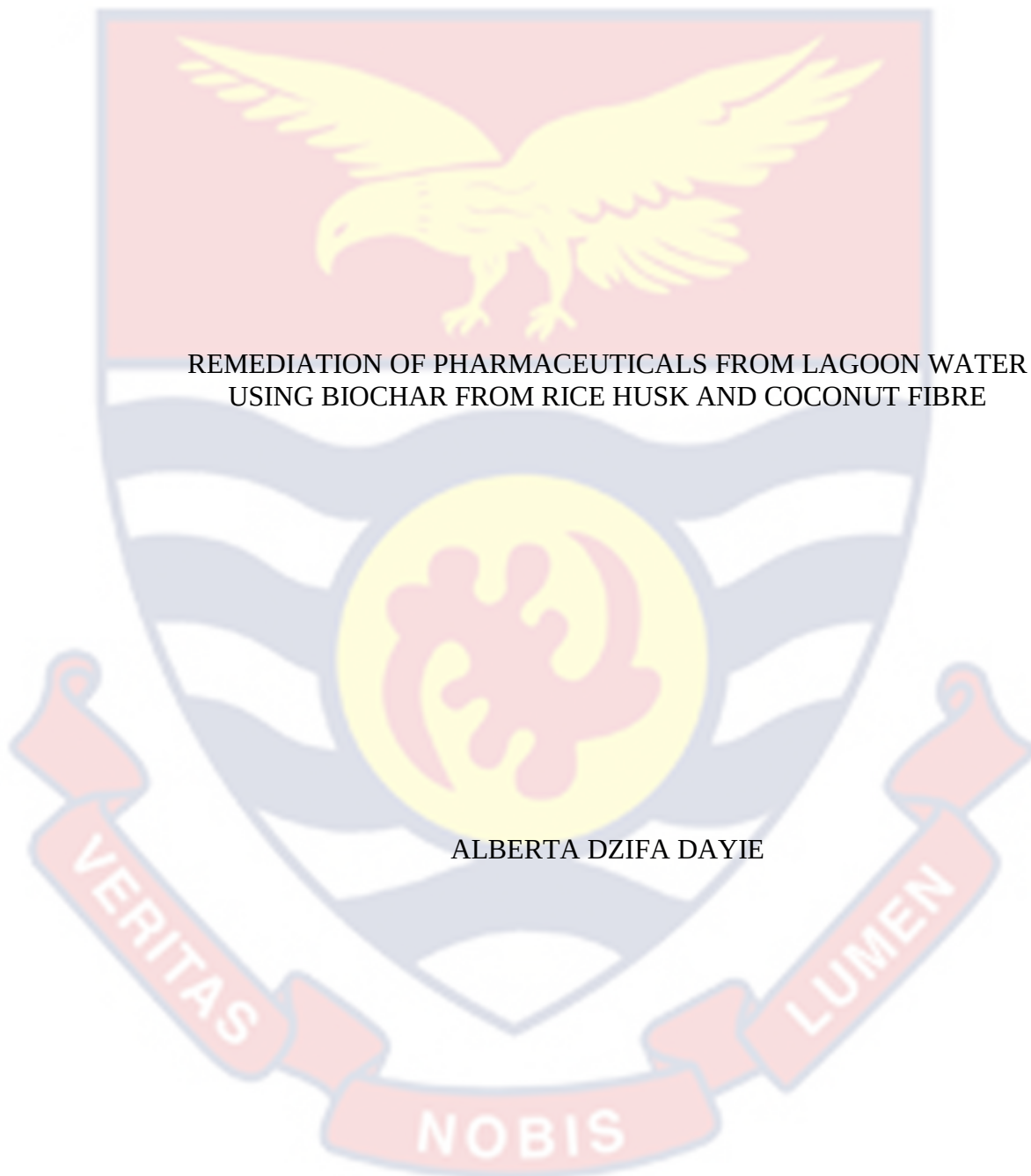


UNIVERSITY OF CAPE COAST

REMEDICATION OF PHARMACEUTICALS FROM LAGOON WATER
USING BIOCHAR FROM RICE HUSK AND COCONUT FIBRE

ALBERTA DZIFA DAYIE



2024



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REMEDICATION OF PHARMACEUTICALS FROM LAGOON WATER
USING BIOCHAR FROM RICE HUSK AND COCONUT HUSK

BY

ALBERTA DZIFA DAYIE

Thesis submitted to the Department of Chemistry of the School of Physical Sciences, College of Agricultural and Natural Sciences, University of Cape Coast, in partial fulfilment of the requirements for the award of Doctor of Philosophy in Chemistry.

APRIL, 2024

DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original research and that no part of it has been presented for another degree in this University or elsewhere.

Candidate's Signature Date.....

Name: ALBERTA DZIFA DAYIE

Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were supervised in accordance with the guidelines on supervision of thesis laid down by the University of Cape Coast.

Principal Supervisor's Signature..... Date.....

Name: PROF. DAVID KOFI ESSUMANG

Co-Supervisor's Signature..... Date.....

Name: PROF. BAAH SEFA-NTIRI

ABSTRACT

The pollution of water bodies by pharmaceutical wastes, particularly from antibiotics, poses a global threat by contributing to antibiotic resistance and toxicity to aquatic life, as traditional wastewater treatment plants fail to remove these contaminants. Therefore, the study explored the possibility of using biochar made from rice husk, coconut fibre and coconut shell in the remediation of eight PHAs (erythromycin, metronidazole, sulfamethoxazole, caffeine, acetaminophen, aspirin, trimethoprim and ciprofloxacin) from lagoon water as most lagoons in Ghana serve as dumping sites for wastewater. The SEM and FTIR analysis revealed the porosity of biochars which were within the micro-meter range and C-O, O-H, C=O as functional groups found on their surfaces respectively. Additionally rice husk biochars contain Si-O-Si. Pharmaceuticals were extracted from water samples using C18 SPE cartridges and analysed using HPLC Shimadzu prominence UFLC 20AD coupled with UV-vis SPD-20AV to determine their levels. After conducting competitive batch adsorption tests on the eight pharmaceuticals, five biochars (CF53, CF61, RH53, RH61, and RH63) were selected based on their mean removal efficiencies (above 75 %). The adsorption kinetics (pseudo first and second order intraparticle diffusion), isotherm (Langmuir, Freundlich and Temkin) and thermodynamics were studied. The adsorption kinetics fitted the pseudo-second-order, and also occurred on both surface and in the pores according to the intraparticle diffusion model. The adsorption of the PHAs did not fit one isotherm suggesting that the adsorption was driven by mixed mechanisms involving both chemical and physical reactions and again the adsorptions were all favourable. The calculated values ΔH° and ΔG° indicated that the adsorption was exothermic and spontaneous. The selected biochars from coconut fibre and rice husk were effective in the removal of the different PHAs and can be used as an alternative to costly adsorbents for the removal of the eight PHAs from water.

KEY WORDS

Adsorption

Biochar

Isotherm

Kinetics

Pharmaceuticals

Remediation



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DEDICATION

To my Husband: Prof. Nicholas T. K. D. Dayie and my children: Eleagbe,

Elinam, Yayra and Eyram.



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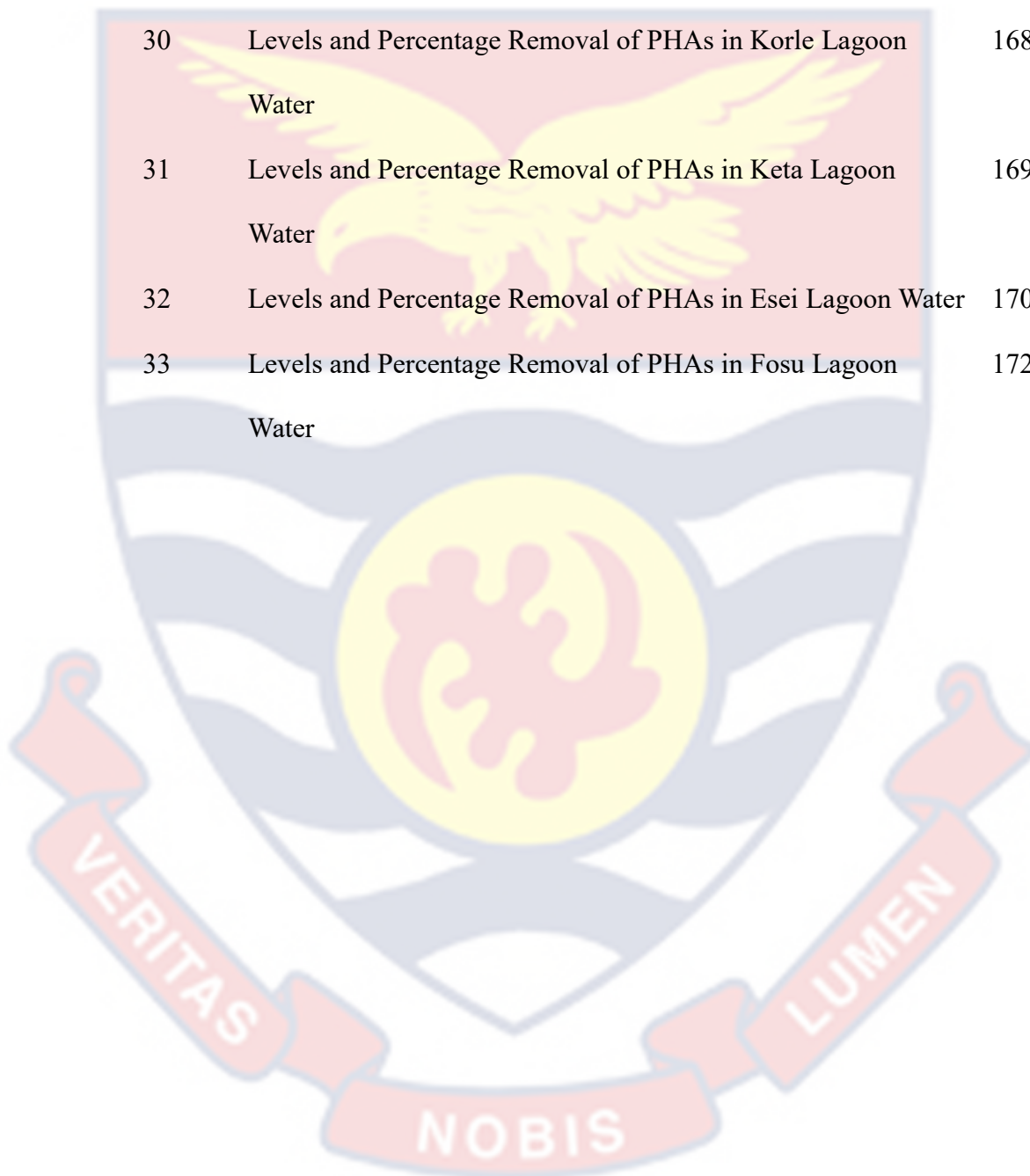


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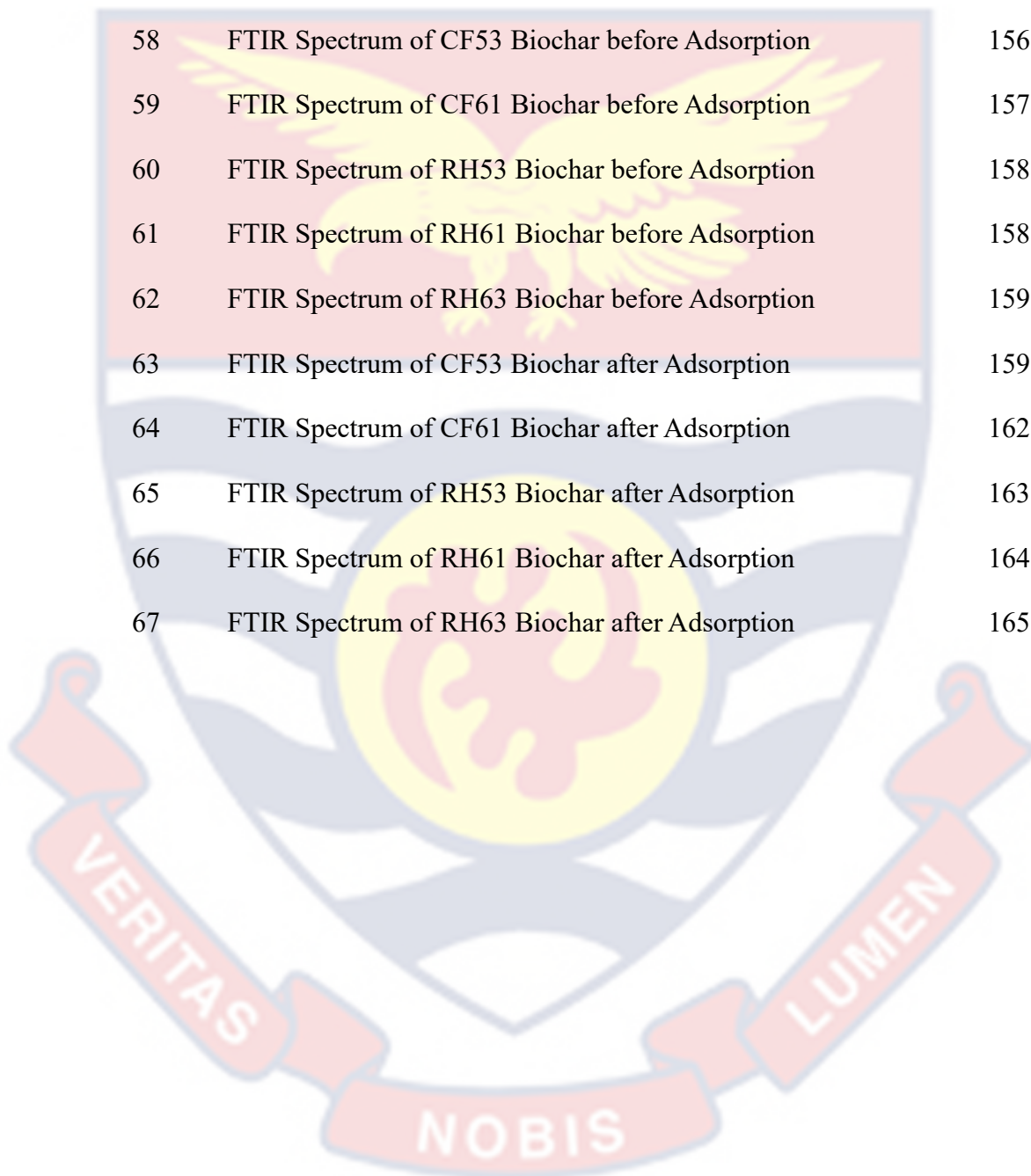
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LIST OF ABBREVIATIONS

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ACE	Acetaminophen
AC	Activated Carbon
AOPs	Advanced Oxidation Processes
ASP	Aspirin
CAF	Caffeine
CNTs	Carbon Nanotubes
CIP	Ciprofloxacin
CF	Coconut Fibre
CFBs	Coconut Fibre Biochars
CS	Coconut Shell
CSBs	Coconut Shell Biochars
EDA	Electron Donor-Acceptor
ERY	Erythromycin
EL	Esei Lagoon
FL	Fosu Lagoon
HELCOM	Helsinki Commission
HPLC	High Performance Liquid Chromatography
IPD	Intraparticle Diffusion
KTL	Keta Lagoon
KL	Korle Lagoon
R _L	Langmuir Dimensionless Parameter
MET	Metronidazole

MWCNTs	Multi-Walled Carbon Nanotubes
OECD	Organization For Economic Co-Operation and Development
PHA	Pharmaceuticals
PFO	Pseudo First Order
PSO	Pseudo Second Order
RH	Rice Husk
RHBs	Rice Husk Biochars
SEM	Scanning Electron Microscopy
SWCNTs	Single-Walled Carbon Nanotubes
SUL	Sulfamethoxazole
SDG	Sustainable Development Goals
VM	Volatile Matter
WHO	World Health Organization



CHAPTER ONE

INTRODUCTION

The presence of pharmaceutical contaminants in water bodies has become a significant environmental and public health concern. Pharmaceuticals, including antibiotics, analgesics, and hormones, are increasingly found in surface waters, groundwater, and even treated drinking water. This problem is urgent due to the potential adverse effects on aquatic ecosystems and human health, such as the development of antibiotic resistance and endocrine disruption. Despite advances in wastewater treatment technologies, conventional treatment plants inadequately remove many pharmaceutical residues, leading to their persistent presence in the environment. Advanced technologies like reverse osmosis and advanced oxidation processes have shown potential in mitigating pharmaceutical pollution but are often costly and complex. In contrast, biochar offers a sustainable and economically viable alternative, with promising results in preliminary studies. Thus, this study explored the use of biochar, a low-cost adsorbent derived from agricultural waste, for removing pharmaceutical contaminants from water.

The practical implications of this study are substantial. Successful implementation of biochar for pharmaceutical removal can enhance water quality, protect aquatic life, and reduce the risk of drug resistance development. This research contributes to the growing body of literature on sustainable waste management and environmental remediation techniques, providing valuable insights into the efficacy of biochar as an adsorbent.

Background to the Study

The need for advanced wastewater treatment has garnered international attention, primarily driven by the rapid population growth, increasing water pollution, and the growing demand for clean water. This heightened focus is essential, particularly in the context of limited water resources and the imperative to protect aquatic ecosystems from the detrimental effects of wastewater disposal. A notable issue that has come to the forefront is the presence of pharmaceuticals in wastewater effluents. Traditional wastewater treatment plants were primarily designed to remove nutrients and easily degradable carbon compounds (Oliveira et al., 2017; Patel et al., 2019). As a consequence, they often exhibit limited capabilities to effectively remove pharmaceuticals. This, in turn, has transformed wastewater treatment plants into significant sources of pharmaceutical contamination in the environment, of particular concern are pharmaceuticals like antibiotics, as their discharge into the environment can exacerbate the spread and development of antibiotic-resistant genes. Various technologies, including reverse osmosis and photolysis, have been considered to address this issue, but their high costs can make them challenging to implement on a large scale.

Therefore, there is a growing need for the development and adoption of simple yet efficient wastewater treatment technologies that are cost-effective. Such technologies can play a pivotal role in reducing global water demands and mitigating the environmental impact of pharmaceuticals. In this context, this research is focused on using low-cost adsorbents derived from agricultural waste, specifically biochar, for the removal of pharmaceuticals. This approach aligns with the broader goal of addressing the global water challenge and

minimizing the environmental impact of pharmaceuticals in a sustainable and economical manner.

Pharmaceuticals

The use of pharmaceuticals has a rich history that spans thousands of years. Early medicines were derived from natural sources, including extracts from herbs, plants, roots, vines, and fungi (Jones, 2011). However, a significant shift occurred after World War II when researchers began to focus on synthesizing chemicals to replace natural extracts. It became evident that synthetic chemicals held the potential to effectively combat parasites, bacteria, and other microorganisms. In 1897, a milestone was reached with the introduction of the first synthetic pharmaceutical, aspirin (Desborough & Keeling, 2017).

Since then, synthetic pharmaceuticals have been developed to address a wide array of health concerns, including extending human lifespans, curing numerous deadly diseases, addressing mental health issues, and enhancing the overall quality of life (Madikizela et al., 2017; Patel et al., 2019). These pharmaceuticals are not limited to human use; they are also extensively employed in veterinary medicine (Caban & Stepnowski, 2021).

Pharmaceuticals encompass a diverse range of compounds, with common categories including antibiotics, lipid regulators, beta-blockers, steroids and related hormones, cancer drugs, diuretics, antiepileptics, antidepressants, tranquillizers, non-steroidal anti-inflammatory drugs, anxiolytics, proton pump inhibitors, and analgesics (Ngqwala & Muchesa, 2020). The successful discovery and mass production of pharmaceuticals has led to their rapid proliferation, both in terms of medical applications and

environmental presence, over the past four decades (Akhbarizadeh et al., 2020; De Andrade et al., 2018; Desbiolles et al., 2018; Gabarrón et al., 2016; Keerthanan et al., 2021; Lach et al., 2018; Oliveira et al., 2017; Peña-Guzmán et al., 2019).

Occurrence of Pharmaceuticals in the Environment.

Pharmaceuticals have emerged as a significant category of emerging contaminants, as recognized by institutions like the European Commission (Deloitte Sustainability, 2018) and the Helsinki Commission (COM, 2017). Emerging contaminants encompass synthetic or naturally occurring chemicals and microorganisms that are potentially known or suspected to have adverse ecological and human health effects. Importantly, these contaminants are not commonly monitored or regulated in the environment (Ahmed et al., 2017; Ndoun et al., 2021; Zandaryaa & Frank-Kamenetsky, 2021). Pharmaceuticals are a key component of these emerging contaminants, and many of them are not subject to comprehensive regulation (Patel et al., 2019). The presence of pharmaceuticals in the environment raises concerns due to their adverse effects on both human health and ecosystems. These compounds include a wide array of drugs, such as lipid regulators, antimicrobial agents, stimulants, steroidal hormones, anti-inflammatory drugs, anti-itching medications, antidepressants, contraceptives, and anticonvulsants (Patel et al., 2019; Snyder et al., 2009; Tushara Chaminda et al., 2018; Yanyan et al., 2018)

Pharmaceuticals have been present in water bodies for some time, but the rapid increase in their production, their widespread availability, and the growth of the human population have significantly contributed to the presence of these chemicals in the environment. Furthermore, many pharmaceutical

compounds are not readily biodegradable, exacerbating the environmental challenges associated with their extensive use (Bilal et al., 2019).

Multiple sources of pharmaceutical contamination have been identified, including pharmaceutical manufacturing plants, wastewater treatment facilities, hospitals, industrial processes, septic tanks, waste management facilities, aquaculture operations, and animal farming activities (Beek et al., 2016; OECD, 2019). Residential wastewater is often recognized as a primary source of pharmaceutical pollution, serving as a marker of surface and groundwater contamination (Tran et al., 2015; Bu et al., 2016). The continual introduction of pharmaceutical waste from these sources into the environment, particularly aquatic systems, has led to the contamination of surface water and groundwater. This contamination has, in turn, affected drinking water sources (Beijer et al., 2017; Ngqwala & Muchesa, 2020).

Effect of Pharmaceutical Waste on the Environment

Organic pharmaceutical compounds constitute a class of emerging contaminants that are consistently found at trace levels in water and soil across the globe, as observed by Keerthanan et al. (2021). Even at these trace levels, these compounds can have significant impacts on both humans and non-target organisms in the environment (Andrade et al., 2018). Their presence has been linked to the development of antimicrobial drug resistance and endocrine-disrupting activities in both humans and animals. The ubiquity of these compounds in the environment poses a significant challenge in terms of control, especially in regions with limited wastewater treatment facilities. As a result, there is currently no immediate solution to this problem.

Additionally, a noteworthy observation is that these pharmaceutical chemicals continue to be continually introduced into the environment. Significant levels of these compounds have been detected in surface water, groundwater, and treated drinking water, spanning urban and rural areas worldwide (Chauhan et al., 2020; Owens, 2015; Wilkinson et al., 2022). This is particularly concerning because the existing water treatment processes in many developing countries do not effectively remove these contaminants (Chauhan et al., 2020).

Once introduced, pharmaceuticals can be adsorbed and subsequently bio-accumulated in organisms, leading to endocrine disruption, antibiotic resistance, and the inhibition of primary productivity (Bilal et al., 2019; Lin et al., 2016). Their presence in the environment can also lead to aquatic toxicity and genotoxicity (Egbedina et al., 2021).

For instance, studies have indicated that exposure to paracetamol can reduce fetal androgen production in rodents (Kilcoyne & Mitchell, 2019). Trace levels of pharmaceuticals have also been associated with hormonal disorders in fish populations and a decline in bird populations in certain regions (Kabbani et al., 2021). An illustrative example is the use of diclofenac as a veterinary pharmaceutical, which has led to a significant decline in the population of Indian vultures since 1996 (Beek et al., 2016). Even low concentrations of antidepressants like fluoxetine have been linked to reduced feeding in starlings during their key foraging time (Kidd et al., 2014).

Organic pharmaceutical waste compounds are primarily water-soluble and are not easily biologically degraded (Bahamon & Vega, 2017; Tony, 2022). With the global population on the rise and a corresponding increase in

pharmaceutical usage, the continuous discharge of these compounds into water bodies is expected to result in a progressive elevation of pharmaceutical levels in these environments, potentially leading to chronic toxicity effects (Patel et al., 2019).

Removal Technologies of Organic Pharmaceuticals

The treatment and remediation of organic pharmaceutical waste and residues have garnered significant interest due to their adverse impact on the environment and human health (Ndoun et al., 2021). Efforts are being made to identify sustainable and cost-effective technologies for effectively removing pharmaceuticals from wastewater. Various methods have been employed to treat wastewater containing pharmaceutical waste, including reverse osmosis, advanced oxidation processes, adsorption, ion exchange, metal-organic frameworks (Lin et al., 2018), ozonation, precipitation, and filtration with coagulation processes (Ambaye et al., 2021; Ngqwala & Muchesa, 2020). While many of these methods are highly efficient, their high cost and operational expenses can make their application challenging, particularly in both developed and developing countries (Ambaye et al., 2021).

Among these methods, adsorption stands out for its effectiveness, versatility, lack of transformation by-products, ease of implementation, and cost-efficiency in eliminating contaminants when compared to alternative techniques (Calisto et al., 2017; Chauhan et al., 2020; Xu et al., 2013). Adsorption is particularly suitable for pollutants with high toxicity that cannot be biologically degraded. Materials for adsorption are readily available, relatively inexpensive, easy to design and operate, and effective in removing organic contaminants such as pharmaceuticals.

Various types of natural and modified porous materials, including nanomaterials, have been studied for extracting pharmaceuticals from water-based solutions. However, their effectiveness, specificity, durability, and cost can limit their use in pollutant removal (Chauhan et al., 2020). As an alternative, biochar derived from agricultural waste has been explored as a potential material for adsorbing pharmaceuticals from aqueous solutions (Ahmed et al., 2017; Li et al., 2018; Qin et al., 2017).

Biochar is a solid, black carbon material produced through the pyrolysis of biomass, such as agricultural residues and organic waste, in the presence or absence of a minimal amount of oxygen (IBI, 2015). Biochar exhibits a porous structure with a high surface area, hydrophobic properties, and a considerable degree of aromaticity, making it an effective adsorbent. Research has shown that biochar is capable of reducing the concentration of both organic and inorganic contaminants in water and soil media. It has proven effective in the removal of various pharmaceuticals, including antiepileptic drugs (Calisto et al., 2017; Meng et al., 2017), anti-inflammatory drugs (Lin et al., 2017), antidepressants (Calisto et al., 2015), antibiotics (Wang et al., 2015), and analgesics (Igwegbe et al., 2021).

Statement of the Problem

The excessive use of pharmaceuticals across the globe has led to high levels of their residues in the environment, a concern documented in various studies (aus der Beek et al., 2016; Wöhler et al., 2020; Kumar et al., 2019; Puga et al., 2022). This significant presence of pharmaceutical residues in water bodies not only compromises water quality but also challenges sanitation systems. Such challenges are directly aligned with the United Nations'

Sustainable Development Goal 6: Clean Water and Sanitation, as outlined in the 2030 Agenda for Sustainable Development (United Nations, 2015). This goal emphasizes the critical need for providing clean water and ensuring effective, sustainable sanitation practices.

Inadequate treatment and improper disposal of pharmaceutical waste, particularly in urban and healthcare settings, lead to further contamination of water resources. The concentrations of these pharmaceuticals, ranging from a few ng/L to mg/L, are associated with acute and chronic toxicological effects on diverse species, disruption of ecological balances, and, most importantly, the facilitation of antimicrobial resistance (Felis et al., 2020; Srivastava & Reddy, 2021) which is a major threat to global health as identified by the World Health Organization (WHO). It has been estimated over that 700,000 deaths in 2016 were attributed to antimicrobial resistance and this number is projected to rise to 10 million annually by 2050 if no effective measures are taken (O'Neill Jim, 2016).

In Ghana, hospitals which are cited near lagoons, serve as dumping sites for hospital waste which are suspected to contain some levels of pharmaceutical residues (Boadi & Kuitunen, 2002). However, the specific types and concentrations of these pharmaceuticals remain largely unexplored, representing a critical gap in environmental health research (Asare, 2022). This study aims to assess the levels of selected pharmaceuticals in contaminated lagoons and explore the efficacy of biochar produced from rice husk, coconut shell, and coconut fibre for their remediation. The outcomes of this study could offer valuable insights for environmental management and public health,

particularly in improving wastewater treatment practices and mitigating the adverse impacts of pharmaceutical contaminants.

Purpose of the Study

The widespread detection of pharmaceuticals in environmental waters globally, including in African countries like Ghana (Azanu et al., 2018; Borquaye et al., 2019; Danner et al., 2019; Galindo-Miranda et al., 2019; Wilkinson et al., 2022), poses a significant public health and leads to the contamination of natural water bodies, including lagoons (Madikizela et al., 2020; Bilal et al., 2019; Lin et al., 2016). This contamination affects aquatic life, disrupts ecosystems, and can have detrimental effects on human health due to the potential for bioaccumulation and the development of antimicrobial resistance (AMR) (Tornimbene et al., 2018). The situation is exacerbated in Ghana by inadequate sanitation, improper disposal of pharmaceutical waste, and the ineffectiveness of existing wastewater treatment plants (Abor, 2013; Sasu et al., 2012). Given the scarcity of effective wastewater treatment facilities, as highlighted in a 2020 survey by the Danish Embassy Trade Council, there is an urgent need for alternative, locally viable treatment methods. Biochar, made from abundant local biomass like coconut shell and rice husk, presents a promising, cost-effective solution for this purpose. Despite its potential, current research in Ghana primarily focuses on biochar's application to soil (Abukari, 2019; Akoto-Danso et al., 2019; Maccarthy et al., 2020; Parker et al., 2021; Steiner et al., 2018), with little knowledge regarding its use in treating wastewater, particularly for pharmaceutical waste removal. This study aims to explore the feasibility and effectiveness of using biochar derived from agricultural waste products such as rice husk and coconut fibre to remove

pharmaceutical pollutants from lagoon water in Ghana. Besides, the scarcity of data on pharmaceutical waste levels in Ghana highlights a critical gap in achieving SDG 6, which emphasizes clean water and sanitation. Research in this area is vital to understand and mitigate water pollution, aligning with SDG 6's goal of ensuring sustainable water management and halving the amount of waste water by 2030. Addressing this data gap is key to protecting water resources in Ghana, directly contributing to the targets set by SDG 6.

Research Objectives

Main Objective

The main objective of the study is to assess the levels and removal of selected pharmaceutical wastes/residues from lagoon water using biochar made from agricultural waste materials (biomass).

Specific Objectives

The specific objectives were to;

1. produce biochar from rice husk, coconut shell and coconut fibre at varying temperatures,
2. determine some physicochemical properties of produced biochars,
3. determine the efficiency of the biochars in removing selected pharmaceuticals from water (lab trials),
4. determine the kinetics and isotherm of adsorption of biochar in removing selected pharmaceuticals from water using batch adsorption.
5. Access the levels of the pharmaceuticals in some lagoon waters and apply appropriate biochars obtained to remediate the pharmaceutical wastes.

Hypothesis

Biochar made from coconut fibre, coconut shell and rice husk can effectively remove pharmaceuticals such as erythromycin, metronidazole, sulfamethoxazole, caffeine, acetaminophen, aspirin, trimethoprim and ciprofloxacin from lagoon water.

Significance of the Study

Successful bioremediation of pharmaceuticals using biochar will lead to improved water quality in lagoons, benefiting aquatic ecosystems and reducing the risk of bioaccumulation of harmful substances in the food chain. By removing pharmaceutical contaminants, the study can contribute to mitigating the development and spread of AMR.

Utilizing rice husk and coconut fibre for biochar production promotes sustainable waste management practices and adds value to agricultural by-products. Implementing biochar for water treatment provides a cost-effective and locally accessible method for addressing pharmaceutical contamination, particularly in low-resource settings.

The findings from this study can inform policymakers and stakeholders about effective strategies for managing pharmaceutical pollutants, leading to the development of guidelines and regulations for wastewater treatment and disposal practices.

Delimitations

This study is delimited to the remediation of pharmaceutical residues, focusing exclusively on eight selected pharmaceuticals: Metronidazole (MET), Acetaminophen (ACE), Trimethoprim (TRI), Caffeine (CAF), Sulfamethoxazole (SUL), Aspirin (ASP), Erythromycin (ERY), and

Ciprofloxacin (CIP). The study also restricts its investigation to four specific lagoon water bodies. The selection of these pharmaceuticals is based on their extensive use in Ghana, while the choice of lagoons is due to their role as common dumping sites for waste. Other pharmaceuticals and water bodies outside of these selected ones are not considered in this research, allowing for a more detailed and focused analysis within the defined scope.

Limitations

The findings of the study may not be applicable to other pharmaceuticals or water bodies not included in the research. The study's results are specific to the selected pharmaceuticals and lagoons, which may limit the broader applicability of the conclusions. Focusing on only four lagoons may not capture the full variability of environmental conditions in different regions, which could affect the generalization of the remediation techniques to other water bodies.

Organization of the Study

This thesis is divided into five chapters. Chapter one covers the background of the study and explains the effect of pharmaceutical waste/residue on the environment and humans. Sections such as the problem of the study, general objective, specific objectives, and significance of the study are also discussed in Chapter One. Chapter two presents the literature review and offers a detailed review of relevant scientific literature. Pharmaceuticals, their classification, usage, fate, and removal are discussed. Methods of preparation of biochar and its applications. Chapter three dives into the preparation of biochar, physiochemical properties, batch adsorption of pharmaceuticals, and environmental application of biochar. Chapter four describes and discusses the results from the preparation of biochar and its physicochemical properties. Also

to be discussed, are the kinetic and isotherm models of the adsorption data obtained. Finally, chapter five will focus on the summary, conclusions, and recommendations of the study.



CHAPTER TWO

LITERATURE REVIEW

Introduction

Chapter two offers an extensive exploration of the literature relevant to the central theme, encompassing pharmaceuticals (PHAs), biochar and its utility in eliminating contaminants, pharmaceutical presence in aquatic environments, their origins, prevalence, and a range of technologies for their comparative removal. In addition, this chapter provides an in-depth analysis of adsorption as a method for eliminating contaminants, with a particular emphasis on its applicability to low-cost adsorbents.

Pharmaceuticals

Pharmaceuticals (PHAs), which encompass both synthetic and naturally occurring compounds, are commonly found in prescription medications, over-the-counter therapeutic drugs, and veterinary treatments intended to prevent, cure, or manage various medical conditions, ultimately contributing to the enhancement of public health (Madikizela et al., 2017; WHO, 2012). This category of substances includes synthetic hormones, antibiotics, anti-inflammatory agents, analgesics, and more. Pharmaceuticals distinguish themselves from other chemical contaminants due to several key characteristics:

Firstly, they consist of numerous complex molecules, each varying in molecular weight, functionality, and form. Additionally, as medications are often polar substances with many ionizable groups, the pH of the environment affects how much they ionise. They also exhibit lipophilic properties and, in some cases, only partial solubility in water. Furthermore, many pharmaceuticals possess the capability to persist in the environment for extended periods, often

becoming biologically active through accumulation; notable examples include erythromycin and sulfamethoxazole.

After administration, pharmaceuticals undergo metabolic reactions that can alter their chemical structure. Those that reach their intended therapeutic effects without being inactivated have the potential to permeate cells and exhibit persistence in the body (Quesada et al., 2019).

Since pharmaceuticals are widely used in aquaculture, agriculture, human and veterinary care, and other fields, pharmaceutical residues and debris have been regularly discharged into the environment. These substances enter the environment through various routes, including human and animal excreta, unused medication, biosolids, landfill leachate, treated sewage sludge, wastewater effluents, medical waste from healthcare, and industrial waste. Globally, it has been demonstrated that wastewater treatment plants often fail to effectively eliminate pharmaceuticals during treatment, resulting in the contamination of water bodies. In regions like Africa, such as Ghana, many communities lack proper sewage treatment facilities, leading to the unmitigated disposal of pharmaceutical waste directly into the environment without prior treatment (González Peña et al., 2021; Madikizela et al., 2017, 2020; Quesada et al., 2019; Silva et al., 2019).

Classification of pharmaceuticals

Pharmaceuticals are categorized based on their therapeutic applications into several distinct groups, including antihistamine drugs and antiulcer like cimetidine and famotidine, hypnotic agents or antianxiety such as analgesics, anti-inflammatories and diazepam exemplified by diclofenac, paracetamol, ibuprofen, and antidepressants including benzodiazines, anticancer drugs like

ifosfamide and cyclophosphamide, antipyretics and stimulants such as estrogens, caffeine, and methylphenidate and hormonal compounds including estriol and estrone, anti-diabetic medications like alpha-glucosidase inhibitors, antibiotics such as trimethoprim, sulfamethoxazole, and metronidazole, β -blockers represented by atenolol and metoprolol, and antimicrobials including penicillin (Ojemaye & Petrik, 2019).

Among the extensive array of pharmaceuticals, there are more than 250 different antibiotics registered globally for human and veterinary applications. The consumption of antimicrobials, encompassing antibacterial, antiviral, and antifungal drugs, is on the rise worldwide, with Ghana being no exception. It's worth noting that antibiotics are most times procured without a prescription, despite legal restrictions against their sale (Azanu et al., 2018). Since many antibiotics are not entirely metabolised by the human body, the ease of access to them in Ghana raises questions regarding the ongoing release of these pollutants into the environment (Madikizela et al., 2017). Moreover, several antibiotics exhibit high environmental persistence due to their continuous discharge (Galindo-Miranda et al., 2019). Compounding this issue is the widespread utilization of antibiotics in poultry farming (Boamah et al., 2016) and aquaculture (Agoba et al., 2018)).

Selected pharmaceuticals and their occurrence in the environment

The antibiotics selected for this study encompass erythromycin (a macrolide), trimethoprim, and sulfamethoxazole (sulfonamides), ciprofloxacin (a quinolone), and metronidazole (a nitroimidazole). These antibiotics hold a place on the Ghana Essential Medicine List (Ministry of Health, 2017) and were chosen due to their frequent prescription and known presence as contaminants

in water, attributed to their persistence in aquatic environments. Acetaminophen, aspirin and caffeine are over the counter drugs which are purchased without prescription.

Sulfamethoxazole and trimethoprim (TRI), both sulfonamides, are widely utilized antibiotics in human and veterinary medicine (Jodeh et al., 2022). They act as bacteriostatic antibiotics, with a history of application dating back to the 1930s in treating and preventing conditions such as urinary tract infections, sinusitis, intestinal infections, and biliary tract infections (Ai et al., 2020; Pei et al., 2021; Prasannamedha & Kumar, 2019). Sulfamethoxazole (SUL) is noteworthy for its potential toxicity even at low concentrations and its reported tendency to induce drug resistance in pathogens. Furthermore, it exhibits persistence in the environment and resistance to biodegradation and hydrolysis (Shimabuku et al., 2016). Trimethoprim, too, lingers in the environment, with approximately 80% of it being excreted in urine, ultimately reaching water systems (Mohammadzadeh & Leiviskä, 2023). Notably, surface water samples in Ghana have registered concentrations of 2861 ng/L (SUL) and 840.0 ng/L (TRI) (Azanu et al., 2018, 2021). To address the presence of sulfonamides like SUL and TRI, various adsorbents have been employed. These include graphite and graphene-based materials (Carrales-Alvarado et al., 2020), iron-modified peat, and magnetite-pine biosorbents (Mohammadzadeh & Leiviskä, 2023), and activated sludge (Ma et al., 2021).

Metronidazole, commonly known as Flagyl, stands out as one of the most frequently consumed over-the-counter antibiotics, produced in large quantities. It may be used to treat infectious disorders brought on by anaerobic bacteria and protozoans as well as to fight parasites in fish and poultry feed. It

has been discovered to cause DNA damage in human lymphocytes, however, and it may be mutagenic and carcinogenic. Even at very low quantities, metronidazole is hazardous to freshwater and marine creatures as well as soybeans. It accumulates in aquatic settings due to its limited biodegradability and high solubility in water; noteworthy amounts of 35 mg/L were found in the effluent treatment plant of a pharmaceutical manufacturing business in Lagos, Nigeria (Yakubu, 2017). Successful treatment methods for metronidazole in water include the use of rice husk biochar (Abbas & Abbas, 2021; Azarpira & Balarak, 2016), sugarcane bagasse (Sun et al., 2017), nanoscale zero-valent iron particles (Qiu et al., 2010), and polypyrrole (Aarab et al., 2019).

Erythromycin is a macrolide antibiotic which inhibits bacterial protein synthesis by attaching to the 50S ribosomal subunit of the bacterium. It is utilised both in human and veterinary medicine. It possesses bacteriostatic properties and may become bactericidal at higher doses (Minski et al., 2021). Unfortunately, its presence in the environment has contributed to the development of antimicrobial resistance. Erythromycin is classified as a highly toxic pollutant in aquatic environments, with a recorded detection of 4.2 µg/L in a river in China (Chen et al., 2018).

Fluoroquinolone antibiotic ciprofloxacin (CIP) is a commonly used fluoroquinolone that slows DNA synthesis and is used in both human and veterinary medicine. Its presence has been detected in various environmental compartments, including raw wastewater (Dong et al., 2016; Östman et al., 2017; Tran et al., 2016), treated wastewater (Dong et al., 2016; Schubert et al., 2014), surface water (Castrignanò et al., 2018; Ding et al., 2017; Tran et al., 2019), and groundwater (Dong et al., 2016; Östman et al., 2017; Tran et al.,

2016). In Ghana, CIP has been identified in select water sources, including hospital effluents, wastewater effluents, rivers, and irrigation water in Kumasi, Ashanti Region. Concentrations ranged from 0.25 in selected rivers to 15.733 µg/L in hospital effluents (Azanu et al., 2018).

Acetaminophen (ACE), a common analgesic and antipyretic drug, finds widespread use both on its own and as a raw material in various pharmaceutical products. ACE, a COX-2 inhibitor, disrupts prostaglandin production and is marketed globally as a pain and inflammation reliever in doses ranging from 200-1000 mg. Due to its incomplete metabolism within the liver, it is excreted in urine and can enter the environment. ACE in water is an indicator of wastewater contamination and is known to be highly toxic to aquatic life (Bilal et al., 2019; Petrie et al., 2015). Its frequent use, over-the-counter availability, and inadequate removal in wastewater treatment plants have led to quantifiable levels of ACE (ppb, ppm) in receiving waters and soils (Azanu et al., 2021). ACE has been detected in water bodies worldwide, including numerous African countries such as Kenya, South Africa, Nigeria, Uganda, Egypt, and Ghana (Abdallah et al., 2019; Agunbiade & Moodley, 2014; De Wispelaere et al., 2016; Matongo et al., 2015; Nantaba et al., 2020; Olaitan et al., 2017; Waleng & Nomngongo, 2022).

Aspirin, or acetyl salicylic acid, is one of the oldest and most affordable nonsteroidal anti-inflammatory drugs used for alleviating fever, colds, and pain. It is available over the counter, resulting in high consumption rates. A US study indicated that about 29 million people take aspirin daily (O'Brien et al., 2019). Aspirin is one of the most commonly found drugs in various water bodies, such

as Greek waters and the Umgeni River in South Africa, as well as in Nigeria (Gumbi et al., 2016; Nannou et al., 2015; Oluwatosin et al., 2016).

Caffeine (1,3,7-trimethylxanthine, CAF) is a psychomotor stimulant present in coffee, tea, soft drinks, and food. It is also a component of numerous prescribed and over-the-counter drugs. Caffeine serves various medicinal purposes, such as a cardiac, cerebral, and respiratory stimulant, and diuretic. It is readily biodegradable in wastewater treatment plants and thus serves as an indicator of raw sewage pollution in surface water. Caffeine enters the environment through unconsumed beverages and rinsing of coffee cups. Several adsorbents, including activated rice husk biochar, engineered tea-waste biochar, coconut fibre, Pelegri Carbon, and activated carbon from *Sargassum* (sp), have been employed to remove caffeine from water (Almeida-Naranjo et al., 2021; Bahrami et al., 2023; Francoeur et al., 2021; Keerthanan et al., 2021; Melo et al., 2020).

The elimination of pharmaceutical residues from water prior to discharge into the environment is vital for both environmental and public health safety. Conventional wastewater treatment processes are often insufficient in removing these pollutants, necessitating the augmentation of such processes with advanced technologies such as oxidation, adsorption, or hybrid water treatment methods, like membrane bioreactors. Among these technologies, adsorption has garnered significant attention from researchers due to its cost-effectiveness and ease of operation (Patel et al., 2019).

Analysis of pharmaceuticals in water

High-performance liquid chromatography (HPLC)

HPLC separates, identifies, and quantifies components in a mixture based on their differential interactions with a stationary phase and a mobile phase. The technique operates on the principle of liquid-solid chromatography), where compounds are separated as they pass through a column. HPLC is widely used in the pharmaceutical industry for quality control and environmental monitoring. Its precision and ability to handle complex mixtures make it indispensable (Dong, 2006; Okafo & Roberts, 2003).

Liquid chromatography-mass spectrometry (LC-MS)

LC-MS combines the separation capabilities of liquid chromatography with the detection power of mass spectrometry. It operates on the principle of ionizing separated compounds and measuring their mass-to-charge ratios. LC-MS is particularly valuable for detecting trace levels of pharmaceuticals in biological and environmental samples. Its high sensitivity and specificity have made it revolutionary in analytical chemistry (Niessen, 2006). It is extensively used in pharmaceutical analysis and environmental studies (Böttcher et al., 2010).

Gas chromatography-mass spectrometry (GC-MS)

GC-MS identifies and quantifies compounds by separating them based on their volatility in a gas chromatography column and then analyzing their mass-to-charge ratios using mass spectrometry. It is ideal for analyzing volatile and semi-volatile pharmaceutical compounds in environmental and forensic samples. GC-MS is considered the gold standard for analyzing small, volatile

molecules (McMaster, 2008). Its reliability makes it widely used in forensic toxicology and drug testing.

Ultraviolet-visible spectroscopy (UV-Vis)

UV-Vis spectroscopy measures the absorption of ultraviolet or visible light by a sample, with absorbance directly related to the concentration of the absorbing species according to Beer-Lambert's law. The technique is widely used in the pharmaceutical industry for quantitative analysis and studying the stability of drugs. UV-Vis is valued for its simplicity, speed, and reliability (Skoog, Holler, & Crouch, 2017). It is commonly employed in quality control and monitoring chemical reactions.

Pharmaceutical removal techniques

Advanced oxidation processes (AOPs)

AOPs are a group of techniques applied in aqueous environments to degrade pollutants, utilizing reactive species like hydroxyl radicals ($\bullet\text{OH}$). These processes typically involve oxidizing agents (ozone, peroxide) and catalysts (iron, manganese, titanium dioxide) and are enhanced by radiation (UV) to oxidize organic contaminants into biodegradable substances and mineral salts (Khan et al., 2020; Rathie et al., 2020; Bang et al., 2019; Puga et al., 2022; Elkacmi & Bennajah, 2019). Common AOPs include Fenton process ($\text{Fe}^{2+,3+}/\text{H}_2\text{O}_2$), UV/ H_2O_2 , photo-Fenton processes $\text{Fe}^{2+,3+}/\text{H}_2\text{O}_2/\text{UV}$ and $\text{Fe}^{2+,3+}/\text{H}_2\text{O}_2$ simulated sunlight), and heterogeneous catalysis. They are effective in completely mineralizing organic pollutants but can produce potentially toxic by-products (Ganiyu et al., 2015; Rizzo, 2015).

Membrane technology

This includes processes like forward osmosis, reverse osmosis, microfiltration, and nanofiltration. These techniques remove contaminants through size exclusion, hydrophobic interaction, electrostatic repulsion, or adsorption. Reverse osmosis, capable of removing particles as small as 1 nanometer, is highly efficient in pharmaceutical waste removal, achieving high rejection rates, except for smaller molecules like acetaminophen (Dhangar & Kumar, 2020; Dolar et al., 2017; Radjenovic et al., 2008). Combining membrane processes with other treatments like catalytic oxidation or adsorption systems enhances effectiveness (Tahterian et al., 2016; Nguyen et al., 2012, 2013).

Constructed wetlands

Constructed wetlands are an economical option for wastewater treatment and reducing various pollutants, including pharmaceutical waste. They come in different types: hybrid, horizontal flow, free water surface, and vertical flow. Effectiveness varies by wetland type and pharmaceutical, with some studies showing over 80% removal efficiency for certain drugs and endocrine disruptors (Wu et al., 2017; Rathi et al., 2020; Ilyas et al., 2020; Vymazal et al., 2016; Ávila et al., 2015).

Adsorption

One of the most effective methods for eliminating impurities from aqueous solutions is adsorption, which also provides a mechanism to restore, reuse, and recycle the adsorbent (Rathi et al., 2020). It is one of the greatest techniques globally (Ngueagni et al., 2019; Nithya et al., 2020; Suganya & Kumar, 2018), due to its flexibility of use, simplicity of operation and

indifference to pollutants, therefore being among the most effective and reliable treatment for pharmaceutical waste (Abbas et al., 2018; Calisto et al., 2015; Moazeni et al., 2020; Patel et al., 2021; Peiris et al., 2017; Yanyan et al., 2018). Activated carbon (Ondarts et al., 2018), zeolite (López-Maya et al., 2019; Martucci et al., 2012), clays (Dordio et al., 2016; Roca et al., 2015), and biochar made from agricultural wastes (Liu et al., 2018), metal organic frameworks (Gao et al., 2018; Li et al., 2017), carbon nanotubes (Wang et al., 2015; Yanyan et al., 2018), etc. have been used as adsorbent for various contaminants (Yaashikaa et al., 2019).

Carbonaceous adsorbents used in adsorption

Graphene-based, carbon nanotubes and activated carbon (AC), and adsorbent are widely employed as carbonaceous adsorbents for the elimination of pharmaceuticals from water, as demonstrated by Teo et al. (2022). Among these, activated carbon stands out as the most extensively studied sorbent for pharmaceutical removal due to its remarkable attributes, including a substantial surface area, interactive capabilities, an abundance of pore structures, and ready availability.

Carbon nanotubes (CNTs)

Carbon Nanotubes are unique carbon allotropes known for their cylindrical structure, high thermal conductivity, electrical resistivity, and mechanical strength. They are classified into single-walled (SWCNTs) and multi-walled (MWCNTs) categories (Teo et al., 2022). CNTs are notable for their functionalization capabilities, enhancing adsorption properties for both organic and inorganic compounds. In pharmaceutical remediation, CNTs have been highly effective, with MWCNTs achieving up to 99.4% removal efficiency

of erythromycin from aqueous solutions (Dashtizade and Balarak, 2018). They are also employed in removing other pharmaceuticals like sulfamethoxazole, tetracycline, ciprofloxacin, acetaminophen, and various others (Zhang et al., 2010; Sophia et al., 2016; Ncibi & Sillanpää, 2015; Yanyan et al., 2018; Zhao et al., 2016).

Graphene-based materials

Graphene, a two-dimensional carbon material, is recognized for its extensive surface area and electron-rich nature. It interacts with hydrophobic pharmaceutical contaminants through van der Waals or π - π interactions. The hydrophilicity of graphene can be increased by converting it to graphene oxide (GO), which is more effective in aqueous environments. Graphene exhibits excellent photoactivity and electrical properties and, when combined with other nanomaterials, forms adsorbents with superior physicochemical characteristics. Despite its effectiveness in pharmaceutical removal, challenges include graphene's susceptibility to aggregation and difficulty in separation and recycling, posing risks of secondary pollution (Li et al., 2019; Sophia et al., 2016; Wang & Wang, 2019).

Activated carbon (AC)

Activated Carbon is a widely used carbonaceous adsorbent derived from various sources, including coal, petroleum, and a range of agricultural (biomass) and industrial residues. Its high adsorption capacity and expansive surface area make it a preferred choice in wastewater treatment (Xiang et al., 2019; Akhtar et al., 2016; Serrano et al., 2011). AC is available in powdered (PAC) and granular (GAC) forms and is effective in removing a wide range of contaminants from water.

Traditionally, AC has been primarily derived from sources like coal, petroleum, coal, lignite, and coke. However, recent advancements have diversified the range of carbon-based materials used in its production. These encompass a variety of agricultural and industrial residues, such as nut shells, corn hulls, rice straw, almond shells, peach stones, oat hulls, cotton stalks, grape seeds, hazelnut shells, corn cobs, cotton residues, cherry stones, rice hulls, apricot stones, straw, pecan shells, olive residues, peanut hulls, and corn stover. Activated carbon can be utilized either in a powdered form (PAC) or a granular form (GAC) (Serrano et al., 2011).

Biochar

Biochar, a carbon-rich residue, is produced through the pyrolysis of biomass in an oxygen-limited environment (Ringer, 2022). This process results in a product with a large surface area, high pH, and an aromatic structure (Gwenzi et al., 2017). Biochar is mainly carbon but also contains organic and inorganic components, including minerals like Mg, Ca, K, and inorganic carbonates. It has various applications, including soil enhancement, greenhouse gas reduction, soil carbon content increase, water retention improvement, and as an adsorbent for metals and organic contaminants in soils and aqueous (Guo et al., 2019; Ho et al., 2017; Khan et al., 2017; Naeem et al., 2019; Shen et al., 2017; Patra et al., 2017; Roberts et al., 2015; Yang et al., 2021; Zhao et al., 2018).

Methods of biochar production (Biomass conversion technologies)

Biochar's characteristics depend on the feedstock and pyrolysis conditions used. Different thermochemical conversion methods are employed, including slow and fast pyrolysis, hydrothermal carbonization, torrefaction,

flash carbonization, and gasification. The yield of biochar is influenced by factors like temperature, heating rate, particle size, and lignin content (Guo et al., 2016; Yaashikaa et al., 2020b; Devakumari, 2021).

Biochar can be produced from plant-based feedstocks (such as wood, peels, straws, husks, cornstalk, coconut shell, palm kernel (Devakumari, 2021; Goswami & Kumar, 2018; Khuenkaeo & Tippayawong, 2019; Mohan et al., 2012; A. A. Rahman et al., 2016; Shen et al., 2017; Solanki & Boyer, 2017; Suman & Gautam, 2017), industrial organic waste, sewage sludge, and organic municipal solid waste (Ahmad et al., 2014; Ahmed et al., 2016; Ali et al., 2022). Biochar yield depends on the pyrolysis temperature, the feedstock, heating rate, particle size and lignin content of the biomass used (Amalina et al., 2022). Using data obtained by Yang et al (2007) from a thermogravimetric analyzer operated at constant heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and swept with 120 mL of nitrogen, hemicellulose was the first to decompose at $220\text{ }^{\circ}\text{C}$ and end at about $315\text{ }^{\circ}\text{C}$. Lignin starts decomposing slowly from $160\text{ }^{\circ}\text{C}$ steadily to $900\text{ }^{\circ}\text{C}$ yielding a solid residue forming about 40 percent of the original sample. Table 1 summarizes the various biomass conversion method into biochar.

Table 1: Summary of Biomass Conversion Processes

Thermochemical process	Temperature range(°C)	Heating rate	Pressure	Residence time	Product distribution (weight %)		
					Solid (biochar)	Liquid (bio-oil)	Gas (syngas)
Slow pyrolysis	350-700	Slow, (<10°C/min)	Atmospheric	Hours	35*	30	35
Torrefaction	200-300	Slow, (<10°C/min)	Atmospheric	Minutes-hours	80*	—	20
Fast pyrolysis	400-1000	Very fast (~1000°C/s)	Vacuum-atmospheric	Seconds	10	70-75*	20
Gasification	700-1500	Moderate-very fast	Atmospheric-elevated	Second-minutes	10	5	85*
Hydrothermal carbonization	175-250	Slow		hours	50-80*	3-20	2-5

* Main product

Source : (Amalina et al., 2022; Mohan et al., 2014; Shaheen et al., 2019)

Slow pyrolysis

Slow pyrolysis takes place between a temperature of 100 to 1000 °C with residence time between 2 to 4 hours at a rate of 1-20 °C per min. Slow pyrolysis produces substantially more biochar approximately 20-40% of the feedstock (Fawzy et al., 2021; Zhang et al., 2017) and other products (Table 1). Slow pyrolysis is preferred if production of biochar is the main goal of pyrolysis (Ajien et al., 2022). This biochar is beneficial for agronomic, treatment of metal and organic waste as well as carbon sequestration.

Fast pyrolysis

During this procedure, biomass undergoes rapid heating within the temperature range of 400-600 °C, a method discussed by Mohan et al., (2014). Without oxygen, this happens, mostly producing bio-oil and charcoal in the end, as reported by Garrido et al. (2017) and Zhang et al. (2014). The resulting biochar typically manifests as a fine powder, as the feedstock is finely ground to facilitate swift heat transfer. Residence time is within seconds (0.5-2 s) and biochar produced is very low. There are no universal minimum heating rate criterion as various authors give different heating rate depending on feedstock and reaction types. According to Yoder et al. (2011), only particle sizes below 2 mm can be used in fast pyrolysis. Fast pyrolysis at low temperatures produces biochar that contain large numbers of oxygenated functional groups both on and below pore surfaces (Patel et al., 2019).

Torrefaction

It is a mild thermochemical process involving heating samples for long period of time between 200-300 °C in the absence of oxygen. Torrefaction reduces

biomass absorptivity of water making it less hygroscopic. Resulting solid is about 70 percent of the initial weight of the biomass. Torrefaction sometimes serves as a pretreatment method for fast pyrolysis the (Garrido et al., 2017). Torrefaction increases biomass density, reduces weight for easy transportation in energy production. Chars produced are not used as adsorbents since they undergo partial decomposition mostly to induce some water loss.

Gasification

Gasification involves the partial combustion of biomass, primarily generating gaseous fuel suitable for applications in heat or electricity generation, as noted by Mohan et al. (2014). The gasification process necessitates the presence of a gasifying medium, such as air, steam, or oxygen, to facilitate the reconfiguration of molecular structures.

Hydrothermal carbonization

By hydrothermally carbonizing biomass in water at low temperatures and high pressures, char water slurry is produced. This process produces hydrochars, as described by Mohan et al. (2014), alongside the production of bio-coal and water-soluble products. This specific technique effectively transforms all of the carbon in the biomass into a material that resembles coal without producing any gaseous emissions. It can be directly applied to wet feedstock, including sewage sludge and moist animal manure. Hydrochar from this process is eco-friendly and gives a higher yield than fast and slow pyrolysis. However, they are less stable compared to biochars and their chemical properties are different from biochars obtained from pyrolysis and gasification.

Factors affecting biochar properties.

The pyrolysis settings (heating rate, temperature, residence time, pressure), the kind of feedstock, and the reactor used in the carbonization process all affect the physical and chemical characteristics of biochar (Ali et al., 2022; Zhang et al., 2016; Amalina et al., 2022). These affect the quality of biochar directly.

Types of biomass (feedstock)

Biochar, a product of biomass pyrolysis, can be derived from diverse feedstocks categorized primarily into woody and non-woody biomass. Woody biomass, like tree and forestry residues, is known for its low moisture and ash content, high calorific value, and density. In contrast, non-woody biomass, including industrial biowastes, agricultural residues, and animal manure, typically has lower calorific value, higher moisture and ash content, and lower density.

The structural components of these feedstocks – cellulose, hemicellulose, and lignin – vary in proportion depending on the source (Tan et al., 2021). For instance, rice husk comprises 20% lignin, 25% hemicellulose, and 35% cellulose (Satbaev et al., 2021). Figure 1 shows some of the sources of biomass for biochar production.

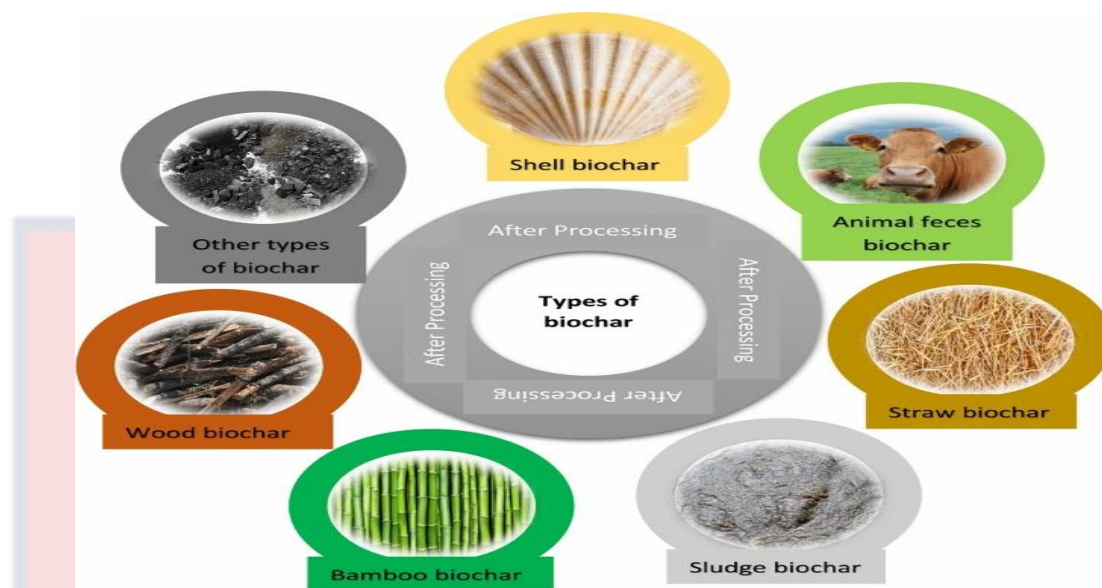


Figure 1: Some Sources of Biomass for Biochar Production.
Source: Ambaye et al., (2021)

The biochar production process involves dehydration and rearrangement of cellulose to form hydroxymethyl furfural, followed by aromatization, polymerization, and intramolecular condensation (Hassan et al., 2020; Lee et al., 2019). Cellulose and hemicellulose break down at lower temperatures (200-350 °C) and yield biochar rich in oxygen-containing functional groups but in lower quantities. Lignin, decomposing between 280 and 500 °C, produces more biochar due to its high fixed carbon content and thermal stability.

Sewage sludge and animal litter, used as alternative feedstocks, produce biochars with higher mineral content but smaller surface area compared to those from agricultural and woody biomass. The biochar's characteristics are heavily influenced by the original feedstock's structure, determining its final properties and macro-porosity (Yavari et al., 2015).

Biochars from less moist biomass have larger surface areas. Woody and agricultural waste-derived biochars generally exhibit larger surface areas than those

from municipal waste and animal dung. Non-woody biochars are alkaline, rich in salts like carbonates, calcium, and potassium chlorides, and have higher ash content than their woody counterparts at the same pyrolysis temperature (Oliveira et al., 2017).

Temperature

Temperature plays a crucial role in defining the sorption capacity and physicochemical properties of biochar. The pyrolytic temperature influences biochar's surface area, pore structure, functional groups, and elemental content, impacting its adsorption capabilities (Chatterjee et al., 2020).

Increase in pyrolysis temperature leads to higher ash content, pH, and total carbon content due to the release of labile components. However, biochar yield, cation exchange capacity, and total nitrogen content decrease (Li et al., 2023; Fouladidordhani et al., 2021). It also results in increased surface area and porosity, enhancing the biochar's ability to adsorb contaminants (Dhar et al., 2022).

Furthermore, higher pyrolytic temperatures result in the development of active functional group sites, both electron donors and acceptors, occurs at elevated temperatures. This results in biochar surfaces with alkaline and acidic properties, improving binding affinity for various compounds in water (Zheng et al., 2013). Biochars produced at higher temperatures are better suited for adsorbing organic contaminants through hydrophobic interactions and precipitation (Nebout et al., 2016). Biochar produced at lower temperatures is more effective for polar organic or inorganic pollutants, utilizing ion exchange, polarization-selective interactions, and electrostatic interactions (Sobik-Szołtysek et al., 2021). For biochar

production, temperatures between 500 °C and 800 °C are generally considered optimal.

Residence time

Slow pyrolysis of biomass produces more biochar but increasing the residence time will result in a gradual decrease of biochar production and high biochar pH. However, increasing the residence time for fast pyrolysis at higher temperatures does not have any effect on the amount of biochar produced or the pH (Amalina et al., 2022; Cao et al., 2018; Wang et al., 2018). Additionally, the largest BET surface areas are seen in biochar formed from high carbon feedstocks with lengthy residence times (Miles et al., 2016).

Pretreatment

Biomass pretreatment is crucial in biochar production, enhancing lignin, cellulose, and hemicellulose conversion and facilitating the transformation of biomass into valuable products. Effective pretreatment methods should preserve cellulose and hemicellulose, avoid generating toxic byproducts, be energy-efficient, and low-cost (Patel et al., 2019; Zadeh et al., 2020).

Pretreatment methods are broadly classified into biological (fungi, archaea and bacteria) and non-biological. Non biological further divided into physical, chemical, and physicochemical methods. Physical methods include milling, microwave, ultrasound, and pyrolysis. Chemical methods encompass acid, alkaline, ozonolysis, ionic liquids, and organo-solvents. Physicochemical methods involve hot water, wet oxidation, CO₂ explosion, ammonia-based treatments, and steam explosion (Yaashikaa et al., 2020).

Chemical pretreatment by immersion of the raw materials in a solution and reduction of the biomass's particle size are the two main pretreatment techniques usually used in the synthesis of biochar. Acid, oxidant, and alkali pretreatments enhance the biochar's pore structure, surface area, and surface functional groups (Amalina et al., 2022; Zhang et al., 2017). Particle size reduction is achieved through chipping, milling, or grinding, significantly influences biochar yield. Smaller particle sizes promote homogeneous heat transfer, resulting in biochar with a larger specific surface area (Maurya et al., 2015; Zadeh et al., 2020).

Biochar Modification

Biochar, a carbonaceous material derived from biomass pyrolysis in an oxygen-restricted atmosphere, can be modified to enhance its adsorptive properties. Both physical and chemical modification techniques are employed to augment its characteristics, influenced by factors like temperature, activation time, and type of activator (Wang & Wang, 2019; Yang et al., 2019).

Physical modification techniques include steam application which enhance the biochar's surface area and porosity by removing impurities and creating surface hydrogen complexes (Sizmur et al., 2017; Wang & Wang, 2019), and ball milling, which involves particle size reduction to increase the biochar's surface area and porosity (Sizmur et al., 2017; Kwak et al., 2019; Liu et al., 2022).

Chemical modifications involve the use of 1. acid functional groups to the biochar surface, using acids like citric, nitric, phosphoric, sulfuric, and hydrochloric acid. This modification alters the surface phase and functional group composition, enhancing adsorption capacities (Ahmed et al., 2016; Vijayaraghavan, 2021); 2.

alkaline agents like potassium hydroxide and sodium hydroxide to increase surface area, pore volume, and oxygen-containing functional group (Rajapaksha et al., 2016; Wang et al., 2020; Li et al., 2018; Shen and Zhang, 2019; Nguyen et al., 2021); 3. metal ions or heteroatoms into biochar's pores and surface, expanding its surface area and enhancing adsorption capabilities. Metals used include silver, manganese, magnesium, aluminium, iron, and zinc. This technique is used to create metal-biochar composites and improve biochar's catalytic properties (Wang & Wang, 2019; Yang et al., 2019; Sizmur et al., 2017) and 4. oxidizing chemicals like hydrogen peroxide and potassium permanganate to increase oxygen-containing functional groups on biochar's surface. This modification can significantly enhance adsorption capacities for specific contaminants but may vary based on the targeted pollutant (Xue et al., 2012; Huff and Lee, 2016; Wang et al., 2015).

Physical and chemical properties of biochars

Surface area

Temperature, feedstock type, and post-treatment processes are key factors influencing the surface area of biochar, which is crucial for its adsorption capacity (Shaheen et al., 2019). The surface area of biochar is directly impacted by pyrolysis conditions. Generally, an increase in pyrolysis temperature leads to an increase in surface area due to the solid matrix shrinking and pore size reduction (Fellet et al., 2022; Li et al., 2016; Weber & Quicker, 2018). For example, a surface area of 590 m²g⁻¹ was achieved at 800 °C (Mendonça et al., 2017). However, the response to temperature can vary with feedstock. In some cases, higher temperatures may reduce the surface area.

Woody biomass typically produces biochar with higher surface area compared to plant-based feedstocks at the same temperature. This was demonstrated when woody material and plant feedstock were pyrolyzed at 600 °C, with the woody biochar exhibiting a larger surface area (Reyhanitabar et al., 2020). The microstructure of the biomass (micro- or mesopores) and physical changes during pyrolysis, such as mass loss and shrinkage, contribute to surface area and porosity (Bruckman, 2013).

Post treatment using heat, acids, and bases can further enhance biochar's surface area. For instance, palm kernel biochar treated with 2.0 M KOH exhibited a surface area of 270.7027 m²g⁻¹, higher than that treated with H₃PO₄ and Fe₂Cl₃.6H₂O (Nasri et al., 2017). Nitrogen doping, as applied to algae-derived biochar, increased the surface area to 433 m²g⁻¹ (González-Hourcade et al., 2022).

pH

The kind of feedstock and pyrolysis temperature employed affect the pH of biochar. Non-woody feedstocks like grass, rice husk, and manure, especially at high pyrolysis temperatures, tend to produce biochar with a higher pH compared to woody feedstocks due to their higher ash content (Ippolito et al., 2020). Algal biomass and poultry litter, for instance, yield biochars with pH values between 7.81 and 13.66, attributed to their high ash content. There's a positive correlation between ash content and pH (Tag et al., 2016).

Increased pyrolysis temperature leads to the loss of acidic functional groups and the formation of alkaline substances like Ca-, Mg-, Na-, and K- bearing oxides, hydroxides, and carbonate minerals, resulting in higher pH values (Weber & Quicker, 2018; Gai et al., 2014).

Biochar produced at temperatures over 300 °C experiences the release of alkali salts from the organic matrix, increasing its pH. A constant pH is usually reached at around 600 °C when all salts are released (Shaheen et al., 2019; Sun et al., 2017).

Electrical conductivity (EC)

Salt concentration in biochar is indicated by electrical conductivity (EC). The EC of biochar is more influenced by the kind of feedstock than by the pyrolytic temperature. This is due to the fact that it depends on the elemental composition and ash concentration, both of which are greatly influenced by the initial feedstock and the pyrolysis conditions (Yargicoglu et al., 2015). High pyrolysis temperature mostly produces biochar with high EC values (Wang et al., 2020). This is a consequence of the ash or residue concentration rising as a result of the pyrolysis's loss of volatile material (Singh et al., 2017).

Ash content

The ash content in biochar, a key indicator of its mineral composition, is significantly influenced by the nature of the feedstock and the pyrolysis temperature. Biochar's ash concentration generally increases with rising pyrolysis temperatures. This trend is consistent across various types of straws (rape, corn, rice, and wheat), where higher temperatures lead to increased ash content due to the formation and deposition of mineral elements (Domingues et al., 2017; Wang et al., 2020; Zhang et al., 2020). The type of feedstock used for biochar production plays a crucial role in determining its ash content. Feedstocks with high lignin content, such as shells and nuts, tend to produce biochar with lower ash content. In contrast,

manure and materials with low lignin content result in biochar with higher ash content (Brewer et al., 2011; Aller, 2016; Hassan et al., 2020). Wood biochar, particularly from hardwoods high in lignin, has been reported to have relatively low ash content (4 - 23 %) compared to biochars made from corn stover and switchgrass (Brewer et al., (2011).

Elemental composition of biochar

Biochar's elemental composition, which includes carbon (C), hydrogen (H), oxygen (O), sulfur (S), nitrogen (N), and inorganic minerals like potassium (K), silicon (Si), calcium (Ca), iron (Fe), magnesium (Mg), phosphorus (P), and sodium (Na), varies based on pyrolysis type, feedstock, and temperature. The carbon content is predominantly aromatic, forming stable rings and is the largest component, accompanied by hydrogen and oxygen. Nitrogen is usually present on the biochar surface within C-N heterocyclic structures (Ravindra et al., 2022).

Slow pyrolysis enhances the production of major minerals compared to fast pyrolysis, but overall, the pyrolysis type has less impact on elemental composition than feedstock type and pyrolysis temperature (Ippolito et al., 2020; Zhang et al., 2017). Woody biochars contain more carbon and fewer plant nutrients due to the inherent characteristics of the wood, while manure-based biochars are richer in minerals like N, S, P, Ca, and Mg.

The H/C and O/C molar ratios are critical indicators of biochar's carbonization, aromaticity, and hydrophilicity. Higher pyrolysis temperatures lead to a reduction in these ratios, indicating increased aromatization, dehydration, structural transformation, and loss of functional groups containing oxygen and

hydrogen. This results in biochars with lower polarity, higher hydrophobicity, and greater stability due to fewer oxygen-based functional groups (Suliman et al., 2016; Gai et al., 2014; Li et al., 2013; Wang et al., 2021; Zhao et al., 2017). The polarity index $[(O+N)/C]$ decreases with increasing temperature, reflecting reduced polarity and increased aromaticity in the biochar (Shaheen et al., 2019).

Surface functional groups of biochar

The surface functional groups of biochar are mainly determined by the feedstock (Choudhary et al., 2019) and the pyrolysis temperature (Amalina, et al., 2022). Feedstock pretreatment and biochar post treatment can also affect the surface functional groups.

Increasing pyrolysis temperature from 200 to 500 °C leads to dehydration, decarboxylation, and de-carbonylation, resulting in the release of water, CO, and CO₂, and formation of hydrocarbons. This process modifies surface functional groups like O-H, C=C, C=O, and C-H. Higher temperatures over 500 °C induce dehydrogenation and de-methanation, increasing aromaticity and carbonaceous character. Aromatization begins around 350 °C, producing hydrophobic groups at higher temperatures and oxygen-containing, hydrophilic groups at lower temperatures (Chen et al., 2017; Gai et al., 2014; Hassan et al., 2020; Zhang et al., 2020). The primary surface functional groups include hydroxyl, methyl, carboxylic, amine, amide, lactonic, and alkene groups, which facilitate ion exchange and adsorption (Wijitkosum & Jiwnok, 2019; Bouaik et al., 2021). Biochar produced in a nitrogen environment has a higher oxygen content than those produced in the presence of air, with the presence of alcohols, phenols, carboxylic acids, ethers,

esters, and carbonyl groups on the surface (Janu et al., 2021). These functional groups are identified using Fourier-transform infrared spectroscopy (FTIR) or X-ray photoelectron spectroscopy (XPS). In this study the FTIR will be used.

Fourier-transform infrared spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a crucial analytical technique for identifying chemical bonds and functional groups by measuring infrared radiation absorption, creating a molecular fingerprint (Griffiths & de Haseth, 1986). It operates based on molecular vibrations, with specific frequencies of infrared light exciting these vibrations. Two common modes, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Attenuated Total Reflectance (ATR), are used to analyze carbon materials, each with distinct advantages (Stuart, 2022). DRIFTS involves grinding the sample with KBr powder, while ATR presses the sample against a crystal for higher sensitivity and less spectral variation (Griffiths & de Haseth, 1986). FTIR is widely used in chemistry, materials science, and environmental analysis, FTIR provides detailed insights into a sample's molecular structure and composition (Zhang et al., 2017).

Surface morphology

Morphology refers to the shape and surface structure of particles, influencing their interaction with other substances and performance in various applications, such as drug delivery and ceramics (Zhang et al., 2017). In biochar, surface morphology is a key property that includes features like porosity, roughness, and the presence of cracks, which significantly affect its adsorption capacity and catalytic activity (Lehmann & Joseph, 2015). These characteristics are

crucial for biochar's effectiveness in applications like environmental remediation and soil amendment (Chen et al., 2020). Tools like Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) are commonly used to analyze and understand biochar's surface morphology (Lehmann & Joseph, 2015). This analysis helps optimize biochar's use in fields such as agriculture and environmental management (Zhang et al., 2017).

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a technique that uses a focused beam of electrons to scan the surface of samples, producing high-resolution images that reveal surface morphology and composition (Chen et al., 2020). Unlike Transmission Electron Microscopy (TEM), which transmits electrons through a specimen, SEM detects electrons emitted from the specimen's surface, making it ideal for surface topography analysis. The method involves directing electrons from a tungsten filament towards the specimen, where they interact to generate signals that are transformed into images. Samples typically require preparation, including fixation, dehydration, and coating with a conductive material, to ensure optimal imaging. SEM is widely used in fields like materials science, nanotechnology, and biomedical research, offering quick data acquisition and high-quality imaging, though it requires stable conditions and a significant investment (Zhang et al., 2017).

Some environmental applications of biochar

The environment has been plagued with diverse contaminants. These contaminants are more toxic and complex. A severe hazard to people, other living

things, and the environment, most of these toxins originate from manmade causes. In order to remove these toxins from the environment, scientists are exploring for environmentally appropriate removal methods. According to Yaashikaa et al. (2019), biochar is popular because it is cost-effective, porous, and has a high adsorption capacity. Different methods, including electrostatic attraction and interactions, hydrophobic interactions, hydrogen bonding, pore filling, and complicated adsorption, are used by biochar to remove pollutants.

Adsorption of Heavy Metals in Water and Soil

Inorganic metals cannot biodegrade and become hazardous to living organisms in larger quantities, they pose a serious threat to both the environment and public health. The most poisonous, cancer-causing, and inorganic pollutants are heavy metals, which include Cu, Cd, Zn, Ni, Hg, and Pb (Oliveira et al., 2017; Uchimiya et al., 2011). Studies have demonstrated that biochar can be used to remove harmful heavy metals from soils and wastewater (Sobik-Szołtysek et al., 2021; Wang et al., 2018). Ion exchange between heavy metals and protons, alkali or alkaline earth metals on the surface of biochar are the main methods by which heavy metals are removed from water (Bolan et al., 2021; Rangabhashiyam & Balasubramanian, 2019; Wang et al., 2020). The mineral component of biochar contributes to the precipitation of heavy metals by acting as another adsorption site in removing contaminants (Yaashikaa et al., 2019). Biochar produced from poultry manure at 575 °C has been used to sufficiently remove Zn, Cd and Pb from water (Sobik-Szołtysek et al., 2021). Pecan shell biochar was also used to sorb Pb from water. Water activated pecan shell adsorb more Pb than the none activated (Crisler

et al., 2019). Diary manure biochar was also more effective in removing Pb, Cu, Zn and Cd from solution than rice husk biochar (Xu et al., 2013). This was due to the abundance of oxygenated groups such as -COOH and OH that showed strong affinity for the heavy metals.

Adsorption of organic pollutants

In recent time, there have been a significant increase of organic pollutants in our water bodies. Some of these include pharmaceuticals (e.g., tetracyclines, acetaminophen, sulfamethoxazole, ibuprofen, etc.), agrochemicals (e.g., pesticides, herbicides, insecticides, fungicides etc.), volatile organic compounds (VOCs) (e.g., benzene trichloroethylene, furan, hexane etc.), and aromatic dyes (e.g., methylene-blue, methyl violet, rhodamine brilliant-blue, congo red etc.)(Oliveira et al., 2017; Shen & Zhang, 2019; Mahmoud et al., 2023). Functional groups of pollutants interact with those on the biochar through chemisorption (electrophilic interactions) and/ physisorption (pore diffusion, hydrophobic, electrostatic attraction/repulsion via π - π electron donor-acceptor and hydrogen bonding), which are the main mechanisms, to cause their removal. (Bartoli et al., 2020). Biochars produced at higher temperatures (>500 °C) have greater surface area, high aromaticity owing to the loss of O- and H-containing functional groups which encourages the removal of non-polar organic contaminants than those produced at lower temperatures (Ahmed et al., 2016; Xiao & Chen, 2016).

Biochar has been used in the removal of organic dyes such rhodamine-B dye from contaminated textile effluent using magnetic chicken bone biochar. Approximately 96.5 mg/g of the dye was removed at pH 10 within 180 min of

contact time (Oladipo et al., 2017). Biochar produced from green seaweed was able to remove over 77.5 % of Remazol dyes (Gokulan et al., 2019). *Wodyetia bifurcate* was used as an adsorbent for the removal of methylene blue and 83 % removal was achieved in 30 min (dos Santos et al., 2019). One mechanism of removal is electrostatic contact between the dye molecule and the surface of the biochar which promotes the removal of the dye. Another preferred interactional method is pore filling (Yaashikaa et al., 2019).

Biochar produced from a mixture of wood chips of maple, elm and oak effectively removed pesticides (atrazine and simazine) from water with adsorption capacities of 435 and 514 mg/g respectively (Zheng et al., 2010). Biochar has also been used in the remediation of several pharmaceuticals such as SUL (Ai et al., 2020; Qin et al., 2019), ACE (Patel et al., 2021; Rahman & Nasir, 2020).

Catalyst and Catalyst Support

Biochar is used as a catalyst are in agriculture, ecology, and energy. It is used in biorefineries to create products with additional value (Mishra et al., 2021). The production of electricity, the production of biodiesel, and the removal of tar all use biochar as a catalyst (Shen et al., 2014). For example, biochar was used in the catalytic transformation of tar into carbon monoxide and hydrogen. High yield of biodiesel (95 %) was obtained from the trans-esterification of waste cooking oil using chicken manure-derived biochar (Jung et al., 2018, 2019) and 88 % yield from waste cooking oil using sulfonated rice husk biochar at 100 °C (Li et al., 2014).

Soil Amendment

Due to its fundamental structure and surface functional groups, biochar has become popular in the soil remediation industry. The following are some of the ways that biochar is used in agriculture: a) improving soil cation exchange capacity and reducing aluminium toxicity (Saha & Basak, 2019); b) increasing productivity by holding onto water; c) encouraging the sequestration of carbon and lessening the effects of greenhouse gasses (Sizmur et al., 2017); d) raising the fertility and structure of the soil (Barnossi et al., 2021); and e) increasing microbial. Additionally, biochar may be used to clean up soil that has been polluted by dangerous contaminants including pesticides, heavy metals, and hydrocarbons. Heavy metals may be effectively absorbed by biochar with high pore volumes, surfaces, and functional groups (Amalina et al., 2022).

Biochar is also added to soil as a supplement. As a consequence, the soil's pore capacity expands, allowing microbial growth that extends nutrients, air and moisture. This promotes the survival, activity, and multiplication of microbes, which benefits plant growth (Sakhiya et al., 2020; Yaashikaa et al., 2020).

Mechanism of remediation/removal/adsorption

The reaction between the adsorbate and the adsorbent surface continues until equilibrium is achieved. The following are the stages involved in the adsorption process: The adsorbate is deposited onto the surface of the adsorbent by three processes: (1) physical adsorption; (2) precipitation and complexation; and (3) condensation, which fills the adsorbent's pores. Three distinct stages make up this process: (a) the clean phase, during which no adsorption happens; (b) the mass

transfer phase, during which adsorption is underway; and (c) the equilibrium or exhausted zone, during which equilibrium is reached (Ambaye et al., 2021).

Some of the methods used to adsorb organic pollutants onto biochar include electron donor-acceptor (EDA) interaction, partitioning, pore filling, hydrophobic interaction and electrostatic interaction.

Pore filling

Biochar is made up of mesopores (2 – 50 nm) and micropores (<2 nm) on the surface. The presence of these pores determines the use of pore filling as a mechanism for adsorption of organic pollutants. This process is influenced by the organic pollutant's polarity, nature, and kind of biochar. Biochar with less volatile matter content and low concentration of organic pollutant increases the efficiency of adsorption through pore filling (Abbas et al., 2018; Ambaye et al., 2021; Puga et al., 2022).

Pore filling was reported by Anton et al. (2022) as one of the main mechanisms used by biochar made from holm tree (HB), and grapevine cane biochar (GB) for the sorption of venlafaxine (VLX), trazodone (TRZ) and fluoxetine (FLX). The HB (59.53 μm) and GB (72.63 μm) used had higher particle size distribution than biochar made from eucalyptus biochar (53.96 μm). Also intra particle size diffusion was considered as the main adsorption mechanism of tetracycline unto biochar produced from alfalfa hay modified with NaOH with adsorption capacity of 302.37mg/g (Jang & Kan, 2019).

Partitioning

The adsorption mechanism of organic pollutants is determined by the characteristics of the carbonised (graphene and crystalline-like) and non-carbonized (organic carbon, non-crystalline, amorphous) components of the biochar. The amorphous phase of biochar separates aliphatic and polyaromatic compounds including sugars, ketones, and phenols (Abbas et al., 2018; Ambaye et al., 2021; Anton et al., 2022). Utilising organic carbon fractions of biochar, dairy and swine dung biochar generated at pyrolysis temperatures of 200 and 350 °C shown significant sorbate partitioning of atrazine pollution Cao et al., 2009). Biochar with high volatile content promotes this mechanism of adsorption.

Electrostatic interaction

Another kind of adsorption is electrostatic contact, which occurs when ionizable organic molecules and the charged surface of biochar are attracted or repelled by one another electrostatically. Organic pollutants that are negatively charged are often drawn to the surface of positively charged biochar and vice versa. The ionic strength and pH of the aqueous solution affect this mechanism's effectiveness (Abbas et al., 2018; Ahmad et al., 2014; Ambaye et al., 2021; Cheng et al., 2021). According to Mukherjee et al. (2011), the surface of the biochar is positively charged at a low solution pH and vice versa. The solution pH therefore controls the net charge on the surface of the biochar. Increase in ionic strength of the adsorbate solution results in electrostatic repulsion interactions between the adsorbate and adsorbent increasing the adsorption while decreasing adsorption by electrostatic attraction.

Electron donor and acceptor (EDA) interaction

The major mechanism of electron donor and acceptor interaction is the adsorption of aromatic chemicals onto graphene-like charcoal. The interaction between aromatic rings is often mild (Cheng et al., 2021). Biomass pyrolyzed at a temperature greater than 1100 °C produces biochar with complete graphitization. Pyrolysis temperature affects the electron density of the biochar and determines whether there is π - electron deficiency or π -electron enrichment within the aromatic rings. Below 500 °C, the π aromatic biochar system acts an electron acceptor while acting as an electron donor above 500 °C (Abbas et al., 2018; Ambaye et al., 2021). Rice straw biochar effectively removed tetracycline and this was attributed to the high surface area and EDA interactions between the tetracycline molecules (which act as π electron acceptors due to its aromatic structure) and biochar's graphitic surface (Wang et al., 2017).

Hydrophobic interactions

By combining partitioning and hydrophobic interaction, this process is exploited in the adsorption of neutral and hydrophobic organic molecules (Abbas et al., 2018; Ambaye et al., 2021). When non-polar groups like C - H are present and cause mutual repulsion between water molecules, this is known as hydrophobic interaction (Cheng et al., 2021), therefore low oxygen content increases hydrophobicity (Puga et al., 2022). This mechanism requires less energy compares to partitioning and it is the main mechanism of adsorption onto the surface of the graphene structure. The adsorption of perfluoro octane sulfonate using maize straw biochar was dominated by hydrophobic interactions. Organic compounds with high

hydrophobicity also enhance their removal by hydrophobic interaction. Figure 2 below, shows the different mechanisms use in the adsorption of organic and inorganic pollutant.

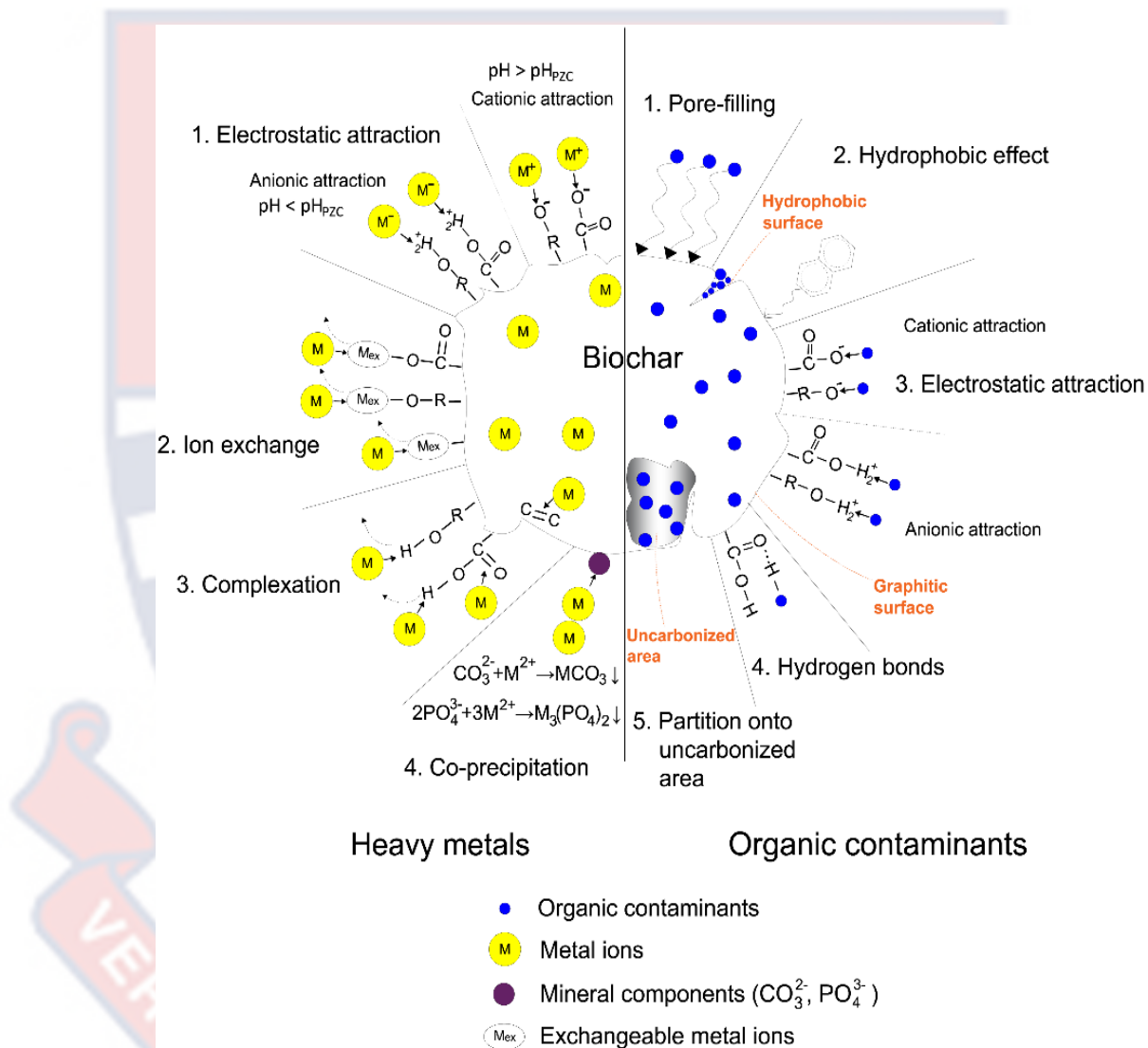


Figure 2: Different Biochar Adsorption Mechanisms for Organic and Inorganic Contaminants.

Source: Ambaye et al., (2021)

Table 2: Examples of Biochar Adsorption of Organic Contaminants

Feedstock	Pyrolysis temperature(°C)	Organic contaminant	Adsorption capacity /removal percentage	Adsorption mechanism	References
Pine wood	425	Salicylic acid, ibuprofen	22.7mg/g 10.74mg/g	Hydrogen bonding π - π interaction	Essandoh et al., (2014)
Waste water sludge	850	sulfamethoxazole	45mg/L	π - π interaction	Shimabuku et al. (2016)
Bamboo	380	chloramphenicol	233mg/L	π - π interaction	Ahmed et al. (2017 a,b)
Eucalyptus wood	500	carbamazepine	104.85 to 867.70mg/L	π - π interaction	Chen et al. (2017)
Bamboo wood					
Rice straw	400-800	anisole Phenol Guaiacol	70.4m/g 17.2m/g 23.3m/g	Pore filling, π - π electron donor acceptor interaction	Li et al. (2017a,b)
Pine sawdust	700	sulfamethoxazole	86.82%	Hydrophobic interaction	Reguyal & Sarmah, (2018)

Table 2 continued

Sugar cane bagasse	400-800	Malachite green	3000mg/L	Diffusion	Vyavahare et al. (2017)
Corn straw	600	atrazine	67.55m/g	Pore filling	Zhang et al. (2018 a,b)
Rice husk	700	Tetracycline hydrochloride	80.9mg/g	π - π interaction, electrostatic interaction	Zeng et al. (2017)
		Doxycycline hydrochloride	85.2mg/g		
		ciprofloxacin	36.1mg/g		
Rice husk	600	Erythromycin	>95%	Not provided	Herrera et al. (2022)
	500	Azithromycin	>95%		
Tea waste	700	Caffeine	15.4mg/g	Electrostatic interaction and nucleophilic attraction	Keerthanan et al. (2021)

Adsorption Kinetics

The adsorption kinetics assesses the removal efficiency with regards to time. It is very important as it clarifies the rate controlling step and also the estimates the rate of adsorption of the PHAs by the biochars (Andrade et al., 2018). Various kinetic models have been used to ascertain the processes and possible stages that govern the rate of adsorption. In this study, pseudo-second order (2) and pseudo-first order (1) and intra-particle diffusion models are utilized to explain the adsorption kinetics of pharmaceuticals. The pseudo-first order model also known as the Lagergren model models an adsorption reaction where the reaction rate is dependent on the concentration of one reactant, while the concentration of the other reactant(s) is in large excess and effectively constant whereas the second order model assumes that the rate of adsorption of a contaminant is proportional to the number of available active sites on the surface of the adsorbent.

$$q_t = q_e(1 - e^{-K_1 t}) \quad (1)$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (2)$$

where:

t ; is time (min), K_1 ; is the rate constant of the pseudo-first order model (min^{-1}),

q_e ; is the amount of solute adsorbed onto the adsorbent at equilibrium (mg/g), and

q_t ; is the amount of sorbent adsorbed onto the adsorbent at any given moment (t) (mg/g).

The intra-particle diffusion (IPD) model is generally applied to determine the rate limiting step of an adsorption reaction. It is represented by equation 3

$$q_t = K_{id} t^{0.5} + C \quad (3)$$

where:

K_{id} ; is the intraparticle diffusion rate constant which is determined from the gradient of the plot of q_t versus $t^{0.5}$, C ; is the thickness of the boundary layer which is determined from the intercept, and q_t ; and t have their usual meaning. A plot of q_t versus $t^{0.5}$ gives a linear function. If the line passes through the origin, it means the adsorption is controlled by diffusion IPD. However, in most cases, the line does not pass through the origin but rather gives multiple linear sections corresponding to different mechanisms. The adsorption of a contaminant in a solution onto an adsorbent involves four main mechanisms, mass transfer (bulk movement) of contaminants as soon as adsorbent is added to solution which is the first, the second is film diffusion, which involves the slow movement of solutes from the boundary layer to adsorbent surface (surface diffusion), then movement in to the pores of the adsorbent which is the third and finally the rapid attachment to the active sites of the pores (pore diffusion)(Peiris et al., 2017).

Several studies have used these kinetic models to examine the efficiency of adsorption of contaminants such as ACE (Al-itawi, 2020), ERY (Herrera et al., 2022; Ndoun et al., 2021), ASP (Essandoh et al., 2014), CIP (Zeng et al., 2017)

Adsorption Equilibrium

When the rates of adsorption and desorption are equal, dynamic adsorption equilibrium is reached. Since the chemical potential in both phases is the same at this moment, there is no mass transfer of solute. Adsorption isotherm is dependent on equilibrium concentration in the liquid phase at a certain temperature and

pressure as well as the quantity of solute adsorbed in the solid phase. Selecting the appropriate isotherm model is crucial for system design and modelling, as it verifies the adsorption process of the investigated adsorbent and adsorbate process (Karimi & Tavakkoli, 2019). Based on their presumptions, the models may provide details on the adsorbent's surface characteristics, the adsorption process, the extent to which adsorption sites are covered, and the degree of affinity between the adsorbent and adsorbate. The accurate assessment and design of adsorption systems are facilitated by the modelling of isotherms. The non-linear versions adsorption isotherms are often used to avoid inaccuracies which would originate from linearization. The non- linear Freundlich (eqn. 4), Langmuir (eqn. 5), and Temkin (eqn. 6) isotherm models are used in this work.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = \left(\frac{RT}{b\tau} \right) \ln(K\tau C_e) \quad (6)$$

where: q_e : concentration in the solid phase at equilibrium (mg/g); q_{max} : Langmuir maximum adsorption capacity (mg/g); K_L : Langmuir isotherm constant (L/mg); C_e : concentration of solute in solution at equilibrium (mg/L); K_F : Freundlich constant associated with adsorption of the adsorbent[(mg/g).(L/mg) $^{1/n}$]; n : Freundlich heterogeneity factor (-); R is the universal gas constant (J/mol/K), T ; is the temperature, $b\tau$ is related to the heat of adsorption (KJ/mol) and $K\tau$; is the Temkin constant (L/g) which corresponds to the maximum binding energy.

Langmuir isotherm model is predicated on several assumptions, such as the existence of a set number of well-defined localised sites where molecules may

adsorb, the equality of all sites with respect to energy, homogenous monolayer adsorption, and the absence of interactions between nearby adsorbed molecules. It also presupposes that when equilibrium is established at a particular location, the rates of adsorption and desorption will be identical (Ajiboye et al., 2021). An essential dimensionless parameter (R_L), a characteristic of the Langmuir isotherm is expressed as:

$$R_L = 1/(1 + K_L C_0) \quad (7)$$

The R_L is a separation factor and it determines whether the adsorption process is favourable or unfavourable. The adsorption process is unfavourable when the separation factor R_L is greater than unity ($R_L > 1$), linear when the separation factor R_L is equal to unity ($R_L = 1$), favourable when the separation factor R_L lies in the range $0 < R_L < 1$. When the separation factor R_L is equal to zero ($R_L = 0$), the adsorption progress is irreversible (Al-ghouti & Da, 2020; Huang et al., 2018; Jodeh et al., 2022; Tang et al., 2018).

The Freundlich isotherm is used to describe multilayer adsorption when the heat of adsorption and affinity are not distributed uniformly throughout the heterogeneous surface. According to Freundlich isotherms, binding strength decreases as site occupancy increases, implying that adsorbate molecules occupy greater binding affinities before weaker sites.

The Temkin isotherm assumes that the adsorption surface is characterized by uniform distribution of binding energies (Sabzehmeidani et al., 2021) and the heat of adsorption decreases linearly with an increase in the surface coverage of the

adsorbent as a result of the adsorbate – adsorbate interactions (Azarpira & Balarak, 2016).

Adsorption Thermodynamics

Determining the spontaneity of the adsorption by the biochars involves analyzing entropy and energy factors, particularly the Gibbs free energy change (ΔG°). A more negative ΔG° indicates favourable adsorption, and it's calculated using the formula

$$\Delta G^\circ = -RT \ln K_L \quad (8)$$

This value is related to both the entropy change (ΔS°) and the heat of adsorption (ΔH°), as shown in the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

Combining equations 8 and 9 gives

$$\ln K_L = \Delta S^\circ/R - \Delta H^\circ/RT \quad (10)$$

where K_L is the equilibrium constant, T is the absolute temperature (K) and R is the universal gas constant ($8.314 \text{ J/mol}^{-1}\text{K}^{-1}$). Thus, enthalpy (ΔH°) and entropy changes (ΔS°) can be derived from the slope and intercept of the linear Van't Hoff plot of $\ln K_L$ against $1/T$, providing insights into the adsorption process's thermodynamics.

Goodness of Fit

This assists to determine which isotherm and kinetics model best describes an adsorption process. The coefficient of correlation R^2 , sum of squared errors (SSE). Spearman's correlation coefficient, average relative error, non-linear chi square, standard deviation of relative errors, Marquardt's percent standard

deviation, hybrid fractional error function, chi square, average percentage error, and composite fractional error function are some of the error functions used to study the fitness of a model.

Chi square

The chi square (χ^2) statistical test procedure establishes how well an isotherm equation best approximate an experimental adsorption system. The chi-square statistic is expressed by the equation:

$$\chi^2 = \sum_{i=1}^N \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,calc}} \quad (11)$$

The isotherm equation that in theory approximates the experimental adsorption system better would have a smaller chi square value (Rahman & Nasir, 2020; Sepehr et al., 2017; Stylianou et al., 2021).

The hybrid fractional error function

The hybrid fractional error function (HYBRID) is composite fractional error which was developed to improve the fit of the sum of the squares of the errors at low residual concentration of the adsorbate (Ayawei et al., 2017; Dhiman, 2022; Fallou et al., 2016; Sivarajasekar & Baskar, 2019). The hybrid fractional error function is expressed as:

$$\sum_{i=1}^N \left[\frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,exp}} \right]_i \quad (12)$$

Residual root means square error

The residual root mean square error (RMSE) was applied to determine the goodness of fit of the selected isotherm models to the experimental data. Smaller residual root mean square error values are indicative of better curve fitting (Azarpira & Balarak, 2016; Bahrami et al., 2023; Sekulic et al., 2019). The equation is given by the expression:

$$\sqrt{\frac{1}{n-2} \sum_{i=1}^N (q_{e,exp} - q_{e,cal})^2} \quad (13)$$

Marquardt's percent standard deviation

The Marquand's percent standard deviation (MPSD) was used to determine the number of degrees of freedom of the adsorption (Ayawei et al., 2017; Cabrera-Lafauriea et al., 2015; Dhiman, 2022; Fallou et al., 2016; Tang et al., 2018). The Marquand's percent standard deviation function is expressed by equation (10) as:

$$\sum_{i=1}^N \left[\frac{(q_{e,exp} - q_{e,calc})}{q_{e,exp}} \right]_i^2 \quad (14)$$

Sum of the squares of the errors

The sum of the squares of the errors (SSE) is expressed as:

$$\sum_{i=1}^N (q_{e,exp} - q_{e,calc})_i^2 \quad (15)$$

where $q_{e,exp}$ is the experimentally determined amount of the adsorbate removed by the adsorbent and $q_{e,cal}$ is the theoretically determined amount of the adsorbate removed by the adsorbent and was estimated using the selected isotherm equations. Though application of sum of the squares of the errors is widespread, for high

residual amount of the adsorbate, the magnitude of this error increase and therefore this error gives a better fit for the isotherm parameters at high residual concentration of the adsorbate when the error function is minimized (Dhiman, 2022; N'diaye et al., 2020).

Akaike information criterion (AICc)

The Akaike information criterion is a statistical method that is used to compare models with different numbers or parameters. A smaller AICc value suggests the model has a better fit (Francoeur et al., 2021; Luconi et al., 2022). It is represented by equation 16

$$AICc = 2k - n \left[\ln \left(\frac{SSR}{n-k} \right) \right] \quad (16)$$

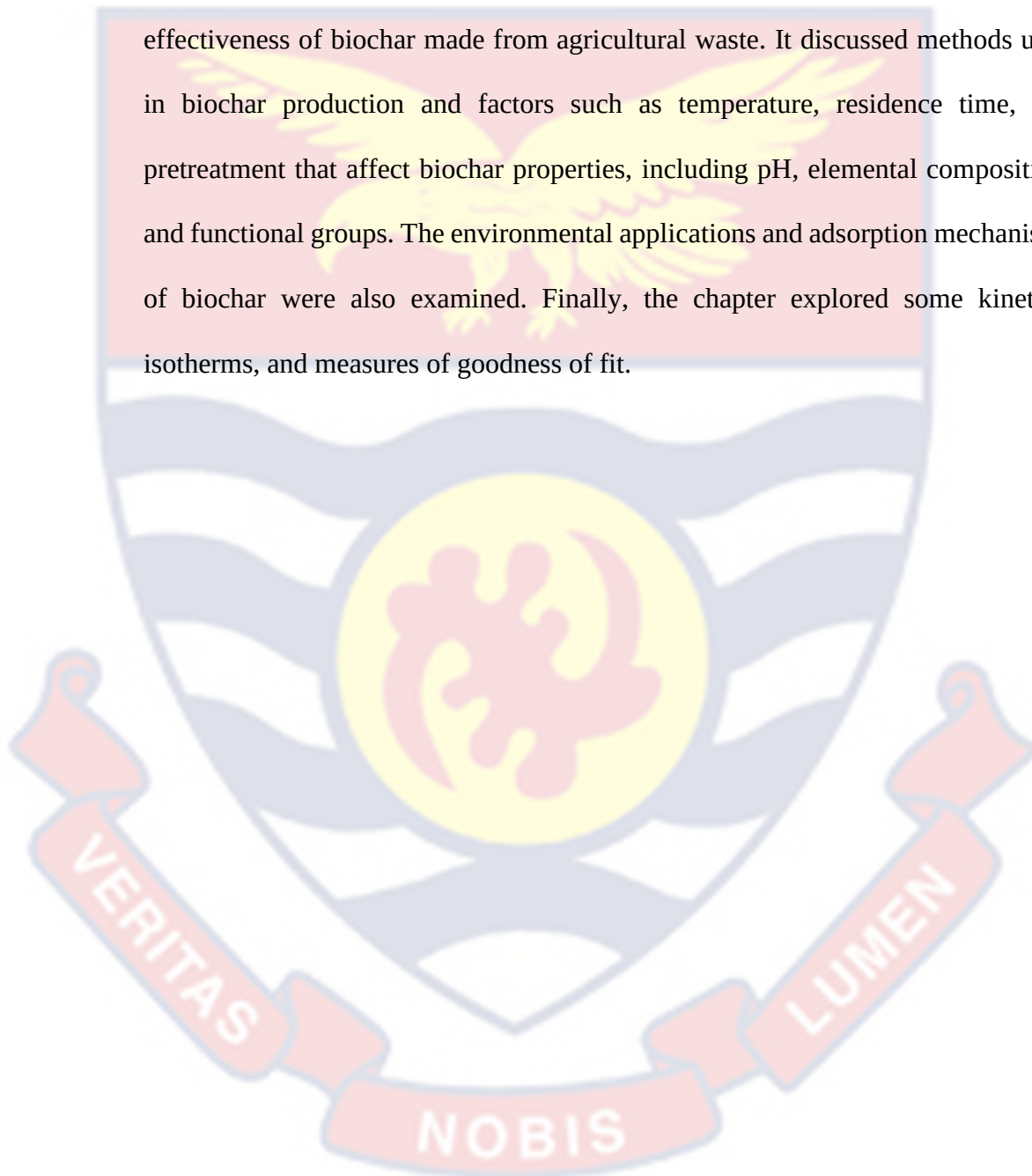
Where k is the number of parameters in the model, n is the number of data point, SSR, the sum of squares for the residual and ln is the natural logarithm.

Sum of normalized errors (SNE)

The Sum of Normalized Errors (SNE) offers a standardized way to compare the goodness of fit across different error functions, which can otherwise yield varying measures of fit quality. By normalizing the error values for each function relative to the highest error observed in a specific kinetic model, SNE simplifies the process of selecting the most suitable model. This normalization involves dividing the error values by the maximum error for each respective kinetic or isotherm model, thereby facilitating an easier and more straightforward comparison (Ayawei et al., 2017; Sivarajasekar & Baskar, 2019).

Chapter Summary

This chapter provided a brief overview of the classification and various removal techniques for pharmaceutical residues from water, emphasizing the effectiveness of biochar made from agricultural waste. It discussed methods used in biochar production and factors such as temperature, residence time, and pretreatment that affect biochar properties, including pH, elemental composition, and functional groups. The environmental applications and adsorption mechanisms of biochar were also examined. Finally, the chapter explored some kinetics, isotherms, and measures of goodness of fit.



CHAPTER THREE

METHODOLOGY

Introduction

This chapter provides an overview of the laboratory equipment and processes used in the study, including solution preparation, biochar production, laboratory trials assessing the effectiveness of biochar in remediating eight selected pharmaceuticals, kinetic and equilibrium studies, thermodynamic properties of the adsorption process, and the application of selected biochars to lagoon water samples.

Standards and Reagents

The antibiotics (metronidazole, trimethoprim, sulfamethoxazole, and ciprofloxacin) were purchased from Fluka (Glostrup, Denmark). Erythromycin (ERY) Acetaminophen (ACE), caffeine (CAF) and aspirin (ASP) were purchased from Sigma-Aldrich. All the analytical standards had a purity above 99 %. Methanol and acetonitrile (HPLC grade) and sodium EDTA analytical grade, were purchased from Merck International. Solid phase extraction was performed using Agilent C18, 6 mL 500 mg cartridges.

Stock Solution Preparation

A 1.0 g/L concentration stock solution of each antibiotic, ACE, CAF and ASP was prepared in deionized water in 1.0 % methanol. The standard solutions were protected from light and stored at 4 °C for further use. Working concentrations of the standard solutions were prepared by appropriate dilution with deionized

water. In case of mixtures of standards, each stock solution was directly added to the aqueous solution and mixed thoroughly to the desired concentration.

Collection and Pretreatment of Feedstock /Biomass

Dried coconut shells and fibre were collected from coconut oil producers at Duakor in the Cape Coast Metro of the Central Region. The shell was removed from the fibre and broken into smaller sizes for easy transfer of heat during pyrolysis. The fibre was ripped into smaller pieces and kept for further work. Rice husk was collected from a rice mill at Ayensudo and brought to the lab for further work.

Coconut shell (CS), coconut fibre (CF), and rice husk (RH) feedstocks were selected because they are readily available and were waste materials that are mostly left in the environment (Duku et al., 2011; Obeng et al., 2020).

Preparation and Treatment of Biochar

Biochar was produced from coconut shell and fibre (Bispo et al., 2018; Dhar et al., 2022) and rice husk biomass through slow pyrolysis in a muffle furnace under limited oxygen and atmospheric pressure. A known mass of biomass determined with Satorius LE 623P balance was packed into metal containers and tightly closed to minimize the oxygen content inside the container. The tightly closed metal containers were placed in the muffle furnace (Dissanayake et al., 2018). The temperature was set at a rate of 10 °C per minute until the set point of 500 and 600 °C for one set and kept at the set temperature for zero, one, two and three hours. Biochar produced at higher temperatures have high surface area, porosity and bulk density and is efficient in removing organic contaminants from

soil and water (Sobik-Szołtysek et al., 2021). Biochar produced was allowed to cool to room temperature before they were removed from the furnace and their masses determined. They were ground and passed through 0.8 mm and 0.250 mm sieves and washed with deionized water till the solution become clear. They were then dried in the oven at 105 °C for 24 hours, placed in airtight containers and labelled for further analysis.

Biochar Characterization

Biochar yield

The biochar yield was calculated using the following expression used by Domingues et al. (2017) and Boadu et al. (2019):

$$\text{Biochar yield}(\%) = \frac{\text{mass of biochar}(g)}{\text{mass of biomass}(g)} \times 100 \quad (16)$$

Determination of pH and electrical conductivity (EC)

The pH and EC of biochar were measured with a biochar-to-deionized water ratio of 1:10 and agitated for one hour using a magnetic bar stirrer. The resultant solutions were allowed to stand for 30 min (Hmid et al., 2014; Singh et al., 2017). The pH and EC values were read using a combined pH/EC meter (Eutech PC 700) that was previously calibrated with standard solution. The pH/EC was done in triplicate for each sample.

Proximate analysis

Proximate analysis was determined according to American Society for Testing and Materials (ASTM) D1762-84 (Conz et al., 2017; Dhar et al., 2022; Zhang et al., 2017).

Moisture content

About 1 g of dried biochar in a crucible was heated in a furnace at a temperature of 105 °C for 2 hours. The samples were placed in a desiccator and allowed to cool. The mass was measured using an analytical balance. Moisture content (MC) was determined by the expression below:

$$\% \text{ MC} = \frac{\text{initial mass of biochar } (M_1) - \text{mass after heating } (M_2)}{\text{initial mass of biochar } (M_1)} \times 100\% \quad (17)$$

Volatile matter

The resultant mass obtained from the moisture content determination was heated at 950 °C for 10 min in the furnace, crucibles were removed and placed in a desiccator to allow them to cool. The volatile matter (VM) was calculated as:

$$\% \text{ VM} = \frac{M_2 - \text{mass after heating } (M_{950})}{M_2} \times 100\% \quad (18)$$

Ash content (AC)

A 1.0 g of biochar was weighed and heated at 750 °C for 6 hours. The ash content was determined by the mass of the residues after cooling in a desiccator using the equation below.

$$\% \text{ AC} = \frac{\text{final mass after ashing}}{\text{initial mass}} \times 100 \quad (19)$$

Fourier transform infrared spectroscopy (FTIR)

A PerkinElmer Spectrum 3 FTIR spectrometer was used to determine the functional groups on the surface of the biochar. The spectra were obtained at 4 cm⁻¹ resolution by measuring the absorbance from 400 to 4000 cm⁻¹ using a combined 40 scans.

Scanning electron microscopy (SEM)

The surface morphology of the biochars were examined using a scanning electron microscope ZEISS Crossbeam 540. The surface of the biochars were coated using a thin layer of gold nano particles to enhance conductivity.

Selection of Pharmaceuticals

The pharmaceuticals studied in this thesis, are commonly used chemicals and are among the essential medicines used in Ghana (Ministry of Health, 2017). The antibiotics (metronidazole (MET), trimethoprim (TRI), sulfamethoxazole (SUL), ciprofloxacin (CIP) and erythromycin (ERY) are obtained mostly over the counter without prescription in Ghana despite regulations against this practice (Azanu et al., 2018). ACE and ASP are easily accessible as they are mainly sold over the counter, in drug stores and public places in the country. CAF is mostly taken in the form of tea which can be obtained in provision stores all over the country. CAF is also a component of numerous medicines. They have also been found in some water bodies in Ghana at high concentrations (Azanu et al., 2021). Table 3 highlights some properties of the selected PHAs.

Table 3: Some Properties of the Selected Pharmaceuticals

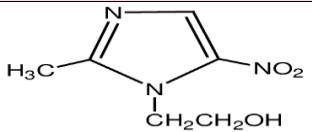
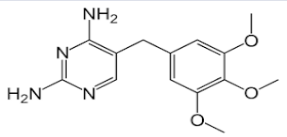
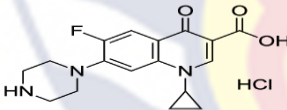
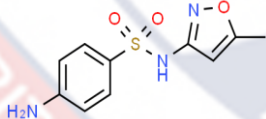
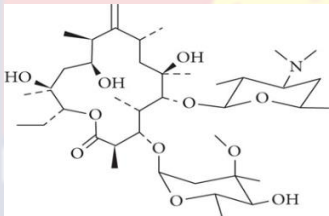
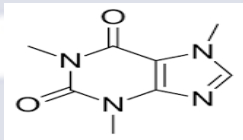
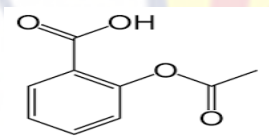
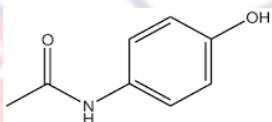
Pharmaceuticals	ID	Structure	Molecular formula	Molecular weight	pKa
Metronidazole	MET		$C_6H_9N_3O_3$	171.15	15.44
Trimethoprim	TRI		$C_{14}H_{18}N_4O_3$	290.32	7-12
Ciprofloxacin	CIP		$C_{17}H_{18}FN_3O_3$	331.34	6.09
Sulfamethoxazole	SUL		$C_{10}H_{11}N_3O_3S$	253.28	6.16

Table 3 continued

Erythromycin	ERY		$C_{37}H_{67}NO_{13}$	733.93	8.9
Caffeine	CAF		$C_8H_{10}N_4O_2$	194.19	14.0
Aspirin	ASP		$C_9H_8O_4$	180.16	3.5
Acetaminophen	ACE		$C_8H_9NO_2$	151.16	9.0-9.5

Source: Azanu et al. (2018)

Batch Adsorption Experiments

Batch adsorption studies were done in a 100 mL Erlenmeyer flask. For the kinetic studies, 0.5 g of biochar was added to 50 mL of individual pharmaceutical solutions containing 10 mg/L to determine the removal efficiency of the various biochar prepared for the selected pharmaceuticals. The adsorption was done at room temperature (25 °C) using a magnetic bar stirrer on a Stuart US151 at 50 rpm. Samples were collected at various time intervals up to 24 hours (15, 30, 60, 120, 240, 360, 480, 720 and 1440 min). The collected samples were conditioned, and filtered through 0.22 µm PES Agilent filters and their concentrations were determined using the Shimadzu UHPLC. Control experiments with no biochar but containing pharmaceuticals were simultaneously carried out to exclude the degradation of the pharmaceuticals. No measurable change was observed in the concentrations of the controls. Also, blank experiments were performed with biochar without the pharmaceuticals, this was to check the potential desorption of pharmaceuticals from the produced biochars. The mass of pharmaceuticals adsorbed was calculated by mass difference. All the experiments were done in duplicates.

The biochars that obtained removal efficiency of above 70 % within 24 hours of stirring were used for the next stage. Here, 0.5 g of biochar was added to 50 mL solution containing a mixture of all the eight selected pharmaceuticals (competitive adsorption). The adsorption process was carried out as in the above. Five biochars that performed well in the competitive adsorption were later used for the removal of PHAs in environmental samples. The pH of the experiments was

not controlled using a buffer. It was done to avoid additional ions in the system that could compete for adsorption sites. Nevertheless, the initial and final pH values of the suspension were recorded (Nielsen & Bandosz, 2016).

Kinetic Studies

The amount of pharmaceuticals adsorbed on the biochar at time t (q_t , mg/g) and removal efficiency (RE) were calculated using the equation 20 and 21 respectively.

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (20)$$

$$RE(\%) = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (21)$$

Where C_0 (mg/L), C_e (mg/L) and C_t (mg/L) are the initial concentration, equilibrium concentration and final concentration at time (t) of pharmaceuticals respectively. V (L) and m (g) are the volume of reaction solution and mass of biochar respectively. To investigate the mechanism of adsorption unto the biochar, measured kinetic data set were fitted into three kinetic models, the pseudo-first pseudo-second models, and intraparticle diffusion. The conformity of the experimental data to the models were evaluated using R^2 , adjusted R^2 , the sum of normalized errors and the AICc values.

Adsorption Isotherms

Adsorption isotherms of the PHAs on the five selected biochars were performed at their inherent pH varying from 9-11.5. The biochars were selected based on their removal efficiencies (above 85 %) in the competitive adsorption of the eight pharmaceuticals within 8 hours were chosen. These were CF53, CF61, RH53, RH61 and RH63. 0.5 g of the biochars were added PHA solutions (50 mL)

of varying initial concentration (5, 10, 15, 20, 25 and 30 mg/L). The solution was stirred for 24 hours and then filtered and prepared for analysis. The experimental data of the pharmaceuticals adsorption onto the adsorbent was fitted to three typical isotherm models: Langmuir, Freundlich and the Temkin.

Study Areas

Fosu Lagoon

Fosu lagoon (5°6'17.87" N, 1°15' 18.68" W) is located in the Cape Coast metropolis, Ghana. It is a closed lagoon with its sand bar occasionally breached by heavy rainfall or manually as part of the celebrations of the 'Fetu' Festival (Dankwa et al., 2016). According to Armah et al. (2012), the lagoon is surrounded by many settlements that serve as point sources for polluting the lagoon. Located at the northern side, is a metropolis transport garage as well as mechanical workshops at the northeastern side of the lagoon which discharge industrial waste into the lagoon. In addition are drains from a nearby educational institution and a hospital, household dumping and sewage. The human activities in the area are immense and have resulted in massive sedimentation in the populated northern sector especially, one can walk many meters on the water weeds as the lagoon has been transformed into waste and marshland (Dankwa et al., 2016).

Korle Lagoon

Korle Lagoon is located in Accra, the capital of Ghana. It is to the southwest side of the central business within longitude 05°35'N and latitude 00°06'W. The lagoon covers a total surface area of about 0.6 km² and an estimated catchment area of 400 km². The Korle Lagoon is fed by the Odaw River and two major drains

on its eastern and western sections. The Odaw River flows through the capital with a catchment area of about 60 % of the metropolitan area. This serves as a location for storm water runoffs resulting in the transportation of pollutants from places such as farms and residential areas (Aglanu & Appiah, 2014; Osae et al., 2022). The two major drains are uncovered and collect silt and debris into the lagoon from all the suburbs of the city. The catchment area of the lagoon is associated with the siting of many industries, markets, mechanical shops and the development of uncontrolled urbanization with many slums and squatters. Due to lack of sanitation facilities, the shores of the lagoon have been turned into defecation site (Aglanu & Appiah, 2014; Boadi & Kuitunen, 2002).

Esei Lagoon

The Esei lagoon is located in Sekondi in the Western Region of Ghana. It is an open lagoon that maintains a permanent contact with the sea as a result of human interferences. Several open drains from settlement around end up in the lagoon, the beaches are used as places of convenience and dumping of human excreta (Coastal Resource Center-Ghana/Friends of the Nation, 2010).

Keta Lagoon

The Keta lagoon is located in Keta, in the Volta Region of Ghana. It lies in the far south-east of the country near the international frontier with Togo with coordinates 5° 55'N 0° 59'E. The lagoon is about 140 km east northeast of Accra on the south coast of the Volta Region. It is an extensive brackish water body situated to the east of the Volta River estuary. It is an open lagoon fed by three main water sources: the Todzie river, the Aka and Belikpa streams and the Volta River

which flows into the lagoon at Anyanui at an unknown discharge rate. It has a total surface area of about 28,400 ha, 27 km long and a variable width of up to 16 km. The lagoon is surrounded by many settlements with flood-plain consisting of marsh, scrub, farmland and substantial mangrove stands which are heavily exploited for fuelwood. The main activities around the lagoon are vegetable farming and fishing (Lamptey & Ofori-Danson, 2014; Lamptey et al., 2013). A map of the various lagoons is presented in Figures 3 and 4.

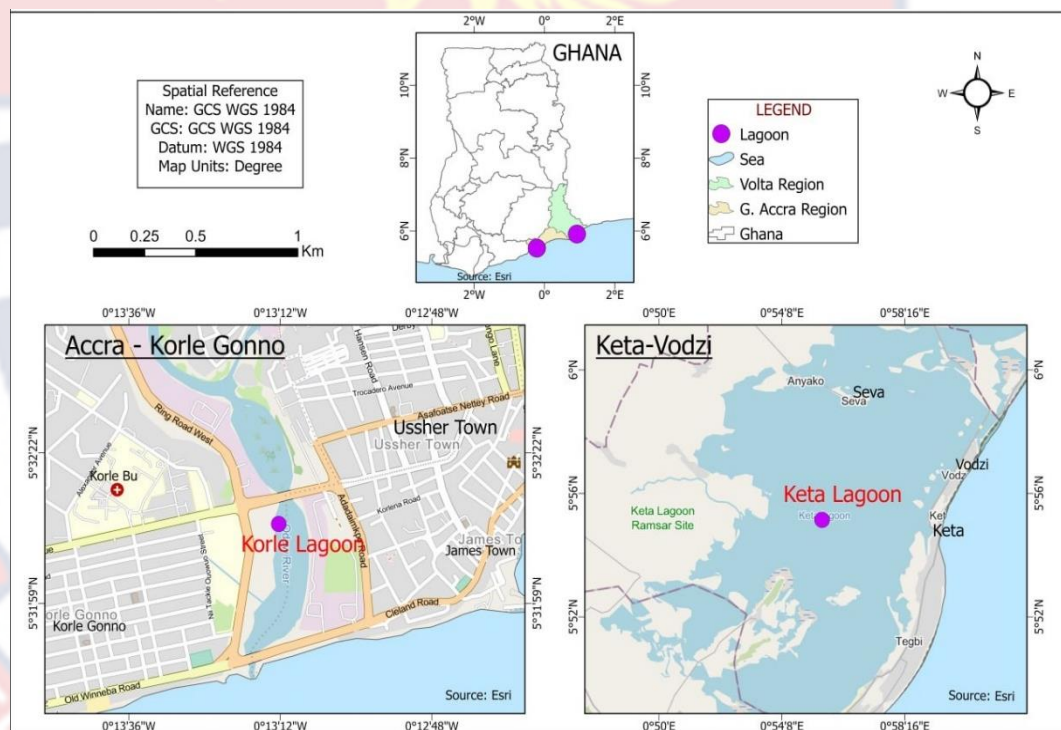


Figure 3: Map of Korle and Keta Lagoons. Source: Author's construction

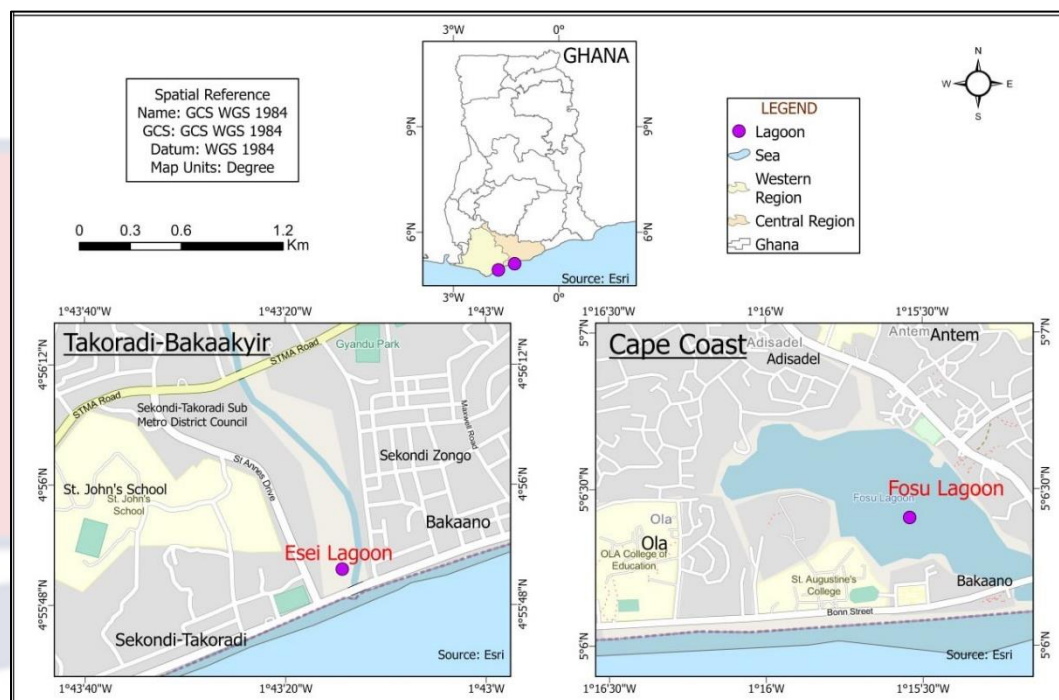


Figure 4: Map of Esei and Fosu Lagoons. Source: Author's construction

Sampling and sample pretreatment

Water samples were taken from Fosu, Keta, Korle and Esei lagoons of the Central, Volta, Greater Accra and Western Regions of Ghana between the month of March and April 2022. Six samples were taken from each site into clean amber glass bottles and were kept on ice while being transported to the lab. Samples were worked on immediately they were brought to the lab.

The water samples were extracted based on USEPA 1694 method. Water samples were acidified with HCl and 0.5 g Na_4EDTA was added to chelate any metal that will interfere with extraction of the PHAs. Solid phase extraction (SPE) cartridges were preconditioned with 10 mL methanol and 6 mL acidified deionized water of pH 2. Cartridges were then loaded with 1.0 L of water samples with the aid of a vacuum manifold at a flow rate of between 8 and 10 mL per min. The

loaded SPE cartridges were washed with 10 mL acidified deionized water of pH 2 and dried under vacuum for 5 min. Three successive elution of analytes were done using 3 mL methanol each and dried under a gentle flow of pure nitrogen gas to near dryness. It was reconstituted with 1 mL methanol and filtered with 0.22 μm syringe filters into 1.5 mL vials before HPLC-UV analysis.

Fixed Bed Column

A borosilicate glass column of length 50 cm and diameter of 3 mm was used for the filtration. The column was held vertically using a clamp stand. About 2 mm of glass wool was placed at the bottom of the column to prevent clogging. About 20 grams of the five selected biochars were carefully packed with the aid of deionized water and glass wool was placed on top to prevent the disturbance of the top layer of the biochar. The adsorbent bed was rinsed with deionized water after the set up to prevent colouration of the effluent due to adsorbent pigmentation (Tejedor et al., 2023). Also, prior to the experiment, deionized water at a flow rate of 3 mL/min was passed the column for 20 min to wet the biochar and to remove trapped air (de Franco et al., 2017). The experiment was performed at room temperature (25 °C). The experiment was done in duplicate. The inherent pH of the PHA solution was used and that of the lagoon water samples were adjusted using an analytical grade HCl to the inherent pH level of the PHA solutions.

The removal efficiency using the column was tested using 20 mg/L of mixed PHA solution at a flow rate of 3 mL/ min and a 1000 mL of the filtrate was collected for analysis to determine its concentration. Real water samples from the

lagoons were passed through the biochar and the effluent was analysed to determine the removal percentage.

HPLC-UV Analysis of Pharmaceuticals

Quality control

Six (6) level external standard calibration curves were created for each of the analyte at concentrations of 0.05, 0.5, 1.0, 2.0, 5.0 and 10 mg/L in acetonitrile except for ERY which was calibrated at concentrations between 1 and 50 mg/L. An initial calibration verification standard (2.5 mg/L) was used to validate the calibration curve. Continuous calibration verification standard (10 mg/L) was also analyzed each day prior to each batch analysis to verify the robustness and accuracy of the instrumental method. System suitability test using US Pharmacopoeia criteria with 10 ppm standards (n=7) were conducted for each batch analysis to ascertain the reliability of the instrumental analysis conditions. A reagent blank (extracted MilliQ deionized water was analysed in replicate at the start of each batch analysis.

Analysis of pharmaceuticals

Following filtration with 0.22 μ m filters, the initial and final concentration of pharmaceuticals were determined using HPLC Shimadzu prominence UFLC 20AD coupled with UV-vis SPD-20 AV detector equipped with auto-sampler and a Phenomenex Luna 3 μ m C18 column (150mm x 4.6mm). The mobile phase consisted of 1 % acetic acid in water at pH 3(A) and 1:1 acetonitrile-methanol (B) mixture at a flow rate of 0.6 mL/min. The column temperature was maintained at 40 °C throughout the analysis. The HPLC gradient solvent elution method was performed: 0-4.1 min 10:90 (A:B v/v); 4.1-23 min 15:85 (A:B v/v); 23-26 min

15:85 (A:B v/v); 26.1- 30 min 10:90 (A:B v/v); and 30-40 min 10:90 (A:B v/v). Sample injection volume was set at 5 μ L and the runtime was 40 min with retention times of 8.11, 8.703, 15.11, 16.41, 19.38, 22.27, 24.14 and 25.66 for ACE, MET, TRI, CAF, CIP, SUL, ASP and ERY respectively. The UV-vis detector was operated in dual wavelengths mode at 275nm (channel 1) and 285nm (channel 2). The flow cell was also kept at 15 °C.

Chapter Summary

This chapter introduced the methodology employed in the study, focusing on biochar production and characterization, the selection of pharmaceuticals, and the experimental procedures for adsorption studies. Biochar was produced from coconut shell, coconut fibre, and rice husk through slow pyrolysis at varying temperatures and residence times. The biochars were then characterized for properties such as pH, electrical conductivity, moisture content, volatile matter, and ash content.

The chapter also outlined the procedures for batch adsorption experiments and kinetic studies to determine the removal efficiency of selected pharmaceuticals. Adsorption isotherms were performed to fit the experimental data to models like Langmuir, Freundlich, and Temkin. The study areas, including Fosu Lagoon, Korle Lagoon, Esei Lagoon, and Keta Lagoon, were discussed, emphasizing their environmental significance and pollution sources.

Finally, the chapter detailed the sampling, sample pretreatment, and HPLC-UV analysis of pharmaceuticals, ensuring quality control and accurate measurement of pharmaceutical concentrations in water samples.

CHAPTER FOUR

RESULTS AND DISCUSSION

Introduction

This chapter deals with some physico-chemical parameters of the biochars produced from rice husk (RH), coconut shell (CS) and coconut fibre (CF), removal efficiencies of pharmaceuticals (PHAs) in both single and multi-component as well as the kinetics, modelling of adsorption data to some isotherms and the thermodynamics of the adsorption. Also, the mechanism of adsorption and application of selected biochars to environmental samples are also discussed.

Biochar Production

Twenty-four different biochars were produced using the slow pyrolysis method which yields char as the major product (Zhang et al., 2017). Eight biochars were produced from rice husk (RH), coconut shell (CS) and coconut fibre (CF) (Bispo et al., 2018; Dhar et al., 2022; Suman & Gautam, 2017) at 500 and 600 °C with residence time of 0, 1, 2 or 3 hours. Biochars were produced at these temperatures because it leads to adsorbent with higher surface area and are more efficient in adsorbing organic contaminants (Zheng et al., 2013) such as pharmaceuticals. Biochar produced were labelled in the format CF5, CF51, CF52, CF53 representing biochar made from coconut fibre, pyrolysed at 500 °C with residence times of 0, 1, 2, and 3 hours respectively.

Physicochemical Properties

Biochar yield

The biochar yield of CF, CS, and RH produced at 500 °C ranged from 34.9978 - 41.2393, 29.9884 - 29.0580 and 37.5536 - 43.1798 % respectively as shown in Figure 3. Lower yields were obtained at 600 °C for all the biochars i.e. RH (36.2039 - 37.3198 %), CS (28.0010 - 28.7453 %) and CF (31.8980 - 28.7453 %). These values were in agreement to the percentage yield obtained by Appazov et al. (2021; Dhar et al. (2022), Fawzy et al. (2021), Hidayat et al. (2023), Scapin et al. 2021, and Wang & Sarkar (2018). Biochar yield of all the biomass reduced with increasing temperature and increasing residence times.

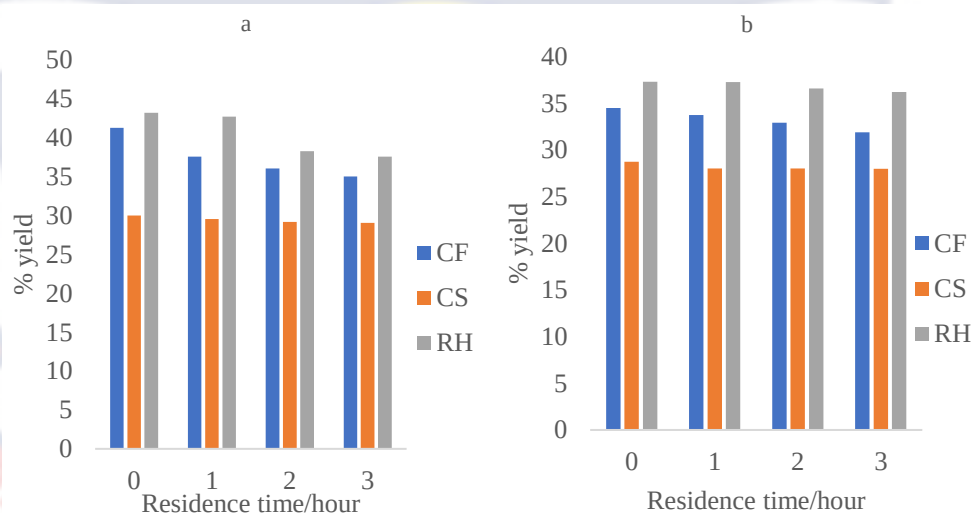


Figure 5: Biochar Yield of RH, CS and CF pyrolyzed at 500 °C (a), 600 °C (b) at different Residence Times

Biochar yield was highest in biochar produced at 500 °C and lowest at 600 °C for all the feedstocks used. Similar results were reported by Dhar, (2020), Guarnieri et al. (2021), Suman & Gautam, 2017, Armynah et al. (2018), Amalina et al., (2022) and Pelleria et al., (2012). Also, the residence time further reduced the

biochar yield as it was increased from 1 to 3 hours. This may be due to the fact that as the residence time increased more organic matter was converted to ash and amorphous form of carbon (Yu et al., 2022). The production of biochar at the selected temperature of 500 and 600 °C, results in the thermal breakdown of hemicellulose at 180-280 °C; cellulose at 240-350 °C, lignin 300-500 °C and formation of carbonaceous compounds above 500 °C (Puga et al., 2022).

According to literature, CF which contains the highest lignin content must have produced the highest yield of biochar but rather the highest yield was from RH biochar (Tan et al., 2021; Wang & Sarkar, 2018). This may be due to the high ash content (Table 4) as a result of the presence of higher levels of potassium and zinc in rice husk (Ahmad et al., 2014). Lower yield observed in CF and CS may be due to degradation of hydroxyl groups and the decomposition of the lignocellulose structures to form aromatic and heteroaromatic compounds as the pyrolysis was done at a higher temperature (Sun et al., 2017b).

The residence time showed slight effect on the percentage yield of the biochar at a particular temperature. The yield reduced slightly as the residence time increased from one hour to three hours (Figure 3). Similar trend was observed in the pyrolysis of 8 different feedstocks with residence time of 0.5 to 8 hours, (Sun et al., 2017a). Generally, residence time has more impact on biochar pyrolyzed at lower temperatures (<500 °C) than higher temperatures (Cao et al., 2018). Residence time at higher temperature conditions is known to impact the efficiency of pyrolysis by causing changes on the biochar surface as well as its internal structure and enlarges porosity (Krasucka et al., 2021).

Proximate analysis

Volatile matter, ashes, and fixed carbon content from the proximate analysis provide basic characteristics of the prepared biochars (Puga et al., 2022).

The moisture content of the biochar reduced with increasing pyrolysis temperature. Biochar made from rice husk contained the lowest moisture content of 5.6 - 6.42 % and coconut fibre, the highest (Table 4). The moisture content of rice husk biochar pyrolyzed at 450 °C was lower than the 16.0 % obtained by Tanko et al. (2020).

The volatile matter (VM) of the biochars decreased with increasing pyrolysis temperature and residence time (Tag et al., 2016; Tomczyk et al., 2020). This agreed with results from Zhao et al. (2017). This was attributed to the cracking of volatile fractions into low-molecular-weight liquids and gases as temperature and residence time increased (Ronsse & Dickinson, 2017). Also, increasing temperature resulted in the dehydration of hydroxyl groups and thermal degradation of cellulose and lignin (Tomczyk et al., 2020). The volatile matter content values ranged from 17.58 - 20.38 %, 18.10 - 22.38 % and 6.08 - 10.35 % for CF, CS, and RH respectively and it affects the stability as well as the sorption capacity of the biochar (Mukherjee et al., 2011; Zimmerman et al., 2010). Biochar with high VM content is said to be highly efficient with partitioning mechanism which involves the diffusion of pharmaceuticals (PHAs) into non-carbonized biomass pores (Puga et al., 2022).

The ash and fixed carbon content (Table 4) increased with increasing in temperature. The Rice husk biochar (RHB) had the highest ash content whiles Coconut Shell biochars (CSBs) contained the least ranging from 1.54 - 3.83 %.

Table 4: Fixed Carbon, Ash, Volatile Matter and Moisture Contents of Biochars produced at Various Residence Times

Pyrolysis Temp (°C)	Residence time (h)	Coconut Fibre				Coconut Shell				Rice Husk			
		Fixed carbon (%)	Ash content (%)	Volatile matter (%)	Moisture content (%)	Fixed carbon (%)	Ash content (%)	Volatile matter (%)	Moisture content (%)	Fixed carbon (%)	Ash content (%)	Volatile matter (%)	Moisture content (%)
500	0	70.5553	9.0690	20.3757	17.6993	76.0854	1.5393	22.3752	6.7287	43.8574	45.7975	10.3451	6.4298
	1	70.1853	9.1133	20.7014	10.9267	76.6335	1.9875	21.3790	6.5346	43.8821	46.4959	9.6220	6.4242
	2	70.4924	9.7861	19.7214	10.1769	77.1348	2.3821	20.4831	6.7573	44.1359	46.7847	9.0794	5.2968
	3	70.5404	10.1449	19.3147	9.0100	77.4648	2.5105	20.0247	6.7428	43.5526	48.3013	8.1461	5.6723
600	0	70.8304	10.3135	18.8561	6.9999	77.4709	3.0503	19.4788	7.4139	44.1287	48.3167	7.5546	5.0377
	1	70.6536	11.3002	18.0462	9.7102	77.5826	3.1727	19.2447	7.1946	43.6424	49.1819	7.1757	5.2997
	2	70.3462	11.3794	18.2744	3.5874	78.0531	3.4364	18.5105	6.3028	43.6974	49.6366	6.6660	5.4543
	3	70.8212	11.5961	17.5827	7.6014	78.0795	3.8199	18.1006	7.1177	43.0912	50.8323	6.0765	5.6269

Source: Laboratory data (2022)

High RH ash content corroborates with work done by Avornyo et al. (2021) where he reported the ash content of 46.55 and 47.82 % for RH biochar pyrolysed at 500 and 700 °C respectively. On the other hand, CS had the highest percentage of fixed carbon with RH having the least set of values. According to Dissanayake et al. (2018), the main component of the high ash content in RH is silica and this was also confirmed by (Islam & Ahiduzzaman, 2016). Increase in ash content is as a result of the deposition of inorganic constituent and organic matter combustion residues which remains in the biochar after pyrolysis (Cao & Harris, 2010; Domingues et al., 2017; Tomczyk et al., 2020; Zhao et al., 2017). Increasing the pyrolysis temperature leads to a higher degree of polymerization (Domingues et al., 2017) resulting in a more condensed carbon structure in the biochar.

pH and conductivity

The pH of the biochars (Table 5) increased with increasing temperature with RH having the least pH. The pH ranged from 9.94 -11.56, 10.82 - 11.48 and 8.95 - 10.73 for CF, CS and RH respectively. All the biochars were alkaline. The high pH values might be due to the loss of acidic functional groups and that may have resulted in the formation of Ca^{2+} , Mg^{2+} , Na^{+} , and K^{+} bearing oxides, hydroxides and carbonate minerals which occur as the temperature increases. Also, pyrolysis at high temperatures causes the release of moisture and volatile matter contents in the feedstock leading to breakage of inter and intra molecular chemical bonds which leads to high ash content resulting in a high pH value (Wang et al., 2013; Weber & Quicker, 2018). High pH biochars produced agreed with work done by Gai et al. (2014), Sun et al. (2017a), Higashikawa et al. (2016) and Wang et al.

(2013). According to Ippolito et al. (2020), non-woody feedstock such rice husk, coconut shell and fibre produce biochar high pH values due to high ash content.

Table 5: pH and Conductivity Values of Biochars produced

Temp/°C	Residence time/hour	Coconut Fibre		Coconut Shell		Rice Husk	
		pH	*Cond (mS)	pH	*Cond (mS)	pH	*Cond (mS)
500.0	0	9.9400	2.0467	10.8167	0.2423	8.9533	0.1585
	1	10.3800	2.0800	10.8867	0.5120	9.0367	0.1679
	2	10.8967	2.1167	10.9300	0.5923	9.2800	0.1690
	3	11.3100	2.1900	11.1067	0.6003	9.6400	0.1989
600	0	11.3500	2.3667	11.2667	0.6343	9.6600	0.2377
	1	11.4833	2.5467	11.2967	0.9373	9.9767	0.2923
	2	11.5433	3.0633	11.3233	1.0637	10.5067	0.2943
	3	11.5567	3.2567	11.4833	1.0797	10.7333	0.4080

*Cond- Conductivity

Source: Laboratory data (2022)

A significant positive correlation (Appendix A) of 0.98, 0.98 and 0.90 was observed between pH and the ash content in RH, CS and CF biochars respectively and this agreed with work done by Tag et al. (2016).

The electrical conductivity (EC) increased as the temperature of pyrolysis was increased for all biochars produced. CF had the highest values ranging 2.05-3.26 mS/cm, followed by CS (0.24 -1.08 mS/cm) and RH (0.15 – 0.41 mS/cm). High pyrolysis temperature mostly produces biochar with high EC values (Wang et al., 2020). However, according to Yargicoglu et al. (2015), EC depends more on the feedstock type rather than the temperature of pyrolysis. This is because the EC is a function of the ash content and elemental composition of the biochar which is significantly determined by the type of feedstock. Varying EC values (Table 5) obtained in this study might be due to the different biomass used as they were all

pyrolyzed under the same condition. The EC indicates the soluble salt content of the biochar. Correlation analysis (Appendix A) showed that there was a significant relationship between the ash content and the EC of all the biochars produced which was in agreement with work done by Reyhanitabar et al. (2020).

Scanning electron microscopy (SEM)

The images from the SEM which show the morphology of the pyrolyzed materials indicated the development of pores in the biochar (Figure 6). For the coconut fibre biochars, their surfaces were rough with tiny heterogenous and longitudinal pores. The CF61 appeared to have thicker walls with less degradation than the CF53 biochar. Also, more fragmentations with more complex pore structure are observed in the CF53 biochar than the CF61, indicating the effect of the holding time of 3 hours on the physical structure of the biochar.

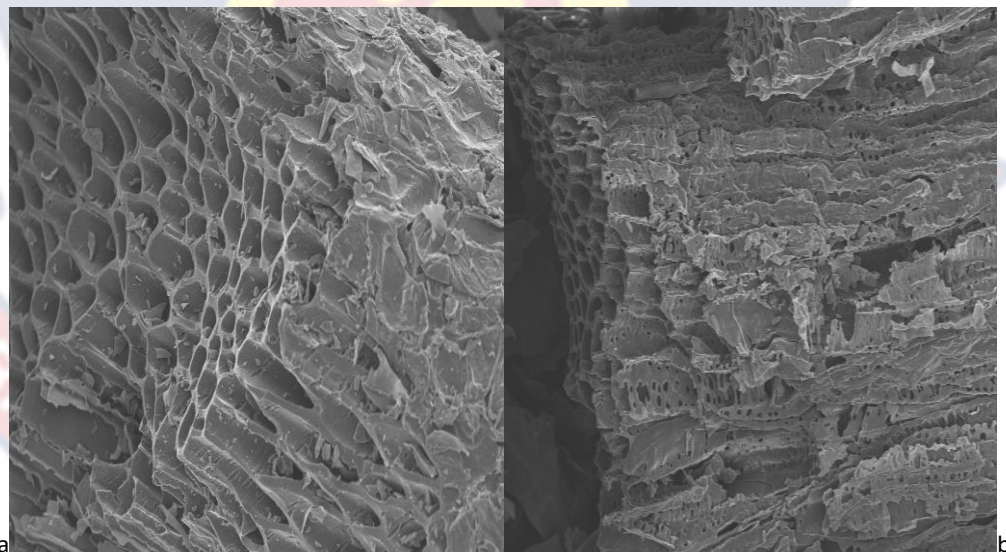


Figure 6: SEM Images of CF61(a) and CF53(b) at 500X magnification

The rice husk biochars (Figures 7-9) showed the surface is conspicuously ridged and punctuated with conical-like protrusions which is in agreement to

previous reports (Abrishamkesh et al., 2015; Hagos et al., 2022; Hariz et al., 2015; Prakongkep et al., 2013). Pores formed were irregular and variably shaped. The pores were in the micro-meter range. The SEM images clearly showed the development of numerous honey comb-like pores in all the biochars.

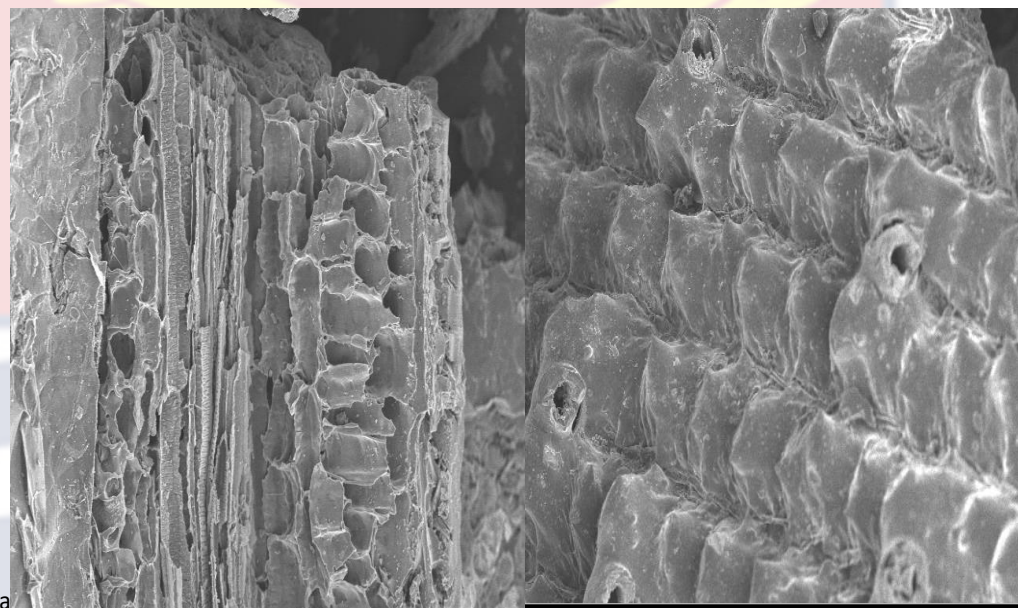


Figure 7: SEM images showing Pore Distribution and Surface Structure of RH53 Biochar

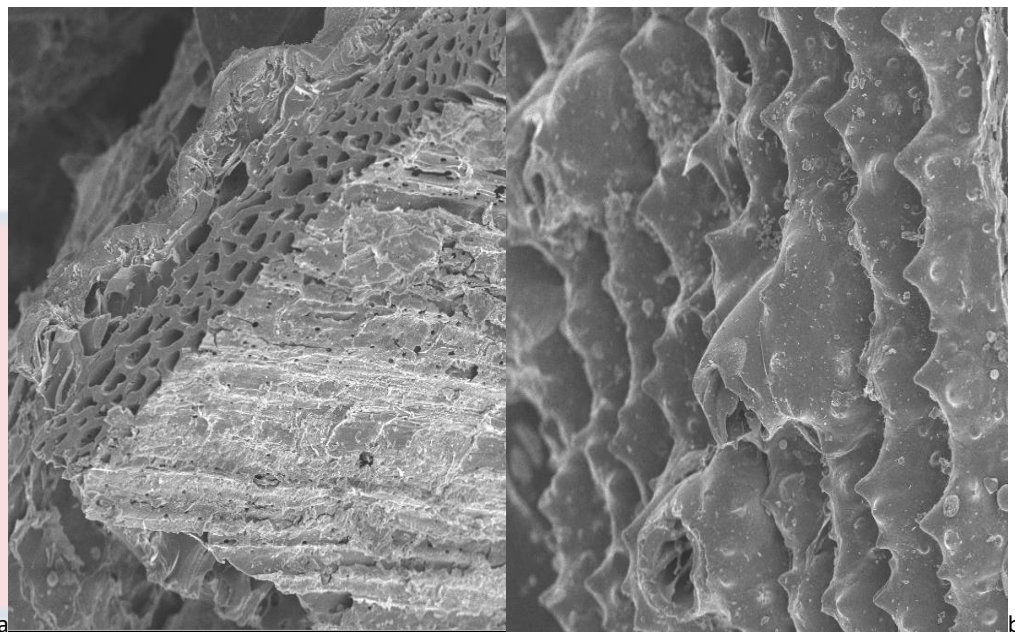


Figure 8: SEM Images showing Pore distribution (a) and Surface structure (b) of RH61 Biochar

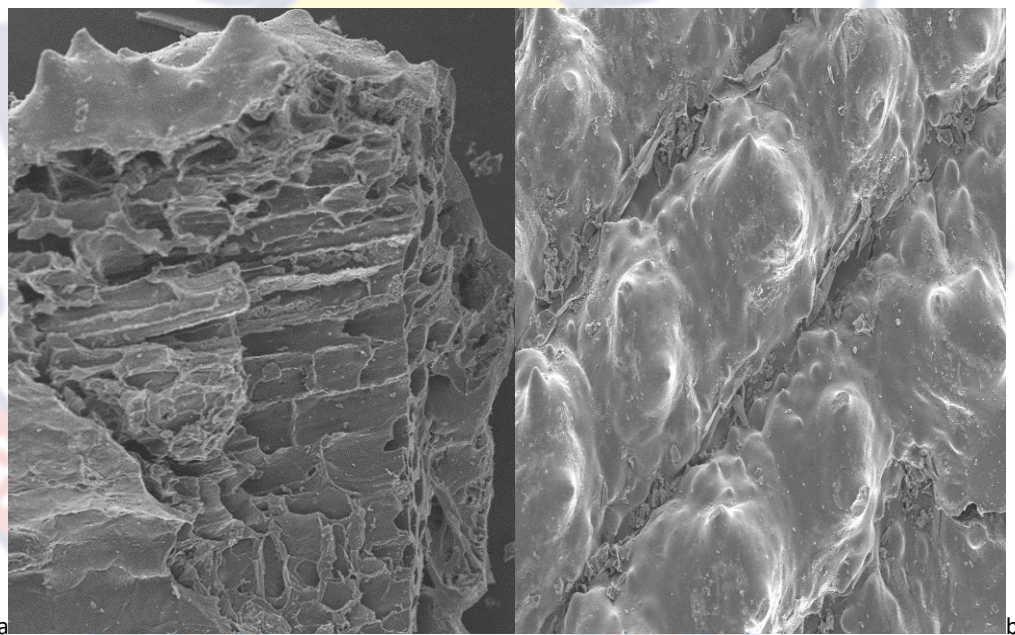


Figure 9: SEM Images showing Pore distribution (a) and Surface Structure (b) of RH63 Biochar

Single-Component Adsorption

The removal efficiency of the pharmaceuticals (PHAs) by the biochars are discussed in this section. The adsorption of eight PHAs was tested using eight different biochars produced from RH, CF and CS. Labels such as RH5, RH51, RH52 and RH53 were used to indicate RH biochar produced at 500 °C with residence times of 1, 2 and 3 hours, respectively. For testing, 0.5 g of biochar, 50mL of 10 mg/L of each pharmaceutical solution was used at room temperature (25 °C). The solutions were magnetically stirred at 50 rpm for 24 hours with their inherent pH monitored.

Removal efficiency of pharmaceuticals

Metronidazole (MET)

Over 70 % removal of Metronidazole was noted within the first hour of stirring, which is likely due to the number of available adsorption sites filling rapidly. After 60 min, however, a slower rate was observed for most of the biochar. The maximum MET removal of 100 % for coconut fibre biochars (CFBs) (Figure 10) occurred at 1440 min for CF61, CF62, CF63, and CF6.

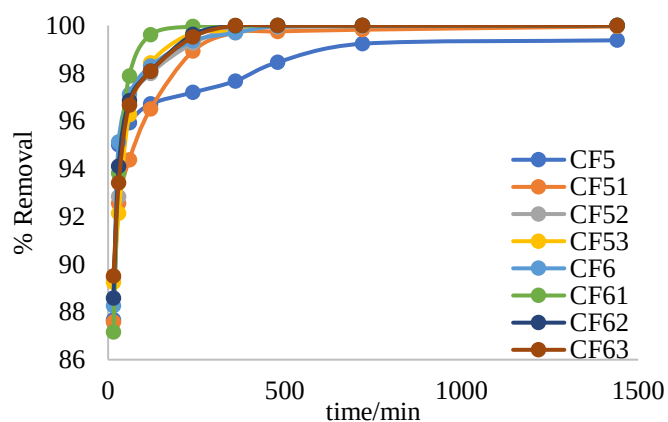


Figure 10: Percentage Removal of MET using CFBs

Additionally, higher pyrolysis temperatures and longer residence times resulted in greater MET removal. For example, CF53 which is pyrolyzed at 500 °C with residence time of 180 min gave a better removal rate than CF5 with no residence time. Also, CF63 which was pyrolyzed at 600 °C and with residence time of 180 min was the best biochar in removing MET among the CFBs with maximum adsorption of 100 % at 480 min. The CFBs were effective in the removal of MET with removal efficiencies increasing with increased residence time, pyrolysis temperature and contact time.

The coconut shell biochars (CSBs) and rice husk biochars (RHBs) performed remarkably well in the removal of MET in the single-component adsorption. A 100 % removal was achieved at 1440 min for all the CSBs (i. e. CS5, CS51, CS52, CS53, CS6, CS61, CS62, and CS63) and RHBs as shown in Figure 11.

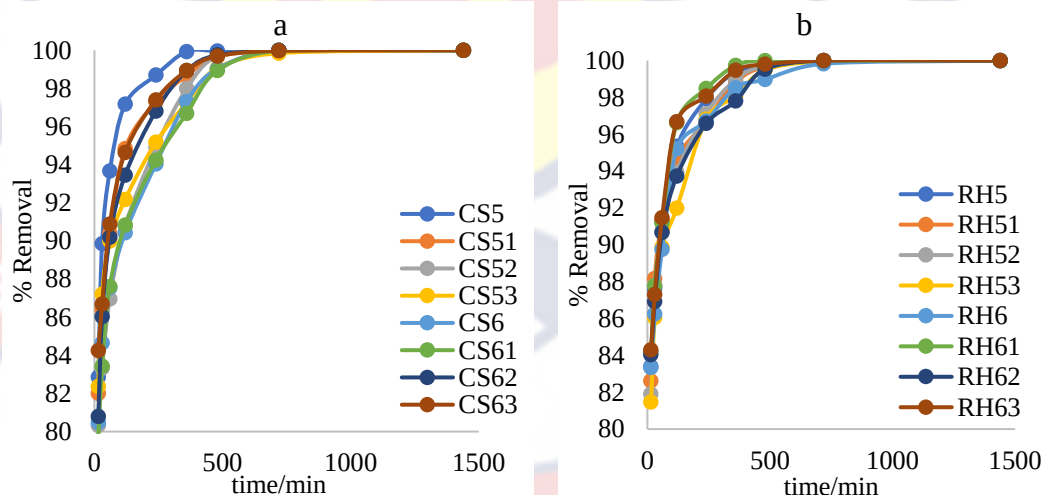


Figure 11: Percentage Removal of MET using CSBs (a) and RHBs (b)

Unlike CFBs, the removal efficiency of MET by RHBs and CSBs showed no consistent trend/relationship with the pyrolysis temperature and residence times.

The adsorption capacity ranged from 0.8757 to 1 mg/g at 1440 min of adsorption. 0.7973 to 1 mg/g and 0.8146 to 1 mg/g for CFBs, CSBs and RHBs respectively. Removal of MET using RH biochar Abbas & Abbas, (2021) and Azarpira & Balarak, (2016) produced similar efficiencies.

Trimethoprim (TRI)

The removal of trimethoprim (TRI) was observed to be quite high with 100% removal at 720 min of stirring for all the CFBs and CSBs (Figure 12) except for CF63 (99.88 %) and CS51 (94.41 %). The most effective biochars for TRI removal were CF61 and CS51 which achieved 100% at 60 min. The RHBs on the other hand, had 100 % removal from some biochars (Figure 13). The adsorption capacity ranged from 0.9675 to 1mg/g for the biochars at 1440 min of adsorption.

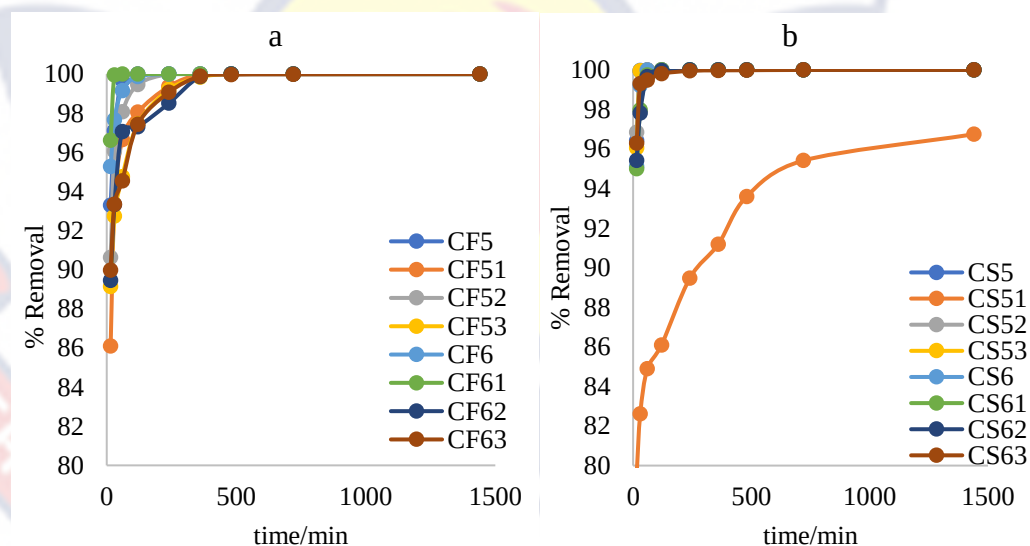


Figure 12: Percentage Removal of TRI using CFBs (a) and CSBs (b)

Similar efficiencies were obtained by Adesokan et al., (2021); Jodeh et al., (2022; Mohammadzadeh & Leiviskä, (2023) when carbonized wood waste, modified silica with pyrazole-3-carbaldehyde, iron-modified peat and magnetite-pine bark respectively were used for the removal of TRI.

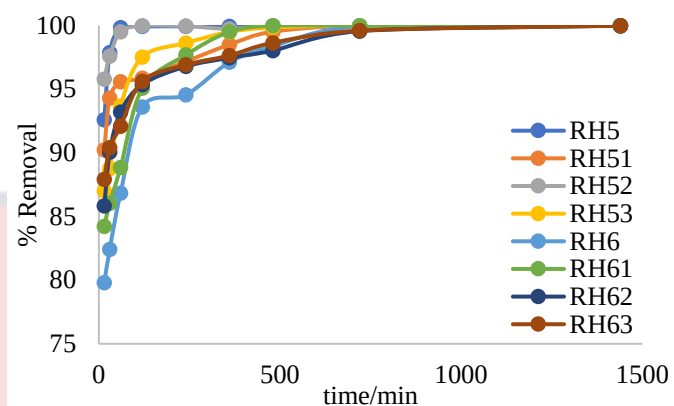


Figure 13: Percentage Removal of TRI using RHBs.

Higher adsorption capacities were however obtained by Jodeh et al., (2022) and Mohammadzadeh & Leiviskä, (2023) than those in this study as biochars were modified thereby increasing their surface area. No particular trend was observed in the percentage efficiency and adsorption capacity of TRI.

Caffeine (CAF)

High removal efficiency was achieved for (CAF) as well; however, 100 % removal was observed in only CF61, RH61 and RH63 at 1440 min of adsorption as shown in Figures 14 and 15. For the CFBs (Figure 14), biochars with higher residence times (CF52, CF53, CF62, and CF63) tend to have higher CAF removal percentages than those produced at lower residence time (CF5, CF51, CF6, and CF61) at a given pyrolysis temperature. Similar trend was observed in the CSBs as well, however biochars pyrolyzed at 500 °C (CS5, CS51, CS52, CS53) had higher percentage removal compared to those pyrolyzed at 600 °C (CS6, CS61, CS62, CS63).

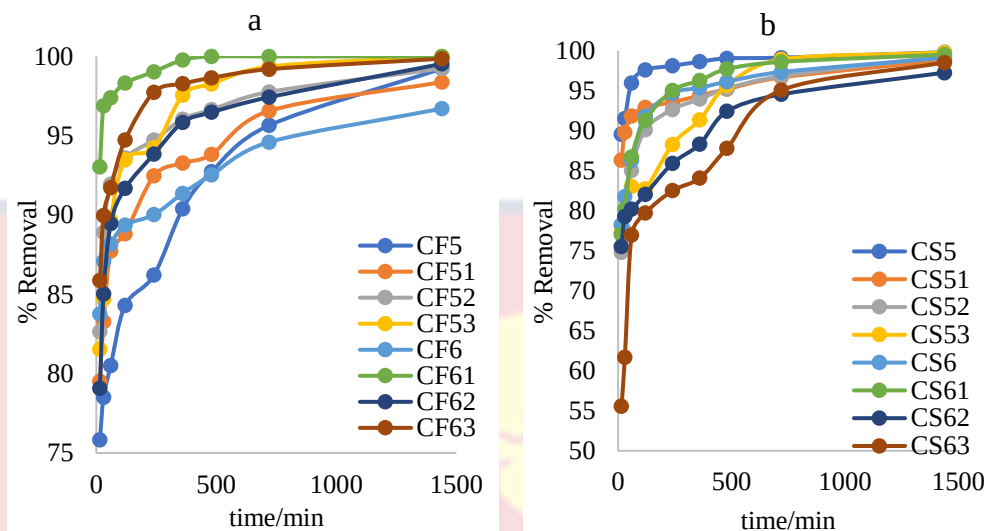


Figure 14: Percentage Removal of CAF by CFBs (a) and CSBs (b)

Rice husk biochars (RHBs) produced at 500 °C (RH5, RH51, RH52, RH53) were observed to have higher removal to efficiency than those produced at 600 °C (RH6, RH61, RH62, RH63) with the exception of RH61 and RH63, which had higher rates. CAF removal efficiencies of 95.5, 90.5, 93.6, 89.2 and 54.8 % were achieved when orange peel, banana peel, orange peel composite, banana peel composite, and magnetite biochar respectively were used (Almeida-naranjo et al., 2021) as well as activated RH which yielded 96.70 % removal (Bahrami et al., 2023). The adsorption capacity ranged from 0.5557 at 15 min to 1 mg/g at 1440 min.

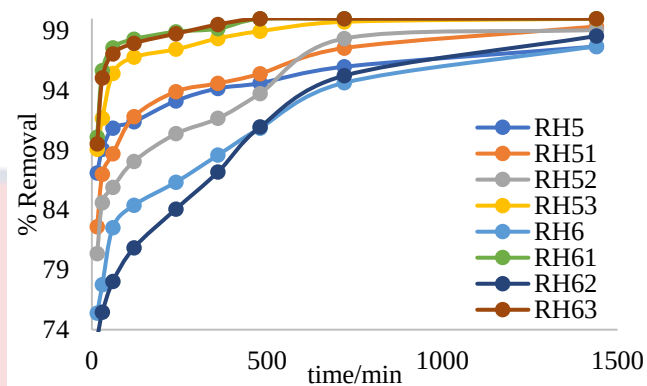


Figure 15: Percentage Removal of CAF using RHBs

Aspirin (ASP)

Coconut fibre biochars (CFBs) pyrolyzed at 600 °C generally show higher percentage removal compared to those pyrolyzed at 500 °C as shown in Figure 16. The residence time had a positive impact on the percentage removal of ASP, with biochars held for longer times generally showing better removal rates. RHBs also exhibited the highest removal efficiencies, reaching 100 % at 120 min and maintaining this level throughout the remaining contact times (Figure 16). Aspirin removal occurred at one of the fastest rates with 100 % removal achieved in CF52, CF53, CF61, CF62 and CF63 as well as for some CSBs (CS51, CS63) in Figure 17 and RHBs (RH51, RH53, RH61 and RH63) at 120 min of stirring. The removal efficiencies were similar to those of Wong et al. (2018) who used spent tea leaves biochar to remove aspirin from water. 94.28 % removal was achieved after 60 min of reaction. The adsorption capacity was low at the beginning but increased with the time of adsorption in all the biochars used.

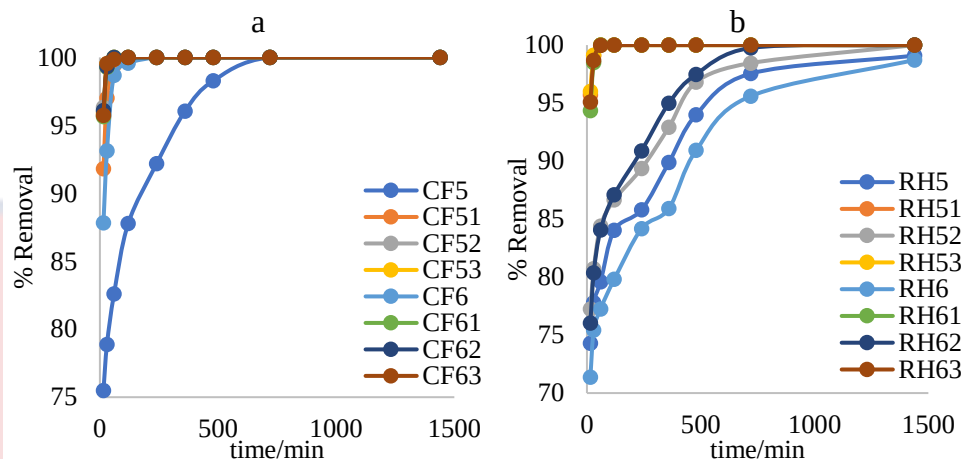


Figure 16: Percentage Removal of ASP using CFBs (a) and RHBs (b)

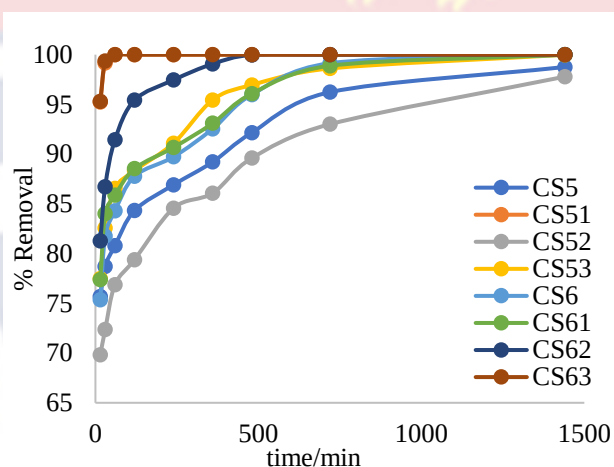


Figure 17: Percentage Removal of ASP using CSBs

Erythromycin (ERY)

With regard to ERY, removal was not rapid as was observed in the removal of other PHAs. Percentage removal ranged from 49.7421 % in 15 to 100 % in 1440 min of stirring for CFBs (Figure 18). 100 % removal was only observed in CF53 and CF61 after 12 hours of stirring. Over 70 % removal occurred in CSBs and RHBs (Figure 19) at 15 min of stirring. 100 % removal was achieved in RH51 and RH62 after 1440 min of stirring whiles RH61 and RH63 after 720 min. It can be concluded that the best biochars for ERY removal are CF61 (coconut fibre biochar

pyrolyzed at 600 °C and held for one hour), RH61 (rice husk biochar pyrolyzed at 600 °C and held for one hour), and RH63 (rice husk biochar pyrolyzed at 600 °C and held for three hours), as they all achieve a 100 % ERY removal rate at 1440 min. The adsorption capacity ranged from 0.4974 - 1 mg/g in CFBs, 0.7015 - 0.9963 mg/g for CSBs and 0.7096 - 1 mg/g. 90 to 100 % removal efficiency was obtained when biochar made from biosolid, cattle manure and ground spent coffee were used for the removal of ERY within 360 min of adsorption (Stylianou et al., 2021).

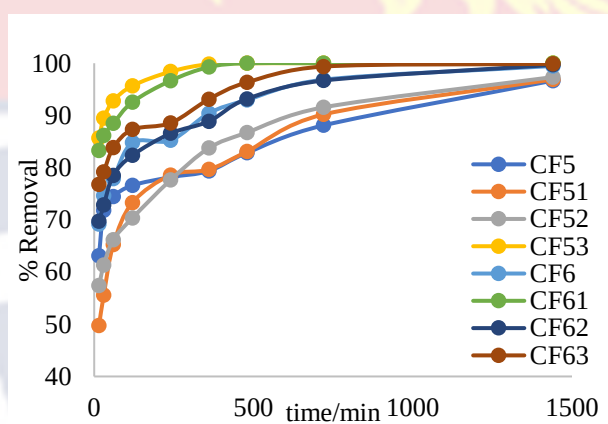


Figure 18: Percentage Removal of ERY using CFBs

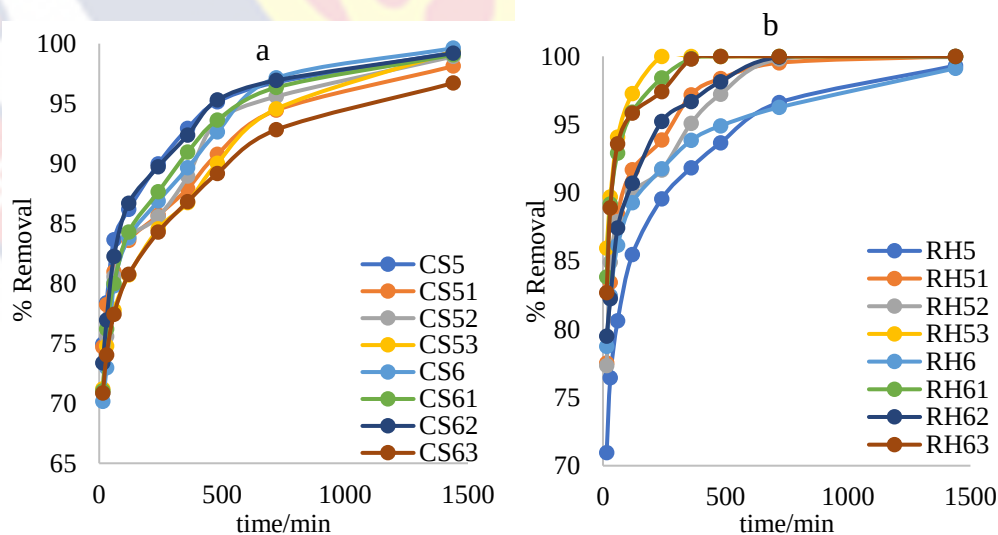


Figure 19: Percentage Removal of ERY using CSBs (a) and RHBs (b)

Sulfamethoxazole (SUL)

Removal efficiency for SUL was high with 100 % removal occurring in few biochars; CF51 at 1440 min, RH53, RH61, RH63 and CF61 in 720 min and CF52 being the best biochar with 100 % removal occurring at 360 min. The removal percentages of CFBs, CSBs and RHBs are shown in Figures 20 and 21 respectively. SUL has been removed using biochar made from orange peel (Ai et al., 2020), wood (Shimabuku et al., 2016), pine sawdust (Reguyal et al., 2017), bamboo, Brazilian pepper wood, sugarcane bagasse, and hickory wood (Yang et al., 2012).

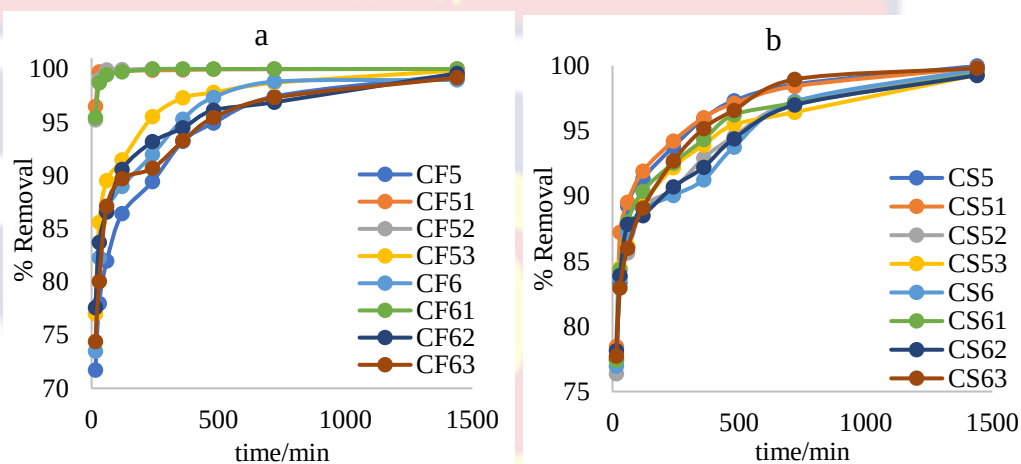


Figure 20: Percentage Removal of SUL using CFBs (a) and CSBs (b)

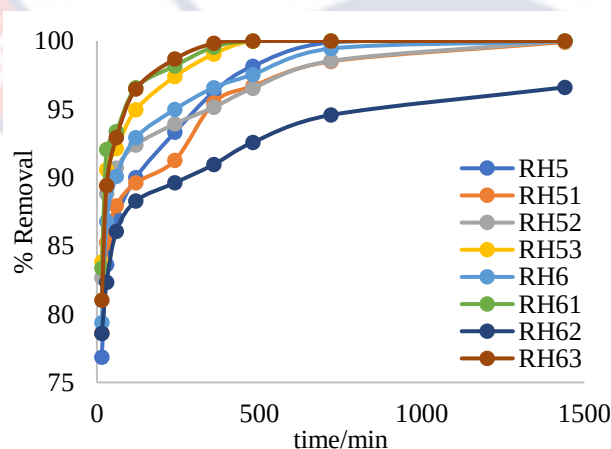


Figure 21: Percentage Removal of SUL using RHBs

Acetaminophen (ACE)

ACE adsorption by the biochars was one of the best removal processes, there was over 90 % removal within the first 15 min of adsorption. About 100 % removal was achieved by most of the biochars (Figures 22 & 23). Similar results was achieved when CS pyrolyzed at a temperature between 400-500°C produced 94 % removal in 1440 min (Solanki & Boyer, 2017),

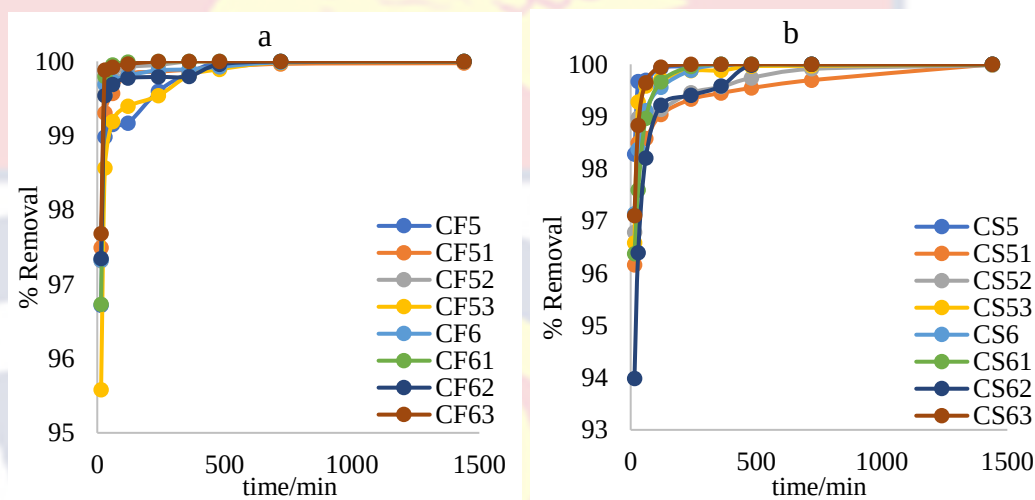


Figure 22: Percentage Removal of ACE using CFBs (a) and CSBs (b)

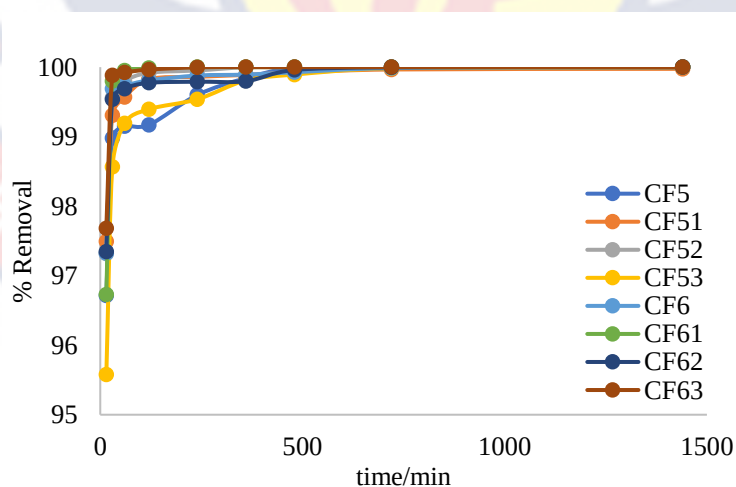


Figure 23: Percentage Removal of ACE using RHBs

About 95 % efficiency was attained when ozone-treated multi-walled carbon nanotubes were used for the removal of 10 mg/L of ACE (Yanyan et al., 2018). Also 52 % removal within 5 min by commercial activated carbon (Nguyen et al., 2020) and 99.88 % removal using Ca(II)-doped chitosan/ β -cyclodextrin (Rahman & Nasir, 2020).

Ciprofloxacin (CIP)

The removal efficiency of CIP generally increased with time for all types of biochar. However, the differences in efficiency between biochars made from CF, CS and RH are more apparent. CFBs (Figure 24) showed the highest removal efficiency, with most samples achieving close to or over 99 % removal within the first hour, and nearly all samples reaching 100 % removal by 240 min. RHBs (Figure 24) also performed well, with most samples achieving over 99 % removal by 120 min (Arun & Maharathi, 2019). CSBs (Figure 25) appears to be the least effective of the three, although it still achieved over 99 % removal in some cases.

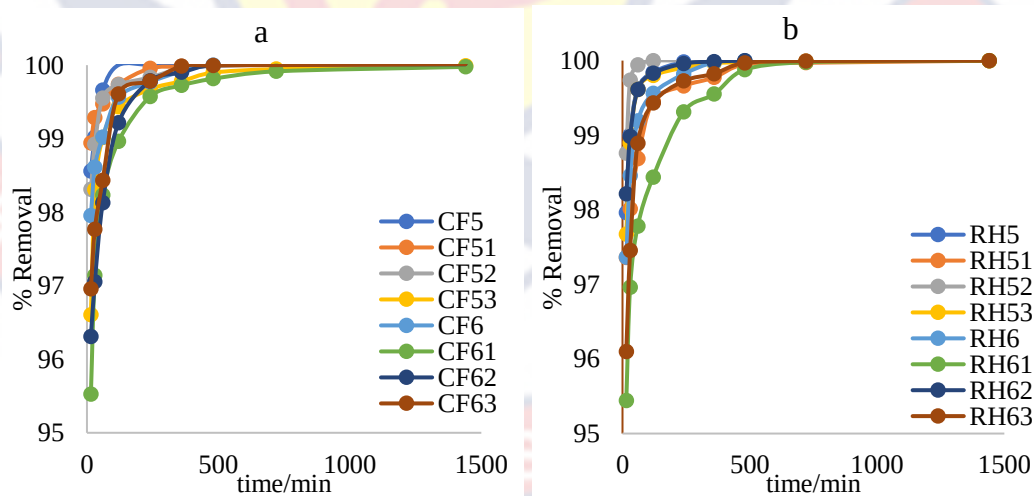


Figure 24: Percentage Removal of CIP using CFBs (a) and RHBs (b)

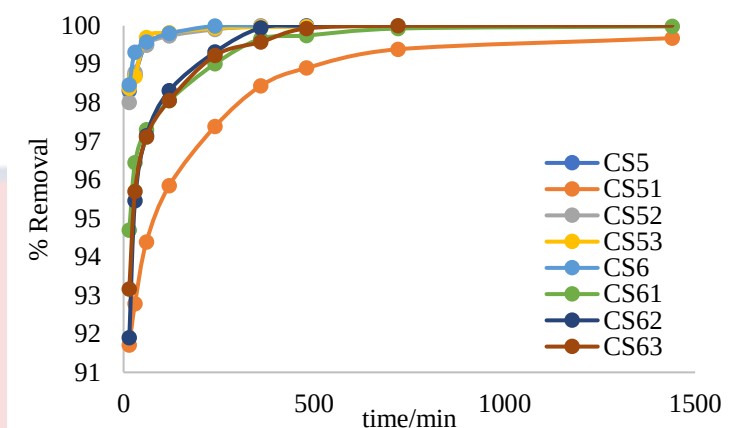


Figure 25: Percentage Removal of CIP using CSBs

Adsorption capacity

The mean adsorption capacity ranged from 0.82 mg/g to approximately 1 mg/g (Appendix B). The adsorption capacity increased with increasing contact time for all biochars. Also, to some extent, the adsorption capacity increased in biochars with high residence time than those with less or no residence time.

The overall performance of the biochars in removing the pharmaceuticals (PHAs) ranged between 89 and 98 % with its corresponding adsorption capacity of 0.89 to 0.98 mg/g (Appendix B)

Effect of Temperature and Residence Time on Removal Efficiency

The pyrolysis temperature showed some effect on the adsorption performance of some of the biochars used. An increase in the removal efficiency was observed for CF biochars produced at 600 °C than at 500 °C within few hours of adsorption. For example, in the adsorption of TRI, CAF, ERY, ASP there was an increase from 93 to 95 %, 63 to 69 %, 75 to 83 %, 75 to 88 % respectively within the first 15 min with complete adsorption at the end of 24 hours (Figures 12, 14, 18 & 16). However slight reduction was observed for biochars produced from CS and

RH. Increase in pyrolysis temperature from 500 to 600 °C did not have much effect on the total adsorption of the PHAs even though it promoted the development of more porous structure.

Residence time significantly affected the removal efficiency and adsorption capacity of all the PHAs within the initial hours of adsorption. Removal efficiency increased with increasing residence time. Biochars pyrolyzed at residence time of 180 min had higher removal efficiencies than those pyrolyzed at 60 min or no residence time. For example, removal increased from 80 to 82 % in the removal of CAF using CF5 biochar, 87 to 89 % for MET using CF6, 84 to 87 % for TRI using RH6 as residence time increased from 60 min to 180 min. Similar trends were observed for other PHAs using other biochars. This increment in adsorption may be due to the formation of well-defined pores in biochar produced at longer residence time and this is consistent with results reported by Sun et al, (2017).

Competitive Adsorption

The results for the simultaneous removal of the eight PHAs showed different removal efficiencies by the biochars.

Acetaminophen (ACE)

All the 24 biochars produced performed very well in the removal of ACE in the competitive mode. Percentage removal ranged from 94 to 99 % (Figures 26-27) for all the biochars with adsorption capacity of 0.945 to 0.999 mg/g. CS62 completely remove ACE after 24 hours.

Comparing both single and competitive adsorption, it showed that the removal of ACE was not affected by the presence of the other PHAs. The best

biochar for the removal of ACE is CS62 which obtained a 100 % removal in both single and competitive adsorption. Biochars from CF and RH also demonstrated high removal efficiencies.

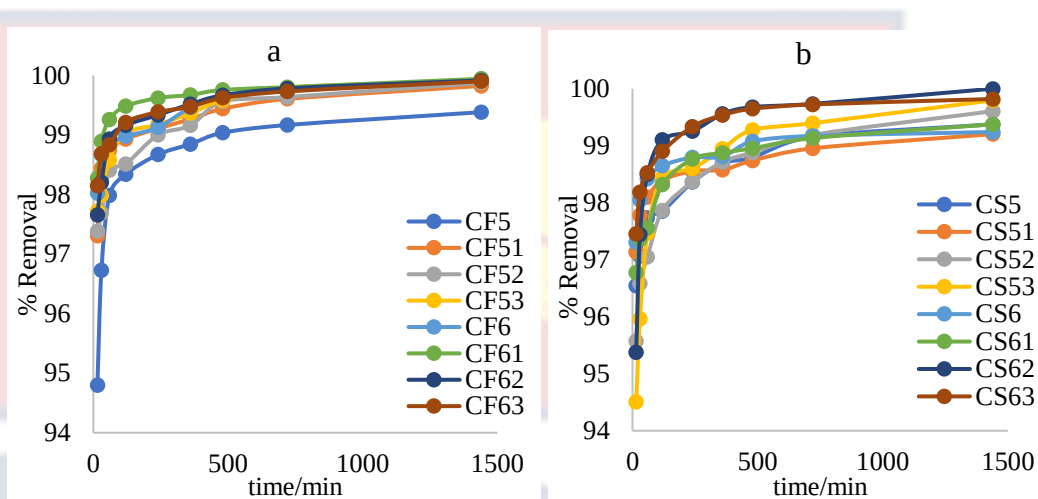


Figure 26: Percentage Removal of ACE using CFBs (a) and CSBs (b)

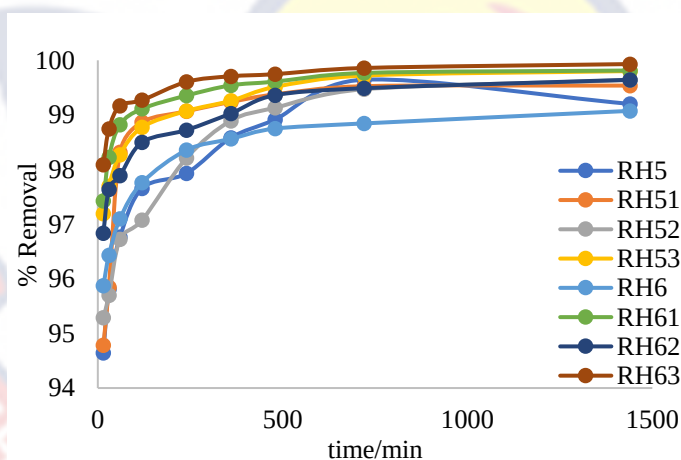


Figure 27: Percentage Removal of ACE using RHBs

Erythromycin (ERY)

A removal percentage of 40 - 99 %, 55 - 84 % and 61- 96 % for ERY were attained in CF, CS and RH biochars respectively. CF53 and CF61 obtained the highest removal efficiency with CF52 with the least percentage of 68 % in 24 hours. CS63 was the highest among the CS biochars with the least removal observed in

CS5 with 74 % in 24 hours. With the RH biochars, the highest removal was observed in RH63 even though the rest also had above 90 % in 24 hours. Figures 28-29 display the removal pattern of the biochars in removing ERY. Adsorption capacities ranged from 0.4 to 1 mg/g. Removal efficiencies reduced in the competitive adsorption and this may be due to the bulky nature of the compound.

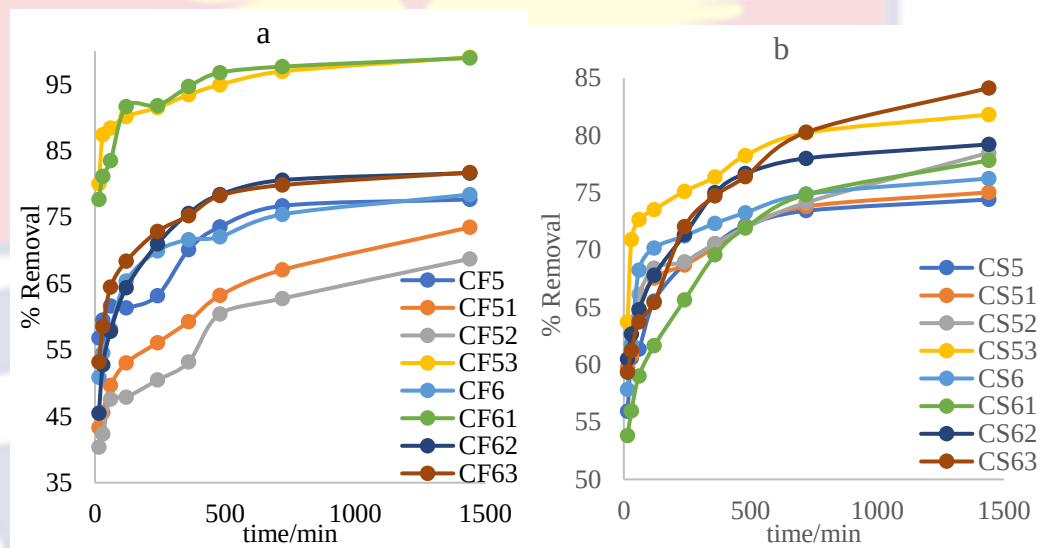


Figure 28: Percentage Removal of ERY using CFBs (a) and CSBs (b)

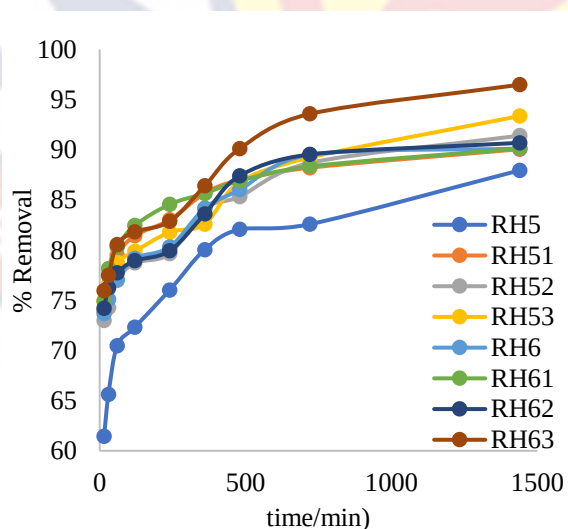


Figure 29: Percentage Removal of ERY in Multi-component using RHBs

Aspirin (ASP)

All the biochars performed well in the adsorption of ASP. The percentage removal ranged from 49 % within 15 min of stirring to 99 % within 24 hours. Most of the biochars removed more than 80 % of ASP after 24 hours of stirring with CF52, CF53, CF6, CF61, CF62, RH51, RH53, RH61 and RH63 attaining 99 % removal within 24 hours. Figures 30 and 31 show the removal efficiency of biochars in the adsorption of ASP. The adsorption capacity was between 0.49 and 0.99 mg/g after 24 hours.

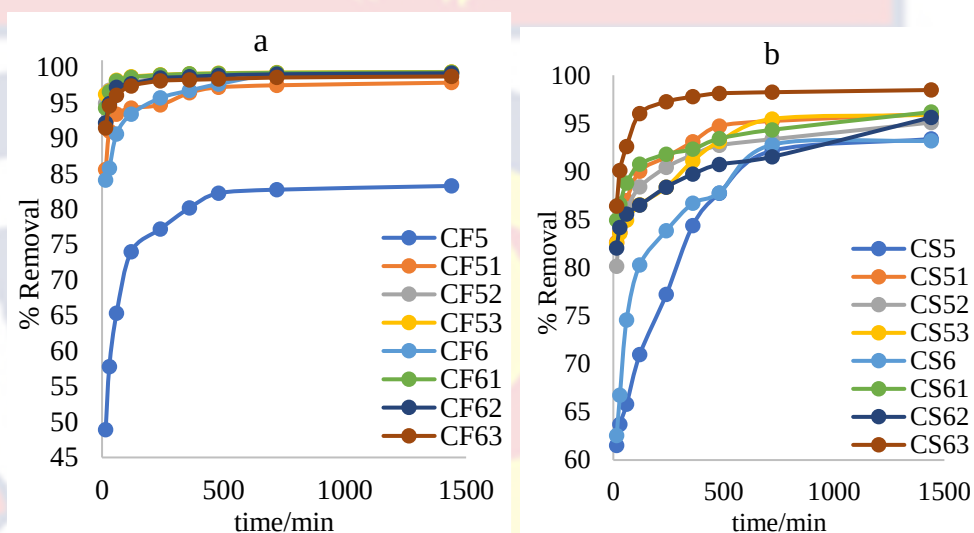


Figure 30: Percentage Removal of ASP using CFBs (a) and CSBs (b)

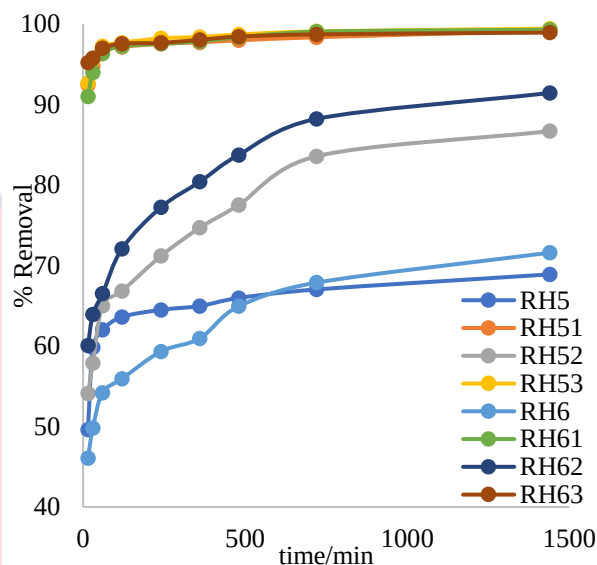


Figure 31: Percentage Removal of ASP using RHBs

Sulfamethoxazole (SUL)

Above 79 % removal was achieved by all biochars within 24 hours of stirring with RH63, RH61, RH53, RH51, CS62, CF51 and CF52 attaining between 93 and 96 % (Figures 32a and 33). The highest efficiency was achieved by RH63 with 96.49 %.

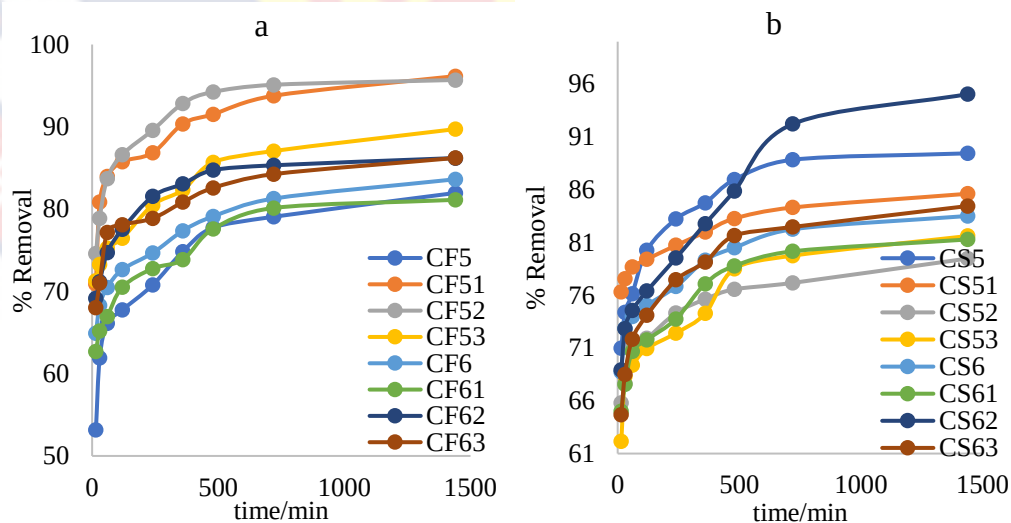


Figure 32: Percentage Removal of SUL using CFBs (a) and CSBs (b)

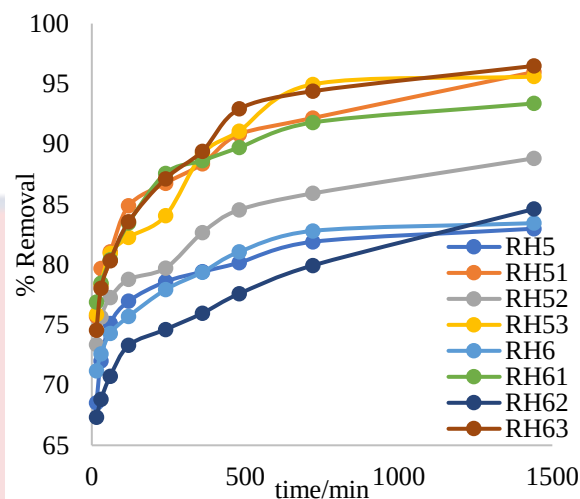


Figure 33: Percentage Removal of SUL using RHBs

Caffeine (CAF)

The percentage removal for CF biochars ranged from 63 % within 15 min of stirring to 95 % in 24 hours with CF52, CF53, CF61 and CF62 attaining above 90 % removal of CAF in 24 hours (Figure 34). CF61 had the highest removal of 95 % as well the highest adsorption capacity of 0.95 mg/g among the CF biochars. The percentage removal ranged from 78 - 83 % within 24 hours among the CS biochars with CS63 being the biochar with the highest amongst them (Figure 34). The RH biochars on the other hand, showed the highest removal in 24 hours (Figure 35). All except RH5 and RH6 had over 90 % removal of CAF with RH63 obtaining almost a 100 % with adsorption capacity of 0.995 mg/g.

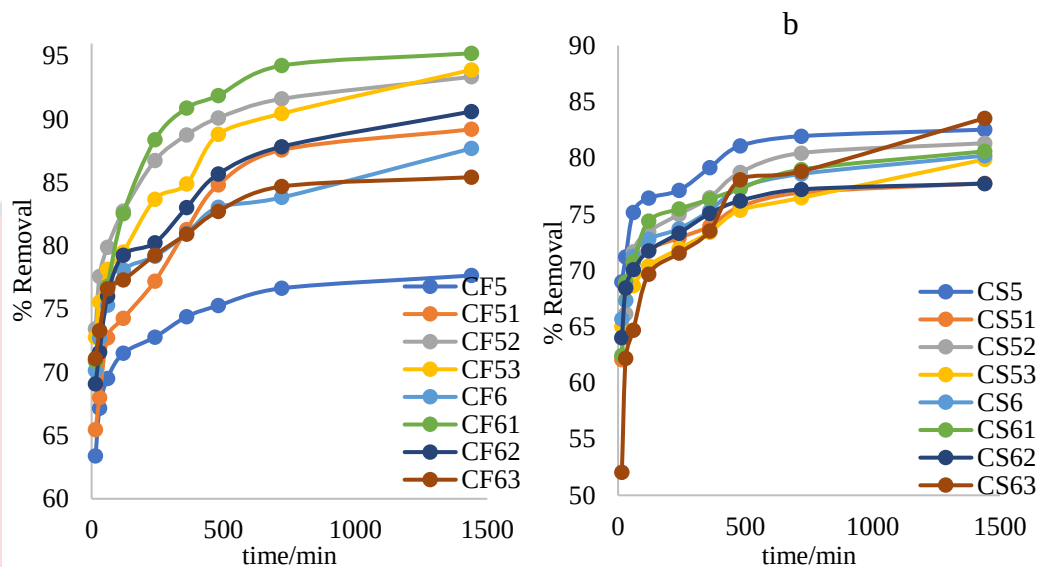


Figure 34: Percentage Removal of CAF using CFBs (a) and CSBs (b)

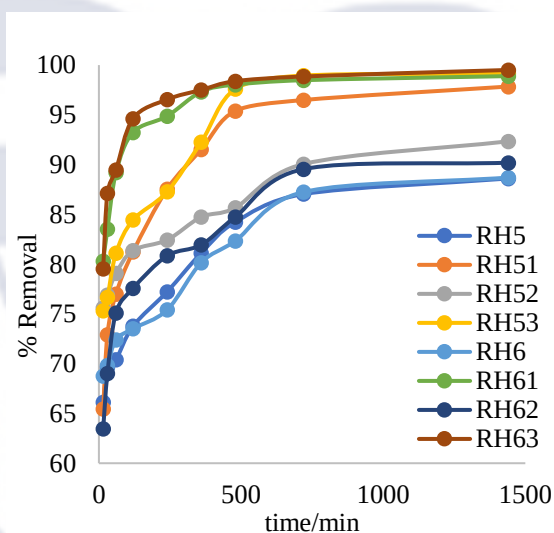


Figure 35: Percentage Removal of CAF using RHBs

Trimethoprim (TRI)

The removal rate for TRI was very high within the first 15 min of adsorption with percentage removal as high as 92 %, in CF6, 97 % in CS53, and 98 % in CS62. The rest ranged from 72 to 88 %. Removal reduced drastically despite the high initial rate of removal resulting in 100% removal only in CF6, CF62, CS53 and CS52 with the rest of the biochars attaining 92 to 99 % in 24 hours as shown in

Figures 36 and 37. In a work done by Nielsen and Bandosz, (2016), competitive adsorption of TRI was highly favoured in basic pH which agrees with the adsorption of TRI in this study. The adsorption capacities of the biochars were between 0.92 and 1 mg/g in 24 hours.

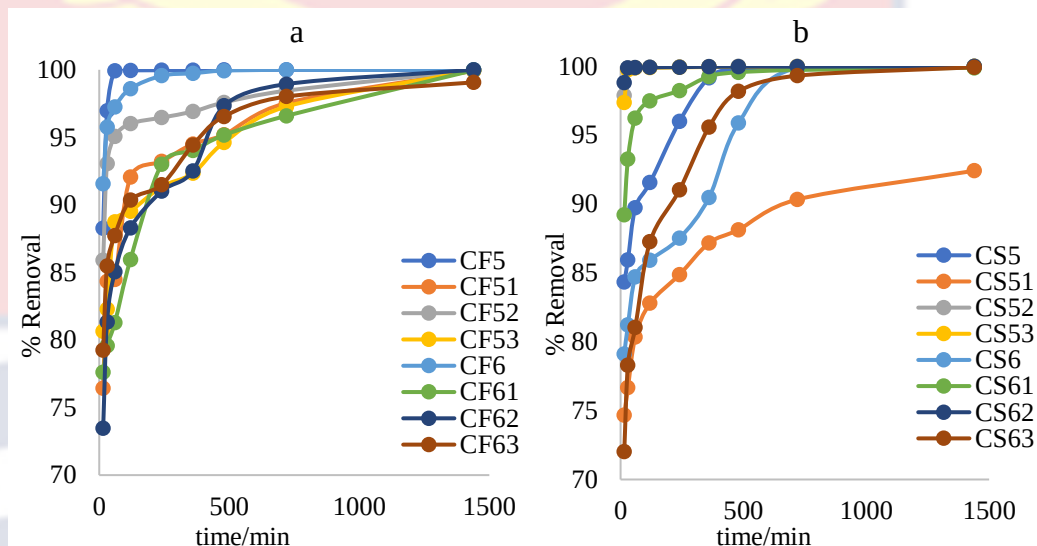


Figure 36: Percentage Removal of TRI using CFBs (a) and CSBs (b)

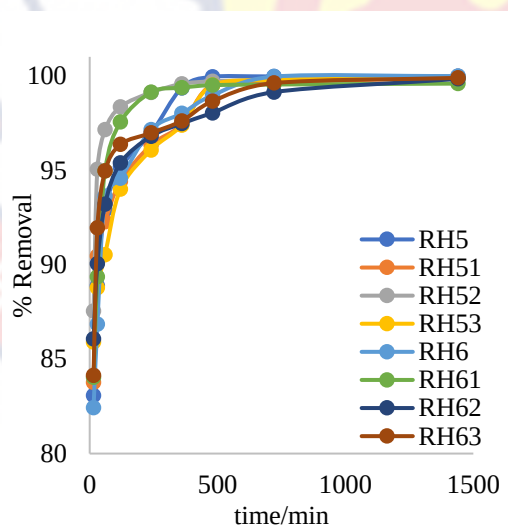


Figure 37: Percentage Removal of TRI using RHBs

Metronidazole (MET)

MET removal by the biochars ranged between 96 and 99 % within the first 15 min of adsorption and to 99 % in 24 hours for all biochars (Figure 38-39), however no biochar attained a 100 % removal. Removal efficiencies reduced comparing the single component adsorption and the competitive adsorption. MET was successively removed with efficiency of 96.4 % and adsorption capacity of 4.79 mg/g by the rice husk biochar modified with H_2SO_4 at 90 min of stirring (Azarpira & Balarak, 2016).

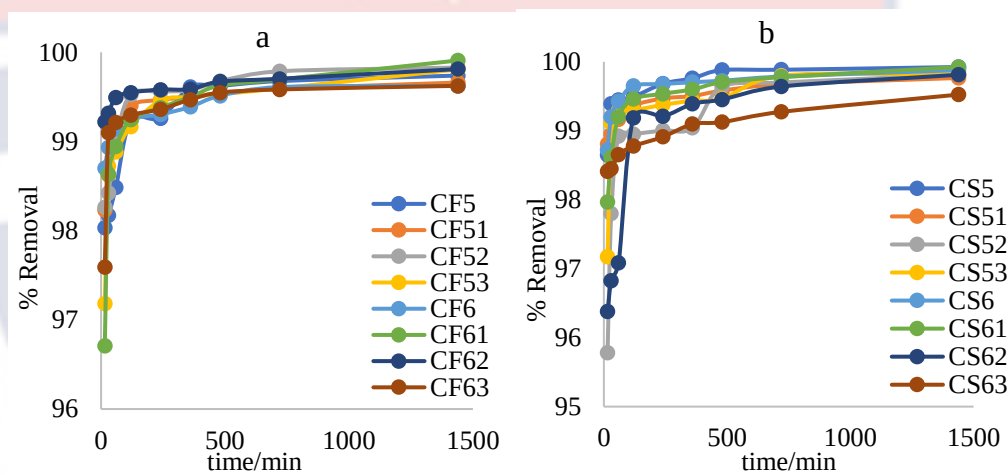


Figure 38: Percentage Removal of MET using CFBs (a) and CSBs (b)

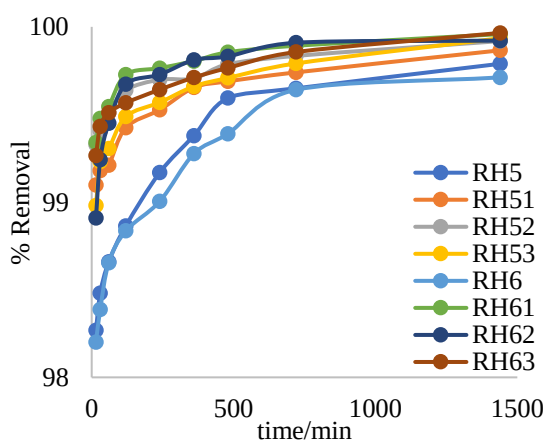


Figure 39: Percentage Removal of MET using RHBs

Ciprofloxacin (CIP)

Ciprofloxacin removal was very fast, 80 % removal efficiency was achieved for all the biochars used (Figure 40 - 41) within the first 15 min of stirring. Within 24 hours, some biochars attained 100 % removal of CIP (CF5, CF51, CF6, CF63, CS5, CS6, RH5, RH52, RH6, and RH62).

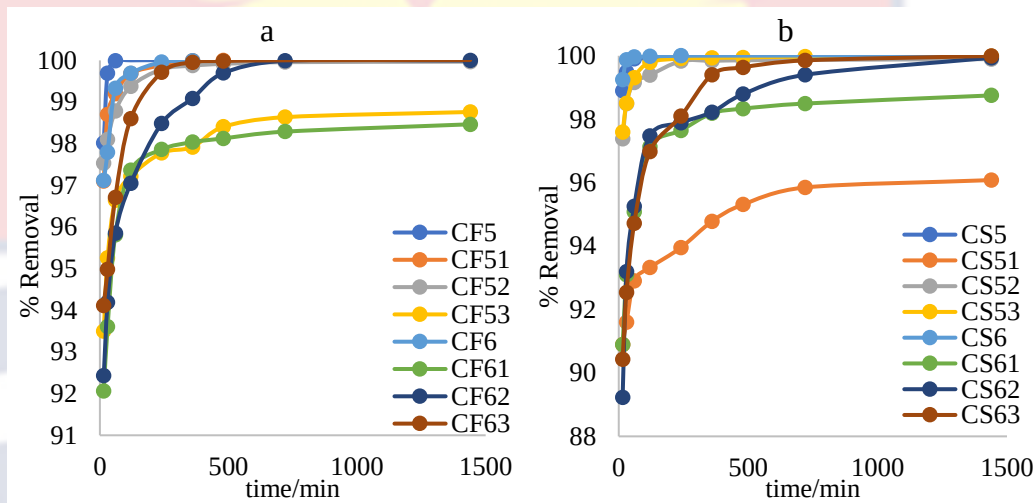


Figure 40: Percentage Removal of CIP using CFBs (a) and CSBs (b)

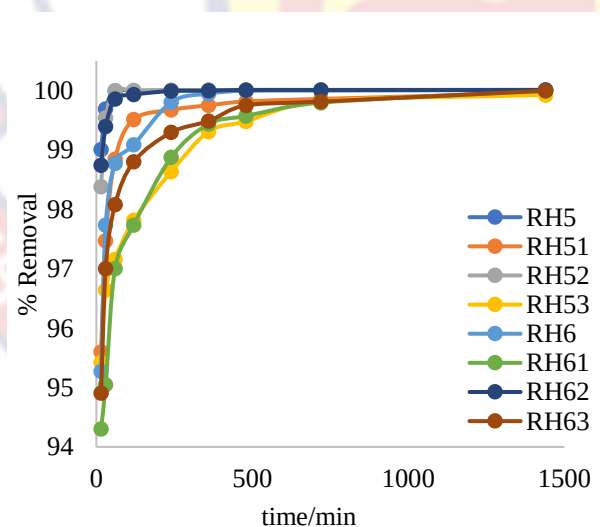


Figure 41: Percentage Removal of CIP using RHBs

Adsorption capacity of multi-component adsorption

The mean adsorption capacity of biochars ranged from 0.7518 to 0.9662, 0.7756 to 0.9373, and 0.7757 to 0.9890 mg/g for the coconut fibre, coconut shell and rice husk biochars respectively (Appendix B). The overall mean adsorption capacity for the removal of the PHAs by the biochars ranged from 7.2 to 7.9 mg/g (Figure 42)

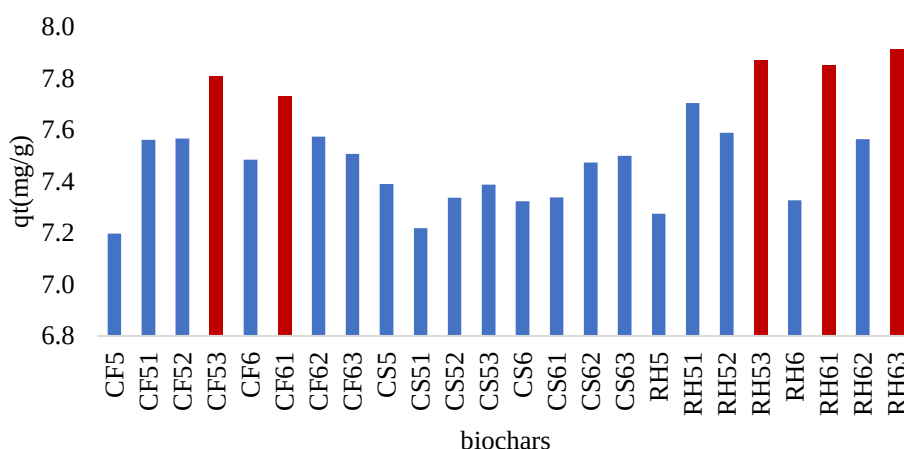


Figure 42: Total Mean Adsorption Capacities of the 24 Biochars at 24 hours

In summary, all the biochars produced were able to remove the PHAs concentration above 70 % in the competitive adsorption. Generally, values obtained suggest that higher percentage removal was realized in biochars produced at higher pyrolysis temperatures (600 °C) than lower temperatures (500 °C). This could be due to the change in physical and chemical properties of the biochar such as enhanced surface area, pore volume and the presence of various functional groups that enhanced adsorption. Also, the residence time positively affected the removal of some PHAs as higher removal efficiencies and adsorption capacities were observed in biochars with higher residence time. Higher residence times may lead

to the development of more and well-defined porous structures which in turn increase the surface area for adsorption. However, according to Wang et al., (2018) higher residence time may have less effect on biochars pyrolyzed at higher temperatures.

The adsorption capacity was also observed to increase with contact time between the biochar and the PHAs. Higher contact time allow for more interaction between the surface of the biochar and the PHAs leading to a more effective removal. However, rate of adsorption reduced over time as pores on the surface were gradually being occupied by the PHAs (Luconi et al., 2022).

MET, TRI, ASP, ACE, and CIP removal were not affected in competitive mode adsorption as close to 99 % and above efficiency was obtained for all biochar. SUL, ERY, and CAF on the other hand had their efficiencies reduced in competitive-mode adsorption for most biochars. Removal efficiency of above 90 % was observed in biochar CF53, CF61, RH53, RH61 and RH63 for all the PHAs and were therefore selected for the next phase of the study.

The removal pattern for the PHAs on the selected biochars are as follows; CF53 (TRI < ACE < MET < ASP < ERY < CIP < CAF < SUL); CF61 (ACE < MET < ASP < ERY < CIP < TRI < CAF < SUL), and RH53 (MET < CIP < TRI < ACE < ASP < CAF < SUL < ERY). The RH61 and RH63 followed the same removal pattern as RH53.

From Figure 42, five biochars were selected (CF53, CF61, RH53, RH61 and RH63) because they had the highest adsorption capacities at 24 hours and therefore were used for the rest of the study.

Adsorption Kinetics of PHAs

The result of the kinetic studies performed on the adsorption data of PHAs in competitive mode are presented in this section. This study was done to determine the effectiveness of the adsorption process and to understand the mechanisms that were involved in the removal process by the five biochars. Three kinetic models: the pseudo first order (PFO), the pseudo second order (PSO) and the Weber-Morris intraparticle diffusion (IPD) were used (Adesokan et al., 2021; Sumalinog et al., 2018; Zhang et al., 2017). The adsorption kinetic model analyzed the adsorption data from 0.5 g of the five biochars in 10 mg/L each of the eight PHAs within 24 hours of uptake time at the inherent pH which was between 7.47-10.37.

The non-linear version of the PFO and PSO models were used. Therefore, to determine the best fitting model, the sum of normalized errors (SNE) (Ayawei et al., 2017) and Akaike's information criterion (AICc) (Gezahegn et al., 2019; Luconi et al., 2022) as well as the graphical interpretation (Luconi et al., 2022) were used. The kinetic model with the least SNE and AICc values together with a good graphical representation indicated the best fit and therefore assumed to be the most appropriate model for the PHA adsorption (Luconi et al., 2022).

Acetaminophen (ACE)

The kinetic parameters for the PFO, PSO and IPD are listed in Table 6-8. The calculated adsorption capacity (q_{tcal}) values were closer to the experimental q_{texp} values from PSO model. Also, the least values of SNE and AICc were those obtained for the PSO model for all the five biochars followed by IPD model. The best graphical presentation was also observed for the PSO model (Figure 43). The

PSO model assumes that the rate of adsorption is proportional to the square of the number of unused adsorption sites, suggesting that the availability of adsorption sites had a greater impact on the adsorption rate rather than the concentration of ACE in the solution. This indicated that chemisorption might have dominated the adsorption process (Dawood et al., 2017). The highest PSO constant (K_2) of 4.1546 g/mg obtained for CF61 which implied the biochar had a very strong affinity toward ACE (Kołodzyńska & Bąk, 2018).

Table 6: PFO Parameters and Best Fit Values for ACE Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qtexp(mg/g)	0.9990	0.9994	0.9980	0.9981	0.9993
qtcal (mg/g)	0.9918	0.9956	0.9902	0.9929	0.9951
K_1 (1/min)	0.2794	0.2893	0.2643	0.2636	0.2822
R^2	0.4051	0.6527	0.4520	0.6122	0.6156
R^2 adjusted	0.2068	0.5370	0.2693	0.4829	0.4875
AICc	-88.5701	-100.2050	-86.2796	-91.8254	-96.8696
SQE	0.0003	0.0001	0.0004	0.0002	0.0001
RMSE	0.0056	0.0029	0.0064	0.0047	0.0035
MPSD	0.6464	0.3369	0.7356	0.5391	0.4057
MSE	0.0000	0.0000	0.0000	0.0000	0.0000
Hybrid	0.0041	0.0011	0.0053	0.0029	0.0016
Chi-square	0.0003	0.0001	0.0004	0.0002	0.0001
SNE	1.0160	1.0126	1.0170	1.0148	1.0134

Source: Laboratory data (2022)

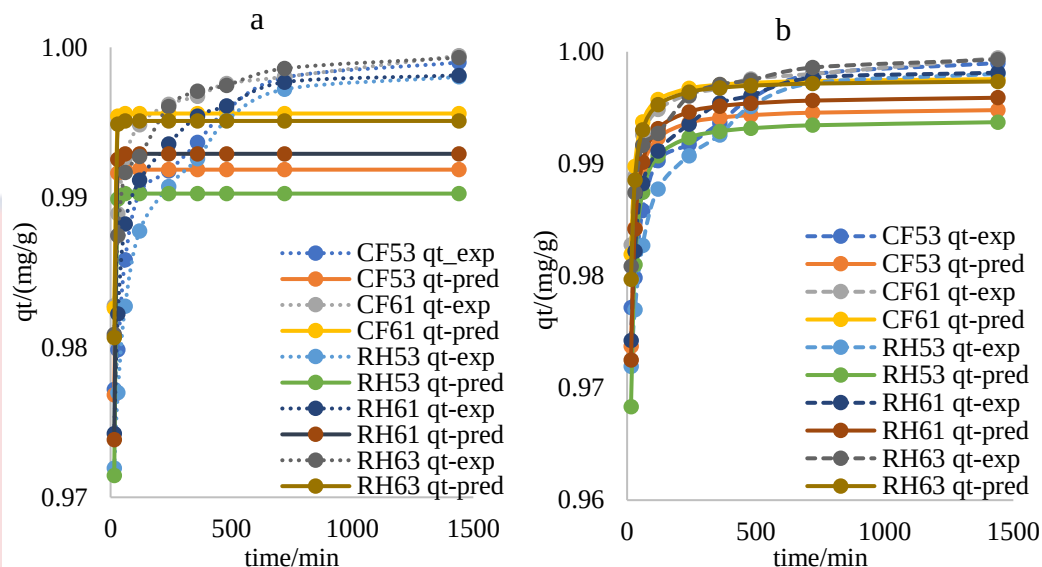


Figure 43: PFO (a) and PSO (b) Models of ACE Removal using Selected Biochars

Table 7: PSO Parameters and Best Fit Values for ACE Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qtexp(mg/g)	0.9990	0.9994	0.9980	0.9981	0.9993
qt cal (mg/g)	0.9950	0.9977	0.9940	0.9961	0.9975
K ₂ (g/(mg min))	3.0637	4.1546	2.5325	2.7540	3.6686
R ²	0.8224	0.9648	0.8520	0.9504	0.9413
R ² adjusted	0.7632	0.9531	0.8026	0.9339	0.9217
AICc	-99.4511	-120.8095	-98.0589	-110.3345	-113.7806
SQE	0.0001	0.0000	0.0001	0.0000	0.0000
RMSE	0.0031	0.0009	0.0033	0.0017	0.0014
MPSD	0.3529	0.1070	0.3820	0.1924	0.1583
MSE	0.0000	0.0000	0.0000	0.0000	0.0000
Hybrid	0.0012	0.0001	0.0014	0.0004	0.0002
Chi-square	0.0001	0.0000	0.0001	0.0000	0.0000
SNE	1.0127	1.0100	1.0130	1.0109	1.0106

Source: Laboratory data (2022)

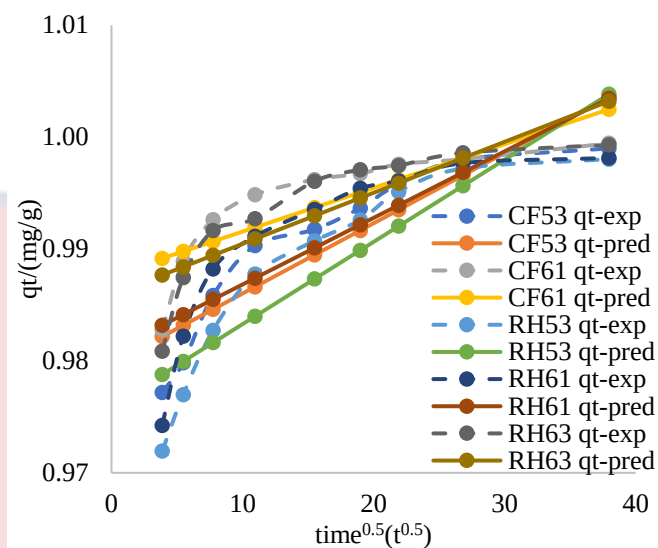


Figure 44: IPD Model of ACE Removal using Selected Biochars

For the adsorption to be solely controlled by IPD, a linear graph of qt against $t^{0.5}$ must pass through the origin giving a zero intercept. The value of the intercept obtained if the linear graph does not pass through the origin represent the boundary layer. A higher value represents a greater contribution of surface adsorption in the rate determining step (Wong et al., 2017). When multiple lines are obtained, it suggest that the adsorption occurred through several mechanisms including IPD (Dashtizade & Balarak, 2018). From adsorption data, graph of qt versus $t^{0.5}$, produced multiple lines with none passing through the origin for all biochars used (Figure 44), which implied that the IPD was not the rate determining step but other mechanisms such as film diffusion and external mass transfer might be involved in the adsorption of ACE onto the biochars.

Table 8: IPD Parameters and Best Fit Values for ACE Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
kwm (mg/g.min ^{0.5})	0.0006	0.0004	0.0007	0.0006	0.0005
B (mg/g)	0.9797	0.9876	0.9759	0.9809	0.9859
R ²	0.8153	0.6720	0.7981	0.6852	0.6980
R ² adjusted	0.7538	0.5626	0.7309	0.5803	0.5973
AICc	-99.0978	-100.7179	-95.2687	-93.7029	-99.0405
ACE	0.0001	0.0001	0.0001	0.0002	0.0001
RMSE	0.0031	0.0029	0.0039	0.0042	0.0031
MPSD	0.3600	0.3287	0.4466	0.4877	0.3610
MSE	0.0000	0.0000	0.0000	0.0000	0.0000
Hybrid	0.0013	0.0011	0.0020	0.0023	0.0013
Chi-square	0.0001	0.0001	0.0001	0.0002	0.0001
SNE	1.0128	1.0124	1.0137	1.0142	1.0128

Source: Laboratory data (2022)

The fitting to PSO corroborates with adsorption of ACE using rice husk biochar (Faisal et al., 2020; Paredes-Laverde et al., 2019), activated hydrochar from spent grain (de Araújo et al., 2020), and municipal waste biochar (Sumalinog et al., 2018).

Ciprofloxacin (CIP)

The parameters for PFO and PSO models are shown in Tables 9 and 10 respectively. The adsorption of CIP by the biochars fitted the PSO. This was because the SNE and AICc values for PSO model were the least indicating its fitness. Also, graphical representation agreed with this conclusion (Figure 45). The PSO rate constant K_2 ranged from 0.9 in CF61 to 1.4563 g/(mg/min) in RH53 indicating that CIP adsorption was fastest unto this biochar.

Table 9: PFO Parameters and Best Fit Values for CIP Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qtexp(mg/g)	0.9876	0.9847	0.9993	1.0000	1.0000
qtcal (mg/g)	0.9762	0.9728	0.9863	0.9850	0.9907
K ₁ (1/min)	0.2079	0.1902	0.2259	0.2059	0.2087
R ²	0.6358	0.5918	0.4677	0.4564	0.7018
R ² adjusted	0.5144	0.4557	0.2902	0.2752	0.6024
AICc	-78.2895	-72.1984	-76.7123	-71.2287	-80.8562
SQE	0.0009	0.0018	0.0011	0.0020	0.0007
RMSE	0.0100	0.0140	0.0109	0.0148	0.0086
MPSD	1.1704	1.6706	1.2580	1.7287	0.9995
MSE	0.0001	0.0002	0.0001	0.0002	0.0001
Hybrid	0.0132	0.0265	0.0155	0.0289	0.0098
Chi-square	0.0009	0.0018	0.0011	0.0020	0.0007
SNE	1.0214	1.0265	1.0228	1.0277	1.0199

Source: Laboratory data (2022)

Table 10: PSO Parameters and Best Fit Values for CIP Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qt exp	0.9876	0.9847	0.9993	1.0000	1.0000
qtcal (mg/g)	0.9832	0.9822	0.9925	0.9937	0.9973
K ₂ (g/(mg min))	1.2188	0.9040	1.4563	1.0429	1.2583
R ²	0.9533	0.9496	0.8306	0.8665	0.9803
R ² adjusted	0.9377	0.9328	0.7741	0.8220	0.9737
AICc	-96.7670	-91.0219	-87.0168	-83.8669	-105.2922
SQE	0.0001	0.0002	0.0003	0.0005	0.0000
RMSE	0.0036	0.0049	0.0061	0.0073	0.0022
MPSD	0.4169	0.5925	0.7097	0.8582	0.2558
MSE	0.0000	0.0000	0.0000	0.0001	0.0000
Hybrid	0.0017	0.0033	0.0049	0.0071	0.0006
Chi-square	0.0001	0.0002	0.0003	0.0005	0.0000
SNE	1.0132	1.0147	1.0166	1.0180	1.0116

Source: Laboratory data (2022)

These results are similar to CIP adsorption onto protein modified nanosilica (Pham et al., 2020), RH and corn cob (Peñafiel et al., 2019), rabbit manure biochar

(Huang et al., 2018) and SiO₂ nanoparticles from RH (Nassar et al., 2019) in which PSO was the best fitting kinetic models.

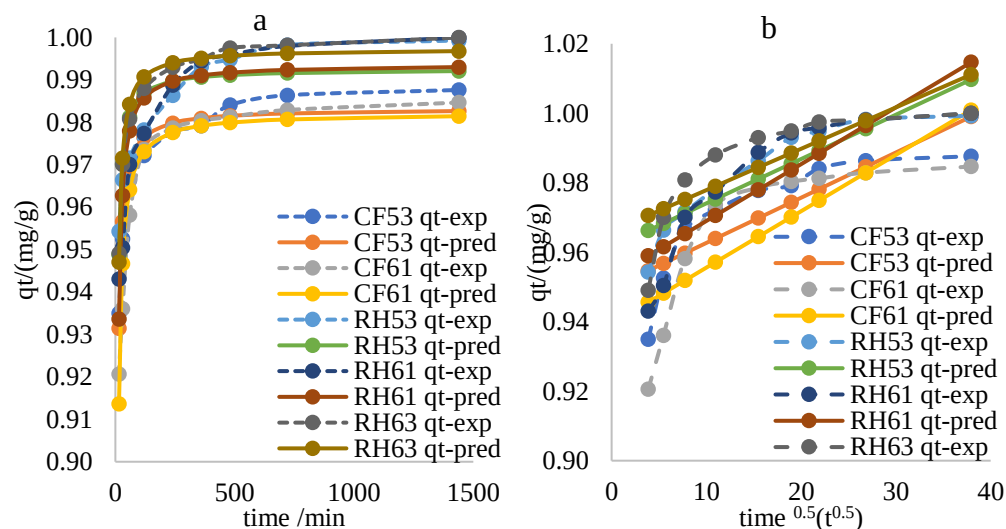


Figure 45: PSO (a) and IPD (b) Models of CIP Removal using Selected Biochars

Further analysis was done on the adsorption data using the IPD model and the parameters obtained in Appendix C to determine the diffusion mechanism and to predict the rate controlling step of CIP. A plot of qt against $t^{0.5}$ (Figure 45) did not pass through the origin for all the five biochars which suggested that the adsorption of CIP was not controlled only by IPD but other mechanisms as indicated by PSO model (Dhiman, 2022; Nassar et al., 2019).

Aspirin (ASP)

Adsorption data for aspirin (ASP) was also analyzed using the PSO, PFO and IPD model, the results (Table 11, Appendix C) showed that just like CIP and ACE, the data from all the biochars fitted the PSO model. The SNE and AICc values were lowest in the PSO model compared to the PFO model. Also, the calculated qt values of the PSO were more compatible with the experimental values for all the biochars. Furthermore, the graphical representation (Figure 46) also

aligned better to PSO model. This is in agreement with removal of ASP by sugarcane bagasse biochar (Romano et al., 2022), graphene nanoplatelets (Al-Khateeb et al., 2014) and activated carbon from spent tea leaves (Wong et al., 2017)

which followed the PSO model.

Table 11: PSO Parameters and Best Fit Values for ASP Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qtexp/(mg/g)	0.9935	0.9932	0.9938	0.9926	0.9890
qtc _{al} (mg/g)	0.9917	0.9930	0.9888	0.9855	0.9827
K ₂ (g/(mg min))	1.8824	1.2366	0.9785	0.7709	1.7841
R ²	0.9173	0.9980	0.9795	0.9662	0.8541
R ² adjusted	0.8897	0.9974	0.9726	0.9550	0.8055
AICc	-98.7819	-125.8919	-100.6545	-92.0870	-92.1173
SQE	0.0001	0.0000	0.0001	0.0002	0.0002
RMSE	0.0032	0.0007	0.0029	0.0046	0.0046
MPSD	0.3738	0.0823	0.3311	0.5387	0.5393
MSE	0.0000	0.0000	0.0000	0.0000	0.0000
Hybrid	0.0014	0.0001	0.0011	0.0028	0.0028
Chi-square	0.0001	0.0000	0.0001	0.0002	0.0002
SNE	1.0127	1.0095	1.0124	1.0146	1.0146

Source: Laboratory data (2022)

The adsorption data was fitted into the IPD model (Appendix C) to gain insight into the rate determining step and the mechanism. In this study (Figure 46), multiple straight lines which did not pass through the origin were obtained. This indicated that the IPD is part of the adsorption mechanism but not the rate determining step for the adsorption of ASP.

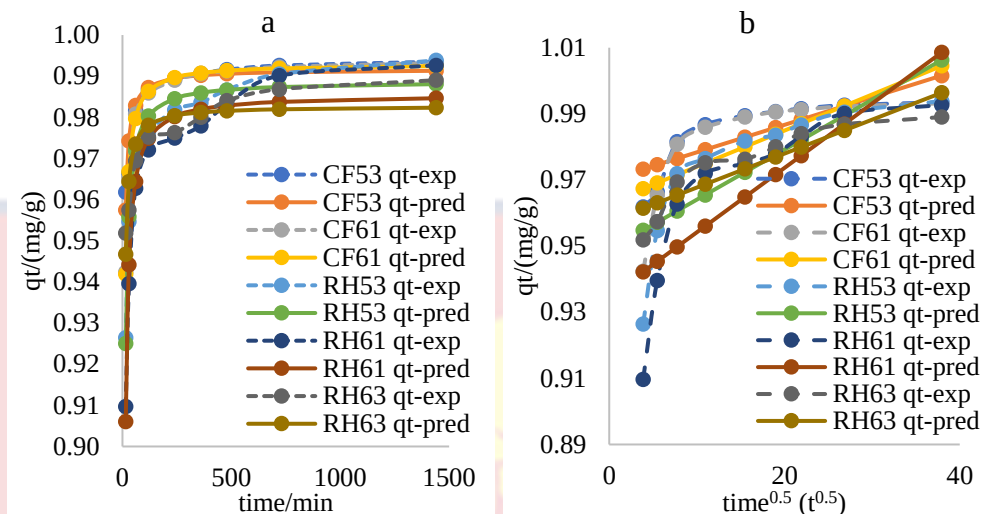


Figure 46: PSO (a) and IPD (b) Models of ASP Removal using Selected Biochars

Erythromycin (ERY)

Erythromycin adsorption data were fitted into PFO and PSO model (Appendix C), it was deduced that all the adsorption data of biochars favoured Pseudo second order (PSO) model (Figure 47). This was because the SNE and AICc values were lower for PSO as compared to PFO. Also, the experimental adsorption capacity values of PSO were very closer to the calculated adsorption capacity (Appendix C). With respect to IPD model (Appendix C & Figure 47), the linear portion of the graph did not pass through the origin implying IPD had an influence on the adsorption process but not the rate controlling step.

Also, higher R^2 values were obtained by all biochars for the IPD model as compared to those of PSO suggesting that the adsorption process was controlled by diffusion dominated mechanisms such as boundary layer and liquid film diffusion (Ahmed et al., 2016; Huang et al., 2018; Nassar et al., 2019).

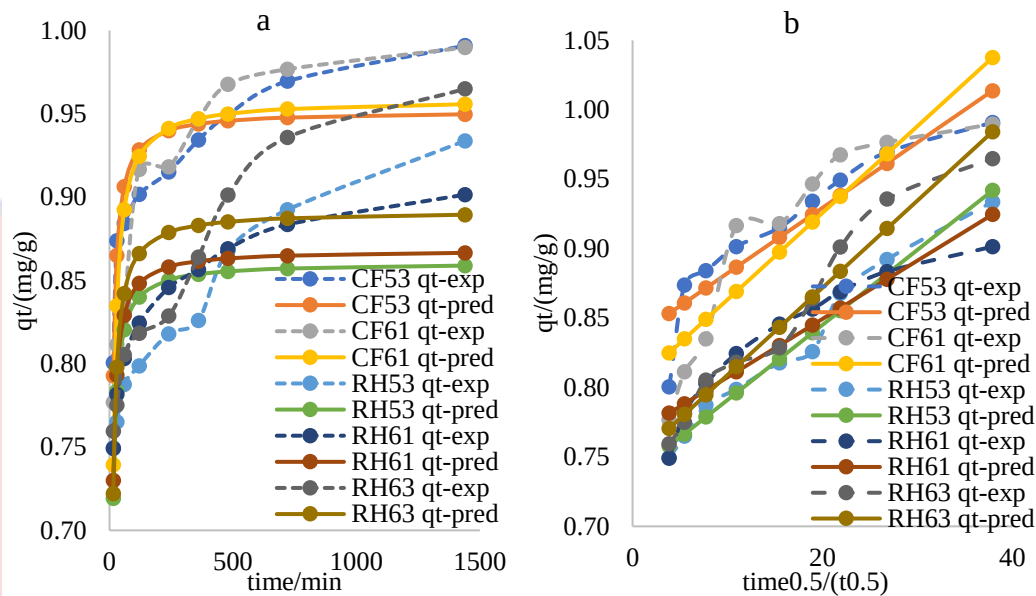


Figure 47: PSO (a) and IPD (b) Models of ERY Removal using Selected Biochars

The PSO constant, K_2 , for the selected biochars was very low, it ranged from 0.2343 in CF61 to 0.4054 g/(mg/min) in RH61 which implied that biochars had low affinity for ERY. This may be as a result of ERY being very bulky as it is the pharmaceutical with the largest molecular structure (Table 3). ERY removal with multi-walled nanotubes (Dashtizade & Balarak, 2018) and BPNB-SiO₂-Chit Hgel nanobiosorbent (Mahmoud et al., 2023) also fitted PSO model.

Metronidazole (MET)

The kinetic fitting results obtained for PFO and PSO for MET are shown in Figure 48 and their kinetic parameters are listed in Appendix C. The correlation coefficients R^2 of PFO and PSO ranged from 0.4526 to 0.8510 and 0.8078 to 0.9833 respectively. Also, the calculated adsorption capacity (q_{tpred}) obtained from PSO were nearer to the experimental q_{texp} as compared to the PFO values. Also, the rate constant for PSO were larger than those of PFO and these were observed in all the biochars. The kinetic analysis data therefore indicates that that the adsorption

of MET onto the different biochars used can be well described by the PSO model: which suggests that the adsorption onto the biochars affected by both biochar adsorption capacity and the substrate concentration (Sun et al., 2017). Sun et al. (2017) found that adsorption of metronidazole onto biochars made from sugarcane bagasse fitted PSO. Also, removal of MET by biochar made from Siris seed pods using microwave assisted K_2CO_3 and KOH activation followed PSO model (Ahmed & Theydan, 2013). Similar results was obtained when eucalyptus sawdust impregnated with 85 % H_3PO_4 was used in the adsorption of MET (Wan et al., 2016).

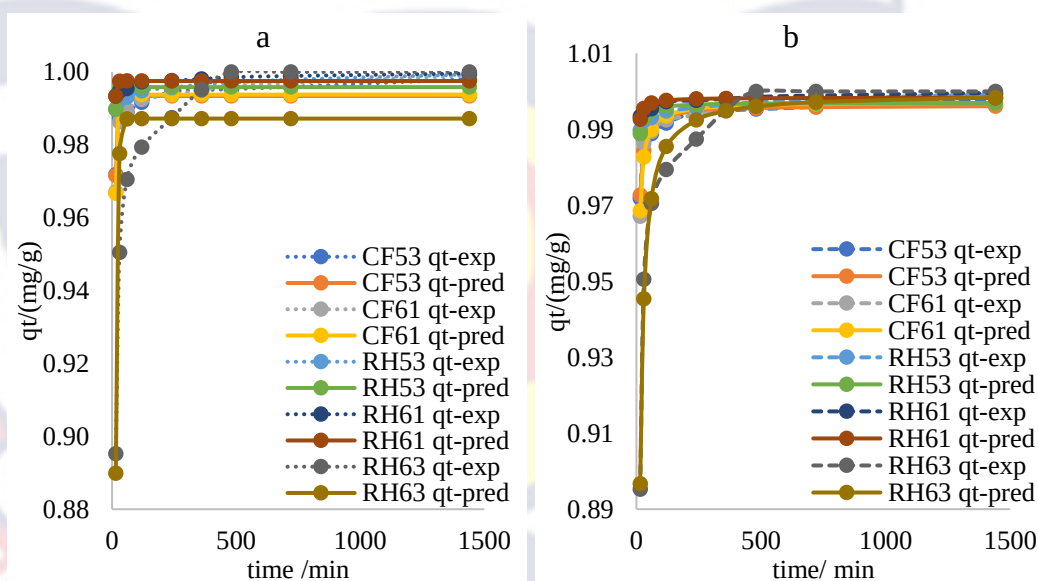


Figure 48: PFO (a) and PSO (b) Models of MET Removal using Selected Biochars

Further analysis was done using the IPD model to gain insight into the mechanism, a graph of qt against $t^{0.5}$ gave straight lines without passing through the origin implying that intraparticle diffusion (IPD) is not the only mechanism affecting the adsorption process (Figure 49).

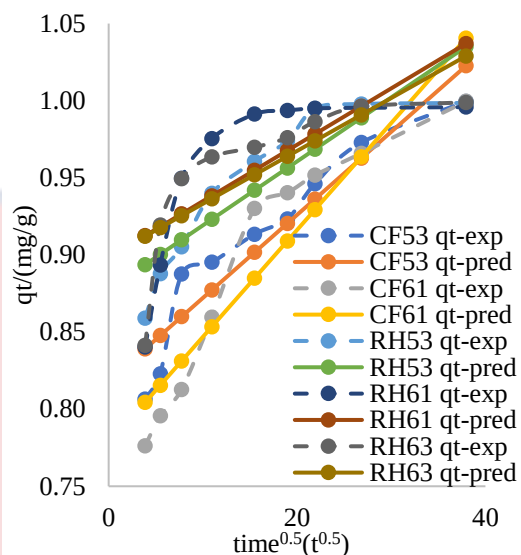


Figure 49: IPD Model for MET Removal using Selected Biochars

Trimethoprim (TRI)

The SNE and the AICc values (Appendix C) as well as graphical presentation (Figure 50) showed that the adsorption of TRI onto the biochars fitted the PSO model. The rice husk biochars (RHBs) removed TRI faster than the coconut fibre (CF) biochars as higher K_2 values were obtained. Analysis using the IPD model (Appendix C & Figure 50) demonstrated that the adsorption of TRI onto the biochars was dominated by diffusion mechanisms such as external mass transfer and internal diffusion but intraparticle diffusion was not the rate determining step as the graph of q_t versus $\text{time}^{0.5}$ adsorption process did not pass through the origin.

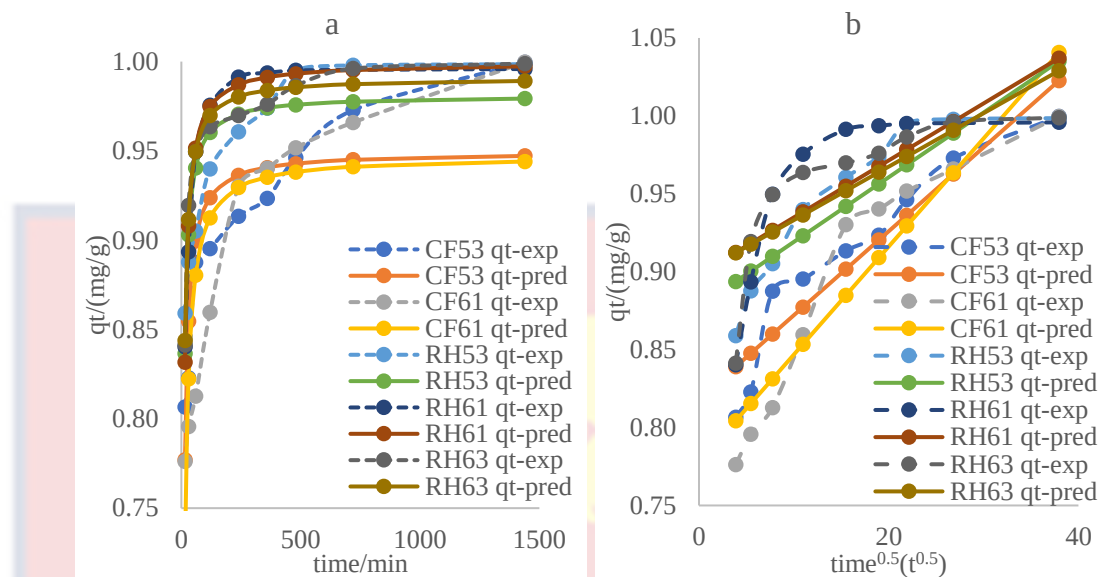


Figure 50: PSO (a) and IPD (b) Models of TRI Removal using Selected Biochars

Fitting of adsorption data to PSO model were similar to results obtained for the removal of TRI using carbonized wood (Adesokan et al., 2021) and modified silica with pyrazole (Jodeh et al., 2022).

Caffeine (CAF)

Caffeine adsorption onto the five biochars were subjected to analysis using PSO, PFO and IPD models. Results showed that adsorption process using the biochars fitted the PSO better (Figure 51) Adsorption fitting PSO model indicated that the process depended on both the biochars and the CAF in solution. Also, diffusion dominated mechanisms occurred in the adsorption process as indicated by the IPD model. The IPD however, was not the rate determining step (Figure 51). The parameters of the models are listed in Appendix C.

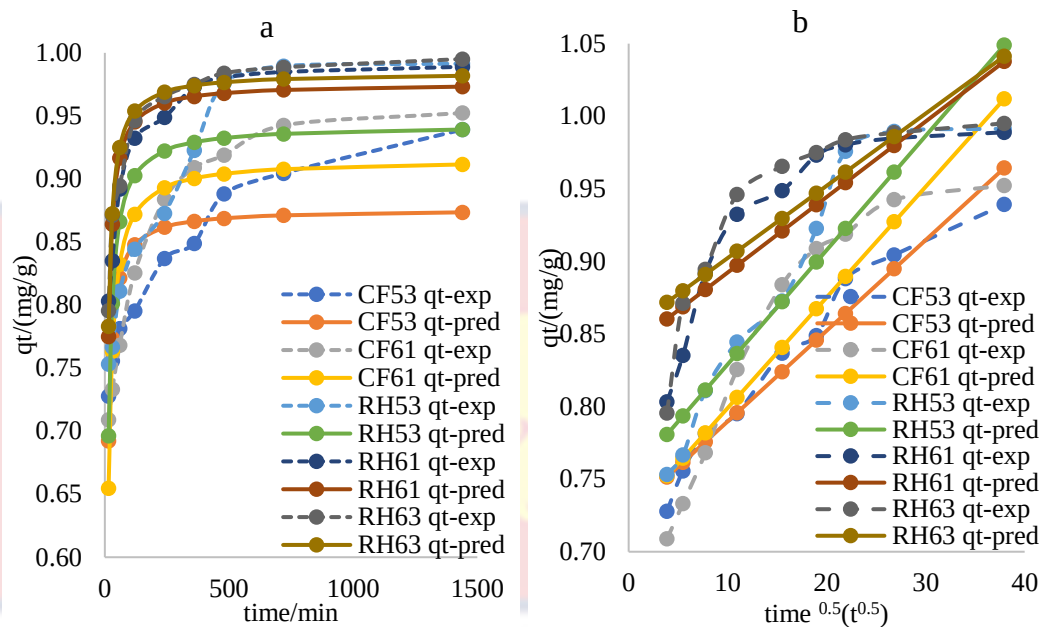


Figure 51: PSO (a) and IPD (b) Models of CAF Removal using Selected Biochars

Similar fitting of adsorption data to PSO model was obtained when rice husk (Bahrami et al., 2023), activated carbon from *Sargassum* sp (Francoeur et al., 2021), and activated biochar from acai seed (Da Silva Vasconcelos De Almeida et al., 2021) were used in the removal of caffeine.

Sulfamethoxazole (SUL)

Adsorption data of SUL were fitted into the three models and the parameters listed in Appendix C. Adsorption of SUL fitted the PSO model and also the IPD model showed that diffusion mechanisms were involved (Figure 52) in adsorption process. However, IPD was not the rate determining step as a graph q_t versus $t^{0.5}$ produced straight lines that did not pass through the origin (Figure 52).

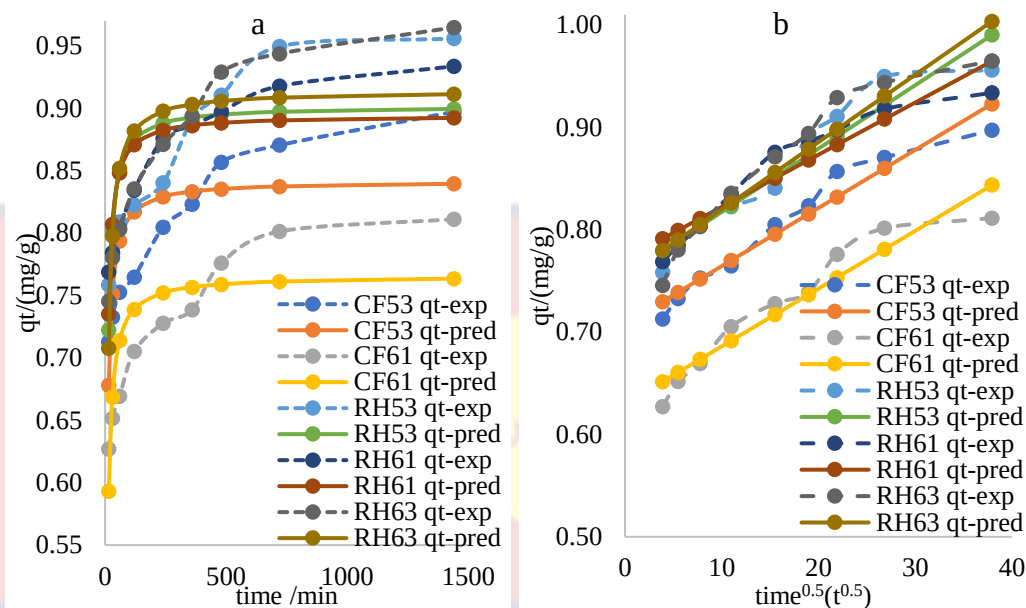


Figure 52: PSO (a) and IPD (b) Models of SUL Removal using Selected Biochars

In summary, the adsorption of the eight PHAs onto the five biochars fitted the PSO model. This suggested that the adsorption process was influenced by the availability of sites than by the concentration of the pharmaceuticals in solution and also an indication of chemical reaction between the PHAs and the functional groups on the surface of the biochars. However, small differences in some of the parameters indicated that there was a likelihood of mixed adsorption processes occurring (i.e., physical and chemical) simultaneously, despite the tendency to occur chemically based on the q_{texp} , R^2 , adjusted R , AICc, and SNE values.

Further analysis using the IPD model suggested that diffusion dominated the mechanism of adsorption but IPD was not the rate determining step as no line passed through the origin (Xiang et al., 2020). Two to three distinct regions were observed indicating, the transfer of external mass or boundary layer diffusion, intra particulate diffusion and diffusion into the biochar interstices. This involves the diffusion of the PHAs from the solution to the surface of the biochar during the first

stage, then entering the pores when the outer surface becomes saturated and finally get adsorbed onto active surfaces in the internal surface. As PHAs move into the pores of the biochar, their concentration reduces thereby reducing the diffusion rate till equilibrium is reached (Bachmann et al., 2021; Da Silva Vasconcelos De Almeida et al., 2021).

Adsorption Isotherms

The Langmuir, Freundlich and Temkin isotherm (Mellah & Harik, 2020) were used to determine the relationship between the residual amount of pharmaceuticals in the aqueous phase and the amount of pharmaceuticals adsorbed by the selected biochars (Kgomo et al., 2022). These isotherm equations were fitted to the adsorption data by non-linear regression using the mentioned errors. The precise values of the parameters for the selected isotherms were computed using the solver add-in application in Microsoft Excel 2010 spreadsheet and values were verified using the CAVS - Adsorption Evaluation software (Sobieraj et al., 2022; Wagassa et al., 2023). The isotherm that fits were determined based on the R^2 , adjusted R^2 , AICc, SNE values and their graphical presentation.

Isotherm studies of PHAs using RH53 biochar

The parameters and best fit values obtained for fitting the equilibrium data to the non-linear models of Langmuir, Freundlich, and Temkin are presented in Tables 12, 13 and 14. The maximum monolayer amount (q_{max}) ranged from 2.9307 to 9.9449 mg/g with ERY obtaining the highest value (Table 12). The (q_{max}) value for MET is comparatively lower than values obtained by Abbas & Abbas, (2021); Ahmadfazeli et al., (2021); Azarpira & Balarak, (2016) and Sun et

al., (2017) who used modified biochar for their studies but favourable with result by Aarab et al., (2019). The Langmuir constant (K_L) and Freundlich constant (K_F) indicated (Table 12 & 13) which signify the degree of affinity / binding strength (Abbas & Abbas, 2021; Xu et al., 2017) and relative adsorption capacity (Inyinbor et al., 2016; Musah et al., 2022) respectively showed that the biochar RH53 had a strong affinity for most of the PHAs (MET, ACE, TRI, CAF, ASP & CIP) but a weak one for SUL and ERY. The highest K_F value was obtained for ACE indicating a stronger affinity for the available active sites. The lowest K_L and K_F values of 0.0869 L/mg and $0.8482 \text{ mg g}^{-1}(\text{L mg}^{-1})^{1/n}$ respectively were obtained by ERY indicating less affinity for adsorption.

Table 12: Langmuir Isotherm Parameters and Best Fit Values for the Removal of PHAs using RH53 Biochar

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
$q_{\text{exp}}(\text{mg/g})$	2.9773	3.0982	2.9587	2.7898	2.6327	2.8328	2.6033	2.9682
$q_{\text{max}}(\text{mg g}^{-1})$	3.6913	4.2581	3.4501	2.9307	4.0363	3.0485	9.9449	3.4446
$K_L (\text{L mg}^{-1})$	22.6531	9.8176	12.6176	4.2405	0.5458	3.6110	0.0869	17.3861
R_L	0.009-	0.020-	0.016-	0.045-	0.268-	0.05-	0.697-	0.011-
	0.001	0.003	0.003	0.008	0.058	0.009	0.848	0.002
R^2	0.7534	0.9457	0.9330	0.9706	0.9210	0.8802	0.9338	0.8887
R^2 adjusted	0.5889	0.9095	0.8884	0.9510	0.8683	0.8004	0.8897	0.8145
SQE	1.0644	0.2338	0.2841	0.1085	0.2662	0.4609	0.2136	0.4762
RMSE	0.4212	0.1974	0.2176	0.1345	0.2106	0.2771	0.1887	0.2817
MPSD	81.7953	25.9620	41.9343	15.4080	43.2847	33.1164	23.4763	32.6937
MSE	0.1774	0.0390	0.0474	0.0181	0.0444	0.0768	0.0356	0.0794
Hybrid	38.5019	5.4811	10.2048	2.1796	9.8756	10.0998	5.2541	11.0772
Chi-square	1.1521	0.2404	1.5323	0.0949	0.2679	0.6011	0.3254	1.0128
SNE	1.5051	1.2385	1.2930	1.1646	1.2464	1.3477	1.2563	1.3954
	-	-	-	-	-	-	-	-
AICc	-5.0428	14.1380	12.9673	18.7435	13.3578	10.0652	14.6794	9.8688

Source: Laboratory data (2022)

ERY is very bulky, therefore the presence of other PHAs with small sizes such as ACE which are also in solution and might be competing for the same adsorption sites leading to a lower K_L and K_F value (Kgomo et al., 2022).

The dimensionless separation factor (R_L) is a vital characteristic of the Langmuir isotherm which evaluates the performance of the adsorption process. The factor ranges from 0 to 1 and indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), irreversible ($R_L = 0$) or favourable ($0 < R_L < 1$) (Musah et al., 2022). The factor was very small ($0 < R_L < 1$) for the all the PHAs and this suggested that the adsorption of the PHAs were favourable (Aarab et al., 2019; Al-ghouti & Da, 2020).

From the parameters obtained for the Freundlich isotherm, the Freundlich exponent, $1/n$, (Table 13) which determines the adsorption intensity or surface heterogeneity was less than 1 for all PHAs indicating a favourable adsorption (Ahmadfazeli et al., 2021) as well as may be an indication of a chemisorption process (Kyzas et al., 2018). The coefficient of variation R^2 of several compounds for the Langmuir and Freundlich isotherms showed good fits. This may suggest that adsorbate monolayer may be formed first followed by the formation of heterogeneous multi-layers (Kgomo et al., 2022).

Table 13: Freundlich Isotherm Parameters and Best Fit Values for the Removal of PHAs using RH53 Biochar

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
$K_F(\text{mgg}^{-1})$								
$^1(\text{Lmg}^{-1})^{1/n}$	5.4035	6.4672	4.1503	2.1837	1.3645	2.3417	0.8482	4.7819
$1/n$	0.3660	0.5152	0.3661	0.3440	0.5483	0.3874	0.7981	0.3778
n	2.7322	1.9410	2.7315	2.9070	1.8238	2.5813	1.2530	2.6469
R^2	0.7208	0.9235	0.9509	0.9205	0.8852	0.9661	0.9448	0.9189
R^2 adjusted	0.5347	0.8724	0.9181	0.8675	0.8086	0.9435	0.9080	0.8648
SQE	1.2049	0.3293	0.2085	0.2949	0.3868	0.1304	0.1782	0.3473
RMSE	0.4481	0.2343	0.1864	0.2217	0.2539	0.1474	0.1723	0.2406
MPSD	87.7899	37.5651	19.2026	29.1212	51.2645	16.0917	24.1657	40.6518
MSE	0.2008	0.0549	0.0347	0.0492	0.0645	0.0217	0.0297	0.0579
Hybrid	42.3353	8.7488	4.1625	6.7556	13.6992	2.5486	4.6986	10.3095
Chi-square	0.8032	0.2560	0.1432	0.2405	0.3408	0.1077	0.2348	0.3148
SNE	1.5125	1.2562	1.2466	1.2597	1.2876	1.1837	1.2199	1.2772
		-	-	-	-	-	-	-
AICc	-4.2990	12.0813	14.8242	14.7864	11.1168	17.6397	15.7671	11.7630

Source: Laboratory data (2022)

The Temkin isotherm assumes that the heat of adsorption decreases linearly with decrease in binding energies which are uniformly distributed over the surface of the biochar. From Table 14, the Temkin constant (b_T) corresponds to the heat of adsorption which ranged from 2643.7353 to 5175.2098 J mol⁻¹. These high values indicated that there was a strong interaction between the PHAs and the RH53 biochar and also, the heat of adsorption decreases more rapidly with increase in adsorption implying a favourable adsorption process. The Temkin equilibrium constant (K_T) which corresponds to the maximum binding energy was highest for TRI implying RH53 showed the highest affinity for TRI and lowest for SUL.

Table 14: Temkin Isotherm Parameters and Best Fit Values for the Removal of PHAs using RH53 Biochar

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
b_T (J/mg)	3716.407	2791.466	5175.210	4210.218	2643.735	4684.809	2646.644	4129.468
K_T (L /mg)	366.3334	69.2770	606.1890	48.8996	4.7834	81.4124	2.9811	357.3818
R^2	0.7043	0.9349	0.8617	0.9789	0.9262	0.9267	0.8827	0.8901
R^2 adjusted	0.5072	0.8915	0.7695	0.9648	0.8770	0.8778	0.8045	0.8169
SQE	1.2761	0.2801	0.5866	0.0780	0.2485	0.2822	0.3786	0.4701
RMSE	0.4612	0.2161	0.3127	0.1140	0.2035	0.2169	0.2512	0.2799
MPSD	95.6819	26.8688	42.8280	16.4274	38.0241	16.7613	26.6239	41.1824
MSE	0.2127	0.0467	0.0978	0.0130	0.0414	0.0470	0.0631	0.0784
Hybrid	49.9381	6.2246	14.7773	1.9319	8.3535	4.2214	7.3733	12.5779
Chi-square	1.0357	0.2643	0.7099	0.0723	0.2747	0.1537	0.3091	0.5284
SNE	1.5531	1.2617	1.3849	1.1345	1.2399	1.2936	1.3146	1.3384
-	-	-	-	-	-	-	-	-
AICc	3.9544	13.0531	8.6176	20.7218	13.7707	13.0086	11.2450	9.9458

Source: Laboratory data (2022)

The large heat of adsorption and the maximum binding energy predicted by Temkin isotherm indicated that the removal of PHAs by the RH53 was a favourable process and it occurred through chemical bonding of PHAs to the RH53 biochar used. The positive values obtained for b_T ($b_T > 1$) was an indication that the adsorption process was exothermic (Nguyen et al., 2020; Kgomo et al. 2022). The large binding energy indicates that RH53 could be an excellent adsorbent for the selected PHAs.

From the experiment data (Table 12, 13, &14), several compounds showed high values of R^2 , adjusted R^2 for all the three isotherms used. According to the R^2 , adjusted R^2 , AICc, the sum of normalized errors (SNE) values, and Figure 53, ACE (de Araújo et al., 2020; Faisal et al., 2020; Paredes-Laverde et al., 2019) and

MET adsorptions best fitted the Langmuir isotherm; TRI (Jodeh et al., 2022), ASP (Wong et al., 2017), CIP, and ERY (Wang et al., 2021) the Freundlich isotherm; SUL and CAF, the Temkin isotherm model.

The fitting of the adsorption data to different isotherms may indicate the heterogeneous nature of the biochar as well as suggesting the formation of adsorbate monolayer first followed by the formation of heterogenous multilayers (Sekulic et al., 2019) as all these processes are occurring on the surface of one biochar. This may have occurred because of solute-solute attractive forces between the adsorbates on the surface of the RH53 biochar and the adsorbate in solution (Kgomo et al., 2022). The process might also be exothermic as several PHAs had high and positive b_T values (Nguyen et al., 2020).



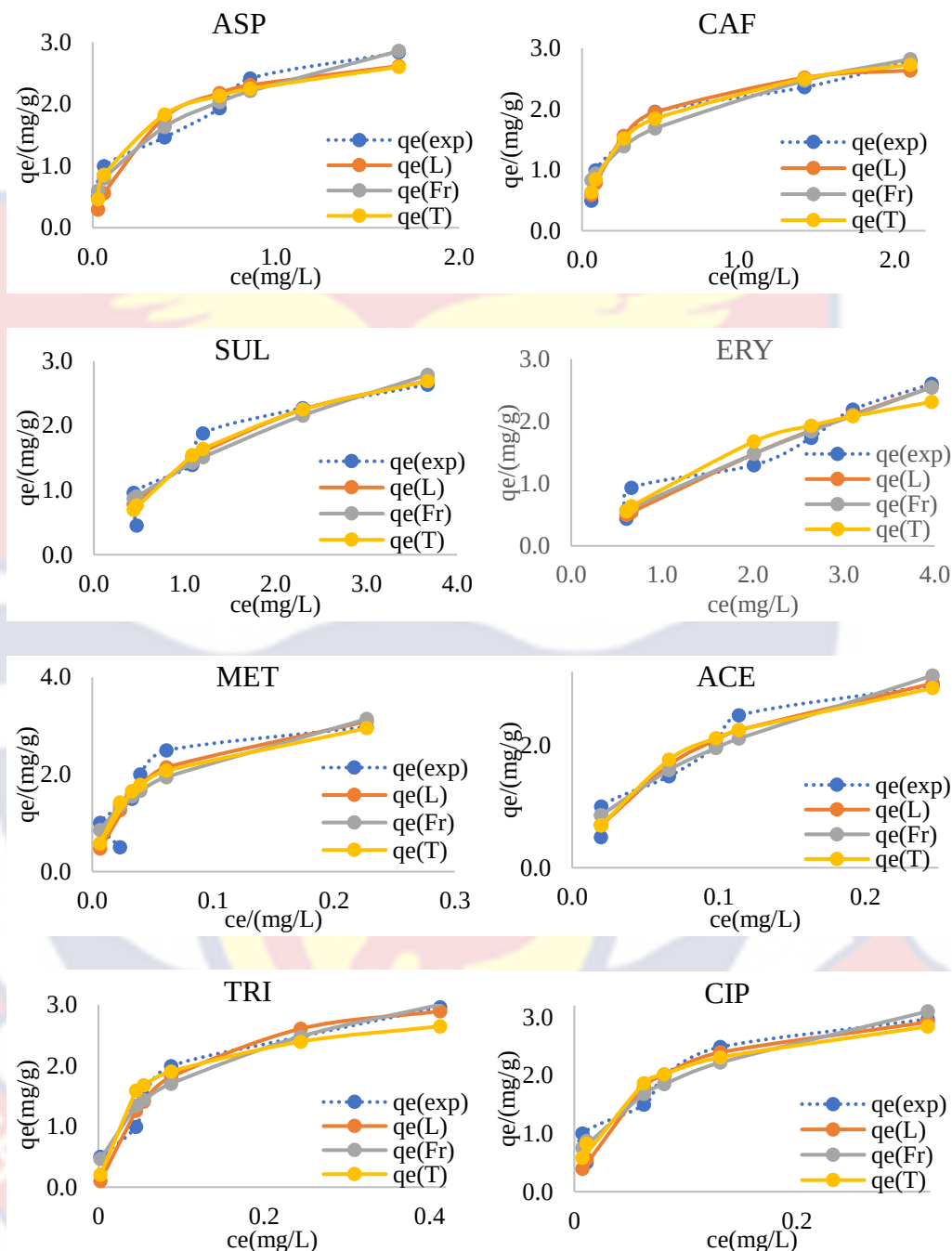


Figure 53: Isotherm Models of PHAs using RH53 Biochar

Isotherm studies of PHAs using RH61 biochar

The Table 15 shows the parameters obtained using non-linear Langmuir isotherm. The model assumes a monolayer adsorption on to homogeneous surface

sites of an adsorbent. The maximum monolayer adsorption capacity $q_{\max}$ was determine to be from 3.3302 for MET to 37.7268 mg/g in ERY adsorption.

Table 15: Langmuir Isotherm Parameters and Best Fit Values for the Removal of the PHAs using RH61

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
$q_{\text{exp}}(\text{mg/g})$	2.9841	2.9799	2.9518	2.8751	2.6902	2.9106	2.6273	2.9589
$q_{\max} (\text{mg g}^{-1})$	3.3302	4.0420	3.6644	3.6916	11.1515	4.1689	37.7268	4.1912
$K_L (\text{L mg}^{-1})$	37.0593	13.1257	7.8846	2.2610	0.1036	2.1880	0.0186	5.4081
R_L	0.005-	0.015-	0.025-	0.081-	0.659-	0.084-	0.914-	0.035-
	0.001	0.003	0.004	0.015	0.243	0.015	0.641	0.006
R^2	0.9029	0.9786	0.9892	0.9664	0.9558	0.9330	0.9606	0.7567
R^2 adjusted	0.8381	0.9643	0.9821	0.9440	0.9264	0.8884	0.9344	0.5945
SQE	0.4199	0.0924	0.0454	0.1331	0.1555	0.2729	0.1298	1.0297
RMSE	0.2645	0.1241	0.0870	0.1489	0.1610	0.2133	0.1471	0.4143
MPSD	39.0964	14.2928	12.1910	14.7173	17.3110	24.2654	18.7863	53.0432
MSE	0.0700	0.0154	0.0076	0.0222	0.0259	0.0455	0.0216	0.1716
Hybrid	11.7760	1.9703	1.0827	2.4670	3.0386	6.0348	2.8500	26.4260
Chi-square	0.8051	0.0902	0.0407	0.1180	0.1336	0.3606	0.1255	89.0298
SNE	1.3411	1.1604	1.1036	1.1963	1.2030	1.2855	1.1743	1.9108
	-	-	-	-	-	-	-	-
AICc	10.6242	19.7088	23.9741	17.5179	16.5857	13.2091	17.6669	-5.2418

Source: Laboratory data (2022)

The $q_{\max}$ values from the Langmuir isotherm model were not nearer to the q_{exp} values indicating might not be the best fitting isotherm model. The Langmuir constant K_L which represents the affinity of RH61 to the PHAs ranged from 0.0186 to 37.0593 L/mg. MET had the strongest affinity and SUL, the least. The Langmuir separation factor was very low ($R_L < 1$) for all the PHAs with values ranging from 0.001 to 0.914, this indicated that the PHAs easily migrated to surface of the adsorbent and the removal of the PHAs with the adsorbent was a favourable process.

The Freundlich model (Table 16) assumes a multi-layered adsorption on to a heterogenous adsorbent (Nasseh et al., 2018). The values of $1/n$ were in the range of 0.3858 to 0.9403, where all the PHAs achieved $1/n < 1$ suggesting normal and non-linear adsorption. Except for ERY, the PHAs showed $K_F > 1$, suggesting a good affinity for the active sites of the RH61. ACE had a strongest affinity for the active sites of the biochar as it obtained the highest K_F value. The K_L and K_F values of ERY were all very low, suggesting the low affinity of the RH61 biochar. Also, the near one value of the $1/n$ indicates it almost unfavourability.

The Temkin Isotherm demonstrates the effect on indirect adsorbate and adsorbate interactions on adsorption and assumes linear reduction in heat of adsorption with increment in extent of adsorption. The Temkin constant which is reported by Mellah & Harik, (2020) as adsorption energy variation b_T ranged between 2104.8344 to 9044.7820 J/mol (Table 17).

Table 16: Freundlich Isotherm Parameters and Best Fit Values for the Removal of the PHAs using RH61

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
K_F								
(mg/g(L/mg) ^{1/n})	6.1480	6.9049	4.2745	2.5686	1.0555	3.0396	0.7096	4.0619
1/n	0.3858	0.5035	0.4575	0.5081	0.8418	0.5414	0.9403	0.3986
R^2	0.9262	0.9836	0.9576	0.9816	0.9568	0.9735	0.9618	0.8212
R^2 adjusted	0.8770	0.9727	0.9294	0.9693	0.9279	0.9559	0.9363	0.7020
SQE	0.3191	0.0707	0.1787	0.0730	0.1521	0.1080	0.1260	0.7568
RMSE	0.2306	0.1085	0.1726	0.1103	0.1592	0.1341	0.1449	0.3552
MPSD	48.2613	14.8175	31.0141	21.5926	18.9663	17.6883	19.9186	48.1950
MSE	0.0532	0.0118	0.0298	0.0122	0.0254	0.0180	0.0210	0.1261
Hybrid	12.8435	1.5319	5.7141	2.7072	3.1170	2.7135	2.9037	20.1090
Chi-square	0.3342	0.0544	0.1688	0.0902	0.1278	0.1239	0.1196	3.4509
SNE	1.2855	1.1199	1.2020	1.1386	1.1888	1.1751	1.1664	1.5145
	-	-	-	-	-	-	-	-
AICc	12.2709	21.3135	15.7512	21.1172	16.7159	18.7735	17.8449	7.0889

Source: Laboratory data (2022)

Table 17: Temkin Isotherm Parameters and Best Fit Values for the Removal of the PHAs using RH61 Biochar

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
$b_T(\text{J/mol})10^3$	3.9905	3.1870	3.0187	3.2225	2.2402	3.3815	2.1048	9.0448
K_T (L/mg) 10^3	0.5882	0.1865	0.0737	0.0264	0.0030	0.0396	0.0019	11.2645
R^2	0.8936	0.9657	0.9954	0.9698	0.922	0.9245	0.9308	0.5758
R^2 adjusted	0.8226	0.9428	0.9924	0.9496	0.87	0.8742	0.8846	0.2931
SQE	0.4600	0.1479	0.0192	0.1198	0.2745	0.3077	0.2283	1.7951
RMSE	0.2769	0.157	0.0566	0.1413	0.2139	0.2265	0.1950	0.5470
MPSD	52.542	15.6053	5.0937	11.6371	17.7666	18.1693	15.0662	96.3293
MSE	0.0767	0.0246	0.0032	0.02	0.0457	0.0513	0.038	0.2992
Hybrid	16.5655	2.521	0.3388	1.8317	4.4351	4.7624	3.3081	55.6248
Chi-square	0.6035	0.102	0.0138	0.0768	0.1629	0.1819	0.1382	1.5118
SNE	1.3423	1.1892	1.0847	1.1881	1.2889	1.3043	1.2594	1.6206
	-	-	-	-	-	-	-	-
AICc	10.0762	16.8861	29.1205	18.1497	13.1749	12.4889	14.281	1.9068

Source: Laboratory data (2022)

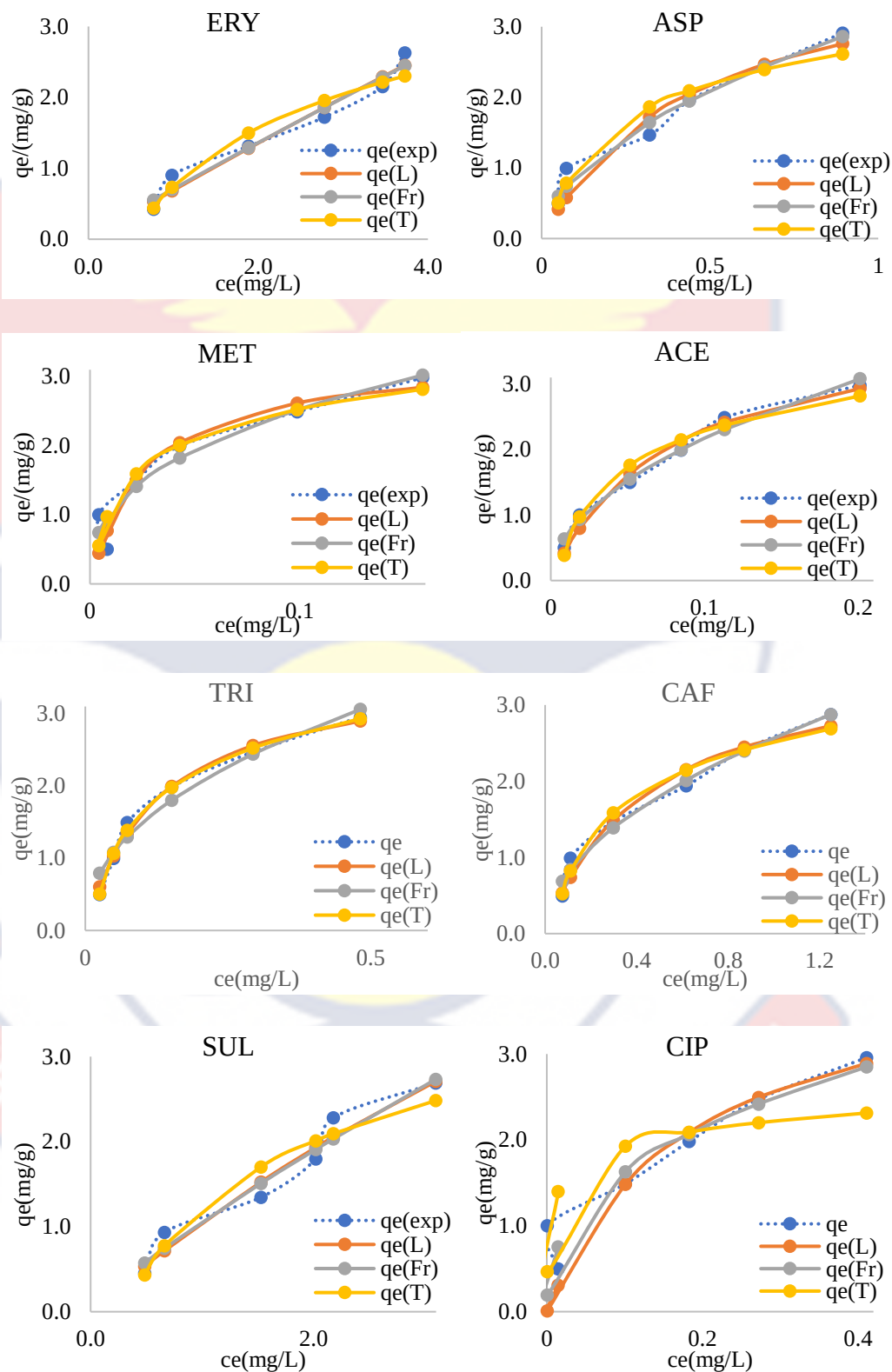


Figure 54: Isotherm Models of PHAs using RH61 Biochar

The positive values of adsorption energy variation b_T means an exothermic adsorption process (Mellah & Harik, 2020). The maximum binding energy K_T was between 1.8917 for ERY and 11264.4627 L/g for CIP. The large heat of adsorption and the maximum binding energy predicted by the Temkin isotherm for some of the PHAs indicate that the PHAs removal by RH61 was a favourable process. RH61 has the lowest affinity for ERY and SUL as they present the lowest K_T values.

Comparing the SNE, R^2 , adjusted R^2 , AICc values from Tables 15, 16, & 17 and the isotherm graphs (Figure 54), and TRI fitted the Temkin isotherm; MET, ACE, SUL, ERY, CAF, ASP and CIP, the Freundlich isotherm.

Isotherm studies of PHAs using RH63 biochar

The result (Table 18) show that the obtained values of R_L (the separation factor) was between 0 and 1 for all the PHAs indicating the adsorption process was very favourable. The q_{max} values were in the range of 2.5722 (CAF) to 5.3950 mg/g (ERY). The highest value of K_L , 22.9393, was obtained for MET and the lowest of 0.1226 L/mg for ERY. The R^2 were above 0.7 for all the PHAs. These values demonstrate that chemical adsorption might play an important role in the adsorption of the PHAs on RH63 biochar. The Langmuir isotherm assumes monolayer adsorption on a uniform surface with identical adsorption sites (Rahman & Nasir, 2020).

Table 18: Langmuir Isotherm Parameters and Best Fit Values for the Removal of the PHAs using RH63

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
q _{exp} (mg/g)	2.9569	2.9710	2.8061	2.7039	2.6017	2.8868	2.4039	2.9392
q _{max} (mg/g)	3.0730	3.3937	2.9192	2.5722	3.4035	3.8459	5.3950	2.9989
K _L (L/mg)	22.9393	20.8407	4.9710	5.5107	0.6255	3.0508	0.1226	22.3690
R _L	0.005-	0.015-	0.039-	0.035-	0.242-	0.062-	0.612-	0.009-
	0.0009	0.003	0.007	0.006	0.051	0.011	0.213	0.001
R ²	0.8398	0.8854	0.7921	0.8785	0.9262	0.9676	0.7679	0.7301
R ² adjusted	0.7330	0.8089	0.6535	0.7975	0.8770	0.9460	0.6131	0.5501
SQE	0.6791	0.4917	0.7834	0.4164	0.2347	0.1316	0.6021	1.1303
RMSE	0.3364	0.2863	0.3613	0.2634	0.1978	0.1481	0.3168	0.4340
MPSD	39.6038	32.6844	42.6868	30.4382	20.5480	14.5164	39.7366	52.4903
MSE	0.1132	0.0820	0.1306	0.0694	0.0391	0.0219	0.1004	0.1884
Hybrid	16.0206	11.1299	18.6350	8.7579	4.6063	2.1490	15.2416	27.2612
Chi-square	2.6937	0.8667	4.5934	0.4953	0.2316	0.0804	2.5109	66.5303
SNE	1.5010		1.5740	1.3286	1.2584	1.1744	1.4724	2.2251
				-	-	-		
AICc	-7.7394	-9.6765	-6.8817	10.6743	14.1139	17.5841	-8.4609	-4.6824

Source: Laboratory data (2022)

The Freundlich constant K_F for the adsorption of PHAs onto RH63 was between 0.7816 and 4.9196 (Table 19). The heterogeneity factor $1/n$, which represent the bond distribution according to Tang et al., (2018) were all less than 1, indicating that the adsorption is facile and favourable. This, also, indicated that physical adsorption might be dominant and existence of heterogeneous high-energy adsorption sites were available.(Conde-Cid et al., 2020).

Table 19: Freundlich Isotherm Parameters and Best Fit Values for the Removal of the PHAs using RH63

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
K_F (mg/g(L/mg) ^{1/n})	3.9318	4.9196	2.3264	1.9391	1.2337	2.9400	0.7816	3.3420
1/n	0.3107	0.3707	0.3017	0.3069	0.5271	0.4534	0.5878	0.2518
R^2	0.9389	0.9068	0.9127	0.9394	0.9546	0.8993	0.8296	0.8206
R^2 adjusted	0.8982	0.8447	0.8545	0.8990	0.9243	0.8321	0.7160	0.7010
SQE	0.2589	0.3996	0.3290	0.2078	0.1444	0.4092	0.4420	0.7513
RMSE	0.2077	0.2581	0.2342	0.1861	0.1552	0.2612	0.2714	0.3539
MPSD	39.7165	42.7054	44.9143	36.7915	23.2428	36.1082	42.9196	67.7550
MSE	0.0431	0.0666	0.0548	0.0346	0.0241	0.0682	0.0737	0.1252
Hybrid	9.3818	11.4906	12.0873	7.7741	3.8321	8.9481	12.9624	27.6415
Chi-square	0.3165	0.3370	0.4442	0.2332	0.1480	0.2819	0.8439	1.2432
SNE	1.2570	1.2939	1.2928	1.2293	1.1852	1.2761	1.3400	1.4445
AICc	13.5261	10.9202	12.0870	14.8457	17.0267	10.7784	10.3155	-7.1329

Source: Laboratory data (2022)

According to the Temkin model, the adsorption sites on the adsorbent have unequal and different adsorption energies as well as different adsorption coefficients. (Gao et al., 2018; Tang et al., 2018). The b_T values (Table 20) which corresponds to the heat of adsorption in the Temkin's model ranged from 2.889 – 9.227 kJ/mol, with the ASP having the least value.

Table 20: Temkin Isotherm Parameters and Best Fit Values for the Removal of PHAs using RH63 Biochar

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
b_T (J/mg)	5395.834	4080.892	6186.162	5403.188	3117.046	2889.372	4695.583	9772.917
K_T (L/mg)	930.2440	387.6271	307.6704	88.4557	5.1827	28.844	7.270	27160.149
R^2	0.8822	0.8892	0.8232	0.9240	0.9272	0.9643	0.6876	0.6209
R^2 adjusted	0.8037	0.8154	0.7054	0.8733	0.8787	0.9405	0.4793	0.3681
SQE	0.4993	0.4751	0.6662	0.2605	0.2316	0.1449	0.8104	1.5875
RMSE	0.2885	0.2814	0.3332	0.2084	0.1965	0.1554	0.3675	0.5144
MPSD	46.7447	41.1500	59.7590	34.9972	19.9888	10.0953	67.0540	102.1867
MSE	0.0832	0.0792	0.1110	0.0434	0.0386	0.0242	0.1351	0.2646
Hybrid	14.8191	12.6262	22.0636	7.9621	4.2400	1.8559	25.7462	58.4886
Chi-square	0.6360	0.5059	0.8342	0.2978	0.1786	0.0725	0.9088	1.4563
SNE	1.3493	1.3394	1.4018	1.2507	1.2444	1.2232	1.4171	1.6098
-	-	-	-	-	-	-	-	-
AICc	9.5845	9.8822	7.8544	13.4873	14.1944	17.0064	6.6789	2.6443

Source: Laboratory data (2022)

From the SNE, R^2 , adjusted R^2 , AICc values in Table 18-20 and Figure 55, ASP data were geared towards Langmuir isotherm. SUL, ERY, MET, ACE, TRI, CAF, and CIP fitted the Freundlich isotherm. The fitting of the PHAs to the different models suggested that there was the formation of monolayer followed by heterogenous layer.

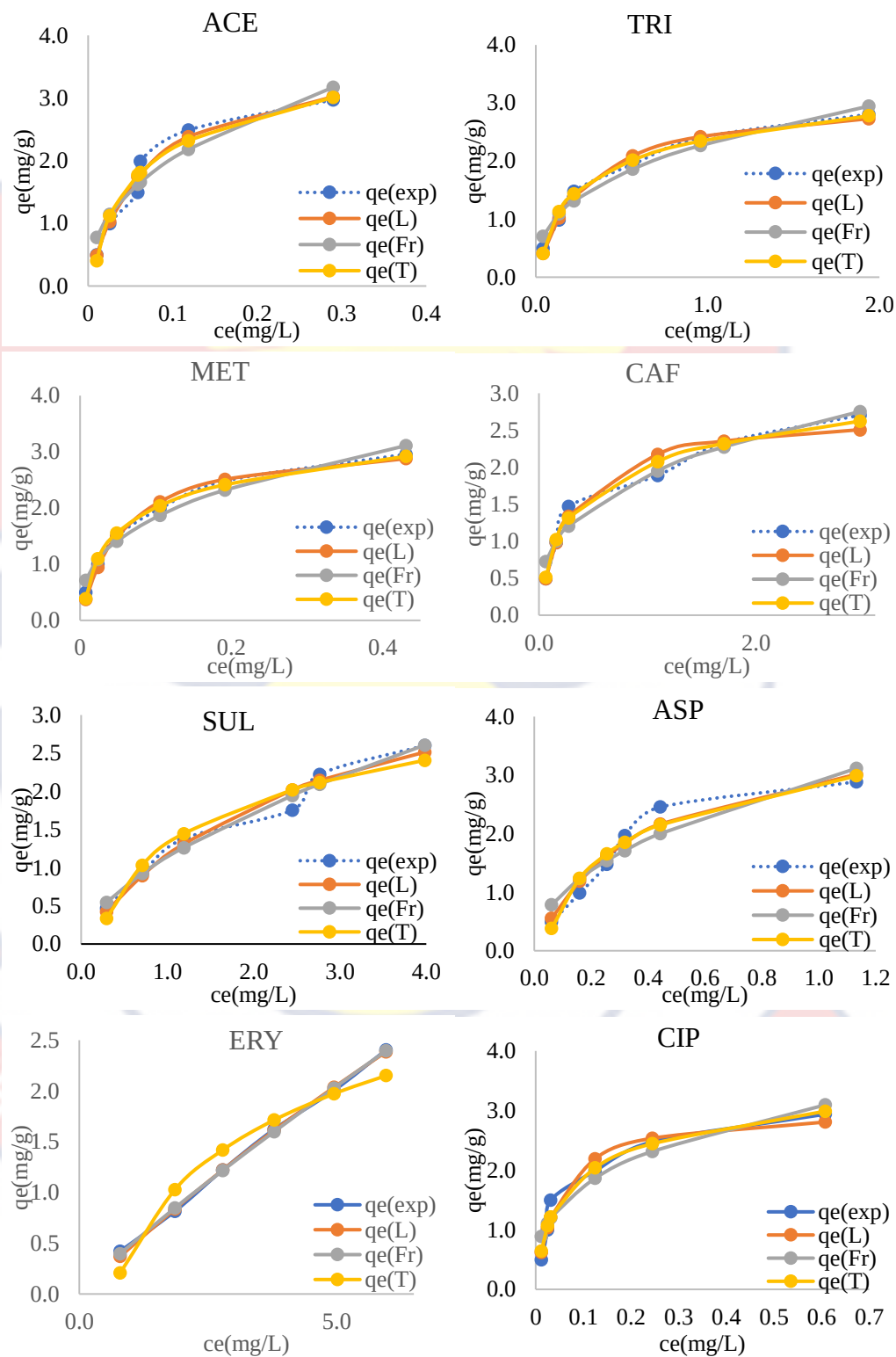


Figure 55: Isotherm Models of PHAs using RH63 Biochar

Isotherm studies of PHAs using CF53 biochar

Parameters obtained for the adsorption of PHAs using CF53 in Table 21, showed the highest $q_{\max}$ value was 3.8224 for ASP and lowest for ERY (1.7127 mg/g). The R_L value was below 1 for all the PHAs indicating that the adsorption of all the PHAs onto the biochar was favourable. The K_L value which expresses the affinity between the adsorbate and adsorbent was highest (13.0770 mg/g) for MET and lowest (0.5586 mg/g) for SUL. Thus, implying that the biochar had the highest affinity for MET.

Table 21: Langmuir Isotherm Parameters and Best Fit Values for the removal of PHAs using CF53

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
$q_{\exp}(\text{mg/g})$	2.9351	2.8299	1.9982	1.8677	1.8128	2.9405	1.9300	2.4947
$q_{\max}(\text{mg/g})$	3.2331	2.9641	1.9785	1.7972	1.9218	3.8224	1.7127	2.3114
$K_L (\text{L/mg})$	13.0770	6.2578	2.5264	0.8060	0.5586	6.2713	4.7260	3.9136
R_L	0.015- 0.003	0.031- 0.005	0.073- 0.013	0.199- 0.040	0.264- 0.056	0.031- 0.005	0.041- 0.007	0.019- 0.008
R^2	0.9394	0.7906	0.3148	0.7725	0.9281	0.9830	0.6310	0.8831
R^2 adjusted	0.8989	0.6510	-0.1420	0.6208	0.8801	0.9716	0.3850	0.8051
SQE	0.2540	0.8096	1.0876	0.2944	0.0888	0.0716	0.5535	0.3326
RMSE	0.2058	0.3673	0.4258	0.2215	0.1216	0.1092	0.3037	0.2355
MPSD	21.2755	47.4589	55.7514	29.9713	15.9186	10.1198	45.5950	22.5980
MSE	0.0423	0.1349	0.1813	0.0491	0.0148	0.0119	0.0922	0.0554
Hybrid	5.2195	20.6033	28.1271	7.4241	2.1753	1.1133	15.3963	5.8974
Chi-square	0.2594	4.0524	42.1006	0.3484	0.0963	0.0462	0.7048	0.2431
SNE	1.2811	1.5472	2.2901	1.2782	1.1569	1.1336	1.3740	1.2993
	-	-	-	-	-	-	-	-
AICc	13.6389	6.6844	4.9131	12.7546	19.9464	21.2364	8.9665	12.0214

Source: Laboratory data (2022)

The adsorption parameters and best fit values for the Freundlich isotherm model obtained using the CF53 biochar in the removal of the PHAs are displayed

in Table 22. According to Luconi et al. (2022), when the empirical parameter ($1/n$) which is related to the adsorption force of the adsorbent is less than 0.5, it means substances are more easily adsorbed. However, when the value is greater than 2, it indicates the difficulty of the adsorption. The values of $1/n$ were below 0.5 for all the PHAs, indicating that the biochar CF53 has a strong affinity for all the PHAs. The K_F value gives an approximate measure of the adsorption capacity of the adsorbent; the higher the value is, the greater the capacity. The K_F values ranged from 0.7148 to 3.9532, the highest value observed for ASP which implied that the CF53 biochar had a greater affinity for ASP.

Table 22: Freundlich Isotherm Parameters and Best Fit Values for the Removal of PHAs using CF53 Biochar

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
K_F (mg/g(L/mg) ^{1/n})	3.6209	2.5096	1.3635	0.7518	0.7148	3.9532	1.1185	1.5496
$1/n$	0.3402	0.2797	0.1433	0.3511	0.3705	0.4384	0.2260	0.3016
R^2	0.9119	0.9332	0.6243	0.8749	0.9476	0.9286	0.8315	0.9810
R^2 adjusted	0.8532	0.8886	0.3738	0.7915	0.9126	0.8811	0.7192	0.9684
SQE	0.3690	0.2584	0.5964	0.1618	0.0647	0.3000	0.2527	0.0540
RMSE	0.2480	0.2075	0.3153	0.1642	0.1039	0.2236	0.2052	0.0948
MPSD	38.3514	34.6505	68.4561	28.7281	22.4698	25.7071	35.8103	16.1361
MSE	0.0615	0.0431	0.0994	0.0270	0.0108	0.0500	0.0421	0.0090
Hybrid	9.3892	7.8565	24.8995	5.2899	2.6753	5.4863	8.2968	1.7199
Chi-square	0.2715	0.2854	0.6158	0.2316	0.0950	0.1953	0.3228	0.0661
SNE	1.2696	1.2497	1.3875	1.2045	1.1313	1.2433	1.2547	1.1205
-	-	-	-	-	-	-	-	-
AICc	11.3993	13.5368	7.1481	16.3443	21.8440	12.6406	13.6696	22.9351

Source: Laboratory data (2022)

From Table 23, the heat of adsorption b_T for CF53 in the removal of the PHAs was between 3.197 and 17.376 kJ/mg. The Temkin constant K_T which

corresponds to the optimum binding energy (Musah et al., 2022) of the PHAs ranged from 5.7221 to 24432 L/mg.

Table 23: Temkin Isotherm Parameters and Best Fit Values for the Removal of PHAs using CF53

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
$b_T(\text{J/mg})10^3$	4.0084	6.1609	17.3770	7.0021	6.0758	3.1978	10.1532	6.1246
K_T								
$(\text{L/mg})10^3$	0.1870	0.4324	24.4327	0.0100	0.0057	0.0756	0.1541	0.0674
R^2	0.9501	0.8864	0.5279	0.8313	0.9522	0.9592	0.7774	0.9641
R^2 adjusted	0.9168	0.8106	0.2131	0.7188	0.9203	0.9319	0.629	0.9402
SQE	0.2091	0.4393	0.7494	0.2183	0.059	0.1717	0.3339	0.1020
RMSE	0.1867	0.2706	0.3534	0.1907	0.0992	0.1692	0.2359	0.1304
MPSD	20.4165	38.4626	80.7731	30.9004	15.9205	21.9355	41.739	11.2873
MSE	0.0349	0.0732	0.1249	0.0364	0.0098	0.0286	0.0557	0.0170
Hybrid	4.1582	11.3329	33.3003	6.4622	1.7502	3.8724	11.0335	1.7376
Chi-square	0.1594	0.4827	0.6636	0.266	0.0735	0.1745	0.3908	0.0666
SNE	1.2326	1.3276	1.4357	1.2322	1.1251	1.2013	1.2887	1.1819
-	-	-	-	-	-	-	-	-
AICc	14.8056	10.352	10.352	14.5485	22.399	15.988	11.9986	19.1116

Source: Laboratory data (2022)

Comparing the R^2 , adjusted R^2 , AICc, SNE values in Table 21-23, and Figure 56, MET and SUL data best fitted Temkin isotherm, and ASP, Langmuir, and ERY, ACE, CIP, TRI and CAF fitted the Freundlich isotherm model.

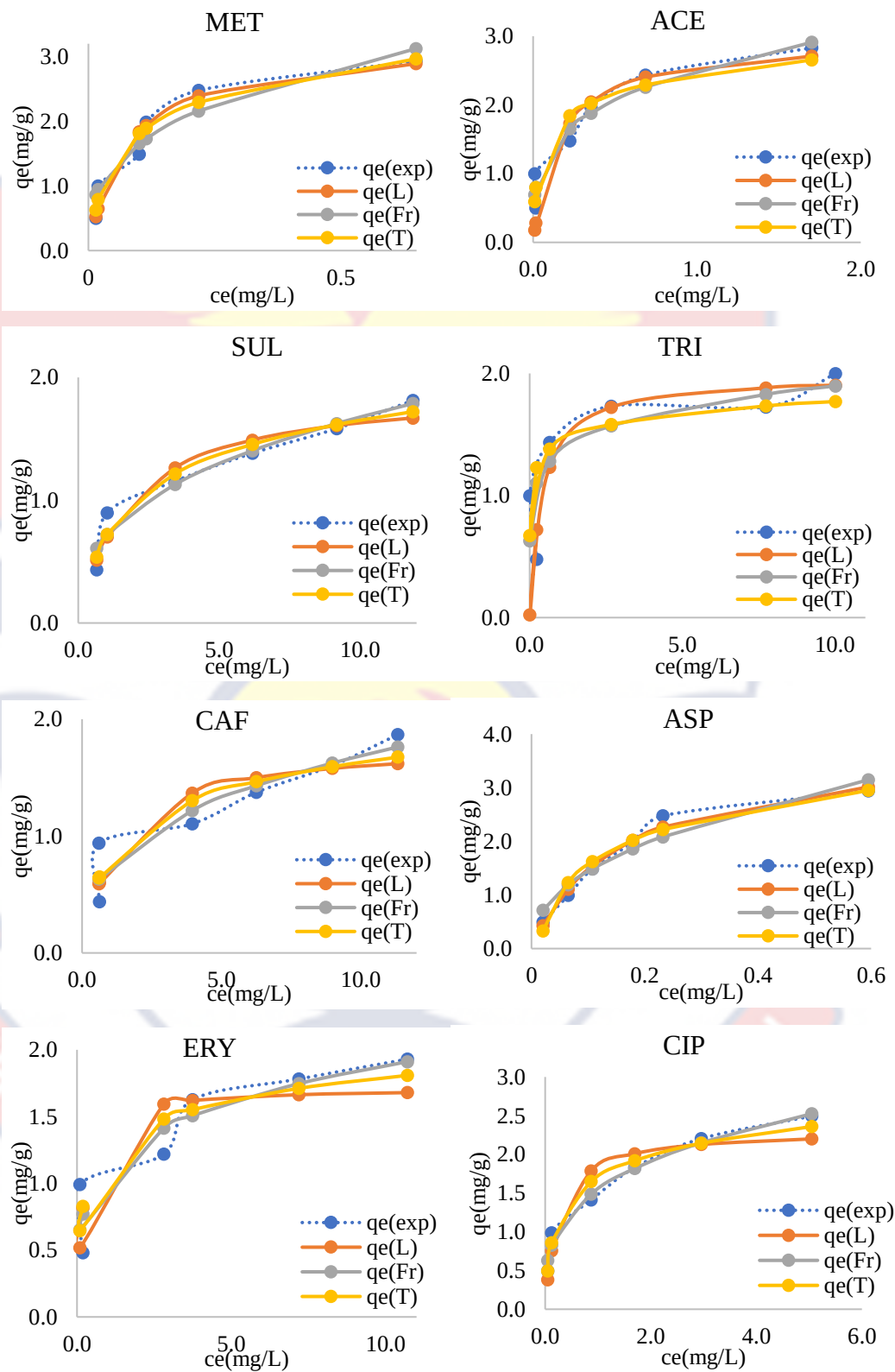


Figure 56: Isotherm Models of PHAs using CF53 Biochar

Isotherm studies of PHAs using CF61 biochar

The maximum adsorption capacity of the PHAs ranged between 2.2399 in ERY to 35.0112 mg/g in SUL (24). The Langmuir constant K_L was between 0.0086 to 38.5989 L/mg. The biochar, CF61, has reasonable affinity for the PHAs. The Langmuir separation factor, R_L was below one for all the PHAs, indicating a favourable adsorption process (Ayawei et al., 2017).

Table 24: Langmuir Isotherm Parameters and Best-Fit Values for the Removal of PHAs using CF61 Biochar

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
$q_{exp}(mg/g)$	2.9168	2.9452	2.4337	2.3122	2.2327	2.9407	2.4828	2.7351
$q_{max}(mg\ g^{-1})$	2.8106	2.9258	2.4113	2.3090	35.0112	3.9502	2.2399	3.9459
$K_L\ (L\ mg^{-1})$	17.2209	38.5989	1.8968	0.9810	0.0086	4.7736	4.1004	0.6646
R_L	0.011- 0.002	0.005- 0.001	0.095- 0.017	0.169- 0.033	0.958- 0.795	0.040- 0.007	0.047- 0.008	0.231- 0.048
R^2	0.8501	0.9249	0.5602	0.8851	0.9364	0.9965	0.8539	0.8027
R^2 adjusted	0.7502	0.8748	0.2669	0.8085	0.8940	0.9942	0.7566	0.6711
SQE	0.6153	0.3170	1.1152	0.2532	0.1509	0.0145	0.3858	0.6889
RMSE	0.3202	0.2299	0.4311	0.2054	0.1586	0.0491	0.2536	0.3388
MPSD	36.7392	26.5713	51.3245	21.0672	18.7963	3.6635	30.3543	46.1685
MSE	0.1025	0.0528	0.1859	0.0422	0.0252	0.0024	0.0643	0.1148
Hybrid	13.2354	7.1062	26.5623	4.6110	3.4668	0.2082	7.9916	17.6636
Chi-square	1.1122	0.4938	65.7475	0.1875	0.1686	0.0082	0.3391	1.6187
SNE	1.4188	1.3086	2.8323	1.2515	1.2112	1.0771	1.2976	1.4424
-	-	-	-	-	-	-	-	-
AICc	8.3316	12.3105	4.7632	13.6584	8.4691	30.8352	11.1324	7.6532

Source: Laboratory data (2022)

The experimental data were fitted into the Freundlich isotherm and its parameters obtained in Table 25 using CF61 biochar. The Freundlich exponent ($1/n$) which expresses the favourability of adsorption were all below 1. The

Freundlich model generally describes physio-sorption heterogeneously occurring at the surface of the biochar with different affinities.

Table 25: Freundlich Isotherm Parameters and Best Fit Values for the Removal of the PHAs using CF61

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
K_F (mg/g(L/mg) ^{1/n})	3.1109	3.6907	1.5136	1.0233	0.3309	3.9852	1.4732	1.6107
1/n	0.3132	0.2698	0.2237	0.3804	0.9171	0.5001	0.2734	0.4648
R ²	0.9333	0.9169	0.7318	0.9090	0.9392	0.9771	0.8918	0.9131
R ² adjusted	0.8888	0.8614	0.5529	0.8484	0.8987	0.9619	0.8197	0.8551
SQE	0.2739	0.3509	0.6801	0.2005	0.1442	0.0959	0.2857	0.3035
RMSE	0.2137	0.2418	0.3367	0.1828	0.1550	0.1264	0.2182	0.2249
MPSD	41.9191	45.9625	62.6558	27.4657	18.6889	21.5351	36.2810	21.7414
MSE	0.0456	0.0585	0.1133	0.0334	0.0240	0.0160	0.0476	0.0506
Hybrid	10.1870	11.7674	23.8398	5.2269	3.2608	2.7798	8.3968	5.7678
Chi-square	0.3077	0.2830	1.1092	0.1829	0.1451	0.0872	0.2669	0.2523
SNE	1.2631	1.2763	1.4162	1.2121	1.1995	1.1442	1.2540	1.3035
-	-	-	-	-	-	-	-	-
AICc	13.1874	11.7006	7.7305	15.0598	16.7637	19.4846	12.9346	12.5709

Source: Laboratory data (2022)

The Temkin constant, b_T , which corresponds to the heat of adsorption was in the range 2718 to 13128 J/mol. The Temkin equilibrium constant, K_T , which correspond to the maximum binding energy ranged from 1.1128 for SUL to 6287 L/mg for TRI. The CF61 biochar had the strongest affinity for TRI as it had the highest K_T . Also, the high b_T values obtained show that the adsorption is a favourable process and might occur through chemical bonding and adsorption was exothermic because b_T was greater than one (Jang & Kan, 2019).

Table 26: Temkin Isotherm Parameters and Best Fit Values for the Removal of PHAs using CF61 Biochar

Parameters	MET	ACE	TRI	CAF	SUL	ASP	ERY	CIP
$b_T(\text{kJ/mg})$	5.2222	4.9732	13.1281	5.0957	2.7188	2.9552	6.4680	4.7536
$K_T(\text{L/mg})$	371.0111	742.2801	6287.8957	10.0448	1.1128	51.9086	66.5691	32.1341
B_T	0.4794	0.5034	0.1907	0.4913	0.9209	0.8472	0.3871	0.5267
R^2	0.9706	0.9531	0.9503	0.9075	0.8861	0.9918	0.8880	0.8482
R^2 adjusted	0.9509	0.9218	0.9171	0.8458	0.8101	0.9864	0.8133	0.7469
SQE	0.1235	0.1980	0.1288	0.2039	0.2704	0.0342	0.2959	0.5301
RMSE	0.1435	0.1817	0.1465	0.1843	0.2123	0.0755	0.2221	0.2972
MPSD	20.0228	32.5443	13.1185	21.1677	19.8065	10.7776	33.3790	22.9754
MSE	0.0206	0.0330	0.0215	0.0340	0.0451	0.0057	0.0493	0.0884
Hybrid	2.9175	6.6020	2.1992	4.0609	4.8776	0.8173	7.7063	7.9790
Chi-square	0.1007	0.2384	0.0963	0.1571	0.1811	0.0365	0.2673	0.2754
SNE	1.1651	1.2229	1.1976	1.2192	1.2821	1.0899	1.2559	1.3991
-	-	-	-	-	-	-	-	-
AICc	10.4015	15.1339	17.7164	14.9594	13.2644	25.6759	12.7237	9.2251

Source: Laboratory data (2022)

Comparing the SNE, the adjusted R , R^2 , AICc, in Tables 24-26, and the graphical presentations of the isotherms (Figure 57), MET and TRI, fit Temkin, ACE and ASP fit Langmuir and the rest, CAF, SUL, ERY, and CIP, the Freundlich isotherm model. This suggests that the adsorption of the PHAs onto the surface of the CF61 biochar was driven by mixed mechanisms involving chemical and physical forces.

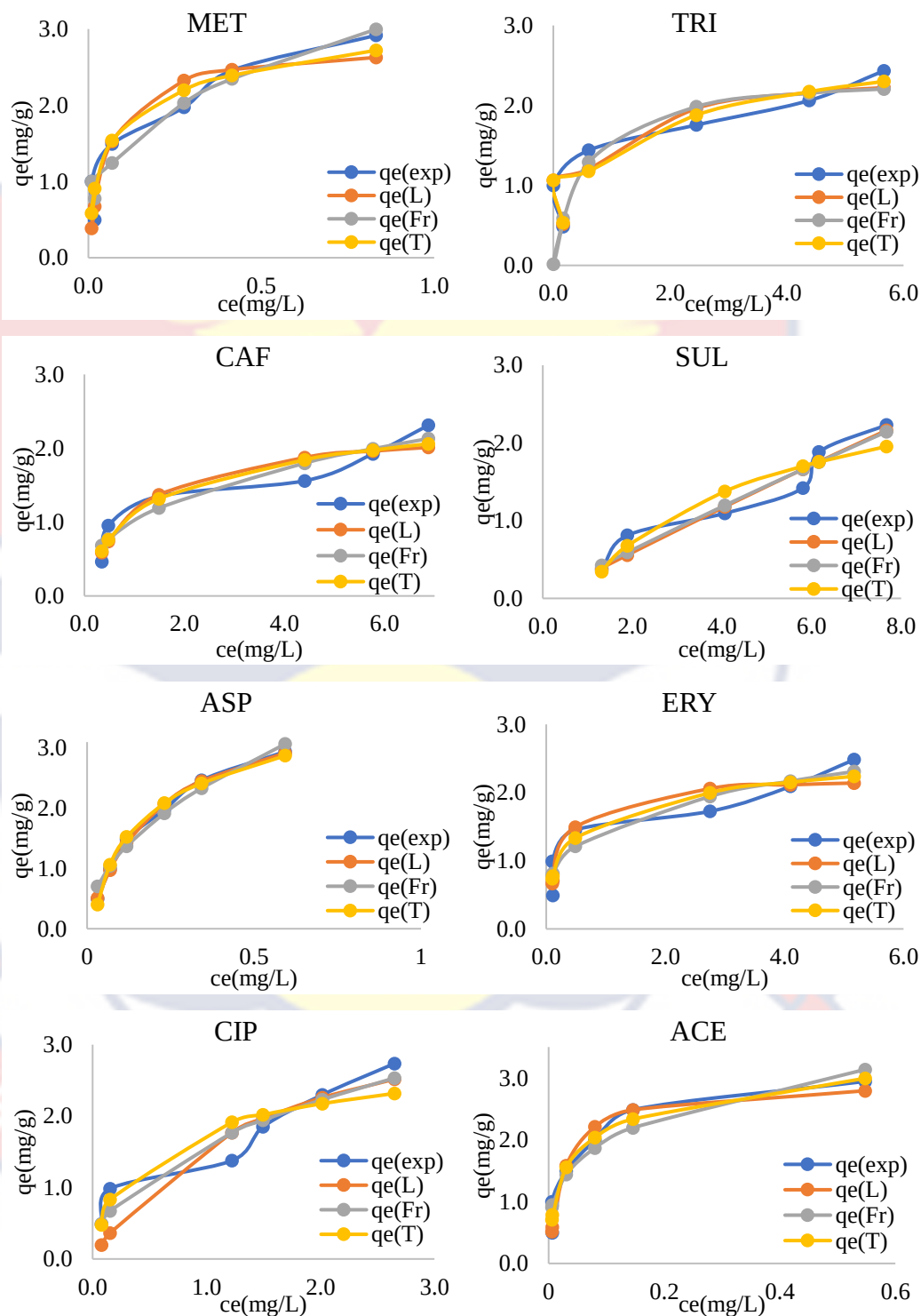


Figure 57: Isotherm Models of PHAs using CF61 Biochar

From the isotherm study using the Temkin, Langmuir and Freundlich models, it can be concluded that the adsorption of the eight pharmaceuticals onto

the five biochars were all favourable. PHAs adsorption data fitted different models on the same biochar which indicated that both physical and chemical adsorption may be occurring on the same biochar. However, according to the models the RHBs showed less affinity for SUL and ERY.

Thermodynamic Studies

The effect of temperature on the adsorption of the PHAs were conducted at 298, 308 and 323 K. The parameters of the thermodynamic studies were calculated based on the van't Hoff equation. The standard Gibb's free energy change (KJ/mol) was determined using equation $(-RT \ln K_c)$ whilst the standard enthalpy change ΔH° (KJ/mol) and the standard entropy change ΔS° (KJ/mol) were determined from the gradient and the intercept respectively of the Van't Hoff thermodynamic plots of $\ln K_c$ versus $1/T$ as reported by Ajala et al. (2023), Faisal et al. (2020), Nguyen et al. (2020), and Pandiarajan et al. (2017). A positive value for change in enthalpy (ΔH°) implied the adsorption process is endothermic whilst a negative value for change in internal energy (ΔG°) shows that the adsorption of the PHAs onto the selected biochars was spontaneous and thermodynamically feasible (Sekulic et al., 2019; Yang et al., 2018). Positive values of the change in entropy (ΔS°) shows the randomness of the solid and liquid interface during the adsorption of PHAs on the adsorbents (Bachmann et al., 2021).

The thermodynamic parameters for the adsorption of PHAs on CF53 are shown in Table 27. From the Table 27, the positive ΔG° values for SUL was an indication that the adsorption of SUL was not spontaneous at all temperatures. On the other hand, the ΔG° values for the rest of the PHA were negative implying the

adsorption was spontaneous for most of the PHAs. However, the ΔG° value increased with increasing temperature indicating that the spontaneity reduced with a rise in temperature (Biswas et al., 2019; Pandiarajan et al., 2017).

Table 27: Thermodynamic Parameters of PHAs using CF53 Biochar

CF53	T/K	Kc	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol)
ACE	298	98.8522	-11.3868	-95.4296	-283.4949
	308	15.6263	-7.0427		
	323	8.9043	-5.7836		
MET	298	51.9793	-9.7934	-49.7279	-134.6637
	308	20.7621	-7.7708		
	323	14.8139	-7.1300		
TRI	298	217.2252	-13.3384	-213.4324	-677.6359
	308	1.2003	-0.4677		
	323	1.0210	-0.0551		
CAF	298	1.5442	-1.0770	-50.3852	-166.3947
	308	0.5492	-1.5355		
	323	0.4338	-2.2090		
CIP	298	7.9745	-5.1466	-129.7525	-416.4484
	308	2.5198	-2.3677		
	323	0.2934	-3.2436		
SUL	298	0.8726	0.3378	-39.7066	-134.1726
	308	0.5458	1.5513		
	323	0.3184	3.0269		
ASP	298	15.2744	-6.7577	-162.1368	-516.5093
	308	10.1079	-5.9266		
	323	0.2410	-3.7641		
ERY	298	10.8175	-5.9025	-90.6650	-286.8643
	308	1.2794	-0.6313		
	323	1.1081	-0.2714		

Source: Laboratory data (2022)

The adsorption process was exothermic for all the PHAs according to the ΔH° with the adsorption mostly physical as ΔH° values were less than 10 (Sekulic et al., 2019). Also, the negative ΔH° values suggest that the physical bond weakens

at higher temperatures. Negative values of ΔS° were obtained for all the PHAs suggesting that there was reduced randomness as PHAs were adsorbed onto the surface of the CF53 biochar suggesting that the adsorption was enthalpy driven (Fountouli & Chrysikopoulos, 2018; Kgomo et al., 2022). The negative values obtained for ΔS° implied that the adsorption process involved an associative mechanism with the formation of more than one layer of adsorption emphasizing chemisorption (Maszkowska et al., 2014; Tran et al., 2016). According to Hagos et al. (2022), negative values could indicate that the adsorption process was controlled by complexation and electrostatic adsorption. The thermodynamic parameters obtained for CF61 (Appendix D) biochar followed the same pattern as CF53. The adsorption was exothermic and spontaneous for all PHAs except for SUL.

For the rice husk (RH) biochars, adsorption of the PHAs onto RH63 was exothermic, spontaneous and less random as all the parameters had negative values (Table 28). The biochar RH53 on the other hand (Appendix D), had the adsorption of PHAs being spontaneous, endothermic (except for MET and ASP) and an increase in randomness at the solid liquid interphase (except MET and ASP). Whilst the adsorption of PHAs onto RH61 (Appendix D) was enthalpy driven (except for CIP and TRI), spontaneous (except for ERY) and exothermic (except for TRI).

Table 28: Thermodynamic Parameters of PHAs using RH63 Biochar

PHA	T/K	Kc	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol)
ACE	298	145.0579	-12.3374	-80.2708	-222.0250
	308	434.8623	-15.5640		
	323	18.0736	-7.6561		
MET	298	289.2267	-14.0480	-107.9150	-316.5728
	308	37.0417	-9.2539		
	323	19.0014	-7.7885		
TRI	298	88.0578	-11.1001	-48.0754	-124.2093
	308	43.6896	-9.6768		
	323	26.0588	-8.6240		
CAF	298	20.3178	-7.4650	-39.5485	-105.2772
	308	28.6130	-8.5925		
	323	7.3135	-5.2630		
CIP	298	4566.1100	-20.8876	-65.1817	-154.2607
	308	237.7744	-14.0173		
	323	915.3994	-18.0379		
SUL	298	2.7449	-2.5030	-40.2852	-127.3801
	308	1.2708	-0.6139		
	323	0.9934	-0.0174		
ASP	298	9.0102	-5.4493	-7.0164	-38.7230
	308	3.1623	-2.9496		
	323	11.0364	-6.3514		
ERY	298	2.7487	-2.5064	-31.2731	-98.4072
	308	0.8978	-0.2761		
	323	1.2631	-0.6178		

Source: Laboratory data (2022)

In summary, the adsorption of the PHAs onto the selected biochars was spontaneous and exothermic suggesting that the adsorption process was thermodynamically feasible and also energy sustainable process. Adsorption of the PHAs involved an associative mechanism with the formation of more than one layer of adsorption emphasizing chemisorption (Maszkowska et al., 2014; Tran et al., 2016).

FTIR Analysis of the Selected Biochars

The coconut fibre biochars (CFBs)

The FTIR spectrum of CF61 and CF53 (Figures 58 and 59) showed the presence of several functional groups. The peak around 750-900 cm^{-1} corresponds to the presence of aromatic C-H. The peak at 1217 cm^{-1} represented aromatic C-O and phenolic hydroxyl stretching (Binh & Kajitvichyanukul, 2019), 1434 cm^{-1} was assigned to COOH and CHO stretching. 1227 cm^{-1} may represents O-H of phenolic compounds (Suman & Gautam, 2019) as well as for C-O stretching vibrations of esters, ethers and alcohols.

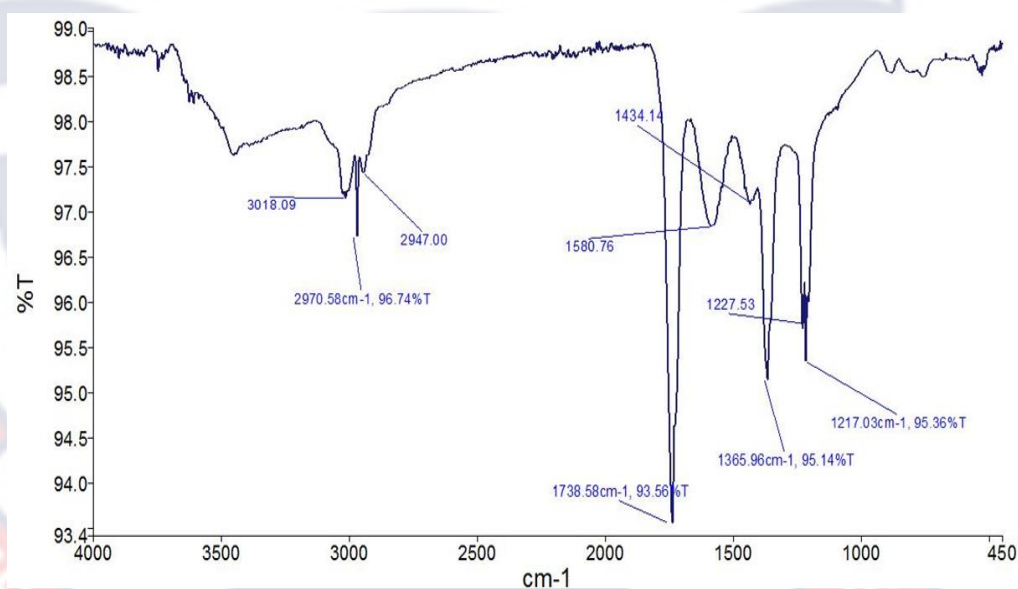


Figure 58: FTIR Spectrum of CF53 Biochar before Adsorption

The peak at 1365 cm^{-1} was ascribed to C-H/C-C stretching(CH_3) (Nguyen et al., 2020), 1580 cm^{-1} to C=C stretching vibrations in aromatic rings or other conjugated systems (Huiqin Li et al., 2020) and at 1738 cm^{-1} to carbonyl group C=O stretching vibrations which indicates the presence of carboxylic acid, esters ketones and aldehydes (Binh & Kajitvichyanukul, 2019; Tejedor et al., 2023).

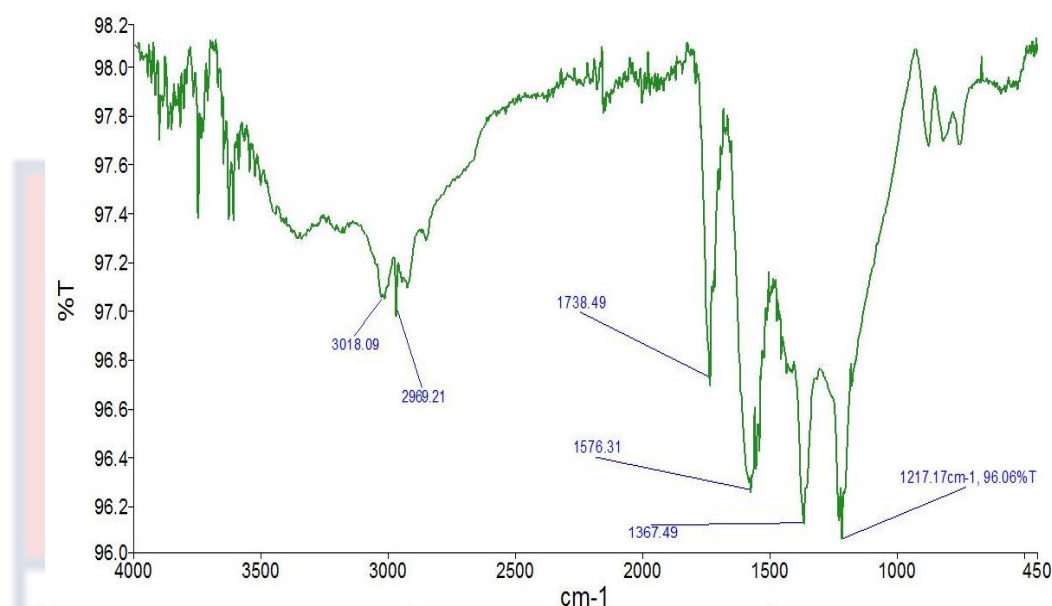


Figure 59: FTIR Spectrum of CF61 Biochar before Adsorption

The band at 2947-3018 cm^{-1} represent C-H stretching of aliphatic CH_x (Ahmadfazeli et al., 2021; Castilla-Caballero et al., 2020). Band around 3500 cm^{-1} indicate the presence of OH groups which may be found in carboxylic, phenols or absorbed water. The biochar contains oxygen containing functional groups which might play a major role in the adsorption of aromatic contaminants through π - π interaction and hydrogen bonding (Binh & Kajitvichyanukul, 2019). The two biochars contain the same functional groups which are C-O stretching of hydroxyl and alcohol, carbonyl and alkyl groups but with varying intensities.

FTIR spectra of rice husk biochars

The FTIR spectra of the rice husk biochars; RH53, RH6, and RH63 as shown in Figure 60, 61, and 62 contained several functional groups. These are Si-H found at 794 cm^{-1} (Shen & Zhang, 2019), an intense peak around 1078-1094 cm^{-1} corresponding also to Si-O-Si (Hossain et al., 2020; Mohadi et al., 2021), peaks

at 1216, 1365, 1434, 1738 cm^{-1} represent aromatic-O and phenolic hydroxyl stretching, C-H/C-C stretching, CHO stretching and C=O stretching respectively.

Peaks around 2949, 2971 and 3015 cm^{-1} which were in found RH53 and RH63

indicate the presence of C-H stretching of aliphatic CH_x .

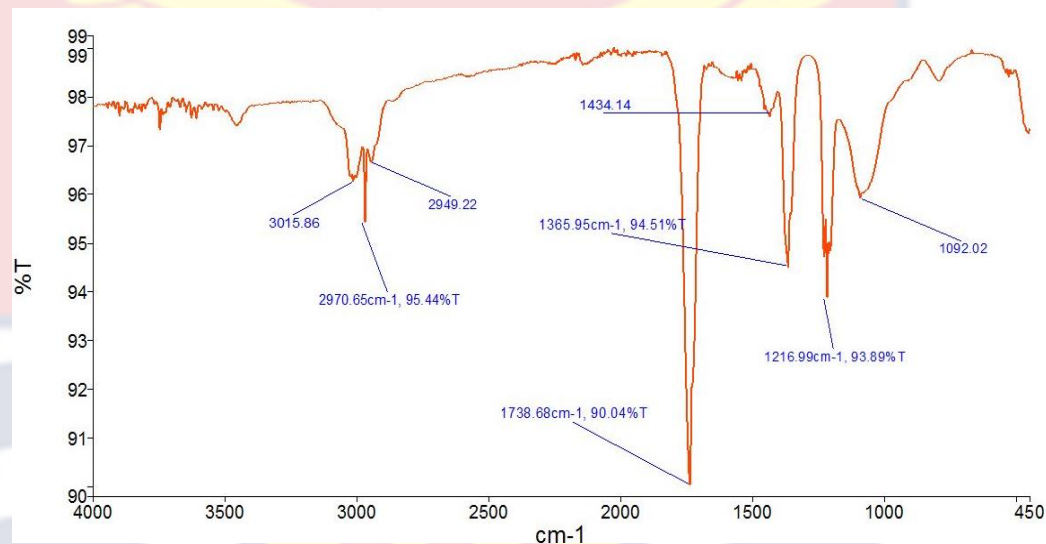


Figure 60: FTIR Spectrum of RH53 Biochar before Adsorption

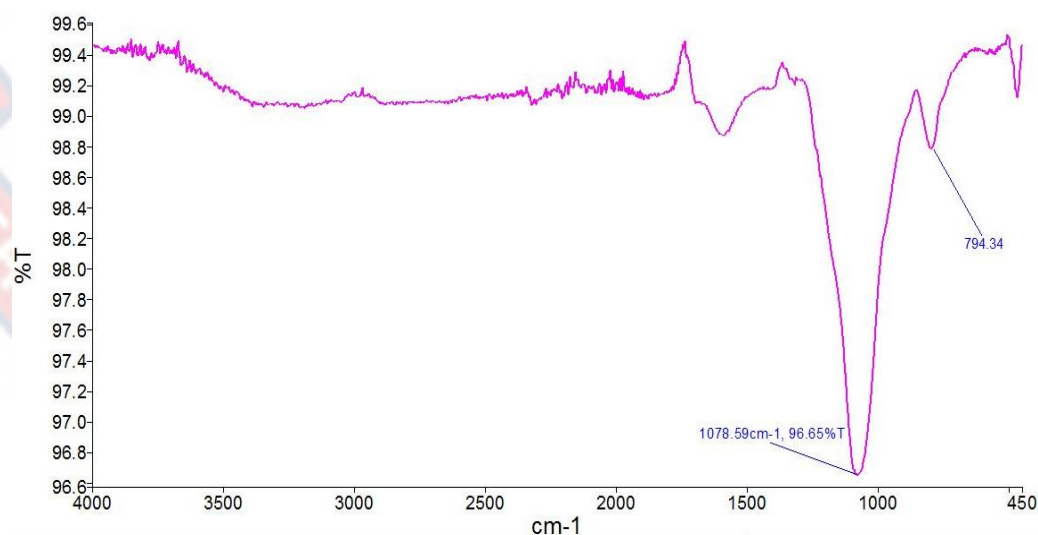


Figure 61: FTIR Spectrum of RH61 Biochar before Adsorption

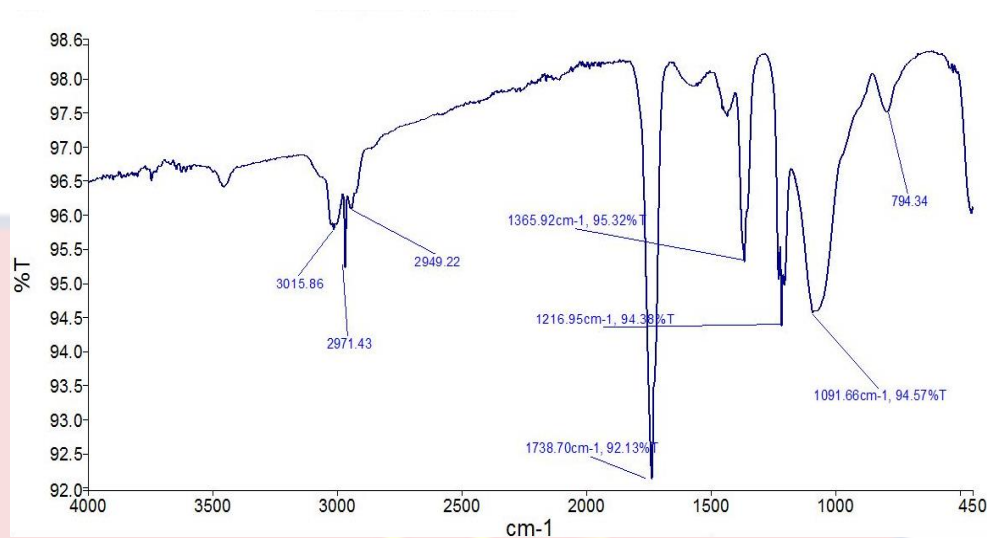


Figure 62: FTIR Spectrum of RH63 Biochar before Adsorption

Mechanism of Adsorption

Mechanism of adsorption onto CF53 biochar

CF53 biochar was made from coconut fibre pyrolyzed at 500°C with residence time of 3 hours. The FTIR spectrum of CF53 biochar before the adsorption process in Figure 58 showed the presence of various functional groups such as O-H, C-O, C=O, C=C, C-H indicating the presence phenolic hydroxyl groups, carbonyl, and aromatic hydrocarbons.

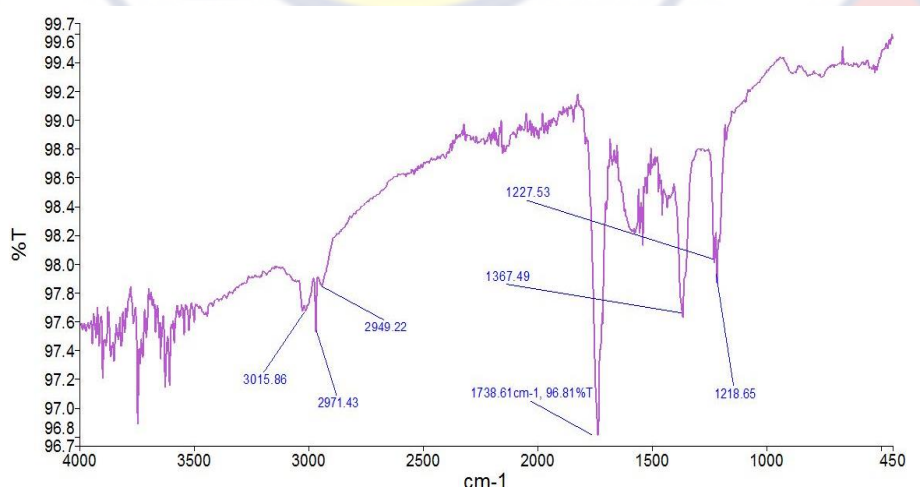


Figure 63: FTIR Spectrum of CF53 Biochar after Adsorption

After adsorption, there were changes in the FTIR spectrum (Figure 63) which indicated that there was interaction between the pharmaceuticals and the functional groups on the surface of the CF53 biochar. There was a change in intensity and the position of the O-H peak suggesting that there was hydrogen bonding between the PHAs and the biochar. Hydrogen bonding can occur between the surface hydrogens of the hydroxyl groups on the surface of the biochar and the appropriate atoms such as oxygen, nitrogen, hydrogen of the PHAs and also between the hydroxyl group on the surface of the biochar and the aromatic ring of the PHAs (Nguyen et al., 2020). ACE, ASP, ERY, TRI have functional groups of hydroxyl, amide and carboxylic acid that can form hydrogen bonds with the carbonyl or hydroxyl groups on the surface of the biochar (Binh & Kajitvichyanukul, 2019; Igwegbe et al., 2021). The change in the intensity and position of C-H stretching of aliphatic hydrocarbons around $2946.22 - 3015.86 \text{ cm}^{-1}$ confirm their interaction with the biochar. This may be as a result of possible π - π interaction (π - π electron donor-acceptor interaction) bonding between the π -electrons of the biochar (donor) and the π -electrons of the aromatic rings of the pharmaceuticals (acceptor) such as CAF, ACE, and ERY (Keerthanan et al., 2020).

Also, alkyl groups in biochar possess hydrophobic properties hence might form hydrophobic bond with the alkyl groups in the PHAs (Binh & Kajitvichyanukul, 2019). The C=O peak at 1738.58 cm^{-1} showed no significant shift but rather a change in intensity suggesting n- π interaction between aromatic rings of phenol (ACE) and the carbonyl oxygen of the biochar. In such a mechanism, the carbonyl oxygen on the surface of the biochar serves as an electron

donor and the aromatic rings of phenol the electron acceptor (Nguyen et al., 2020). The intensity of peaks at 1580.76 and 1227.53 cm^{-1} showed that these sites were involved in the adsorption process and these are associated with C=C stretching due to the interactions of π - π interaction between the aromatic rings of the PHAs and the aromatic rings of the biochar. There was a change in the pH of the solution from 9.35 to 8.23 indicating the possibility of protonation and deprotonation of PHAs like MET, CIP, and SUL which might undergo ionization and interact with charged sites on the biochar through acid-base interactions or ion exchange. Biochar is a porous surface therefore there was a possibility of physical adsorption of the PHAs into the pores of the biochar as indicated by the result from the IPD modelling. Therefore, the mechanisms of the PHAs onto the CF53 biochar include π - π interactions, electrostatic interactions, hydrogen bonding and likelihood of Van der Waals interactions.

Mechanism of adsorption of PHAs onto the CF61 biochar

There were several shifts in the FTIR of the CF61 after adsorption of the PHAs (Figure 64). The peak at 3018.09 cm^{-1} which represent the C-H shifted to 3015.86 cm^{-1} indicating that the alkyl groups were involved in hydrophobic bonding as well as π - π interactions with the PHAs. There was also a shift from 1738.49 to 1736.26 cm^{-1} as well as change in intensity which indicated that C=O functional groups were involved in the reaction. n - π interaction between aromatic rings of phenol and the carbonyl oxygen of the biochar might have occurred (Nguyen et al., 2020).

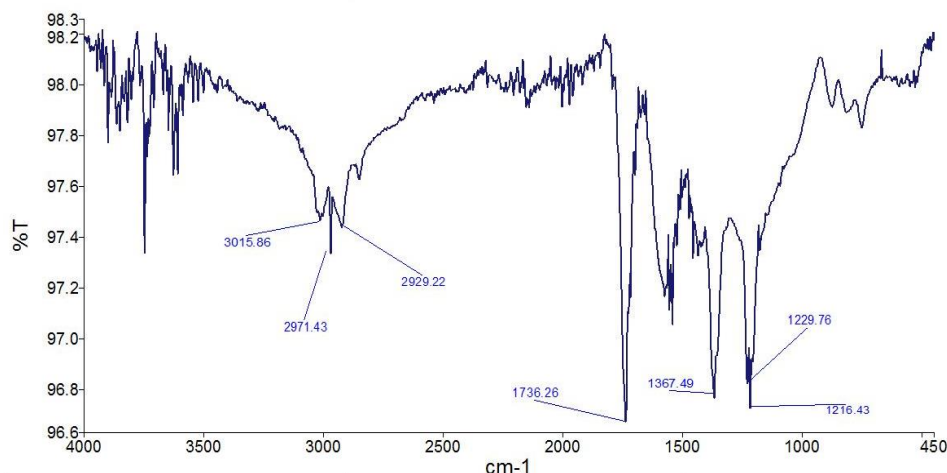


Figure 64: FTIR Spectrum of CF61 Biochar after Adsorption

Also, there is a likelihood of hydrogen bonding. The change in intensity of peak around 1600 cm^{-1} , which represent aromatic $\text{C}=\text{C}$ stretching suggested that π - π interactions between the aromatic rings of the PHAs and the biochar. The diminishing of peaks at around 1200 - 1738 cm^{-1} might be the due to surface complexation or chemical reactions between the PHAs and the biochar. There was change in the pH of the solution from 10.37 to 9.54 which indicated the release of hydrogen ions resulting in ion exchange or electrostatic interactions between biochar and the PHAs.

Mechanism of adsorption of PHAs onto RH53 biochar

Functional groups such as Si-O-Si , C=O and C-H were found on the FTIR spectrum of RH53 biochar before adsorption of PHA, After the adsorption process, certain changes were observed on the spectrum in Figure 65. There was a shift in the position of the C-H stretch from 3015.86 to 3018.09 cm^{-1} as well as from 2970.65 to 2971.43 cm^{-1} which might indicate π - π interactions between the aromatic compound in the PHAs and the aromatic structure of the biochar as all the

PHAs contained aromatic rings (Li et al., 2019). Hydrophobic interactions might also be occurring.

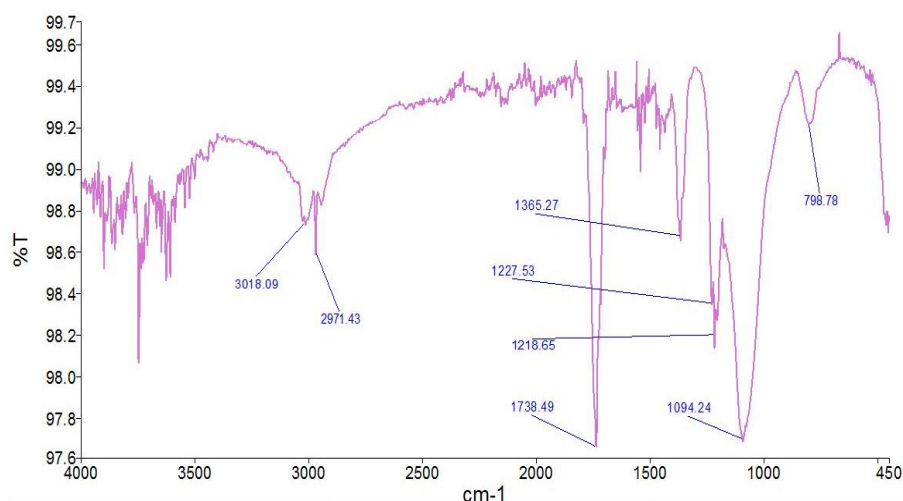


Figure 65: FTIR Spectrum of RH53 Biochar after Adsorption

A minimal shift was also observed in the C=O peak but with an increase in intensity which indicated that the concentration of C=O had reduced because it was utilized in the adsorption process such as through hydrogen bonding. Notable change in intensities and shifts around 1200 to 1400 cm^{-1} might be as a result of hydrogen bonding or electrostatic interactions of C-O, phenolic hydroxide groups on the biochar with the PHAs. There was also a shift in the Si-O-Si peak at 1092.02 to 1094.24 cm^{-1} with a change in its intensity as that of the one found at 798.78 cm^{-1} . The change in intensities of the Si-O-Si peaks suggested that some surface complexation of the PHAs and the silica sites might have occurred.

Mechanism of adsorption of PHAs onto RH61 biochar

The most prominent peaks on biochar RH61 are at peak 1078.59 and 794.34 cm^{-1} representing Si-O-Si. After adsorption (Figure 66), new peaks were found at 3015.86-2942.55, 1738.79, 1367.49, 1227.53 and 1218.65 cm^{-1} , indicating the

presence of C-H stretching (Ahmadfazeli et al., 2021; Castilla-Caballero et al., 2020), carbonyl group (C=O) (Binh & Kajitvichyanukul, 2019; Tejedor et al., 2023), C-C/C-H stretching vibration (Nguyen et al., 2020), O-H of phenolic compounds (Suman & Gautam, 2019 /C-N stretching vibrations of amines (Patel et al., 2019), C-O and phenolic hydroxyl (Binh & Kajitvichyanukul, 2019) respectively. The presence of the carbonyl peak may indicate the adsorption of ERY, ASP, and CIP might contribute to the presence of the carbonyl as these PHAs have the carbonyl functional group in their structure. Presence of O-H of phenolic functional group may be due to the adsorption of ACE onto the biochar (Nguyen et al., 2020).

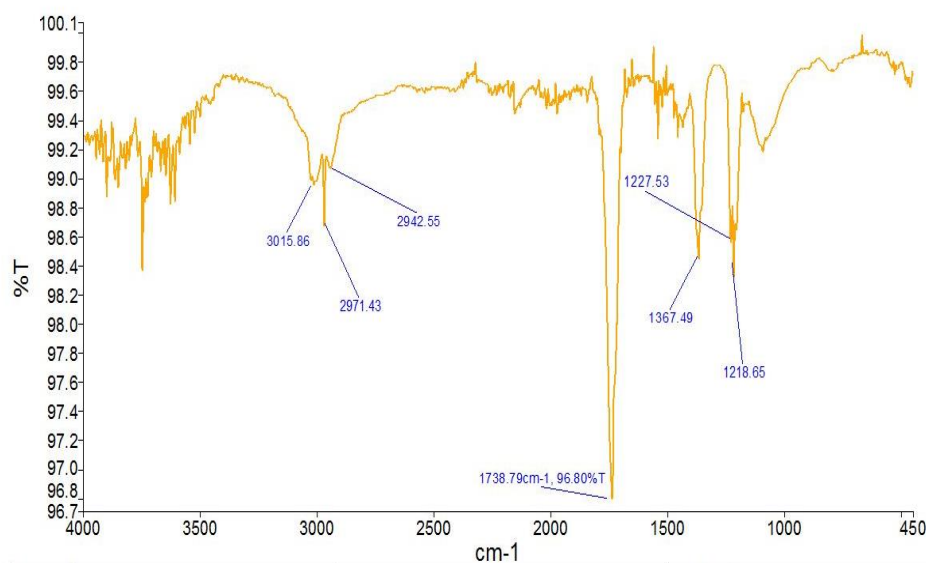


Figure 66: FTIR Spectrum of RH61 Biochar after Adsorption

The presence of the C-N group might be due to the presence of SUL, MET and CIP adsorbed onto the biochar as these PHAs contain the amine group. Also, the peaks around 2942 - 3015.86 and 1365 cm^{-1} which represent C-H of aromatic compounds might indicate the adsorption of the PHAs since they all contain

aromatic rings. There was a slight change in pH of the solution from 8.12 to 7.02 indicating the involvement of electrostatic interactions between the biochar and PHAs. Mechanisms might include hydrogen bonding of OH and COOH of PHAs to the biochar. Also, π - π electron donor acceptor interactions can occur between the aromatic rings of the PHAs and the aromatic sites of the biochar.

Mechanism of adsorption of PHAs onto RH63 biochar

The adsorption of the PHAs onto RH63 biochar resulted in changes on the spectrum (Figure 67). There were changes in the intensities of the peaks (C-H) around 2949.22 - 3015.86 cm^{-1} indicating their involvement of the adsorption of the PHAs such as hydrophobic interactions. There was a shift in the peaks representing the carbonyl (1738 to 1738.61 cm^{-1}), C-C/C-H (1365.92 to 1367.49 cm^{-1}), C-O (1216.95 to 1216.95 cm^{-1}) and the Si-O-Si (1091.66 to 1089.80 cm^{-1}) with change in intensities of adsorption of these functional groups.

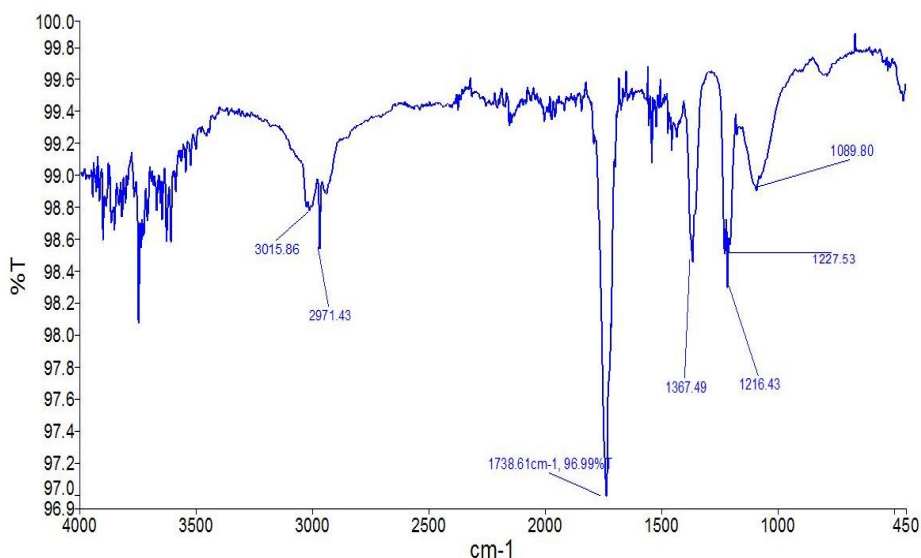


Figure 67: FTIR Spectrum of RH63 Biochar after Adsorption

The O-H group present in the biochar might form hydrogen bonds with the PHAs. Also, π - π electron-donor acceptor interactions might have occurred between

the aromatic structures on the biochar and that of the pharmaceuticals. Surface complexation might occur between carboxyl and hydroxyl functional groups and the PHAs. Lastly change in the pH of the solution from 9.38 to 8.23 indicated the exchange of ions through electrostatic attraction between the PHAs and the biochar.

Application to Environmental Samples

Prior to applying the biochar to environmental samples, the continuous adsorption method was applied to remove the PHAs from laboratory generated waste water containing 20 mg/L of each PHA. One litre of the filtrate was collected and analysed. The data presented in Table 29 focused on the removal efficiencies of the PHAs using the selected biochars. The removal efficiencies varied depending on both the type of biochar and the PHA. Removal efficiencies ranged from 90.0184 to 100 %. The high removal rate observed could be high due to the increased mass of biochar used as this increases the number of pore sizes and available sites for adsorption. Overall, the biochar RH63 gave the highest efficiency.

Table 29: The Removal Efficiencies of PHAs from Water using Fixed Bed

Biochars	Mean % Removal of PHAs							
	ACE	MET	TRI	CAF	CIP	SUL	ASP	ERY
CF53	99.9771	99.9836	99.8113	99.4795	90.0184	99.9947	99.7233	94.1087
CF61	99.9893	99.9780	98.9171	99.4856	97.5909	96.7836	99.8858	96.2064
RH53	99.9541	99.9249	99.4764	99.1351	98.4496	98.1479	99.9841	98.2213
RH61	99.9881	99.9788	99.8658	98.9506	99.8504	98.1672	99.2370	95.1266
RH63	99.9902	99.9812	99.8814	98.6604	100.0000	97.6241	99.9660	96.1927

Source: Laboratory data (2022)

The biochars, RH53, RH61, RH63, CF53 and CF61 were applied to environmental samples from four lagoons in the southern part of Ghana. Lagoons were chosen because they are mostly dumping sites for liquid waste from households and health facilities. Water samples were collected from the Fosu (FL), Korle (KL), Keta (KTL) and Esei lagoons (EL)

Korle Lagoon (KL)

Water samples were passed through columns filled with 20 g of each biochar. The initial concentration and concentration of filtered samples were determined to ascertain the percentage removal of the PHAs from each biochar. Table 30 show the mean concentrations of the PHAs in the untreated water and the mean percentage removed after filtration with the five biochars. For ACE, MET, and TRI, the 'nd' (not detectable) results across all biochars could be due to their low initial concentrations. according to Yang et al. (2018), the effectiveness of biochar in adsorbing certain pharmaceuticals largely depends on the initial pollutant concentration and the adsorbent's properties. This suggests that these compounds were not present in significant amounts in the water (Azanu et al., 2021). Non detection of MET and TRI the KL was also observed by Asare, (2022). ASP had the highest mean concentration of 48.3973 mg/L with the least being CAF (0.2180 mg/L). After treatment, CAF and CIP were not detected in filtrate from CF53 biochar whilst RH61 and RH63 filtrate had concentrations below detection limit for CIP. Varying removal efficiencies were observed for SUL, ASP and ERY with the highest removal from RH61, RH61 and RH63 respectively.

Table 30: Levels and Percentage Removal of PHAs in Korle Lagoon Water

PHAs	Untreated	Mean % Removal by biochars				
	KLRAW (mg/L)	CF61	CF53	RH53	RH61	RH63
ACE	nd	nd	nd	nd	nd	nd
MET	nd	nd	nd	nd	nd	nd
TRI	nd	nd	nd	nd	nd	nd
CAF	0.2180±0.0154	83.8073	nd	87.7523	80.6239	84.5940
CIP	0.8130±0.0365	94.6802	nd	72.1433	nd	nd
SUL	0.7068±0.0926	67.9188	89.7400	82.0175	90.8744	82.1502
ASP	48.3973±0.3887	71.5547	84.8943	61.9916	89.6164	76.5116
ERY	24.2468±0.8762	83.3432	66.7028	51.9988	73.6264	92.9290

nd-not detected; KLRAW- Korle lagoon raw water

Source: Laboratory data (2022)

Keta Lagoon (KTL)

The mean concentrations of the PHAs detected were low, CAF (0.1874 ± 0.0603 mg/L), CIP (0.0248 ± 0.0286 mg/L), SUL (0.6067 ± 0.0343 mg/L), ASP (9.9543 ± 0.5154 mg/L) and ERY (19.4398 ± 0.5800 mg/L) as indicated in Table 31. For ACE, MET, and TRI, the results showed 'nd' (not detectable) across all biochars. This pattern suggests the absence of these compounds in the untreated water. This observation is consistent with previous studies indicating that the adsorption efficiency of biochar is highly dependent on the properties of both the biochar and the target pollutants (Yang et al., 2018). The removal efficiencies for SUL and ASP showed significant variation among the biochars. While CF61, CF53, RH53, and RH61 exhibited similar removal efficiencies for SUL (ranging from 76.7164 % to 82.8979 %), RH63 achieves a complete 100 % removal. This could be due to the unique adsorption properties of RH63, which might be more

compatible with the chemical structure of SUL, as has been observed in other studies where the adsorption capacity was found to be influenced by the interaction between the biochar's surface functional groups and the pollutant's molecular structure (Tan et al., 2021). Finally, the removal of ERY presents a gradual increase in efficiency from RH53 (80.9283 %) to RH63 (87.7235 %), though not achieving complete removal. This gradient suggests a differential interaction of ERY with the surface characteristics of the biochars. The comparatively lower removal efficiencies might be due to the larger molecular size and complex structure of ERY, which can impact its interaction with the biochar surfaces (Ahmed et al., 2016). Removal of the PHAs was above 70 % for all the biochars with 100 % removal of CAF and CIP from all biochars.

Table 31: Levels and Percentage Removal of PHAs in Keta Lagoon Water

PHAs	Untreated KTLRAW(mg/L)	Mean % Removal by biochars				
		CF61	CF53	RH53	RH61	RH63
ACE	nd	nd	nd	nd	nd	nd
MET	nd	nd	nd	nd	nd	nd
TRI	nd	nd	nd	nd	nd	nd
CAF	0.1874 ± 0.0603	100	100	100	100	100
CIP	0.0248 ± 0.0286	100	100	100	100	100
SUL	0.6067 ± 0.0343	76.7164	81.8264	81.0022	82.8979	100
ASP	9.9543 ± 0.5154	76.6457	70.0882	71.9115	71.8763	100
ERY	19.4398 ± 0.5800	83.0592	81.6986	80.9283	81.8362	87.7235

nd-not detected; KTLRAW- Keta lagoon raw water

Source: Laboratory data (2022)

Esei Lagoon (EL)

Table 32 presents the percentage removal of pharmaceuticals from water samples from a Esei lagoon using various biochars. Caffeine, CIP, SUL and ERY were detected in the untreated water from the EL with mean concentrations of 0.95275 ± 0.2683 , 0.3135 ± 0.0734 , 0.9008 ± 0.0775 , 71.4603 ± 1.6366 and 12.5638 ± 1.3620 mg/L respectively. However, ACE, MET and TRI were not detected in the untreated water (Table 32).

Table 32: Levels and Percentage Removal of PHAs in Esei Lagoon Water

PHAs	Untreated ELRAW(mg/L)	Mean % Removal by biochars				
		CF61	CF53	RH53	RH61	RH63
ACE	nd	nd	nd	nd	nd	nd
MET	nd	nd	nd	nd	nd	nd
TRI	nd	nd	nd	nd	nd	nd
CAF	0.9528 ± 0.2683	82.7631	74.4686	84.5447	95.5959	100
CIP	0.3135 ± 0.0734	100.	100	100	92.0255	100
SUL	0.9008 ± 0.0775	95.5593	100	100	95.5037	100
ASP	71.4603 ± 1.6366	94.7053	79.7834	93.3774	95.6308	95.8914
ERY	12.5638 ± 1.3620	67.7326	62.7122	39.8229	83.3947	97.9007

nd-not detected; ELRAW- Esei lagoon raw water

Source: Laboratory data (2022)

CAF and CIP present interesting results. CAF removal efficiency shows a gradient, with RH63 achieving 100 % removal. This high efficiency might be attributed to the specific adsorptive interactions between CAF and the surface properties of RH63, which could include factors such as surface area, pore size, and functional groups (Tan et al., 2015). For CIP, the removal efficiencies were 100 % for CF61, CF53, and RH63. After treatment, CIP was completely removed by all

the biochars except RH61 giving 92 % removal. The initial concentration of CIP was the lowest in the untreated water. ASP concentration was the highest and its removal ranged from 79.7834 to 95.8914 %. Removal percentages for CAF, SUL and ERY ranged from 74.4686 to 100.0, 95.5037 to 100.0 and 62.7122 to 97.9007 % respectively. RH61 was observed to have higher removal efficiency for all PHAs. SUL and ASP showed high removal efficiencies across most biochars, with SUL achieving 100 % removal in CF53, RH53, and RH63. ERY removal efficiency varied significantly across the biochars, with RH63 showing the highest removal of 97.9007 %. The lower removal efficiencies observed with some biochars (such as RH53) could be due to the larger molecular size and complex structure of ERY, which may affect its interaction with the biochar surfaces (Zhang et al., 2018). ASP also showed high removal rates, especially with RH61 and with RH63 giving the highest efficiency of 95.59 %.

Fosu Lagoon (FL)

Table 33 presents the PHA levels of water from Fosu lagoon and their percentage removal. The mean concentrations of PHA in the raw water (FL-untreated) detected were 1.6888 ± 0.1304 , 0.1472 ± 0.0300 , 2.1188 ± 0.3288 , 3.0583 ± 0.2723 , 2.3805 ± 0.0792 , 3.7303 ± 0.7402 , 41.5813 ± 4.4050 and 52.4443 ± 8.1996 mg/L for ACE, MET, TRI, CAF, CIP, SUL, ASP and ERY respectively. For ACE, all biochars achieved a remarkable 100 % removal rate. This exceptional efficiency could be attributed to the molecular simplicity and smaller size of ACE, which might facilitate its complete adsorption onto the surface of the biochars. The biochars likely possess sufficient surface area and appropriate pore sizes that

effectively trap and held the ACE molecules, a phenomenon supported by studies emphasizing the importance of biochar surface area in adsorption processes (Bianco et al., 2021).

Table 33: Levels and Percentage Removal of PHAs in Fosu Lagoon Water

PHAs	Untreated FLRAW	Mean % Removal by biochars				
	(mg/L)	CF61	CF53	RH53	RH61	RH63
ACE	1.6888±0.1304	100	100	100	100	100
MET	0.1472±0.0300	90.9353	83.1947	90.6298	100	100
TRI	2.1188±0.3288	87.8330	80.1758	99.9978	76.2360	93.8997
CAF	3.0583±0.2723	55.2849	53.0982	60.1978	90.1578	93.9590
CIP	2.3805±0.0792	53.1191	54.0643	71.3191	87.2086	87.8807
SUL	3.7303±0.7402	90.3492	86.4821	72.4013	91.8839	87.6483
ASP	41.5813±4.4050	95.5834	92.9187	91.1643	93.9534	96.3686
ERY	52.4443±8.1996	85.4391	82.7593	62.4250	70.3383	78.3994

FLRAW-Fosu lagoon raw water
Source: Laboratory data (2022)

MET and TRI showed varied removal efficiencies across the biochars. For MET, the highest removal was observed with RH61 and RH63 (100 %), which could be due to the presence of specific functional groups on these biochars that have a high affinity for the MET molecule. This could involve electrostatic interactions or hydrogen bonding, considering the amine groups in MET (Yang et al., 2018). For TRI, the highest removal was seen with RH53 (99.9978 %), possibly due to its unique surface chemistry, which might include a higher proportion of functional groups like hydroxyl or carboxyl that can interact effectively with the aromatic structure of TRI (Zhang et al., 2018).

CAF and CIP present a more complex scenario. CAF removal was highest with RH61 and RH63, indicating that these biochars might have higher surface areas or more complex pore networks, which enhance the adsorption of larger, more structurally complex molecules like CAF (Tan et al., 2015). CIP removal, on the other hand, was lower with CF61 and CF53, possibly due to the steric hindrance caused by CIP's bulky structure, which may prevent effective interaction with the biochar surface (Zhou et al., 2017).

Chapter Summary

This chapter discussed the production of biochars from rice husk, coconut shell, and coconut fibre, their physicochemical properties, and their efficiency in removing pharmaceuticals from aqueous solutions. A total of 24 biochars were produced using slow pyrolysis at 500 and 600°C, with varying residence times. The yield decreased with increasing temperature and residence time, and rice husk biochar showed the highest yield due to its high ash content. Proximate analysis revealed reduced moisture and volatile matter with increasing pyrolysis temperatures, while ash and fixed carbon content increased. The biochars displayed a range of pH values, with rice husk biochars having the lowest.

The adsorption of pharmaceuticals was tested in both single- and multi-component systems, with higher temperatures and longer residence times generally improving removal efficiency. Adsorption kinetics fitted best to the pseudo-second-order model, indicating chemisorption as the dominant mechanism. The Langmuir, Freundlich, and Temkin isotherms were used to model adsorption data, showing favorable adsorption processes for most pharmaceuticals. The study revealed that

biochars produced at higher temperatures and longer residence times exhibit improved adsorption capacities, making them effective for removing pharmaceuticals from water.



CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Overview

The study aimed at investigating the use of biochar made from rice husk (RH), coconut fibre (CF) and coconut shell (CS) for the remediation of selected pharmaceuticals from lagoon water. Some physicochemical properties of the biochars were determined such as the volatile content, ash content, the fixed carbon, the pH, electrical conductivity, and the functional groups using the FTIR. Eight pharmaceuticals were selected for their constant use as well being bought without prescription in Ghana. The removal efficiencies of the PHAs using the 24 biochars were tested singly and competitively using batch adsorption. The adsorption data obtained for five best biochars were subjected to adsorption isotherm modelling to get an insight into the adsorption energies and the level of affinity of the biochars produced for the PHAs. The data was also fitted to kinetic models to determine the mechanisms of adsorption of the PHAs. The preferred biochars were used on samples from some selected lagoons for the removal of the selected PHAs that were found in them.

Summary

The five selected biochars were effective in the removal of the eight pharmaceuticals simultaneously from lagoon water. From the isotherm and kinetic studies, it was revealed that both chemical and physical adsorptions were involved in the removal process.

Conclusions

Eight biochars were produced each from the three agricultural wastes, namely the RH, CF and CS at 500 and 600 °C at residence times of 0, 1, 2 and 3 hours totalling 24 biochars in all. Physicochemical properties of the biochars were determined. Biomass pyrolyzed at 500 °C obtained higher yield of biochar than those done at 600 °C. Also, increasing residence time at a particular temperature reduced the yield of all biochars. Rice husk gave the highest biochar yield (36.20-43.18 % followed by CF (31.90-41.23 %) and CS (28.00-29.99 %).

Moisture content of biochars ranged 5.6723 - 17.6993, while the fixed carbon content was 43.8574 - 76.0854 % and the ash content was 1.5393-50.8323 %. the rice husk biochar contained the highest ash content. All the biochars were alkaline with pHs ranging from 9.9400 - 11.5567, 0.8167 - 11.4833, and 8.9533 - 10.7333 for CF, CS and RH biochars respectively. Electrical conductivity of biochars ranged from 0.1585-3.2567 mS.

Fourier Transform Infrared Spectroscopy (FTIR) analysis on the five selected biochars revealed the presence of C-O, C-H, OH, C=O, C-C on their surfaces with Si-O-Si (only on rice husk biochars). Scanning electron microscopy (SEM) images indicated the formation of numerous pores in the micro meter range.

The 24 biochars were subjected to batch adsorption to determine the removal efficiencies of the eight selected PHAs in single and competitive mode. Single-component adsorption of PHAs gave over 95 % removal from all the biochars used with the highest efficiency observed in the first 60 min. However, competitive-mode adsorption involving the simultaneous removal of the eight

selected PHAs was not as efficient as in the single mode adsorption. metronidazole (MET), trimethoprim (TRI), aspirin (ASP), acetaminophen (ACE), and ciprofloxacin (CIP) removal were not affected in competitive mode adsorption as close to 99 % and above efficiency was obtained for all biochar. Sulfamethoxazole (SUL), erythromycin (ERY), and caffeine (CAF) on the other hand had their efficiencies reduced in competitive-mode adsorption for most biochars. Removal efficiency of above 90 % was observed in selected biochars (CF53, CF61, RH53, RH61 and RH63).

Kinetic studies of the adsorption of the PHAs onto the five biochars showed that the adsorption data of the PHAs fitted the Pseudo second order (PSO) model. Further analysis with Intra particle diffusion (IPD) model revealed that IPD was not the rate determining step of the adsorption process but rather adsorption consisted of boundary layer diffusion, IPD or pore diffusion of PHAs from the surface to interior pores.

The equilibrium studies were done using the non-linear forms of Langmuir, Freundlich, and Temkin adsorption isotherms. The adsorption of the pharmaceuticals (PHAs) was declared favourable by the Langmuir's separation factor (R_L) and the Freundlich's heterogeneity factor ($1/n$) as they were all less than one. The PHAs fitted different isotherm models with respect to the different biochars. Adsorption on to RH53 biochar of ACE and MET adsorptions best fitted the Langmuir isotherm; TRI (Jodeh et al., 2022), ASP, CIP, and ERY the Freundlich isotherm; SUL and CAF & the Temkin isotherm model. With the RH61 biochar TRI fitted the Temkin isotherm; MET, ACE, SUL, ERY, CAF, ASP and

CIP, the Freundlich isotherm model. The ACE and ASP adsorption data were geared towards Langmuir isotherm whilst SUL, ERY, MET, TRI, CAF, and CIP fitted the Freundlich isotherm when RH63 was used. MET and SUL data best fitted Temkin isotherm; ASP, Langmuir; and ERY, ACE, CIP, TRI and CAF fitted the Freundlich isotherm model whilst using the CF53 biochar. Adsorption data of PHAs onto CF61 biochar had MET, ACE, and TRI, fitting Temkin; ASP fits Langmuir and the rest, CAF, SUL, ERY, and CIP, the Freundlich isotherm model. The PHAs formed monolayers first on the surfaces and heterogenous multilayers were formed later as all the PHAs did not follow into a single model confirming the heterogenous nature of the biochars

The five selected biochars were applied to remediate environmental samples from four lagoons in Ghana. Mean concentrations (mg/L) of PHAs in water samples from Korle lagoon (KL) prior to treatment with the biochars were 0.2180 ± 0.0154 , 0.8130 ± 0.0365 , 0.7068 ± 0.0926 , 48.3973 ± 0.3887 and 48.3973 ± 0.3887 mg/L for CAF, CIP, SUL, ASP, and ERY respectively. Mean concentrations for water samples from Keta lagoon (KTL) were 0.1874 ± 0.0603 (CAF), 0.0248 ± 0.0286 (CIP), 0.6067 ± 0.0343 (SUL), 9.9543 ± 0.5154 (ASP) and 19.4398 ± 0.5800 mg/L (ERY). For the Esei lagoon (EL), the mean concentrations were 0.95275 ± 0.2683 (CAF), 0.3135 ± 0.0734 (CIP), 0.9008 ± 0.0775 (SUL), 71.4603 ± 1.6366 (ASP), and 12.5638 ± 1.3620 mg/L (ERY). Acetaminophen, MET and TRI were not detected in the water samples from EL, KL and KTL. On the other hand, all the eight PHAs were detected in the water samples from the Fosu lagoon (FL) with mean concentrations ranging from 0.1472 ± 0.0300 (MET) to

52.4443 ± 8.1996 mg/L (ERY). After treatment with CF53, CF61, RH53, RH61 and RH63 biochars, removal efficiencies of the PHAs ranged between 51.9988 and 100 %. From the above it is evident that the selected biochars were able to remove the selected PHAs. Overall, the biochar RH63 made from rice husk pyrolysed at 600 °C and held for 3 hours was the best biochar as it achieved highest removal efficiency for both the batch and environmental application.

Recommendations

Despite the effective performance of the produced biochars, it is necessary to assess their life cycle, potential for reuse and regeneration, as well as their economic viability. Bacteria degradation should be explored for the spent biochars. Also, coconut shell biochars showed high removal efficiency of PHAs therefore should be explored further. Biochar produced can also be mixed in different proportions to ascertain whether removal will occur at a faster rate. Furthermore, with the availability of the raw materials in abundance, biochar from these materials should be produced and applied in treatment plants. Finally, water bodies should be monitored frequently to know the level of contamination by PHA wastes and residues.

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APPENDICES

APPENDIX A

RELATIONSHIP BETWEEN SOME PROPERTIES OF THE BIOCHARS

	pH	Conductivity	Moisture	Volatile matter	Ash content	Fixed carbon
Coconut fibre						
pH	--					
Conductivity(mS)	0.714*	--				
Moisture (%)	-0.866**	-0.670	--			
Volatile matter (%)	-0.895**	-0.871**	0.668	--		
Ash content (%)	0.902**	0.900**	-0.728*	-0.984**	--	
Fixed carbon (%)	0.440	0.326	-0.080	-0.599	0.449	--
Coconut shell						
pH	--					
Conductivity(mS)	0.905**	--				
Moisture (%)	0.419	0.110	--			
Volatile matter (%)	-0.963**	-0.951**	-0.276	--		
Ash content (%)	0.979**	0.950**	0.341	-0.991**	--	
Fixed carbon (%)	0.924**	0.933**	0.197	-0.989**	0.961**	--
Rice husk						
pH	--					
Conductivity(mS)	0.944**	--				
Moisture (%)	-0.511	-0.404	--			
Volatile matter (%)	-0.966**	-0.916**	0.661	--		
Ash content (%)	0.979**	0.948**	-0.555	-0.987**	--	
Fixed carbon (%)	-0.701	-0.765*	-0.100	0.594	-0.715*	--

*. Correlation is significant at the 0.05 level

**. Correlation is significant at the 0.01 level

APPENDIX B

ADSORPTION CAPACITIES

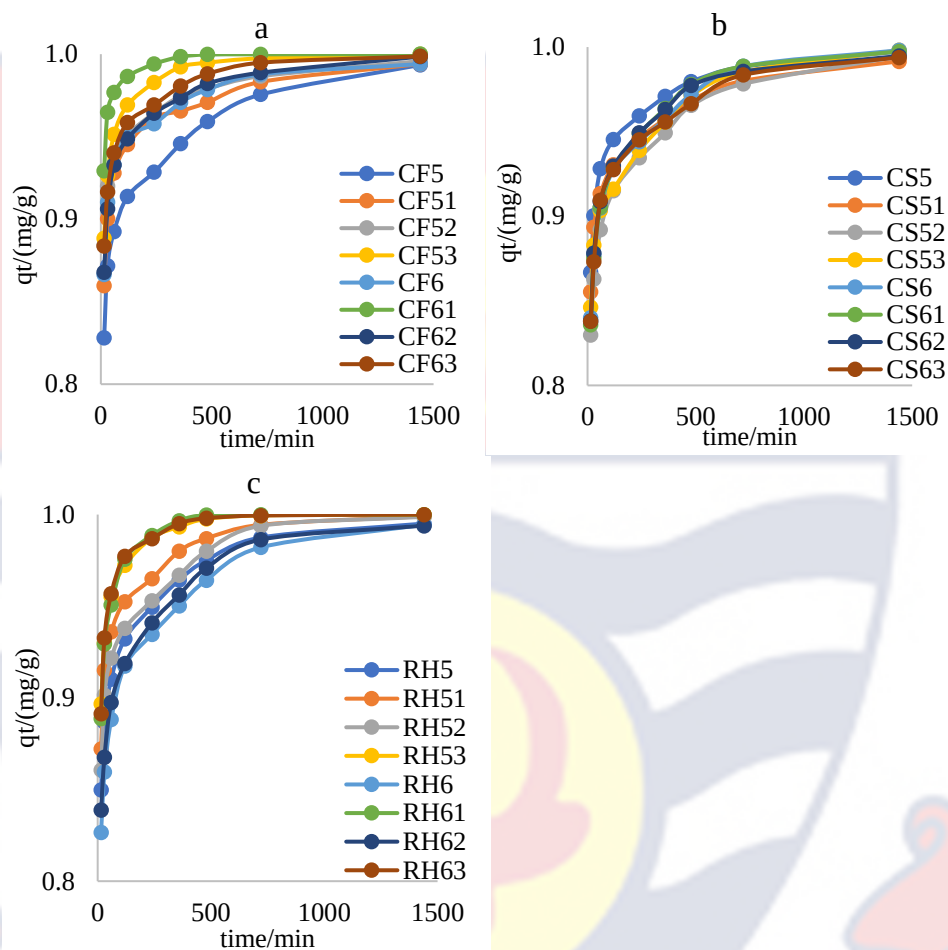


Figure B1: Mean adsorption capacities of coconut fibre(a), coconut shell (b) and rice husk(c) biochars in single component adsorption

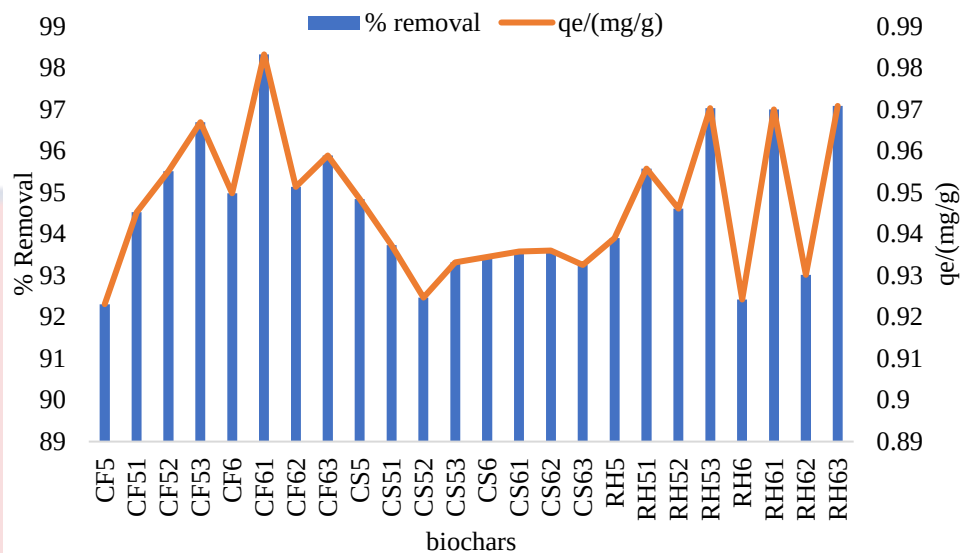


Figure B2: Overall Mean Percentage Removal and Adsorption Capacities of the 24 Biochars in Single Component Adsorption

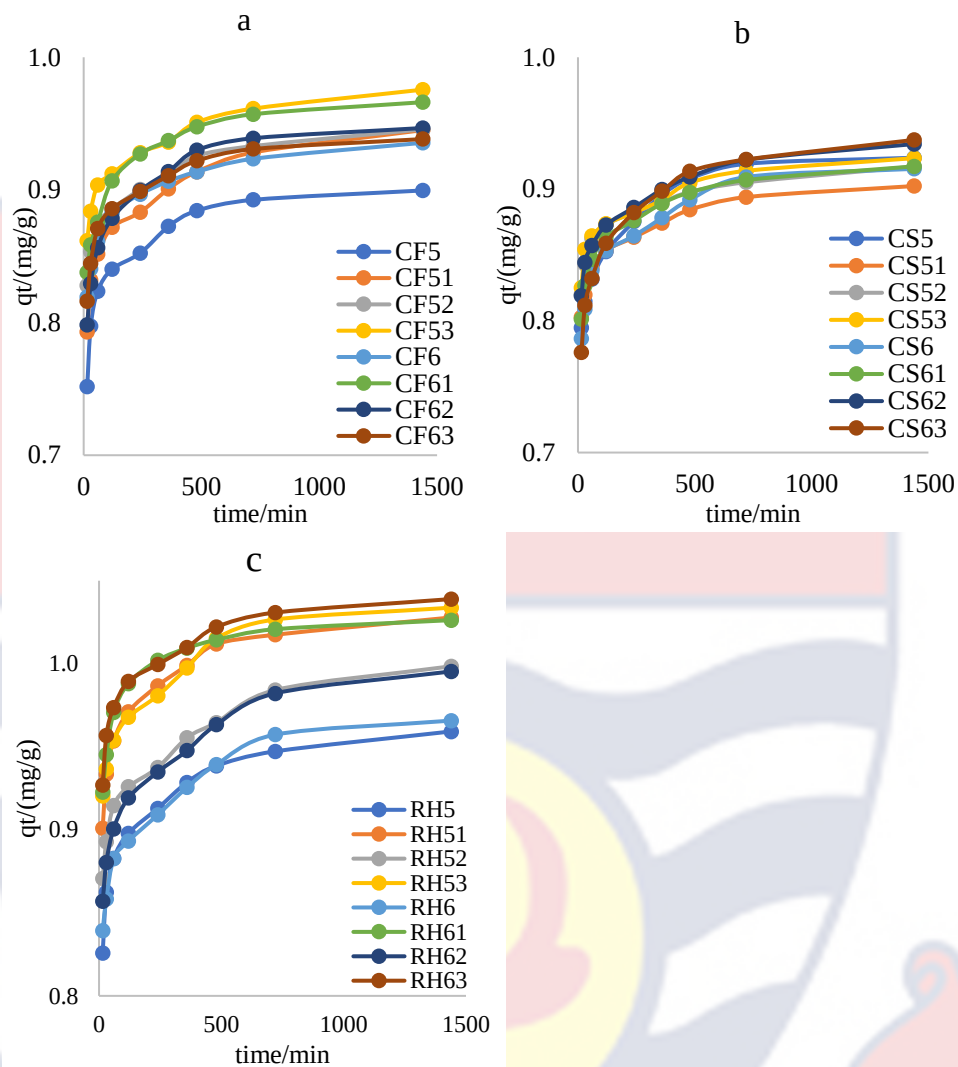


Figure B3: Mean Adsorption Capacities of Coconut Fibre(a), Coconut Shell (b) and Rice Husk(c) Biochars in Competitive Adsorption

APPENDIX C

KINETIC STUDIES OF THE ADSORPTION PROCESS

Table C1: IPD Parameters and Best Fit Values for CIP Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
kwm (mg/g.min ^{^(0.5)})	0.0013	0.0016	0.0013	0.0016	0.0012
qt(exp)	0.9876	0.9847	0.9993	1.0000	1.0000
B (mg/g)	0.9497	0.9393	0.9613	0.9527	0.9660
R ²	0.6843	0.6066	0.8059	0.7356	0.6231
R ² adjusted	0.5791	0.4754	0.7412	0.6475	0.4974
AICc	-79.5766	-72.5301	-85.7937	-77.7159	-78.7465
SQE	0.0008	0.0017	0.0004	0.0010	0.0008
RMSE	0.0093	0.0137	0.0066	0.0103	0.0097
Marquardt	1.1006	1.6343	0.7607	1.1985	1.1375
MSE	0.0001	0.0002	0.0000	0.0001	0.0001
Hybrid	0.0116	0.0254	0.0057	0.0140	0.0125
Chi-square	0.0008	0.0018	0.0004	0.0010	0.0009
SNE	1.0205	1.0262	1.0172	1.0219	1.0211

Table C2: PFO Parameters and Best Fit Values for ASP Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qt exp (mg/g)	0.9935	0.9932	0.9938	0.9926	0.9890
qt cal (mg/g)	0.9868	0.9865	0.9807	0.9753	0.9775
K ₁ (1/min)	0.2425	0.2045	0.1898	0.1756	0.2400
R ²	0.5134	0.7742	0.7432	0.6991	0.4565
R ² adjusted	0.3512	0.6989	0.6576	0.5988	0.2754
AICc	-82.8305	-83.2026	-77.9165	-72.4036	-80.2823
SQE	0.0005	0.0005	0.0009	0.0017	0.0007
RMSE	0.0077	0.0076	0.0102	0.0138	0.0089
Marquardt	0.9024	0.8845	1.1913	1.6355	1.0432
MSE	0.0001	0.0001	0.0001	0.0002	0.0001
Hybrid	0.0079	0.0076	0.0137	0.0256	0.0106
Chi-square	0.0005	0.0005	0.0010	0.0018	0.0007
SNE	1.0186	1.0184	1.0217	1.0264	1.0201

Table C3: IPD Parameters and Best Fit Values for ASP Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
kwm (mg/g.min ^{0.5})	0.0008	0.0011	0.0015	0.0019	0.0010
B (mg/g)	0.9701	0.9631	0.9489	0.9347	0.9575
R ²	0.6172	0.5146	0.6245	0.6577	0.7916
R ² adjusted	0.4896	0.3529	0.4993	0.5436	0.7222
AICc	-84.9902	-76.3157	-74.4957	-74.2428	-88.9110
SQE	0.0004	0.0011	0.0014	0.0020	0.0003
RMSE	0.0069	0.0111	0.0123	0.0147	0.0055
Marquardt	0.7971	1.3114	1.4718	1.7812	0.6468
MSE	0.0000	0.0001	0.0002	0.0002	0.0000
Hybrid	0.0062	0.0165	0.0205	0.0298	0.0041
Chi-square	0.0004	0.0011	0.0014	0.0020	0.0003
SNE	1.0175	1.0229	1.0243	1.0273	1.0157

Table C4: PFO Parameters and Best Fit Values for ERY Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qtexp(mg/g)	0.9908	0.9897	0.9337	0.9015	0.9649
qtcal (mg/g)	0.9315	0.9292	0.8397	0.8494	0.8667
K ₁ (1/min)	0.1251	0.1066	0.1379	0.1334	0.1267
R ²	0.6156	0.5000	0.2754	0.4962	0.2901
R ² adjusted	0.4875	0.3334	0.0339	0.3282	0.0535
AICc	-56.4993	-48.5952	-49.6849	-56.5525	-47.0157
SQE	0.0101	0.0242	0.0215	0.0100	0.0289
RMSE	0.0334	0.0519	0.0488	0.0333	0.0566
Marquardt	4.0701	6.8086	6.4928	4.5453	7.3886
MSE	0.0011	0.0027	0.0024	0.0011	0.0032
Hybrid	0.1541	0.3991	0.3582	0.1715	0.4724
Chi-square	0.0109	0.0267	0.0257	0.0119	0.0335
SNE	1.0515	1.0741	1.0703	1.0501	1.0805

Table C5: PSO Parameters and Best Fit Values for ERY Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qtexp(mg/g)	0.9908	0.9897	0.9337	0.9015	0.9649
qcal(mg/g)	0.9517	0.9587	0.8606	0.8682	0.8916
K ₂ (g(mg min))	0.3494	0.2343	0.3937	0.4054	0.3184
R ²	0.8384	0.8370	0.5661	0.8232	0.5877
R ² adjusted	0.7845	0.7827	0.4215	0.7642	0.4502
AICc	-64.2973	-58.6821	-54.3008	-65.9766	-51.9057
SQE	0.0042	0.0079	0.0128	0.0035	0.0168
RMSE	0.0217	0.0296	0.0378	0.0197	0.0432
Marquardt	2.6146	3.9134	4.9994	2.6658	5.6181
MSE	0.0005	0.0009	0.0014	0.0004	0.0019
Hybrid	0.0642	0.1310	0.2135	0.0596	0.2739
Chi-square	0.0045	0.0090	0.0153	0.0042	0.0195
SNE	1.0364	1.0456	1.0562	1.0328	1.0632

Table C6: IPD parameters and Best Fit Values for ERY Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
kwm (mg/g.min ^{0.5})	0.0047	0.0062	0.0054	0.0042	0.0063
B (mg/g)	0.8352	0.8008	0.7370	0.7653	0.7463
R pearson	0.9162	0.8931	0.9885	0.9383	0.9798
R ²	0.8395	0.7976	0.9771	0.8805	0.9600
R ² adjusted	0.7859	0.7301	0.9694	0.8406	0.9466
AICc	-64.3567	-56.7330	-80.7692	-69.5019	-72.8908
SQE	0.0042	0.0098	0.0007	0.0024	0.0016
RMSE	0.0216	0.0330	0.0087	0.0162	0.0135
Marquardt	2.9201	4.2126	1.1728	2.2805	1.7184
MSE	0.0005	0.0011	0.0001	0.0003	0.0002
Hybrid	0.0713	0.1569	0.0115	0.0419	0.0261
Chi-square	0.0048	0.0109	0.0008	0.0029	0.0018
SNE	1.0351	1.0503	1.0186	1.0279	1.0252

Table C7: PFO Parameters and Best Fit Values for MET Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qtexp (mg/g)	0.9981	0.9991	0.9994	0.9996	1.0000
qtcal (mg/g)	0.9934	0.9938	0.9959	0.9975	0.9872
K ₁ (1/min)	0.2545	0.2402	0.3396	0.3653	0.1544
R ²	0.8193	0.8510	0.4526	0.4417	0.8245
R ² adjusted	0.7591	0.8013	0.2702	0.2555	0.7660
AICc	-98.7710	-86.7294	-106.3102	-112.7901	-72.7458
SQE	0.0001	0.0001	0.0000	0.0000	0.0017
RMSE	0.0032	0.0035	0.0021	0.0015	0.0136
Marquardt	0.3653	0.4029	0.2393	0.1668	1.5860
MSE	0.0000	0.0000	0.0000	0.0000	0.0002
Hybrid	0.0013	0.0016	0.0006	0.0003	0.0244
Chi-square	0.0001	0.0001	0.0000	0.0000	0.0017
SNE	1.0129	1.0133	1.0115	1.0107	1.0261

Table C8: PSO Parameters and Best Fit Values for MET Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qtexp(mg/g)	0.9981	0.9991	0.9994	0.9996	1.0000
qtcal (mg/g)	0.9964	0.9973	0.9971	0.9984	0.9996
K ₂ (g/(mg min))	2.7490	2.2499	8.0607	11.5161	0.5814
R ²	0.9642	0.9665	0.8078	0.8337	0.9875
R ² adjusted	0.9523	0.9553	0.7438	0.7782	0.9833
AICc	-113.3487	-110.4341	-115.7311	-123.6883	-96.5054
SQE	0.0000	0.0000	0.0000	0.0000	0.0001
RMSE	0.0014	0.0017	0.0012	0.0008	0.0036
Marquardt	0.1628	0.1917	0.1417	0.0910	0.4204
MSE	0.0000	0.0000	0.0000	0.0000	0.0000
Hybrid	0.0003	0.0004	0.0002	0.0001	0.0017
Chi-square	0.0000	0.0000	0.0000	0.0000	0.0001
SNE	1.0106	1.0109	1.0104	1.0098	1.0133

Table C9: IPD Parameters and Best Fit Values for MET Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
Kwm	0.0005	0.0006	0.0003	0.0002	0.0023
(mg/g.min ^{0.5})					
B(mg/g)	0.9821	0.9802	0.9910	0.9943	0.9376
R ²	0.5592	0.5334	0.8750	0.8180	0.5457
R ² adjusted	0.4123	0.3778	0.8333	0.7573	0.3942
AICc	-	-	-	-	-
	90.7436	97.0015	119.5982	122.8764	64.1835
SQE	0.0002	0.0003	0.0000	0.0000	0.0043
RMSE	0.0050	0.0062	0.0010	0.0008	0.0218
Marquardt (%)	0.5779	0.7251	0.1146	0.0953	2.6635
MSE	0.0000	0.0000	0.0000	0.0000	0.0005
Hybrid	0.0033	0.0051	0.0001	0.0001	0.0658
Chi-square	0.0002	0.0004	0.0000	0.0000	0.0045
SNE	1.0151	1.0167	1.0101	1.0099	1.0364

Table C10: PSO Parameters and Best Fit Values for TRI Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qtexp (mg/g)	0.9995	0.9997	0.9985	0.9958	0.9989
qtcal (mg/g)	0.9494	0.9470	0.9811	0.9994	0.9909
K ₂ (g/(mg min))	0.3166	0.2323	0.3932	0.3309	0.3862
R ²	0.7783	0.7346	0.8301	0.9874	0.9770
R ² adjusted	0.7044	0.6462	0.7735	0.9832	0.9694
AICc	59.5285	53.2474	65.6220	87.6928	84.4769
SQE	0.0072	0.0144	0.0037	0.0003	0.0004
RMSE	0.0283	0.0401	0.0201	0.0059	0.0071
Marquardt (%)	3.5007	5.3279	2.4607	0.7538	0.8258
MSE	0.0008	0.0016	0.0004	0.0000	0.0000
Hybrid	0.1118	0.2410	0.0561	0.0050	0.0066
Chi-square	0.0079	0.0166	0.0039	0.0004	0.0005
SNE	1.0445	1.0589	1.0342	1.0155	1.0177

Table C11: PFO Parameters and Best Fit Values for TRI Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qt exp (mg/g)	0.9995	0.9997	0.9985	0.9958	0.9989
qt cal (mg/g)	0.9260	0.9153	0.9609	0.9793	0.9738
K ₁ (1/min)	0.1235	0.1103	0.1407	0.1212	0.1281
R ²	0.4548	0.3765	0.4728	0.7605	0.8362
R ² adjusted	0.2731	0.1687	0.2970	0.6807	0.7816
AICc	-51.4306	-45.5599	-55.4295	-61.1844	-66.8006
SQE	0.0177	0.0339	0.0113	0.0060	0.0032
RMSE	0.0443	0.0614	0.0355	0.0258	0.0189
Marquardt (%)	5.5982	8.0971	4.3277	3.1978	2.2463
MSE	0.0020	0.0038	0.0013	0.0007	0.0004
Hybrid	0.2802	0.5613	0.1739	0.0933	0.0480
Chi-square	0.0194	0.0377	0.0119	0.0063	0.0033
SNE	1.0649	1.0862	1.0540	1.0413	1.0328

Table C12: IPD Parameters and Best Fit Values for TRI Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
kwm (mg/g.min ^{0.5})	0.0054	0.0069	0.0041	0.0037	0.0034
B (mg/g)	0.8182	0.7775	0.8777	0.8983	0.8988
R ²	0.8876	0.8758	0.7937	0.5311	0.5963
R ² adjusted	0.8501	0.8344	0.7250	0.3747	0.4618
AICc	-65.6419	-60.0785	-63.8750	-55.1356	-58.6841
SQE	0.0036	0.0068	0.0044	0.0117	0.0079
RMSE	0.0201	0.0274	0.0222	0.0361	0.0296
Marquardt	2.6290	3.4221	2.6732	4.5053	3.8017
MSE	0.0004	0.0008	0.0005	0.0013	0.0009
Hybrid	0.0598	0.1059	0.0671	0.1837	0.1273
Chi-square	0.0041	0.0075	0.0046	0.0124	0.0085
SNE	1.0335	1.0433	1.0370	1.0544	1.0458

Table C13: PFO Parameters and Best Fit Values for CAF Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
q _{texp}	0.9392	0.9523	0.9914	0.9889	0.9951
q ₁ (mg/g)	0.8499	0.8799	0.9079	0.9499	0.9597
k ₁ (1/min)	0.1168	0.0912	0.1003	0.1113	0.1092
R ²	0.3743	0.4651	0.3720	0.5928	0.7161
R ² adjusted	0.1657	0.2867	0.1627	0.4571	0.6215
AICc	-48.1219	-44.7679	-43.1731	-52.7102	-56.1823
SQE	0.0255	0.0370	0.0442	0.0153	0.0104
RMSE	0.0533	0.0642	0.0701	0.0413	0.0340
Marquardt	7.2201	9.0849	9.2310	5.3122	4.2564
MSE	0.0028	0.0041	0.0049	0.0017	0.0012
Hybrid	0.4341	0.6574	0.7295	0.2480	0.1640
Chi-square	0.0304	0.0439	0.0500	0.0166	0.0111
SNE	1.0756	1.0888	1.0974	1.0608	1.0518

Table C14: PSO Parameters and Best Fit Values for CAF Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
q _{exp} /(mg/g)	0.8759	0.9153	0.9427	0.9758	0.9844
K ₂ (g/(mg min))	0.2871	0.1830	0.2000	0.2638	0.2636
R ²	0.6893	0.8066	0.7039	0.9157	0.9601
R ² adjusted	0.5858	0.7421	0.6052	0.8876	0.9468
AICc	-54.4238	-53.9236	-49.9389	-66.8826	-73.8336
SQE	0.0127	0.0134	0.0209	0.0032	0.0015
RMSE	0.0375	0.0386	0.0481	0.0188	0.0128
Marquardt	5.0664	5.5262	6.3334	2.4435	1.6028
MSE	0.0014	0.0015	0.0023	0.0004	0.0002
Hybrid	0.2147	0.2405	0.3439	0.0519	0.0232
Chi-square	0.0152	0.0167	0.0241	0.0036	0.0016
SNE	1.0555	1.0562	1.0694	1.0318	1.0244

Table C15: IPD Parameters and Best Fit Values for CAF Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
kwm	0.0062	0.0076	0.0079	0.0052	0.0050
(mg/g.min ^{0.5})					
B (mg/g)	0.7273	0.7227	0.7503	0.8403	0.8526
R ²	0.9485	0.8318	0.8721	0.7131	0.6685
R ² adjusted	0.9314	0.7757	0.8295	0.6175	0.5580
AICc	-70.6024	-55.1794	-57.4962	-55.8602	-54.7869
SQE	0.0021	0.0117	0.0090	0.0108	0.0122
RMSE	0.0153	0.0360	0.0316	0.0346	0.0368
Marquardt	2.0618	4.7958	3.8595	4.3991	4.7710
MSE	0.0002	0.0013	0.0010	0.0012	0.0014
Hybrid	0.0355	0.1943	0.1377	0.1721	0.1979
Chi-square	0.0025	0.0134	0.0096	0.0118	0.0133
SNE	1.0270	1.0535	1.0490	1.0524	1.0548

Table C16: PFO Parameters and Best Fit Values for SUL Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qcal/(mg/g)	0.8972	0.8112	0.9560	0.9337	0.9648
qexp/(mg/g)	0.8178	0.7415	0.8761	0.8713	0.8854
K ₁ (1/min)	0.1246	0.1110	0.1217	0.1306	0.1100
R ²	0.3325	0.3944	0.3416	0.3719	0.4260
R ² adjusted	0.1101	0.1925	0.1221	0.1626	0.2347
AICc	-49.2380	-49.9262	-47.5529	-51.2338	-52.7102
SQE	0.0225	0.0209	0.0272	0.0181	0.0272
RMSE	0.0501	0.0482	0.0550	0.0448	0.0549
Marquardt	7.0661	7.5962	7.2085	6.0491	7.2917
MSE	0.0025	0.0023	0.0030	0.0020	0.0030
Hybrid	0.3996	0.4130	0.4476	0.3065	0.4523
Chi-square	0.0278	0.0286	0.0313	0.0209	0.0311
SNE	1.0711	1.0675	1.0783	1.0648	1.0780

Table C17: PSO Parameters and Best Fit Values for SUL Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
qexp/(mg/g)	0.8417	0.7659	0.9019	0.8944	0.9141
K ₂ (g/(mg min))	0.3286	0.2988	0.2974	0.3443	0.2501
R ²	0.6585	0.7201	0.6509	0.7383	0.7522
R ² adjusted	0.5446	0.6268	0.5345	0.6510	0.6696
AICc	-55.2683	-56.8725	-53.2631	-59.1113	-66.8826
SQE	0.0115	0.0097	0.0144	0.0075	0.0117
RMSE	0.0358	0.0328	0.0400	0.0289	0.0361
Marquardt	5.0592	5.1378	5.2557	3.9119	4.7821
MSE	0.0013	0.0011	0.0016	0.0008	0.0013
Hybrid	0.2047	0.1899	0.2377	0.1279	0.1949
Chi-square	0.0144	0.0134	0.0167	0.0089	0.0136
SNE	1.0529	1.0480	1.0591	1.0445	1.0539

Table C18: IPD Parameters and Best Fit Values for SUL Adsorption

Parameters	CF53	CF61	RH53	RH61	RH63
K _w					
(mg/g.min ^{0.5})	0.0057	0.0056	0.0062	0.0051	0.0066
B (mg/g)	0.7078	0.6297	0.7554	0.7714	0.7541
R ²	0.9440	0.9134	0.9194	0.8938	0.9058
R ² adjusted	0.9253	0.8846	0.8926	0.8584	0.8745
AICc	-71.5391	-67.4332	-66.4611	-67.2285	-63.8343
SQE	0.0019	0.0030	0.0033	0.0031	0.0045
RMSE	0.0145	0.0182	0.0192	0.0184	0.0222
Marquardt	1.9692	2.7910	2.4212	2.4146	2.9026
MSE	0.0002	0.0003	0.0004	0.0003	0.0005
Hybrid	0.0323	0.0573	0.0526	0.0503	0.0728
Chi-square	0.0023	0.0040	0.0037	0.0035	0.0050
SNE	1.0260	1.0297	1.0327	1.0313	1.0362

APPENDIX D

THERMODYNAMIC PARAMETERS OF ADSORPTION

Table D1: Thermodynamic Parameters of PHAs using CF61 Biochar

PHAs	T/K	K _c	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol)
ACE	298	179.5267	-12.8659	-105.9680	-311.3868
	308	62.0195	-10.5744		
	323	12.1321	-6.6018		
MET	298	108.5644	-11.6191	-73.2501	-209.7195
	308	13.7185	-6.7091		
	323	17.3566	-7.5490		
TRI	298	307.5876	-14.2006	-261.5844	-837.8043
	308	0.5093	-1.7286		
	323	0.4317	-2.2217		
CAF	298	1.9952	-1.7123	-75.2810	-248.6099
	308	0.3751	-2.5125		
	323	0.3002	-3.1831		
CIP	298	6.4171	-4.6080	-10.5545	-24.3185
	308	1.1131	-0.2746		
	323	5.0865	-4.3025		
SUL	298	0.4298	2.0933	-22.1906	-81.7239
	308	0.2904	3.1679		
	323	0.2454	3.7164		
ASP	298	14.5138	-6.6311	-7.1969	-1.7140
	308	14.1355	-6.7858		
	323	12.0745	-6.5892		
ERY	298	9.6418	-5.6173	-133.3923	-431.2569
	308	0.6217	-1.2176		
	323	0.3345	-2.8964		

Table D2: Thermodynamic Parameters of PHAs using RH53 Biochar

PHAs	T/K	Kc	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol)
ACE	298	50.5474	-9.7242	8.4346	66.2028
	308	398.5495	-15.3406		
	323	59.9833	-10.8292		
MET	298	154.4213	-12.4925	-17.4912	-14.8151
	308	252.2215	-14.1684		
	323	97.5501	-12.1155		
TRI	298	68.8631	-10.4907	20.1537	99.6148
	308	27.8721	-8.5252		
	323	117.7752	-12.6139		
CAF	298	11.5072	-6.0557	11.6826	65.1980
	308	109.9422	-12.0411		
	323	14.7793	-7.1239		
CIP	298	136.0795	-12.1790	31.5664	149.3602
	308	544.2643	-16.1389		
	323	296.6315	-15.0572		
SUL	298	2.1733	-1.9242	1.4692	19.2775
	308	40.7906	-9.5009		
	323	2.1165	-1.9833		
ASP	298	16.1241	-6.8919	-27.8546	-69.4731
	308	15.2434	-6.9791		
	323	7.9024	-5.4679		
ERY	298	1.4090	-0.8500	15.2643	61.6144
	308	28.0561	-8.5421		
	323	1.9522	-1.7694		

Table D3: Thermodynamic Parameters of PHAs using RH61 Biochar

PHAs	T/K	Kc	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol)
ACE	298	53.3814	-9.8594	-54.7689	-148.1565
	308	64.8418	-10.6884		
	323	13.0472	-6.7941		
MET	298	240.8087	-13.5939	-91.4469	-261.8212
	308	56.1645	-10.3203		
	323	23.8204	-8.3864		
TRI	298	23.9402	-7.8716	38.8353	162.9076
	308	399.5323	-15.3469		
	323	60.9461	-10.8713		
CAF	298	8.9393	-5.4297	-62.8239	-187.5047
	308	24.8085	-8.2269		
	323	1.7453	-1.4731		
CIP	298	2054.9760	-18.9085	-11.4500	19.3161
	308	216.0274	-13.7716		
	323	1609.4284	-19.5304		
SUL	298	1.4081	-0.8484	-41.0696	-133.4964
	308	1.3819	-0.8286		
	323	0.4913	1.8797		
ASP	298	13.4538	-6.4431	-65.9928	-204.0807
	308	1.1395	-0.3346		
	323	2.6137	-2.5413		
ERY	298	0.9148	0.2208	-25.7439	-86.2043
	308	0.9041	0.2583		
	323	0.4728	1.9813		