



EXPANDED CLAY AGGREGATES FOR WATER PURIFICATION

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By

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CERTIFICATION

This is to certify that the thesis titled “*EXPANDED CLAY AGGREGATES FOR WATER PURIFICATION*” submitted to the school of postgraduate studies,
African University of Science and Technology (AUST), Abuja, Nigeria
for the award of the Doctorate degree is a record of original research carried out by
Ihekwe, Gina Odochi in the Department of Materials Science and Engineering.

EXPANDED CLAY AGGREGATES FOR WATER PURIFICATION

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ABSTRACT

Most poor and vulnerable people such as the peri-urban, people living in poverty and some internally displaced people (IDPs) are prone to water borne diseases because they drink polluted water. In order to improve water sanitation and hygiene (WASH) and to help achieve sustainable development goal (SDGs) six, a novel nano-adsorbent material, Expanded Clay Aggregates (ECAs) adsorbents produced from clay and biomass was developed. The raw materials for the production of ECAs adsorbents were sourced locally, processed and characterized by multiple means to uncover their salient properties in the first instance. The synthesized materials were formulated to form composites which were calcined to temperatures above 1000⁰C to produce ECA adsorbents. The adsorbents were tested on multi-filtration capabilities of known pollutants (*Eshchericia coli*, Phosphates, Nitrates, Arsenic and Lead). Excellent results with high efficiencies were achieved for both filtration and adsorption studies. The ability of the ECAs to remove contaminants was based on the fact that they are processed to nano-scale, which offered larger surface area, high pore volume and other novel properties required for filtration. The research has contributed towards finding a sustainable solution to the problem of inability of majority of Nigerians, Africans and other third world countries to have sustainable access to potable, safe and affordable drinking water. The research outcome has high potential for commercialization, which can lead to mass production of water filters.

Keywords: Water Purification, Clay Characterization, Filtration Membrane, Expanded Clay Aggregates, Heavy Metals, Bacteria.

This research work is dedicated to God Almighty and Our Mother Mary. Whenever my strength failed, I took delight in singing Psalms, Hymns and Songs of Praise. The rejuvenation from Blessed Sacrament after each visit, kept me going.

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List of Publications

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CHAPTER ONE

1.0 INTRODUCTION

1.1 RESEARCH BACKGROUND

Water (H₂O) is a liquid compound of two hydrogen atoms and one oxygen atom which at room temperature, is colourless, odourless, and tasteless. In its impure form, water exists as rain, ocean, lakes, rivers, etc (Dictionary.com; Anne, 2018). It covers about 71% of the earth's surface (Mahi & Isah, 2016). Water is universally utilized by humans, plants and animals. Clean, uncontaminated, or safe water is very essential to the well-being of humans whose body constitutes about 60% water for adult men and 50-55% in adult women (IOM, 2004; USGS). Adequate water intake per day for men was proposed to be 2.0 liters per day for females and 2.5 liters per day for males (EFSA, 2010). The human body metabolic and catabolic processes need water to optimize their functions (H4H Initiative, 2017). According to United Nation's 2006 report on power, poverty and global water crisis, every human has right to sufficient, safe acceptable, physically accessible and affordable water (Watkins, 2006). Water plays vital roles in socio-economic development, agriculture, domestic, industries and sustainable eco-system. "Water is essential to decent jobs and sustainable development" (WWAP, 2016). Invariably, water is life since all known forms of living and survival largely depends on it. Though it does not add nutrient or calories to the body (Mahi & Isah, 2016). Contaminated water (water that contains pathogens, viruses, chemicals, heavy metals and other toxins) can pose danger to health and hence affect the quality of human life (WHO, 2019). Drinking water which is considered safe must be free from these contaminants or within acceptable range of contamination standard

(Siong et al., 2016). It is important to note that getting water that is 100% 'pure' may be practically impossible even with recent modern developments.

The joint report of World Health Organization (WHO) and United Nations Children's Fund (UNICEF) 2017, estimated that 2.1 billion people globally lack access to safe water for household and other utilities while 4.5 billion people does not have basic sanitation system (WHO and UNICEF, 2017). Contaminated water together with poor sanitation is estimated to cause about 1.8 million deaths and 61.9 million disabilities per year (WHO and UNICEF, 2001). A newborn is lost per day globally as a result of infectious diseases caused by dirty environment and unclean water (WHO and UNICEF, 2015).

Africa, an arid continent of about 1.45 billion has 677 lakes, dams, canals and rivers as sources of surface water together with underground water sources, yet its biggest challenge is poor access to safe drinking water. About 319 million people have no access to safe drinking water and about 159 million people from the region fetch water from sources outside their homes for drinking and other utilities. An average of 30 minutes is spent per trip to the source. Currently, 14 countries in Africa are experiencing water stress while it is estimated that 25 countries will be in serious stress by the year 2025 (WWAP, 2016; WHO, 2019). In situation like this, women and girl children are the ones that suffer most as the domestic demands on water rest on them, forcing some to drop out of school (Graham et al., 2016). Both natural phenomenon and human factors have been identified to be instrumental to lack of access to water (UNWA, 2003).

The most populous country in Africa, Nigeria currently is estimated to have a population of over 209 million as at January 2021 (Worldometers, 2021). This is projected to rise to 392 million by the year 2050 making it the 4th most populous country in the world (CIA, 2017). Nigeria except

the Niger Delta and some part of the Northern regions is currently not among the water- stressed African countries. However the quality and quantity of water together with conflicts among communities over water resources boundaries cannot be over looked.

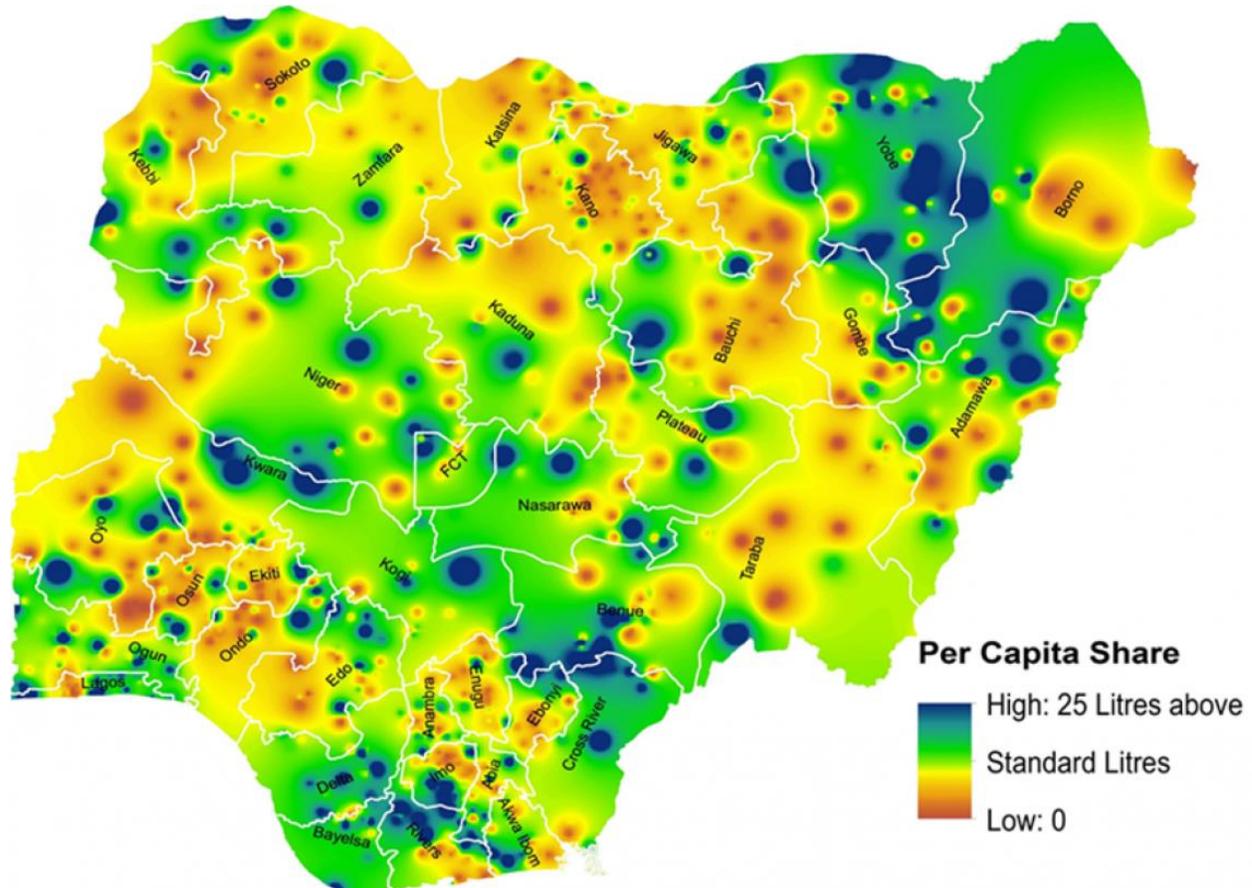


Fig.1.1. Map showing access to water in Nigeria (UNICEF, 2020)

The Federal Ministry of Water Resources and UNICEF in 2020 reported that about one-third of Nigerians drink contaminated water and 46 million still practice open defecation (UNICEF, 2020). Only a few have access to required quantity despite the quality while most states predominantly in the Northern part of the country have poor access to water (Figure 1.1). In fact, since the outbreak of Coronavirus disease (COVID-2019), it has become urgent to improve access to Water Sanitation and Hygiene (WASH) by investing on the expansion of basic washing

facilities to curb the spread of the virus especially in schools (UNICEF, 2020; WHO and UNICEF, 2020). It was also highlighted that access to WASH is not keeping pace with increase in population across Nigeria. WHO and UNICEF emphasized the importance of hygiene for reducing transmission and recommended all schools enforce regular hand washing, ensure daily disinfection and cleaning of surfaces, provide basic water, sanitation and waste management facilities, and follow appropriate environmental cleaning and decontamination procedures (WHO and UNICEF, 2020).

The need for access to clean water for all is therefore imperative to improve the quality of life of people without drinking water by providing safe clean and affordable water using appropriate purification technologies that are cheap to combat the spread of COVID -19 and other health related issues and deaths that are linked with water borne diseases.

1.2 PROBLEM STATEMENT

The need for safe clean drinking water cannot be over emphasized as it is obvious that there is a global water stress despite the efforts of relevant agencies (donor agencies inclusive), organizations (including non- governmental organizations (NGO) and stakeholders. The earth is covered by 71% water out of which only 2.5% is fresh water. The surface water, dams, rivers, streams, ponds, canals, lakes, are only 0.3% while 98.8% is ice and ground water leaving the remaining in biological bodies. Fresh water sources are usually contaminated with chemicals, heavy metals, pathogens, microbes, and other toxicology contaminants as a result of mining, industrial effluents, poor sanitation system and agricultural activities. Drinking water and water for other utilities must be free from these contaminants before it is considered safe for use.

Filtration is one of the methods used in water purification. Many researchers have worked on the filtration of common contaminants found in water which are usually of bacteria, fungi, virus, metals and chemical origin. Preliminary studies show that most water treatment plants are based on sand filtration concept together with chemical additives to provide residents with 'safe water'. In addition, the use of chlorine after the sand filtration can be eliminated by using other earth based techniques. Water disinfection by chlorine and aluminium sulphate (alum) is universally accepted. In fact chlorine disinfection is a yardstick that is used to compare other purification technique in terms of water quality and standard. Such disinfection should be monitored very closely because of the disinfection by products (DBP) that are generated afterwards. Such DBPs are the trihalomethanes (THM's), trichloroacetone (CCl₃COCH₃), chloroamines, chlorophenols and other halogenated intermediate compounds. These chemicals have direct health hazard relationship; unfortunately, there is no equipment/technology to ascertain the level of these DBPs in Nigeria. More so, the cost of purchasing flocculants and coagulants are too high. For instance, aluminium has been linked to Alzheimer disease, Parkinson, memory loss and brain damage diseases while the DBPs are linked to cancer and infertility. One of the techniques to mitigate such problems and that of water borne diseases is the use of expanded clay aggregates.

Summarily, the problem being addressed is lack of access to clean potable and affordable water especially for the peri-urban poor in slums and vulnerable groups such as internally displaced persons (IDPs) and school children. The research tends to provide a solution based on development of novel materials that are locally available, renewable, bio-based, no chemical additive and requires no energy to operate for the removal of known pollutants (bacteria, viruses, nitrates, phosphates, heavy metals, etc) and emerging pollutants (pharmaceuticals) from water and waste water.

1.3 RESEARCH AIM AND OBJECTIVES

The main aim of the research is to contribute towards finding a sustainable solution to the problem of inability of majority of Nigerians and other Africans to have sustainable access to potable, safe and affordable drinking water. By using theoretical modelling and experimental analysis, the adsorbents are to be developed using cheap and available materials processed using the highest level of Science and Nanotechnology to provide clean water. Among other goals, the research will tend towards improvement of WASH, provide data and properties of some the Nigeria clay minerals and biomass, reduce prevalence of waterborne diseases by providing solution to contaminated water filtration and economic recovery through value addition to Nigerian minerals and renewable waste. The outcome can be commercialized since the filter requires no special skill, cheap and no electricity to operate.

The specific objectives are to:

- (i) Prepare and characterize samples (clay and rice husk) by multiple means for the production of Expanded Clay Aggregates. The raw materials for the production of ECA adsorbents will be sourced locally, processed and characterized to uncover their salient properties in the first instance.
- (ii) Synthesize and characterize raw materials which will be formulated to form composites that will be calcined to a temperature above 1000⁰C to produce ECA adsorbents.
- (iii) Produce ECAs, characterize and test on their ability to remove multiple contaminants such as microbes (E.coli), chemicals (Phosphate and Nitrate) and heavy metals (Lead and Arsenic) contaminants and their adsorption studies.

1.4 JUSTIFICATION

The rationale for this research is to decrease the incidence of water borne diseases that are caused by bacteria, phosphate, nitrate and heavy metals (lead and Arsenic) and possibly eliminate the use of chemicals such as alum and chlorine in water treatment purposes. Commercialization of Expanded Clay Aggregates to filter water at point of use and municipal water treatment plants are highly feasible. The technique when adopted for large treatment plants will proffer the following advantages;

- (i) cost benefits and savings from overhead/ running cost. The pressure and energy required for frothing during backwashing will reduce drastically because frequent backwashing will no longer be required as in the case of sand filter medium.
- (ii) the use of chemicals (alum and chlorine) may be eliminated. Huge sum will be saved as the chemicals that are used in Nigeria's water treatment plants are imported. DBPs associated with these will also be eliminated which will in turn reduce the health effect of water borne diseases and the likes.
- (iii) larger pore volume of the expanded clay aggregate will produce water that is safer and cleaner in terms of quantity and quality than sand filter medium.

1.5 RESEARCH GOALS

The project goals include;

- i. To improve water sanitation and hygiene by developing water filters based on available local materials.

- ii. To provide data and information on properties of local minerals (clays and biomass) in relation to their suitability for water filters production and other industrial application.
- iii. To provide water solution to vulnerable groups such as the peri-urban people living in poverty and IDPs.
- iv. To reduce the prevalence of waterborne disease.
- v. To add value to Nigeria's abundant mineral resources (clay) and economic recovery through utilization of non-renewable industrial waste (rice husk).

1.6 SCOPE OF WORK

The scope and organization of the work take the following forms; chapter one is the general introduction about water, its importance, daily intake requirement and other uses. The global, Africa and Nigeria scarcity and projections in the years to come viz-a-viz population growth was discussed peripherally. The problem statements, research aim and objectives, goals and justification for the study were also presented.

Chapter two understudies a detailed literature review on the access to clean drinking water and water bodies globally, in Africa and Nigeria. The factors and challenges of poor access and recommendations to water problems were also reported. The chapter also presented the sources of water, water quality and water contaminants. Water treatment techniques and technologies, raw materials for water purification, taking a holistic look on clay materials both as a ceramic media and in aggregate forms were discussed. The unresolved issues and gaps in knowledge were presented.

The raw materials sources, preparation and characterization by multiple means which reported results of physical assessments, morphologies, functional groups, mineralogies, zeta potentials, etc of different clay minerals were presented in chapter three. Appropriate selection based on the reported properties for use in production of Expanded Clay Aggregates and other industrial applications also were discussed in this chapter.

Chapter four presented the plastic characteristics of the clay samples using compression and Atterberg limits tests. Results were discussed inter-alia moisture contents, chemical compositions and mineralogies. Insight on plastic properties of clay materials and potential uses were provided.

Chapter five reported the process of Expanded Clay Aggregates production at different formulations and calcination temperatures. Characteristic features of the produced ECAs based on morphology, mineral compositions and surface area were reported. Filtration test for E.coli bacteria, Phosphates and Nitrates were examined and removal efficiencies reported. Finally, batch experiments and adsorption studies of Arsenic and Lead were carried out. Results of Isotherm models, and conditional effects such as pH, reaction kinetics, adsorbent dosage and cycle experiment were also reported.

Recommendations and conclusions are presented in chapter six.

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CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 ACCESS TO DRINKING WATER

One of the twenty first century's issues is water. Water is needed by all human, plants and animals for economic productivity and social well-being. Lack of water has enormous consequence and affects the general well-being of humans and limits economic development. Water and its importance has been a subject of discuss and a reoccurring decimal at United Nation's meetings. For instance, in her meeting at Rio de Jainero 1992 (UN, 1992), several programme areas which included; integrated water resources development and management; water resources assessment; protection of water resources, water quality and aquatic ecosystems; drinking water supply and sanitation; water and sustainable urban development; water for sustainable food production and rural development and impacts of climate change on water resources were proposed for freshwater sector. Almost three decades after, water problems are still persistent.

Deeply concerned about the global lack to safe water and sanitation, the United Nations in its 2010 general assembly declared safe, clean and affordable drinking water and sanitation as basic human rights because they are essential to the sustainability of healthy living and fundamental in maintaining the dignity of all human beings (UN, 2010). This resolution was reaffirmed in 2019 and 2020. (Roaf et al., 2019; UN, 2020). Previous declarations such as "International Year of Freshwater" (2003), "International Decade for Action 'Water for Life'" (2005-2015) and International Year of Sanitation (2008) culminated into the 2010 declaration. Despite the efforts of donor agencies, government and all relevant stakeholders on water and sanitation, billions of

people globally still lack access to these basic needs although successes were recorded on improved services from 2000 to 2017 (WHO/UNICEF, 2015 & 2017). Goals and targets are set, monitored and reported from time to time. The Millennium Development Goal 7 worked towards halving the proportion of world population without sustainable access to safe drinking water and basic sanitation by the year 2015. Result indicated that, people without access to clean water reduced to 9% from baseline level of 24% while that of sanitation was missed and only reduced from 46% to 32% (United Nations, 2015). The Sustainable Development Goal 6 targets ensuring that clean, safe and affordable water and sanitation are accessible to all by the year 2030. This goal when actualized, will indirectly affect the attainment of other goals such as goal 1, 3, 5 and 15. The vulnerable, people living in poverty and least powerful are those without access to water and these could impede their potentials and visions (Watkins, 2006).

2.1.1 Global Access to Drinking Water and Challenges

The challenge of access to clean water has been there since time immemorial. In the 1900s about 0.24 billion (14% of global population) are without access to clean water. The figure increased to 3.8 billion (58%) in the 2000s (Kummu et al., 2016). Despite the achievement of the MDG goal 7C, i. e increment on successful access from 71% in 1990 to 91% in 2015 (WHO and UNICEF, 2015), many people are still without access to clean water globally. Global coverage point at 96% success if current indicator trends are maintained (WHO & UNICEF, 2017). Due to growing population, socio-economic development, climate change, industrial and domestic usage, water use has been growing to about 1% since 1980 and it is expected to last up to 2050 (Kummu et al., 2016; UN, 2019). The United Nation's world water development report 2019 also mentioned that over 2 billion people live in countries with high water stressed areas whereas about 4 billion people experience severe water scarcity at least one month in a year.

The disappearing rivers, shrinking lakes and dams will continue to be a global problem if adequate measures are not put in place. Agriculture and in turn food security is being threatened by water scarcity. Climate change has been identified as one of the major nexus of water challenge which give rise to higher temperature of seas, melting of the glaciers and intensification of water cycles that results in more flood and droughts (Solomon, 2011; Elimelech, 2006; Huntington, 2006; Shevah, 2015; Okonkwo, et al., 2015). Population explosion and urbanization contribute to water shortage especially in the arid and semi-arid regions.



Fig.2.1. Disappearing Aral Sea (NASA Earth Observatory Map, 2014)

Aral Sea in Kazakhstan North Uzbekistan Central Asia (Figure 2.1) that used to be the world's fourth largest lake is about 10% its original size (Eric, 2014). In 1998, it was reported that water level was down by 20m and a volume of 210km³ as compared to 1, 060 km³ in 1960 and 68, 000km³ original size causing the lake to split into four lakes. The southern and eastern lakes that

made up the southern Aral Sea shrunk to strip around 2009. While the southern lake keep disappearing and reappearing, the eastern lake dried up completely in 2014 making a history. It is now known as the Aralkum Desert (https://En.wikipedia.org/wiki/Aral_sea). Efforts are being made to salvage the drying north Aral Sea by dam construction around the area that supplies the salty lake with fresh water although some researcher believed that the lake will dry up completely by the year 2020. Drought and irrigational diversions are major causes of such shrinkage (Brain, 2014).

The Sea of Galilee (Figure 2.2) has receded for over 30 years due to drop in annual rainfall. In 2018, water level dropped to the lowest causing the Sea to become more salty and less viable as drinking water (Voiland, 2020). Desalination and expensive purification methods become necessary. However, water level has gradually increased since the rainy season of 2019 and as at April 2020, it rose about 16cm below the upper red line (Tzvi, 2020)



Fig.2.2; Map showing the drying Sea of Galilee (NASA Earth Observatory images by Joshua Stevens, using Landsat data from the U.S Geological Survey and topographic data from the Shuttle Radar Topography Mission (SRTM) 2020.

Poyang Lake in China and Lake Chad have been in the media report for the past decades. Notably, Lake Chad which is the sixth largest lake in the world is fast diminishing (Gao et al., 2011). Bordered by Nigeria, Chad, Niger and Cameroun, the lake became about one tenth of its 1960 original size in 2017 (Figure.2.3). It was reported that the lake spanned at least 22,000 Km² in the 60s (Hansen, 2017) and 25, 000 Km² (Okonkwo et al., 2015). In the 70s, water started disappearing and reappearing in the Northern region depending on the season. However, the northern and southern region never reconnected back again as a whole lake. Hydrological and VIC models which was used to study the water level and extension (Lemoalle et al., 2012; Gao et al., 2011) revealed that shortage of rainfall and continues drought around the basin contributed to drying of the lake. However, a proper management of renewable water resources was

recommended. Models and satellite data are being used by researchers to understudy the lake as insurgency, kidnappings, bombings and wars have made ground-based measurements difficult to achieve.

The means of livelihood of the rural dwellers within the lake which comprises; farming, fishing, livestock farming, suffer a lot of setbacks. The ripple effects of this also forced the herdsmen to migrate down south in search of greener pastures and causing more bloodshed when they are not in peaceful coexistence with their host communities. Lake drying affects the socio-economic activities, draw backs and livelihood opportunities of the dwellers (Okpara et al., 2016). The water resources renewable management, joint inter-governmental efforts, political wills, developmental assistance, agricultural practices, etc are some of the strategies that will revitalize the lake and give succor to the communities that depend on it for survival. Conferences and seminars are being held among international communities as in the case of Lake Chad to save the lake in order to revive the basin's ecosystem for sustainable livelihood security and development

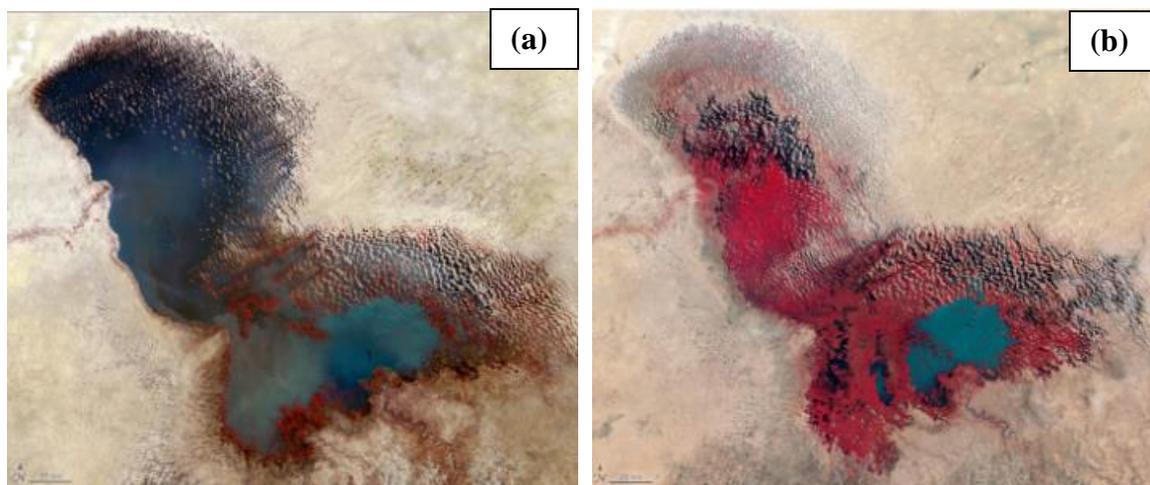


Fig.2.3. Disappearing lake Chad (a) 1973 and (b) 2017 (NASA Earth Observatory, 2017)

Consequently, this public outcry on the disappearing lakes, seas, rivers, dams and streams contribute to water scarcity and access lacked by one third of the world's population. Water productivity is low in most countries and the available ones are poorly managed. It is estimated that when enough water is produced, food production will double by the year 2050 thereby reducing the number of 925 million mal-nourished people on earth (Solomon, 2011; Rosegrant, 2015) since agriculture is the major consumer of fresh water. Research study on impacts on freshwater availability and further implications for global food production reported that 24% of the global population lives in area under chronic scarcity while 19% live under occasional water scarcity which consequently results in about 2.6 billion people living some degree of poor reference diet (Kummu, et al., 2013).

2.1.2 Access to Safe Drinking Water in Africa

It was perceived that Africa has water scarcity which may lead to water crises. Global indicators and statistics are making it more real than myth (Naik, 2017). The Joint Monitoring Program (JMP) report on Progress on household drinking water, sanitation and hygiene, quoted that “in 2017, nine out of ten of the 785 million people who still used limited services, unimproved sources or surface water live in three regions: Sub-Saharan Africa (400 million), Eastern and South-Eastern Asia (161 million), and Central and South Asia (145 million). More than half of the 144 million people who still collected water directly from rivers, lakes and ponds lived in Sub-Saharan Africa” (WHO & UNICEF, 2017).

General household survey using Probit regression in 2014 showed that about 29.68 % of the people living within a study area in South Africa pay for safe drinking water. Also, the survey reported that children under age five suffers diarrhea mobility due to fecal contamination

resulting from lack of basic sanitation and exposure to pathogens via the food chain (Oyekale, 2017). Similar result was reported for Limpopo province, South Africa (Edokpayi et al., 2018). Armah et al (Armah et al., 2018) used a pooled regression analysis of the compositional and contextual factors that systematically vary with access to water and sanitation services over a 25-year time period in fifteen countries across sub-Saharan Africa (SSA) in their study. The study reported provision of access to improved water sources from 1990 to 2015 as against unimproved sanitation facilities over the same period which was attributed to environmental, cultural, economic and human behavior. Similar studies conducted about a poor peri-urban settlements of Abidjan, Côte d'Ivoire, using multivariate logistic regression model showed that about 25% of people do not have access to clean safe water while 57% lack basic sanitation practice (Angoua et al., 2018). In Eswatini (formerly known as Swaziland), Eswatini Multiple Indicator Cluster Surveys (EMCSs) data for access to clean water in 2010 and 2014 was analyzed using Bivariate and Multivariate complementary log-log regression, households' access to improved drinking water sources significantly improved from 73.1% in 2010 to 77.7% in 2014 ($p < 0.0001$) (Simelane et al., 2020). According to the study, in 2010, household heads between ages 35-54 years irrespective of sex had improved access while age 55 years and above had lower odds towards improved drinking water sources whereas in 2014, the lower odds were from households with female heads and more populated household. Successes in both years were attributed to wealth index of household.

2.1.3 Access to Safe Drinking Water in Nigeria

Nigeria is the largest country in Africa with a population of over 182 million people as at 2017 (World Bank, 2017) and over 209 million in early 2021 (Worldometers, 2021). Access to Water Sanitation and Hygiene (WASH) is markedly lower than counterpart countries. 57 million people

continued to live with poor access to clean water while 130 million practice poor sanitation systems. The Nigeria water sector faces significant challenges (WHO & UNICEF, 2017; World Bank, 2017). Drinking water supply and distribution in Nigeria is still low despite being blessed with adequate water sources. Notably, there are variations between water sources availability in the North and the South. Mean number of rainy days decrease from South to North. No part of Nigeria can claim good access to safe and affordable drinking water despite the natural water supply policy whose aim is to ensure adequate supply of quantity, quality and affordable access to safe drinking water for all citizens. National water programmes have been in existence since the 1960s. Lake Chad and the Niger River Basins Commission were set up within the Country and bordered countries while the Sokoto Rima and the Chad Basin Authorities were established in 1976 (Olusumbo, 2001). Other water issues related Agencies and Institutions including international organizations were set up to develop Nigeria's water resources and management to cushion the effect of anticipated population expansion and urbanization, yet most cities and citizens still lack access to clean water as result of poor performance of these agencies (World Bank, 2017).

However, Nigeria recorded improved water supply from 47% in 1990 to 58% in 2008, she did not meet the benchmark of Millennium Development Goal (MDG) of 75% coverage by 2015 (Akpor and Muchie, 2011). Research surveys using different models for analysis on access, quality, quantity, reliable and affordable in different parts of Nigeria showed poor access to quality water (Emenike et al., 2017). Some states like Lagos and Kwara have more access to pipe borne water than the Ebonyi and Taraba (Lukman et al., 2016).

2.1.4 Factors Affecting Access to Drinking Water in Nigeria

The factors that affect access to drinking water in Nigeria are both man-made and natural phenomenon. In 2007, the Inter-Governmental Panel for Climate Change (IPCC), reported that global warming will be more intense in African than the rest of the world (IPCC, 2007). The climate change will be characterized by rising temperature which will amplify water loss with highest increase in the Western Sahara Region. Such proposition is now playing out especially in the non-coastal region of Africa; Nigeria inclusive.

The amount of time spent in collecting water (distance to the water source, queuing, filling of water containers and going back home) is high in countries where access to drinking water supplies located on premises is not common. Time factor associated with water scarcity is a man-made factor. WHO/UNICEF used threshold of 30 minute for water collection, above such time is described as limited access. Cassivi et al.,'s (Cassivi et al., 2018) household survey in seventeen (17) countries with lowest rankings when it comes to on-premises water access, highlighted the burden of time factor which decreased access to water by 13% on the average when a 30 minute collection time was used as a monitor. Similar result was reported for 23 countries where 50% of the population depends on the water sources outside their compounds where the main responsibility of fetching water lies more on women and children (Graham et al., 2016; Geere & Cortobius, 2017). Rapid industrialization, population growth, climate change (Wada et al., 2011; Dinka, 2018; Dos Santos et al., 2017; Alirol et al., 2020), and socio-economic status and slum settlement characteristics such as poor practices of water usage (UN-HABITAT, 2003; Ooi & Phua, 2007; Ezeh et al., 2016), contamination from sewage and latrines have been reported to be part of the factors that affect access to safe drinking water in some localities.

Abubakar utilized descriptive and inferential statistics to evaluate factors that influence household access to drinking water in Nigeria (Abubakar, 2019). The reported regression analytical findings included but not limited to place of residence ($\chi^2=8328.2$), geopolitical zone ($\chi^2=12042.8$), education ($\chi^2=5346.2$), wealth index ($\chi^2=16540.3$), ethnicity ($\chi^2=8649.9$), access to electricity ($\chi^2=8040.9$), and gender ($\chi^2=537.3$). Similar findings ($p < 0.01$) was reported by Akoteyon (Akoteyon, 2019). Other factors reported in literature are; corrupt government, failed central planning and implementation of water policies and standards (Dinka, 2018), poor operation and maintenance practice of existing water treatment plants (Akali et al., 2015; World Bank, 2017), drought due to human water consumption (Wada et al., 2013), insurgency, ethnic and tribal conflicts which often result in communal clashes and war (Emmanuel, 2010; Amnesty International, 2002).

2.1.5 Strategies for Improving Access to Drinking Water in Nigeria

Interdisciplinary research among scholars and research findings domestication by industries should be encouraged (Armah et al., 2018). Socio-economic factors such as improved Gross national Income (GNI), policy interventions and implementation, control of corruption, political stability by the government can help improve access to clean and affordable water (Nwankwoala, 2012; Komolafe and Agboola, 2013; Obeta, 2018; Gomez et al., 2019). Physical aspect of water scarcity can be controlled by better management, establishing water supply infrastructure including mini water scheme, infiltration gallery and rural water collection pattern (Olu, 2014; Jideonwo, 2014; Ingram & Memon, 2020; Hope et al., 2020), increase sustainability to cushion evolving challenges (Kummu et al., 2016; Naik, 2017), good water practices in terms of consumption /use and cost recovery (Ademiluyi and Odugbesan, 2008; Abubakar, 2018) and

recognizing local water vendors through public private partnership and hence control their charges which is higher than the average water board rate (Ahmad, 2017).

2.2 SOURCES OF WATER

The sources of water supply are broadly grouped into surface and ground water sources. Earth's water distribution constituents as shown in figure 2.4. Only about 2.5% is freshwater from which 30.1 % are underground, 1.2% are surface and 68.7% are trapped as glaciers and ice (Shiklomanov, 1993). No wonder the global water crises, the compositions of river water is 0.49% while lake is 20.9%. The water characteristics, importance, resources , issues, challenges and management was discussed extensively in Olusumbo's lecture (Olusumbo, 2001). With increase in drying rivers and lakes due to climatic conditions and other prevailing issues, water recovery and treatment becomes necessary to mitigate such challenges. The sources of water affects the raw water quality which in turn determines the type of treatment and finished product expected. Treatment choice is largely determined by the quality of raw water, available processes, cost and the expected standard.

Where is Earth's Water?

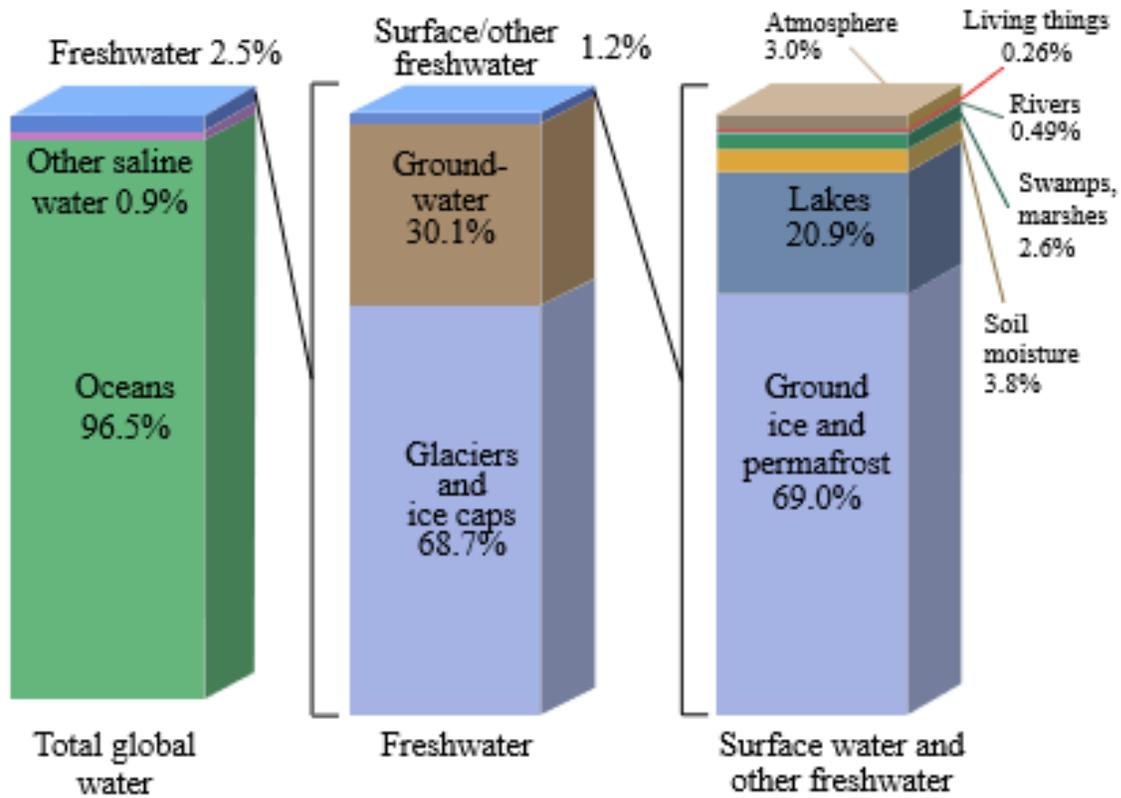


Fig. 2.4. The Earth's Water Distribution.
 (https://en.wikipedia.org/wiki/File:Earth%27s_water_distribution.svg.)

2.2.1 Surface water

Surface water includes; rivers, dams, lakes, canals and streams. They are easily contaminated by bacteria, protozoa and algae. These contaminants may arise as a result of runoff water after rainfall which carries a lot of particles from human habitation, agricultural fertilizers, pesticides, chemicals and industrial waste. Sewage, sludge and industrial effluents are usually discharged in surface water or in landfills in developing countries and quasi-developed countries. It is usually recommended that the water sources be cordoned off from human activities and should be surrounded by buffer zones covering a lot of area. The buffer zones help to filter out the large

particles and prevent them from getting into the source. Rain and fog harvest may be considered sources of surface water (Winter, et al., 2005)

2.2.2 Ground water

This is mainly wells and boreholes dug underneath the earth surface into the water aquifers to extract water. These aquifers may have come to be as a result of rainfall over several years ago. Some aquifers are confined beneath rocks while some are found just some are found just below the water table. The quality of water here is determined by the depth of the well or borehole. Deep ground water is naturally filtered by materials such as soil, clay and rocks. These materials clean the water and present it with clarity and low in turbidity. It is usually free from pathogens and bacteria but contains a lot of dissolved carbonates, sulfates of calcium and magnesium and heavy metals especially cadmium and arsenic for shallow wells (Sharma & Bhattacharya, 2016).

2.3 SAFE DRINKING WATER: STANDARDS AND QUALITIES (WATER SAFETY)

Water has direct impart to human's health, whether used for domestic purposes, drinking, food/beverage production or recreational activities (WHO, 2017; Gorchev & Ozolins, 2011). The quality of water is not to be compromised as the human body is more than 60% water (Mahi & Isah, 2016). Visualization of water such as odour, clarity and taste are not guaranteed ways of ascertaining water quality as clarity does not mean standard. Physical/chemical assessment and monitoring of water quality/standard are necessary and should be done periodically to ascertain the level of contamination at all times. Physical parameters such as pH, turbidity, colour, acidity, alkalinity and chemical contaminants such as levels of chlorides, nitrates, fluorides, nitrates, ammonium, phosphorous, chemical oxygen demand (COD), total dissolved oxygen (TDO), lead, arsenic, cadmium, etc are tested to measure standard. Biological assessments to determine the contaminants like bacteria (*Escherichia coli* (*E.coli*)), algae pathogens viruses and fungi are

equally necessary as exceeding the acceptable limit may pose danger to health (CityWestWater, 2017).

Water quality is not only achieved by purification, deficient minerals may be added to improve the properties. The water quality standards are predominately covered by World Health Organization Guidelines for Drinking Water and other international organizations (Sayato, 1989). However, every nation has its own standard which is usually extracted from international standard with little or no modifications. These standards are subject to change as soon as new water related discoveries are established through research. More so, quality standard depends on the given application of the water which in turn determines the maximum allowable level of pollution. Nigerian standard for drinking water quality was established in 2005 by National Council for Water Resources (NCWR) when it was discovered that the operational standards established by Standards Organization of Nigeria (SON) and Federal Ministry of Environment were not well accepted by all stakeholders (Standards Organization of Nigeria, 2007). It is sad to note that water quality and standards are not been enforced or checked in most developing countries including Nigeria especially around the urban areas.

2.4 WATER CONTAMINANTS

Common contaminants or pollutants found in drinking water may lead to chronic health effects like cancer, liver, bladder and kidney problems when they are above permissible threshold. These contaminants are grouped into microbial, chemical pollutants (organic and inorganic) and disinfection by-products contaminants. Others include biological pollutants such as turbidity, organic matter, natural and anthropogenic which occurs due to seasonal factors. Chemical pollutants include heavy metals and metalloids and other synthetic organic chemicals. They can

be transmitted through food chain that are irrigated with contaminated water or poisonous chemicals that are absorbed by aquatic animals like fishes and sea foods. Swimming frequently in contaminate surface water can also lead to illnesses which affect human health. The global discuss on water pollution was captured in (Schwarzenbach et al., 2010)' review even though it is inexhaustible.

2.4.1 Microbial Contaminants (Pathogens)

Microbes with minute infectious dose (e.g., *Giardia*, *Cryptosporidium*, and *Shigella* species; hepatitis A virus; enteric viruses; and enter hemorrhagic *Escherichia coli*) may cause illnesses no matter how little is swallowed. This is because total immunity does not develop for most enteric pathogens and hence may induce a re-infection (Backer, 2002). *Cryptosporidium* is an emerging pollutant excreted from oocyst from infected animal with currently no specific cure. It is a protozoan, gastrointestinal parasite which gives rise to severe, self-limiting diarrhea when ingested. This has caused waterborne disease outbreaks in United Kingdom and United States of America killing immune-compromised patients (Hoxie et al., 1997). Some pathogens like *Aeromonas* species are harmless (Hunter, 1997). *Pseudomonas aeruginosa* may multiply during distribution and known to cause infection in patients with weak immune system (Fawell & Nieuwenhuijsen, 2003).

Traditionally, it is believed that freezing of water eliminates microorganism. This is not true as most enteric pathogens and organisms including *shigella* species and *salmonella typhosa*, hepatitis A virus, and *cryptosporidium* species can survive for a long period of time in both cold and frozen waters (Dickens et al., 1985).

2.4.2 Inorganic Contaminants

These include heavy metals such as Lead (Pb), Zinc (Zn), Chromium (Cr), Nickel (Ni), Mercury (Hg), Copper (Cu), Cadmium (Cd), Plutonium (Pu) and metalloids such as Arsenic (As) and Selenium (Se). They are highly toxic even when present in small quantities. Their transport mechanisms depend on reactions to varying conditions which include but not limited to oxidation/reduction, adsorption, complexation, and precipitation/dissolution reactions. X-ray spectroscopies have become veritable tool in the study of metal ions and their interaction on mineral surfaces and at such exposes the factors that affect the mobility of metal ions.

2.4.3 Organic Contaminants

Organic contaminants or pollutants are compounds that contain carbon, hydrogen and other elements. They include pesticides, herbicides, pharmaceuticals, hydrocarbons, phenols, plasticizers, tissues of plants and animals. Most organic contaminants originate from domestic sewage (septic tanks, latrines), urban run-off from rains, industrial effluents and agriculture wastewater, sewage treatment plants and industry including food processing, pulp and paper making, agriculture and aquaculture. Presence in traces or quantum of organic contaminants in food, water or environment may pose harmful to health due to their undesirable properties such as toxicity and flammability (The National Academics, 1980; Kookana et al., 1998) especially the Persistent Organic Pollutants (POPs). Organic contaminants exhibit different transport mechanisms from inorganic ones. They exhibit partitioning behavior in environment and therefore require different methodological approach in analyzing them. More complex multi-functional polar chemicals such as biological active compounds (pesticides, biocides, herbicides and pharmaceuticals) are very difficult to analyze. Common materials used in disinfection are

chemical based materials, biochars, activated carbon, clay and composite membranes, etc. There are so many reported research and reviews on the successful use of these materials in the removal of organic pollutants (Zadaka et al., 2005; Zhu et al., 2016; Mandal et al., 2016; Bhomick et al., 2017). Mechanisms of destruction are commonly by oxidation, partition, adsorption or thermal decomposition (Mohamed, 2013; Bhomick et al., 2017)

2.5 WATER TREATMENT (PURIFICATION) METHODS

2.5.1 Straining through Cloths

Filtration through cloth is a physical process and an age long tradition used in the removal of larger particles and insects from water. It is regarded as an emergency water filtration technique which has been reported to reduce the infection of cholera by half (Colwell et al., 2003; Kendall, 2003) and 4.2% bacteria (Odugbemi & Ogunsola, 2002) . Cloth filtration method can serve as pre-filtration method for micro and ultra-filtrations. Old Sari cotton fiber cloths are usually preferred. Other fibers such as nylon, polyesters, vinylon, etc used as cloth filters have been reviewed pointing out their advantages and challenges (Murat et al., 2017; Zerín & Datta, 2018). The cloth is folded at least into four times before usage, washed, rinsed with filtered water and sun-dried after usage to prevent diseases.

2.5.2 Aeration

Aeration is usually the first treatment in municipal treatment plant systems and sometimes pilot plants. Oxygen saturation is maintained in water through aeration. Usually air is infused into the bottom of the water source say pond, lake or lagoon or surface agitation for oxygen exchange thereby releasing gases like carbondioxide, hydrogen sulphide and methane(Wikimedia, 2018). Ferrous iron is converted to filterable ferric iron via oxidation. In the same vein, hydrogen

sulphide is oxidized to elemental sulphur which can easily be removed through filtration. Basic methods of aeration are aerobic and anaerobic while modified methods include; tapered aeration, diffused aeration, deep shaft aeration etc. Different methods are efficient in the removal of Chemical Oxygen Demand (COD), Total Dissolved Solid (TDS), Biological Oxygen Demand (BOD) and other biological contaminants in both freshwater and wastewater (Sabry & Alsaleem, 2010; Aral, 2014; Aral & Gönüllü, 2015; Akhlaque et al., 2017; Kulkarni, 2017).

2.5.3 Coagulation, Flocculation and Sedimentation

Coagulation involves the use of coagulants such as aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$) known as alum, iron salt, calcium and magnesium salts and alkaline liquids, to separate colloidal particles from water which are too small to settle by gravity. When alum is used, the polyelectrolytes converts the aluminum sulphate into polynuclear ($\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$) species forming aluminum complexes which help in the coagulation process (Edzwald, 2011). Addition of these coagulants induces electrostatic and ionic forces which causes the particles to stick together prior to filtration / disinfection. Baking powder and white ash were used in the case of emergency. Recent research has explored the use of *Moringa Oleifera* seeds as coagulants /flocculants which has produced up to 95% efficiency and acceptable results above established standards in reduction of total coliform and turbidity (Amagloh & Benang, 2009; Bichi, 2013; Hendrawati et al., 2016; Karina, 2018; Delelegn et al., 2018; Raja et al., 2019; Taiwo et al., 2020).

Flocculation uses stirring of the water to cause formation of larger particles. Flocculants are mostly added to promote the agglomeration of particles with continuous stirring for about 5 minutes. Then the water is allowed to sit for about 30 minutes for proper settling of colloids.

Coagulation and flocculation have been proven to mitigate the fouling of membrane filters when coupled in the filtration process (Leiknes, 2009).

Sedimentation: When large particles such as sand and silt, settle rapidly at the bottom of the container through gravity, the process is referred to as sedimentation. It was used in the olden days to purify water for clarity before the evolution of modern technologies; however, it is still being practiced by the peri-urban people living in poverty. Sedimentation does not disinfect water rather allows clearer water to be collected through the top of the container while the large particles settle at the bottom of the container.

2.5.4 Filtration

Purifying water by filtration is also common. It involves the use of medium in the form of membrane or aggregates. Filtration utilizes both physical and chemical processes while adsorbing and absorbing contaminants on the medium. Filtration media includes ceramic (clay) membrane for point of use filtration, cloth or fiber membrane, compressed granular activated carbon (GAC), polymer membranes, sand, gravel or crushed rock and clay aggregates. Water quality after filtration depends on the filter media, raw water and flow rate and pore size of the filter (Russell et al., 1978). Table 2.1 displays the microorganisms susceptible to filtration by size. Viruses are very smaller in size than bacteria and are susceptible to passage through filter media with larger pore size which can filter bacteria. More so, electrochemical attraction can cause them to attach themselves on the surface of the filter media. So engineering the filter media taking cognizant of pore size is very important.

Filters are easy to handle and operate. They require no special skill but can clog by suspended colloidal particles after repeated usage. Such particles may cause fouling and reduces water

permeability of the filters. Careful surface cleaning such as back-flushing (reversal of pressure such as pure water applied to the permeate side of the membrane) and/or chemical cleaning (chlorinated water, acid or base solutions, disinfectant and detergents) in the case of natural organic material or bio-fouling is required for point of use filter while backwashing is employed when using aggregates as in the case of treatment plants. Filtration can eliminate bacteria, protozoa, cyst and viruses depending on the porosity of the media (Chelsea, 1989).

Table 2.1
Susceptibility of micro-organisms to filtration by size

Organism	Approximate size (µm)	Maximum recommended filter rating (µm)
Virus	0.03	NA ^a
Escherichia coli	0.5 X 3-8	0.2- 0.4
Campylobacter species	0.2-0.4 X 1.5-3.5	0.2- 0.4
Vibrio cholerae	0.5 X 1.5-3.0	0.2- 0.4
Cryptosporidium oocyst	2-6	1
Giardia cyst	6-10 X 8-15	3-5
Entamoeba histolytica cyst	5-30	3-5
Nematode egg	30-40 X 50-80	20
Schistosome cercariae	50 X 100	Coffee filter or fine cloth
Dracunculus larvae	20 X 500	Coffee filter or fine cloth

^a Not applicable to most portable filters; only reverse-osmosis membranes exclude viruses by virtue of pore size. Retrieved from (Backer, 2002a).

Reverse Osmosis (RO) i.e filtration using a semi permeable membrane was a major breakthrough in membrane filtration technology (Figure 2.5). The earliest RO had salt rejections of approximately 96-97% and could only produce potable water from low concentration brackish water. Subsequent research was able to yield membranes that could reject salt up to 99.7% and could produce potable water from sea water (Baker, 2000). RO membrane feeds under high

pressure (100-800psi) has been used to filter viruses, ions, molecules, solids and achieve a 4-log reduction in viruses whereas mechanical filters can achieve up to 2-3 logs in virus reduction (Backer, 2002a). The results depend on permeation of different species. This is not efficient enough that is why mechanical filtration is used in conjunction with other treatment methods (Gerba & Naranjo, 2000).

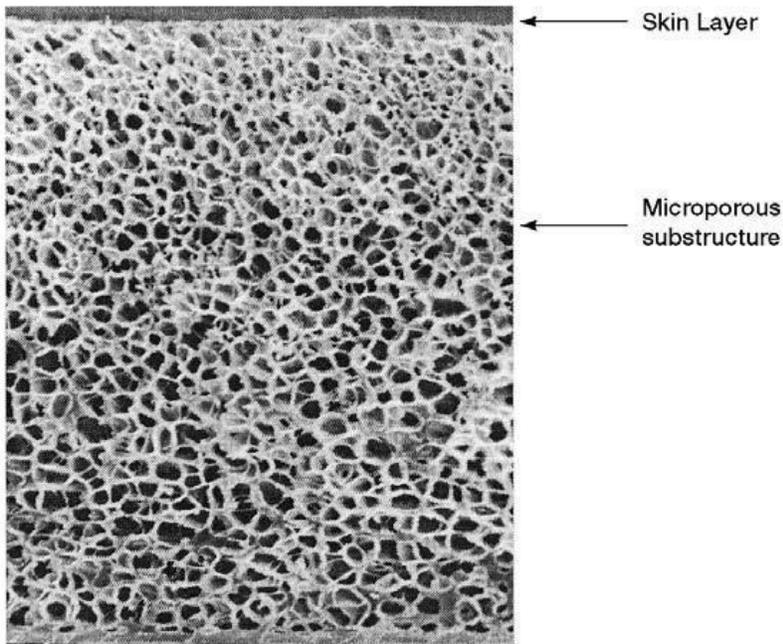


Fig.2.5. Scanning electron micrograph of the cross-section of a Loeb-Sourirajan reverse osmosis membrane. The development of this type of anisotropic membrane was a critical breakthrough in the development of membrane technology. (Reprinted from R. W. Baker, Membrane Technology & Research Inc. (MTR), Menlo Park, CA, USA. Copyright @ 2000 Academic Press)

2.5.5 Disinfection

Disinfection involves the use of chemicals such as chlorine (chlorination), calcium and sodium hypochlorite which readily dissociates in water and is non-carcinogenic, but reacts with other pollutants to form harmful compounds. The technology is easy to use, has strong and wide-spectrum antimicrobial activity and low toxicity to humans when controlled dose is used.

Limitations of chlorine disinfection method are the formation of disinfection by-products (DBPs) such as chloroamines, TriHaloMethanes (THM's), trichloroacetone (CCl₃COCH₃), chlorophenols, chloroforms, chlorinated hydrocarbons and other halogenated intermediate compounds which are very dangerous to health (The National Academics, 1980; Kookana et al., 1998). Iodine is also used in water disinfection of bacteria, cyst and viruses on lower concentration and fungi on higher concentration (Gottardi, 1991). Iodine is known to increase the susceptibility of thyroid problems in certain individuals (e.g, pregnant women). Other chemical disinfectants are ozone (ozonation) and chlorine dioxide. They are highly effective in killing *Cryptosporidium* species (Peeters et al., 1989; Gerba and Johnson 1997).

The use of Ultraviolet (UV) radiation is also very effective in water disinfection. This is commonly used by food and beverage industries. The major challenge with UV disinfection is the power generation which is expected to be in sufficient dose to produce the require energy for disinfection. More so, the water must be free from dissolve solids or particles to avoid interference and shield of organisms (Backer, 2001).

2.5.6 Boiling and Distillation

Bringing water to a boil at 100⁰C is the oldest and effective method of water purification for killing pathogenic bacteria, viruses and protozoa. This helps to eliminate pathogens and microbes-causing intestine diseases up to 100% if done correctly (Backer, 2002a; Idika et al., 2002; Sodha et al., 2011). However; boiling water does not remove inorganic chemical contaminants such as heavy metals and metalloids. Treated water can get re-contaminated if stored or handled improperly (Clasen et al., 2008; Psutka et al., 2011). Boiling is very effective in reduction of E.Coli up to 98.5% when stored in a covered container (Brown & Sobsey, 2012).

However boiling water for purification has its challenges such as the cost of heat source, electricity, biomass, waiting for the water to cool before using and handling to avoid recontamination.

Distilled water is collected in the form of vapour after heating and condensing using distillation method. It is one of the oldest methods of water purification. It is capable of removing bacteria, inorganic and most organic contaminants from water. However organic contaminant such as pesticides and herbicides, benzene and toluene whose boiling points are below 100⁰C cannot be efficiently removed as they vapourize with the distilled water and re-contaminate it. Also, pollutants with boiling points greater than 100⁰C are difficult to remove. These organic compounds are removed prior to condensation (Kamrin et al., 1990). Water purification by distillation is a very slow process, requires a lot of energy, carefulness and large quantity of water to produce and hence is a costly method. Moreover, distilled water lacks oxygen, has low pH (acidic) and also flat to taste which informed its application industrially rather than drinking and other household applications (Kamrin et al., 1990).

2.6 WATER FILTRATION AGGREGATES AND MEMBRANES

Sand is the most common aggregate used in water filtration especially for municipal treatment plants. Other aggregates and granules used in water filtration are charcoal, crushed rocks, blast furnace slags and clay (Library & Land, 2015). These are also used in filtration of wine and other liquids. There are three main types of sand bed filtration namely, rapid gravity, upward flow and slow sand filter (https://en.wikipedia.org/wiki/sand_filter, 2018). While rapid and upward flow sand filters use chemicals for flocculation, slow sand filters do not use chemicals, reduces turbidity, bacteria and organic matters producing high quality clean water (NDWC, 2000). Flocs

and other impurities are trapped within the sand bed by means of absorption or encapsulation. Different grades of sand are used to filter water. Most bacteria and pathogens are removed through this process however; odour and taste may be problems which are effectively removed using activated carbon granules. The sand aggregate is backwashed after series of use and the effluent are dislodged through a septic tank. The frequency of backwashing depends on the shape of grains, packing, depth and the type of flocculants used while the overall performance of the filter is affected by the shape, strength, susceptibility to salts and chemical attacks, resistance to internal erosion of fines, resistance to abrasion and composition of the materials especially during compaction, placing and frothing (Library & Land, 2015).

Membrane filtration involves forcing a liquid through a semi-permeable (porous) membrane. It is utilized in water, beverage and bio-processing industries. The utility of membranes to purify water involves membranes classified by their pore size and separation capabilities (Figure 2.6). The order of pore size increment starts with reverse osmosis membranes, nanofiltration, ultrafiltration and microfiltration membranes. Microfiltration is a size exclusion pressure or vacuum driven membrane filtration which operates at ambient temperature, velocity of about 1-3m/s and pressure ranging from 5psi to 54psi, 100-400kpa (Perry & Green, 2007; Baker, 2012). It is capable of removing bacteria, protozoan's cyst, and suspended particles of 0.1-10 micrometers (Baker, 2000). Ultra filtration filters through a pore size range of 0.1-0.01 micrometers are capable of removing viruses, bacteria, colloids and particles. It shows higher removal of pathogens than microfiltration medium (Molelekwa et al., 2014). Also, the use of coagulants and sludge production are drastically reduced (Leiknes, 2009).

Reverse osmosis involves dense membranes where solution-diffusion governs the separation process (Robeson, 2012). It is preferable during desalination and filters up to 1 nanometer. It is

efficient but an expensive technique. Nano filtration uses organic thin film composite membranes of typical pore size range of 1-10 nanometers. Its properties are found between reverse osmosis and ultra- filtration. Nanofiltration has gained popularity due to the emergency of nanotechnology and nanomaterial and their applications in efficient water and wastewater treatments (Savage & Diallo, 2005; Han, Xu, & Gao, 2013; Das et al., 2014; Konda et al., 2017) . It is efficient in separation of inorganic salts and small organic molecules (Mohammad et al., 2015). It operates at low pressure with excellent properties such as high resistance to fouling, high degree of ions selectivity, capable of reducing hardness, Total Dissolved Solids (TDS), turbidity, sulfates, tannis, etc.

Ceramic membranes commonly called clay membranes have been in existence since time immemorial. They have special attributes of high resistance to heat, chemical attack, performance indices, mechanical strength, good cleaning ability and affordability, applicable over a wide range of pH and are very durable (Scott, 1995). Studies have shown that clay ceramic membranes are very efficient in microbes and fluorides removal (Yinma, 2010 ;Annan, 2016).

Pore size (nm)	0.1	1	10	100	1000	10 ⁴
Membrane type	Reverse osmosis	Nanofiltration	Ultrafiltration	Microfiltration	→	
MW cutoff		200	20K	100K	1MM	
Separation capability	Organic chemicals Salt ions	Sugars	Hemoglobin Virus	Milk proteins	Colloids and clay Bacteria	
Applications	Desalination Ultrapure water	Food/beverage purification Virus removal Pesticide/herbicide removal	Drinking water purification Wastewater reclamation Bacteria removal Food processing Hemodialysis	Sewage water treatment RO pretreatment	Particle removal	

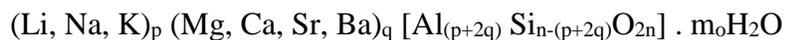
Fig.2.6. Membranes used in water filtration (Reprinted from Polymer Membranes LM Robeson, Lehigh University, Macungie, PA, USA © 2012 Elsevier B.V. All rights reserved)

Polymeric membranes have also been used in water purification studies of water and wastewater (Popescu et al., 2017; Konda et al., 2017). Researchers have conducted reviews on reported advances of polymer membrane in water desalination and purification revealing production processes, opportunities, challenges and way forward (Savage & Diallo, 2005; Shannon et al., 2008; Geise et al., 2010; Madaeni et al., 2015; Mohammad et al., 2015; Werber et al., 2016). Polymers used in the production of membranes can be made from organic, inorganic and composite materials. Examples include polysulfone, poly(ether sulfone), polyacrylonitrile, poly(vinylidene fluoride), aromatic polyamides, sulfonated poly(ether sulfone), and cellulose acetate. Nano and ultrafiltration polymeric membranes are usually produced by phase inversion process (Robeson, 2012).

2.6.1 Adsorbent Materials Used in Water Filtration

Activated Carbon (AC): The use of activated carbon in water filtration dated since time immemorial. Generally, activated carbon has large surface areas and large pore volume (porosity). These characteristics gave rise for its high adsorption and absorption capacities through the porous network of the particle. No wonder it is used in common home-based water filters. The major role of AC is to adsorb contaminants which may affect the odour and taste of drinking water. Several studies have been done on the use of AC for adsorption in aqueous solutions and the removal of total suspended solid (TSS), biological oxygen demand (BOD) and other organic pollutants such as bacteria and viruses. Result indicated high efficiency (99.999%) with improvement in odour and turbidity of the drinking water (Gerba & Naranjo, 2000; Harry & Rodríguez-Reinoso, 2006; Kwiatkowski, 2012; Zaid et al., 2013; Danyuo et al., 2015).

Zeolites: These are three-dimensional structured crystalline aluminosilicates comprising mainly aluminium, silicon and oxygen. Each oxygen atom is shared by two tetrahedral. The presence of water and larger cavities differentiates it from Feldspar mineral (Encyclopaedia Britannica, 2020). Natural occurring zeolites have mono or di-valent cations like sodium, calcium, potassium, magnesium and barium interconnected cavities enclosed in their framework. The honeycomb-like structure consists of pores of order of few atoms in width (~2-10Å) which allows the movement of ions within the cavities, thus, necessitates reversible dehydration and exchange of cation. The widely accepted general formula of natural zeolites is written below:



Where; p- no of monovalent metal ion, q- no of divalent metal ions, n- no of oxygen atom/ 2 and m_o- no of water molecules

Zeolites can be synthesized from Kaolin by calcining it to a high temperature, say above 600°C (Kovo & Edoga, 2005; Atta et al., 2007). Natural zeolites such as Clinoptilolite (Clino zeolites), Mordenite, Chabazite, etc have been used extensively in water treatments due to their exceptional cation-exchange ability, sorption and molecular sieve properties (Ajenifuja et al., 2012; Margeta et al., 2013; Kammerer et al., 2014). They are divided into seven main groups and the division is based on their physical properties, crystal structure, exchangeable ions, pore volume /size, morphology, binding ways, etc.

In the past decades, both natural and modified zeolites have been widely used as adsorbent to purify water. Zeolites and clay matrix (sometimes doped with silver nano-composite) are excellent in adsorption of heavy metal ions such as Pb^{2+} , Cd^{2+} , Cu^{2+} , As^{2+} and Zn^{2+} and have efficiently removed bacteria, heavy metals and other microbial growth from polluted water (Perić et al., 2004; Petrik et al., 2012; Ajenifuja et al., 2012; Delkash et al., 2015; Jiménez-Castañeda & Medina, 2017).

Thermal properties of zeolites (stability, resistance conductivity and heat capacity) depend on SiO_2/Al_2O_3 ratio. Thermal stability increases with increase in crystallinity. Higher silica/aluminum ratio affects the temperature resistance. Depending on type of zeolite, some have been found to be thermally and chemically stable up to 1000°C. Thermal conductivity depends on the particle size, temperature range, degree of packing and voids distribution (Jha and Singh, 2016).

Chitosan: Chitosans are strong adsorbents of heavy metals. They are synthesized from shells of fishery waste such as shrimp shells and crab shells, hence are cheap. Chitosans have molecular structure similar to that of cellulose. Modification of Chitin, a biological polymer from the exo

skeletons of crustaceans, forms Chitosan excellent properties such as biocompatibility, biodegradability and non-toxicity. Researchers have reported its use in the efficient removal of pollutants such as COD, TDS, Turbidity, pathogens and heavy metals. Chitosan concentrations increment from 0 to 1 g 100 ml⁻¹, resulted in decrease in turbidity, TDS, electrical conductivity and from 1.98 to 0.98 NTU, 5.67 to 4.13 g L⁻¹, 10.18 to 5.27 mS cm⁻¹, 6.1 to 5.71 respectively. Coliform bacteria and Staphylococci at different concentrations were completely eliminated (Al-Manhel et al., 2018; Stroparo et al., 2018). Experimental research has reported removal of phosphates reducing it from ~19 µg/ml by 6-30 fold and attenuating dissolved hydrosulfides from 1mM by 100-fold using metal ion modified chitosan (Yep, 2016).

Successes have been recorded for the use of Chitosan as a natural coagulant in remediation of microbes and turbid waters to over 90% efficiency and wastewaters. (Rajendran et al., 2015; Abebe et al., 2016; Frederick, 2016; Nechita, 2017; Junior et al., 2018; Marey, 2019). Adsorption studies of heavy metals (arsenic, copper, zinc, mercury, uranium), dyes and pharmaceuticals from aqueous medium using chitosan including modified form have been reported and reviewed to be successful although results depended largely on the modification method adopted, materials used for the modification and adsorption experimental conditions (Wan Ngah et al., 2011; Jain, 2013; Annaduzzaman, 2015; Kyzas & Bikiaris, 2015; Sutirman et al., 2018; Ismaila et al., 2021). The presence of amino and hydroxyl groups in chitosan molecules serve as attachment sites towards metal ion thereby contributing majorly to its adsorption capabilities. Other parameters of dependent are deacetylation degree, molecular weight, particle size and crystallinity (Benavente, 2008).

Hydroxyapatite (HAp): HAp are naturally synthesized from egg shells, bones of fish and mammals because of high content of calcium and carbonates. The common one is the calcium

hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Adsorption studies have shown their high capabilities to adsorb heavy metals such as lead, Arsenic and Cadmium under varying conditions like initial metal concentration, pH, temperature and reaction time (Takeuchi and Arai, 1990; Meski et al., 2010; Narwade et al., 2014; Mousa et al., 2016; Bailliez et al., 2019). Ion exchange mechanism by substitution of calcium with the heavy metals is commonly proposed by researchers.

2.6.2 Clays: Characteristics and Composites in Water Filtration

Clays occur naturally and are abundant in earth's surface, hence are available and affordable. Generally, clay is formed as a result of weathering process greatly influenced by the parent rock, vegetation, topography, climate conditions and duration. Clay mineral structure may be destroyed or modified at high temperature beyond dehydroxylation. There is tendency for rapid fusion after dehydroxylation temperature when using fluxes such as potassium, iron and magnesium (Britannica Encyclopedia). Clay and clay minerals are the most important industrial minerals whose application is dependent on their microstructural morphology, mineral compositions, phase constitution and chemical composition. Clay minerals are phyllosilicates minerals with layers of silica tetrahedral (Figure 2.7a) and layers of Al, Fe, Mg octahedral, similar to gibbsite or brucite (Figure 2.7b). The arrangements of these layers accounts for major and minor differences in the properties of clay.

There are three main groups of clay mineral are kaolin (usually referred as kaolinite), Illite and Smectite of Montmorillonite, each with specific properties and formation as shown (Table 2.2). Associated clay minerals like vermiculite, quartz, micas, chlorite, etc, do not impart plasticity to clay but interfere with its identification. Montmorillonite are known to adsorb more water than kaolinite, illite, and chlorite (Stratton et al., 1959; Rolfe et al., 1960). The chlorites and illites

have similar water sorption properties. Clay has wide range of utilization and industrial application. Characterization and classifications of clay have been done successfully using technical equipment such as X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Fourier Transmission Infra-Red (FTIR), Differential Scanning Calorimeter (DSC), Scanning Electron Microscope (SEM), Atomic Absorption Spectroscopy (AAS) and others (Velde, 1993; Bergaya & Lagaly, 2013). Documented and reported results are veritable tools and are handy for use and for industrial applications purposes.

Table 2.2
Three Major Clay Minerals Showing Formation, Characteristics and Uses

Group	Examples	Formation	Characteristics	Uses
Kaolin	Kaolinite, nacrite and dickite	Decomposition of orthoclase feldspar	1:1 (figure 2.7c) phyllosilicates, non-swelling with fine texture	Ceramics production, fillers for papers and paints, water treatment
Illite similar to Muscovite	Glauconite	Decomposition of micas and feldspar, predominant in marine clays and shales	2:1 phyllosilicates, commonest clay mineral, possession of exchangeable cations (K, Ca and Mg)	Cosmetics, binders, water treatment
Smectite or Montmorillonite	Bentonite and vermiculite	Alteration of mafic igneous rocks rich in Ca and Mg	2:1 (figure 2.7d) phyllosilicates, weak linkage by cations (e.g. Na ⁺ , Ca ⁺⁺) results in high swelling/shrinking potential and isomorphous substitution	Drilling mud for oil and water wells, binder in pharmaceuticals, feeds for blast furnace, water treatment

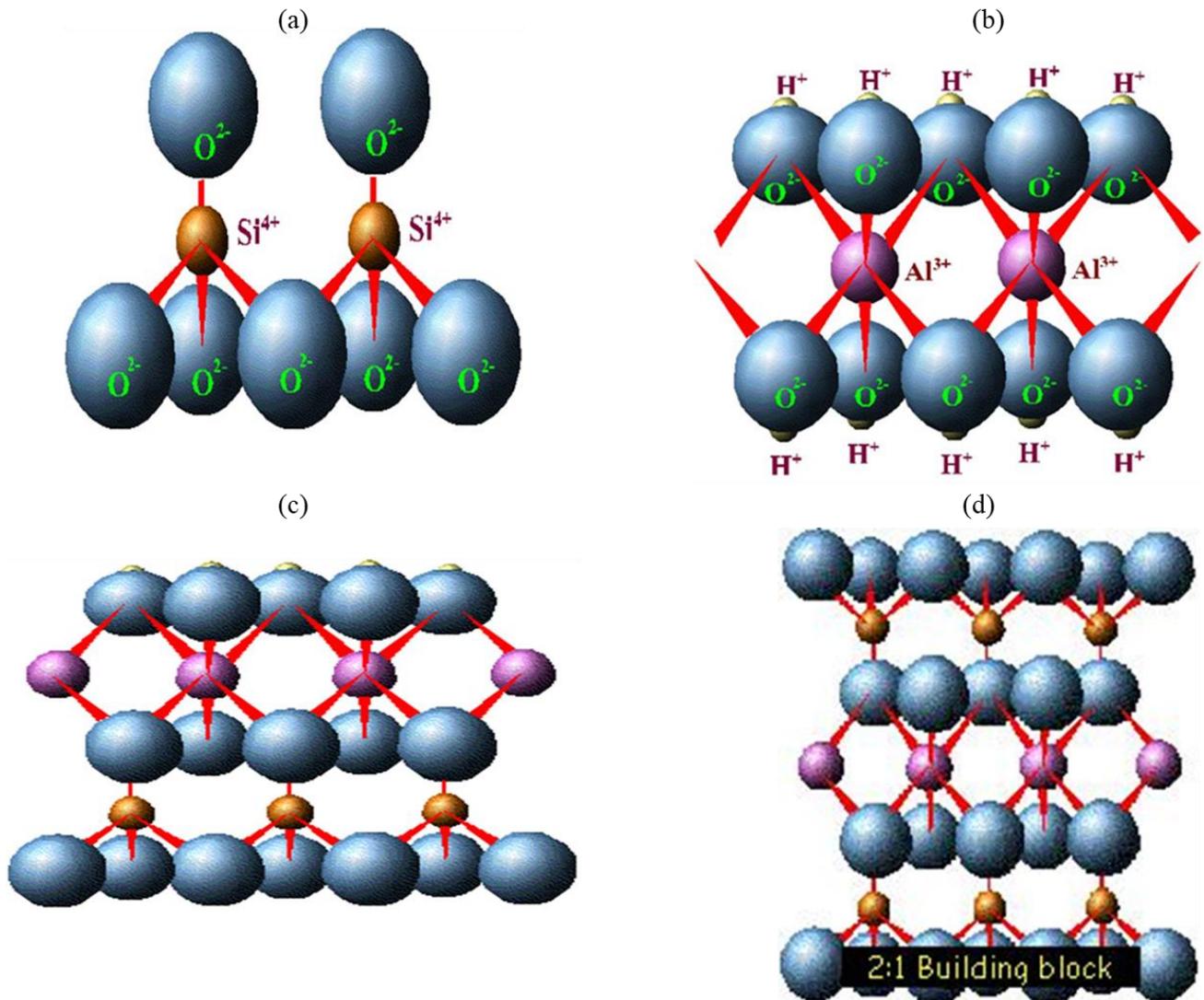


Fig.2.7. Building blocks for clay minerals. (a) Silicon-Oxygen Tetrahedral ($\text{Si}_2\text{O}_5^{2-}$) ; (b) Al-Octahedral (Gibbsite sheet) $\text{Al}(\text{OH})_6^{3-}$; (c) Kaolinite 1:1 Building block; (d) Smectite 2:1 Building block (Science.earthjay.com)

With regards to water treatment, clay has been used extensively since time immemorial in water filtration and purification studies both in sole and modified forms. Some of the reviews on the use of clay in water filtration are reported in the succeeding chapter.

Industrial waste, such as rice husk and saw dust are some of the materials that forms composite with clay in water purification studies. The kernel of rice typically known as rice husk is obtained after separation of rice from paddy in a rice mill and it is a rich source of silica. Other

non-renewable sources are; wheat, oats, barley and maize. Silica is found at the epidermal layer of these crops. They are abrasive and brittle as well. Complete combustion of rice husk gives rise to white ash which contains 86-99% silica (Paragas et al., 2014; Bakar et al., 2016; Todkar et al., 2016). Rice husk has been found useful in so many applications like; polymer reinforcement, water purification, road construction, dye and acid removal, cosmetics and cosmetology, dentistry, building construction, food industry, adsorbents, etc. However, this discussion is limited to water purification using clay-rice husk composite.

Pachauri (2013) prepared column and ball rice husk ash-based filters for water/waste water purification. The treatment efficiency for total suspended solids (TSS) for the waste water were 63, 81 and 88% after 1,2 and 3 hours respectively with ball filter while that of column were 50, 66 and 76% after 1, 2 and 3 hours respectively. The result also showed reduction in chloride content from 283 mg/l to 189 mg/l after 6 hours of retention time. The removal of Cadmium II and Zinc II ions from binary systems was effective using rice husk filter. Higher percentage of the duo ions were absorbed by the adsorbent during filtration (Srivastava et al., 2008). The use of microwave for the incineration of rice husk used in water filtration has been studied for the adsorption of heavy metals, chromium and copper respectively. The results indicated efficient removal of these ions by means of adsorption (Wongjunda & Saueprasea, 2010; Johan et al., 2011). Nitrites removal in water was studied using rice hull- derived zeolites. The husk was washed with distilled water and acids prior to calcinations. Results showed that both the untreated and treated were able to remove nitrite by 97.03% and 97.22% respectively (Paragas et al., 2014).

Rice husk has great potentials as adsorbents due to the presence of functional groups, high porosity and surface area. Its major constituent is silica, carbon and other trace elements like

alumina, potassium oxide, iron oxide, manganese, sulphur, calcium oxide and phosphorous pentoxide, etc. Similarly, clay-sawdust composite as an adsorbent in water purification have been studied and documented by researchers. Results have shown that such composite is very effective in removing heavy metals, oils, dyes and chemicals (Shukla et al., 2004; Annan, 2016; Annan et al., 2018)

2.6.3 Expanded Clay Aggregates (ECA) for Water Filtration

The uses of ECAs in water filtration are still evolving. Their major applications tilt more to sustainable building material than in water filtration studies. New technologies on water treatment have been reported but not much can be found in literature on the use of Expanded Clay Aggregate application in surface water treatment especially biomass-modified ECAs. Some of the reviewed literature centers attention on the use of Light Expanded Clay Aggregate (LECA) and ECA in the adsorption of phosphorous in wastewater (Table 2.3).

Table 2.3

Review of the usage of Expanded Clay Aggregate in Water Purification

Authors	Adsorbent	Contaminant(s) of study	Outcome
(Johansson, 1997)	LECA LECA+CaCO ₃	Phosphorus from wastewater	Higher P-sorption was observed for LECA+CaCO ₃ more than LECA
(Melin and Odegaard 1999)	ECA	TOC, COD, colour and ozonated humid water	Removal rate between 57-75% for all experiment was achieved
(Nath & Goldberg, 2003)	Sintered LECA with addition of carbonates of calcium and or magnesium as flux materials	phosphorus	High phosphorus binding capacity with very good hydraulic conductivity
(Yaghi & Hartikainen, 2014)	LECA Al or Fe oxide coated LECA	Removal of Arsenite (AS ^{III}) and impact of Phosphorous on removal efficiency	Enhanced sorption of AS ^{III} at pH 7, 68µg g ⁻¹ and 114µg g ⁻¹ for LECA and Al or Fe modified LECA respectively
(Noori et al., 2014)	Natural LECA, H ₂ O ₂ and MgCl ₂ modified LECA	Fluoride	At pH 6, fluoride was reduced from 10 g/l initial concentration to 0.39 mg/l, 1.0 mg/l and 0.075 mg/l for Natural LECA, H ₂ O ₂ and MgCl ₂ modified LECA respectively at sorption capacities; 8.53 mg/g, 17.83 mg/g and 23.86 mg/g.
(Bahmanpour et al., 2017)	LECA granules and powder	COD, BOD, TSS, nitrate and phosphate in dairy industry wastewater	Efficiency of COD removed after 20hrs is 65.9% TSS& BOD had great reduction Nitrate=63.87% Phosphate- reasonable reduction
(Łopata et al., 2017)	ECA	Phosphorous and Nitrogen on river water	12-16% removal efficiency for phosphorus and 5-6% for Nitrogen
(Kalhori et al., 2017)	LECA MgO-modified LECA	metronidazole (MNZ)	Removal efficiency of MNZ increased by 8% with addition of carbonates for LECA and total removal of MNZ for MgO/LECA. Maximum adsorption capacity under optimum conditions are 56.31 to 84.55 mg/g for LECA and MgO/LECA respectively
(Gisvold, Odegaard, & Føllesdal, 2018)	Zeolite containing LECA	Ammonium from domestic wastewater	High ammonium removal at high ammonium loading rate by a combination of nitrification and ion exchange

2.7 UNRESOLVED ISSUES AND FUTURE DIRECTIONS OF RESEARCH

Many researchers have worked on the filtration of common contaminants found in water (i.e surface water, well water, wastewater, underground water) which are usually of bacteria, fungi, virus, metals and chemical origin using clays, clay minerals and composites. No study has been reported for the use of Expanded Clay Aggregates in the removal of pathogens and adsorption studies of arsenic and lead. This study looked at the removal characteristics of ECA adsorbent on E.coli bacteria as well as nitrate and phosphate for comparative analysis report. Adsorption studies of arsenic and lead was also carried out and results were compared with other nano adsorbents found in literature.

2.8 CONCLUDING REMARKS

The importance of water to health, education, environment, economic productivity, peace and stability and agriculture cannot be overemphasized. It is finite, indispensable and a vulnerable resource. When sea shrinks, the available one becomes more salty and inhabitable for aquatic creatures that lives in it and for other uses. It becomes pertinent to pump in fresh water or desalinate the salty water for domestic and other uses. Reverse osmosis and other purification methods become necessary at this point. With the shortage of water and scarcity, water management becomes so important. The need to recycle and treat the available ones to combat illness associated with filthy water arises. In water treatment, cheap based effective measures are preferred. Clay was mixed with bio-renewable materials to produce composite which are used to filter some organic and inorganic pollutants found in water. The raw materials were selected based on their availability, affordability, effectiveness and efficiency in water treatment. The expanded forms of clay are targeted to be used in municipal treatment plants and point of use water filtration including filter bottles

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CHAPTER THREE

3.0 MULTIPLE CHARACTERISATIONS OF CLAY MATERIALS FOR EXPANDED CLAY AGGREGATES PRODUCTION AND OTHER INDUSTRIAL APPLICATIONS

3.1 INTRODUCTION

Clean uncontaminated water is essential for the well-being of both plants and animals. The human body metabolic and catabolic processes need water to optimize their functions. According to the United Nation's 2006 report on power, poverty and the global water crisis, water plays vital roles in socio-economic development, agriculture, domestic life, industry and a sustainable eco-system. Every human being has the right to sufficient, safe acceptable, physically accessible and affordable water (Watkins, 2006; WHO and UNICEF, 2015). Fresh water sources are usually contaminated with chemicals, heavy metals (from wastewater, fertilizers, pesticides, mining activities industrial pollution, and others), pathogens, microbes, and other toxicology contaminants.

The joint report of the World Health Organization (WHO) and United Nations Children's Fund (UNICEF) estimated that 2.1 billion people globally lack access to safe water for household and other utilities, while 4.5 billion people does not have a basic sanitation system (WHO and UNICEF, 2017). Contaminated water together with poor sanitation is estimated to cause approximately 1.8 million deaths and 61.9 million disabilities per year (WHO and UNICEF, 2001). A new born is lost per day globally as a result of infectious diseases caused by a dirty

environment and unclean water (WHO and UNICEF, 2015). These unpalatable reports gave rise to goal number six (6) of the Sustainable Development Goals (SDGs), which is clean water and sanitation for all. The relevant agencies, government, non-governmental organizations and researchers have been instrumental to the successes recorded so far. However, the problem is still prevalent in developing countries, especially those in Africa.

The assessment of water quality using the Water Quality Index (WQI) and every available means are being developed and used by researchers. Lei (2019) and Ismail & Adel, (2018) applied the WQI assessment in the evaluation and the validity of an area of a river with one number that checkmated the different parameters for drinking water. The results were able to certify the water safe or not for use according to the specified standards. Drinking water and water for other utilities must be free from these contaminants before it is considered safe for use to promote a healthy lifestyle that is free from the illnesses that are associated with waterborne diseases (WHO and UNICEF, 2001).

One of the ways of removing these contaminants is through filtration, which is a common method used in water purification. It involves the use of a medium in the form of a membrane or aggregates. Filtration utilizes both physical and chemical processes while adsorbing and absorbing contaminants on the medium. Filtration media include but are not limited to ceramic (clay) membranes for point of use filtration, cloth or fibre membranes, compressed granular activated carbon (GAC), polymer membranes, sand, gravel or crushed rock, and clay aggregates. Amongst the other economic benefits of clay such as artefacts, medicines, building materials, electrochemical science, cosmetics, pharmaceuticals, earthen wares and agriculture (Lim et al., 2013; Manukaji, 2013; Iyasara et al., 2016), clay has played a vital role in water purification technology.

Clay ceramic water filters have shown capabilities in removing water contaminants such as microbes (Sengco & Anderson, 2004), chemicals (Nwuzor et al., 2018; Cucarella & Renman, 2009; Zereffa & Bekalo, 2017), and heavy metals (Akapomie et al; 2012; Choudhary, 2018; Zereffa & Bekalo, 2017). Ceramic water filters made from clay and clay minerals are very efficient for water filtration through adsorption/absorption, molecular sieving and ion exchange mechanisms (Wang & Peng, 2010; Margeta et al, 2013; Bergaya et al., 2006). More so, clay is inexpensive, abundant, widespread and readily available. Other considerations are user friendliness, cultural acceptability and a low maintenance cost. The characterization of materials to determine their salient properties for effective utilization and application is the key contributor to many research breakthroughs in the field of science and technology. The mineralogy, chemical composition, mechanical properties (such as plasticity), specific surface area, porosity, functionality and structure, as well as the interactive behaviour of clay and clay minerals, determine their suitability for use in water filtration media and other industrial applications.

Previous studies on the samples of study and most Nigerian clays have focused only on physical, chemical (XRF), mineralogical (AAS and XRD), and SEM (Nsu and Ihitte clay only) (Chukwudi, 2008; Chukwujike and Igwe, 2016) investigations. Multiple characterizations of these samples, especially those that have not been reported, will provide information on these clays, while the already reported ones will be validated or refuted by the current study. Several studies have shown that clay can be used as a refractory lining with improved refractory properties such as shrinkage, abrasion resistance and reduced porosity (Iyasara et al., 2016). Nsu clay has been tested for the adsorption of cadmium(II), heavy metals and chemicals (Nwuzor et al., 2018; Akapomie et al., 2012). The results showed a spontaneous and endothermic adsorption

of Cd (II) from aqueous effluents as well as over 60% adsorption of organic and inorganic pollutants from industrial paint effluents.

Characterization reports for Kutigi, Minna and Oboro clay deposits have discussed only their physical analysis and chemical compositions, while there has not been any documented report on Obowo Clay. Nigeria is blessed with clay and clay minerals amongst other abundant natural mineral resources. Unfortunately, value is currently not being added to them except for the ones that are locally mined for art and craft purposes. This paper reports the results of seven Nigerian clay samples investigated for moisture content, morphology, chemical composition, mineralogy, functional groups, zeta potentials and seeks to establish a correlation among them. Multiple techniques were adopted to effectively and efficiently characterize the clay for documentation purposes and to determine their potential suitability in the production of expanded clay aggregate media for water filtration and other suggested industrial applications.

The structure of this article beyond the introduction is materials and methods, which include the initial preparation of samples after their collection from various locations, visual characterization, microscopic measurements, spectroscopy, diffraction and stability analysis. The results and discussion are then presented and then followed by suggested industrial applications and the conclusions.

3.2 MATERIALS AND METHODS

3.2.1 Sample Collection and Preparation

Samples were collected using geological bedrock maps provided by the Geological Survey Agency of Nigeria for locating mineral deposits across the federation. Three clay samples were collected from Imo State, and their locations are Agbaghara Nsu in Ehime Mbano Local

Government Area, Onuiyi River in Obowo Local Government Area and Nkumeato in Ihitte/Uboma Local Government Area. One sample was collected from Isiala Oboro in Abia State. Two samples were collected from Kutigi and Minna in Niger State, while one sample was collected from Afuze in Edo State. The locations covered three out of the six geo-political zones in Nigeria, namely, South-East, North-Central and South-South indicating tremendous deposits in the country. For ease of identification, the samples were named after their locations as indicated in (Figure 3.1).

The samples were crushed using a manual jaw crusher (Model: Retsch BB50, made in Germany) set at a gap width of 0.2 mm at a speed of 850 rpm. The crushed samples were soaked in water for 24 hours and sieved with (Model: Endecotts Octagon 200 Sieve, made in UK) sets of 150 microns, 106 microns and finally 45 microns. They were dried in an oven (Model: Memmert UN110, made in Germany) at 110°C for 24 hours, similar to the procedure of Cullum & Voldinh, (2014). The samples were crushed again into powder form before they were packed in zip-lock polymer bags for storage and further experiments.

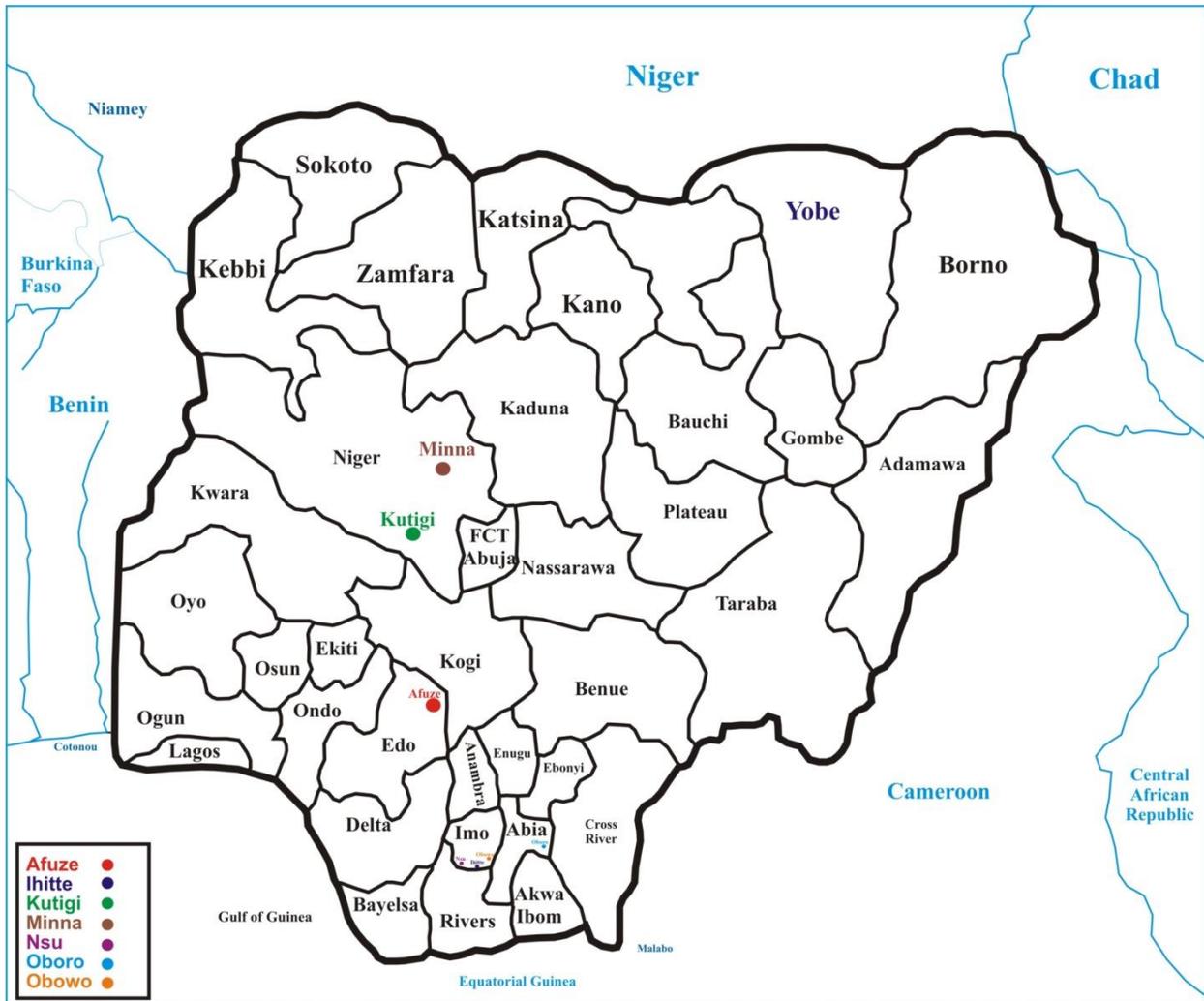


Fig.3.1. Map of Nigeria showing the location of sample sites

3.2.2 Clay Sample Index and Moisture Content Determination

Visual inspection was performed on the clay to determine their colour and feel when wet.

The knowledge of the moisture content of clay or soil is very essential in its classification. It is generally defined as the mass of water in the soil or clay sample expressed as a percentage of the dry mass after heating at a temperature of $105 \pm 5^\circ\text{C}$ (equation 3.1).

$$\text{Moisture Content, } W = \frac{M_W}{M_D} \times 100\% \quad (3.1)$$

where M_W is mass of water

M_D is mass of dry sample.

The moisture content was determined using a moisture analyser (Model: ADAM PMB 53, made in USA). Clay samples (5g) were weighed with an accuracy of 0.01 g and introduced into the sample holder. The temperature was set at 110°C and ran for time intervals of several repeats until stability in the moisture content was achieved.

3.2.3 Electron Microscopy and Energy Dispersive X-ray (SEM-EDX)

Samples were coated with gold nanoparticles in a mini sputter coater (Model: Quorum SC 7620, made in UK) to prevent the samples from charging and reflection. Scanning electron microscope (SEM) coupled with energy dispersive X-ray (EDX) images were captured with a Carl Zeiss SEM (Model: evo10LS-EDAX, made in Germany) at a very high count per second. SEM was carried out to determine the morphology of the samples. The obtained micrographs were mapped by EDX spectroscopy to determine the elemental compositions of the samples.

3.2.4 X-ray Photoelectron Spectroscopy (XPS)

The XPS analysis was carried out to determine the surface chemical composition of the clays. First, 20 mg of each clay sample was measured using a Sartorius microbalance with a precision of 0.001 mg (Model: MC5, made in Germany). The weighed samples were transferred into 20 ml glass bottles containing 5 ml of deionized water to form a dispersion, which was homogenized for 20 seconds with a homogenizer (Model: CV334, made in Germany). Then, 1 cm² silicon wafers were used as substrates. Sonication for 5 minutes was carried out in a sonicator (Model: RK-52, made in Germany) using acetone, for 10 minutes in isopropyl alcohol, and then dried with air and nitrogen to ensure appropriate cleaning (Moulder et al. 1979). Next, 10 µl of the

dispersion was taken from each sample and separately drop-cast onto the substrate. These were air dried for an hour and then placed in a desiccator under vacuum for approximately 48 hours.

XPS measurements were done following the steps already described by Schampera et al., 2015 and Todea et al; 2013 using electron spectroscope (Model: Omicron Full lab System, made in Germany). The C 1s peak binding energy of adventitious carbon was used for the charge referencing correction to 285 eV. The survey spectra were quantified in terms of atomic % for the elements identified with the CasaXPS software (UK) package and a Shirley-type background removal using the element library casaxps_KratosAxisC1s.

3.2.5 X-ray Diffraction (XRD)

The X-ray diffraction measurements were carried out using a Rigaku SmartLab 9kW unit with a rotating anode at 45 Kv and 150 mA to obtain the mineralogy present in the samples. Patterns were recorded at 2 θ degrees with a scan speed of 0.03 degrees per second and a 1.54 Å wavelengths. Mineralogical interpretations were carried out using the PDXL Ver.1.8.1 Integrated X-ray powder diffraction software and the Whole Powder Pattern Fitting (WPPF) empirical peak shape function.

3.2.6 Fourier-transform Infrared Spectroscopy (FTIR)

Analytical grade KBr obtained from Guangzhou Jinjuada Chemical Reagent Company Limited was mixed with each of the clay samples in the ratio of 10:1 and pressed into pellets using a 10-t press. Optimal spectra in the region of 4000-400 Cm⁻¹ were obtained at high resolution, and several scans were recorded with Fourier-transform infrared Thermo Scientific Equipment (Model: Nicolet IS5, made in USA). This was done to obtain the functional groups present in the samples.

3.2.7 UV-vis Spectroscopy

Clay dispersions were prepared by mixing the clay powder with distilled water in cuvette cells and were referenced to a blank. The UV-vis spectra of structural elements and functional groups of samples were recorded in the wavelength range of 195-800 nm using a UV-vis (Model: 6850 UV/Vis-Spectrometer, ANALTIKJENA Germany).

3.2.8 Zeta Potential Measurements

Electrostatic interactions exist at the effective boundary between the particle and its surrounding. The zeta potential is the key indicator of the stability of colloidal dispersions. The potential differences in the surfaces of the clay samples, inter alia, solution stabilities, exchangeable cations/adsorption, electrophoresis and electrokinetics, when dispersed in water have been very relevant in the study of colloidal processes and properties (Celik, 2004; McFadyen & Fairhurst, 1993; Gungor & Dilmac, 1996). A NanoBrook Zetaplus (Model: 220001, made in USA) was used in the measurement. Samples were prepared by dissolving 0.101 g of KNO_3 in 1000 ml of distilled water, followed by the dissolution of 1.0 g of each clay sample in 20 ml of 1 mM KNO_3 . The mixture was sonicated with an ultrasonic cleaner, (Model: SB-4200, made in China) at a working frequency of 40 KHZ, a settling temperature of 25°C and measuring temperature of 21°C for 5 minutes. The supernatant and residue separation was achieved by using an Eppendorf centrifuge (Model: 5804 R, made in Germany) at 3500 rpm and a temperature of 21°C for 2 minutes.

3.3 RESULTS AND DISCUSSIONS

3.3.1 Physical Examination, Morphology and Elemental Composition

The results (Table 3.1) determined by the visual examination, feel when wet and the moisture meter analyser indicate the sample from Obowo has the highest moisture content of 57%, while that of Afuze has the lowest moisture content of 26.8%, which is indicative of the fact that the higher the moisture content is, the more plastic and more mouldable the clay. The colour (Figure 3.2) variations may have resulted from the formation due to weathering (redox reaction), humid climate, excess leaching, presence of impurities, organic matter, moisture content, and the elemental and mineral compositions of the samples (Spielvogel et al., 2004; Leger et al., 1979). This is discussed later in detail with the other results.

Table 3.1
Sample Index of Clays with % Moisture Content

Location	State	M.C	Description
Afuze	Edo	26.8	Non-plastic orange-brown powder
Ihitte	Imo	44.8	Plastic pink powder
Kutigi	Niger	27.2	Non-plastic white powder
Minna	Niger	53.2	Moderately plastic orange-yellow powder
Nsu	Imo	43.6	Plastic light-brown powder.
Oboro	Abia	52.4	Plastic grey-white powder
Obowo	Imo	57.0	Very plastic yellow-brown powder.

The plasticity was determined by touch after wetting with water



Fig.3.2. Clay samples showing colour variations: (a) Afuze (orange-brown), (b) Ihitte (pink), (c) Kutigi (white), (d) Minna (orange-yellow), (e) Nsu (light brown), (f) Oboro (grey-white) and (g) Obowo (yellow- brown)

The SEM micrographs (Figure 3.3) display the silicate flakes of kaolinite and quartz for the Afuze clay mineral, while the EDX spectrum of the mapped area (not displayed) indicates the presence of silica and aluminium in high quantities and traces of potassium, iron and oxygen. The pinkish Ihitte clay mineral shows a spongy-porous tubular surface with an elemental composition from the EDX spectrum revealing a high content of silica and aluminium with trace elements of oxygen and iron. Well-formed stacks of kaolinite layers are observed for the Kutigi sample with silica and aluminium as the major constituents and oxygen and titanium are the minor constituents. The Minna clay mineral show hexagonal flakes surface, while EDX also reveals high contents of aluminium and silica with trace elements of iron, potassium and oxygen. The morphology of Nsu clay shows pseudo-hexagonal sharp edge platelets in a face-to-face arrangement corroborating the work of Chukwudi (2008). The samples from Oboro and Obowo show a honeycomb spherical surface and sheet-like flakes, respectively. Their major elemental constituents are silica and aluminium with minor constituents of iron, potassium, titanium and

oxygen for Nsu and iron, magnesium, gold, titanium, krypton, osmium and oxygen for Oboro, while oxygen is the only trace element for Obowo.

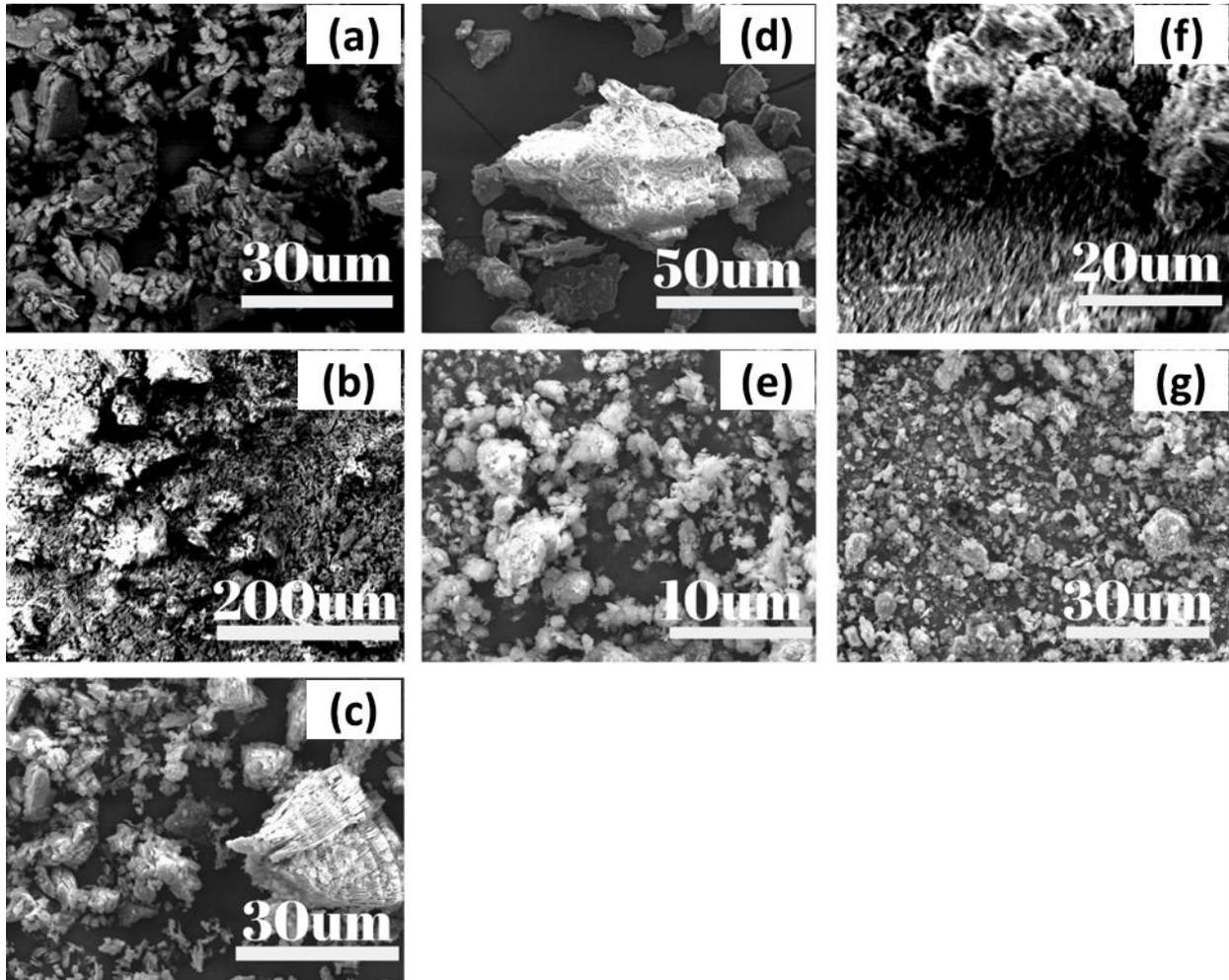


Fig.3.3. SEM images of clay minerals showing their morphological variations. (a) Afuze showing sheets of kaolinite and quartz flakes, (b) Ihitte clay showing a spongy-porous fibrous surface, (c) kutigi- stacked or thick kaolinite platelets, (d) Minna- hexagonal flakes, (e) Nsu- pseudo-hexagonal kaolinite in a face-to-face arrangement, (f) Oboro- honeycomb with porous spherical grains, and (g) obowo- sheet-like flakes

3.3.2. Mineralogy and Chemical Composition

The XPS results of all the clay samples (Figure 3.4a) are typical of spectra of clay and clay minerals. The individual samples with their elemental atomic percentages are presented in Figure 3.4 (b-h). The presence of carbon in varying relatively high concentrations is a result of

weathering during formation and surface-atmosphere interactions or residual precursors (Todea et al., 2013), while that of oxygen is due to the elemental oxygen, oxides, oxygen in water and metal oxides associated with the elements. To evaluate the changes in chemical bonding, the Al 2p and O 1s peaks were deconvoluted into four components to determine the chemical environment of oxygen in silicates, while the Si 2p was deconvoluted into five components for all the samples based on the geometry of the bands, and the interpretation is based on these three energy levels.

The Al 2p shows bonding agreement with the O 1s in the deconvoluted components except those for Oboro. The observed line widths might have resulted from variations in the chemical environment of oxygen since they originate from the coordination of oxygen with the cation(s) (Al^{3+} , Fe^{2+} , K^+ , and Ca^{2+}) present in the samples. The shift in binding energy for the O 1s photoelectrons can be explained by a slight increase in the electron density around the oxygen atoms by surface changes, while the broadening of the full width at half maximum points out a larger distribution of the oxygen sites (Shaikhutdinov & Freund, 2013).

The O 1s high-resolution spectra of the samples are well fitted with four components conforming to the different coordinations of the cations with oxygen. The presence of the components at 532.17-532.21 eV are closely related to the oxygen in Si-O-Si and in Si-O-Al which overlap with the silicone/siloxane bonds between 101.57-102.85 eV except for those for Oboro and that of the silicate bond (oxides) between 101.41-103.67 eV. The O 1s high-resolution spectra of the samples apparently consist of relatively symmetric peaks conforming with established binding energies in the literature (Tissot et al., 2016; Schampera et al., 2015; Boscoboinik et al., 2013; Wanger et al., 1979; Zschornact 2007). The component at ~534 eV is due to the presence of surface C bonded to O, which indicated an organic contaminant or the mineral formation route.

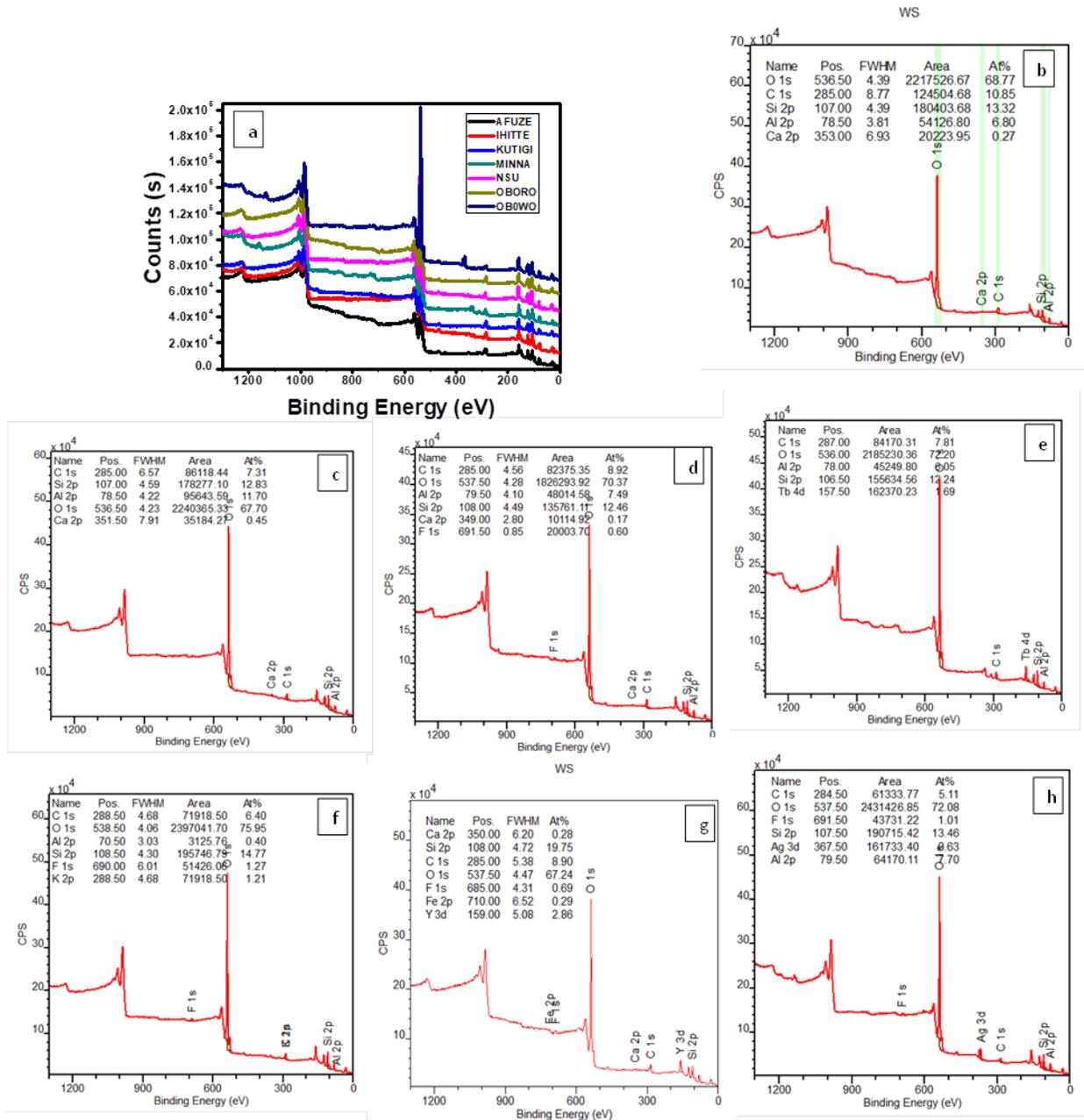


Fig.3.4. (a) XPS Spectroscopy of all the clay samples, (b) spectra of Afuze, (c) spectra of Ihitte, (d) spectra of Kutigi, (e) spectra of Minna, (f) spectra of Nsu, (g) spectra of Oboro, and (h) spectra of Obowo. All elemental compositions are in atomic weight %

The binding energy peak at approximately 533 is attributed to the Si-O-Si bridging oxygen and to adsorbed water resulting from Al-OH groups. Additionally, the peak at 531.75 eV can be correlated with great amount of octahedral Al 2p at 74.83 eV, as reported by Tissot et al., (2016).

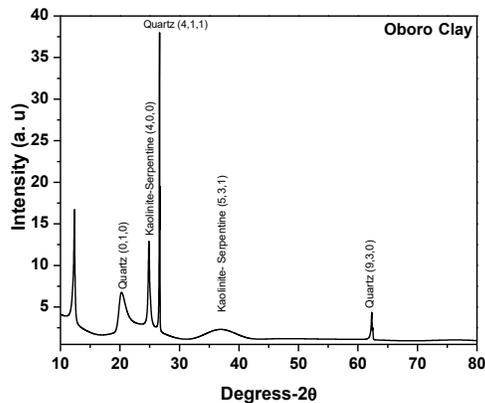
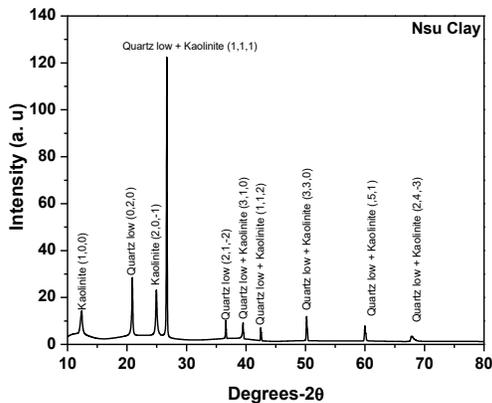
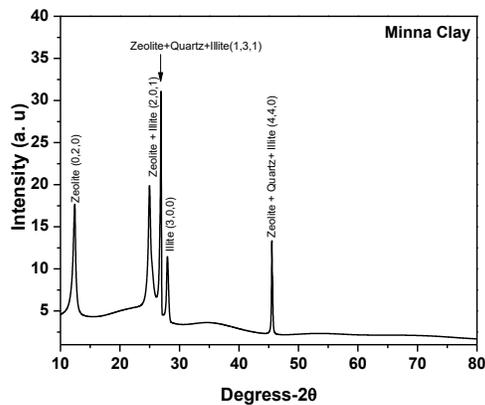
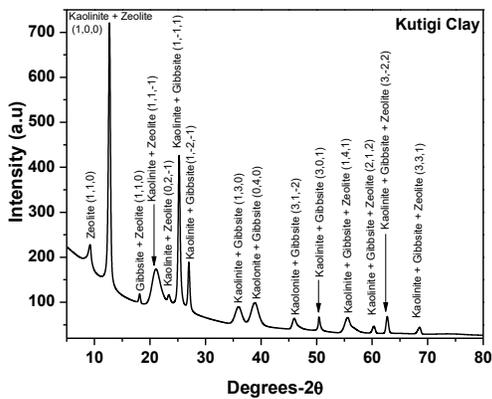
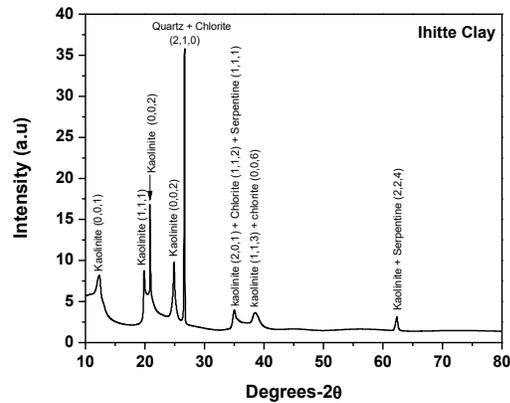
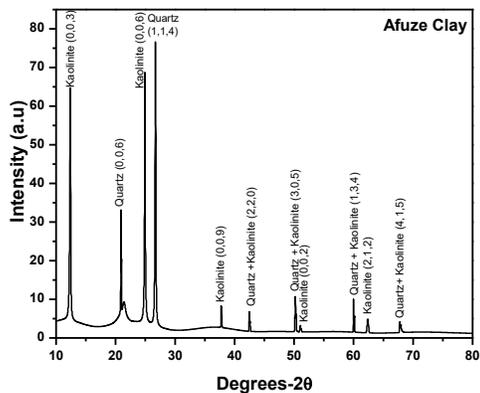
Aluminium in transition alumina can either be present in octahedral sheets (hexacoordinated aluminium) or tetrahedral sheets (tetraordinated aluminium) (Malki et al., 2014). The binding energies of gibbsite ($\text{Al}(\text{OH})_3$) for all the clay samples range from 73.16 eV to 75.53 eV indicating coordination of the octahedral sites of Al to the surface OH groups (531.75-532.24), while the binding energies of tetrahedral sites of Al 2p and Si 2p are influenced by the negative charge on the silicate framework.

Lower binding energies, 71.16 eV to 72.96 eV, recorded for Al metal are in agreement with that already reported (Crist, 2007; Wanger et al., 1979) and the database of elements, <https://xpssimplified/element/aluminum.php>. Aluminium hydroxides present in all samples (except for Oboro) between the range of 74.34 eV to 75.77 eV are typical of binding energies common to kaolinites, which result from the Al-OH translation of gibbsite. The peaks for aluminium oxides are recorded at the binding energies of 74.00, 74.36, 74.33, 72.96, 74.86, and 74.09 for Afuze, Ihitte, Kutigi, Minna, Nsu and Obowo samples, respectively, typical of those recorded by the previous XPS analyses of similar clay and clay minerals (Todea et al., 2013; <https://xpssimplified/element/aluminum.php>; Elmi et al., 2016; Tissot et al., 2016).

Afuzé showed a prominent peak of SiO_2 at a binding energy of 103.67. This value is similar to that mentioned by Elmi et al., (2016)'s review on tetrahedral layer silicates and quartz. The observed chemical shift in the photoelectron binding energies for Si 2p between 99.05 eV to 99.64 are attributed to metal silicates and silicon, while the lower binding energies observed for Oboro could not be explained. Apparently, lower binding energies suggests sputtering damage to the air-cleaved surface by a systematic error due to lower energy positively charged Ar ion bombardment (Elmi et al., 2016) or other random error, although there is no known category that addresses changes in BE numbers (Crist, 2007).

The mineralogical results from XRD patterns (Figure 3.5) reveal that Afuze is predominantly kaolin clay (kaolinite, nacrite and dickite) and quartz mineral. The result conforms with the Si_2O_5 sheets bonded to aluminium oxide/hydroxide layers ($\gamma\text{-Al(OH)}_3$, called gibbsite layers, as shown by the Al 2p XPS (Figure 3. 4) and EDX, which recorded no traces of other elements other than Al, Si and oxygen. High-angle XRD reflections are observed for sudoite-chlorite in the Ihitte clay sample (Figure 3.5). The high content of magnesium-rich dioctahedral chlorites is usually pinkish to white, which is in conformity with the pink colour observed for the sample in Figure 3.2.

The trace elements calcium and iron observed in XPS and EDX, respectively, can be linked to the 20.84% of the transition metal fluoro compound, CaFeF_5 with an octahedral cis-chain structure capable of halogen exchange with or fluorination of organic compounds. The Kutigi clay sample revealed both strong and broad reflections for kaolinite and calcium tecto-dialuminotetrasilicate hydrate (Figure 3.5). Kaolinites possess a dioctahedral structure and are known for their 1:1 silicate layers sandwiching a gibbsite layer. The two characterizations of XPS and XRD confirm this conclusion for this sample, although XPS reveals stronger peaks for aluminium oxides than gibbsite. The 3% Ti recorded for the mapped area in EDX might result from impurities that are associated with dickite during formation due to the weathering of feldspar, whereas the trace of calcium captured by XPS results from hydrated aluminosilicate. Hydrated calcium aluminosilicate mineral, laumontites, and the hydrated phyllosilicate mineral of aluminium and potassium, muscovites, are the major constituents of Minna clay (Table 3.2).



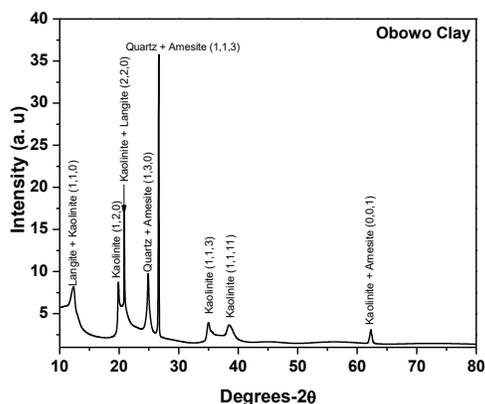


Fig. 3.5. XRD patterns of Afuze, Ihitte, Kutigi, Minna, Nsu, Oboro and Obowo clay and clay minerals

The XRD quantification conforms with the result of EDX of 6% Fe, K₂O-rich contents due to the interlayer K in illite/muscovite, and traces of terbium, which has a resemblance to calcium, as captured by XPS. The impurities of terbium may be a result of secondary mineralization, and iron coloured it brown-yellow (Figure 3.2). Kaolinite and quartz are observed for Nsu clay. The presence of Ti, Fe and K captured by EDX, XPS and XRD indicates a 1:1 layer structure, but trioctahedral sheets filled with Mg²⁺ antigorite confirms the previous publications by Chukwujike and Igwe, (2016); Nwuzor et al., (2018); and Iyasara et al., (2016) in their elemental composition of oxides. Quartz and berlinite minerals dominate Oboro, as seen in the XRD pattern (Figure 3.5). The white-grey colour of the sample might come from potassium tectosilicate and kaolinite. Calcium tecto-dialuminotetrasilicate hydrate is the major component of Obowo with reflections of quartz and the uncommon amesite minerals.

Table 3.2
Quantification of clay minerals as revealed by XRD

Name	Chemical Formula	% Mass Composition	Group
Afuze			
Quartz	SiO ₂	37.44	Silica
Kaolinite	Al ₂ SiO ₅ (OH) ₄	44.40	Kaolin
Nacrite	Al ₂ SiO ₅ (OH) ₄	3.69	Kaolin
Dickite	Al ₂ SiO ₅ (OH) ₄	<u>14.47</u>	Kaolin
		<u>100.00</u>	
Ihitte			
Sudoite	Mg ₂ (Al,Fe ³⁺) ₃ Si ₃ AlO ₁₀ (OH) ₈	45.93	Chlorite
Alpha-Magnesium Sulphate	α -MgSO ₄ 4.2K	14.81	Sulphate
Calcium Iron Flouride	CaFeF ₅	20.84	Fluoro Compound
Guidottiite	MnFe ³⁺ SiFe ³⁺ OH ₄	18.37	Serpentine
Lizardite	Mg ₃ SiO ₅ (OH) ₄	0.01	Kaolin-Serpentine
	Al ₂ CaH _{15.68} O _{11.84}	<u>0.04</u>	Kaolin-Serpentine
		<u>100.00</u>	
Kutigi			
Kaolinite	Al ₂ SiO ₅ (OH) ₄	18.71	Kaolin
Dickite	Al ₂ SiO ₅ (OH) ₄	44.26	Kaolin
Lizardite-2H ₂	Mg ₃ Si ₂ O ₅ (OH) ₄	22.63	Kaolin-Serpentine
Nacrite	Al ₂ SiO ₅ (OH) ₄	<u>14.40</u>	Kaolin
		<u>100.00</u>	
Minna			
Laumontite	Ca(AlSi ₂ O ₆) ₂ · 4H ₂ O	69.85	Zeolite
Muscovite	(KF) ₂ Al ₂ O ₃ 3(SiO ₂) 6(H ₂ O)	<u>30.15</u>	Illite/ Mica
		<u>100.00</u>	
Nsu			
Quartz Low	SiO ₂	80.14	Quartz-
Dickite	Al ₂ SiO ₅ (OH) ₄	<u>19.86</u>	Tectosilicate
		<u>100.00</u>	Kaolin
Oboro			
Quartz	SiO ₂	49.72	Tectosilicate
Berlinite	Al(PO ₄)	44.46	Phosphate
Leucite	K(AlSi ₂ O ₆)	<u>5.82</u>	Tectosilicate
		<u>100.00</u>	
Obowo			
Calcium tecto-dialumotetrasilicate	Ca Al ₂ Si ₄ O ₁₂ (H ₂ O) _{3.02}	92.08	Tectosilicate-Zeolit
Amesite	(Fe, Mg)4Al ₄ Si ₂ O ₁₀ (OH) ₈	<u>7.92</u>	Serpentine
		<u>100.00</u>	

3.3.3 Spectroscopy Analysis

The combined spectra for the seven samples are presented in Figure 3.6 but are outlined in Table 3.3 for clarity. The O-H stretching bands from medium to strong intensities are between 3700-3300 for most kaolinite and illite clays (Fadil-Djenabou et al., 2015; Nayak & Singh, 2007; Bantignies et al., 1997; Frost & Vassallo, 1996; Larkin, 2011). Bands for Si-O stretching occur between 1095-1009 Cm^{-1} in clay minerals, and the Si-O-Si of quartz (Nayak & Singh, 2007; Bishop et al., 2017) and Al-O bending falls within the range of 1200-700 Cm^{-1} . For SiO_2 , a strong band is at approximately 1100 Cm^{-1} , bending bands between 600-150 Cm^{-1} , and medium bands of SiO_2 at approximately 470 Cm^{-1} . Metal O-H bands are seen in the bending mode between 950 and 600 Cm^{-1} (Senoussi et al., 2016; Lenka, Vaculikavo* and Eva, 2005). Water absorbs below 800 Cm^{-1} , and strong infrared transitions from metal-O-metal groups occur at 800-200 Cm^{-1} (Larkin, 2011). Table 3.3 shows the intensities of the O-H stretching, Si-O stretching and bending and Al-OH bending bands for all the samples, indicating that they are mostly kaolinite and illite minerals sensitive to cation exchange (Mbey et al., 2019; Koutnik, 2011; Fadil-Djenabou et al., 2015). The OH stretching of the inner surface and the outer hydroxyl groups are observed at 3696, 3695 and 3651 for sandwiched octahedral sheets between two layers for kaolinites, and the tetrahedral-octahedral-tetrahedral structure is noted for illite. The bands at approximately 3620-3619 cm^{-1} was as a result of low frequency of the inner surface hydroxyls of kaolinites and gibbsite (Frost, 1995; Bantignies et al., 1997; Frost & Vassallo, 1996; Koutnik, 2011). Active Al-OH bending bands at 917-912 Cm^{-1} are observed, thus, validating the previous work on the inner hydroxyls of kaolin and gibbsite (Mbey et al., 2019; Nayak & Singh, 2007). The vibrational modes of the octahedral aluminium ions of kaolinite and gibbsite together with the Si-O stretching of quartz are recorded for all the samples

except Obowo at 798-796 Cm-1. The octahedral vibrations involving Al³⁺ ions and Si-O-Si deformation are also observed below 600 Cm-1

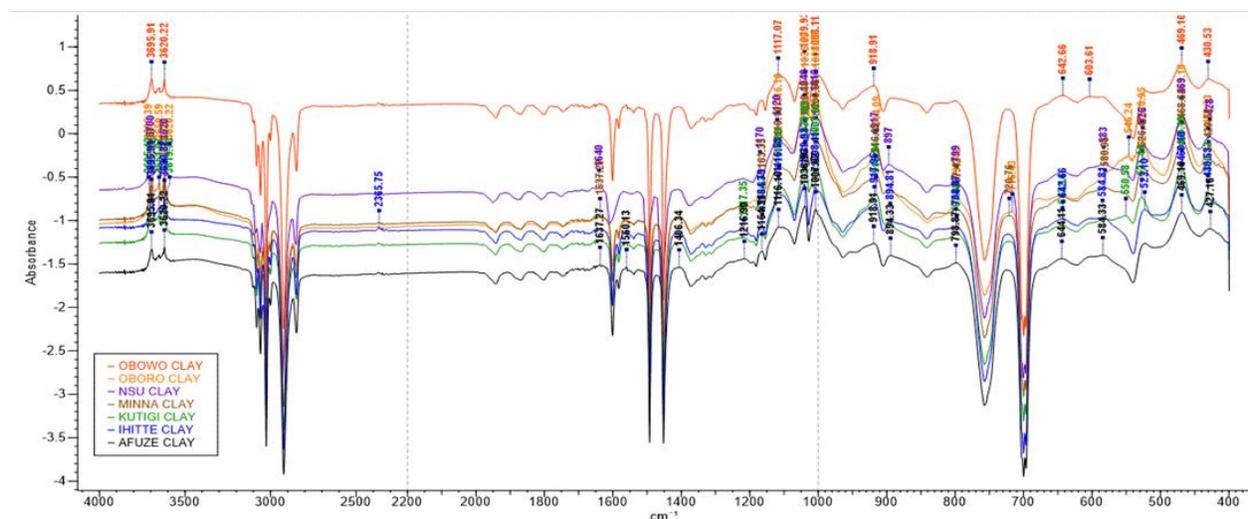


Fig.3.6. FTIR showing combined spectra of all the clay samples

A UV-vis absorption in the 195-800 nm range for clay samples results from transition metal cations either as structural elements of the lattice or exchangeable cations on the clay surface (Karickhoff & Bailey, 1973; Taylor et al., 2006). Water adsorbed on the samples shows a broad background UV band in the clay peaking in the range of 197-267 nm.

Table 3.3

Frequencies and absorbance for various stretching and bending bands for certain Nigerian clay minerals (Cm-1)

Sample Name	O-H Stretching	Si-O Stretching	Al-OH Bending	Deformation Bands (Al-O-Si, Si-O-Si, Si-O)
Afuzo	3695,3619	1047,1039,1012,796	912	561,553,545,527,473,432,428
Ihitte	3695,3620	1039,1009,798	917	585,523,469,430
Kutigi	3695,3651,3619	1037,797	915	550,527,469,430
Minna	3696,3619	1038,797	916	580,526,468,429
Nsu	3696,3619	1038,797	916	581,526,468,427
Oboro	3696,3651,3620	1035,797	914	546,527,469,430
Obowo	3695,3620	1039	916	469,430

This implies that the transition that occurs in the UV-vis region is from π - π^* and the presence of hydroxyl substituents of Si=O functional groups (Tobergte & Curtis, 2013). Weak bands are also noticed between 303-333 nm, however, the appreciable scattering proposed to have resulted from the internal lattice being shielded by the large crystalline particle size confirms that clay generally shows an increase in light scattering and loss of resolution when compared with those of their mineral constituents, which is attributed to amorphous metal oxides and hydroxides (Karickhoff & Bailey, 1973).

3.4 CLAY PROPERTIES AND POTENTIAL INDUSTRIAL APPLICATIONS

The stability and mobility of samples are presented in Table 3.4. A negative electrophoretic mobility is observed for all the clay samples that might have resulted from H^+ and OH^- , which are the potential determinant ions (pdi) for clay minerals, SiO_2 , Al_2O_3 and Fe_2O_3 . The higher the zeta potential is, the more stable the solution is against aggregation. Afuze clay is the most stable and mobile, while the lowest stability and mobility values are recorded for Obowo clay. The hydrophobic neutral siloxane basal surface of kaolin and the hydrophilic “gibbsite like” (OH) layer (Figure 3.7) are more prominent in Afuze than they are in Obowo, as presented earlier using XPS. The terminal OH group found in 2:1 layer silicates, such as chlorite (Minna), has the capacity to adsorb specific species depending on certain types of ions, irrespective of pH. Al-OH and Fe-OH are examples that have a great affinity for phosphate ions (Schoonheydt and Johnston, 2006). A lower stability causes breakage of repulsive forces that result in coagulation or flocculation.

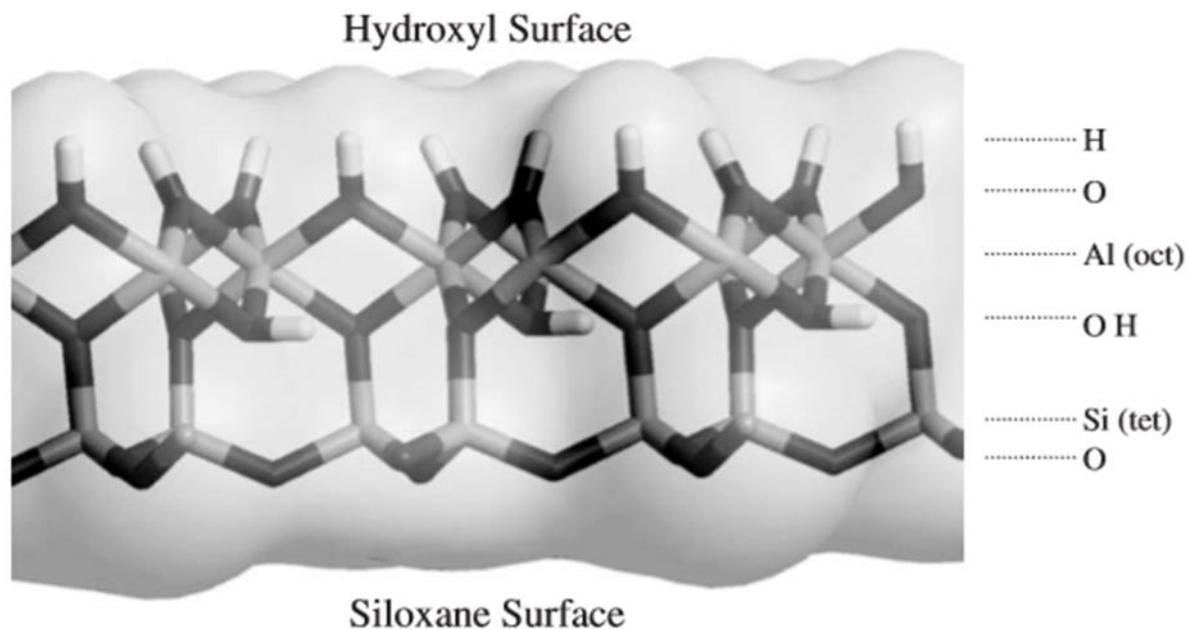


Fig.3.7. Hydroxyl and siloxane surface of kaolinite “ Reprinted from *Handbook of Clay Science. Surface and Interface Chemistry of Clay Minerals* written by R. A. Schoonhedydt and C. T. Johnston. Development in Clay Science vol. 1, Handbook of Clay Science (2006) with permission from Elsevier”

Table 3.4
Zeta potential results for clay minerals in aqueous solution

Sample	Zeta Potential (mv)	Mobility (μs)/(v/cm)	Conductance (μs)
Afuze	-33.64	-2.63	309
Ihitte	-26.64	-2.08	330
Kutigi	-28.42	-2.22	336
Minna	-27.10	-2.12	396
Nsu	-28.50	-2.23	323
Oboro	-26.91	-2.10	313
Obowo	-24.06	-1.88	319

Mean values of 5 tests for each sample

The reactivity of clay minerals and zeolites is controlled by the transition metals present in them. Yttrium-containing aluminosilicate, such as the sample from Oboro, can be used in medical applications such as local radiotherapy and bone reconstruction (Todea et al., 2013).

Kutigi and Minna clay minerals are suitable for the production of ceramic water filters because of their mineral compositions and special properties. Rich in zeolite content and the kaolinite nature of both samples indicate the capability of isomorphous substitution, cation exchange (Bergaya et al., 2006), water softening, removal of odour and molecular sieving through their 3D cage-like framework structure. Heavy metals such as Zn, Cu, and lead are strongly attracted to the negatively charged sites on the 1:1 layer minerals. These are caused by the dissociation of the surface hydroxyls of these minerals.

Furthermore, zeolites are resistant to high temperatures, high pressures, acid and other inorganic solvent attacks, and they do not dissolve in water or oxidize in air. Their flexible porosity can be engineered to suit purpose-driven applications. It is expected that during the production of expanded clay aggregates, the Fe^{2+} content of Minna clay will convert to Fe^{3+} , which is more stable because of its diamagnetic properties due to the half-filled $3d^5$ electron configurations. This is also validated by the zeta potential results for the two clays.

Kaolinite Nsu clay was reported by Akapomie et al., (2012) to have successfully adsorbed cadmium(II) and iron from effluents. Such clay can also be used as an extender in aqueous-based paints and fillers in polymers. Non-plastic kaolinite, such as Afuze and Kutigi, can be used as refractories, ceramics products, paints, fillers for plastics and catalyst (Lopez-galindo- & Viseras, 2004; Bergaya et al., 2006; Douglas, 1993) composites due to their earlier mentioned properties. Apart from Kutigi and Minna clays, Afuze, Nsu and Obowo have great potential for the production water filters, while multi-mineral Ihitte and Oboro are suitable for applications, such as ceramic wares, porcelain, paints, plastic fillers, etc. However, such clays can be modified to suit petrochemical, filtration and catalysis applications.

In addition to using these clays for water filters, refractories, ceramics, etc., they can also be used to synthesize composites with other raw materials, such as agricultural residues and natural fibres. These composites can find suitable application in the construction industry as materials for roads, blocks, and roof and floor tiles. These and other minerals in various locations in Nigeria, with good planning, can provide the raw material base for clusters of small and medium enterprises (SMEs), which can be established in each of the 774 local government areas of Nigeria.

3.5 CONCLUSIONS

A scientific procedure for using the chemical composition, morphology, mineral content, functional groups and stability in determining the industrial application of selected clay minerals was established in this study. Valuable information is extracted from the multiple means of characterization of the Nigerian clays and clay minerals. Based on the above, out of the seven studied clay minerals, two (Kaolin from Kutigi and Fe-rich Minna clay) are found to be more suitable for the production water filter media due to their potential ability to soak up ions and scavenge for heavy metals and chemical contaminants within their structural framework, amongst other special properties. Although the minerals have potential industrial applications, unfortunately they are not contributing much to national development as value is not being added to them at present. All the examined methods of characterization are in tandem with one another except for a slight disparity in Oboro clay (EDX and XPS). Kaolin and Illite are the major clay components, while quartz, gibbsite, antigorite, berlinite, sudoite, amesite, chlorite, lizardite and leucite are the associated minerals. The results of this study are currently being used to select the suitable type of clay to produce expanded clay aggregates to be used to design and fabricate low-cost water filters. The implication of the study is that these clays can be used for various

applications based on their characteristics, thereby increasing local content usage of and value added to minerals in Nigeria. The next chapter will look at characterizing the plastic behaviour of the clays, their mineral oxides and the thermal analysis of the minerals. The expected result will serve as a guide together with the present study to select appropriately the best materials for the filter media. Consequently, the expanded clay aggregate will be produced and tested for efficiencies in various contaminant removals.

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CHAPTER FOUR

4.0 GEOTECHNICAL AND PLASTICITY PROPERTIES OF CLAY

4.1 INTRODUCTION

Plasticity is an essential property of clay that makes it workable or moldable when tempered with water (Brownell, 1977; Andrade et al., 2010). The clay can be transformed into shapes without any tendency to return to its elastic state after moderate applied pressure is withdrawn (Andrade et al., 2010; Perkins, 1995; William, 2017). The study of plasticity of clay and other porous materials are of great values to engineering practices and industrial applications (Corapcioglu, Y and Uz, 1978). Artisans and potters rely on long aged experience and expertise during determination of clay plasticity. This is usually done by making a coil with clay and rolling it around one's finger. Plastic clay will not break while non-plastic clay will break easily (Lagaly, 2006). The behaviors of clay, feel at touch or the potter's wheel are unreliable and do not give dependable plasticity values. Although work experience is valuable, however relying much on experience based learning is arbitrary and not in tune with pace and age of information technology. It is pertinent that systematic approaches which depend on practical measurements based on quantitative expressions be adopted to test the plasticity of clay and catalogue different grades of clay samples with different values. Such information becomes an asset to the user who relies on the specifications before purchasing for use or trial purpose.

Different clay plasticity measurements have been modeled or studied and reported by researchers though with discrepancies in concepts. Perhaps that is why there is no one acceptable technique that can be crystallized into a definition (Hall, 1923). The Atterberg method uses the plasticity index which is determined by varying physical behavior of clay with different moisture content. This method has recorded fair success in comparison with other methods that have been reported

although with much judgment to the person conducting the test (William, 2017; Lagaly, 2006; Hall, 1923; White, 1942; Annan et al., 2014). Clay plasticity is influenced by lots of factors such as the nature of clay (primary or secondary formation), ageing, weathering, mineral compositions and their crystal structures, moisture content and particle size distribution (Andrade et al., 2010; Bergaya & Lagaly, 2013; Mulqueen, 2014; Charkley et al., 2019). Different constituents, structures and wide range of application make it difficult to have a generic reference on clay science (Lagaly, 2006). Plasticity measurements and behavior of extruded clay together with plastic behavior of porous material in any given situation is best analyzed by yield criterion (stress at which plastic deformation is initiated or onset of plastic flow) and constitutive relations (Corapcioglu and Uz 1978). Khlystov & Zheng, (2013) described the uniaxial tension and compression of metals, alloys and ceramics to determine their Young's Modulus, Yield Stress, Ultimate Tensile Strength and Elastic Strain which are used to determine the elasto-plastic behaviors of materials. Measuring and modeling the plasticity of clays subjected to compression loads have been examined and insights on extrusion up-scales /important guidelines and properties were obtained (Andrade et al., 2010; Hall, 1923; Flores et al., 2010; Andrade et al., 2011; Ojuri, 2013)

Geotechnical properties of some of Nigerian lateritic soils and clay minerals have been reported although with major applications in building and construction, recharge sites for regional aquifer, bacterial removal from water and adsorption studies of heavy metals (Onunkwo et al., 2014; Owolabi & Aderinola, 2014; Adeagbo et al., 2016; Oluwapelumi et al., 2017; Oluwatuyi et al., 2018; Innocent, 2018; Onakunle et al., 2019; Ajibade et al., 2019; Ogbuagu & Okeke, 2019). Good results were obtained when the materials are modified with additives.

This chapter understudies the constitutive plastic behaviors of clay samples in Nigeria under compression loads and the plasticity indices in relation to their moisture content, chemical compositions and mineral contents. Although some of the samples from the same study areas have been characterized by physio-chemical means, there are no published works on the plasticity of the samples of study. The presented results are extension of multiple characterization results which have already been published (Ihekweme et al., 2020). The insights and possible adjustment in the development of Expanded Clay Aggregates for water purification purposes was also presented.

4.2 MATERIALS AND METHODS

4.2.1 Theoretical considerations

The clay is considered an isotropic and porous material. The loading condition is an axial symmetry under compression. Every small element deforms homogenously to the same degree at the same instant. (Andrade et al., 2010) Andrade et al's theoretical parts equations (equations 4.1 and 4.2) were adopted for these measurements to evaluate related properties such as force, instantaneous radius and other variables which affect the plasticity of given ceramic bodies.

$$\sigma_z = \gamma \exp 2\mu \frac{(r_f - r_o)}{h} \quad (4.1)$$

$$F = \int_0^{r_f} 2\pi\sigma_z \partial_r \quad (4.2)$$

Where σ_z is the axial stress component; F , axial force; μ , coefficient of friction; γ , effective compressive stress; r_f , radius after compression; r_o , radius before compression; h , height of sample; and r , radial direction.

4.2.2 Experimental Methods

Raw clay samples were collected from seven locations within the south-east, south-south and north- central of Nigeria. Samples were named after their locations i.e Afuze, Ihitte, Kutugi, Minna, Nsu, Oboro and Obowo for ease of identification. Initial preparations were done as stated by Ihekweme et., al (Ihekweme et al., 2020). X-ray result used in discussion was adapted from the earlier publication on the same samples characterization. The chemical compositions were determined by X-ray fluorescence spectroscopy (XRF), (model: XRFEDX3600B).

For the plasticity experimental procedure, 40g of each sample was mixed with varying ml of water according to its moisture content (Ihekweme et al., 2020) and 40% moisture content for comparative analysis. The mixtures were stored in zip lock poly bags for 24 hours for moisture homogeneity. A polyvinyl chloride (PVC) mold of dimensions 20.42mm diameter and 30.06mm height was constructed and used to produce the ceramic bodies. Measurements were taken using a vernier caliper (Model: Mitutoyo series 530). The ceramic bodies were loaded non-eccentrically and subjected to compressive forces at the rate of 3mm/min with Instron model 3345 and a 5KN load cell. Digital photographs were taken at intervals with Nikon D3400 digital camera and the concurrent diameter measurements were determined using image analysis tool (Image Tool). The instantaneous radius and applied forces were determined using equations 4.1 and 4.2. Experimental data was plotted and fitted non-linearly to produce the theoretical curves. The coefficient of friction is assumed to be constant because of the difficulty in its determination and it poses no significant threat in the analysis (Andrade et al., 2010). The pictorial setup and deformation step is shown in figure 4.1. The standard test methods D 4318 (ASTM, 2000) were used to determine the Atterberg limits.

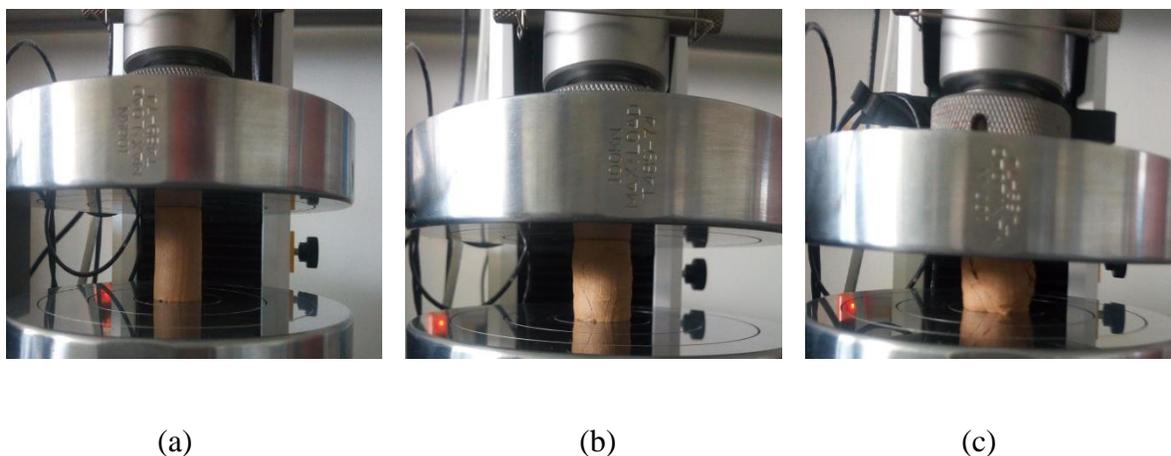


Fig.4.1. Compressive deformation on Minna clay sample at 53% moisture content, (a) point of load; (b) intermediate load; (c) high load

4.3 RESULTS AND DISCUSSIONS

4.3.1 Chemical and Mineral Compositions

Table 4.1

Chemical Composition (Mass %) of Clays Obtained by EDXRF

Oxides	Afuze	Ihitte	Kutigi	Minna	Nsu	Oboro	Obowo
SiO ₂	60.52	51.84	57.31	41.94	67.07	54.91	48.93
Al ₂ O ₃	24.80	27.07	34.74	24.51	22.16	28.38	30.48
Fe ₂ O ₃	5.19	10.13	2.36	17.14	3.91	3.17	5.85
K ₂ O	0.55	0.60	0.67	3.93	0.56	1.11	0.80
P ₂ O ₅	0.35	0.22	0.24	0.19	0.29	0.30	0.24
CaO	0.13	0.12	0.13	0.40	0.09	0.13	0.12
TiO ₂	1.72	1.02	1.19	0.54	0.80	0.98	0.89
MnO	-	0.02	-	0.10	0.01	0.01	0.02
ZnO	0.13	0.14	0.15	0.13	0.14	0.15	0.14
*LOI	6.60	8.83	3.20	11.12	4.95	10.86	12.20
Si/Al	2.4	1.92	1.65	1.71	3.03	1.93	1.61

*LOI- Loss on Ignition @ 1000°C

The samples are predominantly aluminosilicates as shown in table 1. Ihitte and Minna have very high content of iron while the SiO₂/ Al₂O₃ ratio for all the samples ranged from 1.61 to 3.03. Kaolin is the most prevalent clay mineral for Afuze and Kutigi and also present in reasonable

quantities in Ihitte and Nsu (Table 4.2). Quartz is the non-clay mineral in Nsu and Oboro and also high in Afuze. Chlorite clay mineral is prevalent in Ihitte. Illite and zeolite minerals were discerned for Minna. The loss on ignition is highest in Obowo and lowest in Kutigi. This may be attributed to their organic matter and impurities contents which may be traced to their formation and weathering. The ratio of silica to sesquioxides (Fe, Mn, Al, Ti) are 1.91, 1.36, 1.50, 0.99, 2.50, 1.69 and 1.31 for Afuze, Ihitte, Kutigi, Minna, Nsu, Oboro and Obowo respectively. According to Baver (1930), the adsorptive capacity of water molecules on colloidal surfaces decreases with decrease in silica/ sesquioxide ratios, however this was not observed in all cases for samples of study. Other factors like the mineral compositions, high content of organic matters, structure, formation and weathering might have contributed in the differences (Willis, 1946; Baver, 1948; Hough, 1957; Piaskowski, 1963; Bell, 2007).

Table 4.2
Mass % Phase Distribution of Clays Obtained by XRD

Name	Afuzo	Ihitte	Kutigi	Minna	Nsu	Oboro	Obowo
Kaolin	62.56	18.42	77.37	-	19.86	-	-
Illite/Mica	-	-	-	30.15	-	-	-
Quartz	37.44	-	-	-	80.14	49.72	-
Chlorite	-	45.93	-	-	-	-	-
Zeolite	-	-	-	65.85	-	-	92.08
Others	-	36.65	22.63	-	-	50.28	7.92

Adapted from Ihekweme et al., 2020 with permission from Elsevier

The alkali metal oxide, K_2O (flux material) is highest for Minna with 3.93 value followed by Oboro at 1.11 and lowest in Afuze at 0.55. The alkaline earth metal oxide, CaO (auxiliary flux material) during firing and cooling are low in all the samples. This may require an addition of fluxes when producing the expanded clay to bind the clay particles together to avoid disintegration. Transition metal oxides (TiO_2 and ZnO) are present in small quantities too. The

predominant Kaolin samples (Afuze and Kutigi) recorded the highest values for TiO₂ which are necessary for photo catalytic processes during water treatment (Wen et al., 2015), however they do not contain MnO which aid the scavenging of heavy metals within an aqueous system especially in contaminated water.

4.3.2 Compressive Stress Distributions and Plastic Behavior

The plasticity results (Table 4.3) indicate that the liquid and plastic limits range from 29% and 21% for Afuze to 98% and 52% for Obowo respectively. Minna has the highest plastic index of 49% while Afuze possessed the lowest plastic index of 8%. From the fore-going, Afuze and Kutigi can be classified as low plastic clays because their liquid limits (LL) are 30% and below (Hall, 1923; Bain, 1971; Whitlow, 1995; Bell, 2007). This result is not far-fetched as they are predominantly kaolin (Table 4.2) which has low affinity for water, low shrinkage and swelling behavior. Similar findings have been reported (Oluwatuyi et al., 2018; Osinubi et al., 2019). LL for Nsu is 50% which classifies it as having intermediate plasticity or plastic kaolin (Bain, 1971). Ihitte falls within the range of 50-70% with classification as high plasticity. This is due to high content of chlorite and its high affinity for water (Whitlow, 1995). Oboro possessed very high plasticity for falling in between 70-90% while Minna and Obowo are classified as extreme high plastic clay for possessing LL above 90%. The Plasticity indices for all samples are between 8% for Afuze and 49% for Minna and increases in the order of; illite > chlorite > Kaolinite.

The values of compressive stresses parameters from the compression test at different moisture content are presented in table 4.4. Obowo has the highest compressive stress of 0.15Mpa at 57% moisture while Afuze and Kutigi showed the lowest compressive stress of 0.02Mpa. However, at 40% moisture content, Minna exhibited the highest compressive stress of 0.06Mpa.

Table 4.3
Atterberg Plastic Parameters

Sample	Liquid Limits (%)	Plastic Limits (%)	Plastic Index
Afuze	29	21	8
Ihitte	63	41	22
Kutigi	30	19	11
Minna	91	42	49
Nsu	50	36	14
Oboro	82	44	38
Obowo	98	52	46

Despite moisture content, chemical and mineral compositions, all curves showed similar trends apart from kaolinites at 40% moisture content. Such results were comparable to those reported in literature (Ribeiro et al., 2005; Andrade et al., 2010; Vitorino et al., 2014). The values presented showed that moisture content, chemical and mineral compositions exert much influence on clay plasticity (compressive stress parameter). Equipped with such correlations, possible adjustment can be made to obtain desired results.

The different forces with radial variations during compression test of the samples are presented in figures 4.2 and 4.3. The dots are the experimental points which fitted into theoretical curves of plasticity. During compression, internal stress distribution affects the physical structure of the samples with a frictional force between the two opposing plates and the clay sample (Figure 4.1a). Water molecules which are bi-polar are attracted to the tiny particles of clay which are negatively charged and kept them together by means of capillary forces (Gidigas, 1976).

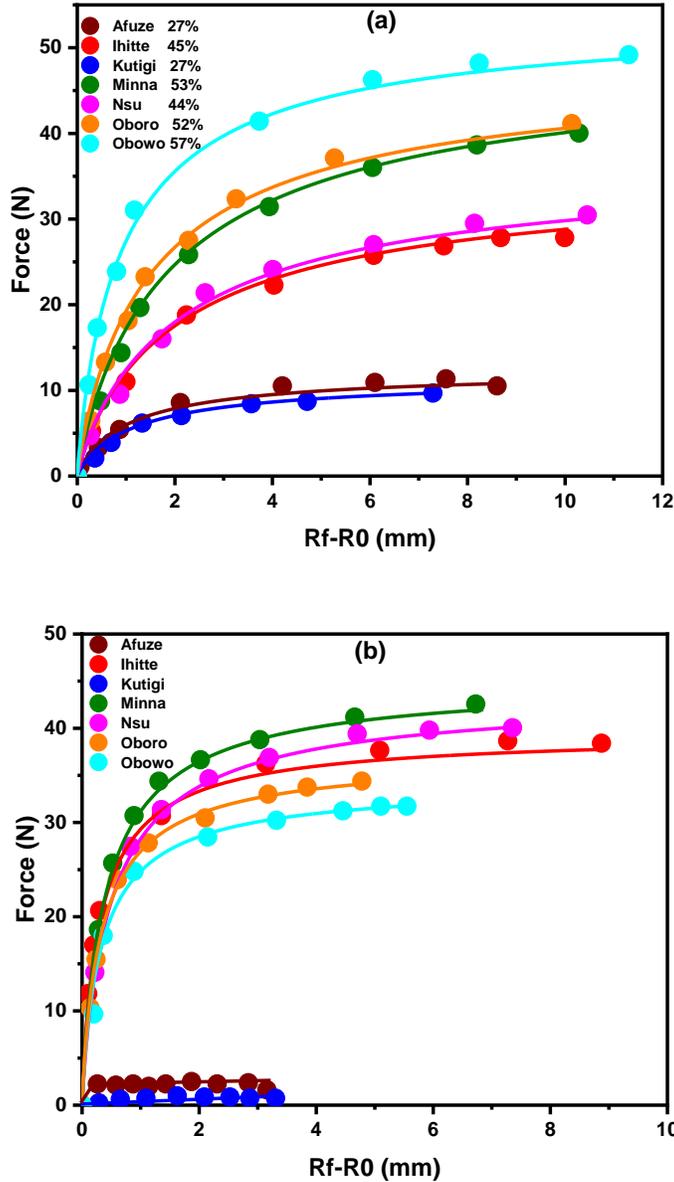


Fig.4.2. Curves of applied force versus radial changes; Rf-R0 are radius after and before compression respectively, the lines represent theoretical fitted curves while the points are experimental data (a) varying moisture content; Obowo has the highest plasticity while kutigi possessed the lowest plasticity (b) 40% moisture content; Minna possessed the highest plasticity curve, Ihitte was more plastic than the others while Obowo has the lowest plasticity outside Kutigi and Afuze that are non-plastic at 40% moisture content

These forces are overpowered upon exertion of more stress causing the water molecules to recede and allow the inflow of air into the pores of the ceramic body (Figure 4.1b).

Table 4.4
Compressive Stresses at different moisture contents

Clay	Moisture (%)	Compressive stress (Mpa)	Coefficient of friction
Afuze	27	0.02	0.15
	40	----	
Ihitte	45	0.05	0.15
	40	0.04	0.15
Kutigi	27	0.02	0.15
	40	----	
Minna	53	0.03	0.15
	40	0.06	0.15
Nsu	44	0.04	0.15
	40	0.03	0.15
Oboro	52	0.11	0.15
	40	0.03	0.15
Obowo	57	0.15	0.15
	40	0.03	0.15

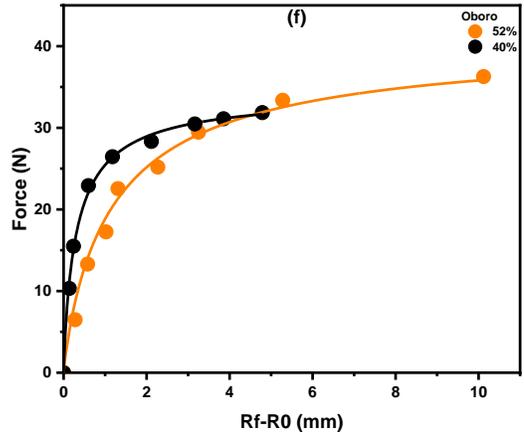
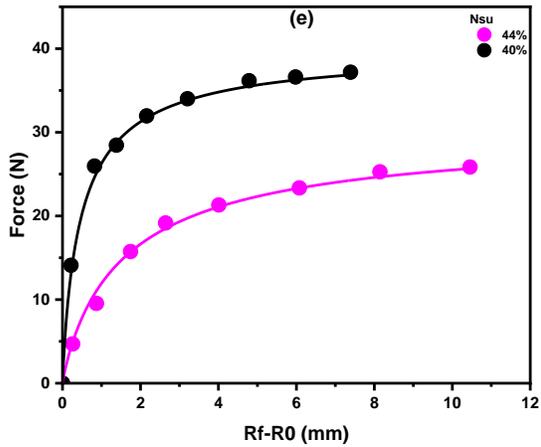
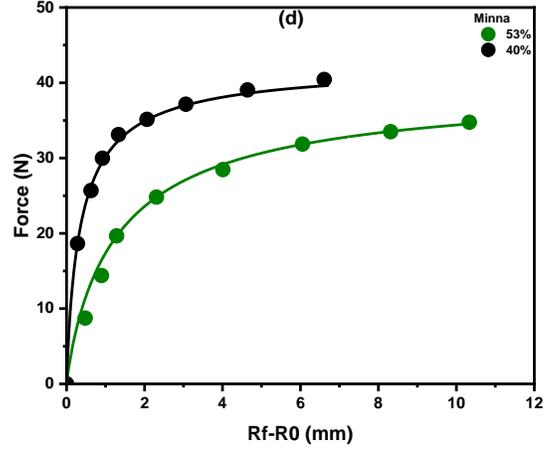
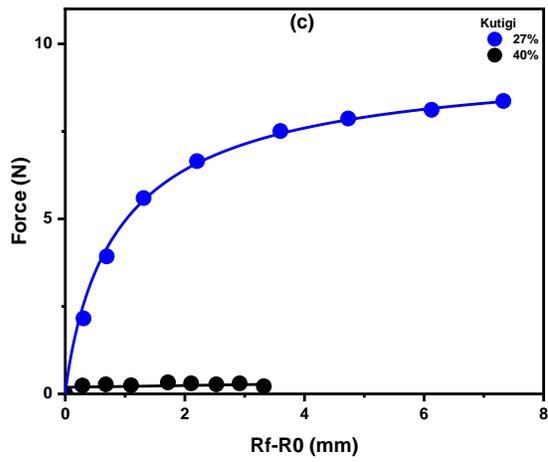
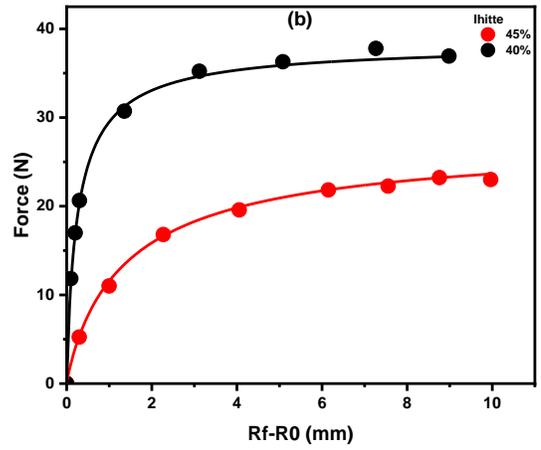
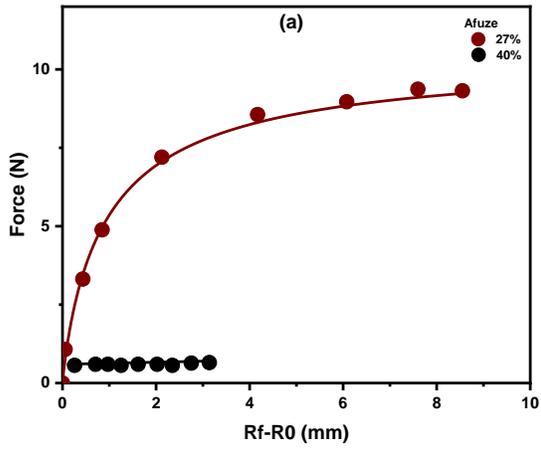
The moisture contents of 27, 45, 27, 53, 44, 52 and 57 for Afuze, Ihitte, Kutigi, Minna, Nsu, Oboro and Obowo were adapted from Ihekwebe et al., 2020 with permission from Elsevier

Deformation occurred gradually until crack was initiated (Figure 4.1c) on the side walls of the samples which propagated as the load increased (barreling). This was possible because the samples were not confined in a die. Although soil exhibit both elastic and plastic behavior, elastic strain was excluded due to insignificant elastic limit which is of no interest in the study.

The behavior exhibited (Figures 4.2 and 4.3) were in agreement with stress-strain curve for elasto-plastic deformation of porous ceramic materials. Straight line part of the graph showed elastic deformation while the curve portion showed plastic deformation. Early cracking was observed for Kutigi and Afuze samples at 27% moisture content which indicated their low-plastic nature. They are non-sedimentary kaolin and lack organic substances which improve the plasticity of clay. Kaolinite clay requires more time for water to penetrate some of the basal plane surfaces to a fix position, an act that aids the development of plasticity and bonding strength (Grim and Culhbert, 1945). However, time factor was not included in the analysis. More

so, at moisture content above 27%, they exceeded their plastic limits and became difficult to mold corroborating the earlier report by Baran et al (2001) and Barnes (2018). Such was observed at 40% moisture (Figure 4.2b) content where they exhibited extreme humidity and do not possess enough green strength for the compression test. Obviously, their optimum water content has been exceeded causing aggregates saturation and pores to be partly filled by free water, hence are represented by the straight line. Minna and Ihitte showed high plastic strength which may be attributed to their high content of iron and swelling potentials due to dry density (Ferber et al., 2009). Fe atoms are known to affect the hardening and shrinkage of clay minerals because they act as an internal source of heat and had effect on reaction kinetics. They also possessed high content of zeolites with special properties (Rhodes, 2010) and chlorite respectively which has high affinity for water.

Different moisture content induce significant changes in plastic behavior of cylindrical clay bodies (Figure 4.2a) due to the rearrangement of clusters of adjacent grains guiding the laminar properties in a flow direction and the separation of attractive and repulsive forces between the clay particles. Obowo showed the highest plasticity i.e highest curve while kutigi showed the lowest plasticity with the lowest curve (Flores et al., 2010). This also conforms to the Atterberg and moisture content results. Producing Expanded Clay Aggregates with the low plastic clay will require the addition of processing binders like sodium salt, Zusoplast C28 or any compatible plasticizers to extend the plastic region (Andrade et al., 2010; Vitorino et al., 2014). This can however be overcome by having a blend of high plastic clay mineral with non-plastic clay mineral since it has been reported that, the adsorption of heavy metals depends on the plasticity of fine-grained soil (Oluwapelumi et al., 2017).



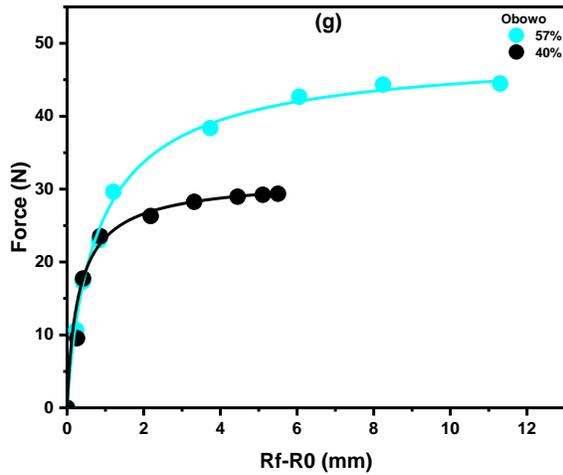


Fig.4.3. Comparative presentation of the clay minerals with varying and 40% moisture content of individual clay mineral. Rf-R0 represents the radius after and before compression respectively; the lines are theoretical fitted curves while the dots are experimental data. Afuze and Kutigi (a and c) showed reasonable plasticity at 27% moisture content; (b) Ihitte exhibited more plasticity at 46% moisture content with lesser force than at 40% moisture content; (d) Minna showed more strength at 40% but lower plasticity, it exhibited high plasticity at 53% moisture content; (e) Nsu was more plastic at 44% than at 40%; (f) Oboro was more plastic at 52% than at 40%; (g) Obowo was more plastic at 57% moisture content however it utilized higher force to achieve that

4.4 CONCLUSION

Direct measurement of clay plasticity by moisture content evaluation and the relationship between the applied force and the resultant deformation has been presented. Compressive test has proven to be suitable to characterize the plastic behavior of extruded clay. Good correlation between the experimental points and theoretical curves were obtained. Optimum water content of 27%, 46%, 27%, 53%, 44%, 52% and 57% are recommended for Afuze, Ihitte, Kutigi, Minna, Nsu, Oboro and Obowo respectively based on the obtained result. Compressive stresses and plastic indices are parameters to predict plasticity in relation with chemical and mineral compositions and moisture content. Thus the clay material properties can be optimized using this

veritable tool for wide industrial applications. Low plastic clay will require addition of plasticizers to bind the particles or working with optimum moisture content to extend their plastic regions. Good plasticity occurs when the material do not present early crack or extreme humidity. From the perspective of water filter application and in order to eliminate the use of chemicals in treatment plants, it is recommended that the low plastic clay (kutigi) be mixed with high plastic clay (Minna) to obtain balanced plasticity that will withstand the frothing pressure during backwashing in treatment plants or water bottles when using Expanded Clay Aggregates. These two samples were also favored in the multiple characterizations previously reported by same authors. Future work will use the selected clay and associated minerals to produce Expanded Clay Aggregates, test on contaminants removal of microbes, organic contaminants and adsorption studies of heavy metals.

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CHAPTER FIVE

5.0 EXPANDED CLAY AGGREGATES MULTI-FUNCTIONALITY FOR WATER PURIFICATION: DISINFECTION AND ADSORPTION STUDIES

5.1 INTRODUCTION

The need for safe clean drinking water cannot be over emphasized as it is obvious that there is global water stress despite the efforts of relevant agencies (donor agencies inclusive), organizations (including non- governmental organizations (NGO) and other stakeholders. The earth is covered by 71% water out of which only 2.5% is fresh water (Shiklomanov, 1993) . Fresh water sources from surface water, dams, rivers, streams, ponds, canals and lakes, are only 0.3% while 98.8% is ice and ground water, leaving the remaining in biological bodies (Khyade & Swaminathan, 2016). These water sources are usually contaminated with chemicals, heavy metals, pathogens, microbes, and other toxicology contaminants resulting from mining, industrial effluents, municipal sewage, septic tanks, flawed sanitation system, latrines, animal feces and agricultural activities.

Clean drinking water is a scarce commodity as world population continues to grow and it is estimated to grow to 9.8 billion by 2050 and 11.2 billion by 2100 (UN, 2017). Such population growth will be concentrated in nine countries including Nigeria according to the report. Proactive measures to address Sustainable Development Goal (SDG) number six i.e. “to ensure availability and sustainable management of water and sanitation for all” are salient. Global report shows that about 2.1 billion and 4.5 billion lack access to safe water and safety managed sanitation respectively (WHO/UNICEF, 2017). About 844 million lack basic drinking water sources whereas 159 million drink untreated water from surface water sources. Estimation shows that about 801,000 children below age 5, mostly rural dwellers, die every day due to gastrointestinal

infection popularly known as diarrhea. This contributes 11% out of 7.6 million deaths among children (Liu et al; 2012).

Lack of clean water for sanitation and safe drinking water is estimated to have caused 88% of these deaths from diarrhea (Prüss-Üstün A et al., 2008). In 1998, about 2.2 million people under age 5 died from diarrhea infection, 8.5% and 7.7% were from Southeast Asia and Africa respectively (WHO/UNICEF, 2001). World health Organisation's report on World Water Day 2020 says that diarrhea deaths are common among infants, young children, malnourished people and those with impaired immunity (WHO, 2020) . Other waterborne diseases such as cholera, dysentery, hepatitis A, typhoid, Trachoma, schistosomiasis and guinea worm are also major contributors to deaths among children (WHO, 2009, 2016; Hotez et al., 2006).

Common contaminants found in drinking water may lead to chronic health effects like cancer, liver, bladder, cardiovascular and kidney problems. These contaminants are grouped into microbial, organic and inorganic, disinfectants, disinfection by-products (DPBs) and heavy metal contaminants. Microbes with minute infectious dose (e.g., *Giardia*, *Cryptosporidium*, and *Shigella* species; hepatitis A virus; enteric viruses; and enterohemorrhagic *Escherichia coli*) may cause illnesses no matter how little is swallowed (Backer, 2002). This is because total immunity does not develop for most enteric pathogens which may induce a re-infection. Incidences of water borne disease outbreak are traceable to microbial pollutants. Excess inorganic contaminants such as nitrate and phosphate in surface and ground water and shallow wells are usually from inorganic nitrogenous fertilizers used for agricultural purposes, erosion, industrial discharge, natural decomposition of rocks and minerals, food preservatives, and oxidation of nitrogenous waste product from mammal's excreta. They are found mainly in aerobic conditions in aquifer especially when there are no growing plants around to take up some

for de-nitrification which depends on temperature and pH in case of surface water. Concentration in surface water for nitrate usually is low (0-18mg/l) but increases above 50mg/l up to hundreds of thousands due to agricultural runoff and environmental waste at the onset of rainfall (WHO, 2011). Excess nitrate, above 10 mg/l (U.S. EPA standard) in water causes methemoglobinemia, cancer and metabolic problems (WHO, 2011; Knobeloch et al., 2000; USEPA, 2011, 2017). Whereas 0.08-0.10mg/l level of phosphate can trigger algae bloom in surface water, 0.5 mg/l may speed up eutrophication and is considered unsafe for drinking water (Fadiran et al., 2008; Fried et al., 2003).

Toxic metals in drinking water even at low concentrations such as Lead and Arsenic have been linked to incidences of cancer, cardiovascular diseases, hypertension and kidney problems. Municipal water treatment plants involve removal of un-dissolved substances, dissolved substances and harmful microbes. Sand filtration is very popular among the Nigerian water purification technologies which only remove un-dissolved material, while chlorination and ozonization are employed to kill harmful microbes and most times form Disinfection By-Products (DBPs). Prior to filtration; coagulants such as aluminum sulphate are added for sedimentation and flocculation purposes. DBPs are the TriHaloMethanes (THM's), trichloroacetone ($\text{CCl}_3\text{COCH}_3$), chloroamines, chlorophenols and other halogenated intermediate compounds have direct health hazard relationship (The National Academies, 1980).

A novel approach that combines disinfection and filtration using Expanded Clay Aggregate (ECA) was developed to eliminate these filtration steps and formation of DBPs. Many researchers have reported new technologies on water treatment but not much can be found in literature on the use of ECA application in surface water treatment especially biomass-modified ECAs. Some of the reviewed literature centers attention on the use of Light Expanded Clay

Aggregate (LECA) and ECA in the adsorption of phosphorous in wastewater (Table 2.3). This chapter presents the results of development of ECA adsorbents, filtration of natural water for bacteria, phosphate and nitrate experiments, including adsorption experiments of lead and arsenic.

5.2 METHODOLOGY

5.2.1 Development of Expanded Clay Aggregate (ECA)

The clay samples selected were from Kutigi and Minna. Rice husk was sourced from Kpakungu rice mill Minna, Niger State. The raw clay samples for the aggregate were prepared and characterized in an earlier work reported (Ihekweme et al., 2020). It was washed with distilled water and dried in a Mimert oven. It was grated and sieved through sieve number 40 to get particle size of 425 μm and below. The following compositions were prepared (Table 5.1). The clay from Kutigi is non-plastic kaolin and therefore was mixed with Minna plastic clay and some portions were modified by addition of plasticizer (Na_2CO_3) to form a geo-polymer composite.

The flow process of production is presented in Figure 5.1. Different mixture compositions according to Table 2 were prepared (Figure 5.1a), pelletized (Figure 5.1b) and dried. A local manual driven rotary furnace with thermocouple was constructed to utilize local content to get good results as there was no functional rotary furnace. It was fired by coal through a blower connected to a battery (Figure 5.1c). The temperature range attained was between 764°C and 809°C . There was rapid heat loss as soon as firing stopped. This was because the furnace was not lagged, so firing was withdrawn gradually in order to get more micro pores than coarse pores. Mixtures were calcined with stepwise temperature increment in a furnace for 6 hours to a

maximum temperature within the earlier mentioned range. Rice husk and other organic matter burnt off when the temperature exceeded 430⁰C creating the pores needed for filtration.

Samples were transferred to a muffle furnace (KSL-1500X) to attain the required temperatures of 1100⁰C and 1200⁰C for another 6 hours to produce the expanded clay adsorbents (Figure 5.1d). They were cracked (Figure 5.1e) to expose the internal pores and stored in zip lock bags for experiments.

Table 5.1
Mixture Design and Description

Code	Clay (vol. %)	Rice Husk (vol.%)	Plasticizer (g)	Calcination Temperature (°C)
GI-1	100% Kutigi	-	5	1100
GI-2	100% Kutigi	-	5	1200
GI-3	100% Minna	-	-	1100
GI-4	40% Kutigi + 40% Minna	20	-	1100
GI-5	40% Kutigi + 40% Minna	20	-	1200
GI-6	85% Kutigi	15	5	1100
GI-7	85% Kutigi	15	5	1200
GI-8	100% Minna	-	-	1200



Fig.5.1. Flow Process of Expanded Clay Production: (a) clay-rice husk mixture, (b) pelletized adsorbent prior to drying and firing, (c) firing in a locally constructed furnace (d) ball-shaped ceramic granulate with porous core, (e) ECA was cracked to expose the surface with internal pores

5.2.2 Characterization of ECA

The samples were characterized for morphology using Scanning Electron Microscope (SEM) (Model: Supra55VP-Carl Zeiss) with EDX attachment after being coated with gold nanoparticle to avoid charging. XRD was done by Rigaku Smartlab 9kw unit with rotating anode at 45 Kv and 150 mA to determine their mineral contents. Patterns were recorded at 2θ and a wavelength of 1.54 \AA . X-ray photoelectron spectroscopy (Model: Omicron Fulllab System; Made in Germany)

was done to determine the chemical compositions of the aggregates. Surface area, pore volume and pore diameter were determined using BET methods (Quantachrome Instruments: version 11.03).

5.2.3 Pilot Testing of ECA Removal on Different Contaminants

5.2.3.1 Filter and ECA Characteristics

The ECA was crushed and sieved through no 5 (4mm), no 10 (2mm) and no 18 (1mm). The finely-grained particles below 1mm were sieved out because of their possibility to prevent free flow of water. It was washed and rinsed several times with distilled water to remove dust. It was then soaked for 24 hours in sterile water to open up the pores. The basic parameters of the soaked water was examined before commencement of experiments. The bench-scale set up for filtration involved a glass filter column of length 1.0m and column diameter of 0.2m. The eight samples were set up in parallel and the experiments ran concurrently. The depth of filter bed is 0.7m with grain size range of 2mm to 4mm which packed with size reduction down the column.

5.2.3.2 E.coli Experiments

The gram negative bacteria, *Escherichia coli* (E.coli) disinfection efficiency was tested using the pour plate technique and serial dilution on real environmental water. 1 ml of raw contaminated water and filtered water were incubated at $35^{\circ}\text{C}\pm 2^{\circ}\text{C}$ on petrifilms for 24 hours and the colony forming units (CFU/ml) were determined. Raw bacterial water was filtered 6 times using the same set up to initiate a cyclic experiment and test for reusability. Log reduction values (LRV) were calculated using equation 5.1.

$$\text{Log Reduction} = \log_{10} \frac{N_i}{N} \quad (5.1)$$

Where; N_i – is the colony forming unit of the bacteria before filtration

N_f is the colony forming unit of the bacteria after filtration

5.2.3.3 Column Experiments for Nitrate and Phosphate

De-nitrification and phosphate removal experiments were done following the set up in section 2.3.1 with fresh ECA. 1000 ml of standard anion mix with an initial concentration of 1.5 mg/l for both nitrate and phosphate were prepared. The pH was controlled using 1% HCl and 1% NaOH to 2 and also tested on increase level up to 12. All experiments were carried out at room temperature. 750 ml of the influent was run through the column containing each ECA sample after holding at different time intervals. The water head was maintained at 0.02m on top of the ECA filter bed to allow even distribution of the influent. The filtrate was collected at 5, 10, 15, 25, 40, 60 and 120 minutes intervals and was analyzed using DX-120 Ion Chromatography. The flow rate was set at 1.2 ml per minute and the duration of each analysis was approximately 10 minutes.

5.2.3.4 Batch Adsorption Experiments

For adsorption of heavy metal experiments, synthetic solutions of Arsenic (As) and Lead (Pb) were prepared by dissolving 1.32g of Arsenic (III) oxide (As_2O_3) in 20 ml of 2M solution NaOH and while lead standard solution was prepared by dissolving appropriate amount of $Pb(NO_3)_2$ and made up with deionized water to stock solutions of 1000 mg/l of metal ions. 100 mg of adsorbents were added to solution containing 1-120 mg/l of Pb (II) and 1-100 mg/l of As (III) for the equilibrium adsorption experiments. pH was adjusted with 1% hydrochloric acid or 1% NaOH to 5.0. Mass of 0.1 g of each sample of adsorbent was added to 100 ml of each of the prepared solution and was shaken at 150 rpm for 12 hours at 25°C. The concentrations were

determined by atomic adsorption spectrometry (nov AA 350; Made in Germany) to ascertain the amount of adsorbed As (III) and Pb (II) at time intervals. Isotherm adsorption data were obtained which was fitted by both Langmuir and Freundlich isotherm models (Luo et al., 2015) represented in equations 5.2 and 5.3 respectively;

$$Q_{eq} = \frac{Q_{max} k_l C_{eq}}{1 + k_l C_{eq}} \quad (5.2)$$

$$Q_{eq} = K_f C_e^{1/n} \quad (5.3)$$

Where C_e is the equilibrium concentration (mg/l) and Q_{eq} is the adsorptive capacity at equilibrium (mg/g). K_L (l/mg) and Q_{max} (mg/g) are the Langmuir parameters; K_L is the binding constant, and Q_{max} is the maximum adsorptive capacity (mg/g); K_f (mg^{1-(1/n)} L^{1/n}g⁻¹) and n are the Freundlich parameters; K_f is the adsorption capacity and n is the adsorption intensity.

100 mg each of the adsorbent was added to fresh solutions with concentrations of 18.6 mg/l for Pb (II) and 12.5 mg/l for As (III) and shaken for 30 minutes at 25⁰C. Regeneration was done adopting the procedure used by (Zhang et al., 2015) with 0.01 M Na₂ EDTA for lead and 0.1 M NaOH for arsenic for five cycles. Effects of experimental parameters such as pH, dosage and contact time were studied by keeping others constant and varying one. pH effect was varied between 2-8, dosage effect ranges from 0.2g/100 ml to 2g/100ml and adsorption kinetics was evaluated between 1-120 mins. The specific quantity adsorbed, Q (mg/g) and adsorption efficiency (R%) were calculated using the equations 5.4 and 5.5 respectively (Gaur et al., 2018);

$$Q = V \times \frac{(C_i - C_e)}{1000 \times W} \quad (5.4)$$

$$R = \frac{(C_i - C_e)}{(C_i)} \times 100\% \quad (5.5)$$

Where V (ml) is the volume of solution used, C_i (mg/l) is the initial concentration; C_e (mg/l) is the equilibrium concentration and W (g) is the amount of adsorbent.

5.3 RESULTS AND DISCUSSIONS

5.3.1 Morphology, Mineralogy and BET Characteristics of ECA

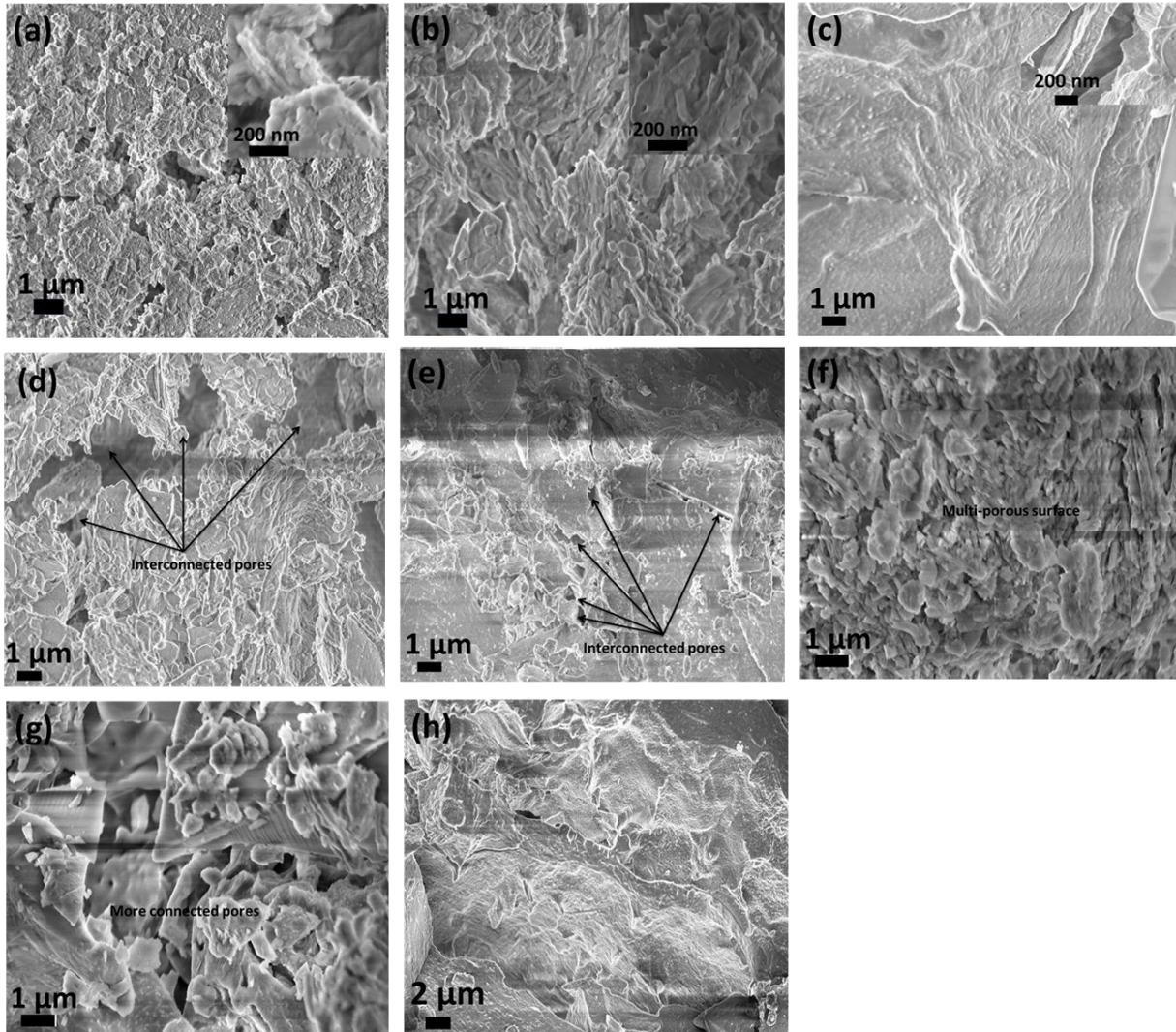


Fig.5.2. Surface image of ECA particle under a scanning electron microscope (SEM) showing cavities; (a) GI-1 exposes the stack sheet structure of kaolin ; (b) GI-2; stack sheet morphology (c) GI-3- showing long, slender and fibrous aggregate of sillimanite and hexagonal flakes; (d) GI-4- mixed surfaces of sheet platelets and hexagonal flakes; (e) GI-5- mixed surfaces of sheet platelets and hexagonal flakes; (f) GI-6- multi-porous well defined flakes; (g) GI-7 multi-porous well defined flakes with more connected pores-; (h) GI-8- possess long, slender and fibrous aggregates of sillimanite with more pores than GI-3

When crushed, SEM examination of ECA revealed that, there is interconnected honeycomb- like cavities (Figure 5.2) and inter granular connected pores of different shapes and sizes. The differences are not far- fetched as they are additive and temperature dependent. Images of GI-1 and GI-2 (Figure 5.2a and 5.2b) show staked structure with inter connected edges. This implies that the calcination temperatures did not present any visible changes on the morphology of the two samples. GI-3 and GI-8 (Figures 5.2c and 5.2h) possessed fibrous aggregate which appear long and slender, however the pores for GI-3 are not as much when compared to GI-8 sample. This means that they are temperature dependent as more pores were created as the temperature increased from 1100⁰C to 1200⁰C. Interconnected pores were observed for GI-4 and GI-5 (Figures 5.2d and 5.2e). The addition of rice husk created these connections as they burnt off during calcination and it was further confirmed from BET analysis (Table 2) as these set contained more pore volume than other samples. The structure of GI-6 and GI-7 changed from stacked sheets (Figures 5.2a and 5.2b) to flakes characterized by irregular distributed pores and shapes (Figures 5.2f and 5.2g) due to the addition of rice husk.

Mineral reflections of XRD examination (Figure 5.3) are presented below. Kaolinite composite reflected strong peaks for Cassiterite (a tin oxide mineral) for both GI-1 and GI-2 (Figure 5.3a) which was also concentrated in high temperature quartz veins as seen in GI-2 only. The EDX of these samples (not shown) though possessed high content (% weight) of silicon (52.89) and aluminium (53.51) respectively; it also recorded 3.44 for titanium (GI-1 only) and 2.31 for potassium. These results conform with the earlier report for Kutigi clay (Ihekweme et al., 2020) which had kaolin as the major mineral then. The present minerals can be attributed to high temperature exposure and addition of Na₂CO₃. The predominant high temperature silicate minerals for GI-3 are Sillimanite, quartz and mullite, however strong reflections were observed

when calcined to 1200⁰C (GI-8) for Pentacalcium bis[dinitridocobaltate (1)] and Spessartine (Figure 5.3b).

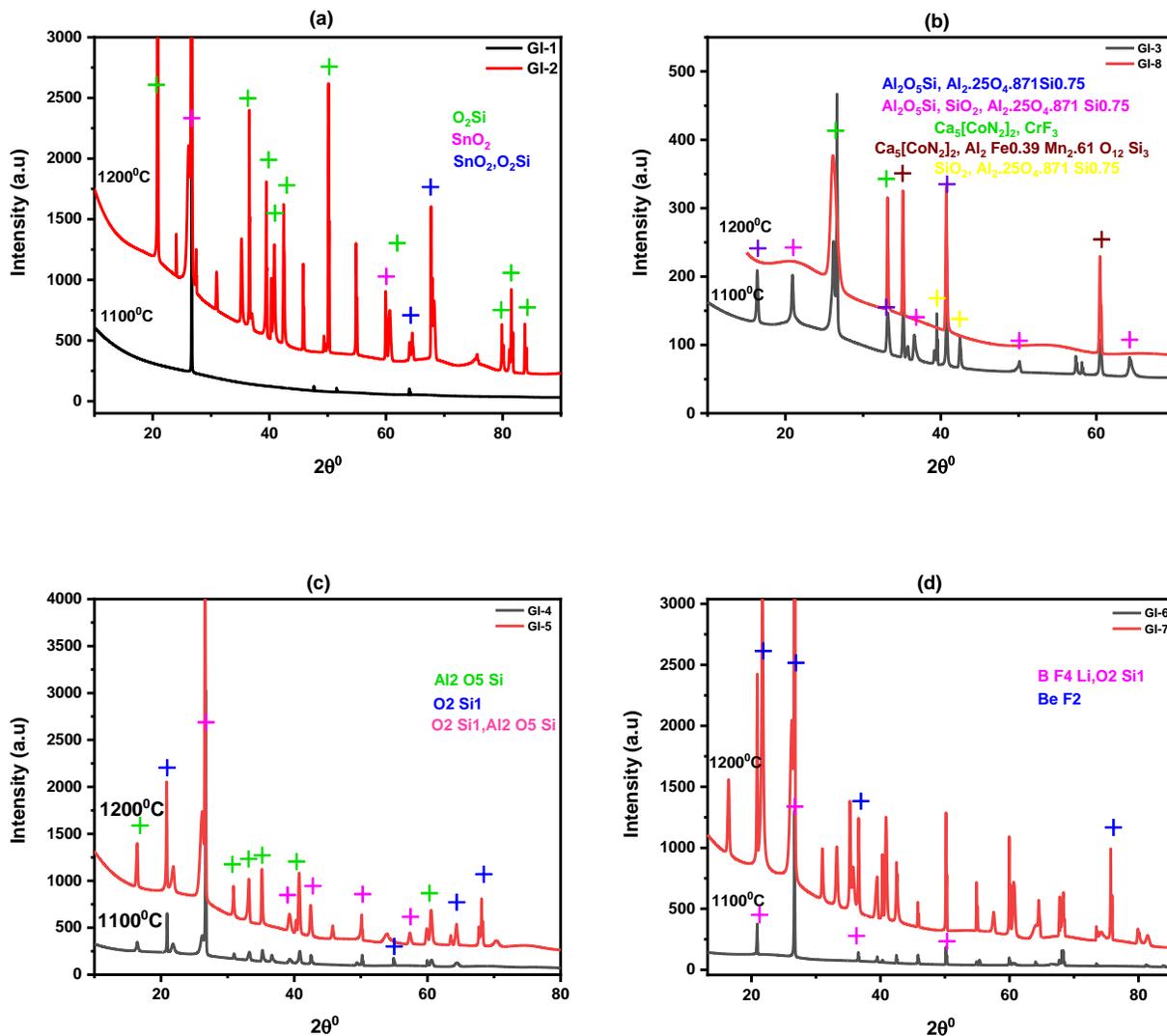


Fig. 5.3. XRD plots of ECA at 1100⁰C and 1200⁰C showing mineralogy. (a) 100% Kutigi clay; (b) 100% Minna; (c) 40% Kutigi+40% Minna + 20% rice husk; (d) 85% Kutigi + 15% rice husk

The mixture of the two clay minerals and rice husk (Figure 5.3c) results in composite with major minerals of silimanite and quartz and traces of beryllium fluoride (GI-5 only) which structurally resembles quartz. The BeF_2 may have come from the addition of rice husk and formed at

temperature above 1100⁰C. The minerals for GI-6 and GI-7 (Figure 5.3d) were Bithium tetraflouride and quartz whereas BeF₂ were observed at 1200⁰C which confirmed the suspicion of rice husk addition at elevated temperature.

The elemental compositions revealed by XPS showed high contents of O 1s and C 1s which could be attributed to the reasons mentioned earlier (Ihekweme et al., 2020) in their raw materials characterization. Other strong reflected elements were silicon, aluminium, fluorine, iron and calcium which are likely to exist in their oxides forms. Trace elements were lanthanides rare earth such as dysprosium and erbium, bismuth, silver and nickel. Chromium (Cr 2p) element was observed for GI-3 and GI-7 which also reflected by XRD as chromium fluoride.

Table 5.2
Surface area / pore analysis of the ECAs

Sample	Surface area (m²/g)	Pore Volume (cc/g)	Pore Size (nm)
GI-1	468.948	0.134	2.131
GI-2	542.265	0.180	2.072
GI-3	530.442	0.136	2.113
GI-4	477.203	0.195	2.853
GI-5	471.270	0.190	2.118
GI-6	475.120	0.128	2.153
GI-7	566.998	0.163	2.132
GI-8	456.143	0.132	2.133

The samples relatively have high surface area (Table 5.2). GI-7 has the highest surface area of 566.998m²/g while GI-8 possessed the lowest with 456.143m²/g. The pore volume ranges from 0.132cc/g to 0.195cc/g with GI-4 possessing the highest value as well as highest pore size of 2.853nm.

Table 5.3
Physical Parameters of sterile water after soaking ECA adsorbents in it for 24 hours

Sample Name	GI-1	GI-2	GI-3	GI-4	GI-5	GI-6	GI-7	GI-8
Temp (°C)	27.2	27.1	27.1	27.0	26.9	26.9	26.9	27.0
Conductivity (µs/cm)	38.6	36.0	48.2	80.8	58.1	62.8	34.1	47.9
TDS (mg/l)	17.2	16.0	21.6	36.7	26.3	28.4	15.2	19.2
Salinity (%)	-0.2	-0.2	-0.1	-0.1	-0.1	-0.1	-0.2	-0.1
pH	6.6	8.0	9.2	8.8	9.2	7.5	8.3	9.0

Table 5.3 shows excellent total dissolved solid (TDS) values for all the samples since they are below 300 mg/l which is perfect for WHO standard for drinking water. This also confirms the absence of harmful elements such as manganese, arsenic, sulphate, etc as revealed by XRD. The pHs are also within WHO range of 6.5-9.5 whereas GI-3, GI-4, GI-5 and GI-8 fell outside the EPA standard range of 6.5-8.5 for drinking water. We suspect that the 80.8 µs/cm conductivity value recorded for GI-4 maybe due to the high presence of the nesosilicate and sillimanite minerals.

5.3.2 E.coli Disinfection

The disinfection result in figure 5.4 shows that using the adsorbents could achieve E.coli bacteria reduction up to log 4. It was also observed that the adsorbents were not consumed after 6 cycles of filtration although there was a decrease in flow rate (not part of the present studies). Similar disinfection assay was published by (Asamoah et al., 2020) using clay-metaloxide / metal composite pellets. We postulate that the high disinfection result might have arisen from bacterial cell wall that possessed amphoteric properties due to the presence of cationic and anionic groups, surface charge and modification of the adsorbent (Londono & Williams, 2016). Other clay-

based materials have successfully removed E.coli from water (Dang-I-Auphedeous., 2010; Unuabonah et al., 2018; Ajibade et al., 2019).

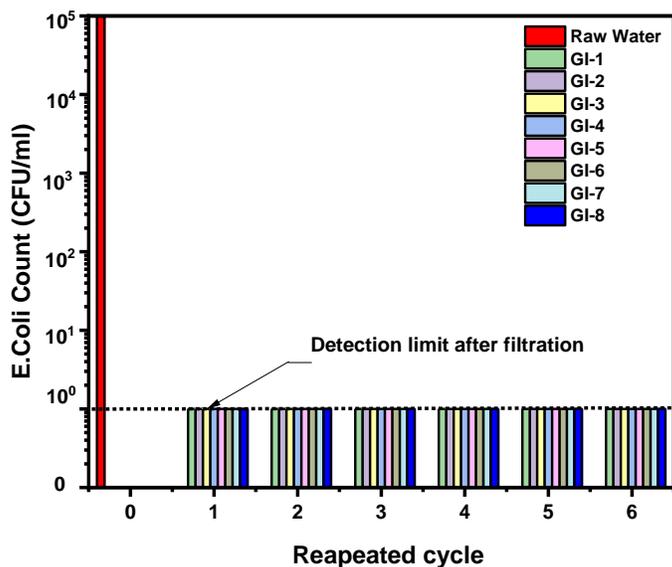


Fig.5.4. The antibacterial efficiency of ECA adsorbent on E.coli bacteria before filtration at 10⁵ CFU/ml raw water and after filtration. The adsorbents have excellent reusability as they maintained high disinfection efficiency after 6 recycling

5.3.3 Phosphate and Nitrate removal

The reduction efficiencies for phosphate and nitrate for the entire adsorbents varied from 27.33% to 76% (Figures 5.5a and 5.5b) and 10.67% to 46% respectively (Figures 5.5c and 5.5d). GI-1 possessed the highest disinfection efficiency of 76% within 10 minutes and consequently attained disinfection equilibrium around 25 minutes for phosphate. The cassiterite mineral and the aluminium complexes were suspected to have adsorbed the phosphorus ions (Johansson, 1997). Other adsorbents calcined to same temperature i.e, GI-3, GI-4 and GI-7 reached disinfection equilibrium around 40 minutes (Figure 5.5a) with highest efficiency values of 36%,

32.67% and 44% respectively. The phosphate % removal efficiency values for GI-2, GI-5, GI-7 and GI-8 were 46.47%, 33.35%, 41.33% and 40% respectively. Higher removal efficiency values attributed to lower pH, high surface area and high pore volume were recorded as against those reported by (Johansson, 1997; Łopata et al., 2017), 79-90% were reported by (Alzeyadi et al., 2019) using Biomass Bottom Ash (BBA), however 57%-75% removal efficiencies was reported for the bio-filtration of ozonated humid water (Melin, and Odegaard, 1999).

The highest % removal efficiency for Nitrate was 46% which was possessed by GI-1 around 5 minutes and attained equilibrium at about 40 minutes. GI-7 possessed the lowest value of 10.67% at about 40 minutes. The lower adsorption efficiencies was due to negative charge of Nitrate (Rezvani & Mehdi, 2018). With increasing pH, the removal efficiencies reduced drastically to as low as 18% for phosphate and 6% for Nitrate (highest values for all the adsorbents). We suspect that OH groups compete with the anions causing the reactive sites to become negatively charged which impedes Nitrate and Phosphate removal due to repulsion (Rezvani & Mehdi, 2018).

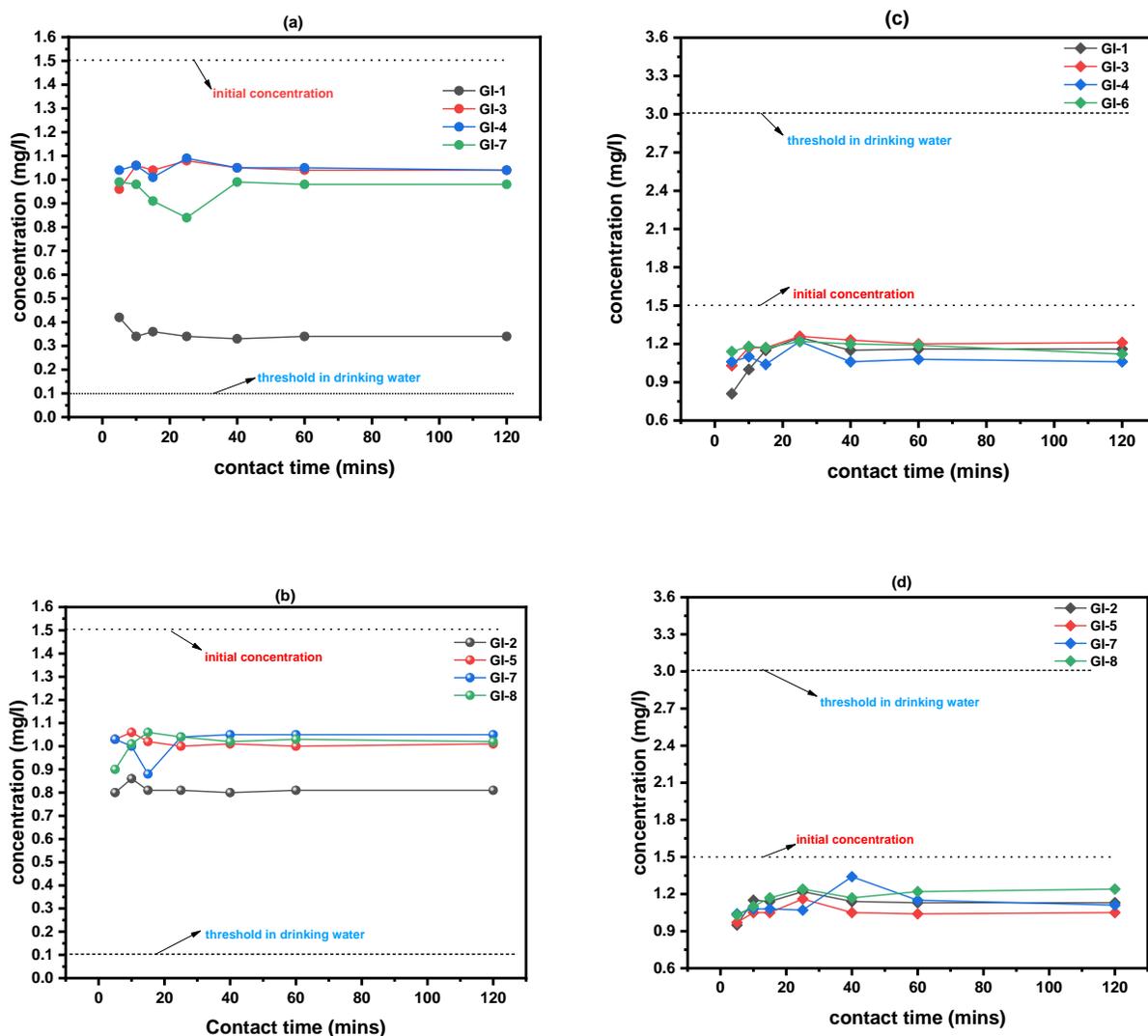


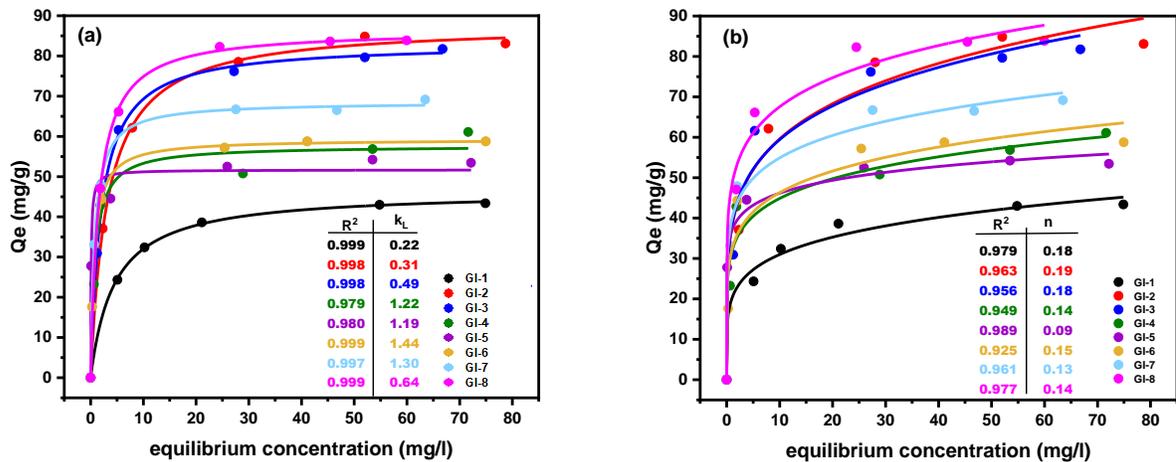
Fig.5.5. Phosphate and Nitrate reduction efficiencies; (a) phosphate concentration reduction for adsorbents calcined to 1100°C: GI-1 > GI-6 > GI-3 > GI-4; (b) Phosphate concentration reduction for adsorbents calcined to 1200°C: GI-2 > GI-7 > GI-8 > GI-5; (c) Nitrate concentration reduction for adsorbents calcined to 1100°C: GI-1 > GI-3 > GI-4 > GI-6; (d) Nitrate concentration reduction for adsorbents calcined to 1200°C: GI-2 > GI-5 > GI-8 > GI-7

5.3.4 Adsorption Isotherm

Langmuir and Freundlich models for both lead and Arsenic are presented in figure 6. The correlation coefficient R^2 suggests that the Langmuir isotherm is more appropriate (all adsorbents) in describing the adsorption process for both lead and arsenic (Figures 5.6a, 5.6b,

5.6c and 5.6d). This implies that the adsorption of lead and arsenic on ECA surface is a monolayer adsorption. The result is similar to those reported in the review of modified clay minerals adsorption processes (Annan et al., 2018; Gu et al., 2019). It was therefore postulated that lead and arsenic removal was achieved by the adsorbate molecular transport to the adsorbent surface by diffusion through the boundary layer, the adsorbate diffuses from the external surface into the pores of the adsorbent, and the adsorbate binds on the multiple active sites of the internal pores (Habuda-stani & Nuji, 2015).

From figure 5.6 also, the maximum adsorption capacity (Q_{\max} (mg/g)) for each of the adsorbent were calculated for lead and arsenic to be 46.40/22.26; 87.93/74.62; 83.16/49.66; 57.66/33.57; 51.69/35.05; 59.28/25.86; 68.55/33.46 and 86.51/54.79 for GI-1, GI-2, GI-3, GI-4, GI-5, GI-6, GI-7 and GI-8 respectively. The adsorption capacity K_f for both lead and arsenic respectively for the 8 adsorbents were 20.13/9.5; 37.89/12.42; 38.38/19.93; 31.81/15.95; 36.98/6,15; 32.22/14.50; 39.84/17.30 and 48.24/22.79.



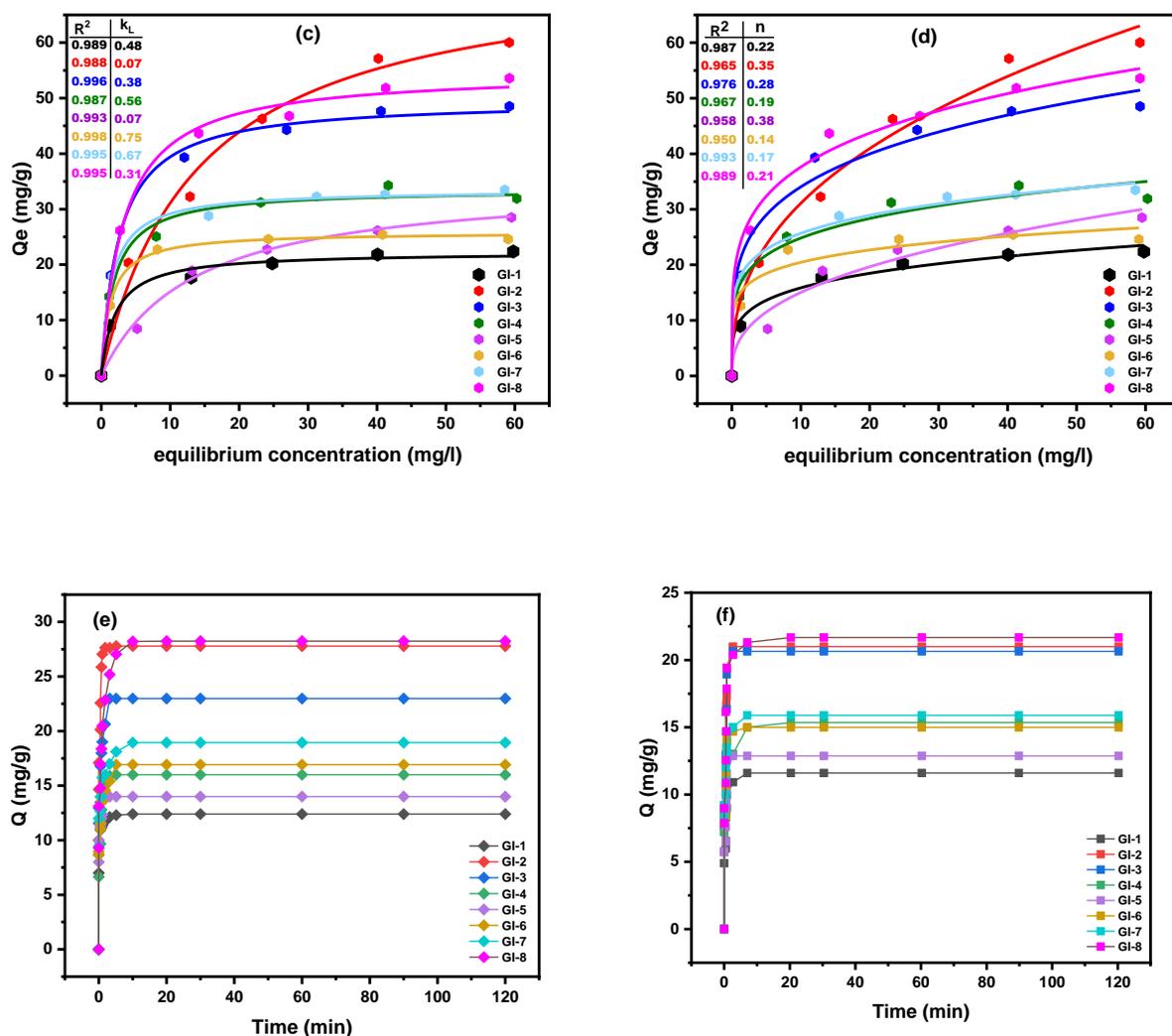


Fig.5.6. Adsorption of Pb (II) and As (III) on ECA, 25⁰C and pH 5.0 (a, c) Langmuir adsorption isotherms for Pb and As respectively; (b, d) Freundlich adsorption isotherms for Pb and As respectively; (e, f) Adsorption kinetics for Pb and As respectively

5.3.5 Adsorption Kinetics

Adsorption kinetics for Pb (II) and As (III) (Figures 5.6e and 5.6f) was rapid. About 90% of adsorption took place within the first minute and equilibrium was attained within ten minutes as a result of active sites saturation. This is highly remarkable and recommendable for real applications. The rapid response to adsorption may be attributed to availability of large surface

areas that exposed more reactive sites with fine particle size, active surface groups and large pore volume. Researchers have reported such response with other nano-adsorbents (Gu et al., 2019; Zhang et al., 2015)

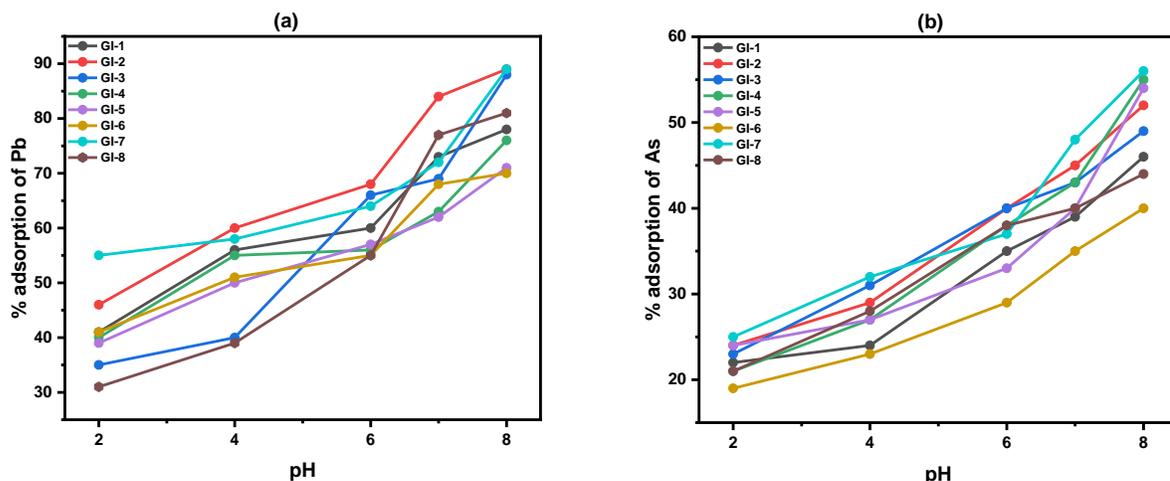


Fig.5.7. Effect of pH on adsorption; (a) Pb II; (b) As III. Experimental conditions: temperature 27 °C, contact time 40 min, adsorbent dose 0.1g/100 ml

5.3.6 Effect of pH

Due to the importance of pH in adsorption studies, the effects on the adsorbents were investigated within the range of 2 to 8. pH activates the anion adsorption sites on clay minerals (Mehmood et al., 2009). When the pH is low, the hydroxyl group exposed on the sites of clay mineral adsorbents becomes protonated causing the positive charge to interact and adsorbed the anions present in arsenic. The lower values of adsorption at lower pH was due to excess H^+ ions which competes with Pb ions on the active sites. However the Pb ions reacts more with OH^- as the pH increases resulting in adsorption increase.

Generally, lead and arsenic adsorption capacity increased with increase in pH (Figures 5.7a and 5.7b) for all the adsorbents. Similar results were presented by (Goldberg, 2002) for arsenic (III) adsorption by kaolinite, illite, smectite and similar nano-adsorbent minerals (Habuda-stani &

Nuji, 2015) and (Gaur et al., 2018) for lead. We suggest that this was due to surface charge of the adsorbents which is closely related to pH of water. Although higher adsorption was achieved at higher pH, this may be as result of pH precipitating at pH above 6 (Taffarel and Rubio, 2009). For further experiments, pH 6 was adopted to avoid precipitation interference.

5.3.7 Effect of Adsorbent Dose

Adsorption of lead and arsenic was more as the dosage increased. Significant difference were observed between the adsorbent calcined to 1100⁰C (figure 8a) and 1200⁰C (Figure 5.8b). For instance, 52% arsenic was adsorbed at 1.0 (g/100ml) on GI-1 whereas it was improved to 62% on GI-2 at the same dosage. We attribute it to more surface area and pore volume recorded in BET result in table 2 and active binding sites. However, it cannot be concluded that the higher the calcined temperature, the higher the arsenic/lead adsorption as GI-3 adsorbed 59%/84% as against GI-8 that adsorbed 55%/82% respectively. Adsorption tends to equilibrium after reaching peak at 1.0 (g/100ml) though except GI-8 arsenic adsorption and a decline in the lead adsorption for GI-1 and GI-2. Generally, it was observed that Pb is adsorbed by ECA more than As. This is due to the positive and negative ionization possessed by the two metals respectively.

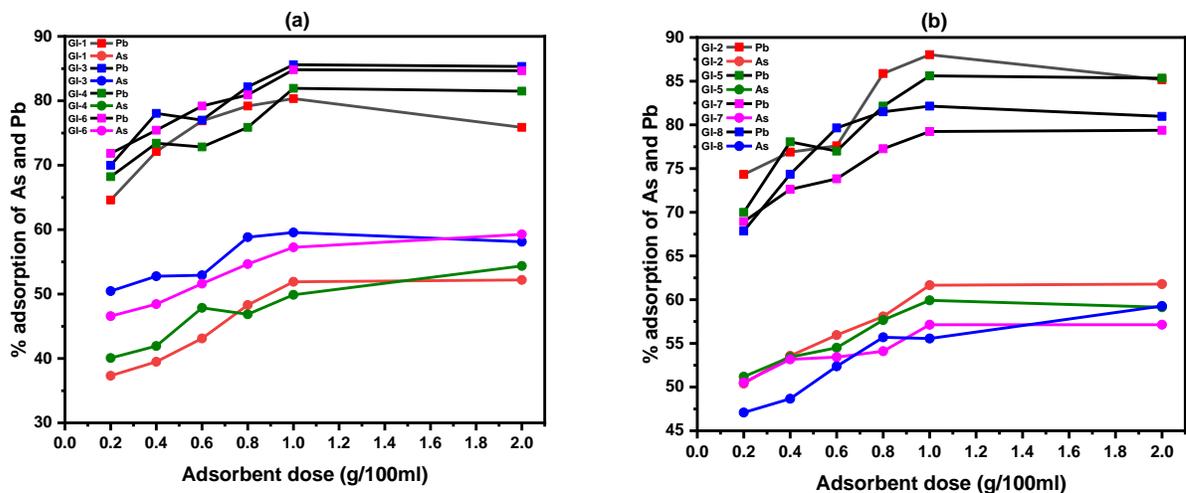


Fig.5.8. Effect of adsorbent dose on adsorption of Pb II and As III. Experimental conditions: temperature 27 °C; contact time 40 min; pH 6; (a) adsorbents are calcined to 1100⁰C; (b) adsorbents are calcined to 1200⁰C

5.3.8 Cycle Experiments

Figure 5.9 reveals the Pb (II) adsorption capacity by all the ECA adsorbents. Their metal uptake was predominantly stable for some after four cycles (Figures 5.9c, 5.9g and 5.9h) whereas there was much significant difference for GI-5 (Figure 5.9e) after two cycles, i.e from 82 (mg/g) to 73 (mg/g). The adsorption for As (III) (Figure 5.10) was more stable for till the fourth cycle for all adsorbent with the exception of GI-3 which exhibited significant difference at the third cycle (Figure 5.10c). GI-7 and GI-8 were not consumed even till the fifth cycle as their adsorption capacity reduced negligibly from 37 (mg/g) to 36 (mg/g) and 38 (mg/g) to 37 (mg/g) respectively. Relatively, the adsorbents had good reusability and possess great potential in the purification of water.

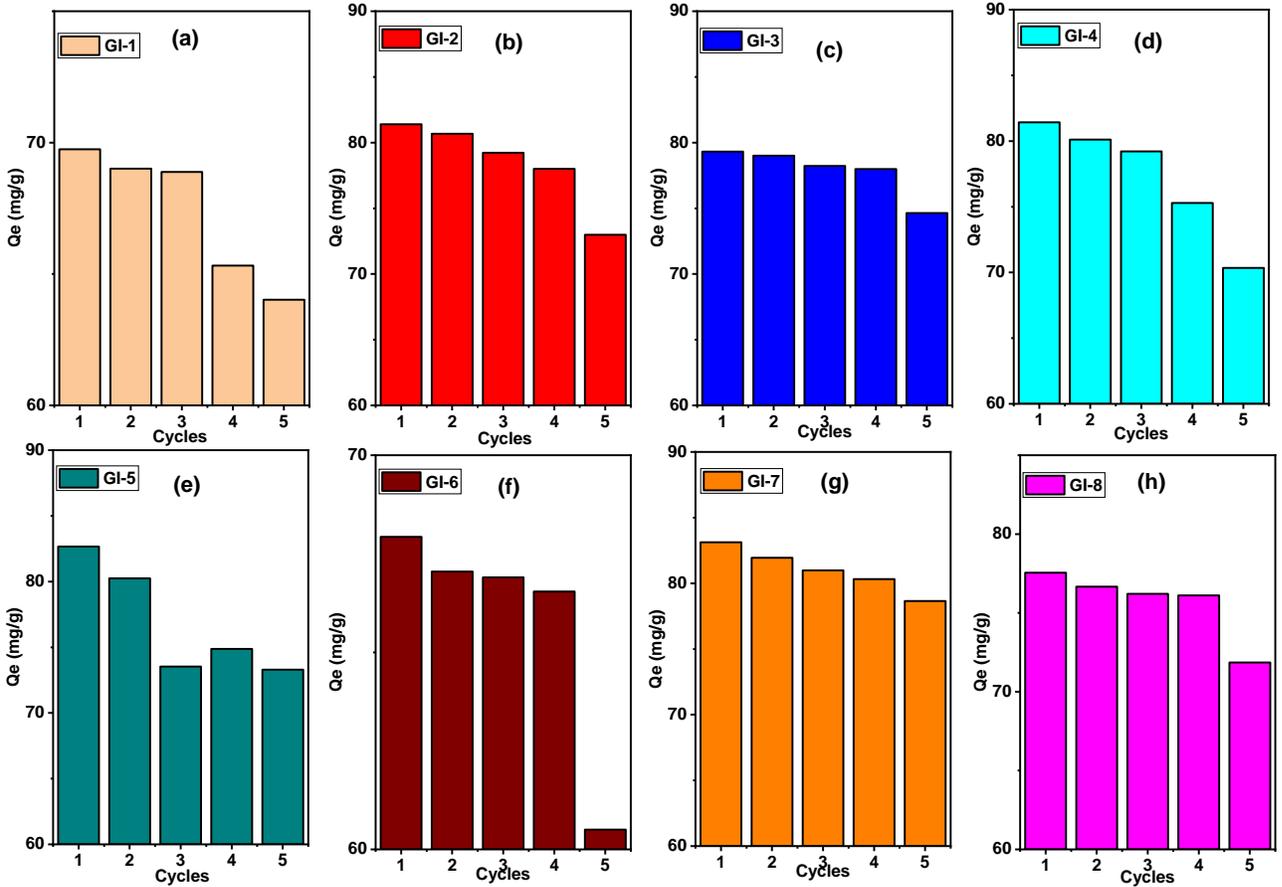


Fig.5.9. Cyclic experiments for the Pb (II) adsorption shaken for 30 minutes at 25⁰C regenerated with 0.01 M Na₂ EDTA

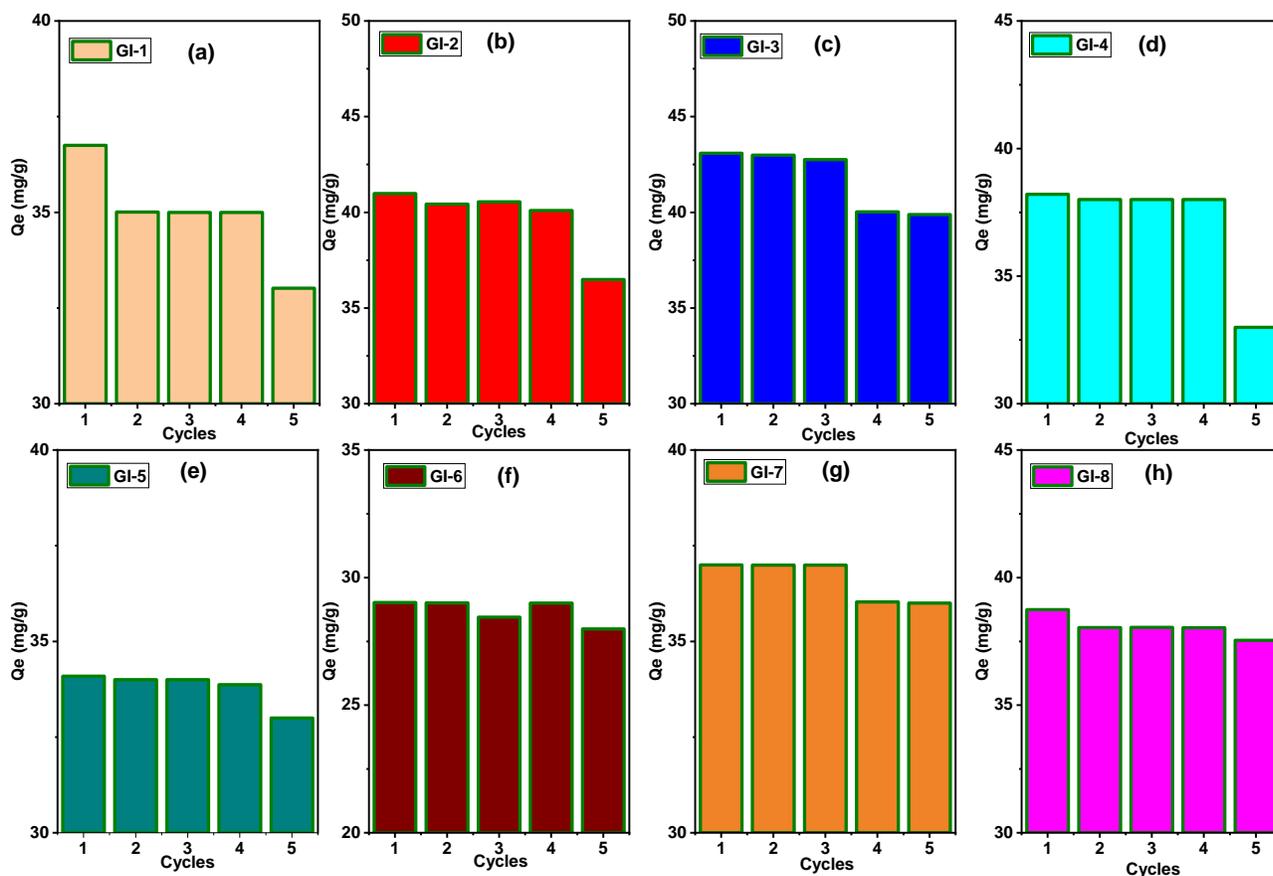


Fig.5.10. Cyclic adsorption experiments for As (III) shaken for 30 minutes at 25⁰C regenerated with 0.1 M NaOH

5.4 CONCLUSIONS

Expanded Clay Aggregates (ECA) in natural and modified forms was used as filter materials for the removal of E.coli bacteria, phosphates and nitrates as well as adsorbents for lead (II) and arsenic (III). Their possession of large surface areas to volume ratio, high pore volume and more reactive sites necessitates high removal rate of E.coli bacteria up to log four, high phosphate (27.33% to 76%) and nitrate (10.67% to 46%) removal compared with previous studies results. Adsorption isotherms for both lead (II) and arsenic (III) fitted better to Langmuir than Freundlich models. Adsorption kinetics was fast and recommendable for real applications. Experimental

factors such as pH, adsorbent dose and contact time obviously affected the adsorption studies. This study has successfully demonstrated the feasibility of modified ECA for use in water treatment and remediation applications thereby eliminating or reducing the use of chemicals to barest minimum. Future work will look at the adsorption mechanisms of interaction between adsorbents and contaminants, development of low cost modified clay adsorbents with other renewable fillers and their exploitation in water remediation for community base applications and municipal treatment plants.

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CHAPTER SIX

6.0 GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 CONCLUDING REMARKS

Part A: Seven Nigerian clays and clay minerals were sourced locally, characterized by multiple means with respect to their potential application in water purification and other industrial uses. The morphology was carried out using Scanning Electron Microscope while chemical/mineral compositions were quantified using Energy Dispersive X-ray, X-ray Photoelectron Spectroscopy and X-ray Diffraction. The equipment used to investigate the functional groups inter-alia other physical and chemical behavior of adsorbed species were Fourier Transform Infrared and Ultraviolet Spectroscopy. Stability studies in aqueous solution were determined by zeta potential measurements.

Combined results revealed that the clays are mostly kaolin and illite while clay minerals are predominantly gibbsite and quartz although other clay associated minerals and elements were also observed. Two out of the characterized samples were found suitable for application in filter media production for water purification due to the possession of exchangeable cations and electrophoresis properties while others possess potential industrial applications for refractory linings, ceramics, medical, beauty and cosmetics products. Results of the study were used to design and facilitate expanded clay aggregates production to be used for the development of low cost water filters to address the challenge of poor access to potable water in Africa and other developing continents.

Part B: The plasticity characteristics which are essential in the determination of clay and clay minerals suitability for water filtration purposes were examined. Preliminary studies on the clays from the locations of study have been reported on their physiochemical characteristics but there are no published works on the plastic behavior of clays. The plastic behavior of the seven clays was characterized using plasticity indices and compressive stress parameters in relation to chemical compositions and moisture content. The objective of this part was to determine the plastic behavior of the seven clay minerals and their suitability in production of Expanded Clay Aggregates (ECA) for water filters.

Compressive stresses and deformation parameters were determined experimentally and compared theoretically. Atterberg limits (D 4318) were used to determine the plasticity indices. Chemical compositions of the samples were examined with XRF and correlated with plasticity and mineral contents of the clays. The aluminosilicate clays possessed $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1.61 to 3.03 and plastic indices of 8 to 49. Low plastic indices (8-11) and low compressive stresses parameters were observed for kaolinite clays (0.002MPa) due to their low affinity for water while zeolite rich clays showed high plastic indices (46 and 49) for Obowo and Minna and sharp difference in their compressive stresses parameters (0.15MPa and 0.03MPa) at optimum moisture contents of 57% and 53% respectively. Despite varying moisture content, chemical and mineral compositions, all curves showed similar trends apart from kaolinites at 40% moisture content. Relationships exist among microstructural properties, chemical composition, moisture content, compressive strength and plasticity indices of the clays. The plastic behavior properties showed that they are all suitable for development of ECA for water filters. However, the two earlier selected were used for further experiments.

Part C: The two selected clays (Kutigi and Minna) in their natural forms and rice husk- Na_2CO_3

modified clay was used to produce expanded clay aggregates adsorbents at different formulations and varying temperatures. Characterizations of the produced adsorbents were done by SEM, XRD, XPS and BET to reveal their salient features. Filtration studies were carried out to ascertain the disinfection assay of E.coli and removal efficiencies of nitrate and phosphate. Batch adsorption experiments were employed to determine the effect of pH, contact time and adsorbent dosage for effective removal of Arsenic (III) and lead (II) including isotherm models. Aluminosilicates and associated minerals with high surface areas between 456.143-566.998m²/g and significant adsorption sites were revealed. Log four bacteria disinfection assay was achieved. Reduction efficiencies for phosphate and nitrate for all adsorbents varied from 27.33% to 76% and 10.67% to 46% respectively. High correlation coefficients made Langmuir isotherm model more favourable than Freundlich model. The adsorption capacities for both lead and arsenic were high and reaction was fast, making the adsorbents suitable for water remediation applications.

6.2 RECOMMENDATIONS FOR FUTURE WORK

Studies on the adsorption mechanisms of interaction between adsorbents and contaminants, flow rate experiments over varying depths, filter designs, prototypes and pilot plants production and testing are very important and hereby recommended for immediate future work. Other formulation ratios for ECA adsorbents may be looked at together with comparative analysis with the ones presented. Production of ECAs using other bio-sorbents fillers such as saw dust, sugar cane bagasse, moringa roots, cellulose fibers, etc and testing on water contaminants removal other than the ones presented in this work is recommended as one of the future works. Transformations studies above 1200⁰C is also recommended for future work although, this may impact on the cost of production. Mathematical model of the filtration process and research on the development of low cost modified clay adsorbents with other renewable fillers and their

exploitation in water remediation for community base applications and municipal treatment plants should be encouraged. Finally, studies on the adsorbents capability to filter wine and fruit juice can be explored.

6.3 CONTRIBUTIONS TO KNOWLEDGE

The research contributed to knowledge through the following highlighted points;

- i. Provision of data and information on properties of local minerals (clays and biomass) in relation to their suitability for water filters production.
- ii. Development of novel nano-adsorbents which are capable of removing multiple contaminants from water which will in turn contribute to the improvement of water sanitation and hygiene programmes, provision of water solution to vulnerable groups such as the peri-urban poor and IDPs and reduction in the prevalence of waterborne diseases. The technology offers a very good prospect for providing affordable potable water in a country where several existing sources are of questionable quality.
- iii. Improvement of savings in overhead and running cost for Municipal Water Treatment Plants. Due to large surface area and high pore volume of the aggregates, more volume is filtered at a time and backwashing will no longer be as regular as in the case of sand filters.
- iv. Economical solution to water filtration in placement of the use of sand and gravel. Reduction to the barest minimum of the cost of importation of coagulants, flocculants or elimination of the use of chemicals in water treatment technologies since ECA adsorbents had high efficiencies in removal rate of multiple contaminants from water.
- v. Economic recovery through local content utilization and value addition to Nigerian minerals and renewable waste.

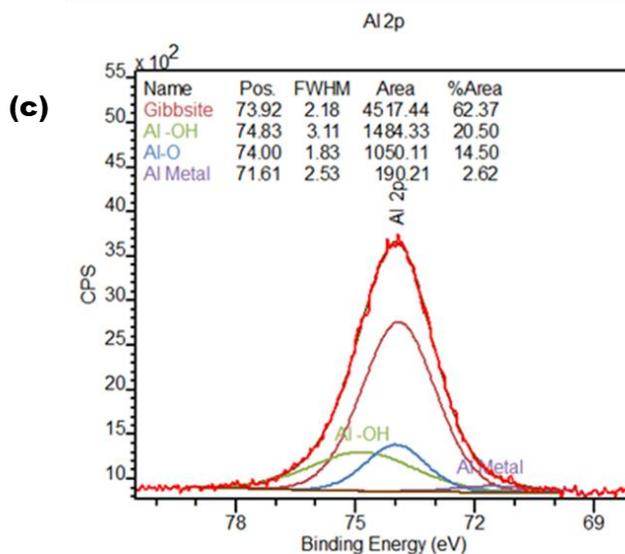
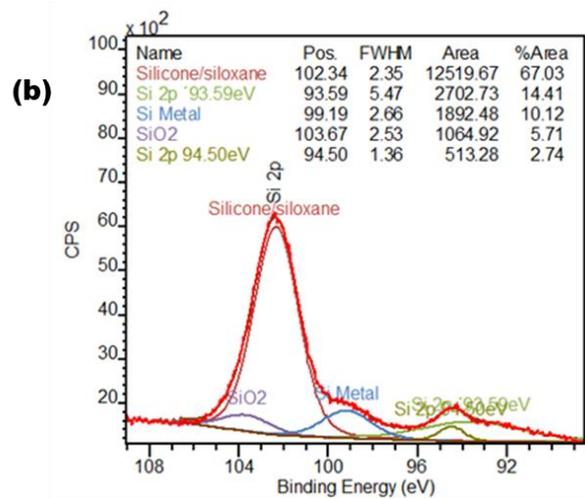
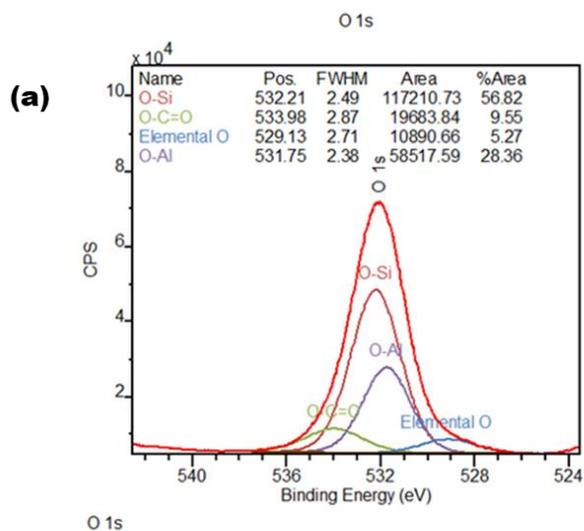
APPENDICES



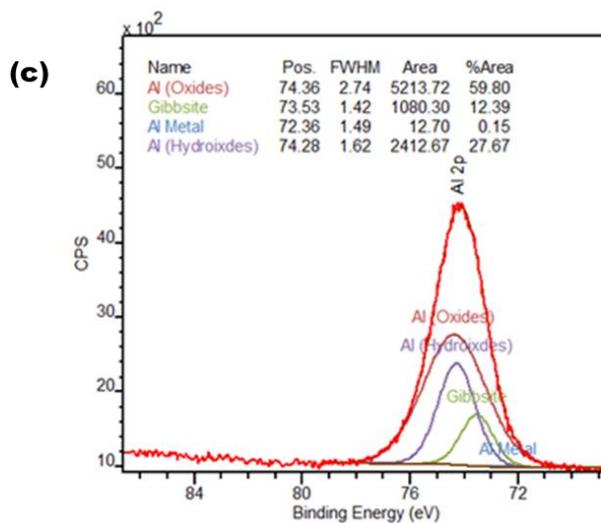
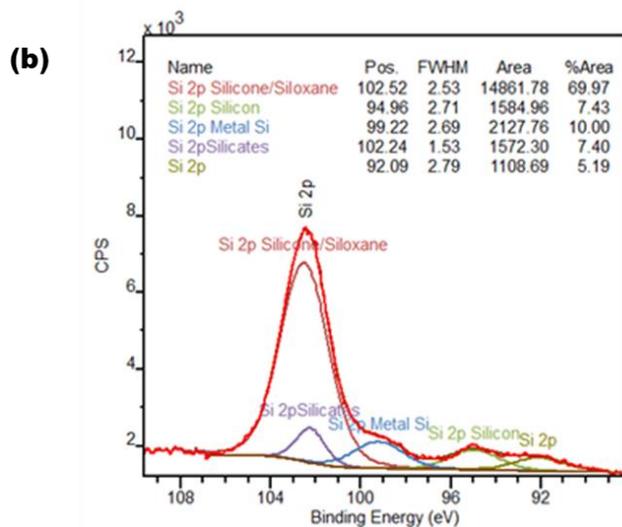
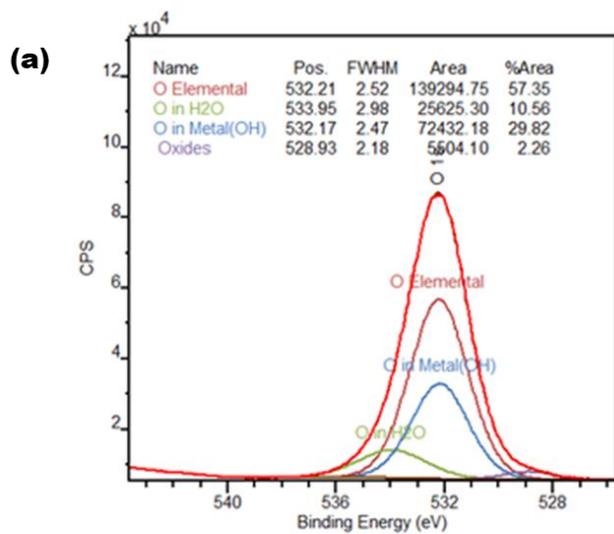
APPENDIX 1. Collection of Clay samples from Nsu, Imo State and Kutigi in Niger State



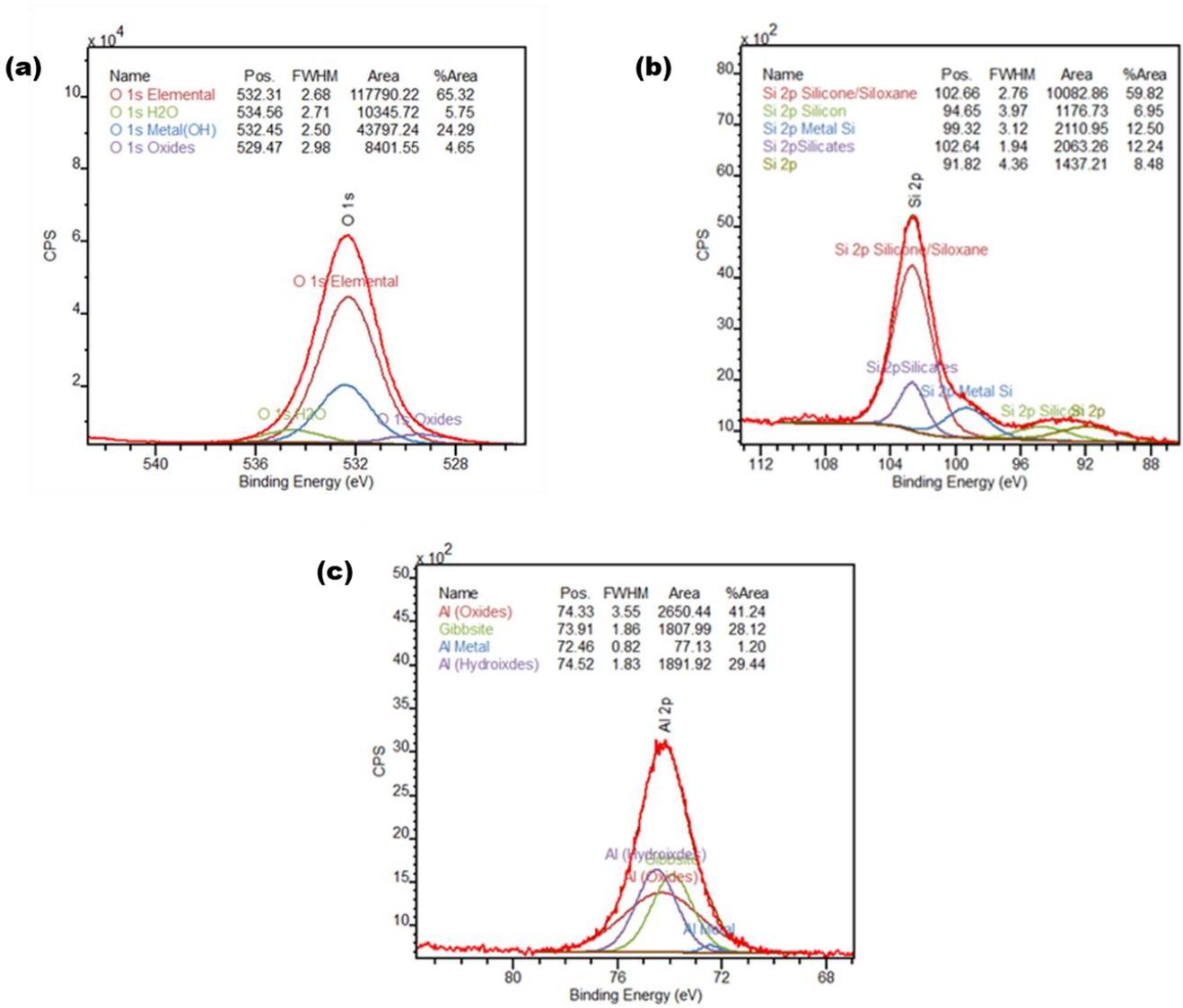
APPENDIX 2. First instance calcination of clay samples in a locally made Furnace



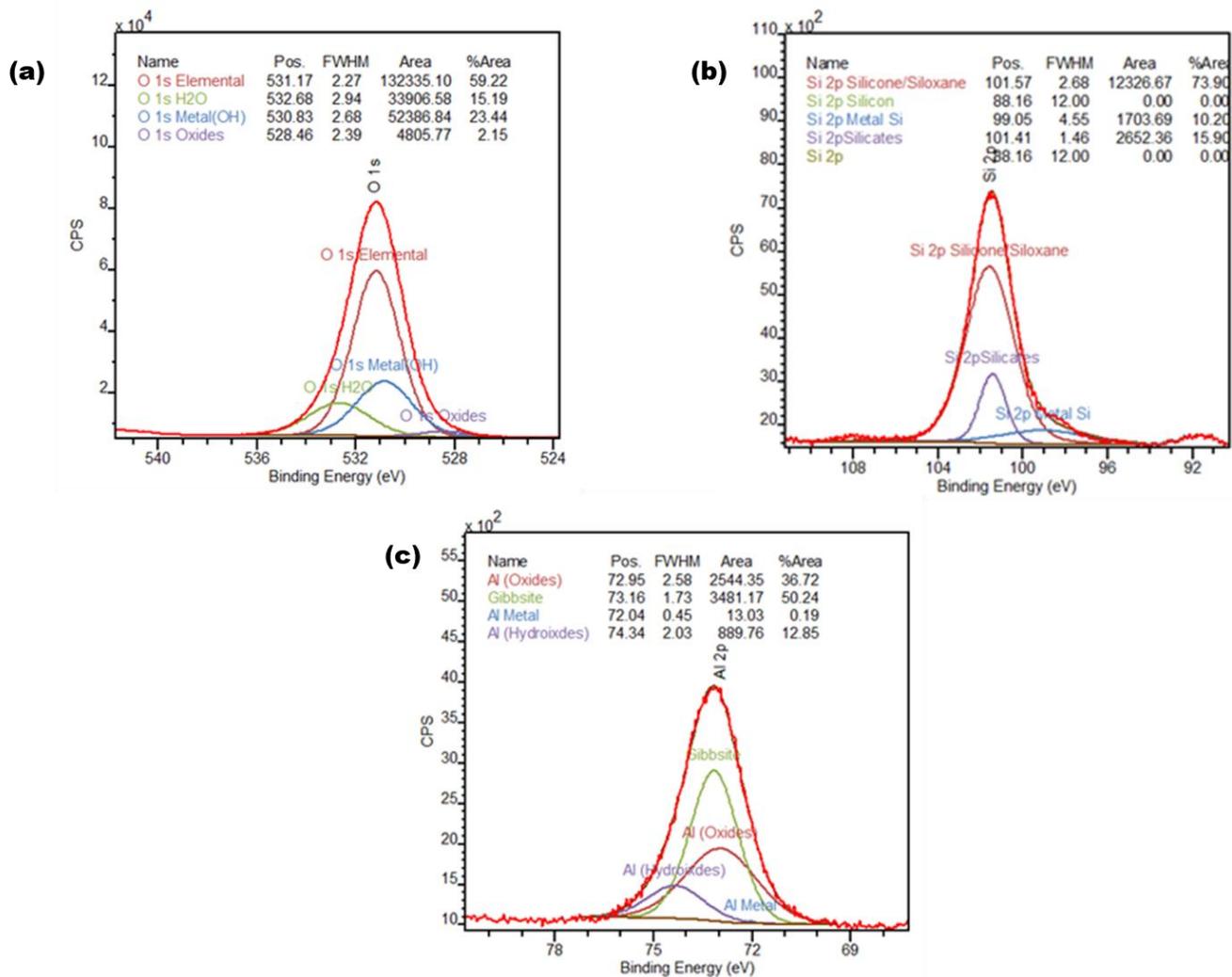
APPENDIX 3. Deconvoluted XPS components of (a) O 1s; (b) Si 2p and (c) Al 2p for Afuze clay



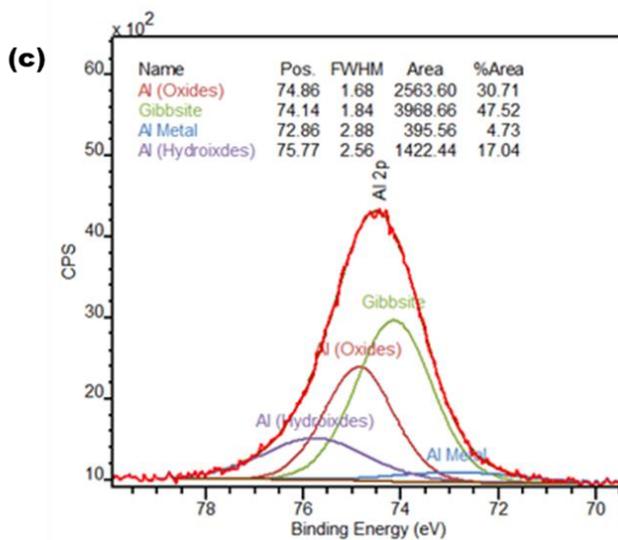
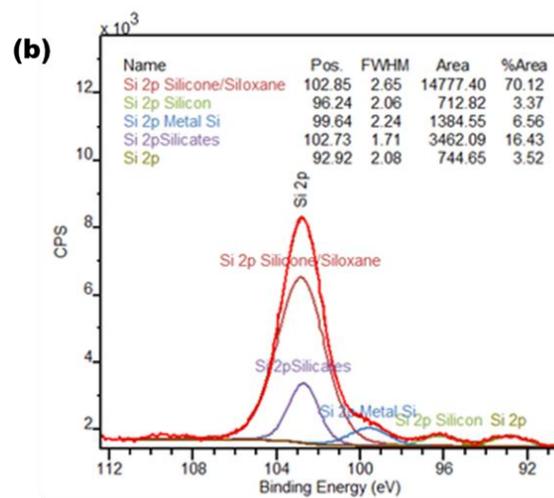
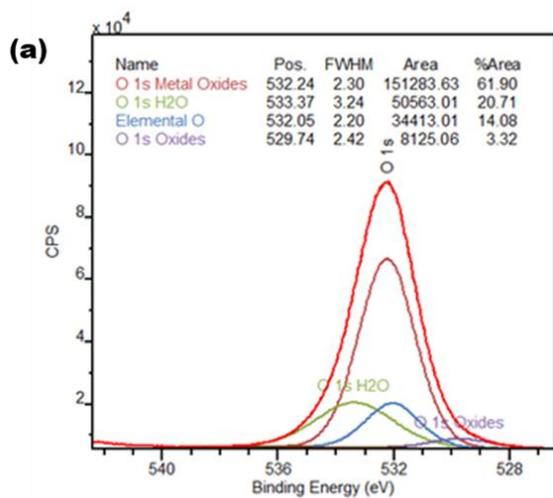
APPENDIX 4. Deconvoluted XPS components of (a) O 1s; (b) Si 2p and (c) Al 2p for Ihitte clay



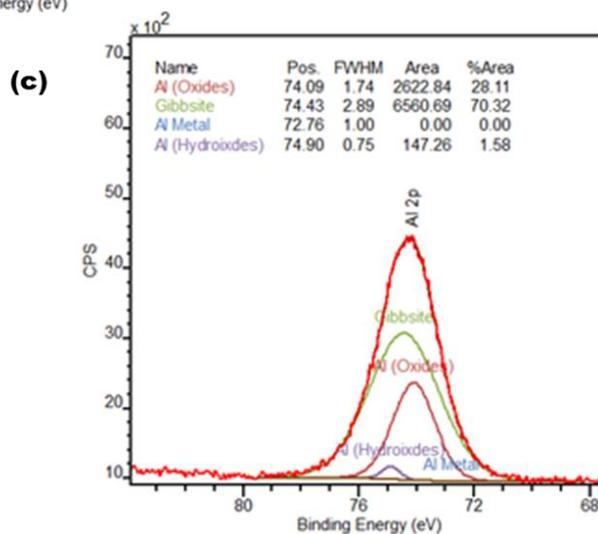
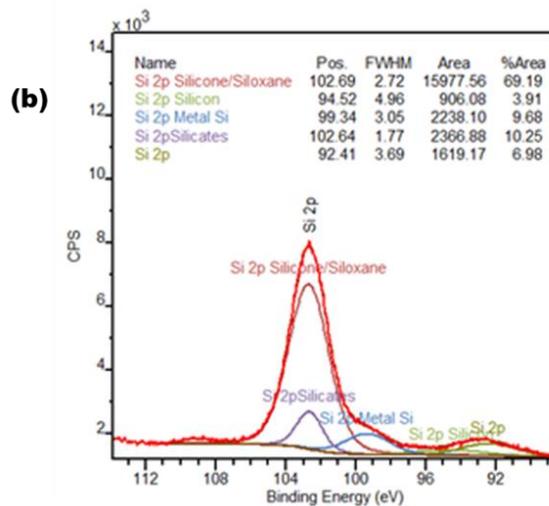
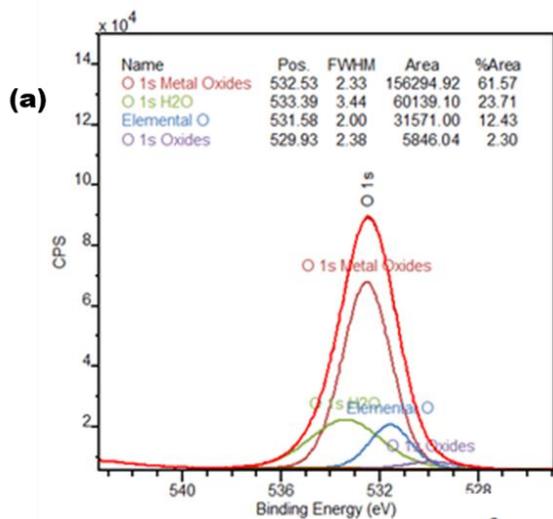
APPENDIX 5. Deconvoluted XPS components of (a) O 1s; (b) Si 2p and (c) Al 2p for Kutigi clay



APPENDIX 6. Deconvoluted XPS components of (a) O 1s; (b) Si 2p and (c) Al 2p for Minna clay



APPENDIX 7. Deconvoluted XPS components of (a) O1s; (b) Si 2p and (c) Al 2p for Nsu clay



APPENDIX 8. Deconvoluted XPS components of (a) O 1s; (b) Si 2p and (c) Al 2p for Obowo clay



APPENDIX 9. Contaminated water at Ruga settlement, FCT, Abuja being utilized by rural dwellers



APPENDIX 10. Team of research students visited Ruga settlement, FCT, Abuja water source



APPENDIX 11. The hospitable people of Bida community in Niger State, Nigeria with the research student