



FACULTY OF ENGINEERING  
Department of Chemical Engineering  
Master in Hydrocarbon Processing Engineering

**SYNTHESIS AND CHARACTERIZATION OF BIODEGRADABLE POLYMER-BASED  
ORGANOCLAYS AND ITS APPLICATION AS ADSORBENT MATERIAL FOR  
WASTEWATER TREATMENT**

A Dissertation Submitted to the Faculty of Engineering in Partial Fulfillment of the  
Requirements for the Degree of Master of Science in Hydrocarbon Processing Engineering

**Student: Theophile Mushimiyimana Mujuri**

Maputo

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**Supervisor: Prof. Afonso Daniel Macheca**

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## **STATEMENT OF ORIGINALITY**

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I, **Theophile Mushimiyimana Mujuri**, hereby declare that the undersigned dissertation submitted for award of the MSc degree in Hydrocarbon Processing Engineering is my own work and has not previously submitted by me or another person for the award of any other degree of the University.

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**(Theophile Mushimiyimana Mujuri)**

## **DEDICATION**

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To my wife Marie Louise, Uwase and my Sons Cedric, Joseph and daughters Mireille, Pascaline. I highly appreciated their love, motivation and unconditional support, especially during those long periods of absence.

## ACKNOWLEDGEMENTS

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My heartfelt thanks to you all!

## PREFACE

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Water scarcity has recently become a major challenge as many fresh water sources have been exhausted due to the rapidly growing population and anthropogenic activities. Anthropogenic activities have been identified as a major threat to the environment as they release a mixture of complex pollutants into environment, being polluted water of great concern. To deal with this situation, researchers all around the world are seeking for alternative sources of fresh water.

Water reuse has emerged as one of the most promising alternatives for this situation, being wastewater treatment the “trump card” to the success. Adsorption-based technology remains the most simple, well studied and efficient method preferred by most researchers. Activated carbon is the most widely used adsorbents, but the production and regeneration costs combined with the fact that it cannot efficiently remove organic contaminants at higher concentrations have limited its application. As an alternative, organo-clays have received enormous attention recently. However, since conventional organo-clays are surfactant-based clays, their use raises concerns as most surfactants are harmful for humans, animals, and environment in the event of unprofessional handling or inadequate disposal.

The present study, therefore, aimed to develop organo-clays based on natural clays and bio-degradable polymers. The focus therefore was given to bentonite clay from Boane Deposit and dimer fatty acid polyamides. The combination of natural clays and bio-degradable polymers such will lead to the development of adsorbent materials that are environmentally friendly and effective in the removal of pollutants from wastewater compared to activated carbon and surfactant-based organo-clays.

The present work was undertaken as a pre-requirement for the completion of the master’s degree in Hydrocarbon Processing Engineering at the Faculty of Engineering of the Eduardo Mondlane University. The work was basically comprised of 6 phases namely: (i) review of the relevant literature for the study; (ii) preliminary processing and characterization of raw clay (bentonite); (iii) activation with soda ash and characterization of the clay; (iv) synthesis and characterization of organo-modified clays; (v) evaluation of the performance of the organo-modified clays in the wastewater treatment; and (vi) compilation and discussion of the results and elaboration of the dissertation.

## **Dissertation outline**

In total, the dissertation comprises five chapters and references. A background to the study, motivation, problem statement, research objectives and methodology are given in Chapter 1. Chapter 2 provides an overview on the water and wastewater related issues. The main wastewater characteristics, including its management, environmental hazards and treatment technologies are given in this chapter. The chapter also provides a review on the clays and clay minerals (with emphasis to bentonite) and their use as adsorbents in wastewater treatment. The chapter introduces the reader to the conventional way for clay surface modification via soda ash procedure and organo-modification route. An overview of the modified clay structure and the common analytical techniques that are used for the characterization of clays is also given. The chapter ends with a brief description about polymeric materials. Chapter 3 outlines the model creation methodology. The results and discussions of the investigation are presented in Chapter 4. The key findings of the study, including recommendations are given in the Chapter 5. The main references consulted for the study are listed in the item of “References”.



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## RESUMO

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No presente trabalho uma amostra de bentonite cálcica branca da região de Boane no Sul de Moçambique foi sucessivamente submetida ao processo de activação sódica e organo-modificação com vista a usar o produto resultante como material adsorvente no tratamento de águas residuais. No processo de organo-modificação, o estudo explorou uma rota de produção de argilas organo-modificadas. Em vez da rota convencional de organo-modificação baseada em surfactantes, o estudo usou a chamada “abordagem de organo-modificação sem surfactante”. Resultados experimentais confirmaram o sucesso da troca iónica de iões  $\text{Ca}^{2+}$  por  $\text{Na}^+$  uma vez que a capacidade de troca catiónica e a razão Na/Ca aumentaram, respectivamente, de 67.5 para 74 meq/100 g de argila e de 2.94 para 15.8, conforme a variação da concentração de  $\text{Na}_2\text{CO}_3$ , temperatura de activação e o do tempo de agitação, respectivamente, de 2 a 6 % w/w, 25 a 65 °C e de 2 a 4 h. Os resultados da difracção de raios-X confirmaram que o processo de organo-modificação teve lugar uma vez que o principal pico de esmectita das argilas modificadas com polímeros se deslocou para o lado esquerdo ate  $18.4\text{Å}$ . As imagens da microscopia electrónica de varredura das argilas modificadas com polímero apresentaram camadas compactas nas suas estruturas, sugerindo que os grupos funcionais localizados nas extremidades da cadeia do polímero aderiram à superfície da argila. O processo de activação sódica e organo-modificação da argila aumentou a capacidade de adsorção de fenol. A capacidade de adsorção de fenol aumentou na ordem do aumento da concentração do polímero. Nas condições actuais do estudo, a quantidade máxima de fenol adsorvido foi observada na amostra com a concentração de polímero de 7.5 % w/w.

**Palavras-chave:** Bentonte; activação sódica; organo-modificação; tratamento de águas residuais;

## ABSTRACT

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In this work, a white Ca-bentonite from Boane region in Southern Mozambique was successively subjected to Na<sub>2</sub>CO<sub>3</sub> activation and organo-modification process aiming to use the resulting hybrids as adsorbent materials in wastewater treatment. In the organo-modification process, the study explored a different route of organoclays production. Instead of the conventional organo-modification route based on surfactants, the study used the so-called “surfactant-free organo-modification approach”. Experimental results confirmed the successful ion exchange of Ca<sup>2+</sup> ions with Na<sup>+</sup> ions since the cation exchange capacity (CEC) and Na/Ca ratio increased, respectively, from 67.5 up to 74 meq/100 g clay and from 2.94 up to 15.8, as the concentration of Na<sub>2</sub>CO<sub>3</sub>, activation temperature and stirring time varied, respectively, from 2 to 6 wt.%, 25 to 65 °C and from 2 to 4 h. X-ray diffraction (XRD) confirmed that the organo-modification process using the “surfactant free approach” has taken place since the main smectite peak of the polymer modified clays shifted to the left side up to 18.4A°. Scanning Electronic Microscopy (SEM) images of the polymer modified clays presented compact layers in their structures, suggesting that the protonated amine functional groups at the ends of the polymer chains have attached the surface of the clay. The sodium activation and organo-modification processes increased the phenol adsorption capacity of the clay. Phenol adsorption capacity increased in the order of increasing polymer concentration. Under the current study conditions, the maximum adsorbed phenol was observed at the maximum polymer concentration, 7.5 wt.% polymer.

**Keywords:** Bentonite clay; sodium activation; organo-modification; wastewater treatment;

## LIST OF ABBREVIATIONS

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CEC: cation exchange capacity

COD: chemical oxygen demand

STSS: total suspended solids

TN: total nitrogen

TP: total Phosphorus

SDGs: sustainable development goals

MMT: montmorillonite

USA: united States of America

XRF: X-ray Fluorescence

TGA: Thermogravimetric analysis

FTIR: Fourier Transformer Infrared

SEM: Scanning electron microscopy

TEM: transmission electron microscopy

ASTM: American Standard Testing Method

FESEM: Field emission scanning electron microscope

ICSD: inorganic crystal structure database

EDX: Energy-Dispersive X-ray Spectroscopy

EDS: Energy-Dispersive Spectroscopy

UV-vis: Ultraviolet Visible Rays

NBDSS: natural bentonite dry sieved sample

SC: sodium carbonate

PA: polyamide

NBWSS: natural wet sieved bentonite sample

pH: hydrogen Potential

HPLC: High Performance Liquid Chromatography





## CHAPTER 1

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### 1. GENERAL INTRODUCTION

#### 1.1. Background

The global supply of drinking water has recently become a major challenge as many fresh water sources have been exhausted due to the rapidly growing population, intensification of agricultural and industrial activities, urbanization, and climatic factors (Benedini & Tsakiris, 2013). The other side of the problem is the deterioration of water quality due to the effects of pollution caused by anthropogenic activities (Kumar Reddy & Lee, 2012). Although approximately 70% of the Earth's surface is covered with water, only a small fraction (2.5%) is freshwater compatible with terrestrial life (Momina et al., 2018; Sotelo et al., 2019).

To deal with this situation, many communities all around the world are working to increase water conservation and seeking alternative sources of fresh water. Among several alternatives, water reuse has emerged as one of the most promising options that could partially substitute fresh water and will help some communities significantly expand their water supplies and needs (NRC, 2012). Water reuse generally refers to the process of using treated wastewater, the so-called "reclaimed water" for beneficial purposes such as agricultural and landscape irrigation, industrial processes, non-potable urban applications (such as toilet flushing, street washing, and fire protection), groundwater recharge, recreation, and direct or undirected water supply (Sun et al., 2011).

An effective availability of water for reuse purposes will require a combination of wastewater treatment technologies and processes that can effectively generate water of a quality, so the treated water has a wide range of potential applications. Several wastewater treatment plants are already installed and in operation across the world, using a wide range of conventional wastewater treatment processes, which includes physical, biological, chemical, and electrochemical (Anderson, 2003; Dolnicar & Hurlimann, 2009; Alqadami et al., 2018). However, since most wastewater treatment plants receive streams from domestic, agricultural, and industrial sources loaded with a wide range of high concentration mixed pollutants, some of these treatment processes have been shown to be ineffective to treat complex and complicated

polluted wastewaters or they are too expensive (Andreozzi et al., 1999; Safoniuk, 2004), making the wastewater treatment process a huge challenge for the entire world.

Among several processes for wastewater remediation, adsorption-based remains the simplest and widely used process with a great potential for treating wastewater and aqueous solutions more effectively and efficiently than other methods. The low operational cost, effectiveness in removing a wide range of pollutants, ease of handling, low energy demand, minimal sludge generation and the possibility of regeneration of the waste material are pointed out as the main factors behind the preference of the technology (Yin et al., 2016; Capra et al., 2018).

Clay minerals stand out among several adsorbents used for wastewater remediation. Clay minerals, in natural and modified forms, such as montmorillonite, diatomite, dolomite, kaolinite, layered double hydroxide, sepiolite, halloysite, vermiculite and zeolite have been found to be good adsorbents for various pollutants in wastewater (Jayabalakrishnan & Raja, 2007; Hascakir & Dölgen, 2008; Tabana et al., 2020; Cavallaro et al., 2019; El Bastamy et al., 2021, Booker et al., 1996; Srimurali et al., 1998; Abollino et al., 2003). However, for the treatment of wastewater containing some organic contaminants such dyes from textile industry streams or surfactants from domestic sewage resulting from sanitation products, due to the relatively low adsorptive capacity, natural clay minerals have limitations (Favre & Lagaly, 1991). To overcome this situation, surfactant-based organo-clays have received enormous attention recently. Surfactant-based organo-clays have proven to be efficient adsorbent for wastewater treatment (Macheca & Uwiragiye, 2020; Beall, 2003; Alther, 2002; Nafees et al., 2013; Guégan et al., 2015; Anirudhan et al., 20129). However, the use of surfactant-based organo-clays raises concerns regarding their negative impacts on human health, aquatic species, and the environment. As an alternative to surfactant-based organo-clays the study aimed to develop organo-clays based on natural clays and bio-degradable polymers for wastewater treatment purpose.

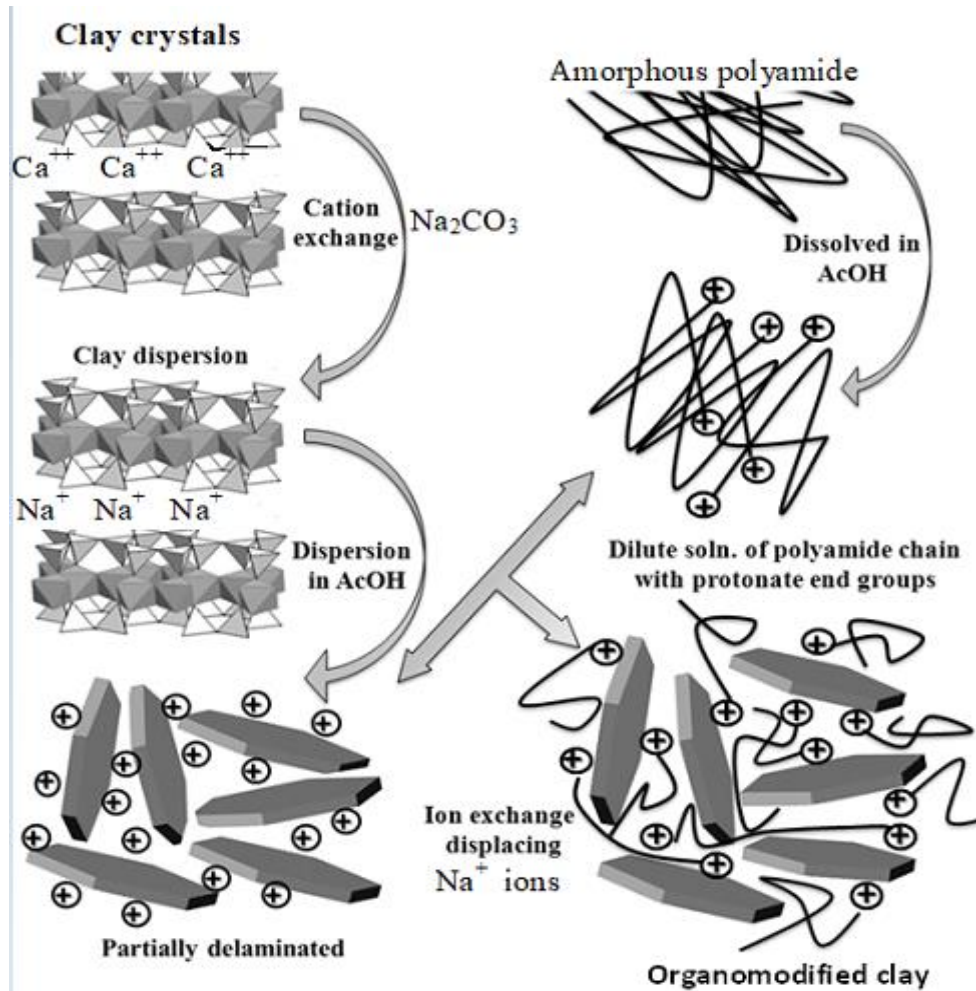
## **1.2. Problem statement and proposed solution**

Water scarcity has become a global problem due to the rapidly growing population, intensification of agriculture, industrialisation, urbanisation, and climate change. Industrial or domestic wastewater contains numerous and complex pollutants including heavy metals, radioactive materials, halogenated compounds, persistent organic pollutants, bio-accumulative and toxic chemicals such as pesticides as well as pathogenic microorganisms, which are dangerous to humans, animals, plants, and the environment.

The deficiency of fresh water and increasing demand for clean water have attracted the attention of researchers globally to find cost-effective and sustainable management solutions. Among several solutions, wastewater treatment and its re-use has emerged as one of the most promising options that could partially reduce the pressure on the fresh water sources and will help communities significantly expand their water supplies and needs. However, water reuse will only be an effective solution if appropriate and sustainable technologies are available. Several wastewater treatment plants are already installed and in operation across the world, using a wide range of technologies but, since most plants receive streams from different sources of activities, loaded with numerous and complex pollutants, most of technologies have been shown to be ineffective in terms of performance and operating costs.

Adsorption remains the most preferred technologies for wastewater treatment industry due to its low operational cost, simplicity, effectiveness in removing a wide range of pollutants, ease of handling, low energy demand and minimal sludge generation. Activated carbon is the most widely used adsorbents, but the production and regeneration costs combined with the fact that it cannot efficiently remove organic contaminants at higher concentrations, i.e., above 3 ppm have limited its application. As an alternative, organo-clays have received enormous attention recently. However, since conventional organo-clays are surfactant-based clays, their use raises concerns as most surfactants are harmful for humans and aquatic organisms and aggressive to the environment in the event of unprofessional handling or inadequate disposal. It is therefore necessary to develop high quality and sustainable adsorbents that can remediate wastewater systems with less or non-negative impacts to humans, animals and without generating other pollution sources. This was the main objective of the present study.

Instead of conventional organoclays, the proposed study focuses on investigating the potential of using dimer fatty acid polyamide-based organoclays for wastewater treatment process. The new polymer-based organoclays will be synthesized using the so-called “surfactant-free organo-modification approach” ( Machecha et al., 2014). In essence, the method will use polyamides with protonated amine end groups as clay surface modifiers of the clay previously dispersed in the liquid medium. Surfactant-free organo-modification method is the intercalation of polymer chains in the clay galleries via solution-dispersion technique, similar to the ion exchange reaction principle. The underlying principle for the success of the above-mentioned method is based on the following ideas: in some polyamides, the polymer chains themselves can provide the required organo-modification when amine functional groups are present e.g., at the chain ends. Dimer fatty acid-based polyamides (chosen for the present study) are of this type of polyamides. Dimer fatty acid-based polyamides are amorphous polymers and are a special class of biopolymers derived from plant oils. They are soluble in lower carboxylic acids. When dissolved in these acidic solvents, the amine functional groups at the ends of some chains become protonated. It should be possible for these cationic molecules to ion exchange with the intercalated cations present in the clay galleries. This means that surface modification of the clay should be possible via solution intercalation of the polymer chains *per se* provided that suitable exchangeable ions are present in the clay. Figure 1 provides a schematic outline of the conceptual approach that was followed in the present investigation.



**Figure 1:** “Schematic representation of the route to clay organo-modification via solution intercalation of the polymer chains Adapted from Machecha et al., (2014)”.

More details about the preparation route are given in section 3.2.3. The clay modification route outlined above will be applied to bentonite from Boane Deposit, Mozambique.

### **1.3. Motivation**

The use of appropriate technologies for effective wastewater treatment can significantly improve the performance of many wastewater treatment processes and may eliminate or minimize problems of possible harm associated with pollutants, thus increasing the availability of this precious liquid to the communities while reducing the pressure on the fresh water sources. Among several technologies for wastewater remediation, adsorption-based technology remains the simplest and widely used technology with a great potential for treating wastewater and aqueous solutions more effectively and efficiently than other methods (Gonzalezspi-Sup et al., 2009). The low operational cost, simplicity, effectiveness in removing a wide range of pollutants, ease of handling, low energy demand, minimal sludge generation and the possibility of regeneration of the waste material are pointed out as the main factors behind the preference of the technology (Yin et al., 2016; Rathnayake, 2017; Capra et al., 2018).

Clay minerals stand out among several adsorbents used for this purpose. The high cation exchange capacity (CEC) and swelling ability, their technical viability which, associated with their abundance and low cost, make clay mineral-based adsorbents very desirable in many industrial and scientific applications. The use of clay-based adsorbents in adsorption and filtration system gives some advantageous related to economic and easiness. However, for some organic and toxic pollutant, the use of natural clay minerals is not efficient due to low adsorption capacity. By nature, clays are hydrophilic because of the presence of inorganic cations located in the interlayer spaces. By this reason, clay will not adsorb organic and relatively hydrophobic compounds (Favre & Lagaly, 1991). The removal capability of natural clay minerals towards organic and inorganic contaminants can be improved by exchanging naturally occurring interlayer cations with other organic cations, getting what is called organo-clays (Cao et al., 2017). This was the primary objective of the present research. The main advantages of using organo-modified clays as an adsorbent in residual water treatment processes is the fact that it can remove a wide range of contaminants, such as microorganisms, heavy metals, organic and inorganic pollutants and sometimes some radioactive materials. Instead of conventional organo-clays, the proposed study focuses on investigating the potential of using biodegradable polymer-based organo-clays as adsorbents for wastewater treatment, as an alternative to the harmful surfactant-based ones and activated carbon. The combination of natural occurring clays and bio-

degradable polymers will certainly lead to the development of adsorbent materials that are environmentally friendly and effective in the removal of pollutants from wastewater.

#### **1.4. Research Objectives**

The main objective of the study is to evaluate the potential of using biodegradable polymer-based organo-clays as adsorbents for wastewater treatment using phenol as water contaminant. The targeted clay is bentonite from Boane Deposit and the organo-modifier polymer is a dimer fatty acid polyamide. In particular, it is intended to:

- Characterize (using appropriate analytical techniques) the clay for the proposed purposes;
- Activate bentonite using sodium carbonate, in order to increase the cation exchange capacity;
- Formulate and characterize the biodegradable polymer-based organo-clay samples at different concentrations; and

Evaluate the performance of the formulated products by assessing the efficiency in removing contaminants from the aqueous solutions.

#### **1.5. Methodology**

Seven main phases were defined in the present research work namely:

- Preliminary processing and characterization of clay samples;
- Sodium activation (with soda ash) of clays and their characterization;
- Synthesis and characterization of organo-modified clays;
- Wastewater treatment and clays performance evaluation;
- Analysis and discussion of the obtained results; and
- Elaboration of the dissertation.



## CHAPTER 2

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### 2. LITERATURE REVIEW

#### 2.1. Water and wastewater

Water is mainly used in everyday life activities like domestic supply, industrial supply, irrigation, animal supply, and preservation of aquatic life, recreation and leisure, breeding of aquatic species, generation of electricity, landscape harmony, navigation and transport of wastes. However, the world is facing the challenges regarding the rising in demand of clean water due to the increase in size of population which is not in line with increase of fresh water sources suppliers. Water scarcity especially affects agricultural irrigation, which represents the largest demand of fresh water worldwide, which accounts about 70% of total used water (Al-Essa, 2018).

Sources of wastewater in many areas are micro industries (like laundries, hotels, hospitals, etc.), macro industries (industrial wastewater) and household activities (domestic wastewater). Wastewater is collected through sewage systems (underground sewage pipes) to one or more centralised sewage system plants for treatment purposes. In cities and towns with old sewage systems treatment plant stations sometimes do not exist or are not well equipped so that they might not be ready for efficient treatment, resulting in less efficient sewage systems and occasional leaks (Popa et al., 2012).

##### 2.1.1. Characteristics of wastewater

Water because of its properties as solvent and its capacity to transport more particles, incorporates in itself many impurities that's affect its quality. Because of its use in domestic supply, breeding of aquatic species, industrial supply, generation of electricity, irrigation, navigation, animal supply, landscape harmony, preservation of aquatic life, dilution and transport of wastes, recreation and leisure it is very important to treat it before its reuse (Cavallini & Campos, 2013).

The chemical, physical or bacteriological characteristics vary from region to another relying on the geographical location of the field. Studies of water quality in various effluents revealed that

anthropogenic activities have an important negative impact for the quality of water in the downstreams of many rivers and this resulted by cumulative effects from upstream development but also from inadequate wastewater treatment facilities. The quality of water decay is generally characterized by important modification of chemical oxygen demand (COD), total suspended solids (TSSs), total nitrogen (TN), total Phosphorus (TP), Iron (Fe), copper (Cu), zinc (Zn), Lead (Pb) etc., which are the results of wastewater discharged in rivers (Popa et al., 2012). Water sewerage is accomplished by either off-site sewerage (separate sewage system and combined sewerage system) or on-site sewerage. The composition of wastewater is a function of its uses to which water was substituted. Domestic sewage 99.9% water and the remaining 0.1% include organic and inorganic, suspended and dissolved solids, together with microorganisms ( Macheca & Uwiragiye, 2020).

### **2.1.2. Wastewater management**

Since the beginning of the 21<sup>st</sup> century the world faces a water quality crisis resulting from continuous population growth, urbanisation, land use change, industrialisation, food production practices, increased living standards and poor water use practices with poor management strategies (National & Press, 2012). Wastewater management has direct impact on the biological diversity aquatic life and acts as support in sustainable development goals (SDGs) with the aim of improving sanitation and marine environment through pollution reduction.

### **2.1.3. Wastewater and the Environment**

Some wastewaters, especially industrial or domestic wastewaters, contain numerous and complex pollutants including dyes, phenols, polychlorinated biphenyls, methyl-tert-butyl ether, plasticizers, heavy metals, pharmaceutical and personal care products, naturally occurring radioactive material, halogenated compounds, persistent organic pollutants, bio-accumulative and toxic chemicals such as pesticides as well as pathogenic micro-organisms (Montemurro et al., 2019; Barceló, 2005, Wang et al., 2008; Huang et al., 2012) , which are dangerous to humans, animals, plants, and the environment. These pollutants can be toxic to humans and aquatic life, radioactive, or corrosive. They can damage ecosystem health by depleting oxygen or causing algal blooms, or they can interact with disinfectants at drinking water plants to form cancer-

causing chemicals (Hammer & Levine, 2012). Thus, an important element of preventing and controlling water pollution by effective management is the existence of reliable and adequate information of concentrations of pollutants in wastewater. The wastewater treatment is so important for protecting the environment ( Machecha & Uwiragiye, 2020).

#### **2.1.4. Wastewater treatment technologies**

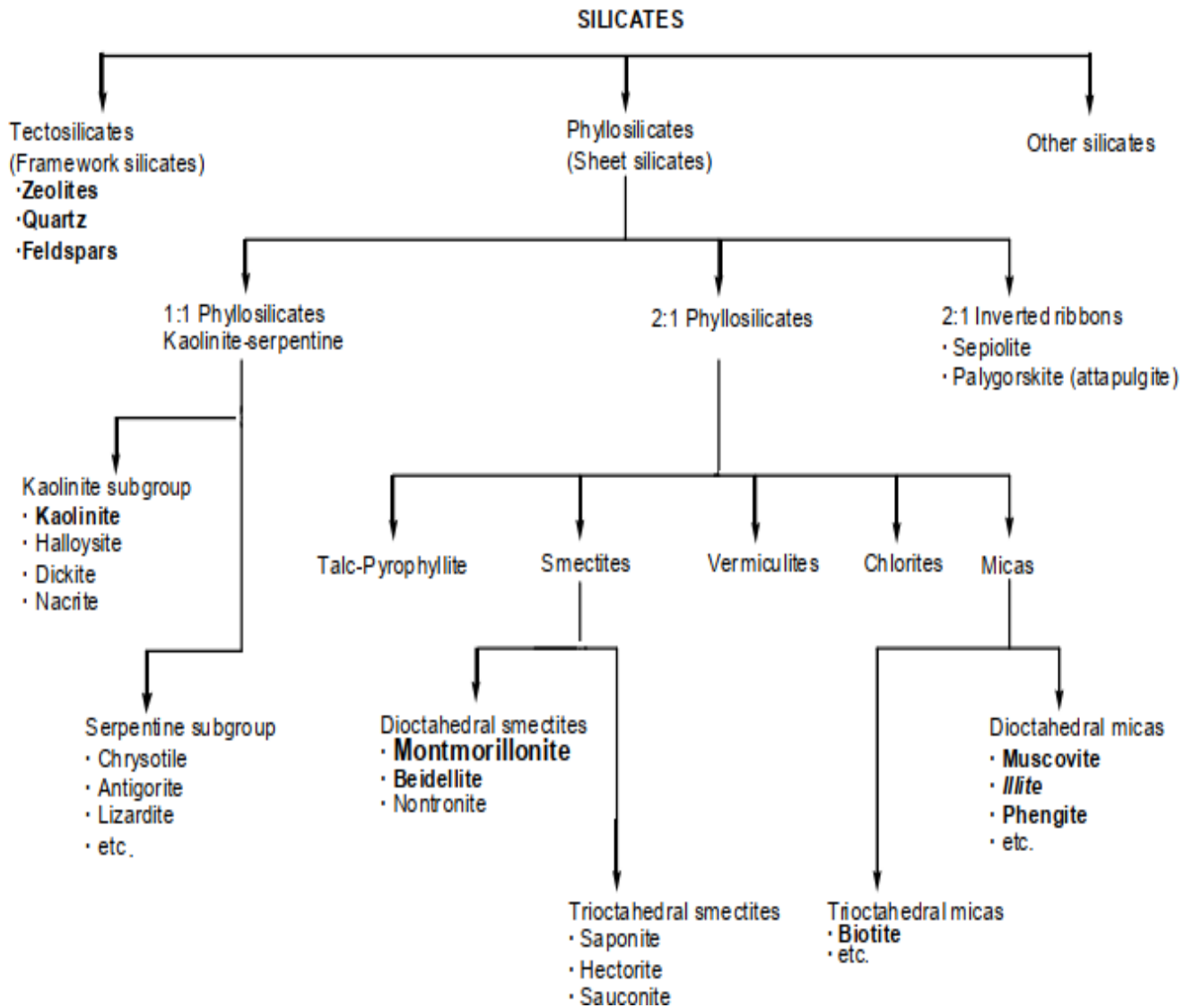
Treatment is the most complex management option. It can be utilized to prepare wastewater for disposal or distinct qualities of finished water or residuals for beneficial reuse and/or be used to generate clean water (Kılıç, 2021). Water treatment technologies can be classified into three main general methods: Physical Methods, Chemical Methods, and Energy Intensive Methods. Physical methods of wastewater treatment represent a body of technologies that is referred largely to as solid-liquid separations techniques, of which filtration plays a dominant role (Environment, 2019).

There are several techniques in wastewater treatment that are specifically used to remove heavy metal ions and other organic pollutants e.g., chemical precipitations, conventional coagulations, reverse osmosis, ion exchange, electro dialysis, electrolysis (Sharma & Bhattacharya, 2016). Most of above techniques are complicated, time consuming and expensive, which prevents their use in developing countries. However, adsorption is the most preferred; is less expensive and more effective, simple in design and environmentally safer technique that removes both organic and inorganic pollutants. Clay minerals stand out among several adsorbents used for wastewater remediation. The use of clay-based adsorbents in adsorption and filtration system gives some advantageous related to economic and easiness.

#### **2.2. Clay and clay minerals**

The term “clay” refers to occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden if dried or fired. Is a naturally occurring mineral aggregate consisting of various minerals (clay minerals) content and degree of purity and are formed on site of parent rocks (Guggenheim, 2016). The formation of clay is a chemical process that is assisted by mechanical breakdown that separates coarse grains into fine

particles. The crystallography of clay show that they have two fundamental units of mineral i.e. tetrahedral unit that belongs to four oxygen enclosing silicon and octahedral that belongs to six oxygen or hydroxyl at corners around metallic ions (Firoozi et al., 2017). Despite their varied chemical composition, clays can be classified in just a few major groups: smectites, vermiculites, micas, kaolin, talcum, chlorites, fibrous and interstratified (López-Galindo et al., 2007). A detailed classification is given in the Figure 2.



**Figure 2:** “Clays classification adopted from Wilson, (1999)”.

Clay mineral in turn is a mineralogical term referring to the part of a family (the phyllosilicates) consisting of hydrated aluminosilicates containing considerable amounts of Mg, Ca, Na, K, and Fe and, occasionally, fewer other metals such as Ti, Mn, or Li (Guggenheim, 2016). They have been part of human existence since antiquity (Murray, 2002) and were used as natural nano-materials along history for industrial and commercial uses. The first recorded applications were more than 5000 years ago, in Cyprus and Greece, for bleaching clothes, and removal of grease and stains from it (Orléans et al., 2000; Beneke & Lagaly, 2002). The high cation exchange capacity (CEC) and swelling ability, their technical viability which, associated with their abundance and low cost, their colloidal size and crystalline structure, their chemical reactivity, their higher adsorption capacity under specific conditions and resistance to environmental make clay minerals very desirable in many industrial and scientific applications.

Clay minerals are crystalline sheet like structure composed by alumina-silicates and metallic ions (Guggenheim, 2016).

A model presentation of a typical clay mineral structure is shown in Figure 3.

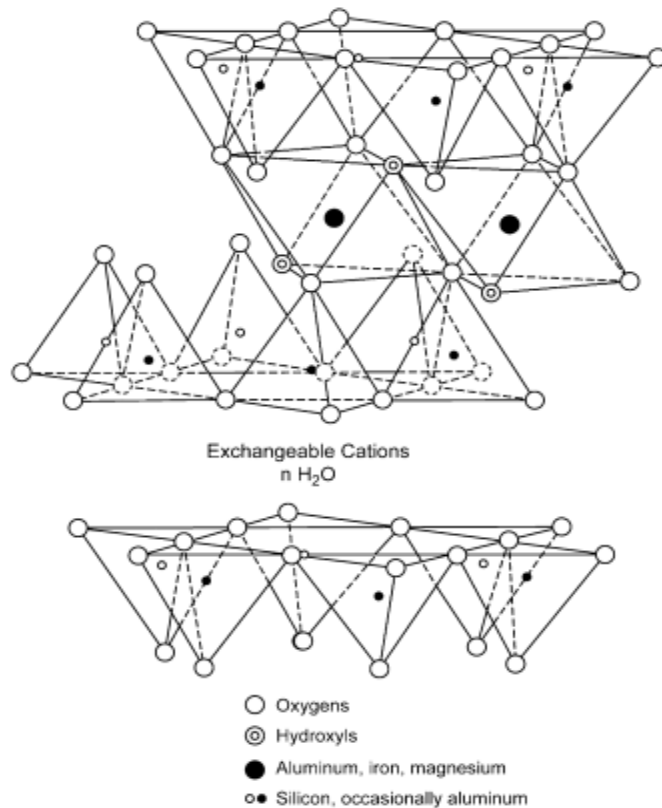


Figure 3: “Diagrammatic sketch of the structure of smectites Adapted from Wilson, (2007)”.

As previously stated, clay minerals stand out among several adsorbents used for wastewater remediation. However, “bentonitic clays” (the clay of choice in the present study) are the most popular among industries and academia.

### **2.2.1. Bentonite**

Bentonite is a rock term used to designate a naturally occurring, very fine-grained material largely composed of the clay mineral, montmorillonite (MMT) (Grim, 1978). Accordingly, a description and discussion of MMT is applicable to bentonite as well. Bentonite, in addition to MMT, contains a small portion of other mineral matter, usually quartz, feldspar, volcanic glass, organic matter, gypsum, or pyrite. MMT is clay mineral from smectite group, a group name for platy phyllosilicates of 2:1 layer with layer charge between 0.2 and 0.6 per formula unit (pfu). Chemically, MMT is described as a hydrous aluminum silicate containing small amounts of alkali and alkaline-earth metals. Structurally, MMT is made of two basic building blocks, the aluminum octahedral sheet and the silica tetrahedral sheet . According to Programme (2005), bentonite feels greasy and soap-like to the touch. Freshly exposed bentonite is white to pale green or blue and, with exposure, darkens in time to yellow, red, or brown. The unique ability of bentonite to absorb more water and swell many times its dry volume and its low water permeability property, makes it an ideal appreciated candidate for many industrial and engineering applications (Magzoub et al., 2020). An interesting and particular characteristic of the MMT clay minerals is the isomorphic substitution of  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  in the crystalline structure with low valence cations. Exchangeable cations located mainly on interlamellar surfaces such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$  and  $\text{Li}^+$ , electrostatically fixed, have the function of compensating negative charges generated by such isomorphic substitution that occur in the reticulate.

Depending on the dominant exchangeable cations present, MMT can be calcium or sodium, exhibiting extremely different uses and properties. Thus, if the predominant exchangeable cations are sodium, MMT is said to be sodium and if the predominant exchangeable cations are calcium, then there is calcium MMT (Inglethorpe et al, 1993). The differences in charge in the layers, their origin and the interlayer cations alter the physic-chemical and technological properties of the clay. The terms non-swelling and swelling bentonite are synonymous with calcium and sodium bentonites, respectively. Sodium bentonites, however, are the most sought-

after materials by industrialists. Due to their high cation exchange and swelling capacity, sodium bentonites are the most preferred for industrial applications. The adsorption capacity of clay is directly linked to these two properties.

However, natural occurrence of sodium bentonites is very rare. Except for the bentonite, mined in South Dakota, Wyoming and Montana in the USA, the vast majority of sodium bentonites available in the world are the result of the activation processes in presence of sodium salts. Many and different sodium salts can be used in the activation process. However, treatment with  $\text{Na}_2\text{CO}_3$ , commonly known as soda ash, is a well-known method that the industry has used for decades. High swelling capabilities, high cation exchange capacity and strong viscosities of a bentonite can be significantly improved by increasing the Na/Ca ratio and this in turn can be reached by adding very small amounts of  $\text{Na}_2\text{CO}_3$ , usually 2 to 4 wt.% (Lebedenko & Plée, 1988; Inglethorpe et al, 1993; Liu et al., 2004; Liu et al., 2018; Yildiz, et al., 1999; Magzoub et al., 2020; Karagüzel et al., 2010; Brandenburg & Lagaly, 1988; Taylor et al., 2007).

### **2.2.2. Swelling capacity**

Bentonite has strong colloidal properties and its volume increases several times when it comes in contact with water, creating a gelatinous and viscous fluid. Both Na and Ca ions are hydrated in this interlayer position. The MMT ability to absorb water is due, in part, to the small grain size of the individual MMT crystals (usually much less than 2  $\mu\text{m}$ ) and the fact that the individual sheets have a negative surface charge that tends to attract polar molecules. This negative charge is also responsible for another essential attribute of MMT - its ability to absorb positively charged ions from solutions, an attribute that, like adhesion, is also widely exploited commercially. Sodium MMTs generally have one layer of water in the interlayer position and calcium MMTs generally have two layers of water (Murray, 2002). The thickness of the interlayer water layer varies with the nature of the adsorbed cation and the amount of water available. If the cation is sodium, swelling can progress from 9.8 Å, when the clay is exposed to air, to a maximum of 40.0 Å, when the clay is fully dispersed in a liquid medium. In the case of calcium or polycationic clays, the amount of water adsorbed is limited and the particles continue to be joined together by electrical and mass interactions. The difference in the swelling of the sodium and calcium MMTs is due to the attraction force between the layers, which is increased by the presence of calcium,

reducing the amount of water that can be adsorbed, while the sodium cation causes a less attractive force, allowing greater amount of water to penetrate between the layers, and then be adsorbed (Silva & Ferreira, 2008).

### **2.2.3. Cation exchange capacity**

Clay minerals have ions fixed on their surface, between layer and within channels of their crystalline structure that can be exchanged to other ions present in surrounding solutions through chemical reactions, without any structural change in their crystalline lattice. This characteristic is called cation exchange capacity (CEC) and is characterized by a two-way diffusion, according to which, each equivalent of an ion adsorbed by the clay mineral causes the release of a previously fixed cation equivalent. Cation exchange capacity is of fundamental significance for the applied properties and is often cited in usage specifications and industrial applications (Murtaza et al., 2020; Calabria et al., 2013). Is a fundamental property for the realization of all processes that use interchangeable cations in the interlayer of the environment of MMTs, besides providing changes in the physico-chemical and technological properties of the clay depending on the absorbed ion. The CEC of natural clay varies from 40 to 150 meq/100g clay, but it is usually greater than 80 meq/100g when the clay is composed exclusively by MMT. The presence in the interplanar medium is also favour to cation exchange process ( Macheca & Uwiragiye, 2020).

### **2.2.4 Clay surface modification**

Surface modification of clay minerals is an important step for improving the practical applications of clay minerals. Properties such as swelling and CEC, for instance, can benefit from clay surface modification. The different approaches used to modify MMT clay minerals or other clay types were listed by Bergaya & Lagaly, (2006) and this include: (i) adsorption; (ii) ion exchange with inorganic cations and cationic complexes (example of  $\text{Na}_2\text{CO}_3$  treatment); (iii) ion exchange with organic cations; (iv) binding of inorganic and organic anions, mainly at the edges; (v) grafting of organic compounds; (vi) reaction with acids; (vii) pillaring by different types of poly (hydroxy metal) cations; (viii) interlamellar or intraparticle and interparticle polymerization; (ix) dehydroxylation and calcination; (x) delamination and reaggregation of smectitic clay minerals; and (xi) physical treatments such as lyophilisation, ultrasound, and plasma. One of the



most explored approaches recently is the ion exchange with organic cations, generating the so-called “organo-modified clays” or alternatively, “organo-clays”. Some of the more important applications of organo-clays include their use in polymer nano-composite technology; as adsorbents of organic pollutants in soil; and in wastewater treatment technology (Carrado, 2000; Paiva et al., 2008).

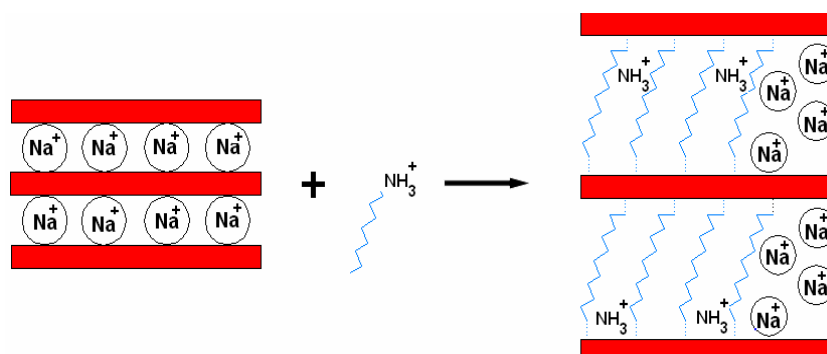
### **2.2.5. Organo-clays**

Organo-clays are hybrids derived from an ion exchange reaction of the inorganic cations located in the interlayer spaces of natural or synthetic clays with surfactants under hydrothermal conditions. In wastewater treatment technology, for instance, the orga-modification process aims to expand the clay galleries but above of all to make the clay surface compatible with organic pollutants such as dyes from textile industry streams, phenolic compounds or surfactants from domestic sewage resulting from sanitation products (Favre & Lagaly, 1991) or even hydrocarbon fractions from oil and gas industry, which cannot efficiently be removed by pristine clays, due to their hydrophilic nature. The reason for this procedure is simple; by nature, clays exhibit a hydrophilic character because of the presence of inorganic cations located in the interlayer spaces. Therefore, clay will not adsorb organic and relatively hydrophobic compounds (Favre & Lagaly, 1991). Organo-clays, therefore, will exhibit a synergistic effect with many commonly utilized water treatment unit processes. Unlike activated carbon, organo-clays can remove organics at higher concentrations, i.e., above 3 ppm (Alther, 2002). The main advantages of using organoclays as adsorbents in wastewater treatment processes is the fact that they can remove a wide range of contaminants, such as microorganisms, organic pollutants, heavy metals, and sometimes some radioactive materials.

#### **2.2.5.1. Organo-clays preparation route**

The clay surface layer is modified through an ion exchange reaction with organic onium ions such as cationic surfactants. The reaction can occur via dry or wet method. The wet method, however, involving the contact of a dilute aqueous dispersion of layered silicates with ammonium salt solutions or melts of the guest compounds seems to be the best for preparing

organo-clays (Breakwell et al, 1995; Bergaya & Lagaly, 2006). The process of such substitution is called intercalation. A typical ion-exchange reaction is illustrated schematically in Figure 4.



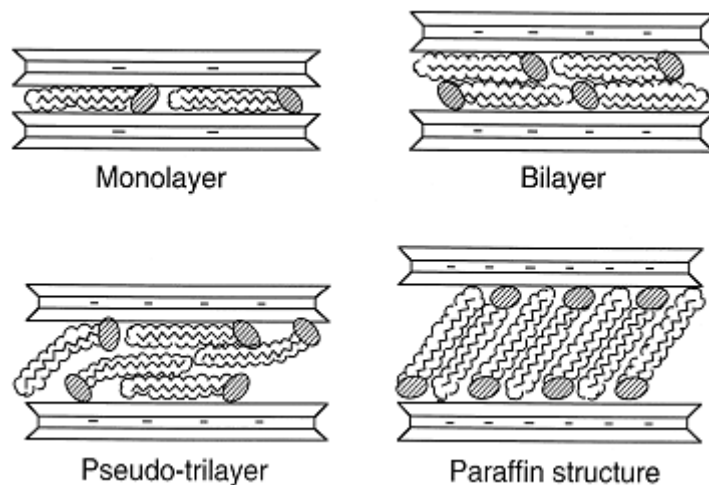
**Figure 4:** “Surface modification of clay by ion exchange reaction (intercalation), where Na cations are replaced by cations of the surfactant Adapted from Singer & Peterson, (2011)”.

The organic compounds most used in the preparation of organo-clays are the quaternary ammonium salts of long chains. Quaternary ammonium salts constitute a wide category of chemical compounds, usually having one or two groups of long-chain hydrocarbons, with 12 to 20 carbon atoms, on average, directly linked to the nitrogen atom where the polar part of the molecule is located. These salts represent the final state in the alkylation of nitrogen amines, where four organic groups are covalently linked to the nitrogen atom and the positive charge of this atom is neutralized by an anion, usually a halogen. In turn, cationic surfactants are surfactants, formed by amphiphilic molecules, whose molecular structures are characterized by presenting at least two distinct regions, one hydrophilic (polar) that has an affinity for water and another hydrophobic (non-polar) that has affinity with fatty acid molecules (Coelho, 2008). Examples of some surfactants include dodecyl sodium sulfate, cetyltrimethyl ammonium bromide, alkyl dimethyl benzyl ammonium chloride, N-alkyl-N, N-dimethyl- $\beta$ -ammonium propionate, tetramethylammonium, tetraethylammonium, and trimethylphenylammonium.

#### 2.2.5.2. Structure of organo-clays

As previously indicated, the organo-modification process aims to make the surface of the clay compatible with organic compounds as well as to expand the clay galleries. However, the success of the procedure is strongly dependent on the CEC and charge density of the clay, the degree of exchange, the concentration of the surfactant, preparation methodology, the chain length of the surfactant, etc. Depending on those factors, different arrangements of organic

molecules between the layers can be formed as shown in Figure 5. The organic ions may lie flat on the silicate surface as a monolayer or bilayer, or depending on the packing density and the chain length an inclined paraffin-type structure, with the chains radiating away from the silicate surface can be formed.



**Figure 5:** “Orientations of alkylammonium ions in the galleries of layered silicates with different layer charge densities Adapted from Lagaly, (1986).”

In the pseudotrimolecular layers, some chain ends are shifted above one another, so that the spacing is determined by the thickness of three alkyl chains (Zanetti et al, 2000;Lagaly, 1986; Brown & Brindley, 1980; Weiss, 1963; Vaia et al., 1994; Lebaron et al., 1999; Pavlidou & Papaspyrides, 2008).

### 2.2.6. Clays and organo-clays characterisation techniques

The first piece of information obtained from a raw or a synthetic clay sample is an X-ray diffraction (XRD) pattern and X-ray Fluorescence (XRF). From these two techniques a mineralogy information and chemical composition of the clay is obtained. In specific case of the organomodified samples, XRD technique allows monitoring the effective intercalation of quaternary ammonium salts between the layers of the clay, observing the increase of basal spacing  $d_{001}$ . The increase in basal spacing is often an indication that organic molecules have been incorporated within the interlayers during clay crystallization. The basal spacing of natural clays varies from values which are generally between 1.2 and 1.6 nm. The basal spacing of the organomodified samples can range between 2.0 and 4.0 nm. However, to confirm the supposition based on basal spacing, more direct evidence of organic uptake is needed.

This can be done by Thermogravimetric analysis (TGA) and Fourier Transformer Infrared. FTIR results reveal the frequency variations in strains and angular deformations of CH<sub>2</sub> and CH<sub>3</sub> groups of organic salts (surfactant) as a function of packing density, chain length and temperature. TGA are used in order to study the thermal stability or behavior of neat clay and their modified hybrids. Since weight loss between 200 and 600 °C is very low for the inorganic clay, any peaks in a derivative plot of this region are indicative of the presence of organics (Carrado, 2000; Sinha Ray & Okamoto, 2003 ; Breakwell et al, 1995). The morphology of neat and organomodified clays can be assed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Vaia et al., 1994).

## CHAPTER 3

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### 3. EXPERIMENTAL

#### 3.1. Materials

Raw Ca-bentonite sample, exhibiting a white colour was obtained from Boane region, Maputo Province, Mozambique and was kindly supplied by Minerais Industriais de Moçambique Lda Company (Mimoc). The CEC of original sample (wet sieved clay) determined by a methylene blue test (Standard Test Method for Methylene Blue Index of Clay.. Methylene blue, acetic acid (glacial) and a pure fine powder form of sodium carbonate were obtained from Tecnotraguas-Mozambique and used as received. The dimer fatty acid polyamide (Euremelt 2140) was kindly given by the University of Pretoria, South Africa.

#### 3.2. Methods

##### 3.2.1. Raw bentonite beneficiation

Dry and wet sieving are the most well-known traditional methods for the purification of clays. However, wet sieving combined with sedimentation processes is the most recommended one. According to Magzoub et al.,( 2020), in wet sieving process using a 75  $\mu\text{m}$  mesh No. 200, stable colloidal suspensions are formed when bentonite is dispersed in water (1:5 by weight) for 24 h. Sedimentation disperses the particles and allows pure clay to be easily separated. Any sand or quartz impurities will not be suspended and will rapidly settle down during this process. Wet sieving avoids the grinding of the impurities to a fine powder that can pass through during dry sieving. Using wet sieving and sedimentation higher amount and pure bentonite can be recovered compared to dry sieving. Thus, taking advantage of the benefits described above, in the present work raw bentonite samples were purified using a combined wet sieving (75  $\mu\text{m}$  mesh No. 200) and sedimentation processes.

### **3.2.2. Sodium carbonate treatment**

$\text{Na}_2\text{CO}_3$  activation process aimed to increase the CEC. The process was thermochemically carried out.  $\text{Na}_2\text{CO}_3$  was added to water before the wet sieved bentonite and the mixture was then stirred using a high-speed mixer for 10 minutes. Bentonite clay and  $\text{Na}_2\text{CO}_3$  solution were mixed in a 500 mL Erlenmeyer flask. The activation process was performed at three different times (2, 3 and 4 h) at three different temperatures (25, 45 and 65 °C) and at three different concentrations of  $\text{Na}_2\text{CO}_3$  (2, 4 and 6 wt.%  $\text{Na}_2\text{CO}_3$ ). About 2.5% of water is expected to evaporate at the end of the thermal stirring process. To compensate the lost water and maintain the same bentonite concentration in the suspension, distilled water was added to the mixture (Magzoub et al., 2020). After completing the activation process, the suspension was filtrated and washed with abundant distilled water to obtain bentonite cake relatively free from excess of  $\text{Ca}^{2+}$  ions. The sodium modified samples were then dried at 60 °C in a convection oven for 24 h. Finally, the dried bentonite samples were ground into powder with an aggregate particle size of <75  $\mu\text{m}$ . The best performing clay sample (with highest CEC), evaluated by means of CEC determinations was chosen for the organo-modification stage.

### **3.2.3. Formulation of polyamide-based organoclays**

Dimer fatty acid polyamide was used as a clay surface modifier. A typical preparation procedure for the dimer fatty acid polyamide-based organoclays was as follows as (per described in section 1.2): A weighed amount of the dimer fatty acid polyamide was first dissolved in acetic acid, corresponding to 10 wt.% of dimer fatty acid polyamide solution. In an 500-mL glass container, the clay powder (chosen in the previous step 3.2.2) were dispersed in acetic acid at a solids content of 5 wt.%. A predetermined amount of the resulting dispersion was stirred at room temperature using a high-speed mixer for 5 min. Then, 10 wt.% of dimer fatty acid polyamide solution was added drop by drop for 5 minutes while stirring the mixture. After this time, mixing was continued for another 10 min. Distilled water was added to the mixture to loosen the clay. After completing the mixing process, large amount of distilled water was added to the mixture for 2 days in order to eliminate the acetic acid. The water was replaced with fresh water on a daily basis. The organo-clay was separated from the solution by decantation. Following these steps organo-clays corresponding to targeted loads of ca. 2.5, 5.0 and 7.5 wt.% polyamide were

generated. Finally, they were dried in a convection oven at 60 °C for 24 h and then collected for further tests and analysis.

### **3.3. Samples characterization**

Elemental composition was determined using X-ray fluorescence (XRF) spectroscopy. Major elemental analysis was executed on fused beads using a (XRF) spectrometer. The samples were milled in a tungsten carbide milling pot to achieve particle sizes <75 µm and dried at 100 °C and roasted at 1000 °C to determine the loss on ignition (LOI) values. Then 1 g sample was mixed with 6 g of lithium tetraborate flux and fused at 1050 °C to make a stable fused glass bead. X-ray diffraction (XRD) analysis were conducted on a PANalytical X'Pert Pro powder diffractometer with an X'Celerator detector and variable divergence- and fixed receiving slits with Fe-filtered Co-K $\alpha$  radiation ( $\lambda=1.789\text{\AA}$ ). The mineralogy was determined by selecting the best-fitting pattern from the ICSD database to the measured diffraction pattern, using X'Pert High Score Plus software.

Thermogravimetric analysis (TGA) were performed on a Perkin Elmer Pyris 4000TGA instrument using the dynamic method. About 15 mg of the sample was placed in open 150 µL alumina pans. Temperature was scanned from 25 to 950 °C at a rate of 10 °C/min with air flowing at a rate of 50 mL/min.

A Zeiss Ultra 55 FESEM Field emission scanning electron microscope was used to study the morphology of the clay samples at 1 kV. The clay samples were coated with carbon prior to analysis.

### **3.4. Determination of cation exchange capacity (CEC) and Na/Ca ratio**

The response of the bentonite to sodium activation was determined through CEC via Methylene Blue Test (Standard Test Method for Methylene Blue Index of Clay. ANSI/ASTM C 837-76) accomplished with an Energy-Dispersive X-ray Spectroscopy (EDX) aimed to verify the Na/Ca ratio. Na/Ca ratio test was conducted using a scanning electron microscopic (SEM-EDS, Jeol Instruments).

### **3.5. Wastewater treatment (clays performance evaluation)**

The wastewater used in the present study was phenol contaminated water. The water was produced in the laboratory according to Tabana and co-workers (2020). The first set of phenol adsorption tests compared the adsorption efficiencies of the neat clay and the organo-modified ones. In these tests, 100 mL of simulated wastewater containing 40 mg/L phenol was contacted with 10 g/L of clay in a 250 mL glass beaker. The resulting suspension was stirred continuously for 24 h to allow for maximum adsorption. The resulting suspensions were then centrifuged at 4,000 rpm for 20 min. The concentrate was further polished by filtering through a 0.45  $\mu\text{m}$  millipore filter. The solids remaining from centrifuging were dried in a convection oven at 60 °C for 24 h, after which they were milled and taken for further analysis (phenol determination).

### **3.6. Phenol adsorption studies**

Phenol adsorption experiments were conducted using an UV-vis spectrophotometer analyzer 6850 JENWAY at 268 nm. Calibration curve using phenol solutions in the concentration range between 15 and 75 mg/l were used for the quantification of phenol after adsorption process.



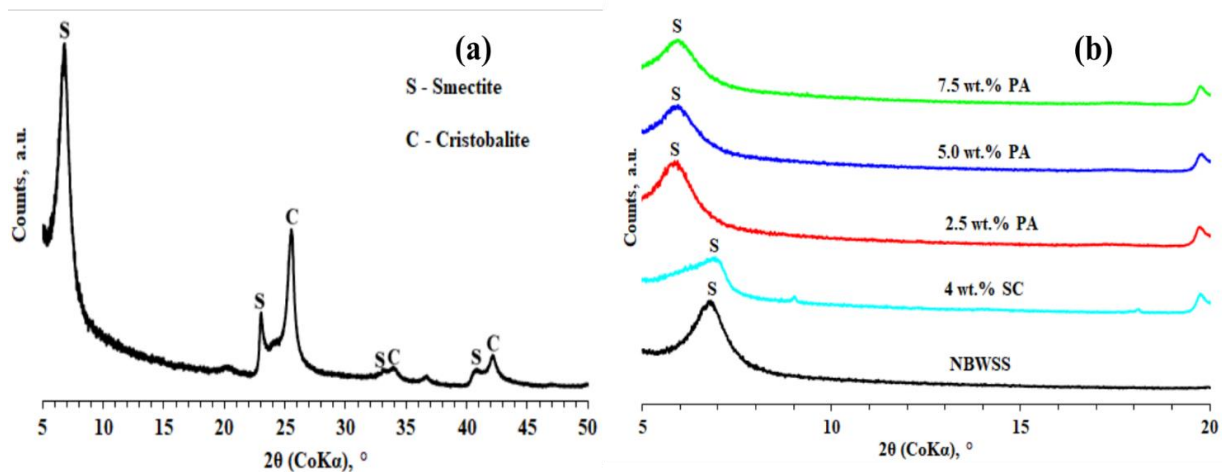
## 4. RESULTS AND DISCUSSION

### 4.1. X-ray fluorescence (XRF) chemical composition

In order to verify the consistency of the chemical composition of the clay under study, a replica of the elemental chemical analysis was carried out on the natural wet sieved sample. XRF measurements (on dry basis) indicated chemical compositions very close to those previously found by Malai et al. (2020) and these are as follow: 79.6 wt.% SiO<sub>2</sub>, 13.4 wt.% Al<sub>2</sub>O<sub>3</sub>, 2.52 wt.% Fe<sub>2</sub>O<sub>3</sub>, 0.49 wt.% CaO, 0.21 wt.% K<sub>2</sub>O, 0.64 wt.% Na<sub>2</sub>O, 2.97 wt.% MgO, 0.01 wt.% MnO, 0.17 wt.% TiO<sub>2</sub>, and 0.01 wt.% P<sub>2</sub>O<sub>5</sub>. Previous analyses established that the high silica and low contents in Al<sub>2</sub>O<sub>3</sub> and MgO, when compared to typical bentonites are features that are strictly related to the parent rocks of dominantly rhyolitic composition. The cristobalite phase present as a major impurity in the clay is the responsible for the higher content of silica (Muchangos, 2000). The differences observed in the XRF analyses evident here reflect natural variations rather than composition changes caused by the processing of the samples.

### 4.2. X-ray diffraction (XRD)

Figure 6 presents the XRD pattern of the raw wet sieved bentonite, showing only the most abundant phases namely, smectite (S) and cristobalite (C) and the most salient peaks.



**Figure 6:** XRD patterns for the natural bentonite wet sieved sample (NBWSS) (a) and sodium (SC) and polymer (PA) samples (b).

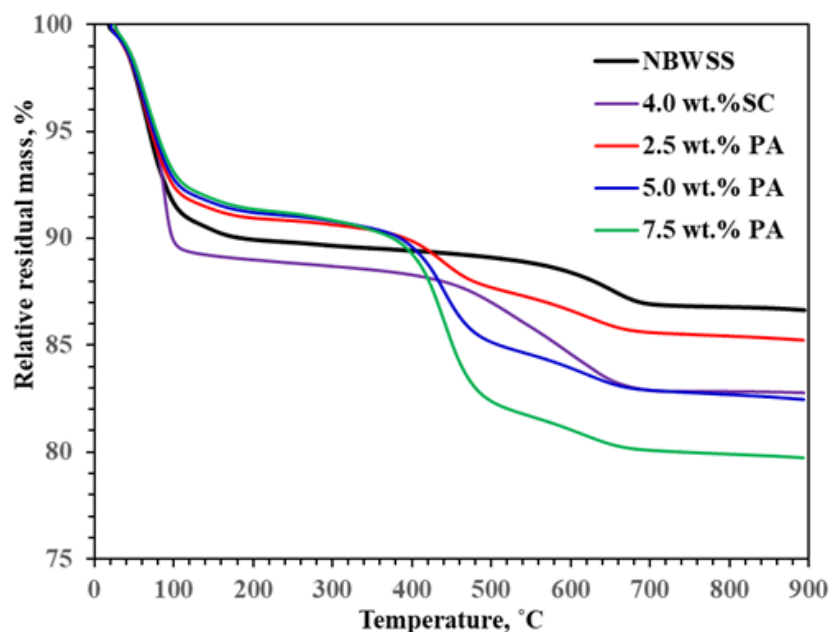
The main smectite phase reflection  $d_{001}$  was found at 15.1Å for the raw bentonite (NBWSS), a value which is in agreement with the theoretical value of the  $\text{Ca}^{2+}$  saturated smectites. This interlayer spacing suggests characterizing this smectite as the one having a mixture of monovalent/divalent exchangeable cations (Inglethorpe et al., 1993). According to these authors, the basal spacing  $d_{001}$  of smectites having a mixture of monovalent/divalent exchangeable cations is between 15.4 and 12.6Å. For the selected sodium activated sample (4.0 wt.%  $\text{Na}_2\text{CO}_3$ ) the smectite peak was found at about 14.1Å. This implies that, despite the introduction of  $\text{Na}^+$  ions, the clay remains with a mixture of monovalent/divalent exchangeable cations. The smectite peak of the polymer modified samples shifted to the left as the organo-modification is carried out, indicating that the basal distance increases with the introduction of the polymer molecules. When the polymer molecules are incorporated into the clay, its basal distance increased from 14.1Å to about 18.4Å. However, from the figure it can be concluded that the variation of the polymer concentration from 2.5 to 7.5 wt.% polymer seems to have no influence in  $d$ -spacing, suggesting that at this stage any additional quantity of polymer is simply adsorbed on the surface of the clay particles. The increase in the interlayer spacing of the organic modified bentonite sample suggests that the organic modification treatment has created a greater disorder of the clay particles when compared to the neat of natural bentonite (Macheca, 2016).

### 4.3. Thermogravimetric analysis (TGA)

The TGA curves of (NBWSS) sample, the selected sodium activated sample (4 wt.%  $\text{Na}_2\text{CO}_3$ ) and polymer modified hybrids at different polymer concentrations are shown in Figure 7. Mass loss proceeded stepwise throughout the analysed temperature range. All samples exhibited an intense loss of mass at about 120 °C, indicating the loss of adsorbed water, characteristic of smectite clays. However, for the same temperature (120 °C), the sodium-modified clay lost more mass than natural and polymer-modified clays. This was expected since sodium bentonites absorb more water than calcium ones and others.

The mass loss from 100 °C to about 450 °C in both samples is due to the releasing of the interlayer water and to the releasing of some remaining free water. However, the organo-modification process appears to have reduced amounts of these two forms of water. The occasional presence of organic materials inherent to the clay can also be released in this

temperature range. In the range between 450 °C and 750 °C there was also a loss of mass that can be associated with aluminosilicate dehydroxylation. The mass loss observed above 700 °C can be related with the destruction of the crystal lattice (formation of new crystalline phases of the clay). However, in the two temperature ranges indicated above, except for sodium modified clay (SC), the organo-modified bentonite sample showed higher mass loss when compared to natural clay (NBWSS). This behaviour could be attributed to the thermal decomposition of the dimer fatty acid polyamide used as bentonite clay organo-modifier. The most pronounced mass loss of the sodium modified clay when compared to the sample modified with 2.5 wt.% polymer (2.5 wt.% PA) may be related to the presence of other carbonated species (carbonate minerals) such as trisodium hydrogendicarbonate dihydrate ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) and calcite ( $\text{CaCO}_3$ ).

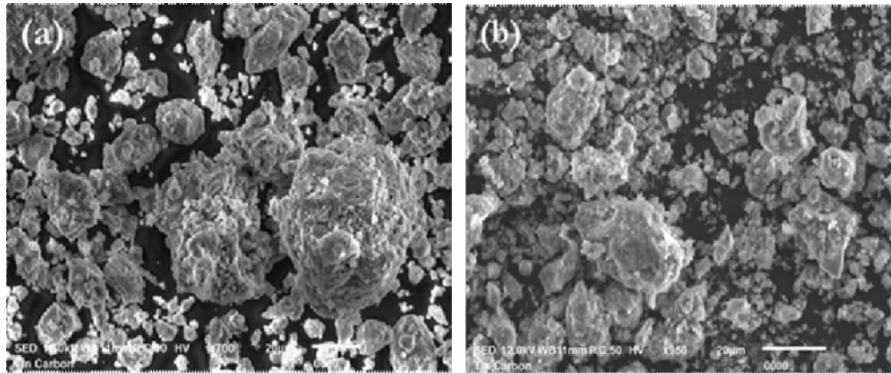


**Figure 7:** Thermogravimetric analysis curves for the NBWSS (a), 4 w.% SC (b), 2.5 wt.% PA (c), 5.0 wt.% PA (d) and 7.5 wt.% PA (e).

#### 4.4. Scanning electron microscopy (SEM)

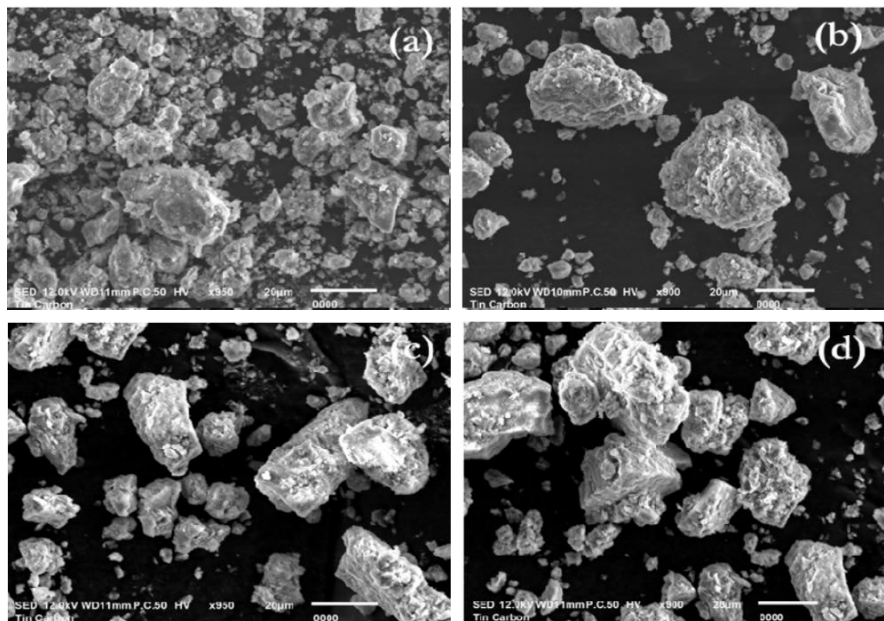
SEM micrographs of raw dry sieved (a) and wet sieved (b) bentonite samples are shown in Figure 8. The strains exhibit similar morphologies. The two samples presented some crystalline pseudo-hexagonal edges and semi rounded micro-sized particles on the surface of the clay mineral particles. However, stacks of the dry sieved sample appeared significantly larger than

those for wet sieved sample, reaching a particle size between 20 and approximately 50  $\mu\text{m}$ . In wet sieved sample the particles appeared much looser and with smaller size than those in dry sieved sample. Most of the particles were much smaller than 5  $\mu\text{m}$  in size. This was expected since wet sieving process disperses the clay particles and allows pure clay to be easily separated (Magzoub et al., 2020).



**Figure 8:** SEM micrographs of raw dry sieved (a) and wet sieved (b) bentonite samples at 20  $\mu\text{m}$ .

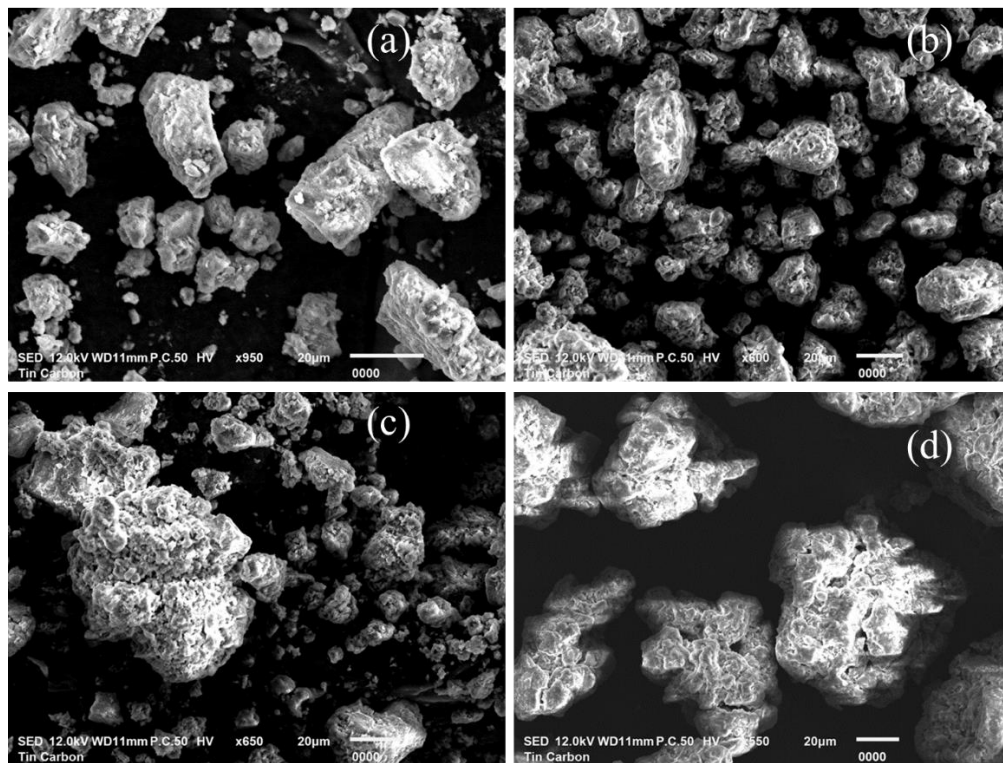
SEM micrographs of wet sieved bentonite (a) and  $\text{Na}_2\text{CO}_3$  modified samples at 2 wt.% (b), 4 wt.% (c) and 6 wt.% are shown in Figure 9.



**Figure 9:** SEM micrographs of raw wet sieved bentonite (a) and  $\text{Na}_2\text{CO}_3$  modified samples at 2 wt.% (b), 4 wt.% (c) and 6 wt.% (d) at 20  $\mu\text{m}$ .

As can be seen in the figure, in the three treated samples the clay particles appeared even much looser and softer than those in wet sieved sample. However, the particles became larger in size, a scenario that is not surprising as the treatment process of bentonite in the presence of  $\text{Na}_2\text{CO}_3$  leads to an increase in particle size due to their swelling (Magzoub et al., 2020).

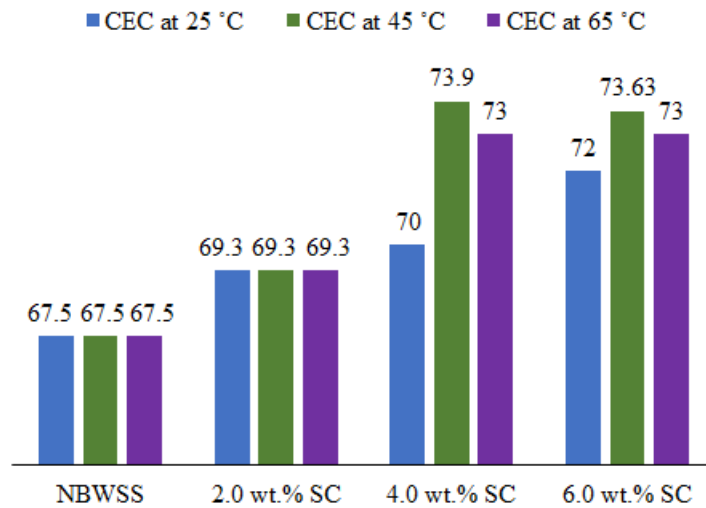
The micrographs samples of 4 wt.%  $\text{Na}_2\text{CO}_3$  bentonite and clay polymer modified samples at 2.5 wt.% PA, 5.0 wt.% PA and 7.5 wt.% PA are shown respectively in Figure 10 (a), (b), (c) and (d). From the micrographs it is clear that the aggregates of the organo-modified samples appeared significantly larger and are more wrinkled than that for the raw bentonite (wet sieved sample) and the sodium modified ones. The particle size tends to increase with increasing polymer concentration. This confirms the hydrophobic character of the clays. The hydrophobized clay particles tends to gather more easily than those of natural clay because the polymer chains compensate the negative charge and thus, eliminating the repulsive electrostatic forces between the layers (Praus et al., 2006).



**Figure 10:** SEM micrographs of 4 wt.%  $\text{Na}_2\text{CO}_3$  bentonite (a), and clay polymer modified samples at 2.5 wt.% (b), 5.0 wt.% (c) and 7.5 wt.% (d).

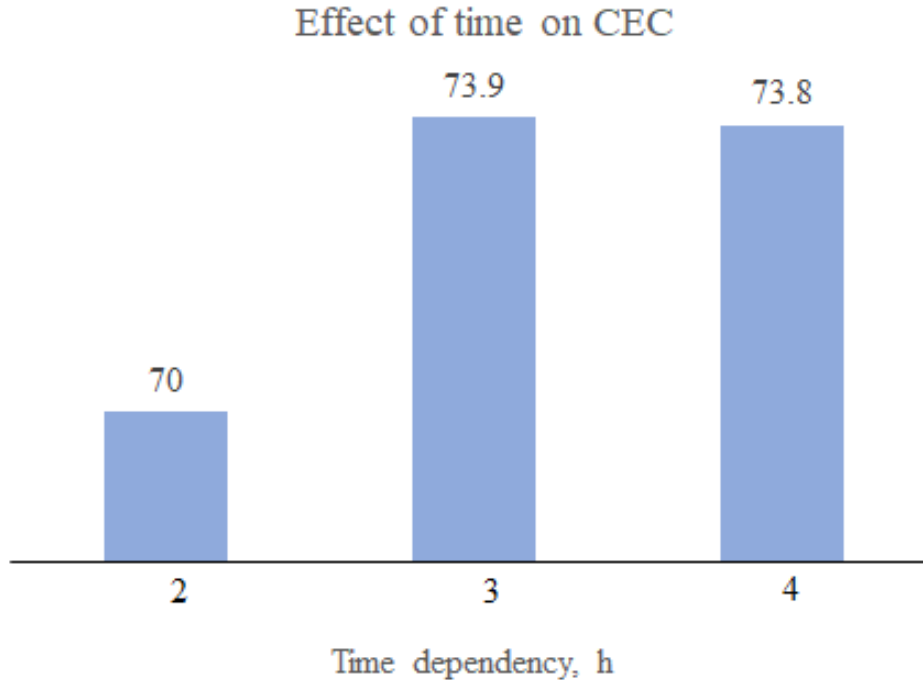
#### 4.5. Cation exchange capacity (CEC) determination

The results of the CEC determined by the Methylene Blue Test indicated a good response of the clay to the thermal treatment process in presence of  $\text{Na}_2\text{CO}_3$  as shown in the Figures 11 and 12. As can be seen from Figures 11, the wet sieved bentonite exhibited a CEC of about 67.5 meq/100 g clay. After  $\text{Na}_2\text{CO}_3$  activation process the CEC increased from 67.5 up to almost 74 meq/100 g clay as the concentration of  $\text{Na}_2\text{CO}_3$  varied from 2 to 6 wt.%, indicating that the sample Ca-Bentonite was effectively modified into Na-Bentonite.



**Figure 11:** Effect of temperature and wt.%  $\text{Na}_2\text{CO}_3$  on CEC at fixed time (3 h).

The value of 74 meq/100 g clay obtained here lies within the range presented by the so-called “relatively pure montmorillonites” (70 and 130 meq/100 g clay) (Inglethorpe et al., 1993).



**Figure 12:** Effect of time on CEC at a fixed Na<sub>2</sub>CO<sub>3</sub> content (4 wt.%) and temperature (45 °C).

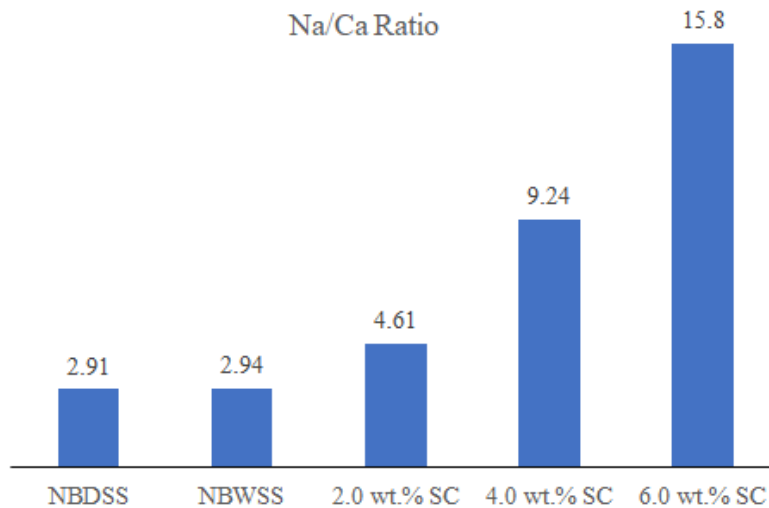
The study confirmed that the sodium activation process, in addition to being dependent on sodium concentration, is also temperature and time dependent as shown in the Figures 11 and 12. This is in agreement with Magzoub and co-workers (2019). The results show that high CEC values (about 74 meq/100 g clay) can be obtained at sodium concentrations of 4 or 6 wt.%, at temperatures of 45 or 65 and °C and with stirring time 3 or 4 hours. However, in an economic context and in matters of optimization, where the objective is to maximize the CEC saving resources such as energy so the best option would be to get higher response (74) using 4 wt.% Na<sub>2</sub>CO<sub>3</sub> at 45 °C and 3 h.

#### **4.6 swelling capacity**

The raw bentonite showed an intermediate swelling behaviour, since the result presented by Foster's Swelling Index was 7.0 mL/g of clay.

#### 4.7. Na/Ca ratio determination

The successful ion exchange of  $\text{Ca}^{2+}$  ions with  $\text{Na}^+$  ions was confirmed by the results of the sodium/calcium ratio determined using Energy-Dispersive X-ray Spectroscopy (Figure 13). From the figure it can be seen that the sodium/calcium ratio of raw and purified bentonite samples is in the range of 2.91 to 2.94. This ratio increased from 2.94 up to 15.8 as the concentration of  $\text{Na}_2\text{CO}_3$  varied from 2 to 6 wt.%, similar to previous observations (Magzoub et al., 2020; Singh & Sharma, 1991).



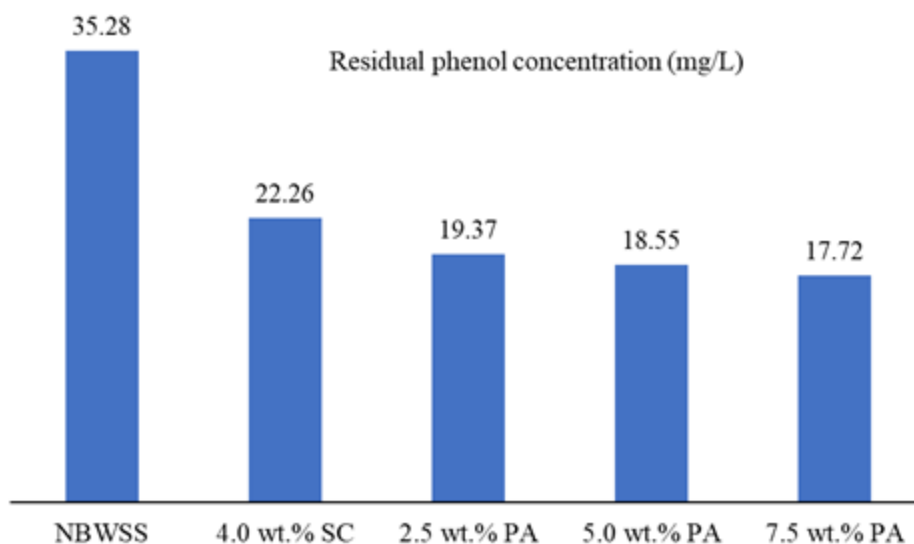
**Figure 13:** Na/Ca ratio for natural dry/wet sieved clays (NBDSS and NBWSS) and  $\text{Na}_2\text{CO}_3$  activated samples.

#### 4.8. Adsorption studies

Figure 14 shows the extent of phenol adsorption for various clays and loading. From the figure it is clear that the wastewater treatment with NBWSS and the modified samples led to a significant reduction in phenol concentration to less than half of the initial concentration (40 mg/L). The natural wet sieved clay sample (NBWSS) was able to reduce the phenol concentration by 11.8% compared to the initial value, confirming what was stated in section 1.1 that clay minerals even in their natural state have been found to be good adsorbents for various pollutants in wastewater. There was a significant improvement in adsorption efficiencies up to 44.4% (17.74 mg/L) when the neat clay was treated with 4 wt.%  $\text{Na}_2\text{CO}_3$ , showing clearly that the modification with soda ash is an extremely important step. The amount of adsorbed phenol changed from 17.74 mg/L



(44.4%) to 20.63 (51.6%), 21.45 (53.6%) and 22.28 mg/L (55.7%) when the clay was subjected to polymer modification process at the concentrations of 2.5, 5.0 and 7.5 wt.% polymer, respectively, showing clearly that these new polymer-based organo-clays (synthesized using the so-called “surfactant-free organo-modification approach”) have enormous potential to be applied as adsorbent materials for wastewater treatment.



**Figure 14:** Phenol adsorption efficiency for various clays and loading.

### 5. CONCLUSIONS AND RECOMMENDATIONS

#### 5.1. CONCLUSIONS

Based on the experimental results of the work, the following conclusions can be drawn:

- The clay showed a good response to the sodium activation process in the presence of  $\text{Na}_2\text{CO}_3$ . The CEC increased from 67.5 meq/100 g clay for the wet sieved sample (natural bentonite) up to ~74 meq/100 g clay for the activated samples as the concentration of  $\text{Na}_2\text{CO}_3$ , activation temperature and stirring time varied, respectively, from 2 to 6 wt.%, 25 to 65 °C and from 2 to 4 h;
- The CEC is strongly dependent to changes in three parameters evaluated here namely temperature,  $\text{Na}_2\text{CO}_3$  concentration and stirring time;
- For the same variation range of the parameters under analysis (2 to 6 wt.%  $\text{Na}_2\text{CO}_3$ , 25 to 65 °C and from 2 to 4 h), the Na/Ca ratio increased from 2.94 up to 15.8, confirming the successful ion exchange of  $\text{Ca}^{2+}$  ions with  $\text{Na}^+$  ions;
- For the activation conditions used in the study the CEC passes through a maximum of about 74 meq/100 g clay. High values of CEC of about 74 meq/100 g clay can be obtained at optimal activation conditions are 4 wt.%  $\text{Na}_2\text{CO}_3$ , 45 °C and 3 h and for commercial production those conditions are recommended.
- XRD confirmed that the organo-modification process, using the “surfactant free approach” has taken place since the main smectite peak of the polymer modified clays shifted to the left side. SEM images of the polymer modified clays presented compact layers in their structures, suggesting that the protonated amine functional groups at the ends of the polymer chains have attached the surface of the clay; and
- Modification of neat clay with soda ash at a concentration 4 wt.%  $\text{Na}_2\text{CO}_3$  increased the phenol adsorption capacity of the clay, having reached 44% of the adsorbed phenol. Phenol adsorption capacity was further increased from 44.4% to 51.6%, 53.6% and 55.7% when the clay was subjected to polymer modification process at the concentrations of 2.5, 5.0 and 7.5 wt.% polymer, respectively, demonstrating that sodium modification route and organo-modification with biodegradable polymers are key steps to produce adsorbent materials with great potential to be used in the wastewater treatment process.

## 5.2. RECOMMENDATIONS

- Adsorption studies over residence times of more than 24 h such as 48, 72 h, etc., need to be carried out for optimization purposes;
- The influence of solution pH using sodium hydroxide need to be investigated. Values of pH of 7, 9 and 12 are the most recommended;
- Adsorption kinetics using Langmuir-Freundlich isotherms need to be investigated in order to investigate the adsorption efficiency in terms of percentage of phenol as well as the maximum adsorption capacity;
- For comparison purposes phenol adsorption studies using High Performance Liquid Chromatography (HPLC) is recommended;
- Recycling and reusability of an adsorbent is an important aspect for the viability of the adsorption process.

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## APPENDIX

### Appendix1. Sodium/Calcium Ratio Analysis by EDX for raw, purified and activated bentonite samples

<b>Element</b>	<b>NBDSS</b>	<b>NBWSS</b>	<b>2 wt.% SC</b>	<b>4 wt.% SC</b>	<b>6 wt.% SC</b>
Na	1.31	1.44	1.89	3.51	4.89
Ca	0.45	0.49	0.41	0.38	0.31
Na/Ca ratio	2.91	2.94	4.61	9.24	15.8

**Appendix 2: Effect of temperature and wt.% Na<sub>2</sub>CO<sub>3</sub> on CEC**

Temperature (°C)	CEC, meq				STDEV
	wt.% Na <sub>2</sub> CO <sub>3</sub>	Run 1	Run 2	Average	
-	0	67.50	67.50	67.50	0.0000
25	2	69.00	69.50	69.25	0.1250
	4	70.00	70.00	70.00	0.0000
	6	71.50	72.50	72.00	0.5000
45	2	69.00	69.50	69.25	0.1250
	4	73.75	74.00	73.90	0.0325
	6	73.75	73.50	73.63	0.0313
65	2	69.50	69.00	69.25	0.1250
	4	72.50	73.50	73.00	0.5000
	6	72.50	73.50	73.00	0.5000

**Effect of time on CEC**

Temperature (°C)	CEC, meq				STDEV
	Time (hrs)	Run 1	Run 2	Average	
45 (4wt% Na <sub>2</sub> CO <sub>3</sub> )	2	70.00	70.00	70.00	0.0000
	3	73.75	74.00	73.90	0.0325
	4	73.50	74.00	73.75	0.1250