets. It is least reactive clay, has no side effects, no health problems till the fine dust particle is controlled, so it is safe environmentally *(Nandi and Boswani, 2008; Nandi and Boswani, 2009).*

- *Montmorillonite Clay:* it is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay *(Jaafar, 2006).* Its structural unit is made up of a gibbsite layer that is sandwiched between two silica sheets [85]. It has been described as belonging to the family of the smectite with the general formula $(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_2(OH)_2 \cdot nH_2O$ *(Grim 1962).* This means that its chemical composition is based on hydroxyl-aluminosilicate network where substitutions are mainly within the octahedra layer (Mg^{2+}, Fe^{2+}) and to a much less extent within the silicate layer *(Kausar et al., 2018).*

The individual crystals of montmorillonite clay loosely bound hence water can penetrate into its layers, causing the clay to swell. The water content of montmorillonite is variable and it increases greatly in volume when it absorbs water. Chemically, it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2\cdot nH_2O$ *(Wikipedia, 2021*). Common substituents are potassium, iron, and other cations and their exact ratio varies with source *(Jaafar, 2006)*. It has been characterized as having an octahedral charge greater than 50% with cation exchange capacity due to isomorphous substitution of magnesium for aluminium in the central alumina plane. When lower valence cations are substituted in such instances, the nearby oxygen atoms are left with a net negative charge that can attract cations. This will automatically make it a good adsorbent for cationic species *(Wikipedia, 2021*).

Montmorillonite clays have reportedly been used extensively in catalytic processes. For over 60 years, cracking catalysts have used montmorillonite clays. Other acid-based catalysts use acid-treated montmorillonite clays *(Lloyd and Lawrie 2011)*. There are also other uses of montmorillonite clay based on the aforementioned properties viz, in the oil drilling industry as a component of drilling mud where it makes the mud slurry and viscous, thus, helping in keeping the drill bit cool and removing drilled solids. It is also used as a soil additive to hold soil water in drought-prone soils, in the construction of earthen dams and levees, prevention of leakage fluids, component of foundry sand, and as a desiccant in the removal of moisture from air and gases *(Wikipedia, 2021).*

Plate 1.0 Image of Montmorillonite

- *Bentonite Clay:* this is an absorbent swelling clay consisting mostly of montmorillonite. It has high water retention capacity and it is able to swell increasing its volume by up to a factor of 8 *(Jackson, 1997).* This high swelling capacity has made it unsuitable for building and road construction *(Wikipedia, 2021).* The fact that it belongs to the class of montmorillonite clay, characterized by it aluminium phyllosilicate structure which takes the form of microscopic platy grains gives it a very large total surface area making it a very good adsorbent. It possess forces of cohesion that makes it useful as a binder and as an additive to improve the plasticity of kaolinite clay used for pottery *(Nesse, 2000).*

It is differentiated from true montmorillonite clay due to the presence of other impurities. It is usually formed from weathering of volcanic ash in seawater, which converts the volcanic glass present in the ash to clay minerals *(Adeyemo et al., 2015)*.

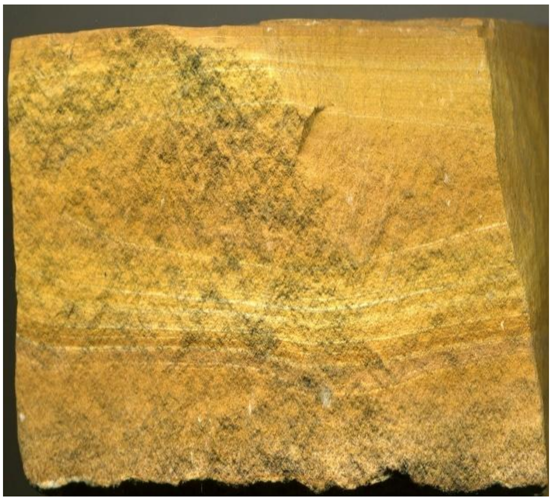

Plate 1.1 Image of Bentonite

1.2.2 Modification of Clay

In many cases, pre-treatment is required to enhance the adsorption capacity of clays and hence modified to increase metal uptake (O'Connell *et al.,* 2010). This pretreatment improves the surface area, pore volume, and number of active sites present on the surface. Through modification, the clay minerals become hydrophobic, organophilic, and thus leads to enhanced uptake of small non-ionic organic compounds *(Ismadji et al., 2015*). There are many methods for clay treatment or activation with a goal to increase the adsorption capacity of the raw clay material. However, some researchers have also present results that treatment or modification did not increase the adsorption properties

(Bhattacharyya and Gupta 2009; Al-Jlil and Alsewailem, 2009). The various methods that has successfully been used for clay modification are chemical treatment, biogenic modification, mechanochemical treatment, and physical treatment.

1.2.2.1 Chemical Modification

This method has been widely used for the activation and improved functionality of clay. It is usually achieved through intercalation or pillarization *(Shen et al., 2015)*.

In pillaring, a layered compound is transformed into a thermally stable micro- and, or mesoporous material with retention of the layered structure *(Schoonheydt and Jacob, 2001)*. The product obtained from the process is a pillared compound or a pillared layered solid. They are considered as special class of clays due to their improved property. The introduction of micro and or mesopores into clay is achieved by combination of clay and a pillaring agent via an ion-exchange reaction, in which a two-dimensional channel network is formed *(Schoonheydt and Jacob, 2001)*. Heating the clay stabilizes the pillared clay as a result of enhanced permanent bonding between the pillar and the layers. The resulting materials have small cavities and a large surface area. The low cost of pillaring materials along with these properties, make pillared clays ideal for use as alternative catalysts to zeolites *(Kloprogge et al., 2002)*. There are numerous oligomeric cations that could be used as pillars, some of which are Al, Zr, Ti, Cr, Fe and Ce and these cations can be used individually or mixed in different ratios.

In intercalation, there is a reversible inclusion or insertion or molecules or ions into layered materials.

Chemical modification involves the use of acids, salts, bases, and metallic oxides which introduces exchangeable cations or anions into the layers of clays via the pillaring or intercalation process. The acids used may be organic or mineral acids usually oxo acids or Lewis acids.

1.2.2.1.1 Acid Activation

During the treatment of clays with acids exchangeable cations are replaced with H^+ ions and cations are leached out of both tetrahedral and octahedral sites, leaving the SiO_4 group intact for binding with cations and anions *(Theocharis et al., 1998).* Acid treatment of clay materials have been widely studied as a form of chemical treatment method for the improvement of heavy metals adsorption properties. This treatment involves leaching of the clay material with either organic or inorganic acids of which the result is disaggregation of clay particles, elimination of mineral impurities, and dissolution of the external layers so that the chemical composition and structure of the clays are altered *(Kayode et al., 2019).* The benefits of acid treatment are observed in terms of increased surface area, porosity and number of acid sites with respect to the parent clays.

1.2.2.1.2 Modification with Organic Compounds

In this method, organic surface active species (surfactants) are introduced into the clay structure via ion exchange mechanism. This done to convert the hydrophilic silicate surface to an organophilic one, making the intercalation of polymeric chain between silicate layers possible. This modification has been explored by some researchers and the modified clay was found to possess improved properties. For instance, result of a study on Cr (VI) removal using batch adsorption techniques conducted by Gładysz-Płaska et al. (2012), exploring the adsorptive properties of the natural red clay after modification by hexadecyl-trimethylammonium bromide (HDTMA) showed improved adsorption properties of the modified clay over the raw red clay.

1.2.2.2 Biogenic Modification

This method of modification involves fortification of clay with organic biomass and composites that could possibly enhance heavy metals adsorption by improving the surface area of the clay. In fortification with organic biomass, additional reactive sites for cation exchange and or surface are provided for complexation. A study conducted by Akpomie et al. (2017) on investigation of the effect of cassava peel modified kaolinite clay compared to the unmodified kaolinite clay on the adsorption of Cr (III) ion gave result show indicating that cassava peel modified kaolinite clay was suitable for chromium ion sorption from aqueous solution.

1.2.2.3 Physical Treatment

Modification of clay by this method is applied in order to disrupt the chemical structure of the clay material. The clay material is usually subjected to a very high temperature capable of breaking some chemical bonds and altering the arrangement of molecules in the lattice structure of the clay. The major ways of doing this are calcination and microwave heating.

1.2.2.3.1 Calcination

Clays are strongly dependent on temperature, and the high temperature treatment of clays destructs the crystalline structure of the clay minerals. This serves as the basis of its functionalization via calcination. In calcination also referred to as conventional heating, the clay materials are exposed to high temperature capable of breaking the bonds of the components contained in its structure. The limitation of this method is that the outermost parts of the materials experience the energy before the interiors, stimulating a thermal gradient amid the inner and the outer surface of individual particle. This may eventually lead to overheating of the materials causing substrate and reagent degradation and heterogenous microstructure of materials at high heating temperature, high energy consumption and time wastage.

1.2.2.3.2 Microwave Heating

Almost all reactions have been tested under classical conditions (thermal heating) for comparison with reactions that proceeds in the microwave field which is an improved alternative for conventional heating. Observations from experimental results obtained from microwave–initiated chemical reactions has shown that reactions occur at faster rates as great as 1000-folds of the conventional methods *(Hayes, 2004)*. Thus, the microwave heat treatment of clay provides an advantage over calcination due to low energy consumption, fast activation, and less time consumption.

1.2.3 Fluoride

Fluoride is an ion of fluorine, the most reactive halogen characterized by an oxidation state of -1. It has been reported to be one of the essential micronutrients enhancing human health via facilitation of the mineralization of bone and preventing dental caries if consumed at a recommended dosage *(Tan et al., 2020; Fantong et al., 2010).* Irrespective of its health benefits, it has been reported to possess some detrimental effects if consumed at dosages exceeding the standard set by the world health organization *(Tan et al., 2020).*

It exists in natural water such as fresh and see water at low concentration, as well as in rainwater, particularly in urban areas. Seawater fluoride levels are usually in the range of 0.86 to 1.4 mg/L, and average 1.1 mg/L *(Wikipedia, 2021).*

An excess of it in water and other sources if consumed causes fluorosis, a condition that has been incurable until now that makes teeth and bones extremely hard and brittle *(Tewari and Dubey, 2009).* The main constituent of teeth is hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) and fluoride can substitute the hydroxide ion present in the hydroxylapatite to form fluorapatite which is responsible for the hardness, increased density, and brittles of bones and teeth *(Saikia et al., 2017).* The major sources of fluoride in ground water are fluoride bearing rocks such as fluorspar, cryolite, fluorapatite. The fluoride content in ground water is a function of many factors such as availability and solubility of fluoride minerals, velocity of flowing water, pH, temperature, concentration of calcium and bicarbonate ions in water *(Malay and Salim, 2011).*

It is a major contaminant found in some major industrial effluents which when deposited into water bodies poses a risk to the environment. For example, if it is consumed by Pisces on which man depends for food, when deposited into water bodies, it becomes detrimental to human health as a result of consumption of high dosages exceeding regulatory standards. Thus, while water is the major source of fluoride ingested by man, food and air are also other media through which fluoride can be ingested. The quantity released by some major industries has been documented in recent reports as tabulated below.

Sources	Emission (Tons/year)
Steel	40,100
Ceramics	21,200
Phosphate fertilizer and processing industries	18,700
Aluminium industries	16,000
Combustion of coal	16,000

Non-ferrous metal fluorides	4,000

Table 1.1 Fluoride emission from some major industries

Different technologies have been used for the defluoridation of drinking water viz, precipitation/coagulation, ion-exchange methods, membrane based techniques such as reversed osmosis, and adsorption methods but all of these methods are requires technical expertise and are expensive except adsorption used clay materials which has been reported to be very effective *(Akafu et al., 2019).*

1.2.4 Methods Used for Quantitative Determination of Fluoride

Several methods have been used for the quantitative determination of fluoride in water depending on the source and concentration of the fluoride. They include but not limited to the potentiometric method, colourimetry, and gas chromatographic methods.

1.2.4.1 Potentiometric Method

This method is based on the electrical conductivity of fluoride in solution which is a function of its concentration. It employs the use of a modern pH meter or an ion meter with the use of a fluoride ion selective electrode (ISE).

The fluoride electrode is an ion-selective sensor having the laser-type doped lanthanum fluoride crystal across which a potential is established by fluoride solutions of different concentrations as its key element. The crystal contacts the sample solution at one face and an internal reference solution at the other. The cell may be represented by:

Ag|AgCl, Cl^- (0.3*M*), F^- (0.001*M*) |LaF_3| test solution|reference electrode

The fluoride electrode can be used with a standard calomel reference electrode and almost any modern pH meter having an expanded millivolt scale. Calomel electrodes contain both metallic and dissolved mercury; therefore, dispose of them only in approved sites or recycle. The issue of proper disposal is settled with preference to Ag|AgCl electrode over the calomel electrode. The fluoride electrode measures the ion activity of fluoride in solution rather than concentration. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complexing species. Adding an appropriate buffer provides a nearly uniform ionic strength background, adjusts pH, and breaks up complexes so that, in effect, the electrode measures concentration.

The presence of some polyatomic cations would reduce the concentration of fluoride in solution due to the formation of complexes of notably iron and aluminium. To avoid this interference, the use of chelating agents is employed while preparing the test solutions since they chelate the polyvalent cations to form stable complexes. The chelates thus formed leaves the fluoride free in the solution and the formation and stability of these complexes is hinged on the pH of the solution.

Also, fluoride being a strong Lewis base forms a weak acid (hydrofluoric acid) with a poorly ionized complex (HF·HF) in acidic medium hence, a buffer is required to keep the pH above 5. On the other hand, interference occurs with the fluoride in a basic medium due to the hydroxide formed. At the pH maintained by the buffer, no hydroxide is formed hence, the used of a buffer to calibrate the ion selective electrode is necessary to avoid interferences. The buffer called total ionic strength adjusting buffer (TISAB) is usually prepared by mixing 4g Of EDTA or CDTA (1,2 cyclohexylenediaminetetraacetic acid), 57ml glacial acetic acid, 58g sodium chloride, in about 500ml deionized water and adjusting the pH to 5-5.5 by slowly adding about 125ml of sodium hydroxide after which the solution is diluted to 1000ml in a standard flask.

1.2.4.2 Colourimetric Method

The colourimetric method for the determination of fluoride is based on its tendency to form complexes with certain inorganic species. A typical colourimetric method uses the SPADNS (sodium2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate) and acidified zirconyl oxychloride solution mixed in equal volumes to measure the concentration of fluoride in solution by filter photometry of UV-Vis spectroscopy.

The SPADNS colourimetric method is based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless hexafluorozirconate(IV) ion, a complex anion (ZrF_6^{2-}); and the dye. As the amount of fluoride increases, the color produced becomes progressively lighter. The reaction rate between fluoride and zirconium ions is influenced greatly by the acidity of the reaction mixture. If the proportion of acid in the reagent is increased, the reaction can be made almost instantaneous. Under such conditions, however, the effect of various ions differs from that in the conventional alizarin methods. The selection of dye for this rapid fluoride method is governed largely by the resulting tolerance to these ions.

1.2.4.3 Gas Chromatographic Method

A gas chromatograph (GC) with flame ionization detector (FID) or electron capture detector (ECD) is a relatively common instrument in brewery laboratories, offering good robustness, precision, selectivity and sensitivity. Before the GC-FID analysis, the sample (standard) is derivatized using trimethylchlorsilane (TMCS) in toluene.

Fluoride ions are converted to trimethylfluorosilane (TMFS)

through a two-step reaction.

$$CH_3 - Si - Cl + H_2O \leftrightarrow CH_3 - Si - OH + HCl$$

$$CH_3 - Si - OH + H^+ + F^- \leftrightarrow CH_3 - Si - F + H_2O$$

TMCS is converted to trimethylsilanol by hydrolysis. Under acidic conditions, trimethylsilanol reacts further with free fluoride ion to form volatile TMFS. n-Pentane can be used as an internal standard for accurate quantification. TMFS is extracted with an organic solvent (toluene) and the organic layer is injected into the gas chromatographic system. The TMFS peak is quantified using a calibration curve prepared from standard solutions. This method is often used for determination of fluoride in toothpaste (*Wejnerowska et al., 2007*). Gas chromatography has also been reported as a suitable method for the determination of trace amounts of fluoride because of its simplicity, accuracy and sensitivity *(Lipka et al., 2000).*

1.2.5 Adsorption

Adsorption simply is the phenomenon where the molecules of a substance referred to as adsorbate adheres to the surface of a solid. The solid surface on which the adsorbate adheres is referred to as the adsorbent. It follows that a solid is able to adsorb molecules of gases or solutes from a solution as a result of the residual forces existing on its surface. When such solid materials have unsatisfied valences, the adsorbate may undergo a bond breakage and chemically bind to the surface of the solid, the basis for solid catalysis.

The adsorbing properties of a solid is hinged on certain factors which are the surface properties, the nature of the adsorbent, and the nature of the adsorbate. The surface properties of the adsorbent are usually characterized in terms of the pore sizes, volume, and surface area in m^2/g. The surface area is proportional to the extent to which adsorbates will adhere to the surface of the adsorbent. Apart from the surface area, the pore volumes or size plays a major role in the adsorbent's capacity. For example, an adsorbent characterized by micropores only will be limited in its affinity for adsorbates when they are mesoporous. This is evidenced from the fact that carbon based microporous materials can not readily adsorb methylene blue, a dye that is characterized by its large molecular size compared to iodine which could readily be used to determine the index (iodine index) of carbon-based microporous materials. Surface charge and acidity of and adsorbent is another factor to be considered in choosing a material for adsorption. A surface with positive charge distribution would readily adsorb a negatively charged specie and vice versa.

1.2.5.1 Types of Adsorption

There are two types of adsorption namely physical adsorption (physisorption) and chemical adsorption (adsorption).

Physical adsorption occurs when the adsorbate is bound to the surface of the adsorbent by Van der Waal's forces. Here the heat of adsorption is equivalent to the heat required to condense a gas on the surface of a solid thus making the heat of physical adsorption small. It is therefore obvious that at elevated temperatures, physical adsorption will become difficult, in fact the reverse will take place known as desorption since the molecules of gas or solute ions are in adsorptive equilibrium with the surface of the adsorbent. Therefore, it could be generalized that physical adsorption is reversible.

Chemical adsorption takes place when the adsorbates molecules/ions are chemically bound to the surface of the of the adsorbent. In this case, the force of attraction between the solid adsorbent and the adsorbate is chemical in nature, usually covalent bonds. This makes chemical adsorption irreversible and just like chemical reactions, it is accelerated at elevated temperatures and becomes the pathway to catalysis when the solid adsorbent possesses unsatisfied valences. It is characterized by a high enthalpy or differential heat of adsorption.

1.2.5.2 Adsorption Isotherms

Adsorption isotherms are curves that expresses the relationship between the equilibrium pressure of gasses or the concentration of solutes to the extent of adsorption at constant temperature. These curves define the behavior of gases or solutes on an adsorbent's surface as they help predict the nature of adsorption.

Several isotherms have been developed by some scientists commonly Langmuir, Freundlich, the B.E.T isotherms.

- *Langmuir's Isotherm:* according to Langmuir, there is adsorptive equilibrium between the adsorbent and the adsorbate because as the adsorbate strike the surface of the solid adsorbent, some molecules are desorbed such that when monolayer coverage is attained, the at equilibrium, the rate of adsorption is equal to the rate of desorption. This led to the theoretical equation

  $$\theta = \frac{KC_{eq}}{1 + KC_{eq}}$$

  The above equation relates the number of moles of solute per unit mass adsorbent required for monolayer coverage to the number of moles per unit mass adsorbed as

  $$\frac{N}{N_m} = \frac{KC_{eq}}{1 + KC_{eq}}$$

  The equation is then linearized as

  $$\frac{C}{N} = \frac{C_{eq}}{N_m} + \frac{1}{KN_m}$$

  When the extent of adsorption a_{eq} is used, the equation takes the form

  $$\frac{C_{eq}}{a_{eq}} = \frac{C_{eq}}{N_m} + \frac{1}{KN_m}$$

  Where N_m is the number of moles of solute required for monolayer coverage, K , is Langmuir's constant, and C_{eq} is the equilibrium concentration of solute. Thus, a plot of $\frac{C}{a_{eq}}$ as a function of C_{eq} gives a straight line graph whose slope is $\frac{1}{N_m}$ with an intercept of $\frac{1}{KN_m}$ from where the constants N_m and K can be evaluated *(Raghav and Kumar, 2018; Akafu et al., 2019).*

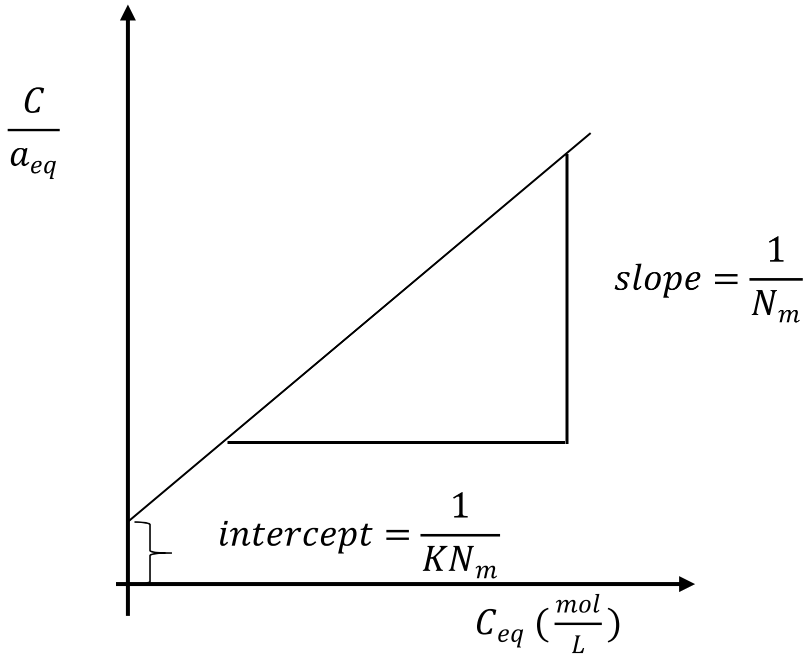

Figure 1.0 A Sketch of Langmuir's isotherm

- *Freundlich Isotherm:* this isotherm is based on the assumption that the adsorbent had a heterogeneous surface composed of different sites with adsorption on each site following the Langmuir's isotherm. The equation was given theoretically as

  $a = KC^{1/n}$

  Where a is the extent of adsorption, C is the concentration of adsorbate, K and n are constants.

  Taking the logarithm of both sides yields

$$loga = logK + \frac{1}{n}logC$$

Thus, a plot of $loga$ against $logC$ would give a straight line graph whose slope is $1/n$ and intercept is $logK$ as shown below *(Raghav and Kumar, 2018)*

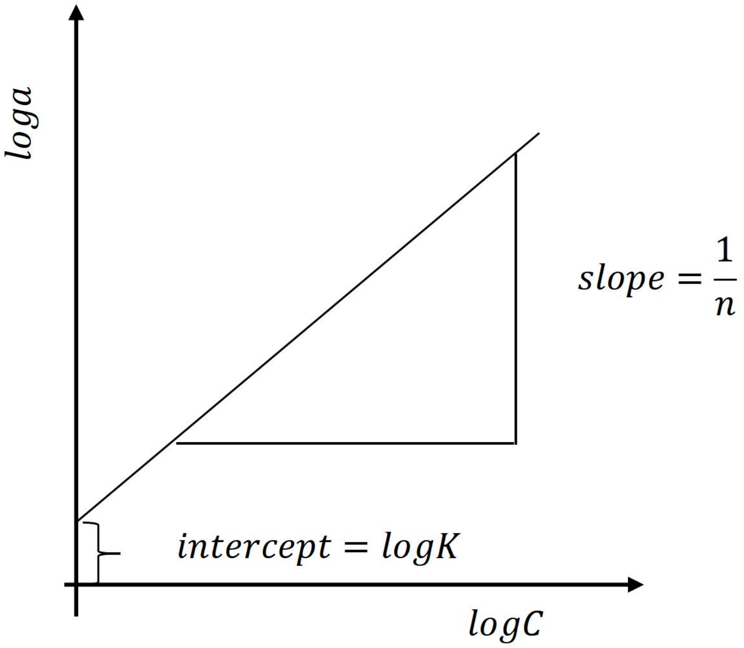

Figure 1.1 A sketch of Freundlich' isotherm

1.2.5.3 Thermodynamics and Kinetics of Adsorption

Thermodynamics helps to ascertain the feasibility/spontaneity of a reaction and in adsorption studies, it helps in determining the feasibility and the type of adsorption that occurred between the adsorbate and adsorbent. The major factor assessed in the thermodynamics of adsorption is the isosteric enthalpy of the differential heat (ΔH) of adsorption. Its value helps predict weather adsorption is physical or chemical and coupled with the free energy term ΔG, it helps assess the spontaneity of adsorption using the thermodynamic formulae

$\Delta G = \Delta H - TS.$

According to Vant-Hoff isotherm equation,

$$\frac{dlnC}{dT} = \frac{-\Delta H}{RT^2}$$

Which translates to

$$\frac{d}{dT}\left[\frac{lnC}{1/T}\right] = \frac{-\Delta H}{R}$$

Thus, a plot of lnC against $1/T$ at a constant concentration would give a straight line graph whose slope is $\frac{-\Delta H}{RT}$ as shown below

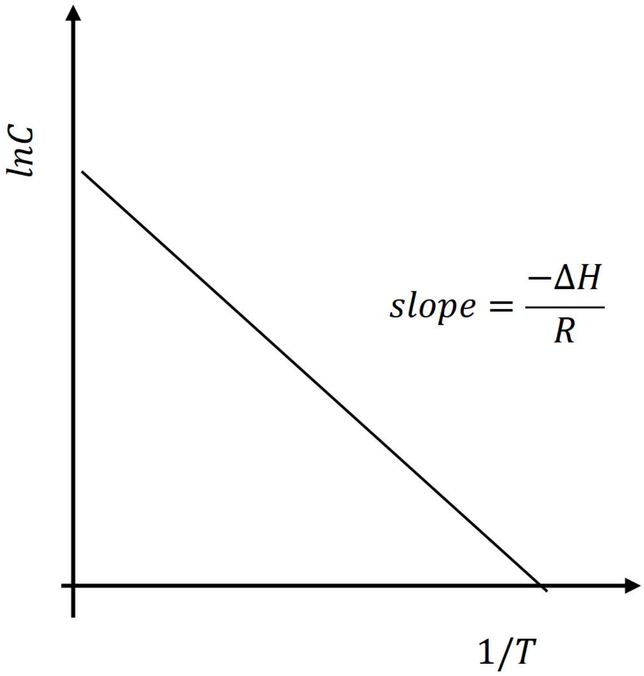

Figure 1.2 A sketch of Vant-Hoff isotherm

The kinetics of adsorption helps predict the pathways through which adsorption has taken place under a given set of conditions. Just like kinetics of chemical reactions, it takes place at rates which may be larger or smaller depending on the conditions of adsorption which could be temperature, pressure, pH, contact time, amongst others. For the fact that the kinetics is solely dependent on the surface properties of the adsorbent under a set of conditions, the pseudo first order model is given as

$$\ln(q_e - q_t) = lnq_e - kt$$

While for a pseudo second order model, the linearized form is given as

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$

Thus, plotting $\ln(q_e - q_t)$ against would give a straight line and when this happens using experimental data, the reaction follows the pseudo first order kinetic model but if the correlation coefficient is closer to unity for a plot of $\frac{t}{q_t}$ against t, the kinetics follows a pseudo second order model *(Saikia et al., 2017; (Raghav and Kumar, 2018; Akafu et al., 2019).*

1.2.6 The Edible Clay

The edible clay is also known as calabash chalk and has been called different names depending on locality such as Ulo, Ndom, Mabele, Nzu, Argile, Poto, Lacraie, and Eko *(Ukwueze and Ochuba, 2017).* It best fits into the description of kaolinite clays having extremely flat card-like crystals that are stacked together with weak electronic bonds and possesses a negative charge making it a good adsorbent for cationic species. It has been reported to contain some traces of heavy metals which majorly are mercury, lead, chromium, and cadmium all of which accumulates with time in those practicing geophagy, a eating disorder characterized by the craving for clay, and exerts some toxicological effects *(Ukwueze and Ochuba, 2017).*

It is commonly eaten by pregnant women in Africa where they conceive it as a remedy for morning sickness although, it has not been medically established. Other than this reason, people in other parts of the word also consume it for differing reasons and it is location dependent. This practice is as old as mankind and is a reflection of cultural practices, religious belief, and physiological needs.

CHAPTER TWO

MATERIALS AND METHODS

2.1 MATERIALS

Volumetric flasks

Erlenmeyer flasks

Beakers

Plastic funnel

Measuring cylinder

Aluminium foil

25µm sieve

2ml and 10ml syringes

Suction tube

Retort stand and clamp

Magnetic stirrer

Mechanical shaker

Thermostatic oven

pH indicator paper

Sample bottles

Burette

Pipette

Test tubes

Glass stirring rod

Desiccator

Centrifuge machine

2.2 REAGENTS

Oxalic acid

Edible clay

Sodium hydroxide

Phosphoric acid

Sodium fluoride

SPADNS

Zirconyl oxychloride octahydrate

Sodium arsenite

Hydrochloric acid

2.3 PREPARATION OF RAW EDIBLE CLAY SAMPLE

The edible clay was obtained in the clustered form, crushed using a mortar and a pestle to break down aggregates and obtain fine powder. The powder obtained was then sieved using a 125µm mesh sieve after which it was transferred to an air tight container for storage.

2.4 PREPARATION OF MODIFIED EDIBLE CLAY

100g was weighed from the raw edible clay prepared from above into a beaker containing 3M oxalic acid and stirring was done for an hour. The modified clay was then separated from the mixture via decantation after which it was washed with distilled water followed by subsequent decantation until a pH of 7 was attained. The acid modified clay slurry obtained was then dried at temperatures ranging from 60-80°C after which it was homogenized using a mortar and pestle and stored in an airtight container.

2.5 PREPARATION OF SOLUTIONS

All reagents used are of analytical grade with minimum assay of 98% and solutions were prepared following standard methods as described below

2.5.1 Preparation of 3M Oxalic Acid

138.0759g of oxalic acid was weighed as calculated into a 500ml beaker, 250ml distilled water was added to dissolve the solid with stirring after which the solution was transferred into a 500ml standard flask. The beaker and the stirring rod were rinsed thrice into the standard flask and the solution was made up to mark after which it was transferred to a 500ml plastic reagent bottle for storage.

2.5.2 Preparation of Acidified Zirconyl chloride-SPADNS Solution

0.958g of SPADNS was weighed into 100ml beaker, distilled water was added to dissolve solid and the solution was transferred into a 500ml standard flask. The beaker was rinsed thrice with distilled water into the flask using wash bottle and the solution was made up to mark after which it was stoppered, shaken, and transferred into plastic reagent bottle labelled SPADNS.

0.133g zirconyl oxychloride was weighed into a beaker, dissolved in 25ml distilled water and 350ml concentrated hydrochloric acid was pipetted into this solution after transferring to a 500ml volumetric flask. The solution was then made up to mark. Equal volumes of the SPADNS solution and the acidified zirconyl oxychloride solution and SPADNS were then mixed and stored in a labelled reagent bottle.

2.5.3 Preparation of 100mg/L Fluoride Solution

A calculated weight of 0.221g of sodium fluoride was weighed directly into a beaker and was dissolved by adding distilled water. The resulting solution was then transferred into a 1000ml volumetric flask, the beaker was rinsed thrice into the flask and the solution was made up to mark. It was then transferred into a 1000ml reagent bottle and labelled prior to use.

2.6 PREPARATION OF STANDARD CALIBRATION CURVE

A dilute solution of 10mg/L was made by withdrawing 10ml from the stock prepared above into a 100ml standard flask and diluting to mark. 1, 2, 3, 4, 5, and 6ml were then withdrawn into 50ml standard flasks, 10ml acidified zirconyl oxychloride-SPADNS solution and the solutions were made up to mark.

A reference solution was prepared by withdrawing 10ml from the mixed solution and adding 7ml of concentrated hydrochloric acid already diluted to 10ml. the solution was then made up to mark in a

The absorbance was read at 570nm after which the values were plot as a function of the various concentrations to obtain a calibration.

2.8 BATCH ADSORPTION STUDIES

The batch adsorption study was carried out considering the effect of contact time concentration, pH, and adsorbent dosage.

2.7.1 Effect of Contact Time

0.5g of the adsorbent was weighed into Erlenmeyer flask containing 50ml of 10mg/L fluoride solution. The mixture was then agitated at 200rpm using a mechanical shaker and sampling was done from the 15th minute at intervals of 5 minutes till a maximum time of 35 minutes. The mixture was centrifuged to determine the concentration of fluoride left at each time interval following similar procedure used for the preparation of the standard calibration curve.

2.7.2 Effect of Concentration

Various serial dilutions of 20mg/L, 25mg/l, 30mg/l, 35mg/l, 40mg/l, 45mg/L, and 50mg/l were prepared from the fluoride stock solution and 0.5g of the prepared clay material was added. Each mixture was then agitated at 200rpm for a predetermined equilibrium time after which centrifugation was done to separate each solution for determination of the final concentration of fluoride.

2.8.3 Effect of Adsorbent Dosage

0.1g, 0.3g, 0.5g, 0.7g, 0.9g, and 1.3g of the adsorbent were weighed into conical flasks containing 50ml of 35mg/L fluoride solution. The mixtures were agitated at 200rpm for a predetermined equilibrium time, centrifuged, and the final concentration of fluoride was determined.

2.7.4 Isotherm Studies

50ml fluoride concentrations of 20, 25, 30, 35, 40, 45, and 50mg/l were transferred into Erlenmeyer flasks containing 0.5g of raw clay. The same procedure was repeated using activated clay and all flasks were agitated at 200rpm for 25 minutes and 15 minutes respectively for raw and activated clay. The final concentration of fluoride after centrifugation were then determined.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 RESULTS FROM EFFECT OF CONTACT TIME

The calibration curve obtained is given in figure 3.1

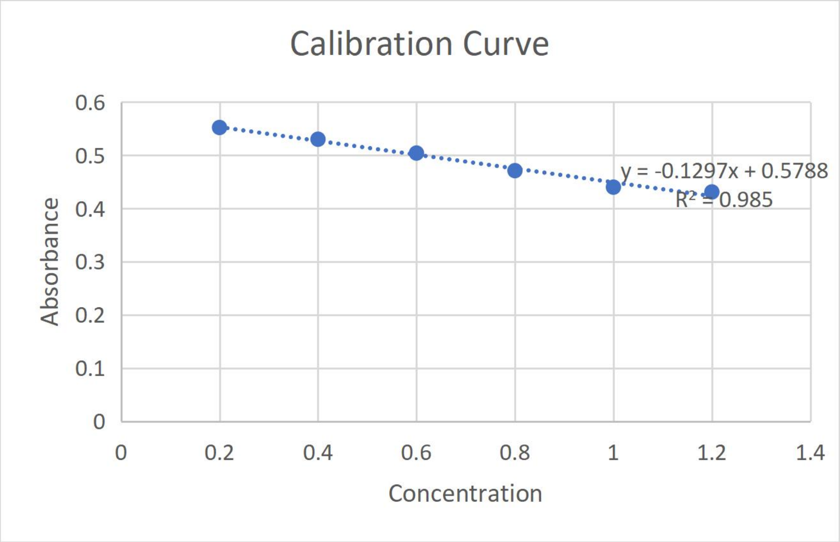

Figure 3.1 Calibration curve of fluoride at 570nm

The extent of adsorption was calculated from the results obtained from the concentration of fluoride after adsorption using the relationship

$$\% \, removal = \frac{(C_0 - C_e)}{C_0} \times 100$$

Where V is the volume of adsorbate's solution in litres, W is the adsorbent's weight, C_0 is the initial adsorbate's concentration, and C_t is the adsorbate's concentration at time 't'.

The values are tabulated as shown on table 3.1

Table 3.1 Table of values from study of the effect of time

These values indicate that the extent of adsorption is maximum at a time of 25 minutes as further represented in the graph below

Time (mins)	C_e (mg/L) Raw Clay	% Removal Raw Clay	C_e (mg/L) Activated Clay	% Removal Activated Clay
5	2.49	92.89	2.26	93.54
10	2.39	93.18	2.02	94.23
15	2.28	93.49	1.62	95.37
20	2.22	93.66	2.14	93.89
25	2.12	93.98	2.38	93.20
30	2.17	93.80	2.39	93.18
35	2.22	93.66	2.40	93.16

Table 3. 1 Tables of values from effect of contact time

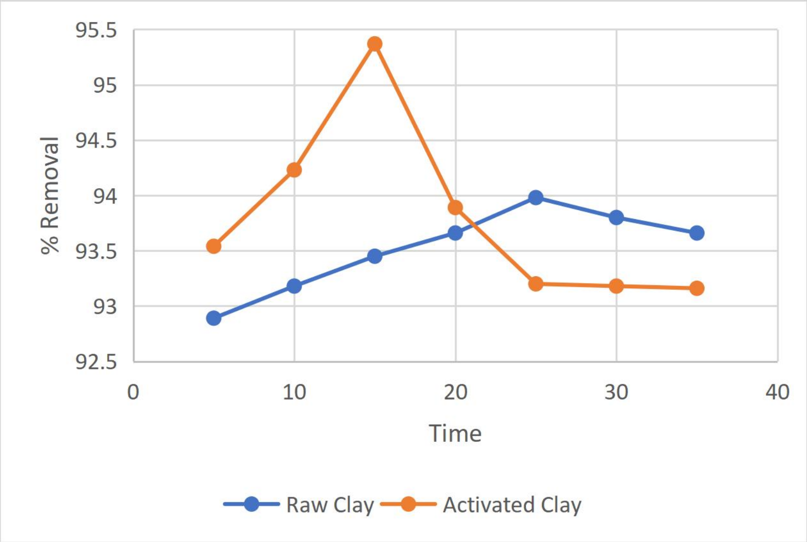

Figure 3.2 Graph of percentage removal as a function of time

From the graph, it is obvious that adsorption increased with time until a peak is reached at 25 minutes and the peak was maximum for activated clay at 15 minutes. From these maximum values, the peaks started to decrease indicating that there was no further adsorption.

3.2 EFFECT OF ADSORBATE'S CONCENTRATION

The values obtained from the study are shown on the table below.

Co (mg/L)	C_e (mg/L) Raw Clay	% Removal Raw Clay	C_e (mg/L) Activated Clay	% Removal Activated Clay
20	2.07	89.65	2.56	87.20
25	1.89	92.44	1.84	92.64
30	1.01	96.63	1.99	93.37
35	1.38	96.06	1.87	94.66
40	1.72	95.70	1.79	95.53
45	1.65	96.33	1.65	96.33
50	1.76	96.48	1.63	96.74

Table 3.2 Tabulated values from study of adsorbent's dosage

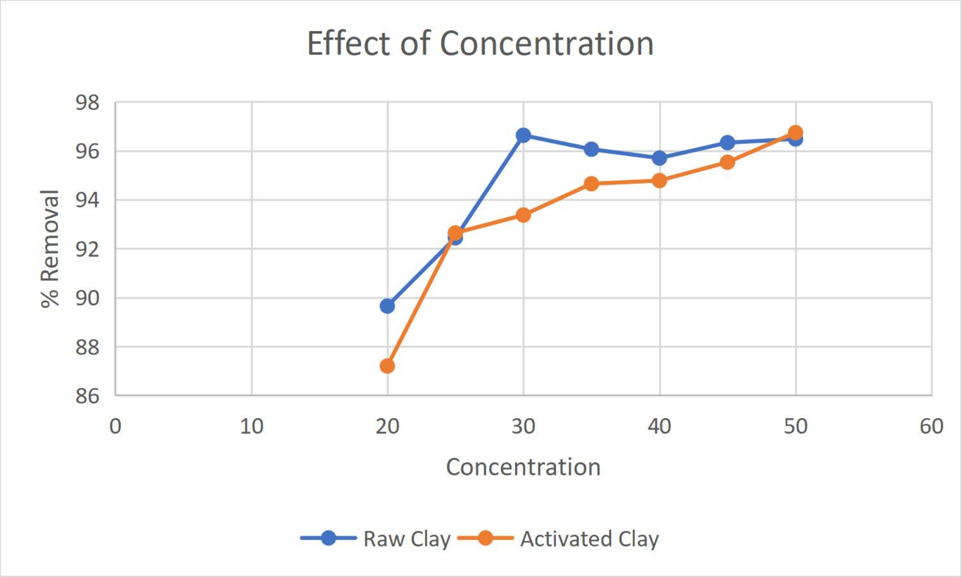

Figure 3.3 A plot of % removal as a function of adsorbate's concentration

From the plot, percentage removal was maximum for concentrations of 30mg/L and 25mg/L for raw and oxalic acid treated clays. While the increase was less marked from 25mg/L for the activated clay, a deviation was observed for the raw clay from 30mg/L fluoride concentrations. At low initial concentration, the ratio of the number of ions to the number of available adsorption sites is small and consequently the adsorption is independent of the initial concentration, but as the concentration increases, the situation changes and the competition for adsorption sites becomes fierce. As a result, percentage removal decreases appreciably.

3.3 RESULTS FROM THE STUDY OF EFFECT OF ADSORBENT DOSAGE

The values are tabulated on the next page.

Dosage (g)	C_e (mg/L) Raw Clay	% Removal Raw Clay	C_e (mg/L) Activated Clay	% Removal Activated Clay
0.1	2.11	93.97	2.25	93.57
0.3	1.90	94.57	1.65	95.29
0.5	1.69	95.18	1.41	95.98
0.7	1.57	95.51	1.25	96.43
0.9	1.42	95.94	1.16	96.69
1.1	1.34	96.16	1.10	96.87
1.3	1.28	96.34	1.08	96.92

Table 3.3 Table of values from effect of adsorbent dosage

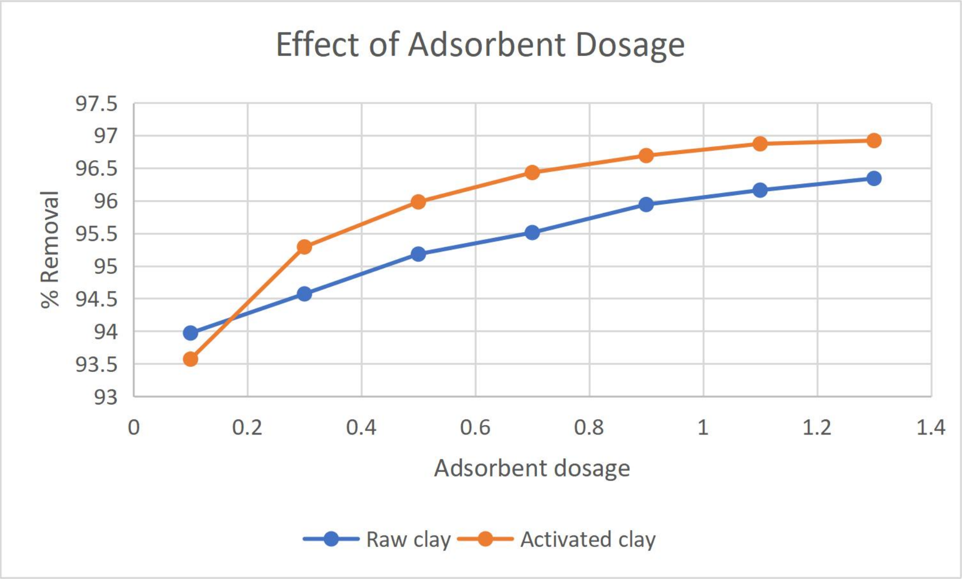

Figure 3.4 A plot of percentage removal as a function of adsorbent dosage

The graph shows a plot of percentage removal as a function of adsorbent dosage and an increase could be visualized from the tabulated values. This should be expected because as the amount of adsorbent increases, the ratio of active sites to the adsorbate increases. The activated clay had better sorption affinity for fluoride compared to the raw clay.

3.4 RESULTS FROM ISOTHERM STUDIES

The results obtained from the isotherm studies for raw clay are tabulated below and data were fit into the Langmuir's and Freundlich's isotherms.

C_0	C_e	C_e/q_e	$\log C_e$	$\log q_e$
20	2.07	1.16	0.32	0.25
25	1.89	0.82	0.28	0.32
30	1.01	0.35	0.01	0.46
35	1.38	0.41	0.14	0.53
40	1.72	0.45	0.24	0.58
45	1.65	0.38	0.22	0.64
50	1.76	0.37	0.25	0.68

Table 3.4 Table of values from isotherm studies of raw clay

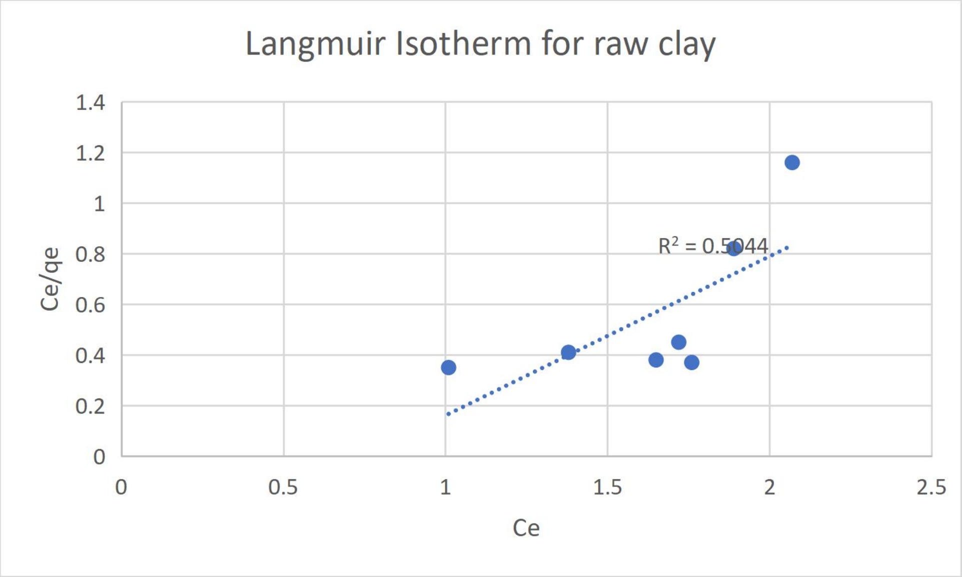

Figure 3.5 Langmuir isotherm for raw clay

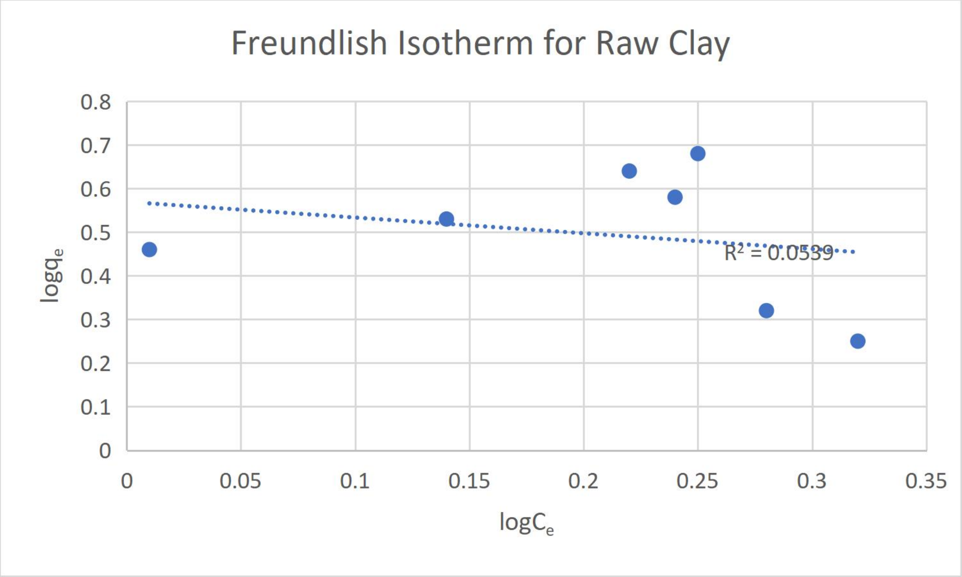

Figure 3.6 Freundlich's isotherm for raw clay

From the plots, it shows that the values obtained from isotherm studies of the raw edible clay could not fit into the Langmuir's and Freundlich's isotherms although a better correlation was found for Langmuir's isotherm. It is obvious then that adsorption does not follow a monolayer coverage following these isotherms.

C_0	C_e	C_e/q_e	$\log C_e$	$\log q_e$
20	2.56	1.47	0.41	0.24
25	1.84	0.79	0.30	0.37
30	1.99	0.70	0.30	0.45
35	1.87	0.57	0.27	0.52
40	2.09	0.47	0.25	0.58
45	1.65	0.38	0.22	0.64
50	2.08	0.34	0.21	0.67

Table 3.5 Table of Values from isotherm study of oxalic acid treated Clay

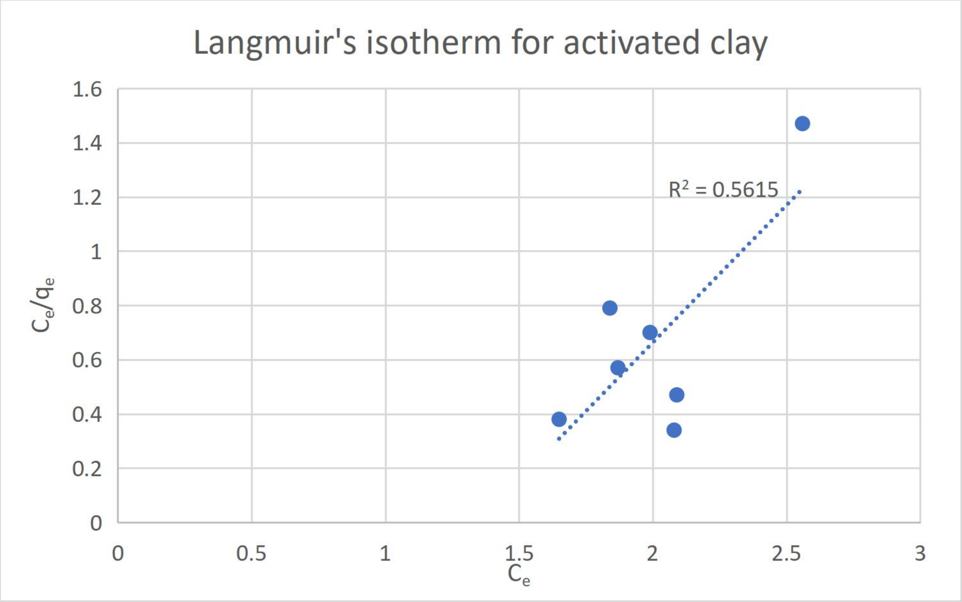

Figure 3.7 Langmuir's isotherm for oxalic acid treated clay

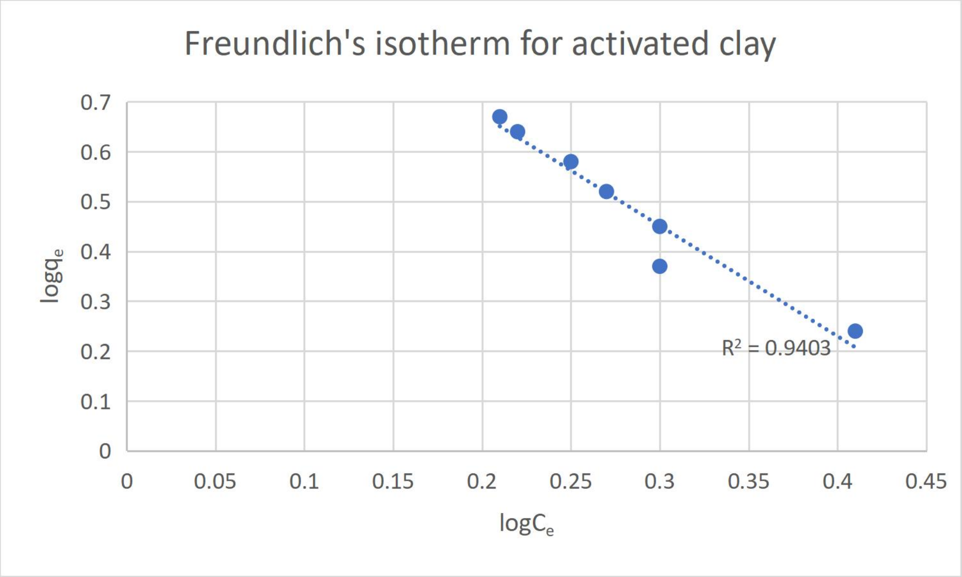

Table 3.8 Freundlich's isotherm for activated clay

The isotherms shown above are indications that adsorption does not follow a monolayer coverage, a similar observation for the raw clay sample.

3.4 CONCLUSION

From the results obtained, edible clay in the raw and oxalic acid treated form had a high sorption capacity for fluoride in solution. The sorption capacity of the clay was improved following its modification with oxalic acid. This could be attributed to the incorporation of functional groups from the acid into the clay thus modifying its surface and increasing the number of sites.

It is therefore imperative to conclude that edible clay in its natural and treated forms can be used to treat effluents containing fluorides due to its availability and it's a cheaper alternative compared to industrially manufactured adsorbents.

REFERENCES

Adeyemo, A. A., Adeoye, I. O., and Bello O. S. 2015 Adsorption of Dyes Using Different Types of Clay: A Review. *Applied Water Science 20(2).*

Akafu, T., Chimdi, A., and Gomoro, K. 2019. Removal of Fluoride from Drinking

Water by Sorption Using Diatomite Modified with Aluminum Hydroxide. *Journal of Analytical Methods in Chemistry*.

Akpomie, K. G., Odewole, O. A., Ibeji, C. U., Okagu., O. D., and Agboola., I. I. 2017. Enhanced Sorption of Trivalent Chromium unto Novel Cassava Peel Modified Kaolinite Clay. *Der Pharma Chemica. 9(5):48-55.*

Al-Jlil, S. A. and Alsewailem, S. A. (2009). Saudi Arabian Clays for Lead Removal in Waste-Water. *Applied Clay Science. 42: 671–674.*

Amini, M., Mueller, K., Abbaspour, K. C., Rosenberg, T., Afyuni, M. Møller, K. N., and Sarr, M. 2008. Statistical Modeling of Global Geogenic Fluoride Contamination in Groundwaters. *Environ. Sci. Technol. 42:3662 -3668*

Bhattacharyya, K. G. and Gupta, S. S. 2009. Calcined Tetrabutylammonium Kaolinite and Montmorillonite and Adsorption of Fe(Ii), Co(Ii) and Ni(II) from Solution. *Applied Clay Science. 46216–46221.*

Chaudry, M., Prabhakar, I., Gupta, B., Anand R., Sehrawat, P., and Thakar, S. S.

2017 Prevalence of Dental Fluorosis Among Adolescents in Schools of Greater Noida, Uttar Pradesh. *J Indian Assoc Public Health Dent 15(1):36-41*

Chen, B., Hui, C. W., and McKay, G. 2001 Pore Surface Diffusion Modelling for

Dyes from Effluents on Pith. Langmuir 17: 740-748.

Ehsan, A., Bhatti, H. N., Iqbal, M., and Noreen, S. 2017 Native, Acidic Pre-Treated and Composite Clay Efficiency for the Adsorption of Dicationic Dye in Aqueous Medium. *Water Sci Technol 75 (4):753–764.*

El-Maghrabi, H. H., and Mikhail, S. 2014 Removal of Heavy Metals via Adsorption using Natural Clay Material. *Journal of Environment and Earth Science 4(19):224-3216*

Fantong, W. Y., Satake, H., and Ayonghe, S. N. 2010 "Geochemical Provenance

and Spatial Distribution of Fluoride in Groundwater of Mayo Tsanaga River Basin, Far North Region, Cameroon: Implications for Incidence of Fluorosis and Optimal Consumption Dose," *Environmental Geochemistry and Health 32(2):147–163.*

Gładysz-Płaska, A., Majdan M., Pikus, S. and Sternik, D. (2012). Simultaneous Adsorption of Chromium(VI) and Phenol on Natural Red Clay Modified by HDTMA, *Chemical. Engineering Journal. 179 140–150.*

Gomes, F. S. C. (2018) Healing and Edible Clays: A Review of Basic Concepts, Benefits, and Risks. *Environ Geochem Health 40(5):1739-1765*

Grim, R. E. 1962 Applied Clay Mineralogy. McGraw-Hill, New York

Grim, J. D., Bessarobov, and Sanderson, R. 1998 “Review of Electro-assisted Methods for Water Purification,” Desalination 115:285–294.

Grim, R. E (1962) Applied clay mineralogy. McGraw-Hill, New York

Guggenheim, S., and Martin R.T (1995) Definition of Clay and Clay Mineral: Joint Report of the AIPEA Nomenclature and CMS Nomenclature Committees. Clay Miner 43:255–256

Hayes, B. L. 2004. Recent Advances in Microwave Assisted Synthesis. *Aldrichimica ACTA*. 37(2).

Ismadji, F. E. Soetaredjo, A. and Ayucitra, A. 2015. Clay Materials for Environmental Remediation, in: *Springer Briefs in Green Chemistry for Sustainability*

Jaafar S. N. B. S. 2006. Adsorption study—dye removal using clay. A B. Chem. Eng. Thesis, Faculty of Chemical Engineering and Natural Resources, University College of Engineering & Technology

Jaafar, S. N. B. S. 2006 Adsorption Study—Dye Removal Using Clay. A B.Chem. Eng. Thesis, Faculty of Chemical Engineering and Natural Resources, University College of Engineering &Technology

Jackson, J. A., ed. 1997 "Bentonite". Glossary of geology (Fourth ed.).

Joo, J. B., Park, B., and Yi, J. 2009 Preparation of Polyelectrolyte Functionalized

Mesoporous Silicas for the Selective Adsorption of Anionic Dye in an Aqueous Solution. *J Hazard Mater 168:102–107.*

Kayode, A. D., Sunday, A. S., Oluyemi, A. S., Adegalu, A. A., Samson, O. O., Abidemi, O. I., and Hellen, O. A. 2019. Clay Soil Modification Techniques for the Adsorption of Heavy Metals in Aqueous Medium: A Review. *International Journal of Advanced Research in Chemical Science 6(6):14-31*

Kloprogge, J. T., Evans, R., Hickey, L. and Frost, R. L. 2002 Characterization and Al-pillaring of smSectites from Miles, Queensland (Australia). *Applied Clay Science. 20:157–163*

Kloprogge, J. T., Komarneni, S., and Amonette, J. E. 1999. Synthesis of Smectite

Clay Minerals: Acritical Review. *Clay Miner. 47:529–554.*

Kumar, M., Goswami, R., Patel, A. K., Srivastava, M., and Das, N. 2020 Scenario, Perspectives and Mechanism of Arsenic and Fluoride Co-Occurrence in the Groundwater: A Review. Chemosphere 249.

Lipka, R., Sobezak, M., Kuś, S., Oszwaldowski, S., and Jarosz, M. 2000. Determination of Fluoride Impurities in Leuprolide. Comparison of Analytical Methods. *Microchem. J. 65:51–58.*

Liu, P., and Zhang, L. 2007Adsorption of Dyes from Aqueous Solutions or Suspensions with Clay Nano-Adsorbents Sep. *Purif. Technol. 58 (1):32–39*

Lloyd and Lawrie 2011. Handbook of Industrial Catalyst. New York Springer pp.

181-182

Malay, D. K., and Salim A. J. 2011 Comparative Study of Batch Adsorption of Fluoride Using Commercial and Natural Adsorbent. *Research Journal of Chemical Sciences 1(7):68-75.*

Markovska, L., Meshko, V., Noveski, V., and Marinovski, M. 2001 Solid Diffusion Control of the Adsorption of Basic Dyes onto Granular Activated Carbon and Natural Zeolite in Fixed Bed Columns. *J. Serb Chem Soc 66:463-475*

Moore, D.M., and Reynolds, R.C. 1989 X-ray Diffraction and the Identification of Clay Minerals, Oxford university press, Oxford.

Nandi, B. K., Boswani, A., Das, A. K. Mondal, B., and Purkait, M. K. 2008 Adsorption Kinetics and Equilibrium Studies on the Adsorption of Crystal Violet Dye using Kaolin as an Adsorbent. *Separation Science and Technology 43(6):1386-1403*

Nandi, B. K., Boswani, A., Mondal, B., and Purkait, M. K. 2009. Adsorption Characteristics of Brilliant Green Dye on Kaolin. *Journal of Hazardous Materials 161(1):387-395*

Nesse, 2000 pp. 252-257.

Noida, Uttar Pradesh. *J. Indian Assoc. Public Health Dent. 15:36–41*.

O'Connell D.W., Birkinshaw C, O'Dwyer T.F (2008). Heavy metal adsorbents prepared from the modification of cellulose: a review, *Bioresources and Technology. 99 6709–6724.*

Raghav, S., and Kumar, D. 2018 Adsorption Equilibrium, Kinetics, and Thermodynamic Studies of Fluoride Adsorbed by Tetrametallic Oxide Adsorbent. *J. Chem. Eng. Data 63(5):1682-1697*

Saikia, P., Bharali, K. R., and Baruah, K. H. 2017 Kinetic and Thermodynamic Study of Fluoride Removal Using a Novel Bio-sorbent from Possotia (Vitex negundo) Leaf. *Journal of Analytical Science and Technology 8(23).*

Schoonheydt, R. A. and Jacobs, K. Y. 2001. Clays: From Two to Three Dimensions. In Studies in Surface Science and Catalysis; Elsevier Science B.V.: Amsterdam, The Netherlands; pp. 299–343.

Shen, B., Chen, J. and Yue, S. (2015). Removal of Elemental Mercury by Titanium Pillared Clay Impregnated with Potassium Iodide. *Microporous and Mesoporous Mater. 203 216–223.*

Sheng, G., Shen, R., Dong, H., and Li, Y. 2013 Colloidal Diatomite, Radionickel,

and Humic Substance Interaction: A Combined Batch, XPS, and EXAFS Investigation. *Environ Sci Pollut Res 20:3708–3717*

Tan, T. L., Krusnamurthy, P., Nakajima, H., and Rashid, S. A. 2020. Adsorptive, Kinetics and Regeneration Studies of Fluoride Removal from Water Using Zirconium-Based Metal Organic Frameworks. *RSC Adv.10***:***18740-18752*

Tewari, A., and Dubey, A. 2009 “Defluoridation of drinking water: efficacy and need,” *Journal of Chemical and Pharmaceutical Research 1(1):31–37*

Theocharis, C. R., Jacob, K. J., and Gray, A. C. 1988. Enhancement of Lewis Acidity in Layer Aluminosilicates. *Journal of Chemical Society. Faraday Trans 84:1509-1516*

Ukwueze, S. E., and Ochuba, C. O. 2017. Chemical and Toxicological Evaluation

of Edible Clay (Ulo) Sourced from Southern Nigeria. *European Journal of Pharmaceutical and Medical Research 4(7):231-235*

Wejnerowska, G., Karczmarek, A., and Gaca, J. 2007. Determination of Fluoride in Toothpaste Using Headspace Solid-Phase Microextraction and Gas Chromatography-Flame Ionization Detection. J. Chromatography. 1150:173–177.

WHO 2017 Guidelines for Drinking-Water Quality—Fourth Edition Incorporating the Forst Addendum. https://apps.who.int/iris/bitstream/handle/10665/254637/9789241549950-eng.pdf?sequence=1

Wikipedi, 2020. Montmorillonite https://en.m.wikipedia.org/wiki/Montmorillonite

World Health Organization 2011 Guidelines for Drinking-water Quality, World Health Organization, pp. 1–541

Zakaria, R. M., Hassan, I., El-Abd, M. Z., and El-Tawil, Y. A. 2009 Lactic Acid Removal from Wastewater by Using Different Types of Activated Clay. *Thirteenth International Water Technology Conference (IWTC), Hurghada 13:403–416*

Zhang, Y., Xiong, L., Xiu, Y., and Huang, K. 2019. Defluoridation in Fixed Bed

Column Filled with Zr (Iv)-Loaded Garlic Peel. *Microchem. J. 145:476—485*

APPENDIX

Calculation of Mass of Oxalic Acid Required to Prepare 3M Solution in 500ml

Given that the molecular formula of oxalic acid is $C_2H_4O_4$, its molecular weight is 92.0506g/mol. The volume to be prepared is 500ml (0.5L). Thus, the mass required to prepare the solution is calculated as

$$mass = molarity \times molecular\ weight \times volume\ (L)$$

$$mass = 3mol/L \times 92.0506g/mol \times 0.5L = 138.0759g$$

Calculation of Mass of NaF Required to Prepare 100mg/L Fluoride Solution

This solution is to be prepared in 1000ml (1L) flask. Thus, the amount of fluoride required is

$$mass = 1L \times 100mg/L = 100mg = 0.1g$$

The amount of NaF containing 0.1g of fluoride would therefore be

$$mass = \frac{0.1g \times 41.9882g/mol}{18.9984g/mol} = 0.221g$$

Where 41.9882g/mol and 18.9984g/mol are the formula weight and atomic weight of NaF and fluoride respectively.