



**EDUARDO MONDLANE UNIVERSITY**

Faculty of Engineering

Department of Chemical Engineering

Master Dissertation in Hydrocarbon Processing Engineering

**EVALUATION OF THE EFFICIENCY OF OKRA ADSORBENT FOR HEAVY  
METALS REMOVAL FROM WASTEWATER IN NATURAL GAS PRODUCTION.**

Jean d'Amour Barasikina

Maputo, November 2021



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**Supervisor:** Prof. Dr. João Chidamoio, Eng.

Maputo, November 2021

## **DECLARATION OF DOCUMENT ORIGINALITY**

I, Jean d'Amour Barasikina, hereby declare that this research report is my own work towards the MSc degree in Hydrocarbon Processing Engineering and that, to the best of my knowledge, it contains no material previously published by another person nor material, which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in text.

**Jean d'Amour Barasikina**

**Signature: .....**

**Maputo...../...../.....**

## ABSTRACT

Nowadays, one of the leading environmental pollutants is heavy metals. This is due to the rapid development of industry and the over-exploitation of natural resources in many countries. Hence, heavy metals in wastewater must be removed before discharge because they are toxic even at low concentrations.

This research aims to evaluate the efficiency of okra waste as an adsorbent for heavy metals removal from wastewater in natural gas production. The FTIR was used to characterize the okra-activated carbon and the peaks showed the presence of functional groups such as Hydroxyl (OH), Amino (N-H), Carboxyl (C=O, C-O-C), C-O stretching and M-O. Furthermore, the batch adsorption experiments were conducted via varying agitation speed, contact time, adsorbent dose and adsorbent particle sizes. After extraction and adsorption batch process, samples were analyzed using Inductively Coupled Plasma-Optical (or atomic) Emission Spectrometry (ICP-OES).

The results showed that the maximum removal percent of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^{2+}$  and  $\text{Ba}^{2+}$  metal ions had been observed to be at an agitation speed of 1000 rpm, contact time of 90min, okra adsorbent dose of 0.25 g and particle size of 1.00mm. Then, the Langmuir isotherm model was applied to describe the maximum adsorption capacity ( $Q_{\text{max}}$ ) calculated for Cd (II), Pb (II), Zn(II), Cu(II), Ba(II) and Ag(II) metal ions. The maximum adsorption capacity ( $Q_{\text{max}}$ ) has been addressed to evaluate the fitting ability of the Langmuir isotherm model, wherever it yielded a better fit to the experimental data with higher correlation coefficients ( $R^2$ ) belongs between (0.888-0.999). Thus, the okra adsorbent showed a very high adsorption capacity for  $\text{Ba}^{2+}$  as 64.102 mg/g following for  $\text{Cu}^{2+}$  as 14.8 mg/g followed by  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ag}^{2+}$  as 8.37 mg/g 7.09 mg/g, 1.79 mg/g and 0.90 mg/g respectively and the  $R_L$  value in the present study for  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^{2+}$  and  $\text{Ba}^{2+}$  ions were found to be 0.0003 , 0.0027 , 0.0001 , 0.0002, 0.0002 and 0.2705 respectively . Therefore, all values of  $R_L$  were less than one, indicated that the adsorption of these heavy metals ions onto okra adsorbent is favorable.

The experimental results prove that due to its high efficiency for  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^{2+}$  and  $\text{Ba}^{2+}$  ions removal from wastewater, okra wastes from agricultural by-products are promised to be used as a low-cost adsorbent for further studies to remove other heavy metals.

**Keywords:** Heavy metals, pollutants, Toxic, Non-biodegradability, Agricultural by-products, Okra waste, Wastewater, Batch adsorption, Langmuir isotherm

## RESUMO

Hoje em dia, um dos principais poluentes ambientais são os metais pesados. Isso se deve ao rápido desenvolvimento da indústria e à super-exploração dos recursos naturais em muitos países. No entanto, os metais pesados nas águas residuais devem ser removidos antes da descarga porque são tóxicos mesmo em baixas concentrações.

Esta pesquisa tem como objetivo avaliar a eficiência de adsorvente a base de resíduo de quiabo na remoção de metais pesados em águas residuais produzidas durante a extração de gás natural. Para o efeito, foi utilizado o FTIR para caracterizar o adsorvente produzido, e os picos mostraram a presença de grupos funcionais como Hidroxila (OH), Amino (N-H), Carboxila (C = O, C-O-C), C-O alongamento e M-O. Adicionalmente investigou-se o efeito da velocidade de agitação, tempo de contato, dose de adsorvente e tamanhos de partículas na eficiência da adsorção. Após o processo de extração e adsorção, as amostras foram analisadas usando espectrometria de emissão de plasma acoplado indutivamente (ou atômica) (ICP-OES).

Os resultados mostraram que a percentagem máxima de remoção de íons metálicos  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ag^{2+}$  e  $Ba^{2+}$  foi observada em uma velocidade de agitação de 1000 rpm, tempo de contato de 90min, dose de adsorvente de 0,25 g e tamanho de partícula de 1,00mm. Em seguida, o modelo de isoterma de Langmuir foi aplicado para descrever a capacidade máxima de adsorção ( $Q_{max}$ ) calculada para os íons metálicos *Cd (II)*, *Pb (II)*, *Zn (II)*, *Cu (II)*, *Ba (II)* e *Ag (II)*. Avaliou-se a adequabilidade dos resultados ao modelo cinético de adsorção de *Langmuir* onde obteve-se coeficiente de correlação ( $R^2$ ) entre (0,8884-0,9999). O adsorvente a base de quiabo mostrou uma capacidade de adsorção muito alta para  $Ba^{2+}$  com 64,102 mg / g seguida de  $Cu^{2+}$  com 14,8 mg / g seguido por  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  e  $Ag^{2+}$  com 8,37 mg / g, 7,09 mg / g, 1,79 mg / g e 0,90 mg / g respectivamente e o valor *RL* no presente estudo para  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ag^{2+}$  e  $Ba^{2+}$  são respectivamente 0,0003, 0,0027, 0,0001, 0,0002, 0,0002 e 0,2705. Todos os valores de *RL* são menores que um, indicando que a adsorção desses íons de metais pesados no adsorvente de quiabo é favorável.

Os resultados experimentais provam que o adsorvente a base de quiabo é eficiente no processo de remoção de metais pesados em águas residuais provenientes da produção de gás natural.

**Palavras-chave:** Metais pesados, poluentes, Tóxico, Não biodegradabilidade, Subprodutos agrícolas, Resíduos de quiabo, Águas residuais, Adsorção em lote, Isoterma de Langmuir.

## **DEDICATION**

I would like to dedicate this thesis to: Almighty God, my beloved mother who always supports me and my siblings, all my friends for the love and unconditional support you never stopped showing.

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## **LIST OF ABBREVIATIONS**

**AAS:** Atomic Absorption Spectrometry

**AC:** Activated Carbons

**ATSDR:** Agency for Toxic Substances and Disease Registry

**BET:** Brunauer Emmett and Teller

**CCD:** Charge Capacitive Discharged arrays

**CO<sub>2</sub>:** Carbon Dioxide

**CRM:** Certified Reference Materials

**EDAX:** Energy Dispersive Analysis X-Ray

**EPA:** Environmental Protection Agency

**ETAAS:** Electrothermal Atomic Absorption Spectrometry

**FAAS:** Flame Atomic Absorption Spectroscopy

**FTIR:** Fourier Transform Infrared

**GAC:** Granular Activated Carbon

**GFAAS:** Graphite Furnace Atomic Absorption Spectroscopy

**ICP-OES:** Inductively Coupled Plasma-Optical

**IUPAC:** International Union of Pure and Applied Chemistry

**LIBS:** Laser-Induced Breakdown Spectroscopy

**PAC:** Powder Activated Carbon

**PMT:** Photomultiplier

**PW:** Produced Water

**PWW:** Produced Wastewater

**RF:** Radio Frequency

**SASOL:** South African Synthetic Oil Limited

**SEM:** Scanning Electronic Microscopy

**SRM:** Standard Reference Method

**STL:** Spent Tea Leaves

**THM:** Total Heavy Metals

**UEM:** Universidade Eduardo Mondlane

**USEPA:** United States Environmental Protection Agency

**WHO:** World Health Organization

**XRD:** X-Ray Diffraction

# CHAPTER I

## INTRODUCTION

### 1.1. Background

Due to the rapid development of industry and the over-exploitation of natural resources in many countries, the levels of pollution have been steadily increasing (Ranck *et al.*, 2005).

One of the most critical challenges worldwide is the rapid increase in water consumption due to population growth, urbanization and industrialization. Nowadays, water resources are contaminated by industrial effluents, affecting the quality of ecosystems and the health of all living forms (Bulgariu *et al.*, 2019). For instance, one of the leading wastewater contaminants is the presence of heavy metals such as Cadmium, Lead, Copper, Zinc, Silver and Barium, which have been extensively used as targeted pollutants in this research study not only due to their high toxicity but also because of the known human health problems related to those mentioned heavy metals compounds (Departament & Qu, 2015).

Generally, heavy metals are defined as metallic elements with a relatively high density greater than  $6.0 \text{ g/cm}^3$  compared to water. Consequently, heavy metals above acceptable limits in wastewater will often direct to disadvantageous effects on humans, other organisms and the environment at large (Kinuthia *et al.*, 2020). Heavy metal-contaminated wastewater can generally be originated from metal plating, mining operations, tanneries, chloralkaline, radiator manufacturing, smelting, alloy industries, storage batteries industries, etc. Other sources of heavy metals are pharmaceuticals, as well as body care and cleaning products. Moreover, illegal wastewater discharges are also an essential source of sewage sludge pollution with heavy metals (Tytła, 2019).

The removal of heavy metals from contaminated wastewater has become an important research topic due to their toxicological problems Singha & Guleria, (2015) reported that the heavy metal ions are considered as non-biodegradable and can accumulate in biological tissues, resulting in a variety of illnesses and ailments. They must be therefore removed before disposal since they are harmful even at low concentrations, and that is why their levels in water, wastewater, and farming water must be kept to a minimum.

The Ion exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration and adsorption on activated carbon and biological materials were all mentioned in the literature as reliable ways for removing heavy metals from wastewater before discharge into the environment (Departament & Qu, 2015). In order to minimize the metal to an acceptable level for discharge and long-term environmental consequences , each technique requires a large number of chemicals as described by Jayan & Aryasree, (2008) in their study.

In general, most of the available processes have costly disadvantages, are challenging to use on the wide-scale application, are technically complex, used for wastewater treatment in specific cases and produce a considerable quantity of toxic sludge that needs additional treatment (Esgair, 2018). Because of its convenience, ease of operation and simplicity of design, adsorption was chosen as the preferable approach in this study (Jayan & Aryasree, 2008) as well as its effectiveness in lowering heavy metal ion concentrations to inadequate levels and the usage of low-cost adsorbent materials (Saka *et al.*, 2012).

Adsorption can be defined as the accumulation of a substance at a surface or interface. The adsorption process in wastewater treatment happens when a solid adsorbent and polluted wastewater are in contact. The pollutant that is being adsorbed is referred to as an adsorbate and the adsorbing phase is referred to as an adsorbent (Desta, 2013). The effectiveness of adsorption was determined not only by the characteristics of the okra adsorbent used , but also by various parameters such as contact time, adsorbent particle size, adsorbent amount and agitation speed that are commonly used during the adsorption process and these factors have been taken into account when evaluating the potential of okra as low-cost adsorbent. Normally, the adsorption process is particularly attractive in fact that the adsorbent used is not expensive and does not require pre-treatment (Hall *et al.*, 2009). Recently, a great deal of interest in the research for removing heavy metals from industrial effluent has been focused on using agricultural by-products as adsorbents (Hegazi, 2013). For instance , agricultural by-products used as adsorbent material to purify heavy metal contaminated wastewater have become increasingly popular through the past decade because they are less expensive, biodegradable, abundant and efficient as reported by Saka *et al.*,( 2012). Furthermore, by reusing solid waste, the use of agricultural or fruit waste as a raw material lowers total costs and prevents surface water contamination (Shafiq *et al.*, 2021).



To date, various waste materials, such as rice husk, wheat straw, wood waste biomass, sawdust, okra waste, wasted tea leaves, peanut husk, orange peels, and fruit debris, have been identified as agricultural by-products, with biochar being used to remove metals or metalloids from polluted wastewater (Esgair, 2018). The functional groups like carboxyl, phenol, methyl and hydroxyl are the based composition of agricultural wastes, which may be treated chemically and physically for increasing the adsorption capacities to heavy metals (Dai *et al.*, 2018). In notion, cellulose and protein are the structural components of okra waste (O. & E., 2014a), and it is a crucial fruit vegetable crop grown worldwide. Moreover, okra fruit contains 86% water, 2.2% protein, 10% carbohydrate, 0.2% fat, and vitamins A, B, and C (Ash *et al.*, 2019).

In this research, the efficiency of a new, environment-friendly, cost-effective, and locally available raw okra waste originates from agricultural by-products was prepared and activated by using phosphoric acid as activating agent. Furthermore, the powdered okra has been used as adsorbent for removal of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^{2+}$  and  $\text{Ba}^{2+}$  heavy metals ions from wastewater in natural gas production sampled from Petroleum Temane SASOL plant locates in Inhambane, south province of Mozambique. The batch method was employed by varying parameters including contact time, agitation speed, particle size of okra adsorbent material and the amount of okra adsorbent were studied in order to obtain the maximum heavy metals removed from wastewater and then after, the Langmuir isotherm model was applied to describe the adsorption isotherm (Emenike *et al.*, 2016).

## 1.2. Research Problem

Typically, Temane SASOL natural gas processing plant produces huge amount of wastewater approximately  $60 \text{ m}^3$  per day. This wastewater produced contains a variety of inorganic compounds characterized as toxic, carcinogenic and mutagenic, which, when persisting in the environment, may have the potential effect on man and vegetation (Bobade & Eshtiagi, 2015). The heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons as they are non-biodegradable and often accumulate in the environment, causing both short and long term adverse effects, even at low concentrations (Department & Qu, 2015). Bobade & Eshtiagi (2015) stated heavy metals such as Lead, Cadmium, Copper, Nickel, Zinc, and Arsenic among the most toxic and dangerous of the hazardous compounds found in industrial wastewater.

Mostly, the exposure to heavy metals may occur via inhalation or ingestion through food, drink, fume or dust, which affects human health (Qasem & Mohammed, n.d.).

Zeiner, (2007) studied the accumulation of heavy metals in body tissue and their binding to enzymes disrupt the functioning of cells, which later leads to tumors or cancers. For this reason, it is significant to monitor heavy metals in/on textile materials. The adverse effects of heavy metals in people, for example, are dependent on their dose, rate of emission, duration of exposure, and type of metal absorbed through wastewater, therefore this study focused on the impacts of Pb, Cd, Cu, and Zn heavy metals on human health (Kinuthia *et al.*, 2020).

Consultants & Africa (2001) mentioned that heavy metals produced in SASOL had been disregarded as possible hazardous water pollutants. As a result, it is generally recommended that the amounts of heavy metals in industrial wastewater be investigated more thoroughly. In many cases, surface discharge of this water is a more realistic way of disposal due to environmental and financial issues. In other circumstances, reinjection is not an option, and the only way to dispose of this water is by surface discharge. For offshore wells, for example, release to the surrounding water is the most cost-effective method of disposal.

In addition to the previously described disadvantages of heavy metals, there are certain challenges to removing heavy metals on a broad scale since several commonly used methods for removing heavy metals from wastewaters need huge volumes of chemicals to minimize the metal to an acceptable level for disposal, which has long-term environmental consequences (Jayan & Aryasree, 2008). They are also expensive, difficult to utilize on a large scale, technically sophisticated, only employed for wastewater treatment in particular instances and produce a large amount of hazardous sludge that requires extra treatment (Esgair, 2018).

It is therefore essential that this research was conducted to remove heavy metals pollutants, especially  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^{2+}$  and  $\text{Ba}^{2+}$  ions from wastewater in Temane SOSOL natural gas processing plant using more effective cleanup or containment methods such as adsorption method using low-cost okra waste from agricultural by-product (amount of okra and cost required are detailed in the literature P20-21) to reduce as much as possible the adverse effects caused by heavy metals contaminated wastewater to the environment, animals and humans being.

### **1.3. Research objectives**

#### **1.3.1. Main objective**

The main objective of this research is to evaluate the efficiency of okra waste used as an adsorbent for heavy metals removal from wastewater in the Petroleum Temane SASOL plant located in Inhambane, south province of Mozambique.

#### **1.3.2. Specific objectives**

- ✓ To investigate the effect of adsorption variables, including contact time, agitation speed, the particle size of okra adsorbent material, and the amount of okra adsorbent to obtain the maximum removal of heavy metals from wastewater.
- ✓ To conduct the laboratory experiment to determine the removal efficiency of heavy metals adsorption onto okra adsorbent using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).
- ✓ To analyze the suitability of the Langmuir isotherm to carry out an experimental removal calculation to predict how much heavy metals have been adsorbed by okra adsorbent.

### **1.4. Motivation**

Recently, Temane SASOL plant is generating huge volumes of wastewater approximately 60 m<sup>3</sup> each day. A timeline looking at regulatory changes over this period, and disposal options of this wastewater produced in order to avoid their massive injection into the environment still a big challenge. Based on this assessment of wastewater production, disposal options and future effects on human health of those wastewaters produced in Temane Sasol Plant, needs to focus on improving wastewater recycling and advanced wastewater treatment options that remove heavy metals from wastewater prior to disposal. This research focused on the removal of heavy metals from wastewater in Temane SASOL natural gas processing plant by using the low price, available (described on p20-21) and effective non-conventional adsorbent materials from agricultural by-products which are raw okra waste for heavy metals removal from wastewater in Temane SASOL natural gas processing plant locates in Inhambane, southern province of Mozambique.

So far, the majority of okra plants are produced and consumed in Mozambique, but a significant proportion of okra wastes are still transported to open areas for burning or dumping, resulting in the release of toxic materials and pollutants, as well as carbon dioxide (CO<sub>2</sub>), into the environment. Furthermore, by reusing okra waste as adsorbent for heavy metals from wastewater in Temane SASOL natural gas processing plant, might be a preferable choice for reducing landfill waste and environmental concerns associated with okra wastes while also saving money for the country (Sulyman *et al.*, 2017).

Because of the high affinity of the different adsorbents for inorganic contaminants, adsorption was chosen as the most effective method for removing heavy metals from wastewater in this investigation (Zango *et al.*, 2020). Additionally, the process has been also preferred due to its simplicity, low cost, availability of multiple adsorbents materials, non-environmental toxicity, ease of design, high efficiency, ease of operation and ability to treat a selection of heavy metals in a variety of concentrated forms (Hall *et al.*, 2009).

The okra adsorbent activated carbon has been selected to be used in this study during the adsorption process due to its effectiveness, high surface area and high adsorption capacity. This process is costly due to the required regeneration after each adsorption process. Therefore, its use in different wastewater treatment applications is limited to expensive renewal (Crini *et al.*, 2019).

Moreover, natural sorbents are characterized by limited oil capacity and low cost and its disposal method criterion was the crucial critical issue when selecting this okra adsorbent material. The cost of natural adsorbents such as okra waste is several tens of times lower than conventional adsorbent cost include Activated alumina, Silica gel, Zeolites, Molecular sieves as well as ion-exchange resins, etc. Natural adsorbents do not require their regeneration which reduce their cost (Olga *et al.*, 2015).

Esgair (2018); Hashem (2007), O. & E. (2014a) and Khaskheli *et al* (2016) evaluated the performance of okra adsorbent for Heavy Metals removal from wastewater and they found that okra waste was the best adsorbent material for removal of cadmium and copper ions from wastewater and Bobade & Eshtiagi (2015) studied and stated the literature on various adsorbents such as natural materials, an industrial by-product, agricultural and biological waste, biopolymers and hydrogels used to remove heavy metals from and the parameters affecting heavy metals adsorption in wastewater.

## **1.5. Research questions**

- ✓ Can the adsorption method efficiently and effectively treat heavy metals contaminated wastewater to compliance limit?
- ✓ Is raw Okra waste adsorbent suitable for heavy metals removal from wastewater in natural gas production?
- ✓ Can heavy metals removal efficiency of adsorption be enhanced with subsequent loading of raw Okra waste adsorbent during the removal of heavy metals contaminated wastewater when embedded with an activated agent?
- ✓ What will be the effect of the adsorption variable, which includes contact time, agitation speed, the particle size of each adsorbent material and amount of okra adsorbent, on the removal efficiency of heavy metals adsorption?

## **1.6. Hypothesis**

The wastewater in natural gas production may contain various heavy metals. The okra wastes from agricultural products are more efficient low-cost adsorbent to remove these heavy metals from wastewater by a variant of different adsorption parameters including: agitation speed, contact time, adsorbent dose and adsorbent particle size.

## CHAPTER II

### LITERATURE REVIEW AND THEORETICAL FRAMEWORK

#### 2.1. Introduction to heavy metals contaminants

Due to a deficiency of safe drinking water, the globe is experiencing a water crisis. Heavy metals including Cadmium, Lead, Copper, Zinc, and others are a major source of worry. Because of their high toxicity and well-documented human health issues, these chemicals have been widely employed as target pollutants in research investigations. Wastewater treatment has long been an important component of study due to growing environmental consciousness and severe environmental legislation. Water is an essential component of every country's economic growth (Bobade & Eshtiaghi, 2015).

The terminology "heavy metals," for general, refers to any metallic element with a relatively high density that is toxic (non-biodegradable) or hazardous even at low quantities. This is due to the fact that many inorganic metals are non-biodegradable and may cause cancer even at low quantities. Heavy metals such as Cd (II), Pb (II), Cu (II), and Zn (II), which are widely found in the effluents of mining, battery, and other industries, have been designated as priority and hazardous pollutants by the USEPA. As a result, they should be treated before being discharged into municipal sewers (Department & Qu, 2015).

Consequently, when these metals are passed to people through the food chain, they may accumulate in various bodily organs and tissues, potentially causing life-threatening disease and damage to essential systems. Activated carbon, despite its widespread usage in the water and wastewater treatment sectors, is still a costly commodity. The necessity for safe and cost-effective technologies to remove heavy metals from polluted waters has prompted research on low-cost alternatives to commercially available activated carbon in recent years. As a result, all feasible sources of Agro-based cheap adsorbents must be investigated as soon as possible (Hegazi, 2013).

Matouq *et al.*, (2018) and Department & Qu, (2015) reported the guidelines for the maximum permissible discharge into the environment established by the World Health Organization (WHO) and the Environmental Protection Agency (EPA). Wherever, the maximum acceptable concentrations of some heavy metals such as Lead (Pb), Chromium (Cr) and Cadmium (Cd) in drinking water are indicated in the table 1.

**Table 1.** Standards and guidelines for some heavy metals in drinking water allowed by the WHO and EPA (Department & Qu, 2015).

| Metals    | WHO (mg/l) | EPA (mg /l) | EU (mg/l) |
|-----------|------------|-------------|-----------|
| <b>Pb</b> | 0.01       | 0.015       | 0.01      |
| <b>Cr</b> | 0.05       | 0.10        | 0.05      |
| <b>Cd</b> | 0.003      | 0.005       | 0.005     |

## **2.2. Sources and health effects of heavy metals contaminated Wastewater**

### **2.2.1. Sources of heavy metal contaminated wastewater**

Unlike organic wastes, heavy metal-contaminated wastewater typically comes from a variety of sectors including printing, dyeing, metallurgical engineering, electroplating, photographic materials, fuels, power operations, semiconductors, and battery production (Singha & Guleria, 2015). Other sources for the metal wastes as reported by Department & Qu, (2015) include the wood processing industry, where a chromate copper arsenate wood treatment produces arsenic-containing wastes; inorganic pigment manufacturing has pigments containing chromium compounds and cadmium sulfide. These generators make a large quantity of wastewaters, residues, and sludges that can be categorized as hazardous wastes requiring extensive waste treatment.

Despite of the use of automobile parts (tires, brakes), fuel combustion, and road infrastructure (e.g. road surface-layer fraying, corrosion of galvanized road buffers). Zinc originates from ZnO-containing tires and galvanized automobile parts, whereas nickel comes from metal abrasion in cars and fuel use (Grd *et al.*, 2012). The exposure to heavy metals may generally occur through inhalation or ingestion through food, drink, fume or dust, affecting human health (Bobade & Eshtiaghi, 2015).

### **2.2.2. Effects of heavy metal contaminated wastewater**

Heavy metals, in general, can rapidly enter the food chain through a variety of channels and induce increasing harmful effects on living species over the course of their lives (Department & Qu, 2015). Possible carcinogens; harm to the brain, lungs, and kidneys; damage to growing fetuses; high blood pressure or heart rate; vomiting and diarrhea; skin rashes and eye irritation are some of the negative health effects connected with various heavy metal compounds in humans (Kinuthia *et al.*, 2020).

Heavy metals can also cause disease in the gastrointestinal, renal, and cardiovascular systems, as well as cancer, liver and kidney disease, melancholy, and osteoporosis, among other things (Ida & Eva, 2021). Qasem and Mohammed reported the permissible quantity of various heavy metals, their sources, and affected organs as suggested by the World Health Organization (WHO) and they are shown in table 2

**Table 2.** Heavy metals sources, organs affected and the permitted amounts in drinking water base on the world health organization (WHO) recommendations (Qasem & Mohammed, n.d.).

| <b>Heavy metal</b>   | <b>Main sources</b>  | <b>Main organ and System</b>  | <b>Permitted amount(mg/l)</b> |
|----------------------|--|---|-------------------------------|
| <b>Lead (Pb)</b>     | Lead-based batteries, solder, alloys, cable sheathing pigments, rust inhibitors, ammunition, glazes and plastics stabilizers.  | Bones, liver, kidneys, brain, lungs, spleen, Immunological system, hematological system, cardiovascular system and reproductive system. | <b>10</b>                     |
| <b>Arsenic (As)</b>  | Electronics and glass production   | Skin, Lungs, brain, kidneys, metabolic system and endocrine.  | <b>10</b>                     |
| <b>Copper (Cu)</b>   | Corroded plumbing systems, electronic and cables industry.   | Liver, brain, kidneys, cornea, gastrointestinal system, lungs, immunological system, and hematological system.                          | <b>200</b>                    |
| <b>Zinc (Zn)</b>     | Brass coating, rubber products, some cosmetics and aerosol deodorants.   | Stomach cramps, skin irritations, vomiting, nausea and anemia and convulsions   | <b>300</b>                    |
| <b>Chromium (Cr)</b> | Steel and pulp mills and tanneries   | Skin, lungs, kidneys, liver, brain, pancreas, tastes, gastrointestinal system   | <b>50</b>                     |
| <b>Cadmium (Cd)</b>  | Batteries, paints, steel industry, plastic industries, and metal refineries and corroded galvanized pipes.   | Bones, liver, kidneys, lungs, Testes, brain, immunological system and cardiovascular system.  | <b>3</b>                      |
| <b>Mercury (Hg)</b>  | Electrolytic production of chlorine and caustic soda, runoff from landfills and agriculture, electrical appliances, industrial and control instruments, laboratory apparatus and refineries. | Brain, lungs, kidneys, liver, immunological system, cardiovascular system, endocrine and reproductive system.                           | <b>6</b>                      |
| <b>Nickel (Ni)</b>   | Stainless steel and nickel alloy production.   | Lung, kidney, gastrointestinal distress, pulmonary fibrosis, and skin   | <b>70</b>                     |



### 2.3. Adsorption process description

In this investigation, one of the heavy metals removal methods employed was adsorption. Adsorption is defined as the attachment of gas, liquid, or solid atoms, molecules, or ions to a surface material. The minimal space requirements for batch and continuous fixed bed units, simplicity of design and ease of operation, non-pollutant to water, no odor emissions, and the inexpensive cost of the adsorbent are only a few of the benefits of adsorption (Sulyman *et al.*, 2017). Many studies sought to find a low-cost and workable material for the adsorption process in order to lower the cost of wastewater treatment.

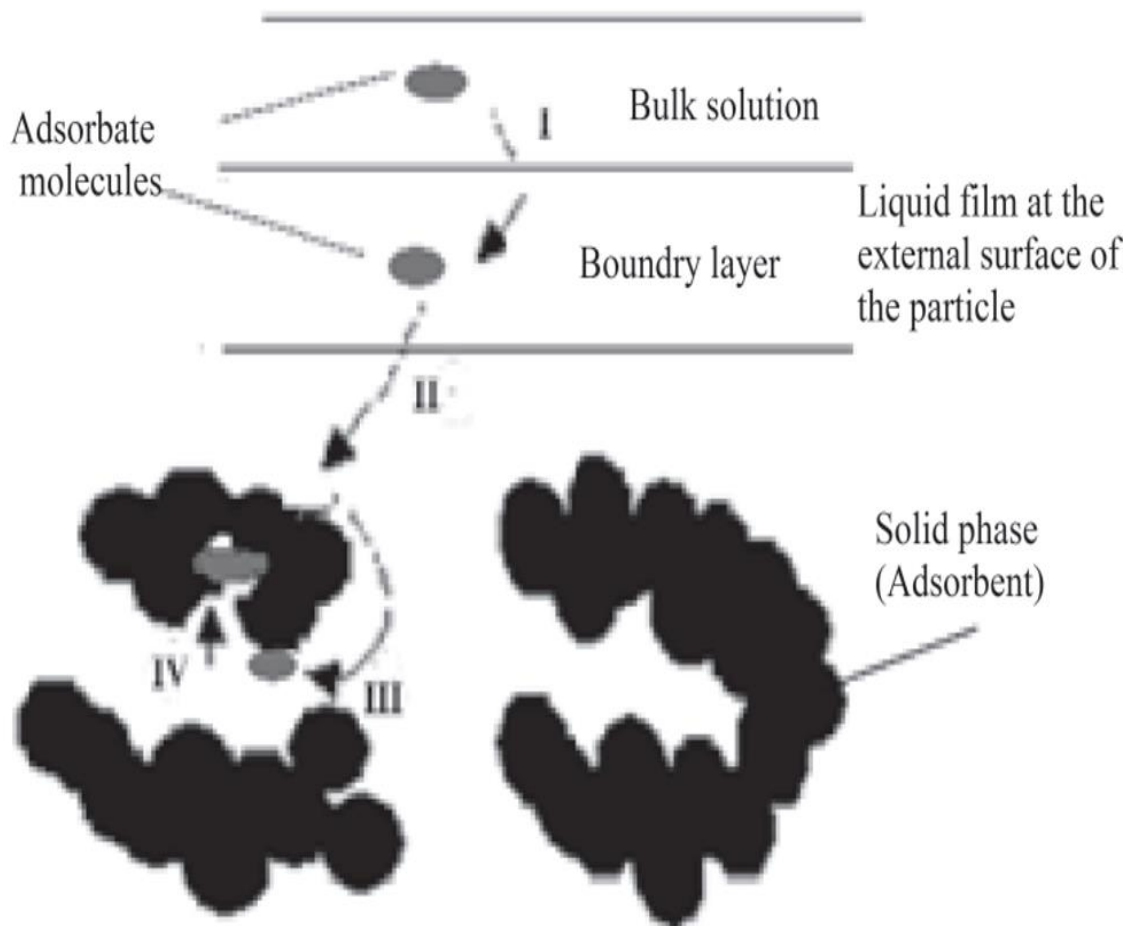
Physical adsorption and chemical adsorption are the two types of adsorption processes. Physical adsorption is achieved by Van der Waals forces, dipole interactions, and hydrogen bonding, there is no electron exchange between adsorbent and adsorbate. This is because physical adsorption does not need any activation energy, the time necessary to reach equilibrium is short. Thus, physical adsorption is a non-specific and reversible process whereas chemical adsorption occurs when an adsorbent and an adsorbate molecule form a chemical bond; it is selective and irreversible, and the chemical and electronic characteristics of the adsorbent are modified. The binding between the adsorbent and adsorbate by the covalent bond is called weak chemical adsorption, and that by ionic bonds is called strong chemical adsorption (Sulyman *et al.*, 2017). The adsorption method efficiently removes inorganic compounds since it reaches the limits established by legislation for discharging these effluents to water bodies.

In the last step of water and wastewater treatment, adsorption onto activated carbon is employed to remove remnants of harmful pollutants that were not released during the main treatment and therefore, the adsorption experiments on heavy metal removal have often been conducted on pure components (De Arruda Guelli Ulson De Souza *et al.*, 2012).

### 2.3.1. Adsorption Mechanisms

The adsorption process of the adsorbate molecules from the bulk liquid phase into the solid (adsorbent) phase is described by the following four steps (Sulyman *et al.*, 2017):

- ✓ The mass transfer of the adsorbate molecules across the external boundary layer toward the solid particle.
- ✓ Adsorbate molecules are transported from the particle surface into the active sites by diffusion within the pore-filled liquid and migrate along the solid surface of the pore.
- ✓ Solute molecule adsorption on the active sites on the interior surfaces of the pores.
- ✓ The molecule gets approached inside the pores of the adsorbent, as presented by Figure1.



**Figure 1.** The mechanism of molecule adsorption using micro porous adsorbent (Sulyman *et al.*, 2017).

### **2.3.2. Affecting factors on the rate of the adsorption process**

Referring to Saka & Mas, (2012) study, they described the adsorptive removal of organic and inorganic substances from wastewater by activated carbons depends upon the surface area, the pore volume and the pore-size distribution carbons. The effectiveness of the adsorption relies not only on the characteristics of the adsorbent but also on different parameters, including pH, temperature, initial concentration, contact time, the particle size of adsorbent, etc. These parameters should also be considered while examining the potential of low-cost adsorbents (Saka *et al.*, 2012). The following paragraphs represent the most common and effective factors on the rate of the adsorption process.

#### **✓ Effect of Solution pH**

In the adsorption process of Synthetic Dyes (SD) and Heavy Metals (HM) employing either batch mode or fixed-bed column, the pH value of the aqueous solution is an important regulating parameter. During adsorption, these pH levels impact the surface charge of the adsorbent, the degree of ionization, and the speciation of the adsorbate. Most metals adsorption on Activated Carbon adsorbents increased with increasing pH in general. This was due to the fact that the protonation of the active sites at the carbon surface was increased at low pH (<4). According to some authors, metal complexes form at higher pH levels and precipitate, so the separation may not be due to adsorption (Hashem, 2007).

#### **✓ Effect of Agitation Speed and Contact Time**

When contemplating an economical wastewater treatment application, equilibrium time is a critical factor to consider. Simply described, the sorption process is divided into three steps (phases): Because of the huge amount of adsorbate connected to the sorbent during the early period of adsorption, the sorption process is highly quick at initially, and the rate of removal is often greater as reported by Sulyman *et al.*, (2017) . Normally, the higher sorption rate at the beginning can be attributed to the presence of a larger surface area represented by the adsorbent and the availability of free active sites at the beginning time for the adsorption of the adsorbate. After this time, as the contact time rises, the sorption rate slows down and eventually approaches a constant value, at which point no more adsorbate is taken from the solution (transition phase). Finally, due to the dearth of free active sites on the adsorbents at the time, the process reaches a condition of equilibrium (saturation phase).

### ✓ Effect of Adsorbent amount

When using the batch mode approach, on the other hand, the number of adsorbents (concentrations) is always and theoretically regarded as a proportion of the bed height factor.

With increasing adsorbent dose, the percentage of adsorption rose, while the quantity of molecules adsorbed per unit mass of adsorbent dropped. The number of adsorbents grows, which increases the number of adsorption sites and hence the adsorbent surface area. On Activated Carbon and modified Activated Carbon made from okra agricultural waste, heavy metals were removed from aqueous solution (Sulyman *et al.*, 2017).

### ✓ Effect of Particle Size

Adsorbent material particle sizes are a critical parameter in the adsorption process. Because of its bigger pores and higher adsorption rate, powder activated carbon (PAC) outperformed granular activated carbon (GAC) in metal adsorption capacity. The bigger pores of PAC enable for more removal of these pollutants from their aqueous phase by entry; the authors also interpreted the result to the larger pores of PAC, which allow HMs to be more rapidly adsorbed within internal sites and so completely occupy these active sites. Contaminant adsorption capability diminishes as particle size rises. As a result, when various natural materials are used as adsorbents for the adsorption of pollutants, the proportion of contaminants removed decreases (Sulyman *et al.*, 2017).

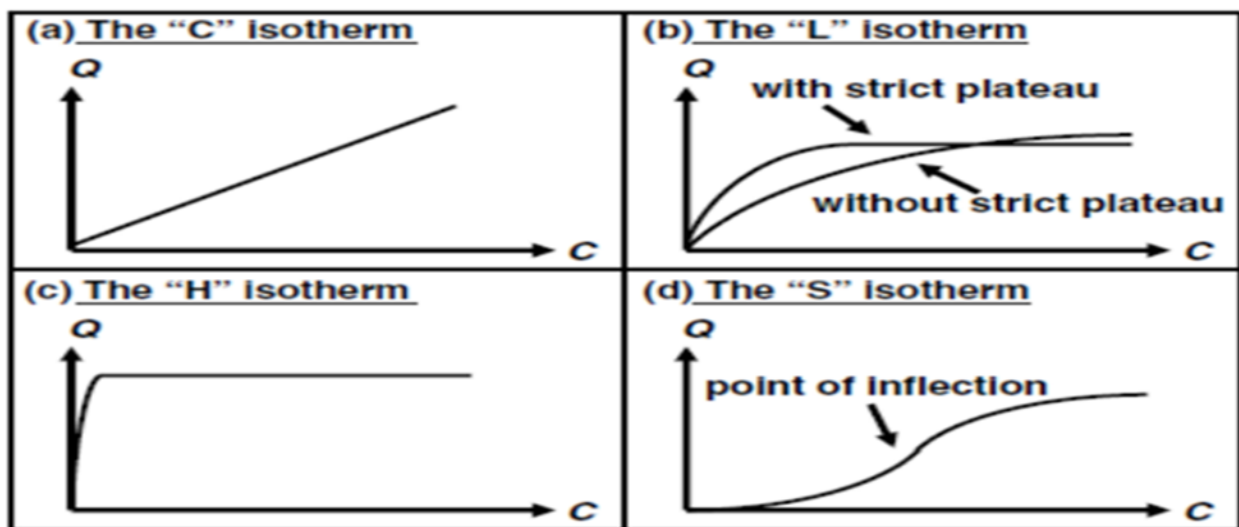
### 2.3.3. Adsorption isotherm model.

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase since the adsorption isotherms are essential to describe how adsorbents will interact with the adsorbate and so are critical for design purposes; therefore, the correlation of equilibrium data using an equation is essential for practical adsorption operation (Abdel & Reiad, 2011). Shafiq *et al.*,(2021) demonstrated how to calculate the adsorption capacity at equilibrium using the Equation 1 shown below:

$$q_e = \frac{C_i - C_e}{\frac{m}{v}} \quad (1)$$

Where  $C_i$  (mg/L) denotes the initial concentration of the heavy metals and  $C_e$  (mg/L) is the effluent concentration),  $q_e$ : Adsorption capacity at equilibrium (mg/g) ,  $m$ : dry weight adsorbent (g),  $V$ : volume of wastewater solution (L).

Generally, when the solute's retention on solid particles is investigated, the remaining solute concentration of compound C (mg/L) can be compared with the concentration of this compound retained on solid particles q (mg/g). The relationship  $q = f(C)$  is named the "sorption isotherm"(Department & Qu, 2015). The uniqueness of this relation requires several conditions to be met including: **(i)** the various reaction equilibrium of retention/release must have been reached, and **(ii)** all other Physico-chemical parameters such as pH, temperature, and heavy metals initial concentration must remain constant. The word "isotherm" was specifically chosen because of the influence of the temperature on sorption reactions; the temperature has been kept constant at 60°C. Department & Qu,( 2015) distinguished between high affinity (H), Langmuir (L), constant partition (C), and sigmoidal-shaped (S) isotherm classes. The “C” isotherm: the curve is a line of zero-origin. It means that the ratio between the concentration of the compound remaining in solution and adsorbed on the solid ( $K_d$ ) remain the same at any concentration. For instance, this isotherm is often used as an easy-to-use approximation (for a narrow range of concentration or low concentrations such as observed for trace pollutants) rather than an accurate description. For example, if the solid has a limited quantity of adsorption sites, the isotherm could be nonlinear because of a possible saturation plateau. The "L" isotherm: corresponds to a decrease of site availability as the solution concentration increases, providing a concave curve, suggesting a progressive solid saturation. One usually makes two sub-groups: **(i)** the solid has a limited sorption capacity, and **(ii)** the solid does not show clearly a limited sorption capacity (Department & Qu, 2015).



**Figure 2.** The four main types of Isotherms (Department & Qu, 2015).

The ‘‘H’’ isotherm: this is only a particular case of the ‘‘L’’ isotherm, where the initial slope is very high (Figure 2 c). This case was distinguished from the others because the compound sometimes exhibits such a high affinity for the solid that the initial slope cannot be determined from infinity, even if it does not make sense from a thermodynamic point of view. The ‘‘S’’ isotherm: the curve is sigmoidal and thus has a point of inflection (Figure 2 d). This type of isotherm implies that adsorption becomes more straightforward as the concentration in the liquid phase increases (Departament & Qu, 2015).

As far as adsorption is concerned, it means that the solute molecule has a reasonably sizeable hydrophobic part and a marked localization of the force of attraction for the substrate.

For a given molecule, this character may depend on both the nature of the adsorbent surface and the nature of the solvent. The inflection point illustrates the concentration for which the adsorption overcomes the complexation (Departament & Qu, 2015).

#### 2.3.4. Langmuir isotherm equation

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The Langmuir equation is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface (Abdel & Reiad, 2011). The linear Langmuir isotherm model is presented by the following equation 2:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (2)$$

Where  $K_L$  (**L/mg**) is the Langmuir constant related to adsorption energy and  $q_{max}$  (**mg/g**) is the maximum adsorption capacity,  $q_e$  is the adsorption capacity at equilibrium in mg/g,  $C_e$  is the equilibrium concentration of the adsorbate in mg/l.

Frequently, the sorption process of metal ions on okra adsorbent follows the Langmuir isotherm model, where the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the sorption of the following ion (Abdel & Reiad, 2011).

## **2.4. Low-cost adsorbents**

Human activities such as industrial, agricultural, and home activities have had an impact on the environment, resulting in serious issues such as global warming and the development of wastewater carrying high levels of pollutants. Water of excellent quality is a limited resource, thus it's become critical to treat wastewater to remove contaminants. Furthermore, society's fast modernization has resulted in the production of a large volume of low-value resources that are useless. Such materials are commonly regarded as garbage, and disposing of them is a challenge.

Because all of these materials may be used as low-cost adsorbents for wastewater treatment, they may have some benefit. A brief overview of a wastewater treatment technique has been provided, with a focus on explaining and emphasizing the low-cost alternative adsorbents that may be used with these waste / low-cost materials (Gupta *et al.*, 2009).

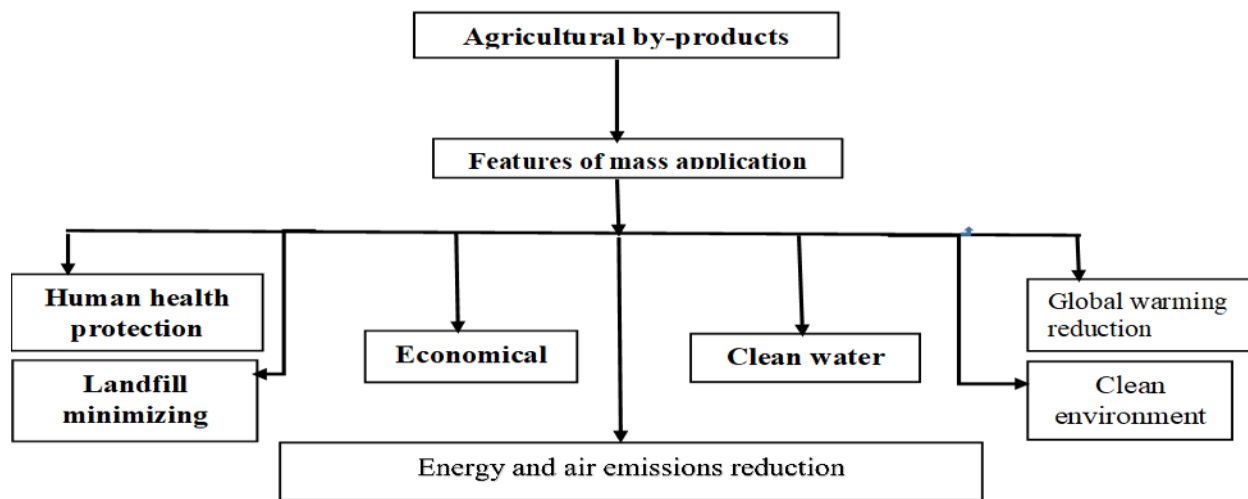
Therefore, numerous biological material such as wheat bran, rice husk, sawdust, okra waste, spent tea leaves, peanut husk, orange peels,...etc., are formed of principal formation of cellulose, starch, lignin .lipids, proteins and hemicelluloses that produce an effective adsorbent for heavy metals removal from wastewater (Esgair, 2018).

### **2.4.1. Low-cost adsorbent from agricultural waste**

So far, the majority of fruit and other food materials are produced and consumed globally, but a significant proportion of their wastes are still transported to open areas for burning or dumping, resulting in the release of toxic materials and pollutants, as well as carbon dioxide (CO<sub>2</sub>), into the environment. Recycling such wastes as raw materials for creating activated carbon might be a preferable choice for reducing landfill waste and environmental concerns associated with agricultural by-products/wastes while also saving money (Sulyman *et al.*, 2017).

As a result, agricultural and forest adsorbents serve as low-cost adsorbents, generating the most extensive renewable resources on the planet. Agriculture by-products are therefore one of the richest sources of low-cost adsorbents, as they comprise hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, all of which contain diverse functional groups (acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphhydryl groups). These groups can bind pollutant ions in wastewater solutions by donating an electron pair and forming complexes with them (Saka & Mas, 2012).

According to Dai *et al.*, (2018), oxygen functional groups in hemicellulose and cellulose, such as carbonyl groups, hydroxyl groups, and ether, can bind inorganic contaminants by chelating, completing, coordinating, hydrogen bonding, and other mechanisms, all of which are important in the preparation of adsorbents. Figure 3 depicts how agricultural by-product applications contribute to human health protection, economic growth, water purification, and global warming mitigation.



**Figure 3.** Representation of features of mass application derived from agricultural by-products /wastes (Rene *et al.*, 2007).

Recently, there has been a lot of focus on using natural, affordable, and eco-friendly sorbents to replace conventional and expensive sorbents from an economic and environmental standpoint. Activated Carbons are what they're called. The pyrolysis of carbonaceous materials from plants and agricultural residues/wastes, followed by either physical or chemical activation of the chars formed, is how these chemicals are primarily created and generated (Sulyman *et al.*, 2017). Environmentally friendly utilization of agricultural by-products/waste materials either as raw materials or in the production of so-called activated carbons (AC) is an important issue.

Referring from our literature review, the main factors characterizing Activated Carbons materials are their affordability, local availability (P20-21) and efficiencies in removing many unwanted toxins and pollutants they, therefore, could be utilized instead of more conventional but expensive adsorbent materials, particularly in developing countries especially in Mozambique where many industries lack appropriate individual sewage treatment systems; even where they exist, they lack satisfactory functioning and maintenance because of the lack of reasonable budgets (Sulyman *et al.*, 2017).



### 2.4.2. Adsorption performance of some non-conventional low-cost adsorbent

Non-traditional low-cost adsorbents for removing pollution chemicals should be capable of firing a wide range of heavy metals compounds. As a result, they must be tolerant to a variety of effluent characteristics. Every low-cost adsorbent has intrinsic advantages and drawbacks in wastewater treatment, regardless of where it is used. Their adsorption capabilities change as the experimental circumstances change (Amuda *et al.*, 2007).

Non-conventional adsorbents have the potential to be widely available, affordable, and effective adsorbents, according to Amuda *et al.* (2007). Agricultural by-products like nutshells, wood, bone, peat, coconut shells, okra wastes processed into activated carbons, and biomass like *Aspergillus Tereus Rhizopus arrhizus* have been reported to be important adsorbents for the removal of inorganic pollutants from municipal and industrial wastewater.

### 2.4.3. Okra agriculture waste description

Okra waste may be described as agricultural by-product which is made of  $\alpha$ - cellulose and protein (O. & E., 2014a). It is an important fruit vegetable crop grown worldwide. Moreover, okra is one of the most widely known and utilized species of the family Malvaceae (Ash *et al.*, 2019) and it is currently ranked as the second main fruit and vegetable produced in the world. It is rated as one of the important vegetables and is a native to Africa. This crop is mainly grown in tropical, subtropical, and warm temperate climates in different countries from Africa to Asia, Southern Europe, and America (Moses, 2020). Today, apart from Africa, the okra plant is successfully grown in the southern part of the USA, the Caribbean, South America, the Middle East, Greece, and Turkey. However, the okra plant is mainly produced in underdeveloped countries across the globe. According to the Fact fish database, total okra production was almost 10 million tons in 2017. That year, the top three okra producers were India, Nigeria, and Sudan. More than half of the ten biggest okra producers were from African countries (Yilmaz & Stawski, n.d.).



**Figure 4.** Picture of freshly harvested Okra (Yilmaz & Stawski, n.d.)

#### **2.4.3.1. Amount of okra wastes for heavy metals removal in wastewater from Petroleum Temane SASOL plant.**

According to the SASOL database, the Temane SASOL natural gas processing facility in Inhambane, Mozambique's southern region, produces a considerable volume of wastewater, over 60 m<sup>3</sup> each day. Because this amount of wastewater must be treated before being discharged into the environment, the amount of okra wastes from agricultural by-products must be illustrated in order to determine how much it will cost the government to remove heavy metals from wastewater produced by the Temane SASOL processing plant. In this work, heavy metals were removed from wastewater generated at the Temane SASOL natural gas processing facility using locally available okra waste purchased in Maputo.

This study reported that 3kg of okra materials generates 707.2g of okra powder once all okra adsorbent procedures are completed. In addition, the ideal removal efficiency revealed that 0.5 g of okra adsorbent is required to remove heavy metals from 0.015L of wastewater generated at the Temane SASOL facility. The question is to know the amount of okra wastes required to treat wastewater generated in the Temane Sasol facility during a one-year period. As previously indicated, SASOL's database reveals that the plant generates 2.19x10<sup>7</sup> dm<sup>3</sup> of wastewater over a one-year period. As a result, 7.3x10<sup>8</sup> g of okra adsorbent will be required to treat the quantity of wastewater produced by Temane SASOL in a year, according to the mass balance. The okra adsorbent was made from okra trash collected in Mozambique, yielding 7.3x10<sup>8</sup> g of okra adsorbent per year from 3,097 tons of okra wastes.

#### **2.4.3.2. Cost estimation for okra wastes produced in Mozambique**

The okra market in Mozambique shows the price of flesh okra, however, this research deals with the use of okra wastes produced from consumed flesh okras, unfortunately, the previous studies for the recycling of these okra wastes to be used as adsorbent were not yet studied in Mozambique, For this reason, the price of okra waste was estimated to be 10 meticaais per kilogram (10 MT/kg) this is approximately USD158.73 per ton of okra wastes. The cost of okra wastes required to treat wastewater from Temane SASOL plant over the course of a year is estimated to be over USD 491587 / 3097 tons of okra wastes.

This budget for okra waste over the course of a year is not excessive when compared to the cost might be required when using traditional adsorbents such as Activated alumina, Silica gel, Zeolite, and others, which are the most expensive owing to their operation, regeneration requirements, sewage treatment and technological design.

### 2.4.3.3. Local availability of okra waste

According to the agro-database and okra market in Mozambique, the quantity of okra harvested in 2020 was 1.18 million tons per year (1.18MT/Y). Referring to the literature, 10% of produced agro-products are wastes. Thus, 10% of flesh okras harvested in Mozambique are thrown away as okra wastes, as result 118,000 tons of okra wastes are produced each year. This means that okra materials are reasonable in Mozambique. Furthermore, the amount of okra materials needed for wastewater treatment at the Temane SASOL plant are enough and available in Mozambique. This is due to the fact that the amount of okra wastes required for wastewater treatment over the course of a year is quite little in comparison to the amount of okra wastes produced from flesh okras harvested in Mozambique on a seasonal basis. Therefore, agricultural by-product okra waste is a low-cost, readily available, and effective non-conventional adsorbent material for removing heavy metals from wastewater generated at the Temane SASOL facility.

**Table.3:** Summary of the amount and cost estimation for heavy metals removal from wastewater produced in Temane SASOL plant

| Amount   |  | Cost estimation             |               |
|--|--|-----------------------------|---------------|
| Okra wastes required in period of year (tons/year) | Amount of wastewater might be treated in year ( dm <sup>3</sup> /year) | Price / 1 ton of okra waste | Cost/ year    |
| 3,097  | 2.19×10 <sup>7</sup>   | USD158.73                   | USD<br>491587 |

## **2.5. Adsorbent preparation and activation**

### **2.5.1. Adsorbent Preparations**

Before being employed for heavy metals removal in wastewater samples, the okra adsorbent will be produced and modified as previously stated. These adsorbent materials adsorption capacity was raised as a result of the alteration. For example, numerous activation agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate), mineral and organic acid solutions (hydrochloric acid, phosphoric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycolic acid), organic chemicals (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agents (hydrogen peroxide) and dye (Reactive Orange 13), *etc* (Ali *et al.*, 2012).

Pyrolytic destruction of the precursor happens during carbonization, as does the simultaneous removal of several non-carbon molecules (H, N, O and S). Low molecular weight volatiles are emitted first, followed by light aromatics and hydrogen gas in this process. However, the end product is a carbonaceous char that is permanently deposited. The holes created during carbonization are filled with tarry pyrolysis leftovers that must be activated in order to develop the char's interior surface (Ali *et al.*, 2012).

The voids between the primary crystallites are unfilled during the activation phase by eliminating less structured loosely bound carbonaceous material. The porous structure with a large internal surface area is formed by the channels that run through the graphitic areas, the gaps between the primary crystallites, and fissures inside and parallel to the graphite planes (Rangabhashiyam *et al.*, 2013). High surface area, microporous structure, consistent pore size distribution, high porosity, high surface reactivity, 85 excellent mechanical strength, and great adsorption capacity are all advantages of activated carbon (Dai *et al.*, 2018).

### **2.5.2. Activation methods**

Activated carbon is the oldest known adsorbent and is often made from a variety of sources, including coal, coconut shells, okra farm waste, lignite, and wood, among others. As a result, it's critical to understand the various factors that influence Activated Carbon's adsorption capacity before modifying it, so that it can be designed to their unique physical and chemical properties to improve their affinity for metals, inorganic, and organic species present in aqueous solutions.

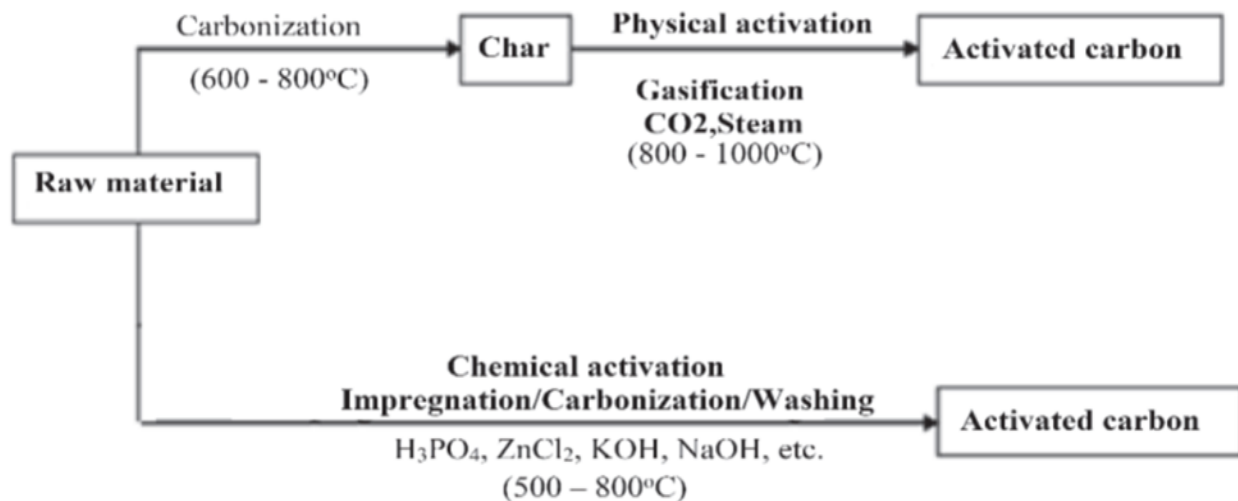
The following are some of these factors: Specific surface area, pore-size distribution, pore volume, and the presence of surface functional groups are all factors to consider (Sulyman *et al.*, 2017) , Therefore, activation may be accomplished via chemical or physical treatment methods.

✓ **Physical activation.**

This is a procedure in which the precursor is converted into activated carbons utilizing gases, and then the precursor is generally carbonized and activated. Carbonization is the initial stage, in which the precursor is pyrolyzed in an inert atmosphere (nitrogen, argon) at temperatures ranging from 600 to 900 degrees Celsius, resulting in the development of char, which is generally non-porous. The activation process involves exposing the material to oxidizing atmospheres (carbon dioxide, oxygen, or steam) at temperatures between 600 and 1200 degrees Celsius, which causes the more disorganized carbon to be removed and a well-developed porous structure to form, resulting in a high surface area (Gupta *et al.*, 2009).

✓ **Chemical activation.**

This procedure comprises impregnation with chemicals such as H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, KOH, or NaOH, followed by heating at temperatures ranging from 450 to 900 degrees Celsius under a gas (usually nitrogen) flow. In chemical activation, the carbonization and activation stages are thought to occur concurrently. Chemical activation is often chosen over physical activation since it requires a lower temperature and a shorter time to activate the material (Gupta *et al.*, 2009). Figure 5 depicts how each activation method is handled from the raw material to the manufacture of activated carbon .The top direction process denotes the physical activation technique, while the bottom direction process indicates the chemical activation approach.



**Figure 5.** The process of activated carbon manufacturing (Sulyman *et al.*, 2017).

## **2.6. Characterization of the adsorbent.**

To acquire microscopic insight on how PW pollutants adsorb, it's typically required to characterize the adsorbent system. A solid with a high adsorption capacity should have specific properties linked to the surface area of the adsorbent and an internal network of pores (Yousef & Qiblawey, 2020).

Some of the techniques used to characterize the adsorbent include BET surface area analysis, FTIR, XRD, SEM, EDAX, and others. The BET (Brunauer, Emmett, and Teller) surface area analyzer can determine the adsorbent's specific surface area. The adsorption capacity increases as the surface area increases. Before and after adsorption, the FTIR spectrum can disclose the different functional groups present on the adsorbent surface. One of the most extensively utilized diagnostic methods is scanning electron microscopy (SEM). It reveals whether the adsorbent's surface is heterogeneous or homogeneous, as well as the degree of porosity of the adsorbent for adsorbate entrapment.

The crystalline phase of the adsorbent will be determined by analyzing XRD patterns and diffraction peaks. Characterization of adsorbents includes determining the elemental composition (C, H, N, and O). The proximate analysis of the adsorbent includes the examination of moisture content, ash content, volatile matter content, and fixed carbon content (Gayatri & Ahmaruzzaman, 2010). The chemical composition and most functional groups found in okra wastes are shown in table 4, as well as the wave number ranges of bands that indicate the kind of each functional group present in okra waste.

**Table 4.** Chemical Analysis of dry okra wastes

| Chemical composition of okra  |      | Chemical groups present in okra       |                                     |
|-------------------------------|------|---------------------------------------|-------------------------------------|
| Compound                      | %    | Wave number of bonds $\text{cm}^{-1}$ | Chemical groups                     |
| CaO                           | 3.8  | 3700-3200                             | OH                                  |
| P <sub>2</sub> O <sub>5</sub> | 3.8  | 3000-2900                             | C-H                                 |
| MgO                           | 1.5  | 1800-1650                             | C=O                                 |
| Carbohydrate                  | 64.4 | 1620                                  | Aromatic ring                       |
| Fat                           | 2.3  | 1550-1500                             | N                                   |
| Protein                       | 18.9 | 1485-1440                             | CH <sub>2</sub> and CH <sub>3</sub> |
| Fibre                         | 7.6  | 1390-1360                             | CH <sub>3</sub>                     |
|                               |      | 1300-1200                             | C-O-C                               |
|                               |      | 1200-1000                             | C-O                                 |
|                               |      | 900-960                               | Cyclic comp                         |
|                               |      | 850-800                               | C=C                                 |
|                               |      | 800-700                               | Alkyl group                         |
|                               |      | 700-400                               | Sub-in-aromatic ring                |

## 2.7. Analytical methods description

### 2.7.1. Description

Heavy metals in water samples can be qualitatively examined using a variety of analytical procedures, including FAAS, ETAAS, ICP-OES, ICP-MS, anodic stripping, and, more recently, laser-induced breakdown spectroscopy (LIBS). The steps of an analysis are (i) representative sampling, (ii) to prevent analyte contamination, (iii) contamination from the environment, wares, and chemicals added to the sample, (iv) transfer the sample to the lab, (v) sample treatment before analysis (leaching, extraction, pre-concentration/separation of the analytes), (vi) choose the method while considering its limitations, (vii) calibration of the vessels, instrument, (viii) The rings of a chain consist of accurately preparing the sample, all solutions, and standards, (ix) testing the correctness of the procedure using Certified Reference Materials (CRM), and (x) statistically evaluating and reporting the findings. These stages are all necessary and can be a cause of mistake if not followed correctly (Baysal *et al.*, 2013).

The most crucial phase is sample preparation, which should be done promptly, conveniently and securely. Particulates or organic compounds may be present in wastewater samples, necessitating pre-treatment prior to spectrometric analysis.

The concentration of metals inorganically and biologically bonded, dissolved or particulate components should be determined to determine the overall metal content. To reduce interferences, the sample's organic matrix should be removed by digestion, and metal-containing compounds should be degraded to yield free metal ions, which may be measured more simply using atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP).

Wet digestion by acid mixes before elemental analysis, dry ashing followed by acid dissolution of the ash, and microwave-assisted digestion are the three methods for eliminating organic material and dissolving heavy metals (Baysal *et al.*, 2013). Table 5 contrasts two digesting procedures (wet and microwave) based on the circumstances that each approach employs throughout the application 4 as reported by Baysal *et al.*, (2013)

**Table 5.** Comparison of digestion techniques (Baysal *et al.*, 2013).

| <b>Conditions</b>              | <b>Wet digestion</b>         | <b>Microwave digestion</b>   |
|--------------------------------|------------------------------|------------------------------|
| Time consumption               | Slow                         | Rapid                        |
| Temperature                    | Low                          | High                         |
| Pressure                       | Atmospheric                  | Above atmospheric            |
| Operator skills                | High                         | Moderate                     |
| Safety                         | Corrosive-explosive reagents | Corrosive-explosive reagents |
| Operating cost                 | Low                          | High                         |
| Environmental effect           | High                         | Low                          |
| Analyte loss and contamination | High                         | Low                          |

### **2.7.2. Inductively Coupled Plasma Optical Emission Spectrometry.**

ICP-OES or ICP-AES (inductively coupled plasma-optical (or atomic) emission spectrometry) is an analytical method for determining trace metals. A plasma source is used to excite the atoms in samples in this multi-element approach. These excited atoms produce light of a certain wavelength, which is measured by a detector, and the intensity of the emitted light is proportional to the concentration (Baysal *et al.*, 2013).



### ✓ **Advantages of ICP-OES**

To atomize effectively, samples are heated to 10000°C, which is required for the ICP method. Multi-element analysis is another benefit. With the ICP method, 60 elements can be evaluated in less than a minute or a few minutes consecutively in a single sample run. Aside from that, the equipment is only optimized for one set of metal analysis at a time. Interferences are reduced when the working temperature is high. Because background interferences are minimized, ICP-OES assures reliable results (Baysal *et al.*, 2013).

### ✓ **Limitations of icp-oes**

Refractory elements may be measured at low concentrations, and measurements can be made over a large linear range (B, P, W, Zr and U). Inert gas consumption, on the other hand, is substantially higher than AAS procedures, resulting in high operational expenses. Depending on the plasma arrangement, ICP equipment can be 'axial' or 'radial.' The plasma source is observed from the side in the radial arrangement. Because axial plasma emissions are examined horizontally over its length, background signals are reduced, resulting in lower detection limits. Both viewing modes are available on some instruments. (Baysal *et al.*, 2013).

### ✓ **ICP-OES operating conditions**

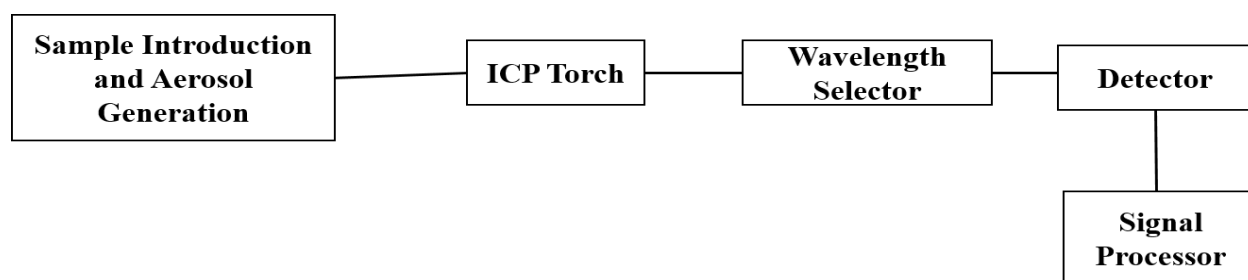
Dimpe *et al* ( 2015) and Didukh-Shadrina *et al* ( 2019) stated the ICP-OES conditions include :The ICP-OES system's RF power (Kw), Plasma gas flow (L min-1), Auxiliary Ar (L min-1), Nebulizer Ar (L min-), Pump rate (mL min-1), Readings / replicate, and Wavelength (nm) were used during the identification and quantification of heavy metals in the extracted wastewater. The following table 6 shows the amount required for each condition:

**Table 6.** Wavelengths and operating conditions used for ICP-OES determination of heavy metals.

| Conditions                            | Amount   |
|---------------------------------------|--|
| RF power ,Kw                          | 1.3  |
| Plasma gas flow , L min <sup>-1</sup> | 15   |
| Auxiliary Ar , L min <sup>-1</sup>    | 0.2  |
| Nebulizer Ar , L min <sup>-1</sup>    | 0.8  |
| Pump rate , mL min <sup>-1</sup>      | 1.5  |
| Readings / replicate                  | 3  |
| Wavelength , nm                       | Cu:324.752, Fe:238.2014, Co:238.892, Ni:231.604,<br>Al:308.215 , Zn:213.857 , Pb:220.353 ,Mn:257.610 and<br>Cr:267.709 |

### ✓ Components of ICP-OES instrument

The ICP-OES instrument is made up of five primary components, which are listed below: a) Aerosol Generation part is where the liquid sample introduced in Nebulizer has been converted into an aerosol that can be transported to the plasma, b) ICP torch is designed to extend the capability of the instrument while providing optimized performance and ease of use ,c) Wavelength Selector is used to select the optimal wavelength that exhibit suitable intensities and that are also free from spectral interferences, d) Detector is used to measure the intensity of the light emissions and e) Signal Processor is a computer with software for calculation and display of emissions spectra and concentration values. The figure 6 shows a typical ICP-OES instrument as described by Didukh-Shadrina *et al* (2019).



**Figure 6.** Block diagram of ICP-OES (Didukh-Shadrina *et al.* 2019).

## CHAPTER III

### RESEARCH METHODS AND STRATEGIES

#### 3.1. Introduction to methods and strategies

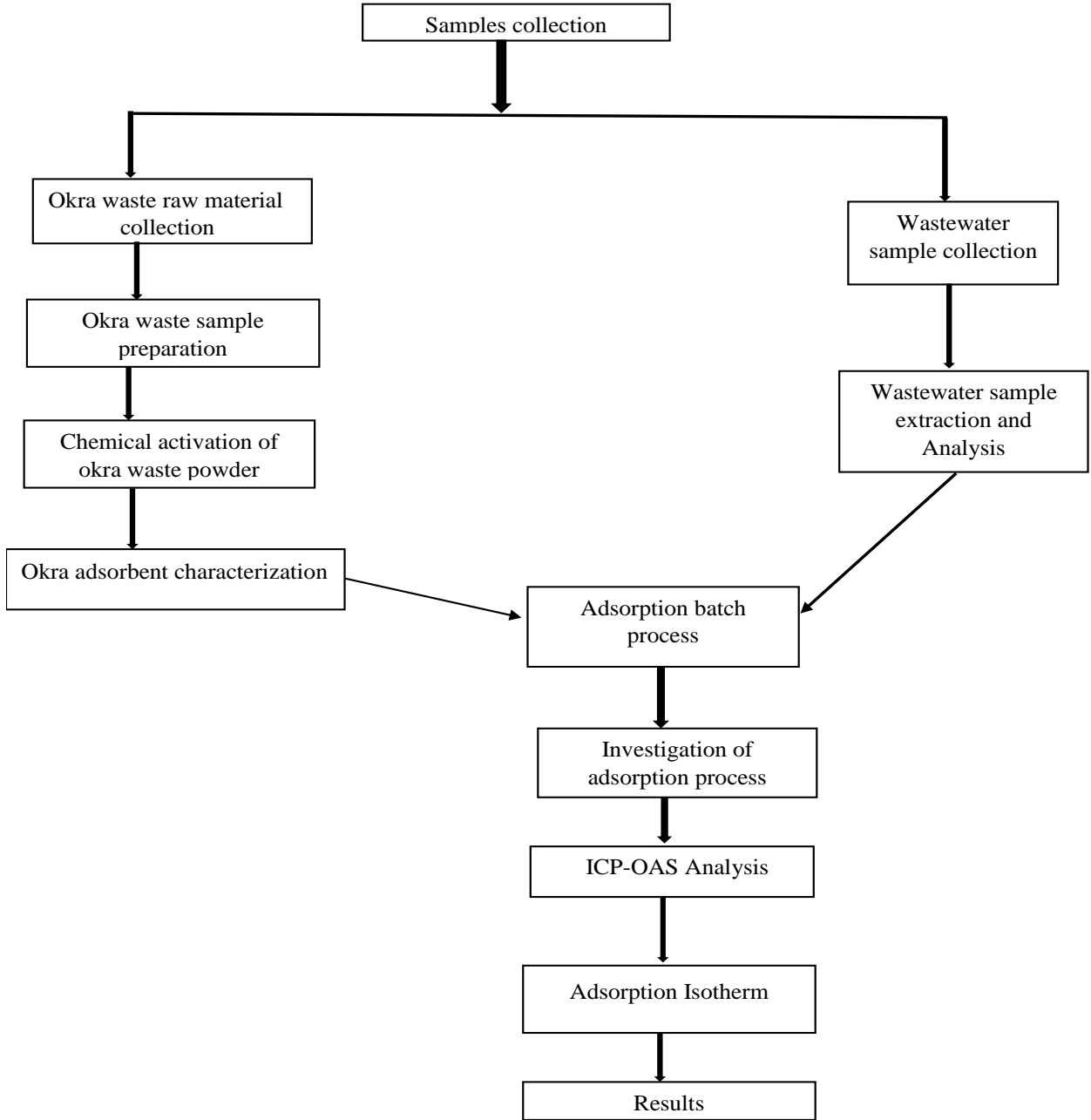
The goal of this chapter is to go through some of the most well-known analytical methods for detecting, quantifying, and monitoring heavy metals in wastewater. The phrase "total heavy metals" (THM) refers to the overall amount of heavy metals found in the environment, particularly in wastewater from natural gas extraction. As a result, the THM data obtained is dependent on the analytical method utilized (Tytła, 2019). Heavy metal concentrations were measured using inductively coupled plasma optical spectrometry (ICP-OES) (Ida & Eva, 2021). As a result, knowing how the determination was achieved is required for interpretation of analytical data (Zhang *et al.*, 2013).

The materials, chemicals, and processes utilized to adsorb heavy metals from wastewater in natural gas production onto okra adsorbent are described in this chapter. The research was carried out at the chemical engineering and chemistry departments of Eduardo Mondlane University in Mozambique. The experimental area is in Maputo, Mozambique, and is located at 18.6677° S, 35.5296° E on Africa's Southeast coast.

All of the chemical reagents employed in this research were analytical grade, such as deionized water, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), and nitric acid (HNO<sub>3</sub>), which were all found at the UEM, chemical engineering, and chemistry departments' laboratories and they were utilized immediately without any further purifications.

### 3.2. Study design

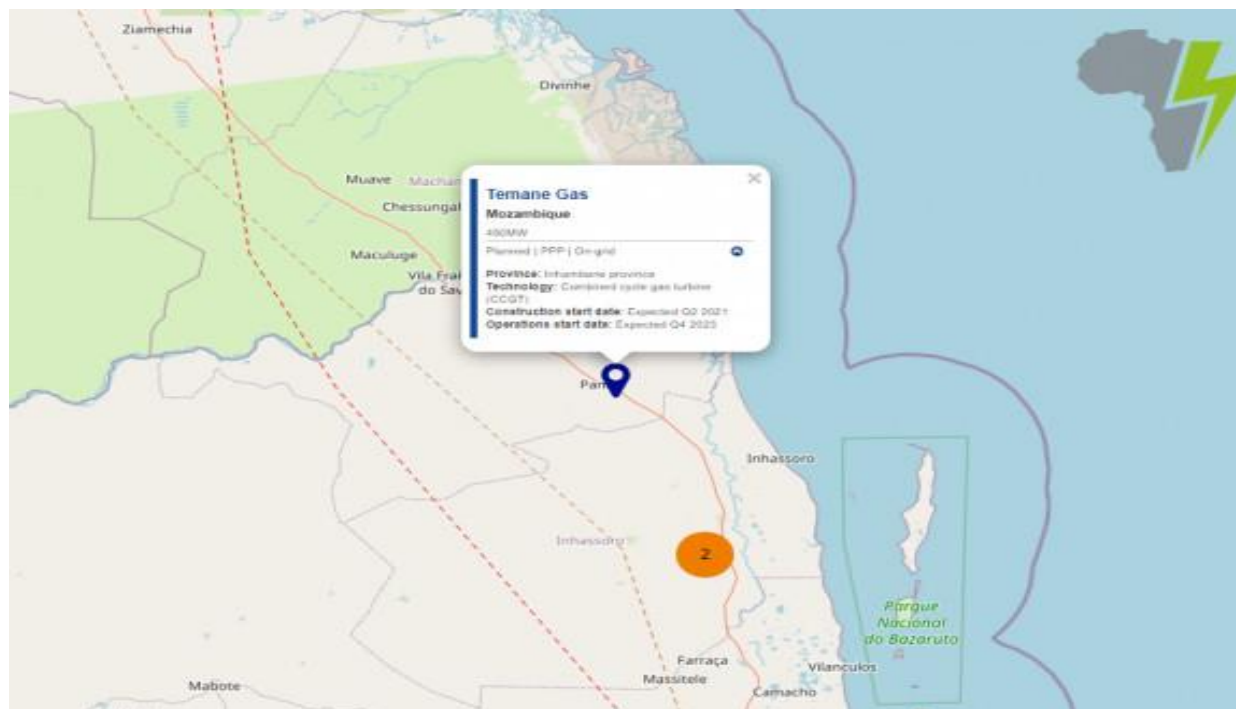
This research was carried out step wise. Figure 7 shows all of the experimental stages that this study went through, from sample collection through ICP-OES instrument analysis.



**Figure 7.** Experimental design of the study.

### 3.2.1. Samples collection

There were two types of raw materials samples utilized in this study: okra waste raw materials and wastewater samples. Okra plant producers in Mozambique, Maputo area, and various agricultural food concern marketplaces in Maputo gathered raw okra wastes originating from agricultural by-products. Wastewater samples were taken from the Petroleum Temane SASOL facility in Inhambane, Mozambique's southern region.



**Figure 8.** A map showing the study area (Maputo & Petroleum Temane SASOL plant location).

### 3.2.2. Okra waste sample preparation

The collected okra wastes from agricultural by-products source were sorted, cleaned; seeds were removed and cut into small pieces to facilitate the drying process. The pieces were dried at 110 °C in an oven to reduce humidity for 6 hours to remove moisture and other volatile impurities (Chen *et al.*, 2015). After that, it was grinded with a laboratory milling ball at 200–300 r/min for 5–6 h to reduce the size of particles so that they become less than or equal to 1 mm. The okra waste powder was sieved into four different particle sizes include 0.125 mm, 0.25 mm, 0.5 mm and 1mm particle size (Geetha & Belagali, 2013).

### **3.2.3. Okra adsorbent activation**

The okra adsorbent has to be activated before it could be utilized to remove heavy metals from wastewater samples. Activation enhances the adsorption capacity of adsorbent materials in general. As previously discussed in the literature, there are several approaches for alteration.

In this study, chemical activation of okra adsorbent was processed to increase the surface area of okra adsorbent for better adsorption, wherever the impregnation of the powdered okra waste was performed out using phosphoric acid ( $H_3PO_4$ ) as the impregnating agent. The okra powder was impregnated at a rate of 4: 1 (v / m), respectively. And then, the acid-treated adsorbent was dried for 4 hours at 105 ° C; After drying, it was cooled and washed with distilled water to remove different residual organic and mineral matter, and was dried in an oven at 110°C for 24 h and finally, samples were packed in an airtight container, and the adsorbent was ready for use.

### **3.2.4. Characterization of okra adsorbent**

Characteristics of okra waste activated carbon such as physical structure (e.g. particle size, specific surface area, porosity), chemical nature and functional groups (e.g. surface charge, pH at the point of zero control), and mechanical properties were studied. As a result, the prepared okra adsorbents were characterized with Fourier Transform Infrared (FTIR), which provided better information on the quality of the functional groups available on the surface of the okra adsorbent.

### **3.2.5. Wastewater samples extraction and analysis**

Typically, water sample preparation is essential for PWW analysis. This step was performed due to several goals described as following: To concentrate or dilute target analytes (heavy metals) to meet the capability of analytical instrumentation and to remove materials in the matrix that might interfere with the chromatographic separation, ionization, or detection of target analytes. For instance, inorganic analysis, which is the concern, these goals are usually met by removing particles and diluting the sample to meet instrument performance(Jiang *et al.*, 2021). After completion of the sequential wastewater extraction procedure, the residual heavy metal contents were determined. The concentrations of heavy metals in wastewater extracts were analyzed with inductively coupled plasma optical spectrometry (Avio 200 ICP-OES, PerkinElmer Inc., Waltham, MA, USA) wherever, the experiments were performed in duplicate.

### 3.2.5.1. Sample digestion procedures

Closed digestion methods concerning various acid mixtures were conducted using a hot plate. The acid digestion procedures were investigated to determine their reliability in extracting six heavy metals ions (Cd, Cu, Pb, Zn, Ag and Ba) in the influent wastewater sample spiked with SRM (either CWW-TM-A or CWW-TM-B). The acid digestion mixture HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> was tested with slight modification with both hot plate and conventional microwave methods. Thus, the filtration was made using the cellulose-acetate filter paper and the syringe acrodisc filter (0.45 μm) and finally analyzed with ICP-OES (Dimpe *et al.*, 2015). The samples were digested in triplicate for each procedure to quantify the closeness (precision) of the results obtained under the same conditions. The blank solutions, with identical reagents, subjected to the same treatment as the reference material were prepared before contact with okra adsorbent. The concentrations of heavy metals in blank solutions were considered initial concentrations of heavy metals in wastewater.

### 3.2.5.2. Hot plate digestion

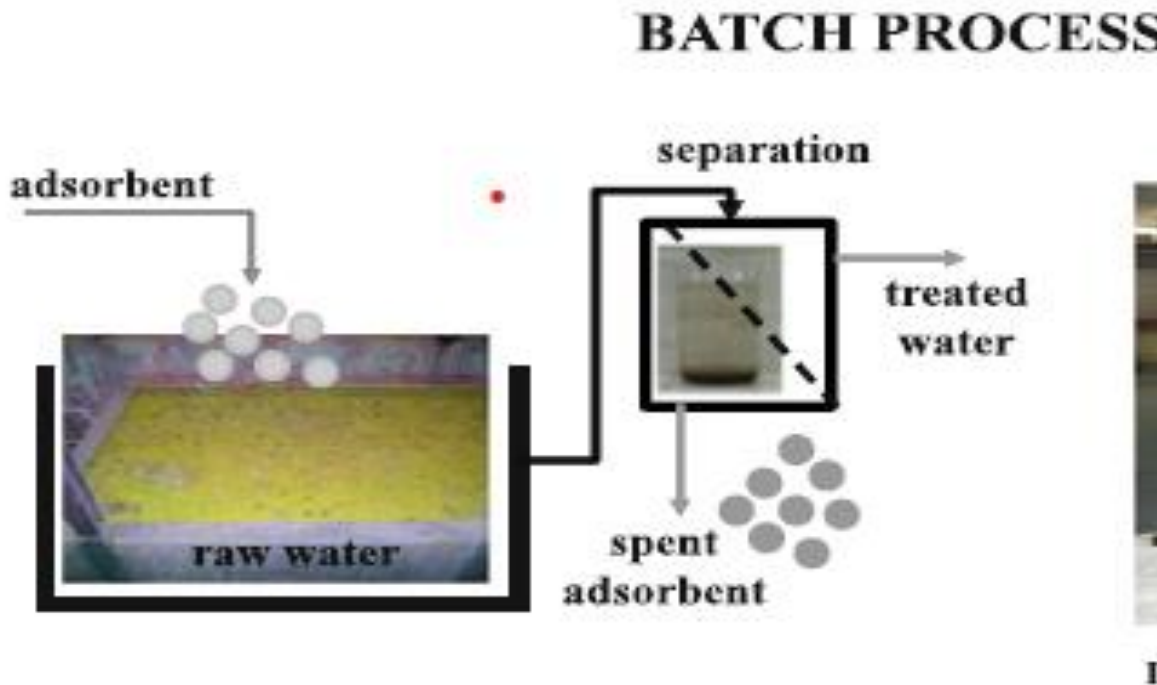
As previously described, the acid mixture of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> method was used for hot plate digestion. In this study, the sample to be digested was in an aqueous form; wet digestion was performed for both blank and adsorbed wastewater samples. The temperature was maintained at 120°C for 2 h during digestion of wastewater test sample with 16 mL (12 mL HNO<sub>3</sub> and 4 mL H<sub>2</sub>O<sub>2</sub>) of 6:2 HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> mixtures on the hot plate. After cooling the sample, 10 mL of deionized water was added to the sample and mixed thoroughly. The inclusion of H<sub>2</sub>O<sub>2</sub> in this method was made to enhance the destruction of organic matter. After digestion, the solutions were filtered with the cellulose-acetate filter paper and the syringe acrodisc filter (0.45 μm), then transferred into a 100 mL volumetric flask and diluted to the mark with deionized water (Dimpe *et al.*, 2015).



**Figure 9.** Mixture of waste water sample with HNO<sub>3</sub> / H<sub>2</sub>O<sub>2</sub> solution on the Hot Plate

### 3.2.6. Adsorption batch process

In the present research, the Adsorption batch process was conducted to investigate the adsorption efficiency of okra adsorbent for heavy metals in wastewater from the Petroleum Temane SASOL plant. The batch adsorption method was preferred on the laboratory scale because, apart from their simplicity and ease of operation, it is limited to treating small volumes of solution. (Desta, 2013). The batch method is also widely used because this technology is cheap and operates and, consequently often favored for small and medium-size process applications using simple and readily available mixing tank equipment. Simplicity, well-established experimental methods, and easily interpretable results are the main reasons frequently evoked for the extensive use of these methods. Another attractive advantage is that, in batch systems, the parameters of the solution/effluent, such as contact time, pH, strength ionic, temperature, etc., can be controlled and adjusted (Desta, 2013).



**Figure 10:** Adsorption batch process



### 3.2.7. Investigation of adsorption batch process

The adsorption of heavy metal ions by okra adsorbents was evaluated under various conditions such as agitation speed, contact time, particle size and amount of adsorbent through isotherm studies. The effect of changing those parameters mentioned above was carried out include : Effect of agitation speed, the effect of contact time, effect of particle size and impact of adsorbent amount. In this study, the adsorption batch process was performed by varying four at a constant temperature of 60°C: The agitation speed was changed from 500 to 1500 revolutions per minute (rpm). Varying contact times of 30, 60, 90 min and the amount of okra adsorbent varied between 0.25g to 1.5g and adsorbent particle size of 0.125, 0.250 and 0.500 1.00 mm, respectively. Moreover, the influence of any mentioned above variables for the adsorption efficiency was varied gradually while keeping the other variables constant to obtain the maximum removal percent of heavy metals in wastewater by okra adsorbent (O. & E., 2014b).

After each adsorption batch process at different variable change, the wastewater samples were removed from the spent adsorbent with a micropipette after reaching the desired contact time; The samples were filtered then, proceeded to the wet sample's digestion process following the steps which were previously described, figure 14 shows the filtered solution obtained after an adsorption process and the residual metal concentration at equilibrium ( $C_e$  (mg / L) was measured using ICP-OES.



**Figure 11.** Filtration of waste water samples from the spent adsorbent after each parameter variation.

### 3.2.8. Inductively coupled plasma – optical emission spectrometry (ICP-OES) analysis.

Generally, the inductively Coupled Plasma-Optical (or atomic) Emission Spectrometry (ICP-OES or ICP-AES) is an analytical technique used to quantify trace metals. This method was preferred because is a multi-element technique uses a plasma source to excite the atoms in samples, wherever samples are heated through 10000 °C to atomize effectively, which is an essential advantage for the ICP technique compared to other methods. ICP-OES also ensures accurate data due to the minimization of background interferences. The operating conditions on the ICP-OES spectrometer during the measurements were as follows. RF power: 1400 W, Plasma argon flow rate: 13 L min<sup>-1</sup>, Auxiliary argon flow rate: 2.00 L min<sup>-1</sup>, and Nebulizer argon flow rate: 0.95 L min<sup>-1</sup>. The analytical lines were chosen: Cd 226.438 nm, Cu 213.598 nm, Pb 216.999nm and Zn 202.548 nm (Dimpe *et al.*, 2015). Therefore, this study has used it to determine the concentration of heavy metals ions such as Cu, Pb, Cu, Zn, Ag and Ba in wastewater samples.

## 3.3. Adsorption Isotherm

### 3.3.1. Description of Adsorption Isotherm

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase since the adsorption isotherms are essential to describe how adsorbents will interact with the adsorbents and so are critical for design purposes; therefore, the correlation of equilibrium data using an equation is necessary for practical adsorption operation (Abdel & Reiad, 2011).

In addition, Desta (2013) described an adsorption isotherm as a graphical representation showing the relationship between the amount adsorbed by a unit weight of okra adsorbents and the amount of adsorbate remaining in a test medium at equilibrium, and it shows the distribution of an absorbable solute between the liquid and solid phases at various equilibrium concentrations. For the calculation of removal efficiency (%) of okra waste adsorbent and the amount of Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, zn<sup>2+</sup>, Ag<sup>2+</sup> and Ba<sup>2+</sup> ions sorption at equilibrium ( $q_e$ , mg/g), the following equation were used (Khaskheli *et al.*, 2016).

$$RE(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (3)$$

Where  $C_i$  (mg/l) denotes the initial concentration of heavy metals, and (mg/l) is the effluent concentration. The experiments were carried out in duplicate to ensure the reproducibility of the findings; then, the mean of two measurements was calculated. The equilibrium isotherm was demonstrated by the plot of equilibrium adsorption potentials. The adsorption capacity was calculated using the equation described above.

$$q_e = \frac{C_i - C_e}{\frac{m}{v}} \quad (4)$$

These relationships depend on the type of adsorption that occurs; multilayer, chemical or physical adsorption. Where  $q_e$ : Adsorption capacity at equilibrium (mg of ions/g of okra adsorbent),  $C_i$ : initial concentration of metal ions in solution (mg/L),  $C_e$ : equilibrium concentration of metal ions in solution (mg/L),  $m$ : dry weight adsorbent (g),  $V$ : volume of wastewater solution (L) (Matouq et al., 2018).

### 3.3.2. Langmuir isotherm equation

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The Langmuir equation assumes that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface due to the high  $R^2$  values (0.96–0.99) and nearly perfect fitting using both regression forms as shown by the following equations (Abdel & Reiad, 2011).

$$Q_e = \frac{bQ_m C_e}{1 + bC_e} \quad (5)$$

and in linearized form is:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{bQ_{max}} \quad (6)$$

Where  $C_e$  is the equilibrium concentration (mg/l),  $q_e$  is the adsorption capacity (mg/g) and  $Q_{max}$  is the maximum adsorption capacity (mg/g) and  $K_L$  or  $b$  is the energy of adsorption about the heat of adsorption (L/mg), respectively.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1. Introduction to results and discussion

This chapter presents and discusses the main results concerning the efficiency of okra adsorbent for Cadmium, Copper, Lead, Zinc, Silver and Barium heavy metals removal in wastewater from natural gas production under process, which was clearly explained in previous chapters. The results described are obtained from the characterization of okra adsorbent by FTIR, Effect of the adsorption parameters (agitation speed, contact time, adsorbent dose and particle size) and adsorption isotherm model on okra adsorbent for those heavy metals removal in wastewater.

#### 4.2. Okra adsorbent characterization using FTIR

Characteristics of okra waste activated carbon such as physical structure (e.g. particle size, specific surface area, porosity), chemical nature and functional groups (e.g. surface charge, pH at the point of zero charges), and mechanical properties have been studied. The FTIR is a spectroscopic method used to collect information about a possible interaction between the metals ions and the functional groups present in the okra sorbent. FTIR analyses were performed on both okra powder and okra activated carbon, and results are depicted in Figure 12.

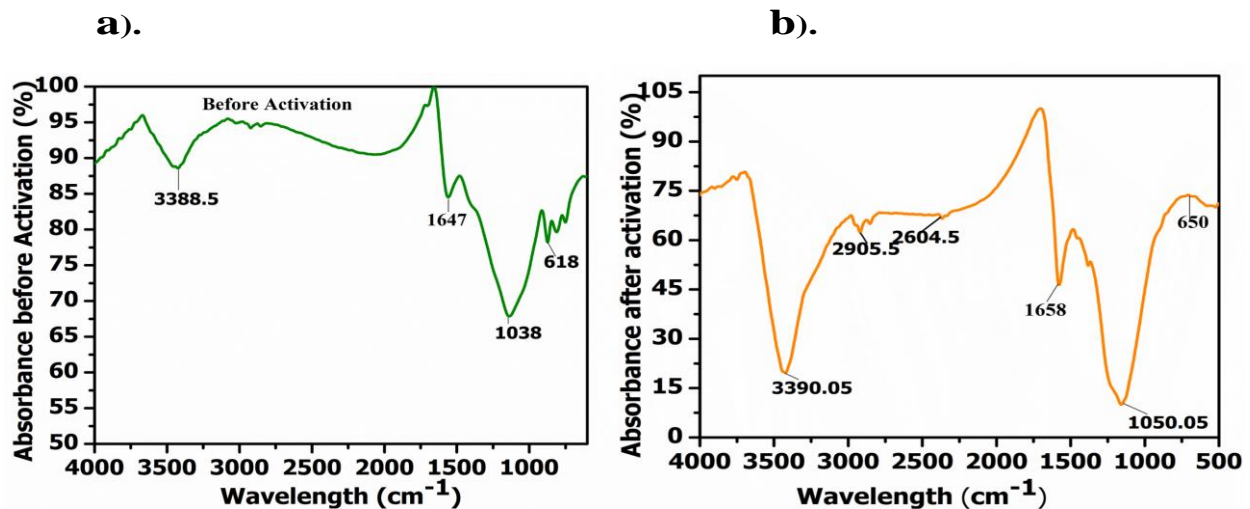


Figure 12. Infrared spectrum of okra a) before activation b) after activation with phosphoric acid

The performance of activated carbons from okra wastes was studied using the FTIR spectrum, and the findings are displayed in Figure 12. The primary goal of the FTIR research was to discover functional groups as part of the characterization of okra before and after phosphoric acid activation. The FTIR spectra for okra powder shows peaks at  $3388.5\text{ cm}^{-1}$ ,  $1647\text{ cm}^{-1}$ ,  $1038\text{ cm}^{-1}$  and  $618\text{ cm}^{-1}$ , which were identified as Hydroxyl(OH), Amino(N-H), Carboxyl(C-O-C,C=O), and M-O groups respectively, as shown in Figure 12.a). Nevertheless, as shown in Figure 12.b), the peak spectra of okra activated carbon were  $3390.05\text{ cm}^{-1}$ ,  $2905.5\text{ cm}^{-1}$ ,  $1640\text{-}1658\text{ cm}^{-1}$ ,  $1050.05\text{ cm}^{-1}$  and  $650\text{ cm}^{-1}$ , which were attributed to the O-H , N-H , C-O-C , C=O , C-O and M-O groups respectively. The activated carbon material prepared by  $\text{H}_3\text{PO}_4$  activation reveals more functional groups than the okra powder before activation, according to the infrared spectrum peak height comparison, because  $\text{H}_3\text{PO}_4$  increases the oxygen-containing groups on the surface of okra powder during carbonization, and this is also due to the elimination of part of the volatile matter present, making the adsorbent better for the adsorption of metals ions.

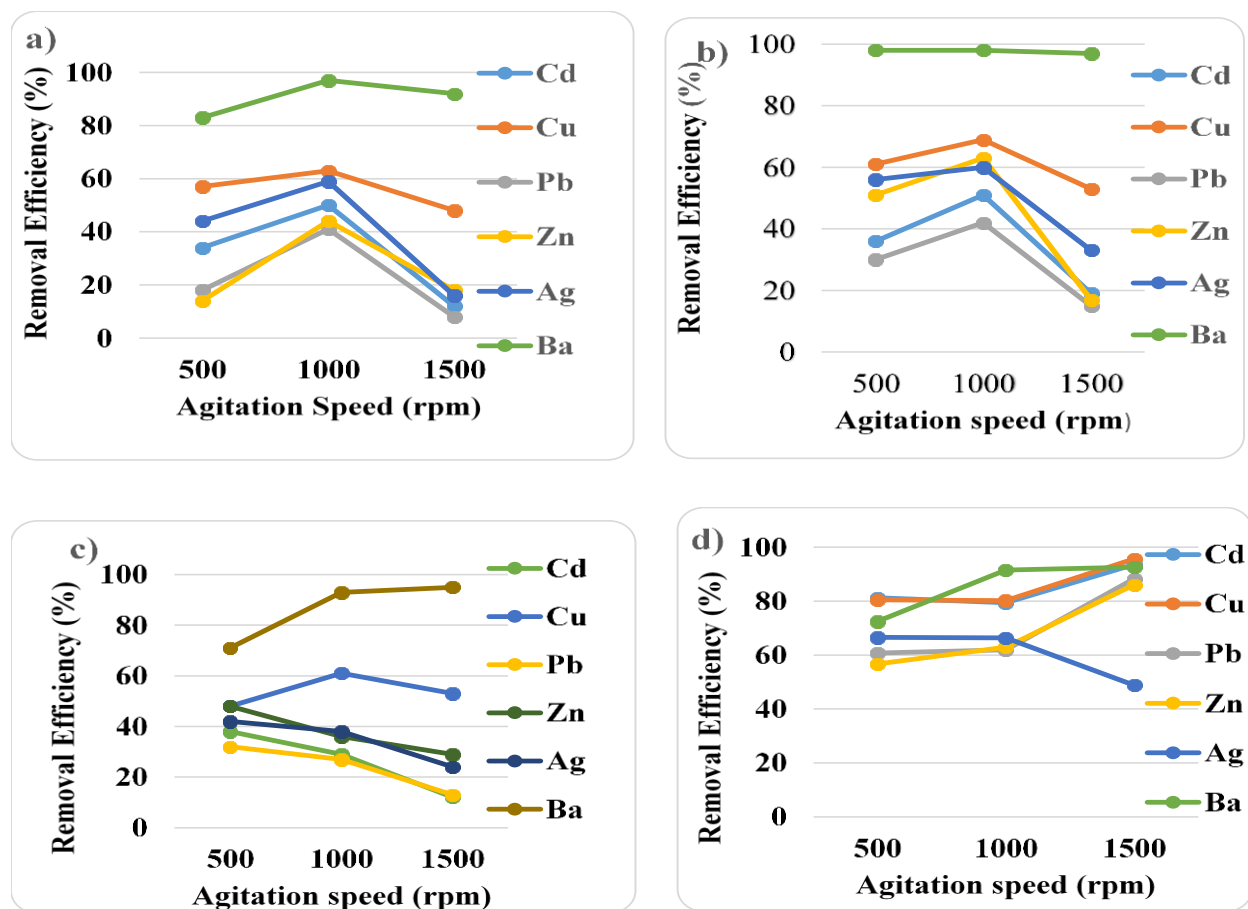
The functional groups on the surface of these materials increase the affinity to the heavy metals, wherever, these metals ions are all positive charge, while the functional groups present in the okra showed negative charge due to a pair of electrons in the oxygen atoms and nitrogen. Lone pair of electrons on oxygen and nitrogen atoms supplies electrons to the electron-deficient positively charged metals, which made adsorption by okra waste possible; hence positively charged metals of Cadmium, Copper, Lead, Zinc, Silver and Barium ions could be removed.

#### **4.3. Effects of adsorption parameters on Cd, Cu, Pb, Zn, Ag and Ba metals ions removal onto four different Okra adsorbent particle sizes.**

The initial concentrations for Cd, Cu, Pb, Zn, Ag and Ba metal ions in wastewater are 125 mg/l, 1001 mg/l, 1600 mg/l, 1000 mg/l, 125 mg/l and 2375 mg/l respectively, in the blank solution. By varying four adsorption parameters such as agitation speed, contact time, amount of adsorbent, and okra particle size, the equilibrium concentration and removal percentage of each metal ion onto four different okra adsorbent particle sizes of 0.125 mm, 0.250 mm, 0.500 mm and 1.00 mm were obtained. In reality, the number of parameters performed were insufficient to determine their impact on the removal efficiency of heavy metals from wastewater. Only a few parameter variations were employed because the amount of wastewater sampled in Temane natural gas processing plant was not large enough to prepare a large number of test solutions.

### 4.3.1. Effect of agitation speed

The influence of agitation speed on the removal percent of cadmium, copper, lead, zinc, Silver and Barium ions onto four different okra waste particle sizes were investigated at variant agitation speed 500 , 1000 , 1500 revolution per minute and the results offered in figure (13).



**Figure 13.** Effect of agitation speed for Cd, Cu, Pb, Zn, Ag and Ba ions removal percent onto okra adsorbent **a)** with 0.125 mm, **b)** with 0.250mm, **c)** with 0.500mm and **d)** with 1.00mm.

The experimental results show that the removal percent of cadmium, copper, lead, zinc, silver, and Barium ions increased to the maximum shaking speed. For cadmium, copper, lead, zinc, silver, and Barium ions, the removal percent was 34, 57, 18, 14, 44 and 83% respectively, at 500 revolutions per minute. It increased to 50, 63, 41, 44, 59 and 97% respectively at 1000 revolutions per minute (rpm). The removal percent decreased to 12, 48, 8, 18, 16 and 92%, respectively, at 1500 revolutions per minute (rpm) when using okra adsorbent with particle size 0.125 mm, as shown in figure 13. a).

Figure **13. b)** Shows the effect of agitation speed on Cd, Cu, Pb, Zn, Ag and Ba ions using okra adsorbent with particle size 0.250 mm. The results show that the removal percent are 36 ,61 ,30 ,51 ,56 and 98 % respectively at 500 revolution per minute and increased to 51 ,69 ,42 ,63 ,60 and 98 % respectively at 1000 revolution per minute wherever decrease to 19, 53 ,15 ,17 ,33 and 97 % respectively at 1500 revolution per minute (rpm).

The effect of agitation speed on Cd, Cu , Pb, Zn, Ag, and Ba ions using okra adsorbent with particle size 0.500 mm is shown in figure **13. c)** wherever the removal percent are 38 ,48 ,52 ,48 ,42 and 71 % respectively at 500 revolutions per minute(rpm) and decrease to 29 , 61 , 27 , 36 , 38% for Cd, Cu, Pb, Zn, Ag ions respectively and increases from 71 to 93% for Ba ion respectively at 1000 revolution per minute (rpm) wherever decrease more to 12 , 53 , 13 , 29 , 24 for Cd, Cu , Pb ,Zn, Ag ions respectively and increases from 93 to 95% for Ba ion at 1500 revolution per minute(rpm).

Figure **13.d)** shows the effect of agitation speed on Cd, Cu, Pb, Zn, Ag, and Ba ions using okra adsorbent with particle size 1.00 mm, and the results show that removal percent are 81 , 81 , 61 ,57 , 67 and 72 % respectively at 500 revolutions per minute (rpm) and increased to 79, 80, 66 % for Cd, Cu Ag ions respectively and increase to 62 , 63 and 91% for Pb, Zn, Ba ions respectively at 1000 revolution per minute (rpm) wherever increase to 94 , 96 , 88 , 86 and 93 % for Cd, Cu, Pb, Zn and Ba ions and decrease to 49% for Ag ion at 1500 revolution per minute (rpm). This impact of agitation speed may be explained as follows: Increasing agitation speed increases the mobility of Cd, Cu, Pb, Zn, Ag and Ba ions which causes increases the diffusion coefficients subsequently increase the mass transfer rate of Cd, Cu, Pb, Zn, Ag and Ba ions to the surface of okra waste adsorbent with a large particle size which increases the removal percent with increasing shaking speed.

After that, the increasing of agitation speed from 500 to 1000 revolutions per minute (rpm), the removal percent are generally decreased due to the fracturing of the bonding between the Cd, Cu, Pb, Zn, Ag and Ba ions and the surface site of okra adsorbent which causes desorbing the Cd, Cu, Pb, Zn, Ag and Ba ions from the surface site. Moreover, the higher agitation speed distributes the adsorbent particles in the solution and adsorption time will not be adequate for giving the adsorbent a chance to bind metal ions (Esgair, 2018).

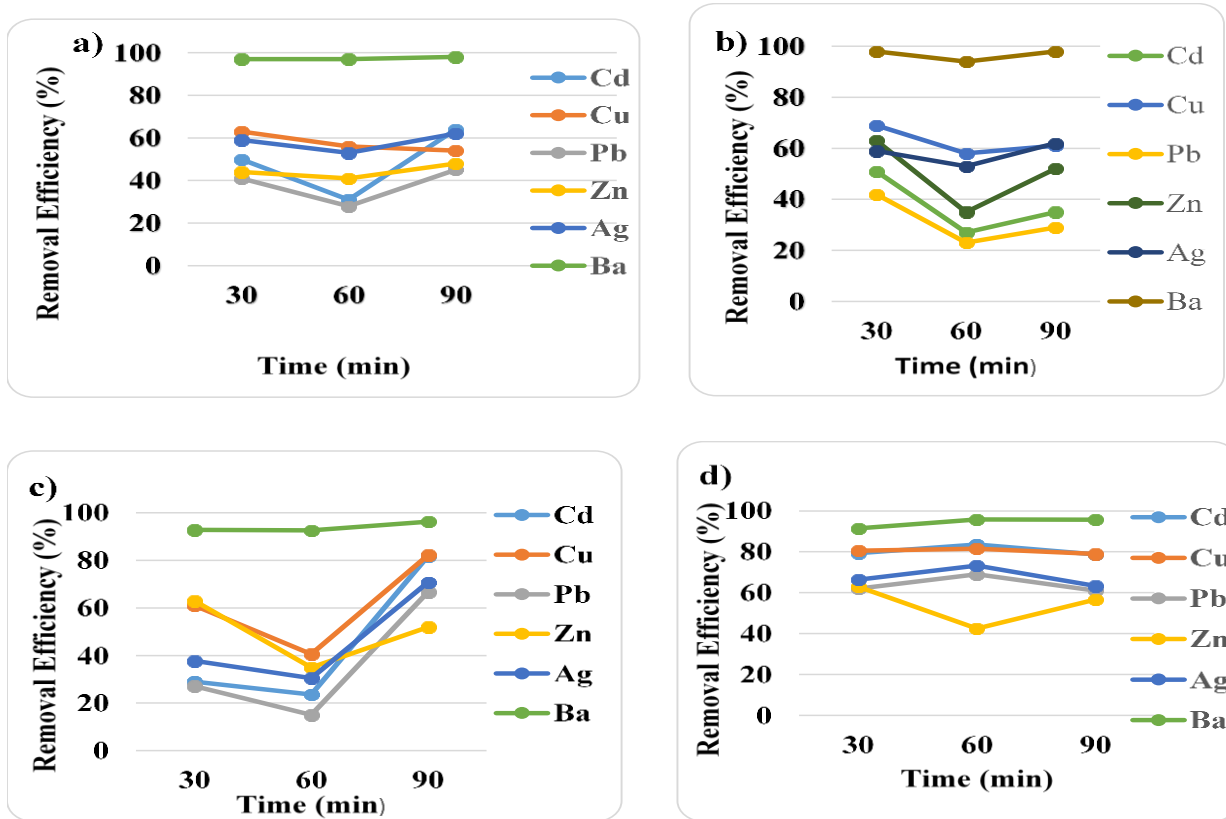
Therefore, an enhanced probably physical adsorption is occurring rather than chemical adsorption. However, the agitation speed of 1000 revolutions per minute (rpm) using okra adsorbent with 1.00 mm particle is highly preferred due to its high removal efficiency for Cd, Cu, and Pb, Zn, Ag and Ba ions removal from wastewater.

A similar trend was reported by Esgair, (2018) who studied the effect of agitation speed of okra agricultural waste compared with wheat bran on adsorption of cadmium and copper ions from wastewater. In the range of 50-250 rpm, the results showed that the adsorption percentage cadmium and copper ions was 45.8 and 23.4 at 50 revolutions per minute and increased to 59.6 and 34.7 respectively at 150 revolutions per minute when using okra waste and the shaking speed 150 revolutions per minute has been recommended as the best for cadmium and copper ions removal from wastewater by using wheat bran and okra waste. These results trends are also supported by the previous work done by Khaskheli et al., (2016) who studied the Removal of Cr(III) and Cr(VI) from Contaminated water using okra Leaves—Agricultural waste, and the results showed that the trend of sorption of both chromium species (Cr(III) and Cr(VI)) are increased up to 200rpm (~20%) and then decreased at high shaking. These results are also in the same line with the results found by Length (2018) in his study to study equilibrium, kinetic and thermodynamic of biosorption of zinc ions from industrial wastewater use derived composite bio sorbents from the walnut shell, where he found that the removal efficiency of Zn (II) ions using the four prepared adsorbents increased as the agitation speed increased until the optimum value and then decreased when the agitation speed further increased.



### 4.3.2. Effect of contact time

The removal percent of cadmium, copper, lead, zinc, Silver and Barium ions from wastewater was investigated in the adsorption batch process at different contact times from 30 to 90 min. The relationship between removal percent of cadmium, copper, lead, zinc, Silver and Barium ions on four different okra particle sizes and adsorbed time shows in figure (14).



**Figure 14.** Effect of contact time for Cd, Cu, Pb, Zn, Ag and Ba ions removal percent onto okra adsorbent **a)** with 0.125 mm, **b)** with 0.250mm, **c)** with 0.500mm and **d)** with 1.00mm

The figure 14.a) shows the effect of contact time for cadmium, copper, Lead, zinc, Silver and Barium ions removal onto okra adsorbent with 0.125 mm particle size, it shows that the removal percent are 50 , 63 , 41 , 44 , 59 and 97% respectively at 30 min and decrease to 31 ,56 ,28 ,41 ,53 and 94% respectively and increased to 64 , 54 ,45 , 48 ,62 and 98% respectively at 90 min. The effect of contact time on Cd, Cu, Pb, Zn, Ag and Ba ions onto okra adsorbent with particle size 0.250 mm is shown in figure 14. b) wherever the removal percent are 51 , 69 , 42 , 63 ,60 and 98% respectively at 30 min and decrease to 27 , 58 , 23 , 35 , 35 and 94 % respectively at 60 min and 90 min and increase to 35, 61, 29, 52 , 46 and 98% respectively at 90 min.

Figure 14. c) shows the effect of contact time on Cd, Cu, Pb, Zn, Ag and Ba ions using okra an adsorbent with particle size 0.500 mm, and the results show that removal percent are 29 ,61, 27, 36 , 38 and 93 % respectively at 30min and decrease to 24 , 41 ,15 , 30 % for Cd ,Cu ,Pb and Ag ions respectively increases to 44% for Zn ion and remains constant at 93% for Ba ion at 60 min wherever increase to 82 , 82 , 67 , 69, 71 and 96 % respectively at 90 min . Whereas, the effect of contact time on Cd, Cu, Pb, Zn, Ag and Ba ions using okra adsorbent with 1.00 mm particle size is shown in figure 14. d). The removal percent are 79, 81, 62, 63, 66 and 91 % Respectively at 30 min and increase to 84, 69 , 73 , 96% for Cd , Pb , Ag , Ba ions, remains constant 81% for Cu ion and decrease to 43% for Zn ion.

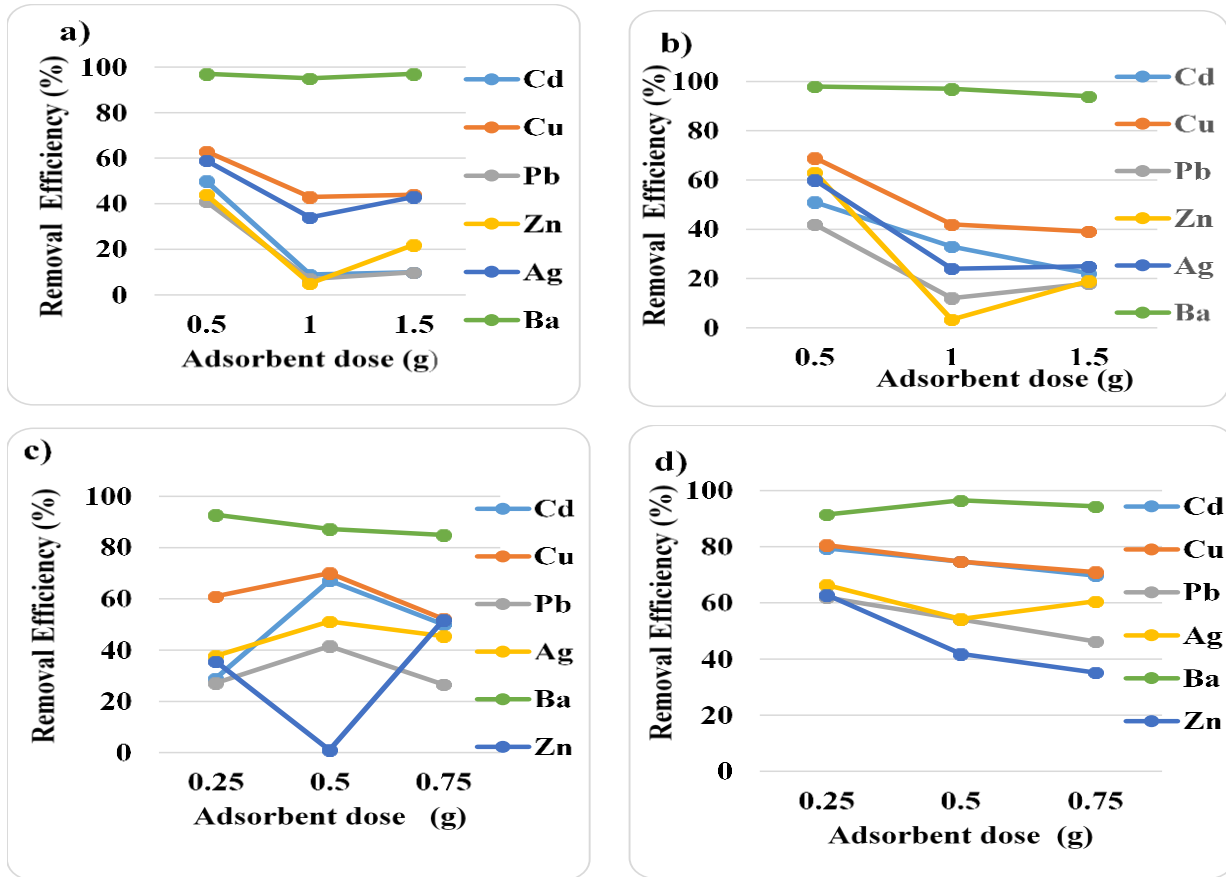
These results may be interpreted as follows: The rate of adsorption concerning residence time on the surface of okra adsorbent shows that the percentage removal of the metal ions is firstly increased with increasing contact time; this trend is because the adsorption processes are fast until they reach their optimum times. This is attributed to the availability of large surface areas of the okra adsorbent. Wherever the equilibrium times were attained. After the plateau, the surface pores of the adsorbent became enclosed, and desorption began. The slow rate of adsorption at this stage, also known as the desorption process, may be due to the accumulation of metal ions on the surface of the okra adsorbent. Moreover, the removal percent of Cd, Cu, Pb, Zn, Ag and Ba ions on some okra adsorbent remained constant with increasing the agitation time from 500 pm to 1000 rpm due to access to the equilibrium state, which occurs when the saturation of the active centers and the inability to absorb more Cd, Cu, Pb, Zn, Ag and Ba ions.

Therefore, the adsorption of Cd, Cu, Pb, Zn, Ag and Ba ions on okra adsorbent with 1.00 mm particle size at 90 minutes was chosen for the later experiments to remove Cd, Cu, Pb, Zn, Ag and Ba ions from wastewater using okra waste as adsorbing the material.

The findings in figure 14, which show the trends of contact times effect on four okra adsorbent particle sizes for Cd, Cu, Pb, Zn, Ag and Ba ions removal, are in the same line with the previous study reported by Esgair, (2018) who studied the removal of cadmium and copper by using okra waste and found the best time is 90 min. The contrast trend was reported by Jellali *et al.*, (2021) who studied the effect of contact time for Cadmium and Copper ions removal from Aqueous Solutions using lignite as a Low-Cost Material. The results from his study showed that the low contact times of 5 and 20 min for Cd and Cu, respectively, ensuring percentages removal of more than 80% of the adsorbed Cd or Cu amounts could be used in actual case application.

### 4.3.3. Effect of Adsorbent dose

The okra adsorbent dosage is an essential parameter because this determines the capacity of okra adsorbent. The amount of adsorbent employed was found to influence the efficiency of the adsorption process. Due to its direct impact on the adsorption performance, the okra adsorbent dose for the batch experiments was optimized using ranges of 0.25–1.5g for Cd, Cu, Pb, Zn, Ag and Ba ions to enhance its removal efficiency. This parameter was optimized in conjunction with the other optimized parameters (Contact time= 30 min, agitation speed=1000 rpm) by shaking different amounts of okra wastes with different particle sizes, and the results are depicted in Figure (15).



**Figure 15.** Effect of adsorbent dose for Cd, Cu, Pb, Zn, Ag and Ba ions removal percent onto okra adsorbent **a)** with 0.125 mm, **b)** with 0.250mm,**c)** with 0.500mm and **d)** with 1.00mm.

The effect of adsorbent dose on Cd, Cu, Pb, Zn, Ag and Ba ions removal onto okra adsorbent with particle size 0.125 mm is shown in Figure **15. a)** It is elaborated that removal percent attained at adsorbent dosage 0.5 g/15 mL is 50, 63, 41, 44, 59 and 97% for Cd, Cu, Pb, Zn, Ag and Ba ions respectively and decrease to 1g are 9, 43, 7, 5 and 95% respectively at adsorbent dosage 1g /15ml and increasing slowly to 22, 18, 19, 25 % for Cd, Pb, Zn, Ag respectively, while decreases to 39, 94% for Cu, Ba ions respectively at adsorbent dosage 1.5 g / 15ml.

The effect of adsorbent dose on Cd, Cu, Pb, Zn, Ag and Ba ions using okra adsorbent with particle size 0.250 mm is shown in figure **15. b)** wherever the removal percent are 51, 69, 42, 63, 60 and 98% respectively at adsorbent dose 0.5g /15ml and decreased to 33, 42, 12, 3.3, 24 and 97% respectively at adsorbent dose 1g / 15 ml and decreasing to 22, 39, 94 % for Cd, Cu, Ba respectively and increases slowly to 18, 19, 25 % for Pb, Zn, Ag ions respectively at adsorbent dose 1.5g / 15 ml. Figure **15. c)** shows the effect of adsorbent dose on Cd, Cu, Pb, Zn, Ag, and Ba ions using okra adsorbent with particle size 0.500 mm, and the results show that removal percent are 29, 61, 27, 36, 38 and 93% respectively at adsorbent dose 0.25 g / 7.5 ml and increases to 50, 52, 45 for Cd, Zn, Ag ions respectively and decrease to 52, 85% for Cu, Ba ions respectively at adsorbent dose 0.5 g / 7.5 ml while remains constant 27% for Pb ion at adsorbent dose 0.5 g / 7.5 ml.

Whereas the effect of adsorbent dose on Cd, Cu, Pb, Zn, Ag and Ba ions using okra adsorbent with 1.00 mm particle size is shown in figure **15.d)**.The removal percent are 79, 81, 62, 63, 66 and 91% respectively at adsorbent dose 0.25 g / 7.5 ml and decreases to 75, 75, 54, 42, 54 for Cd, Cu, Pb, Zn, Ag ions respectively and decreases to 96 % for Ba ion at adsorbent dose 1g / 7.5 ml , whereas decreases to 70, 71, 46, 35 ,94% for Cd , Cu ,Pb ,Zn , Ba ions respectively and increases to 61% for Ag ion.

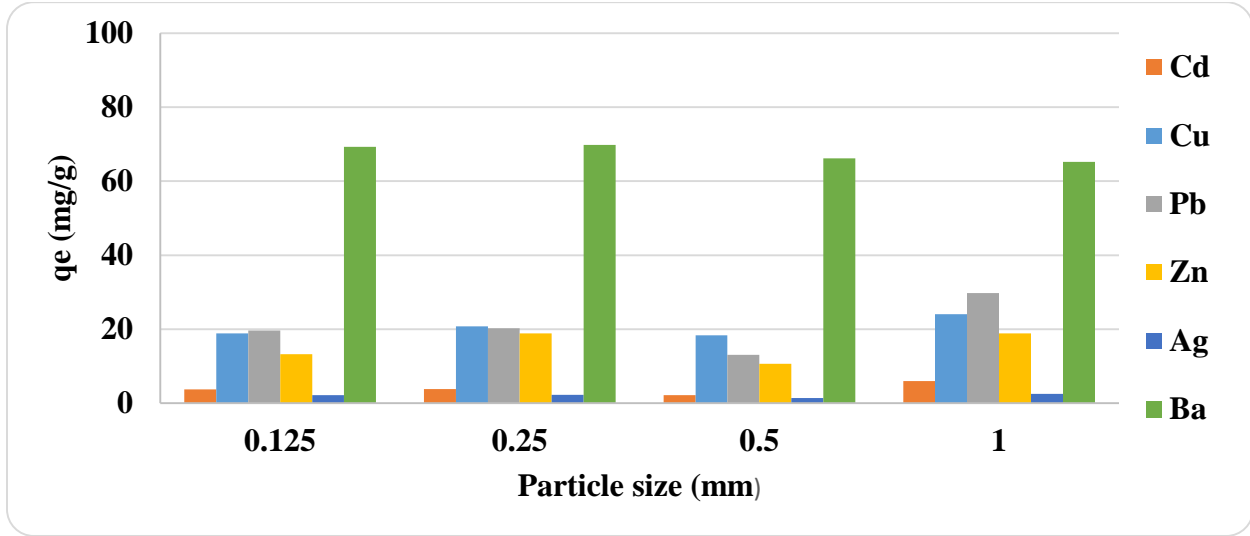
These results may be interpreted as follows: Generally, the effect of okra adsorbent dose on removal percent for Cd, Cu, Pb, Zn, Ag and Ba ions removal in wastewater increases with increasing the okra amount for okra adsorbent with small particle size and decreases with increasing the okra adsorbent amount with large particle size. The trend of increase in removal capacity can be associated with the availability of more adsorption sites for the metal ions (Science, 2020).

This also happened due to the accretion in a number of unsaturated binding active sites, which are ready for adsorption with the adsorbent dose increment. Consequently, the number of Cd, Cu, Pb, Zn, Ag and Ba ions in wastewater solution became insufficient with respect to the available binding sites. Moreover, increasing the adsorbent mass upon a certain limit causes aggregation of adsorbent particles, and as a result, the adsorbent total surface area exposed to the adsorption process decreases and the diffusion path length increases (El-araby *et al.*, 2019). Therefore, 0.25 g of okra adsorbent with 1.00 particle size was the optimal adsorbent doses to achieve the optimal percentage removal and adsorption capacity for Cd, Cu, Pb, Zn, Ag and Ba ions removal. And Ba ions are highly removed on all four adsorbent particle sizes doses (0.25g-1.5g).

These results are in alignment with a previous study reported by Khaskheli *et al.*, (2016) who used okra adsorbent for removal of Cr (III) and Cr (VI) from Contaminated Water, and their results show that the removal percent almost increased 20% as the amount of adsorbent increased from 50 mg to 100 mg and they found that 100 g dose is better for further study and the findings of this study are in the same line with the previous study done by Shafiq *et al.*, (2021) who studied the effect of Eucalyptus camdulensis—Derived Biochar doses for Kinetic and Isotherm Studies of Ni<sup>2+</sup> and Pb<sup>2+</sup> Adsorption from Synthetic Wastewater. Their results showed that 0.6 g and 0.15 g were the optimal EU-biochar doses to achieve the optimal percentage removal and adsorption capacity for Ni<sup>2+</sup> and Pb<sup>2+</sup> respectively. A similar trend was also reported by Hashem, (2007) who studied the effect of okra wastes dose for lead ion Removal from Aqueous Solution by Adsorption; he found that the percentage removal of lead ion increases with increasing the okra amount for groups of different particle sizes.

### 4.3.4. Effect of Particle Size

The particle size is an important parameter in the adsorption process.



**Figure 16.** Effect of wastes particle size on the equilibrium capacities of Cd, Cu, Pb, Zn, Ag and Ba ions (at constant conditions: Agitation speed =1000rpm, contact time=30min, adsorbent dose 0.5 mm)

**Figure 16** shows the comparison of adsorption capacity of different okra adsorbent particle sizes for  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^{2+}$  and  $\text{Ba}^{2+}$  ions. On okra adsorbent with 0.125 mm particle size, the adsorption capacities are 3.765, 18.87, 19.665, 13.23, 2.2065 and 69.291 mg/g respectively. From these results, the decreasing order of Okra adsorbent with 0.125 mm for the metal ions removal is  $\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^{2+}$ . On okra adsorbent with 0.250 mm particle size, the adsorption capacities are 3.795, 20.73, 20.235, 18.9, 2.268 and 69.768 mg/g, respectively. From these results, the decreasing order of Okra adsorbent with 0.250 mm for the metal ions removal is  $\text{Ba}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^{2+}$ . On okra adsorbent with 0.500 mm particle size, the adsorption capacities are 2.175, 18.33, 13.05, 10.695, 1.4145 and 66.135 mg/g, respectively. From these results, the decreasing order of Okra adsorbent with 0.500 mm for the metal ions removal is  $\text{Ba}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^{2+}$ . On okra adsorbent with 1.00 mm particle size, the adsorption capacities are 5.9535, 24.09, 29.73, 18.87, 2.4885 and 65.19 mg/g, respectively. From these results, the decreasing order of Okra adsorbent with 0.125 mm for the metal ions removal is  $\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^{2+}$ .

The affinity of different okra adsorbent particle sizes for  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^{2+}$  and  $\text{Ba}^{2+}$  ions removal, the results show that the okra adsorbent with 0.125 and 1.00 mm particle size has the same order for heavy metals removal, which is  $\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^{2+}$  for both 0.125 and 1.00 mm adsorbent particle size and the results also show the same order for heavy metals removal which is  $\text{Ba}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ag}^{2+}$  for both 0.250 and 0.500 mm adsorbent particle size. Therefore, the similarities for all four different okra adsorbent particle sizes such as 0.125, 0.250, 0.500 and 1.00 mm have the high and the low affinity for  $\text{Ba}^{2+}$  and  $\text{Ag}^{2+}$  ions, respectively.  $\text{Ba}^{2+}$  ion was highly removed on okra adsorbent 0.250 mm particle with 69.768 mg/g of the adsorption capacity ( $q_e$ ), and the  $\text{Ag}^{2+}$  ion is more least removed on okra adsorbent 0.500 mm particle with 1.4145 mg/g of the adsorption capacity ( $q_e$ ).

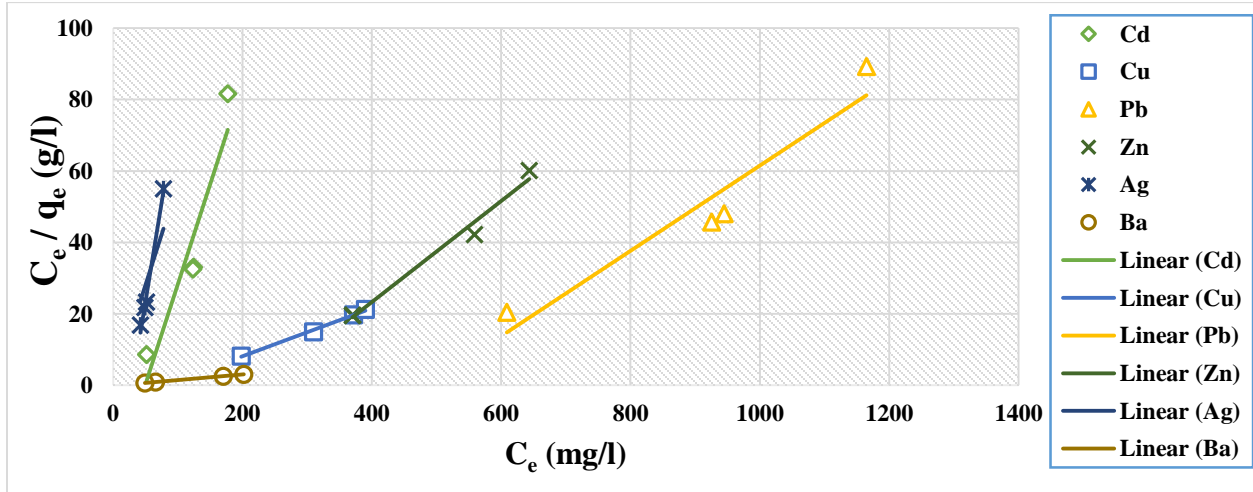
These results may be interpreted as follows: Figure 16 shows that the adsorption capacity for  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^{2+}$  and  $\text{Ba}^{2+}$  ions increase as increasing okra adsorbent particle size and decreasing in some cases. Thus, the smaller the particle sizes of the okra adsorbent, the higher its adsorption rate. As the particle size decreases, the adsorption capacity increases.

Therefore, the okra adsorbent with 0.125 mm adsorbed more amount than the okra adsorbent with a larger particle size, such as 0.500 mm of particle size. This happened due to the surface area increases as the particle size decreases (Yuan *et al.*, 2021). A similar trend was reported by Jellali *et al.*, (2021) who studied the use of lignite as a Low-Cost Material for Cadmium and Copper Removal from Aqueous Solutions. They found that the highest adsorbed amount of Cd (26.1 mg/g) and Cu (18.6 mg/g) was observed for the lignite with particle size less than 63  $\mu\text{m}$ , which is very small and observed that these adsorbed Cd and Cu amounts decreased by about 25% and more than 65%, respectively when lignite particles of 1–2 mm size were used. This outcome could be attributed to the lower microporosity and surface area generally observed for coarser media.

#### **4.4. Langmuir isotherm model**

Adsorption isotherms were investigated for different initial metal ions concentrations of 250 mg/l, 1001 mg/l, 1600 mg/l, 1000 mg/l, 125 mg/l, and 2375 mg/l for  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^{2+}$ , and  $\text{Ba}^{2+}$  metals ions onto a different type of okra adsorbent particle size at constant conditions of 0.5 g of okra adsorbent. The equilibrium data for those heavy metal ions.

The equilibrium adsorption capacity for Cd, Cu, Pb, Zn, Ag, and Ba ions removal using several kinds of okra adsorbent particles was estimated using the equation (4). Moreover, the linear Langmuir model in linear form was expressed using the equation (6). Figure 17 depicts the plot of  $C_e/q_e$  versus  $C_e$  for the removal of heavy metal ions (Cd (II), Cu (II), Pb (II), Zn (II), Ag (II) and Ba (II) by using the okra adsorbent with different particle size.



**Figure 17.** Langmuir isotherm for Cd (II), Cu (II), Pb (II), Zn (II), Ag (II) and Ba (II) ions removal at various concentrations.

From the plot, it is noticed that the sorption data are adequately fitted to the Langmuir equation with average regression coefficients ( $R^2 = 0.888-0.999$ ). The Langmuir parameter was computed from the slopes and intercepts of the linear plot of  $C_e$  as the x-axis and  $C_e/q_e$  as the y-axis, as displayed in Figure 17.

$$q_{\max} = \frac{1}{\text{Slope}} \quad (8)$$

$$b = \frac{1}{\text{Intercept} \times q_{\max}} \quad (9)$$

Figure 17 shows negative intercepts for the Langmuir linearized equation. Negative intercepts defy physical logic and are most likely linked to significant deviations in experimental data that occurred during the laboratory experiment and linearized isotherm models utilized. In this situation, absolute values were employed. In addition, the Langmuir non-linear regression is recommended, making non-linear regressions substantially more accurate.



The Langmuir isotherm parameters were used to calculate the affinity between the adsorbent and adsorbate via dimensionless separation factor,  $R_L$  as determined using the following equation:

$$R_L = \frac{1}{(1 + bC_i)} \quad (10)$$

Where  $b$  is the Langmuir constant and  $C_i$  is the initial concentration of metal ions. The  $R_L$  values promulgate whether the adsorption is irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ) or linear or unfavorable ( $R_L = 1$  or  $R_L > 1$ ) (Mustapha *et al.*, 2019).

**Table 7.** Langmuir isotherm constants for the removal of Cd, Cu, Pb, Zn, Ag and Cu ions from wastewater by Okra adsorbent.

| Isotherm model    | Langmuir parameters     | Metals ions      |                  |                  |                  |                  |                  |
|-------------------|-------------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                   |                         | Cd <sup>2+</sup> | Cu <sup>2+</sup> | Pb <sup>2+</sup> | Zn <sup>2+</sup> | Ag <sup>2+</sup> | Ba <sup>2+</sup> |
| Langmuir isotherm | q <sub>max</sub> (mg/g) | 1.8              | 14.8             | 8.4              | 7.1              | 0.9              | 64.1             |
|                   | K <sub>L</sub> (L/mg)   | 15.404           | 0.363            | 6.924            | 4.709            | 35.23            | 0.001135         |
|                   | R <sub>L</sub>          | 0.0003           | 0.0027           | 0.0001           | 0.0002           | 0.0002           | 0.2705           |
|                   | R <sup>2</sup>          | 0.888            | 0.995            | 0.921            | 0.984            | 0.989            | 0.999            |

The literature states that the equation is: Linear:  $R_L = 1$ ; Favorable:  $0 < R_L < 1$ ; Irreversible:  $R_L = 0$ . The Langmuir constants obtained were computed in Table 7, and Langmuir isotherm showed better fit to the experimental data with higher correlation coefficients ( $R^2$ ) for all the metal ions belongs between (0.888-0.999), wherever the maximum adsorption capacity of okra adsorbent for Cd<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>2+</sup>, Ba<sup>2+</sup> metal ions were 1., 14.8, 8.4, 7.1, 0.9 and 64.102 mg/g respectively as indicated in table 7. The maximum adsorption capacities of the okra adsorbent were found to be between 0.9 and 64.1 mg/g. The values for  $R_L$  in the range of 0–1 decreased with increasing initial metal ion concentration, which indicates favorable uptake of metal ions. However, the  $R_L$  value in the present study for Cd<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>2+</sup> and Ba<sup>2+</sup> were found to be 0.0003, 0.0027, 0.0001, 0.0002, 0.0002 and 0.2705 respectively, the calculated equilibrium parameter,  $R_L$ , of the Langmuir isotherm was in the range between 0 and 1 for all the six heavy metal ions. Therefore, these values of  $R_L$  obtained indicating that the adsorption of the Cd<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>2+</sup> and Ba<sup>2+</sup> ions onto okra adsorbent are favorable.

## CHAPTER V

### CONCLUSION AND RECOMMENDATIONS

#### 5.1. Conclusions

According to the results found out and the objective of this research, the present study has demonstrated that the okra agricultural waste adsorbent exhibited the most effective removal efficiency of cadmium, copper, lead, zinc, silver and Barium ions from wastewater. Wherever, FTIR used to analyze for the functional groups present in okra adsorbent showed the presence of functional groups such as Hydroxyl (OH), Amino (N-H), Carboxyl (C=O, C-O-C), C-O stretching and M-O groups. Moreover, the batch adsorption method was performed varying four parameters and the results showed that the optimum value of adsorption parameters for maximum removal of Cd, Cu, Pb, Zn, Ag and Ba metal ions with initial concentrations of 250 mg/l, 1001mg/l, 1600 mg/l, 1000 mg/l, 125mg/l and 2375 mg/l in wastewater solution, respectively), found at agitation speed of 1000 rpm, contact time of 90min, okra adsorbent dose of 0.25 g and particle size of 1.00mm. Then, equilibrium adsorption isotherms were measured for all components system, and the experimental data were analyzed with the Langmuir isotherm model.

The examination of the linear isotherm plot suggested that the Langmuir isotherm model yielded a better fit to the experimental data with higher correlation coefficients ( $R^2$ ) for all metal ions belong between (0.888-0.999) and the maximum adsorption capacity ( $q_{max}$ ) of okra adsorbent for  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ag^{2+}$ ,  $Ba^{2+}$  metal ions were 1.8, 14.8, 8.4, 7.1, 0.9 and 64.1 mg/g respectively. Thus, the okra adsorbent showed a very high adsorption capacity for  $Ba^{2+}$  as 64.102 mg/g following for  $Cu^{2+}$  as 14.8 mg/g followed by  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Ag^{2+}$  as 8.3 mg/g, 7.092 mg/g, 1.79 mg/g and 0.903 mg/g respectively. Moreover, the  $R_L$  values in the present study for  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ag^{2+}$  and  $Ba^{2+}$  were found to be 0.0003, 0.002, 0.0001, 0.0002, 0.0002 and 0.2705 respectively. These  $R_L$  values are all less than one, indicating that the adsorption of the  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ag^{2+}$  and  $Ba^{2+}$  ions onto okra adsorbent is favorable.

Based on the findings of this study, I believe that readily available okra agricultural wastes, which are a nuisance to the environment, could be used as a natural adsorbent due to its high removal efficiencies for the  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ag^{2+}$  and  $Ba^{2+}$  ions involved in this study, as well as the undeniable advantages of the okra adsorbent, such as its low cost of preparation and easy separation on the application of adsorption batch process.

## 5.2. Recommendations

- ✓ The same future study is recommended using other instruments such as SEM, XRD and BET to characterize the okra adsorbent,
- ✓ The effect of parameters such as PH and Temperature is recommended in the future study for heavy metals removal from wastewater using okra from agricultural wastes.
- ✓ Further studies should be done on the removal of heavy metals from wastewater using coconut shells and Moringa seeds as natural adsorbents.
- ✓ The wastewater samples should be well stored and kept in the laboratory before being analyzed to avoid the deterioration and evaporation of some volatiles hydrocarbons for those studies which will be focusing on the removal of hydrocarbons from wastewater from natural gas production.

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## Appendices

1. **Appendix A:** Tables showing removal efficiency and equilibrium capacities of okra adsorbent for removal of heavy metals ions from wastewater.

**Table 8.** Band shifts of some important functional groups in the raw okra waste before and after activation.

| Raw okra waste                  |                |                                  |                |
|---------------------------------|----------------|----------------------------------|----------------|
| <i>Before activation</i>        |                | <i>After activation</i>          |                |
| Wave number( $\text{cm}^{-1}$ ) | Absorbance (%) | Wave number ( $\text{cm}^{-1}$ ) | Absorbance (%) |
| 3388.5                          | 87.5           | 3390.05                          | 22.5           |
| 2900                            | 95             | 2905.5                           | 66.8           |
| 1647                            | 85             | 1658                             | 45             |
| 1640                            | -              | 1640                             | 67.5           |
| 1038                            | 67.5           | 1050.05                          | 52.5           |
| 618                             | 80             | 650                              | 7.5            |

**Table 9.** Equilibrium adsorption capacity for Cd, Cu, Pb, Zn, Ag and Ba ions removal using different types of okra adsorbent particle.

| Particle size(mm) | volume (l) | Ads or bent dose(g) | Cd       |          |          | Cu       |          |          | Pb       |          |          | Zn       |          |          | Ag       |          |          | Ba       |          |          |
|-------------------|------------|---------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|                   |            |                     | Ci(mg/l) | Ce(mg/l) | qe(mg/g) | Ci(mg/l) | Ce(mg/l) | qe(mg/g) | Ci(mg/l) | Ce(mg/l) | qe(mg/g) | Ci(mg/l) | Ce(mg/l) | qe(mg/g) | Ci(mg/l) | Ce(mg/l) | qe(mg/g) | Ci(mg/l) | Ce(mg/l) | qe(mg/g) |
| 0.125             | 0.015      | 0.5                 | 250      | 124.5    | 3.765    | 1001     | 372      | 18.87    | 1600     | 944.5    | 19.665   | 1000     | 559      | 13.23    | 125      | 51.45    | 2.2065   | 2375     | 65.3     | 69.291   |
| 0.25              | 0.015      | 0.5                 | 250      | 123.5    | 3.795    | 1001     | 310      | 20.73    | 1600     | 925.5    | 20.235   | 1000     | 370      | 18.9     | 125      | 49.4     | 2.268    | 2375     | 49.4     | 69.768   |
| 0.5               | 0.015      | 0.5                 | 250      | 177.5    | 2.175    | 1001     | 390      | 18.33    | 1600     | 1165     | 13.05    | 1000     | 643.5    | 10.695   | 125      | 77.85    | 1.4145   | 2375     | 170.5    | 66.135   |
| 1                 | 0.0075     | 0.25                | 250      | 51.55    | 5.9535   | 1001     | 198      | 24.09    | 1600     | 609      | 29.73    | 1000     | 371      | 18.87    | 125      | 42.05    | 2.4885   | 2375     | 202      | 65.19    |



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