SURFACE MODIFICATION OF COCONUT SHELL BIOCHAR FOR Pb AND CD ADSORPTION

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DEPARTMENT OF CHEMISTRY

FACULTY OF PHYSICAL SCIENCES

UNIVERSITY OF BENIN

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A PROJECT THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY, FACULTY OF PHYSICAL SCIENCES, UNIVERSITY OF BENIN, BENIN CITY, NIGERIA, IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF MASTERS OF SCIENCE (M.SC) DEGREE IN INDUSTRIAL CHEMISTRY

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CERTIFICATION

I hereby certify that this work was carried out by **Okogun, Alexander Courage** with matriculation number **PGPSC2015618** in the Department of Chemistry, faculty of Physical Science, University of Benin, Edo state, Nigeria.

_____ _____

Prof. J. Iyasele **Date**

Head of Department

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Project Supervisor

DEDICATION

This work is dedicated to my wonderfully awesome God, whose grace, guidance and protection kept me to fulfill the requirements of this expedition.

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I wish to appreciate to my lovely parents Mr. and Mrs. Okogun , my siblings and my family for their love, support and prayers which have been of immense help to me throughout my sojourn in school.

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May God bless you all and reward your individual and collective efforts. AMEN!

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ABSTRACT.

Air and water pollutants are often treated with activated carbon. This project inspects this sorbent for heavy metal or inorganic compound removal. Production of activated carbon. Physical and chemical activation and raw material pyrolysis are discussed. Biochar has a surface area of 226.380m2/g and a modified Biochar of 248.650m2/g, pore volume of 0.134cm3/g and 0.150cm3/g, pore size of 2.08nm and 2.118nm distribution, and chemical surface structure. Biochar and modified biochar FTIR spectra were analyzed for functional groups. Spectrum intensity enhanced with acid alteration. Peaks at 3200-3550 cm−1 indicate O-H stretching vibrations, as well as C=C stretching vibrations of alkane functional group at 1600-1660 cm−1 and -=CH3 group at 1430-1470 cm�� Modified biochar improved wastewater treatment and soil remediation by increasing specific surface area, pore volume, and pore size. Scanning electron microscopy revealed a rough modified biochar structure, increasing adsorption sites. Modification increased FTIR intensity, indicating functional group changes. Adsorption testing indicated modified biochar eliminates Pb and Cd from water. Adsorption efficiency depended on initial concentration, pH, dose, and contact time. The Langmuir adsorption isotherm model fit the data better than the Freundlich model, implying monolayer adsorption onto a homogenous surface. These studies demonstrate that acid-modified biochar can remove heavy metals from water.

CHAPTER ONE

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 BACKGROUND OF STUDY

Carbon ranks fifteenth in the earth's crust and fourth in the cosmos by mass after hydrogen, helium, and oxygen. Scientific, industrial, and consumer uses of carbon and carbon-containing substances vary. Activated carbon is famous for cleaning water and other applications. Porous activated carbon has a wide surface area for adsorption or chemical reactions. This microcrystalline, non-graphitic, amorphous carbon material has been carefully processed to increase its internal porosity through linked pores.
Biochar is primarily carbon with hydrogen, oxygen, ash, nitrogen, and sulfur, according to Ahmad et al. (2016). Composition and qualities of biochar depend on feedstock, reactor design, and production conditions. The most important characteristics affecting biochar adsorption include chemical structure, porosity, feedstock inorganic metal content Kong, et al. (2014), and process conditions. Biochar surface heterogeneity resembles activated carbon. Biochar removes pathogenic organisms, organic matter, surfactants, nitrogen, micropollutants, heavy metals, and other pollutants better than activated carbon due to its large surface area, higher carbon content, high cation and anion exchange capacity, and stable structure Kaetzl, et al., 2018. Biochar has a wide surface area and an equally distributed pore network with micropores as large as 2nm, mesopores between 2-50 nm, and macrospores as small as 50nm Mukherjee, et al., 2011. It adsorbs heavy metals and organic ammonia nitrogen in water due to its huge specific surface area Han, et al., 2020. Biochar outperformed activated carbon in several cases despite having a lower surface area. Water absorption expands biochar's inner surface. Ahmad et al. (2020) noted

that expansion increases adsorption capacity. Numerous research have examined modified biochar adsorption and functional group effects. Vijay, et al. (2008) found that some functional groups form hydrogen bonds and respond. Hydrogen bonds have high binding energy, making them difficult to break. Microwaves, oxidation, reduction, and metal ion loading are common modifications Yang, et al., 2019. -CHO, -COOH, and -OH are common functional groups in modified biochar. Wu, et al., 2019 found it effective in eliminating metals and organic pollutants. Cheng et al., 2021 discovered modified biochar physically and chemically adsorbs. Adsorption mechanisms vary by contaminant and property. Biochar pores and surface area can be increased with iron oxides for structural benefits Ren, et al., 2015.
Coconut shell and husk biomass contains mainly lignin, cellulose, and hemicelluloses, according to Borel et al. (2021). Li et al. (2020) say accelerating cellulose breakdown increases biochar porousness. Jiang et al. (2020) found that increasing lignin breakdown speeds biochar synthesis, increasing its specific area, fixed carbon (FC) concentration, and exquisite scent. The percentage of lignin, cellulose, and hemicellulose in coconut shell and husk biomass strongly affects biochar characteristics. A unique coconut waste biomass technique produces biochar, a black, carbon-rich, porous material with high aromatization and anti-decomposition properties.
Columbus' sailors burned wooden water containers in the 15th century to preserve water. People probably relied on intuition without knowing the effect's mechanics. The mechanism was found in 18th century.
In 1862, Lipscombe invented a portable water purifying carbon compound. This milestone enabled the commercial use of activated carbon in portable water treatment and wastewater. Current research on this chemical is vital. The urgent need to treat home and industrial wastewater drives this.

Activated carbon cleanses water, including cooking and commercial vegetable oils. The slow pace of technical improvement in the country has depleted national resources by importing activated carbons for local chemical and process companies and municipal and industrial water treatment plants. Industrialization, agriculture, and population development have caused ecosystem contamination. Many pollutants harm living things, thus wastewater treatment is needed. Water treatment technology are often flawed. Because it eliminates contaminants, activated carbon treatment was developed for water purification.

A problem

Because organic and inorganic substances pollute waterways, wastewater must be purified before discharge. Adsorption is one of the most effective conventional methods for treating organic compound-contaminated wastewater. Activated carbon effectively reduces organic load.

JUSTIFICATION

Benefits of completing this research include:

I. Coconut shell is common in Nigeria.

Boost agricultural waste-to-activated carbon industry.

iii. Job creation will lower national unemployment.

Iv. Industrial uses of activated carbon will bring Nigeria foreign exchange.

1.16 Goals and objectives.

1.16.1 AIM.

This study creates and modifies coconut shell biochar for Pb and Cd absorption.

1.16.2 Goal.

i. To evaluate modified biochar (BET, SEM EDS, FTIR of activated carbon).

II. Treatment of coconut shell biochar surfaces with HCl

III. Measure activated carbon pH, bulk density, and conductivity.

Literature Review

Heat treatment turns carbon precursors into activated carbon, a porous, highly adsorbent material with a large surface area. An linked network of pores increases internal porosity in this microcrystalline, non-graphitic, amorphous carbon. Thus, many applications use it as an adsorbent.

Europe pioneered industrial activated carbon production in the early 1900s. In 1900 and 1901, Swedish chemist von Ostreijko patented the chemical and thermal or physical activation of carbon with metal chloride and carbon dioxide and steam. Dutch Norit introduced Norit and Purit activated carbon in 1911 by activating peat with steam in a chemische werke facility. That age, powdered activated carbon was mostly used for decolorizing solutions in the chemical and food industries, and the sugar business recognized this invention.

In 1913, the US created the first activated carbon from soda byproduct blast ash, along with European developments. This breakthrough came from accidentally discovering ash decolored liquids. In WWI, granular activated carbons were mass-produced for gas masks to absorb hazardous gasses.

After WWI, Europe made great strides in coconut and almond shell activated carbons. Zinc chloride produced activated carbon with strong mechanical strength and gas and vapor adsorptive ability. Zinc chloride activation of sawdust produced pelletized carbons to recover volatile solvents and eliminate benzene from town gas from 1935 to 1940.

Cheng et al. (2021) note that biochar can adsorb several pollutants, however they stress the need to understand the mechanisms. They expect more challenges as biochar research and

development continue. Staying abreast of modern treatment technology requires more biochar-based pollutant removal technologies, especially for wastewater. For advanced wastewater treatment, consider biochar.

Discussing biochar alteration to optimize pollutant removal is crucial (Varjani et al., 2021). Adapting the modification procedure and understanding each modification agent's processes need more research. This research is crucial for optimizing biochar's environmental rehabilitation performance. The study of biochar modification is early, but its applications are huge. Biochar research technology will expand its use as it advances. Recent nanotechnology advances offer several chances to improve water treatment systems.

Biofilters improve biochar's environmental remediation adsorption (Gautam et al., 2021). Biochar serves many wastewater treatment purposes. However, scientists must monitor its environmental effects (Wiedemeier et al., 2014). Biochar's environmental effects must be studied to maximize its benefits and minimize its drawbacks. Biochar released during wastewater decontamination may raise treated water carbon. Biochar is a biomass pyrolysis product produced at 300-800°C without activation and may not be fully carbonized. In addition, biochar can contain toxic elements and nanoparticle pollution. Especially from sludge, biochar may release heavy metals.

More research is needed to optimise biochar production and reduce pollution (Han et al., 2020). This includes studying ways to optimize biochar carbonization and reduce hazardous compound emissions during wastewater treatment. Biochar can continue to be used for environmental remediation while minimizing risks by addressing these concerns. The cost and efficiency of biochar production depend on feedstock availability and composition. Biochar can be made from agricultural biomass, urban waste, paper waste, aquatic, and woody biomass (Gabhane et al.,

2020). Many agricultural wastes are used, including rice straw, cotton stalks, and coconut shells. Biochar is also made from municipal waste like paper mill and sewage sludge (Van Zwieten et al., 2010; Yuan et al., 2016). Examples of woody biomass include pine sawdust and waste wood chips (Lai et al., 2013), while aquatic biomass such as Macroalgae sp. and seaweed (Roberts, 2015) are often utilized as feedstock. Traditional methods of biochar production involve piling biomass in soil pits and allowing it to burn slowly with limited airflow (Barrow et al., 2013). Another method is to burn biomass outdoors and cover it with soil (Emrich et al., 2013). These approaches may be inefficient or environmentally harmful but have been used historically. As biochar production evolves, innovative and sustainable methods that maximize resource utilization and minimize environmental impact are needed. The process described is known as pyrolysis, a thermal degradation technique that utilizes heat to decompose biomass while minimizing the presence of oxygen (Basu et al., 2010). Traditional approaches to pyrolysis include slow pyrolysis and fast pyrolysis. To produce biochar, the selected biomass undergoes thorough drying before being pulverized. Pulverized particles are milled to 40 mesh (Rambli et al., 2018). Slow pyrolysis entails heating the biomass within the range of 300–600°C at a pace of 5 to 7°C per minute for at least 24 hours or longer. This process is typically carried out in a continuous auger/screw pyrolyzer reactor, resulting in biochar as the primary product (35–45%), along with bio-oil (25–35%) and syngas (20–30%) (Verma et al., 2012). However, fast pyrolysis operates at temperatures above 500°C and heating rates above 300°C per minute without oxygen (Dai et al., 2017). This process promotes rapid decomposition of biomass, providing mostly bio-oil as the principal product, with biochar produced in lower quantities.

1.2.1 PROPERTIES OF ACTIVATED CARBON.

The features of activated carbon can be explored within physical and chemical perspective.

PHYSICAL PROPERTY.

The surface area of activated carbon is one of its most crucial physical properties, as it directly influences its adsorption capacity. The available surface area for adsorption is determined by both the molecular size of the adsorbate and the pore diameter of the activated carbon. In applications requiring specialized adsorption, such as liquid-phase processes, the pore size distribution becomes paramount. Liquid-phase carbons typically possess a majority of holes with sizes of 3mm or smaller to permit rapid diffusion of the liquid adsorbate. The density of activated carbon, in conjunction with its specific adsorptive capacity for a particular substance, helps determine the grades of activated carbon required for a given system. This consideration provides optimal performance and cost-effectiveness. Additionally, mechanical strength and particle resistance play crucial roles, particularly in applications where pressure drop and carbon losses are concerns. Activated carbon particles must maintain their integrity under varying conditions to ensure efficient operation and longevity of the system. Therefore, selecting activated carbon with suitable physical properties is essential for achieving desired performance and minimizing operational issues.

1.2. Chemical property.

1. The iodine number, or adsorption capacity, is an important statistic for activated carbon performance. It is defined as the number of milligrams of iodine absorbed by one gram of carbon when the iodine concentration in the remaining filtrate is 0.02 normal. Iodine values are reported in mg/g to reflect activated carbon activity. It is directly related to the surface area of the carbon, as it represents the ability of the carbon to adsorb iodine molecules. Higher iodine values suggest more adsorption capacity and, by extension, a bigger surface area available for adsorption. Thus, the iodine value shows activated carbon's efficacy in water, air, and industrial operations.

2. MOLASSES NUMBER: The Molasses number, also known as molasses efficiency, is a measure of the mesopore content of activated carbon through the adsorption of molasses from solution. This test assesses carbon's propensity to absorb larger molecules. A high Molasses number implies a strong adsorption capacity for bigger molecules, often within the range of 95 to 600. Molasses efficiency is stated as a percentage, ranging from 40% to 185%. Regional differences exist in Molasses numbers. The European Molasses number normally runs from 525 to 1100 and is inversely connected to the North American Molasses number. This mismatch underlines the need of adopting regional standards and testing techniques when evaluating the performance of activated carbon for specific applications.

3. The apparent density of activated carbon impacts its quality and performance. Higher density often denotes greater volume activity, indicating a higher concentration of carbon within a particular volume. This often correlates with better quality activated carbon, as it implies a higher mass of adsorbent material available for adsorption.Apparent density is a key parameter used to assess the physical characteristics of activated carbon and is influenced by factors such as particle size, pore structure, and production method. Activated carbon with higher apparent density tends to have stronger mechanical strength and resistance to attrition, making it more suited for applications where physical durability is crucial, such as in fluidized bed reactors or packed columns.

4. Hardness or abrasion number is a key indicator of activated carbon's durability and physical integrity. Carbon resists frictional forces like backwashing and handling. The raw material and activated carbon activity can greatly affect hardness or abrasion number. Different activated carbon sources vary in hardness according to pore structure, particle size, and production processes. Product hardness can also be affected by activation. To ensure durability and

practicality, choose activated carbon with enough hardness. Harder carbon resists abrasion and degradation, improving filtration, purification, and adsorption performance.
5. Particle Size Distribution: Finer activated carbon particles allow better surface area access and faster adsorption kinetics. Vapor phase systems must address pressure drop, which affects energy cost.

2.2.3 Activated carbon.

Carbon surface chemistry is simpler due to its molecular and crystalline forms. Carbon black can do this, but it has less internal surface area than activated carbon. Activated carbon structure depends on carbonization and activation temperatures.
Several aromatic, nuclear structures become microcrystalline carbon atoms united hexagonally during carbonization. Prepared impurities and methods affect microcrystalline manufacturing. Active micro crystallites release free valences by breaking carbon-bonds on their surfaces. Three types of pores form in activated carbon micro crystallites: macropores, transitional pores, and micropores. Macropores are formed by burning off the edge groups of the crystallites, while micropores are formed by burning off the micro crystallite planes. Dubiet observed two stages of oxidation. Tridisperse activated carbon has maro, transitional, and micropores. From micropores to macropores, particle surfaces are directly accessible. The adsorptive property of active carbon depends on its chemical makeup. Imperfect (half burnt-off) graphite layers may affect the electron cloud configuration in the carbon skeleton, causing unpaired electrons. This greatly affects carbon adsorptive power for polarized compounds.
Adsorption occurs mostly in micropores and mesopores, with macropores transporting. Gas-phase adsorption uses microporous carbon, while liquid-phase processes use mesoporous carbon (Benaddi et al., 2000). Adsorption is largely driven by mesopores (Hu et al., 2001). Typically,

mesopores have 0.1 to 0.5 cm3 volume and 20 to 100 m2 surface area per gram (Hu et al., 2001). Oxidizing gases can create mesopores in activated carbon (Marsh, 1989). Large parts of the carbon surface are pore barriers that only tiny molecules can enter. Selective accessibility determines molecular adsorption and carbon material efficacy in many applications.

Activated Carbon Microstructure

Amorphous or activated carbon has a highly disordered microcrystalline structure with randomly oriented graphitic microcrystals (Gomez-Serrano et al., 2005). This structure is called "turbostratic," resembling a graphite with random layer plane translation along the axis and rotation along the c-axis. Turbostratic structures have 0.344 nm interlayer spacing, bigger than graphite (0.3354 nm). High-resolution transmission electron microscopy (HRTEM) research has produced several microporous models (McEnaney, 2002). Small stacks of two or three carbon layer planes separate the interlayer gap in nongraphitizing carbons heated to 900°C. Micropores are inherent to activated carbon's microstructure, contributing to its large surface area and adsorption capacity.

The Activated Carbon Process

The chars from pyrolyzing carbonaceous materials like wood, coal, peat, fruit stones, shells, or synthetic polymers are activated to make activated carbon (Manocha, 2003). Pyrolysis decomposes organic molecules without air, producing tarry and gaseous compounds and a solid porous carbon mass. The carbonized material is activated physically or chemically to create an adsorbent with high porosity and surface area. Chemical activation involves acid or alkali treatment, whereas physical activation involves steam or carbon dioxide heating. Activated carbon processing involves selecting raw material, carbonization process variables (such as temperature and heating rate), and activation method. To make activated carbon for water

treatment, air purification, and industrial processes, these factors must be optimized.

1.4 Activated Carbon Production Factors

1.4.1 Raw Material

Activated carbon can be made from most carbon-rich organic molecules that do not fuse during carbonization (Rodriguez-Reinoso, 2002). This wide range of feedstocks includes synthetic polymers and carbonaceous vegetal resources like wood, coal, peat, fruit stones, and shells. When choosing raw material for porous carbon, many factors are considered. These factors:

i. Rich in carbon
ii. low inorganic content (ash)
iii. Lots of volatiles and density
iv. Country supply stability
The activation potential
vi. Affordable stuff
vii. Low storage degradation

Wood, sawdust, coconut shells, and other plant-based materials are used to generate activated carbon. They comprise 45% of activated carbon raw materials. Properties make coconut shells and fruit stones good for activated carbon production. Many applications use microporous activated carbons made from coconut shells, peach stones, and olive stones.

1.4.2 Heat

Quality of activated carbon relies on temperature, notably final activation temperature. Commercial activation employs steam and CO2 at 800°C (San Miguel et al., 2003). However,

experts are researching ways to optimize the final activation temperature to boost production and cut expenses. Many studies have revealed that activation temperature impacts activated carbon output and surface area. San Miguel et al. (2003) reported activation temperatures of 1100°C, while Haimour and Emeish (2005) reported 200°C. Poor activation temperatures may limit production yields and surface areas but save energy and speed up processes. Higher activation temperatures boost manufacturing yields and surface areas but require more energy and processing time.

Optimising activation temperature maximises activated carbon properties and reduces manufacturing costs. The correct characteristics for the intended purpose and the cost-effectiveness of the production method must be assessed.

Many studies show that activated carbon is best formed around 400–500°C (Srinivasakannan and Zailani, 2003). Guo and Lua (2003) found that raising the activation temperature from 500°C to 900°C releases more volatiles and produces activated carbon with high surface area and adsorption capacity. Haimour and Emeish (2005) found that volatile matter reduces with carbonization temperature, with the greatest fluctuation between 200°C and 800°C due to fast carbonization. They also found that carbonization temperatures beyond 800°C may not be appropriate for activated carbon preparation since volatile matter lowers little.

BET surface area is another significant aspect of activated carbon properties affected by activation temperature. Activation temperature increases BET surface area. The activation temperature increases BET surface area and activated carbon adsorption capacity and efficiency by releasing volatile materials and widening pores. More active adsorption sites improve carbon surface adsorbate molecule availability.

1.4.3 Activation Time

Another important factor in carbonization and activated carbon characteristics is activation time. Srinivasakannan and Zailani (2003) found that palm shell and coconut shell precursor activation times range from 1 to 3 hours. As activation time increases, activated carbon BET surface area increases. Carbon pores expand and broaden with longer activation durations, increasing adsorption surface area. Long activations may reduce returns. Kim et al. (2001) found that high activation minimizes product yield drop.

1.4.4 Carbonised

Carbonization gasifies non-carbon components like hydrogen and oxygen from starting materials through pyrolytic breakdown. Unbound elemental carbon atoms reorganize form elementary graphite crystallites, according to Manocha (2003). Primary graphite crystallites and thermo-stable aromatic structures are essential for the activation process, which increases carbon structure porosity and surface area.

1.5 Activated Carbon.

Heavy metals, organic compounds, and toxic chemicals can be in industrial sewage. These contaminants can cause cancer, toxicity, mutagenicity, and teratogenicity in individuals and the environment. Common wastewater treatment methods include adsorption, chemical precipitation, membrane separation, artificial wetlands, and ion exchange. Adsorption is a diverse and effective wastewater treatment method for various pollutants. Researchers study biochar adsorption. Bu et al. (2021) said biochar's large specific surface area and functional groups make it a promising wastewater pollutant adsorbent. Biochar is a cost-effective wastewater treatment option because its surface properties may be altered to improve adsorption. Being generated from solid waste and agricultural residues, biochar is cheap. Fdez-Sanroman et al. (2020) found modified biochar adsorbs like activated carbon at half the cost. Biochar cleans wastewater of organic matter,

surfactants, and nitrogen. According to Kopecký et al. (2021), biochar has promise as a phosphorus (P) sorbent in wastewater treatment. Biochar absorbs phosphorus, reusing fertilizers and improving soil. Water includes diverse micropollutants that harm health and the environment. These pollutants come from pharmaceuticals, antibiotics, cosmetics, endocrine disruptors, and industrial chemicals, according to Bo et al. (2015). Wastewater treatment systems must be effective since micropollutants are omnipresent and hazardous. Biochar may work because of its cost-effectiveness, flexibility, and toxin targeting. Research and develop biochar-based wastewater treatment technologies to address micropollutants and protect human and environmental health. Even in little amounts, antibiotics, personal care products, and psychiatric drugs are micropollutants that affect persons and ecosystems. Gomes et al. (2015) indicated that these poisons can accumulate in food chain organisms, threatening people and animals. Researchers used modified biochar to remove micropollutants from water, including medicines like tetracycline, personal care products like triclosan, and psychoactive drugs like coffee. Biochar eliminates heavy metals and other inorganic pollutants from wastewater. Bioaccumulation of heavy metals harms ecosystems and humans. Organic contaminants like colors and heavy metals are a problem in water. Bio-oil biochar has been studied to remove chromium (Cr), including hexavalent (Cr(VI)) compounds used in color pigments. Wastewater treatment with biochar-based Cr(VI) adsorbents is promising. As an excellent adsorbent, biochar removes methyl violet from wastewater. Biochar-based adsorption technology must be developed to protect humans and the environment from a wide range of micropollutants in water.

i. Using ethanol solutions (5–50%) as mobile phase and activated carbon in 50% w/w

combination with celite as stationary phase, low-pressure chromatographic separation of carbohydrates (mono-di-tri saccharides) is possible.
ii. Medical uses: Activated carbon relieves oral toxicity and overdoses. It may blind poison and block digestion. Medical professionals bring activated carbon to poisoning scenes or emergency rooms. Empirical dose is 1g/kg (50–100g for teens and adults).
iii. Recrystallization with activated carbon purifies colored impurities in organic chemistry. iv. Most people utilize portable activated carbon water filtering. It removes pesticides, herbicides, chlorinated hydrocarbons, and phenols from water. It cleans electroplating baths, reaction catalysis, and aquarium filters.
Activated carbon is being investigated for hydrogen and natural gas storage. Porous material absorbs gases. Van-der Waals attractions attract gas to carbon. We found carbons with 5–10 kJ/m bonding energy. Gas can be desorbed at high temperatures and burned or used in a hydrogen fuel cell. vi. Iodine or sulphur-laced activated carbon traps mercury from coal fire power stations, medical incinerators, and natural gas well heads.

1.6 Activated carbon use.

After activation, activated carbon becomes powdered and granular. PAC is produced by grinding activated carbon in mills until 65-90% pass through a 325 mesh (45μm) screen. Finely split particles with a high surface area-to-volume ratio are employed in fast adsorption procedures. However, water treatment plants employ GAC in packed bed contact basins. GAC particles are larger and less surface-to-volume than PAC. SOCs, NOM, and substances that affect water taste and odor can be absorbed by GAC. Bansal et al. (2002) say GAC is a versatile and effective municipal and industrial water quality solution. Pesticides and other synthetic organic compounds (SOCs) can pollute ground and surface water supplies, causing neurological, renal,

and cancer complications with continuous exposure (Hammer and Hammer, 2001). Phenol, a typical organic molecule removed by activated carbon, comes from plastics manufacture and natural sources. Due of its environmental prevalence, effective removal strategies are needed (Jung et al., 2001). Natural organic matter (NOM) including fulvic and humic acids, hydrophilic acids, and carbohydrates can discolor water and generate carcinogenic disinfection byproducts (DBPs) like chloroform when disinfected with chlorine. Reducing NOM levels before chlorination. Calcium-NOM compounds enhance activated carbon NOM adsorption (Frederick, 2001).

1.6.1 Reactivated Carbon

When activated carbon becomes saturated with adsorbates after regular use, treated water exceeds the desired level, triggering breakthrough. Reactivating activated carbon recovers its adsorption capacity, making it useable instead of disposable. The most typical approach, thermal reactivation, comprises drying, desorption, pyrolysis, and gasification. Granular activated carbon (GAC) bed breakthrough time depends on adsorbate type, influent concentration, and treatment degree (Kawamura, 2000). Warmer thermal desorption vaporizes volatile adsorbates and decomposes unstable ones after drying removes water and some. Pyrolysis transforms heavy or non-volatile adsorbates into char, while gasification at higher temperatures removes vapors and gaseous products from reactivated carbon pores (Cannon et al., 1993 Before bringing reactivated GAC to service, virgin GAC can replace 10-15% mass loss from GAC transfer to regeneration locations or burning (Clark and Lykins, 1989). Reactivation at high temperatures in an inert atmosphere alters surface chemistry by removing oxygen-containing functional groups (Pereira et al., 2003). During GAC operation, inorganic substances like calcium may be adsorbed and not released after reactivation, limiting adsorption sites and efficiency (Clark and Lykins, 1989).

Reactivation with calcium catalysis increases carbon surface active sites, mass loss, and pore enlargement, which may alter adsorption effectiveness (Knappe et al., 1992). Reactivated carbon raises treated water pH, but its length and extent dictate its system impact (Farmer et al., 1998).

1.7 Carbon activation production.

Thermal or chemical processes can make activated carbon granules, powders, fibers, or beads from thermosetting precursors. Carbonization at 600–650°C and partial gasification (activation) in steam or carbon dioxide at 800–900°C provide the right pore structure in the most typical thermal method. This procedure enhances the raw material's pore structure, which varies by kind. Most reactions are thermal. The second commercial method heats cellulose precursor and hydrochloric acid in one step. Activation by chemicals. Despite having no formal name, thermal and chemical activation are called such. Both involve high temperatures.

1.8 Thermalizing.

Precursor material selection affects activated carbon product adsorptive and physical properties. Cost, availability, quality, mineral matter, and sulfur content are crucial when choosing coal, peat, and lignite sources.

Thermal activation normally requires two steps:

Carbonization happens at 600–650°C in an inert atmosphere. Organic solids lose hydrogen and create free radicals that condense into stiff cross-linked solid char between 400 and 600°C. This method enhances porosity but not enough for practical use. It mostly alters precursor material pores. Mill the carbonization char before continuing.

b) High-temperature activation: CO2, steam, or nitrogen heats milled char to 700–1200°C. It gradually raises the temperature to give each activation step time before going on. High-temperature activation prioritizes burning carbon particles blocking pores, creating the optimal

pore shape in activated carbon.

1.9 Chemoactivation.

Most chemical activation uses sawdust and phosphoric acid. Other activators and dehydrators include zinc chloride, sulfuric acid, calcium hydroxide, manganese chloride, and sodium hydroxide. In a 600°C rotary furnace, a paste of raw material and reagent is dried and carbonized. Phosphoric acid activators heat carbonized products to 800–1000°C, oxidizing carbon. After activation, most acid can be reused at the correct strength. Activated product is rinsed and dried. Changing the raw material-to-activating agent ratio, commonly 1:5 to 1:4, affects activated carbon activity. Increasing activating chemical concentration, furnace temperature, and stays can boost activity.

1.10 STEM activation.

Steam activates many raw minerals. Several procedures involve carbonization at 500–600°C and steam activation at 800–1100°C. Since carbon to carbon dioxide is exothermic, this energy can be employed to produce a self-sustaining process. Steam gasifies carbonized material in this water-gas reaction:

To maintain temperature, C + H2O (g) ----> CO + H2 (-31 Kcal). Rotary (fired directly or indirectly), vertical multi-hearth furnaces, fluidized bed reactors, and vertical single throat retorts can carbonize/activate.

Activated Carbon Surface Chemistry

Adsorption, electrochemical behavior, catalytic activity, acid-base properties, redox processes, and hydrophilic-hydrophobic interactions are altered by activated carbon's chemical surface. Unlike graphite, activated carbons' adsorption is largely affected by dispersion forces due to their random aromatic sheet organization. This unpredictable configuration causes unpaired electrons

and incompletely saturated valences, affecting adsorption. Oxygen, hydrogen, nitrogen, chlorine, and sulfur are inherited or added during carbonization and activation. At aromatic sheet edges or heterocyclic ring systems in carbon layers, heteroatoms form surface compounds, complexes, and groups. Oxygen from air or oxygen can only be desorbed as carbon oxide at high temperatures by all activated carbons. Chemically bonded hydrogen in activated carbons cannot be eliminated at 1000°C. Ammonia and nitrogen-rich organics add nitrogen, whereas hydrogen sulfide and carbon disulfide add sulfur. Halogens are introduced by halogen gasses or liquids.

1.10.1 Activated Carbon Surface Group

Pore size distribution and surface chemistry determine activated carbon adsorption selectivity. Due to its neutral surface, activated carbon absorbs organic molecules better than polar and ionic species. Raw material chemistry impacts activated carbon surface chemistry, improving efficiency. Activated carbon has oxygen, nitrogen, and other heteroatom surface functional groups due to its porosity and disordered areas. Network and plane periphery heteroatoms mimic aromatic compound functional groups. They underpin activated carbon surface chemistry. Oxygen on activated carbon is acidic and basic. Bases neutralize lactone, fluorescein-like lactone, and carboxylic acid anhydride carboxyl, phenolic hydroxyl, quinone-type carbonyl, ether, peroxide, and ester groups. Acids neutralize uncharacterized chromene or pyrone basic groups. Infrared spectroscopy identifies surface functional groups. Basic properties of activated carbon include oxygen-rich areas, basal planes, and nitrogen functional groups.

1.11). Adsorption.

Adsorption is necessary in natural, physical, biological, chemical, and industrial systems, including water filtering. The main adsorption mechanisms are dispersion-driven physisorption and electron exchange or sharing between the adsorbate and activated carbon surface. Adsorbate

buildup is easy on activated carbon due to its huge surface area and internal pore structure. Adsorption kinetics depend on bulk transport, film resistance, internal pore transfer, and physical adsorption. How fast adsorbate grows on activated carbon depends on these phases. Adsorption rate depends on concentration gradient, temperature, and hydrophobicity. Adsorption efficacy depends on activated carbon pore size. Large pores eliminate NOM, while micropores absorb small molecules. Mesopores enable chemicals diffuse to micropores for adsorption. Activated carbon's porous, cheap, and abundant nature makes it a good, wide-surface adsorbent. This material has the most physical adsorption surface area per gram. One teaspoon of activated carbon has more surface area than a football field. Color, taste, odor, and toxicity-causing water-dissolved contaminants are well collected. Activated carbon has graphitic platelets that absorb contaminants. Induced dipole interactions and Van der Waals forces drive these interactions. In neutral organic compounds, activated carbon graphitic platelets form intramolecular dipoles. The molecules attach to the activated carbon's surface and precipitate out of solution in its nano-pores or adsorption gaps. Activated carbon accelerates condensation. [1,12] Adsorption.

As a "molecular sponge," activated carbon contains millions of pores and a vast surface. Adsorption uses chemical and physical processes to concentrate fluid molecules on this surface. An absorbing liquid or solid distributes fluid molecules throughout its structure. Physical adsorption holds molecules to activated carbon via Van der Waals forces. This method does not chemically change carbon or adsorbate. Chemical bonds hold molecules in situ in chemisorption when they react with carbon or an impregnate. The molecule to be adsorbed must match the adsorbent's pore size. This maximizes molecule-pore wall attractive forces beyond energy. Coconut shell carbon with small pores may not decolorize well because larger color molecules

cannot access them. Carbon cannot adequately absorb them. Coconut shell carbons absorb small molecules due to their tiny pores. Coconut shell carbon absorbed Krypton and Xenon better than wood. The liquid packing capacity of pores determines adsorption. Capillary condensation in 25-angstrom mesopores can result via multilayer adsorption under high vapor pressures. At constant temperature, an isotherm displays the relationship between adsorption capacity and pressure (gases) or concentration (liquids). Chemical families with higher pressure and molecular weight adsorb better. Methane (CH4) absorbs less than propane (C3H8). Competition or preferred adsorption occurs in multi-component systems when heavier molecules are adsorbed after equilibrium. Lower molecular weight species desorb from the surface and are replaced by higher ones. Pressure and temperature affect vapor phase physical adsorption. Adsorption is more efficient at lower temperatures and higher pressures because molecules are less mobile. Wet and organic systems display this effect. The carbon surface absorbs moisture but desorbs it after choosing organic molecules. This is usually due to molecular size and charge. Carbon surfaces prefer organic over ionic water molecules. Charge determines primary, secondary, and tertiary amine adsorption. Less nitrogen-charged primary amines adsorb better than secondary or tertiary ones. Adsorption is better for large bulky molecules without charges than tiny charged ones. Though minuscule, molecular form matters. Some species are weakly physically adsorbed regardless of operation. Impregnating carbon with a target species-reacting chemical boosts its performance. Such chemicals spread over a broad surface area when coated on carbon, increasing reaction possibilities. Chemistry removes adsorbate in chemisorption.

1.12.1 Absorption

Granular activated carbon adsorbs organic compounds based on molecular surface attraction, total surface area per unit weight, and wastewater pollutant concentration. An adsorption

isotherm is needed to measure activated carbon consumption. Pollutant adsorption per unit carbon weight and equilibrium water concentration are linked by this isotherm. A relationship expression is:

X/M=KCl/n

Where:

Adsorption of contaminant per carbon weight

Concentration of water stream pollutants

Contaminant empirical constants

Plotting experimental logarithms with contaminant concentration on the X-axis and adsorbed amount on the Y-axis yields K and n. The resulting line has 1/n slope and K intercept. These dimensionless empirical constants compare chemical and activated carbon adsorption.

1.13 Adsorption/Surface Chemistry.

Oxygen on activated carbon impacts adsorption, wettability, catalysis, and electrical properties. Due to limited diffusion into micropores, acidic oxygen-containing functional groups on the basal plane's outer surface or edge are essential for adsorption. Because most of the adsorption surface is outside, oxygen content impacts carbon adsorption. Oxygen makes activated carbon polar. More polar components are removed during adsorption. Polar molecules adsorb better than non-polar ones on activated carbon with oxygen-containing functional groups. H2O. Your study illustrates the complex link between surface chemistry and activated carbon adsorption. Carbon surfaces with oxygen-containing functional groups like carboxylic groups can provide physical barriers that inhibit hydrophilic adsorption of valeric acid and phenol. Delocalized n-electrons can be destroyed by oxygen chemisorption in phenol and acidic anionic dyes. These studies underline the importance of activated carbon surface

chemistry for improving adsorption performance in various applications.

Characterizing Surface Functional Groups.

TPD, FTIR, and XPS determine activated carbon surface oxygen functional groups. These methods disclose activated carbon's surface chemistry and adsorption capabilities by detecting carboxyls, lactones, phenols, anhydrides, ketones, quinones, hydroquinones, aldehydes, and ethereal structures.

Desorption thermal.

Thermal stability helps characterize activated carbon surface functional groups. Chemical bond breakage requires different energies, affecting thermal stability. Normal heat treatment of activated carbon in vacuum or inert gas breaks down surface compounds into CO2, CO, H2O, and H2. Carboxylic acid and lactone groups breakdown around 200-800°C to form CO2. CO is produced by quinone, phenol, and ether decomposition at 500-1000°C. Phenolic group breakdown (200-500°C) produces H2O. Splitting C-H bonds (500-700°C) releases hydrogen atoms that create H2. In 1956, Puri et al. studied sugar and coconut charcoals before and after outgassing and oxidation. At 1200°C evacuation, oxygen functional groups produced as CO2 and charcoal base neutralization capacity were linked. Carbon's alkali neutralization was linked to CO2 evolution, the CO2 complex. Base neutralization was impacted by CO2 complex alterations during outgassing or oxidation. Heat treatment desorbed oxygen as CO2 after nitric acid oxidation. CO2 complex production increased base neutralization, while its breakdown during outgassing decreased base adsorption (Zhuang et al., 1994).

1.15 FTIR.

IR is commonly used to analyze coal, carbon black, char, and activated carbon chemical structures. The bulk structure and surface functional groups of carbon compounds are shown.

Carbon compounds have IR bands at 3400-3500, 1760-1880, 1700-1720, 1550-1675, and 1100-1200 cm^-1.

As an example:

Carbon gasification-induced surface oxygen complexes were examined by Zhuang et al. (1994) using diffuse reflectance infrared Fourier transform spectroscopy. At 1770 cm^-1, 1610 cm^-1, and 1250 cm^-1, there were obvious and broad bands. Specific functional groups, such as carboxylic acid and lactone (1770 cm^-1), carboxyl groups (1610 cm^-1), and C-O stretching bands (1250 cm^-1), were found.

The 1994 investigation of HNO3-oxidized carbon by Bautista-Toledo et al. related the 3500 cm^-1 band to carboxylic acid groups (v OH) and the 1717 cm^-1 band to carbonyl groups. Ishizaki et al. (1981) attributed the 1760-1710 cm^-1 band to carboxylic groups and the 1600 cm^-1 band to carboxylate groups after alkali neutralization.

In 1983, Starsinic et al. reported FTIR bands for carboxylic acid carbonyl groups (1720 cm^-1), C-O stretching, and OH bending modes (1250 cm^-1) in oxidized Saran char. A band at 3400 cm^-1 may indicate water adsorption in carbon or KBr during grinding. Another effective method for detecting oxygen functional groups in carbonaceous materials is Oxygen K-edge XANES. Turner et al. (1997) discovered carbonyl-type chemicals in partially combusted char using oxygen XANES. Characterizing carbonaceous materials' chemical composition and surface functions helps understand their adsorption properties.

1.15. Good Adsorption:

These findings support adsorption. Because adsorbate molecules bind to the adsorbent surface, the adsorbate concentration is frequently larger than in the bulk solution. Adsorption from

solution rises with solution temperature and concentration because adsorbate molecules have more kinetic energy to interact with the adsorbent surface. On heterogeneous surfaces like activated carbons, the Freundlich adsorption equation is applied. The adsorbate on the adsorbent is compared to its equilibrium concentration in the bulk solution. Adsorption occurs when charcoal absorbs KCl from a concentrated solution. Because of its porousness and large surface area, charcoal can absorb KCl molecules from the solution. At the charcoal surface, KCl molecules lower the solution's KCl concentration. Many purification and separation methods use this phenomenon.

1.15.2 Negation:

where the adsorbent surface contains less adsorbate than bulk. In dilute KCl solutions, charcoal prefers water. While KCl remains in the solution, water molecules adsorb onto charcoal, increasing salt concentration. Negative adsorption is unusual but possible under specific conditions and adsorbent-adsorbate combinations.

CHAPTER TWO

2.0 MATERIALS

2.1 Equipment

The equipment used in the study includes various glassware and laboratory apparatus such as measuring cylinders, coconut shell, 250ml and 500ml beakers, 250ml conical flasks, funnels, Whatman filter paper, and 250µm sieves. is as presented in Table 3.1

2.1.1 Reagents and Raw Materials Used

The materials and raw materials employed in this study are shown in Table 3.1

Table 2.2: Reagents and Raw Materials

S/N	MATERIALS	SOURCES	USES
1	Hydrochloric acid	98% pure AR, produced by JHD, Shatou, Guondghuo China.	To be used as activating agent
2	Potassium chloride	Pure AR, produced by Fisons, Loughborough England	For calibration of conductivity and salinity meters
3	Distilled water	Laboratory grade	For preparation of solutions

The equipment/apparatus used in this study are given in Table 3.2.

Table 2.3: Equipment/apparatus used for the experiment

S/N	Equipment	Manufacturer and model number	Use
1	Cycling Vibrator (Orbital shaker)	HY-4A PEC Medical, England	Mixing of adsorbent and adsorbate
3	Thermostatic Hot Air-Drying Oven	DHG-0A Jinotech Instrument Co. China	drying of adsorbent
4	Electric Muffle Furnace	PEC Medical, USA Model SX-5-12	carbonization, charring and calcination of adsorbent
	Fourier Transform Infrared (FTIR)	Cary 630 Spectroscopy. Agilent Technologies, Scientific, CA, USA	Functional group identification
	Scanning Electron Microscope (SEM).	BC43 Benchtop Confocal Microscope. Oxford Instrument, England	Surface morphology of adsorbent
	Brunauer-Emmett-Teller (BET).	NovaWin version 11.03. Quantachrome Instrument	Surface Area, Pore Volume, and Pore Size
	Atomic Absorption Spectrometer	INESA AA320 AAS, Shandong, China	Heavy metal analysis

Plate. 2.1 Cycling vibrator (Orbital shaker)

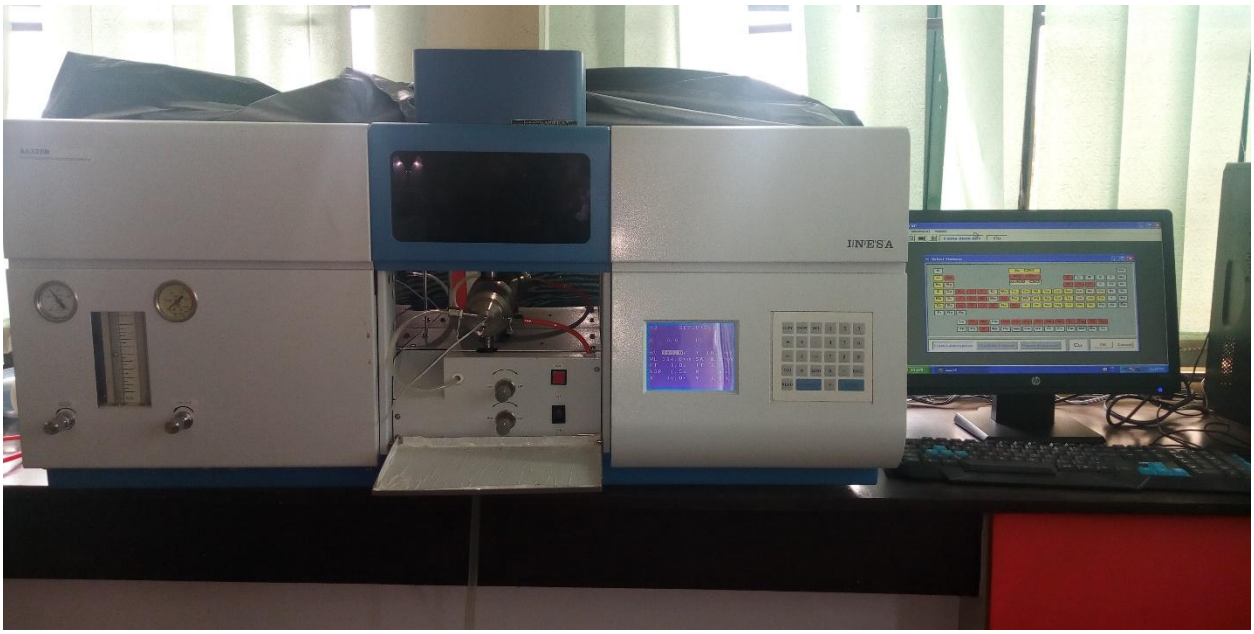

Plate 2.2 Atomic absorption spectrometer

2.3 MATERIALS

The coconut shells used in this study came from Idumagho, Ewohimi, Ubiaja, Edo State, Nigeria. Shells were used as experimental substrates. Laboratory-grade hydrogen chloride (HCl) was obtained from the University of Benin Department of Chemistry in Benin City. The impregnation process relied on this high-quality chemical, which influenced the study's results.

2.4 Making biochar

Get the coconut nut shell by removing the bark. Wash it with distilled water, sun-dry it for 3 weeks, and oven-dry it at 60°C for 24 hours. Ground biochar will be sieved through a 0.5mm filter before carbonization. Prepared precursor samples were cooked at 500ºC for 2 hours in a muffle furnace before cooling. They will smash, grind, sieve, and reduce carbonized materials in

a 250Um mechanical sieve before storing in an airtight jar.

2.5 Activator Chemical

Measure and pour 1M HCl acid into a beaker. Adding 200g carbonized biochar to acid makes a slurry.Adding 10ml of distilled water and stirring for 30 minutes fully mixes and dissolves the slurry. Chanapet 2012 Pouring fluid into crucible permits following reactions or operations. Activating chemical samples are oven-dried at 105°C for 24 hours to remove moisture and boost activation. Cooled dry samples are activated in a 700°C muffle furnace for 30 minutes. This phase is crucial for biochar surface area and reactivity. Finally, sealed jars keep activated samples for analysis and prevent contamination. Bhaskar et al (2015)

2.6 Bulk

Two grams of coconut shell biochar are carefully weighed into 10ml cylinders. Tap the biochar samples in the measurement cylinders to ensure consistent density. Per measurement cylinder, densely packed biochar samples' milliliter volume is measured. Mary et al. (2016) determine bulk density:

Dried activated carbon weight/volume = BD. 2.6.1 PH

Small modifications will be made to Singh et al.'s (2017) pH technique. 2g coconut shell Biochar is properly measured into 100ml beakers. Each beaker gets 20ml distilled water. Gently whirling the solution for 15 minutes disperses it. After spinning, foil-wrapped mixes are left for 10 minutes to avoid contamination. Parts can settle properly. The electrode is immersed in the mixture and pH is measured from the upper suspension.Calibration: Before measuring pH, check activated carbon surface shape and elemental content (2.7).

Scanning electron microscope JESM-7600F images sample surfaces. Prepared samples are secured to the SEM sample holder with double-sided carbon tape. The mounted samples will be

accelerated by a 15 keV electron beam. SEM signal production is optimized at this energy. SEMs take high-resolution images of sample surfaces for morphology and structure study. Micromarkers in SEM micrographs assess pore diameter, exposing material porosity. SEM analyzes element composition to determine sample element presence and distribution. This will disclose the volume's atomic and weight percent elemental makeup. Bello etal. (2015) 2.8 Electrical conductivity measurement

2g coconut shell biochar will be measured into a 100ml beaker, 20ml of distilled water added, and gently swirled for 15 minutes to determine EC using Singh et al. (2017). The stirred mixture will be covered with foil paper and left to settle for 10 minutes to avoid contamination. Finally, each sample's conductivity will be measured from the mixture's top.

2.8.3 SEM

The sample shape was evaluated by SEM (Hitachi SU 3500, Tokyo Japan).

2.8.4 FTIR

Coconut shell biochar functional group alterations are detected by FTIR. Before analysis, sample tablets will be prepared by mixing the sample with 1:100 hydrogen chloride. The Varian 660MidIR Dual MCT/DTGS Bundle with ATR FTIR spectrometer records 400–500cm-1 spectra. The detector will scan each sample 200 times at 4cm-1. Tabulate the wave number-absorption FTIR spectroscopy refractogram. Spectrum will be obtained via IR solution software.

2.8.5 BET Surface Area

The BET glass sample tube will receive 0.3g of accurately weighed sample. The tube's weight before and after loading will be recorded for accuracy. Nitrogen-powered Micromeritics FlowPrep 067s degass loaded samples at 473K for 3 hours. A sample's physically adsorbed water molecules are eliminated. After degassing, the sample will be reweighed for weight changes. A

liquid nitrogen-cooled Micromeritics TriStar 3000 V4.02 analyzes samples. BET surface area and pore volume/size are calculated from the nitrogen adsorption isotherm by the instrument software. For analysis and interpretation, the instrument's computer will record BET results, including surface area and pore characteristics.

2.8.6 Heavy Metal Water Treatment

Batch-adsorption was done on 100ml of contaminated water. In 250ml conical flasks, 0.2–1.20g activated carbon per 100ml water was weighed. The flasks were shaken at 120rpm on an orbital shaker at room temperature. The experiment varied adsorbent dosage, contact time, and pH to assess efficiency. Each experimental condition involves filtering flask samples with Whatman paper. An AAS assessed water lead (Pb) and cadmium (Cd) in the filtrate. Experimental settings were carefully manipulated to assess impact:

2.8.7 Adsorbent dose

Activated carbon 0.2–1.2 g per 100ml was used to study adsorbent dosage. Each dosage was given to four 250ml conical flasks containing 100ml of contaminated wastewater at room temperature. A fixed time of agitation helped adsorption. The mixture was filtered to remove the adsorbent from wastewater. Filtrate analysis measured pollutants. This experiment changed adsorbent dosage and analyzed pollutant removal using activated carbon to determine its effect on wastewater treatment efficiency. Heavy metal uptake percentage (Pr):(3.1)

Equation (3.2) calculates metal ion uptake per gram of adsorbent, q (mg/g): q=((C_o-C_f)*V)/m. Where Co and Cf are the starting and ending mg/l concentrations, V is the contaminated water volume in liters, and m is the adsorbent dose in grams.

The effect of contact duration on dirty water was tested using activated carbon at 1.0g/100ml for 15, 30, 45, 60, 75, and 90 minutes. Filtered sample and immediately tested for heavy metal ions.

CHAPTER THREE

3.0 RESULTS AND DISCUSSIONS

3.1. Effects of Modification on the Physicochemical Properties of Biochar

Table 3.1. Physicochemical Properties of Biochar (BC) and Modified Biochar (MBC).

Parameters	BC	MBC
pH	6.26	5.88
Electrical Conductivity (µS/cm³)	230	164
Bulk Density (g/cm³)	0.66	0.56
Surface Area(m²/g)	248.650	379.004
Pore Volume (cm³/g)	0.150	0.237
Pore Size (nm)	2.118	2.115

***BC*- Biochar**
***MBC*- Metal doped biochar**

Table 3.1 compares biochar physicochemical properties before and after acid modification. Acidity and alkalinity are determined by pH. Biochar is mildly acidic to neutral at 6.26 pH. After modification (MBC), pH drops to 5.88, indicating acidity. Adding acidic functional groups to biochar during alteration may reduce pH (Wang et al., 2018).

Electrical conductivity (EC) measures solution soluble salt concentration. Acid modification (MBC) reduced the electrical conductivity of BC from 230 µS/cm³ to 164 µS/cm³ in this investigation. Its soluble salt concentration dropped. This fall may be due to acid alteration reducing biochar surface ash. Ash dissolving in BC adds greatly to EC (Rehrah et al., 2014). This confirms Peiris et al. (2019) findings on untreated and adjusted tea waste biochar EC.

Biochar had a bulk density of 0.66 g/cm³, while modified BC had a lower density of 0.56 g/cm³. Modifying structures or removing components may reduce bulk density.

BC and MBC had 248.650m2/g, 0.150cm3/g, 2.118nm and 397.00m2/g, 0.237cm3/g,

2.115nm specific surface area, pore volume, and pore size. Acid treatment exposed more pores and surfaces, increasing surface area and pore volume over charcoal. Fig. 3.1 shows BC pores were larger than MBC pores. Lui et al. (2020) found acid alteration reduced walnut shell biochar pores. Biochar surface area and porosity are essential for wastewater and soil remediation (Leng et al., 2021). Adsorption, chemical reactions, and other interactions are more frequent on larger surfaces.

3.2 Scanning Electron microscopy (SEM) / Elemental composition

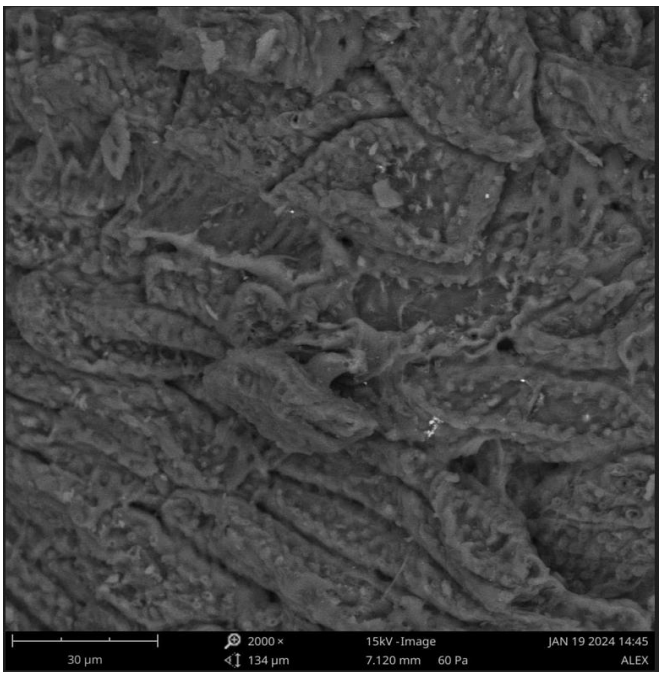

Fig. 3.1: SEM of BC

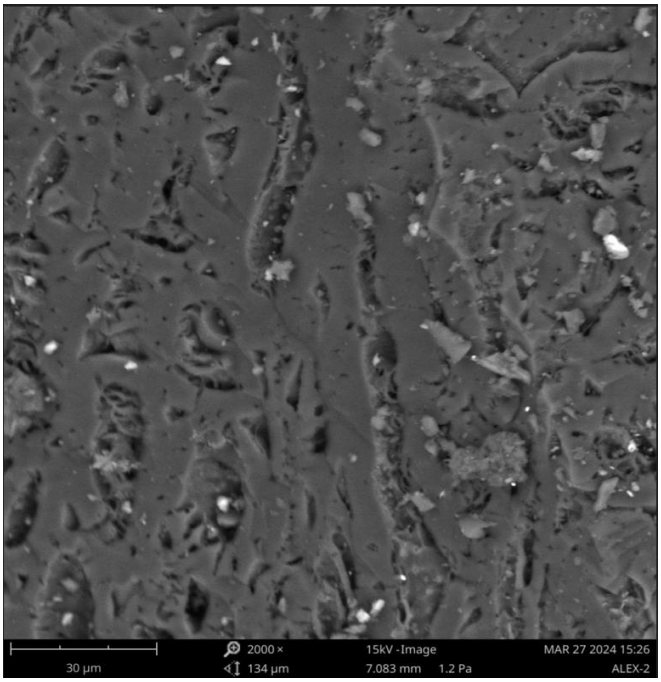

Fig. 3.2: SEM of MBC

Table 3.1: Elemental composition of BC

Element Symbol	Element Name	Atomic Conc.	Weight Conc.
C	Carbon	96.49	94.84
N	Nitrogen	2.54	2.91
Al	Aluminum	0.22	0.49
Si	Silicon	0.18	0.41
Na	Sodium	0.17	0.32
Mg	Magnesium	0.12	0.24
K	Potassium	0.06	0.19
S	Sulfur	0.07	0.18
Cl	Chlorine	0.06	0.17
P	Phosphorus	0.06	0.16
Ca	Calcium	0.02	0.08

Table 3.2: Elemental composition of MBC

Element Symbol	Element Name	Atomic Conc.	Weight Conc. (wt%)
C	Carbon	89.19	82.15
N	Nitrogen	5.12	5.49
Al	Aluminum	1.11	2.30
Mg	Magnesium	1.08	2.01
Si	Silicon	0.82	1.76
Cl	Chlorine	0.64	1.73
Na	Sodium	0.91	1.61
P	Phosphorus	0.53	1.26
S	Sulfur	0.46	1.12
Ti	Titanium	0.15	0.56

SEM was used to determine biochar (BC) and modified biochar (MBC) surface morphology. Figures 3.1 and 3.2 show the samples' various surface morphologies. The acid-modified biochar has more holes than the biochar, which may improve MBC sorption in aqueous solutions (Tejada-Tovar et al., 2021). Tables 3.1 and 3.2 list biochar and modified biochar elemental compositions. Carbon (94.84%, 82.15%) and nitrogen (2.91%, 5.49%) dominate BC and MBC,

with other elements in trace levels.

3.3 Functional groups

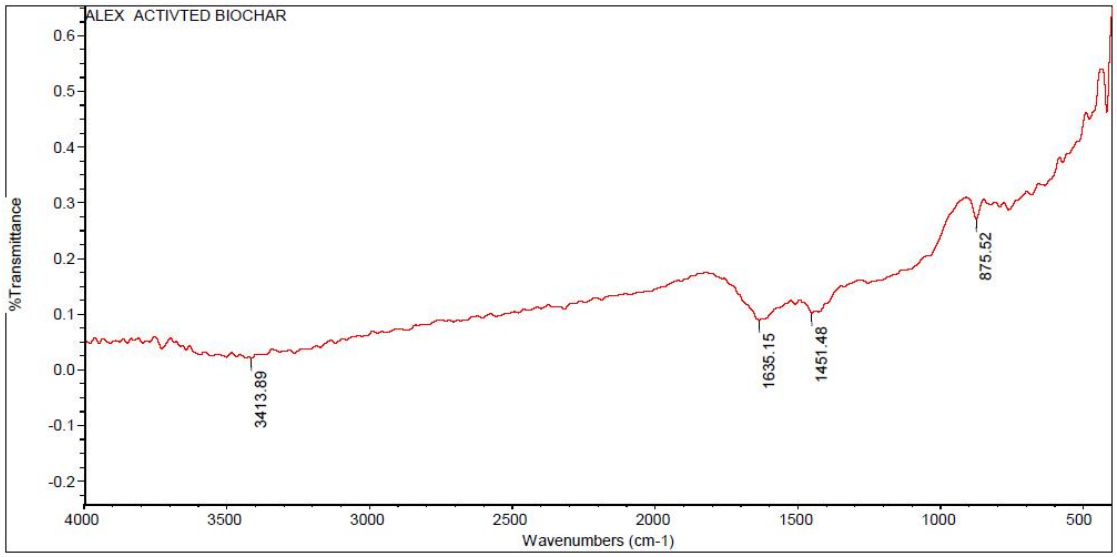

Fig 3.2: FTIR spectrum of biochar (BC)

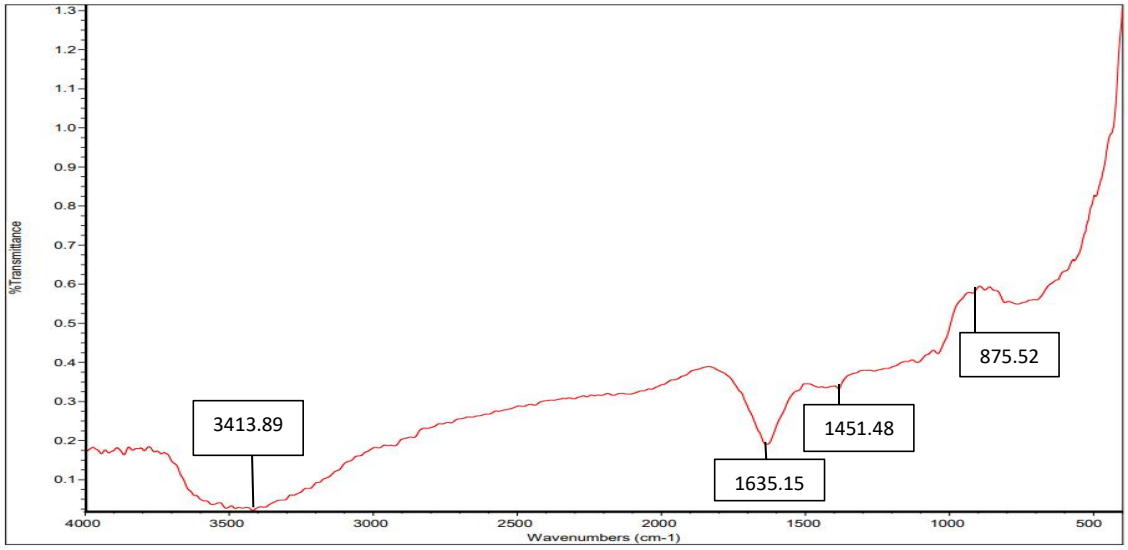

Fig 3.3: FTIR spectrum of modified biochar (BC)

Biochar and modified biochar FTIR spectra were examined to establish their functional groups (fig3.2 and 3.3). Acid modification increased spectrum intensity. Peaks at 3200-3550 cm−1 represent O-H stretching vibrations, 1600-1660 cm−1 represent C=C stretching vibrations of alkane functional group, and 1430-1470 cm−1 represent -=CH3 group.

3.3 Effect of concentration

Table 3.1: Effect of initial concentration on Pb and Cd ions at constant time (60mins), dosage(1g), and adsorbate volume(100ml)

Initial Pb/Cd Conc (mg/L)	Final Pb Conc (mg/L)	Final Cd Conc (mg/L)	Pb Removal (%)	Cd Removal (%)
2.5	0.294	0.435	88.24	82.6
7.5	0.068	0.047	99.09	99.37
10	0.052	0.038	99.48	99.62
12.5	0.036	0.027	99.712	99.78
15	0.035	0.021	99.76	99.86

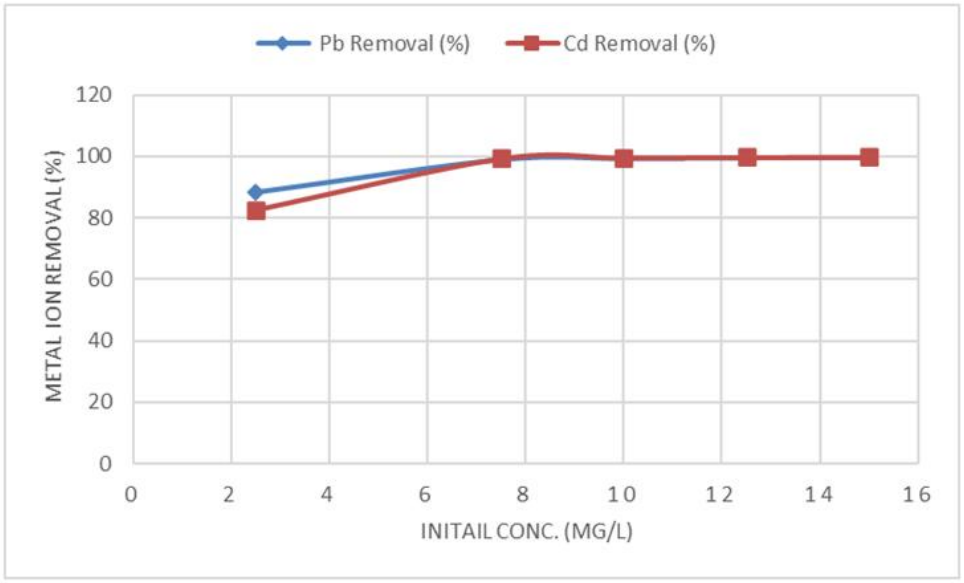

Fig. 3.4: Effects of initial concentration on competitive sorption of Pb and Cd ions

Chromium initiality impacts adsorption efficiency. Pb and Cd absorption studies with initial chromium levels are shown in Figure 3. Higher starting Pb and Cd concentrations improve the % removal of both metals, making the adsorption process more successful. Stronger concentrations may drive adsorption. The experimental adsorption method is effective for Pb and Cd, as shown by their high removal percentages.

3.4 Effect of pH

Table 3.2: Effect of pH at constant dosage on Pb and Cd ions (1g) , initial concentration(5mg/L), and adsorbate volume(100ml)

pH	Final conc. Pb (mg/l)	Final conc. Cd (mg/l)	Pb Uptake (%)	Cd Uptake (%)
3	0.041	0.068	99.18	98.64
5	0.049	0.074	99.02	98.52
7	0.057	0.078	98.86	98.44
9	0.052	0.072	98.96	98.56
11	0.055	0.066	98.9	98.68

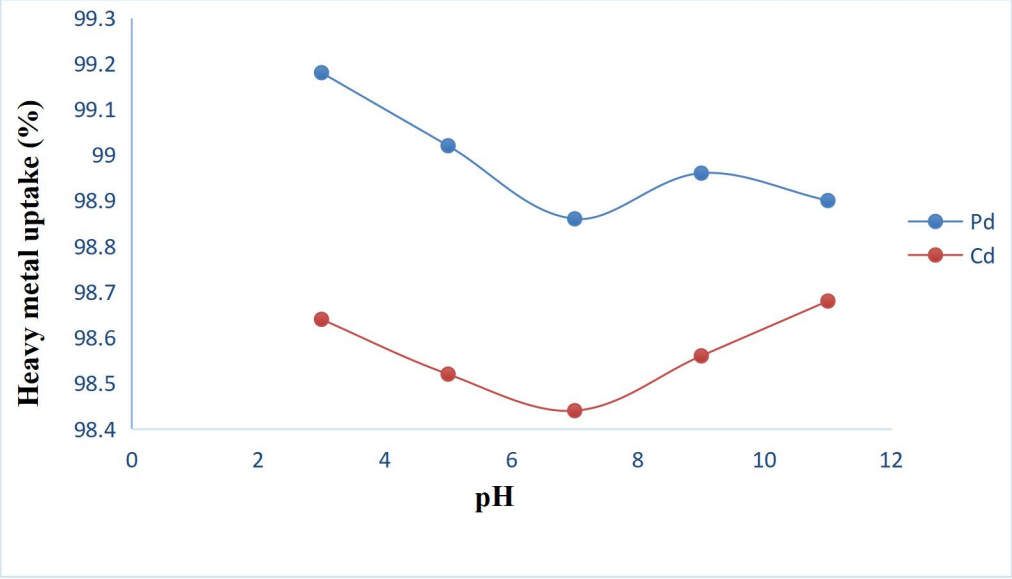

Fig. 3.5: Effects of pH on competitive sorption of Pb and Cd ions

pH impacts metal ion competition for natural sorption sites. pH affects biochar surface charges and solution metal ion speciation. Functional groups in metal absorption and chemistry explain pH-dependent adsorption (Kumar et al., 2011). Figure 1 illustrates pH-dependent Pb and Cd adsorption. Pb and Cd uptake rises at pH 3 and 11, respectively. Heavy metal uptake was 99.18% Pb and 98.68% Cd. Strangely, both metals absorb least at pH 7. Adsorbent absorbs Pb ions better than Cd ions. Lower pH favors neutral or positively charged metal ion adsorption on the adsorbent. Higher pH promotes metal hydroxide complexes and adsorption. Metal absorption varies due to metals' chemical tendencies at different pH conditions and their interaction with the adsorbent surface.

3.5 Effect of adsorbent dose

Table 3.3: Effect of adsorbent dose on Pb and Cd ions at constant time (60mins), initial concentration(5mg/L), and adsorbate volume(100ml)

Dosage (g)	Final conc. Pb (mg/L)	Final conc. Cd (mg/L)	Pb Uptake (%)	Cd Uptake (%)
0.2	3.596	3.157	28.08	36.86
0.4	2.034	2.442	59.32	51.16
0.6	0.841	1.105	83.18	77.9
0.8	0.257	0.621	94.86	87.58
1	0.056	0.074	98.88	98.52
1.2	0.063	0.073	98.74	98.54

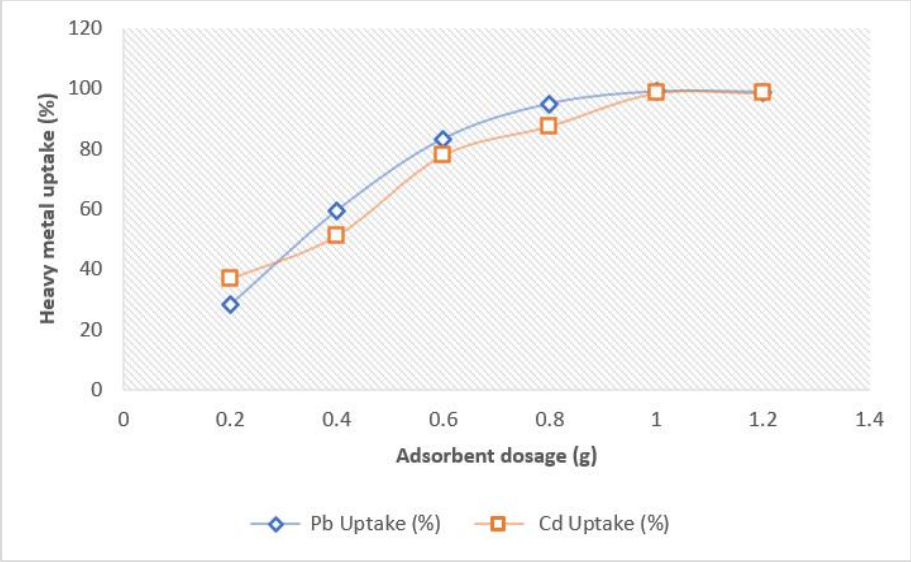

Fig. 3.6: Effects of dosage on competitive sorption of Pb and Cd ions

Figure 3.4 shows that adsorbent dose impacts Pb and Cd ion adsorption. Metal ion adsorption depends on dose. Pb and Cd were removed with 0.2–1.2 g of adsorbent. Pb ions adsorb best at 1g/L (98.88%) and Cd at 1.2g/L (98.54%). Pb uptake dropped 98.74% at 1.2g/L. Pb ions favored adsorbent surface adsorption over Cd. More sites and surface area improve adsorption with adsorbent dose (Wasewar et al., 2009). Similar results (Choudhury et al., 2012; Nameni, 2008; Igwe, 2011).

3.6 Effects of Time of Adsorption

Table 3.5: Effect of contact time on Pb and Cd ions at constant dosage (1g), initial concentration(5mg/L), and adsorbate volume(100ml)

Time (min)	Final conc. Pb (mg/L)	Final conc. Cd (mg/L)	Pb Uptake (%)	Cd Uptake (%)
15	4.046	4.352	19.08	12.96
30	2.171	2.857	56.58	42.86
45	0.845	1.075	83.1	78.5
60	0.056	0.143	98.88	97.14
75	0.036	0.094	99.28	98.12
90	0.039	0.078	99.22	98.44

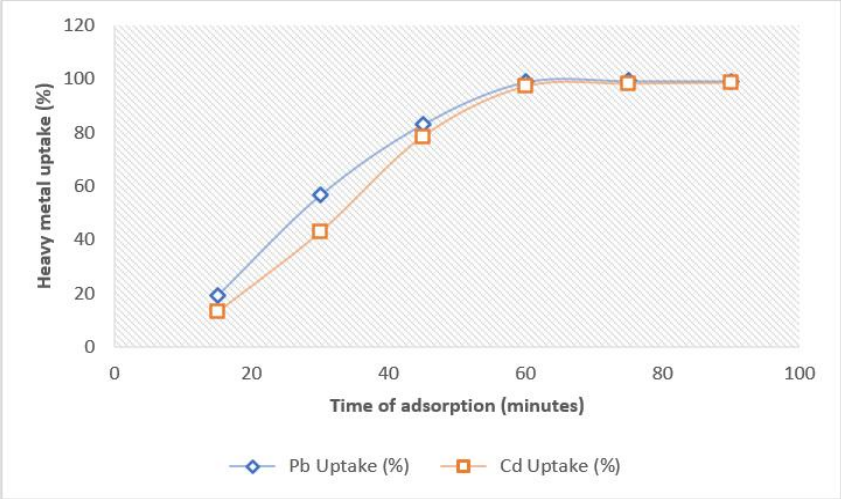

Fig. 3.7: Effects of contact time on competitive sorption of Pb and Cd ions

Contact time is critical in all transfer processes, including adsorption. Therefore, its effect on coconut shell adsorbent Pb and Cd retention must be examined. Contact time depletes Pb and Cd uptake in Figure 3.5. This study demonstrates metal absorption is immediate at touch and rises slowly until saturation. Free adsorption space may explain. This experiment raised adsorption rate and Pb ion removal efficiency to 99.28% in 75 min. Over time, adsorbate molecules repel one other, making surface vacancies difficult to fill. Thus, mass transfer between liquid and solid phases reduces, whereas metal ions penetrate pores and encounter increasing resistance, limiting subsequent adsorption (Choudhury et al., 2012). Cd ions rose 12.96–98.44% from 15–90 min.

3.7 Isotherm studies of Pb(II) and Cd(II) ions

Tables 6: Adsorption isotherm tables (langmuir) for lead and cadmium.

Ce (mg/L)		Qe(mg/g)		Ce/Qe (g/L)	
Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb	Cd^{2+}
0.294	0.435	0.2206	0.2065	1.332729	2.106538
0.068	0.047	0.7432	0.7453	0.091496	0.063062
0.052	0.038	0.9948	0.9962	0.052272	0.038145
0.036	0.027	1.2464	1.2473	0.028883	0.021647
0.035	0.021	1.4965	1.4979	0.023388	0.01402

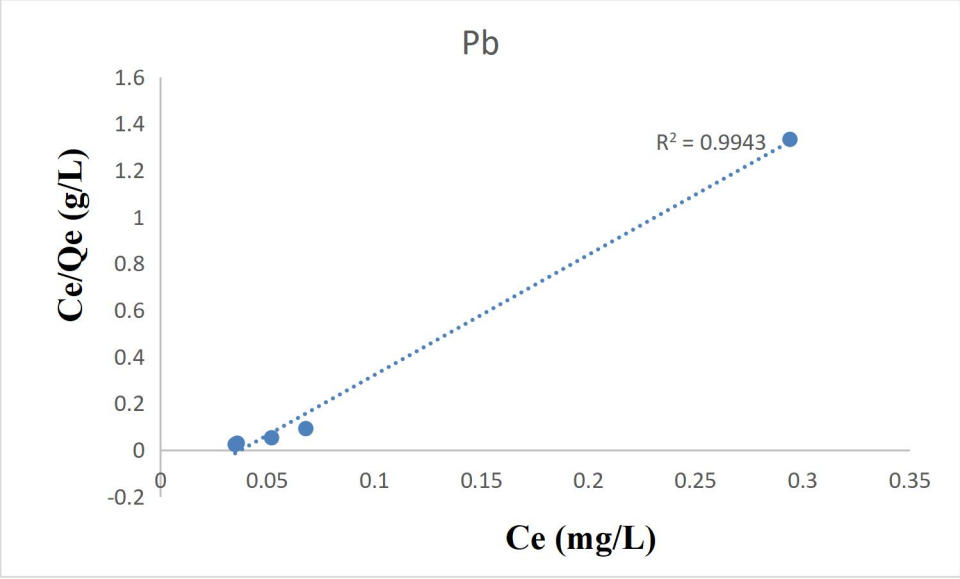

Fig. 3.8: Adsorption isotherm (Langmuir) for lead ions

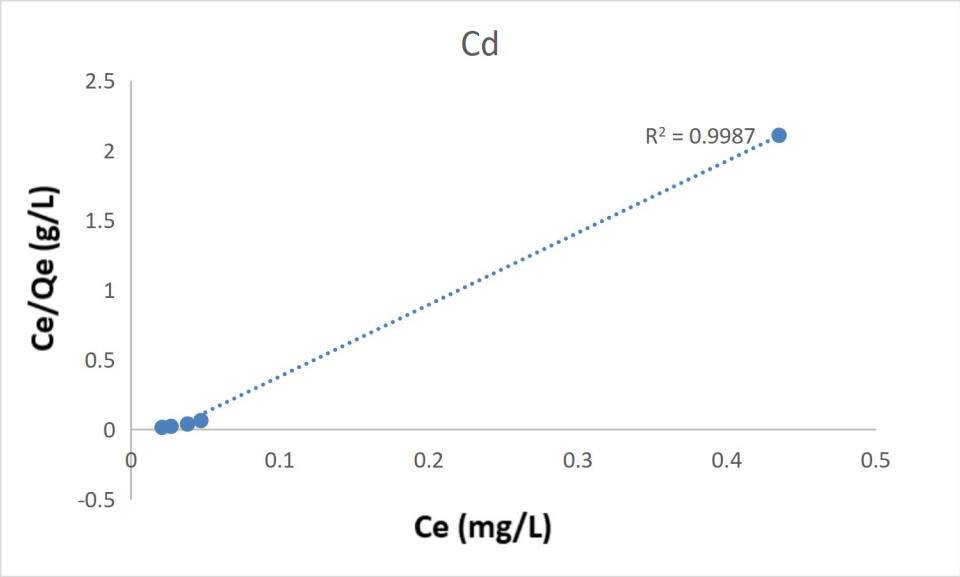

Fig. 3.9: Adsorption isotherm (Langmuir) for cadmium ions

Tables 6: Adsorption isotherm tables (Freundlich) for lead and cadmium.

Ce (mg/L)		Log Ce		Log Qe	
Pb^{2+}	Cd^{2+}	Pb	Cd	Pb	Cd
0.294	0.435	-0.53165	-0.36151	-0.65639	-0.68508
0.068	0.047	-1.16749	-1.3279	-0.12889	-0.12767
0.052	0.038	-1.284	-1.42022	-0.00226	-0.00165
0.036	0.027	-1.4437	-1.56864	0.095657	0.095971
0.035	0.021	-1.45593	-1.67778	0.175077	0.175483

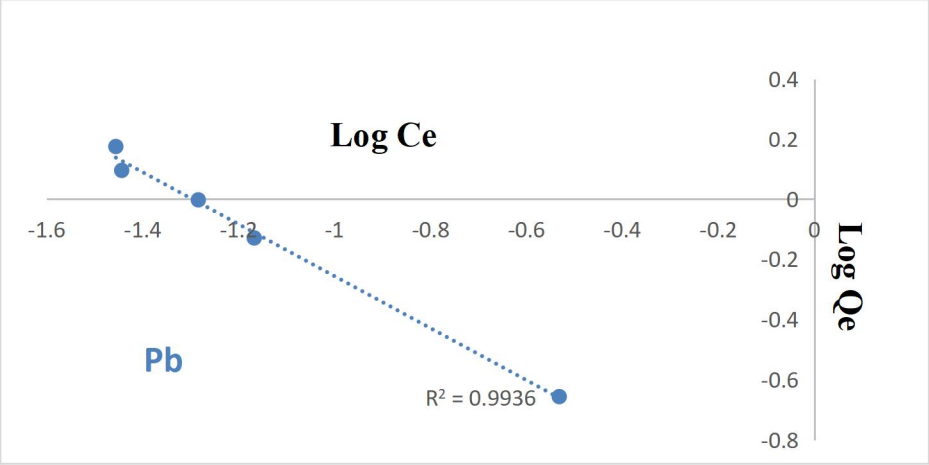

Fig. 4.0: Adsorption isotherm (Freundlich) for lead ions.

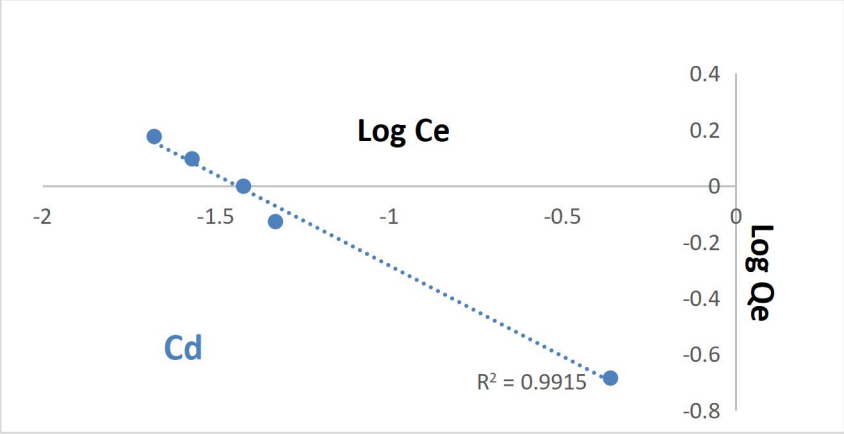

Fig. 4.1: Adsorption isotherm (freundlich) for cadmium ions

Figures 3.8, 3.9, 4.0, and 4.1 compare lead and cadmium adsorption isotherms to Langmuir and Freundlich equations. The Langmuir isotherm fit lead and cadmium data better than the Freundlich isotherms, indicating monolayer adsorption onto a homogenous surface. Lead and cadmium obtained Freundlich coefficients of 0.9936 and 0.9915 and Langmuir regression values of 0.9943 and 0.9987.

Conclusion

The studies show that acid treatment modified biochar's physicochemical properties. Adding acidic functional groups during alteration lowered pH from 6.26 to 5.88, increasing acidity. The correction decreased electrical conductivity from 230 $\mu S/cm^3$ to 164 $\mu S/cm^3$, indicating a decrease in soluble salts. The modification reduces bulk density from 0.66 to 0.56 g/cm^3, indicating structural changes.

Modified biochar improved wastewater treatment and soil remediation by increasing specific surface area, pore volume, and pore size. Scanning electron microscopy revealed a rough modified biochar structure, increasing adsorption sites. Modification increased FTIR intensity, indicating functional group changes.

Adsorption testing indicated modified biochar eliminates Pb and Cd from water. Adsorption efficiency depended on initial concentration, pH, dose, and contact time. The Langmuir adsorption isotherm model fit the data better than the Freundlich model, implying monolayer adsorption onto a homogenous surface. These studies demonstrate that acid-modified biochar can remove heavy metals from water.

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