# EQUILIBRIUM STUDY OF THE ADSORPTION OF 2CHLOROPHENOL FROM AQUEOUS SOLUTION USING BONE CHAR

BY

**Ezekiel Osahenrumwen IDEHEN**

**PSC1808646**

**A PROJECT WRITTEN IN THE DEPARTMENT OF CHEMISTRY AND SUBMITTED TO THE FACULTY OF PHYSICAL SCIENCES IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF DEGREE OF B.SC CHEMISTRY OF THE UNIVERSITY OF BENIN, BENIN CITY. EDO STATE, NIGERIA**

**SEPTEMBER, 2023**

## CERTIFICATION

This is to certify that this project work was carried out and presented by Ezekiel Osahenrumwen IDEHEN in partial fulfillment of the requirement for the award of Bachelor of Science degree (B.Sc.) Chemistry, in the Department of Chemistry, University of Benin, Benin City, Nigeria.

_____ _____

IDEHEN OSAHENRUMWEN EZEKIEL Date

_____ _____

DR. (Mrs.) S.I OMONMHENLE Date

PROJECT SUPERVISOR

_____ _____

PROF. J.U. IYASELE Date

HEAD OF DEPARTMENT

## DEDICATION

I dedicate this project work to God Almighty for his infinite favors, strength and grace to pull through and to my parent Mr. IDEHEN JEFFREY for his support prayers and assistance.

## ACKNOWLEDGEMENT

My greatest gratitude goes to God Almighty, the infinity of goodness, who has given me everything, for the gifts of life and knowledge and who allowed the success and completion of this report.

I also express my gratitude to my supervisor, Dr. (Mrs.) S.I Omonmhenle, who made this project work a success through her, constant criticism, encouragement, patience and support. Also to my incredible course adviser Dr. K. O. Ogbeide for his encouragement and prayers during these times.

My gratitude goes out to the Head of Department, Prof. Julius Iyasele for creating an enabling learning environment for all chemistry students and the entire staff of the Department of Benin, Benin City, also to the Professors, Lecturers and staff in the Department of Chemistry whose efforts in producing great leaders of tomorrow will never be in vain.

I also express my profound gratitude to my parent Mr. Idehen Jeffrey and my Aunt, Mrs. Nkpen Benedict Ona and also to my siblings whose prayers and support went a long way in the success of this project work and during my course of study in the University of Benin.

My gratitude to my friends, my well-wishers, and my project colleague, Miracle Augustine, Oyibo Victoria, Adoga Evelyn, Edmund Deborah, Thomas Precious, Hope, Kachi, Desiri and Cole for their encouragements and prayers during this research project work, also Azubuike Favour, Oshoma Ayomide, Adeniyi Bolaji, Nathaniel Kome, Aluya Ehijator, Alfreda Ehijie and Okereke Deborah for making my stay in the university a memorable one, may Almighty God bless and protect every one of them in all that they do, Amen.

# TABLE OF CONTENTS

## ABSTRACT

This study was carried out to evaluate the Equilibrium of the removal of 2-Chlorophenol from aqueous solution onto bone char and the parameters that were studied were Concentration, Adsorbent dosage and Time. The bone char was obtained from by calcination process occurring at 500ºC for 2hours. This char was characterized by using FT-IR, XRD, SEM/EDS and BET. Batch adsorption experiment was carried out to investigate the following variables, pH, Concentration and Adsorbent dosage. The morphology of the bone char showed fine hexagonal shaped particles and a have homogenous structure with rough edges also the presence of elements Carbon, Oxygen, Silicon, Phosphorus, Aluminum, Potassium and Calcium was observed. It was observed that as the concentration increased the amount adsorbed increased, the pH study showed that the adsorption capacity was highest at pH 7.3, lowest at acidic condition and followed by the basic condition. It revealed that cow bone char has good adsorption properties and could be utilized for the treatment of 2-Chlorophenol in waste water.

# CHAPTER ONE

## 1.0 INTRODUCTION

### 1.1 Background of the Study

Pollution has a destructive impact on all levels of the ecosystem. In the modern day, essential human necessities such as colors and paints, medications, numerous insecticides, germicides, defoliants, disinfectants, and so on have become damaging to the environment. Halogenated aromatic chemicals are a very stable class of contaminants. Incurable diseases can be brought on by halogenated aromatics due to their mutagenic and carcinogenic qualities. (Mahapatra. M.K.et al., 2022)

2-Chlorophenol (2-CP) is a halogenated aromatic compound and has been proactively used in many industrial sectors such as pesticides, polymer, pharma, petroleum, assorted chemicals, etc.(Huong P.T. et al., 2016) The United States Environmental Protection Agency (USEPA) has classified 2-CP as a priority organic pollutant and enacted a permissible limit of 0.1 ppb for drinking water (Pera-Titus. M. et al., 2022). 2-CP enters the environment by industrial effluents, agricultural runoffs, and leachates from contaminated sites and landfills (Shen. T. et al., 2021). 2-CP tends to biomagnify owing to its poor biodegradability. As a potent mutagenic and carcinogenic agent, 2-CP has devastating effects on the aquatic ecosystem (Barakat, M. A. et al., 2021) Hence, the abatement of 2-CP is an essential activity in environmental protection (Kumar A. et al., 2022).

Reverse osmosis (RO), oxidation-reduction, adsorption, chemically induced precipitation, and other techniques have all been used to reduce 2-CP in wastewater. Adsorption has emerged as the most popular technique among those investigated because of its affordability and superior efficacy in treating wastewater (Liu T. et al., 2021).

Efforts to identify less expensive replacements for more expensive synthetic adsorbents have recently increased. Adsorbents generated from waste biomass are gaining popularity as useful removal methods for harmful pollutants like 2-Chlorophenol .

An adsorbent is a substance commonly porous in nature and with a high floor vicinity that can adsorb substance onto its floor with the aid of intermolecular forces (Barrett, E.B et al., 2021) because solutes may be distributed between the adsorbent surface and a mobile section, adsorbents are used as stationary levels in gasoline-solid and liquid-solid chromatography.

Adsorption is the collection of substance unto the face of the adsorbent solids. It's a removal technique in which certain debris is bound to an adsorbent particle surface via either chemical or physical enchantment and is frequently harassed with absorption wherein the substance being absorbed penetrates the alternative strong (Joyner, L.G et al., 2002) The solid surface in touch with a solution tends to collect a surface large to strong molecules because of the distinction of surface forces. Consequently, this reasons an adsorption to take region, the adsorption results in the formation 0of a molecular layer of the adsorbate at the surface of the adsorbent. Frequently an equilibrium awareness is soon formed at the surface and is commonly observed with the aid of slow diffusion onto debris of the adsorbent (Wayne, T.B et al., 2002)

This phenomenon includes an accumulation of substances at the interface that may either be liquid-liquid, liquid-gas, fuel-stable, or liquid-strong. The substance appearing in the adsorption (stable, liquid, fuel, amorphous) is the adsorbent; the adsorbate is a combination of substances or solutions on which the adsorbent is used. Many strong substances are recognized to possess this strength of attracting and keeping molecules or ions upon the surface on exposure e.g. Activated clay, fuller's earth, silica gel, activated carbon, bauxite, and activated alumina, etc.

Animal bones are burned to create animal charcoal, also known as bone black, bone char, or abaiser. Animals' bodies are made up of part of their bones (the skeletal systems), which essentially provide them shape and support. It is made up of 80% calcium, 10% magnesium, and other inorganic components that are present in the bones (Bhargava, D.S. et al., 1991). To draw, animal charcoal is

employed in the form of fine, compressed, and powdered charcoal (Gao X. et al., 2022). Animal charcoal has a higher degree of ability to remove coloring substances from solutions.

The process of converting an organic material into carbon or a residue containing carbon via pyrolysis or destructive distillation is known as carbonization (Julie M. E. et al., 2022). It frequently refers to the production of coal gas and tar from raw coal in organic chemistry. Activated carbon is a form of carbon that has been processed to make it extremely porous and thus has a very large surface area available for absorption or chemical reaction. Though there are many commercially available activated carbons, these are still quite expensive (Chen, Y.N. et al., 2008). Various researchers (Wang, H. et al., 2020) have carried out studies for simplified and cost-effective methods of activation carbon. The advantage of cow Bone Char over other adsorbents comes from its distinctive features such as cost-effective adsorbent, rejuvenation ability, and alternative fuel usability potential. Cow bones are considered waste and can be easily accessible due to the high rate of consumption of cow meat in Nigeria. It can be purchased at very low prices, making the whole adsorption process cheaper by preparing cost-effective adsorbents. (Kozyatnyk I. et al., 2020)

This study carried out the detailed procedure of BC preparation and its characterization. Parameter optimization was carried out to achieve the highest abatement on pH, adsorbent dose, adsorbate-adsorbent contact time, adsorbate concentration, and adsorption system temperature. The experimental data were modeled with various models about adsorption equilibrium, kinetics, and thermodynamics to enunciate the characteristics of 2-CP adsorption onto the BC.

### 1.2 Problem Statement

The primary concern is the increasing contamination of water bodies due to industrial and domestic waste, leading to the presence of hazardous pollutants like 2-Chlorophenol . This compound is toxic and persistent, posing a significant threat to aquatic ecosystems and human health. Conventional wastewater treatment methods often struggle to effectively remove such recalcitrant organic

compounds, warranting the exploration of alternative and efficient treatment techniques. In this context, the utilization of adsorption processes, specifically employing bone char as an adsorbent, has gained attention due to its potential to adsorb organic pollutants.

### 1.3 Relevance of study

Bone char adsorption can effectively remove the dangerous substance 2-Chlorophenol , which is frequently present in industrial wastewater. This procedure enhances the extraction of contaminants while also enhancing the quality of wastewater that is released. The potent adsorption capacity of bone char makes it beneficial for developing effective remediation strategies. This keeps pollutants out of water bodies, which is essential for safeguarding aquatic life, ecosystems, and community well-being. The associated health hazards are diminished by removing this chemical, in compliance with stringent environmental regulations. Additionally, equilibrium studies aid in determining the ideal 2-Chlorophenol removal conditions, leading to cleaner water, healthier ecosystems, and improved public safety. For instance, the efficient removal of 2-Chlorophenol from industrial effluent by bone char adsorption ensures that dangerous chemicals are not released into the water.

### 1.4 Scope of study

This study delves into various aspects, including investigating adsorption kinetics to understand how quickly 2-Chlorophenol attaches to bone char under different conditions. It also employs isothermal modeling, employing models like Langmuir and Freundlich, to connect equilibrium 2-Chlorophenol concentrations with the amount adsorbed on bone char. The impact of factors like pH, adsorption dosage, and initial concentration on adsorption is explored. Optimal conditions encompassing these factors are determined. The translation of equilibrium behavior to real-world wastewater treatment scenarios is investigated.

## 1.5 AIM AND OBJECTIVES

This research aims to determine the optimal conditions and mechanisms for achieving efficient removal of the pollutant through adsorption, using bone char obtained from cow bones.

To accomplish this aim the following, objectives were obtained;

1. Investigating the adsorption kinetics to understand how quickly the process occurs under different conditions.

2. Applying isotherm models (e.g., Langmuir, Freundlich) to establish the relationship between equilibrium concentrations of 2-Chlorophenol and its adsorption onto bone char.

3. Examining the impact of varying variables such as pH, initial concentration of 2-Chlorophenol , and adsorption dosage on the adsorption efficiency.

4. Exploring the molecular-level adsorption mechanisms that occur between 2-Chlorophenol molecules and bone char.

5. Determining the optimal conditions (e.g., pH, temperature, time) to achieve the highest possible adsorption efficiency.

6. Understanding how the equilibrium adsorption behavior observed in laboratory settings translates to dynamic real-world scenarios in wastewater treatment processes.

7. Evaluating the cost-effectiveness of using bone char adsorption in comparison to alternative treatment methods.

## 1.6 LITERATURE REVIEW

### 1.61 Introduction to Bone Char

Animal bones are carbonized to generate bone char, which is referred to in Latin as carbo animeis. The method of construction affects its makeup. However, it largely consists of 6–10% calcium carbonate, 7–10% carbon, and 57–80% tricalcium phosphate (or hydroxyapatite). (J. D. Russell et al., 2005) mostly utilized for decolorization and filtering. Due to its exceptional qualities, bone char is a wonderful but sometimes disregarded substance that has been used in a variety of sectors. Bone char has been used for ages in a variety of applications and is made from the bones of animals, especially cattle (M. P. Marzocchi et al., 2017). This review explores bone char's production method, chemical makeup, potential uses, and environmental implications.

### 1.62 Production Process

Bone char is mainly made from cow and pig bones. To stop the spread of Creutzfeldt-Jakob disease, however, the skull and spine are no longer used.. Bones are heated up to 500 °C (932 °F) in a closed container. Oxygen concentration should be kept low during this operation, as it affects product quality, especially adsorption capacity. Heat is used to remove the majority of the organic matter present in bones, which was formerly collected as dippel oil. In the finished product, what is not eliminated is still there as activated carbon. Heating the bone in an oxygen-rich atmosphere yields chemically quite different bone ash (Jhuma Sadhukhan et al., 2001). Spent bone char can be regenerated by washing it in hot water to remove impurities and then heating it in a furnace to 500 °C (932 °F) (Lee, C. C et al., 2011) controlled air volume. The calcined bones are finely ground to create a powder with increased surface area, which improves the material's reactivity and adsorption capacity. The char is then sieved to ensure a consistent particle size and remove any large or irregular pieces that might not be suitable for the adsorption process. This improves its effectiveness as a filtration medium. This helps in maintaining the quality and efficiency of the

filtration process, ensuring that the bone char particles effectively remove 2Chlorophenol from aqua (Kinniburgh, D. G. et al., 1987)

### 1.63 Composition and Structure of Bone Char

Bone char, derived from cow bones, is a substance primarily composed of calcium phosphate minerals, collagen, and various trace elements. It is known for its diverse applications, ranging from its use in sugar refining to its utilization in soil improvement. The animal bones are composed of 65%-70% of inorganic substances, mainly hydroxyapatite. The chemical composition of hydroxyapatite is $Ca_{10}(PO_4)_6(OH)_2$. The remaining part of bones is composed of organic matter, mainly fibrous protein collagen (K. Chojnacka et al., 2005)

### 1.64 Regulation and Safety

Regulation of bone char varies across different applications and regions. In the context of water purification, for example, regulations exist to ensure that the use of bone char does not introduce additional contaminants. Additionally, food-grade bone char used in sugar refining undergoes stringent quality control measures to ensure its safety.

### 1.65 Conclusion on Bone Char

Bone char, derived from animal bones through a carbonization process, boasts a unique composition and structure that lend themselves to various applications. Its exceptional adsorption capabilities have found use in water purification, sugar refining, environmental remediation, and more. However, environmental considerations and ethical concerns underscore the need for responsible sourcing and production practices. As industries continue to evolve and address these challenges, bone char's versatility and utility remain integral to a range of sectors.

## 1.66 Introduction to 2-Chlorophenol

Phenol and phenolic compounds with high toxicity in contaminated water resources are considered the most important pollutants and therefore vital threats to the environment, and human and animal health (Hamad B.K. et al., 2011) 2-Chlorophenol as a phenolic organic aromatic compound is used in wastewater of many industries such as plastics, polycarbonate, resins, etc (Buddhika G et al., 2011) and Larger industries with high concentrations of phenol and its derivatives include oil refineries (6-500 mg/l), coal furnaces (9-6800 mg/l), petrochemical facilities (2-1220 mg/l), and coking (28-3900 mg/l), such as 2-Chlorophenol (Peter S. et al., 2011) Due to the importance of environmental pollutants, strict standards are exerted on phenolic compounds in some countries (Zhao J. et al., 2011)United States Environmental Protection Agency (EPA) has listed phenol and its derivatives as the priority environmental pollutants. The standard concentration of phenol allowed by EPA in drinking water is 1 mg/l and in wastewater, industries is 500 mg/l (Chen S. et al., 2010) moreover, the concentration of chlorophenols allowed by WHO guidelines in drinking water is 1g/1 (Dionysios D. et al., 2010) Therefore, removing phenolic compounds from contaminated water is considered necessary and important before discharging wastewater into the environment (Maria G. et al., 2012).

## 1.67 Physical and Chemical Properties:

Physical properties

A colorless to amber liquid with an unpleasant, penetrating odor. Density 1.265 g / cm3. Sinks in water and slowly dissolves. Freezing point 7°C (46°F). Boiling point 175°C (347°F).

Very soluble in water

Combustion products pose special risks because they emit harmful chloride vapors. In fire, it burns and emits harmful and unpleasant fumes. (USCG, 1999)

**Physical data:**

Vapor Pressure: 2.2 mm Hg at 68ºF (20ºC)

Flash Point: 147ºF (63ºC)

Water Solubility: Slightly soluble

**Other commonly used name;**

O-chlorophenol

**Health Hazard**

**Acute Health Effects**

The following acute (short-term) health effects may occur immediately or shortly after exposure to 2-Chlorophenol:

- Contact can irritate and burn the skin and eyes.
- Breathing 2-Chlorophenol can cause coughing, wheezing, and/or shortness of breath by irritating the nose, throat, and lungs.
- High exposure can cause headaches, dizziness, fatigue, restlessness, muscle weakness, tremors, seizures, coma, and even death.

**Other Long-Term Effects**

2-Chlorophenol may cause liver and kidney damage.

Chemical properties

2-Chlorophenol is a halogenated aromatic compound with a chlorine atom substituted at the second position of the phenolic ring. Its chemical properties are influenced by the presence of the chlorine atom and the phenolic functional group. Here are some key chemical properties of 2-Chlorophenol:

1. **Acidity and Phenolic Behavior:**

The phenolic hydroxyl group (OH) in 2-Chlorophenol causes the acidic properties of the compound. It can donate a proton to form a phenolate ion in the presence of a base. This phenolic behavior contributes to its ability to undergo various types of reactions

2. **Substitution Reactions:**

The chlorine atom in 2-Chlorophenol makes it susceptible to substitution reactions. It can undergo electrophilic aromatic substitution reactions, here the chlorine atom is replaced by other substituents. These reactions are common in organic synthesis and are enhanced by the electron-rich nature of the phenolic ring.

3. **Oxidation Reactions**:

2-Chlorophenol can undergo oxidation reactions, primarily at the phenolic group. The hydroxyl group can be oxidized to form quinones or other oxidation products. These reactions are of interest in the synthesis of various organic compounds and in understanding the chemical reactivity of phenols.

4. **Esterification and Etherification:**

The phenolic hydroxyl group can participate in esterification and etherification reactions. It can react with carboxylic acids to form esters and with alkyl halides to form ethers. These reactions are utilized in the modification of 2-Chlorophenol chemical structure for various applications. (Carey, F. A. *et al.,* 2007)

Overall, the chemical properties of 2-Chlorophenol are diverse and versatile, enabling it to participate in a wide range of reactions and applications in various industries, including organic synthesis, pharmaceuticals, and chemical manufacturing. The presence of both the phenolic hydroxyl group and the chlorine atom makes it a chemically interesting compound for researchers and practitioners alike.

### 1.68 Applications of 2-Chlorophenol

2-Chlorophenol , despite its toxicity and potential environmental concerns, finds applications in various industries due to its unique chemical properties. Here are some of its notable applications, along with relevant citations:

1. **Synthesis of Pharmaceuticals and Agrochemicals:**

2-Chlorophenol serves as a versatile building block in the synthesis of pharmaceuticals and agrochemicals. It can be utilized as a precursor in the preparation of various biologically active compounds. For example, 2-Chlorophenol has been used in the synthesis of fungicides and herbicides. (A. F. Pozharskii, *et al.,* 2007)

2. **Dye and Pigment Production:**

2-Chlorophenol is employed in the manufacturing of dyes and pigments, where it serves as a precursor for various colorants. It can undergo coupling reactions to produce azo dyes and other colored compounds. (J. Hunger *et al.,* 2007)

3. **Chemical Intermediates**:

The compound is used as a chemical intermediate in the synthesis of other compounds with diverse applications. It can be modified to introduce functional groups and create molecules with desired properties. (H. P. Gregor *et al.,* 2000)

4. **Laboratory Reagents:**

2-Chlorophenol is utilized as a reagent in organic synthesis and research laboratories for various chemical transformations. It can be involved in substitution, oxidation, and coupling reactions.(F. G. Mann *et al.,* 1994)

5. **Wood Preservation**:

Despite environmental concerns, 2-Chlorophenol has been used historically as a wood preservative due to its antimicrobial properties. It shields wood from degradation and fungus development. (K. L. Zadrazil, *et al.,* 2002)

6. **Analytical Chemistry**:

2-Chlorophenol is employed in analytical methods, including chromatography and spectrometry, as a reference compound or standard for calibration purposes. (T. Skoog, *et al.,* 2017)

**1.69 Conclusion of 2-Chlorophenol**

2-Chlorophenol, a chlorinated aromatic compound, has a range of applications in chemical synthesis, wood preservation, and laboratory work. However, its environmental impact and potential health risks have prompted regulatory measures and a decrease in some of its uses. As research continues, a deeper understanding of the compound's properties, effects, and safe handling will guide its responsible use in various industries while minimizing its adverse impact on the environment and human health.

**1.70 Introduction to Adsorption Studies**

These molecules are only found on the water's surface and do not penetrate any deeper. Adsorption is the word used to describe the concentration of molecular species at the surface of a solid or liquid rather than in the bulk of the solid or liquid.

The adsorbate is the molecular species or substance that concentrates or accumulates at the surface, and the adsorbent is the material on which the adsorption takes place on the surface of which the adsorption takes place. As previously noted, adsorption is mostly a surface phenomenon. Because solids, particularly those that have been finely split, have a large surface area, adsorbents such as charcoal, silica gel, alumina gel, clay, colloids, and metals in solution have a high surface area.a finely divided state, and others, such as silica gel and alumina gel, are effective.

By attaching to gas or liquid molecules, solid surfaces can hold them. Desorption is the process of removing an adsorbed substance from a surface on which it has been adsorbed. Adsorption occurs when a substance is concentrated only on its surface and does not penetrate through it to reach the bulk of the adsorbent, whereas absorption occurs when the material permeates through it to reach the bulk of the adsorbent.**1.72 Difference between Adsorption and Absorption**

If the material is concentrated just on its surface and does not permeate through it to reach the bulk of the adsorbent, it is called adsorption, whereas in absorption, the substance is uniformly dispersed throughout the solid's bulk and is referred to as absorption. A chalk stick dipped in ink will, for example, retain the colour of the ink due to adsorption of coloured molecules on the surface, but the ink's solvent will penetrate deeper into the stick due to absorption of the ink's solvent. In rare cases, adsorption and absorption can occur simultaneously. In the scientific literature, these processes are referred to as sorption.

### 1.71 Types of Adsorption

In general, there are two types of adsorption on solids.

**Physical Adsorption (Physisorption):** Physisorption is a type of adsorption where weak van der Waals forces, such as London dispersion forces, are responsible for the interaction between the adsorbate and the adsorbent. This type of adsorption occurs at relatively low temperatures and is

usually reversible. The adsorption isotherm for physisorption typically follows the Freundlich or Langmuir equation. (Atkins, P. *et al.,* 2010).

**Chemical Adsorption (Chemisorption):** Chemisorption involves stronger chemical bonds forming between the adsorbate and the adsorbent. Covalent or ionic bonds are often created during this process, leading to a more stable and specific adsorption. Chemisorption usually requires higher activation energy and can lead to irreversible adsorption. (Balzhiser, R. E. *et al.,* 1967)

### 1.72 Applications of Adsorption

1. **Gas Purification and Separation:**

Adsorption is extensively used to purify gases by removing impurities, such as removing CO2 from natural gas. It's also employed in air separation processes to extract nitrogen or oxygen from air using adsorbents like zeolites. (Ruthven, D. M. *et al.,* 1984).

2. **Water Treatment:**

Adsorption is employed in water treatment to remove contaminants like heavy metals, organic pollutants, and dyes. Activated carbon and other adsorbents are used to adsorb and remove these impurities from water.(Crittenden, J. C *et al.,* 2011)

3. **Catalysis**:

Many heterogeneous catalytic reactions involve chemisorption of reactant molecules onto a catalyst surface. The formation of strong bonds between reactants and catalysts enhances reaction rates and efficiency. (Chorkendorff, I. *et al.,* 2017)

4. **Gas Storage and Delivery**:

Adsorption is used in gas storage applications, such as storing hydrogen for fuel cells. Porous materials like metal-organic frameworks (MOFs) are used to adsorb and release gases efficiently. (Yaghi, O. M. *et al.,* 2003)

5. **Chromatography**:

Chromatographic techniques like gas chromatography and liquid chromatography rely on the differential adsorption of components in a mixture onto a stationary phase. This separation process is widely used in analytical chemistry. (Skoog, D. A. *et al.,* 2013)

### 1.7.3 Conclusion on Adsorption

Adsorption can occur in the presence of physical forces or chemical bonds. Usually, it is reversible (the reverse process is referred to as desorption); therefore, it is responsible not only for the removal of compounds, but also for the release of substances. In the majority of circumstances, this process is characterised at equilibrium by a set of equations that quantify the amount of substance attached to the surface given the concentration of the substance in the fluid present in the fluid. Isotherms (the most renowned of which are the Langmuir and Freundlich equations) are used to describe the behaviour of adsorption equations because their parameters are dependent on temperature, which is one of the most important environmental elements that affect adsorption. Adsorption must be considered for ecological systems to function properly. It regulates exchanges between geospace and the hydrosphere as well as between atmosphere and water, accounts for the transport of substances in the ecosystem, and triggers Ionic exchange and enzymatic activities are examples of crucial processes.

### 1.7.4 **Introduction to Equilibrium Study**

Equilibrium study is a fundamental concept in chemistry and physics that seeks to understand the balance between opposing forces or processes in a system. It involves observing how different properties within a system, such as concentrations, pressures, or temperatures, reach a state of balance over time. Equilibrium is a crucial concept in various scientific disciplines, and its study provides insights into chemical reactions, physical processes, and even economic systems. (Guldberg, C. M., et al., 1864)

### 1.7.5 Equilibrium in Chemical Reactions

In the context of chemical reactions, equilibrium is governed by the Law of Mass Action, which states that the rate of a chemical reaction is proportional to the product of the concentrations of the reactants, each raised to the power of its coefficient in the balanced chemical equation. The equilibrium constant (K) quantifies the position of the equilibrium **for a given reaction.**

For a generic reaction $aA+bB \rightleftharpoons cC+dD$, the equilibrium constant expression is given by:

$$K=(A)a(B)b \div (C)c(D)d$$

### 1.7.6 Analytical Techniques for Equilibrium Study

1. **Spectroscopy: Peering into Concentrations and Absorbance**

Spectroscopic techniques, such as UV-Vis spectroscopy, infrared spectroscopy (IR), and nuclear magnetic resonance (NMR), allow researchers to monitor changes in concentrations and interactions within a system. Absorbance spectra provide valuable information about the distribution of species and their concentrations.(Skoog, D. A. *et al.,* 2017).

2. **Chromatography: Separating and Quantifying Components**

Chromatographic techniques, including gas chromatography (GC) and liquid chromatography (LC), excel at separating and quantifying components within a mixture. These methods are invaluable for analyzing complex mixtures, identifying species, and understanding equilibrium dynamics. (Skoog, D. A. *et al.,* 2017).

3. **Electrochemical Methods: Probing Redox Equilibria**

Electrochemical techniques, such as cyclic voltammetry and potentiostatic methods, are essential for studying redox equilibria and electrochemical reactions. These methods offer insights into electron transfer processes and the behavior of ions in solution.( Newman, J. *et al.,* 2012).

4**. Mass Spectrometry: Unraveling Molecular Structures**

Mass spectrometry (MS) techniques, including gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS), provide information about molecular structures, compositions, and fragmentations. These techniques aid in identifying species and understanding equilibrium changes. (Skoog, D. A. *et al.,* 2017).

5. **Nuclear Magnetic Resonance (NMR): Characterizing Molecular Environments**

NMR spectroscopy offers insights into molecular environments and interactions. By analyzing chemical shifts and coupling constants, researchers can deduce molecular structures and dynamic equilibria.(Levitt, M. H., 2008).

### 1.7.7 Applications of Equilibrium Study

1. **Chemical Engineering: Optimizing Reaction Conditions**

Equilibrium concepts guide chemical engineers in designing optimal reaction conditions for industrial processes. By understanding how different factors influence equilibrium, engineers can tailor reaction conditions to achieve desired product yields and efficiencies.(Fogler, H. S. 2015).

2. **Environmental Chemistry: Unraveling Complex Systems**

Equilibrium studies play a crucial role in environmental chemistry, shedding light on chemical equilibria in natural systems. Understanding processes like acid-base equilibria and metal ion speciation is essential for addressing environmental challenges such as pollution and ecosystem health.( Baird, C. *et al.,* 2012).

3. **Biological Systems: Deciphering Molecular Interactions**

Equilibrium studies reveal the intricate dance of molecular interactions in biological systems. From enzyme-substrate equilibria to protein-ligand binding, equilibrium concepts help us understand the dynamics that underpin biochemical processes. (Cooper, A. *et al.,* 2000)

4. **Atmospheric Chemistry: Understanding Gaseous Equilibria**

Equilibrium principles play a vital role in atmospheric chemistry, especially in understanding gaseous equilibria and reactions that impact air quality and climate. Equilibrium constants help predict the behavior of pollutants and greenhouse gases. (Seinfeld, J. H. *et al.,* 2016).

### 1.7.8 Calculations in Equilibrium Study

Equilibrium study isn't just about observing a delicate balance; it involves rigorous quantitative analysis to uncover insights into the dynamic interplay between reactants and products.

1. **Equilibrium Constant (K): Quantifying Balance**

The equilibrium constant (K) is a numerical value that describes the equilibrium position of a given reaction. It's calculated using the concentrations of reactants and products at equilibrium (Atkins, P. *et al.,* 2010). For a generic reaction $aA+bB \rightleftharpoons cC+dD$ the equilibrium constant expression is:

$$K=(A)a(B)b \div (C)c(D)d$$

2. **Reaction Quotient (Q): Snapshot of the System**

The reaction quotient (Q) is similar to the equilibrium constant but is calculated using concentrations at any point in the reaction, not just at equilibrium. Q helps assess the direction in which a reaction will shift to achieve equilibrium. The reaction is in equilibrium if Q = K.. (Atkins, P. *et al.,* 2010).

3. **Calculating Equilibrium Concentrations: ICE Tables**

ICE (Initial, Change, Equilibrium) tables are used to calculate equilibrium concentrations when given initial concentrations and the reaction's stoichiometry. These tables help determine the changes in concentrations as the reaction progresses and reach equilibrium. (Atkins, P. *et al.,* 2010).

4. **Le Chatelier's Principle: Predicting Shifts**

Le Chatelier's principle is often used to predict the effect of changes in conditions on equilibrium. By considering the impact of concentration, pressure, and temperature changes, one can anticipate the direction in which the equilibrium will shift to counteract the change. (Levine, I. N. 2017).

5. **Equilibrium Calculations with Partial Pressures: Gaseous Reactions**

For gaseous reactions, equilibrium calculations can be based on partial pressures instead of concentrations. The equilibrium constant expression is modified to use partial pressures, often denoted as Kp (Atkins, P. *et al.,* 2010)

6. **Equilibrium Calculations Involving Solubility: Precipitation and Dissolution**

Solubility equilibrium involves calculating the concentration of ions in a saturated solution. Equilibrium constants, like the solubility product constant (Ksp ) are used to describe these equilibrium processes. (Levine, I. N. 2017).

7. **Equilibrium Calculations in Acid-Base Reactions: pH and pOH**

Equilibrium calculations are essential in acid-base equilibria. The pH and pOH of a solution can be calculated using concentrations of hydrogen ions (H+) and hydroxide ions (OH-), which are affected by the ionization of water and any acid or base present. (Skoog, D. A. *et al.,* 2017).

**1.79 Adsorption Isotherm Studies**

Langmuir Isotherm: Monolayer Adsorption

The Langmuir isotherm describes the adsorption of molecules onto a solid surface forming a monolayer. It assumes that adsorption occurs on specific sites and that once a site is occupied, no further adsorption can take place on that site. (Atkins, P. *et al.,* 2010). The Langmuir equation is given by:

$$\theta_A = \frac{V}{V_\mathrm{m}} = \frac{K^A_\mathrm{eq}\, p_A}{1 + K^A_\mathrm{eq}\, p_A},$$

where:

θ is the fractional surface coverage,

C is the equilibrium concentration of the adsorbate,

K is the Langmuir adsorption equilibrium constant.

Freundlich Adsorption Isotherm: Multilayer Adsorption

The Freundlich adsorption isotherm is used for systems where multiple layers of adsorbate molecules can form on the surface. It accounts for non-uniform adsorption energies and is often used for heterogeneous surfaces.

Equation:

$$q = K \cdot C^n$$

where:

q is the amount of adsorbate adsorbed per unit mass of adsorbent,

C is the equilibrium concentration of the adsorbate,

K and n are Freundlich constants.

# CHAPTER TWO

# MATERIALS AND METHODS

## 2.1 Materials

The materials were obtained from the Department of Chemistry, University of Benin, Edo State.

1. Bone char adsorbent
2. 2-Chlorophenol ( 98% pure )stock solution
3. UV-Vis spectrophotometer
4. Magnetic Stirrer
5. Weighing balance
6. Filtration setup
7. pH meter
8. Muffle Furnance
9. Safety equipment (lab coats, gloves, safety goggles, fume hoods)

Table 1: List of Instruments

| Type of Analysis | Model |
|---|---|
| X-ray Diffraction (XRD) | XDS 2400H X-ray diffractometer equipped with MiniFlex2 goniometer and detector |
| Scanning Electron Microscopy (SEM) | SEM, Hitachi SU 3500 |
| FTIR Spectra | Infrared Spectrometer Varian 660 MidIR Dual MCT/DTGS Bundle with ATR |
| UV-Visible Spectrophotometer | UV-6300PC Double Beam Spectrophotometer |
| Brunauer-Emmett-Teller (BET) | ASAP 2023 V4.02(V4.02 H) |
| pH meter | HANNA pHeP pocket-sized pH meter |

## 2.2 Method

## 2.3 Preparation and Characterization of Adsorbent

Fresh cow bones was obtained from Government Slaughter House at Ikpoba Hills, Ikpoba Okha LGA, Benin City,Edo State. The bones were carefully washed with water severally, cleaned from the meat, broken and later washed again repeatedly to remove impurities on the surfaces. The bones were rinsed with de-ionized water and transferred to the oven at 105◦c to dry. The dried bones were crushed and ignited at 500◦c for 2 hours. The bone char produced was further reduced using mortar and pestle. Finally the average particle size of 45µm was used and was obtained using the 45µm sieve size. The XDS 2400H X-ray diffractometer was used to determine the crystal structure, crystalline size and strain of the bone char. The SEM, Hitachi SU 3500 was used to imagine the microstructure and morphology of the bone char. The Infrared Spectrometer Varian 660 MidIR Dual MCT/DTGS was used in identifying the types of chemical bonds (functional groups) present in the bone char, while the BET ASAP 2023 V4.02(V4.02 H) was used in generating the specific surface area of the bone char expressed in $m^2/g$.

## 2.4 Adsorbate

The 2-Chlorophenol stock solution (98% pure) used in the study was obtained from  The sample was stored in a 100ml dark bottle and was transported and stored in laboratory away from the influence of light on the sample. The wavelength of the stock solution of 2-Chlorophenol was determined using UV-6300PC Double Beam Spectrophotometer.

## 2.5 Batch Study

The batch adsorption experiment was carried out at 27◦c.

Prepararion of Calibration curve

A standard solution of 0.97M was prepared from the stock solution and used to prepare the working solutions of 0.09M, 0.08M, 0.07M, 0.06M, 0.05M, 0.04M and 0.02M, using the dilution formula

$C_1V_1 = C_2V_2$

Where: $V_1$ = Volume of stock solution

C1 = Concentration of stock solution.

$V_2$ = Final volume of new solution.

The wavelength of the stock solution was determined using the UV-6300PC Double Beam Spectrophotometer which produced a result of 299nm. The Absorbance of the working solutions was determined using the wavelength of the stock solution which result (see result in Table 2.0) was used to produce the calibration curve (see figure 11.0)

Effect of Contact Time

0.5g of the bone char was weighed and poured into a 100ml glass beaker, 10ml of 0.06M 2-Chlorophenol was poured into the glass beaker and stirred at a rate of 45rpm at 1min, 3mins, 5mins, 10mins, 15mins, 30mins, 45mins, 60mins, 90mins, 120mins, 180mins and 240mins. After each time, the solution was filtered using the Whatmann 1 filter paper and the absorbance of the filterate was read and recorded (see result in Table 3.0). A graph of qe against Contact time was plotted (see figure 5.0) to get the optimum time.

Effect of pH

0.5g of the bone char was weighed and poured into a 100ml glass beaker, 10ml of 0.06M 2-Chlorophenol was poured into the glass beaker and stirred at a rate of 45rpm at varying pH (3, 5, 7, 9 and 11). 0.5M NaOH and 0.5M $HNO_3$ was used to regulate the pH of the solution. The solution after

40mins was filtered and the absorbance was determined (see result in Table 4.0). A graph of qe against pH was plotted (see figure 6.0) and the optimum pH was determined.

Initial Concentration

0.5g of the bone char was weighed and poured into a 100ml glass beaker, 10ml of 0.06M 2-Chlorophenol was poured into the glass beaker and stirred at a rate of 45rpm at a pH of 7.3 at concentrations (0.09M, 0.08M, 0.07M, 0.06M, 0.05M, 0.04M and 0.02M). After 40mins the solution was filtered and the absorbance was determined (see result in Table 5.0). A graph of qe against initial concentration was plotted (see figure 7.0) and the optimum concentration was determined.

Absorbent Dosage

Different weights (0.9g, 0.7g, 0.5g, 0.3g and 0.1g) were weighed and poured into the 100ml glass beaker and stirred at the rate of 45rpm at a pH of 7.3. 40mins after each weights the solution was filtered and the absorbance was determined (see result in Table 6.0). A graph of qe against weight in grams was plotted (see figure 8.0) and the optimum weight was determined.

2-Chlorophenol sorption

The experiments were carried out in 100 ml volumetric flasks, each using 0.5g of bone char and 10ml of 0.06mol/L 2-Chlorophenol . The flasks were placed on a magnetic stirrer running at 300 rpm, 30°C for 40mins. Adsorption of 2-Chlorophenol was determined by using UV/VIS Spectrophotometer. The amount of 2-Chlorophenol adsorbed by the bone char, (qe), was calculated for each run by the following equation:

$$qe = \left(\frac{Co - Ce}{m}\right) V \qquad (1)$$

Equilibrium adsorption isotherms

The Langmuir isotherm model.

The Langmuir isotherm model equation was:

$$qe = \frac{qmaxK_LCe}{1+K_LCe} \qquad (2)$$

where q (mg/g) was the amount of 2-Chlorophenol adsorbed onto the unit mass of the bone char; $K_L$ was the Langmuir equilibrium constant which is related to the affinity of binding sites; Ce was the equilibrium 2-Chlorophenol , and qmax was the maximum adsorption capacity (theoretical monolayer saturation capacity) (Aksu, Z. *et al.,* 2000). The main characteristics of the Langmuir equation, constants $K_L$ and qmax, could be determined from a linearized form of the Langmuir equation as follows:

$$\frac{Ce}{qe} = \frac{1}{qmaxK_L} + \frac{Ce}{qmax} \qquad (3)$$

Therefore, a plot of Ce/qe versus Ce gave a straight line with slope of 1/qmax and intercept of 1/(KL.qmax). The Langmuir isotherm was used to describe observed sorption phenomena. The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules (Ozsoy, H. D. *et al.,* 2006).

**The Freundlich isotherm model.**

The Freundlich isotherm model was based on adsorption on a heterogeneous surface, developed an empirical equation (4):

$$qe = K_FCe^1/n \qquad (4)$$

where qe is the adsorption (mg/g); Ce was the concentration of adsorbate in the solution (mg/L); $K_F$ and n were empirical constants that are characteristics of the system, indicating the adsorption

capacity and the adsorption intensity, respectively. The above equation can be linearized as the following form, also used to confirm the applicability of the model (5):

$$lnqe = lnK + \frac{1}{n} lnCe \qquad (5)$$

where $K_F$ denoted sorption capacity and 1/n denoted sorption intensity. The plot of ln qe versus ln Ce had a slope with the value of 1/n and an intercept magnitude of ln $K_F$.

# CHAPTER THREE

# 3.0 RESULTS AND DISCUSSIONS.

## 3.1 Characterization Result

X-ray diffraction (XRD).

The XRD pattern of the bone char was used to identify the amorphous phases. Fig. 1a, indicates several distinct peaks at 2θ intervals corresponding to the diffraction planes.

**XRD DIFFRACTION PARTERN OF SAMPLE**

**Sample 01: BG**

| Peak | 2θ/degree | Plane | Intensity $I/I_0$ | d-Valve (A°) | % Composition |
|---|---|---|---|---|---|
| 1 | 11.56 | 0 0 1 | 4.34 | 7.7208 | 1.98 |
| 2 | 20.86 | 1 0 0 | 14.42 | 4.2530 | 6.57 |
| 3 | 26.52 | 1 0 1 | 79.21 | 3.3618 | 36.14 |
| 4 | 36.58 | 1 1 0 | 8.11 | 2.4563 | 3.70 |
| 5 | 39.50 | 0 0 2 | 12.19 | 2.2815 | 5.56 |
| 6 | 40.27 | 1 1 1 | 7.84 | 2.2394 | 3.58 |
| 7 | 42.51 | 2 0 0 | 7.92 | 2.1267 | 3.61 |
| 8 | 45.92 | 2 0 1 | 5.82 | 1.9762 | 2.66 |
| 9 | 50.19 | 1 1 2 | 11.80 | 1.8178 | 5.38 |
| 10 | 54.98 | 0 2 2 | 8.14 | 1.6701 | 3.71 |
| 11 | 60.00 | 1 2 1 | 8.20 | 1.5418 | 3.74 |
| 12 | 62.38 | 2 1 1 | 7.23 | 1.4949 | 3.29 |
| 13 | 64.09 | 1 1 3 | 4.31 | 1.4529 | 1.96 |
| 14 | 68.23 | 0 2 3 | 4.60 | 1.3746 | 2.09 |

| | | | | | |
|---|---|---|---|---|---|
| 15 | 73.54 | 1 0 4 | 4.53 | 1.2879 | 2.06 |
| 16 | 75.80 | 3 0 2 | 8.02 | 1.2550 | 3.65 |
| 17 | 77.52 | 3 1 1 | 4.51 | 1.2314 | 2.05 |
| 18 | 79.98 | 2 1 3 | 5.97 | 1.1996 | 2.72 |
| 19 | 81.26 | 1 1 4 | 6.05 | 1.1839 | 2.76 |
| 20 | 84.00 | 2 0 4 | 5.94 | 1.1521 | 2.71 |

Figure 1a: XRD of bone char

. X-ray diffractogram of the adsorbent confirms the presence of hydroxyapatite as shown by a sharp peak at about 33o 2Ɵ. Also, the presence of well-defined peaks observed between 25o and 60o on the 2Ɵ axis are characteristic of the apatite phase (12). Furthermore, the presence of carbonates and silicon groups on the surface of the adsorbent suggest possible ionic substitution which may further influence the crystalline nature of the apatite phase

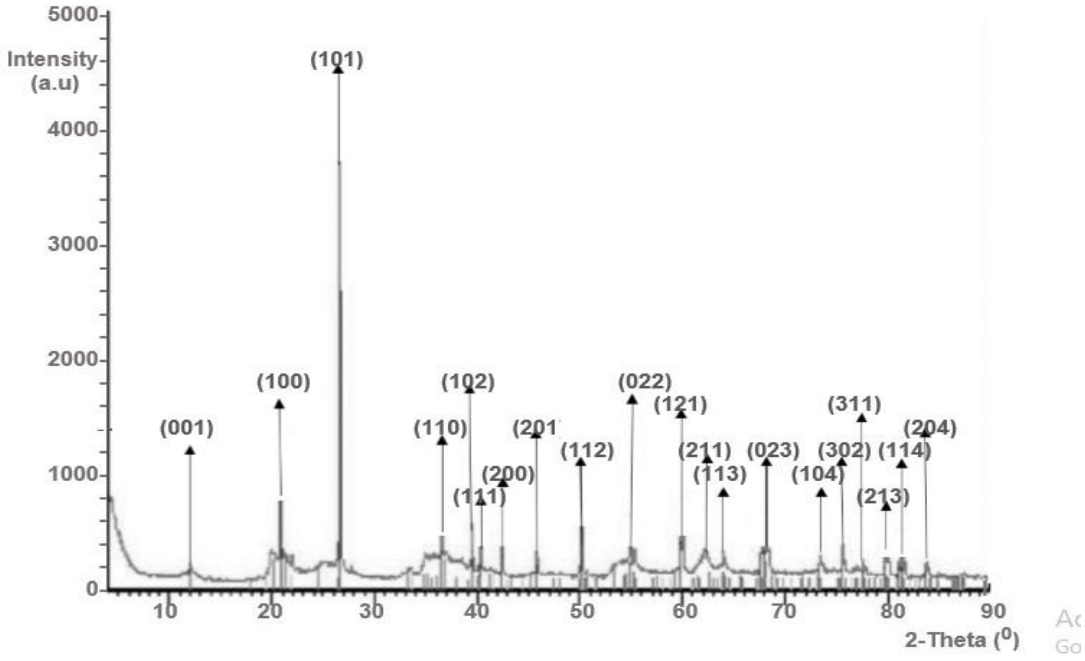



Figure 1b: XRD pattern of bone char

Fourier-transform infrared (FTIR) spectroscopy:

Figure 2, shows the surface functionalities of the bone char. Results indicate the presence of hydroxyl groups, 3708.25 $cm^{-1}$, which may be attributed to the presence of water molecules or hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (Manalu J. L. *et al*., 2015). 2710.01$cm^{-1}$ related C-H stretching vibrations in aromatic structures which indicates the presence of an alkene. Also at wavelength 2600 $cm^{-1}$ C=O stretching vibration is observed indicating the presence of a carboxylic group. The presence of anime group was indicated at peak 1240.55$cm^{-1}$..

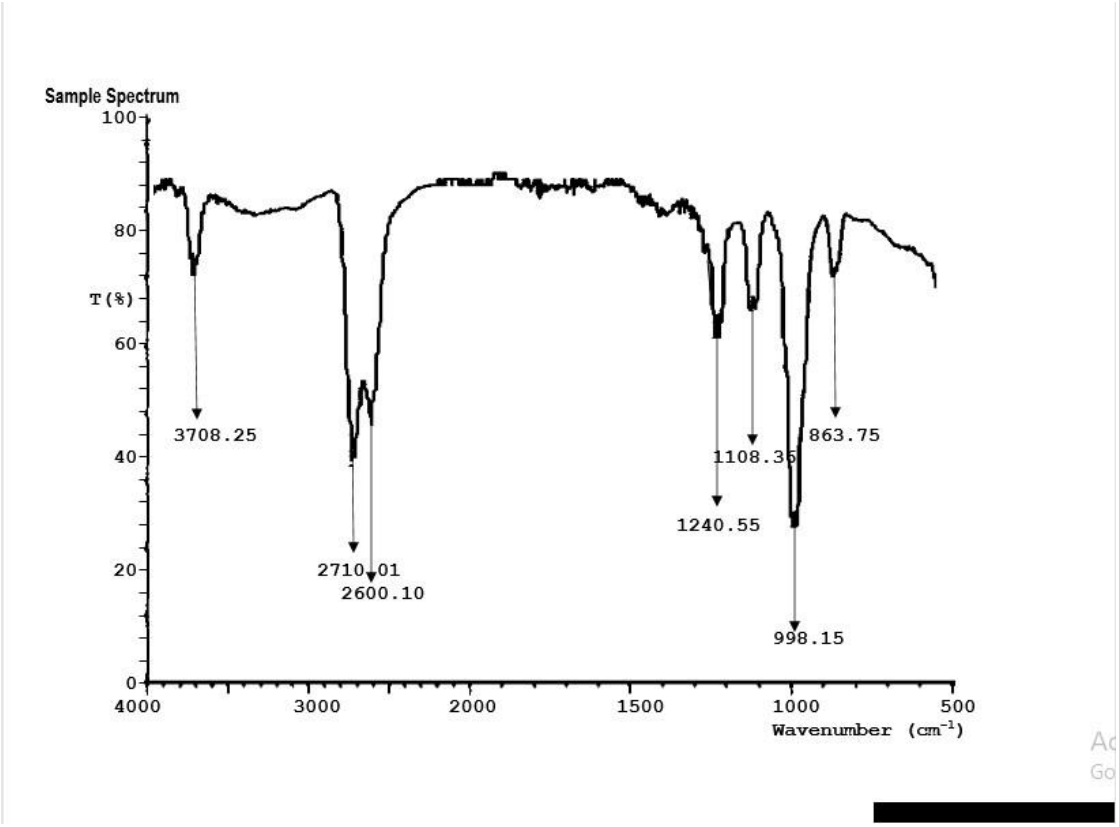



Figure 2: FTIR Spectra of bone char

Brunauer-Emmett-Teller (BET) surface area.

The observation of the result of samples shows the idea about the texture of the bone char. It is observed that the values of specific surface area of the bone char is 50.54 $m^2/g$ having a Molecular Cross Sectional Area: 0.1600 nm2

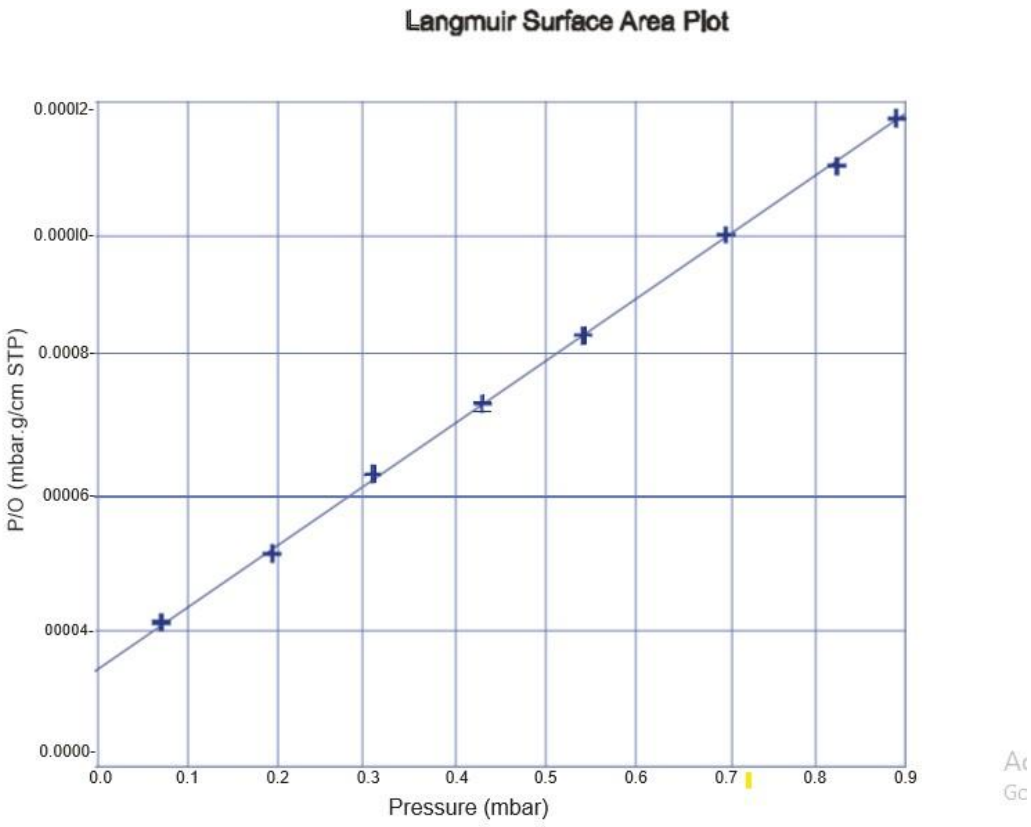



Figure 3: Langmuir surface area plot of bone char.

Scanning Electron Microscopy (SEM/EDS):

The characterization of the bone char by SEM showed a maginified image of 500nm indicating the large surface area, with fine irregular shaped particles and homogenous structure of the bone char. EDS measurement confirms the presence of the major elements Carbon, Oxygen, Silicon, and trace elements Phosphorus, Aluminium, Potassium and Calcium in the bone char.

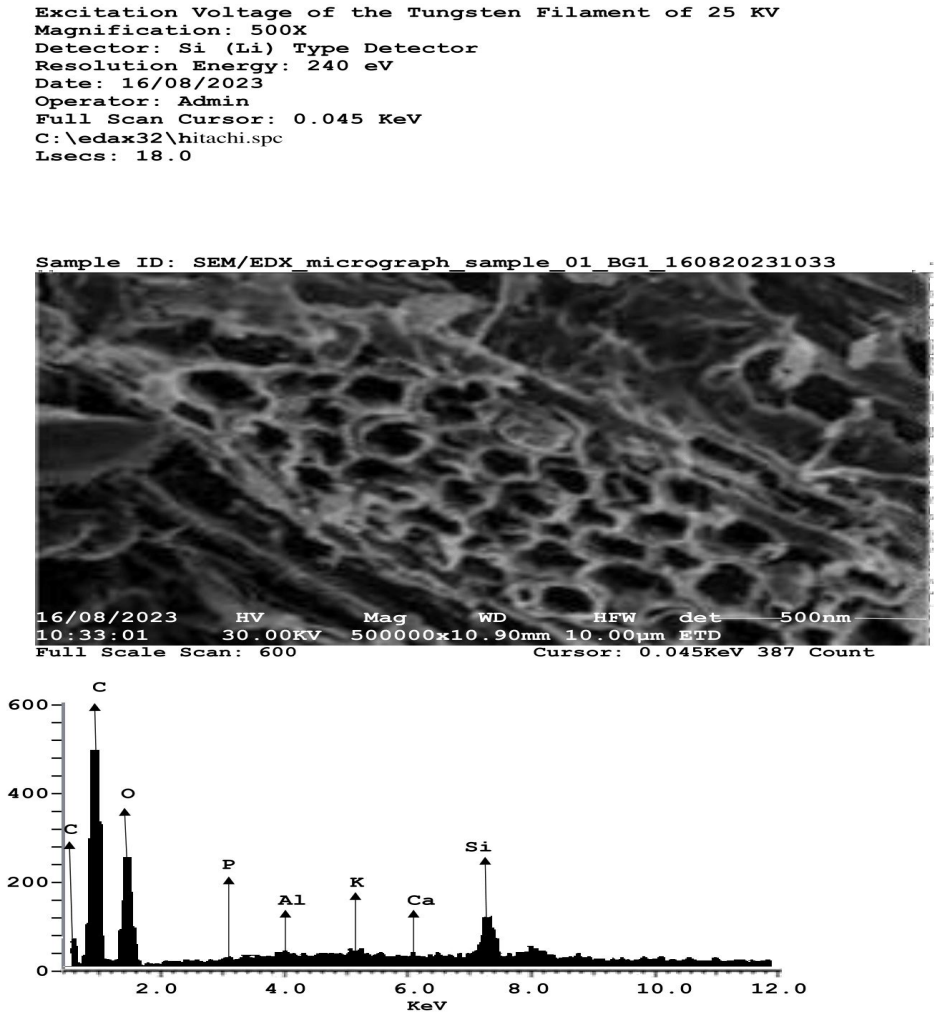



Figure 4.0: Scanning Electron Microscopy (SEM/EDS) image

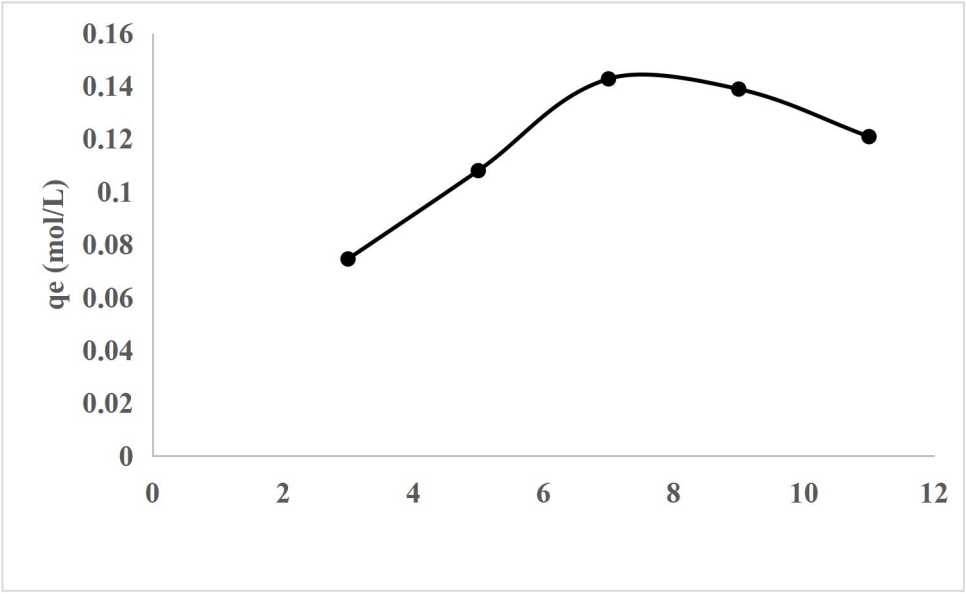
### 3.2 Batch adsorption studies of the Bone Char:

Equilibrium studies including:

Preparation of Standard and Working Concentrations:
A standard concentration of 0.946M was prepared from the stock solution

Effects of solution pH:

Increasing adsorbent dosage and increasing 2-Chlorophenol concentration were conducted to evaluate the adsorption potential of the bone char. The results of the influence of varying pH on the adsorption is shown in Figures 6.00




.

Figure 5.0: A plot of qe against pH

It was observed that maximum adsorption occurred at pH 7.3. At lower pH 2-Chlorophenol will exist primarily in its molecular form. However as the pH increases, 2-Chlorophenol undergoes deprotonation, forming negatively charged ions. At higher pH, the surface of the Bone Char is negatively charged, which adsorbs the deprotonated, negatively charged form of 2-Chlorophenol. This implies that the pH of the solution can affect the adsorption of 2-Chlorophenol onto Bone Char by influencing the charge of both the adsorbent (Bone Char) and the adsorbate (2-Chlorophenol).

Adsorbent Dosage:

The Bone Char displayed a high adsorption potential with maximum adsorption at 0.5 g where almost all the 2-Chlorophenol molecules at the concentration under consideration were removed from the system. The corresponding increase in adsorption may be attributed to the availability of adsorption sites by which the 2-Chlorophenol adhere. A gradual decrease in adsorption was observed as the concentration of the 2-Chlorophenol was increased. This is attributed to the gradual filling of

the adsorption sites as the concentration of the 2-Chlorophenol increased. The result of the influence of Adsorbent dosage on adsorption is shown in figure 8.0

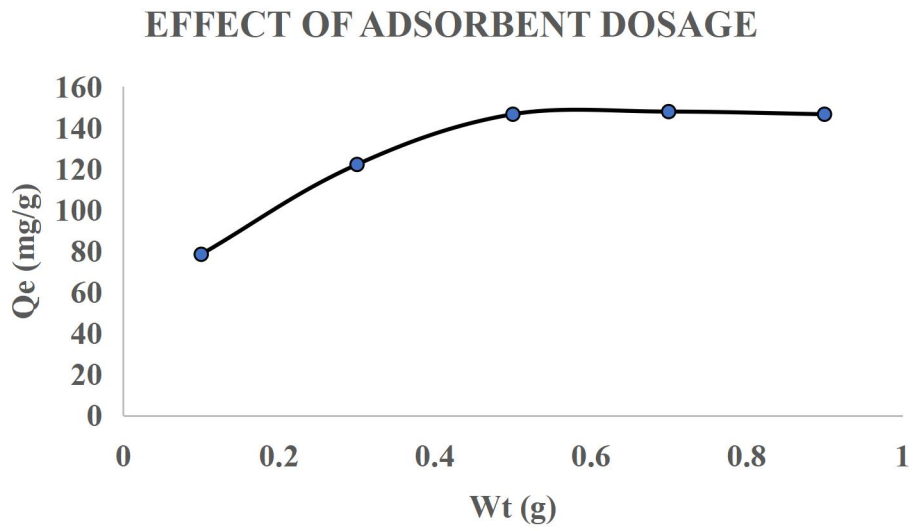



Figure 6.0: A plot of qe against Adsorbent Weight in grams

At 0.06M 2-Chlorophenol solution, saturation point is reached where the driving force of the 2-Chlorophenol started decreasing and the surface of the adsorbent might have been completely filled at this threshold. Increase in adsorption at different adsorbent dosages may be attributed to availability of sorption sites.

Initial Concentration

It was observed that as the concentration of 2-Chlorophenol increases, the adsorption capacity of bone char increases as shown in Figure 7.0. The optimum concentration observed is 0.06mol/L. Also, the efficiency of the adsorption capacity decreased after equilibrium was reached due to saturation. The significant differences in adsorption potentials at different adsorbate concentrations may be attributed to a shift in equilibrium

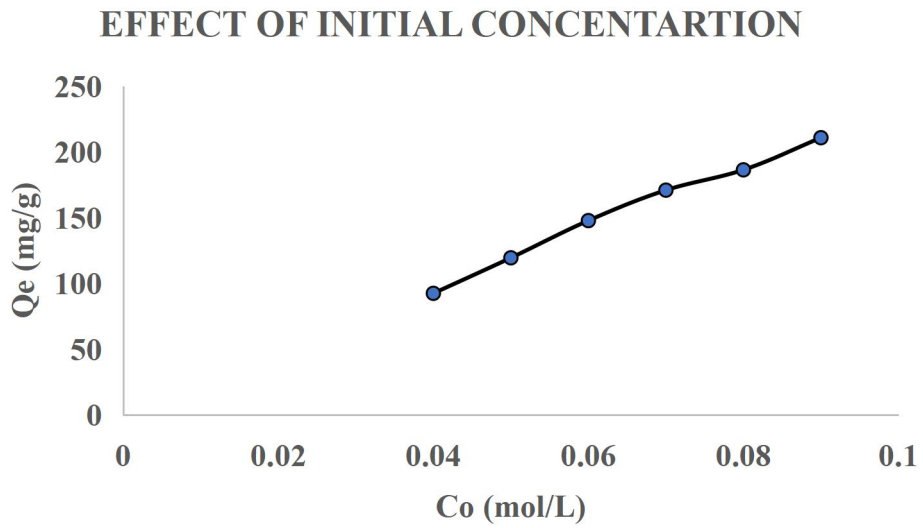



Figure 7.0: A plot of qe against Initial Concentration in mol/L

Adsorption isotherm:

To investigate the adsorption capacity as a function of aqueous concentration of the 2-Chlorophenol , adsorption isotherms are widely employed for fitting the data using representation of the adsorption (expressed as mg metal adsorbed per g of bone char) versus concentration of the 2-Chlorophenol at equilibrium Ce. Adsorption isotherm for 2-Chlorophenol on different concentrations are shown in Figure 8.0.

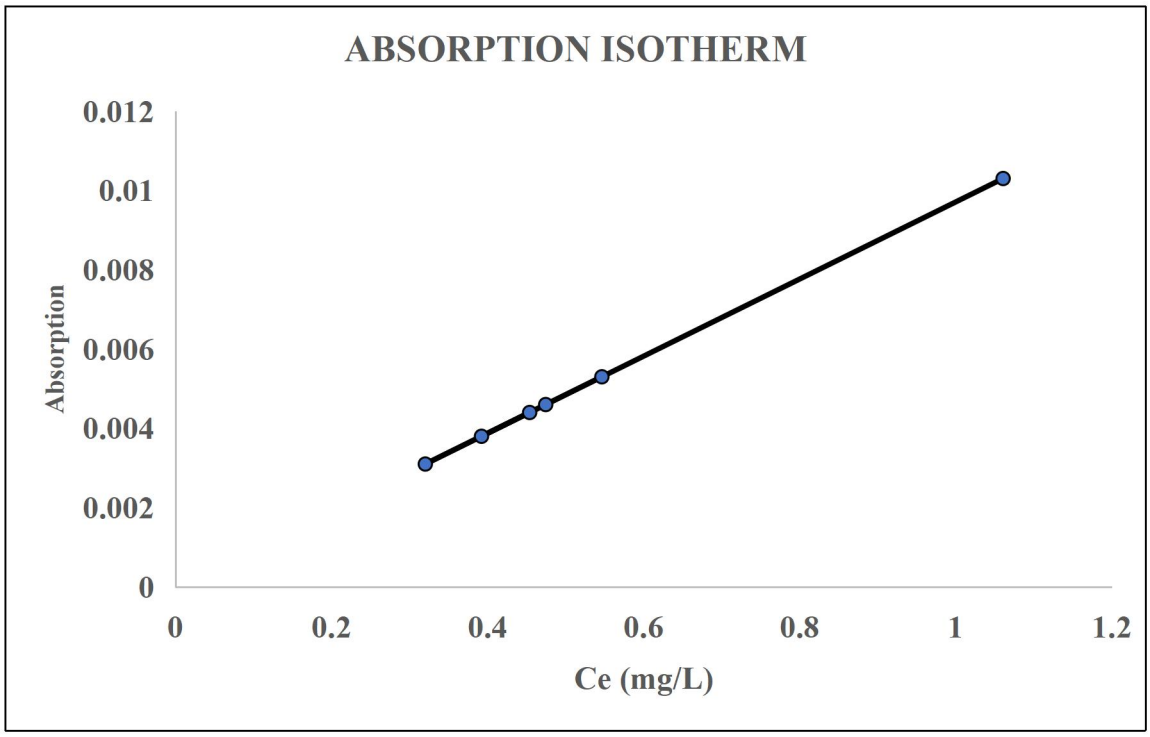



Figure 8.0: Adsorption Isotherm for 2-Chlorophenol on Bone Char

In batch adsorption processes, the initial 2-Chlorophenol concentration provided an important driving force to overcome the mass transfer resistance between the aqueous solution and the bone char surface. As a result, the amount of 2-Chlorophenol adsorbed was expected to be higher with a higher initial concentration, hence improving the adsorption process (Nita I *et al.,* 2007). From Figure 8.0, It is observed that when the initial Chlorophenol concentration increased from 0.320 to 1.061 mg/L, the uptake capacity of the bone char from 92.563 to 210.834 mg/g. This could be explained from two aspects. Firstly, the higher initial 2-Chlorophenol concentration increased the driving force to overcome the mass transfer resistance of 2-Chlorophenol between the aqueous and solid phases. Secondly, the increase 2-Chlorophenol uptake capacity of the bone char with increasing initial concentration might also be attributed to a more intense interaction between the adsorbate ions and the absorbant (Nita I *et al.,* 2007).

Langmuir Model:

The Langmuir equation has been frequently used to give the sorption equilibrium. According to the Langmuir model, metal ion absorption happens on a homogeneous surface via monolayer adsorption with no interaction between the deposited ions. All surface sites are alike and can only accommodate one adsorbed molecule, the ability of a molecule to be adsorbed on a given site is independent of its neighboring sites occupancy, adsorption is reversible, and the adsorbed molecule cannot migrate across the surface or interact with neighboring molecules (L Anah *et al.,* 2018). To get the equilibrium data, initial 2-Chlorophenol concentrations were varied while the adsorbent mass in each sample was kept constant (Shanmugapriya A *et al.,* 2011). The linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by Equation (3) The adsorption constants of the Langmuir isotherm model parameters, qmax and $K_L$, were calculated from the intercept and slope of Ce/qe against Ce using Equation (3) and were found to be 212.76mg/g related to adsorption capacity and 0.00273 1/mg related to the rate of adsorption, respectively. The correlation coefficient of Langmuir isotherm ($R^2$) was 0.9834 (Figure 9.0), which shows correlation or linear relationship. With $R^2$ levels closer to one, the relationship becomes more linear. Thus, it was found that adsorption of 2-Chlorophenol onto bone char correlated well with Langmuir equation (Nita I *et al.,* 2007).

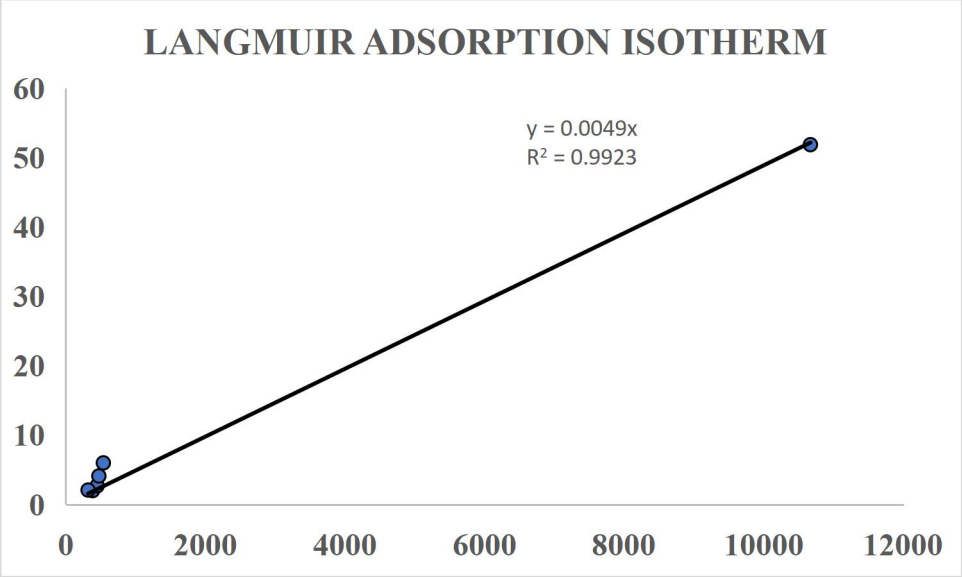



Figure 9.0: The Langmuir adsorption isotherm for 2-Chlorophenol adsorption by bone char

Freundlich Model

The Freundlich isotherm was originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces or surface supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that binding strength decreases with increasing degree of site occupation. The Freundlich isotherm can describe the adsorption of organic and inorganic compound on a wide variety of adsorbents (L Anah. *et al*., 2018). On average, a favorable adsorption tends to have Freundlich constant, n, between 1 and 10. Larger value of n (smaller value of 1/n) implies a stronger interaction between the adsorbent and the adsorbate while 1/n equal 1 indicates linear adsorption leading to identical adsorption energies for all sites. Linear adsorption generally occurs at a very low solute concentration and low loading of the adsorbent (L Anah. *et al*., 2018). The value of n of this model fell in the range of 1–10, indicating favorable biosorption. The numerical value of 1/n <1 suggested that at lower equilibrium concentrations, adsorption capacity was only modestly suppressed. This isotherm did not anticipate adsorbent saturation by adsorbate. Freundlich isotherm model parameters $K_F$ and n, calculated according to Equation (7), were 26.728 for adsorption capacity and 0.7474 for

intensity of the adsorption. The correlation coefficient of Freundlich isotherm ($R^2$) was 0.174 (Figure 10.0).

The Freundlich isotherm model depicts multilayer adsorption, in which adsorbate molecules are maintained at more than one adsorption site on the adsorbent's surface. The linear and non-linear mathematical expressions of this model are given in equations 6 and 7 respectively. The low correlation coefficient of the isotherm suggests that the mechanism of removal is more of a monolayer adsorption than adherence of dye molecules to a multiple adsorption site. The slope of the graph represented by the value of 1/n (Table 2) indicating moderate non-linearity. (Markandeya, A. *et al.,* 2015).

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \quad (7)$$

Where:

qe is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g-1)

kL is the Langmuir constant related to the adsorption capacity (L g-1),

Ce is the concentration of adsorbate in the solution at equilibrium (mg L-1),

qm is the maximum uptake per unit mass of adsorbent (mg g-1),

$C_o$ is the highest initial concentration of adsorbate

Where $K_F$ (mg g-1) (L mg-1) n and 1/n are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

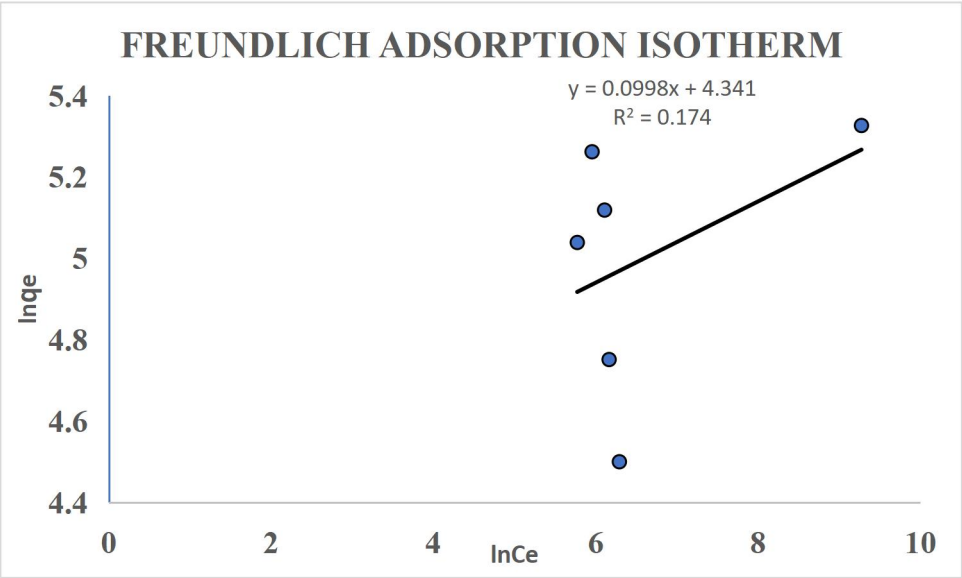



FIGURE 10.0: Freundlich Isothermal model for 2-Chlorophenol adsorption by bone char

Table2: Isotherm parameters for the adsorption of 2-Chlorophenol onto activated bone char.

| Isotherm | Parameters | Value |
|---|---|---|
| Langmuir | $q_{max}$ (mg/g) | 212.76 |
| | $K_L$ (L/mg) | 0.0027 |
| | $R_L$ | 0.9998 |
| | $R^2$ | 0.9963 |
| Freundlich | KF ($mg^{-1-1/n}\ L^{1/n}\ g^{-1}$) | 26.728 |
| | n | 1.3380 |
| | $R^2$ | 0.1740 |
| | 1/n | 0.7474 |

Table 2 shows the properties of the Langmuir and Freundlich equations. In Table 2, Langmuir model seems to fit the experimental data well. The $R^2$ value is low at 0.1740, suggesting that this model does not describe the data accurately. 1/n is approximately 0.7474, representing a degree of non-linearity in this model (Gad H. M. H. *et al.,* 2014)

## CONCLUSION

This study revealed that cow bone char has good adsorption properties and could be utilized for the treatment of 2-Chlorophenol in waste water before discharge into the environments, also the Langmuir model appears to be better fit for the adsorption of 2-Chlorophenol onto bone char due to its higher correlation coefficient, 0.9963 compared to Freudlich model of correlation coefficient 0.174.

## REFERENCES


A. F. Pozharskii, A. T. Soldatenkov, A. R. Katritzky (1997), Heterocycles in Life and Society, John Wiley & Sons,

Adewuyi, A., Göpfert, A., Adewuyi, O. A., & Wolff, T. (2016). Adsorption of 2-chlorophenol onto the surface of underutilized seed of Adenopus breviflorus: A potential means of treating waste water. *Journal of Environmental Chemical Engineering*, *4*(1), 664-672. https://doi.org/10.1016/j.jece.2015.12.012

Adkins, S. S., Chen, X., Nguyen, Q. P., Sanders, A. W., & Johnston, K. P. (2010). Effect of branching on the interfacial properties of nonionic hydrocarbon surfactants at the air–water and carbon dioxide–water interfaces. *Journal of Colloid and Interface Science*, *346*(2), 455-463. https://doi.org/10.1016/j.jcis.2009.12.059

Adkins, S. S., Chen, X., Nguyen, Q. P., Sanders, A. W., & Johnston, K. P. (2010). Effect of branching on the interfacial properties of nonionic hydrocarbon surfactants at the air–water and carbon dioxide–water interfaces. *Journal of colloid and interface science*, *346*(2), 455-463.

Adkins, S. S., Chen, X., Nguyen, Q. P., Sanders, A. W., & Johnston, K. P. (2010). Effect of branching on the interfacial properties of nonionic hydrocarbon surfactants at the air–water and carbon dioxide–water interfaces. *Journal of colloid and interface science*, *346*(2), 455-463

Aksu, Z. (2000). Equilibrium and kinetic modelling of cadmium(II) biosorption by C. Vulgaris in a batch system: Effect of temperature. *Separation and Purification Technology*, *21*(3), 285-294. https://doi.org/10.1016/S1383-5866(00)00212-4

Argese, E., Bettiol, C., Ghelli, A., Todeschini, R., & Miana, P. (1995). Submitochondrial particles as toxicity biosensors of chlorophenols. *Environmental Toxicology and Chemistry*, *14*(3), 363-368. https://doi.org/10.1002/etc.5620140302

Balaban, M. O., Zuritz, C. A., Singh, R. P., & Hayakawa, I. (1986). Estimation Of Heat Of Moisture Sorption And Improved Criteria For Evaluating Moisture Sorption Isotherm Equations For Foods. *Journal of Food Process Engineering*, *10*(1), 53-70. https://doi.org/10.1111/j.1745-4530.1987.tb00004.x

Batool, F., Mohyuddin, A., Amjad, A., Ul Hassan, A., Nadeem, S., Javed, M., Hafiz Dzarfan Othman, M., Wayne Chew, K., Rauf, A., & Kurniawan, T. A. (2023). Removal of Cd(II) and Pb(II) from synthetic wastewater using Rosa damascena waste as a biosorbent: An insight into adsorption mechanisms, kinetics, and thermodynamic studies. *Chemical Engineering Science*, *280*, 119072. https://doi.org/10.1016/j.ces.2023.119072

Bhargava, D., & Killedar, D. (1992). Fluoride adsorption on fishbone charcoal through a moving media adsorber. *Water Research*, *26*(6), 781-788. https://doi.org/10.1016/0043-1354(92)90009-S

Carey, F. A. (2000). Organic Chemistry, 4th Edition, McGraw–Hill, USA

Chaisoontornyotin, W., Haji-Akbari, N., Fogler, H. S., & Hoepfner, M. P. (2016). Combined asphaltene aggregation and deposition investigation. *Energy & Fuels*, *30*(3), 1979-1986.

Chen, X., Jeyaseelan, S., & Graham, N. (2002). Physical and chemical properties study of the activated carbon made from sewage sludge. *Waste Management*, *22*(7), 755-760. https://doi.org/10.1016/S0956-053X(02)00057-0

Chun-Ting He, Jing-Yu Tian, Si-Yang Liu, Gangfeng Ouyang, Jie-Peng Zhang* and Xiao-Ming Chen (2013). A porous coordination framework for highly sensitive and selective solid-phase microextraction of non-polar volatile organic compounds Chemical Science DOI: 10.1039/C2SC21181E

Cui, X., Wang, X., Yang, L., Chen, B., Chen, J., Andersson, A., & Gustafsson, Ö. (2016). Radiative absorption enhancement from coatings on black carbon aerosols. *Science of the Total Environment*, *551*, 51-56.

Daraei H, Kamali H (2014) Experimental Design and Response Surface Modeling for Optimization of 2-Chlorophenol Removal from Water by Nanoscale Iron and Fe Powder. *J Environ Anal Toxicol* 4: 228. doi: 10.4172/2161-0525.1000228

Dedovets, D., Li, Q., Leclercq, L., Nardello-Rataj, V., Leng, J., Zhao, S., & Pera-Titus, M. (2022). Multiphase Microreactors Based on Liquid–Liquid and Gas–Liquid Dispersions Stabilized by Colloidal Catalytic Particles. *Angewandte Chemie International Edition*, *61*(4), e202107537. https://doi.org/10.1002/anie.202107537

Dong, J., Shen, L., Shan, S., Liu, W., Qi, Z., Liu, C., & Gao, X. (2022). Optimizing magnetic functionalization conditions for efficient preparation of magnetic biochar and adsorption of Pb(II) from aqueous solution. *Science of The Total Environment*, *806*, 151442. https://doi.org/10.1016/j.scitotenv.2021.151442

Dos Reis, G. S., Thivet, J., Laisné, E., Srivastava, V., Grimm, A., Lima, E. C., Bergna, D., Hu, T., Naushad, M., & Lassi, U. (2023). Synthesis of novel mesoporous selenium-doped biochar with high-performance sodium diclofenac and reactive orange 16 dye removals. *Chemical Engineering Science*, *281*, 119129. https://doi.org/10.1016/j.ces.2023.119129

Duan, F., Li, Y., Cao, H., Wang, Y., Crittenden, J. C., & Zhang, Y. (2015). Activated carbon electrodes: Electrochemical oxidation coupled with desalination for wastewater treatment. *Chemosphere*, *125*, 205-211. https://doi.org/10.1016/j.chemosphere.2014.12.065

Duan, J., Ji, H., Xu, T., Pan, F., Liu, X., Liu, W., & Zhao, D. (2021). Simultaneous adsorption of uranium(VI) and 2-chlorophenol by activated carbon fiber supported/modified titanate nanotubes (TNTs/ACF): Effectiveness and synergistic effects. *Chemical Engineering Journal*, *406*, 126752. https://doi.org/10.1016/j.cej.2020.126752

Emir Martínez-Gutiérrez , Humberto González-Márquez , Sergio Martínez-Hernández , Anne-Claire Texier , Flor de María Cuervo-López & Jorge Gómez dani (2012) Effect of phenol and acetate addition on 2-chlorophenol consumption by a denitrifying sludge, *Environmental Technology*, 33:12, 1375-1382, DOI: 10.1080/09593330.2011.627882

Gad H M H and Nabila A M 2014 Int. J. Advanced. Sci. Technol. Res. 4 184-201

Hamad BK, Noor AMD, Rahim AA (2011) Removal of 4-Chloro-2-Methoxyphenol from Aqueous Solution by Adsorption to Oil Palm Shell Activated Carbon Activated with K2CO3. J *Physic Sci* 22: 39-55.

Huong, P., Lee, B., & Kim, J. (2016). Improved removal of 2-chlorophenol by a synthesized Cu-nano zeolite. *Process Safety and Environmental Protection*, *100*, 272-280. https://doi.org/10.1016/j.psep.2016.02.002

Huong, P., Lee, B., & Kim, J. (2016). Improved removal of 2-chlorophenol by a synthesized Cu-nano zeolite. *Process Safety and Environmental Protection*, *100*, 272-280. https://doi.org/10.1016/j.psep.2016.02.002

Hyder, A., Begum, S. A., & Egiebor, N. O. (2015). Adsorption isotherm and kinetic studies of hexavalent chromium removal from aqueous solution onto bone char. *Journal of Environmental Chemical Engineering*, *3*(2), 1329-1336. https://doi.org/10.1016/j.jece.2014.12.005

Kozyatnyk, I., Yacout, D. M., Van Caneghem, J., & Jansson, S. (2020). Comparative environmental assessment of end-of-life carbonaceous water treatment adsorbents. *Bioresource Technology*, *302*, 122866. https://doi.org/10.1016/j.biortech.2020.122866

Kumar, R., Taleb, M. A., & Barakat, M. A. (2022). Design of BiOCl/WO3@Polyaniline Organic–Inorganic Nanocomposite Photocatalyst for the Efficient Decontamination of 2-Chlorophenol from Wastewater. *Catalysts*, *13*(1), 175. https://doi.org/10.3390/catal13010175

L Anah & N Astrini (2018) *IOP Conference Series: Earth and Environmental Science. Sci.* 160 012017DOI 10.1088/1755-1315/160/1/012017

L.I. Suárez-García, F.M. Cuervo-López, A.-C. Texier (2019) Biological removal of mixtures of ammonium, phenol, cresol isomers, and sulfide in a sequencing batch reactor, 1189-1202

Levitt, M. H. (2008). Symmetry in the design of NMR multiple-pulse sequences. *The Journal of chemical physics*, *128*(5).

Mahapatra, M. K., & Kumar A. (2022). Studies on the Adsorption of 2-Chlorophenol onto Rice Straw Activated Carbon from Aqueous Solution and its Regeneration. Department of Chemical Engineering, National Institute of Technology, Rourkela -769008, Odisha, India. https://doi.org/10.15255/CABEQ.2021.2004

Markandeya, A. Singh, S.P. Shukla, D. Mohan, N.B. Singh, D.S. Bhargava, R. Shukla, G. Pandey, V. P. Yadav & G.C. Kisku | Alberto Bezama (Reviewing Editor) (2016) Adsorptive capacity of sawdust for the adsorption of MB dye and designing of two-stage batch adsorber, Cogent Environmental Science, 1:1, DOI: 10.1080/23311843.2015.1075856

Maureen Tang, Sida Lu and John Newman (2012) *J. Electrochem. Soc.* 159 A1775 DOI 10.1149/2.025211

Muhammad Asif Hanif, Hafiz Muhammad Tauqeer , Nabiha Aslam , Asma Hanif, Muhammad Yaseen and Rasheed Ahmad Khera (2017). Correct Interpretation of sorption mechanism by Isothermal, Kinetic and Thermodynamic models. *International Journal of Chemical and Biochemical Sciences*, 12:53-67.

Nand, V., Maata, M., Koshy, K., & Sotheeswaran, S. (2012). Water purification using moringa oleifera and other locally available seeds in Fiji for heavy metal removal. *International Journal of Applied*, *2*(5), 125-129.

Ng, K. S., Head, I., Premier, G. C., Scott, K., Yu, E., Lloyd, J., & Sadhukhan, J. (2016). A multilevel sustainability analysis of zinc recovery from wastes. *Resources, Conservation and Recycling*, *113*, 88-105. https://doi.org/10.1016/j.resconrec.2016.05.013

Nita I, Iorgulescu M, Spiroiu M F, Ghiurea M, Petcu C & Cintezã O 2007 Analele Universitatii din Bucuresti-Chimie 1 59-67

Ozsoy, H. D., & Kumbur, H. (2006). Adsorption of Cu(II) ions on cotton boll. *Journal of Hazardous Materials*, *136*(3), 911-916. https://doi.org/10.1016/j.jhazmat.2006.01.035 (14) Chen J H, Xing H T, Guo H X, Li G P, Weng W and Hu S R 2013 J. Hazard. Mat. 248-249 28594

Ramos, R.L., Lebron, Y.A.R., Moreira, V.R. *et al.* Phenolic compounds in surface water: methodology and occurrence in Doce River, Brazil. *Environ Monit Assess* 193, 687 (2021). https://doi.org/10.1007/s10661-021-09420-4

Reimann, C., Bjorvatn, K., Frengstad, B., Melaku, Z., Tekle-Haimanot, R., & Siewers, U. (2003). Drinking water quality in the Ethiopian section of the East African Rift Valley I—Data and health aspects. *Science of The Total Environment*, *311*(1-3), 65-80. https://doi.org/10.1016/S0048-9697(03)00137-2

Rosales, E., Anasie, D., Pazos, M., Lazar, I., & Sanromán, M. A. (2018). Kaolinite adsorption-regeneration system for dyestuff treatment by Fenton based processes. *Science of The Total Environment*, *622-623*, 556-562. https://doi.org/10.1016/j.scitotenv.2017.11.301

Sandrin, T.R., Hoffman, D.R. (2007). Bioremediation of Organic and Metal Co-contaminated Environments: Effects of Metal Toxicity, Speciation, and Bioavailability on Biodegradation. In: Singh, S.N., Tripathi, R.D. (eds) Environmental Bioremediation Technologies. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-540-34793-4_1

Scott G. Huling, Robert G. Arnold, Raymond A Sierka, Patrick K. Jones, and Dennis D. Fine Contaminant Adsorption and Oxidation via Fenton Reaction Journal of Environmental Engineering Volume 126, Issue 7 https://doi.org/10.1061/(ASCE)0733-9372(2000)126:7(595)

Shanmugapriya A, Ramya R, Ramasubramaniam S & Sudha P N 2011 Arch. Appl. Sci. Res. 3 424-35

Shen, T., Xu, H., Miao, Y., Ma, L., Chen, N., & Xie, Q. (2021). Study on the adsorption process of Cd(II) by Mn-diatomite modified adsorbent. *Materials Letters*, *300*, 130087. https://doi.org/10.1016/j.matlet.2021.130087

Skoog, D. A., Holler, F. J., & Crouch, S. R. (2017). *Principles of instrumental analysis*. Cengage learning.

Tang, B., Yang, Z., Song, Z., Shi, G., Fu, D., Sun, X., Zou, J., & Qi, H. (2021). Self-built field induces surface electrons to reduce H+ to atomic H* for photocatalytic hydrodechlorination of 2-chlorophenols. *Chemical Engineering Journal Advances*, *8*, 100194. https://doi.org/10.1016/j.ceja.2021.100194

Tao, W., Zhong, H., Pan, X., Wang, P., Wang, H., & Huang, L. (2020). Removal of fluoride from wastewater solution using Ce-AlOOH with oxalic acid as modification. *Journal of Hazardous Materials*, *384*, 121373. https://doi.org/10.1016/j.jhazmat.2019.121373

Tegoulia, V. A., & Cooper, S. L. (2000). Leukocyte adhesion on model surfaces under flow: effects of surface chemistry, protein adsorption, and shear rate. *Journal of Biomedical Materials Research: An Official Journal of The Society for Biomaterials, The Japanese Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials*, *50*(3), 291-301.

Wu, Z., Zhong, H., Yuan, X., Wang, H., Wang, L., Chen, X., Zeng, G., & Wu, Y. (2014). Adsorptive removal of methylene blue by rhamnolipid-functionalized graphene oxide from wastewater. *Water Research*, *67*, 330-344. https://doi.org/10.1016/j.watres.2014.09.026

Xiao, W., Jiang, X., Liu, X., Zhou, W., Garba, Z. N., Lawan, I., Wang, L., & Yuan, Z. (2021). Adsorption of organic dyes from wastewater by metal-doped porous carbon materials. *Journal of Cleaner Production*, *284*, 124773. https://doi.org/10.1016/j.jclepro.2020.124773

Xu, Q., Owens, G., & Chen, Z. (2020). Adsorption and catalytic reduction of rifampicin in wastewaters using hybrid rGO@Fe/Pd nanoparticles. *Journal of Cleaner Production*, *264*, 121617. https://doi.org/10.1016/j.jclepro.2020.121617

Yang, Y., Sun, C., Lin, B., & Huang, Q. (2020). Surface modified and activated waste bone char for rapid and efficient VOCs adsorption. *Chemosphere*, *256*, 127054. https://doi.org/10.1016/j.chemosphere.2020.127054

Zhou, Y., Liu, G., Liu, J., Xiao, Y., Wang, T., & Xue, Y. (2021). Magnetic biochar prepared by electromagnetic induction pyrolysis of cellulose: Biochar characterization, mechanism of magnetization and adsorption removal of chromium (VI) from aqueous solution. *Bioresource Technology*, *337*, 125429. https://doi.org/10.1016/j.biortech.2021.125429

Zhu, M., Li, N., Lu, Y., Hu, Z., Chen, S., & Zeng, R. J. (2020). The performance and microbial communities of an anaerobic membrane bioreactor for treating fluctuating 2-chlorophenol wastewater. *Bioresource Technology*, *317*, 124001. https://doi.org/10.1016/j.biortech.2020.124001