Characterization and Adsorption Performance of New Zealand Biochar for the Removal of Paracetamol and Ibuprofen from Synthetic Solutions in Batch and Column Systems

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Abstract

Pharmaceuticals are a significant class of emerging organic contaminants that have been increasingly detected in aquatic environments. Their persistence and limited removal by conventional treatment methods poses considerable risks to both flora and fauna. The study investigates the adsorption performance of New Zealand-sourced biochar both raw and surface-modified for the removal of two widely used pharmaceuticals, paracetamol and ibuprofen, from aqueous solutions. With its local availability and carbon-rich structure, biochar was evaluated as an innovative solution to address the growing challenge of emerging pharmaceutical pollutants in aquatic environments. The research aimed to characterize the physicochemical properties of biochar and evaluate its adsorption capacity under batch and column configurations, addressing removal efficiency, equilibrium behaviour, kinetic mechanisms, and dynamic breakthrough performance. The biochar was instrumentally analysed by BET surface area analysis, Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX) to examine the biochar's surface structure and functional groups. Premium Biochar demonstrated the highest BET surface area (308.3 m^2/g), which further increased to 354 m^2/g after 30% KOH activation, indicating enhanced porosity and improved availability of adsorption sites. Batch adsorption experiments revealed that paracetamol achieved higher removal efficiencies and adsorption capacities (up to 8.5 mg/g) compared to ibuprofen (maximum of 2.8 mg/g), largely due to its smaller molecular size and greater polarity. The non-linear technique using isotherm and kinetic model was used to validate the process efficiency of pharmaceuticals removal. Kinetic modelling indicated pseudo-second order and Elovich models best described the adsorption mechanisms ($R^2 > 0.997$), confirming chemisorption on heterogeneous surfaces as the dominant process. Isotherm analysis showed multilayer Freundlich adsorption for paracetamol and monolayer Langmuir adsorption for ibuprofen reflecting differences in multilayer versus monolayer adsorption behaviour. Column experiments were conducted under single-pass, closed-loop recirculation, and semi-continuous dosing modes. Single-pass continuous flow showed in rapid breakthrough at short empty bed contact times (1.6–4.5 minutes) due to hydraulic limitations. In contrast, closed-loop recirculation columns achieved up to 90% paracetamol removal and 58% ibuprofen removal under extended operation, specifically, the optimal condition when using 1 mm particle size KOH-activated biochar (1 mm KOH-modified biochar, 15 L/min flow, 500 min runtime). Semi-continuous dosing experiments demonstrated gradual adsorbent saturation with final adsorption capacities of approximately 0.43–0.57 mg/g, supporting the need for regeneration strategies in long-term applications.

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alongside me, and for reminding me what truly matters. I couldn’t have done this without you; we overcame every challenge together.

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List of Abbreviations

EOCs	Emerging Organic Contaminants
PPCPs	Pharmaceuticals and Personal Care Products
PFAS	Per- and Polyfluoroalkyl Substances
WWTP	Wastewater Treatment Plant
PhACs	Pharmaceutical Active Compounds
AC	Activated Carbon
GAC	Granular Activated Carbon
PAC	Powdered Activated Carbon
SF	Surface Flow
EBCT	Empty Bed Contact Time
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
BET	Brunauer–Emmett–Teller (surface area analysis)
UV	Ultraviolet
ng/L	Nanograms per Liter
µg/L	Micrograms per Liter
mg/g	Milligrams per Gram

Chapter 1

Introduction

Chapter One present an overview of the study, outlines the background, research problem, objectives, and the overall structure of the thesis. The background section highlights the environmental concern posed by emerging organic contaminants (EOCs), particularly pharmaceuticals of ibuprofen and paracetamol, and outlines the motivation for this research. It also identifies key research gaps and presents the problem statement that this study aims to address.

1.1 Background

Over the past three decades, increasing research has classified pharmaceuticals and personal care products (PPCPs) as a significant group of emerging organic contaminants (EOCs) (Yang et al., 2017). Despite being used daily all over the world, pharmaceuticals represent a significant class of chemicals that are frequently disposed of inappropriately (Beek et al., 2015). Emerging contaminants in aquatic systems, especially pharmaceutical substances, have become a growing environmental issue in recent years. This trend is mainly driven by changes in human lifestyles and the increased use of synthetic compounds in medicine and pharmaceuticals and personal care products. PPCPs exhibit endocrine-disrupting effects indicate that they may have the potential interfere hormonal regulation in both humans and wildlife (EU, 2023).

For instance, research demonstrates that exposure to both individual and combined PPCP residues results in adverse reproductive outcomes and histopathological abnormalities in zebrafish (Galus, Kirischian, et al., 2013). Additionally, these contaminants may pose risks to human health through indirect pathways, including the consumption of contaminated drinking water and the accumulation of residues within the food. This raises concerns regarding potential detrimental effects on public health, aquatic organisms, and the propagation of antibiotic resistance (Yanan et al., 2022).

The predominant pharmaceutical groups pollute water systems, including Ibuprofen and paracetamol, commonly found in the environment, are anti-inflammatories and analgesics, respectively (Falahi et al., 2022). It was observed that the toxic effect of ibuprofen at 265.9 μg/L and paracetamol at 2.5 μg/L can cause an imbalance in fish reproduction systems. It has been recorded that around 69% of excreted ibuprofen undergoes hydroxylation and carboxylation in

the human body, generating metabolites with higher toxicity than the original compound (Islam et al., 2024).

Pharmaceutical compounds infiltrate the environment through various routes, including domestic wastewater, hospital effluent, and wastewater treatment plants. These compounds may also enter surface waters through drinking water treatment facilities, general water treatment systems, aquaculture activities, and agricultural runoff. Additionally, runoff from animal farming operations, land applications of manure, and improper disposal practices by manufacturers further contribute to their presence. Notably, hospital discharges tend to exhibit higher pharmaceutical concentrations compared to domestic wastewater (Price et al., 2010).

The frequent detection of pharmaceuticals in water sources is indicated by the excessive usage of these substances in both human and animal medicine. Conventional wastewater treatment systems are not fully effective in removing these substances, allowing residues to pass through the treatment processes. Consequently, traces of pharmaceuticals such as paracetamol and ibuprofen are still detected in rivers, groundwater, and occasionally in drinking water supplies with concentrations level ranging from (ng/L) parts-per-trillion to(µg/L) parts-per-billion (Patel et al., 2019).

Pharmaceutical contamination is challenging to manage because of the diverse group of compounds involved, each with unique physicochemical properties that impact their removal efficiency, persistence, and interactions to the environment (Patel et al., 2019). Ibuprofen and paracetamol, for instance, exhibit differences in solubility, degradation, and adsorption behaviour, which influence how effectively they are removed during wastewater treatment (Patel et al., 2022). Such variability highlights the need to develop innovative and sustainable treatment technologies that can effectively reduce pharmaceutical concentrations in aquatic systems.

Recent scientific studies have emphasized advanced technologies, such as advanced oxidation processes (AOPs), to facilitate pharmaceutical removal from water (Anjali & Shanthakumar, 2019), membrane filtration processes (Gu et al., 2018), Biological treatment process (Dogan et al., 2019), Ion exchange process (Ahmed & Hameed, 2019), Electrocoagulation process (Song et al., 2017). However, in practical use, these technologies and methods are costly and challenging to implement due to the necessity of extreme conditions, including high pressures, elevated temperatures, low pH, and strong oxidizing radicals (Liu et al., 2019). For instance, membrane filtration is limited by high energy consumption, frequent maintenance, and significant operational costs. Advanced oxidation processes and ozonation, while effective, are

generally confined to laboratory-scale applications due to their high economic demands. Biological treatments tend to be slow and require tightly controlled environmental conditions to be effective. Additionally, coagulation and flocculation produce large quantities of sludge, increasing overall treatment and disposal costs (Rashid et al., 2021).

In search of better alternatives, adsorption has become a widely recognised and economically viable method for removing emerging pollutants (EPs) from wastewater. Its effectiveness, operational simplicity, and flexibility make it a strong alternative to conventional treatment approaches. An additional advantage is the potential for adsorbent regeneration, which contributes to minimizing the formation of undesirable secondary pollutants (Melo et al., 2023).

Activated carbon is the most used adsorbent in water treatment due to its high adsorption capacity. However, its use is restricted by high production costs, which typically range from USD 1,100 to 1,700 per ton, and by environmental concerns associated with its production from non-renewable fossil-based materials (Lee et al., 2024; Ali et al., 2012). These limitations emphasise the need to develop low-cost, renewable, and environmentally sustainable carbon-based adsorbents for effective treatment applications.

Earlier centuries' studies mainly focused on natural chars and black carbon. However, in recent years, there has been a steady increase in research on the use of biochar for environmental purposes, especially in water and wastewater treatment. According to Lehmann and Joseph (2015), publications in this area have now exceeded those in more traditional topics like compost science. This trend shows that biochar is gaining recognition as a sustainable option for removing contaminants from the environment.

Among various sorbent materials investigated for contaminant removal, carbon-based substances have shown especially promising performance. Biochar, a carbon-rich material generated by pyrolyzing of organic waste, because of its high surface area, porous structure, and versatility. Biochar can be produced from a variety of biomass feedstocks, including agricultural residues, forestry by-products, municipal solid waste, and sludge originate from biological wastewater treatment processes (Ihsanullah et al., 2021). Therefore, biochar's potential has been investigated as a more sustainable alternative to activated carbon for water quality improvement, owing to its wide availability, low production cost, and comparable adsorption capacity (Kearns et al., 2014). The use of biochar as an adsorbent aligns with the goals of sustainable development (SDG) by offering, renewable and effective solution for

mitigating the risks associated with pharmaceutical contaminants in wastewater (Patro et al., 2024).

There are several types of interactions that control how pharmaceutical chemicals react to biochar, which consist of electrostatic forces, hydrophobic interactions, and π-π stacking. These procedures depend on the surface chemistry of the biochar, as well as the molecular properties of the pollutants (H. Patel, 2021). Essandoh et al. (2014) studied that pine wood-derived biochar has demonstrated a three-dimensional adsorption capacity and can be able to remove pharmaceutical contaminants up to 50 times more effectively per unit mass than activated carbon when applied to contaminated water. In addition to assessing the performance of raw biochar, Chauhan et al. (2022) also examine the impact of surface modification on enhancing its adsorption capacity. The surface chemistry and porosity of biochar are critical parameters that significantly influence its ability to adsorb contaminants from aqueous solutions.

To assess the performance of biochar and other adsorbents, experimental studies commonly use both batch and column systems. Batch experiments are useful for understanding adsorption kinetics and equilibrium capacity, while column studies offer a more realistic evaluation of performance under continuous flow conditions, similar to those in real-world treatment systems. The presence of co-contaminants, such as humic substances and inorganic ions, may affect adsorption efficiency by competing for active sites or modifying the solution chemistry (S. Wang et al., 2021).

In summary, the investigation of New Zealand biochar for the removal of pharmaceuticals such as ibuprofen and paracetamol addresses a critical need for innovative water treatment materials. By evaluating the adsorption performance in both batch and closed-loop column systems, the findings of this study will not only improve the understanding of biochar's practical application in water treatment but also provide valuable data to support the future design of full-scale column systems for the efficient removal of pharmaceutical contaminants.

1.2 Problem Statement

In New Zealand, pharmaceuticals such as ibuprofen and paracetamol have been frequently detected in groundwater and wastewater across both rural and urban catchments, including areas like Waikato, Whakaraupō, and Canterbury. This contamination is largely attributed to domestic sewage from onsite wastewater treatment systems (Coxon et al., 2024).

In 2019, a comprehensive baseline survey in New Zealand examined 61 groundwater sites across the Waikato region. The survey found emerging organic contaminants (EOCs) in 91% of these sites' pharmaceuticals being present in common, with 11 different pharmaceutical compounds identified among 723 substances screened. Detected concentrations ranged widely, from 0.1 to 11,000 ng L^{-1}. Although emerging contaminants have been recognized as one of New Zealand's top 20 environmental research priorities, few studies have specifically investigated biochar produced from local feedstocks, particularly under realistic operational conditions (Moreau et al., 2019).

Globally, Biochar produced through biomass pyrolysis has shown significant promise as an effective adsorbent for eliminating pharmaceuticals from water. Previous studies mentioned that good adsorption performance of biochar for ibuprofen and paracetamol. However, most of these studies used biochar produced from international feedstocks and conducted experiments primarily in batch settings. Batch experiments often overestimate biochar performance because they fail to replicate real-world conditions, such as continuous flow dynamics and practical operational limitations.

There is limited research into raw biochar and surface-modified biochar specifically derived from local biomass from New Zealand. Furthermore, very few studies have evaluated the performance of locally sourced biochar under realistic operational conditions, especially using continuous column systems. Consequently, there is a crucial gap in understanding the effectiveness and practicality of New Zealand-produced biochar in treating pharmaceutical contaminants in real-world water treatment scenarios.

Therefore, this study aims to comprehensively characterize between pretreatment biochar and raw biochar produced from New Zealand feedstocks. It will investigate its effectiveness in removing ibuprofen and paracetamol from aqueous solutions through both batch and column experiments. Addressing this research gap will provide meaningful insights to advance the development of sustainable and locally relevant water treatment solutions.

1.4 Research Question

This research aims to address the following significant questions:

1. What are the key physicochemical characteristics of New Zealand biochar that influence its adsorption capacity for ibuprofen and paracetamol?

2. How effectively does New Zealand biochar remove ibuprofen and paracetamol from water in batch adsorption experiments, and what are the associated adsorption kinetics and isotherms?
3. What is the breakthrough behaviour and cumulative adsorption performance of ibuprofen and paracetamol in a closed-loop recirculating column system using New Zealand biochar?
4. How do operational parameters such as biochar dose, flow rate, influent concentration, and contact time affect the removal efficiency of ibuprofen and paracetamol in both batch systems?

1.5 Research Objectives

It is crucial to consider innovative and sustainable solutions to address the challenges of eliminating emerging contaminants of pharmaceuticals from the aquatic system. Motivated by this challenge, a strong research interest in exploring more sustainable and cost-effective treatment options, focusing on the use of New Zealand biochar as a cost effective and environmentally sustainable adsorbent. Its local availability and environmental benefits make it a promising solution.

This research is projected to contribute to the development of practical treatment options by evaluating the potential of raw biochar and surface-modified biochar for the adsorption process to remove pharmaceutical residues from water systems. Moreover, this study supports innovative water treatment strategies for not only environmental protection but also resource recovery.

The following is an outline of the objectives that this study aims to discover:

1. To design, construct, and operate a column adsorption system to evaluate the dynamic performance of biochar in contaminant removal processes.
2. To characterize the physicochemical properties of selected biochar sourced from New Zealand, with a focus on parameters such as surface area, porosity, particle size and surface functional group.
3. To assess the effect of alkaline surface modification using 30% KOH on the adsorption capacity and removal efficiency of New Zealand biochar for paracetamol.

4. To analyse the isotherm, kinetic, and adsorption capacity of biochar for ibuprofen and paracetamol in batch and column experiments.
5. To evaluate column performance under low feed and high recirculation conditions to simulate a continuous treatment system.
6. To interpret the adsorption data to identify optimal operational conditions for pharmaceuticals removal using biochar in practical real wastewater treatment setups.

1.6 Thesis Structure

The thesis is structured into five chapters; each is designed to explore the research objectives and deliver a thorough understanding of how effectively New Zealand biochar removes pharmaceutical contaminants from aqueous solutions.

The first chapter introduces the background and context of the study. It outlines the growing concern of pharmaceutical pollution in aquatic environments, highlights the limitations of conventional treatment technologies, and presents biochar as a promising alternative adsorbent. The initial section also defines the research problem, states the aims and objectives, and explains the motivation for conducting this research.

Following the Introduction, Chapter 2 provides a detailed review of relevant literature. This includes an overview of emerging organic contaminants (EOCs), with a focus on pharmaceuticals, their environmental occurrence, persistence, and adverse impacts on the environment. The chapter reviews current treatment methods of both conventional and advanced and emphasises adsorption technologies. Particular attention is given to biochar, its production, physicochemical properties, and previous applications in water treatment with the effect of raw biochar and surface-modified biochar. Additionally, an overview of the pharmaceuticals of interest including Ibuprofen and Acetaminophen (Paracetamol). The chapter also identifies research gaps and justifies the scope of this study.

Subsequently, Chapter 3 is dedicated to the experimental research, which describes the methodology employed throughout the research. It includes the materials used, preparation, and characterisation of New Zealand-sourced biochar, and procedures for conducting batch and column adsorption experiments. The design, construction, and operation of the contact column system are also detailed, along with the parameters measured to assess adsorption performance and system efficiency. Analytical techniques used for contaminant detection, such as UV-Vis spectrophotometry, BET, SEM, EDS, and FTIR, are also presented for the total experiment 16.

Chapter 4 presents and discusses the experimental results in relation to previous studies. It includes findings from biochar characterisation, batch adsorption performance, and breakthrough behaviour in the column system. The data are analysed to evaluate the effects of contact time, biochar dosage, particle size, and system configuration on the removal efficiencies of ibuprofen and paracetamol. In addition, adsorption behaviours observed in this study are compared with those reported in the literature, highlighting both the effectiveness and limitations of the selected biochar. The feasibility of implementing biochar-based systems for continuous water treatment is further assessed, considering key operational factors and long-term sustainability.

Chapter 5 concludes the thesis by summarising the key findings and their implications for water treatment practices. It also outlines the study's limitations and provides recommendations for future research, including optimisation of column design, long-term performance monitoring, and potential integration of biochar with other treatment technologies.

Chapter 2

Literature Review

2.1 Emerging Organic Contaminants (EOCs)

Emerging organic contaminants (EOCs) include natural or synthetic chemicals that commonly originate from the wastewater effluent of hospitals, factories, and residential areas, as well as agricultural runoff. Moreover, these contaminants comprise a variety of chemical , including pharmaceuticals and personal care products (PPCPs), endocrine-disrupting compounds (EDCs), pesticides, hormones, per- and polyfluoroalkyl (PFAS) substances (García et al., 2020). The global annual production of pharmaceuticals and personal care products (PPCPs) has been estimated at approximately 20 million tons, with projections indicating continued growth. This trend is largely driven by societal development, including the broader use of pharmaceuticals in both human and veterinary medicine, along with increasing demand for personal hygiene products. Commonly detected PPCPs in the natural environment include nonsteroidal anti-inflammatory agents, hormones, antibiotics, lipid-regulating compounds, beta-blockers, anticonvulsants, preservatives, disinfectants, ultraviolet filters, and insect repellents (Wang & Wang, 2016).

This study will focus on two commonly detected pharmaceutical emerging organic contaminants (EOCs) of ibuprofen and acetaminophen (paracetamol). These compounds were selected from the wider category of EOCs group based on their common presence in aquatic environments and their potential risk to ecological systems.

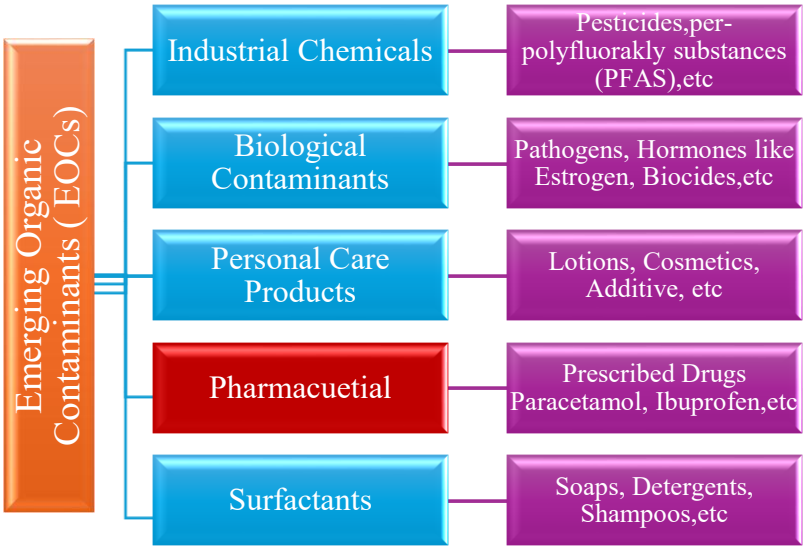

Figure 2.1 Categories of Emerging Organic pollutants (EOCs) discharged via domestic and industrial wastewaters

Moreover, EOCs are routinely utilized by persons and industries worldwide, resulting in significant quantities being discharged into various environmental matrices, including water, soil, and air. There is increasing global concern about the adverse effect of EOCs on both environment quality and food chain. The widespread presence of EOCs adversely affects human health and the resilience of freshwater and marine ecosystems (Coxon et al., 2024).

Pharmaceuticals such as antibiotics and hormones, along with PFAS (often utilized in industrial applications), are progressively discovered in surface water, groundwater, wastewater, and leachate. For instance, Martín et al. (2012) conducted a study that demonstrated the frequent finding of prescription as well as over-the-counter medications, including paracetamol, ibuprofen, diclofenac, and antibiotics, in water systems because of human and veterinary use.

These compounds have been developed for stability in applications, their constant discharge into the environment, along with their primary supply of municipal and industrial sewage, can make them extremely dangerous, keeping them resistant to environmental degradation, resulting in accumulation and potential adverse effects on animal and human populations (Snyder et al., 2003).

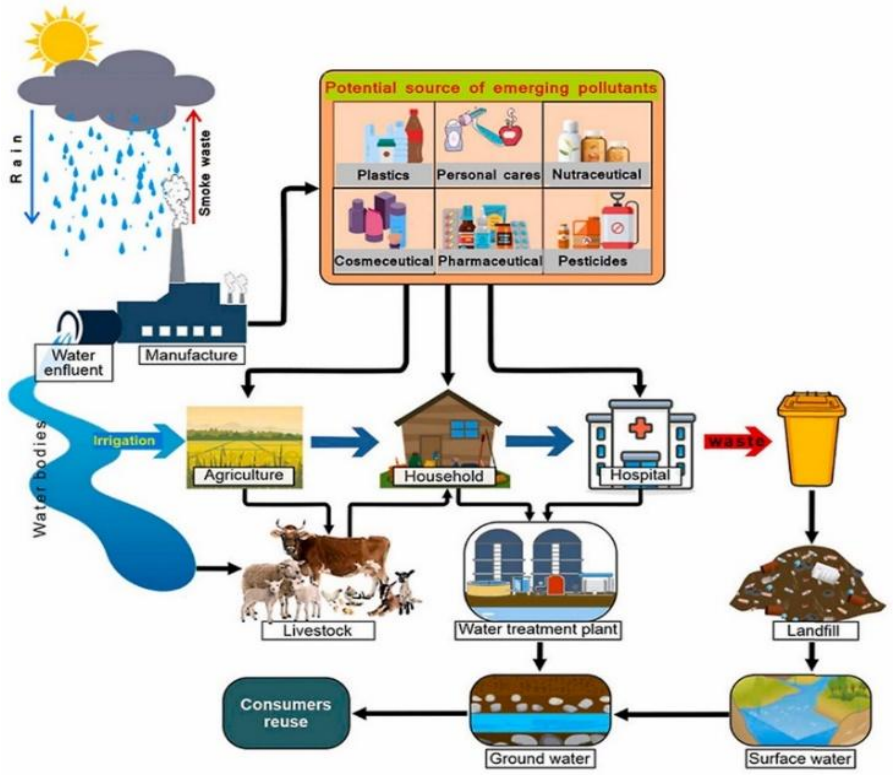

Figure 2.2 Schematic of Emerging Organic Contaminants (EOCs) from sources to receptors, Rasheed et al. (2018).

The diverse range of EOCs will exhibit physico-chemical properties that span from hydrophilic ("water-loving") to hydrophobic ("water-fearing"). The transport and ultimate destiny of EOCs depend upon their physicochemical properties: hydrophilic EOCs will mostly be solubilized in the aqueous phase and have a more ephemeral character, whereas hydrophobic EOCs will predominantly be associated with particulates and have greater persistence (Stewart, Northcott, Gaw, & Tremblay, 2016).

2.1.1 Pharmaceuticals and Personal Care Products (PPCPs)

The substantial amounts of acetaminophen (paracetamol) are commonly prescribed and purchased over the counter in New Zealand. So, the concentrations reported in following table 2.1 for this substance may provide as a reference for what could be detected in New Zealand's municipal wastewater. These findings, together with data from the 2010 Pharmac list of the most prescribed pharmaceuticals in the country (Pharmac 2010) as shown in the table. Some of these pharmaceuticals were also investigated in the US EPA study, offer valuable insights into compounds that might be detected in the influent and effluent of typical urban wastewater systems in New Zealand, including samples collected from the Hawke's Bay wastewater treatment facilities.

Table 2.1 Ranking of the 20 most prescribed pharmaceuticals in New Zealand in 2010 (adapted from Pharmac, 2010).

Rank	Pharmaceutical Compound	Treatment Indication
1	Paracetamol	Analgesic / Antipyretic
2	Aspirin	Analgesic / Anti-platelet
3	Simvastatin	Cholesterol and cardiovascular control
4	Omeprazole	Dyspepsia, peptic ulcer disease
5	Amoxicillin	Broad spectrum antibiotic
6	Metoprolol succinate	βblocker for blood pressure control
7	Amoxicillin clavulanate	Broad spectrum antibiotic
8	Salbutamol	Asthma (inhaled)
9	Diclofenac sodium	Analgesic/Anti-inflammatory
10	Cilazapril	ACE inhibitor

11	Zopiclone	Hypnotic
12	Ibuprofen	Analgesic
13	Prednisone	Steroid
14	Flucloxacillin	Antibiotic
15	Quinapril	ACE inhibitor
16	Bendroflumethiazide	Diuretic
17	Felodipine	Calcium channel blocker
18	Alendronate sodium	Osteoporosis
19	Metformin	Type II diabetes
20	Fluticasone	Asthma (inhaled)

Research in New Zealand has been investigated the presence of pharmaceuticals and personal care products (PPCPs) the in wastewater and related environmental media. For example, A doctoral research project at the University of Canterbury (Gielen 2007) evaluated 12 pharmaceutical and personal care products in treated wastewater effluent, sewage sludge (biosolids), soil environments, and pore water. The study also evaluated the removal efficiencies of three treatment methods: activated sludge, composting, and land application. Pharmaceuticals and personal care products were identified in all environmental areas; however, the reported concentrations did not exhibit acute toxicity toward soil organisms or affect lettuce seed germination. Research indicated that pharmaceutical contaminants produced immediate and prolonged effects on soil microbial communities. Initial short-term microbial effects transitioned to long-term (12-year) adaptation to three pharmaceutical active compounds (PhACs) namely, paracetamol (acetaminophen), tetracycline, and aspirin was also noted.

In a partnership with the National Institute of Water & Atmospheric Research (NIWA) and Dr. Mira Petrović in Barcelona, Spain, a study analysed 46 pharmaceutical active compounds (PhACs) in sediments and 68 PhACs in biosolids using archival sediment samples from Auckland (Stewart et al., 2009) and biosolids collected from five wastewater treatment plants across New Zealand. Although PhAC concentrations in biosolids showed considerable variability, levels exceeding 3000 ng/g were reported at a larger WWTP, while concentrations up to 780 ng/g were recorded at a facility with a catchment area comparable to Hawke's Bay.

Sediment analyses revealed that a substantial number of PhACs had entered the marine receiving environment around Auckland, with concentrations reaching up to 10.8 ng/g (Stewart et al., 2009).

Pharmaceutical residues in New Zealand were identified in effluent from the Rotorua wastewater treatment plant through analytical monitoring (Gielen, 2007). Detected compounds included naproxen (analgesic), carbamazepine (nervous system), diltiazem (cardiovascular), ibuprofen (analgesic), and amitriptyline (antidepressant). The average concentrations of these substances in the treated effluent ranged from 30 ng/L for amitriptyline to 990 ng/L for naproxen.

The pharmaceutical profile of coastal sediments in the Auckland region exhibited some variation (Stewart et al., 2014). Acetaminophen and naproxen were reported at mean concentrations of 7.5 µg/kg and 5.5 µg/kg, respectively. Other pharmaceuticals, including metoprolol (cardiovascular), diclofenac (analgesic), fenofibrate (cardiovascular), clarithromycin (antibiotic), roxithromycin (antibiotic), ranitidine (alimentary tract), cimetidine (alimentary tract), and sotalol (coronary), were detected at mean concentrations of 2 µg/kg or lower.

Stewart (2016) further examined EOCs in effluent from the Omaha wastewater treatment plant, located north of Auckland. The analysis targeted three analgesics, all of which were detected at concentrations of 145 ng/L for ibuprofen, 51 ng/L for diclofenac, and 6 ng/L for paracetamol (acetaminophen).

2.1.2 PFAS (Per- and Poly-Fluoroalkyl Substances)

PFAS stands for per- and poly-fluoroalkyl substances, a class comprising thousands of chemical compounds that are widely used in both industrial and domestic settings. PFAS, also known as "forever chemicals," are characterized by an exceptionally persistent carbon-fluorine link and at least one hydrophobic fluoroalkyl component in each molecule. They are commonly categorized according to the number of carbon atoms in their molecular backbone as long-chain (> 7 carbons), short-chain (4–6 carbons), or ultrashort-chain (< 4 carbons) (Vlad et al., 2023).

Before being banned in 2006, firefighting foams in New Zealand had been using two of the PFAS chemicals, PFOS and PFOA, for more than 50 years. In New Zealand, they have been applied to flammable liquid fires in fire training facilities and airports. In these circumstances, they were frequently utilized at great quantities, in open areas, and on bare ground. Due to

PFAS's high environmental mobility, these locations are a clear initial option for possible soil, surface water, and groundwater contamination. Early studies on PFAS revealed connections to conditions like thyroid, cholesterol, cancer, problems with reproduction, and low birth weights. According to Australia's most recent health advise, there is insufficient evidence to connect exposure to PFAS to human illness (Vlad et al., 2023).

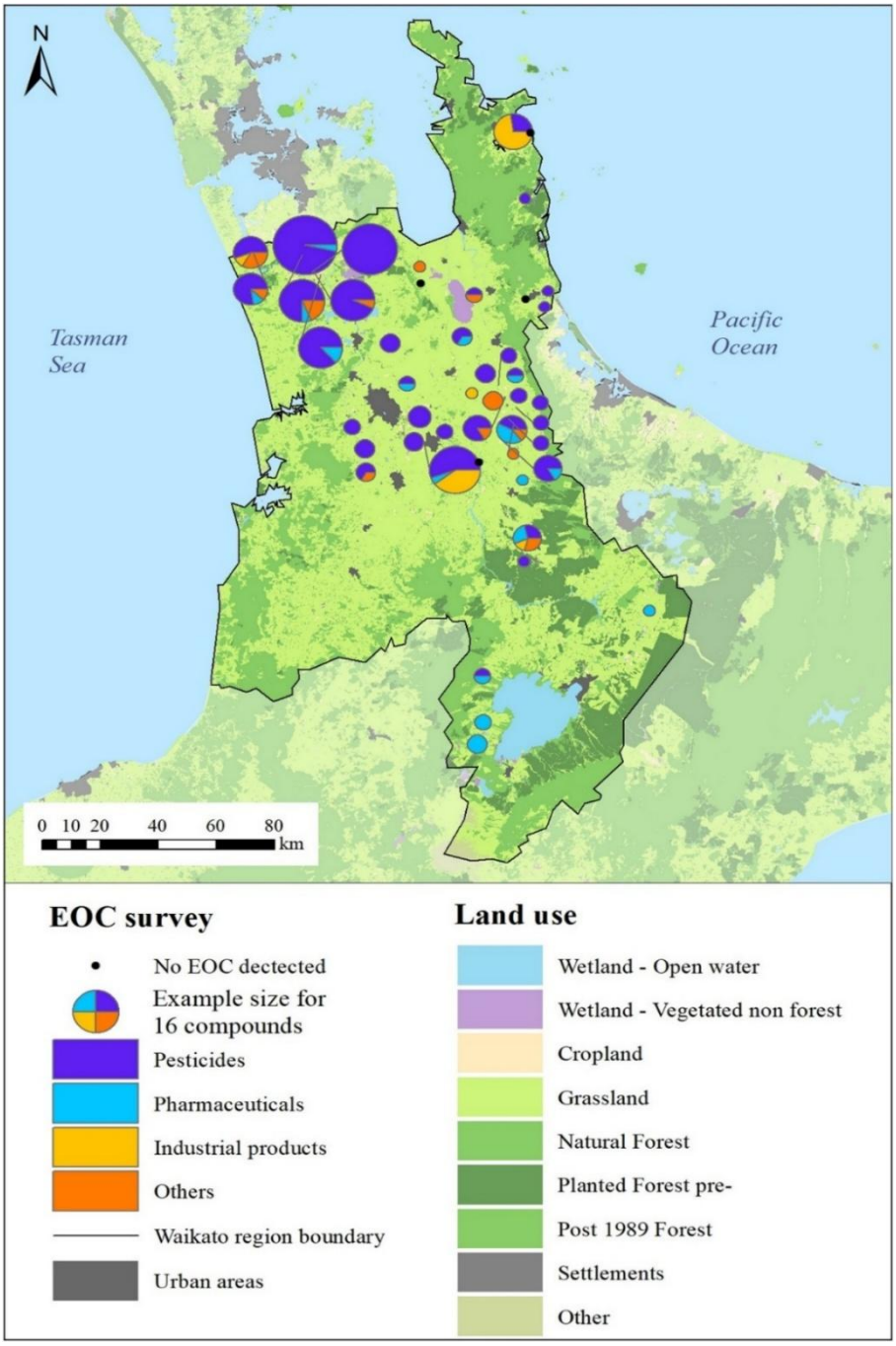

Figure 2.3 (Moreau et al., 2019) Spatial distribution of EOC detections at SOE groundwater sites in the Waikato region, New Zealand. The size of the circle is proportional to the number

detected compounds; a scaled example displaying 16 compounds is shown in the legend for reference.

2.2 Occurrence and Prevalence in Water Bodies

The widespread application of pharmaceuticals in human and veterinary medicine has led to their frequent occurrence in surface water, groundwater, and even drinking water supplies. The presence of these substances in aquatic ecosystems represents a global environmental challenge rather than a problem confined to specific regions. Numerous studies have documented the detection of various pharmaceutical substances in water bodies across the world, including common analgesics such as ibuprofen and paracetamol, as well as antibiotics, hormones, and antiepileptic drugs (M. Patel et al., 2019). Since pharmaceutically active compounds were first identified in aquatic environments in the 1980s, a wide range of these substances has been detected in diverse water bodies. Bush (1997) categorised these therapeutic compounds into several major groups:

(i) anti-inflammatories and analgesics, including ibuprofen, paracetamol, and diclofenac.
(ii) antibiotics such as sulfonamides, tetracyclines, penicillins, β-lactams, macrolides, fluoroquinolones, and imidazoles;
(iii) antiepileptics like carbamazepine;
(iv) antidepressants, including benzodiazepines;
(v) lipid-lowering agents such as fibrates;
(vi) antihistamines, including famotidine and ranitidine;
(vii) β-blockers like metoprolol, atenolol, and propranolol; and
(viii) other compounds such as barbiturates, narcotics, antiseptics, nd contrast media.

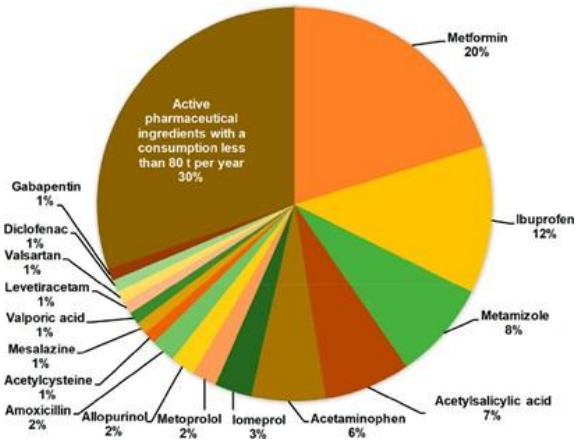

Figure 2.4 Global consumption trends of pharmaceuticals usage (M. Patel et al., 2019)

An assessment commissioned by Germany's Ministry for the Environment identified 631 out of 713 tested pharmaceutical compounds were detected above analytical detection limits. These substances were identified in surface waters across 71 countries can be seen in Figure 2.4. In a separate global evaluation, 203 pharmaceutical compounds were reported in 41 countries (Hughes et al., 2012). Several nationwide studies have also been conducted to assess emerging organic contaminants (EOCs), including pharmaceutically active compounds, especially in countries such as Germany, the United States, and Japan. In Japan, a nationwide survey investigated the presence of 12 antibiotics across 37 rivers, with combined cumulative concentrations reaching as high as 626 nanograms per litter (Murata et al., 2011).

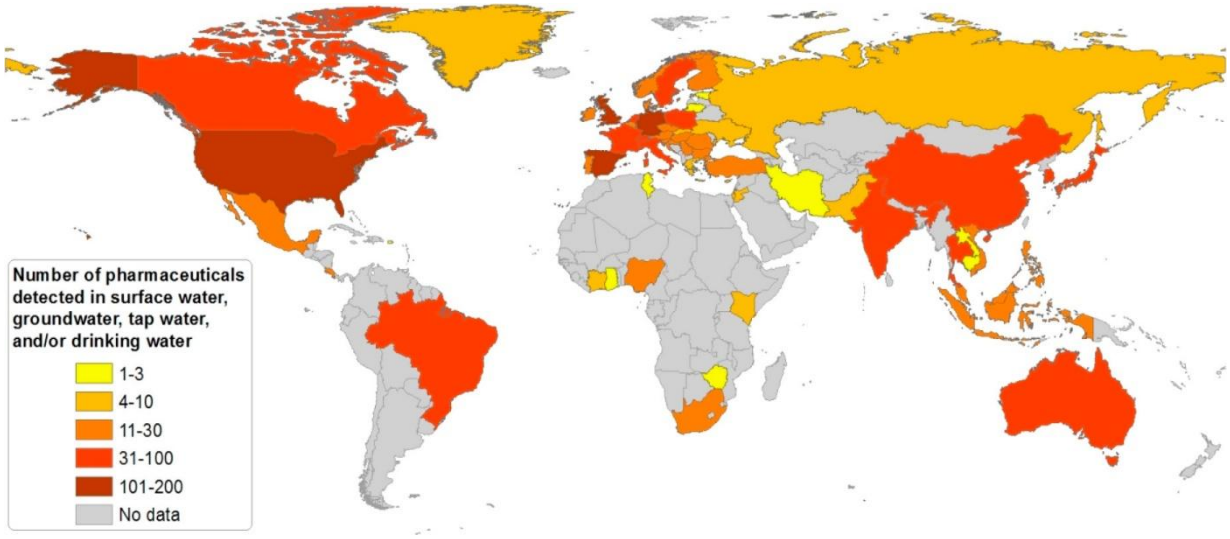

Figure 2.5 Worldwide presence of pharmaceutical compounds in drinking water, tap water, groundwater, and surface waters, based on findings by Beek et al. (2015b). Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA (2016).

2.3 Sources and Pathways of Pharmaceuticals

Pharmaceutical compounds in aquatic systems are now recognized as a serious environmental issue. As part of the broader group of emerging contaminants, they have a detrimental effect on the aquatic ecosystems and may also pose risks to human health (Das et al., 2024). Moreover, these pollutants are derived from a variety of pathways, which can be broadly classified as point and non-point sources. Point sources refer to clearly identifiable origins, such as discharges from hospitals, pharmaceutical industries, and wastewater treatment facilities (Lapworth et al., 2012).

Even small sources, such as residential disposing of expired or unused medicines, including antibiotics, analgesics like paracetamol and ibuprofen, down sinks or restrooms, can contribute

to pharmaceutical concentrations in wastewater and emerge as point sources (Kümmerer, 2009b). Ibuprofen and paracetamol were identified within a concentration range of 1.7–373.1 µ.g/L and 0.35–180 µ.g/L (Vymazal et al., 2016).

According to studies conducted in New Zealand, a significant portion of the population disposes of medications in toilets or sinks. For example, according to a poll, over a quarter (19%) of participants poured pills down the drain, and more than half (55%) reported doing the same with liquid drugs (Braund et al., 2009). Similarly, a survey of pharmacies in New Zealand revealed that the wastewater system was most frequently used to dispose of unwanted liquid medications (52%) and some prohibited substances (73%). (Tong et al., 2011).

Wastewater treatment plants are considered as a primary source of pharmaceutical pollution because conventional treatment systems lack the specific design to remove these compounds. Consequently, pharmaceutical residues frequently remain in the treated effluent and are released into surface water resources(Rodríguez-Serin et al., 2022).

According to Murray et al. (2010), non-point sources typically experience natural attenuation in the soil profile, which lessens their environmental impact. The pathways by which pharmaceuticals are released from sources and transported to receptors are presented in Figure 2.6.

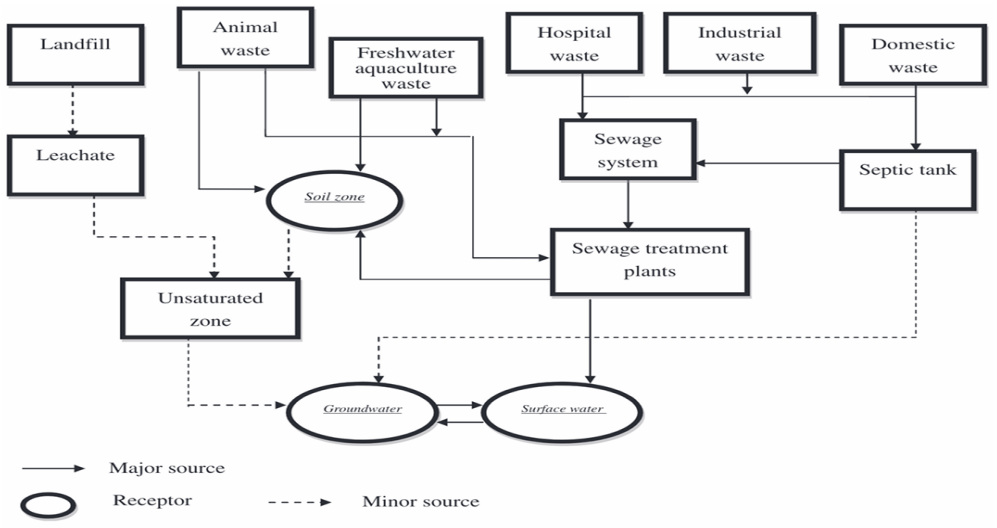

Figure 2.6 (Li, 2014) Potential origins and pathways of pharmaceutical pollution in soil and water.

2.3.1 Domestic Wastewater

Residential sources comprise a mixture of emerging organic contaminants (EOCs)in water bodies, including disposal of personal care products compounds. Multiple pharmaceuticals,

including antibiotics, analgesics like paracetamol and ibuprofen, and endocrine disruptors such as estrogen are partially excreted in bioactive or unchanged forms, entering the wastewater stream through sinks and restrooms (Jelic et al., 2012).

These pollutants are frequently resistant to standard wastewater treatment methods, which leads to their release into water systems at low but significant source of EOCs in aquatic environment (Jelic et al., 2012).

As consumer demand for pharmaceuticals continues to increase, awareness of their potential to degrade environmental quality is also emerging serious problem. Pharmaceuticals residue have been found in nearly every continent's environmental matrix, including surface water (lakes, rivers, streams, wetlands, and seas), sludge, groundwater, and influents and effluents from wastewater treatment operations (Patel et al,2019; Bedoya-Ríos et al., 2017). In addition, these are found in wastewater is classified as a micropollutant, which is a diverse group of organic compounds detected in the environment at low levels of concentration (μ g/L or ng/L) (Hind M. Ewadh*, Siti Rozaimah Abdullah, Nurina Anwar, Hassimi Abu Hasan, 2017).

2.3.2 Industrial Wastewater Effluent

The key industries sector includes pharmaceuticals, textiles, and chemical production significantly contribute to the release of diverse pollutants, such as pharmaceuticals and synthetic chemicals, into aquatic systems. These effluents frequently pose a diverse range of chemical substances and high levels of contaminants, primarily because from insufficient on-site treatment methods (United Nations Environment Programme, 2016).

Significant emerging organic contaminants (EOCs) detected in industrial wastewater include synthetic estrogens, including 17α-ethinylestradiol, which can be found in oral contraceptives. These compounds are introduced into aquatic environments through industrial effluents as well as domestic wastewater. Studies has demonstrated that these estrogens can cause endocrine disruption in aquatic organisms, resulting in harmful biological effects, including the feminization of male fish populations that are observed downstream of effluent discharge points (Kidd et al., 2007). Conventional wastewater treatment plants (WWTPs) are unable to effectively remove these compounds, which contributes to their persistence in aquatic systems and leads to their ecological impact.

2.3.3 Agricultural Runoff

A notable route through which EOCs enter water systems is agricultural runoff. Activities involving veterinary drugs, insecticides, and hormonal treatments both natural and synthetic applied in livestock and crop production often provide the source of this contamination. These

compounds are frequently released into the environment by animal's waste and the utilization of manure or slurry as fertilizer, which may contain unmetabolized residues (Sarmah et al., 2006). When contaminated manure is applied to agricultural fields, it serves as a source of EOCs that can infiltrate surrounding water systems via surface runoff and soil leaching. Aspects include soil composition, rainfall intensity, and the presence of organic matter define the kinetics of EOC transfer (Kümmerer et al., 2018). In comparison to other nations, agriculture in New Zealand is expected to contribute less significantly to the influx of veterinary drugs into waterways (Weiss et al., 2008).

The dairy farming sector in New Zealand is a significant contributor to steroid hormones released into the environment (Gadd et al., 2009b). The levels of estrogenic steroid hormones in dairy shed effluents discharged into waterways or used for pastures surpass those observed in wastewater treatment plant effluent. The vast majority of dairy cow waste passes straight onto the pasture by defecation and urination without any treatment. Steroid hormones are contained in animal waste, effluents from irrigated oxidation ponds, and slurry. These are applied to pasture and may penetrate soil into groundwater or be conveyed from pasture to nearby water bodies (Gadd et al., 2009). Consequently, estrogenic steroid hormones have been discovered in groundwater and stream waters in extensively irrigated dairy catchments in New Zealand (Gadd et al., 2009).

The findings from the case study by Ginebreda et al. (2009b) documented an increasing number of pharmaceutical residues in European rivers, largely related to agricultural activities, especially in regions with substantial use of medicated feed and animal manure. These studies emphasized the necessity for improved animal waste management and runoff legislation to minimize EOC contamination in aquatic systems and conserve ecosystems and public health.

2.3.4 Landfill Leachate

Leachates from landfills are another pathway that EOCs could reach marine ecosystems (Ramakrishnan et al., 2015). As deposited waste products decompose, a variety of EOC classes are projected to be discharged into landfill leachates. Pharmaceuticals, musk perfumes, insect repellents, flame retardants, UV filters, and perfluorinated chemicals are a few examples of EOCs that have been measured in landfill leachates. When this contaminated leachate seeps into surrounding soils and groundwater, it can lead to significant and persistent contamination issues posing long-term ecological and health risks. (Eggen et al., 2010).

Commonly used medications for pain relief and fever reduction, like ibuprofen and paracetamol, are frequently found in landfill leachates. Inappropriate disposal methods, such

as flushing expired medications down the toilet or throwing them out with regular trash, allow these chemicals to end up in landfills. These medications could pass through the leachate of landfills and perhaps enter the groundwater systems. According to research, these chemicals' partial resilience to natural degradation processes results in their persistence in leachate and subsequent occurrence in downstream water supplies (Eggen et al., 2010).

2.4 Environmental and Health Impacts of Pharmaceuticals

Pharmaceutical contamination in water systems affects not only human health but also aquatic life and ecosystem balance. These effects are not always straightforward and pose an immediate threat to human health, which remains considerable due to limited data on long-term exposure and the combined effects of chemical mixtures.

Many pharmaceuticals remain active even at low concentrations and disrupt the endocrine systems of aquatic organisms. For example, estrogen-based compounds have been linked to reproductive abnormalities in fish (Krasucka et al., 2020). Endocrine-disrupting compounds (EDCs) have been demonstrated to interfere by certain pharmaceuticals. This disruption has the potential to lead to modifications to the reproductive such as feminization of male fish and reduced fertility rates and developmental processes of aquatic species. Furthermore, Adegoke et al. (2023) noted that these contaminants have the potential to migrate into groundwater and soil. This not only increases the risk of bioaccumulation through the food chain but also affects their environmental impact.

The discharge of antibiotics into aquatic environments contributes to the rise of antimicrobial resistance (AMR). This represents a serious and growing global health issue. AMR reduces the effectiveness of antibiotics in treating infections and places added strain on public health systems (Qiu et al., 2022). Beyond direct health risks, long-term exposure of aquatic organisms that are exposed to pharmaceutical traces over a long time can accumulate these substances in their bodies (bioaccumulation) and the food chain (biomagnification). Furthermore, the chronic exposure of aquatic organisms to pharmaceutical residues can lead to amplifying their ecological consequences (Díaz et al., 2024).

In addition to impacting wildlife, pharmaceuticals can impair plant health by disrupting symbiotic relationships with soil microorganisms, which are crucial for nutrient cycling and overall plant resilience (Gaw et al., 2014). These disruptions can lead to reduced plant growth and productivity, ultimately affecting entire terrestrial ecosystems can see in figure 2.7.

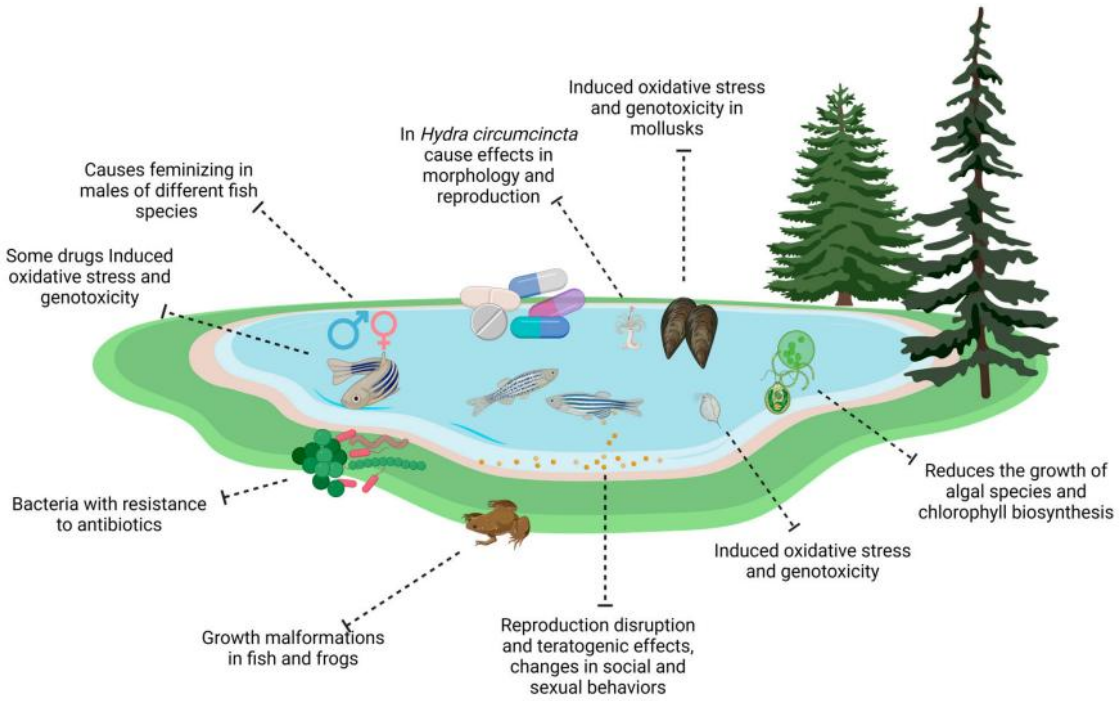

Figure 2.7 Environmental risks of pharmaceuticals on freshwater and marine organisms (Estrada-Almeida et al., 2024).

2.5 Management Strategies for Pharmaceutical Pollution

The management of pharmaceutical contaminants remains a growing challenge, driven by the continuous emergence of new compounds and uncertainties regarding their chronic ecological effects. Regulatory agencies face difficulties in ranking emerging pollutants based on their environmental and health risks (Nataraj, 2022b). Risk assessment is further complicated by chemical mixtures, fluctuating environmental conditions, and possible interactions between contaminants. Conventional wastewater treatment systems are generally ineffective at eliminating pharmaceuticals, resulting in their persistent detection in treated wastewater and aquatic environments (Coxon et al., 2024).

Addressing the challenges presented by pharmaceutical contamination requires a comprehensive and integrated strategy, incorporating source control measures, advanced treatment technologies, and thorough ecological risk assessments. Source control strategies focus on minimizing the input of these pharmaceuticals into the environment by promoting responsible usage practices, implementing drug return programs, and exploring the development of more biodegradable drug formulations (Patel et al., 2019).

Nonetheless, several source control measures are currently being implemented globally to reduce the discharge of contaminants of emerging concern (CECs) into the environment. For

instance, several countries have introduced national-level measures to address the environmental risks associated with pharmaceutical waste. In the United States, specific regulations guide the disposal of hazardous pharmaceutical waste within the healthcare sector. Germany has established an environmental checklist aimed at managing the use and release of veterinary pharmaceuticals. In Sweden, a "Wise List" has been developed to promote the use of commonly prescribed pharmaceuticals, incorporating environmental impact as a criterion in the selection process (“Pharmaceutical Residues in Freshwater,” 2019).

This inefficiency highlights the necessity for innovative remediation and the development of sustainable and efficient treatment methods. Therefore, advanced treatment technologies, including membrane bioreactors and adsorption-based methods, have shown potential for improving the removal of contaminants. Among these, biochar-based adsorption stands out as a sustainable option due to its strong adsorption capacity for both organic pollutants and heavy metals (Zeghioud et al., 2022). Biochar has gained interest as a cost-effective, eco-friendly adsorbent capable of removing various contaminants, including pharmaceutical residues (Dong et al., 2023; Qiu et al., 2022). In countries like New Zealand, where protecting aquatic ecosystems and public health are key priorities, the use of biochar presents a practical, sustainable solution and potential to mitigate the environmental and health impacts of pharmaceutical pollution (Dong et al., 2023).

Although research into pharmaceutical ecotoxicity is ongoing, concerns about environmental persistence, metabolic transformation pathways, and bioaccumulation potential underscore the critical need for enhanced removal mechanisms (M. Patel et al., 2019). Utilizing advanced adsorbent materials such as biochar in the treatment systems is considered an effective strategy for addressing the challenges posed by pharmaceutical contamination (Qiu et al., 2022).

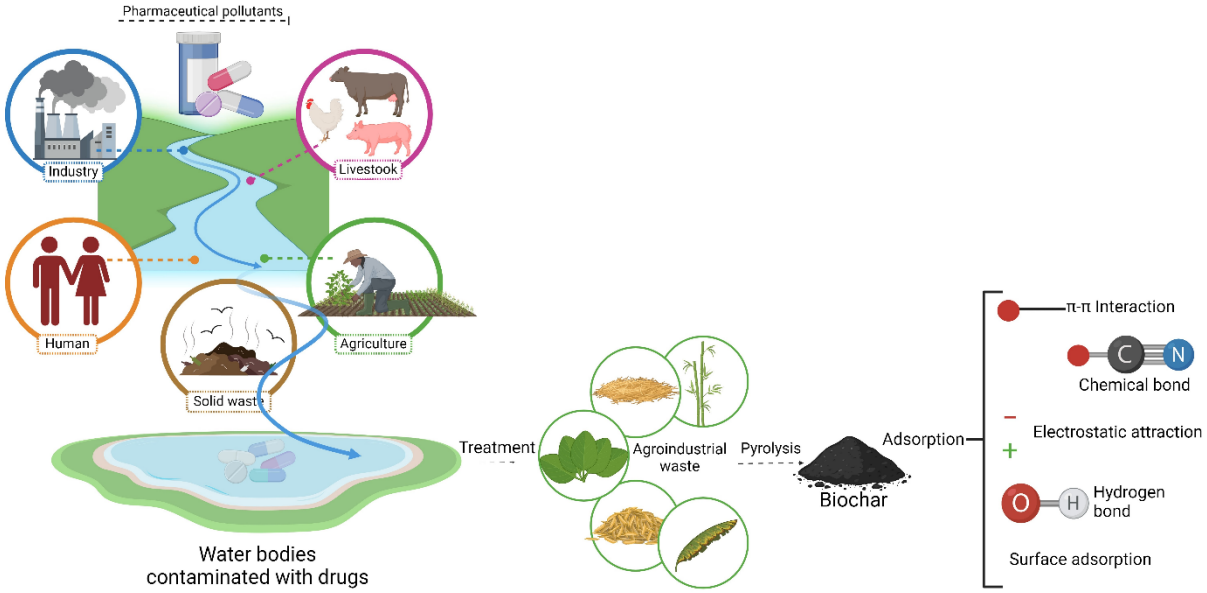

Figure 2.8 Pharmaceutical Contamination and Treatment Method of Adsorption with Biochar (Estrada-Almeida et al., 2024).

2.6 Treatment Technologies for Pharmaceuticals

Pharmaceuticals are increasingly detected in various water sources due to their widespread use and incomplete removal during wastewater treatment. Their chemical stability and low biodegradability make many of these compounds resistant to conventional treatment processes. As a result, there is growing interest in identifying effective technologies capable of removing pharmaceutical residues from water. Treatment methods can be broadly classified into conventional approaches, such as activated sludge and filtration, and advanced techniques, including adsorption, membrane processes, and advanced oxidation (Renita et al., 2017).

All treatment technologies for removing contaminants of emerging concern, such as pharmaceuticals, offer specific advantages and limitations. Among these, adsorption has emerged as a promising approach due to its operational simplicity, ease of design, and effectiveness. Unlike some advanced treatments, adsorption does not generate harmful by-products, making it a safer and more environmentally sustainable option for wastewater purification (D. S. Tong et al., 2010). The following sections Table 2.2 will discuss the current and new strategies and treatments designed to tackle the issue of pharmaceutical elimination, focusing on their effectiveness, benefits, and drawbacks.

Table 2.2 Overview of Wastewater Treatment Technologies for Pharmaceutical Contaminant Removal

Treatment Technology	Advantages	Limitations	References
Adsorption Process	Operates under simple conditions, requires low energy input, generates minimal sludge, and provides high removal efficiency.	High cost is associated with the use of commercial activated carbon.	(Garba et al., 2019; Zaied et al., 2020)
Membrane Filtration Process	Provides rapid treatment and efficient removal of salts and organic pollutants; suitable for large-scale applications.	High operational costs and susceptibility to membrane fouling.	(Gu et al., 2018)
Electrocoagulation Process	Suitable for continuous operations and large-scale treatment; highly effective in removing colloidal and ionic contaminants.	Generates sludge and requires frequent electrode maintenance or replacement.	(Song et al., 2017)
Advanced Oxidation Process	Capable of effectively degrading organic pollutants and precipitating heavy metals in aqueous environments.	Involves high operational costs and substantial reagent use; some methods require pretreatment to ensure consistent performance.	(Anjali and Shanthakumar, 2019)

Biological Treatment Process	Features simple reactor design and operation; produces bioenergy (methane) and achieves high removal efficiency, even under low temperature conditions.	Time-intensive due to the slow microbial activation process; post-treatment often necessary to eliminate residual nutrients and pathogens.	(Dogan et al., 2020)
Ozonation Process	Efficiently removes organic pollutants and enhances disinfection through oxidation.	May disrupt radical scavengers, requires high energy input, and can produce harmful oxidative by-products.	(Gomes et al., 2017; J. Wang & Bai, 2016)
Ion Exchange Process	Highly effective for water softening and can be utilized for treating wastewater.	High operational costs due to the need for regular regeneration and cleaning of ion exchange media to maintain performance.	(Ahmed and Hameed, 2019)

2.7 Adsorption Process

Adsorption is considered one of the most promising technologies for removing emerging organic contaminants (EOCs) from water. Its popularity is due to several advantages, including low energy use, simple operation, and the ability to treat different types of water. The process relies on the interaction between contaminants and the surface of solid adsorbents, enabling effective removal through surface attachment. Because of these benefits, adsorption is widely seen as a practical and effective method for removing EOC compounds in both laboratory research and real-world applications. This approach also demonstrates strong potential for the adsorption of various pharmaceutical compounds (PCs) onto the surface of the adsorbent. A wide range of materials can serve as suitable adsorbents, provided they are cost-effective and possess a high capacity for contaminant removal from wastewater (Chauhan et al., 2022).

Biochar, a carbon-rich material generated by the pyrolysis of biomass, is increasingly recognised as an efficient, sustainable, and low-cost adsorbent. Its adsorption capacity for specific emerging organic contaminants (EOCs) can be enhanced through surface modification techniques (Zhang et al., 2019). The growing interest in biochar stems from its potential for resource recovery and its environmental sustainability. This study focuses on the application of biochar produced from locally sourced organic waste in New Zealand. The aim is to evaluate its effectiveness in adsorbing selected EOCs, including pharmaceuticals from aqueous solutions. By investigating the performance of New Zealand-derived biochar, this research not only explores its potential as a practical and eco-friendly adsorbent but also highlights the benefits of utilising regionally available materials in environmental remediation efforts.

2.7.1 Adsorption Mechanism

Adsorption is a physicochemical process whereby molecules from a fluid phase accumulate on the surface of a solid material, termed the adsorbent. This mechanism involves a relatively straightforward mechanism in which the interactions between the adsorbate molecules of pharmaceutical compounds and the surface sites of the adsorbent, including van der Waals forces, electrostatic interactions, hydrogen bonding, and, in some cases, covalent bonding, as illustrated in Figure 2.9. The efficiency of adsorption is influenced by several factors, such as the surface area, porosity, and surface chemistry of the adsorbent, as well as the physicochemical properties of the adsorbate and the solution environment (Yan et al., 2020a).

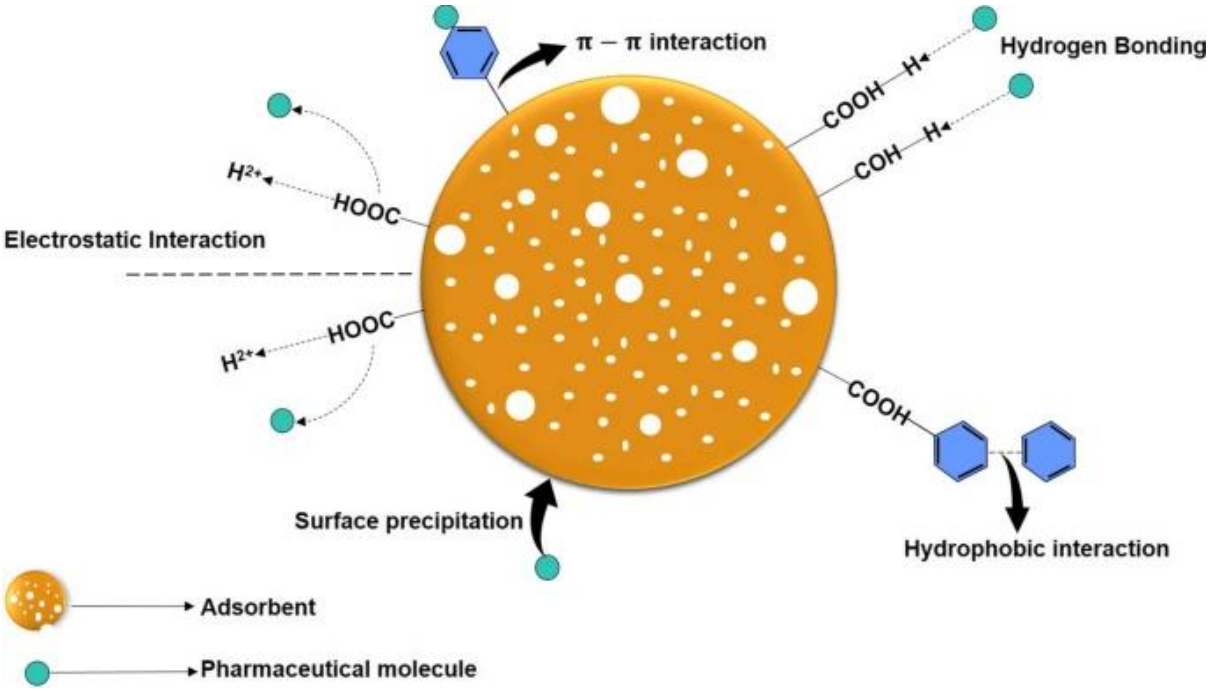

Figure 2.9 Adsorption Mechanisms of Pharmaceutical Compounds on Solid Surface (Chauhan et al., 2022).

2.7.2 Adsorption Isotherms

Adsorption isotherms describe the equilibrium relationship between a contaminant's concentration in solution and its amount adsorbed on the biochar surface at a fixed temperature (M. B. Ahmed et al., 2016). They offer valuable insights into the adsorption capacity of the biochar and help characterise the underlying adsorption mechanisms. Among the various isotherm models, the Langmuir and Freundlich models are the most commonly applied to describe the adsorption behavior of contaminants onto biochar (Xiao & Chen, 2015).

2.7.3 Adsorption Kinetics

Adsorption kinetics explores the rate how quickly a contaminant, or adsorbate, is transferred from a liquid solution onto the surface of a solid adsorbent such as biochar (Ocampo-Pérez et al., 2012). This type of analysis is useful for determining the time required for the system to reach adsorption equilibrium. While adsorption isotherms describe the equilibrium relationship between the adsorbent and adsorbate, kinetic studies focus on the time-dependent behaviour of the process. Understanding these dynamics helps reveal how fast adsorption occurs and what mechanisms may be controlling the rate of removal (Ray et al., 2020).

Adsorption kinetic models are generally classified into two main categories: diffusion-based models and reaction-based models. Diffusion models describe the movement of adsorbate molecules through three distinct phases such as external diffusion (boundary layer transport),

internal or pore diffusion, and adsorption onto active sites. Although several complex diffusion models have been proposed, their practical application is often limited due to mathematical complexity and difficulty in interpretation. As a result, simplified empirical models, such as the Weber and Morris intraparticle diffusion model, are commonly used to represent diffusion-controlled adsorption behaviour. In contrast, adsorption reaction kinetic models are also empirical but are developed to describe the overall adsorption process over time. These models are based on the interaction mechanisms between the adsorbate and the adsorbent, providing insights into the rate-controlling steps throughout the entire adsorption period (H. Qiu et al., 2009; J. Wang & Guo, 2020).

2.8 Adsorption of Pharmaceuticals Using Biochar

Adsorption is a commonly applied technique for removing pharmaceutical pollutants from water, with carbon-based materials such as activated carbon, carbon nanotubes, reduced graphene oxide, and biochar serving as effective adsorbents (Baccar et al., 2012). Among these, biochar stands out due to its low cost, well-developed porous structure, and abundance of surface functional groups, including –OH, –COOH, and $–NH_2$. These features have led to biochar being recognised as a promising functional carbon material for future environmental technologies (Monisha et al., 2021).

Recent studies have confirmed the effectiveness of both unmodified and surface-modified biochar in adsorbing pharmaceutical compounds from aqueous media. Key factors that influence its adsorption efficiency include surface area, pore volume, and the chemical nature of its functional groups. These characteristics influence the interaction mechanisms between the biochar surface and pharmaceutical compounds in solution (Monisha et al., 2021).

Several studies have investigated the use of biochar derived from various biomass sources for the removal of ibuprofen from aqueous systems as shown in the Table 2.3. In the following table section outlines the adsorption capacities of different biochar types that have been studied for the elimination of pharmaceutical contaminants in the aquatic system. For instance, pinewood biochar produced at 425 °C with a residence time of 20–30 minutes was shown to effectively adsorb ibuprofen, following pseudo-second-order kinetic behaviour and exhibiting optimal performance under acidic pH conditions. Its maximum Langmuir adsorption capacity was reported at 10.74 mg/g, surpassing that of commercial activated carbon (Essandoh et al., 2014).

In another study, biochar derived from pepper stems (PS-biochar) demonstrated high adsorption efficiency for ibuprofen, attributed to its well-developed mesoporous structure and

favourable surface chemistry. The adsorption mechanism was primarily governed by π–π interactions, hydrogen bonding, and pore-filling, with a Langmuir monolayer capacity of 569.6 mg/g, and kinetics consistent with the pseudo-second-order model (Naima et al., 2022).

Additionally, sugarcane bagasse-derived biochars, including steam-activated (SPAB) and chemically activated (SCAB) variants, were evaluated for ibuprofen removal. Both Langmuir and Freundlich isotherm models were applicable, with SCAB and SPAB showing adsorption capacities of 13.51 mg/g and 11.90 mg/g, respectively. After 18 and 12 hours of contact time, SPAB and SCAB achieved removal efficiencies of 82% and 91%, respectively (Chakraborty et al., 2018).

The rising number of publications, illustrated in Figure 2.10, reflects the growing interest in applying biochar or modified biochar to remove pharmaceutical contaminants from water and wastewater through adsorption. In 2009, simply two literary works were published, however, in 2023, the quick growth trend signifies an increasing number was published compared to 2015 (Aziz et al., 2024).

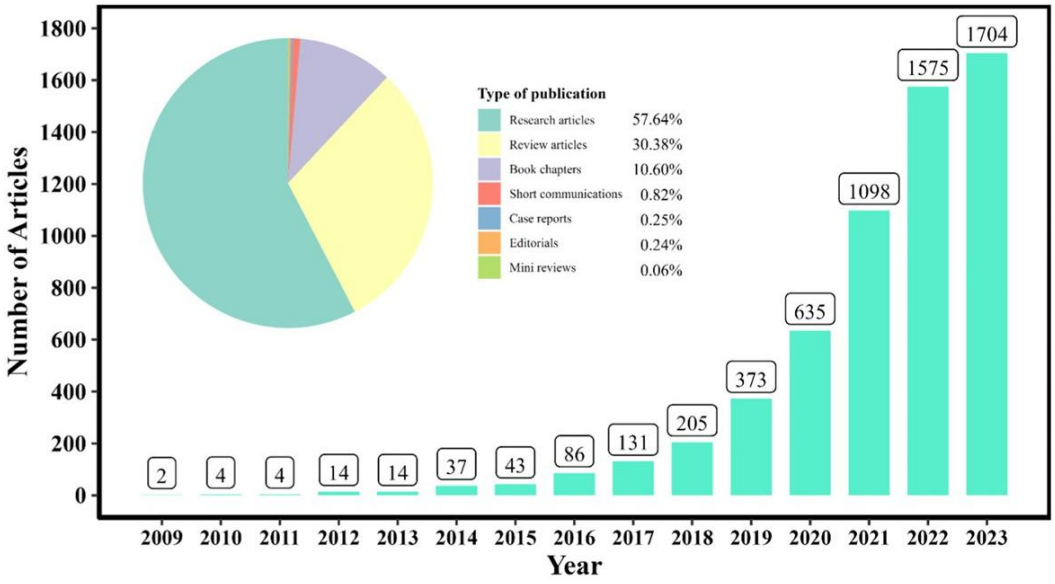

Figure 2.10 The articles published in the past 12 years with the topic of (Biochar and Adsorption and Pharmaceuticals) in 2011–2023

Table 2.3 Adsorption Performance of Different Biochar for Removing Pharmaceuticals from Water

Biochar Feedstock	pH	Time	Concentration	Temperature	Pharmaceutical Pollutant	Adsorption Capacity	Isotherm Model	Kinetic Model	Reference
Sugarcane bagasse	2	12 h	20 mg/L	20 °C	Ibuprofen	13.51	Freundlich isotherm	Pseudo-second-order	(Chakraborty et al., 2018)
Bamboo biomass	3.5	10 h	100 mg/L	25 °C	Sulfonamide	88.10	Freundlich isotherm	Pseudo-second-order	(M. B. Ahmed, Zhou, Ngo, Guo, Johir, et al., 2016)
Spirulina residue biochar	3	4 h	50 mg/L	25 °C	Sulfathiazole	13.56	Langmuir isotherm	Pseudo-second-order	(K. Wang et al., 2022)
Fiber industry wastes	3.5	6 h	50 mg/L	25 °C	Sulfamethoxazole	24.06	Langmuir isotherm	pseudo-second-order	(Fernandez-Sanroman et al., 2020)
Maple leaf	3	5 h	100 mg/L	20 °C	Tetracycline	34.05	Liquid film	Pseudo-second-order	(Kim et al., 2020)
Fiber industry wastes	3	6 h	50 mg/L	25 °C	Methylparaben	23.15	Langmuir isotherm	Pseudo-second-order	(Fernandez-Sanroman et al., 2020)
Cauliflower leaves	3	18 h	50 mg/L	25 °C	Oxytetracycline	33.31	Langmuir model	Pseudo-second-order	(Zhang et al., 2022)
Pepper stem	2	2 h	20 mg/L	20 °C	Ibuprofen	569.6	Langmuir	Pseudo-second-order	(Naima et al., 2022)

2.9 Biochar Production and Activation Techniques

2.9.1 What is biochar?

Biochar is a carbon-rich material that resembles charcoal but is produced through a controlled process known as pyrolysis. This process involves heating organic biomass, typically sourced from agricultural and forestry waste, in an environment with limited oxygen. Unlike conventional charcoal, biochar is manufactured using specific methods that reduce contamination and help retain carbon in a stable form. During pyrolysis, organic materials such as wood chips, leaf litter, or plant residues are converted into biochar, which locks carbon in a solid state and reduces its release into the atmosphere (Spears, 2018). Although biochar has been explored for various purposes, including reducing greenhouse gas emissions and supporting energy production, its use in agriculture and environmental remediation has gained particular attention in recent years. It is increasingly considered a sustainable alternative to activated carbon in several of these applications (Weber and Quicker, 2018). Due to its wide-ranging applicability, biochar has been utilized extensively as an innovative and sustainable adsorbent to remove both organic and inorganic contaminants from the environment (Oliveira et al., 2017; Wang et al., 2017).

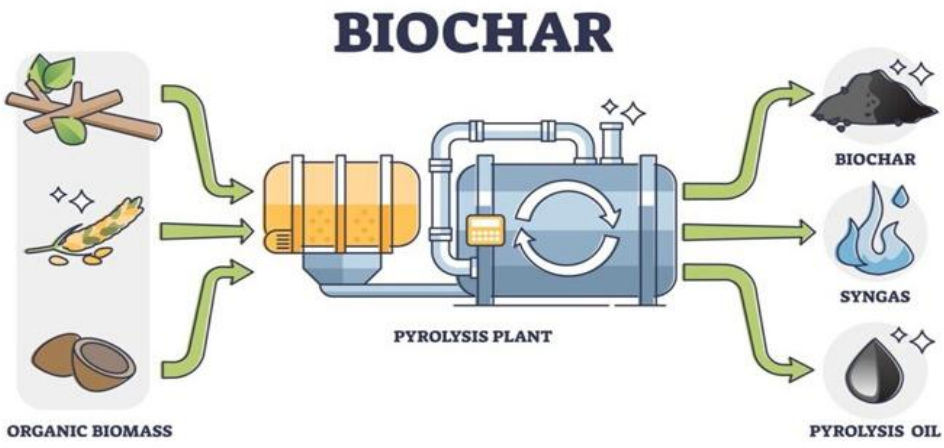

Figure 2.11 The pyrolysis of organic biomass yields biochar, syngas, and bio-oil as valuable products (Skip Shapiro Enterprises, 2024).

2.9.2 Biochar Feedstocks and Production

Biochar, a renewable material produced from biomass, has gained increasing attention for its effectiveness in treating a wide range of environmental contaminants. Its high porosity, large surface area, and abundance of functional groups contribute to its strong adsorption capabilities (Hashem et al., 2020). Biochar is typically derived from three primary sources: plant residues, sewage sludge, and animal litter, as illustrated in Figure 2.12. These feedstocks are

thermochemically converted into biochar through pyrolysis, a process conducted in an oxygen-limited environment at temperatures generally below 1000°C (Hagemann et al., 2018). Biochar derived from agricultural waste often retain a higher concentration of oxygen-containing functional groups, which increases their polarity and may enhance their affinity for polar contaminants (Oliveira et al., 2017).

Municipal solid waste (MSW) is a significant feedstock for biochar production, sourced from residential, commercial, and industrial sectors. Sewage sludge is also widely used, particularly in soil remediation applications. Furthermore, animal and poultry manure, due to their high nutrient content, serve as effective precursors for biochar synthesis (Zubair et al., 2023).

Figure 2.12 Potential Biomass for Biochar Production (Zubair et al., 2023)

Biochar can be produced through several thermochemical methods that utilize a wide range of biomass sources, including pyrolysis, gasification, torrefaction, microwave-assisted processes, and hydrothermal carbonization. The choice of production method is influenced by the desired properties of the final biochar and the availability of technical resources. Among these methods, pyrolysis is the most widely applied, involving the thermal decomposition of biomass in the absence or limited presence of oxygen, often under an inert atmosphere such as nitrogen (Bianasari et al., 2024).

Engineered biochar and hydrochar differ in their surface characteristics due to the conditions under which they are produced. Biochar, generated through dry pyrolysis, typically exhibits greater pore diameter, surface area, and pore volume. In contrast, hydrochar, produced via hydrothermal carbonization under wet conditions, retains higher levels of surface-bound oxygen and hydrogen. This suggests a greater abundance of functional groups and carbon–oxygen complexes on the hydrochar surface (Z. Liu et al., 2009).

2.10 Post-Processing Modification of Biochar

Post-modification methods for biochar are commonly grouped into four main categories as depicted in Figure 2.13. There are (1) enhancing surface area and porosity; (2) introducing positive surface charges; (3) increasing oxygen-containing functional groups; and (4) magnetizing biochar to improve particle recovery. Some treatments may simultaneously enhance multiple properties. For instance, sulfuric acid (H_2SO_4) treatment not only increases the specific surface area but also enriches the surface with oxygen-containing functional groups. Various classification systems for biochar modification exist in the literature, including those based on targeted physicochemical properties (Cheng et al., 2021; X. Li et al., 2021).

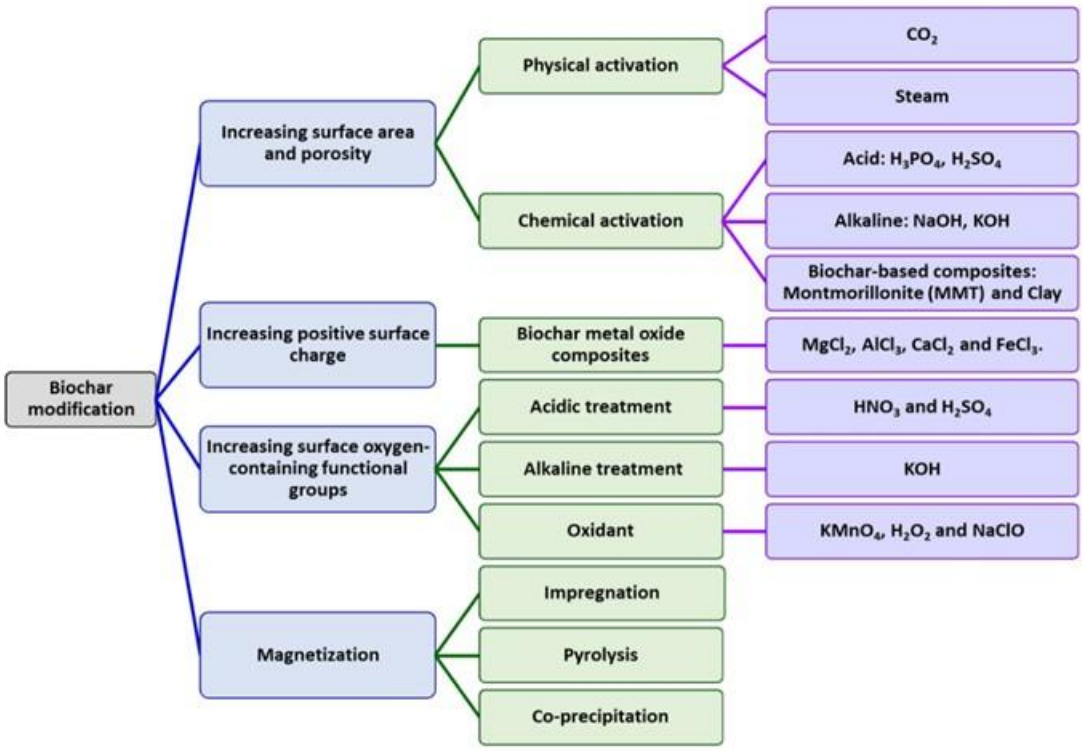

Figure 2.13 Typical Classifications of Biochar Modifications (Zeghioud et al., 2022)

2.10.1 Alkaline Treatment

Alkaline modification improves the non-polar surface properties of the material, enhances its adsorption efficiency, and increases the relative abundance of alkali functional groups. This surface modification can be achieved using KOH, NaOH, or other alkaline oxides. Such treatment also promotes the adsorption of positively charged species onto the adsorbent surface (Rehman et al., 2019). Various methods, including alkaline activation with KOH, can modify biochar to improve its performance. Besides KOH, chemical activation can involve oxidizing agents (like hydrogen peroxide and potassium permanganate), organic agents (such as ethanol),

salts (like sodium chloride and zinc chloride), and metal impregnation (using chromates, carbonates, hydroxides, and nitrates) (Gęca et al., 2023). These treatments alter the material's surface chemistry, biology, and physics, boosting surface area, reactivity, and functional groups, and ultimately improving adsorption (Zhu et al., 2018). Furthermore, thermal and mechanical processes also serve as effective surface modification techniques.

In this research, a pre-treatment was conducted by soaking the biochar in 30% KOH solution for 8 hours, after rinsing and drying. This approach was chosen due to its simplicity, reproducibility, and proven ability to enhance the adsorptive removal of emerging contaminants in aqueous systems. Unlike thermal activation or complex composite modifications, alkaline treatment offers a practical solution for improving biochar performance while maintaining scalability and environmental compatibility.

2.11 Biochar Characterization Techniques

A criterion for determining the application of biochar is its composition. The wide distribution of micro- or mesopores in biochar may contribute to their high surface area. Tan et al. (2015) and Sizmur et al. (2017) have both observed that biochar’s porous structure, large specific surface area, enriched surface functional groups, and mineral components make it suitable for use as an adsorbent in the removal of pollutants from aqueous solutions.

Depending on its properties, including specific surface area, surface functional groups, stability, structure, and, to a lesser size, elemental composition, biochar has a wide range of applications (Zhou et al., 2021). Biochar properties can be structured into four primary categories:

i) Physical properties (porosity, pore size distribution, specific surface area)
ii) Chemical properties (chemical composition, functional groups, pH, ion exchange capacity)
iii) Structure, surface, and morphology
iv) Thermal stability properties

Each category involves specific characterization techniques as illustrated in the following Figure 2.14 (Zeghioud et al., 2022).

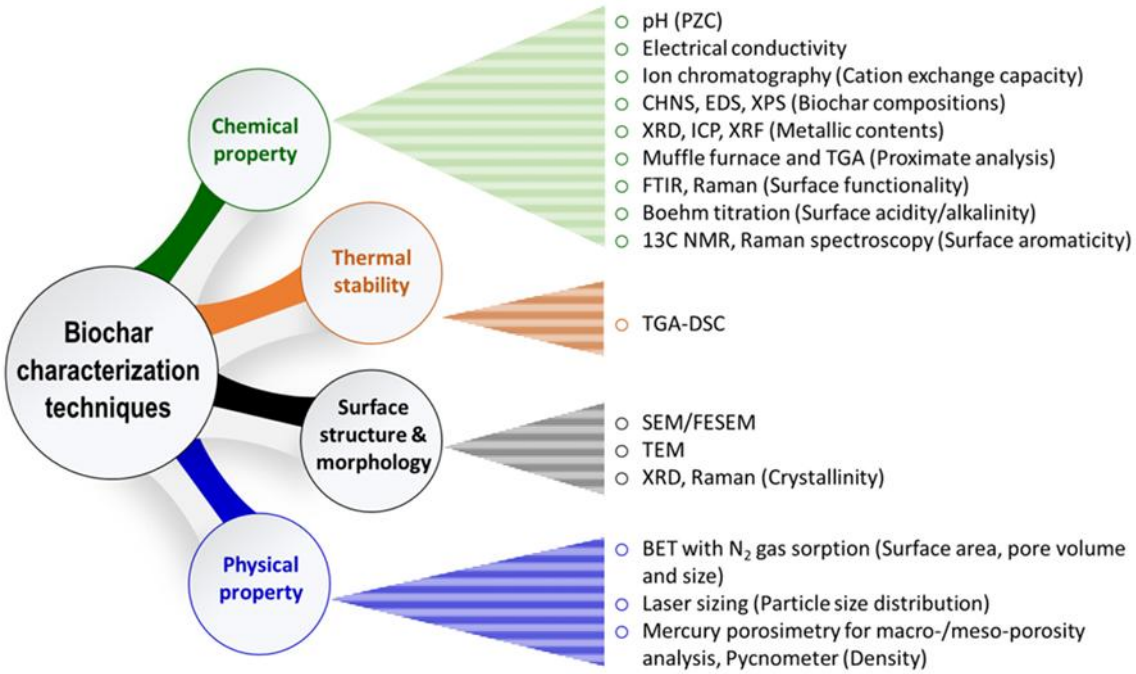

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Figure 2.14 Classification of Characterization Techniques and Biochar Properties

Biochar characterization techniques are essential for evaluating material performance and optimizing treatment processes. Based on a review of 100 scientific articles published between 2018 and 2021, Figure 2.15 shows the reporting frequency (%) of various characterization methods in the biochar literature. Surface imaging techniques, such as SEM and TEM, were the most frequently reported (92%), followed by BET surface area analysis (83%), FTIR spectroscopy (81%), and XRD, XPS, and porosity measurements at 63%, 55%, and 47%, respectively (Zeghioud et al., 2022).

However, the Boehm titration, XRF, and CEC are still the least popular methods for assessing the physicochemical characteristics of biochar. The most desired qualities and determining elements in biochar engineering for the removal of emerging organic contaminants are determined by surface shape, crystallinity, specific surface area, and surface functional groups. Inductively Coupled Plasma (ICP) is used far more frequently than XRF for quantifying the number of heavy metals (Zeghioud et al., 2022).

In this study, SEM, FTIR, and BET analyses were conducted both before and after the adsorption process to evaluate changes in surface morphology, functional groups, and specific surface area of the biochar. is multi-technique approach allowed for a detailed understanding of the mechanisms influencing adsorption performance.

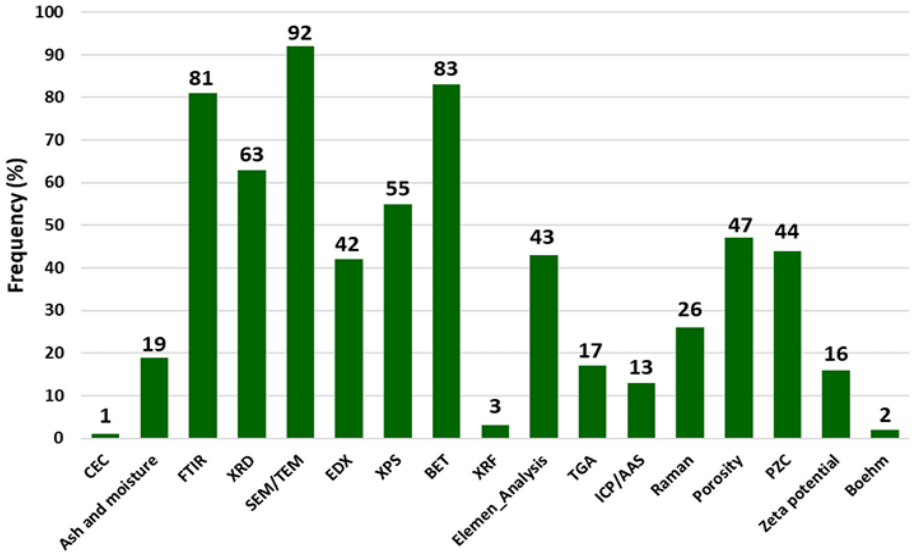


Figure 2.15 Frequency of applying certain techniques for biochar characterization (data recorded from 100 studies).

2.11.1 Physical Properties

Physical parameters consist of specific surface area (SSA), particle size distribution, bulk density, pore size, and pore volume distribution (Ding et al., 2020). These variables are closely related to the conditions under which biochar is produced, including reactor temperature and residence time, the addition of oxygen-containing media (air, pure oxygen, CO_2, and steam), and/or post-production processing that influences the outcome product. (Hu et al., 2021)

Surface area and porosity are key physicochemical parameters that significantly influence the adsorption performance of biochar, especially for pharmaceutical contaminants like ibuprofen and paracetamol in aqueous systems. These properties are commonly measured using the Brunauer–Emmett–Teller (BET) method, which determines specific surface area, and porosity analysis, which reveals the pore size distribution and total pore volume within the biochar structure (Brunauer et al., 1938).According to the International Union of Pure and Applied Chemistry (IUPAC), pore size refers to the internal diameter of a pore. Based on this classification, pores are categorized into three types: micropores (less than 2 nm), mesopores (between 2 and 50 nm), and macropores (greater than 50 nm) (Sing, 1985).

For example, case studies of Xiong et al. (2020) investigated the adsorption of the fungicide epoxiconazole (EPC) using five types of biochar derived from different feedstocks. The findings revealed that adsorption capacity was strongly influenced by the total pore volume and specific surface area of the biochar. Additionally, Patel et al., (2021) observed a positive correlation between the sorption efficiency of biochar towards antibiotic medicine

ciprofloxacin and acetaminophen and its surface area and total pore volume, highlighting the importance of these textural properties in adsorption performance.

2.11.2 Chemical Properties

Biochar's chemical characteristics include electrical conductivity, surface functional groups, capacity for cation exchange, and point of zero charge (PZC). In order to determine how biochar may affect the environment, structural and elemental study is crucial (Xiang et al., 2021).

Scanning Electron Microscopy (SEM), in combination with Energy-Dispersive X-ray Spectroscopy (EDS or EDX), is used to analyse the oxygen-to-carbon (O/C) atomic ratio, as well as the surface elemental composition of biochar. This information facilitates to understand how production conditions influence the material's properties. For instance, the oxygen-to-carbon (O/C) atomic ratio serves as an indicator of the carbonization degree of biochar and signifies the quantity of aromaticity present within the biochar. This characteristic is associated with the stability of the biochar and, consequently, its potential for carbon storage (Ma et al., 2016).

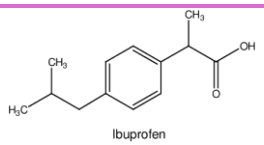
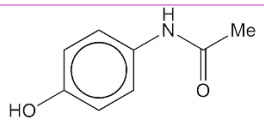
Fourier Transform Infrared (FTIR) spectroscopy is widely employed in the surface characterization of biochar. It provides detailed insights into the presence of oxygen-containing functional groups and is useful for assessing the effectiveness of metal binding during surface modifications. Additionally, FTIR can detect changes in surface functional groups in the adsorption of pollutants (S. Liu et al., 2019).

2.12 Pharmaceuticals of Interest

This study focuses on paracetamol and ibuprofen due to their widespread use, frequent detection in aquatic environments, and potential ecological impact. Paracetamol (acetaminophen) is a commonly used analgesic and antipyretic, often identified in surface waters at concentrations ranging from nanograms to micrograms per litre. Although it is considered less persistent than other pharmaceuticals, its high usage and continuous discharge raise concerns regarding chronic exposure (Vieira et al., 2024).

Ibuprofen, a non-steroidal anti-inflammatory drug (NSAID), is known for its environmental persistence and ability to induce toxic effects in aquatic organisms even at low concentrations. Its incomplete removal in conventional wastewater treatment processes further contributes to its prevalence in water bodies. Both compounds are representative of commonly consumed pharmaceuticals that may pose long-term risks to aquatic ecosystems (Islam et al., 2024).

Table 2.4 Physico-Chemical Properties of Acetaminophen, Ibuprofen (Westerhoff et al., 2005)

Compound	*Structure*	*Molecular weight (g mol⁻¹)*	*Boiling point (°C)*	*Water solubility (mg L⁻¹)*	*Log K_{ow}*	*pKa*
Ibuprofen (IBU)	 Ibuprofen	206.3	157.0	21	3.97[a]	4.4/4.9[a]
Acetaminophen (AAP)		151.2	387.7	14000	0.46[a]	9.4[a]

2.12.1 Paracetamol (Acetaminophen)

Paracetamol, also referred to as acetaminophen, is a widely used pharmaceutical available over the counter for the treatment of pain and fever. The molecular formula is $C_8H_9NO_2$, and the molecular weight of approximately 151.2 g/mol. Its chemical structure features a benzene ring with a hydroxyl group and an acetamide group, giving the molecule both hydrophilic and hydrophobic characteristics. As shown in Figure 2.4, Key physicochemical properties such as solubility, stability, and hydrophobicity significantly influence its environmental behaviour. These characteristics affect how paracetamol interacts with water, soil, and sediments (Gerriets et al., 2024).

The Global Acetaminophen Market Insights, forecast to 2025 report predicts a large increase in paracetamol production. China and India are expected to contribute around 64.4% and 21.2% of the global supply, with the market value reaching 780 million USD by 2025 (Tran et al., 2020). Up to 90% of ingested acetaminophen is excreted unchanged in human waste. Its presence in the environment has raised concerns. Measured concentrations include 0.055 ± 0.051 µg/L in surface water, 6 µg/L in effluents from European treatment plants, 10 µg/L in natural waters in the USA, 65 µg/L in the Tyne River (UK), and up to 150 µg/L in raw hospital wastewater (Fuentes et al., 2020). These levels pose potential risks to environmental and public health, highlighting the need for effective removal strategies. Therefore, current research is exploring the development of advanced treatment materials such as biochar to improve paracetamol removal and reduce its environmental impact (Yanan et al., 2022).

2.12.2 Ibuprofen

Ibuprofen ($C_{13}H_{18}O_2$) is another widely used pharmaceutical and ranks as the third most consumed drug globally. It is commonly prescribed for the treatment of rheumatic conditions, migraines, muscle pain, toothaches, and fever (Baccar et al., 2012). Ibuprofen is, non-steroidal anti-inflammatory drug (NSAID) that contains an aromatic ring and a carboxylic acid group, giving it both slightly acidic and hydrophobic properties. It has moderate solubility in water and a low octanol–water partition coefficient, which means it can change between water and organic matter depending on environmental conditions such as pH and salt concentration. Due to its weakly acidic nature (pKa ~4.9), ibuprofen mainly presents in its anionic form at neutral or slightly alkaline pH. This ionic state influences its mobility in aquatic systems and its interaction with adsorbent materials. (Almuntashiri, 2024).

The occurrence of ibuprofen in the environment is well established, with frequent detection in surface water, wastewater effluents, and occasionally groundwater, typically at concentrations ranging from nanograms to several micrograms per litre (M. Patel et al., 2019). The state-of-the-science review in highlights that pharmaceuticals such as ibuprofen are not only abundant in the environment but also biologically active, which increases the likelihood of adverse ecological outcomes. The persistence and bioactivity of ibuprofen require the development of advanced treatment technologies to ensure effective removal strategies, such as adsorption onto biochar, to mitigate its impact on aquatic ecosystems and human health (M. Patel et al., 2022).

In conclusion, ibuprofen's chemical characteristics, such as weak acidity, moderate hydrophobicity, and specific structural attributes, significantly influence its environmental behaviour. Its frequent detection in aquatic environments results from widespread usage, partial removal during treatment processes, and chemical stability, making it a key target for water quality research and the development of sustainable treatment solutions (Osman et al., 2023).

2.13 Conclusion

This chapter has reviewed current literature on the use of biochar for the removal of emerging organic contaminants (EOCs), with particular emphasis on pharmaceutical compounds, notably paracetamol and ibuprofen. Numerous studies have demonstrated the adsorption capabilities of various biochar, especially in batch adsorption systems, and explored the influence of physicochemical properties, surface modifications, and process conditions. While biochar shows significant potential as a sustainable adsorbent for pharmaceutical removal, its effective application requires further investigation into adsorption mechanisms, standardization of methodologies, and large-scale feasibility assessments. Despite these

advances, most of the existing research has centred around laboratory-scale batch studies, with limited investigation into column-based applications that better reflect real-world scenarios. Particularly in the context of New Zealand, there is a lack of studies evaluating biochar produced from local feedstocks and its integration into existing water treatment infrastructure.

These observations highlight the need for a comprehensive evaluation of New Zealand biochar in dynamic systems, including closed-loop columns. This study aims to fill this research gap by characterizing the properties of premium New Zealand biochar and assessing its performance in removing ibuprofen and paracetamol under both batch and column conditions. The findings from this work are expected to contribute valuable insights into the development of sustainable, low-cost adsorbents for water treatment applications.

Chapter 3

Methodology

3.1 Overview of Research Methodology

This chapter outlines the materials, experimental procedures, equipment, and analytical methods used to evaluate the adsorption performance of New Zealand biochar. During the first three months of the research process, a custom bench-scale fluidized bed column system was designed and constructed as the starting point for the project. Column experiments were designed to simulate real-world treatment scenarios, including single-pass flow, closed-loop recirculation, and semi-continuous treatment. A total of 16 fluidized column experiments were conducted to systematically evaluate the effects of key operational parameters, including biochar dosage, particle size, flow rate, pharmaceutical type, and surface modification of the adsorbent.

Along with the development of the column, a variety of biochar derived from different New Zealand feedstocks were selected and screened by using Brunauer–Emmett–Teller (BET) surface area analysis. The selection process aimed to identify the most suitable type of biochar with optimal surface properties for pharmaceutical adsorption. After selection, the process began with surface modification of biochar using potassium hydroxide (KOH), followed by detailed physicochemical characterization. Batch experiments were conducted to determine the influence of key parameters on adsorption capacity and kinetics. Finally, a series of characterization techniques were applied to determine key properties of the adsorbent, including specific surface area, pore volume, surface morphology, and chemical functionality.

Due to time constraints and unexpected technical issues, including repeated piping modifications and water leakage at the top of the fluidized bed column, some experiments could not be completed as planned. As a result, column adsorption experiments with ibuprofen could not be completed. Consequently, column studies were conducted exclusively using paracetamol as the target contaminant. However, batch adsorption experiments were successfully performed for both ibuprofen and paracetamol, enabling a comparative assessment under controlled conditions. This limitation is acknowledged and further discussed in the Results and Discussion chapter.

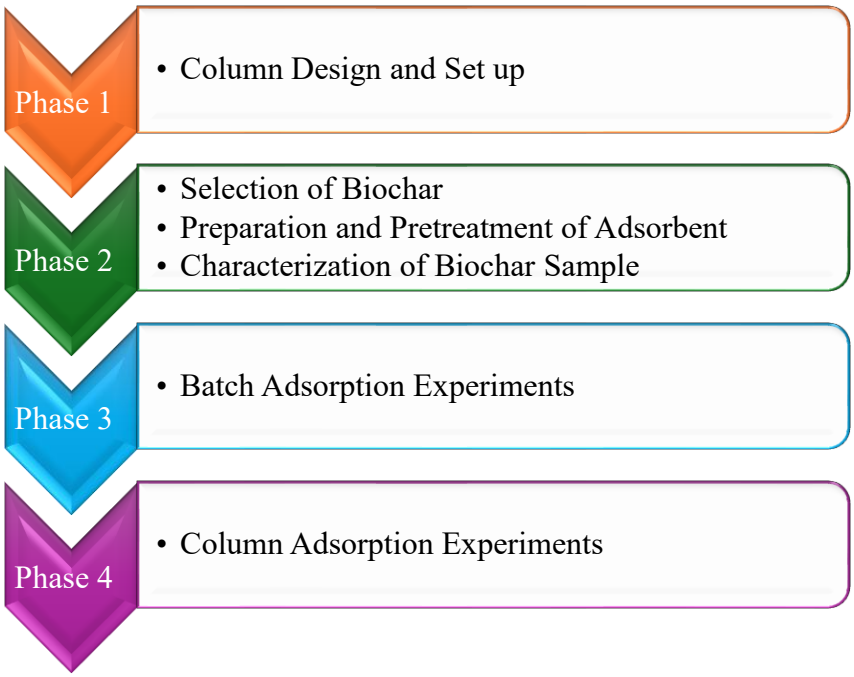


Figure 3.1 The Experimental Workflow of the Four Major Phases

3.2 Materials and Chemicals

The biochar used in this study was sourced from Southern Carbon, a commercial supplier based in the South Island, New Zealand. Sold as "Premium Biochar," it is classified as Grade 1 with a reported carbon content exceeding 85%, aligning with international standards for high-quality adsorbents. According to the manufacturer, the biochar is produced from locally sourced, untreated woody biomass without any chemical additives, making it suitable for environmental uses such as water treatment and soil improvement. The material was received in granular form with a mixture of particle sizes (Southern Carbon, 2024).

The pharmaceuticals used in this study were commercial-grade ibuprofen and paracetamol, purchased over the counter from a local pharmacy. For column experiments of continuous dosing system, a 2000 mg/L stock solution of paracetamol was prepared by dissolving it in distilled water. An ibuprofen stock solution (1000 mg/L) was prepared using a solvent mixture of 1% ethanol and 99% distilled water, due to its limited solubility. Synthetic aqueous solutions were prepared by diluting these stock solutions accordingly.

For batch adsorption studies, a 250 mg/L paracetamol stock solution was prepared in distilled water, and a 200 mg/L ibuprofen stock solution was prepared using the same ethanol–water mixture. For column experiments, tap water was used to replicate real environmental conditions better. The adsorbent used was premium biochar from Southern Carbon, sourced locally in New Zealand, and was used as the adsorbent material. This biochar was sieved to a

particle size of approximately 1 to 2 mm. Potassium hydroxide (30% KOH) was employed for alkaline surface modification. Distilled water, tap water, and ethanol were used throughout the study for solution preparation and washing procedures.

3.3 Column Design and Setup

A custom fluidized bed column was designed and constructed in the Science Engineering Workshop building, Large Scale Lab (LSL Lab), specifically for this study. The experiment setup was in Room C.3.11 of the C Building at the University of Waikato, Hamilton, New Zealand. Most analytical procedures were conducted in Room C3.11, designated as the Environmental Engineering Laboratory.

The development of the column design involved selecting appropriate materials, assembling components, and conducting system testing to ensure operational stability. The final setup consisted of a vertically aligned transparent acrylic column with a height of 1.2 meters and an internal diameter of 0.25 meters. The system included a plywood support plate, biochar-retaining mesh, inflow and outflow ports, a sampling valve, and tubing connections compatible with a peristaltic pump. A static mixer was placed along the inlet line before the column to ensure thorough mixing of the pharmaceutical stock solution with tap water, promoting uniform contaminant distribution across the biochar bed.

A Concept 420 peristaltic pump was used to regulate the influent dosing rate, allowing continuous recirculation of the synthetic pharmaceutical solution through the biochar-packed column. This setup facilitated real-time observation of breakthrough behaviour under dynamic flow conditions. A Grundfos ALPHA2 E high-efficiency circulator pump (230V, 50/60 Hz, 3–34 W) was fitted to maintain a consistent water flow within the column system. Its precise flow control was essential for ensuring stable operation under both recirculation and single-pass conditions. Water flows upward through the column, allowing for biochar fluidization and effective contact with the contaminant solution.

Flow rates were monitored using both a manual stopwatch method and an in-line flow meter for cross-validation. To monitor environmental conditions during column operation, digital pH and temperature sensors were integrated with an Arduino microcontroller. This system provided real-time tracking and display of pH and temperature values, allowing for improved control of operating conditions and consistent data logging throughout the recirculation process. The system is installed on a mobile platform for ease of operation and flexibility in laboratory-scale simulation of real-world adsorption processes.

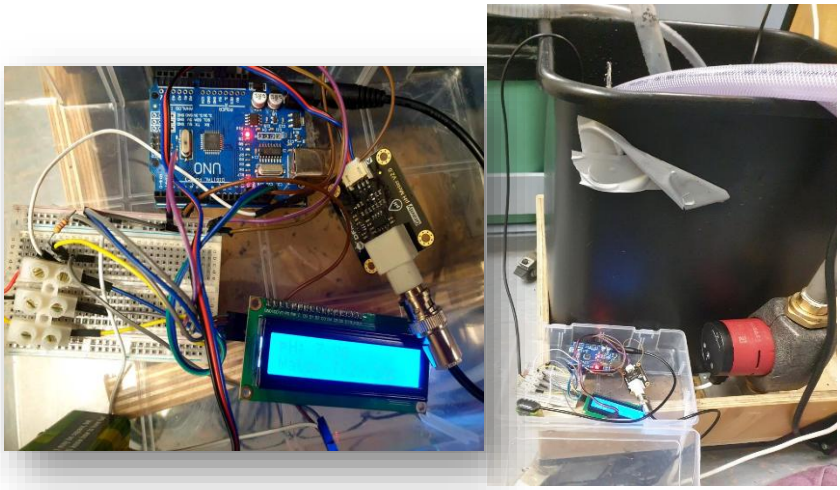


Figure 3.2 pH and temperature monitoring system using Arduino, including sensor probes, microcontroller, and display, integrated with the column experimental setup.

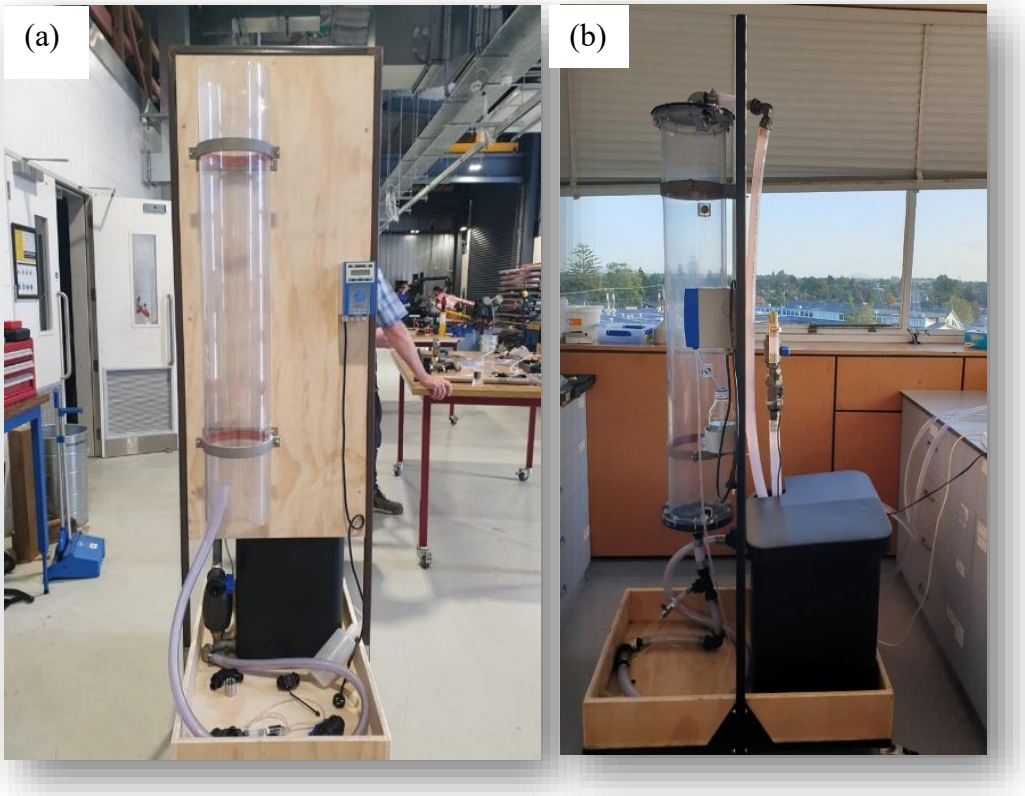


Figure 3.3 Fluidized bed column system set up (a) during construction and assembly in the workshop, (b) fully assembled and installed in the laboratory for continuous adsorption experiments.

In order to provide a detailed visual reference of the system's structure and component layout, standard engineering drawings were developed, including side, front, and back views of the

setup. The schematic diagrams, presented in Figures 3.4-3.6, include dimensional annotations in millimetres(mm). These schematics serve as a technical guide for system construction, operation, and potential scale-up in future applications.

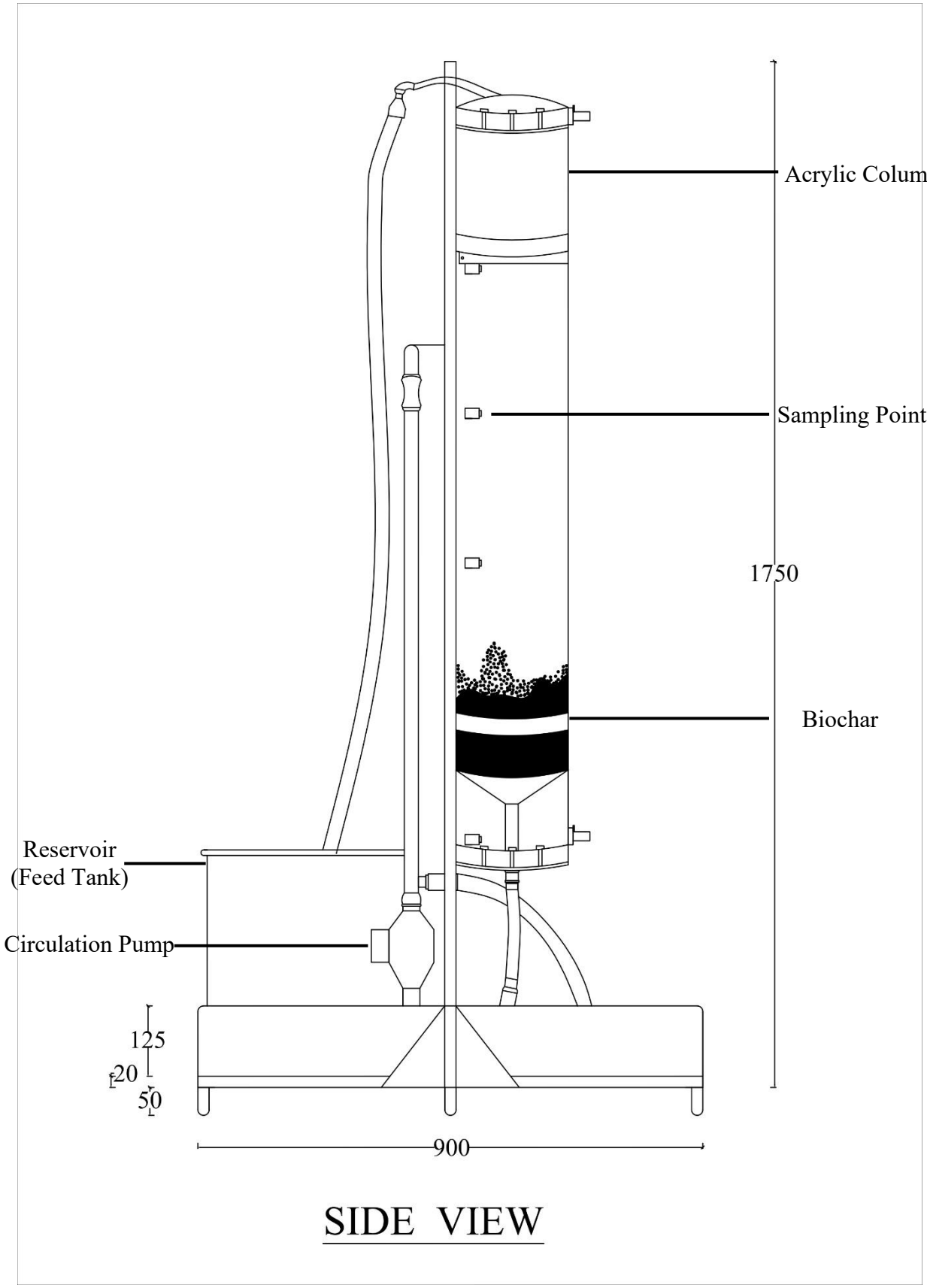


Figure 3.4 Side View of the Fluidized Bed Column

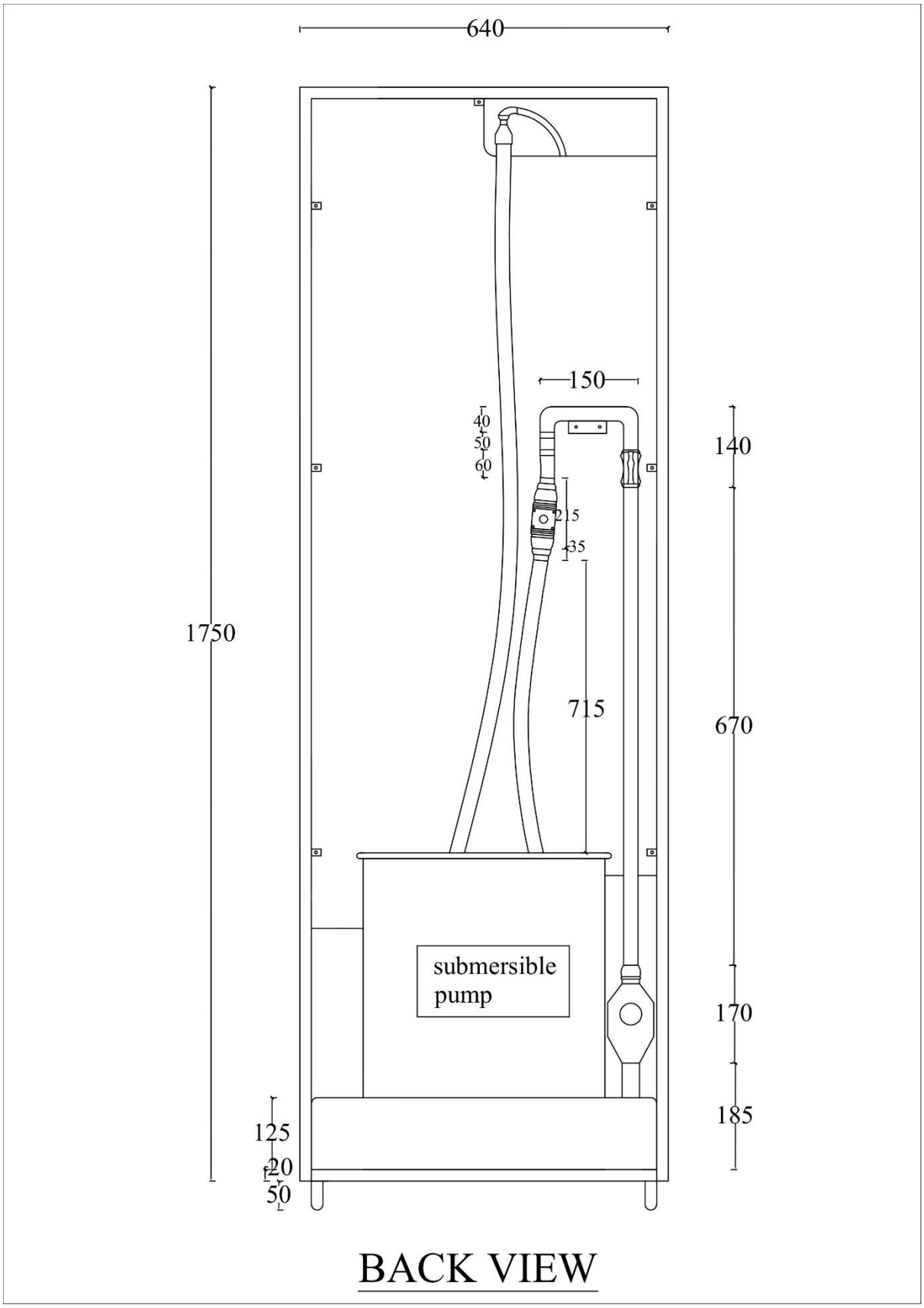


Figure3.5 Back View of the Fluidized Bed column

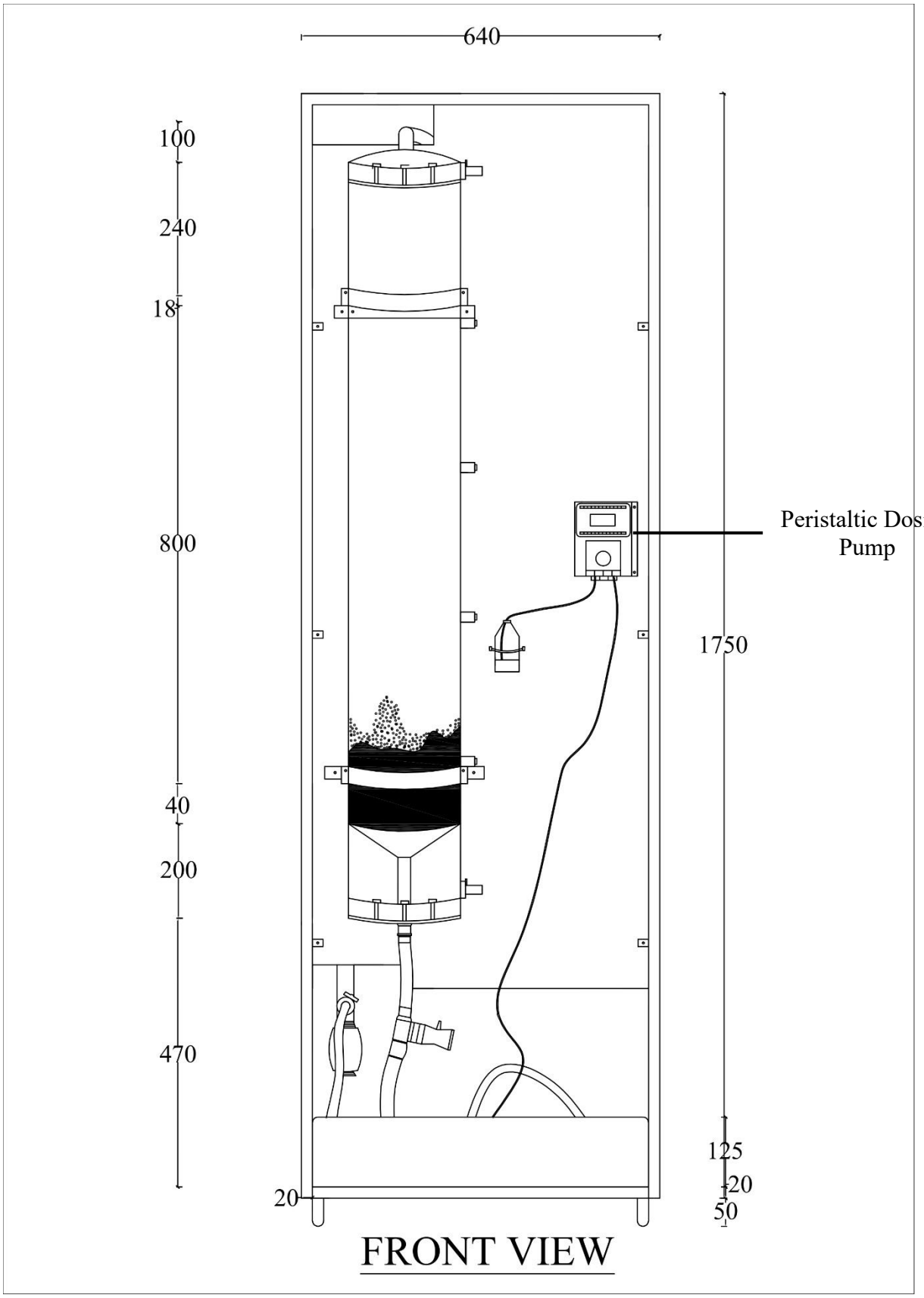


Figure 3.6 Front View of the Fluidized Bed Column

3.4 Preparation and Selection of Biochar

Several types of commercially available biochar produced in New Zealand were purchased and obtained for evaluation in this study. These included Premium biochar from Southern Carbon, Pine biochar, High-Grade biochar, and Plain biochar from the CoolStaff community, as shown in Figure 3.7. Initial screening was carried out based on observable physicochemical properties and known production characteristics.

To identify the most suitable material for pharmaceutical adsorption, each biochar sample was analysed using Brunauer–Emmett–Teller (BET) surface area testing and Scanning Electron Microscopy (SEM). The premium biochar from Southern Carbon demonstrated the highest surface area and a well-developed porous structure. As a result, it was selected for use all further adsorption experiments.

Figure 3.7 Different Types of Tested Biochar Samples

After the premium New Zealand biochar was selected, the unprocessed raw biochar was prepared for analysis by a standardized washing and drying process. Large chunks of raw biochar were thoroughly washed with tap water approximately 15 times to remove surface ash and fine particulate matter.

The washing process was continued until the rinse water became clear, as the presence of ash and fine dust can cause the release of black particles if not thoroughly removed. Following this, the biochar was rinsed again using distilled water (DI) and soaked overnight in DI water to remove any residual soluble impurities. After washing, the biochar was dried at 100 °C for 12 hours in a laboratory oven. Once dried, they are crushed using a laboratory grinder to achieve a smaller particle size. The biochar was sieved using a mechanical sieve shaker to obtain a uniform particle size range between 2 mm and 1 mm.

Prior to column operation, the biochar was pre-soaked in deionized water for 18 hours to allow for complete pore saturation and to minimize hydrophobic behaviour. This pretreatment step ensured that air trapped within the pore network was displaced, thereby improving the wettability, reducing floating tendencies, and promoting a more uniform and stable particle distribution within the column. Such soaking is critical to achieve consistent flow dynamics and reliable adsorption performance in fluidized or packed bed systems involving low-density biochar materials.

3.5 Biochar Pretreatment and Surface Modification

Alkaline surface modification has been shown to significantly enhance the specific surface area and increase the abundance of oxygen-containing functional groups on biochar. These changes contribute to improved adsorption capacities for a wide range of organic pollutants, including pharmaceuticals. Additionally, such chemical treatments can alter the surface polarity of biochar, thereby changing its hydrophilic or hydrophobic character. After alkali pretreatment, the surface hydrophilicity typically decreases, which favours the adsorption of hydrophobic pharmaceutical compounds through hydrophobic interactions (Qiu et al., 2022).

In this study, after sieving the biochar to 1 mm and 2 mm sizes, the sieved premium biochar was washed and soaked in a 30% KOH solution for 8 hours and 16 hours. After the treatment, the biochar was thoroughly rinsed with DI water until the pH of the rinse water was neutral. There is no thermal treatment or high temperature drying applied after soaking, so the process is considered an alkaline surface modification rather than full chemical activation.

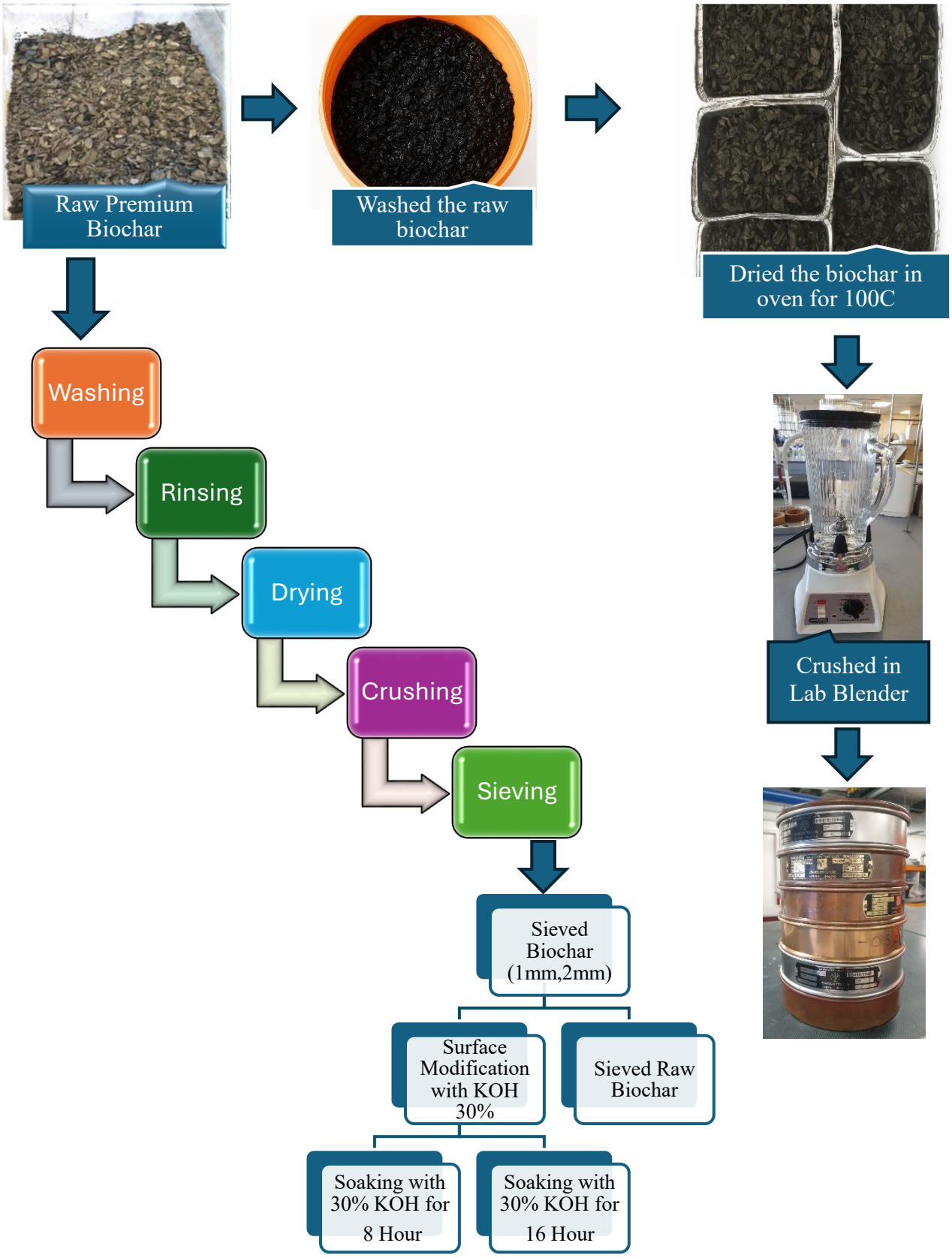


Figure 3.8 Flowchart of the Preparation and Surface Modification Process of Premium Biochar

3.6 Characterization of Biochar

3.6.1 BET Surface Area

Brunauer–Emmett–Teller (BET) surface area analysis was performed to determine the specific surface area, total pore volume, and pore size distribution of the biochar, as these properties are crucial for evaluating its adsorption performance. BET surface area analysis was performed using a Nova 2000e Surface Area and Pore Size Analyzer (Quantachrome Instruments, Florida, USA). Nitrogen adsorption–desorption measurements were performed at 77.35 K. Prior to analysis, the samples were degassed overnight at 220°C to remove moisture, followed by heating to 220 °C and maintaining the temperature for a minimum of six hours to ensure complete outgassing.

3.6.2 SEM-EDX Spectroscopy

The biochar samples were characterized using Scanning Electron Microscopy (SEM) and equipped with an Oxford AZtec X-Max50 SDD energy-dispersive X-ray (EDX) detector with HITACHI Regulus 8230. Pre-adsorption imaging provided baseline information on the biochar's surface structure, porosity, and elemental distribution. Post-adsorption analysis allowed for the assessment of surface modifications resulting from contaminant uptake, such as pore blockage, surface coverage, or shifts in elemental signals. This comparative evaluation helped to better understand the adsorption mechanisms and the interaction between pharmaceutical molecules and the biochar surface's functional groups. EDX analysis was carried out to examine the elemental composition and distribution on the biochar surface. This semi-quantitative method has a detection limit of approximately 0.5 wt% and can identify a wide range of elements. The spectra were processed using a vector-based algorithm to estimate the relative abundance of ten elements commonly present in biochar: carbon (C), oxygen (O), sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), potassium (K), calcium (Ca), titanium (Ti), and iron (Fe).

3.6.3 Fourier Transform Infrared Spectroscopy (FTIR)

The surface functional groups of the biochar samples, both before and after adsorption, were characterized using FTIR. Spectral measurements were performed across the wavenumber range of 400 to 4000 cm^{-1}, with a resolution of 1 cm^{-1}. The resulting transmittance peaks were identified and compared with reference spectra to determine the presence of specific chemical bonds and functional groups associated with adsorption activity.

3.7 Preparation of Solution and Standard Curves

Before conducting the experiments, all pharmaceutical stock solutions were freshly prepared. The required mass of each compound was accurately weighed using an analytical balance and dissolved in appropriate solvents to ensure complete dissolution. Calibration curves were established for ibuprofen and paracetamol to quantify their concentrations in aqueous solutions. Standard solutions with known concentrations ranging from 0 to 15 mg/L were prepared for each compound, and their absorbance values were measured using a UV-Vis spectrophotometer at their respective maximum absorbance wavelengths (typically 225 nm for ibuprofen and 245 nm for paracetamol). Linear regression was applied to generate calibration equations with high coefficients of determination ($R^2 > 0.99$), confirming their suitability for accurate and precise quantification of pharmaceutical concentrations throughout the adsorption experiments.

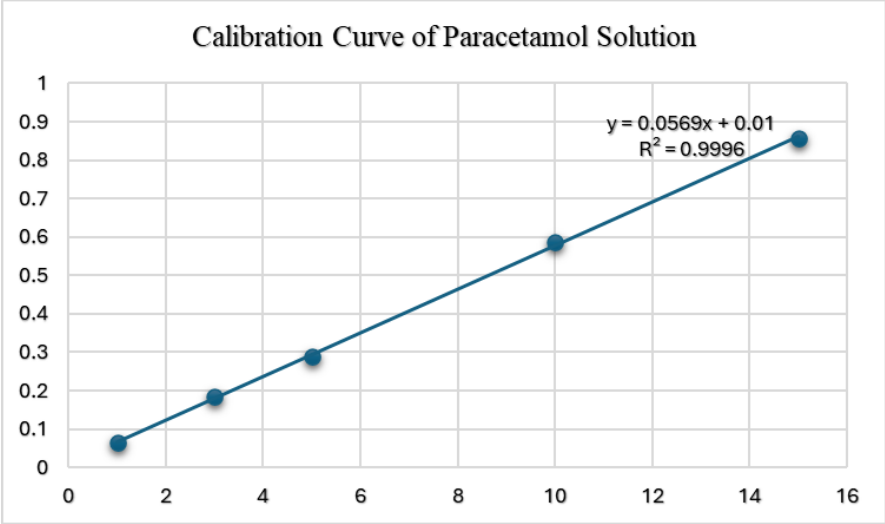


Figure 3.9 Calibration Curve of Paracetamol Solution

For the paracetamol solution, 250 mg of the compound was mixed with 100 mL of distilled (DI) water in a 250 mL beaker. The mixture was sonicated for 30 minutes until fully dissolved. The solution was then transferred to a volumetric flask, and DI water was added to reach the desired volume. After mixing, the solution was poured into a 1 L amber bottle, shaken for a few minutes, and stored in a dark place until required.

For the ibuprofen solution, 200 mg of the compound was first dissolved in a small volume of 1% ethanol solution and sonicated until no visible particles remained and the solution was visually clear. This concentrated solution was then diluted by adding it into 990 mL of DI water

in a 1 L volumetric flask to achieve a final concentration of 200 mg/L. The flask was shaken thoroughly, and the solution was stored in a dark brown bottle.

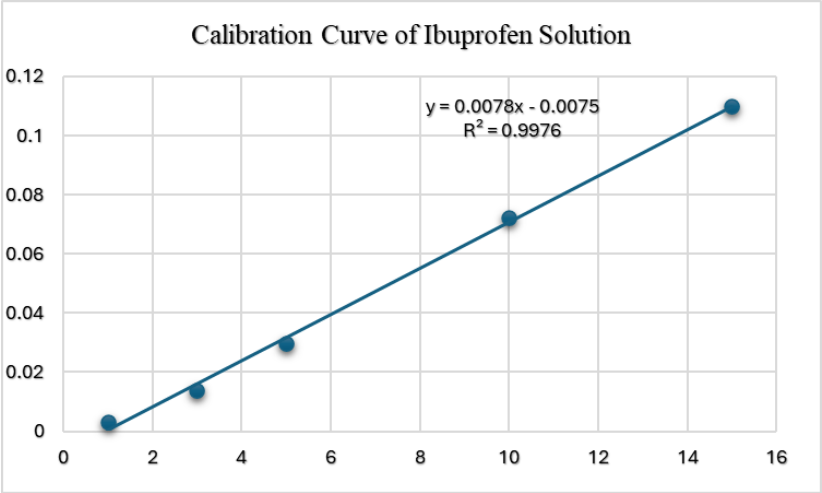


Figure 3.10 Calibration Curve of Ibuprofen Solution

All solutions were prepared using analytical-grade reagents and stored in light-resistant containers to prevent photodegradation. Calibration standards for UV-Vis spectrophotometric analysis were prepared by serial dilution of the stock solutions to the required concentrations.

3.8 Batch Adsorption Experiment

The batch adsorption experiments in this study were performed in five phases: (1) optimization, (2) kinetic analysis, (3) isotherm modelling, (4) investigation of biochar dosage, and (5) evaluation of initial concentration effects. To maintain consistency and accuracy, each experiment followed a standardized protocol:

1. A measured quantity of biochar was added to a 150 ml conical flask.
2. A predetermined volume of pharmaceutical solution was introduced into the flask.
3. The flask was sealed with parafilm and shaken at the orbital shaker and set for a defined duration and temperature.
4. After mixing, the solution was filtered using a 0.45 µm syringe filter. A fresh syringe and filter were used for each sample to prevent cross-contamination.
5. The filtered samples were analysed using a Shimadzu UV-1900 model UV-Vis spectroscopy to determine residual pharmaceutical concentrations.
6. Concentrations were calculated using standard curve equations based on calibration data.

7. Adsorption capacity and removal efficiency were calculated using the following formulas:

Adsorption Capacity, (q, mg/g)

$$q = \frac{(C_0 - Ce)}{m} \cdot v$$

----------(1)

Where, qe (mg/g) is the adsorption capacity at equilibrium, Ci (mg/L) is the initial concentration, Ce (mg/L) is the equilibrium concentration, m (g) is the weight of sorbent, and V (L) is the total volume.

Removal efficiency (R, %)

$$R = \left(\frac{C_0 - Ce}{C_0}\right) \cdot 100$$

----------(2)

Where Ci (mg/L) is the initial concentration and Ce (mg/L) is the equilibrium concentration.

During agitation, the biochar and solution mixture was periodically checked to ensure proper mixing. All experiments were performed at ambient temperature (around 23°C), under natural pH conditions, and repeated in triplicate unless specified otherwise.

3.8.1 Optimization of Experimental Variables

Before conducting detailed batch adsorption studies, key operating variables, including adsorbate concentration, adsorbent dosage, and contact time, were systematically optimized. This optimization process was essential to identify the conditions that yielded the highest removal efficiency and adsorption capacity. For each parameter, a range of values was tested to evaluate their influence on performance. The optimal conditions were selected based on the most effective balance between adsorption rate and equilibrium uptake. All batch experiments were conducted at room temperature (25 ± 1 ºC) and at the natural pH of the solution without any adjustment. A constant solution volume of 100 mL was used for each run.

Experiments were carried out to study:

- Effect of contact time (0 to 180 min)
- Effect of initial concentration (2,6,10,14,18 mg/L)
- Effect of adsorbent dosage (0.05–1 g)
- Effect of particle size (1mm to 3 mm)

To ensure statistical reliability and account for experimental variability, each batch adsorption condition was conducted in triplicate. For every parameter tested, three identical samples were prepared and analysed independently. The resulting values were averaged, and the corresponding standard deviations were calculated and reported.

3.8.2 Batch Adsorption Kinetic Study

Kinetic studies were conducted to assess the rate and mechanism of pharmaceutical adsorption onto biochar. Although 0.5 g of biochar achieved the highest removal efficiency (~96.6%), a dose of 0.1 g was selected for further adsorption studies to evaluate the material's performance under lower dosage conditions. This allows for the assessment of adsorption efficiency per unit mass and provides more conservative estimates of performance, which are relevant for real-world optimization and cost-effective applications.

The constant adsorbent mass of 0.1 g and an initial pharmaceutical concentration of 10 mg/L. For these experiments, 1 mg of biochar was added to 100 mL of solution (Ci = 10 mg/L). Samples were agitated at 200 rpm and collected at various contact times, with a maximum duration of 300 minutes. It was determined that samples were to be taken at fifteen-time interval, initially 0,5,10,15,20,25,35,45,60,90,120,150,180,210,250 minutes for analysis with UV/Vis. The resulting data were used to fit pseudo-first order and pseudo-second-order kinetic models.

The adsorption kinetic models applied in this study are outlined below.

Pseudo-First Order (PFO) Model

The pseudo-first order kinetic model, originally introduced by Lagergren in 1898, is commonly used to describe adsorption kinetics at the solid–liquid interface (Lagergren, 1898). This model assumes that the adsorption rate is directly proportional to the availability of unoccupied adsorption sites. In other words, the rate of adsorbate uptake is directly dependent on the difference between the amount of adsorbate adsorbed at equilibrium and at any given time.

The non-linear form of the pseudo-first order (PFO) kinetic model, which is expressed as Equation (3) (J. Wang & Guo, 2020b),

$$qt = qe * (1 - e^{-k1t}) \quad \text{----------(3)}$$

Where, q_t is the amount of adsorbate adsorbed at time t,

q_e is the equilibrium adsorption capacity,

k_1 is the pseudo-first order rate constant, and

t is the contact time.

Pseudo-Second Order (PSO) Model

The pseudo-second-order kinetic model was originally proposed by Ho and McKay (1998) to describe the chemisorption behaviour of dyes onto peat. This model assumes that the adsorption rate is proportional to the square of the number of unoccupied adsorption sites, reflecting the predominance of chemical interactions in the rate-limiting step, reflecting a chemisorption mechanism. The non-linear form of the pseudo-second order model is obtained and expressed as Equation (4) (J. Wang & Guo, 2020b),

$$q_t = \frac{((k2 * qe^2) * t))}{(1 + k2 * qe * t)}$$

----------(4)

This model is widely applied to systems where chemisorption is the dominant mechanism, and it often provides a better fit to experimental data than the pseudo-first-order model.

Elovich Kinetic Model

The Elovich kinetic model is commonly used to describe chemisorption processes on highly heterogeneous adsorbent surfaces. The non-linear form of the Elovich equation is expressed as:

$$q_t = \left(\frac{1}{\beta}\right) * \ln(1 + \alpha * \beta * t)$$

----------(5)

where qt (mg/g) represents the amount of adsorbate adsorbed at time t (min), α\alphaα (mg/g·min) is the initial adsorption rate, and β\betaβ (g/mg) is a constant associated with the extent of surface coverage and activation energy of chemisorption. The model assumes that the adsorption sites increase exponentially with adsorption, which is suitable for describing the initial fast uptake followed by a slower adsorption phase. The Elovich model was fitted to the kinetic experimental data using a non-linear regression approach.

Intra-Particle Diffusion (IPD) Model

To further investigate the rate-limiting steps of the adsorption process, the intra-particle diffusion (IPD) model proposed by Weber and Morris was applied. The model is expressed in its non-linear form as:

$$q_t = k_{diff} * t^{0.5} + C$$

----------(6)

where k_{diff}(mg/g·$min^{0.5}$) is the intra-particle diffusion rate constant, and C(mg/g) is the intercept that reflects the thickness of the boundary layer. This model considers the possibility of intra-particle diffusion resistance controlling the overall adsorption rate. A multi-linearity pattern of the plot of qt versus $t^{0.5}$ can indicate multiple stages during adsorption, such as external surface adsorption, gradual intra-particle diffusion, and equilibrium.

These models were employed to evaluate the experimental kinetic data, enabling a detailed assessment of the potential mechanisms governing the adsorption of the pharmaceuticals onto biochar in the studied systems.

3.8.3 Batch Adsorption Isotherm Study

The experimental study was aimed to evaluate the best interactions between biochar and selected pharmaceuticals based on varying concentration and time. For isotherm analysis, the initial concentration of the pharmaceutical was varied while maintaining constant biochar dosage and contact time. Batch experiments were carried out using 0.1g of biochar in 100 mL of solution, with a fixed contact time of 18 hour. Initial adsorbate concentrations ranged from 2 to 18 mg/L. After equilibrium was reached, the adsorption capacity was plotted against the equilibrium concentration, and the data were fitted to nonlinear isotherm models, such as Langmuir and Freundlich. The model parameters were estimated using linear regression, and R^2 values evaluated the goodness of fit.

Langmuir Isotherm Model

The Langmuir isotherm model, originally proposed by Langmuir in 1917, was developed to describe gas adsorption onto solid surfaces (Langmuir, 1917). Over time, it has been widely adopted to explain adsorption phenomena in liquid-phase systems, including slurry-based adsorption processes. The model assumes that the adsorbent surface contains a finite number of identical and energetically equivalent adsorption sites, each capable of binding one adsorbate molecule. It also assumes that there are no interactions between adsorbed molecules, and once a site is occupied, no further adsorption can occur at that location.

The Langmuir isotherm nonlinear equation represented as:

$$q_e = \frac{(q_m \ K_L \ Ce)}{(1 + K_L \ Ce)}$$

----------(7)

where, K_L [L/mg] , the Langmuir constant

qm [mg/g] , the maximum adsorption capacity.

Freundlich Isotherm Model

The Freundlich isotherm model, proposed by Freundlich in 1924, is an empirical equation developed to describe adsorption onto surfaces with heterogeneous energy distributions (Freundlich, 1924). In contrast to the Langmuir model, which assumes uniform surface sites and monolayer adsorption, the Freundlich model accounts for adsorption on surfaces with varying affinities toward the adsorbate. As such, it allows for multilayer adsorption and is particularly suited for heterogeneous systems.

This model remains widely used for describing the adsorption of organic pollutants onto porous materials, such as activated carbon, where surface heterogeneity plays a significant role in the adsorption process. The mathematical representation of the Freundlich isotherm can be written as follows, according to Foo and Hameed (2009),

$$qe = K_F \ Ce^{\frac{1}{n}}$$

----------(8)

where, qe , the equilibrium adsorption capacity (mg/g),

K_F , the Freundlich constant related to adsorption capacity

n , the heterogeneity or intensity parameter (dimensionless),

Ce, the equilibrium concentration of adsorbate in solution (mg/L).

3.9 Column Adsorption Experiments

3.9.1 Column Setup Modification and Troubleshooting

During the early phase of column testing, several technical issues were encountered that required adjustments to the column setup. The initial design featured a base mesh intended to retain the biochar while allowing fluid to pass through. However, high internal pressure and frequent clogging were observed during preliminary tests. To resolve this, the mesh was removed and replaced with a free-flow base supported by a downward tapering funnel. A physical modification was made by inserting a conical funnel section between the base inlet and the main body of the column. This adjustment helped redirect the upward flow and minimize settling. This modification ensured smoother fluidization and reduced the risk of blockage.

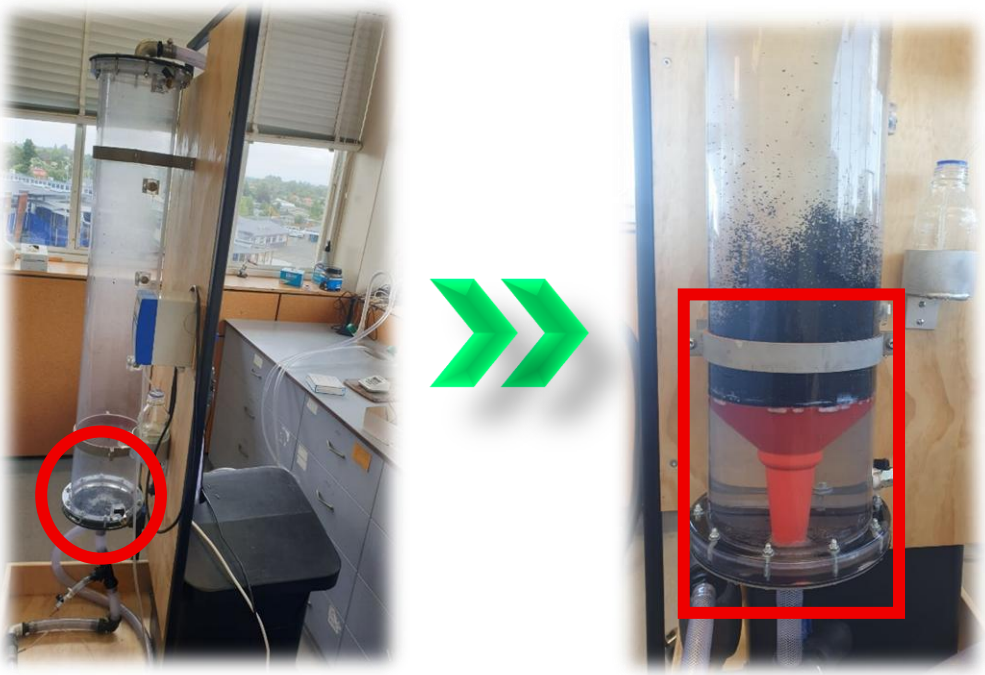


Figure 3.11 Column Modification by Cone shaped Funnel

Additional improvements included reinforcing pipe joints, sealing leak-prone areas with waterproof adhesive, and replacing flexible tubing with rigid connectors to improve flow stability. Initially, a Grundfos centrifugal pump was used for recirculating water through the system however, the flow output was inconsistent and insufficient to maintain stable fluidization at higher dosages. To address this, the pump was placed with an AL-KO submersible pump in the reservoir tank, which provided a more stable and higher flow rate suitable for continuous operation across all experimental modes. These operational modifications were essential for achieving reliable column performance and ensuring repeatability of experimental conditions.

Figure 3.12 Column Modification with Pump

Specifically, the top of the fluidized column experienced repeated water leakage due to seal failure under variable flow pressures. This necessitated multiple cycles of disassembly, resealing, and pressure testing. Additionally, modifications to the piping system were made to improve the flow uniformity and ensure proper fluidization of the biochar bed. Although time-consuming, these design iterations and hand-on adjustments reflect the considerable effort invested in overcoming experimental challenges and ensuring research consistency and reliability of the fluidized column system. The operation of all 16 experimental runs was made possible through extensive troubleshooting, meticulous monitoring, and persistent refinement of the system under real-world constraints.

3.9.2 Single Pass Column Treatment

The single-pass column system was designed that the influent solution passes only once through the adsorption column without recirculation. This represents a typical open-loop flow system, where treated water exits the system and is not returned. Experiments 1 through 7 were conducted using a single-pass column system with continuous pharmaceutical dosing.

In this setup, a paracetamol solution is continuously dosed into the incoming fresh tap water stream using a Concept 420 peristaltic pump. The mixed solution then flows through a static mixer through the pipe to ensure homogeneity before entering the column packed with biochar adsorbent.

The contact time between the solution and the adsorbent is determined by the flow rate and column dimensions, resulting in relatively short retention times compared to closed-loop systems. This configuration is particularly suited for mimicking real-world continuous flow treatment processes used in municipal or industrial water treatment plants.

Effluent samples are collected directly from the column outlet, and influent samples are withdrawn immediately after the static mixer but before entering the column. Both are analysed using UV-Vis spectrophotometry to monitor contaminant concentrations.

The influent concentration remains relatively constant over time, while the effluent concentration increases as the adsorbent becomes saturated. This change is used to generate breakthrough curves, which provide insight into the adsorption dynamics, breakthrough time, and bed exhaustion characteristics.

3.9.3 Closed-loop Recirculation Column

The single-pass systems, where the contact time is limited and fixed, however, the closed-loop system allows the exact solution to be recirculated repeatedly through the column. The closed-loop recirculation column system was employed in this study to enable accurate kinetic analysis of pharmaceutical adsorption onto biochar. This configuration ensured continuous contact between the contaminant solution and the adsorbent, allowing for the observation of time-dependent adsorption behaviour, which is essential for kinetic modelling. Unlike single-pass systems, the closed-loop setup more closely mimics realistic treatment scenarios, such as batch reactors and industrial recirculation processes. Furthermore, by reusing a single batch of pharmaceutical solution without continuous dosing, the system reduced water and chemical usage, making it a more sustainable and resource-efficient approach for extended adsorption studies.

Experiments 8 through 13 were studied using a closed-loop recirculation column system to evaluate the adsorption kinetics of two pharmaceuticals, paracetamol (Experiments 8–12) and ibuprofen (Experiment 13). This system allowed for repeated contact between the adsorbate and biochar, simulating a continuous mixing environment to observe the time-dependent removal performance.

A pharmaceutical solution of 1 g/L concentration was prepared by dissolving 1 g of paracetamol per liter in 100 L of tap water, which was then poured into a large-capacity reservoir. The solution was continuously circulated through the column system using a submersible pump, ensuring constant mixing and flow without the need for continuous dosing.

The influent passed through a static mixer before entering a fluidized bed adsorption column packed with either raw or alkaline-activated biochar. Surface modification of biochar was conducted using a 30% KOH solution for activation. The configuration of the system allowed

the solution to recirculate without interruption, which helped maintain a stable concentration over the 6.5 to 7 hour duration of the experiment.

Sampling ports were installed before and after the column to collect influent and effluent samples at regular time intervals. These samples were analysed immediately using UV-Vis spectrophotometry to monitor the concentration of pharmaceuticals over time, allowing for kinetic modelling of the adsorption process.

3.9.4 Semi-Continuous Closed-Loop Column Mode

This experiment was designed to bridge the gap between idealized batch or single-pass systems and real-world continuous treatment operations. While batch and standard closed-loop kinetic tests help understand adsorption capacity and rate, they do not simulate how a treatment column behaves under intermittent contaminant loading in continuous recirculation.

Experiments 14 to 16 were performed using the semi-continuous closed-loop column system to further assess the progressive saturation behaviour of biochar under repeated dosing conditions. Each experiment utilized raw biochar with a particle size of 1 mm and a constant biochar mass of 100 g. The system was operated with a recirculation flow rate of 15 L/min, with a total water volume of 75 L, and maintained over an 8-hour runtime.

In this experiment, a semi-continuous dosing strategy was integrated into a closed-loop recirculation system to simulate the dynamics of a full-scale continuous treatment process. Rather than introducing the entire pharmaceutical load at once, the total contaminant solution was divided into equal portions and dosed incrementally at fixed time intervals. Between each dosing event, effluent samples were collected from the outlet to monitor changes in concentration over time. This alternating sequence of dosing and sampling was maintained throughout the experiment, allowing for a gradual build-up of pharmaceutical load within the system.

The approach maintains a high internal recirculation rate while applying a low external loading rate, thereby mimicking operational conditions in continuous flow systems with periodic contaminant input. This setup showed the evaluation of the column's progressive saturation behaviour under controlled conditions. The resulting concentration profile provides valuable insight into potential efficiency of the biochar and helps predict how frequently spent adsorbent would need to be replaced or regenerated in a practical treatment scenario.

3.10 Analytical Method

The concentration of ibuprofen and paracetamol in all batch and column adsorption experiment samples was determined using UV-Visible spectrophotometry, a standard analytical method for quantifying organic compounds in aqueous solutions. A Shimadzu UV-1900 UV-Vis spectrophotometer was used throughout the study, operated in photometric mode.

Figure 3.13 Shimadzu UV-1900 spectrophotometer for concentration analysis

Prior to quantification, the maximum absorbance wavelengths (λ_{max}) for each compound were identified using full spectrum scans from 190 to 500 nm. The λ_{max} values were found to be 225nm for ibuprofen and 245 nm for paracetamol, and all absorbance measurements were subsequently performed at these wavelengths. For example, multiple studies have reported λ_{max} values of ibuprofen ranging from 221 nm to 228 nm, depending on solvent and experimental conditions. The recent spectroscopic characterization found the highest coefficient of determination for ibuprofen at $\lambda = 225$ nm, further validating with current result (Rajendiran et al., 2025). For paracetamol, reported λ_{max} values in the literature typically range between 243 nm and 246 nm. For example, a standard operating procedure from Shimadzu UK specifies UV detection of paracetamol at around 243 nm. For example, a study published in the Research Journal of Pharmacy and Technology reported maximum paracetamol absorption at 245 nm, selecting this wavelength for analysis, thereby confirming its suitability for quantitative spectrophotometric determination.

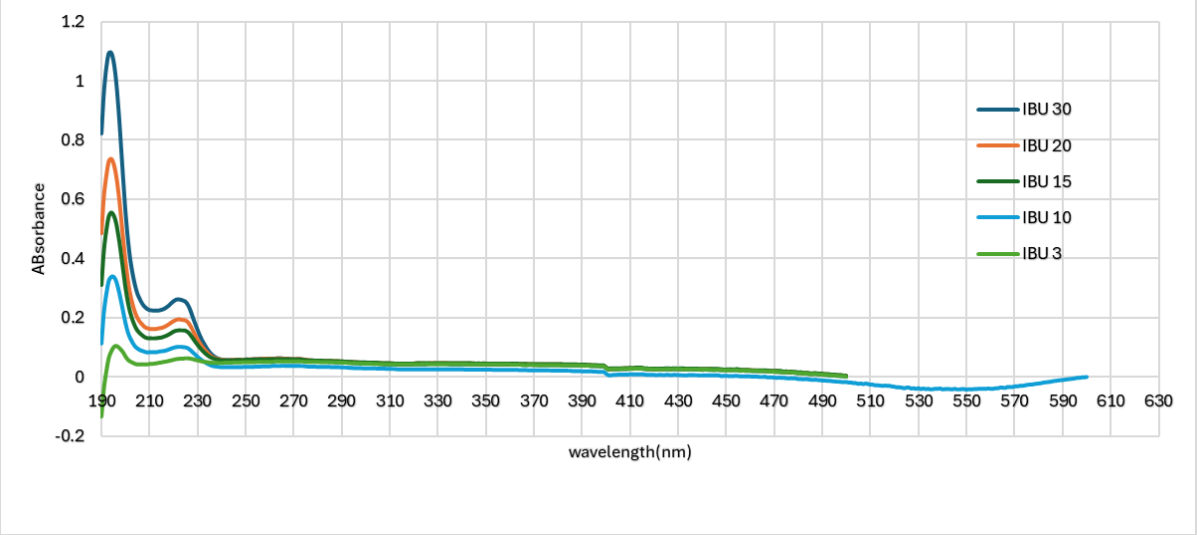


Figure 3.14 UV-Vis absorbance spectra of ibuprofen solutions at varying concentrations (1–30 mg/L), showing maximum absorption near 225 nm.

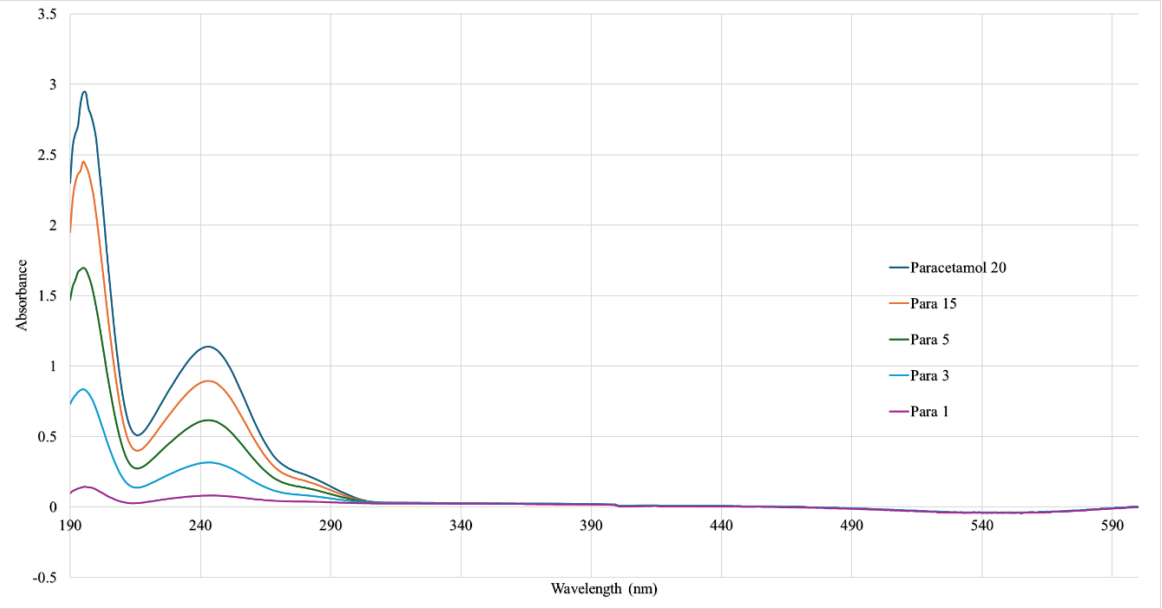


Figure 3.15 UV-Vis absorbance spectra of paracetamol solutions at varying concentrations (1–20 mg/L), showing maximum absorption near 245 nm.

To establish a reliable correlation between absorbance and concentration, a series of standard solutions were prepared by diluting a stock solution to known concentrations (ranging from 1 to 30 mg/L). The absorbance of each standard was recorded at its wavelength and Calibration curves were generated by relating absorbance to concentration. The linear regression equation derived from each curve (typically with an R^2 value ≥ 0.99) was used to calculate the unknown concentrations of all experimental samples. Only absorbance values falling within the validated

linear range of 0.1 to 1.2 absorbance units (AU) were used for quantification, ensuring compliance with the Beer–Lambert law and minimizing measurement errors.

During batch studies, samples were withdrawn at defined time intervals to monitor the adsorption kinetics. In the column experiments, inlet concentrations were verified periodically, while effluent (outlet) samples were collected continuously or at scheduled intervals to construct breakthrough curves. All samples were promptly filtered through 0.45 μm syringe filters to eliminate residual biochar particles and prevent scattering or interference in the absorbance reading. Each sample was transferred into a 10mm path length quartz cuvette for measurement, and distilled water was used as the reference blank throughout all measurements to establish baseline correction.

Each sample was measured in duplicate to ensure data reliability, and calibration standards were checked regularly for stability. The spectrophotometer was calibrated before each session, and all glassware and cuvettes were rinsed thoroughly with distilled water between measurements to avoid cross-contamination. This method provided consistent, accurate determination of pharmaceutical concentrations in both inlet and outlet streams, enabling the calculation of removal efficiency, adsorption capacity, and modelling of kinetic and equilibrium behaviour.

Although high-performance liquid chromatography (HPLC) is the preferred technique for measuring pharmaceutical concentrations at nano- to microgram per liter (ng/L to μg/L) levels due to its high sensitivity and specificity, it was not available for use in this study due to instrumental malfunction and time constraints. As a result, UV–Visible spectrophotometry was employed as an alternative method for quantifying ibuprofen and paracetamol in the aqueous phase. While UV-Vis is less sensitive than HPLC and generally suited for higher concentration ranges, it remains widely used for adsorption studies involving synthetic solutions at mg/L levels.

3.11 Adsorption Models for Column

The adsorption performance within the column systems was interpreted using a combination of kinetic and breakthrough models selected according to each operational mode. In the single-pass flow configuration (Experiments 1–7), In the single-pass column experiments, the adsorption performance was evaluated by plotting breakthrough curves expressed as the ratio of effluent to influent concentration (C_t/C_o) versus time. This approach provides a direct visual assessment of column saturation, breakthrough behaviour, and the effectiveness of biochar

under varying flow rates, bed depths, and particle sizes. Only breakthrough curves were presented for these experiments, as they provide the most practical representation of dynamic performance.

For the closed-loop recirculation setup (Experiments 8–13), adsorption kinetics model were assessed using pseudo-first-order(PFO), pseudo-second order(PFO), and intraparticle diffusion models (IPD). These formulations are well-suited to characterizing time-dependent adsorption rates under batch-like recirculation, enabling insights into rate-limiting steps and diffusion mechanisms.

In the semi-continuous dosing system (Experiments 14–16), breakthrough response to repeated contaminant input was analysed cumulative adsorbed mass performance. This configuration was designed to simulate of real-world treatment dynamics and the estimation of the frequency of adsorbent replacement in continuous systems.

Model fitting was conducted using Microsoft Excel, and Origin Pro 2025, parameters were estimated through linear regression with R^2 values used to assess goodness-of-fit.

Chapter 4

Results and Discussion

4.1 Overview

This chapter outlines the key findings from the experimental work and discusses the results, beginning with a comprehensive evaluation of the adsorbent's physicochemical properties. Analytical techniques, including BET, FTIR, and SEM-EDX, were used to characterize the surface structure, composition, and functional groups of the biochar, both before and after surface modification.

The performance of the biochar was then assessed through batch and column adsorption studies. Batch experiments explored adsorption kinetics, isotherms, and the effect of biochar dosage and particle size, while column tests provided insight into real-time behaviour under continuous flow conditions, including single-pass, recirculation, and semi-continuous dosing modes.

Method validation was carried out to confirm the accuracy and consistency of the experimental setup and measurements. Experimental data were fitted to appropriate kinetic and isotherm models in batch mode, and to breakthrough models in column configurations, allowing for quantitative interpretation and performance prediction.

The chapter concludes with a discussion on potential adsorption mechanisms, drawing from both characterization and modelling outcomes to explain the interactions between pharmaceuticals and biochar surfaces.

4.2 Biochar Characterization

4.2.1 BET Surface Area

The BET surface area and pore characteristics of four selected biochar raw samples, including Pine Biochar, High Grade Biochar, Premium Biochar, and Plain Biochar from the CoolStaff community, are presented in Table 4.1. The result analysis revealed that among the four selected biochar, Premium Biochar demonstrated the highest porosity metrics, with a BET surface area of 308.3 m^2/g, micropore volume of 0.1573 cc/g, and micropore area of 448 m^2/g. In contrast, Plain and Pine Biochar exhibited the lowest values in all categories (BET surface areas of 58.63 m^2/g and 52.27 m^2/g, respectively), suggesting limited adsorption capabilities.

These findings demonstrate that the Premium Biochar, owing to its superior textural properties, is the most promising adsorbent for pharmaceutical adsorption in aqueous systems. The differences in performance can be attributed to feedstock type, particle size, and pyrolysis or activation conditions. High Grade Biochar offers an intermediate solution that balances performance with production cost, making it suitable for moderate adsorption needs or soil enhancement. In contrast, Pine Biochar and Green Circle Biochar may be more appropriate for bulk applications such as low-cost soil amendment, where surface area is not a critical factor.

Table 4.1 BET Analysis of Selected Different Biochar Samples

Sample	BET Surface Area (m^2/g)	Micropore Volume (cc/g)	Micropore Area (m^2/g)
Pine Biochar	58.63	0.0285	80.31
High Grade Biochar	104	0.0519	146
Premium Biochar	308.3	0.1573	448
Plain Biochar	52.27	0.0206	57.88

For instance, previous studies report that biochar derived from hardwoods or subjected to chemical/physical activation can achieve surface areas exceeding 300 m^2/g due to improved porosity and structural uniformity (Ahmad et al., 2016; Tan et al., 2015). In contrast, pine-derived and unmodified biochar generally exhibit lower BET areas, often below 100 m^2/g, limiting their capacity for adsorbing small organic molecules (Zhao et al., 2013). The low BET values observed in Plain Biochar also align with literature attributing weak performance to lower-temperature pyrolysis processes.

Based on the comparative analysis of BET surface area, micropore volume, and micropore area, Premium Biochar demonstrated the highest values across all measured parameters. Its well-developed porous structure indicates strong potential for adsorption applications. As a result, Premium Biochar was selected as the most suitable material among the New Zealand-sourced biochar for use in this study's adsorption batch and column experiments. Furthermore, considering its high performance and local availability, Premium Biochar offers a cost-effective alternative to commercial activated carbon, making it a practical and sustainable option for removing emerging contaminants from aqueous environments.

In order to further enhance its adsorption efficiency, the selected biochar was chemically modified through surface activation. The biochar was treated with 30% potassium hydroxide (KOH) by soaking to increase surface modification and improve its pore structure. KOH activation is a widely recognized method to increase surface area and develop microporosity through carbon etching and expansion. The treated biochar was then used in the adsorption process to evaluate its capacity for removing pharmaceutical contaminants. For example, Jedynak et al. (2024) showed that biochars activated with KOH possess a highly developed porous architecture dominated by micropores, along with a greater abundance of oxygen-containing functional groups such as carboxyl and carbonyl moieties. These modifications enhance the specific surface area while introducing both acidic and basic surface functionalities, thereby improving selectivity and adsorption capacity for diverse contaminants, including ammonia and heavy metals.

A comparative analysis of BET surface area before and after the adsorption process is illustrated in figure 4.1, highlighting the structural changes that occurred because of both chemical activation and contaminant uptake.

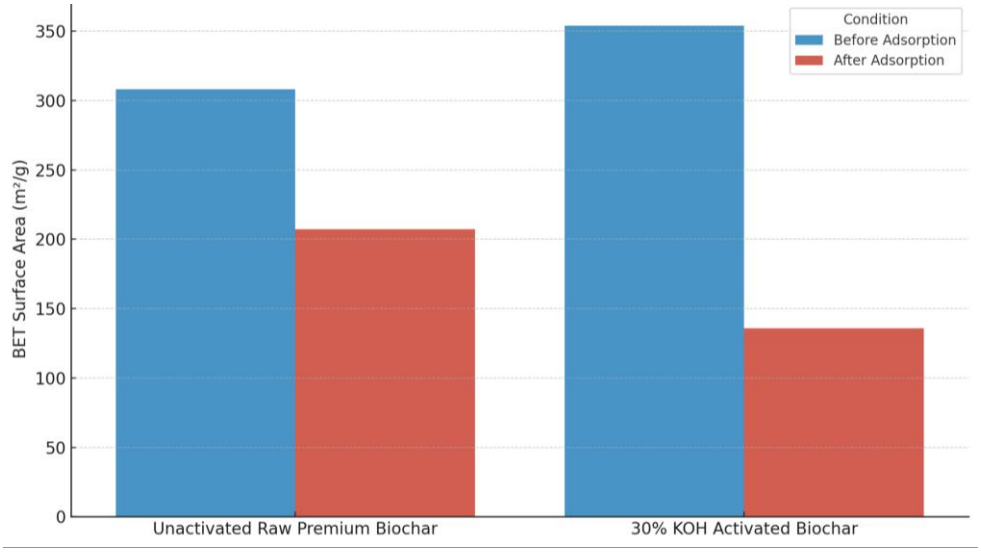


Figure 4.1 Comparison of BET Surface Area of Unactived and 30% KOH Activated Premium Biochar Before and After Adsorption

As shown in the comparative BET analysis (Figure 4.1), the BET surface area of both Unactivated Raw Premium Biochar and 30% KOH Activated Biochar showed a notable decline after pharmaceutical adsorption, indicating effective surface occupation by contaminants.

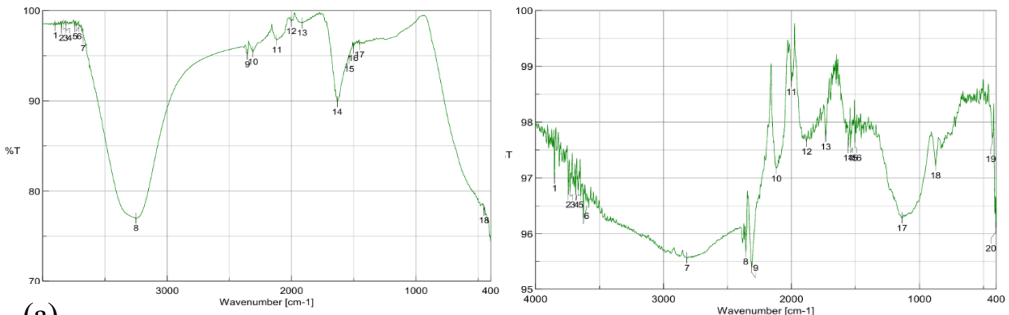
Before adsorption, the 30% KOH activated biochar exhibited a significantly higher BET surface area (354.2 m^2/g) compared to unactivated raw biochar (308.3 m^2/g). This improvement

is attributed to the removal of tar residues and the expansion of existing pores, which is consistent with findings by (Jedynak & Charmas, 2023), who reported that KOH activation enhances pore connectivity and facilitates the diffusion of adsorbates into the internal matrix. After using the surface-modified biochar in the adsorption process of pharmaceuticals removal, a noticeable reduction in surface area (137 m^2/g) was observed, indicating effective interaction between the pharmaceutical and the adsorbent surface.

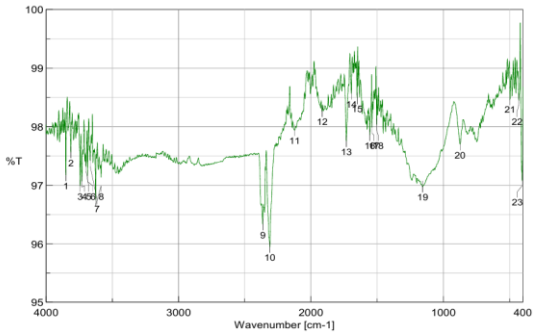
After adsorption, both materials showed a reduction in surface area, but the drop was more dramatic in the activated biochar (down to 135.7 m^2/g, a 62% decrease) compared to the unactivated biochar (207.3 m^2/g, a 33% decrease). This greater decline in the activated sample suggests that its larger surface area and micropore volume facilitated more extensive adsorption of pharmaceutical compounds. The observed reduction supports the mechanism of physical adsorption, where adsorbate molecules fill and block micropores, thereby reducing measurable surface area (Tan et al., 2015).

Overall, these results indicate that while surface activation enhances the adsorption capacity of biochar, it also leads to greater saturation and faster reduction of effective surface area after use. In contrast, unactivated biochar, though less efficient initially, retains more of its surface characteristics post-adsorption. Therefore, 30% KOH-activated biochar is preferable for high-performance, short-duration treatment, while unactivated biochar may be more suitable for cost-effective, moderate-use scenarios.

4.2.2 FTIR Analysis



(a) (b)



(c)

Figure 4.2 FTIR Spectra of (a) Raw Premium Biochar (b) 30% KOH modified Biochar (c) After Adsorption Biochar

The FTIR analysis revealed significant differences in surface functional groups among the raw premium biochar, 30% KOH surface-modified biochar, and the post-adsorption biochar. Figure 4.2 presents the FTIR spectra for the Raw Premium Biochar, 30% KOH Surface Modified Biochar, and After Adsorption Biochar, covering the range from 4000 to 400 cm^{-1}.

In the raw biochar sample, the presence of broad –OH stretching bands around 3400 cm^{-1} was relatively showed, indicating a limited number of hydroxyl groups. After KOH activation, these bands intensified, suggesting an increase in surface oxygenated functional groups such as alcohols and phenols. The modified biochar also exhibited enhanced C=O stretching vibrations around 1730 cm^{-1} and stronger C–O bands near 1150 cm^{-1}, corresponding to carboxylic acids, esters, and ethers. These changes confirm that KOH activation significantly enriched the biochar surface with polar functional groups capable of interacting with contaminants.

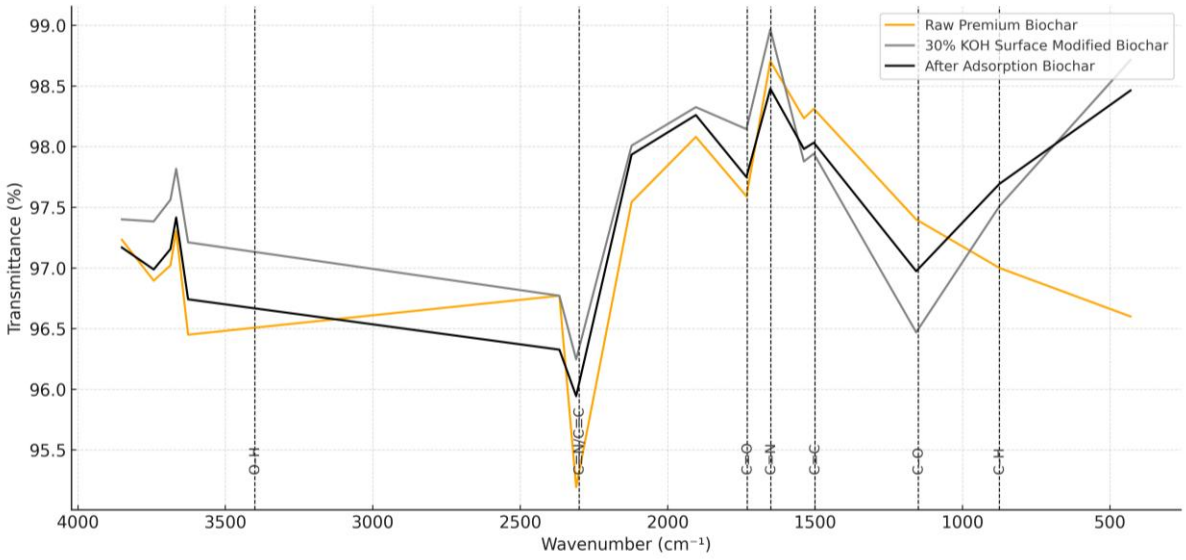


Figure 4.3 FTIR Spectra Comparison Raw, Surface Modified, After Adsorption Biochar

Table 4.2 Functional Group and Wavenumber of Biochar Samples

Wavenumber (cm^{-1})	Functional Group	Raw Premium Biochar	30% KOH Surface Modified Biochar	After Adsorption Biochar

~3850–3600	–OH stretch (alcohols, phenols)	Very strong, sharp, highly hydrophilic	Broad and strong – KOH enhanced	Still present – intensity slightly lower
~2367–2310	CO_2 asymmetric stretch (adsorbed gases)	Moderate bands present	Moderate – clearer doublet	Strong enhancement – possible CO_2 or nitrile uptake
~2120–1900	C≡C or C≡N (alkynes/nitriles)	Faint/weak	More defined – oxidative sites	Slightly diminished – bonding or coverage possible
~1730	C=O stretch (carboxylic acids, esters)	Moderate peaks (~1694, 1632 cm^{-1})	Strong, distinct peaks (1733, 1652 cm^{-1})	Lower intensity, shifted – indicates active site use
~1650–1500	Aromatic C=C and C–N stretch	Strong peaks at 1556, 1504 cm^{-1}	Similar pattern + shoulder	Slight red shift (to 1575 cm^{-1}) → π–π stacking
~1150	C–O stretch (ethers, esters)	Modest signal (~1157 cm^{-1})	Pronounced ether band	Band reduced or disappears evidence of binding
< 600	Metal–O or phosphate lattice	Single band (~453 cm^{-1})	874, 430 cm^{-1} bands from residual K	New bands (531–497 cm^{-1}) indicate metal or phosphate coordination

The raw premium biochar spectrum showed a strong, sharp O–H stretching band around 3850–3600 cm^{-1}, indicating a hydrophilic surface dominated by surface hydroxyl groups. However, it exhibited only moderate carbonyl (C=O) peaks and relatively weak ether (C–O) signals, demonstrated a limited number of oxygenated functional groups. The presence of a single band at 453 cm^{-1} in the low-frequency region indicates minimal inorganic content. Although the aromatic backbone was preserved, which allows for π–π interactions with pharmaceutical molecules, the overall surface reactivity was low. This likely contributed to the lower removal efficiency observed in batch experiments, where fewer polar or reactive functional sites were available to bind pharmaceutical contaminants.

In a literature study, Sun et al. (2022) observed that unmodified coconut-shell biochar exhibited relatively low adsorption capacity for sulfonamide antibiotics. FTIR analysis indicated a limited presence of oxygen-rich functional groups, constraining the development of hydrogen

bonds and other interactions essential for efficient adsorption. Following KOH activation, the biochar demonstrated significant improvements in surface area, porosity, and functional group diversity, leading to a five- to seven-fold enhancement in its antibiotic adsorption capacity

The 30% KOH surface-modified biochar demonstrated significantly enhanced surface functionalization. FTIR spectra revealed intensified peaks in the regions corresponding to hydroxyl (~3700 cm^{-1}), carbonyl (~1730 cm^{-1}), and ether (~1150 cm^{-1}) groups, all of which are critical for adsorptive interaction with pharmaceutical molecules through hydrogen bonding, Lewis's acid–base interaction, and electrostatic attraction.

The presence of residual potassium-based salts, evident from distinct bands near 874 cm^{-1} and 430 cm^{-1}, introduced surface basicity, further promoting affinity for acidic pharmaceuticals. These modifications result in superior performance in both batch and column systems, where the activated biochar exhibited faster adsorption kinetics and higher capacities due to its chemically active surface.

The after-adsorption Biochar spectrum exhibited clear signs of functional group consumption and new surface complex formation. Notably, the intensity of –OH and C=O bands decreased, and the C–O band at 1157 cm^{-1} weakened or disappeared, suggesting that these groups were directly involved in binding pharmaceutical molecules. New bands emerged in the 531–497 cm^{-1} range, indicative of possible phosphate complexes formed during adsorption. Additionally, the aromatic region (~1575 cm^{-1}) became more pronounced and slightly red-shifted, supporting the role of π–π stacking interactions in the adsorption mechanism. These spectral changes validated the adsorption pathways and supported the saturation patterns observed in the breakthrough curves from column tests. Li et al. (2023) reported a decrease in O–H and C=O stretching vibrations following dye adsorption, confirming their involvement in the adsorption mechanism. Similarly, Azzam et al. (2023) observed reduced intensities of these bands after ciprofloxacin adsorption, attributing this to hydrogen bonding and surface complexation with the pharmaceutical molecules.

In summary, FTIR analysis confirmed that the evolution of surface functional groups, especially the enhancement of oxygen-based chemical groups (such as –OH, C=O, and C–O) on the biochar surface, plays a critical role in the adsorption of pharmaceutical compounds. The chemical activation step was essential for improving adsorptive affinity, while post-adsorption spectra provided molecular-level evidence of successful binding. These findings are consistent with experimental trends in both batch and continuous flow systems and emphasize

the importance of surface chemistry in the design of effective biochar-based adsorbents for pharmaceutical removal.

4.2.3 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Analysis

Scanning Electron Microscopy (SEM) was conducted to examine the surface morphology of unactivated raw biochar, surface-modified biochar before and after pharmaceutical adsorption. Micrographs were obtained at magnifications ranging from 200× to 2000× to assess structural and morphological changes associated with the adsorption process as depicted in figure 4.4.

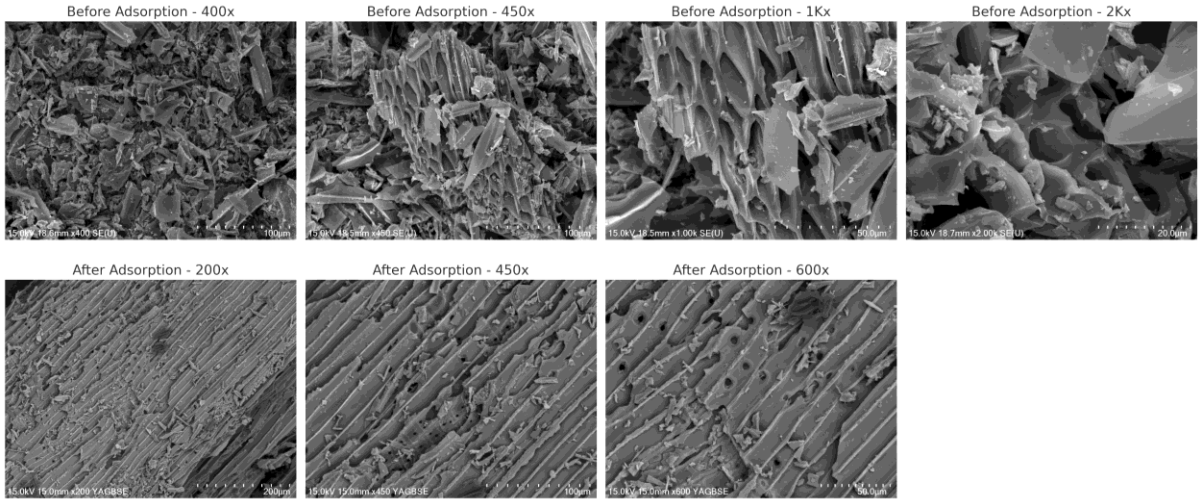


Figure 4.4 SEM Images of Unactivated Raw Premium Biochar Before and After Adsorption

Before adsorption, the biochar exhibited a highly irregular and heterogeneous surface, characterized by jagged edges, fragmented structures, and a substantial presence of surface debris. These surface features suggest that the biochar retains a significant amount of the original plant structure, which is typical for biochar produced via pyrolysis of lignocellulosic biomass due to the characteristic nature of the untreated biochar (woody biomass). Barszcz et al. (2024) mentioned that SEM analysis in that study confirmed that biochar derived from plant biomass displays an irregular, fibrous, three-dimensional surface morphology. This structure is attributed to the retention of plant anatomical features during pyrolysis, particularly at moderate temperatures, with surface debris and heterogeneity commonly observed in biochar produced from woody biomass.

At lower magnifications (400× and 450×), the surface appeared disordered with scattered loose particles. Higher magnification images (1,000× and 2,000×) revealed partially visible pores, many of which were irregular and obstructed by fine residues, suggesting limited initial pore accessibility. The pronounced surface roughness and sharp-edged morphology indicate a

potentially high surface area, although the blocked pores may restrict immediate adsorption efficiency.

In the post adsorption, notable changes in surface morphology were observed. The post-adsorption biochar surface appeared smoother and more organized, with a marked reduction in loose debris. SEM images at 200× and 450× magnification revealed the emergence of elongated, channel-like structures, indicating surface alignment or reconfiguration. At 600×, the pore structures became more defined, exhibiting round and regular shapes. The surface roughness was reduced, and the overall structure appeared more consolidated, likely due to the occupation of adsorption sites by pharmaceutical molecules and the displacement or compaction of surface fragments. These transformations suggest that the adsorption process not only involves contaminant uptake but also promotes physical restructuring of the biochar surface, enhancing pore visibility and accessibility. The shift from a chaotic, debris-laden morphology to a cleaner, channel-rich surface highlights the role of adsorption in modifying the biochar matrix and reinforces its potential as an effective, low-cost adsorbent for pharmaceutical contaminants in aqueous environments.

These morphological features, such as irregular surface topology, high porosity, and interconnected voids, are consistent with literature findings on the efficacy of biochar as an adsorbent for aqueous contaminants (Inyang et al., 2015). The natural porosity and carbonaceous composition of the raw premium biochar suggest it can effectively accommodate both surface adsorption and intraparticle diffusion mechanisms.

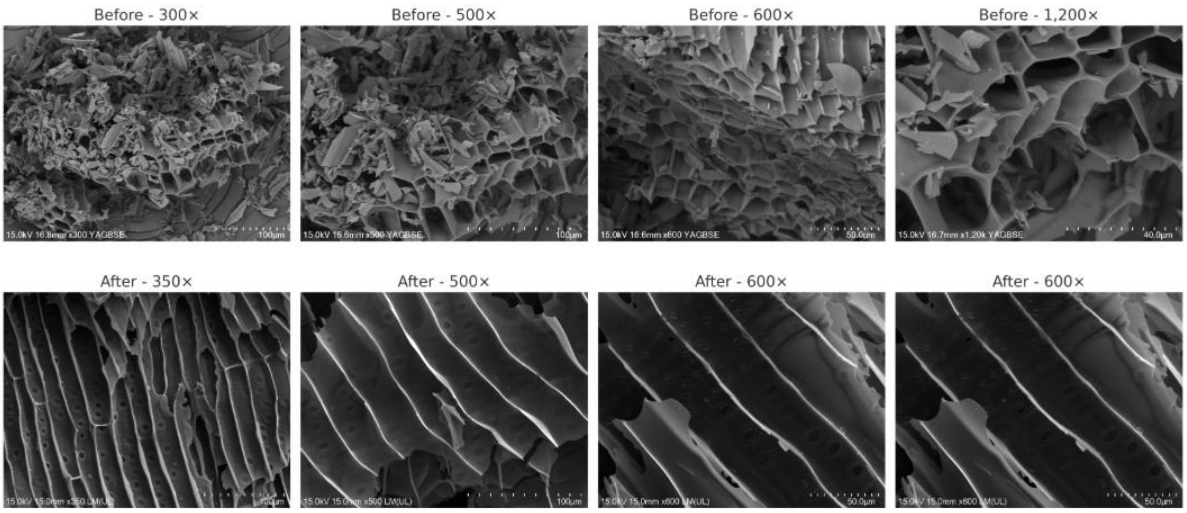


Figure 4.5 SEM Images of 30% KOH Activated Biochar (8hr soaked) Before and After Adsorption

The morphological differences between the KOH-activated biochar before and after adsorption are clearly illustrated in the SEM micrographs at comparable magnifications (180× to 1,200×) of Figure 4.5. These structural changes provide insight into the physical effects of pharmaceutical adsorption on the biochar surface. Before adsorption, the biochar surface exhibited a highly porous, honeycomb-like structure interspersed with irregular fragments and residual debris. After adsorption, the surface appeared smoother, more consolidated, and showed well-defined, clean pores and aligned channel-like features, indicating structural refinement.

These findings are consistent with previous studies on KOH-activated biochar. For example, Zhang et al. (2019) and Mestre et al. (2007) reported that chemical activation with KOH enhances pore development and surface area by etching away amorphous carbon and exposing internal channels. Similar to observations, Wang et al. (2015) noted that post-adsorption SEM images often show cleaner and more organized pore networks due to the displacement of loosely bound particles and improved surface accessibility.

The shift from a debris-covered, irregular surface to a well-defined, organized morphology indicates that adsorption induces not only surface interactions but also subtle physical restructuring. This process appears to improve pore accessibility and reduce diffusion resistance, particularly relevant for continuous adsorption applications such as fluidized bed systems. At lower magnifications (180×–350×), the removal of surface debris and exposure of carbon layers point to an increase in available adsorption sites. At higher magnifications (500×–600×), clearer and more uniform pores confirm structural consolidation and enhanced internal diffusion paths. Collectively, these results underscore the efficacy of 30% KOH-activated biochar as a structurally responsive and high-capacity adsorbent for pharmaceutical removal.

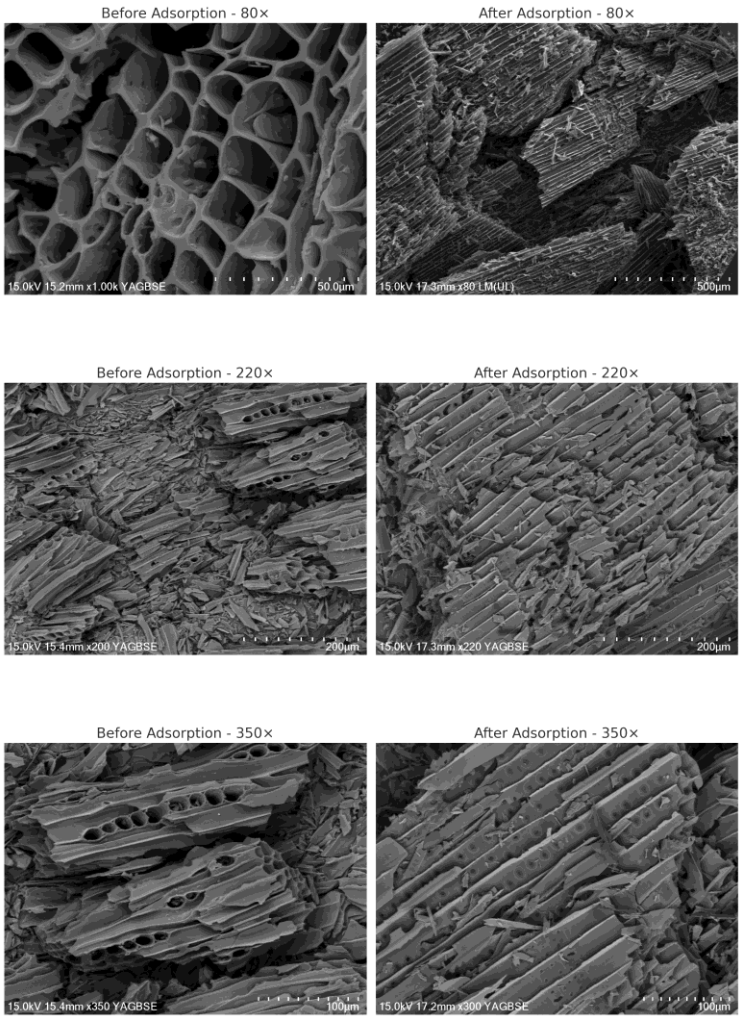


Figure 4.6 SEM Images of 30% KOH Activated Biochar (16 hr soaked) Before and After Adsorption

The SEM images of the 30% KOH-activated premium biochar soaked for 16 hours reveal significant morphological alterations compared to the unactivated raw biochar and 8-hour-soaked activated biochar. Before adsorption, the biochar exhibited a highly porous, honeycomb-like structure with interconnected channels and well-defined pore walls. At higher magnifications, the structure revealed elongated fibrous layers and aligned microchannels, suggesting a high surface area and abundant adsorption sites. After adsorption, notable morphological changes were observed that the surfaces became rougher and more compact, with partially blocked or narrowed pores. At 350×, surface irregularities and adsorbed particulate films were apparent, suggesting successful occupation of internal and external adsorption sites.

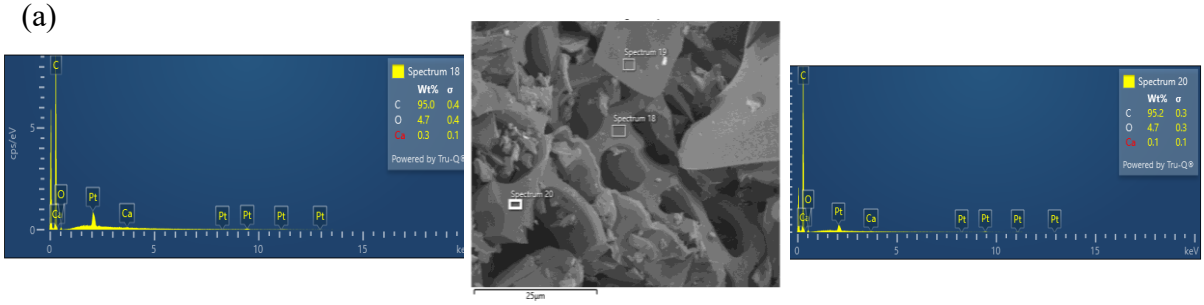
These observations are consistent with findings from Zhang et al. (2019) and Wang et al. (2015), who reported enhanced pore clarity and surface organization in KOH-activated carbon

materials following adsorption of organic contaminants. Unlike biochar activated with alternative agents such as HCl or $ZnCl_2$, KOH-activated biochar demonstrates pronounced pore development and structural realignment after adsorptive interactions.

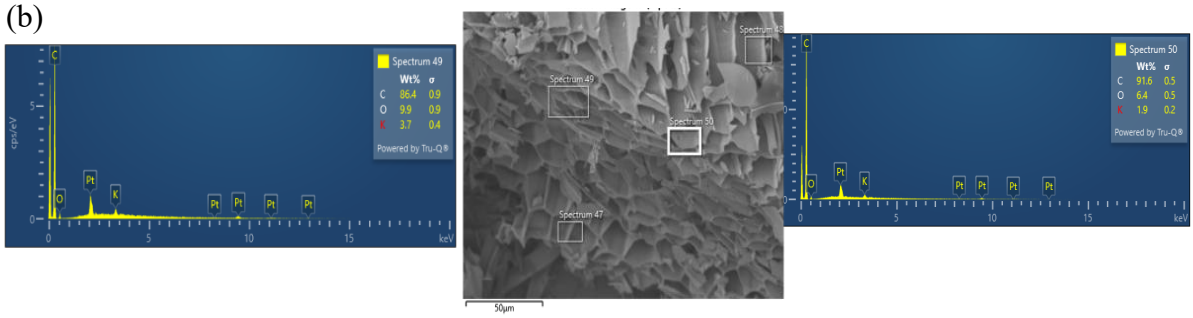
The changes observed are primarily attributed to the chemical activation mechanism of KOH, which creates an interconnected network of micropores by reacting with carbonaceous structures during pyrolysis. The adsorption of pharmaceutical compounds likely promoted further pore exposure and the dislodgement of surface-bound debris. This results in a visibly cleaner morphology, revealing internal porosity and enhancing accessibility of adsorption sites.

The post-adsorption restructuring implies a beneficial self-cleaning effect,wherein adsorptive interactions facilitate partial surface reorganization. This enhances the adsorbent's efficiency in dynamic systems by reducing mass transfer resistance and promoting internal diffusion. The findings underscore the potential of 30% KOH-activated biochar as a high-performance adsorbent, particularly for fixed-bed column applications in water treatment, where sustained accessibility of pore networks is critical for adsorption efficiency.

(a)



(b)



(c)

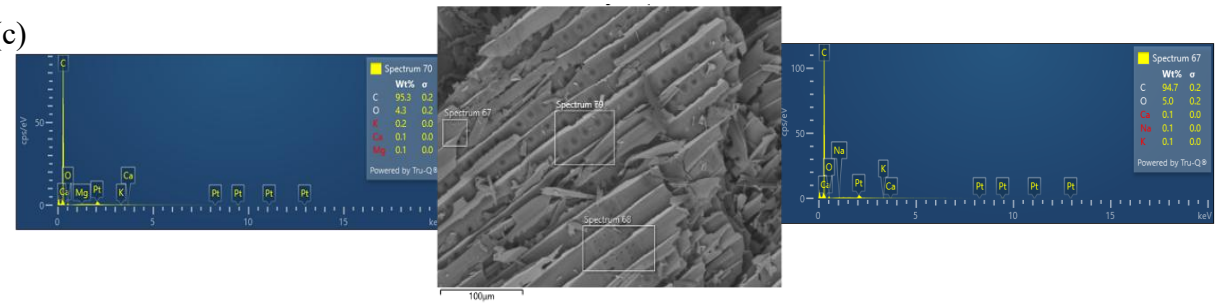


Figure 4.7 Elemental Composition of Biochar Samples (EDS Analysis) (a) raw unactivated biochar (b) KOH surface activation Biochar (c) Post adsorption Biochar

The comparative EDS analysis of the raw, activated, and post-adsorption biochar reveals important changes in elemental composition. Raw biochar shows a high carbon content (~95 wt%) with minor oxygen and traces of silicon originating from the biomass precursor. After KOH activation, carbon content slightly decreases (~85 wt%) while oxygen content increases to ~7 wt%, and potassium appears at ~3 wt%, confirming successful chemical activation. Following adsorption, the carbon content remains high (~94 wt%), while oxygen is slightly elevated compared to raw biochar, and trace elements such as Na and Mg are detectable.

Wang et al. (2021), mentioned in the *Polish Journal of Environmental Studies*, similarly observed through EDS analysis that the elemental composition of biochar changed consistently after adsorption, showing higher oxygen content and the emergence of trace elements.

The increased oxygen content after activation suggests more oxygenated functional groups, which are favourable for adsorption via hydrogen bonding and polar interactions. The presence of potassium after activation is a typical indicator of residual activating agent, which can enhance surface polarity and adsorption sites. After pharmaceutical adsorption, the slight rise in oxygen and trace Na/Mg implies either adsorption of pharmaceutical species carrying ionic groups or cation exchange during the treatment process.

The analysis results indicated that KOH activation successfully modifies the biochar surface to be more oxygen-rich and introduces alkali elements (potassium), enhancing its adsorption capacity. Post-adsorption, the surface largely retains its integrity, showing that the biochar is structurally robust and reusable. The presence of trace elements after adsorption suggests the biochar may accumulate co-contaminants from solution, which should be considered for regeneration and long-term applications.

4.3 Batch Adsorption Performance

4.3.1 Effect of Contact Time

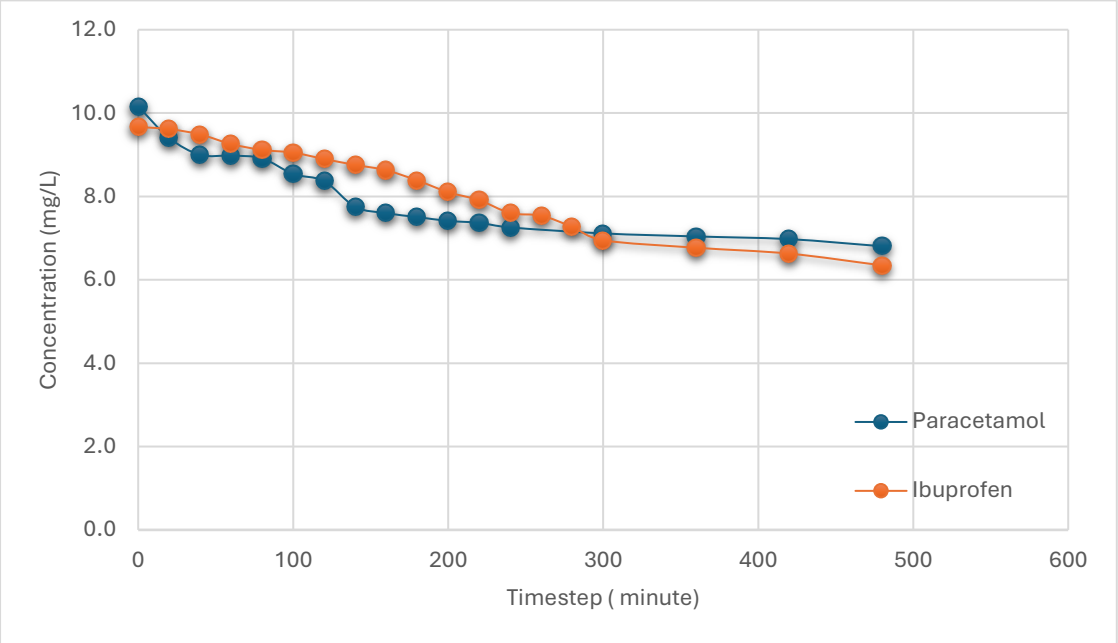


Figure 4.8 Equilibrium time for dose 1g/L of biochar with Paracetamol and Ibuprofen.

The initial concentrations of both pharmaceuticals were set to 10 mg/L to match the influent concentration planned for the column experiments. In order to provide continuity and realistic treatment conditions which involved scaling of batch kinetic data to the dynamic column system. A biochar dose of 0.1 g/100 mL and pH 7.4 was applied. Figure 4.8 clearly shows a two-phase adsorption pattern for both pharmaceuticals with a rapid initial decline in concentration within the first 100–200 minutes, followed by a slower approach to equilibrium beyond 300 minutes.

Paracetamol displayed a more rapid initial concentration decline within the first 100–200 minutes, suggesting its stronger affinity and faster mass transfer toward the biochar surface. In contrast, ibuprofen demonstrated a more gradual and linear decline in concentration, consistent with lower adsorption rates. After about 300 minutes, both pharmaceuticals approached a steady concentration around 6–7 mg/L, suggesting that near-equilibrium was reached at approximately 480 minutes under these batch conditions.

The kinetic patterns observed that external surface adsorption is rapid initially, followed by slower intraparticle diffusion into biochar pores. This is supported by the characteristic two-phase decay of a steep initial drop due to abundant free sites, then a flattening trend as sites become occupied and concentration gradients decrease. Paracetamol's relatively smaller

molecular size and greater hydrophilicity would facilitate its more rapid transfer into the adsorbent micropores compared to ibuprofen.

Overall, a contact time of around 480 minutes is sufficient to reach close to equilibrium for both pharmaceuticals in batch mode, and biochar at this dosage maintains moderate removal efficiency at a realistic influent concentration. From a process design perspective, the selection of 480 minutes as an approximate equilibrium contact time is justified for future modelling, as extending contact time beyond this point offers only marginal improvements in contaminant removal. Moreover, aligning batch conditions with the target influent concentration for column experiments ensures comparable mass transfer driving forces, supporting a more realistic scale-up.

4.3.2 Effect of Initial Concentration

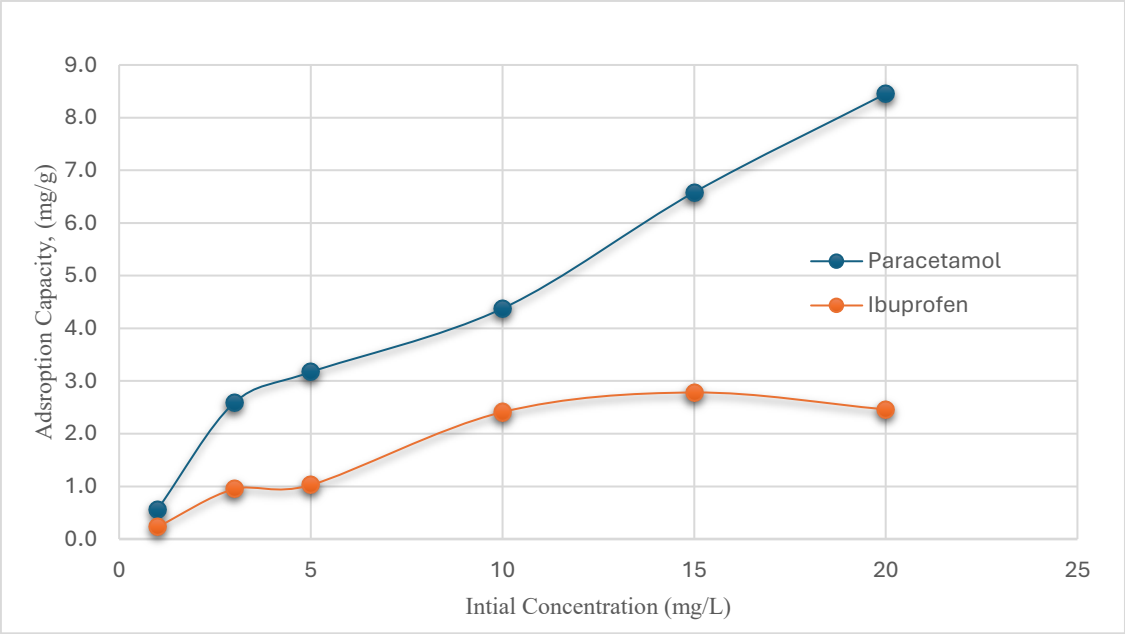


Figure 4.9 Effect of initial concentration on the adsorption capacity of paracetamol and ibuprofen at varying initial concentration of 1 to 20 mg/L, biochar dosages 0.1 g/L, pH 7.4 under batch conditions of 24 hour.

The adsorption capacity of the biochar toward paracetamol and ibuprofen was investigated over a range of initial concentrations from 1 to 20 mg/L, as shown in Figure 4.9. For paracetamol, the adsorption capacity increased progressively, attaining approximately 8.5 mg/g at the highest initial concentration of 20 mg/L. This trend indicates that the available adsorption sites on the biochar were not fully saturated within the tested concentration range. The higher driving forces at elevated concentrations enhanced the mass transfer of paracetamol to the adsorbent surface. Similar findings have been reported for biochar produced from agricultural wastes,

which exhibit gradually increasing adsorption capacities for paracetamol due to its relatively small molecular size and good water solubility, facilitating pore diffusion (Sarker et al., 2025).

The nearly linear increase of *qe* with concentration implies that the biochar possesses a high affinity for paracetamol, and that the adsorbate readily interacts with available surface functional groups, possibly through hydrogen bonding or π–π electron donor–acceptor interactions (Ahmad et al., 2014). These interactions are consistent with the presence of oxygen-containing functionalities and aromatic structures on activated biochar, as reported in prior characterisation studies (Tan et al., 2015). The absence of observable plateauing in *qe* suggests that monolayer coverage was not fully achieved and that multilayer or progressive site occupation may have occurred at higher concentrations.

In contrast, the adsorption capacity of ibuprofen showed a distinct trend, increasing moderately up to 2.8 mg/g at 15 mg/L before plateauing or slightly decreasing at 20 mg/L. This indicates a more limited adsorption affinity and a lower number of effective binding sites for ibuprofen on the biochar surface. Ibuprofen's larger molecular size and more hydrophobic character could hinder its diffusion into micropores and reduce the availability of active sites within the biochar matrix. As a result, once the outer sites were saturated, further increases in concentration did not significantly improve the adsorption capacity, reflecting a limiting behaviour. Moreover, ibuprofen's lower solubility and higher tendency to form hydrophobic aggregates in aqueous media could reduce the effective contact between adsorbate and adsorbent, further constraining its adsorption performance. Such behaviour has been observed in other pharmaceutical adsorption studies, where ibuprofen adsorption generally approaches site saturation at lower *qe* values compared to smaller, more hydrophilic pharmaceuticals (Liu et al., 2019).

Overall, according to the studies and plot results, biochar is generally more effective at removing smaller, polar pharmaceuticals compared to bulkier, hydrophobic ones, primarily due to differences in molecular dimensions, polarity, and interaction mechanisms with the carbon surface. It's highlighted that the biochar shows greater adsorption effectiveness for paracetamol than ibuprofen. These observations are important in understanding the suitability of biochar for treating multi-contaminant wastewater streams and indicate the need for process optimisation to address the less favourable removal of larger, hydrophobic pharmaceuticals.

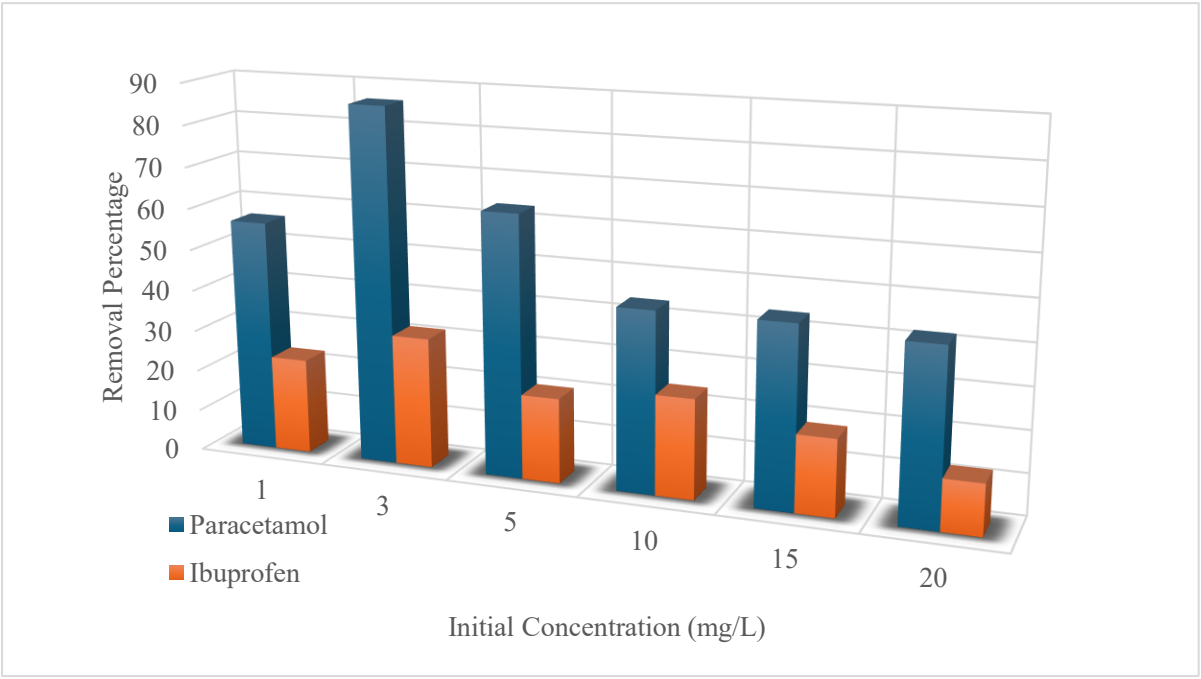


Figure 4.10 Effect of initial concentration on the removal percentage of paracetamol and ibuprofen at varying initial concentration of 1 to 20 mg/L, biochar dosages 0.1 g/L, pH 7.4 under batch conditions of 24 hour.

The removal efficiency for paracetamol was highest at lower initial concentrations, achieving up to approximately 86% removal at 3 mg/L, but progressively decreased to about 42% at 20 mg/L. In contrast, ibuprofen exhibited consistently lower removal percentages across the entire concentration range, with a maximum of around 30% at 3 mg/L, declining to roughly 12% at 20 mg/L.

At lower initial concentrations, the large number of available active sites on the biochar relative to the amount of adsorbate facilitated high removal efficiency, particularly for paracetamol, whose smaller molecular size and higher polarity promoted easier pore diffusion and stronger surface interactions. As the initial concentration increased, the fixed dose of 0.1 g biochar in 100 mL became insufficient to provide enough active sites to adsorb all available molecules, leading to site saturation and a sharp decline in removal percentage. This was more pronounced for ibuprofen, which likely experienced additional limitations and weaker affinity for the biochar surface, further constraining its removal performance as concentrations rose.

These findings indicate that under the studied conditions, the biochar performs effectively for paracetamol removal at lower concentrations but becomes progressively less efficient at higher concentrations due to site saturation effects. The much lower removal of ibuprofen highlights

the challenge of adsorbing larger, more hydrophobic pharmaceuticals, suggesting that adjustments to adsorbent dosage, contact time, or treatment strategy would be required for effective removal in mixed-contaminant wastewater streams. This result indicated the importance of optimising biochar quantity relative to anticipated pollutant loads to maintain satisfactory removal efficiencies for a broader range of pharmaceutical compounds.

The literature also align with this finding of Ibuprofen's lower removal efficiency is linked to its larger molecular size and higher hydrophobicity, limiting interactions with oxygenated biochar surfaces. While adsorption mechanisms such as π–π stacking, hydrogen bonding, and pore filling exist, its affinity is generally lower than that of more polar compounds like paracetamol. Even with surface modification, ibuprofen often requires higher dosages or longer contact times for effective removal (A. L. B. Fuentes et al., 2022).

4.3.3 Effect of Biochar Dosage

Figure 4.11 illustrates the influence of biochar dosage on the removal efficiency of paracetamol and ibuprofen from aqueous solutions, each at an initial concentration of 10 mg/L. The results reveal an enhancement in removal performance for both pharmaceuticals with increasing adsorbent mass, which is the critical role of adsorbent dose in determining treatment efficacy.

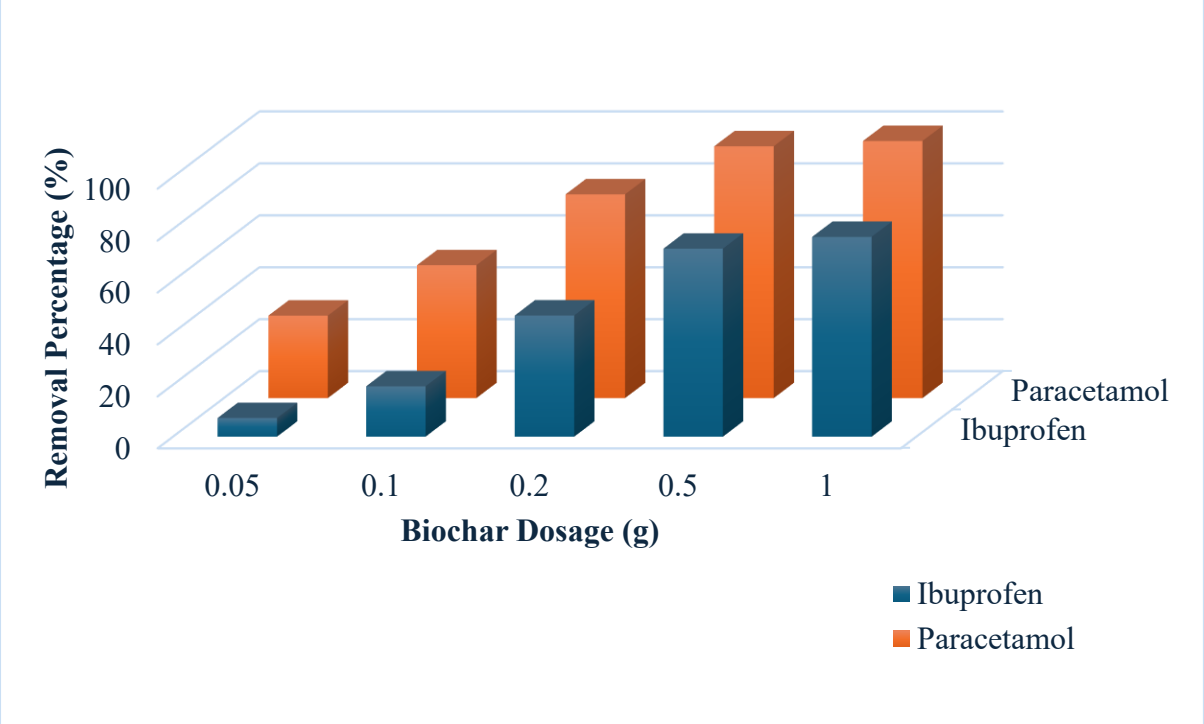


Figure 4.11 Effect of biochar dosage on the removal efficiency of paracetamol and ibuprofen at an initial concentration of 10 mg/L, varying biochar dosages from 0.05 to 1 g, pH 7.4 under batch conditions of 24 hour.

At the lowest dosage of 0.05 g, the removal efficiency for paracetamol reached approximately 35%, while ibuprofen removal was considerably lower, around 10%. This correlated that paracetamol exhibits a greater affinity toward the biochar surface, potentially due to its smaller molecular size, higher polarity, or stronger interactions with the available surface functional groups compared to ibuprofen.

As the biochar dosage was raised to 0.1 g, paracetamol removal improved to 55%, whereas ibuprofen removal increased modestly to around 20%, reflecting a consistent advantage in paracetamol's adsorption behaviour. Further dosage increments to 0.2 g and 0.5 g continued to elevate the removal efficiency for both contaminants, with paracetamol achieving approximately 75% removal at 0.2 g and near-complete elimination (close to 100%) at 1 g of biochar. Ibuprofen removal also rose substantially, reaching around 85% at 1 g, but still slightly below than the paracetamol performance.

This consistent improvement with higher adsorbent mass is attributed to the abundance of available adsorption sites, which promotes greater interaction between the pharmaceutical molecules and the sorbent surface. Nevertheless, the more significant removal of paracetamol even at low dosages implies that adsorption may be additionally determined by the compound's molecular characteristics, including its hydrophilicity, electrostatic interactions, and molecular dimensions.

The observed results align with previously reported trends, in which elevated adsorbent dosage typically boost removal efficiency by increasing the total surface area and functional sites available for contaminant uptake (Nguyen et al., 2022; Bashir et al., 2021). However, it should be noted that beyond a certain dosage, the adsorption capacity per unit mass generally declines due to aggregation of particles or overlapping of active sites, which restricts effective surface exposure. Although this effect was not explicitly shown here, it remains an important consideration for optimising cost and performance in larger-scale systems.

From a practical standpoint, these findings underscore that although higher dosages yield superior removal, an optimal dose balancing cost-effectiveness and performance should be established for implementation at a treatment scale. Moreover, the difference in removal efficiencies between paracetamol and ibuprofen highlights the necessity to tailor adsorbent design for multi-contaminant removal, considering the distinct physicochemical profiles of diverse pharmaceutical pollutants.

4.3.4 Effect of Particle Size

The particle size of biochar plays a crucial role in controlling adsorption performance by influencing surface area and pore accessibility. Figure 4.12 presents the removal efficiencies of paracetamol and ibuprofen at various biochar particle sizes under identical experimental conditions. This comparison helps clarify how particle size affects pharmaceutical uptake in batch systems.

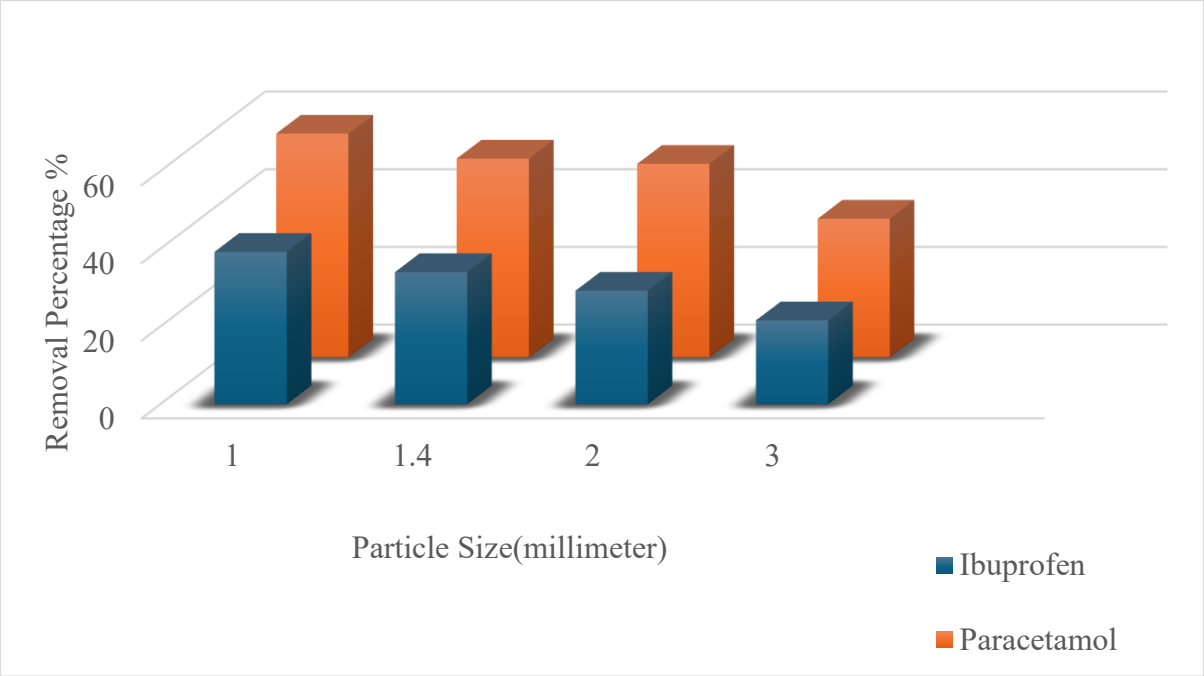


Figure 4.12 Effect of biochar particle size (1mm to 3mm) on the removal efficiency of paracetamol and ibuprofen at an initial concentration of 10 mg/L, biochar dosages 0.1 g/L, pH 7.4 under batch conditions of 24 hour.

The results indicated a clear trend where smaller particle sizes achieved higher removal performance for both compounds. At a particle size of 1 mm, paracetamol reached nearly 70% removal, while ibuprofen achieved around 45%. As particle size increased to 3 mm, removal efficiencies for both pharmaceuticals declined noticeably, with paracetamol dropping to approximately 50% and ibuprofen to about 30%.

This trend can be observed by the greater surface area and higher availability of active sites associated with smaller particles, which enhance contaminant interaction and mass transfer. Larger particles tend to offer reduced external surface area and fewer accessible pores, limiting adsorption performance. These findings are consistent with other studies reporting that smaller adsorbent particle sizes typically promote improved removal efficiency due to enhanced sorption kinetics and greater external diffusion rates (Ali et al., 2020; Chen et al., 2019).

The consistently higher removal of paracetamol across all particle sizes suggests its stronger affinity for the biochar, potentially due to its molecular structure and higher polarity compared to ibuprofen. From a practical perspective, selecting a suitable particle size involves balancing removal efficiency with considerations of hydraulic behaviour and pressure drop in packed or fluidized bed systems.

4.4 Adsorption Mechanism

4.4.1 Kinetic Adsorption Study

In order to better understand the adsorption mechanisms of paracetamol and ibuprofen on biochar surfaces, the data obtained from the contact time experiments were analysed using various kinetic models. Figure 4.13 illustrates the findings of reaction kinetic modelling for Ibuprofen and Paracetamol.

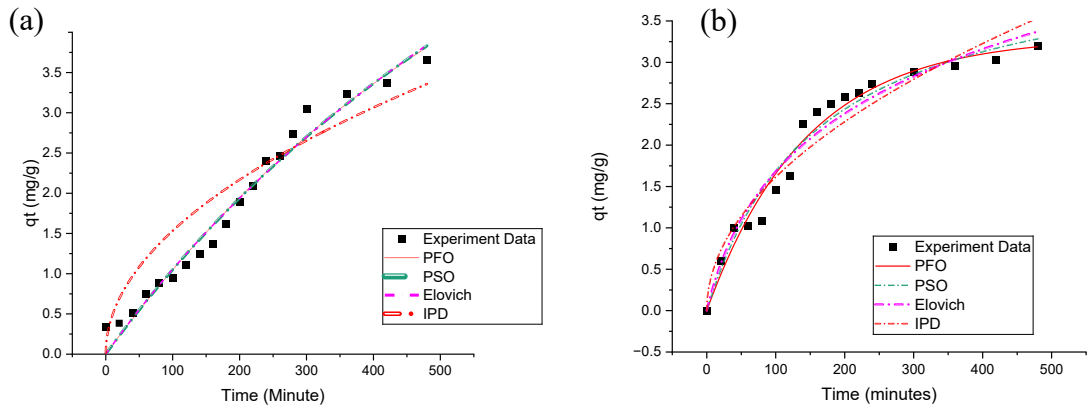


Figure 4.13 Adsorption kinetics of (a) ibuprofen and (b) paracetamol onto biochar at an initial adsorbate concentration of 10 mg/L, an adsorbent dosage of 1 g/L, and pH 7.4.

The kinetic behaviour of ibuprofen (a) and paracetamol (b) onto biochar, compared with four common kinetic models: pseudo-first order (PFO), pseudo-second order (PSO), Elovich, and intra-particle diffusion (IPD). The mathematical forms of these models are described in Section 3.8.2. The experimental data for ibuprofen display a moderately gradual rise in adsorption capacity over time, reaching about 3 mg/g by 500 minutes. Among the fitted models, the PSO (green dashed line) and Elovich (magenta dashed line) closely track the data trend, suggesting that chemisorption (electron-sharing or chemical bond-like interactions) and a heterogeneous surface adsorption process are dominant. The PFO model (red solid line) underpredicts the adsorption at intermediate time points, implying that a purely physisorption-controlled process is insufficient to explain ibuprofen's kinetic behaviour. The intra-particle diffusion (IPD) fit

(red dots) matches reasonably well in the initial stage but deviates later, indicating that pore diffusion contributes but is not the sole rate-limiting step.

According to the data for paracetamol, the trends show a steeper initial rise in adsorption capacity, reaching about 3.3 mg/g at equilibrium within 480 minutes. The PSO model again captures the trend best across the entire time, consistent with chemisorption as the dominant mechanism. The Elovich model also fits well, reinforcing that surface heterogeneity and multilayer interactions may contribute. The PFO model fits less well than PSO and Elovich, especially in the middle stage, suggesting that paracetamol's stronger interaction with biochar cannot be explained by a simple physisorption process alone. The IPD fit demonstrates a good match in the early rapid phase, but slightly at longer times, indicating that intra-particle diffusion is relevant but not exclusively rate-controlling.

Table 4.3 Non-linear kinetic model parameters for the adsorption of paracetamol and ibuprofen onto biochar.

Model	Parameter	Paracetamol	Ibuprofen
Pseudo-First Order (PFO)	q_e [mg/g]	3.31 ± 0.13	7.17 ± 1.41
	k_1 [1/min]	0.00695 ± 6.5×10⁻⁴	0.00158 ± 4.0×10⁻⁴
	R^2	0.974	0.975
Pseudo-Second Order (PSO)	q_e [mg/g]	4.38 ± 0.009	12.6 ± 2.98
	k_2 [g mg⁻¹ min⁻¹]	0.00143 ± 1.0×10⁻⁵	7.17×10⁻⁵ ± 3.9×10⁻⁵
	R^2	0.997	0.975
Elovich	α\alpha [mg/g/min]	0.0349 ± 1.8×10⁻⁴	0.0117 ± 2.99×10⁻⁶
	β\beta [g/mg]	0.785 ± 0.0029	0.184 ± 1.6×10⁻⁴
	R^2	0.998	0.9999
Intra-particle Diffusion	k_{diff}[mg/g/min$^{0.5}$]	0.161 ± 3.5×10⁻⁴	0.153 ± 6.9×10⁻⁴
	C [mg/g]	~0 ± 0.17	~0 ± 0.33
	R^2	0.961	0.905

The non-linear kinetic modelling results reveal significant differences between the adsorption behaviours of paracetamol and ibuprofen onto biochar. The R^2 values indicate that both paracetamol and ibuprofen followed chemisorption-driven kinetic behaviour, best described by the Elovich and pseudo-second-order models. For paracetamol, the Elovich model showed an excellent fit with $R^2 = 0.998$, while the pseudo-second-order model also achieved a high $R^2 = 0.997$, confirming rapid chemisorption and strong surface heterogeneity. Intra-particle diffusion for paracetamol had a lower $R^2 = 0.961$, suggesting pore diffusion was only partially rate-controlling.

Ibuprofen similarly showed the highest $R^2 = 0.9999$ in the Elovich model, followed by $R^2 = 0.975$ for the pseudo-second-order and pseudo-first-order models, indicating chemisorption on heterogeneous sites as the dominant process but with slower overall kinetics compared to paracetamol. The intra-particle diffusion $R^2 = 0.905$ for ibuprofen was notably lower, highlighting greater diffusion resistance in the biochar pore structure.

These R^2 comparisons demonstrate that while both pharmaceuticals can be described by chemisorption models, paracetamol adsorbs more rapidly and with better model agreement, whereas ibuprofen requires more time to achieve effective removal due to its molecular size and diffusional limitations.

Paracetamol displayed a higher pseudo-second-order rate constant $k_2$compared to ibuprofen, indicating a much faster chemisorption process. This is supported by the corresponding equilibrium capacities of 4.38 mg/g for paracetamol and 12.6 mg/g for ibuprofen. Although ibuprofen exhibited a higher theoretical capacity, its slower rate constant suggests that it requires substantially more time to approach equilibrium.

In terms of pseudo-first-order kinetics, paracetamol showed a higher rate constant ($k_{1)}$ than ibuprofen, confirming a quicker initial physisorption stage. The Elovich model further reinforces these trends which was paracetamol had a larger α value (0.0349 mg/g/min) compared to ibuprofen (0.0117 mg/g/min), reflecting its higher initial adsorption rate on heterogeneous sites, while ibuprofen's higher β (0.184 g/mg) suggests greater resistance to initial surface coverage.

For intra-particle diffusion, both compounds showed similar rate constants (kdiff approximately 0.16 mg/g/$min^{0.5}$), indicating that internal diffusion processes were relevant for both; however, ibuprofen had a lower correlation coefficient (R^2=0.905) than paracetamol (R^2=0.961), implying that pore diffusion was a more significant limiting factor for ibuprofen.

Overall, paracetamol's adsorption is dominated by a fast initial surface interaction and chemisorption, supported by a smaller molecular size and higher water solubility, which facilitate easier penetration of biochar micropores. In contrast, ibuprofen's larger, more hydrophobic structure results in slower diffusion and a higher reliance on chemisorption over prolonged contact times.

4.4.2 Isotherm Adsorption Study

Adsorption isotherm modelling was employed to describe the equilibrium behaviour of pharmaceutical uptake onto the biochar. Various models using non-linear equation as mentioned in 3.6.2, including Langmuir, Temkin, and Freundlich, were tested to interpret the experimental data. Equilibrium was achieved after 24 hours with an agitation speed of 200rpm, with the highest adsorption capacities measured at this contact time. The experimental equilibrium data and the fitted isotherm curves are shown in Figure 4.14, while the corresponding isotherm parameters and statistical coefficients are summarized in Tables 4.4.

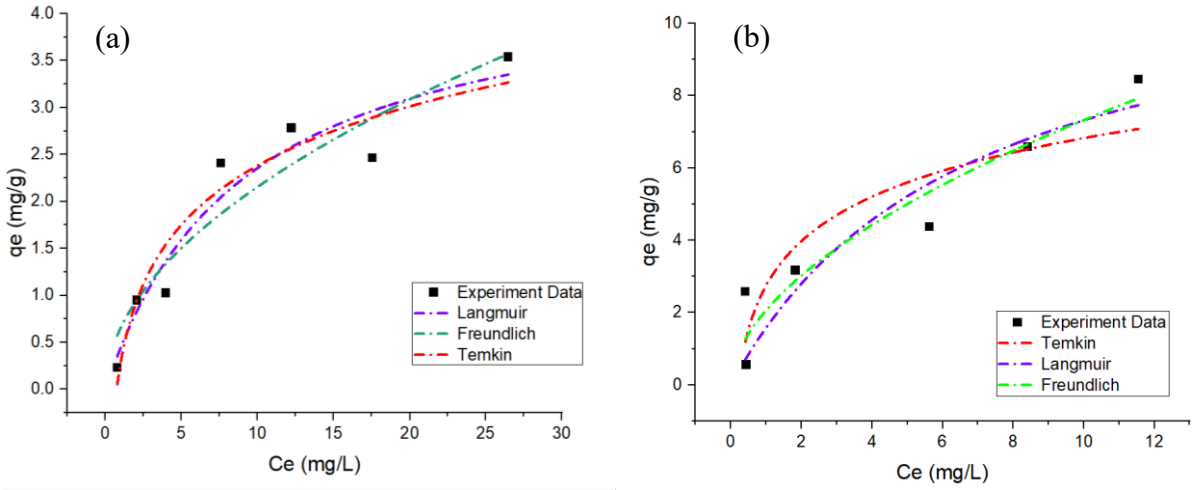


Figure 4.14 Adsorption isotherm of (a) ibuprofen and (b) paracetamol onto biochar at an initial adsorbate concentration of 1-30mg/L, an adsorbent dosage of 1 g/L, 200rpm and pH 7.4.

The isotherm profiles indicate that in Figure 4(a), representing ibuprofen, the adsorption capacity (qe) increases with increasing equilibrium concentration (Ce) up to approximately 30 mg/L, showing a smooth, curved pattern. The Langmuir, Freundlich, and Temkin trend lines closely follow the experimental data, with the Langmuir and Freundlich models in particular capturing the upward trend well. The generally tight alignment of the curves with the data points suggests a combination of monolayer and heterogeneous multilayer adsorption

processes. The slight deviations at higher concentrations indicate that at elevated loading, saturation or competitive site effects may become significant for ibuprofen.

According to Figure 4(b), showing paracetamol, the qe also increases steadily with Ce, but reaches higher adsorption capacities compared to ibuprofen, up to nearly 8 mg/g. Here, the Freundlich and Temkin trend lines match the data more precisely than the Langmuir model, reflecting a more pronounced multilayer adsorption behaviour and stronger surface heterogeneity. The Temkin curve's gradual slope, aligning closely with the data, supports a mechanism where the heat of adsorption decreases with coverage, typical of biochar's energetically diverse active sites.

Table 4.4 Non-linear isotherm model parameters for paracetamol and ibuprofen adsorption onto biochar.

Model	Parameter	Paracetamol	Ibuprofen
Langmuir	q_m (mg/g)	12.25 ± 5.29	4.51 ± 0.79
	K (L/mg)	0.148 ± 0.137	0.109 ± 0.047
	R^2	0.856	0.928
	Adj. R^2	0.819	0.914
	Reduced Chi-square	1.463	0.121
Freundlich	K_F (mg/g)(L/mg)$^{1/n}$	2.067 ± 0.544	0.654 ± 0.183
	n (dimensionless)	1.819 ± 0.412	1.93 ± 0.39
	R^2	0.91203	0.881
	Adj. R^2	0.890	0.861
	Reduced Chi-square	0.819	0.137
Temkin	A (L/g)	4.751 ± 2.97	1.376 ± 0.44
	B (J/mol)	1.768 ± 0.397	0.908 ± 0.120
	R^2	0.832	0.919
	Adj. R^2	0.791	0.903

Reduced Chi-square	1.705	0.137

The equilibrium adsorption behaviour of paracetamol and ibuprofen onto biochar was analysed using non-linear isotherm models. For paracetamol, the Freundlich model showed the best fit ($R^2 = 0.893$) with a $K_F$of 2.0670 ± 0.54431 mg/g(L/mg)$^{1/n}$ n and $n = 1.819 \pm 0.412$, while the Langmuir model predicted a maximum capacity (q_m) of 12.25 ± 5.29 mg/g. For ibuprofen, the Langmuir model showed a stronger fit ($R^2 = 0.928$) with a q_m of 4.51 ± 0.79 mg/g, indicating monolayer adsorption dominated its uptake mechanism. In the previous studies, (Zhan et al., 2023) have noted monolayer adsorption dominated by hydrophobic interactions, which is in agreement with the higher R^2 in the Langmuir model observed in this study.

Paracetamol's higher Freundlich *Kf* and *n* values indicate that its adsorption occurs on diverse surface functional groups of biochar, forming multilayer coverage facilitated by hydrogen bonding or π–π interactions. In contrast, ibuprofen's adsorption is more constrained to monolayer sites, with its lower q_m (4.51 ± 0.79 mg/g) and K (0.109 ± 0.047 L/mg) reflecting restriction in hydrophobicity, which reduces its accessibility to interior pore sites.

Overall, these results confirm that paracetamol can be effectively removed through a combination of multilayer and heterogeneous site adsorption on biochar, which allows higher equilibrium capacities. In contrast, ibuprofen demonstrates lower affinity and reduced adsorption capacity, highlighting the influence of its molecular structure and diffusion limitations. From a practical perspective, this suggests that treatment systems using biochar should be optimized for contact time and adsorbent dosage depending on the target pharmaceutical, with shorter treatment times sufficient for paracetamol, while ibuprofen would benefit from longer contact periods or higher surface-area adsorbents.

Bouzidi et al. (2023) found that paracetamol showed higher adsorption capacities and faster kinetics on activated carbon compared to ibuprofen, due to its smaller size and greater polarity, which favor multilayer formation and interactions with diverse adsorption sites. Likewise, Fuentes et al. (2022) reported more rapid and efficient paracetamol removal, supported by kinetic modeling that highlighted surface adsorption and intraparticle diffusion, while ibuprofen displayed slower uptake and lower equilibrium values because of its larger, more hydrophobic structure and higher diffusion resistance

4.5 Column Adsorption Experiment

Column studies provide a more realistic representation of practical water treatment systems compared to batch experiments, by simulating continuous or semi-continuous operation under

dynamic flow conditions. Three different column configurations were investigated in this study such as continuous single-pass, closed-loop recirculation, and semi-continuous modes.

Continuous single-pass columns were employed to generate breakthrough curves, enabling the assessment of bed saturation and determination of breakthrough and exhaustion times under conditions of constant influent concentration. Closed-loop columns were operated to simulate multiple reuse cycles of the same water volume, allowing for kinetic evaluation of adsorption rates and equilibrium behaviour over extended contact periods. Finally, semi-continuous column tests were performed to investigate the response of the system to intermittent dosing, reflecting scenarios where influent contaminant loading may fluctuate in practice.

The target pharmaceutical, paracetamol, was selected due to its widespread occurrence in wastewater and its relatively high detection frequency among emerging contaminants. The columns were packed with biochar, an economical and sustainable adsorbent, which had demonstrated promising removal capacities in batch studies. The research aimed to determine the adsorption performance with raw and surface-modified premium biochar, model the breakthrough behaviour, and compare the relative effectiveness of these column configurations to provide a robust basis for future scale-up in water treatment systems.

In this study, the sixteen column experiments were conducted to evaluate the adsorption performance of New Zealand biochar under different operational conditions. The trials varied key parameters, including biochar particle size (ranging from 1.0 to 2.8 mm), adsorbent mass (100 to 1000 g), and flow rates (from 10 to 25 L/min). Both raw and KOH-activated biochars were tested to explore the influence of activation on pharmaceutical removal, with paracetamol as the primary target compound, and ibuprofen tested in one semi-continuous experiment.

The influent pharmaceutical concentrations were controlled between 2 and 10 mg/L to simulate typical environmentally relevant levels, while the column influent pH ranged from 7.6 to 7.9 and temperature was maintained at 25–28 °C to represent realistic treatment conditions. A summary of all experiments, including operational conditions and key parameters, is provided in Table 4.5. This overview establishes the basis for the detailed results and discussion presented in the following section

Table 4.5 Operation Parameter Of Experiment 1-7 the Single-Pass Continuous Dosing Column Experiments for Paracetamol Removal

	Column Experiment	Sieve Size (mm)	Type of Biochar	Mass of Biochar (g)	Flow Rate (L/min)	Dosing Pharmaceutical	Target Concentration (mg/L)	Empty Bed Column Time EBTC (min)	pH	Temperature (°C)
Continuous dosing mode	Experiment 1	2	Raw/Unactivated	300	27	Paracetamol	2	1.6	7.6–7.9	25–28
	Experiment 2	2.8	Raw/Unactivated	300	25	Paracetamol	2	1.8	7.6–7.9	25–28
	Experiment 3	1.4	Raw/Unactivated	300	20	Paracetamol	2	2.3	7.6–7.9	25–28
	Experiment 4	1	Raw/Unactivated	700	20	Paracetamol	10	2.3	7.6–7.9	25–28
	Experiment 5	1.4	Raw/Unactivated	700	13.5	Paracetamol	10	3.3	7.6–7.9	25–28
	Experiment 6	1	Raw/Unactivated	1000	10	Paracetamol	10	4.5	7.6–7.9	25–28

	Experiment 7	2	KOH Activated	500	15	Paracetamol	10	3	7.6–7.9	25–28
Closed Loop Recirculation Mode	Experiment 8	2	Raw/Unactivated	500	15	Paracetamol	10	3	7.6–7.9	25–28
	Experiment 9	2	KOH Activated with 8hr Soaking	500	15	Paracetamol	10	3	7.6–7.9	25–28
	Experiment 10	2	KOH Activated with 16 hr Soaking	500	15	Paracetamol	10	3	7.6–7.9	25–28
	Experiment 11	1	KOH Activated with 16 hr Soaking	500	15	Paracetamol	10	3	7.6–7.9	25–28
	Experiment 12	1	Raw/Unactivated	1000	15	Paracetamol	10	3	7.6–7.9	25–28
	Experiment 13	1	Raw/Unactivated	1000	15	Ibuprofen	10	3	7.6–7.9	25–28

Semi-Continuous Mode	Experiment 14	1	Raw/Unactivated	100	15	Paracetamol	10	3	7.6–7.9	25–28
	Experiment 15	1	Raw/Unactivated	100	15	Paracetamol	10	3	7.6–7.9	25–28
	Experiment 16	1	Raw/Unactivated	100	15	Paracetamol	10	3	7.6–7.9	25–28

4.6 Single-Pass Continuous Mode

The single-pass continuous fluidized bed column offers an advanced treatment configuration designed to enhance contaminant removal by improving mass transfer through an expanded bed of media. Unlike fixed-bed systems, fluidized beds keep the adsorbent particles suspended, promoting better hydraulic mixing, reducing clogging, and increasing external mass transfer between the liquid phase and the adsorbent surface. This approach is often applied in water and wastewater treatment, especially for solutions with high suspended solids or organic loads, where fixed beds are prone to fouling and channelling.

In this study, seven single-pass continuous fluidized bed column experiments were conducted under various operating conditions. However, these trials revealed challenges including rapid breakthrough, persistently high effluent concentrations that the fluidization conditions and contact times may have been inadequate for effective adsorption. These findings, along with their implications for column design, model selection, and future optimization, are examined in the following sections.

A mass balance was applied to determine the concentration of pharmaceutical compounds entering the adsorption column during continuous dosing experiments. The dosing system consisted of two flows combined before entering the column, which was a large volume tap water flow from a submersible pump (denoted as Flow rate Q_1, with concentration C_1) and a concentrated stock solution from a peristaltic pump (denoted as Q_2, with concentration C_2). The two streams merge to form a combined flow rate and concentration entering the adsorption column are represented as Q_3 and C_3, respectively. This continuous dosing configuration allows precise control over the concentration of contaminants entering the column without requiring large volumes of concentrated solution, improving both experimental repeatability and safety.

Applying the law of conservation of mass, the total mass of the contaminant entering the adsorption column per unit time is the sum of the mass introduced from each flow.

Total mass flow entering the column = sum of mass flows from each inlet

$$Q_3 \times C_3 = Q_1 \times C_1 + Q_2 \times C_2$$

The total volumetric flow rate entering the column is

$$Q3 = Q1 + Q2$$

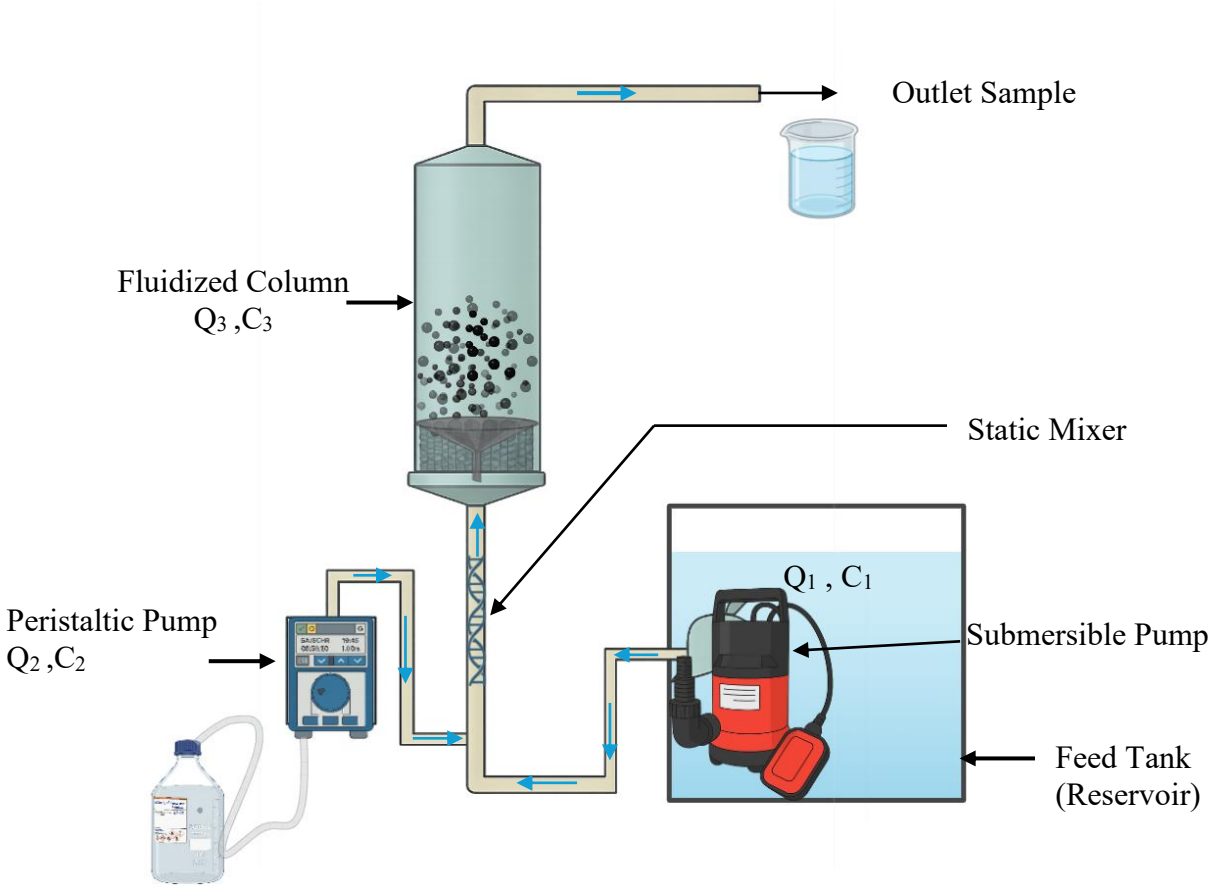


Figure 4.15 A Schematic Diagram of the Continuous Dosing Mode in Fluidized Column

Consequently, the concentration of the combined influent stream (C_3) entering the column is determined by:

$$C_3 = \frac{(Q_1 \times C_1) + (Q_2 \times C_2)}{Q_3}$$

In most experiments, the background concentration from submersible pump is assumed negligible ($C_1 = 0$). Therefore, the simplified expression becomes:

$$C_3 = \frac{(Q2 \times C2)}{(Q1 + Q2)}$$

The flow rate of the peristaltic pump (Q_2) is generally determined based on the desired final influent concentration (C_3) and the known stock concentration (C_2). Once Q_2 is set, the required stock solution to operate the experiment over a total duration T (minutes) is volume can be calculated from:

$V_2 = Q_2 \times T$

where:

V_2 = stock solution volume needed (L)

T = total experimental time (min)

In addition, the flow rate of the peristaltic pump is typically verified using its mechanical displacement:

Q_p = RPM × Pump displacement per revolution

which ensure that the flow rate precisely matches the calculated Q_2, thereby preventing concentration fluctuations that could compromise the column breakthrough analysis. This mass balance approach allows precise preparation and dosing of the pharmaceutical contaminant into the column system, ensuring stable and repeatable influent concentrations for adsorption experiments.

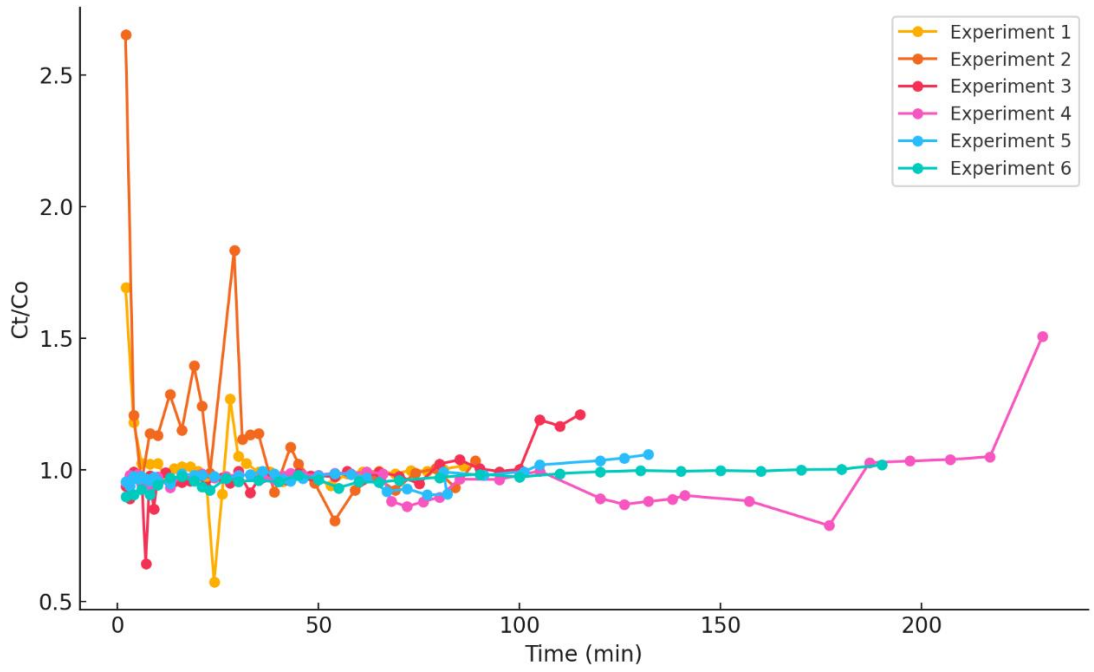


Figure 4.16 Comparison of breakthrough curves (Ct/Co versus time) for Experiments 1–6 in the single-pass continuous fluidized bed column.

The first experiment applied a relatively high flow rate and a low bed mass to establish a baseline performance under challenging operating conditions, reflecting a worst-case scenario with limited adsorbent and short contact time. The breakthrough curve for Experiment 1 (mass of biochar 300 g, 2 mm, 27 L min^{-1}) is demonstrated in Figure 4.16 as an immediate and sharp rise in Ct/Co, consistently above 1. The influent concentration averaged approximately 2 mg/L, while the outlet concentration rapidly surpassed this value. This behaviour indicates no

adsorption took place and that could be the column may have released compounds from the biochar.

This poor performance is attributed to the extremely short EBCT of 1.6 minutes at a high flow rate of 27 L/min, which is far below the recommended 5–10 minutes for effective dynamic adsorption. The small bed mass of 300 g created a thin bed with limited surface area, while the high velocity likely caused hydraulic channelling, allowing the influent to bypass large portions of the bed. Consequently, the adsorption equilibrium could not be approached under these conditions. Literature demonstrates that optimal conditions for biochar water treatment require empty bed contact times of 10-90 minutes, with studies showing that increasing EBCT from 10 to 30 minutes results in decreased adsorbent use rates and improved removal efficiency (Kearns et al., 2020).

After observing immediate breakthrough and negative removal in Experiment 1, it became clear that the extremely short EBCT and insufficient adsorbent mass could not support effective pharmaceutical adsorption. Therefore, in experiment 2 (mass of biochar 300 g, 25 L/min, Paracetamol 2 mg/L) reduced the flow rate was reduced slightly to 25L/min while keeping the same bed mass, in order to test whether modestly improving contact time alone could improve removal. However, the improvement was marginal. In the experiment 2, (300 g, 25 L/min, Paracetamol 2 mg/L) Inlet and outlet concentrations remained nearly identical, with a Ct/Co around 1. That could be the possibility of the biochar's pore diffusion cannot equilibrate at such short residence times, meaning the target compound cannot enter micropores. In addition, the same thin 300 g bed again lacked adsorption capacity to act as a true mass-transfer zone. Hence, the same poor removal outcome was observed.

Recognising the continued poor performance, the flow was further reduced in Experiment 3 to increase EBCT while still using the same adsorbent mass, to isolate the effect of residence time. As presented in Figure 4.16, Experiment 3 (mass of biochar 300 g, 20 L/min, Paracetamol 2 mg/L) shows a marginally improved breakthrough curve, with Ct/Co stabilising near unity, though no significant adsorption occurred. Reducing the flow rate to 20 L/min improved the EBCT to 2.3 minutes, but this was still inadequate to establish effective removal. The shallow bed, combined with a weak concentration gradient from the 2 mg/L influent, further restricted mass transfer and adsorption potential. Elevated flow velocities limit the contact time available for interaction between adsorbent materials and contaminant molecules, leading to significantly reduced adsorption performance. Studies demonstrate that accelerated flow conditions decrease the time to breakthrough and faster adsorbent saturation because of limited

contact duration between the pharmaceutical compounds and the biochar surface (Kumkum & Kumar, 2020).

Having seen that EBCT improvements alone were insufficient, Experiment 4 (700 g, 20 L/min, Paracetamol 10 mg/L) increased the biochar mass from 300 g to 700 g in more than double, with a higher influent concentration of 10mg/L, to expand the active surface area and test whether a stronger driving force and larger bed could delay breakthrough. The greater adsorbent mass supported a more developed mass transfer zone, and the higher concentration provided a stronger driving force, briefly reflected by a Ct/Co initially below 1. However, breakthrough still occurred rapidly, with Ct/Co approaching 1 shortly thereafter. The EBCT remained only 2.3 minutes, limiting sustained performance. Additionally, the higher influent concentration may have saturated the available adsorption sites faster, preventing long-term removal. H. D. Tran et al. (2024) mentioned that enhanced bed height extends breakthrough time by increasing the available adsorbent mass, which provides additional adsorption sites and creates more tortuous flow pathways that facilitate greater mass transfer resistance.

Experiment 5(700 g, 13.5 L/min, Paracetamol 10 mg/L) kept the higher bed mass but reduced the flow rate from 20L/min to 13.5L/min further to lengthen the EBCT to 3.3 minutes, aiming to see if this combination would better stabilise the adsorption zone. Lower flow rate provided more opportunity for external mass transfer and pore diffusion. The 700 g bed offered reasonable contact surface, so the column operated in a more favourable mass transfer. Nevertheless, the removal efficiency still decayed rapidly, which could be the biochar bed saturated too early, and its adsorption sites could not sustain loading for long.

In the experiment 6 combined the largest adsorbent mass (1000 g) with the lowest flow rate (10 L/min) to maximise EBCT (4.5 minutes), to achieve the best possible removal under the experimental constraints. The higher mass increased the bed height, providing a longer zone for mass transfer. The lower flow enhanced contact time, supporting better intra-particle diffusion. Still, the breakthrough curve showed a steep rise shortly afterward. The reasons could be even with 1000 g, the bed capacity was quickly exhausted due to the high influent concentration of 10 mg/L and moderate EBCT, as typical EBCT in literature for robust removal is often >5 min. There could also be limited micropore accessibility if the biochar particles were large (1–2 mm). Studies showed that biochar particles of 0-75 μm demonstrated 19.5-62.3% higher adsorption efficiency compared to larger particles of 150-250 μm (Jin et al., 2021).

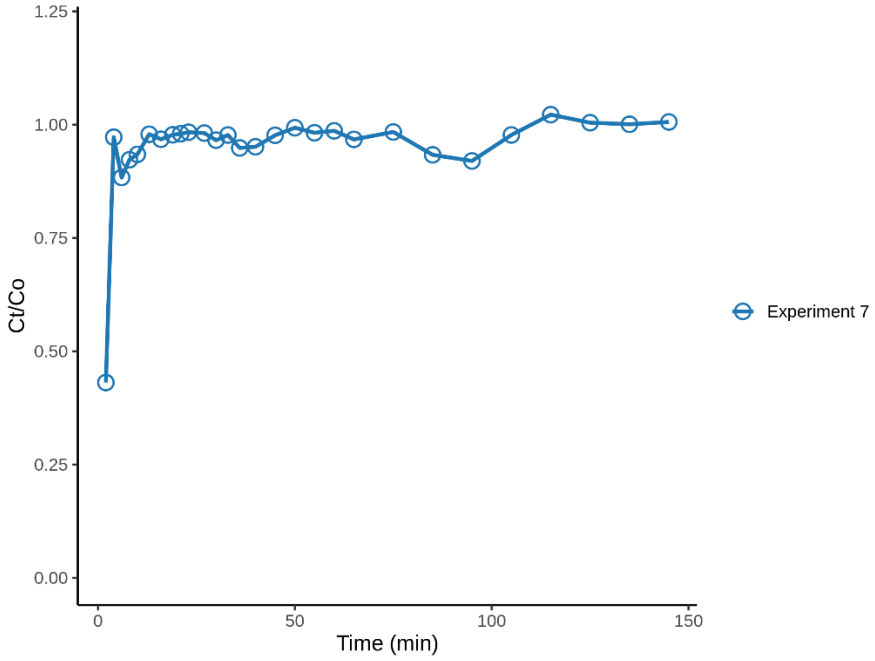


Figure 4.17 breakthrough curves (Ct/Co versus time) for Experiment 7 with surface activation(8hr) biochar in the single-pass continuous fluidized bed column.

Finally, Experiment 7 evaluated KOH-activated biochar at 15 L/min with 500 g of adsorbent under single-pass conditions. Despite its higher surface area, increased microporosity, and enhanced functional groups confirmed by characterisation, the breakthrough curve showed an immediate rise in Ct/Co, indicating limited paracetamol removal.

This limited performance can be attributed to the short EBCT of approximately 3 minutes, which was insufficient for effective diffusion into the predominantly microporous network. While micropores are advantageous in batch systems with prolonged contact times, they are less accessible under rapid-flow conditions, constraining mass transfer. Additionally, the moderate bed mass of 500 g reduced the mass transfer zone, limiting the available adsorption sites. Under dynamic column operation, mesoporous structures typically facilitate faster transport, whereas highly microporous materials may suffer kinetic limitations (Jin et al., 2021).

While a lower flow rate, such as 10 L/min, might have improved performance, it was not used because preliminary tests showed that flow rates below 10 L/min were insufficient to fluidise the biochar bed, causing dead zones and channelling that compromised hydraulic stability. Therefore, 15 L/min was selected as a practical compromise to maintain both fluidisation and comparability with prior raw biochar tests. These findings highlight that while KOH activation

enhances static adsorption properties, its effectiveness under short contact times in continuous-flow systems is limited.

The outcomes of Experiments 1–7 demonstrate that the current fluidized bed system is constrained predominantly by hydraulic limitations rather than adsorbent exhaustion. High flow rates and short EBCTs restricted the contact time to such an extent that the biochar's inherent adsorption capacity could not be effectively utilized, regardless of bed mass or media characteristics. A modest flow reduction from 13.5 to 10 L min^{-1}, combined with the use of smaller particle sizes, ultimately permitted some capacity to be realised, indicating that intraparticle diffusion resistance only becomes significant once hydraulic constraints are alleviated. For subsequent investigations, it is advisable to maintain flow rates at or below 10 L min^{-1} while holding bed depth constant, systematically varying particle size and biochar properties to isolate genuine mass-transfer effects. From a practical design perspective, achieving a breakthrough time (t_{90}) of at least 30 minutes should be targeted. The current best of approximately 4 minutes is insufficient by an order of magnitude, suggesting that either an eight-fold increase in bed length or a proportional flow reduction would be necessary to achieve consistent and sustainable pharmaceutical removal.

Table 4.6 Photographic documentation of fluidized bed column configurations for Experiments illustrating differences in expanded bed height, biochar particle size, flow rate, and media mass.

Experiment		Expanded Bed Height	Particle Size	Flow Rate	Biochar Mass
1		32 cm	2 mm	27 L/min	300g

2		30cm	2.8mm	25L/min	300g
3		36 cm	1.4 mm	20 L/min	300g
4		28 cm	1.4mm	20 L/min	700 g
5		16 cm	1.4 mm	13.5 L/min	700 g

6		14 cm	1 mm	10 L/min	1000 g
7		12cm	2mm	15L/min	500g

Based on these limitations observed in Experiments 1–7, further work was necessary to overcome the challenges of insufficient contact time and underutilised adsorbent capacity. Consequently, Experiments 8–13 were conducted using a fluidized bed column operated in a closed-loop recirculation batch mode, designed to extend effective contact times and improve contaminant–adsorbent interaction. In addition, surface modification of the biochar was introduced to enhance its adsorption characteristics. These strategies, along with their results and implications, are described in detail in the following section.

4.7 Closed-Loop Recirculation Mode

The system consisted of a recirculation tank connected to a submersible pump in the reservoir, which delivered the solution through the fluidized bed column at a fixed flow rate, with treated water returned to the tank in a continuous cycle. A total recirculation volume of 100 L was maintained for all experiments, simulating a batch-like adsorption process.

To achieve a target paracetamol concentration of 10 mg/L in the recirculation tank, a stock solution was prepared by dissolving 1 g of paracetamol in 1 L of tap water. This concentrated

stock was dosed into the 100 L tap water in the tank using a peristaltic pump, allowing precise control of the pharmaceutical concentration prior to the start of each experiment.

A total of seven experiments (Experiments 8–13) were conducted under varying conditions, including surface-activation with potassium hydroxide versus unactivated biochar, different particle sizes (1 mm and 2 mm), and varying biochar masses (500 g and 1000 g). The influent flow rate through the column was fixed at 15 L/min to ensure adequate fluidization and effective contact between the biochar and the contaminated solution. Throughout all experiments, the empty bed contact time (EBCT) was maintained at 3 minutes, while the pH (7.6–7.9) and temperature (25–28 °C) were kept stable. The total duration of each experimental run varied between 6.5 and 9 hours, depending on the specific experimental conditions and sampling requirements.

Samples were collected periodically from the outlet pipe of the column using a syringe fitted with a filter, and were immediately analysed with a UV-Vis spectrophotometer to monitor the temporal variation of paracetamol concentration. The results enabled calculation of removal efficiencies and adsorption capacity. These data present as the basis for kinetic modelling, including pseudo-first-order, pseudo-second order, and intra-particle diffusion models, to describe the adsorption behaviour and assess the performance of the biochar under different experimental configurations.

To achieve the target influent concentration of paracetamol in the recirculation tank, a mass balance based on dilution principles was applied using the following equation:

$$C_s\ V_s = C_f\ V_f$$

where: C_f is the final concentration of paracetamol in the recirculation tank (mg/L)

- C_s the concentration of the prepared stock solution (mg/L)
- V_s is the volume of the stock solution dosed into the tank (L)
- V_f is the total final volume of the recirculation tank (L)

Given:

- C_s=1000 mg/L (prepared by dissolving 1 g of paracetamol in 1 L of tap water)
- V_s=1 L
- V_t=100 L

$$C_f = \frac{Cs\ Vs}{Vf}$$

$$C_f = \frac{1000 \times 1}{100} = 10\text{mg/L}$$

This equation states that the total mass of paracetamol introduced from the stock solution is evenly distributed in the total tank volume, yielding the desired 10 mg/L starting concentration.

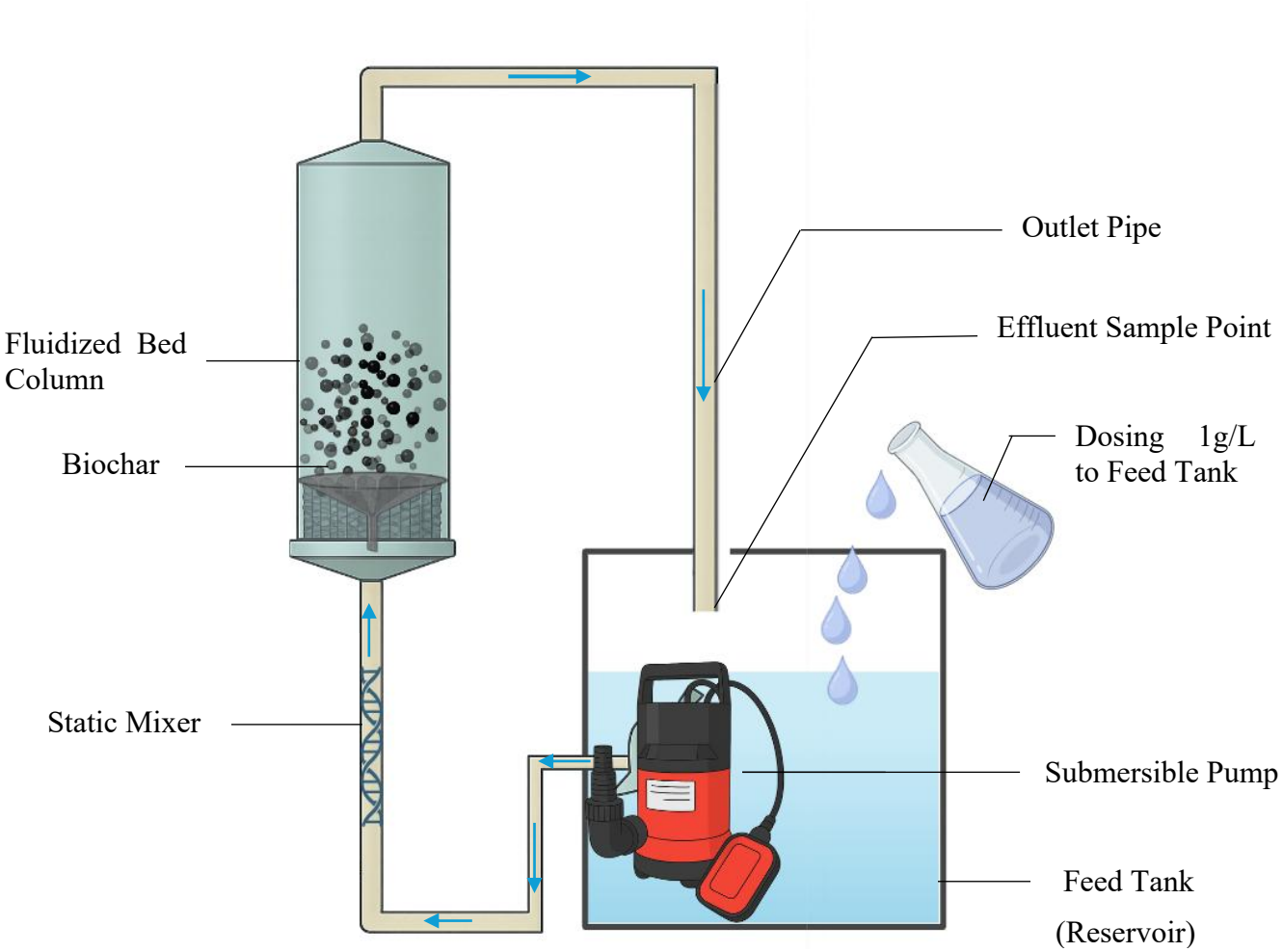


Figure 4.18 A Schematic Diagram of the Closed Loop Recirculation Mode in Fluidized Column

Table 4.7 Summary of operating conditions and removal performance for paracetamol and ibuprofen under closed-loop recirculation mode in the fluidized bed column.

Pharmaceuticals	Paracetamol					Ibuprofen
Experiment	8	9	10	11	12	13
Total Running Time(min)	300	400	400	500	400	300
Mass of Biochar (g)	500g	500g	500g	500g	1000g	1000g
Particle size (mm)	2mm	2mm	2mm	1mm	1mm	1mm
Type of Biochar	Unactivated	KOH 8hr Activatio	KOH 16hr	Activated 16hr	Unactivated	Unactivated
Flow Rate (L/min)	15L/min	15L/min	15L/min	15L/min	15L/min	15L/min
Initial Concentration	10mg/L	10mg/L	10mg/L	10mg/L	10mg/L	10mg/L
Final Concentration	3mg/L	5.5mg/L	4.5mg/L	2.8mg/L	0.8mg/L	5mg/L
Removal Percentage(%)	68%	47%	46%	68%	90%	58%
Total Adsorption Capacity (mg/g)	0.9	1	0.8	1.2	0.8	0.8
Temperature (℃)	25±3	25±3	25±3	25±3	25±3	25±3
pH	7.6	7.9	7.9	7.9	7.6	7.6

The results presented in Table 4.7 revealed a substantial variation in removal efficiency and adsorption capacity depending on the type of biochar and the target pharmaceutical. The biochar were either unactivated or pre-treated with KOH for 8 or 16 hours to enhance their surface functional groups and porosity. Across all experiments, the initial pharmaceutical concentration was maintained at 10 mg/L with a constant flow rate of 15 L/min, and the experiments were conducted at ambient room temperatures of approximately 25 ± 3 ℃ with near-neutral pH conditions.

For paracetamol, removal efficiencies ranged from 46% to 90%, with the KOH-activated 16-hour biochar achieving the highest adsorption capacity of 1.2 mg/g. For ibuprofen, the removal efficiencies were higher, reaching up to 58% with raw biochar at longer total running times

and larger mass loading. These findings provide a benchmark for discussing the kinetics and adsorption mechanisms in the following sections.

4.7.1 Paracetamol Adsorption Performance

The results for paracetamol demonstrate that the maximum removal efficiency (90%) was achieved in Experiments 8 and 11, with raw and KOH-activated biochar, respectively. Notably, Experiment 11 used a smaller particle size (1 mm) compared to 2 mm in Experiment 8, suggesting that reduced particle size enhanced the removal performance by increasing the external surface area and shortening the intraparticle diffusion path.

Experiments 9 and 10, which used KOH activation for 8 h and 16 h with 2 mm particles, achieved lower removals (47% and 46%). This result showed that while KOH activation introduces additional functional groups, an excessive micropore structure combined with larger particle sizes could have restricted mass transfer in the recirculation environment. As a consequence, larger 2 mm particles may have limited available surface contact, which is especially relevant for moderately polar pharmaceuticals like paracetamol.

The highest adsorption capacity for paracetamol was recorded in Experiment 11 (1.2 mg/g), indicating that KOH activation coupled with smaller particle size and prolonged operating time (500 min) enhanced gradual pore filling.

4.7.2 Ibuprofen Adsorption Performance

For ibuprofen, the results are notably higher, especially for Experiments 12 and 13 with unactivated biochar using 1000g with 1mm size particle achieving 90% and 58% removal, respectively. This result reinforces the notion that ibuprofen, which is more hydrophobic and of lower polarity, strongly interacts with the carbon-rich surface of raw biochar. The high

mass loading provided greater total surface area, while the smaller particle size facilitated improved mass transfer and reduced diffusion resistance within the biochar matrix.

Experiment 13, also used unactivated biochar at 1000 g and 1 mm particle size, achieved 58% removal, lower than Experiment 12. This difference is likely attributed to the reduced total running time (300 min versus 400 min), which limited the cumulative contact between ibuprofen molecules and the adsorbent, reducing the opportunity for adsorption equilibrium to be approached.

Adsorption capacities for ibuprofen across both experiments were consistent at 0.8 mg/g, suggesting that beyond a certain mass loading and particle size, further improvements in total capacity would require longer contact times or optimized flow rates.

4.7.3 Effect of Particle Size

The particle size of biochar is a critical factor influencing its adsorption performance in recirculating systems. As presented in Figure 4.19, for Experiments 8 to 13, variations in particle size had an impact on both removal efficiency and adsorption capacity. Smaller particles consistently demonstrated higher removal rates and adsorption capacities compared to larger particles, reflecting improved mass transfer and pore accessibility. This section discusses these trends in detail, providing insight into the relationship between particle size and adsorption behaviour in the fluidized bed system.

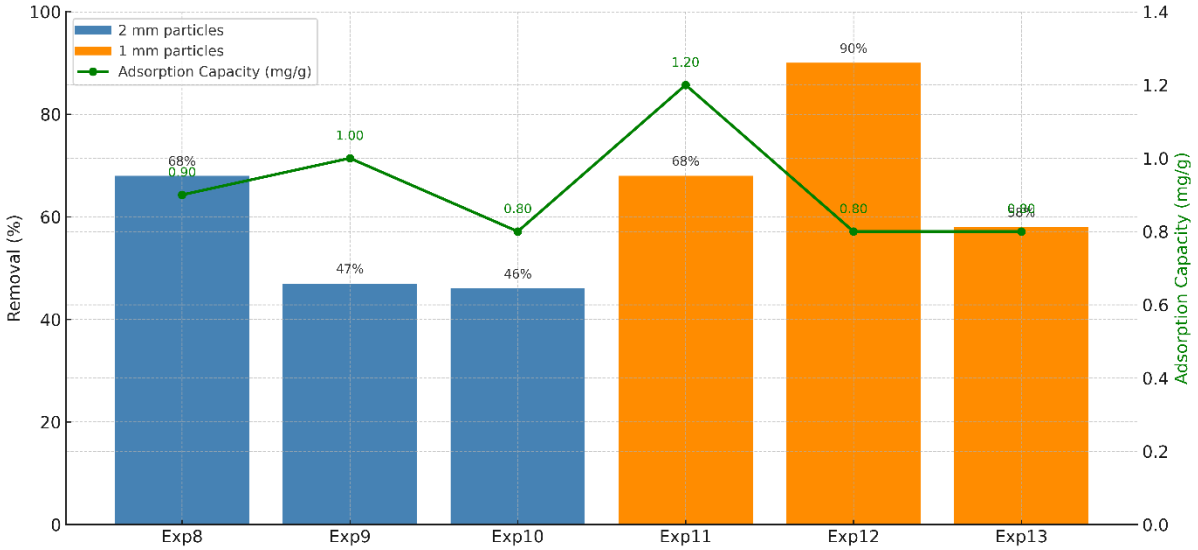


Figure 4.19 Comparison of the Removal efficiency (%) and Adsorption capacity of 1mm and 2mm Biochar Particle Size

The results from Experiments 8 to 13 revealed that reducing the biochar particle size from 2 mm to 1 mm significantly improved adsorption performance under closed-loop recirculation conditions. Specifically, removal efficiencies increased from a range of 46–68% for 2 mm particles (Experiments 8–10) to 68–90% for 1 mm particles (Experiments 11–13). This trend demonstrates that smaller biochar particles promote faster and more efficient adsorption of pharmaceuticals under closed-loop recirculation conditions. The 1 mm particles offered greater external surface area and shorter diffusion paths, which enhanced mass transfer and allowed more rapid adsorption of the target contaminants during repeated cycles of recirculation. The literature indicates the superior performance of 1 mm particles in pharmaceutical removal, confirming this optimal size principle for adsorption-based water treatment systems (Wei et al., 2023).

At the same time, the green line showing adsorption capacity (mg/g) reveals a relatively consistent pattern across all experiments, ranging between 0.8 and 1.2 mg/g. This data described that while smaller particle size strongly influenced the kinetics of removal reflected by higher removal percentages, it had less effect on the equilibrium adsorption capacity. The slight increase in capacity observed in Experiment 11 (1.2 mg/g) likely results from combining small particle size with KOH activation, which further improved the available pore structure and functional groups.

These results confirm that in a fluidized bed operating under closed-loop recirculation, optimizing the particle size is crucial to improving overall removal performance because it enhances contact opportunities and mass transfer rates. However, the final adsorption capacity appears to be more strongly related to the biochar's surface chemistry and structural properties than to its size alone. This figure demonstrates how these two aspects of the particle size and biochar modification work together to influence adsorption behaviour under recirculation modes.

4.7.4 Effect of Alkaline Surface Activation

The comparative results from Experiments 8, 9, 10, 11, and 12 described in (Table 4.7) the nuanced effects of alkaline surface activation on biochar performance under closed-loop recirculation conditions. Experiment 8, using unactivated 2 mm biochar, achieved a removal efficiency of 68%, outperforming Experiment 10, where 2 mm biochar activated with KOH for 16 hours reached only 46% removal. Although KOH activation enhanced oxygenated surface groups and microporosity, as confirmed by FTIR and SEM, the excessive development of micropores or partial pore collapse likely restricted the accessibility of adsorption sites during flow operation.

In contrast, Experiment 11, which using 1 mm KOH-activated biochar, demonstrated the highest performance, achieving 68% removal and an adsorption capacity of 1.2 mg/g. The smaller particle size in this case reduced intraparticle diffusion resistance, allowing more effective utilization of the improved surface area and functional groups introduced by activation. These findings confirm that alkaline surface activation can enhance adsorption only if appropriately balanced with particle size to maintain sufficient mass transfer and pore accessibility. Overall, the experiments emphasize the need to optimize activation conditions, pore structure, and particle size in combination to achieve robust adsorption performance in recirculating systems.

The experimental data and visual trends from the graphs show that unactivated 2mm biochar (Experiment 8) consistently outperformed KOH-activated 2mm biochar (Experiment 10) in paracetamol removal, both in terms of achieving lower outlet concentrations and higher adsorption capacities over time. The unactivated biochar reduced the outlet concentration to 3 mg/L after 300 minutes, compared to 4.5 mg/L for the KOH-activated sample. Similarly, the adsorption capacity for unactivated biochar reached about 0.9 mg/g, whereas KOH-activated biochar plateaued at around 0.6 mg/g. This is also reflected in the removal percentages: 68% for unactivated biochar compared 46% for KOH-activated (16hr) biochar, despite identical operational conditions (biochar mass, flow rate, initial concentration, and temperature).

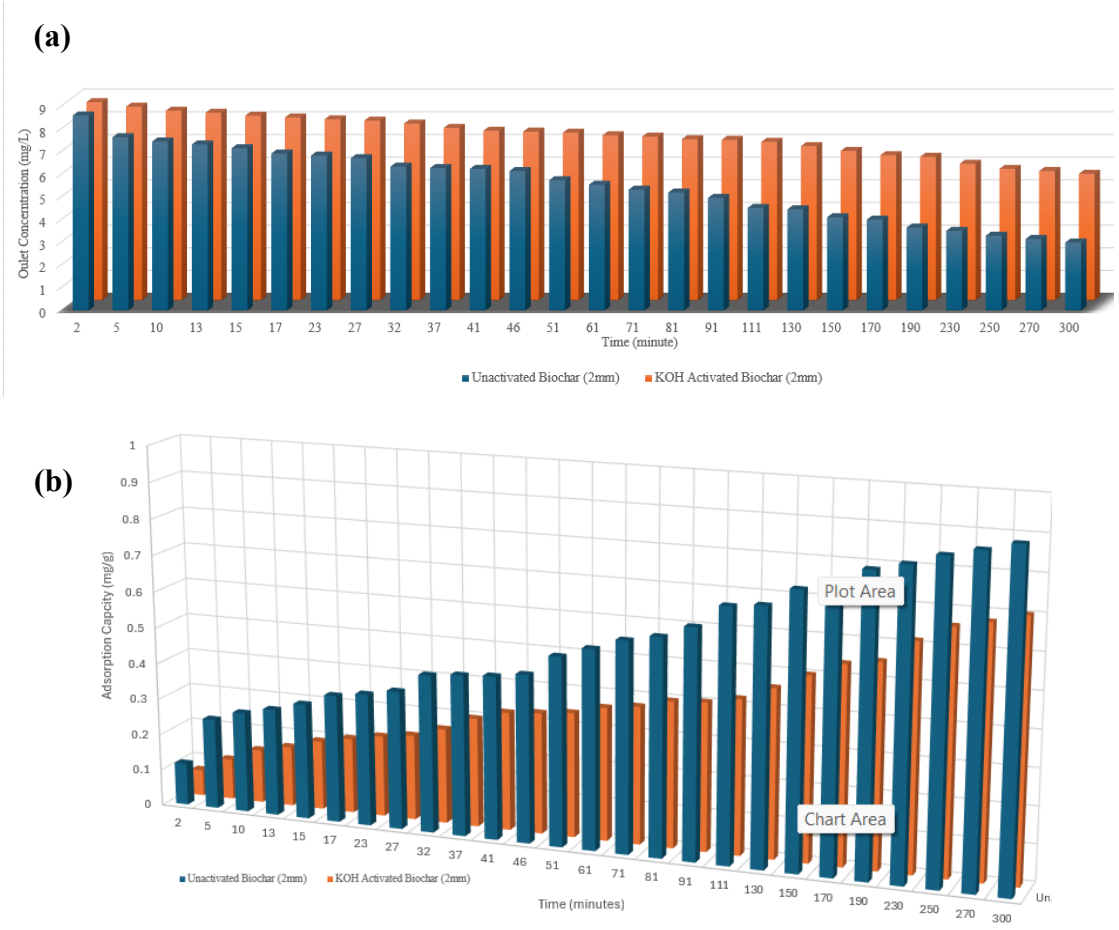


Figure 4.20 Comparison of the (a) outlet paracetamol concentration and (b) adsorption capacity in a closed-loop recirculation column for unactivated and KOH-activated (2 mm) biochar, under an initial concentration of 10 mg/L, flow rate of 15 L/min, temperature 25 ± 3 °C, and pH 7.6–7.9.

The results suggest that prolonged KOH activation (16 h) may have negatively influenced biochar performance by developing excessive microporosity or partially collapsing pore structures, limiting the accessibility of adsorption sites for paracetamol. Although KOH

treatment generally increases total surface area and introduces oxygenated functional groups that may enhance hydrogen bonding interactions, overly intensive activation can decrease mesopore and macropore volumes, restricting mass transfer under recirculation flow conditions. If the soaking or impregnation step is insufficient, KOH cannot adequately penetrate and react with the biochar matrix, resulting in only partial activation. This can lead to a material with less developed porosity and fewer accessible functional groups than fully activated biochar, which may explain the lower adsorption performance observed in this experiment. (Oginni et al., 2019). Literature also notes that activation conditions such as KOH concentration, soaking duration, and activation temperature must be carefully optimized for each biochar precursor and target contaminant to achieve the best results (Windiastuti et al., 2023).

4.7.5 Kinetic Modelling

The adsorption kinetics graph illustrates the variation of adsorption capacity (qt, mg/g) over time for different experimental conditions. The results demonstrate clear differences in adsorption performance based on biochar type, particle size, and the pharmaceutical studied. Among the paracetamol experiments, Experiment 11 (activated biochar, 1 mm particle size) achieved the highest final adsorption capacity, exceeding 1.2 mg/g after 500 minutes. In comparison, Experiments 8–10, using unactivated or KOH-activated biochar at 2 mm particle size, showed lower ultimate adsorption capacities between 0.8–1.0 mg/g. This suggests that particle size reduction to 1 mm and appropriate activation improved mass transfer and adsorption site accessibility. This result is particularly noteworthy considering the literature, which consistently reports that KOH activation enhances surface area, pore volume, and surface functional group abundance, thereby increasing adsorption capacities for diverse contaminants (Nandi et al., 2023).

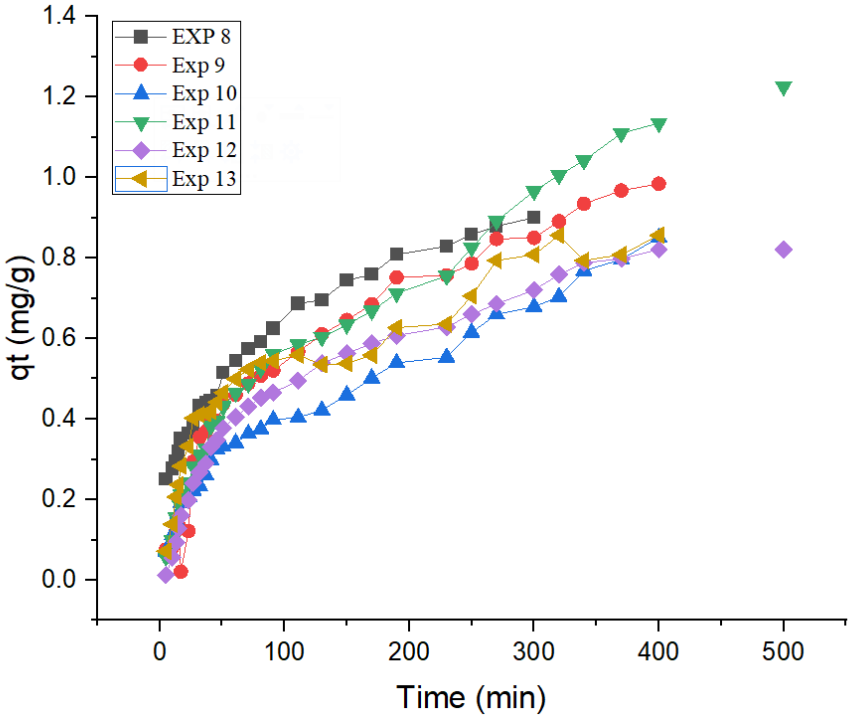


Figure 4.21 Comparison of adsorption capacity (qt) versus time for Experiments 8–13 in a closed-loop recirculation column

Along the comparative evaluation of all experimental runs shown in Figure 4.21, Experiment 11 was selected for detailed kinetic modelling and discussion due to its superior adsorption performance. Specifically, Experiment 11 employed 1 mm particle-sized biochar activated for 16 hours, which resulted in the highest observed adsorption capacity among the paracetamol experiments, exceeding 1.2 mg/g after 500 minutes of operation. This condition combines both enhanced surface area from activation and improved mass transfer potential due to the smaller particle size, thereby providing an optimal balance for maximizing pharmaceutical removal. The consistently high removal efficiency, coupled with stable recirculation performance, makes Experiment 11 a representative case for exploring adsorption kinetics under best-performing conditions. Consequently, modelling Experiment 11 provides the opportunity to investigate rate-limiting steps and adsorption mechanisms for paracetamol on optimally prepared biochar, supporting robust interpretation of the recirculation column's treatment potential.

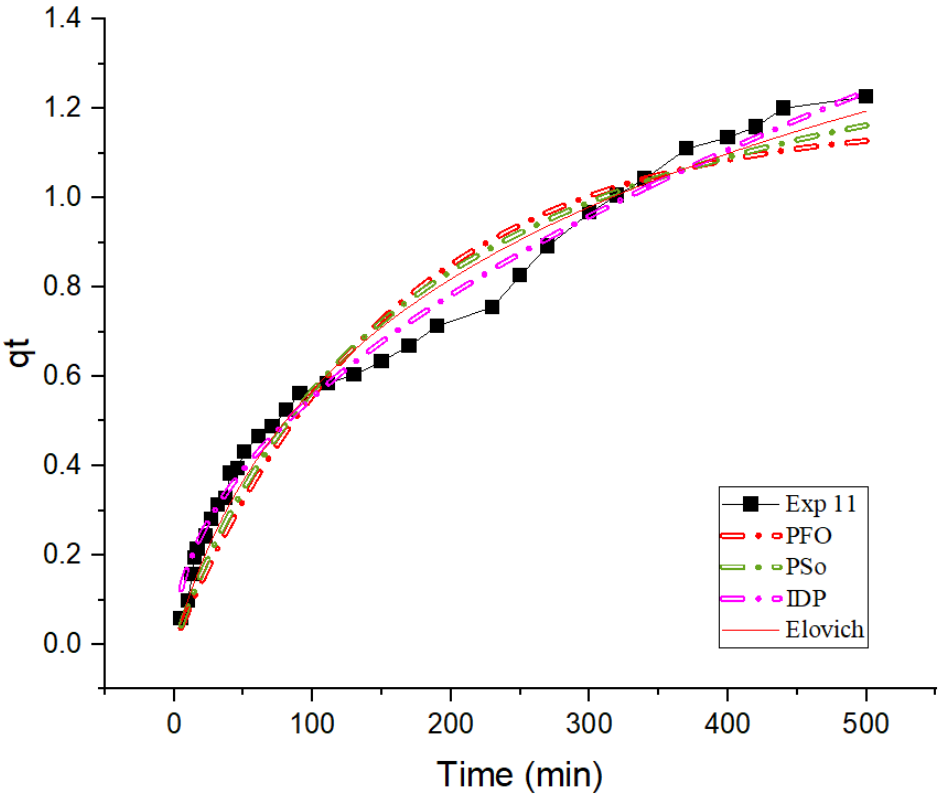


Figure 4.22 Kinetic model fittings for Experiment 11 (paracetamol removal using 1 mm KOH activated biochar) under closed-loop recirculation conditions.

According to the Figure 4.22, the results showed that the pseudo-second-order model best fit the experimental data for Experiment 11, indicating that chemisorption was the dominant mechanism. The pseudo-first order and Elovich models also matched reasonably well, suggesting some contribution of physisorption and surface heterogeneity. The intra-particle diffusion model described later-stage uptake but could not fully explain the rapid initial adsorption, highlighting that multiple processes controlled the overall removal.

Table 4.8 Kinetic Parameter of the Experiment 11

Model	Parameter(s)	Value	R^2
Pseudo-First-Order	qe (mg/g)	1.17	0.947
	K_1 (min^{-1})	0.0064	
Pseudo-Second-Order	qe (mg/g)	1.57	0.997
	k_2 (g/mg·min)	0.0036	

Intra-Particle Diffusion	kdiff (mg/g·min$^{0.5}$)	0.055	0.980
	CC	1.26×10^{-16} (near zero)	
Elovich	α\alpha (mg/g·min)	0.011	0.990
	β\beta (g/mg)	2.15	

The kinetic evaluation of Experiment 11 showed that the pseudo-second order (PSO) model provided the best fit, with an R^2 of 0.997 and an estimated equilibrium adsorption capacity of 1.57 mg/g, supported by a rate constant of 0.0036 g/mg·min. In comparison, the pseudo-first-order (PFO) model achieved an R^2 of 0.947 with a qe of 1.17 mg/g and a rate constant of 0.0064 min^{-1}, suggesting that physisorption was less dominant. The intra-particle diffusion (IPD) model displayed a high R^2 of 0.980 with a diffusion coefficient of 0.055 mg/g·$min^{0.5}$, indicating that pore diffusion contributed but was not solely rate limiting. The Elovich model also fit well ($R^2 = 0.990$), with an initial sorption rate of 0.011 mg/g·min and a desorption constant of 2.15 g/mg, highlighting surface heterogeneity. Overall, these results confirm that chemisorption dominated the removal of paracetamol on the 1 mm activated biochar under closed-loop recirculation conditions, validating its superior adsorption performance for potential process scaling. Overall, the high fit of the PSO model supports the role of active surface sites and optimized pore structures in achieving the maximum adsorption capacity.

4.8 Semi Continuous Dosing Mode

The performance of biochar-based adsorption columns is strongly influenced by the operating mode, with traditional batch or closed-loop systems often failing to fully represent the dynamics of a continuously fed treatment process. To address this limitation, a semi-continuous dosing mode was implemented in this study, designed to more realistically mimic full-scale continuous water treatment applications. A semi-continuous adsorption strategy was designed to better replicate a realistic continuous water treatment process while still using a laboratory-scale setup. In this approach, 100 g of 1 mm unactivated biochar will be packed into the column, with a recirculation flow rate of 15 L/min maintained to ensure adequate fluidization and mass transfer. Unactivated 1 mm biochar was used in the semi-continuous mode due to time limitations and the unavailability of KOH for activation during the experimental period.

Separately, a 1.6 L stock solution containing mass of paracetamol was prepared, corresponding to a concentration of 100 mg/L. This stock was subdivided into sixteen 100 mL beakers, each

containing 10 mg of paracetamol. At the start of the experiment (t = 0), the first 100 mL beaker will be dosed into the recirculation reservoir. After 15 minutes, a 100 mL effluent sample will be collected from the outlet pipe. At 30 minutes, the next beaker will be dosed, followed by a sample collection at 45 minutes, continuing this alternating pattern until all sixteen beakers have been added and sixteen samples have been collected.

This procedure, illustrated schematically in Figure 4.23, enables a semi-continuous mode of operation where the biochar is repeatedly exposed to fresh doses of paracetamol solution, while the recirculation loop ensures consistent contact and mixing. This setup mimics a continuous treatment system with periodic fresh contaminant loading, providing valuable insights into the progressive saturation of the biochar and its removal efficiency over time.

Furthermore, the results provide practical insights into when the adsorbent's capacity would become exhausted, requiring withdrawal of spent biochar and replacement with fresh biochar. In this way, these experiments help predict the operational lifespan of the adsorbent and inform strategies for periodic biochar renewal to maintain consistent removal performance.

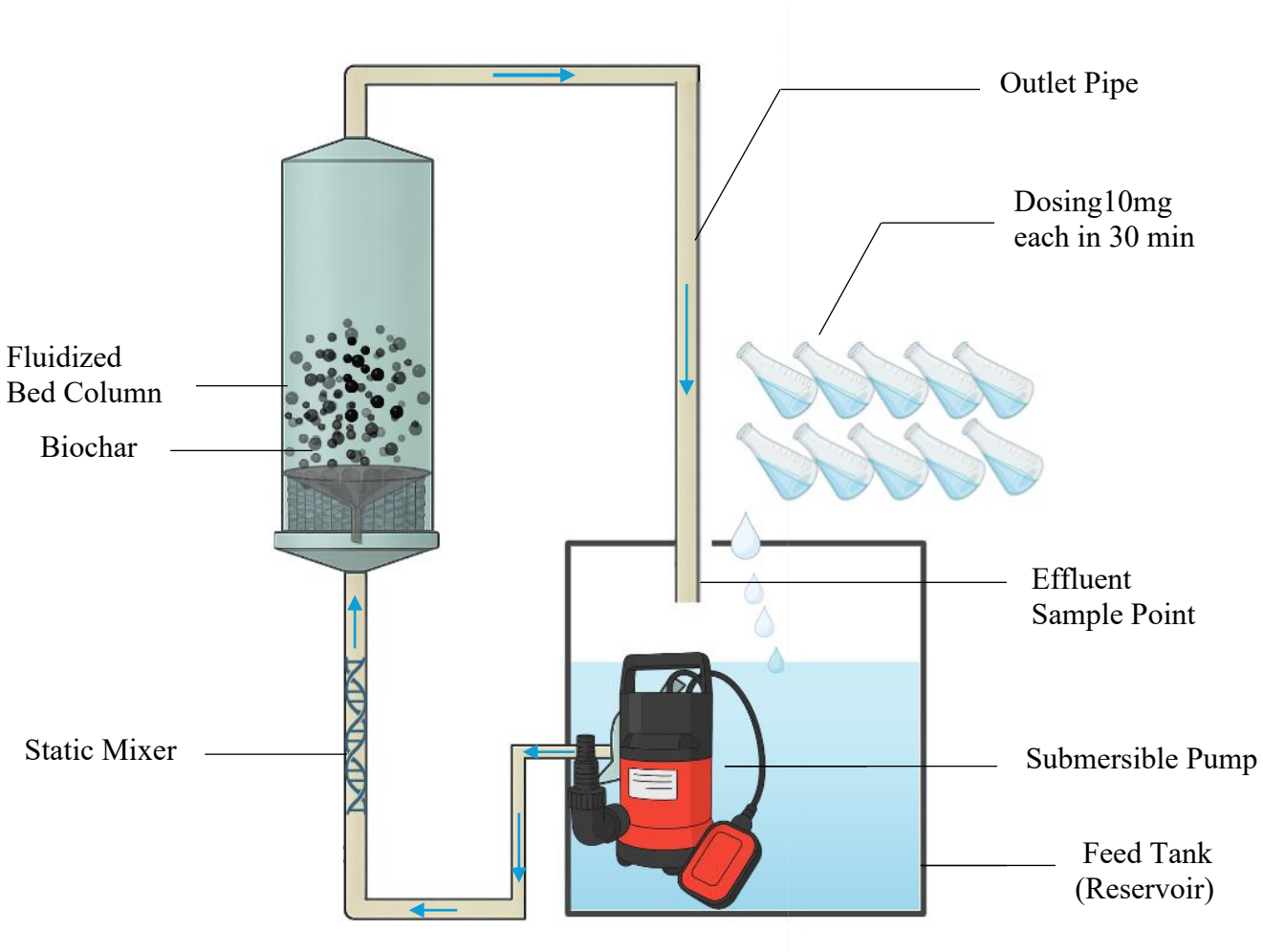


Figure 4.23 A Schematic Diagram of the Semi-Continuous Dosing in Closed Loop Recirculation Mode in Fluidized Column

The semi-continuous experiments (14–16) summarized in the table above evaluated the adsorption performance of unactivated biochar under closed-loop recirculation conditions. All experiments maintained consistent operating parameters, including a 100 g biochar mass, 1 mm particle size, 15 L/min flow rate, and a 10 mg/L dosing concentration for each semi-continuous dosing event.

In Experiment 14, the total mass of paracetamol introduced to the system was only 16 mg over 480 minutes. This low total mass, relative to the high adsorbent dose of 100 g, meant that the pharmaceutical concentration was likely below detection sensitivity after the initial pass. As a result, the changes in effluent concentration were too small to reliably measure, and the calculated adsorption was not significant. This limitation reflects a mismatch between the biochar dosage and the amount of pharmaceutical present; essentially, the adsorbent was in vast excess compared to the contaminant load, making removal indistinguishable from

measurement error. Consequently, no meaningful adsorption mass could be reported for Experiment 14.

In contrast, Experiments 15 and 16 applied higher cumulative pharmaceutical loads (160 mg and 320 mg, respectively), which allowed the system to demonstrate measurable adsorption behavior and breakthrough. Experiment 15 achieved an adsorbed mass of 43 mg, corresponding to an adsorption capacity of approximately 0.43 mg/g, while Experiment 16 reached 57 mg total adsorbed mass with a capacity of about 0.57 mg/g. These results indicate that the semi-continuous closed-loop recirculation mode can progressively load the adsorbent as more pharmaceutical mass is introduced over time, gradually approaching saturation.

Table 4.9 Summary of Semi-Continuous Closed-Loop Recirculation Experiments (Experiments 14–16) for Paracetamol Removal Using Unactivated Biochar

Pharmaceuticals	Paracetamol		
Experiment	14	15	16
Total Running Time(min)	480min	480min	480min
Mass of Biochar (g)	100g	100g	100g
Particle size (mm)	1mm	1mm	1mm
Type of Biochar	Unactivated	Unactivated	Unactivated
Flow Rate (L/min)	15L/min	15L/min	15L/min
Total Dosing stock Volume(L)	1.6 L	1.6 L	1.6 L
Dosing Concentration per time (mg/L)	10mg/L	10mg/L	10mg/L
Mass in (mg)	16mg	160mg	320mg
Adsorbed mass(g)	-	43mg	57mg
Adsorption Capacity (mg/g)	-	0.4	0.6
Temperature (℃)	25±3	25±3	25±3
pH	7.6	7.9	7.9

4.8.1 Cumulative Mass Balance Comparison

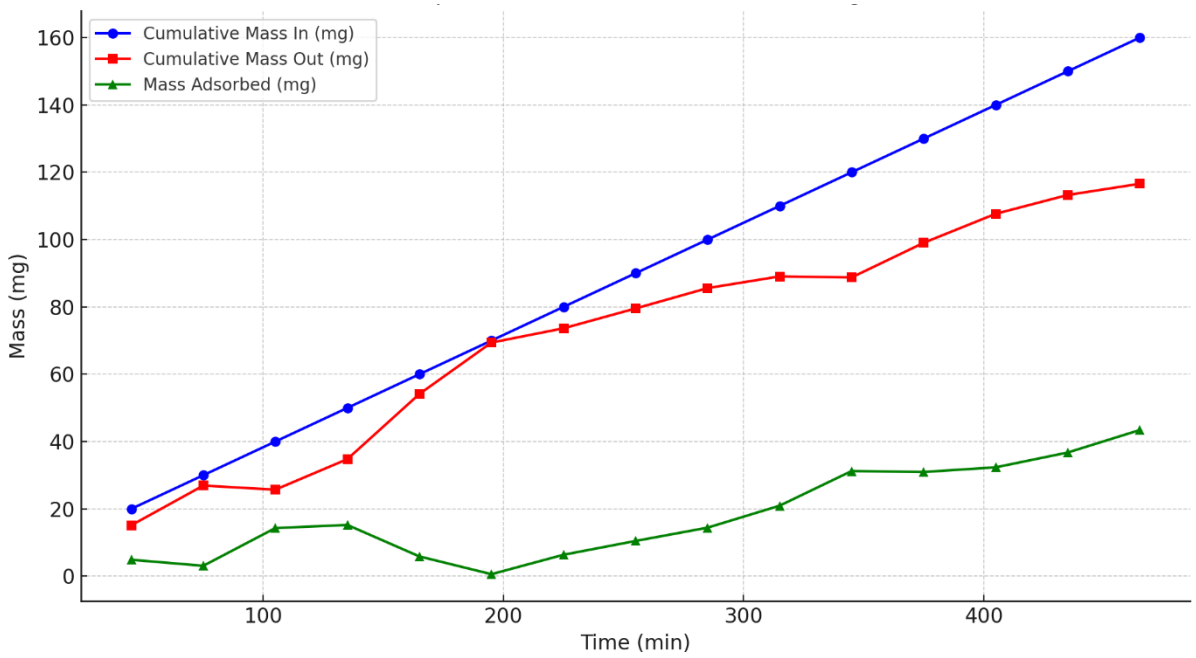


Figure 4.24 Comparison of cumulative paracetamol mass input, output, and adsorbed on biochar over time in semi-continuous dosing under closed-loop recirculation (Experiment 15)

The cumulative mass in (blue line) rises linearly with each repeated 20 mg dosing event over time, reaching 160 mg by the end of 480 minutes. The cumulative mass out (red line) similarly increases but lags behind the input curve, reflecting partial removal of paracetamol by the biochar.

The difference between the cumulative mass in and the cumulative mass out is shown by the green line, representing the mass adsorbed by the biochar at each time point. Initially, the green line increases, indicating active adsorption of the pharmaceutical. However, after approximately 180–240 minutes, the slope of the adsorbed mass curve begins to flatten, and even fluctuates slightly, suggesting that the biochar is gradually approaching saturation. This is consistent with the expectation that as active sites become increasingly occupied, the rate of additional paracetamol removal declines, leading to a reduced adsorption increment over time. This behaviour aligns with literature on biochar adsorption of pharmaceuticals in column systems, where breakthrough and eventual saturation are typical as the active sites become occupied and the removal efficiency declines over time (Ndoun et al., 2023) .

Despite this progressive saturation, the biochar continued to adsorb paracetamol to some extent across the entire experiment, demonstrating its capacity to capture pharmaceuticals over multiple recirculation cycles. The separation between the cumulative mass in and cumulative mass out curves visually confirms that the closed-loop recirculation system enables extended

contact between the pollutant and the biochar, improving overall removal even with repeated pollutant loading. the observed fluctuations in the adsorbed mass may also be attributed to preferential flow paths or changes in concentration gradients, phenomena that have been documented to impact adsorption efficiency in column studies (Brito et al., 2021).

Overall, the data show that unactivated biochar maintained a cumulative adsorbed mass of about 43 mg by the end of Experiment 15, with an estimated final adsorption capacity of approximately 0.43 mg/g. These results highlight the potential of semi-continuous dosing strategies to sustain pharmaceutical removal over extended timeframes, while also pointing to the need for timely replacement or regeneration of the adsorbent once its capacity is largely exhausted.

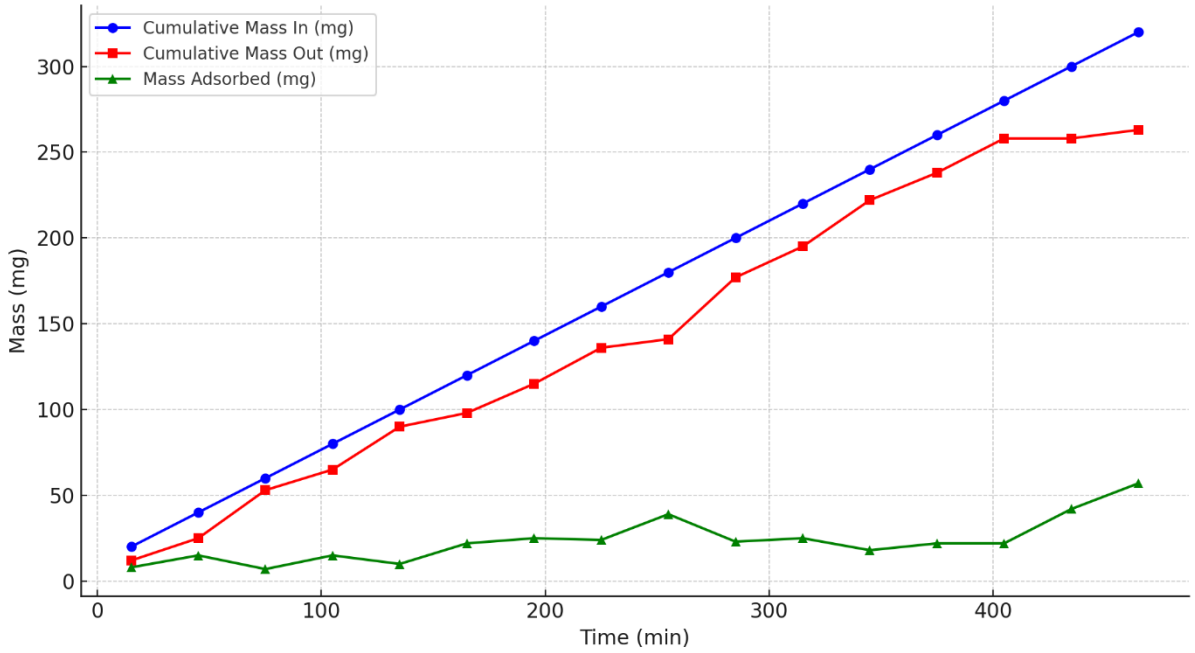


Figure 4.25 Comparison of cumulative paracetamol mass input, output, and adsorbed on biochar over time in semi-continuous dosing under closed-loop recirculation (Experiment 16)

The pharmaceutical load was increased to mass 320 mg double through repeated semi-continuous dosing events in a closed-loop recirculation fluidized bed. As expected, the cumulative mass in (blue line) increased steadily with each dosing step, reaching 320 mg after 480 minutes. Notably, the green line of adsorbed mass shows a pattern of plateauing in several time segments, especially after 300 minutes, suggesting that the biochar was approaching partial saturation under the higher pollutant load. Despite this, by the end of the experiment, the adsorbed mass reached approximately 57 mg, confirming that unactivated biochar retained its capacity to adsorb paracetamol even under more challenging repeated loading conditions.

When compared to Experiment 15, which likely operated under different dosing rates, same biochar mass, or influent concentration, several distinctions may be observed. If Experiment 15 demonstrated a higher or more sustained mass adsorbed, this would indicate either a lower influent concentration, a greater adsorbent mass, or more favourable operating conditions for paracetamol uptake. Conversely, the plateauing and fluctuations in the adsorbed mass observed in Experiment 16 are characteristic of systems approaching breakthrough and saturation, as described in the literature for fixed-bed and fluidized-bed adsorption columns. Studies such as Haro et al. (2021) and Nascimento et al. (2020) have shown that at higher influent concentrations or with insufficient adsorbent mass, the removal efficiency declines more rapidly, and the system reaches equilibrium or breakthrough sooner, resulting in lower overall adsorption capacity and more pronounced fluctuations in the adsorbed mass curve. This behaviour is attributed to the exhaustion of available adsorption sites and possible preferential flow paths within the column, which can limit the effective utilization of the biochar bed.

In the nutshell, Experiment 16 demonstrates typical semi-continuous adsorption dynamics at higher pollutant loads or near-saturation conditions, while Experiment 15 may serve as a reference for improved or baseline performance under less demanding conditions.

Chapter 5

Conclusion and Recommendations

5.1 Overview

This chapter provides a synthesis of the key results presented in Chapter 4, linking them directly to the research questions and objectives defined of this study. It summarises the overall findings, interprets their significance in the broader context of sustainable pharmaceutical wastewater treatment, and reflects on how the research aim has been successfully addressed. Finally, this chapter offers practical recommendations for future research and operational improvements based on the experimental results and identified knowledge gaps.

5.2 Conclusion

This research comprehensively investigated the adsorption performance of New Zealand-sourced premium biochar for the removal of paracetamol and ibuprofen from synthetic aqueous solutions. As a sustainable and low-cost adsorbent of locally available biochar used for both raw and chemically modified in all the experiments. Premium Biochar demonstrated the most favourable physicochemical characteristics, with a BET surface area of 308.3 m^2/g and micropore volume of 0.1573 cc/g, further enhanced to 354.2 m^2/g after 30% KOH activation, confirming improved porosity and increased active site availability. Characterization analyses (FTIR, SEM–EDX) confirmed the enrichment of oxygenated functional groups and the development of more organized pore structures, improving the material's adsorptive affinity. SEM–EDX observations revealed an initially heterogeneous pore structure that became more organized and cleaner following chemical activation, indicating improved accessibility of adsorption sites.

Batch experiments demonstrated superior removal of paracetamol, with maximum adsorption capacities reaching approximately 8.5 mg/g at an higer initial concentration of 20 mg/L, and removal efficiencies of up to 86% at 3 mg/L. In contrast, ibuprofen removal was more limited, with capacities of around 2.8 mg/g and maximum removal efficiencies of 30% under similar conditions. Removal efficiencies for paracetamol were highest (86%) at 3 mg/L initial concentration but declined to 42% at 20 mg/L, whereas ibuprofen removal peaked at 30% and dropped to 12% at higher loads, suggesting site saturation effects. Increasing biochar dose from 0.05 g to 1 g significantly improved paracetamol removal from 35% to nearly 100%, while ibuprofen removal improved from 10% to about 85% under similar conditions, emphasizing the crucial role of adsorbent quantity. Smaller particle size (1 mm) consistently achieved better

removal (paracetamol 70%, ibuprofen 45%) than larger particles (3 mm), attributed to higher external surface area and faster mass transfer. Paracetamol displayed rapid uptake within the first 100–200 minutes, approaching equilibrium by 480 minutes, while ibuprofen adsorbed more gradually due to its larger molecular size and hydrophobicity.

Kinetic modelling supported pseudo-second order ($R^2 > 0.997$ for paracetamol; $R^2 = 0.975$ for ibuprofen) and Elovich models ($R^2 > 0.998$ for both), indicating dominant chemisorption on heterogeneous surfaces. The intra-particle diffusion model contributed partially at later stages but did not solely control adsorption rates. Isotherm studies showed paracetamol followed Freundlich behaviour with $Kf = 2.067$ mg/g(L/mg)^n and $n = 1.82$, indicating multilayer adsorption on diverse sites. In contrast, ibuprofen fitted best to Langmuir isotherm ($q_m = 4.5$ mg/g, $K = 0.109$ L/mg), confirming monolayer, limited-site adsorption governed by hydrophobic interactions.

Column experiments provided valuable insights into dynamic system behaviour. In single-pass continuous flow mode, short EBCTs (1.6–4.5 min) at higher flow rates led to immediate breakthrough ($Ct/Co \approx 1$) due to hydraulic bypassing and inadequate residence time, regardless of biochar mass. However, in closed-loop recirculation mode, removal efficiencies increased substantially that paracetamol removal improved to 68–90%, with final concentrations reduced to as low as 0.8 mg/L (Experiment 12), while ibuprofen achieved up to 58% removal under the same conditions. These improvements were attributed to smaller particle sizes (1 mm), extended recirculation times (up to 500 min), and optimized mass transfer conditions. The best-performing experiment (Experiment 11) achieved an estimated adsorption capacity of 1.57 mg/g, with a pseudo-second-order rate constant of 0.0036 g/mg·min and $R^2 = 0.997$. All the data confirmed chemisorption as the principal removal mechanism supported by intra-particle diffusion contributions ($kdiff = 0.055$ mg/g·min$^{0.5}$).

Finally, semi-continuous dosing experiments simulated real-world loading conditions, revealing progressive adsorbent saturation over repeated dosing events, with final adsorption capacities of 0.43–0.57 mg/g. These results highlight the need for periodic regeneration or replacement strategies to maintain consistent treatment efficiency over time. The cumulative mass balance indicated active adsorption continued throughout dosing, although approaching equilibrium conditions after 300 minutes.

In summary, the findings demonstrate that New Zealand premium biochar, particularly with KOH activation and fine particle size (1 mm), provides high removal efficiencies for paracetamol and moderate for ibuprofen under both batch and dynamic recirculation modes.

Process parameters such as contact time (≥480 min in batch), sufficient biochar dosage (≥1 g/L), small particle size, and appropriate EBCT (≥10 min recommended) were critical to maximizing performance. These outcomes confirmed New Zealand premium biochar has strong potential as a sustainable, cost-effective adsorbent for pharmaceutical removal from water systems. The results provide a foundation though further studies on real wastewater matrices, regeneration, and long-term column stability are recommended to confirm its viability at pilot and full scale.

5.3 Recommendations

Based on the experimental outcomes presented in this study, several recommendations are proposed for future research to enhance the practical and further development of biochar-based water treatment systems.

First, future research should prioritise the regeneration and reuse of spent biochar. Although KOH-activated premium biochar demonstrated high adsorption capacities for paracetamol, saturation effects were evident under repeated contaminant loading, particularly in semi-continuous dosing configurations. Investigating thermal or chemical regeneration protocols could extend the functional lifespan of the adsorbent and improve the economic feasibility of full-scale applications.

Second, further studies should evaluate biochar performance under realistic wastewater conditions. The current experiments were conducted in controlled aqueous systems with single-compound dosing, which may not fully replicate the complexity of actual effluents containing diverse pharmaceutical residues, natural organic matter, and competing inorganic ions. Comparative testing under authentic environmental matrices will help confirm biochar's robustness and refine design parameters for treating heterogeneous contaminant mixtures.

Third, a diverse range of pharmaceutical compounds should be assessed to establish the versatility of New Zealand biochar. While paracetamol and ibuprofen provided valuable contrasts in molecular size and polarity, extending investigations to include antibiotics, endocrine-disrupting chemicals, or persistent pharmaceuticals and personal care products (PPCPs) could support the development of tailored activation strategies and expand biochar's potential applications.

Fourth, improvements to column design of rig of the top and bottom of the side of column and hydraulic parameters should be explored for scalable improvement. The single-pass fluidized

bed columns showed limited removal due to short empty bed contact times. Enhance variation such as increased bed depth, reduced flow rates, or hybrid media layering could improve breakthrough behaviour and overall adsorption capacity in continuous-flow systems.

Upgrade Design for enhanced biochar handling

- Incorporate a variable-speed pump, plus flow meters and pressure gauges, to precisely manage the fluidisation velocity and hydraulic retention time, avoiding channeling or dead zones.
- Add side dosing ports or a screw feeder with an airlock system to enable continuous addition of fresh biochar and automatic removal of spent biochar, moving the system toward a fully continuous process.
- Install a conical base with a controlled drain valve to automate waste biochar withdrawal.
- Integrate programmable logic controllers (PLCs) to automate biochar addition, waste withdrawal, and flow rate control.

Fifth, Future studies should consider further scale selection through pilot-scale to validate the adsorption performance of biochar under realistic operational conditions. Such scale-up investigations should consider for parameters including bed depth, hydraulic retention time, and regeneration cycles, thereby supporting the practical implementation of continuous water treatment systems

Finally, the integration of biochar adsorption with complementary treatment technologies such as advanced oxidation processes or membrane filtration should be considered. Combining biochar with oxidative or physical separation techniques could achieve synergistic removal of complex contaminant mixtures and support modular treatment approaches suitable for decentralised or rural water treatment systems.

By addressing these recommendations, future research and engineering applications can further advance the sustainable use of New Zealand biochar for emerging pharmaceutical contaminant removal, helping to safeguard water resources in an affordable and environmentally responsible manner.

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