STUDY OF ADSORPTION OF SPILLED CRUDE OIL IN AQUATIC TERRITORYUSING MODIFIED BENTONITE CLAY

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(MEng/SEET/2017/7602)

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MINNA

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A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL FEDERAL UNIVERSITY OF TECHNOLOGY MINNA, NIGERIA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF ENGINEERING (MEng) IN CHEMICAL ENGINEERING

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ABSTRACT

Over the past decades, the removal of crude oil from water and wastewater has been of primary interest across the world. The locally available materials such as bentonite clay used as adsorbent in removing crude oil from aqueous solution are limited due to their low affinity to adsorb organic molecules such as crude oil constituent and the fact that the active site of bentonite is not uniform, hence the need to improve its adsorption performance through its modification into organoclay as a functional material for crude oil adsorption. It was in view of this that the study investigated theadsorption of spilled crude oil in aquatic territory using modified bentonite clay. The primary objectives of the study are to developed organo modified bentonite clay adsorbent, characterization of the developed adsorbent, determine the adsorption efficiency of the adsorbent in adsorption of crude oil and to investigate the adsorption isotherm, kinetics and thermodynamics of the developed adsorbent. The XRD diffractograms shows that quartz and albite content of the acid pretreated CTMABr modified bentonite clay is higher than untreated CTMABr modified bentonite, the surface morphology of the acid pre-treated CTMABr modified bentonite clay shows that oxalic acid pre-treatment has impact on the surface morphology of the modified bentonite clay with favourable channels and voids for adsorbing crude oil, the EDX analysis shows that acid pre-treated CTMABr modified bentonite clay has higher silica content with lower alumna, Fe, K, Ti and Ag content compared to raw bentonite and untreated CTMABr modified bentonite clay. The FTIR bands confirm the intercalation of CTMABr in the interlayer of galleries of the bentonite clay mineral in both acids pretreated and untreated CTMABr modified bentonite clay. Also, oxalic acid pretreatment of bentonite clay prior to modification with CTMABr result in higher adsorption capacity compared to untreated CTMABr modified and raw bentonite clay adsorbents.In addition, the effect of time, temperature, dosage, pH and initial concentration on the adsorption of crude oil shows a maximum removal efficiency of 97.52 %at 50 min, 98.05 % at 75 ^{o}C, 95.04 % at an adsorbent dosage of2g, 85.11 % at a pH of 9 and 83.87 % at aninitial concentration of 0.30 mg/Lfor acid pre-treated CTMABrmodified bentonite clay followed by those of untreated CTMABr modified bentonite clay while raw bentonite clay shows the least percentage adsorption and uptake. Furthermore, the adsorption of crude oil in raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay shows that Redlich-Peterson isotherm (acid pre-treated CTMABr: β is 0.8076, A0.7091 is L/g, R^2 is 0.9979; untreated CTMABr: β is 0.7886, A0.8461 is L/g and R^2 is 0.9998; raw bentonite: β is 0.8135, A2.1285 is L/g and R^2 is 0.9992), followed by Freundlich (acid pre-treated CTMABr: 1/n is – 0.2989, K_f is 1.3772 is L/mg, R^2 is 0.9871; untreated CTMABr: 1/n is – 0.1265, K_f is 1.0752 is L/mg, R^2 is 0.9832; raw bentonite: 1/n is – 0.1622, K_f is 0.8378 is L/mg, R^2 is 0.9611) and then Tempkin isotherm model best described the adsorption process while kinetic study shows that pseudo-second order kinetics models (acid pre-treated CTMABr: k_2 is 0.54 is g/mg min, q_e is 41.32mg/g; untreated CTMABr: k_2 is 0.37 is g/mg min, q_e is 31.25mg/g; raw bentonite: k_2 is 0.05 is g/mg min, q_e is 30.85mg/g) best describe the adsorption kinetics, followed by Intra-particle diffusion model, Elovich model, Boyd model and pseudo-first order kinetics model, and the adsorption process is diffusionally control and not kinetically. Hence, oxalic acid pretreated CTMABrorganomodified bentonite clay has good potential for crude oil andother pollutant removal from polluted water.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Over the years, global population growth and industrialization have led to release of different contaminants into environment, which in most cases are toxic even in trace levels. As a result, environmental pollution, particularly water pollution has become a prime concern for developed and developing countries. Water is increasingly being polluted by anthropogenic activities including urbanization, population growth, poor land use, agricultural activities and oil spillage have led to rapid degradation of surface and ground water quality. Of these sources of pollution, oil spillage remains a serious concern in oil producing regions of the world despite recent focus on renewable energy which has resulted in decrease in oil processing activities in some countries. The elimination of these contaminants from water resources is usually done to reduce their amounts down to a safe level (Foroutan *et al.*, 2018).

Crude oil contamination affected both aquatic and terrestrial ecosystems with serious environmental consequences on human health and aquatic life. Major environmental contamination may occur due to accidental losses associated with extraction or transportation, or even intentional discharge by illegal refineries (Vollaard, 2017). These activities have increased the threat of crude oil pollution to the environment and subsequently concomitant discharged into the natural environment, thereby resulting in major ecological problem throughout the world. Oil spillage are major environmental hazards and cause the death of sea birds and other aquatic animals. Many species of fish, birds and marine animals have been adversely affected and over 2 billion dollars have been spent on cleaning up (Linan *et al.*, 2018). Water contaminated by crude oil can be lethal depending upon the nature of the petroleum fraction, the way of exposure to it, and the time of exposure.

Crude oil comprises of complex mixture that often contains toxic pollutants that are hazardous to human and environmental health (Foroutan *et al.*, 2018, Linan *et al.*, 2018). The removal of pollutants from water is very vital and is becoming more important with recurring oil spillage and illegal refinery activities particularly in the Niger Delta region of Nigeria (Osin *et al.*, 2017). This necessitate the need for treatment of waste water contaminated by crude oil. Though crude oil can be generally removed from wastewater by means of conventional methods such as physical or chemical methods, however, these methods are usually expensive and difficult to maintain, even with advanced technologies (Linan *et al.*, 2018).

Physical method, such as sorption is considered a simple and suitable strategy for crude oil removal in polluted effluents because of its high efficiency, easy handling, and economical feasibility (Foroutan *et al*., 2018). Other technologies have been used for the removal of pollutant from wastewater and these include membrane processes and biological materials. These techniques have been reported to be very expensive and economically unfavorable or technically complicated, and are used only in special cases of wastewater treatment. Relatively, an easy and green technology for the removal of contaminants such as crude oil from aqueous solutions has been adsorption using natural material. Adsorption process using natural material has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low cost, availability, profitability, easy operation and efficiency (Foroutan *et al*., 2018). Thus, the preparations of adsorbent from natural material is motivated by cost considerations (relatively cheaper), local generation in countries such as Nigeria and effectiveness in crude oil removal from waste effluents.

Several materials such as activated carbon from agricultural waste, industrial waste and clay materials as well as hybrid diatomite/carbon composites have been used as adsorbent for treatment of crude oil polluted water (Momina *et al.*, 2018, Runtti *et al.*, 2014, Uddin, 2017, Foroutan *et al*., 2018, Momina *et al.*, 2018). However, the use of these materials with the exception of clay materials as adsorbent are limited due to high production cost (Uddin, 2017, Foroutan *et al*., 2018, Momina *et al.*, 2018). Thus, the development and production of other adsorbents from low cost raw materials such as clay, readily available in abundance in Nigeria is needed. These clay materials have been found to be good adsorbent and as a result, several studies have been reported on the use of clay materials such as natural clay, bentonite and kaolin clay in treatment of wastewater effluents (Momina *et al.*, 2018, Foroutan *et al*., 2018). Bentonite, which has high content of montmorillonite, a layered structure, porous, mechanically and chemically stable, large surface area and high cation exchange capability has been found to be useful as an adsorbent compared to other clay type.

Bentonite is one of the materials which has been considered to be of great significant in adsorption of pollutant from aqueous solutions and has been in use in recent years (Foroutan *et al*., 2018, Hokkanen *et al.*, 2018). Bentonite is a natural clay which is found all over the world. In Nigeria, bentonite is found majorly in Edo, Kebbi, Ogun, Ondo, Adamawa, Gombe and Borno states with an estimated bentonite reserves of over 700 million tonnes available in many states of the Federation ready for massive development and exploitation with the largest single deposit at Afuze in Edo State holding 70–80 million tonnes (Nigeria Extractive Industries Transparency Initiative Report, 2016). The abundance of bentonite in Nigeria which has been found to be of great significance in adsorption of pollutant from aqueous solutions motivated the need to investigate the organic modification of bentonite clay for the adsorption of crude oil from aqueous solution.

1.2 Statement of the Research Problem

Over the past decades the removal of various toxic substances such as crude oil from water and wastewater has been of primary interest to many researchers (Uddin, 2017, Momina *et al*., 2018). Materials used as adsorbent in removing crude oil from aqueous solution have been reported to be limited due to high production cost, as a result, clay materials especially bentonite have been found to be good adsorbent alternatives over the years (Hokkanen *et al.*, 2018, Foroutan *et al*., 2018). Bentonite have proven to be efficient in removing many toxic material particularly metal ions and organic contaminants from an aqueous solution (Uddin, 2017, Foroutan *et al*., 2018, Hokkanen *et al.*, 2018, Momina *et al*., 2018). However, its ability to absorb organic molecules such as crude oil constituent is very low and the active site of bentonite is not uniform. In addition, there is scarce studies or even literature on the adsorption of crude oil from aqueous solution using organo modified bentonite clay. It is against this background that this study seeks to investigate the adsorption of crude oil from aqueous solution using organo modified bentonite clay.

1.3 Aim and Objectives of the Study

The aim of this study is to investigate the adsorption of crude oil from aqueous solution using developed organo-modified bentonite clay. The aim can be achieved through the following objectives;

1. Pretreatment and characterisation of raw materials and synthesed organo-modified bentonite adsorbent.
2. Physiochemical analysis of polluted water before and after treatment.
3. Performance evaluation of adsorbents on crude oil adsorption using batch method.
4. Adsorption isotherm, kinetics studies and thermodynamic studies of the adsorption process

1.4 Justification of the Study

Bentonite is in abundance in Nigeria with an estimated reserve of over 700 million tonnes (Raw Material Research and Development Council, 2010). It will help in addressing the environmental problems of large quantity of oil spillage in water and oil contaminated wastewater disposal within the country which has led to rapid degradation of surface water quality. This will also aid in reducing the amounts of the pollutant down to a safe level.

1.5 Scope of the Study

The scope of the study is limited to the use of bentonite sourced locally for developing organomofidifed clay adsorbent. It is also limited to characterization techniques such as Fourier Transform Infra-Red (FTIR), Scanning Electron Microscopy/Energy Dispersive Spectrum (SEM/EDS), X-Ray Diffraction Technique (XRD), X-Ray Fluorescence

Technique (XRF), Thermogravimetric Analysis (TGA) and BET technique. The scope of the study also, covers adsorption isotherm studies with focus on Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm, and kinetics studies with focus on Pseudo first, second-order, Elovich, Intra-particle and Boyd kinetic model.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

The exploitation of crude oil and gas reserves has not always been without some ecological side effects. One particular effect of oil exploration and exploitation is oil spillage which come with attendant impact on environment and even human health. Virtually every aspect of oil exploration and exploitation has deleterious effects on ecosystem stability and local biodiversity. Oil spills damaged land and results in accidents, fires, and incidents of air and water pollution have all been recorded at various times and places across the globe. The crude oil spills have resulted in the massive contamination of water with severe effects in humans in a manner that is often not acknowledged.

The threat to human and aquatic lives posed by crude oil spillages cannot be overemphasized. Oil spillage is the release of liquid petroleum hydrocarbon into the environment due to human activities, and is a form of pollution (Ndeh *et al.*, 2017). The term often refers to marine oil spills, where oil is released into the ocean or coastal waters and it includes releases of crude oil from tankers, offshore platforms, drilling rigs and wells, as well as spills of refined petroleum products (such as gasoline, diesel) and their by-products, and heavier fuels used by large ships such as bunker fuel, or the spill of any oily white substance refuse or waste oil. Spills may take months or even years to clean up. Oil also enters the marine environment from natural oil seeps.

Public attention and regulation have tended to focus most sharply on seagoing oil tankers. Oil spillage is one of the greatest environmental problems as host communities have been at the receiving end of this environmental problem. The problems have generated a lot of concerns within the three tiers of government especially in oil producing states. Oil spillage is one of the contentious issues facing the government, the oil industry and the host communities of the oil producing region, the Niger Delta region of Nigeria.

Crude oil spill either from exploration or processing facilities into the aquatic environment often contaminate the water body with both organic and inorganic contaminants. However, a number of conventional techniques have been employed in the treatment crude oil contaminated which includes; adsorption, advanced oxidation processes, aeration, aerobic and anaerobic treatment, chlorination, coagulation, electrolysis, filtration, flocculation, foam flotation, ion exchange, membrane processes, microbial reduction, and precipitation, reverse osmosis, solvent extraction and bioremediations (Sdiri *et al.*, 2012). Among these crude oil contaminated water treatment techniques, adsorption has been one of the most easily applicable and inexpensive technique, particularly, the use of naturally available materials such as clay materials as low-cost adsorbents.

In recent years, petroleum based organic contaminants are becoming more and more observable in water surface. This is very heterogeneous group of substances containing compounds from various chemical groups. Their impact on living organisms in general have proved their negative influence on vitality, life span, and reproductive success (Karpinska and Kotowskam, 2019). Some of the common use of adsorption process in water purification has led to the development of various adsorbents such as; ion-exchange resins for petroleum based organic substance removal and organically modified clay.

Naturally abundant clay such as bentonite clay have been widely used as adsorbents in wastewater treatment due to their unique properties such as high cation exchange capacity (CEC), high surface area, micro– and meso–porosity and swelling properties. Despite the high adsorption properties of these clays, modification of the clay with organic compound has been found to enhanced their adsorption capacity (Rathnayake, 2017). This chapter therefore, make a review of existing literatures on clay materials with focus on bentonite. It also reviews literatures on organic modification of clay material and the types of organic compound for clay materials modification.

2.2 Clay Materials

According to Adeyemo *et al.* (2015), clay refers to a naturally occurring material composed primarily of fine-grained minerals, which might be plastic in nature at appropriate water contents and will harden when dried or fired. Although clay usually contains phyllosilicates, it may contain other materials that may impart plasticity and harden when dried or fired. Although clay usually contains phyllosilicates, it may contain other materials that may impart plasticity and harden when dried or fired. Associated phases in clay may include materials that do not impart plasticity and organic matter. Clay materials are a diverse group of hydrous layer aluminosilicates that constitute the greater part of the phyllosilicate family of materials. 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).

They are commonly defined by geologists as hydrous layer aluminosilicates with a particle size <2mm, while engineers and soil scientists define clay as any mineral particle <4mm (Huggett, 2015). However, clay materials are commonly >2mm, or even 4mm in at least one dimension. According to Adeyemo *et al*. (2015), clay is a naturally occurring material composed of layered structures of fine-grained minerals which exhibit the property of plasticity at appropriate water content but becomes permanently hard when fired. Their small size and large ratio of surface area to volume gives clay materials a set of unique properties, including high cation exchange capacities, catalytic properties, and plastic behaviour when moist.

Clay materials are the major constituent of fine-grained sediments and rocks (mudrocks, shales, claystones, clayey siltstones, clayey oozes, and argillites). The clay material is formed from chemical weathering processes on the earth's surface, and contributes about 40% of the fine-grained sedimentary rocks (mudrocks) which includes mud stones, clay stones and shales (Ochieng, 2016). They are an important constituent of soils, lake, estuarine, delta, and the ocean sediments that cover most of the Earth's surface. They are also present in almost all sedimentary rocks, the outcrops of which cover approximately 75 % of the Earth's land surface and clays which form in soils or through weathering principally reflect climate, drainage, and rock type (Huggett, 2015). It is now recognized that re-deposition as mudrock only infrequently preserves these assemblages, and clay assemblages in ocean sediments should not be interpreted in terms of climate alone, as has been done in the past. Most clay in sediments and sedimentary rocks is, in fact, reworked from older clay-bearing sediments, and many are metastable at the Earth's surface. This does not preclude the use of clays in stratigraphic correlation; indeed, it can be a used in provenance studies.

A few clays, notable the iron-rich clays form at the Earth's surface either by transformation of pre-existing clays or from solution. These clays are useful environmental indicators, so long as they are not reworked. Clay minerals are generally composed of aluminum silicates which are formed by tetrahedral and octahedral sheets that are linked together through sharing of apical oxygen atoms and the formation of clay minerals is dependent on physicochemical conditions of the immediate weathering environment, nature of the starting materials and other related external environmental factors (Ochieng, 2016), thus resulting into various types of clay materials. Consequently, the application potential of any clay mineral type in nature will depend on its chemical composition, structure and other inherent properties (Landoulsi *et al.*, 2013). On this regard, clay minerals are classified into different groups as follows; Kaolinite, Smectite, Vermiculite Illite and Chlorites.

2.2.1 Types of clay materials

Clays are distinguished from other fine-grained soils by differences in size and mineralogy. Silts, which are fine grained soils that do not include clay minerals, tend to have larger particle sizes than clays, but there is some degree of overlap in both particle size and other physical properties and there are many naturally occurring deposits which include silts and also clay. The distinction between silt and clay varies by discipline. Geologists and soil scientists usually consider the separation to occur at a particle size of 2 µm (clays being finer than silts); sedimentologists often use 4–5 µm and colloid chemists use 1 µm (Adeyemo *et al.*, 2015).

Depending on the academic source, there are three or four main groups of clays: kaolinite, montmorillonite, smectite, illite 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 group includes the clay micas. Illite is the only common mineral (Jaafar, 2006). Chlorites are not always considered clay; sometimes they are 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. Varve (or varved clay) is clay with visible annual layers, formed by seasonal differences in erosion and organic content. This type of deposit is common in former glacial lakes. When glacial lakes are formed, there is very little movement of the water that makes the lake and these eroded soils settle on the lake bed. This allows such an even distribution on the different layers of clay. Quick clay is a unique type of marine clay indigenous to the glaciated terrains of Norway, Canada, Northern Ireland, and Sweden. It is a highly sensitive clay, prone to liquefaction, which has been involved in several deadly landslides (Adeyemo *et al.*, 2015). These differences among the clays provide an opportunity to investigate the impact of structure and layer charge on metal ion coordination to permanent charge sites. In addition, this choice of minerals provided various arrangements of aluminol and silanol surface hydroxyl sites.

2.2.2 Clay structure and chemistry

Clays can be envisaged as comprising sheets of tetrahedra and sheets of octahedra (Figure 2.1). The general formula for the tetrahedral is T_2O_5, where T is mainly Si^4, but Al^{3+} frequently (and Fe^{3+} less frequently) substitutes for it (Huggett, 2015). The tetrahedra as shown in Figure 2.1 have a hexagonal arrangement, if not distorted by substituting cations. The octahedral sheet comprises two planes of close-packed oxygen ions with cations occupying the resulting octahedral sites between the two planes shown in Figure 2.1 b. These cations are most commonly Al^{3+}, Fe^{3+}, and Mg^{2+}, but the cations of other transition elements can occur. The composite layer formed by linking one tetrahedral and one octahedral sheet is known as a 1:1 layer (Figure 2.1 c). In such layers, the upper-most unshared plane of anions in the octahedral sheet consists entirely of OH groups and a composite layer of one octahedral layer sandwiched between two tetrahedral layers, both with the tetrahedra pointing towards the octahedral layer, known as a 2:1 layer (Banković *et al.*, 2013).

A 2:1 clays of the mica and chlorite families have multiple polytypes defined by differences in stacking parallel to the c axis. If the 1:1 or 2:1 layers are not electrostatically neutral, due to substitution of trivalent cations for Si^{4c} or of divalent for trivalent cations, the layer charge is neutralized by interlayer materials. These can be cations, most commonly K^+, Na^+, or NH^{4+}, and hydrated cations, most commonly Mg^{2+}, Ca^{2+}, or Na^+, or single sheets of hydroxide octahedral groups ($Al(OH)_3$ or $Mg(OH)_2$ (Huggett, 2015). These categories approximately coincide with the illite, smectite, and chlorite-vermiculite families of clays. It is evident that the different types of interlayer cation will have a direct affect upon the thickness of the clay unit cell in the 001 dimension. This property, together with the ease with which the interlayer cations are hydrated or will interact with organic compounds, is much used in X-ray diffraction to identify clay minerals.

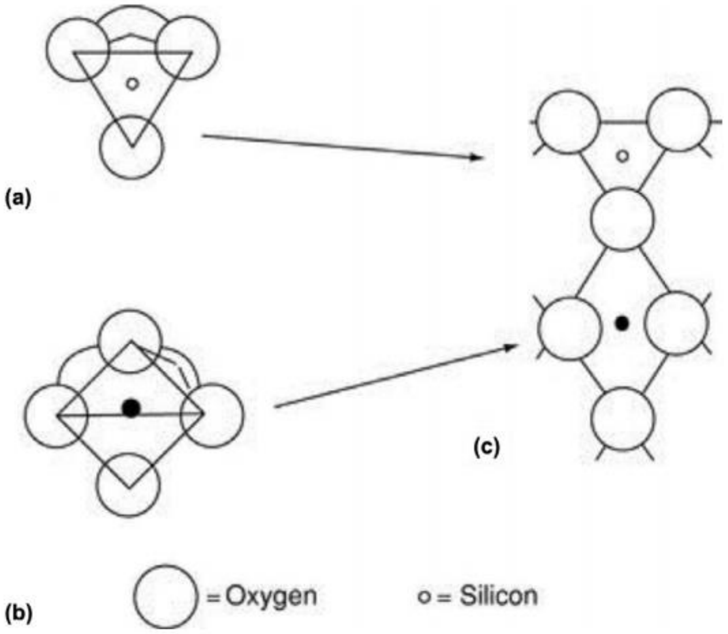


Figure 2.1: (a) Tetrahedrally co-ordinated cation polyhedrons; (b) octahedrally co-ordinated cation polyhedrons; (c) linked octahedral and tetrahedral polyhedrons (Huggett, 2015).

The principal clay physical properties of interest to the geologist are cation exchange capacity and interaction with water. Clays have charges on (001) layer surfaces and at unsatisfied bond edge sites. An important consequence of these charges is that ions and molecules, most commonly water, are attracted to and weakly bonded to clay mineral particles. In most cases cations are attracted to layer surfaces and anions to edge sites. If the interlayer charge is low, cations between 1:1 layers can be exchanged for other cations and these cations can be hydrated by up to two water layers (Huggett, 2015). Water in the interlayer site is controlled by several factors including the cation size and charge. In ‘normal’ pore fluid, one layer of water is associated with monovalent cations, two layers with divalent cations. Water can also weakly bond to the outer surface of clay particles. The relative ease with which one cation will replace another is usually: $Na^+ < K^+ < Ca^{2+} < Mg^{2+} < NH_4^+$. This implies that, NH_4^+ is usually more strongly fixed in the interlayer sites than is Na+.

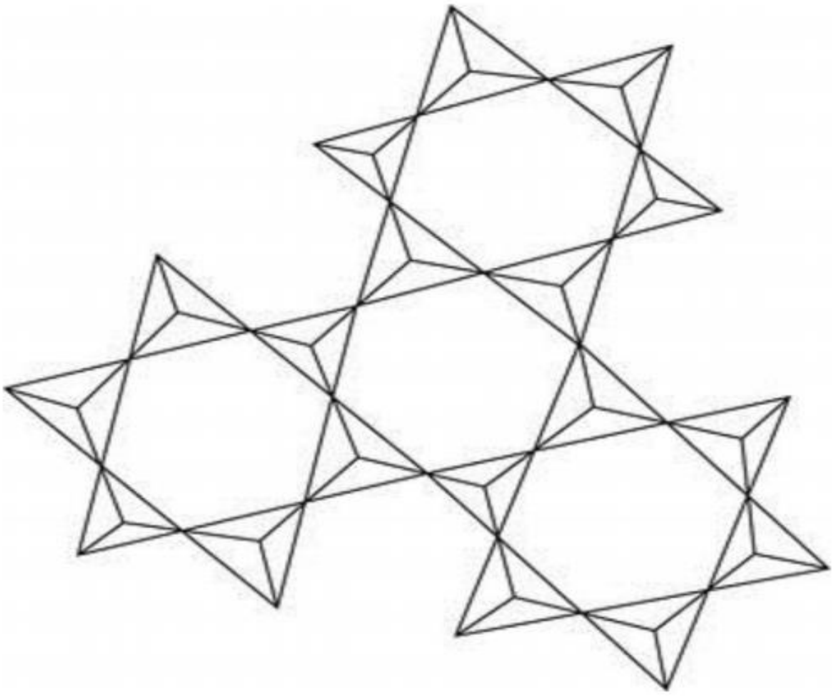


Figure 2.2: Hexagonal arrangement of edge-linked tetrahedral (Huggett, 2015)

The exchangeability of cations is measured as the cation exchange capacity (CEC). This technique is used to characterise clay reactivity, and each clay mineral has a characteristic range of CEC values. The chemical formulae for montmorillonite can be presented as $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}n(H_2O)$ and the chemical structure is given in Figure 2.1. Montmorillonite exhibits one octahedral sheet sandwiched between two tetrahedral sheets (2:1 structure). Several octahedrons $[AlO_3(OH)_3]^{6-}$ and tetrahedrons $[SiO_4]^{4-}$ are linked together by sharing three oxygen atoms to form octahedral sheets and tetrahedral sheets with hexagonal openings, respectively (Rathnayake, 2017). Clay minerals belonging to the smectite group, particularly montmorillonite and beidellite, have the highest CEC. The smectite group represents phyllosilicate/layer silicate minerals and the most widely used smectite as adsorbent is montmorillonite**.** Table 2.1 shows the typical values for cation exchange capacities of some clay materials.

Table 2.1: Values for cation exchange capacities of some clay materials

Clay Material	**CEC (meq/100g)**	**Surface area (m^2/g)**
Kaolinite	3 – 18	12
Halloysite	5 – 40	189
Chlorite	10 – 40	105
Illite	10 – 40	57
Montmorillonite (Bentonite)	60 – 150	750
Vermiculite	100 – 215	254

Source: Huggett (2015); Park (2013)

2.2.3 Classification of clay

According to Huggett (2015), clays are generally classified according to their layer type, with layer charge used to define subdivisions as shown in Table 2.2. Because of their fine particle size, clay minerals are not easily identified by optical methods, though the distinctive chemistry (and sometimes habit or morphology) of most allows identification by X-ray analysis in electron microscope studies. The most reliable method of clay identification, particularly in very fine-grained rocks is X-ray diffraction, either of the bulk sample, or more reliably, of the fine fraction (usually <2mm). The response of the clays to glycol or glycerol solvation, cation saturation, and heat treatment is used to determine which clays are present and the extent of any interlayering.

Table 2.2: Clay classification by layer type

Layer type	Group	Sub-group	Species (clays only)
1:1	Serpentine-kaolin (x~0)	Serpentines (Tr) Kandites (di)	Berthierine, odinite Kaolinite, dickite, 7 A° & 10 A° halloysite, nacrite
2:1	Talc-pyrophyllite (x~0)	Talc (Tr)	
2:1	Smectite (x~0.2–0.6)	pyrophyllite (Di) Tr smectites Di smectites	Montmorillonite (Bentonite), hectorite, saponite beidellite, nontronite
2:1	Vermiculite (x~0.6–0.9)	Tr vermiculites Di vermiculites	
2:1	Mica-illite (x~0.8)	Tr illite	
		Di illite	Illite, glauconite
2:1	Chlorite (x variable)	Tr-Tr chlorites	Chamosite, clinochlore, ripidolite etc donbassite
		Di-Di chlorites	
		Tr-Di chlorites	
		Di-Tr chlorites	Sudoite, cookeite
2:1	Sepiolite-palygorskite (x variable)	Sepiolites palygorskites	Sepiolite palygorskite (syn. attapulgite)

Source: Huggett (2015). Tr = trioctahedral, Di = dioctahedral, x = layer charge,

1:1 Layer Type Clay Minerals: The 1:1 layer minerals contain one tetrahedral and one octahedral sheet in their basic structural unit. This two-sheet mineral type is represented by the kaolin group, with the general formula $Al_2Si_2O_5(OH)_4$. Kaolinite, the most common mineral in this group, is dioctahedral, exhibiting Al^{3+} octahedral and Si^{4+} tetrahedral coordination. The sheets are held together by vander Waals bonds between the basal oxygens of the tetrahedral sheet and the hydroxyls of the octahedral sheet. Layers are held together tightly by hydrogen bonding, which restricts expansion and limits the reactive area to external surfaces. Isomorphic substitution for Si^{4+} and Al^{3+} in this mineral is negligible. As such, soils dominated by 1:1 mineral exhibit a low capacity for adsorbing cations.

2:1 Layer Type Clay Minerals: The joining of two tetrahedral sheets (one from each side) to one octahedral sheet produces a three-sheet mineral type, which is called 2:1

and is represented by the mica, smectite, and vermiculite groups. Talc [$Mg_3Si_4O_{10}(OH)_2$] and pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] are typical representatives of electrically neutral 2:1 type mineral in which adjacent layers are joined to each other by vander Waals bonds. Although these two minerals are found in frequently in soils, their structure serves as a model for discussing transitions leading to the formation of other more common 2:1 clay mineral.

2.3 Bentonite Clay

Bentonite clay are highly colloidal and plastic clays materials composed mainly of montmorillonite which belongs to clay mineral of the smectite group and in addition to montmorillonite, bentonite may contain feldspar, cristobalite, and crystalline quartz. According to Adeyemo *et al.* (2015), bentonite is an absorbent aluminium phyllosilicate, which is essentially impure clay consisting mostly of montmorillonite. There are different types of bentonite, each named after the respective dominant element, such as potassium (K), sodium (Na), calcium (Ca) and aluminium (Al). Montmorillonite, which is an extremely flat crystal flake that carries a relatively strong negative ionic charge (Huggett 2015) The negative charge is compensated for by adsorbing a cation (Na, Ca, K) to the interior of the molecule as shown in Figure 2.3, which what makes it base-metal containing Bentonite clay mineral. The clay can be acid activated. Experts debate a number of nomenclatorial problems with the classification of bentonite clays. Bentonite is usually formed from weathering of volcanic ash, most often in the presence of water. However, the term bentonite, as well as a similar clay called tonstein, has been used to describe clay beds of uncertain origin.

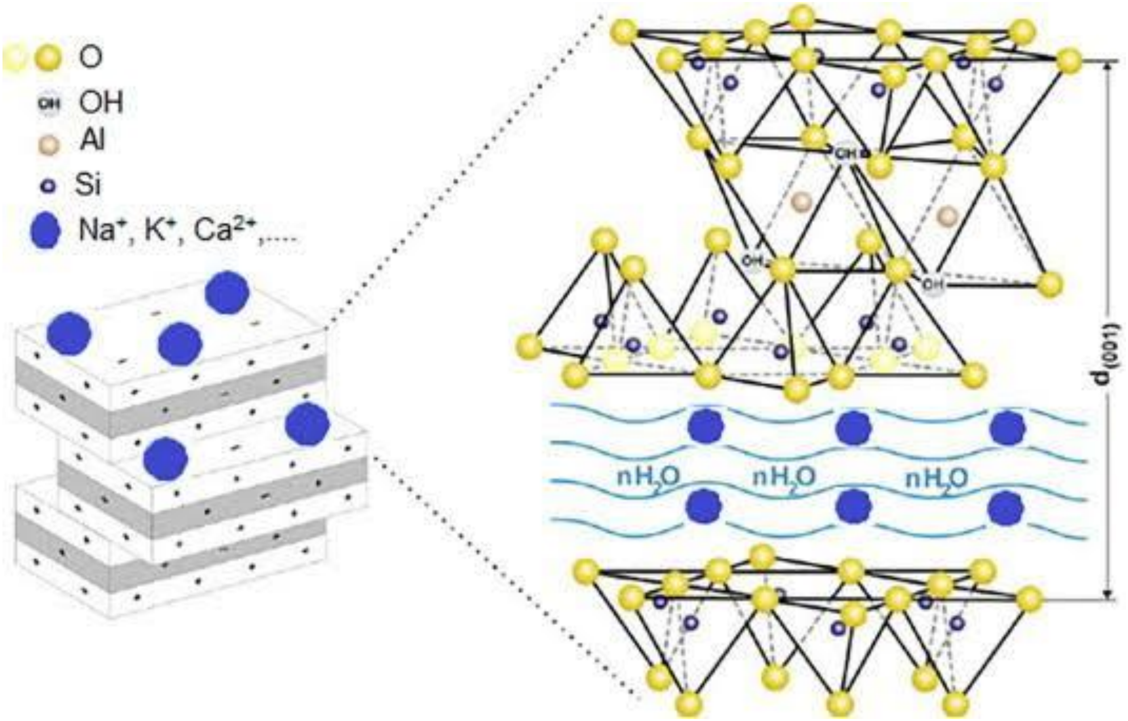


Figure 2.3: Bentonite Structure (Huggett *et al.*, 2015)

Bentonites have excellent rheological and absorbent properties. For industrial purposes, two main classes of bentonite exist: sodium and calcium bentonite. Sodium bentonite expands when wet, absorbing as much as several times its dry mass in water. Because of its excellent colloidal properties, it is often used in drilling mud for oil and gas wells and for geotechnical and environmental investigations (Adeyemo *et al.*, 2015). Calcium bentonite is a useful adsorbent of ions in solution, as well as fats and oils, and is a main active ingredient of fuller’s earth, probably one of the earliest industrial cleaning agents. Calcium bentonite may be converted to sodium bentonite, termed sodium beneficiation or sodium activation to exhibit many of sodium bentonite’s properties by a process known as ‘‘ion exchange’’ (Huggett 2015, Adeyemo *et al.*, 2015). Bentonites are environmentally safe providing dust abatement procedures which are used in processing and handling.

Bentonite also has the interesting property of adsorbing relatively large amounts of protein molecules from aqueous solutions (Huggett 2015, Adeyemo *et al.*, 2015, Afolabi *et al*., 2017). Therefore, it is uniquely useful in the process of wine making, where it is used to remove excessive amounts of protein from white wines. Were it not for this use of bentonite, many or most white wines would precipitate undesirable flocculent clouds or hazes upon exposure to warmer temperatures as these proteins become denatured. It also has the incidental use of inducing more rapid clarification of both red and white wines. Bentonite can also be used as a desiccant due to its adsorption properties. Bentonite desiccants have been successfully used to protect pharmaceutical, nutraceutical and diagnostic products from moisture degradation and extend shelf life. In fact, in most common packaging environments, bentonite desiccants offer a higher adsorption capacity than silica gel desiccants. Bentonite complies with the FDA for contact with food and drugs (Food and Drug Administration, 2011).

As far as adsorptive properties are concerned, bentonite clay has an overall neutral charge; it has an excess negative charge on its lattice and is characterized by a three-layer structure with two silicate layers enveloping an aluminate layer. This arises from the partial replacement of tetravalent silica with trivalent aluminium that leads to the replacement of trivalent aluminium with divalent calcium. Since opposite charges attract, the negatively charged surface lattice of the bentonite clay may have an affinity for cationic dye. Thus, it could be assumed that bentonite clay may have a greater capacity to adsorb cationic dye as it exhibited high removal of cationic Basic Blue 9 and Thioflavin T dyes. Bentonite has been used to remove a number of chemical species: amines; organic pigments (bcarotenes); cations (Ni, Zn), phenol and ketones;

phosphates; pesticides; chlorophyll; and non-ionic contaminants (Espantaleon *et al.*, 2003, Adeyemo *et al.*, 2015, Afolabi *et al*., 2017). Bentonite has proven to be a promising economic material for the removal of dyes due to its abundance and availability.

2.3.1 Types of bentonite

There are different types of bentonite and are each named after the respective dominant element, such as potassium (K), sodium (Na), calcium (Ca), and aluminium (Al).

Sodium bentonite: Sodium bentonite expands when wet, absorbing as much as several times its dry mass in water. Because of its excellent colloidal properties, it is often used in drilling mud for oil and gas wells and boreholes for geotechnical and environmental investigations. The property of swelling also makes sodium bentonite useful as a sealant, since it provides a self-sealing, low permeability barrier. It is used to line the base of landfills. Various surface modifications to sodium bentonite improve some rheological or sealing performance in geoenviroonmental applications (Karnland *et al.*, 2006).

Calcium bentonite: Calcium bentonite is a useful adsorbent of ions in solution, as well as fats and oils. It is the main active ingredient of fuller's earth, probably one of the earliest industrial cleaning agents. Calcium bentonite may be converted to sodium bentonite through what is termed as sodium beneficiation or sodium activation, to exhibit many of sodium bentonite's properties by an ion exchange process. In common usage, this means adding 5 – 10 % of a soluble sodium salt such as sodium carbonate to wet bentonite, mixing well, and allowing time for the ion exchange to take place and water to remove the exchanged calcium (Guyonnet *et al.*, 2005). Some properties, such as viscosity and fluid loss of suspensions, of sodium-beneficiated calcium bentonite or sodium-activated bentonite, may not be fully equivalent to those of natural sodium bentonite. For example, residual calcium carbonates formed if exchanged cations are insufficiently removed, may result in inferior performance of the bentonite in geosynthetic liners (Guyonnet *et al.*, 2005).

Potassium bentonite: Also known as potash bentonite or K-bentonite, potassium bentonite is a potassium-rich illitic clay formed from alteration of volcanic ash.

2.3.2 Bentonite clay availability in Nigeria

According to Afolabi *et al.* (2017), there are about 40–50 different types of solid minerals scattered across the country in varying quantities with bentonite been one of the major metallic mineral. The origin and formation of bentonites is often traced to weathered volcanic ash but there is still the question surrounding the genesis of the numerous clay deposits in Nigeria since there has not been any reported volcanic activity in time past and Nigeria is not a country prone to such geologic activity. Nigeria as a nation is blessed with abundant bentonite resources and the deposits spans the length and breadth of the Nigerian nation. Every region in Nigeria has been reported to have a substantial deposit of bentonite clays, however, some regions of the country may have more deposits than the other.

Bentonite deposits have been discovered in many Nigerian states, cutting across the entire Nigeria. According to Nigeria Extractive Industries Transparency Initiative (NEITI) (2016), large bentonite reserves of over 700 million tonnes are available in many states of the Federation ready for massive development and exploitation. Bentonite deposit have been reported in large deposit in Adamawa, Bomo, Edo, Ogun, Ondo, Plateau, Taraba and Yobe state (Table 2.3). Over 80 million tons of bentonite have been reported in Afuze, Ekpoma-Igunebon, Ovibiokhuan and Okpebho in Edo State (Huggett 2015, Afolabi *et al.*, 2017). Some occurrences have also been reported in Abia, Ebonyi and Anambra States (Table 2.3). Appreciable deposits of bentonite clays are also available in the North-East region. The Abakaliki Formation in South-East Nigeria is a notable formation with substantial quantities of bentonite clays (Nweke, 2015, Afolabi *et al.*, 2017). Besides the proven reserve of bentonite deposit identified, other locations with bentonite deposits in different parts of Nigeria have been found but needs further investigation for reserve estimation, quantification and characterization. The availability of Bentonite in nearly all the states in Nigeria with the wide range of industrial applications enhances the attractiveness of the bentonite utilization as adsorbent for treatment of contaminated water.

Table 2.3: States and Locations of Bentonite Deposit in Nigeria

S/No.	State	Location
1	Edo	Afuze, Ekpoma-lgunebon road, Ovibiokhuan, and Ok ebho.
2	Anambra	Awka
3	Borno	Dikwa, Ngala, New Marte, Mongonu and Mafa
4	Sokoto	Dukamaje and Kalambaina
5	Lagos	Ibeshi LGA
6	Yobe	Fika
7	Taraba	Ibi and Dumgel
8	Adamawa	Mayo Belwa
9	Abia	Umuahia South, Umuahia North
11	Gombe	Pindiaga

Source: Huggett (2015), NEITI (2016), Afolabi *et al.* (2017)

2.3.3 Physical and chemical properties bentonite

Bentonite feels greasy and soap-like to the touch. Freshly exposed bentonite is white to pale green or blue and, with exposure, darkens in time to yellow, red, or brown. The special properties of bentonite are an ability to form thixotrophic gels (reversible behavior of gels that liquefy when shaken) with water, an ability to absorb large quantities of water with an accompanying increase in volume of as much as 12–15 times its dry bulk, and a high cation exchange capacity (Adamis and Williams, 2005). Substitutions of silicon by cations produce an excess of negative charges in the lattice, which is balanced by cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) in the interlayer space as a result, these cations are exchangeable due to their loose binding and, together with broken bonds (approximately 20 % of exchange capacity), give montmorillonite a rather high (about 100 meq/100 g) cation exchange capacity, which is little affected by particle size (Huggett, 2015). This cation exchange capacity allows the mineral to bind not only inorganic cations such as caesium but also organic cations such as the herbicides diquat, paraquat, and striazines, and even bio-organic particles such as rheoviruses and proteins, which appear to act as cations. Variation in exchangeable cations affects the maximum amount of water uptake and swelling which is greatest with sodium and least with potassium and magnesium. Interstitial water held in the clay mineral lattice is an additional major factor controlling the plastic, bonding, compaction, suspension, and other properties of montmorillonite-group clay minerals (Adamis and Williams, 2005). Within each crystal, the water layer appears to be an integral number of molecules in thickness.

Physical characteristics of bentonite are affected by whether the montmorillonite composing it has water layers of uniform thickness or whether it is a mixture of hydrates with water layers of more than one thickness. Loss of absorbed water from between the silicate sheets takes place at relatively low temperatures (100–200 °C). Loss of structural water (i.e., the hydroxyls) begins at 450–500 °C and is complete at 600–750 °C (Adamis and Williams, 2005). Further heating to 800–900 °C disintegrates the crystal lattice and produces a variety of phases, such as mullite, cristobalite, and cordierite, depending on initial composition and structure. The ability of montmorillonite to rapidly take up water and expand is lost after heating to a critical temperature, which ranges from 105 to 390 °C, depending on the composition of the exchangeable cations. The ability to take up water affects the utilization and commercial value of bentonite. Montmorillonite clay minerals occur as minute particles, which, under electron microscopy, appear as aggregates of irregular or hexagonal flakes or, less commonly, of thin laths. Differences in substitution affect and, in some cases, control morphology.

These clay materials have been found to be good adsorbent alternatives that can remove contaminant from water in a water removal system and as a result, several studies have been reported on the use of clay materials such as natural clay, bentonite and kaolin clay in treatment of wastewater effluents (Adeyemo *et al.*, 2015). The fate and mobility of adsorbates are greatly affected by their strong interaction with natural clay and oxide minerals that are widely present in the natural environment (Sheng *et al.*, 2013). The uptake process is generally affected by several environmental factors such as quantity and type of ions, solution pH, ionic strength, temperature and type of dye (Sheng *et al.*, 2013, Adeyemo *et al.*, 2015). Temperature plays a significant role in the dynamic uptake of metal ions in particular, the transformation of surface complexation structures and the stability of various metal precipitates.

2.3.4 Adsorbent characteristic of bentonite

Bentonite is a clay mainly constituted by the clay mineral montmorillonite. Montmorillonites are swellable di-octahedral 2:1-layer silicates which consist of stacks of several so-called 2:1 layer. This clay mineral has a permanent negative charge that arises from isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+} for Al^{3+} in the octahedral sheet (Parolo *et al.*, 2014). This negative charge is naturally compensated by exchangeable cations, particularly Na^{+} and Ca^{2+}, located in the interlayer space. Montmorillonite has a high cation exchange capacity (CEC), marked swelling and high specific surface area leading to a strong adsorption/absorption capacity of ionic or polar compounds (Ikhtiyarova *et al.*, 2012). Along the edges of this clay mineral, another surface having variable charge is developed where Si–O–Si and Al–O–Al bonds are 'broken' and may convert into Si–OH and Al–OH groups (Parolo *et al.*, 2014). The hydration of inorganic cations at the exchange sites causes its surface to be hydrophilic and provides appropriate properties for it to act as a natural adsorbent for several pollutants in the treatment of contaminated waters.

Sorption has an important effect on the transport, reactivity and bioavailability of contaminants, as a result, there is great interest nowadays in the removal of organic compounds from water by sorption processes. A large number of effective sorbent clays have been developed for organic contaminants retention. Montmorillonite surface is hydrophilic in character and has low affinity for nonpolar liquids. In order to enhance their applicability, this clay mineral has to be modified or functionalized. There are different ways to modify clay minerals, i.e., adsorption, ion exchange with organic/inorganic cations and grafting with organic compounds (Parolo *et al.*, 2014). Montmorillonites can suffer ion exchange reactions with long-chain or short-chain quaternary amine cations to obtain organo-bentonites.

2.4 Organo-Modified Clay

These clay materials have been found to be good adsorbent alternatives and as a result, several studies have been reported on the use of clay materials such as natural clay, bentonite and kaolin clay in treatment of wastewater effluents (Momina *et al.*, 2018, Foroutan *et al*., 2018). Of this clay materials, bentonite, which has high content of montmorillonite, a layered structure, porous, mechanically and chemically stable, large surface area and high cation exchange capability has been found to be useful as an adsorbent.

Bentonite have proven to be efficient in removing many toxic material particularly metal ions and organic contaminants from an aqueous solution (Uddin, 2017, Foroutan *et al*., 2018, Hokkanen *et al.*, 2018, Momina *et al*., 2018). However, its ability to absorb organic molecules such as crude oil constituent is very low and the active site of bentonite is not uniform, so a solution is needed to improve its adsorption performance. The adsorption capacity of bentonite can be increased through its modification into organoclay as a functional material for crude oil adsorption. In the modification of bentonite clay materials by ion exchange, the interlayer accessible compensating cations could be exchanged with a wide variety of hydrated inorganic cations or organic cations including those of amines or quaternary ammonium salts such as oxonium, sulfonium, phosphonium ions. By exchanging of sodium cations for organic cations that are also called surfactants, the surface energy of montmorillonite type bentonite decreases and the interlayer spacing expands resulting in an organoclay materials.

Surfactant-modified bentonites have been extensively used for a wide variety of environmental applications (Parolo *et al.*, 2014, Uddin, 2017, Foroutan *et al*., 2018, Hokkanen *et al.*, 2018, Momina *et al.*, 2018). Numerous studies have been focused on the adsorption of nonionic organic compounds onto organo-clays as a function of surfactant type and loading.

Examined the use of modified bentonite clay for the adsorption of nitrate. The clay mineral was modified with surfactant; hexadecyltrimethylammonium bromide. It was reported that modifying the adsorbent gave the possibility of its use for the adsorption of nitrate, and it showed a good adsorption capacity, although, a decrease in the surface area of the adsorbent was observed when the modification occurred. The use of a zero-valent iron and pillared bentonite for the removal of nitrate has been examined (Li *et al.*, 2010). Pillared and zero-valent iron bentonite was prepared by intercalating poly (hydroxo Al (III)) cations with zerovalent iron into the interlayers of the clay-based material. It was reported that the modified material gave a better adsorption capacity compared with the unmodified material, and a distinguishable high removal of nitrate was observed when a uniform mixture of the modifiers was used.

Ma *et al.* (2012) prepared a novel bentonite-based adsorbent the removal of anionic pollutants from water. Bentonite was modified with calcium oxide to produce a novel adsorbent. The material was used for the adsorption of phosphate, fluoride, and other anionic contaminants using a batch adsorption process. The material showed good adsorption capacity for both fluoride and phosphate and the mechanism of adsorption was reported to be an anion/hydroxyl (anion/OH-) exchange reaction. El-Zahhar and Al-Hazmi (2015), also investigated organically modified clay by exchanging hexadecyltrimethylammonium bromide (HDTMA) onto kaolinite clay for adsorption of petroleum hydrocarbons. The study shows that the adsorption capacity of the prepared organoclay was potentially enhanced than that of unmodified clay. The study established that the adsorption efficiency of the prepared organoclay using HDTMA is highly dependent on hydrocarbon type, surfactant concentration on the clay surface, amount of adsorbent and time. Despite the in depth of the studies carried out by several researchers on the adsorption of contaminant in water using organically modifies clay, studies on the adsorption of crude oil from aqueous solution using organo modified bentonite clay are scarce in existing literatures.

2.4.1 Sorption of petroleum substances by organo modified clay adsorbents

The modification of minerals using organic compounds influences their sorption abilities towards oils in various ways, depending on the essential properties of the mineral such as; its type, surface area, CEC, External Cation Exchange Capacity (ECEC) among others. It also depends on the properties of the organic compound (the length and multiplicity of an organic chain), and lastly on the process and efficiency of the incorporation of the organic compound into the mineral structure. The recent literature reports that the sorption of petroleum products on mineral adsorbents is affected by factors such as the textural properties of the adsorbent (specific surface area, the contribution and surface of mesopores, mesopore diameters), particle size distribution and bulk density of the adsorbent, and the density and viscosity of an adsorbate (Bandura *et al.*, 2017). Low bulk density and fine particles favour the formation of capillaries between the material grains, and the contact area between the grains increases with a decrease in their diameter. This leads to an increase in the surface area available for petroleum substances. It can be assumed that the sorption of oil products on porous mineral adsorbents occurs via two mechanisms.

The first is associated with the filling of the available pores and capillaries between the sorbent grains using capillary action (mass transfer/flow). Capillary action depends on the effective diameter of the capillary, the surface energy of the interior wall of the capillary, and the viscosity of the oil. The second mechanism is sorption on the outer surface of the sorbent through the formation of an oil layer around the sorbent grains (or optionally around the agglomerates of grains). As in the case of surface adsorption on quartz sand, oil can create a uniform layer (film) or irregular clusters, depending on the morphology of the surface, its irregularities and roughness, and the properties of the oil (Bandura *et al.*, 2017). Adsorbents with a well-developed mesoporous structure exhibit relatively higher sorption capacity in relation to oils. Micropores present in the structure of minerals are unavailable for large oil particles. In addition, sorption capacity is generally higher for oils of higher density and viscosity (Kenes *et al*., 2012). This phenomenon can be explained by the fact that the substances with a higher molecular weight tend to be preferentially adsorbed over those of lower molecular weight. Generally, long-chain hydrocarbons of relatively high molecular weight dominate the chemical composition of higher-density oils (such as spent engine oil). However, the most popular method of sorption capacity (SC, g/g) determination are weighing the sorbent before and after saturation with the petroleum substance. Sorption capacity is calculated using the Equation 2.1.

$$SC = \frac{W_f - W_i}{W_i} \tag{2.1}$$

where W_f is the weight of the sorbent after sorption of petroleum product, and W_i is weight of the sorbent before sorption.

2.4.2 Application of organoclays as adsorbents

Over the years, organo clay materials have been used as adsorbent in several studies. It has been shown that replacing the inorganic exchange cations of a clay material such as bentonite with organic cations, can result in greatly enhanced abilities of modified clay material in removing organic contaminant from water. This study therefore, considered the application of organo clay materials in removal of aromatics compounds phenol and its derivatives.

According to Sheng *et al.* (2001), clay minerals have excellent capabilities for cations and polar molecules that arise from the large specific surface area and negative charges caused by isomorphic substitution. In addition, polar organic compounds such as alcohols, amines, and ketones were adsorbed into the external clay surface, interlayer space and probably on clay particle edges by electrostatic attraction and ion exchange reactions. However, clay minerals still have a greater tendency to adsorb inorganic cations in wastes than organic constituents due to the large size of organics and hydrophilic nature of clays. Hence, the clay minerals are generally ineffective sorbents for hydrophobic or non-polar organic pollutants. Since the hydrophilicity of clay minerals decreased through the addition of quaternary ammonium compounds, the resulting organoclays can adsorb non-ionic organic compounds from aquatic solutions and have been suggested for wastewater treatments (Yu, 2013).

Banat *et al.* (2000) studied the potential of natural bentonite for the adsorption of phenols from aqueous solutions has been studied. The study revealed that the adsorption capacity of bentonite was limited to the adsorption of phenols from water in the treatment of wastewaters. They investigated the main factors that influence the adsorption capability of phenols. From their study the adsorption capacity was increased at low pH. It was also found that the type of solvent in which phenol was dissolved affected the uptake of phenol-bentonite. Among the prepared solvents (cyclohexane, water, and methanol), the affinity of phenol for bentonite in the presence of cyclohexane was greater than that in water. However, organic modification of bentonite clay will enhance the adsorption capacity of the bentonite in removing contaminant from contaminated water. Several studies have reported the effectiveness of organoclays materials on the uptake of organic contaminants of crude oil-based constituents, including aromatic organic compounds and phenolic compounds among other.

2.5 Adsorption Isotherms

An adsorption isotherm provides a relation between total mass of adsorbed adsorbate per unit mass of sorbent and concentration at constant ambient conditions. In order to develop adsorption isotherms, adsorption experiments are performed. The relationship that exists at a given temperature between the quantities of substance adsorbed as well as the remaining concentration can be explained using adsorption isotherms. Several equations have been used in analyzing equilibrium data obtained from experimental adsorption. A proper insight into the surface characteristics and adsorption mechanism of the adsorbent depends on certain thermodynamic postulates and equilibrium parameters of the equilibrium adsorption models. Langmuir adsorption isotherm and Freundlich adsorption isotherm are the most common isotherms used for adsorption studies (Gulistan, 2014).

The adsorption study plays a vital role and also helps to find the uptake rate and capacity. Adsorption equillibrium is typically explained by the isotherm Equations. The parameters of isotherms describe the surface properties and affinity at a constant temperature and pH. In this study, Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich adsorption isotherm models were considered.

2.5.1 Langmuir isotherm

The Langmuir isotherm model regards adsorption as a chemical process involving monolayer adsorption with fixed number of identical sites attracting the adsorbates to the surface. The model also assumes that all sites possess equal energy and an ion can only be attracted to one site. In the same vein, the model stands on another assumption that ions do not interact with each other (Langmuir, 1918).

2.5.2 Freundlich isotherm

The Freundlich isotherm model describes the equilibrium parameter and adsorption properties for a heterogeneous surface (Freundlich, 1928). Being different from the Langmuir model, the Freundlich model cannot be restricted by saturation limitation and Henry's law. This indicates that multilayer sorption occurs on the heterogeneous surface, which can be predicted mathematically.

2.5.3 Tempkin isotherm

Temkin isotherm model takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process; it is also assumed that the heat of adsorption (ΔH_{ads}) of all molecules in the layer decreases linearly as a result of increase surface coverage (Gulistan *et al.*, 2017). The Temkin isotherm is valid only for an intermediate range of ion concentrations.

2.5.4 Dubinin-radushkevich isotherm

Dubinin-Radushkevich isotherm model is an empirical adsorption model that is commonly applied to describe adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces and is only suitable for intermediate range of adsorbate concentrations because it exhibits unrealistic asymptotic behavior and does not predict Henry's laws at low pressure (Gulistan *et al.*, 2017). The model is a semiempirical equation in which adsorption follows a pore filling mechanism and it presumes a multilayer character involving Van Der Waal's forces, applicable for physical adsorption processes, and is a fundamental equation that qualitatively describes the adsorption of gases and vapours on microporous sorbents (Gulistan *et al.*, 2017). It is usually applied to distinguish between physio sorption and chemo sorption of metal ions and a distinctive feature of the Dubinin-Radushkevich isotherm is the fact that it is temperature dependent and as such, adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed versus the square of potential energy which enables all suitable other data to be obtained (Gulistan *et al.*, 2017).

2.5.5 Redlich-Peterson isotherm

The Redlich-Peterson isotherm model is an empirical isotherm incorporating three parameters, from both Langmuir and Freundlich model whose mechanism of adsorption does not follow ideal monolayer adsorption.

2.6 Adsorption Kinetics

One-way to describe the potentials of an adsorbent for the removal of pollutant from an aqueous phase is by studying the adsorption kinetics. The conclusion grafted from the kinetic studies tend to provide adequate information on the adsorption mechanism of the system (Rashidi *et al.*, 2013). This study also, examine the kinetics of adsorption by using the Pseudo first, second-order, Elovich, Intra-particle and Boyd kinetic model. Several reports have shown that most adsorption system conforms to the Pseudo-second-order model.

2.6.1 Pseudo-first-order model

The Lagergren's pseudo-first-order models describes the adsorption of solute onto adsorbent following the first order mechanism (Kajjumba *et al.*, 2018). It is used to evaluate the kinetic behaviour of an adsorbent and conformity of the experimental work with the kinetic model.

2.6.2 Pseudo-second-order model

The Lagergren's pseudo-second-order models assumes that the rate of adsorption of solute is proportional to the available sites on the adsorbent and the reaction rate is dependent on the amount of solute on the surface of the adsorbent (Kajjumba *et al.*, 2018). It is used to assess the kinetic behaviour of an adsorbent and its conformity of the experimental work.

2.6.3 Intra-particle diffusion model

Intra-particle diffusion model has been widely applied to examine the rate limiting step during adsorption. The adsorption of solute in a solution involves mass transfer of adsorbate (film diffusion), surface diffusion, and pore diffusion. Film diffusion is an independent step, whereas surface and pore diffusion may occur simultaneously (Kajjumba *et al.*, 2018). The intra-particle diffusion model is vital in assessing the adsorption of pollutant by an adsorbent which involves diffusion process (Alhassan *et* *al.* 2017), and is also used to assess the kinetic behaviour of an adsorbent and its conformity of the experimental work.

2.6.4 Elovich model

To further understand the chemisorption nature of adsorption, Elovich model (developed by Zeldowitsch) is applied to assess the kinetic behaviour of an adsorbent. According to Kajjumba *et al.* (2018), the model helps to predict the mass and surface diffusion, activation and deactivation energy of a system. Although the model was initially applied in gaseous systems, its applicability in wastewater processes has been meaningful.

2.6.5 Boyd model

Boyd developed a single-resistance model that can be used to assess the effect of film diffusion in order to understand if film diffusion is the rate controlling step and he assumes that the boundary layer surrounding the adsorbent has a greater effect on the diffusion of solute (Kajjumba *et al.*, 2018).

2.7 Thermodynamic Studies

Thermodynamic studies were also performed on the adsorption of crude oil by the synthesis adsorbents in order to estimate the feasibility of the adsorption process was performed and the activation energy of the adsorption process.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Introduction

This chapter presents the description of materials, chemicals and equipment used in the course of the study. It also presents the experimental procedures for the development of organo modified bentonite clay adsorbent as well as characterization of the produced adsorbent. Furthermore, this chapter present the experimental procedures to investigate the adsorption efficiency of the developed adsorbent as well as the adsorption isotherm models and adsorption kinetics of the developed adsorbent in adsorption of crude oil in polluted water.

3.2 Equipments and Materials

3.2.1 List of chemicals

The major materials and reagents used in the course of the research work are shown in Table 3.1.

Table 3.1: List of Materials

S/N	Materials	Sources
1.	Bentonite clay	Shabu, Lafia LGA, Nassarawa State
2.	Cethyl Trimethyl Ammonium Bromide (CTMABr)	Loba Chemie PVT. Ltd.
3	Oxalic Acid	
4	HCl	Chem. Eng'g. Lab. Kaduna P0lytechnic
5	Distilled Water	Chem. Eng'g. Lab. Kaduna P0lytechnic
6	Crude Oil Polluted Water	Khana LGA, Rivers State.

3.2.2 List of equipment

The major equipment and apparatuses that would be used in the course of the research work are shown in Table 3.2.

Table 3.2: List of Equipment

S/N	Equipment	Model	Manufacturer
1.	Funnel	Pyrex Glass	Pyrex, England
3.	Weighing balance	EK-200i	Gallenkamp, UK
4.	Oven	DHG9030	Bioevopeak, China
5.	pH meter	475343 Benchtop	Corning Ltd., U.S.A.
6.	Thermometer	Glass Thermometer	Zeal, England
7.	Measuring cylinder, beaker	Pyrex Glass E8R04440	Pyrex, England
8.	Thermogravimetric Analyzer	Model DTG-60H	Shimadzu, USA
9	BET Surface Area Analyzer	Micromeritis Tristar 3000	Quantachrome, Canada
10	FTIR	FTIR-8400S	SHIMADZU, UK
11	Scanning Electron Microscopy (SEM)/EDS Analyzer	S-3400N	HITACHI, UK
12	XRD Machine	XPERT-PRO	Malven Panalytical, UK
13	UV Spectrophotometer	S800 Diode Array Spectrophotometer	Biochrom, UK

3.3 Methodology

This methodology for the investigation of the adsorption of crude oil from polluted water using organo modified bentonite clay are depicted in this section. The experimental procedures for this study is as shown in Figure 3.1.

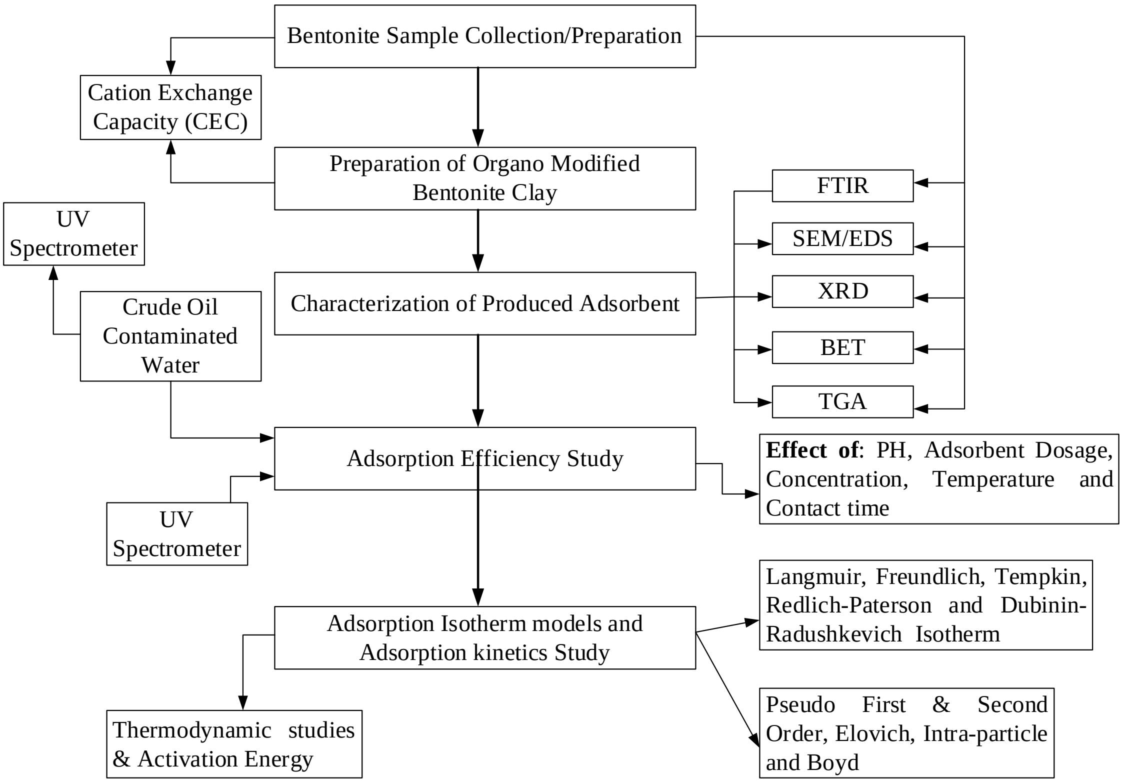


Figure 3.1: Experimental Procedure

3.3.1 Preparation and characterization of raw materials

Bentonite clay was obtained, stones and other non-clay particles was removed from the samples by hand picking and then crushed and sieved using a meshed sieve to further remove the larger non-clay fractions. The sieved bentonite clay samples were dispersed in distilled water acidified with HCl and stirred continuously with a stirrer to form two layers (a settle able heavier particulate layer and a colloidal suspension which is the bentonite clay). The suspended layer was carefully and completely decanted after which the colloidal layer was recovered. The supernatant is to be decanted and the bentonite clay washed thoroughly with distilled water to remove traces of impurities. The impurity free bentonite clay was recovered and oven dried at 100 ^{o}C to obtain dried clean bentonite clay samples. The prepared bentonite clay was grounded, sieved to mesh size <350 µm mesh size and then kept in a closed container ready for use in the preparation of organo modified bentonite clay adsorbent. The cleaned raw bentonite sample was characterized to determined its Cation Exchange Capacity (CEC) according to the procedure described in section 3.4.1.

Also, a gallon of crude oil contaminated water was collected from Khana Local Government Area of Rivers State for the adsorption study. The contaminated water was digested prior to any analysis on the contaminated water. Sample of the digested contaminated water was analyze using S800 Diode Array UV Spectrophotometer by Biochrom, UK to determine the Total Petroleum Hydrocarbon (TPH) and the hydrocarbon constituent in the contaminated water. Afterward, the treated water was also analyzed to determine the concentration of Total Petroleum Hydrocarbon (TPH) remaining in the polluted water and the amount removed by the adsorbent. The remaining quantity of the digested contaminated water was stored for use during adsorption studies.

3.3.2 Synthesis of modified bentonite adsorbents

3.3.2.1 Oxalic Acid Pretreatment of Bentonite

A measured quantity of 200 g of cleaned bentonite clay was measured into a 1-liter beaker and 2 mol/L oxalic (126.06 g/L oxalic acid) solution was prepared using deionized water. 500 mL of the prepared oxalic acid solution was measured and added to the measured bentonite clay material in a beaker at room temperature and the mixture was stirred continuously at 900 rpm for 30 min to ensure uniform mixing which in turn form two layers (a settleable heavier particulate layer and a colloidal suspension which is the acid treated bentonite clay. The suspended layer was carefully and completely decanted after which the colloidal layer was recovered and the supernatant was decanted and the acid treated bentonite clay washed thoroughly with distilled water until the pH is almost neutral. The oxalic acid treated bentonite clay was recovered and oven dried at 100 ^{o}C for 30 min to obtain dried bentonite clay samples. The dried oxalic acid treated bentonite was grounded to 450 µm mesh size and then kept in a closed container ready for use in the preparation of organo modified bentonite clay adsorbent. This procedure was repeated in triplicate.

3.3.2.2 Adsorbent Preparation

The organo modified bentonite clay was prepared by a cation exchange reaction according to procedure reported by El-Zahhar and Al-Hazm (2015). A measured quantity of 200 g of cleaned bentonite clay was measured and dispersed into 1-liter deionized water. The mixture was stirred thoroughly at 900 rpm for 20 min and then left to settle. A measured quantity (69.25 g) of CTMABr equivalent to prepared 0.190 mol/L of CTMABr solution was added to the cleaned bentonite clay mixture and the mixture was stirred thoroughly at 900 rpm for 20 min and left to settle for 24 h at room temperature. After 24 h, the CTMABr modified bentonite clay products was washed with deionized water to remove excess surfactants, filtered and dried at 60 ± 5 ^{o}C till constant weight is achieved. The dried the CTMABr modified bentonite clay products was stored at room temperature for characterization and adsorption study. The modify bentonite clay was done in triplicate. The same procedure was repeated using oxalic acid pretreated bentonite clay. The concentrations of CTMABr was reported as a ratio of bentonite clay cation exchange capacity (CEC). The synthesized modified bentonite adsorbents were stored at room temperature for characterization and the adsorption study.

3.4 Characterization of Raw and Synthesized Organo-Modified Bentonite Clay

The cleaned bentonite clay, pretreated and untreated organo-modified bentonite clay were characterized using CEC, FTIR, SEM/EDS, XRD, BET and TGA. The procedures are discussed subsequently.

3.4.1 Determination of cation exchange capacity

The cation exchange capacity (CEC) of the raw bentonite, pretreated and untreated organo-modified bentonite clay adsorbent were determined according to the ASTM C 837-81 (ASTM, 1988). This test is based on the linear relationship between the methylene blue (MB) index and fundamental clay properties such as CEC and specific surface. In accordance with this procedure, 1.5 g of cleaned raw bentonite clay was measure into a 500 mL beaker with the addition of 300 mL of distilled water and sufficient sulfuric acid to bring the pH to the range of 2.5 – 3.8. After adjusting the pH, the burette was filled with a prepared 0.028 N of methylene blue solution from which 5 mL of the solution was added to the raw bentonite clay slurry in the 500 mL beaker, and stirred for 1min. After one-minute stirring, a drop of the bentonite slurry solution was placed on the edge of a filter paper to check for the formation of light blue sunshine like halo around the dark blue MB colour. The addition of MB and stirring continues for the next 1 min and droplet of slurry solution placed on the filter paper after each addition. The process continues until the end point was reached by the formation of a light blue sunshine like halo around the drop (Jaqueline *et al.*, 2013). The process was repeated in triplicate. The same procedure was repeated for the pretreated and untreated organo-modified bentonite clay adsorbent. The CEC was then determined according to Equation 3.1.

$$CEC\left(\frac{meq}{100g}\right) = \frac{EV}{W} x\ 100 \tag{3.1}$$

where:

CEC = cation exchange capacity in meq/ 100 g of clay

E = milliequivalents of methylene blue per milliliter = 0.028 Normality

V = milliliters of methylene blue solution required for the titration, and

W = grams of dry material

3.4.2 Fourier transform infra-red analysis

Fourier transform infrared (FT-IR) spectroscopy was performed on a SHIMADZU FTIR-8400S, UK to characterize the raw bentonite, pretreated and untreated organo-modified bentonite clay adsorbent samples into the various organic functional groups present in the adsorbent. The FTIR spectra was collected using KBr pellet technique in the wavelength range of 400 – 4000 cm^{-1} at a resolution of 4.0 cm^{-1}.

3.4.3 Brunauer–emmett–teller (BET) surface area analyzer

Prior to adsorption study, the surface area, pore volume and micro-pores were obtained by N_2 physisorption (BET method) at 77 K. These analyses were performed using Micromeritis Tristar 3000 surface area analyzer device using the BET method. Samples of the raw bentonite clay adsorbent was placed in an oven at low temperature to ensure that they have as little remaining water vapor as possible. A measured quantity of the dried raw bentonite samples was introduced into the sample tube of BET surface area analyzer and then de-gassed for 1 h before starting the analysis. The raw bentonite sample was immersed in a liquid nitrogen bath while the Quantachrome instrument performs the nitrogen adsorption tests. During the analysis, a known quantities of ultra-pure nitrogen gas was introduced into the tube while recording the pressure (P/P_0), this enables the plotting and determination of parameters therein. The same procedure was repeated for pretreated and untreated organo-modified bentonite clay adsorbent.

3.4.4 Scanning electron microscopy (SEM) analysis

The surface and microstructure analysis of the raw bentonite clay was carried out using a SEM instrument (model HITACHI, S-3400N). The raw bentonite powder was mounted onto the SEM stubs (layered with sticky carbon tape). The stub was then placed in a sputter coater (EMITECH, K550X) for five minutes for coating with gold to provide high reflectivity during the scanning process. The sample is then placed at 40 °C in an oven before SEM images and EDS result of the sample was generated. The same procedure was repeated for pretreated and untreated organo-modified bentonite clay adsorbent.

3.4.5 X-Ray diffraction analysis

X-ray diffraction (XRD) was also performed on the dried raw bentonite clay powder. The raw bentonite was grounded into fine powder prior to XRD measurements. The scans were performed for each sample and the values reported for the basal spacing. The x-ray diffraction patterns were obtained using a XPERT-PRO x-ray diffractomer with CuKα radiation (λ=1.54 Å). The experiment was run at room temperature with an angle range (2θ) and step size of 0.02° with the machine operating at 40 kV and 40 mA. The same procedure was repeated for pretreated and untreated organo-modified bentonite clay adsorbent.

3.4.6 Thermogravimetric analysis

Thermogravimetric analysis of the raw bentonite clay was carried out with the aid of a thermogravimetric analyzer (Shimadzu Model DTG-60H) system. The powder sample was placed in an alumina crucible (6 mm diameter). A constant heating rate of 5 °C/min was applied from 20 – 1000 °C under nitrogen atmosphere with a flow rate of 50 mL/min. The same procedure was repeated for pretreated and untreated organo-modified bentonite clay adsorbent.

3.5 Performance Evaluation of Adsorbents Using Batch Adsorption Method

The performance of the of the adsorption capacity of the raw bentonite, pretreated and untreated organo-modified bentonite clay adsorbent were evaluated using batch adsorption. Also, the adsorption isotherm and kinetic studies were performed using different models to the determine the adsorption and kinetic mechanism of the raw bentonite clay, repeated for pretreated and untreated organo-modified bentonite clay adsorbent.

3.5.1 Adsorption study

A measured quantity of 2 g of raw bentonite clay was placed in 100 mL beaker at constant temperature (29.8 ^{o}C), constant concentration (effluent concentration), constant mixing (900 rpm) and pH (8.36). 50 mL of the contaminated water was measured and added to the beaker. The contaminated water was made to contact the raw bentonite clay in the adsorption unit for 10 min contact time. After 10 min of continuous mixing, the liquid and the solid phases was separated and the supernatant stored in sample bottle for analysis. The same procedure was repeated for 20, 30, 40, 50 and 60 min contact time using the same raw bentonite clay adsorbent. Samples of the supernatant liquid was taken and the concentration of unabsorbed crude oil constituent in aqueous phase was analyzed using UV-visible spectrophotometer. Data generated from the adsorption studies was then utilized in determining the equilibrium adsorption capacity and percentage removal. The same procedure was repeated with the synthesis oxalic acid pretreated and untreated organo-modified bentonite clay adsorbent. The percentage removal and equilibrium adsorption capacities (qe) of the different samples were determined using the Equation 3.2 and 3.3 respectively.

$$\text{Percentage Removal (\%)} = \frac{C_o - C_f}{C_o} x\ 100 \qquad (3.2)$$

$$q_e\left(\frac{mg}{g}\right) = \frac{(C_o - C_f)\ x\ V}{M} \qquad (3.3)$$

where

q_e = the adsorption capacity of crude oil constituent aqueous solution (mg/g),

C_o and C_e = initial and equilibrium crude oil constituent concentrations in the solution (mg/L),

C_f = final concentration after adsorption (mg/L)

V = the aqueous solution volume (ml) and

M = the mass of adsorbent (g).

The similar procedure was employed to study the effect of concentration (0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 mg/L) at constant temperature (29.8 ^{o}C), time (40 min), mixing (900 rpm), dosage (2 g) and pH (8.36) for raw bentonite, acid pretreated and untreated organo-modified bentonite clay adsorbent and the percentage removal were determined using the Equation 3.2.

The same procedure was utilized to study the effect of temperature (25, 35, 45, 55, 65 and 75 ^{o}C) at constant time (40 min), concentration (effluent concentration), mixing (900 rpm), dosage (2 g) and pH (8.36) for raw bentonite, pretreated and untreated organo-modified bentonite clay adsorbent and the percentage removal were determined using the Equation 3.2.

The same procedure was utilized to study the effect of dosage (0.5, 1, 1.5, 2, 2.5 and 3 g) at constant time (40 min), concentration (effluent concentration), mixing (900 rpm), temperature (35 ^{o}C) and pH (8.36) for raw bentonite, acid pretreated and untreated organo-modified bentonite clay adsorbent and the percentage removal were determined using the Equation 3.2.

The same procedure was utilized to study the effect of pH (4, 5, 6, 8, 9 and 10) at constant time (40 min), concentration (effluent concentration), mixing (900 rpm), temperature (35 ^{o}C) and dosage (2 g) for raw bentonite, acid pretreated and untreated organo-modified bentonite clay adsorbent and the percentage removal were determined using the Equation 3.2.

3.5.2 Adsorption isotherm

Adsorption isotherm was used to describes the equilibrium of the adsorption material at the surface of adsorbent, particularly at the surface boundary at constant temperature and obtained from experimentally measured data by means of regression analysis (Chen *et al.*, 2011). In this study, Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm models were considered to predict the behavior of crude oil adsorption by the adsorbents.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results of the preparation and characterization of organically modified bentonite clay adsorbent as well as the adsorption studies. Furthermore, the discussion of the results obtained are presented in this chapter.

4.2 Characterization of Adsorbent

The raw bentonite, pretreated and untreated CTMABr modified bentonite clay adsorbent were characterized using CEC Analysis, Scanning Electron Microscope (SEM)/ Energy Dispersive X-Ray Spectroscopy (EDX), X-Ray Diffraction Technique (XRD), Brunauer Emmett Teller (BET), Thermogravimetric Analysis (TGA) and Fourier Transform Infra-Red (FTIR) analysis. The result obtained are discussed subsequently.

4.2.1 Cation exchange capacity

The cation exchange capacity of the raw bentonite, pretreated and untreated CTMABr modified bentonite clay adsorbent was investigated in order to determine the capacity of the ions that can be exchanged around the alumina silica clay minerals. The results of CEC obtained for bentonite, pretreated and untreated organo-modified bentonite clay are presented in Table 4.1. Cation exchange capacity for the raw bentonite was found to be 74.85 meq/100 g on average which is within the range of 60 – 150 meq/100 g reported for Montmorillonite bentonite (Park, 2013, Huggett, 2015).

Table 4.1: CEC result for adsorbents

Run	Raw Bentonite	Acid Pre-treated Modified Bentonite	Untreated Modified Bentonite	% Cation Exchange	
				APMB	UMB
1	74.29	7.47	16.05	89.95	78.50
2	74.67	7.09	16.43	90.50	78.00
3	75.60	7.09	16.80	90.62	77.61
Average	**74.85**	**7.22**	**16.43**	**90.36**	**78.04**

APMB: Acid Pre-treated Modified Bentonite and **UMB**: Untreated Modified Bentonite

The CEC of the raw bentonite which is 74.85 meq/100 g is dependent on its mineralogical composition and the value obtained is comparable to 75 meq/100 g reported by Gaucher and Blanc (2006) and Jaqueline *et al.* (2013) for raw bentonites with high montmorillonite content (>80 %), which is in agreement with the CEC results obtained for raw bentonite (74.85 meq/100 g) using methylene blue method. However, the obtained CEC value for the raw bentonite was slightly lower than 76.4 meq/100 g (Choo and Bai, 2016) and 82.59 meq/100 g (Shaha *et al.*, 2017) for raw bentonite clay sourced from Korea and Russia respectively. Whereas the obtained CEC in this study (74.85 meq/100 g) is higher than 67.5 meq/100 g bentonite clay reported by Makhoukhi *et al.* (2010).

The CEC of the untreated modified bentonite clay is 16.43 meq/100 g bentonite clay on average and in the range of 16.05 – 16.80 meq/100 g modified bentonite clay while that of acid pretreated CTMABr modified bentonite clay was found to 7.22 meq/100 g modified bentonite clay on average and in the range of 7.09 – 7.47 meq/100 g modified bentonite clay. The CEC of the acid pretreated CTMABr modified bentonite clay adsorbent was observed to have reduced significantly to 7.22 meq/100 g on average compared to 16.43 meq/100 g for the untreated organically modified bentonite clay. The difference between the CEC of the pretreated and untreated CTMABr modified bentonite clay could be attributed to the acid pretreatment enhancing the exchangeability of cations in the acid pretreated CTMABr modified bentonite clay adsorbent (Huggett, 2015). Additionally, the reduction in CEC values of the oxalic acid pretreated and untreated CTMABr modified bentonite clay showed that cations of CTMABr have participated in the ion exchange process.

4.2.2 XRD analysis

The crystal structure of the raw bentonite, pretreated and untreated CTMABr modified bentonite clay adsorbent were characterized by XRD. Figure 4.1 shows the XRD pattern of the raw bentonite, pretreated and untreated CTMABr modified bentonite clay. It can be seen that the diffraction peak at 2θ angle of 26.67° was the typical diffraction peak of albite and quartz and shows that the acid pretreated CTMABr modified bentonite is mainly crystalline silica of quartz and albite. From the XRD analysis, the basal spacing of the acid pretreated CTMABr modified bentonite clay at 2θ angle of 26.67° was 3.343 Å, indicating the 1 0 1 plane of quartz. Also, the peak at 2θ angle of 20.89° was typical of quartz and microcline. The basal spacing of the acid pretreated CTMABr modified bentonite clay at 2θ angle of 20.89° was 3.189 Å, indicating the 0 0 2 planes of albite (Zhang *et al.*, 2019). From Figure 4.1, it can be seen from the diffractograms that the crystal structure comprises mainly of quarts and albite with the highest intensity of 21803 count and small amounts of microcline with the highest intensity of 4859 count. Meaning that the quarts and albite content of the acid pretreated CTMABr modified bentonite clay is higher than microcline content. In addition, the higher basal spacing in the presence of the quaternary salt (CTMABr) is known to facilitate the intercalation of the organomodified bentonite clay.

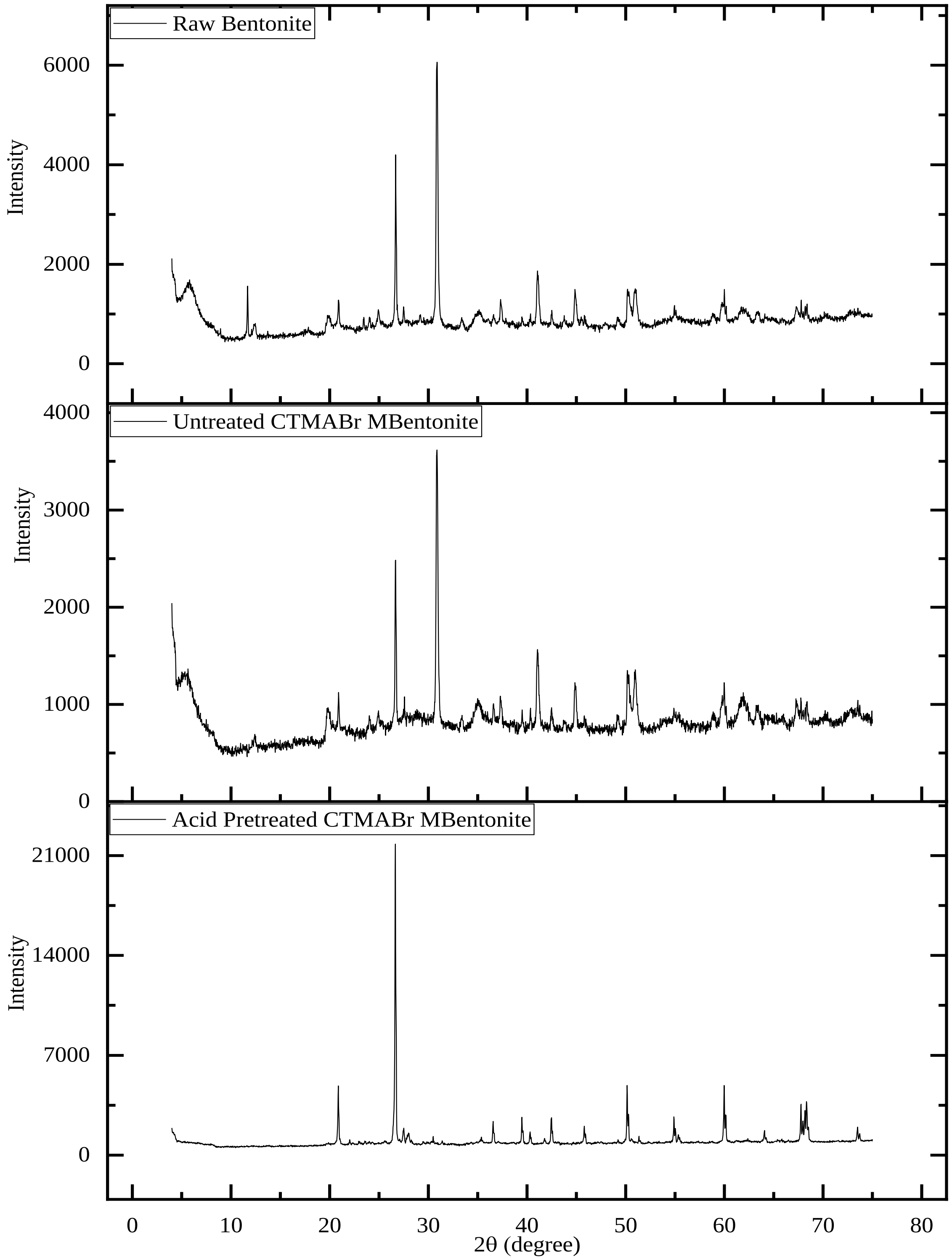


Figure 4.1: XRD pattern of raw bentonite, untreated CTMABr modified bentonite and acid pretreated CTMABr modified bentonite.

Figure 4.1 also shows the XRD pattern of the raw bentonite clay. From Figure 4.1, it can be seen that the diffraction peak at 2θ angle of 5.82°, 11.70°, 17.84°, 20.92°, 26.69°, 30.87°, 35.15°, 44.87°, 50.20°, 50.96°, 54.95°, 58.81°, 59.99°, 61.73°, 63.43°, 67.79°, and 68.37° corresponds to diffraction peak of montmorillonite. The most intense peak observed at 2θ angle of 30.87° which corresponds to those of montmorillonite and vermiculite, shows that the raw bentonite clay comprises mainly of montmorillonite and vermiculite silicate phase with monoclinic and arnothic structures respectively. These peaks correspond to (001), (002), (003), (012), (110) and (111) crystallographic planes assigned to montmorillonite phase respectively. These peaks are consistent with basal spacing reported in literatures for montmorillonite silicate phase (Oueslati *et al.*, 2014, , Milinovic *et al.*, 2020). Also, the peaks of the raw bentonite at 2θ angle of 12.46°, 20.92°, 23.46°, 24.93°, 26.69°, 30.87°, 33.39°, 37.33° and 41.06° correspond to those of vermiculite. These peaks are consistent with basal spacing of (004), (114), (008), reported in literatures for vermiculite silicate phase.

The basal spacing for montmorillonite and vermiculite phase was observed to be 15.004 Å and 14.334 Å respectively, indicating the (001) and (002) plane respectively shows both montmorillonite and vermiculite phase are in almost equal quantity (Oueslati *et al.*, 2014). The XRD analysis shows that the raw bentonite comprises mainly of montmorillonite and vermiculite silicate phase in almost equal quantity as shown in Figure 4.1. It was observed that the crystal system of the raw bentonite clay comprises both anorthic and monoclinic crystal system with three unequal axes with unit cell parameter of a = 5.18 Å, b = 8.98 Å and c= 15.0 Å for montmorillonite phase and a unit cell parameter of a = 5.35 Å, b = 9.26 Å and c= 28.72 Å for vermiculite phase. The analysis further shows that the degree of crystallinity of the raw bentonite clay is 11.96 % with 88.04 % amorphous silica phase. The high amorphous silica phase in the raw bentonite portend high adsorptive capacity (Parolo *et al.*, 2014, Adeyemo *et al.*, 2015).

Figure 4.1 further presents the XRD pattern of the untreated CTMABr modified bentonite clay. It can be seen from Figure 4.1, that the diffraction peak at 2θ angle of 5.66°, 20.92°, 25.01°, 26.69°, 30.87°, 35.15°, 36.59°, 37.30° and 44.87° are typical of those of montmorillonite and similar to the diffraction peak of montmorillonite in the raw bentonite clay. The most intense peak observed at 2θ angle of 30.87° which corresponds to those of montmorillonite, which shows that the untreated CTMABr modified bentonite do not have significant effect on the montmorillonite structure.

However, it was observed that the XRD pattern of the vermiculite phase in the raw bentonite clay change after modification with CTMABr to kaolinite phase. Figure 4.1 shows that the diffraction peak at 2θ angle of 12.43°, 24.96°, 39.51°, 49.12° and 70.10 are typical of kaolinite phase. The characteristic peaks of the kaolinite were similar to that reported by Ajayi *et al*. (2010), Panda *et al*. (2010), Salahudeen (2015) and Milinovic *et al.* (2020) for crystalline silicate. The other peaks which represent the kaolinite phase were much lower; they generally had intensity of less than 900 counts and even lower, which implies that the kaolinite content is lower than montmorillonite content in the molded bentonite balls. The change in the phases present in the untreated CTMABr modified bentonite clay indicates that the CTMABr utilized relatively affected the crystal structure of the bentonite from vermiculite phase to kaolinite phase. In addition, it was observed that the crystal system of the untreated CTMABr modified bentonite clay is anorthic crystal system. The analysis further shows that the degree of crystallinity of the untreated CTMABr modified bentonite clay reduces to about 9.98% with 90.02% amorphous silica phase. The slight increase in amoorphous silica phase would further enhance the adsorptive properties of the untreated CTMABr modified bentonite clay (Parolo *et al.*, 2014, Adeyemo *et al.*, 2015).

4.2.3 SEM/EDX analysis

The morphology of raw bentonite, pretreated and untreated CTMABr modified bentonite clay was studied using SEM/EDX analysis. The SEM imaging was used to study the surface morphology and pore development of the synthesis bentonite clay adsorbent while EDX was used to study the elemental map of the bentonite adsorbents. Figure 4.2 shows the SEM image of the raw bentonite clay at different magnifications of 500 (a) and 750 (b). It was observed that the SEM image of the raw bentonite clay shows a scattered and rough surface morphology with the formation of a nanocrystalline particle. The surface roughness observed from Figure 4.2 (a and b), is attributed to the relatively high amorphous silicate phase associated with raw bentonite clay phase, which validate the high amorphous phase established from XRD analysis.

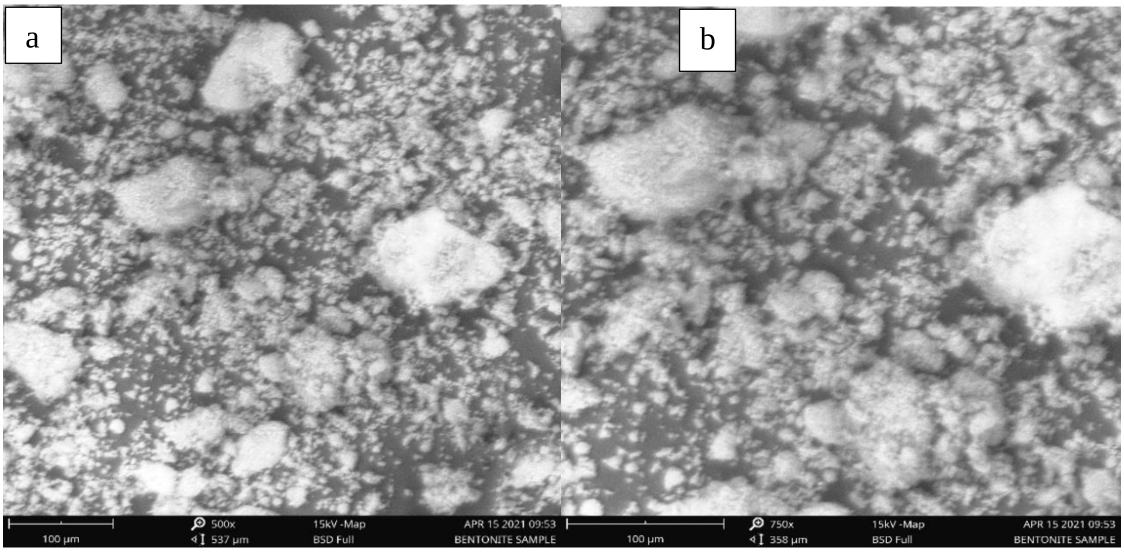


Figure 4.2: SEM image of the raw bentonite clay at (a) 500x and (b) 750x

Figure 4.3 shows the SEM image of the untreated CTMABr modified bentonite at different magnifications of 500 x and 750 x as shown in Figure 4.3. It was observed that the SEM image of the untreated CTMAB modified bentonite shows a crystalline and smooth surface morphology. The SEM images showed the formation of a dense and slightly rough surface with smaller pores. The change in surface morphology could be attributed to the effect of CTMABr modification which was established from the XRD analysis to have relative affect the crystal structure of the bentonite. From Figure 4.3, it can be seen that the surface shows some pore development, this could be attributed to the presence of kaolinite formation identified after modification with CTMABr as established from the XRD analysis. This is because, kaolinite phase has empty framework structure of almost 50% of which is void and makes the special structure of kaolinite to have a lot of micropores and mesopores of less than one nanometer (Aroke *et al.*, 2013).

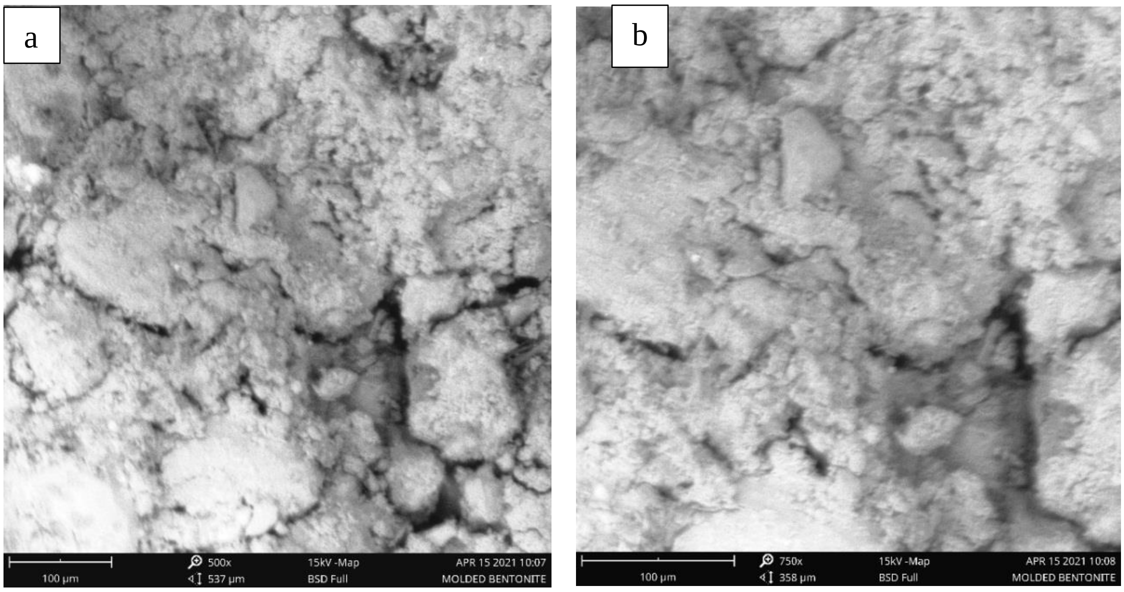


Figure 4.3: SEM image of untreated CTMABr modified bentonite at (a) 500x and (b) 750x

Figure 4.4 shows the SEM image of the acid pretreated CTMABr modified bentonite clay at different magnifications of 500 (a) and 750 (b) with pore development. Figure 4.4 (a) and (b) shows that acid pretreated CTMABr modified bentonite clay shows some pores development. The surface of the acid pretreated CTMABr modified bentonite clay was relatively flat and smooth; a regular and compact stacked lamellar structure was observed with slightly thicker lamellae and fewer pores. However, the structure of Acid-CTMABr organomodified bentonite clay were remarkably altered by developing more pores and cracks with more exfoliated, loose, and curled layers. The view from the side shows that there is a certain distance between the layers, accompanied by some sharp edges, and there are more fine particles between the layers. The surface morphology directly affects the adsorption capacity for organic pollutants such as crude oil. The surface morphology of acid pretreated CTMABr modified bentonite clay shows that oxalic acid pretreatment of the bentonite clay has impact on the surface morphology of the modified bentonite clay. The structure of acid pretreated CTMABr modified bentonite clay showed favorable channels and voids for adsorbing oil.

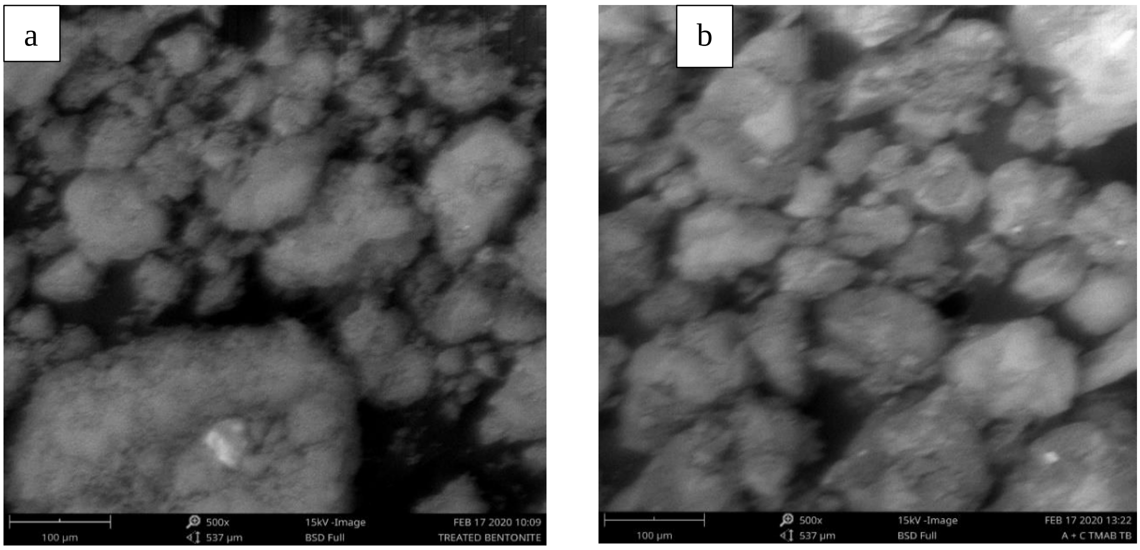


Figure 4.4: SEM image of acid pretreated CTMABr modified bentonite at (a) 500x and (b) 750x

The EDX analysis of the raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay was studied to determine the elemental composition of the adsorbents (Scimeca *et al.*, 2018). Table 4.2 shows the EDX results of the raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. It was observed from the elemental analysis that the raw bentonite contains 31.91 % Si, 12.41 % Al, 16.36 % Fe, 3.93 % K, 1.55 % Ti, 3.57 % Mg, 4.08 % Ag and 15.62 % Ca, untreated CTMABr modified bentonite contains 41.76 % Si, 17.29 % Al, 16.22 % Fe, 7.26 % K, 3.07 % Ti, 1.9 % Ag and 1.62 % Ca while acid pretreated CTMABr modified bentonite contains 51.05 % Si, 11.59 % Al, 9.74 % Fe, 7.18 % K, 0.68 % Ti, 4.3 % Ag and 2.73 % Ca. The high composition of Si and Al in both untreated and acid pretreated CTMABr modified bentonite clay further confirm the XRD result, that the modified bentonite clay constitute primary aluminum silicate material. Also, the high Ca content in the raw bentonite compared to that of untreated and acid pretreated CTMABr modified bentonite clay further indicates ion exchange between Ca and the CTMABr. However, it was observed that oxalic acid pretreated CTMABr modified bentonite clay has higher silicate content with lower alumna, Fe, K, Ti and Ag content. The reductions in acid pretreated CTMABr modified bentonite clay likely occurred as result of washing off of soluble salts of Al, Fe, K, Ti and Ag during the acid pretreatment with oxalic acid.

Table 4.2: EDX Analysis

Element Symbol	Element Name	Raw Bentonite	Untreated CTMABr Modified Bentonite	Acid Pretreated CTMABr Modified Bentonite
Si	Silicon	31.91	41.76	51.05
Al	Aluminium	12.41	17.29	11.59
Fe	Iron	16.36	16.22	9.74
K	Potassium	3.93	7.26	7.18
Ti	Titanium	1.55	3.07	0.68
Ag	Silver	4.08	1.95	4.3
Y	Yttrium	3.02	1.78	2.03
Ca	Calcium	15.62	1.63	2.73
Zr	Zirconium	2.08	1.54	–
Cr	Chromium	–	1.44	–
Mg	Magnesium	3.57	1.34	1.11
Nb	Niobium	1.97	1.3	3.57
S	Sulfur	2.23	1.3	1.15
Cl	Chlorine	–	1.28	–
Na	Sodium	0.37	0.84	0.38
P	Phosphorus	0.0	0	2.17
V	Vanadium	0.9	–	0.68
C	Carbon	–	–	1.19
O	Oxygen	–	–	0.45
Mn	Manganese	–	–	0

4.2.4 FTIR analysis

The FTIR is a measure of the organic and inorganic functional group present in a material. The FTIR spectrum of the raw bentonite, untreated and pretreated CTMABr modified bentonite clay are shown in Figure 4.5 and 4.7 respectively. The FTIR spectra of the raw bentonite clay is as shown in Figure 4.5. It was observed that band at 689.6 cm^{-1} indicates the presence of Si–O–Si and Si–O–Al bending vibration while the band at 726.8 cm^{-1} and 797.7 cm^{-1} are due to Si-O stretching and Si–O stretching vibration respectively that are attributed to the presence of quartz silicate montmorillonite and vermiculite phase in the bentonite (Fernández *et al.*, 2014). Also, the band at 875.9 cm^{-1} and 913.2 cm^{-1} are associated with Al–Al–OH vibrations, Si–O–Al stretching mode for montmorillonite and Al–Mg–OH in the structure of octahedral sheet of montmorillonite. The band in the region of 998.9cm^{-1} is due to Si-O stretching and out of plane Si–O–Si stretching mode for montmorillonite. This band indicate the presence of silicate type of montmorillonite and vermiculite.

From Figure 4.5, the band at 1438.8 cm^{-1} is due to Ca-O broad band vibration which is attributed to montmorillonite phase (Fernández *et al*., 2014), and the band at 1632.6 cm^{-1}, 3391.9 cm^{-1} and 3623 cm^{-1} are due to the –OH bending mode, –OH vibration and –OH stretching mode respectively for the interlayer adsorbed water in montmorillonite and vermiculite phase. This is consistent with OH band for water reported in the literatures (Fernández *et al*., 2014), Furthermore, the band at 3693.8 cm^{-1} is associated with O-H stretching vibrations in the Si-OH and Al-OH groups of the tetrahedral and octahedral sheets of montmorillonite and vermiculite phase of bentonite clay. This is consistent with the bands reported for Si-OH and Al-OH group of tetrahedral sheets of montmorillonite and vermiculite silicate (Fernández *et al*., 2014), This corroborate with the presence of montmorillonite and vermiculite in the bentonite clay established from XRD analysis.

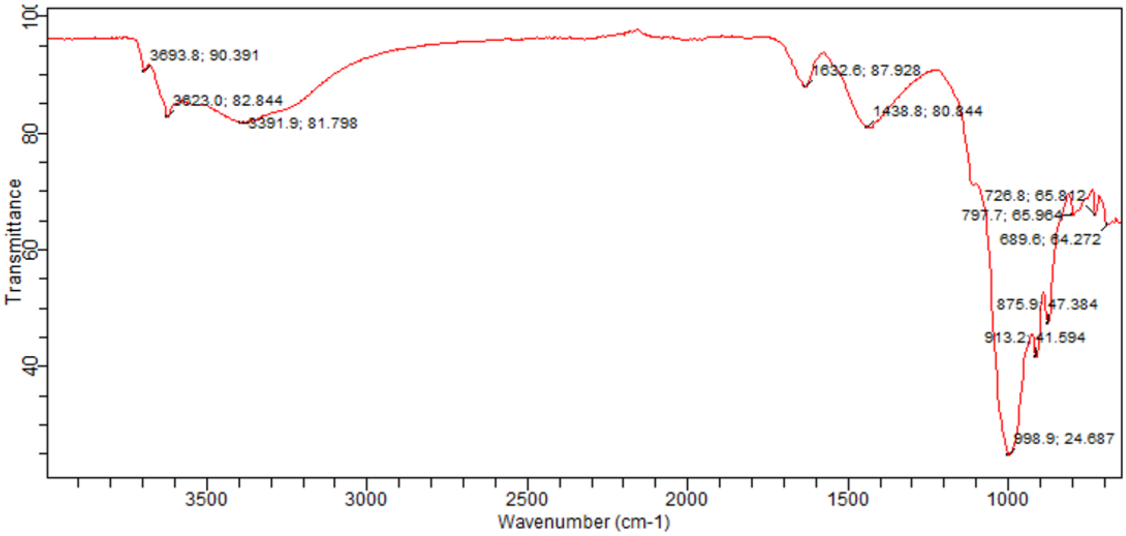


Figure 4.5: FTIR analysis of raw bentonite clay

Figure 4.6 and 4.7 presents the FTIR analysis of the pretreated and untreated CTMABr modified bentonite clay. It was observed that there was a change in the structural orderliness in the number and sharpness of peak with the oxalic acid pretreated CTMABr modified bentonite clay shown in Figure 4.6 compared to that of untreated CTMABr modified bentonite clay shown in Figure 4.7. It is known that the main infrared characteristic peaks of quartz, albite and microcline occur at 400 –1300 cm^{-1} (Ravisankar *et al.*, 2010, Zhang *et al*, 2019). In this range, there were similar bands in the range of 650 – 700 cm^{-1} in the acid pretreated CTMABr (689 cm^{-1}) and untreated CTMABr (678 cm^{-1}) modified bentonite clay. These peaks indicated the presence of Si-O-Si bending vibration and the coupling between the O–Si–O deformation stretching (Wang *et al.*, 2015).

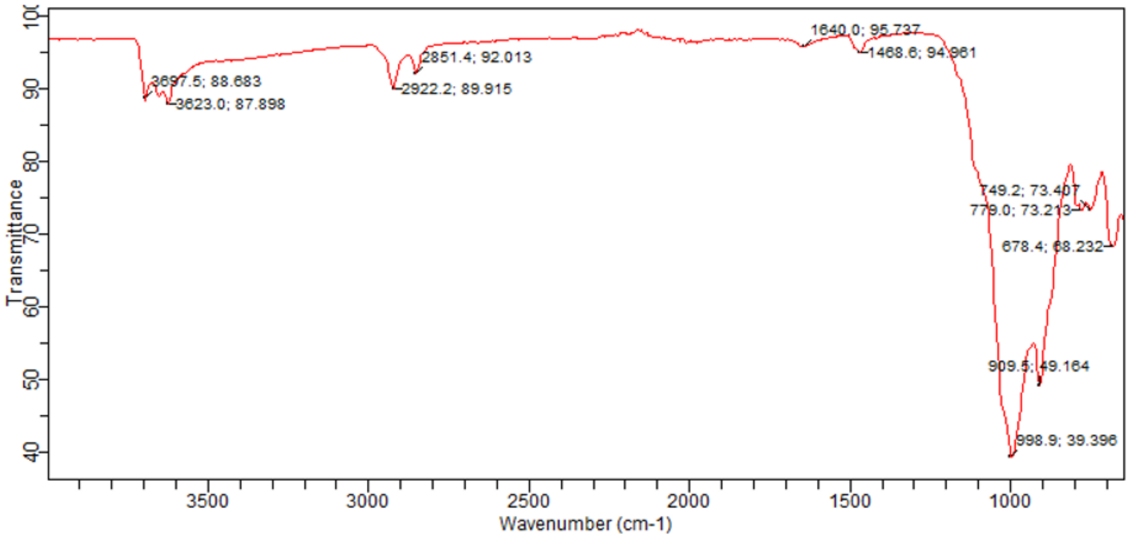


Figure 4.6: FTIR analysis of acid pretreated CTMABr modified bentonite clay

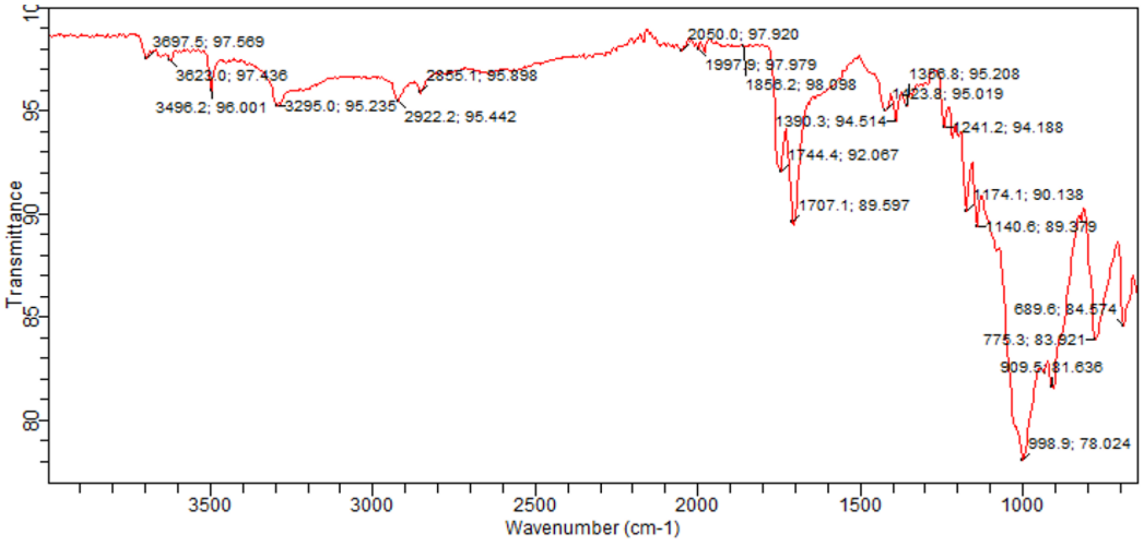


Figure 4.7: FTIR analysis of untreated CTMABr modified bentonite clay

The band between 740 – 800 cm^{-1} indicated the Si-O-Al, particularly 779 cm^{-1} for acid pretreated CTMABr (Figure 4.6) and 775 cm^{-1} for untreated CTMABr (Figure 4.7) modified bentonite clay, and the band between 900 – 1100 cm^{-1}, particularly the peak at 909 cm^{-1} and 998 cm^{-1} for both acid pretreated CTMABr and untreated CTMABr modified bentonite clay indicated Si-O symmetric bond stretching. The peak centered at 1640 cm^{-1} for acid pretreated CTMABr (Figure 4.6) and 1707 cm^{-1} for untreated CTMABr (Figure 4.7) modified bentonite clay correspond to the bending and stretching vibrations of O-H and C–N group (Zhang *et al*, 2019). This meant that there were H-bonded hydroxyls and physically adsorbed water attached as well as amine presence on the organomodified bentonite clay surfaces. The band between 2800 – 3000 cm^{-1}, particularly 2851 cm^{-1} and 2922 cm^{-1} for acid pretreated CTMABr (Figure 4.6) and that between 2855 cm^{-1} and 2922 cm^{-1} for untreated CTMABr (Figure 4.7) modified bentonite clay, indicates C-H stretch for amine and methyl C=O for acid respectively. The bands located at 3697 cm^{-1} and 3623 cm^{-1} for acid pretreated CTMABr and untreated CTMABr modified bentonite clay are the typical indications of inner-surface hydroxyls (O-H) group and the one at 3623 is attributed to the stretching frequency of the internal hydroxyl groups and N-H amine group. These bands confirm the intercalation of alkylammonium in the interlayer of galleries of the bentonite clay mineral (Zhang *et al.*, 2019).

4.2.5 Brunauer–emmett–teller (BET) analysis

Micro porosity of adsorbent materials is significant into the effectiveness of an adsorbent, as such, the surface area and pore size of the raw bentonite, oxalic acid pretreated CTMABr and untreated CTMABr modified bentonite clay material is a fundamental criterion for effective crude oil pollutant removal. The BET technique was used to evaluate the total pores surface area and volume using Quantachrome instrument. The BET analysis was also used to evaluate the cumulative adsorption surface area and volume of the meso and macropores of the raw bentonite acid pretreated CTMABr and untreated CTMABr modified bentonite adsorbent materials while the t-method was used to examine the external surface area and the DR method to examine the micropore area. According to International Union of Pure and Applied Chemistry (IUPAC), porosity is classified into three different groups of pore sizes which are micropores (width < 2 nm), mesopores (width: 2 – 50 nm) and macropores (width > 50 nm) (Zhang *et al.*, 2019). Table 4.3 present the BET surface area analysis of the raw bentonite, acid pretreated CTMABr and untreated CTMABr modified bentonite clay adsorbent.

Table 4.3: BET Surface Area Analysis

Adsorbent	**BET (m^2/g)**	**Pore Volume (cm^3/g)**	**Pore Size (nm)**
Raw Bentonite	513.8	0.2590	2.027
Untreated CTMABr modified bentonite clay	528.7	0.2566	2.046
Acid pre-treated CTMABr modified bentonite clay	566.9	0.2665	2.132
Park (2013) and Huggett (2015)	750	0.1833	1.383

Table 4.3 present the surface area, pore volume and pore size of the raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. The BET surface area for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay are 513.8 m^2/g, 528.7 m^2/g and 566.9 m^2/g respectively. Slight increase in surface area was noticed with the untreated CTMABr modified bentonite clay while a significant increase in acid pretreated CTMABr modified bentonite clay was noticed compared to that of the raw bentonite clay. This could be due to the fact that oxalic acid pretreatment enhances the pore development and high amorphous formation in the modified bentonite clay adsorbent crystal structure which conform with the XRD analysis. The specific surface area of 513.8 m^2/g, 528.7 m^2/g and 566.9 m^2/g obtained for raw bentonite, untreated CTMABr modified bentonite and acid pretreated CTMABr modified bentonite clay respectively are lower compared to 750 m^2/g reported for raw bentonite in the literature (Park, 2013, Huggett, 2015). The specific surface area of oxalic acid pretreated CTMABr modified bentonite clay (566.9 m^2/g) was observed to be higher than that of untreated CTMABr modified bentonite clay (528.7 m^2/g) which could be attributed to the enhancement of pore development by oxalic acid pretreatment. However, raw bentonite was observed to have the lest specific surface area of 513.8 m^2/g compared to that of untreated and acid pretreated CTMABr modified bentonite clay. The high surface area of 750 m^2/g reported by Park (2013) for

montmorillonite, compared to that obtained in this study could be attributed to the source of the raw bentonite clay as the 750 m^2/g was reported for bentonite sourced from Morocco.

Pore volume an adsorbent is another crucial parameter of adsorbent materials. From Table 4.3, substantiating the adsorption surface area of the adsorbents is the micropore volume of the raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. It was observed that the pore volume of the raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay are 0.2590 m^3/g, 0.2665 m^3/g and 0.2566 m^3/g respectively. The poe volume of the untreated CTMABr organomodified bentonite clay was found to be slightly less than that of the raw bentonite which could be attributed to the slight reduction in the degree of crystallinity of the untreated CTMABr modified bentonite clay from the XRD analysis while that of acid pretreated CTMABr modified bentonite clay increase. This further shows that acid pretreated CTMABr modified bentonite clay adsorbent possess higher adsorption capacity than raw bentonite and untreated CTMABr modified bentonite clay. This could be attributed to the high development of the pores in acid pretreated CTMABr modified bentonite clay adsorbent compared to that in obtainable for raw bentonite and untreated CTMABr modified bentonite clay.

The pore size of adsorbent is also another significant parameter that give insight to the adsorption capacity of an adsorbents. From Table 4.3, the pores diameter of the raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay are 2.027 nm, 2.132 nm and 2.046 nm respectively which are mostly in the range of mesoporous pore size 2 – 50 nm classification by IUPAC (Guo *et al.*, 2014, Zhang *et al.*, 2019).).

These observations show that acid pretreatment of bentonite clay modified with CTMABr result in enhanced surface structure of the adsorbent. It also indicates that adsorption would take place mainly in the mesopores, as mesopores are important and also help in transport of fluids to and from the micropores present. Hence, from the adsorbent characterization, it can be concluded that acid pretreatment of bentonite clay modified with CTMABr will result in higher adsorption capacity compared to untreated CTMABr modified bentonite clay and raw bentonite clay as adsorbent.

4.2.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of raw, oxalic acid pretreated and untreated CTMABr modified bentonite clay was carried out and the TGA curves of the raw and CTMABr modified bentonite clay adsorbent is as shown in Figure 4.8. The TGA curve of the raw, oxalic acid pretreated and untreated CTMABr modified bentonite clay decomposition began at 28 °C with a corresponding weight percent of 99.99 for raw bentonite, 99.99 for acid pretreated CTMABr modified bentonite clay and 99.85 for untreated CTMABr modified bentonite clay and the TGA curve shows gradual decomposition at different temperatures for raw, oxalic acid pretreated and untreated CTMABr modified bentonite clay. At 400 ^{o}C, raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay experienced 19.57 %, 1.50 % and 12.51 % loss respectively.

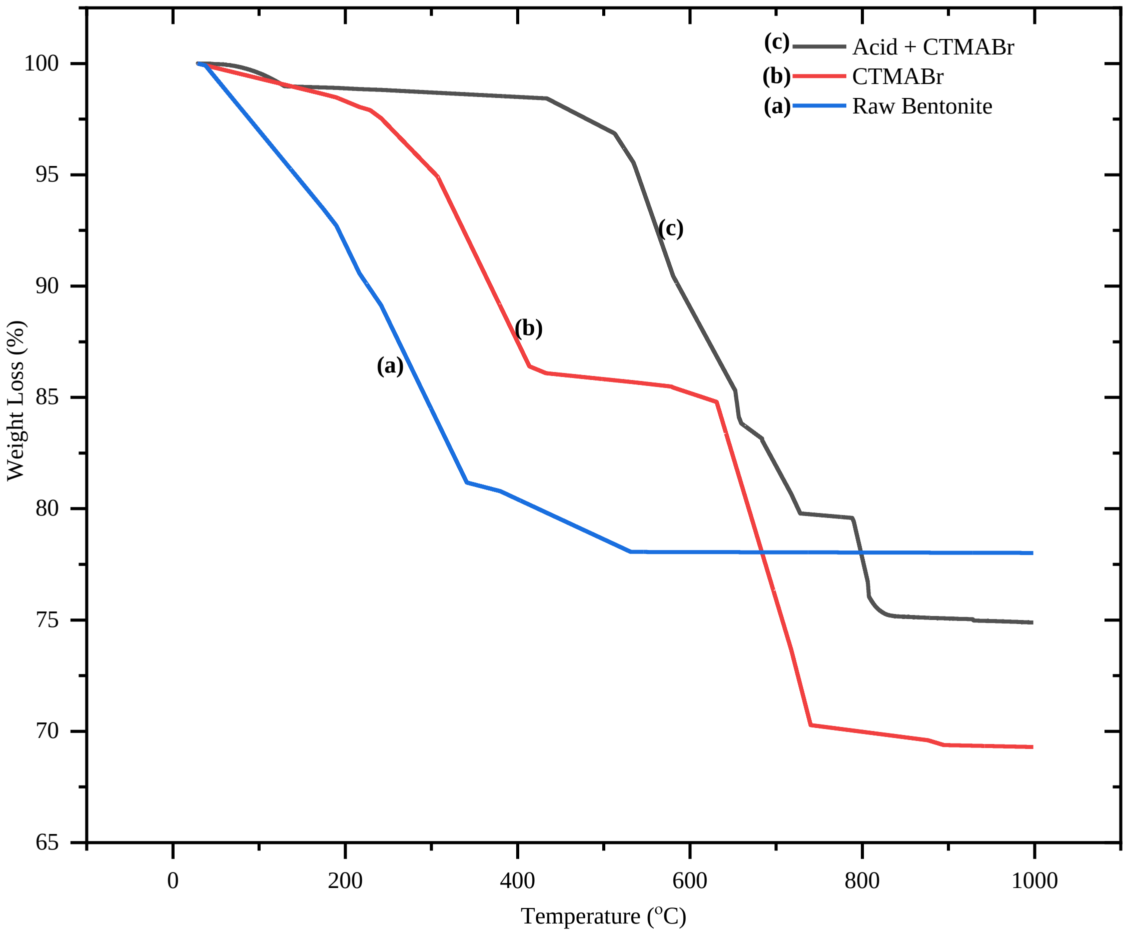


Figure 4.8: TGA curves of (a) raw bentonite, (b) untreated CTMABr modified bentonite and (c) pretreated CTMABr modified bentonite clay

Between 400 °C and 700 °C, raw, oxalic acid pretreated and untreated CTMABr modified bentonite clay adsorbent exhibits decomposition of 2.38 %, 16.58 % and 11.57 % weight loss while raw bentonite experiences no weight loss till 1000 °C. However, acid pretreated and untreated CTMABr modified bentonite clay shows a weight loss of 5.625 % and 2.1698 % until 740 °C and the untreated CTMABr modified bentonite clay almost no weight loss still 1000 °C while a sharp loss of 4.45% was observed in the temperature range of 800 – 840 °C and no significant loss was observed as temperature rises to 1000 °C for acid pretreated CTMABr modified bentonite clay, indicating equilibrium decomposition was attained at about 600 °C for raw bentonite, 800 °C for acid pretreated CTMABr modified bentonite clay and 740 °C for untreated CTMABr modified bentonite clay. The losses experienced by the adsorbent could be attributed to surface water loss and dehydration of the adsorbent materials (Aroke *et al.*, 2014; Aroke and Hamidu, 2020).

The TGA traces of raw, oxalic acid pretreated and untreated CTMABr modified bentonite clay adsorbent show two peaks, the first, in the temperature range of 30 – 540 °C, which corresponds to the dehydration of adsorbed water and interlayer water and the second peak observed between 540 – 840 °C show that the decomposition of other liquid/water molecules in the raw, oxalic acid pretreated and untreated CTMABr modified bentonite clay adsorbents structure started at 540 ^{o}C for raw bentonite, 780 °C for acid pretreated CTMABr modified bentonite clay and 630 ^{o}C for untreated CTMABr modified bentonite clay and was completed at 840 °C. The results are in general agreement with similar behavior was observed by (Boumediene *et al.*, 2016, Aroke and Hamidu, 2020).

4.3 Adsorption Study

The raw bentonite, pretreated and untreated CTMABr modified bentonite clay was used to investigate adsorption of crude oil from polluted water collected from Ejama-Ebubu, Eleme LGA in Rivers State. Details of the results of the polluted water analysis using UV spectrophotometer before and after treatment at the varying adsorption conditions are presented in Appendix A. The initial concentration of crude oil in the polluted water was determined using Spectrophotometry analysis as 53.21 mg/L which is comparable to 52.22 mg/L reported by United Nations Environment Programme (2011). This value is higher than acceptable limit for ground and surface water. Adsorption study was carried out to determine the effect of variation in contact time, temperature, adsorbent dosage, pH and concentration on the adsorption efficiency of raw bentonite, pretreated and untreated CTMABr modified bentonite clay.

4.3.1 Effect of contact time on adsorption of crude oil

The effect of contact time on the adsorptive capacity of raw bentonite, pretreated and untreated CTMABr modified bentonite clay was investigated. Figure 4.9 shows the effect of contact time on the percentage removal of crude oil from the waste effluent using raw bentonite, pretreated and untreated CTMABr modified bentonite clay as adsorbents. The contact time was varied between 0 – 60 min at constant adsorbent dosage of 2 g, 29.8 °C temperature, 8.36 pH, raw effluent concentration and mixing rate of 900 rpm. From Figure 4.9, it was observed that the percentage removal of crude oil from the polluted water rise rapidly and linearly to 28.92 % for raw, 60.83 % for acid pretreated CTMABr modified and 59.04 % for untreated CTMABr modified bentonite clay as contact time increases 0 – 10 min.

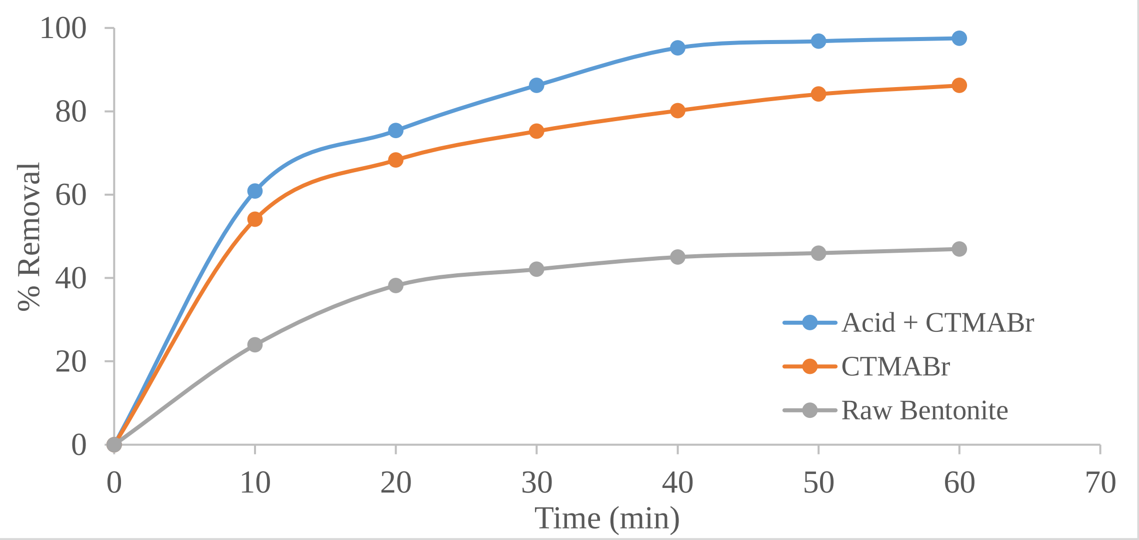


Figure 4.9: Effect of contact time on raw, acid pretreated and untreated CTMABr modified bentonite clay removal efficiency

However, from 10 – 50 min, it can be seen that the rate of crude oil removal from the polluted water rises slowly 28.92 – 46.97 % for raw, 60.83 – 96.81 % for acid pretreated CTMABr modified and 59.04 – 82.09 % for untreated CTMABr modified bentonite clay and while from 50 – 60 min, the rate of crude oil removal from the polluted water remain almost constant at a maximum percentage removal of 46.96 %, 86.17 % and 97.52 % for raw, acid pretreated CTMABr modified and untreated CTMABr modified bentonite clay respectively. It could be inferred that equilibrium is reached at about 50 min adsorption time for raw, acid pretreated CTMABr modified and untreated CTMABr modified bentonite.

It can be seen that the modification of bentonite clay using CTMABr enhances the adsorption capacity of bentonite in removing crude oil constituent from water. This indicates, that pretreatment of the bentonite clay with organic acid such as oxalic acid could increase the adsorptive properties of the organomodified bentonite clay. This is because cation surfactant retention occurs within the interlayer space of bentonite clay minerals after modification resulting in an increase of the basal spacing which provides an increase in the tendency of the adsorbents to adsorb organic molecules (Parolo *et al.*, 2014, Foroutan *et al.*, 2018, Hokkanen *et al.*, 2018, Momina *et al.*, 2018). Also, the oxalic acid pretreatment of CTMABr modified bentonite clay further enhances the removal efficiency of acid pretreated CTMABr modified bentonite clay compared to the untreated CTMABr modified bentonite clay.

Hence, increase in contact time beyond 45 min does not have significant effect on the percentage removal of crude oil constituent in polluted water. This showed that further increase in contact time above 40 min resulted in the adsorption sites getting saturated gradually and the uptake rate will be controlled by the rate at which the adsorbates (crude oil) is transported from the exterior to the interior sites of the raw and organomodified bentonite clay adsorbents, thus, the adsorption became much slower (Gulistan *et al*., 2011). Also, the high removal of crude oil from the polluted water could also be attributed to higher ion exchange observed with acid pretreated CTMABr modified bentonite clay followed by untreated CTMABr modified bentonite clay while the lowest pollutant removal was observed with raw bentonite clay due to the fact that no ion exchange takes place (William, 2012). This shows that pretreatment of bentonite clay before modification with CTMABr improves the adsorption capacity of organomodified bentonite clay.

4.3.2 Effect of temperature on adsorption of crude oil

The influence of temperature on the adsorptive capacity of raw, acid pretreated CTMABr modified and untreated CTMABr modified bentonite clay was investigated as well. Figure 4.10 shows the effect of temperature from on the percentage removal of crude oil from the polluted water using raw, acid pretreated CTMABr modified and untreated CTMABr modified bentonite clay adsorbents. The temperature was varied between 25 – 75 ^{o}C at constant time of 40 min, 900 rpm mixing speed, 2 g adsorbents and pH of 8.36. It was observed that there was rapid increase in the percentage removal of crude oil to 53.78 % for raw bentonite, 86.70 % for acid pretreated CTMABr modified and 80.82 % untreated CTMABr modified bentonite clay as temperature rises from 0 – 45 ^{o}C. The rapid rise in percentage removal could be attributed to the availability of sufficient adsorption site as the temperature rises (Emam, 2013, El-Zahhar and Al-Hazmi, 2015).

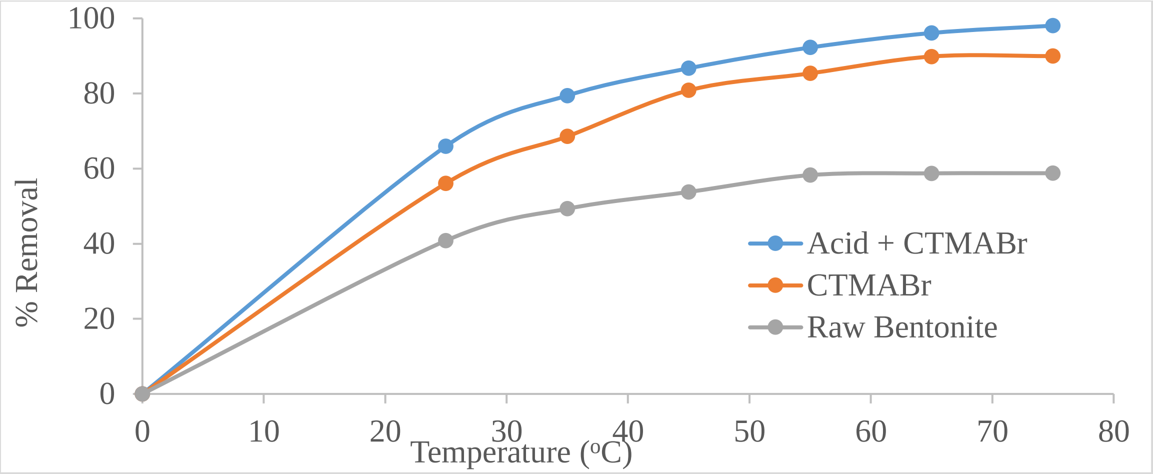


Figure 4.10 Effect of temperature on raw, acid pretreated and untreated CTMABr modified bentonite clay percentage removal

Furthermore, it can be seen that, rise in temperature from 45 – 55 ºC show a very slow rise in removal efficiency of raw and untreated CTMABr modified bentonite clay to 58.26 % and 89.11 % removal respectively and then remains almost constant at a maximum value of 58.77 % and 89.95 % for raw and untreated CTMABr modified bentonite clay respectively as the temperature rises from 55 – 75 ºC whereas, that of acid pretreated CTMABr modified bentonite clay rises to 96.10 % as temperature rises from 45 – 65 ºC and remains almost constant at a maximum value of 98. 05 % as temperature rises from 65 – 75 ºC. The slow rise in percentage removal of crude oil from the contaminated water between 55 – 75 ºC could be attributed to the fact that the adsorption site is almost filled up and saturated. This shows that the rate of adsorption of crude oil into the pores of raw, pretreated and untreated CTMABr modified bentonite clay were enhanced with rise in temperature which could be attributed to the fact that at higher temperature, the molecule of the crude oil gets lighter and could move freely and fast in to the pores of the adsorbent. Hence, increase in temperature, increases adsorption capacity of raw, pretreated and untreated CTMABr modified bentonite clay.

4.3.3 Effect of adsorbent dosage on adsorption of crude oil

The effect oof adsorbent dosage on the adsorptive capacity of raw, pretreated and untreated CTMABr modified bentonite clay was investigated. Figure 4.11 shows the effect of variation of adsorbent dosage on the percentage removal of crude oil from contaminated water using raw, pretreated and untreated CTMABr modified bentonite clay. The adsorbent dosage was varied between 0.5 – 3g at constant time of 40 min, initial concentration of contaminated water, 8.36 pH, mixing speed of 900 rpm and temperature of 35 ^{o}C. It was observed that the percentage removal crude oil using from contaminated water using raw, pretreated and untreated CTMABr modified bentonite clay rises rapidly to 67.93 %, 94.86 % and 89.86 % respectively as the adsorbent dosage increase from 0 – 2.5 g and then remains almost constant at 67.99 %, 95.04 % and 90.35 % re respectively as the adsorbent dosage rises from 2.5 – 3 g.

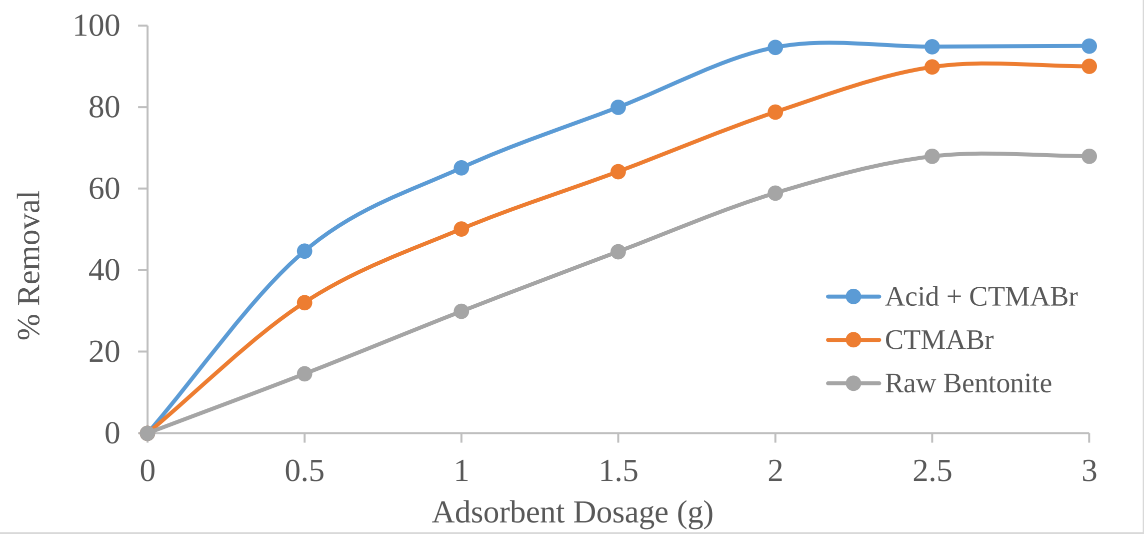


Figure 4.11 Effect of adsorbent dosage on raw, acid pretreated and untreated CTMABr modified bentonite clay removal efficiency

The rapid rise in percentage removal for raw, pretreated and untreated CTMABr modified bentonite clay as adsorbent dosage increases from 0 – 2.5 g could be attributed to the high number of adsorption sites per unit mass of adsorbents (Emam, 2013, Gandhi *et al*., 2014, El-Zahhar and Al-Hazmi, 2015). However, the almost constant and same percentage removal observed between 2.5 – 3 g of adsorbent dosage could be explained by the fact that, at low adsorbent dosage, the adsorption sites are diluted in the solution and available for interaction with crude oil from the polluted water while at high adsorbent dosage no significant removal due to possible aggregation of adsorbent in the polluted water (Emam, 2013; El-Zahhar and Al-Hazmi, 2015). Consequently, the availability of free adsorption sites is limited for removal of crude oil.

4.3.4 Effect of pH solution on the adsorption of crude oil

The influence of pH on the adsorptive capacity of raw, pretreated and untreated CTMABr modified bentonite clay was investigated. The pH of a solution is one of the significant parameter when considering adsorption capacity from contaminated water because, the pH of an aqueous solution controls the adsorption capacity due to its influence on the surface properties of the adsorbent (Emam, 2013). Figure 4.12 shows the effect of variation in pH on the percentage removal of crude oil from the polluted water. The pH was varied between 4 – 10 at constant time of 40 min, constant initial concentration of crude oil in the contaminated water, 2 g adsorbent dosage and 35 ^{o}C temperature.

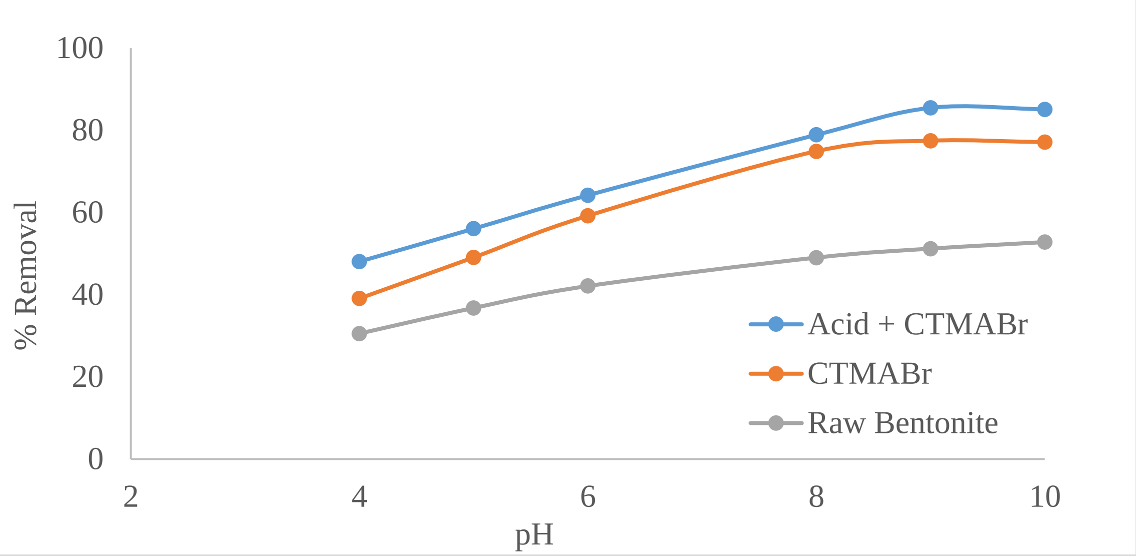


Figure 4.12 Effect of pH on raw, acid pretreated and untreated CTMABr modified bentonite clay removal efficiency

It was observed that, the percentage removal of crude oil using raw, pretreated and untreated CTMABr modified bentonite clay increases rapidly and almost linearly to 51.20 %, 85.46 % and 77.47 % respectively as the pH increases from 4 – 9, and tends to remain almost constant at a maximum value of 52.80 %, 85.11 % and 77.12 % for raw, pretreated and untreated CTMABr modified bentonite clay respectively as the pH rises from 9 – 10. The maximum percentage removal occurred at 9 (alkaline medium) raw, pretreated and untreated CTMABr modified bentooite clay adsorbent. The increase in crude oil percentage removal with increase in pH is attributed to the fact that the surface functional groups of the raw, pretreated and untreated CTMABr modified bentonite clay ionizes which results in greater retentive power to wards the crude oil adsorbate (Emam, 2013, Aroke *et al*., 2016).

4.3.5 Effect of initial concentration on adsorption of crude oil

The effect of initial concentration on the adsorptive capacity of raw, acid pretreated and untreated CTMABr modified bentonite clay was also investigated. The initial concentration of the solution has been found to impact adsorption capacity of adsorbent. Figure 4.13 shows the effect of initial concentration on the percentage removal of crude oil pollutant from the polluted water. The initial concentration was varied from 0.05 – 0.30 mg/L at constant time, pH, dosage and temperature. It was observed that, the removal of crude oil using raw, acid pretreated and untreated CTMABr modified bentonite clay increases rapidly to 43.18 %, 62.77 % and 59.56 % for raw, acid pretreated and untreated CTMABr modified bentonite clay respectively from an initial concentration of 0.05 – 0. 10 mg/L.

The high percentage removal at the initial concentration of 0.05 – 0.1 mg/mL could be attributed to the high number of adsorption sites available at the initial adsorption stage (Gandhi *et al.*, 2014). However, the percentage removal remains constant for raw bentonite clay as the concentration increases from 0.1 – 0.3 mg/mL while the percentage removal for acid pretreated and untreated CTMABr modified bentonite clay rises very slowly to 83.51 % and 78.30 % for acid pretreated and untreated CTMABr modified bentonite clay respectively and remains almost constant at a maximum concentration of 83.87 % and 78.66 % respectively.

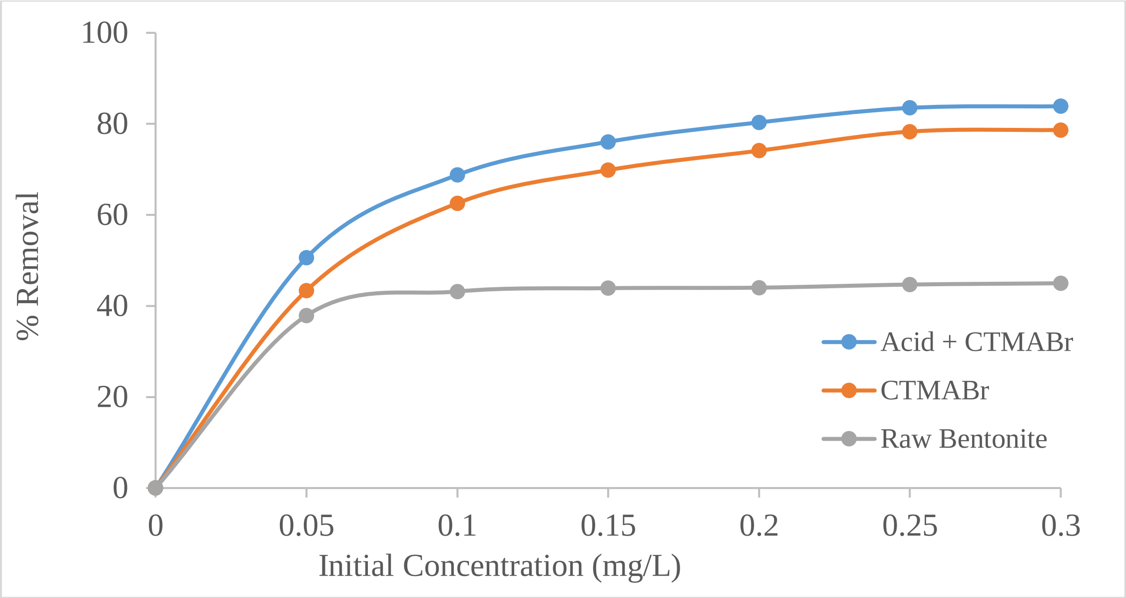


Figure 4.13 Effect of initial concentration on raw, acid pretreated and untreated CTMABr modified bentonite clay removal efficiency

The slow rise in the percentage removal of crude oil as the initial concentration increases from 0.10 – 0.25 mg/L is because the adsorption sites become saturated gradually as initial concentration increases and the uptake rate will be controlled by the rate at which the adsorbates is transported from the exterior to the interior sites of the raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent and as such, the adsorption became much slower (Talaat *et al*., 2011). Hence, the number of free adsorption sites tends to decease, under this condition and the percentage of crude oil removed tends to reached equilibrium when no further uptake of the adsorbate was observed.

4.4 Adsorption Isotherm

The adsorption isotherm of the raw, pretreated and untreated CTMABr modified bentonite clay adsorbent was investigated to describes the equilibrium of the adsorption material at the surface of adsorbent and, particularly at the surface boundary at constant temperature. The isotherm model considered in this study are Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich and Redlich-Peterson isotherm models which are presented and discussed subsequently.

4.4.1 Freundlich isotherm

Freundlich isotherm model was used to investigated the surface heterogeneity and relative distribution of energy of the adsorbate site of the adsorption of raw, pretreated and untreated CTMABr modified bentonite clay adsorbent at constant temperature. Figure 4.14 presents the plot of the Freundlich isotherm model for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent for the removal of crude oil from the polluted water. The study shows that the experimental data for acid pretreated and untreated CTMABr modified bentonite clay adsorbent fits well with the Freundlich isotherm model with a R^2 value of 0.9871 and 0.9832, indicating that 98.71 % ($R^2 = 0.9871$) and 98.32 % ($R^2 = 0.9832$) of the experimental data can be explained by the Freundlich isotherm model for acid pretreated and untreated CTMABr modified bentonite clay. Similarly, the raw bentonite relatively fits well with the Freundlich isotherm model with a R^2 value of 0.9611 (96.11 %).

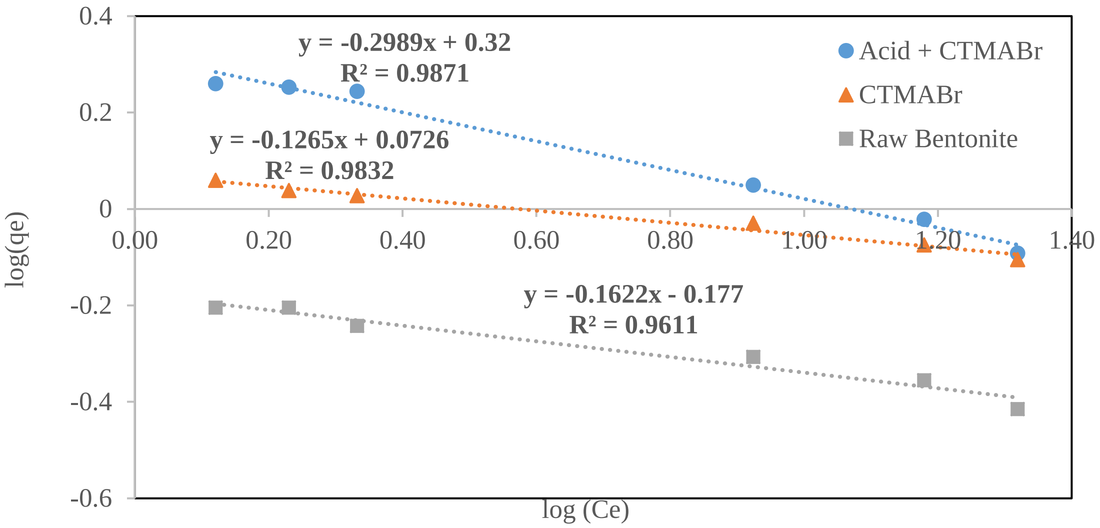


Figure 4.14: Freundlich isotherm model for adsorption of crude oil pollutant

From Table 4, the slope, 1/n, which is a measure of adsorption intensity or surface heterogeneity was found for raw, acid pretreated and untreated CTMABr modified bentonite clay to be – 0.1622, – 0.2989 and – 0.1265 respectively. A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption (Okoli, 2014). The value of 1/n obtained in this study is below 1, indicating the raw, acid pretreated and untreated CTMABr modified bentonite clay is favorable for adsorption of crude oil under conditions used in this study and further indicated that adsorption is the predominant process taking place.

Table 4.4: Freundlich isotherm model parameter

Parameters	Acid + CTMABr	CTMABr	Raw Bentonite
1/n	– 0.2989	– 0.1265	–0.1622
K_f, L/mg	1.3772	1.0752	0.8378
R^2	0.9871	0.9832	0.9611

4.4.2 Langmuir isotherm

Langmuir isotherm model was used to investigated the surface equilibrium of the of raw, pretreated and untreated CTMABr modified bentonite clay adsorbent at constant temperature. Figure 4.15 presents the plot of the Langmuir isotherm model for of raw, pretreated and untreated CTMABr modified bentonite clay adsorbent for the removal of crude oil from the polluted water. The study shows that the experimental data for of raw, pretreated and untreated CTMABr modified bentonite clay adsorbent fairly fits the Langmuir isotherm model with a R^2 value of 0.8152, 0.6804 and 0.8685 and indicating that and 81.52 % (R^2 = 0.8192), 68.04 % (R^2 = 0.6804) and 86.85 % (R^2 = 0.8685) of the experimental data can be explained by the Langmuir isotherm model for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent respectively.

Table 4.5 present the model parameters, K_L and q_m for Langmuir isotherm which are the adsorption equilibrium constant (L/mg) and monolayer adsorption capacity of the adsorbent (mg/g) and their values computed from the slopes and intercepts of the Langmuir plots (Figure 4.15). The Langmuir isotherm model parameter for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent respectively are presented in Table 4.5. The negative nature of the value for the adsorption equilibrium constant (k_L) for the adsorption of crude oil pollutant onto the raw, pretreated and untreated CTMABr modified bentonite clay adsorbent respectively is because the adsorption of the crude oil into the adsorbent didn’t fit well with the Langmuir model which results in the low values for the monolayer coverage (q_m). Therefore, the adsorption of crude oil in by raw, pretreated and untreated CTMABr modified bentonite clay adsorbent was found to fit better with Freundlich isotherm model compared to Langmuir isotherm model.

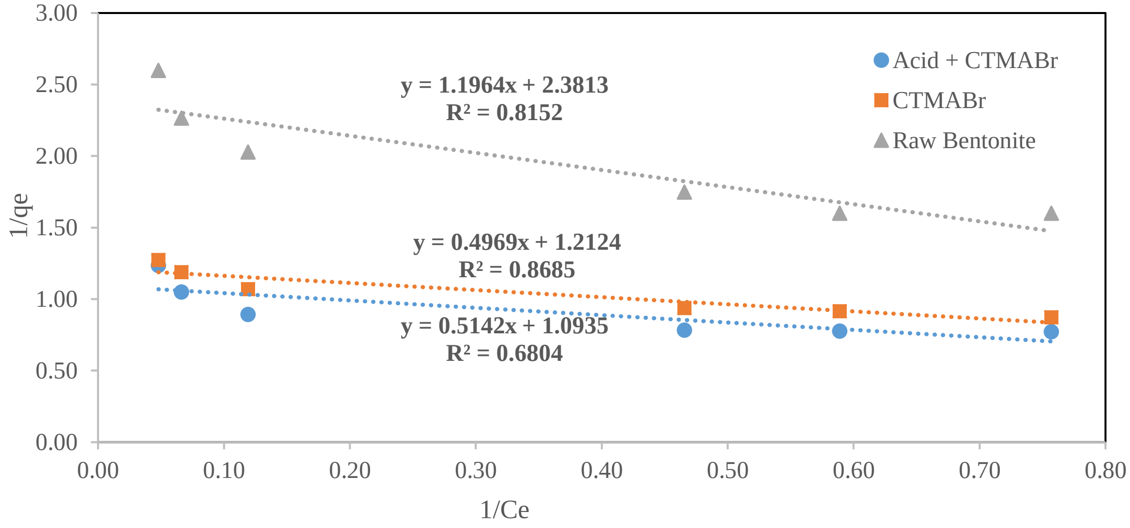


Figure 4.15: Langmuir isotherm model for adsorption of crude oil pollutant

Also, from Table 4.5, R_L, which is indicative of the isotherm shape that shows whether an adsorption system is favourable or unfavourable was determined as 0.0094, 0.0088 and 0.0078 for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. According to Aroke *et al*. (2015), there are four probabilities for the R_L value, adsorption nature to is unfavourable ($R_L>1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L value for crude oil removal by raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent are all in the rage of 0 – 1, indicating the adsorption process favours Langmuir model. However, the R^2 value obtained are slightly higher (0.6 – 0.82), suggesting that Langmuir model fairly fit well with experimental data.

Table 4.5: Langmuir isotherm model parameter

Parameters	Acid + CTMABr	CTMABr	Raw Bentonite
q_m, mg/g	0.9145	0.8248	0.4199
K_L, mg/g	2.1267	2.4397	1.9904
R_L	0.0088	0.0078	0.0095
R^2	0.6804	0.8685	0.8152

4.4.3 Tempkin isotherm

Tempkin isotherm model was used to investigated the effects of indirect adsorbate/adsorbate interactions on the adsorption process of the raw, pretreated and untreated CTMABr modified bentonite clay adsorbent at constant temperature. Figure 4.16 presents the plot of the Tempkin isotherm model for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent for the removal of crude oil from the polluted water. The study shows that the experimental data for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent fits well with the Tempkin isotherm model with R^2 value of 0.9739, 0.9260 and 0.9891, indicating that 97.39 % (R^2 = 0.9739), 92.60 % (R^2 = 0.9260) and 98.91 % (R^2 = 0.9891) of the experimental data can be explained by the Tempkin isotherm model for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent respectively.

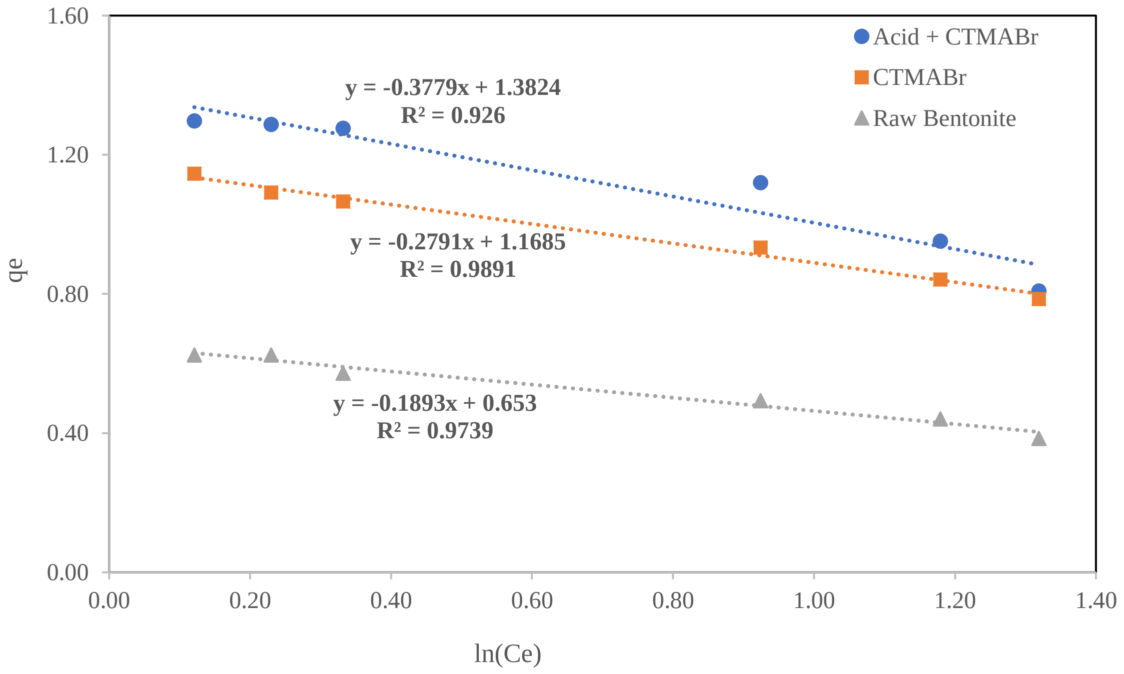


Figure 4.16: Tempkin isotherm model for adsorption of crude oil

Table 4.6 present the isotherm model parameters for the raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. From Table 4.6, the Temkin constant which is related to heat of adsorption (ΔH_{ads}) are determined as 13529.338 J/mol, – 6776.003 J/mol and – 9175.6817 J/mol which is related to the heat that is to released or require when an adsorptive bind to or detaches from the solid surface of an adsorbent (Gulistan *et al.*, 2017). Hence the negative sigh shows the that heat is been released. It was observed that high amount of heat will be required to be released by the raw bentonite for adsorption to take place, this also attest to the low crude oil removal rate observed in this study for raw bentonite due to the high heat required for adsorption to take place.

Table 4.6: Tempkin isotherm model parameters

Parameters	**Acid + CTMABr**	**CTMABr**	**Raw Bentonite**
b, kJ/mol	– 6.7760	– 9.1757	– 13.5293
K_T, L/g	0.0002	0.0001	0.0004
R^2	0.9260	0.9891	0.9739

4.4.4 Dubinin-Radushkevich isotherm

Dubinin-Radushkevich isotherm model which is an empirical adsorption model that is generally applied to express adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces (Gulistan *et al.*, 2017), was used to investigated using raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. Figure 4.17 presents the plot of the Dubinin-Radushkevich isotherm model for of raw, pretreated and untreated CTMABr modified bentonite clay adsorbent for the removal of crude oil from the polluted water. The study shows that the experimental data for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent fits fairly well with the Dubinin-Radushkevich isotherm model with a R^2 value of 0.7838, 0.7961 and 0.8278, indicating that 78.38 % (R^2 = 0.7838), 79.61 % (R^2 = 0.7961) and 82.78 % (R^2 = 0.8278) of the experimental data can be explained by the Dubinin-Radushkevich isotherm model for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent respectively.

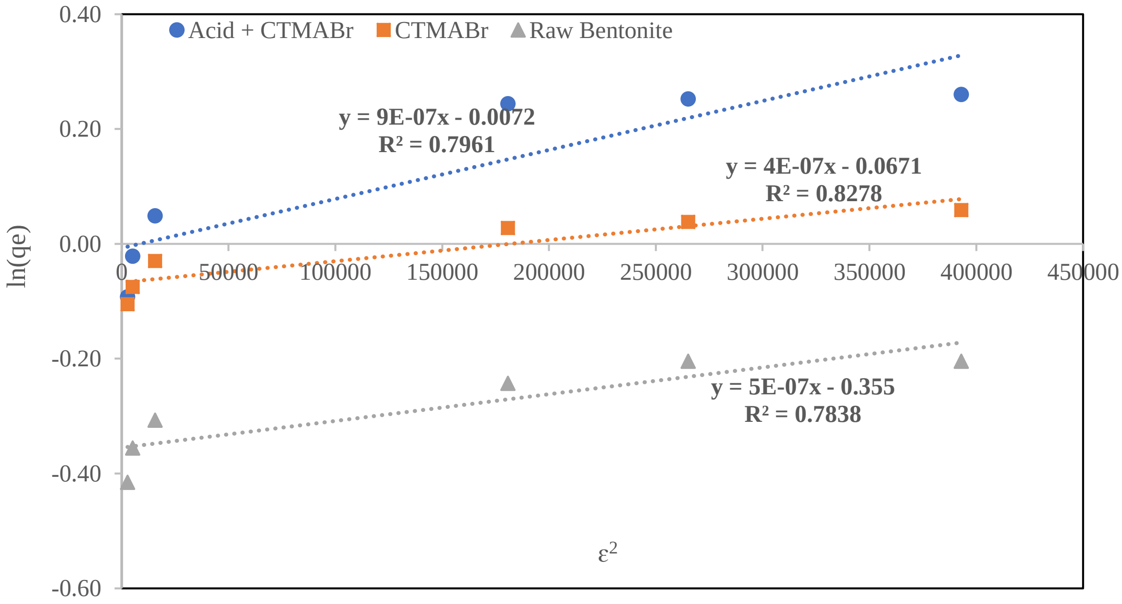


Figure 4.17: Dubinin-Radushkevich isotherm model for adsorption of crude oil

Table 4.7 present Dubinin-Radushkevich the isotherm model parameters for the raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. From Table 4.7, presents the Dubinin-Radushkevich constant for crude oil adsorption into raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent.

Table 4.7: Dubinin-Radushkevich isotherm model parameters

Parameters	**Acid + CTMABr**	**CTMABr**	**Raw Bentonite**
β	8.54×10^{-7}	3.69×10^{-7}	4.66×10^{-7}
q_m, mg/g	0.9836	0.8569	0.4416
R^2	0.7961	0.8278	0.7838

4.4.5 Redlich-Peterson isotherm

Redlich-Peterson isotherm model which is a mix of the Langmuir and Freundlich isotherms model (Gulistan *et al*., 2017), was used to investigated using raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. Figure 4.18 presents the plot of the Redlich-Peterson isotherm model for of raw, pretreated and untreated CTMABr modified bentonite clay adsorbent for the removal of crude oil from the polluted water. The study shows that the experimental data for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent fits very well with the Redlich-Peterson isotherm model with a R^2 value of 0.9992, 0.9979 and 0.9998, indicating that over 99 % of the experimental data can be explained by the Redlich-Peterson isotherm model for raw, pretreated and untreated CTMABr modified bentonite clay adsorbent respectively.

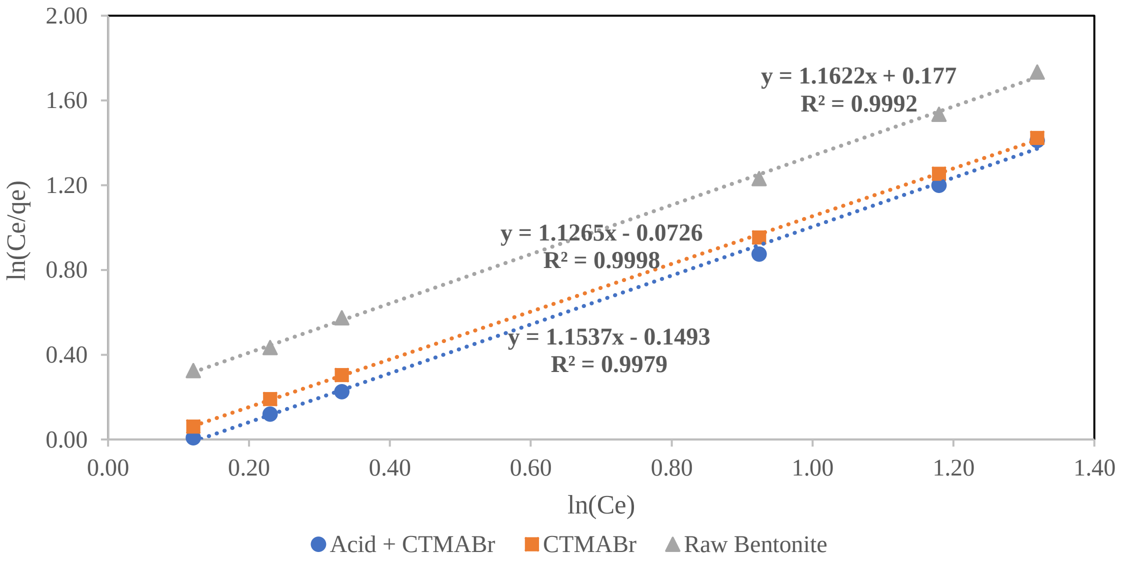


Figure 4.18: Redlich-Peterson isotherm model for adsorption of crude oil

Table 4.8 present the Redlich-Peterson isotherm model parameters for the raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. From Table 4.8, the Redlich-Peterson constant, β which is an exponent that lies between 0 and 1, shows that β is 0.8135, 0.8076 and 0.7886 for raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. The β values obtained is in line with 0 – 1 range supported for the Redlich-Peterson constant (Gulistan *et al.*, 2017). This shows that the adsorption mechanism is closer Langmuir isotherms as β value are closer to 1 for raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent and also, confirmed that the surface of the prepared adsorbent was heterogeneous in nature. Therefore, the Redlich-Peterson isotherm fits best in describing the adsorption of crude oil in raw, acid pretreated and untreated CTMABr modified bentonite clay adsorbent followed by Freundlich and Tempkin isotherm.

Table 4.8: Redlich-Peterson isotherm model parameters

Parameters	**Acid + CTMABr**	**CTMABr**	**Raw Bentonite**
β	0.8076	0.7886	0.8135
A, L/g	0.7091	0.8461	2.1285
R^2	0.9979	0.9998	0.9992

4.5 Adsorption Kinetics

Adsorption kinetic, which is a measure of the adsorption uptake with respect to time at constant pressure and a measure of the diffusion of adsorbate in the pores is very vital in adsorption studies. Hence, the adsorption kinetics of raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent were examined to in order to establish the adsorption uptake rate and the residence time for the adsorption process to be accomplished and to determine the adsorption dynamics as well as adsorbent performance in real application.

4.5.1 Pseudo first-order kinetics

Adsorption kinetic studies was investigated using the pseudo-first-order kinetic models to examine the adsorption kinetics of crude oil adsorption from polluted water using raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. The pseudo-first-order model describes the initial phase and progress of adsorption. Figure 4.19 presents the plot of the pseudo-first-order kinetic model for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. Figure 4.19, shows that experimental data for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent relatively fairly fits well with the model with R^2 value of 0.7765, 0.7533 and 0.7728 respectively.

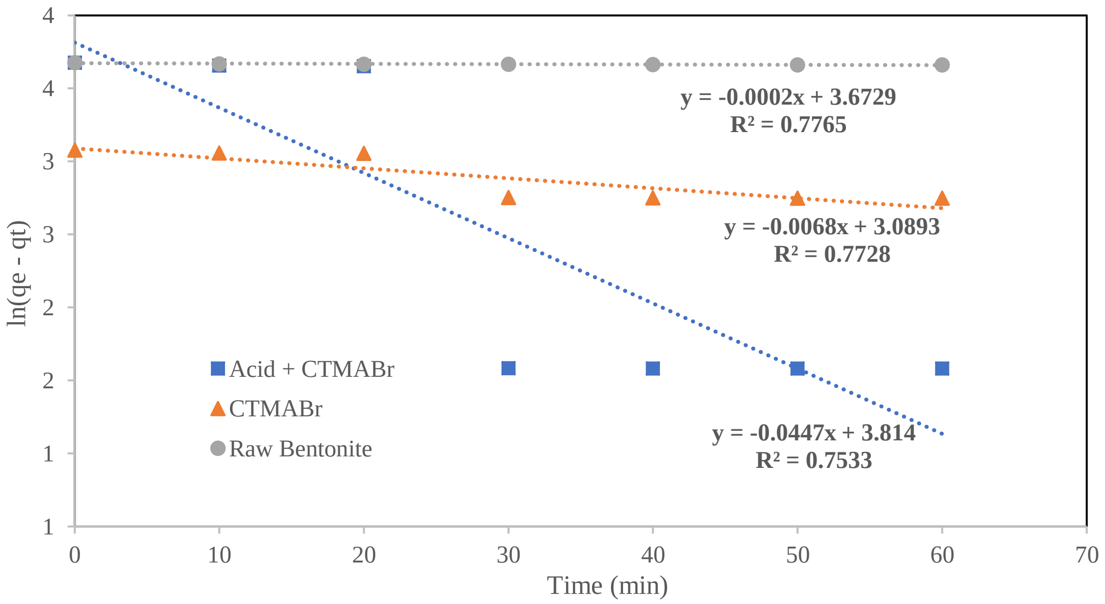


Figure 4.19: Pseudo first-order kinetic model for adsorption of crude oil.

Table 4.9 present the kinetics parameters of pseudo first-order kinetic models for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. The kinetic rate constant was highest in acid pretreated CTMABr modified bentonite clay with a rate constant of 0.091 min^{-1}, followed by that of the untreated CTMABr modified bentonite clay with a rate constant of 0.014 min^{-1}, while raw bentonite clay has the least rate constant of 0.0005 min^{-1}. This implies that crude oil removal by acid pretreated CTMABr modified bentonite clay adsorbent is fastest for first order kinetics compared to untreated CTMABr modified bentonite clay and raw bentonite cay and that experimental data fairly obeyed the pseudo-first-order model.

Table 4.9: Pseudo first-order kinetic model parameters

Parameter	**Acid + CTMABr**	**CTMABr**	**Raw Bentonite**
k_1, min^{-1}	0.091	0.014	0.000
q_e, mg/g	45.33	21.96	39.37

4.5.2 Pseudo second-order kinetics

Adsorption kinetic studies of raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent was investigated using the pseudo-second-order kinetic models to study the adsorption kinetics of crude oil from polluted water. The pseudo-second-order kinetic describes the chemisorption as the rate limiting step in an adsorption process. Figure 4.20 presents the plot of the pseudo-second-order kinetic model for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. Figure 4.19, shows that experimental data for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent fits well with the model with R^2 value of 0.9699, 0.9806 and 0.9816 respectively.

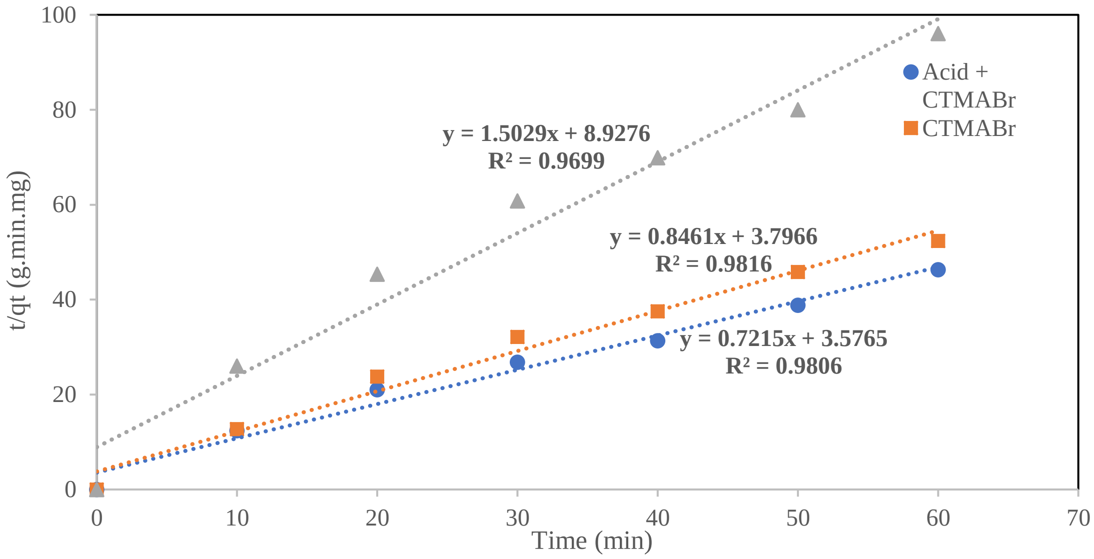


Figure 4.20: Pseudo second-order kinetic model for adsorption of crude oil.

Table 4.10 present the kinetics parameters of pseudo second-order kinetic models for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. The kinetic rate constant was highest in acid pretreated CTMABr modified bentonite clay with an equilibrium rate constant of 0.537 g/mg.min, followed by that of the untreated CTMABr modified bentonite clay with an equilibrium rate constant of 0.368 g/mg.min, while raw bentonite clay has the least rate constant of 0.05 g/mg.min. It was observed that the equilibrium rate constant for the pseudo second-order kinetic model are higher compared to those of pseudo first-order and this implies that crude oil removal by raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent is fastest following pseudo second-order kinetic. The calculated equilibrium adsorption capacity of 41.32 mg/g, 31.25 mg/g and 30.85 mg/g for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay are relatively comparable to experimental equilibrium adsorption capacity of 39.55 mg/g.

The high rate constant for the pseudo-second-order kinetic when compared to that of pseudo-first-order could be attributed to the high uptake rate observed in the second order model which results from the higher pore surface area and volume of the structure of particularly acid pretreated and untreated CTMABr modified bentonite clay adsorbent. This confirms that the rate limiting step in acid pretreated and untreated CTMABr modified bentonite clay adsorption is chemical adsorption. Based on the R^2 value, the pseudo-second order kinetics model is found to best describe the adsorption kinetics of crude oil uptake into raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay when compared to pseudo-first order and suitable for fitting the adsorption kinetics data.

Table 4.10: Pseudo second-order kinetic model parameters

Parameter	**Acid + CTMABr**	**CTMABr**	**Raw Bentonite**
k_2, g/mg min	0.54	0.37	0.05
q_e, mg/g	41.32	31.25	30.85

4.5.3 Intra-particle diffusion model

Intra-particle diffusion model was used to assess the adsorption kinetics of raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay in order to gain insight to the mechanism in adsorption process because, different mechanisms are often involved in adsorption process. These mechanisms are described in basic three steps which are; superficial external adsorption, intra-particle diffusion corresponding to the limiting step and the final equilibrium, which is very fast (Romero *et al.*, 2018). Hence, if the plot of the experimental data exhibit multilinear plots, two or more steps influences the adsorption process as shown in Figure 4.21. Figure 4.21 presents the plot of intra-particle diffusion model for raw bentonite, acid pretreated and untreated

CTMABr modified bentonite clay and shows the variation of the slope with respect to time. The R^2 value of 0.9714, 0.9411 and 0.968 for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay and show that the experimental data is describable by the intra-particle diffusion model.

Theoretically, for an adsorption process to obey the intra-particle diffusion model, a straight linear plot that passes through the origin is expected (Rashidi *et al.*, 2013; Alhassan *et al*, 2017). However, Figure 4.21 clearly shows a variation of gradient with respect to time. Two regions, the first steeper region from 3.16 – 6.32 $min^{1/2}$ which can be attributed to the surface sorption while the second region from 6.32 – 7.75 $min^{1/2}$ can be attributed to intra-particle diffusion indicating that the adsorption process followed two steps. In this case, the rate of adsorption can be said to be influence by external or surface adsorption (film diffusion) and intra-particle diffusion as the gradient did not pass through the origin (Nethaji *et al*, 2013, Kajjumba *et al*, 2018).

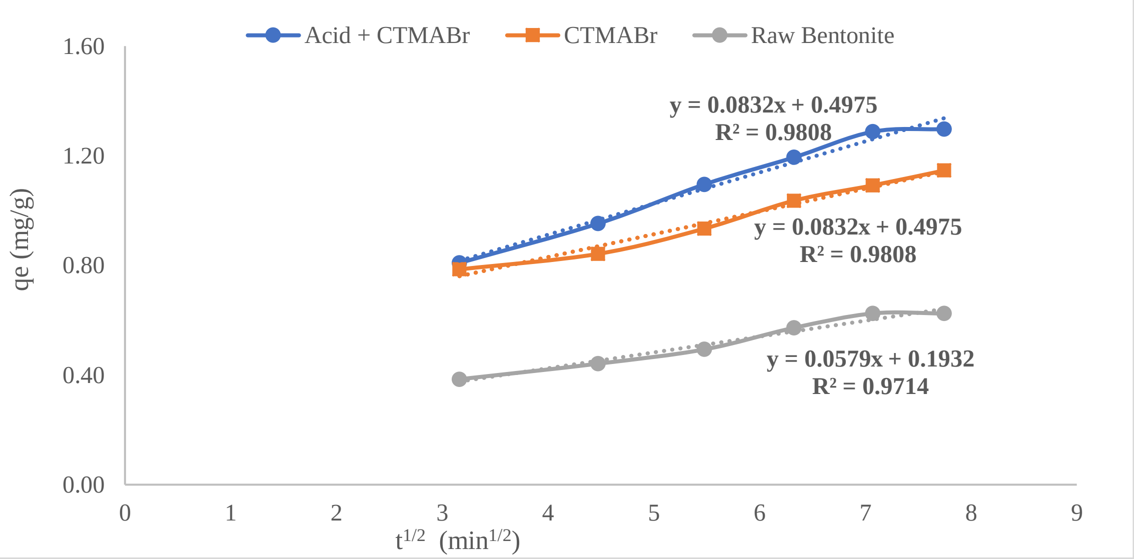


Figure 4.21: Intra-particle diffusion models for the adsorption of crude oil.

Table 4.11 present the intra-particle diffusion rate constants for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay with K_{id1} and K_{id2} as 0.058 mg/g.min$^{1/2}$ and 0.037 mg/g.min$^{1/2}$ respectively for raw bentonite, 0.148 mg/g.min$^{1/2}$ and 0.015 mg/g.min$^{1/2}$ respectively for acid pretreated CTMABr modified bentonite clay and, 0.087 mg/g.min$^{1/2}$ and 0.056 mg/g.min$^{1/2}$ respectively for untreated CTMABr modified bentonite clay which describes the speed of diffusion in the different stages of the adsorption process. This further shows that, as adsorption time rises, the rate of intra-particle diffusion reduces which justifies the high adsorption rate recorded in the first (initial) stage of the adsorption process because the intra-particle diffusion takes place in the micro and meso pores which results in the very high adsorption rate at the initial stage (Yan *et al.*, 2015, Romero *et al.*, 2018). At the second stage, considering the rate of adsorption, K_{id2} = 0.037 mg/g.min$^{1/2}$, K_{id2} = 0.015 mg/g.min$^{1/2}$ and K_{id2} = 0.056 mg/g.min$^{1/2}$ for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay respectively, crude oil adsorption are slowly transferred with intra-particle diffusion into the adsorbent particles, indicating that the rate of adsorption is controlled by intra-particle diffusion. Therefore, the crude oil adsorption process using raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent is diffusionally control and not kinetically.

Table 4.11: Intra-particle diffusion model parameters

Parameter	**Acid + CTMABr**	**CTMABr**	**Raw Bentonite**
k_{id1}, mg/g.min$^{1/2}$	0.148	0.087	0.058
k_{id2}, mg/g.min$^{1/2}$	0.015	0.056	0.037
Ci	0.458	0.495	0.193
k_{id}, mg/g.min$^{1/2}$	0.117	0.084	0.058

4.5.4 Elovich model

Elovich model was used to further understand the chemisorption nature of the adsorption process with raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. Figure 4.22 presents the plot of Elovich kinetic model for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. Figure 4.21, shows that experimental data for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent fits well with the Elovich model with R^2 value of 0.9466, 0.9597 and 0.9317 respectively. Indicating that the Elovich model well describe the adsorption process.

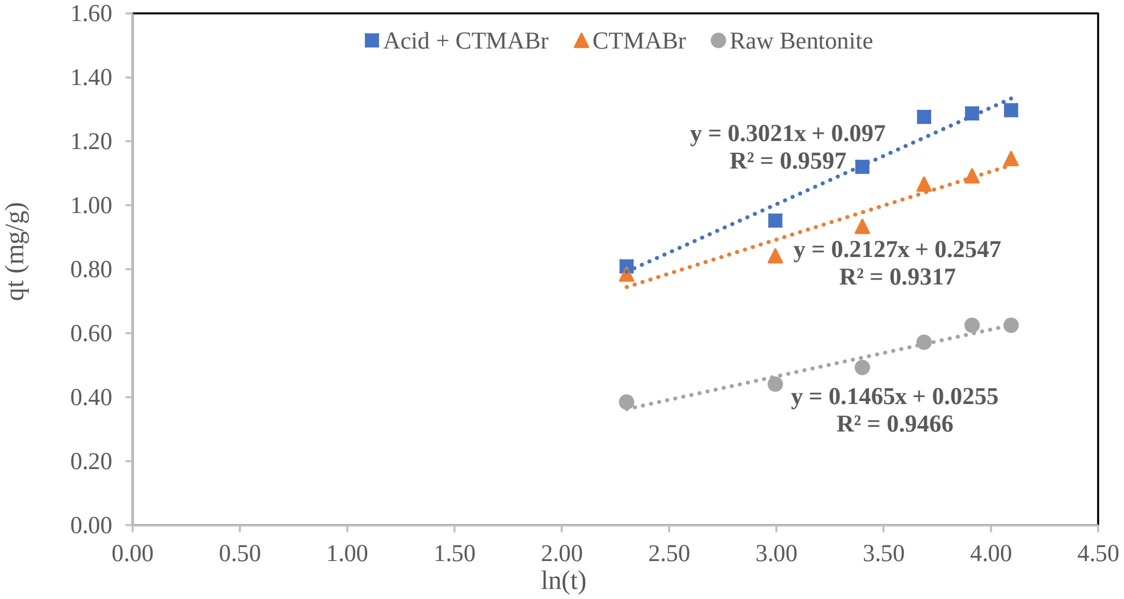


Figure 4.22: Elovich model for the adsorption of crude oil.

Table 4.12 present the Elovich model parameter, α (initial adsorption rate) and β (desorption constant) which are relates to the extent of surface coverage for chemisorption for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. Table 12 present the Elovich model parameter for the adsorption study. The desorption constant (β) were found to be 6.83 g/mg, 3.31 g/mg and 4.70 g/mg for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay while the initial sorption rates were found to be 0.22 mg/g.min, 0.63 mg/g.min and 3.35 mg/g.min for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. This further confirms that crude oil adsorption process using raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent is diffusionally in nature. Also, R^2 value for the Elovich model fits well with the experimental data further indicating that diffusional rate limiting is predominant in the sorption of crude oil pollutant from contaminated water by raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay.

Table 4.12: Elovich model parameters

Parameter	**Acid + CTMABr**	**CTMABr**	**Raw Bentonite**
B, g/mg	3.31	4.70	6.83
α, mg/g.min	0.63	3.35	0.22

4.5.5 Boyd model

The Boyd plot was use to predicts the actual slow step involved in the adsorption of crude oil from contaminated water by raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. Figure 4.23 presents the Boyd plots for the adsorption of crude oil using raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay. From Figure 4.23, it was observed that the plot is approximates $y = mx + 0.0$, indicating that the rate limiting step is more of intra-particle diffusion than film diffusion. Therefore, the Boyd plots suggested that the rate-determining step is the external mass transfer since the plots were linear and does not pass through the origin (Nethaji *et al*., 2013).

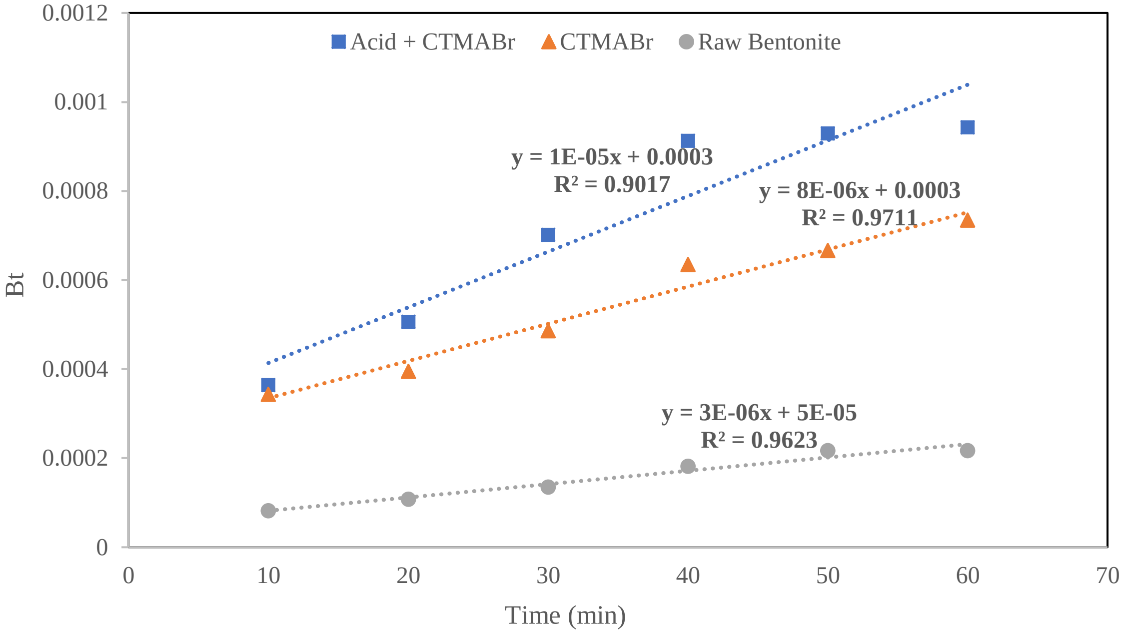


Figure 4.23: Boyd plots for the adsorption of crude oil.

Table 4.13 shows R^2 value of the plot of the experimental data for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent using Boyd model. The R^2 value shows that the experimental data fits well with the Boyd plot with R^2 value of 0.9623, 0.9017 and 0.9711 respectively. Indicating that the Boyd plot well describe the adsorption process.

Table 4.13: Boyd model parameters

Parameter	Acid + CTMABr	CTMABr	Raw Bentonite
R^2	0.9017	0.9711	0.9623

4.6 Thermodynamic Studies

Thermodynamic studies were carried out in order to evaluate the feasibility of the adsorption process and the activation energy of the adsorption process.

4.6.1 Thermodynamic evaluation

Thermodynamic parameters which including enthalpy change (ΔH°), Gibb's free energy (ΔG°), and entropy change (ΔS°) were evaluated for the synthesis adsorbents. Table 4.14 present the thermodynamic parameter obtained for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent in the temperature range of 25 °C (298 K) to 75 °C (348 K). The Gibb's free energy obtained for all the adsorbents were negative, indicating the spontaneous nature of crude oil adsorption by raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent. Detail of the plot are shown in Appendix C.

Table 4.14: Thermodynamic parameters of adsorption of crude oil from polluted water

Adsorbent	**Temperature (K)**	**ΔG (kJ/mol)**	**ΔH (kJ/mol)**	**ΔS (kJ/mol/K)**	**R^2**
Acid + CTMABr	298	-12.9979	9.0421	0.0740	0.9909
	308	-13.7397			
	318	-14.5013			
	328	-15.2286			
	338	-15.8605			
	348	-16.7613			
CTMABr					
	298	-8.1378	14.6474	0.0768	0.9811
	308	-8.9724			
	318	-9.8169			
	328	-10.6689			
	338	-11.4980			
	348	-11.7805			
Raw Bentonite					
	298	-5.6177	26.4745	0.1073	0.9811
	308	-6.7003			
	318	-7.2342			
	328	-8.8212			
	338	-9.8743			
	348	-10.9448			

Table 4.14 shows negative enthalpy (ΔH), indicating that the adsorption of the pollutants in raw bentonite, acid pretreated and untreated CTMABr modified bentonite

clay adsorbent is endothermic in nature, which is in agreement with the effect of temperature on adsorption of crude oil from polluted water (Figure 4.10), indicating increase in adsorption rate with rise in temperature. The highest value of ΔH was observed to be 26.4845 kJ/mol for raw bentonite and lowest of 9.0421 kJ/mol for acid pretreated CTMABr modified bentonite clay, which indicates that raw bentonite requires more energy for crude oil adsorption to take place. Also, the ΔH value obtained for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent are less than 40 kJ/mol, indicating physio-sorption mechanism in the uptake of crude oil by the adsorbents (Liu *et al.*, 2009, Belhamdi *et al.*, 2016, Alhassan *et al.*, 2017).

Furthermore, entropy change (ΔS) which is used to assess randomness at the solid–liquid interface during adsorption was also investigated. The ΔS value obtained for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent are all positive, indicating an increased disorderliness and randomness of the adsorbate in the solid-liquid interface. It was observed that the ΔS value for raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent are 0.1073 kJ mol^{-1} K^{-1}, 0.0740 kJ mol^{-1} K^{-1} and 0.0768 kJ mol^{-1} K^{-1} and respectively, indicating more disorderliness and randomness in the uptake of crude oil by raw bentonite and less by acid pretreated and untreated CTMABr modified bentonite clay adsorbent. The thermodynamic studies show that crude oil adsorption by raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay was spontaneous and endothermic in nature with more disorderliness and randomness by raw bentonite and all suggest a physio-sorption mechanism.

4.6.2 Activation energy

The magnitude of the activation energy (E_a) is also vital in adsorption studies, as it gives information on adsorption mechanism. Value of E_a for physical adsorption are generally in the range of 5 – 40 kJ/mol, while in chemisorption process which involves the formation of strong bonding requires 40 – 800 kJ/mol energy (Alhassan *et al.*, 2017). Arrhenius equation (Equation 3.20) was used to evaluate the E_a of the adsorption process. Table 4.15 clearly shows the activation energy for both adsorbents that was used in this research for CO_2 adsorption.

Table 4.15: Activation energy parameters for the adsorption of crude oil from polluted water

Parameter	**Acid + CTMABr**	**CTMABr**	**Raw Bentonite**
E_a, kJ/mol	8.6592	14.7753	26.5009
k_o, g/mg.min	1.0088	1.0093	1.0120

From Table 4.15, the E_a energy for the adsorption of crude oil by raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay adsorbent are 26.5009 kJ/mol, 8.6592 kJ/mol and 14.7753 kJ/mol respectively, indicating that the adsorption mechanism falls in the range of 5 – 40 kJ/mol for physio-sorption (Alhassan *et al.*, 2017). The lowest E_a value obtained for acid pretreated CTMABr modified bentonite clay suggest that lesser energy of activation is required for the adsorption of crude oil from polluted water compared to 26.5009 kJ/mol for raw bentonite clay. This further show that the adsorption mechanism for the three adsorbents are diffusion-controlled and not chemically-controlled.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The study investigated the adsorption of spilled crude oil from polluted water using raw bentonite, acid pretreated and untreated CTMABr organomodified bentonite clay adsorbent. From the study carried out, the following conclusion were made;

The acid pre-treated CTMABr modified bentonite clay adsorbent shows that organic acid (oxalic acid) enhances the adsorption capacity and adsorptive properties of the adsorbent, the XRD diffractograms shows that quartz and albite content of the acid pretreated CTMABr modified bentonite clay is higher than untreated CTMABr modified bentonite clay and microcline content, the surface morphology of the acid pre-treated CTMABr modified bentonite clay shows that pretreatment of bentonite with oxalic enhances the surface structure of acid pre-treated CTMABr modified bentonite with favorable channels and voids for adsorbing crude oil, the EDX analysis shows that acid pre-treated CTMABr modified bentonite clay has higher silicate content with lower alumna, Fe, K, Ti and Ag content compared to raw bentonite and untreated CTMABr modified bentonite clay while the FTIR bands confirm the intercalation of alkylammonium in the interlayer of galleries of the adsorbents in both acid pretreated and untreated CTMABr modified bentonite clay. Hence, acid pretreatment of bentonite clay modified with CTMABr result in higher adsorption capacity compared to untreated CTMABr modified bentonite clay and raw bentonite clay as adsorbent.

The assessment of the crude oil polluted water shows that the concentration of crude oil in the polluted water before treatment is 53.21 mg/L which was found to reduce significantly after adsorption.

The effect of time, temperature, dosage, pH and initial concentration shows a maximum removal efficiency of 97.52 %, 98.05 %, 95.04 %, 85.11 % and 83.87 % at 50 min, 75 ^{o}C, 2g adsorbent dosage, 9 pH and 0.30 mg/L initial concentration respectively for acid pre-treated CTMABr modified bentonite clay followed by those of untreated CTMABr modified bentonite clay while raw bentonit clay performs the least with adsorption sites become saturated gradually with increase in percentage removal and uptake.

The adsorption of crude oil by raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay shows that Redlich-Peterson isotherm model best described the adsorption process, followed by Freundlich and then Tempkin isotherm model while the kinetic study show that the models describe the adsorption process in pseudo-second order kinetics > Intra-particle diffusion model > Elovich model > Boyd model > pseudo-first order kinetics model and the adsorption process is diffusionally control while the thermodynamic studies show that crude oil adsorption by raw bentonite, acid pretreated and untreated CTMABr modified bentonite clay was spontaneous, endothermic in nature with more disorderliness and randomness by raw bentonite and all suggest a physio-sorption mechanism and the activation energy also shows that the adsorption mechanism for the three adsorbents are diffusion-controlled.

5.2 Recommendation

The study recommends the optimization of the adsorption study using CTMAB organomodified bentonite clay with RSM Central Composite design of experiment considering temperature, adsorbent dosage, time and pH as process parameter.

It also recommends a study on the potential removal of emerging contaminants (ECs) arising from a variety of extensively used synthetic compounds such as cosmetics, pesticides, pharmaceuticals, steroid hormones, and personal care products in wastewater.

5.3 Contribution to Knowledge

The study has contributed to adsorption studies of spill crude oil in water using organically modified bentonite clay which was treated with 2 mol of Oxalic acid solution.

It also contributed to adsorption kinetics and isotherm studies and the activation energy parameter analysis was carried out as followed; Acid + CTMABr, TMABr and Rawn Bentonite which was calculated to be 8.6592 kJ/mol, 14.7753 kJ/mol and 26.5009 kJ/mol respectively.

In addition, the effect of time, temperature, dosage, pH and initial concentration on the adsorption of crude oil was studied and it shows a maximum removal efficiency of 98.05 for Acid + CTMABr adsorbent, 97.52 % for CIMABr adsorbent and 83.865 % for Raw Bentonite adsorbent. All at optimum or at the same operating condictions at temperature of 29.8 °C, time of 40 mins, mixing rate 900 rpm, dosage 2 g. pH 8.36 and concentration of 0.30 mg/L.

REFERENCE

Adamis, Z. and Williams, R. B. (2005). Bentonite, Kaolin, and Selected Clay Minerals, Environmental Health Criteria 231, World Health Organization, Geneva: 1 – 35.

Adeyemo, A. A., Adeoye, I. O. and Bello, O. S. (2015). Adsorption of dyes using different types of clay: a review, *Applied Water Science*, 1 – 26. DOI 10.1007/s13201-015-0322-y

Afolabi, R. O., Orodu, O. D. and Efeovbokhan, V. E (2017). Properties and application of Nigerian bentonite clay deposits for drilling mud formulation: Recent advances and future prospects, *Applied Clay Science,* 143: 39–49.

Ajayi, A. O., Atta, A. Y., Aderemi, B. O. and Adefila, S. S. (2010*)*. Novel Method of Metakaolin Dealumination Preliminary Investigation. *Journal of Applied Sciences Research*, 6(10): 1539-1546.

Alhassan, M., Andrew, I., Auta, M., Umaru, M., Garba, U. G., Isah, A. G. and Alhassan, B. (2017). Comparative studies of CO_2 capture using acid and base modified activated carbon from sugarcane bagasse, *Biofuels*, DOI:10.1080/17597269.2017.1306680.

American Society for Testing and Materials (1988). ASTM C 837-81. Standard Test Methods of Methylene Blue Index of Clay.

Aroke U. O., Osha O. A., Aliyu U. M. and Shuaibu, U. (2016). Removal of Pb^{2+} onto HDTMA-Br Modified Kaolinite Clay as function of pH: Batch Sorption, Isotherms and Kinetics. *IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT),* 10(10): 25-34.

Aroke, U. O. and Hamidu, L. A. J. (2020). Instrumental Characterization of Unmodified and HDTMA-Br Modified Kaolinite Clay: SEM-EDX, Quantachrome and TGA-DTA. Traektoriâ Nauki = Path of Science. 6(6): 2001 – 2010.

Aroke, U. O., Abdulkarim, A. and Ogubunka, R. O. (2013). Fourier-transform Infrared Characterization of Kaolin, Granite, Bentonite and Barite, ATBU Journal of Environmental Technology, 6(1), p. 45 – 51.

Aroke, U. O., El-Nafaty, U. A. and Osha, O. A. (2013). Removal of Oxyanion Contaminants from Wastewater by Sorption onto HDTMA-Br Surface Modified Organo-Kaolinite Clay. *International Journal of Emerging Technology and Advanced Engineering*, 4(1): 475–482.

Aroke, U. O., Ibrahim, M., Osha, O. A. and Yunus, M. H. (2015). Parametric studies of sulphate ion sorption at different pH on HDTMA-Br modified kaolinite clay, *International Journal of Emerging Trends in Engineering and Development*, 3(5): 250-260

Auta, M. and Hammed, B. H. (2014). Optimized and Functionalized Paper Sludge Activated Carbon with Potassium Fluoride for Single and Binary Adsorption of Reactive Dye, *Journal of Industrial and Engineering Chemistry,* 20: 830- 840.

Banat, F.A., Al-Bashir, B., Al-Asheh, S. and Hayajneh, O. (2000). Adsorption of phenol by bentonite. *Environmental Pollution*, 107(3): 391-398.

Bandura, L., Woszuk, A, Kołodynska, D. and Franus, W. (2017). Application of Mineral Sorbents for Removal of Petroleum Substances: A Review. *Minerals*, 7(37): 2 – 25.

Banković, P., Milutinović-Nikolić, A., Mojović, Z., Jović-Jovičić, N., Perović, M., Spasojević, V. and Jovanović, D. (2013). Synthesis and characterization of bentonites rich in beidellite with incorporated Al or Al–Fe oxide pillars, *Microporous & Mesoporous Mater*. 165: 247-256.

Belhamdi, B., Merzougui, Z., Trari, M. and Addoun, A. (2016). A kinetic, equilibrium and thermodynamic study of l-phenylalanine adsorption using activated carbon based on agricultural waste (date stones). *Journal of Applied Research and Technology*, 14 (2016): 354 – 366.

Boumediene, H., Didier, V., Karima, D., Habib, B., Taqiyeddine, M., Serge, B., Ahmed, H. and Mustapha, R. (2016). Preparation and thermal properties of organically modified bentonite with ionic liquids. *ChemXpress*, 9(4): 295 – 203.

Chen, S., Yue, Q., Gao, B., Li, Q., & Xu, X. (2011). Removal of Cr from aqueous solution using modified corn stalks:Characteristic, equilibrium, kinetic and thermodynamic study. *Chemical Engineering Journal*, (168), 909–917.

Choo, K. Y. and Bai, K. (2016). The Effects of The Mineralogy Composition of Various Bentonites on CEC Value Determined by Three Different Analytical methods. *Applied Clay Science. Korea*, 126: 153- 159.

El-Zahhar, A. A. and Al-Hazmi, G. A. (2015). Organically Modified Clay for Adsorption of Petroleum Hydrocarbon, *European Chemical Bulletin*, 4(2): 87-91

Emam, A. E. (2013). Modified activated carbon and bentonite used to adsorb petroleum hydrocarbons emulsified in aqueous solution, *American Journal of Environmental Protection*, 2(6): 161 – 169.

Espantaleon, A. G., Nieto, J. A., Fernandez, M. and Marsal, A. (2003). Use of activated clays in the removal of dyes and surfactants from tannery waste waters. *Applied Clay Science*, 24: 105–110.

Fernández, R., González, L., Ruiz, A. I. and Cuevas, J. (214). Nature of C-(A)-S-H Phases Formed in the Reaction Bentonite/Portlandite, *Journal of Geochemistry*, Hindawi Publishing Corporation, Volume 2014, Article ID 145425, 8 pages http://dx.doi.org/10.1155/2014/145425.

Food and Drug Administration (2011). Database of select committee on GRAS substances (SCOGS). Reviews Bentonite. FDA, Database. Retrieved 15 Aug 2011.

Foroutan, R., Zareipour, R. and Mohammadi, R. (2018). Fast adsorption of chromium (VI) ions from synthetic sewage using bentonite and bentonite/biocoal composite: A comparative study. *Materials Research Express*, October: 1 – 26.

Freundlich (1928). “Colloid and Capillary Chemistry”. New York, E.P. Dutton and Co.

Gaucher, E. C. and Blanc, P. (2006). “Cement/clay interactions: A review: Experiments, natural analogues, and modeling.” *Waste Management*, 26: 776-788.

Gulistan, A. S. (2014). Oil Removal from Produced Water Using Natural Materials. M.Sc. Thesis in Chemical Engineering, Sharjah, United Arab Emirates: 32 – 25.

Guo, M., Wang, H., Huang, D., Han, Z., Li, Q., Wang, X. and Chen, J. (2014). Amperometric catechol biosensor based on laccase immobilized on nitrogen-doped ordered mesoporous carbon (N-OMC)/PVA matrix. *Science and technology of advanced materials*, 15(3), 035005. https://doi.org/10.1088/1468-6996/15/3/035005.

Guyonnet, D., Gaucher, E., Gaboriau, H., Pons, C., Clinard, C., Norotte, V. and Didier, G. (2005). “Geosynthetic Clay Liner Interaction with Leachate: Correlation between Permeability, Microstructure, and Surface Chemistry”. *Journal of Geotechnical and Geoenvironmental Engineering*. 131 (6): 740. doi:10.1061/(ASCE)1090-0241(2005)131:6(740).

Hokkanen, S., Bhatnagar, A., Srivastava, V., Suorsa, V. and Sillanpää, M. (2018). Removal of Cd^{2+}, Ni^{2+} and $PO4^{3-}$ from aqueous solution by hydroxyapatite-bentonite claynanocellulose composite, *International Journal of Biological Macromolecules*, 118: 903-912.

Huggett, J. M. (2015). Clay Materials, *Reference Module in Earth Systems and Environmental Sciences*, Elsevier, 22-July-15. doi: 10.1016/B978-0-12-409548-9.09519-1.

Ikhtiyarova, G. A., Ozcan, A. S., Gok, O. and Ozcan, A. (2012). Characterization of natural- and organo-bentonite by XRD, SEM, FT-IR and thermal analysis techniques and its adsorption behaviour in aqueous solutions, *Clay Miner*, 47: 31–44

Jaafar, S. N. B. S. (2006). Adsorption study: dye removal using clay. A BSc. Chemical Engineering Thesis, Faculty of Chemical Engineering and Natural Resources, University College of Engineering & Technology.

Jaqueline, A. A. C., Daniela, N. A., Ana-Cláudia, Q. L., Stela, D. S. C. and Talita, S. S. S. (2013). Determination of The Cation Exchange Capacity of Bentonite Exposed to Hyperalkaline Fluid. *International Nuclear Atlantic Conference - INAC 2013*, Brazil, November: 24 – 29.

Kajjumba, G. W., Serkan, E., Atakan, Ö., Özcan, H. K. and Aydın, S. (2018). Chapter: Modelling of Adsorption Kinetic Processes—Errors, Theory and Application. *Advanced Sorption Process Applications*. IntechOpen, p. 1 – 12. DOI: http://dx.doi.org/10.5772/intechopen.80495

Karnland, O., Olsson, S. and Nilsson, U. (2006). Mineralogy and sealing properties of various bentonites and smectite-rich clay materials. SKB Technical Report TR-06-30. Stockholm, Sweden.

Karpinska, J. and Kotowskam U. (2019). Removal of Organic Pollution in the Water Environment, *Water*, 11: 1 – 7. doi:10.3390/w11102017

Kenes, K., Yerdos, O., Zulkhair, M., and Yerlan, D. (2012). Study on the effectiveness of thermally treated rice husks for petroleum adsorption. *Journal of Non-Crystal Solids*, 358: 2964–2969.

Landoulsi, O., Megriche, A., Calvet, R., Espitalier, F., Ferreira, J. M. F. and Mgaidi, A. (2013). Effect of heating and acid activation on the structure and surface properties of a kaolinite-illite-Smectite clayey mixture. *Miner Processing Journal*, 6:13-20.

Langmuir, I. (1918). "The adsorption of gases on plane surfaces of glass, mica and platinum," *Journal of the American Chemical Society*, vol. 40, no. 9, p. 1361–1403.

Li, J., Li, Y. and Meng, Q. (2010). Removal of nitrate by zero-valent iron and pillared bentonite. *Journal of Hazardous Materials*, 174: 188-193

Linan, L., Lihua, W., Wenhong, S., Liang, Y., Liming, Y., Shaopan, X., Hailong, W., Peter, J. S. and Zhaoliang, S. (2018). Crude oil removal from aqueous solution using raw and carbonized Xanthoceras sorbifolia shells. *Environmental Science and Pollution Research*, 25: 29325 – 29334. https://doi.org/10.1007/s11356-018-2895-0

Liu, R., Frost, R. L. and Martens, W. N. (2009). Near Infrared and mid infrared investigations of adsorbed phenol on HDTMAB organoclays, *Mater. Chem. Phys*. 113: 707–713.

Ma, J., Qi, J., Yao, C., Cui, B., Zhang, T., and Li, D. (2012). A novel bentonite-based adsorbent for anionic pollutant removal from water. *Chemical Engineering Journal*, 200-202: 97-103.

Makhoukhi, B., Didi, M. A., Moulessehoul, H., Azzouz, A. and Villemin, D. (2010). *Applied Clay Science*, 50: 354

Milinovic, J., Dias, Á. A., Janeiro, A. I., Pereira, M. F. C., Martins, S., Petersen, S. and Barriga, F. J. A. S. (2020). XRD Identification of Ore Minerals during Cruises: Refinement of Extraction Procedure with Sodium Acetate Buffer, *Minerals*, 10 (160), February, p. 1 – 17. doi:10.3390/min10020160.

Momina, M., Mohammad S and Suzylawati, I. (2018). A review on Regeneration performance of clay-based adsorbents for the removal of industrial dyes. *Journal of royal society of chemistry*: 24571-24587.

Ndeh, E. S., Okafor, J. O., Akpan, G. U. and Olutoye, M. A. (2017). Environmental Impacts of Crude Oil Spillages on Water in Ibeno Local Government Area of Akwa Ibom State, Nigeria. *Bayero Journal of Pure and Applied Scienc*es, 10(1): 315 – 319. http://dx.doi.org/10.4314/bajopas.v10i1.49

Nethaji, S., Sivasamy, A. and Mandal, A. B. (2013). Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass. *International Journal of Environmental Science and Technology*, 10: 231–242. DOI 10.1007/s13762-012-0112-0

Nigeria Extractive Industries Transparency Initiative (NEITI) (2016), *The Nigerian Mining Industry - The Untapped Goldmine,* 08 February.

Nweke, O.M., 2015. Evaluating the suitability of clays from Abakaliki Area, Southeastern Nigeria for oil industrial application using geotechnical and rheological properties. *Science Innovation*, 3 (2):22–31. http://dx.doi.org/10.11648/j.si.20150302.11.

Ochieng, O. (2016). Characterization and classification of clay minerals for potential applications in Rugi Ward, Kenya. *African Journal of Environmental Science and Technology,* 10(11): 415-431. November, DOI: 10.5897/AJEST2016.2184.

Osin, O. A., Yu, T. Y. and Lin, S. J. (2017). Oil refinery wastewater treatment in the Niger Delta, Nigeria: current practices, challenges, and recommendations. *Environmental Science Pollution Research*, 24: 22730 – 22740. https://doi.org/10.1007/s11356-017-0009-z

Oueslati, W, Ammar, M. and Chorfi, N. (2014). Quantitative XRD Analysis of the Structural Changes of Ba-Exchanged Montmorillonite: Effect of an in Situ Hydrous Perturbation, *Minerals,* 5, p. 507-526; doi:10.3390/min5030507.

Panda, A. K., Misha, B. G., Misha, D. K. and Singh, R. K. (2010). Effect of Sulfuric Acid Treatment on the Physico-Chemical Characteristics of Kaolin Clay. *Colloids and Surfaces A: Physicochem. Eng. Aspects,* 363: 98–104.

Park, Y. R. (2013). Synthesis, Characterisation and Application of Organic Surfactants Modified Clays for Water Purification. Ph.D. Thesis, School of Chemistry, Physics and Mechanical Engineering Faculty of Science and Engineering. Queensland University of Technology: 40 – 67.

Parolo, M. E., Pettinari, G. R., Mussoa, T. B., Sánchez-Izquierdo, M. P. and Fernández, L. G. (2014). Characterization of organo-modified bentonite sorbents: The effect of modification conditions on adsorption performance, Applied Surface Science, 320: 356–363.

Rashidi, N.A., Yusup, S. and Lam, H. L. (2013). Kinetic Studies On CO_2 Capture Using Activated Carbon. *Chem Eng Trans*. 35, p. 361–366.

Rathnayake, S. I. (2017). Synthesis, Characterization and Application of Inorganic–Organic Clays for Water Purification. PhD thesis in Nanotechnology and Molecular Science, School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology.

Ravisankar, R., Kiruba, S., Eswaran, P., Senthilkumar, G. and Chandrasekaran, A (2010). Mineralogical Characterization Studies of Ancient Potteries of Tamilnadu, India by FT-IR Spectroscopic Technique. *E-Journal Chemistry,* 7(S1), S185 – S190.

Raw Material Research and Development Council, RMRDC (2010). *Raw Materials Sourcing for Manufacturing in Nigeria*, 3rd edition, Abuja.

Romero, J. R. G., Moreno-Piraján, J. C. and Gutierrez, L. G. (2018). Kinetic and Equilibrium Study of the Adsorption of CO2 in Ultramicropores of Resorcinol-Formaldehyde Aerogels Obtained in Acidic and Basic Medium. *Journal of*

Carbon Research, 4 (52): 1 – 17. doi:10.3390/c4040052 www.mdpi.com/journal/carbon.

Runtti, H., Tuomikoski, S., Kangas, T., Lassi, U., Kuokkanen, T. and Rämö, J. (2014). Chemically activated carbon residue from biomass gasification as a sorbent for iron (II), copper (II) and nickel (II) ions, *Journal of Water Process Engineering*, 4: 12 – 24.

Salahudeen, N. (2015). Development of Zeolite Y and ZSM5 Composite Catalyst from Kankara Kaolin, Ph.D Thesis, Department of Chemical Engineering, Ahmadu Bello University, Zaria Nigeria: 70 – 90.

Scimeca, M., Bischetti, S., Lamsira, H. K., Bonfiglio, R. and Bonanno, E. (2018). Energy Dispersive X-ray (EDX) microanalysis: A powerful tool in biomedical research and diagnosis. *European Journal of Histochemistry*, 62 (2841): 1 – 10.

Sdiri, T., Higashi, F. J. and Bouaziz, S. (2012). Effects of impurities on the removal of heavy metals by natural limestonesin aqueous systems. *Journal of Environmental Management*, 93: 245-253.

Shaha, M. V., Pandyab, H. J. and Shukla, A. D. (2017). Influence of chemical additives on shrinkage and swelling characteristics of bentonite clay. *Procedia Engineering*, 189: 932 – 937.

Sheng, G., Shen, R., Dong, H. and Li, Y. (2013). Colloidal diatomite, radionickel, and humic substance interaction: a combined batch, XPS, and EXAFS investigation. *Environmental Science Pollution Research*, 20: 3708–3717.

Talaat, H. A., El-Defrawy, N. M., Abulnour, A. G., Hani, H. A. and Tawfik, A. (2011). Evaluation of Heavy Metals Removal Using Some Egyptian Clays. *2011 2nd International Conference on Environmental Science and Technology (IPCBEE)*, Singapore, 6: 37 – 40.

Uddin, M. K. (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Journal of Chemical Engineering*, 308: 438–462.

UNEP (2011). Environmental Assessment of Ogoniland, United Nations Environment Programme Report, 80 – 220. Retrieved from https://postconflict.unep.ch/publications/OEA/UNEP_OEA.pdf, Accessed: 20/05/2021

Vollaard, B. (2017) Temporal displacement of environmental crime: evidence from marine oil pollution. *Journal of Environmental Economics and Management*, 82: 168. 180.https://doi.org/10.1016/j.jeem.2016.11.001.

Wang, J. P., Li, Q. F., Dong, F. Q., He, X., Zhang, W., Yang, L. J. and Zhang, W. J. (2015). Study on Effect Characteristics and Mechanism of Staphylococcus aureus on Albite. *Advance Materials Research*, 1092–1093, 635–640.

William, F. B. (2012). Adsorption Surface Chemistry. *Soil Environmental Chemistry*, Elsevier: 205 – 234.

Yan, L. G., Qin, L. L., Yu, H. Q., Li, S., Shan, R. R. and Du, B. (2015). Adsorption of acid dyes from aqueous solution by CTMAB modified bentonite: Kinetic and isotherm modeling. *Journal of Molecular Liquid*. 211, p. 1074–1081.

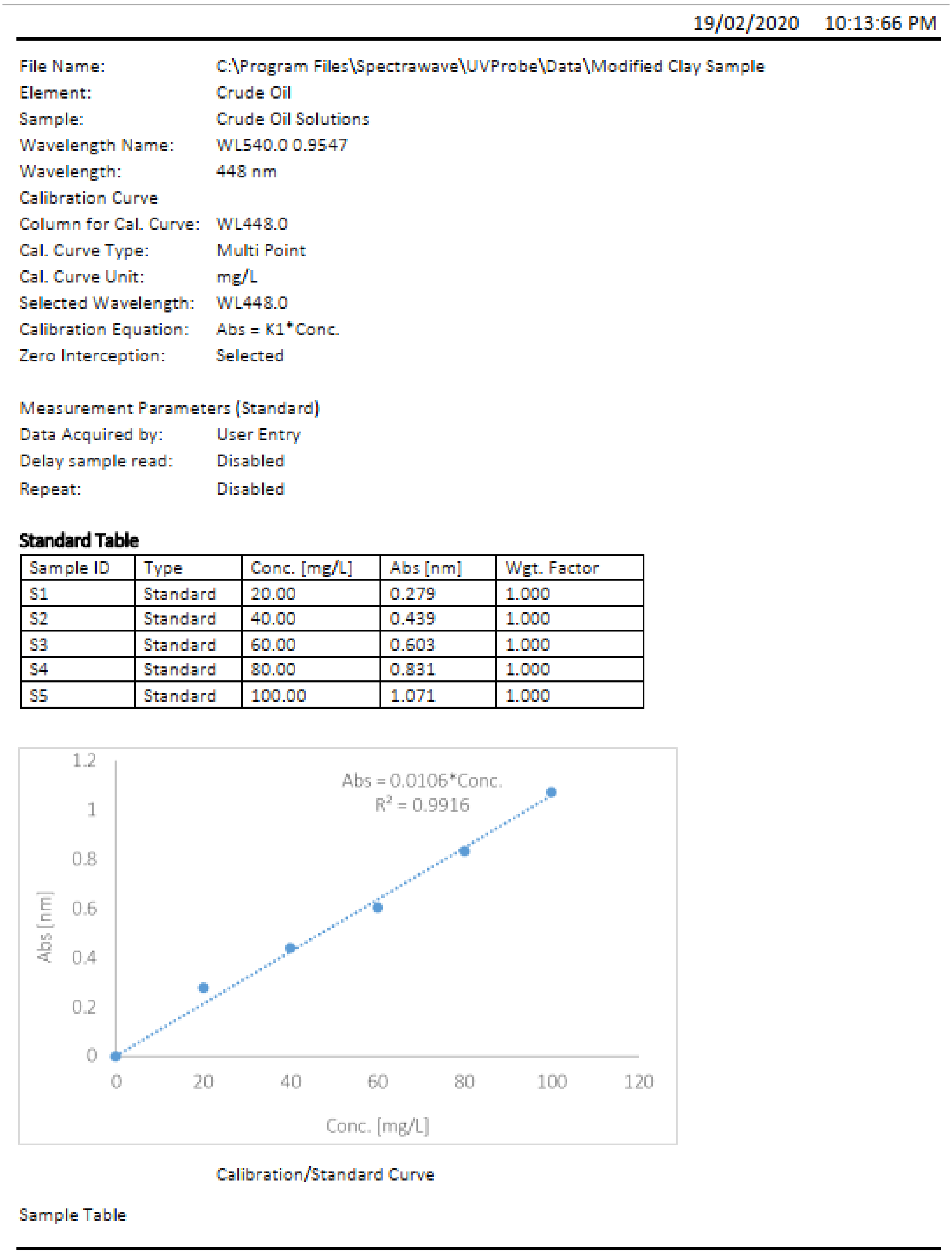
Yu, R. P. (2013). Synthesis, Characterisation and Application of Organic Surfactants Modified Clays for Water Purification. Ph.D. Thesis, School of Chemistry, Physics and Mechanical Engineering, Faculty of Science and Engineering, Queensland University of Technology: 20 – 30.

Zhang, W., Zhang, S., Wang, J., Dong, J., Cheng, B., Xu, L. and Shan, A. (2019). A Novel Adsorbent Albite Modified with Cetylpyridinium Chloride for Efficient Removal of Zearalenone, *Toxins*, 11(674), p. 1 – 15. doi:10.3390/toxins11110674.

APPENDICES

APPENDIX A

WASTEWATER UV-SPECTROPHOTOMETER ANALYSIS



19/02/2020 10:13:66 PM

File Name:	C:\Program Files\Spectrawave\UVProbe\Data\Modified Clay Sample
Element:	Crude Oil
Sample:	Crude Oil Solutions
Wavelength Name:	WL540.0 0.9547
Wavelength:	448 nm
Calibration Curve	
Column for Cal. Curve:	WL448.0
Cal. Curve Type:	Multi Point
Cal. Curve Unit:	mg/L
Selected Wavelength:	WL448.0
Calibration Equation:	Abs = K1*Conc.
Zero Interception:	Selected

Measurement Parameters (Standard)

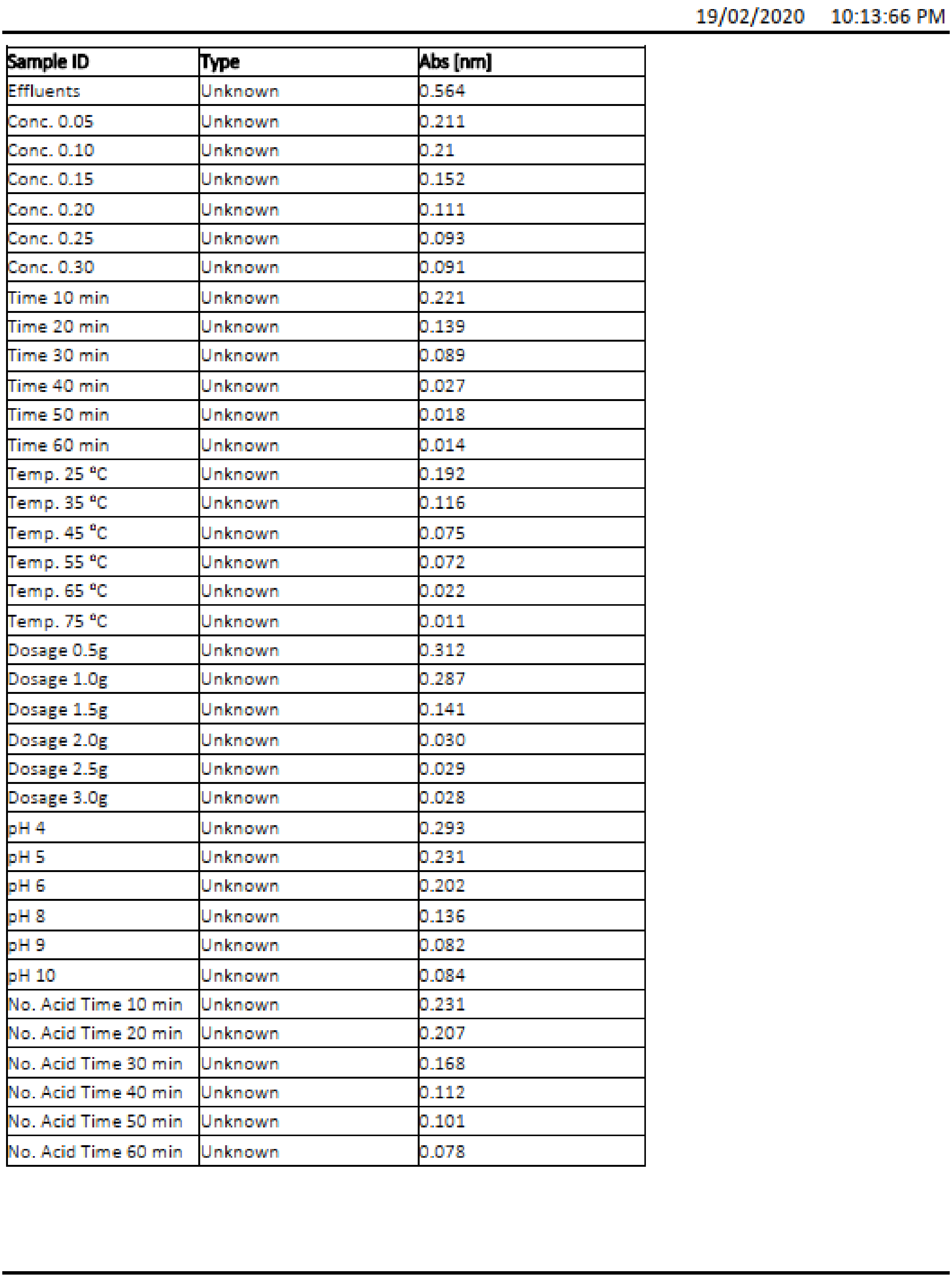
Data Acquired by:	User Entry
Delay sample read:	Disabled
Repeat:	Disabled

Standard Table

Sample ID	Type	Conc. [mg/L]	Abs [nm]	Wgt. Factor
S1	Standard	20.00	0.279	1.000
S2	Standard	40.00	0.439	1.000
S3	Standard	60.00	0.603	1.000
S4	Standard	80.00	0.831	1.000
S5	Standard	100.00	1.071	1.000

Calibration/Standard Curve

Sample Table



19/02/2020 10:13:66 PM

Sample ID	Type	Abs [nm]
Effluents	Unknown	0.564
Conc. 0.05	Unknown	0.211
Conc. 0.10	Unknown	0.21
Conc. 0.15	Unknown	0.152
Conc. 0.20	Unknown	0.111
Conc. 0.25	Unknown	0.093
Conc. 0.30	Unknown	0.091
Time 10 min	Unknown	0.221
Time 20 min	Unknown	0.139
Time 30 min	Unknown	0.089
Time 40 min	Unknown	0.027
Time 50 min	Unknown	0.018
Time 60 min	Unknown	0.014
Temp. 25 °C	Unknown	0.192
Temp. 35 °C	Unknown	0.116
Temp. 45 °C	Unknown	0.075
Temp. 55 °C	Unknown	0.072
Temp. 65 °C	Unknown	0.022
Temp. 75 °C	Unknown	0.011
Dosage 0.5g	Unknown	0.312
Dosage 1.0g	Unknown	0.287
Dosage 1.5g	Unknown	0.141
Dosage 2.0g	Unknown	0.030
Dosage 2.5g	Unknown	0.029
Dosage 3.0g	Unknown	0.028
pH 4	Unknown	0.293
pH 5	Unknown	0.231
pH 6	Unknown	0.202
pH 8	Unknown	0.136
pH 9	Unknown	0.082
pH 10	Unknown	0.084
No. Acid Time 10 min	Unknown	0.231
No. Acid Time 20 min	Unknown	0.207
No. Acid Time 30 min	Unknown	0.168
No. Acid Time 40 min	Unknown	0.112
No. Acid Time 50 min	Unknown	0.101
No. Acid Time 60 min	Unknown	0.078

APPENDIX B

ADSORPTION STUDY DATA

Table B1: Effect of Concentration

Initial Concentration (mg/L)	Percent Removal		
	Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
0	0.00	0.00	0.00
0.05	62.59	53.38	37.89
0.1	62.77	59.56	43.18
0.15	73.05	66.84	43.91
0.2	80.32	71.11	44.02
0.25	83.51	78.30	44.70
0.3	83.87	78.66	44.98

Table B2: Effect of Time

Time (min)	Percent Removal		
	Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
0	0.00	0.00	0.00
10	60.82	59.04	28.92
20	75.35	63.30	33.18
30	84.22	70.21	37.09
40	95.21	80.14	43.02
50	96.81	82.09	46.97
60	97.52	86.17	46.96

Table B3: Effect of Temperature

Temperature (°C)	Percent Removal		
	Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
0	0.00	0.00	0.00
25	65.96	56.08	40.82
35	79.43	68.55	49.30
45	86.70	80.82	53.78
55	87.23	89.11	58.26
65	96.10	89.84	58.74
75	98.05	89.95	58.77

Table B4: Effect of Dosage

Dosage (g)	Percent Removal		
	Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
0	0.00	0.00	0.00
0.5	44.68	32.09	14.55885
1	49.11	40.11	27.8977
1.5	75.00	64.22	40.5754
2	94.68	78.81	58.93081
2.5	94.86	89.86	67.93081
3	95.04	90.04	67.99081

Table B5: Effect of pH

pH	Percent Removal		
	Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
4	48.04965	39.06165	30.53
5	59.04255	50.05455	41.76
6	64.1844	59.1964	43.10
8	75.88652	74.89852	49.02
9	85.46099	77.47299	51.20
10	85.10638	77.11838	52.80

APPENDIX C

KINETIC STUDY DATA

Table C1: Pseudo-First Order Model

t (min)	$\ln(q_e - q_t)$		
	Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
0	3.6776	3.0776	3.6776
10	3.6569	3.0575	3.6678
20	3.6532	3.0560	3.6663
30	1.5847	2.7537	3.6650
40	1.5829	2.7502	3.6630
50	1.5828	2.7496	3.6616
60	1.5827	2.7482	3.6616

Table C2: Pseudo-Second Order Model

t (min)	t/qt		
	Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
0	0.00	0.00	0.00
10	12.36	12.73	25.99
20	21.00	23.75	45.32
30	26.78	32.12	60.81
40	31.34	37.52	69.90
50	38.83	45.79	80.03
60	46.25	52.35	96.06

Table C3: Intra-Particle Diffusion Model

t (min)	$t^{1/2}$	qt (mg/g)		
		Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
10	3.16	0.8090	0.7854	0.3847
20	4.47	0.9524	0.8420	0.4413
30	5.48	1.1203	0.9340	0.4934
40	6.32	1.2765	1.0660	0.5722
50	7.07	1.2877	1.0920	0.6248
60	7.75	1.2972	1.1462	0.6246

Table C4: Elovich Model

t (min)	ln(t)	qt (mg/g)		
		Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
10	2.30	0.8090	0.7854	0.3847
20	3.00	0.9524	0.8420	0.4413
30	3.40	1.1203	0.9340	0.4934
40	3.69	1.2765	1.0660	0.5722
50	3.91	1.2877	1.0920	0.6248
60	4.09	1.2972	1.1462	0.6246

Table C5: Boyd Model

t (min)	Bt		
	Acid Pre-treated CTMAB	CTMAB	Raw Bentonite
10	0.00036	0.00034	8.194×10^{-05}
20	0.00051	0.00039	1.079×10^{-04}
30	0.00071	0.00049	1.350×10^{-04}
40	0.00091	0.00064	1.818×10^{-04}
50	0.00093	0.00067	2.168×10^{-04}
60	0.00094	0.00074	2.167×10^{-04}

APPENDIX D

THERMODYNAMICS STUDY DATA

Table D1: Pseudo-First Order Model

Temperature (K)	k_c		
	Acid Pre-treated CTMAB	**CTMAB**	**Raw Bentonite**
298	1.0053	1.0033	1.0023
308	1.0054	1.0035	1.0026
318	1.0055	1.0037	1.0027
328	1.0056	1.0039	1.0032
338	1.0057	1.0041	1.0035
348	1.0058	1.0041	1.0038

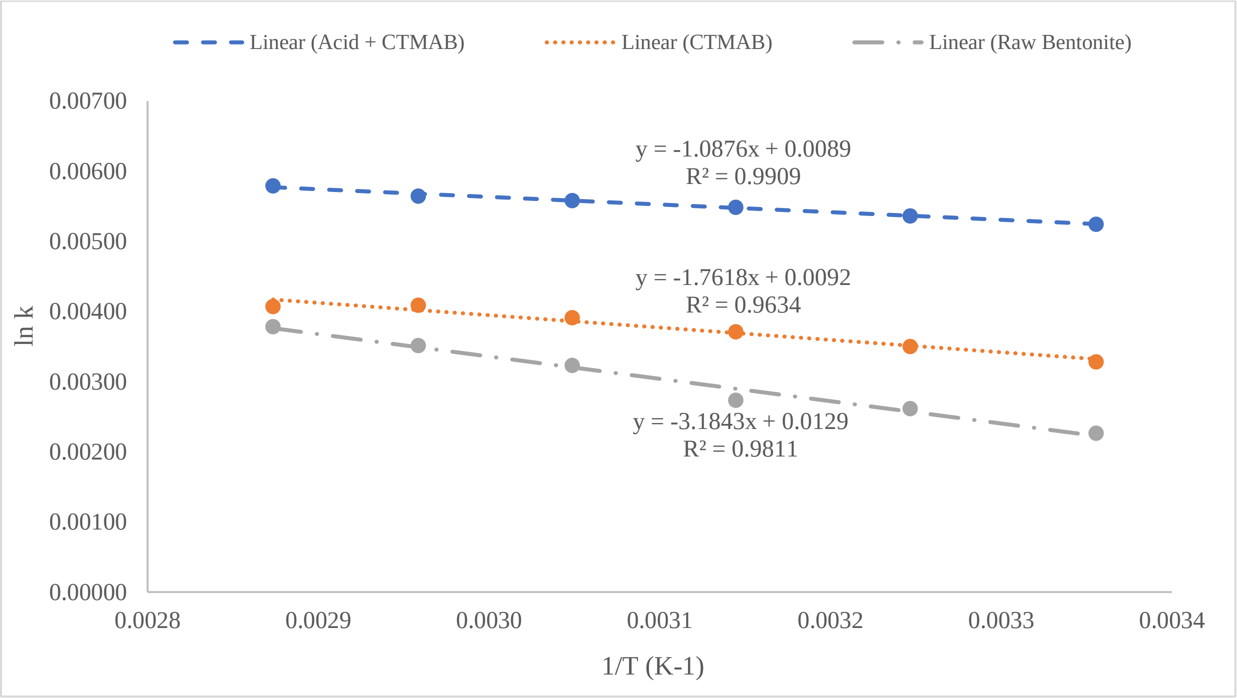


Figure D1: Thermodynamic plots for the adsorption of crude oil pollutant