

**CHEMICALLY MODIFIED BIOCHARS FOR THE
REMOVAL OF IBUPROFEN AND DICLOFENAC FROM
WATER**



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ISLAMABAD, PAKISTAN

2022

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This work is submitted as a dissertation in partial fulfilment for the award
of the degree of

**Master of Philosophy
in
Environmental Sciences**



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2022

DEDICATION

*This thesis is dedicated to my beloved parents
for their endless love and support and for
always being a source of inspiration and
courage to me*

DECLARATION

I, “**Nudrat Ehsan**” (Registration No. 02312013007) hereby declare that my M.Phil. thesis titled as “**Chemically modified biochars for the removal of Ibuprofen and Diclofenac from water**” is entirely my own work carried out in Environmental Waste Management Laboratory, Department of Environmental Sciences, Quaid-i-Azam University, Islamabad and it has not been submitted, in whole or in part, in any previous application for a degree. All the investigations, findings, results, conclusions of this research have neither been previously presented anywhere nor published in any local or international forum.

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ACKNOWLEDGEMENT

No acknowledgment could ever express my deepest gratitude and indebtedness towards our master, cherisher and sustainer, for His countless blessings upon us. I am extremely grateful to Allah Almighty, our propitious and benevolent for endowing with me the required knowledge and necessary provisions for the accomplishment of this work.

I would like to take the opportunity to express my deep gratitude towards my worthy supervisor Dr. Mahtab Ahmad. His expert guidance, humbleness and continuous encouragement made the completion of this work possible. I am highly obliged to him for critically reading the manuscript and providing valuable suggestion to improve it. Without his sympathetic cooperation, accomplishment of this work would have merely been a dream.

I am cordially thankful to Dr. Abida Farooqi, chairperson Department of Environmental Science, for all her support and for providing us academic base to take up this work.

No words can repay my obligations towards my parents for their unconditional love, endless affection and staunch support. I am also thankful to my brother and sisters for their care and moral support. I am grateful to my dearest friends Gulnaz Shah and Anees Amin for cheering me up throughout this journey.

My special thanks to all my friends Sana Rubab, Sabih Uddin Hakal, Subul Huda, Ahmed Attiullah and Safa Jarral who were always there to help me during my research work. I would also like to thank my lab mates Basit Khan, Fath Ullah, Hafsa Tahir, Hina Imtiaz, Iflah Nadeem and Sehrish for their valuable guidance, moral support and motivation to complete my dissertation.

NUDRAT EHSAN

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ACRONYMS AND ABBREVIATIONS

EC	Emerging Contaminants
WWTPs	wastewater treatment plants
NSAIDs	Non-steroidal anti-inflammatory drugs
PCs	pharmaceutical compounds
API	active pharmaceutical ingredients
OTC	Over-the-counter
NEQS	National Environmental Quality Standards
IBU	Ibuprofen
DCF	diclofenac
MWCNTs	multiwalled carbon nanotubes
nZVI	nano zero valent iron
LDH	layered double hydroxide
NET	negative emission technique
LEV	levofloxacin
NPX	Naproxen
CPX	cephalexin
AC	Activated carbon
HTC	Hydrothermal carbonization
SDGs	Sustainable Development Goals
UNGA	United Nations General Assembly
IPCC	Intergovernmental Panel on Climate Change
DW	Distilled Water
D-R	Dubinín–Reduškevič
RQ	Risk quotient
HQ	Hazard quotient
EC	Electrical Conductivity
FTIR	Fourier transform infrared spectroscopy
NTO	Non-target organisms
PEC	Predicted environmental concentration
MEC	Measured environmental concentration (MEC)
PNEC	Predicted no-effect concentration
mg/g	Milligram per gram

l/kg	Litre per kilogram
kV	Kilo volt
mg/l	Milligram per litre
mg	Milligram
ml	Millilitre
$\mu\text{g/ml}$	Microgram per milliliter
g/l	Gram per litre
kJ^2/mol^2	Kilo joule square per mole square
J/K/mol	Joule per Kelvin per mole
kJ/mol	Kilo joule per mole
l/g	Litre per gram
ng/l	Nanogram per litre
$\mu\text{g/l}$	Microgram per litre
$\mu\text{g/kg}$	Microgram per kilogram
mg/l	Milligram per litre
mg/g	Milligram per gram
$\mu\text{S/cm}$	Micro Siemens per centimeter

ABSTRACT

Non-steroidal anti-inflammatory drugs like ibuprofen and diclofenac are recognized as contaminants of emerging concern since they have been found in various environmental matrices and have long-lasting ecotoxic impacts on biotic components of the ecosystem. Owing to their persistence in wastewater treatment, their elimination is desirable. Adsorption is one of the most promising methods for the removal of pollutants from water. In present research, three different biochars were prepared from pine cones, apricot shells and walnut shells at 500 °C and 800 °C via pyrolysis, which were chemically modified with ZnCl₂ and FeCl₃ mineral salts. Batch adsorption studies were performed to assess the effect of biochar dose, initial concentration and contact time. Results showed that FeCl₃ modified walnut biochar, removed a higher percentage (78.30%) of diclofenac. Contrarily, ZnCl₂ modified pine cone biochar removed higher percentage (75.97%) of ibuprofen from water at a dose of 5 g/L among other biochars. Monolayer and multilayer adsorption on the biochars was predicted by Langmuir and Freundlich isotherm models, which best fitted the sorption data. The adsorption kinetics data of ibuprofen and diclofenac fitted well to the power function, Elovich and pseudo-second-order models suggesting a variety of mechanisms were likely at play in the adsorption of ibuprofen onto biochars. This study demonstrates that modified biochars have the ability to adsorb emergent pollutants such as ibuprofen and diclofenac from water.

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction to Pharmaceuticals

Pharmaceuticals are natural or artificial substances that are used to treat or prevent various diseases in both human and veterinary. They are mostly polar molecules containing more than one ionizable group and diverse structural and functional characteristics that are more likely to be lipophilic or moderately soluble in water (Fernandes *et al.*, 2021).

Pharmaceuticals are widely utilized in medical, biotechnology and agriculture i.e. as hormones, drugs, and antibiotics. The pharmaceutical sector has grown to become one of the most important and well-known industries in the world due to widespread use of various types of pharmaceuticals to maintain human and animal health. The global average annual pharmaceutical consumption per capita is estimated to be around 15 g. Developed countries, have consumption as high as 50 to 150 g. The global consumption of active compounds is estimated to be 100,000 tons or more per year (Lonappan *et al.*, 2016). In 2019, the worldwide production of pharmaceutical product was valued at 324.42 billion dollars while forecasted annual growth rate as of 14 percent from 2020 to 2027 (Alessandretti *et al.*, 2021). Usually, drugs are made to benefit the organism to which they have been administered, but most of these compounds end up in the environment, where they can have an undesirable biological effect (Lonappan *et al.*, 2016).

Over recent decades, pharmaceuticals have gained prominence as the foremost emerging contaminants in natural water and wastewater due to their persistent release and resistance to degradation (Ouyang *et al.*, 2020). These are significant group of emerging contaminants (ECs) and their occurrence in drinking water has negative effects on endocrine systems of human and wildlife. In environmental research, only a tiny portion of these ECs has been investigated (Rodriguez-Narvaez *et al.*, 2017).

1.2. Classification of Pharmaceuticals

Pharmaceuticals are split into 24 therapeutic classes, which includes approximately 10,000 diverse pharmaceuticals including roughly 3000–4000 distinct active

ingredients (AI). Antibiotics, analgesics, antidepressants, anti-inflammatories, antiepileptics, lipid regulators, beta blockers, steroids and hormones, antiulcer medicines, and antihistamines are commonly used ones (Fernandes *et al.*, 2021).

1.3. Sources and Routes of Pharmaceuticals in Environment

The pathways by which pharmaceutical compounds (PCs) are continuously released into the environment along with their active metabolites are wastewater treatment plants, discharges from hospitals, municipalities, veterinaries, pharmaceutical industries, unlawful untreated effluents, improper disposal of expired and unwanted drugs, spill accidents during manufacturing, use of sludge and manure as organic fertilizer, treatment of diseases in crops and occasionally via solid waste landfill leachates (Fig. 1; Finley *et al.*, 2013; Eslami *et al.*, 2015; Changotra *et al.*, 2019; Fernandes *et al.*, 2021).

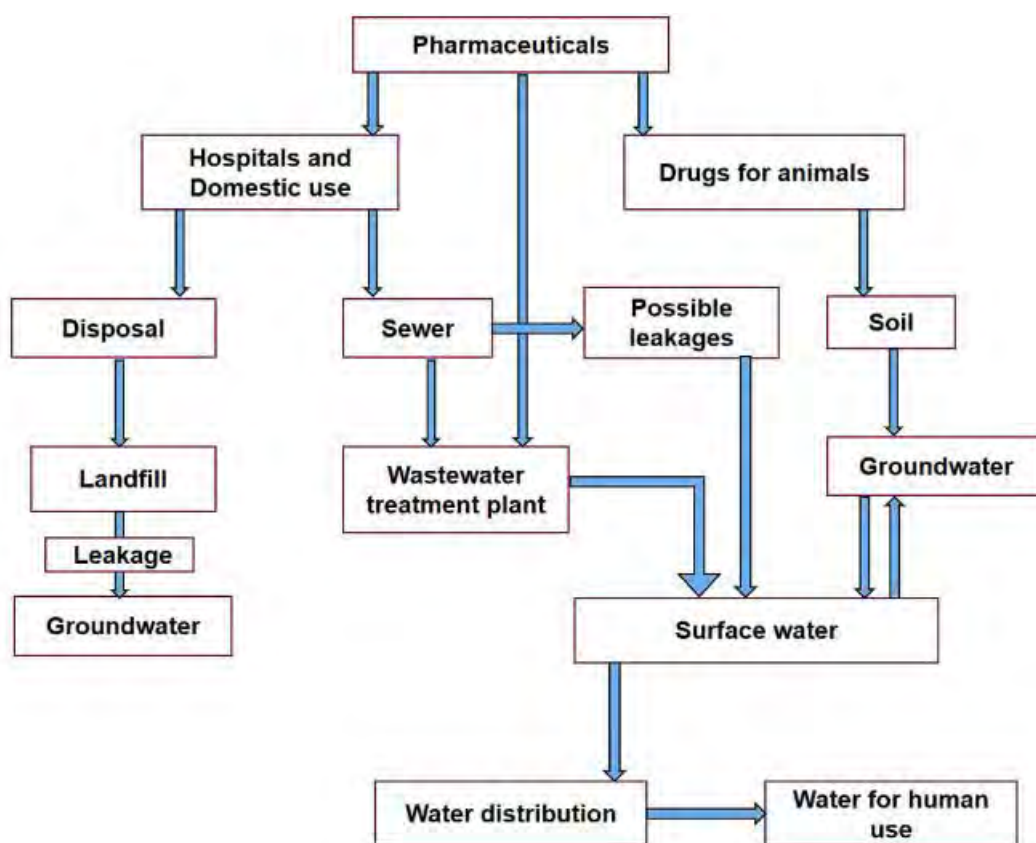


Fig. 1.1: Routes of pharmaceutical pollutants in the environment (Samal *et al.*, 2022)

Surface waters, groundwaters, coastal waters, human consumption water, soils, and sediments have all been found to contain pharmaceuticals and their metabolites.

However, metabolites and transformation products have not received much attention. Additionally, due to their widespread usage, pharmaceuticals are now more prevalent in metropolitan areas' groundwater, wastewater, surface water and stormwater runoff (Rodriguez-Narvaez *et al.*, 2017). Even when their concentration is very low, ng L⁻¹ to µg L⁻¹ in wastewater, they can cause long-term harmful effects on environment (Ouyang *et al.*, 2020).

1.4. Toxicity and Ecotoxicological Effects of Pharmaceuticals

Accumulation of active pharmaceutical residues occurs following excretion, presenting notable hazards to the food chain, human well-being, and the overall ecosystem health. The release of these bioactive compounds into the environment contributes to the emergence of antimicrobial-resistant strains, foreseeably entailing significant risks in future (Deb *et al.*, 2019). Studies have shown that pharmaceuticals may disturb the endocrine system, alter the structure and vital activities of innate microbial communities, affect invertebrates and fishes negatively and result in emergence of genes and bacteria that are resistant. Pharmaceuticals are able to cross the cell membranes and remain as active molecules when they are excreted into the environment. Their persistence in the environment, widespread and growing usage and manufacturing, continuous input at low concentration into the environment, and possible toxicological effects on non-target organisms (NTO) have raised concerns among scientists. Concerns have also been raised about the negative effects that these compounds may have on human health as well as the functions and structures of the ecosystem (Fernandes *et al.*, 2021). This is due to the fact that the majority of them have strong hydrophilicities and long-lasting stability in water (Xie *et al.*, 2014; Khanday *et al.*, 2019). Such substances are regarded as being highly undesirable and are categorized as a potential toxicological pollutants.

1.5. NSAIDS in our Environment

NSAIDs or non-steroidal anti-inflammatory drugs are heterogenous class of pharmaceuticals, used world widely to treat variety of diseases in both humans and animals. They are frequently used for treatment of inflammation and pain, reducing fever and occasionally for treating rheumatic diseases (Embrandiri *et al.*, 2016). These are weak acids that non-selectively inhibit one of the two cyclooxygenase enzymes that

is involved in the synthesis of prostaglandins that mediates inflammation, pain, and fever (Batucan *et al.*, 2022).

Like other pharmaceuticals, NSAIDs enter the aquatic environment via a number of paths, they might enter the environment either directly or via sewage treatment facilities. They may remain unchanged or undergo metabolization to produce other intermediate products (Mulkiewicz *et al.*, 2021). NSAIDs can also be released unintentionally through household, hospital and municipal solid waste management (MSWM) plants, mainly via leachate from solid waste landfills that include digested sludge for agricultural use. A high parent chemical presence in the adjacent aquatic environment may result from manufacturing facilities generating active pharmaceutical ingredients (API) accidentally discharging it into water (Paga *et al.*, 2016).

NSAIDs are commonly used all over the world and have been found in various environmental compartments with their quantities from ng L^{-1} to mg L^{-1} . Furthermore, in majority of the countries, they are over-the-counter (OTC) drugs, which enhances the likelihood of usage and thus their prevalence in the environment (Lonappan *et al.*, 2016). More than fifty different NSAIDs are now available in globally and nearly 35 million people use them on a daily basis. In the UK, USA, France, Italy, Japan and Spain, the consumption of NSAIDs is rising 11.9 percent per year that is equivalent to 30 M people taking NSAIDs daily (Feng *et al.*, 2013). More than six million packages of NSAIDs were used in Portugal in 2016, diclofenac and ibuprofen were two of the most used NSAIDs (Fernandes *et al.*, 2021).

Increased contamination with NSAIDs and their metabolites were observed in all continents' waters prior to the pandemic. But it appears that COVID-19 infections were a factor in the progression of this issue. Between 2019 and 2021, many NSAIDs were found in the water systems of all the world from a few ng ranges to hundreds of mg L^{-1} . The most commonly discovered drugs were diclofenac, ibuprofen, acetaminophen, naproxen, and ketoprofen (Wojcieszynska *et al.*, 2022).

Pharmaceuticals' presence in the environment is directly related to their growing global use, as seen by their market size. With near 48 billion US dollars and 46 billion US dollars, respectively, NSAIDs and analgesics held the major market share in 2020, while antidepressants, antihypertensives, antifungals and anaesthetics had noticeably smaller market shares i.e. 28.60 billion US dollars, 24.1 billion US dollars, 13 billion

US dollars, and 2.0 billion US dollars, respectively. In recent years, NSAIDs have emerged as a novel category of pollutants due to their incomplete degradation in wastewater treatment plants (WWTPs) and their inherent ability to induce physiological concerns in humans, even at low concentrations. Majority of them can be obtained off the counter, they are environmentally significant group of pharmacologically active compounds. Owing to their prevalence in aquatic environments and lasting toxic effects on ecosystem's living components, they are regarded as contaminant of emerging concern (Rastogi *et al.*, 2021). The ecosystem is severely threatened by their increased concentration in water bodies. The negative impact of NSAIDs includes unwanted growth of cells in humans, prostration of gills and liver in fishes (Monisha *et al.*, 2022). Major NSAIDs available in the market are diclofenac, ketoprofen, ibuprofen, celecoxib, salicylic acid, naproxen and mefenamic acid (Rastogi *et al.*, 2021). However, the commonly found drugs includes naproxen, ibuprofen, and diclofenac.

1.6. Toxicity of NSAIDs to humans and non-target organisms

Despite their undeniable effectiveness for treatment of pain and inflammation, the NSAIDs could potentially cause adverse effects, particularly because they are among the most commonly overdosed drugs (Hunter *et al.*, 2011). Topical NSAIDs used in ophthalmology have reportedly been linked to epithelial abnormalities, corneal melt, and superficial punctate keratitis (Rigas *et al.*, 2020). Except for naproxen, using NSAIDs is associated with a higher risk of cardiovascular disease (Li *et al.*, 2020). During oxidation and conjugation reactions, NSAIDs are metabolized in the liver of humans and other mammals. Cytochrome P-450 is responsible for the oxidation of the majority of NSAIDs in human, plants, fishes, and aquatic invertebrates (Parolini, 2020). During metabolism, reactive intermediates are formed that have the potential to bind covalently to DNA, proteins, or other macromolecules causing negative effects (Niu *et al.*, 2015). Finally, the NSAID metabolites, along with 10–20 percent of the parent NSAID are excreted with urine (Hunter *et al.*, 2011). Due to their extensive usage, improper disposal, and ineffective sewage treatment facilities, they have become one of the most frequently detected environmental micropollutants (Lonappan *et al.*, 2016; Parolini, 2020). Additionally, NSAIDs may also have teratogenic effects. The Oxidative stress can damage DNA and modifications at the cellular level (Świacka *et al.*, 2020).

NSAIDs accumulation in aquatic creatures has also been noted. They have been found in the tissue of various creatures including, *potamopyrgus antipodarum*, *gammarus fossarum*, *hyalella azteca*, *chironomus riparius*, *corbicula fluminea*, *utterbackia imbecillis*, *exopalaemon modestus*, etc. Therefore, their acute and chronic toxicity to non-target organisms has received an increasing amount of attention in recent years. The hazardous effects of paracetamol, diclofenac, ibuprofen, acetylsalicylic acid and naproxen on freshwater invertebrates have been reported by many researchers in recent years (Parolini, 2020). Figure 2 illustrates some of the typical harmful impacts of NSAIDs on aquatic organisms.

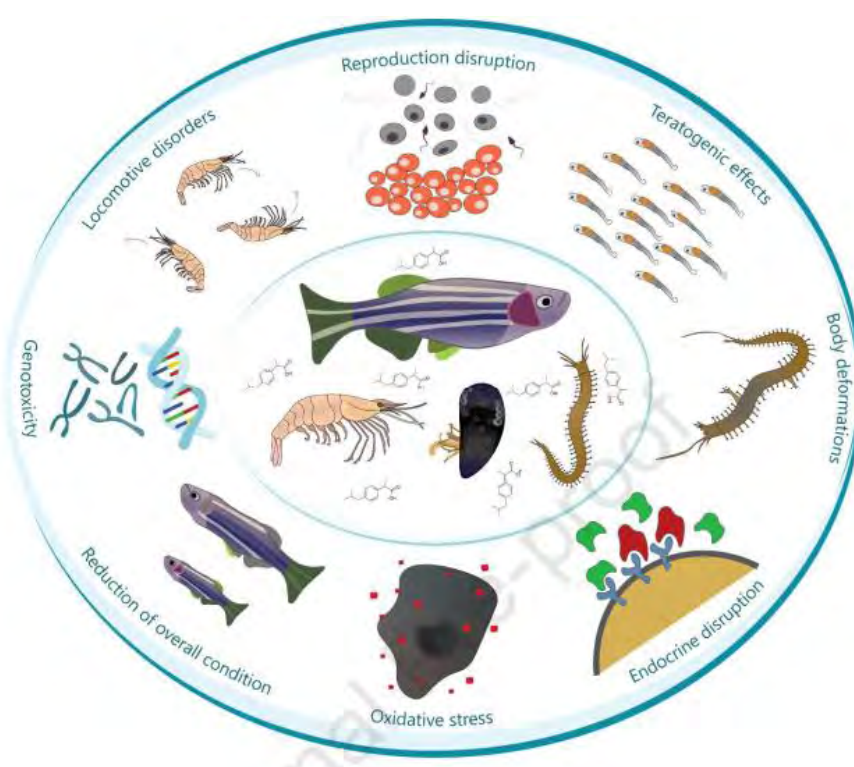


Fig. 1.2: NSAIDs common toxic effects in aquatic organisms (Świacka *et al.*, 2020)

The nephrotoxicity of NSAIDs in birds is one specific illustration of its toxicity in non-target organisms. This kind of harm in cranes and flamingos has been connected to flunixin. Similar results were seen after diclofenac treatment in broiler chicken as well. *Gyps indicus*, *gyps bengalensis*, and *gyps tenuirostris*, the vulture's species found in South Asia, have shown population declines of up to 97 percent between 1990 and 2007. It was due to administration of diclofenac in cattle treatment whose carcasses were a source of food for the vultures.

Additionally, some studies have shown that Even at minimal levels, NSAIDs have the potential to cause toxicity to aquatic creatures, including the cyprinus carpio, oncorhynchus mykiss, gasterosteus aculeatus, salmo trutta fario and tinca tinca (Wojcieszynska *et al.*, 2022).

1.7. Presence and Persistence of NSAIDs

Since NSAIDs typically do not have strict monitoring requirements or discharge levels maintained, they can be detected in water bodies and in wastewater treatment facilities all over the world ranging from few ng/L to µg/L. Based on the elements toxicity, occurrence, and persistence, NSAIDs such as ibuprofen, diclofenac and naproxen are regarded as high-priority pharmaceutical compounds by the European Union (Rastogi *et al.*, 2021). Once they enter the environment, the persistence can be influenced by 1) environmental factors (temperature, pH, light incidence, soil characteristics), 2) physicochemical properties (solubility, polarity, molecular structure, pKa or pKb, photostability, chemical stability, volatility, 3) other pharmaceuticals' presence in the same medium, and 4) occurrence and activity of microorganisms etc. (Fernandes *et al.*, 2021).

Generally, NSAIDs are classified as persistent although contradictory outcomes have been reported by a few. Different results are reported for the persistence of NSAIDs. In the field, the half-life of ibuprofen and diclofenac ranged from 4.6–32 days and <8 - < 30 days (Bu *et al.*, 2016). However, for diclofenac, under specific conditions, a lower half-life was reported in lake and river water, and for ibuprofen, under river water considerably high half-life was reported (63.6 days) (Araujo *et al.*, 2014). For ibuprofen, Yamamoto *et al.* (2009) observed an extended photolysis half-life (413 days) while numerous investigations have reported a half-life below the persistence threshold (Bu *et al.*, 2016). Diclofenac's half-life fell within the range in soil as it was in water although, a comparatively high persistence was reported in soil than water for ibuprofen with half-life of maximum 49.9 days (Lin and Gan, 2011). Inconsistent data on the half-lives in water bodies is unavoidable. The variations in reported NSAID levels can be due to a number of factors that include demography, NSAID consumption per capita in a specified region, illegal disposal of pharmaceutical industry waste, wastewater treatment processes and efficiency, retention period in WWTPs, and characteristics of influent water quality in wastewater treatment plants (Rastogi *et al.*, 2021).

1.8. NSAIDS in Pakistan

The pharmaceutical sector is one of Pakistan's key industries, expanding at a rate of 10% annually. This industry exports a range of PCs to more than 27 nations worldwide. There are variously sized pharmaceutical units totaling over 386. Despite these encouraging economic indicators, the resident pharmaceutical industries do not meet the National Environmental Quality Standards (NEQS). The wastewater is released without any pretreatment into domestic wastewater systems (Rehman *et al.*, 2015).

NSAIDs consumption is higher globally and are known for their persistence and recurrent occurrence in aquatic environments (Cortes *et al.*, 2013). The usage of NSAIDs is also high (38%) in Pakistan in comparison to other groups of pharmaceuticals (Nasir *et al.*, 2012). Sewage treatment is generally inadequate or nonexistent. Additionally, there is a general lack of data regarding the prevalence of pharmaceuticals in water bodies in Pakistan. Wastewater comprising these chemicals is discharged directly into irrigation canals or into rivers and streams through open drains, endangering the aquatic life as well as contaminating soil and groundwater through infiltration (Khan *et al.*, 2018). Due to lack of systematic annual data in Asia, it is difficult to quantify the concentration of NSAIDs in natural environment (Yan *et al.*, 2014).

Khan *et al.* (2018) investigated the occurrence of a few NSAIDs and benzodiazepines in sewage as well as surface water in Mardan region, Pakistan. The NSAIDs were detected at higher quantities particularly paracetamol, ibuprofen, and diclofenac. The highest concentration was detected for paracetamol (32.4 µg/L), while diclofenac and ibuprofen concentrations were 0.16 and 0.21 µg/L, respectively. Likewise, maximum concentrations of ibuprofen and diclofenac found in untreated sewage were higher as compared to the sewage that's treated in some countries i.e. France. Ibuprofen concentration in surface water was low in comparison to the USA (1000 ng/L), Germany, (530–1200 ng/L) and South Korea (336 ng/L) and some other countries while equivalent to that in France. The concentration found in surface waters was lower than toxic values reported for diclofenac i.e., 0.5-50 µg/L above which it causes harm to gills and kidney tissues of freshwater fish. It is possible that some of the chemicals' comparable concentration results from their relatively low use as developing nations like Pakistan only use 20% of the world's pharmaceuticals (Khan *et al.*, 2018). A higher

usage of these drugs has been reported in comparison to other groups of pharmaceuticals (Nasir *et al.*, 2012).

Fifty-two PCs were found, and their risks evaluated in water and sediment samples taken from Lahore, Pakistan, urban drains and canals. NSAIDs were the most common PCs found in the surface water of canals and wastewater from urban drains. Ecological risk assessment showed NSAID acetaminophen posed the greatest threat to aquatic species followed by ibuprofen and diclofenac that exhibited high risk to one or more aquatic species (Ashfaq *et al.*, 2019).

Six pharmaceuticals were detected in sediments, wastewater and solid waste samples belonging to 5 hospitals of Gujrat, Pakistan. Paracetamol was found in highest concentration (696 ng/mL). The maximum concentrations detected for diclofenac, ibuprofen and naproxen were 186 ng/mL, 596 ng/mL and 220 ng/mL, respectively (Ashfaq *et al.*, 2017a) which were quite higher than studies reported by Kosma *et al.* (2014) and Yan *et al.* (2014).

In an investigation near pharmaceutical industrial sector in Lahore, samples of soil, wastewater, sludge, and solid waste were examined for the presence of eleven human pharmaceuticals. Risk evaluations against several species prevalent in fresh water and wastewater were also conducted. NSAIDs were detected in wastewater, sludge, solid waste, and soil samples at very high quantities, including ibuprofen (610 µg/kg, 1673 µg/L, 6046 µg/kg and 1229 µg/kg), diclofenac (257 µg/kg, 836 µg/L, 4968 µg/kg, and 6632 µg/kg) and naproxen (199 µg/kg, 464 µg/L, 7273 µg/kg and 4819 µg/kg) (Ashfaq *et al.*, 2017b). Various species present in wastewater and freshwater were assessed for their hazard quotient (HQ). or risk quotient (RQ). In this investigation, the predicted no effect concentration (PNEC) of potentially poisonous chemicals (PCs) was compared to the predicted environmental concentration (PEC) or measured environmental concentration (MEC) of those compounds. For the majority of PCs and the majority of the species, the RQ values were quite high, particularly for diclofenac in case of *O. mykiss* (12,600) and ibuprofen in case of *O. latipes* (167,300). The RQ values $\gg 1$ suggest a significant risk to these species (Ashfaq *et al.*, 2017b).

Scheurell *et al.* (2009) found that diclofenac and five of its transformation products had relatively high quantities (micrograms per liter range) in various water samples obtained from Karachi compared to other research in developed nations because of

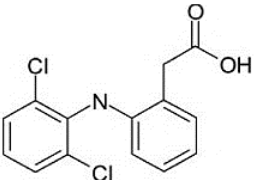
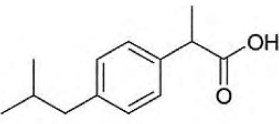
complete lack of wastewater treatment. Diclofenac concentrations of up to 116 $\mu\text{g L}^{-1}$ and 216 $\mu\text{g L}^{-1}$ have been observed in surface water and wastewater of Rawalpindi and Islamabad, Pakistani twin cities. High usage and lack of effective wastewater treatment facilities were indicated by the samples' higher diclofenac concentrations (Hanif *et al.*, 2020).

1.9. Diclofenac and Ibuprofen

Ibuprofen (IBU) and diclofenac (DCF) belong to the category of NSAIDs that are used as analgesics and were synthesized for the first time in the 1960s and 1970s. IBU and DCF are weak acids, both are biodegradable but are not completely eliminated by modern sewage treatment methods. Due to their widescale and extensive use, these are among the most frequently studied pharmaceuticals (Batucan *et al.*, 2022).

IBU and DCF both have similar structures that consists of carboxylic acid group attached to an aromatic ring. DCF structure has two aromatic rings in it that is connected via amine group and two chlorine (Cl) atoms. The Structure and properties of both NSAIDs are presented in Table 1.1.

Table 1.1: Structure and properties of diclofenac and ibuprofen.

Drug/Chemical Name	Molecular Formula	Structure	Molecular Weight (g/mol)	pKa	Log K _{ow}
DICLOFENAC					
2-[2-(2, 6-dichloroanilino) phenyl] Acetic Acid	C ₁₄ H ₁₁ Cl ₂ NO ₂		296.15	4.15	4.51
IBUPROFEN					
2-(4-(2-methylpropyl) phenyl) Propanoic Acid	C ₁₃ H ₁₈ O ₂		206.29	4.91	3.97

Almost all of the administered doses of IBU and DCF are metabolized in humans, but a small percentage of each compound enters the WWTPs unmetabolized. These compounds can be used as gels as well which causes the unmetabolized compounds to

wash off. These drugs inevitably enter the environment because conventional wastewater treatment facilities cannot entirely transform them (Kråkström *et al.*, 2022). IBU and DCF removal from water in traditional WWTPs is difficult because their structure is polar and their solubility is less in water (Bhadra *et al.*, 2017).

Depending on the treatment strategy, different NSAIDs in WWTPs have different removal efficiency. IBU removal rates varied between 75 and 85 percent, while DCF removal rates were low and inconsistent, ranging from 10 to 50 percent, according to Tiwari *et al.* (2017). Additionally, Kummerov'a *et al.* (2016) reported DCF removal efficiencies from WWTP from 20 to 40% while higher removal efficiencies up to 80% have also been observed in some places (Aissaoui *et al.*, 2017). IBU's elimination was significantly more effective than NPX and DCF, typically above 90% (Rutere *et al.*, 2020) which may be explained by IBU removal in the form of metabolites i.e., carboxyl and hydroxyl IBU (Tiwari *et al.*, 2017). This does not imply that the toxicity is necessarily eliminated. The metabolites of IBU are biochemically active and moderately toxic, especially on invertebrates and algae (Ai *et al.*, 2020). DCF's environmental transformation products may be more hazardous than DCF itself (Kråkström *et al.*, 2022). The presence of chlorine atom in DCF structure can contribute to its persistence in the effluent of the WWTP (Tiwari *et al.*, 2017). Due to the large consumption of IBU and the high toxicity of DCF, it is imperative to improve their removal from wastewater (Kråkström *et al.*, 2022).

An estimated 940 tons of DCF is used up annually around the globe with an average of 65 percent of the oral dosage being passed through the urine with its active metabolisms that are sent to conventional WWTPs (Alessandretti *et al.*, 2021).

1.10. Removal Technologies

An emergent goal for environmental technologies is to efficiently remove PCs from waters which comprises variety of polar organic molecules that can undergo chemical transformations during the process of treatment (Muter *et al.*, 2019). Numerous techniques have been developed to eliminate pharmaceuticals from wastewater at the laboratory and the industrial level. These include membrane filtration (Kamrani *et al.*, 2018), biodegradation (Wang *et al.*, 2018), coagulation and flocculation (Sluiter *et al.*, 2010), ozonation (Gomes *et al.*, 2017), electrochemical catalysis (Gholami *et al.*, 2020),

ultrasonic treatment, solid-phase extraction by molecular recognition, solid extraction etc.

The drawbacks of these techniques are the complex structure of the pharmaceuticals, the origination of toxic by-products, increased expense of operation or maintenance (Suriyanon *et al.*, 2015) and the requirement of large systems, infrastructure, and engineering expertise, which makes them ineffective, time-consuming, and costly (Olufemi *et al.*, 2020). Compared to these techniques, adsorption is viewed as a promising method for eliminating various pollutants from wastewater due to its affordable, renewable, and adaptable operation (Ouyang *et al.*, 2020).

Currently, several materials are utilized as adsorbents for organic and inorganic pollutant's removal including Activated carbon (AC), agro-industrial wastes, polymeric matrices, inorganic matrices, zeolites, mesoporous silicas, soil/clays and hybrid nanoporous solids (Isaeva *et al.*, 2021).

1.11. Biochar- a promising adsorbent

Biochar's history can be traced back 2000 years ago to the indigenous Amazonians' Terra preta-man made soil modifiers used to improve the soil that was prepared by in-situ burning of agricultural wastes, however biochar in modern times is created from the carbonaceous residues of thermochemical operations (Isaeva *et al.*, 2021). Terra preta differs from biochar in terms of composition and carbon structure. It is critical to note that the discovery of Terra preta's nutritional value sparked interest in the use of biochar (Kamarudin *et al.*, 2022).

Biochar is lately being recognized for being an effective material for treating contaminated water, managing waste, reducing the effects of climate change, and enhancing soil quality. Biochar has high carbon content and pores with oxygen functional groups and aromatic surfaces and depending on the feedstock and pyrolysis technique, it can have varying physical and chemical properties. The ability of biochar to adsorb any pollutant depends on several factors, including biochar's feedstock, pyrolysis condition and technology, and mainly temperature employed for pyrolysis (Tan *et al.*, 2016). The biochar's pore size, aromaticity, surface area, polarity and surface chemistry could all be affected by the pyrolysis temperature (Ahmad *et al.*, 2014).

The biochar's function as an adsorbent is attributed to the organized carbon matrix possessing a moderate to high surface area, almost like AC which is not only cost effective, but also convenient due to the wide availability of feedstock and the lack of activation processes compared to AC (Ahmad *et al.*, 2021). As the pyrolysis temperature increases, the organic matter breaks down and transforms into biochar, which possesses elevated surface area, carbon content, pH, and porosity (Tomczyk, 2020).

The primary source of the feedstocks for biochar is agricultural biomass, one of the world's most abundant renewable resource. Crop wastes, solid wastes, wood biomass and animal wastes have all been used as feedstocks in production of biochar using a variety of thermochemical processes such as hydrothermal carbonization (HTC), flash carbonization, slow and fast pyrolysis, gasification and torrefaction (Tan *et al.*, 2015). Compared to biochars made from animal waste and municipal solid waste, biochars made from agricultural biomass have higher surface areas, mobile matter, and carbon contents due to their high cellulose, hemicellulose, and lignin contents. These properties thus influence the sorption capabilities towards organic contaminants (Tomczyk *et al.*, 2020). Additionally, the surface functional groups can bind to PCs by physisorption, chemisorption, or occasionally by both (Monisha *et al.*, 2022).

The bio-waste utilized to produce biochar will also reduce the waste burden and aids in waste management. In fact, doing so may help us achieve the Sustainable Development Goals (SDGs) by the United Nations General Assembly (UN-GA), in terms of good health and well-being (G-3), clean water and sanitation (G-6), affordable and clean energy (G-7), responsible consumption and production (G-12) climate action (G-13), Life below water (G-14) and life on land (G-15) (Murad *et al.*, 2022).

In order to achieve SDGs, biochar has emerged as an efficient, eco-friendly, and economically viable strategy. Biochar has been regarded as a potential negative emission technique (NET) in the IPCC assessment report 2018. Production of biochar from agricultural biomass has many benefits over combustion of it directly i.e., long-term carbon storage, offsetting fossil energy, prevention of biomass decay, and decreased emissions of harmful greenhouse gases. It also enhances soil quality, crop yields, physicochemical and biological properties and the production of bioenergy (Neogi *et al.*, 2022).

When it comes to waste treatment, biochar serves as an adsorbent. The sorption characteristics are influenced by the type of raw materials used in its production. Studies have found a large number of feedstocks from various origins that fall under the following three categories: 1) crops, trees and plants, 2) animals, microorganisms etc., and 3) industrial discharges and domestic discharges (Monisha *et al.*, 2022).

Different types of contaminants including metals, dyes, polynuclear aromatics, and pesticides, have been removed via biochar adsorption (Reddy *et al.*, 2017). Numerous studies have reported the removal of various pharmaceuticals like anti-inflammatory drugs, antibiotics (Jung *et al.*, 2015) and other over-the-counter medications with biochar.

For treating numerous PCs like norfloxacin, tetracycline, oxytetracycline, sulfamethoxazole, sulfonamides, etc. barks from trees, leaves and stems and seeds from plants, wood biomass and remains of crops like cotton, wheat, rice and maize straws have been demonstrated as potential sources of feedstock. In addition, shells of camellia oleifera, cotton, walnut, aegle marmelos, terminalia catappa peanut and almond have drawn interest for the preparation of biochar. Shells of terminalia catappa and aegle marmelos were used for treating IBU (Chakraborty *et al.*, 2018b; Show *et al.*, 2021). Peanut shells were used as raw material for biochar to treat naproxen and sulfamethoxazole (Zhang *et al.*, 2019a, b; Tomul *et al.*, 2020). Almond shell efficiently removed DCF (Lonappan *et al.*, 2018a). Adsorption of sulfamethazine, sulfadiazine and sulfachloropyridazine were effective by walnut and cotton shells (Meng *et al.*, 2020; Geng *et al.*, 2021). Biochar made from pine plant materials played significant role in the efficient sorption of PCs (Jang *et al.*, 2018). Removal of sulfamethoxazole, sulfonamides, naproxen, diclofenac and ibuprofen were achieved by pine wood and pine chips (Jung *et al.*, 2013, 2015; Xie *et al.*, 2014; Essandoh *et al.* 2015; Lonappan *et al.*, 2018a, b). Sorption of ibuprofen proved effective using biochar derived from mung bean husk (Mondal *et al.*, 2016b).

One of the most frequent drawbacks of utilizing biochar for adsorption is that its efficiency is low, particularly for anionic pollutants in water. This is because the negative charge on the biochar surface electrostatically repels the anionic contaminants (Tomczyk *et al.*, 2020). To address this problem, biochar is now being developed

(engineered) to increase its adsorption ability by modifying the surface functional groups, surface area and surface charge respectively (Li *et al.*, 2020).

1.12. Engineered Biochar

Development of engineered biochar is trending and gaining attention for the efficient removal and mitigation of contaminants of emerging concerns, heavy metals and toxic dyes from municipal wastewater and industrial effluents, as reported by several researchers (Neogi *et al.*, 2022).

A range of engineering techniques, such as physical activation, chemical processing, impregnation and magnetic modification can be used to produce engineered biochar (Rajapaksha *et al.*, 2016). By providing functional groups that can enhance its chemical interaction with both organic and inorganic contaminants, biochar's surface chemistry can be altered when it is impregnated with inorganic minerals (such as silica, zeolite, and iron salts) (Ahmad *et al.*, 2019).

Engineered biochar also called biochar composites undergo modification with materials as nanomaterials, metals, hydroxides, microorganisms, etc. in order to improve the properties of pristine biochar. They can be categorized as metal biochar, mineral biochar, microorganism biochar, layered double hydroxide (LDH) biochar composites and nano-composites (Wang *et al.*, 2021). Struvite, montmorillonite, attapulgite and other minerals are immobilized, co-pyrolyzed and co-precipitated to create mineral biochar. These are utilised to increase soil fertility and also help in gradient fertilizer release (Chen *et al.*, 2017; Hu *et al.*, 2019; Wang *et al.*, 2021). In addition to MnO_x, MgO and MoS₂ coated biochar composites, metal doped biochars such as nano zero valent iron (nZVI), iron-oxide, and iron-sulphide biochar are among the most notable metal biochar composites. The catalytic activity of biochar is supported by transition metals. It is well known that metal biochar has improved adsorption capacity for removing pollutants and heavy metals (Shen *et al.*, 2019; Lyu *et al.*, 2020; Hamid *et al.*, 2020; Wang *et al.*, 2021).

Biochar infused with microorganisms i.e. mycobacterium gilvum and bacillus siamensis known as microorganism biochar are used to enhance the degradation of persistent pollutants, decompose soil PAHs, immobilize soil metals, and fix nitrogen. The modified nano composites are better candidates for adsorption-dependent

applications as they have large amount of π electrons. So, for the adsorption of organic pollutants including phthalic esters, sulfamethazine, and methylene blue graphene-based biochar and multiwalled carbon nanotubes (MWCNTs) are frequently used (Inyang *et al.*, 2014; Wang *et al.*, 2021). LDH biochar composites are formed of biochar and anionic clay minerals where minerals supply the layers of positive charged metal hydroxide and the anions in the interlayer area are needed for neutralization, Mg-Al, Mg-Fe, Ca-Al, Zn-Al and Ni-Fe are widely used in LDH-biochar composites to enable co-precipitation, enhance anion-exchange capacity and facilitate surface complexation by means of providing hydroxyl groups (Ma *et al.*, 2016; Wan *et al.*, 2017; Gao *et al.*, 2019; Bolbol *et al.*, 2019).

1.13. Biochar for the Removal of NSAIDs

The affinity of sewage sludge-derived biochars towards pharmaceuticals was evaluated in water systems. In order to produce cost effective engineered biochar, the organic waste existing in sewage sludge was utilized by Czech *et al.* (2021). DCF and NPX were removed with 92.7 mg g^{-1} , and 127 mg g^{-1} adsorption capacity, respectively. It was concluded that affinity of the materials depends on the pyrolysis conditions and characteristics of the pollutant. Shirani *et al.* (2020) explored the adsorption of DCF and cephalexin (CPX) by anthriscus sylvestris-derived activated biochar. The porosity and functional groups were increased by activation causing effective removal of DCF and CPX from water in batch and column scale. In another batch adsorption experiment conducted by Filipinas *et al.* (2021), to remove DCF from aqueous solutions using rice hull biochar as adsorbent showed higher DCF removal at low pH (97% at pH 2). FTIR revealed that C=O stretching vibrations were mainly responsible for the adsorption process. Activated biochar, cross-linked magnetic chitosan have also been studied to remove IBU, DCF, and NPX from the aqueous solution (Mojiri *et al.*, 2019).

Pig manure and pinewood biochar produced at temperature $400 \text{ }^{\circ}\text{C}$ and $525 \text{ }^{\circ}\text{C}$ were utilized for DCF sorption without activation (Lonapan *et al.*, 2018b). It was concluded that the biochar derived from pig manure biochar was better than the pine biochar having removal efficiency of 99.6 %. The performance of the pine wood biochar was altered by pH, but not of the other. It was discovered that co-existing ions played a key role in the sorption process. According to a thermodynamic analysis, the sorption for pine wood was endothermic while exothermic for pig dung (Lonapan *et al.*, 2018b).

Bagheri *et al.* (2020) prepared biochar by modifying moringa oleifera seed powder with phosphate for the adsorption of DCF. Removal efficiency and adsorption capacity reached 83 % and 95.38 mg g⁻¹ at 40 mg L⁻¹. Pristine and activated coffee bean waste biochars were studied by Maged *et al.* (2021) for the elimination of DCF and levofloxacin (LEV) from water.

Chakraborty *et al.* (2020) showed adsorption of IBU by date rice stone biochar pyrolyzed at 700 °C and activated via steam and H₃PO₄. Adsorption of IBU was performed using sugarcane bagasse by modifying it in two ways, one with phosphoric acid (chemical) and other using steam (physical). The pore count increased by activations, which in return increased the rate of adsorption. Sorption by chemical activation was greater compared to physical activation. H₃PO₄ and steam biochar both had maximal adsorption capacities of 13.51 mg g⁻¹ (Removal 91 %) and 11.90 mg g⁻¹ (Removal 82 %) which were reached at 12 and 18 hours respectively (Chakraborty *et al.*, 2018a). IBU elimination was successfully tested using shells of aegle marmelos derived biochar generated at 650 °C via steam activation. According to morphological research, activation by steam enlarged the pores and activated the adhesion sites on the biochar's surface (Chakraborty *et al.*, 2018b).

For the removal of IBU, chemically modified biochar was prepared by pyrolysis of parthenium hysterophorus weeds at temperature 300 °C with nitrogen flow and NaOH for activation. Under ideal operating conditions, this biochar's maximal adsorptive capacity was 90.46 mg/g. Low pH and a very low temperature facilitated the adsorption process (Mondal *et al.*, 2016a). Mondal *et al.* (2016b) investigated IBU sorption using mung bean husk-based biochar modified by pyrolyzing at 550 °C using steam, which under ideal operating conditions had a 99.16 % removal efficiency. The sorption process was more favourable at lower temperatures. Essandoh *et al.* (2015) showed that the adsorption of IBU and salicylic acid was highest at low pH levels when treated with biochar derived by pine wood created at temperature 424.87 °C. The highest adsorption uptakes found were 22.7 and 10.74 mg g⁻¹ correspondingly. In a study, 18 different PCs from untreated municipal wastewater samples were treated by wood-derived biochar where the highest absolute removal was attained by IBU (Muter *et al.*, 2019).

Methanol-modified magnetic orange peel powder biochar (Ai *et al.*, 2020), tamarind seed derived pristine and activated biochar (Show *et al.*, 2020), pepper stems biochar

(Naima *et al.*, 2022), rice straw biochar (Salem & Yakoot, 2016), chili seeds (capsicum annum) biochar (Ocampo-Perez *et al.*, 2019), pine wood biochar (Essandoh *et al.*, 2015), plane tree leaf-derived biochar (Yang *et al.*, 2022), douglas fir biochar (Liyanaage *et al.*, 2020), waste wood-derived biochar etc. have been investigated for the removal of IBU.

1.14. Problem statement

Pharmaceuticals are considered contaminant of emerging concern as a result of their widespread presence, elevated concentrations in the aquatic environment and long term ecotoxic effects on biotic components of ecosystem. Inefficiency of the conventional WWTPs for removal of these pharmaceutical micropollutants from wastewater has become one of the most difficult issue, necessitating the development of new technologies. Adsorption is regarded as a promising potential method for removing pharmaceuticals from wastewater, and biochar could take the role as adsorbent due to its affordable, renewable, and adaptable operation.

1.15 Hypothesis

Simple biochars may not be efficient in removing PCs from water due to net-negative charge on their surfaces. Modifying the biochars with mineral salts may introduce additional functional groups on their surfaces, which could form complexes with the PCs in water, thereby enhancing their adsorption potential.

1.16 Study objectives

The objectives of the current research are:

1. Production and engineering of biochars from different feedstocks (pinecone, apricot shells and walnut shells).
2. Investigation of biochars' potential as adsorbent for removing ibuprofen and diclofenac sodium from water

CHAPTER 2

MATERIALS AND METHODS

2.1. Chemicals and Glasswares

Chemicals that were used in this study included: methanol (analytical grade reagent), iron (III) chloride by Chem Lab, ibuprofen (200 mg tablets) by Abbott Laboratories and diclofenac sodium (Dicloran 50 mg) by Sami Pharmaceuticals.

Glassware used in this study included: volumetric flasks, beakers, funnels, crucibles, glass pipettes, micro pipette, Erlenmeyer flasks, measuring cylinders, stirring rod, spatulas, falcon tubes, amber glass bottles etc. Whatman Filter papers, nylon syringe filters and aluminum foil were also used in the study. Distilled water (DW) was utilized for the preparation of all solutions.

2.2. Instrumentation

Mechanical grinder was used to crush the feedstock to small fractions. Grain/spice grinder was used to grind the biochar to obtain desired particles size. Uniform sized biochars were obtained by laboratory test sieves. Biochar production and proximate analysis was done by using muffle furnace (Vulcan D-550). Drying oven (UN-55) was used for the drying purpose. Orbital shaker (OSM-747) was used for smooth mixing of samples. Hot plate stirrer was used for stirring purposes. The pH of the solution was measured by 8000 Adwa (Hungary) pH meter. Shimadzu weighing balance (ATY-244) and micro balance was used to weigh the biochar doses and other chemicals. The EC meter (Adwa, AD8000, and Hungary) was used to measure the electrical conductivity of the samples. The surface functional groups of biochar were identified through FTIR (Fourier transform infrared spectroscopy). UV/visible spectrophotometer (HALO DB-20 UV-VIS Double Beam Spectrophotometer) was opted for the analysis of IBU and DCF in samples. SEM/EDX (SEM; TASCAN, VEGA3 LMU SEM, Czech Republic) was used to examine surface physical morphology and elemental composition of biochar samples.

2.3. Production of Engineered Biochars

Pinecones, walnut shells and apricot kernel shells were selected as feedstocks for biochar production. Pinecones were gathered from Islamabad's forest area. To remove dust and debris, pine cones were rinsed and washed with distilled water (DW), dried in oven and grinded in mechanical grinder. The processed biomass was thermally converted to biochar in a muffle furnace in low oxygen presence by slow pyrolysis. The biomass was pyrolyzed slowly in covered crucibles at the heating rate of 5 °C min⁻¹ at temperature of 600 °C for 3 hours. The resultant biochar was cooled and stored in air-tight zipper bags.

Apricot and walnut shells were obtained from Khyber village, Gilgit Baltistan. The collected biomass was sun-dried for two days to minimize the moisture and grinded by mechanical grinder. The processed feedstocks were thermally converted to biochar by slow pyrolysis in the muffle furnace. The biomasses were separately placed in a covered crucible and pyrolyzed at 500 °C, under restricted oxygen supply at 5 °C per minute temperature rise. The biochars produced were placed to cool at room temperature and preserved in zipper bags. The biochars were grinded in a locally purchased grain/spice grinder and sieved through 0.5 mm sieve to get uniform sized particles.

The measurement of weight loss during pyrolysis was used to determine the biochar yield. The biochar yield was calculated as:

$$\text{Biochar yield (\%)} = \text{Weight of Biochar} / \text{Weight of Biomass} \times 100 \dots \dots \dots \text{(Eq. 1)}$$

2.3.1. Engineered Pinecone Biochar

Pinecone biochar produced at 600 °C was chemically modified with ZnCl₂ mineral salt. The produced biochar was soaked in mineral salt solution of 3 M ZnCl₂, at the ratio of 1:10 (w/v) for 24 hours. To remove excess ZnCl₂, the biochar was washed with DW and placed in an oven until it was dry. Later on, it was pyrolyzed again in furnace for 4 h at 800 °C temperature with heating rate of 20 °C min⁻¹ (Ahmed *et al.*, 2022). The modified biochar was cooled to room temperature and to prevent moisture it was placed in airtight zippers bags. The ZnCl₂ modified pinecone biochar was named as PB.

2.3.2. Engineered Apricot and Walnut Shells Biochars

Prior to modification, both the apricot and walnut biochars were acid washed. To prepare 1N solution of HCl, 81.8 ml of HCl was added in 1000 ml distilled water. Both biochars were separately mixed with the 1 N solution of HCl in 1 L glass bottles, tightly sealed and placed on shaker for 14-15 hours. After shaking the solutions were filtered with Whatman filter paper no. 40. For washing purpose, the biochars were transferred to glass bottles and 1 L distilled water was added to each bottle and placed on shaker for 1 hour. The solution was filtered again and was additionally rinsed using DW to completely remove the excess acid.

Fe-impregnated apricot and walnut biochars were produced by mixing of the acid washed biochars with 1 M ferric chloride (FeCl_3) mineral salt solution. 1M FeCl_3 was prepared by slowly adding Iron (III) chloride hexahydrate (M.W 270.33 g/mol) in DW, stirred through a magnetic stirrer at room temperature. Both biochars were separately mixed with 1M FeCl_3 solution and placed on orbital shaker for 24 hours for uniform mixing. The resultant biochars were washed by DW to remove excess iron and kept for drying in oven at 110 °C for 24 hours (Runtti *et al.*, 2016). The FeCl_3 modified apricot and walnut biochars were named as AB and WB respectively.

2.4. Characterization of Engineered Biochars

Biochars were characterized for proximate analysis (mobile matter, moisture content, ash content and resident matter), ultimate analysis, FTIR (Fourier Transform Infrared Spectroscopy), SEM (Scanning Electron Microcopy) and EDX (Energy-dispersive X-ray spectroscopy) analysis. pH and EC were also measured.

2.4.1. Proximate Analysis

Proximate analysis of biochar was performed based on the methods reported in Ahmad *et al.* (2013). Moisture content of biochars were determined by keeping the sample in crucible at 105 °C for 24 h, to achieve a constant weight. The moisture was calculated by subtracting the weight loss after heating the samples. The mobile matter, the non-carbonized part of biochar was measured by heating the biochar sample at 450 °C for 1 h in covered ceramic crucible in muffle furnace. The content of ash in biochars were determined as the samples were heated at 750 °C for 1 h in open crucibles in the muffle

furnace. Resident matter (fixed matter), the non-ash part of biochar, was calculated by the difference in ash content, mobile matter and moisture content via following formula:

$$\text{Resident matter (\%)} = 100 - (\text{Mobile matter} + \text{Moisture content} + \text{Ash content})$$

EC and pH of the modified biochar samples were measured by taking 1 g of biochar in 20 mL DW (1:20) and shaking at 200 rpm for 1 h. Zeta potential measurements offer insight into the surface charge of the adsorbent material. The point of zero charge (PZC) is the pH value where the material surface reaches a state of equilibrium between its net positive and negative charges (Sulaiman & Al-jabari, 2021). Method by Uchimiya et al. (2011) was opted to measure the point of zero charge pH (pH_{PZC}). A fixed amount of 0.01 g of the biochar samples were put in a falcon tube containing 10 mL of 0.1 M KCl solution. The pHs of the solutions were adjusted to 2, 4, 6, 8, and 12 with NaOH or HCl (0.5 M) solutions accordingly. The pH_i , initial pH of the solutions was recorded, and solutions were shaken for 24 hours and the final pH of the solutions was measured after completion (pH_f). Lastly, the achieved pH values of the biochars after shaking were note down and pH_{PZC} values were determined by the plot between pH_i and ΔpH ($\text{pH}_i - \text{pH}_f$).

2.4.2. Ultimate Analysis

In order to determine the occurrence of functional groups on the surface of these modified biochars, Fourier transform infra-red (FTIR) spectrometer was used. The surface structure was determined using Scanning Electron Microscopy (SEM). For identification of elemental composition of the modified biochars Energy-dispersive X-ray spectroscopy (EDX) analysis was performed.

2.5. Pharmaceutical Compounds' Solution Preparation and Maximum Absorbance Tests

2.5.1. Ibuprofen

IBU stock solution (100 mg/L) was made by mixing a required amount of the powdered IBU tablets in DW in a standard 1 L volumetric flask. IBU is less soluble in water i.e. up to 21 mg L⁻¹. Therefore, firstly 100 mg of ibuprofen was dissolved in 100 ml of methanol to create a homogenous IBU solution (Chakraborty *et al.*, 2018). The solution was filtered through Whatman filter no. 40 to filter out any residue or insoluble fractions

and the volume was made up to 1000 mL with DW. Batch adsorption experiments were performed using this solution. Working solutions of desired concentrations were prepared by dilutions of the stock solution in DW.

Standard solutions of 0.5 to 10 mg/L IBU were prepared by taking required amount from stock solutions in 50 ml measuring flasks and volume was filled up to the mark with DW. The maximum absorbance was measured by taking the spectrum between 190 nm to 400 nm on a UV-Visible spectrophotometer. Distilled water was taken as blank. It was found that 220 nm was the wavelength at which IBU showed maximum absorbance. The relationship between concentration and absorbance was utilized to construct the calibration curve. In concentration range of 0.5 to 10 mg/L, the calibration curve was significantly linear ($R^2=0.999$).

2.5.2. Diclofenac

DCF' stock solution (100 mg/L) was prepared by crushing 100 mg of Diclofenac Sodium tablet (Dicloran) into fine powder and dissolving it in 1000 mL DW. The solution was covered to prevent photo-degradation. Working solutions were obtained by dilution of the stock solution with distilled water. The solutions were stored in refrigerators.

By taking the spectrum between 190 nm to 400 nm through UV-Visible spectrophotometer, DCF's maximum absorbance was found to be at 276 nm. Required amount of solutions were taken from the stock solutions to prepare concentrations of 0.5 mg/L to 10 mg/L. Calibration curve was constructed between concentration and absorbance with a correlation coefficient of 0.999.

2.6. Batch Adsorption Experiments

In order to examine the influence of four adsorption variables, namely initial pollutant concentration, biochar dosage, contact time, and pH, a series of batch mode adsorption experiments were carried out.

2.6.1. Initial Concentration

To study the effect of initial concentration of IBU and DCF, six different concentrations of 1, 5, 10, 20, 30 and 40 mg/L with fixed doses of biochars (2 g/L) and 40 mL volume were prepared in falcon tubes. DCF experiments were carried out in amber glass bottles.

The samples were agitated in shaker for 24 h at 150 rpm. Each batch experiment consisted of three replicates of samples and blanks (without biochar). After 24 h of shaking, the samples were filtered by Whatman filter no. 40 and nylon syringe filters and analysed on UV-visible spectrophotometer at wavelength 220 nm for IBU and 276 nm for DCF. From the standard calibration curves, the residual IBU and DCF concentrations were calculated. The equilibrium adsorption capacity and the removal % were calculated as:

$$Q_e = (C_0 - C_e) \times \text{volume of solution} / \text{weight of biochar} \dots \dots \dots (\text{Eq. 2})$$

$$\text{Removal} = (C_0 - C_e) / C_0 \times 100 \dots \dots \dots (\text{Eq. 3})$$

The amount of pollutant adsorbed at equilibrium by biochar is Q_e (mg/g), C_0 is the initial concentration of pollutant in mg/L in the solution, C_e is the final concentration of pollutant remaining in solution at equilibrium (mg/L).

2.6.2. Adsorbent Dose

The outcome of adsorbent dose was explored by taking 10 mg/L concentration of each IBU and DCF in 40 mL falcon tubes and adding different doses of biochars i.e., 0.5, 1, 2 and 5 g/L. The samples were kept on shaker for 24 h at 150 rpm and filtered through Whatman filter no. 40 and nylon syringe filters. Analyses were done on UV-visible spectrophotometer at 220 nm for IBU and 276 nm for DCF. Each batch experiment was performed in triplicate with blanks.

2.6.3 pH

To examine the impact of pH on adsorption, experiments were conducted at four different pH levels: pH 3, pH 5, pH 7 and pH 9. With 0.1 M HCl and 0.1 M NaOH, the pH was adjusted. The 20 mg/L DCF and IBU solutions were mixed separately with different biochars at 2 g/L dosage and placed on shaker at 150 rpm for 24 hours. The samples were filtered and analysed using a spectrophotometer at 276 nm for DCF and 220 nm for IBU. The residual concentration was determined using a calibration curve.

2.6.4. Contact Time

To check the effect of contact time on adsorption rate, fixed concentrations of the IBU and DCF and amount of biochars were taken in separate batch experiments. The 40 mL solution containing 20 ppm concentration of either IBU or DCF was mixed with 0.08 g

of the modified biochars. The samples were kept on shaker for seven different time intervals i.e., 30 min, 1, 2, 5, 10, 20 and 24 h. At specific time intervals, a sample was extracted, filtered, and its absorbance was measured using a spectrophotometer at 220 nm for IBU and 276 nm for DCF. The residual concentrations were determined by calculating them from the standard calibration curve. The adsorption capacity and removal percentage were calculated from above given equations.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Characterization of Biochars

Chemically modified pinecones (PB), apricot kernel shells (AB) and walnut shells biochars (WB) were subjected to proximate and ultimate analysis, as they are extremely important when examining the properties of carbonaceous materials.

3.1.1. Proximate and Chemical Analysis Results

The results of proximate analysis, yield percentage, pH, pH_{PZC} and EC of the modified biochars are presented in Table 3.1. The yield of PB was comparatively higher (36%) than AB and WB. Biomass having high lignin content produces high yield biochar (Ahmad *et al.*, 2014). PB biochar was derived from pine cones, which contains 37.4% of lignin, 46.5% hemicellulose etc. (Ahmed *et al.*, 2022), thereby resulting in greater production yield. The yield of WB was 30.69% and that of AB was 30.13%. This is because of the decomposition of cellulose and hemicellulose which are the main components of fruit kernels. A yield of 32.5 percent was obtained by pyrolysis of waste apricot kernels at 500 °C for 1 h in a study by Pap *et al.* (2021). It shows longer pyrolysis times and higher temperatures decrease the yields.

Table 3.1: Yield percent, proximate and physico-chemical analyses of biochars derived from pine cone (PB), apricot shells (AB) and walnut shells (WB).

Parameters	PB	AB	WB
Yield (%)	36.00±0.91	30.13±0.02	30.69±0.04
Moisture (%)	5.39±0.03	2.28±0.07	2.42±0.14
Mobile matter (%)	9.23±0.16	11.43±0.92	14.03±1.7
Ash (%)	1.79±0.006	0.61±0.02	1.76±0.7
Resident matter (%)	83.65±0.12	85.67±0.98	81.77±0.93
pH	6.64±0.17	2.27±0.02	2.11±0.04
EC (dS m ⁻¹)	0.354±0.7	0.652±0.7	1.084±1.41
pH _{PZC}	6.3	6	6

The total moisture content for PB, AB and WB biochars were 5.39%, 2.28% and 2.42%. During pyrolysis, moisture and volatiles are evaporated, hemicellulose breaks down

and at temperatures exceeding 500 °C, lignin and other organic materials with stronger chemical bonds degrade (Ca'rdenas-Aguiar *et al.*, 2017). Mobile matter of biochars were 9.23%, 11.43% and 14.03% for PB, AB and WB, respectively. The decrease in volatile matter was caused by the conversion of volatile substances into pyrolysis byproducts. The ash contents were 1.79% for PB, 0.61% for AB and 1.76% for WB, respectively. The resident matter for PB, AB and WB were 83.65%, 85.67% and 81.77% comparable with walnut shells, palm char shells and wheat straw biochar reported by Alfattan *et al.* (2021). The resident matter of all biochars were greater than the mobile matter, demonstrating the stability of biochars as it makes up a significant component of the biochar's overall carbonised organic matter (Ahmed *et al.*, 2022).

Biochars often have an alkaline pH (ranging from 7.1 to 10.5). Different biomass types can have different effects on pH (Tomczyk, 2020). The pH was 6.64 for PB, 2.27 for AB and 2.11 for WB modified biochars. Their acidic nature was because of FeCl₃ and ZnCl₂, two Lewis acids that were impregnated into the biochars. The EC values were 0.354±0.7 dS/m, 0.652±0.7 dS/m and 1.084±1.41 dS/m for modified PB, AB and WB respectively. The variations may be attributed to the composition of biomass, production process and raw materials that have a significant impact on the properties of the biochar (Li *et al.*, 2013). The pH_{PZC} values for PB, AB and WB were 6.3, 6 and 6 respectively. The pH_{PZC} data is extremely useful in figuring out the optimal pH for adsorption and fully understanding the adsorption mechanisms (Naima *et al.*, 2022).

3.1.2 Surface Morphology of Modified Biochars

The SEM images of PB, AB and WB biochars at resolution of 10 µm are shown in Fig. 3.1. Porous structure was observed in all the modified biochars.

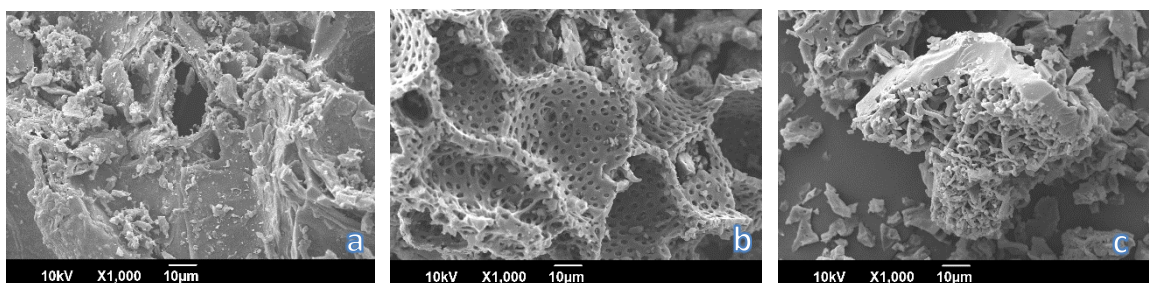


Fig 3.1: Scanning electron microscopy (SEM) images of modified biochars derived from (a) pinecones (PB), (b) apricot shells (AB) and (c) walnut shells (WB).

The surface morphology revealed that PB developed a rough irregular surface, AB consisted of numerous small sized pores, while WB had a fibrous porous structure, all resulting in an increase in surface porosity. Presence of micropores in biochars generally results in high surface area, which is a key factor in controlling the adsorption of contaminants in water.

The EDX spectra of the modified biochars are presented in Fig. 3.2. Different areas were focused and the peaks in EDX spectra confirmed the presence of Zn and Fe in the modified biochars.

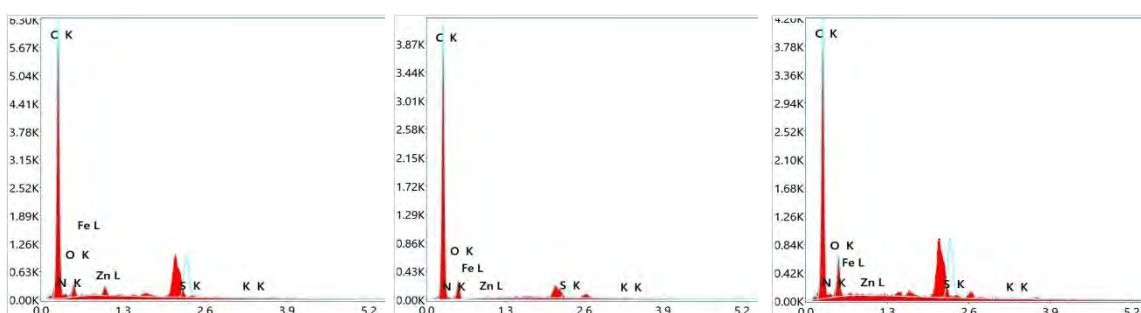


Fig. 3.2: EDX spectra of modified biochars derived from (a) pine cone (PB), (b) apricot shells (AB) and (c) walnut shells (WB).

The elemental analysis of the modified biochar revealed that carbon (C) and oxygen (O) were the most prevalent elements in its composition. The high carbon contents indicated that the modified biochars are carbon-rich adsorbents (Naima *et al.*, 2022). For PB, the weight percent values of Zn, C and O were 0.5, 75.9 and 10.4%.

Table 3.2: EDX elemental analysis (weight%) of modified biochars derived from pine cone (PB), apricot shells (AB) and walnut shells (WB).

Elements	PB	AB	WB
C	75.9	76.1	66.6
N	7.7	4.0	5.6
O	10.4	16.8	20.8
S	4.9	1.9	5.4
K	0.2	0.2	0.2
Zn	0.5	-	-
Fe	-	0.6	0.7

The values were 0.6, 76.1 and 16.8% for Fe, C and O in case of AB while for WB the values were 0.7, 66.6 and 20.8% measured in weight percent respectively. Details of EDX quantitative results analysis are presented in Table 3.2.

3.1.3. Surface Chemistry of Modified Biochars

A flexible versatile tool used for surface characterisation of biochars is FTIR spectroscopy. It was performed to determine the functional groups existing on the modified biochars' surface. A few narrow absorption bands and relatively low intensity peaks were observed for all modified biochars. The FTIR spectra of modified PB, AB and WB are shown in Fig. 3.3.

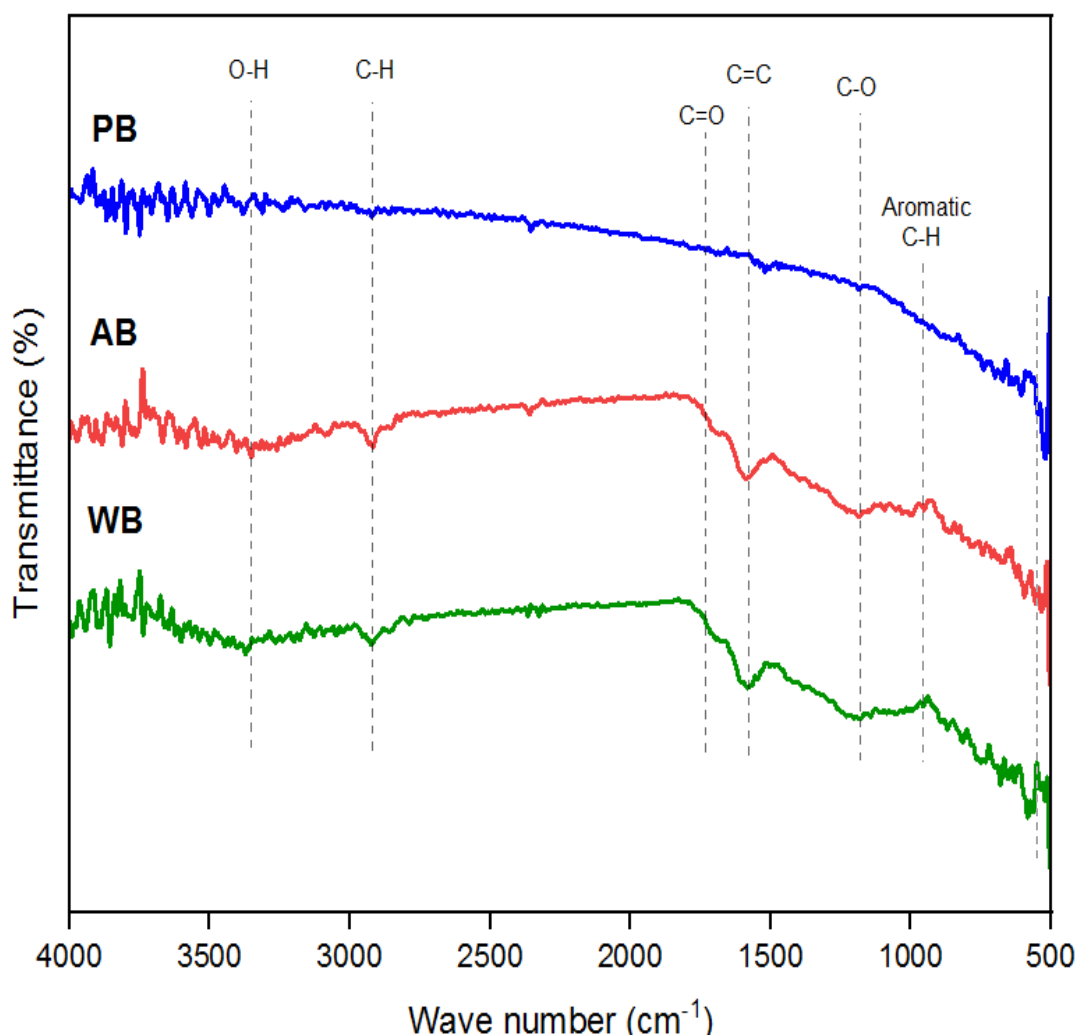


Fig. 3.3: Fourier Transform Infrared (FTIR) spectra of modified biochars derived from pinecones (PB), apricot shells (AB) and walnut shells (WB).

Pyrolysis temperature influenced the surface chemistry of biochars as few prominent peaks were observed for PB pyrolyzed at 800 °C. Peak intensities decreased with increasing pyrolysis temperature, according to the FTIR spectra. Similar weak to medium narrow bands were observed for AB and WB. The band at 3355 cm⁻¹ corresponded to hydroxyl group (O-H) vibrations which indicated the presence of H₂O, carboxylic acids and phenols (Costa *et al.*, 2021). C-H bond stretching of band at 2927 cm⁻¹ corresponded to vibration of alkyl structure of aliphatic group (Elnour *et al.*, 2019). The peaks at 1735 cm⁻¹ and 1575 cm⁻¹ represented the stretching of carbonyl bonds (C=O) and aromatic (C=C) vibrations (Malhotra *et al.*, 2018; Bagheri *et al.*, 2020) which are stronger when carboxyl and carbonyl groups are present (Costa *et al.*, 2021). The peaks at 1193 cm⁻¹ indicated C-O (esters) stretching vibrations (Yang *et al.*, 2022; De Luna *et al.*, 2017). The presence of Zn-O was indicated by the band around 556 in PB (Ying *et al.*, 2020). The special absorbance peaks in AB and WB at 515, 533, and 552 indicate Fe-O complexes in these biochars due to Fe impregnation. These findings support the successful modification of biochar (Ahmed *et al.*, 2022; Sulaiman & Al-jabari, 2021; Din *et al.*, 2021).

3.2. Removal of NSAIDs from Water with Modified Biochars

Modified PB, AB and WB biochars obtained from different feedstocks and produced at different temperatures were used to determine their efficiency for the removal of two NSAIDs, i.e. diclofenac (DCF) and ibuprofen (IBU). To ascertain the impact of starting concentration, dose of adsorbent, contact time and pH on the adsorption of DCF and IBU from water, batch adsorption studies were conducted.

3.2.1 Removal of Diclofenac

3.2.1.1 Effect of Biochar Dose on DCF Removal

The process of adsorption is significantly influenced by dosage of the adsorbent. The impact of dose on the removal percentage and adsorption rate of DCF from modified biochars is shown in Fig. 3.4 (a) and (b), respectively.

It is apparent from the figure that removal percentage of DCF increased as biochar dose increased. The removal percentage of WB was higher than PB and AB in order WB > PB > AB. DCF removal percentage increased from 6.50% to 62.2 % for PB, 1.5% to 59.39 % for AB and 4.76% to 78.30% for WB as dosage was raised from 0.5 g/L to 5

g/L. ZnCl₂ modified AC derived from tea waste also demonstrated a maximum removal of 60% at dose of 300 mg/L as reported by Malhotra *et al.* (2018). Improved DCF removal at higher dosage can be credited to increased active sites available for adsorption.

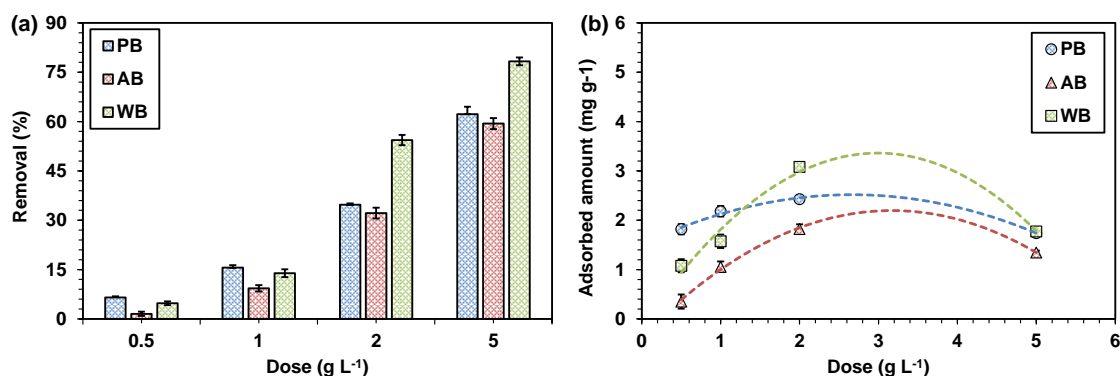


Fig. 3.4: Effect of biochar dose on (a) removal and (b) adsorption of diclofenac sodium. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

There is an overall trend that removal efficiency will increase when adsorbent dosage is raised because the surface area as well as the adsorption sites of the adsorbent will rise too (Akhtar *et al.*, 2021). Consequently, the adsorption capacity of the modified biochars were dropped at higher adsorbent doses. Similar pattern was reported by Costa *et al.*, (2021) and Tam *et al.*, (2020). The adsorption capacity increased in the beginning but as the dose was further increased, it started to decrease, which could be due to the reason that during adsorption more sites remain unsaturated and adsorbent material agglomerates which reduces the available surface area for adsorption and increases diffusion path length (Malhotra *et al.*, 2018). The DCF adsorption capacity was highest among all at dose 2 g/L i.e. PB (2.43 mg g⁻¹), AB (1.82 mg g⁻¹), and WB (3.08 mg g⁻¹). Hence, 2 g/L dose was chosen as fixed dose for other adsorption experiments.

3.2.1.2 Effect of Initial Concentration on DCF Removal

The adsorption potential of the adsorbent is impacted by the initial concentration of the adsorbate, which in turn affects the availability of binding sites. Fig. 3.5 (a) and (b) Figure illustrates the impact of initial concentration on both DCF removal and adsorption in water using modified biochars. It was observed that rate of removal of

DCF decreased with increasing concentration for PB and AB. Similar trend was observed by Malhotra *et al.*, (2018), where DCF removal efficiency was decreasing with an increase in its initial concentration in case of all the adsorbents beyond its optimum level. In contrast, an increase in removal percentage was observed for WB with an increase in the initial concentration of DCF. A similar trend in how the initial concentration affects the removal of DCF is reported by De Luna *et al.* (2017) and Jodeh *et al.* (2016). Elevated DCF concentrations fostered enhanced interactions between the adsorbent and adsorbate, consequently yielding higher removal percentages. However, the adsorption capacity was increased for all modified biochars. This resulted from more solute molecules being available and competing for a fixed number of binding sites on the biochars surface. Resultantly, the number of unsaturated sites decreased, thereby increasing the adsorption capacity (Malhotra *et al.*, 2018).

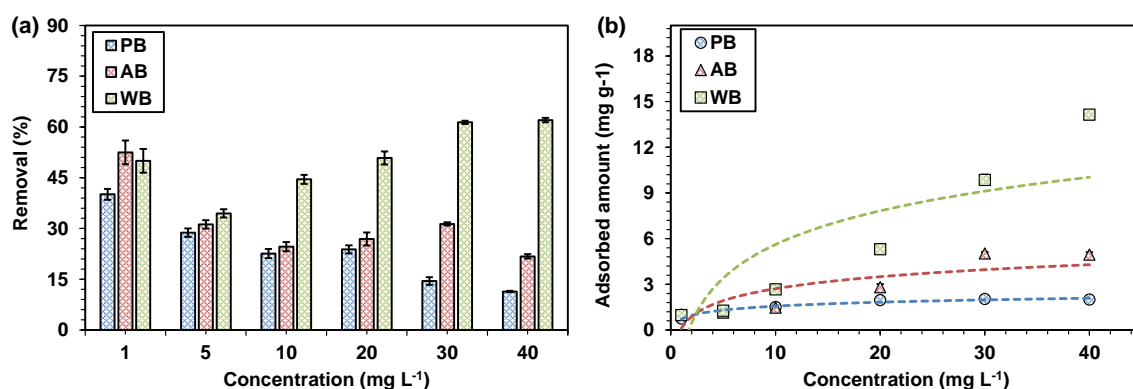


Fig. 3.5: Effect of initial concentration on (a) removal and (b) adsorption of diclofenac sodium. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

From the results, it is clear that WB biochar showed better adsorption performance than PB and AB at different initial concentrations of DCF. Also, WB exhibited higher removal and adsorption performance at highest initial concentration of 40 mg/L i.e., up to 62.04%, and 14.15 mg g⁻¹, respectively. The adsorption capacity of PB and AB observed at 40 mg/L were 2 mg g⁻¹ & 4.96 mg g⁻¹ respectively.

3.2.1.3 Application of Adsorption Isotherm Models

Various isotherm models were used to anticipate the mechanisms involved in the adsorption process. The four most used isotherm models are Langmuir, Freundlich, Temkin and Dubinin-Radushkevich model.

According to Langmuir isothermal model, every adsorption is homogeneous, occurring in monolayers, and each active site has an equal amount of energy (Alessandretti *et al.*, 2021). The Langmuir model can be expressed by the following equation:

$$Q_e = Q_{max} K_L C_e (1 + K_L C_e)^{-1} \dots \dots \dots \text{(Eq. 4)}$$

where, maximum amount of pollutant adsorbed is shown as Q_{max} , expressed in mg/g and K_L is the sorption equilibrium constant expressed in L/mg.

The Freundlich isotherm model describe the multilayer adsorption on heterogeneous surfaces (Murad *et al.*, 2022). The Freundlich isotherm can be stated as:

$$Q_e = K_F C_e^{1/n} \dots \dots \dots \text{(Eq. 5)}$$

where, n is a constant associated to the adsorption intensity. K_F is the Freundlich constant that represents the adsorption capacity of the adsorbent.

The Temkin isotherm model is designed to specifically elucidate the adsorption heat within the adsorption process, offering insights into potential indirect linkages between the adsorbate and adsorbent. This model investigates the correlation between increased surface coverage and a linear reduction in the heat of adsorption across all molecules within the layer, as expressed by equation below (Ahmad, Lee, Rajapaksha, *et al.*, 2013):

$$Q_e = \frac{RT}{B} \ln (AC_e) \dots \dots \dots \text{(Eq. 6)}$$

where R , T , B , and A are the universal gas constants. Heat of adsorption is represented by B and the binding constant (L/mg) is represented by A .

The adsorption process was also explored using Dubinine Redushkevich isotherm model. Its equation is given as:

$$\ln Q_e = \ln Q_m - \beta e^2 \dots \dots \dots \text{(Eq. 7)}$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \dots \dots \dots \text{(Eq. 8)}$$

$$E = (2\beta)^{-1/2} \dots \dots \dots \text{(Eq. 9)}$$

where, \mathcal{E} is Polanyi, ideal gas constant (8.314 J/K/mol) is R , T (K) indicates thermodynamic temperature, average adsorption free energy is presented as E (kJ/mol), β (kJ²/mol²) is a constant of adsorption energy, Q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium and Q_m (mg/g) is the maximum adsorption capacity (Kong *et al.*, 2017).

The utilization of these adsorption isotherm models yielded essential insights into the adsorption characteristics of the modified biochars, including their pollutant removal affinity and capacity. To evaluate the adsorption data, all four models were employed, with the selection of the best-fit model determined by the presence of a high R^2 value. (correlation coefficient).

For DCF adsorption, modeling curves are given in Fig. 3.6. The constant parameters and values of R^2 for the models are listed in Table 3.3.

The Langmuir model exhibited values of R^2 as 0.974 for PB, 0.949 for AB and 0.982 for WB. The Langmuir model projected the highest adsorption capacity (Q_{\max}) of 13641 mg g⁻¹ for WB, a significantly greater value of Q_{\max} stated by Bernardo *et al.* (2016), Tam *et al.* (2020) and Filipinas *et al.* (2021) for DCF, while PB and AB showed Q_{\max} of 2.666 mg g⁻¹ and 14.67 mg g⁻¹ respectively. In Freundlich model, the R^2 values observed for PB, AB and WB were 0.948, 0.944 and 0.977, respectively. It demonstrates that adsorption increases as DCF concentration increases, and that this adsorption takes place in a multilayered system (Jodeh *et al.*, 2016). Further, the n parameter of the model showed the adsorption intensity, $n < 1$ which indicated normal adsorption, while $n > 1$ indicated cooperative adsorption (Kamga *et al.*, 2019). For PB and AB biochar, the n value was below 1, signifying normal adsorption behavior. In contrast, the n value for WB was above 1, indicating cooperative adsorption. The K_F values of 0.547, 0.274 and 0.134 were observed for PB, AB and WB. The R^2 values of Temkin isotherm model were 0.918 for PB, 0.855 for AB and 0.853 for WB biochar. The value of B was lower for the WB (203.2 J mol⁻¹) as compared to AB (578.5 J mol⁻¹) and PB (1749 J mol⁻¹) which indicated greater adsorption of DCF onto WB due to a decrease in the adsorption heat and a uniform sharing of the binding energies (Murad *et al.*, 2022).

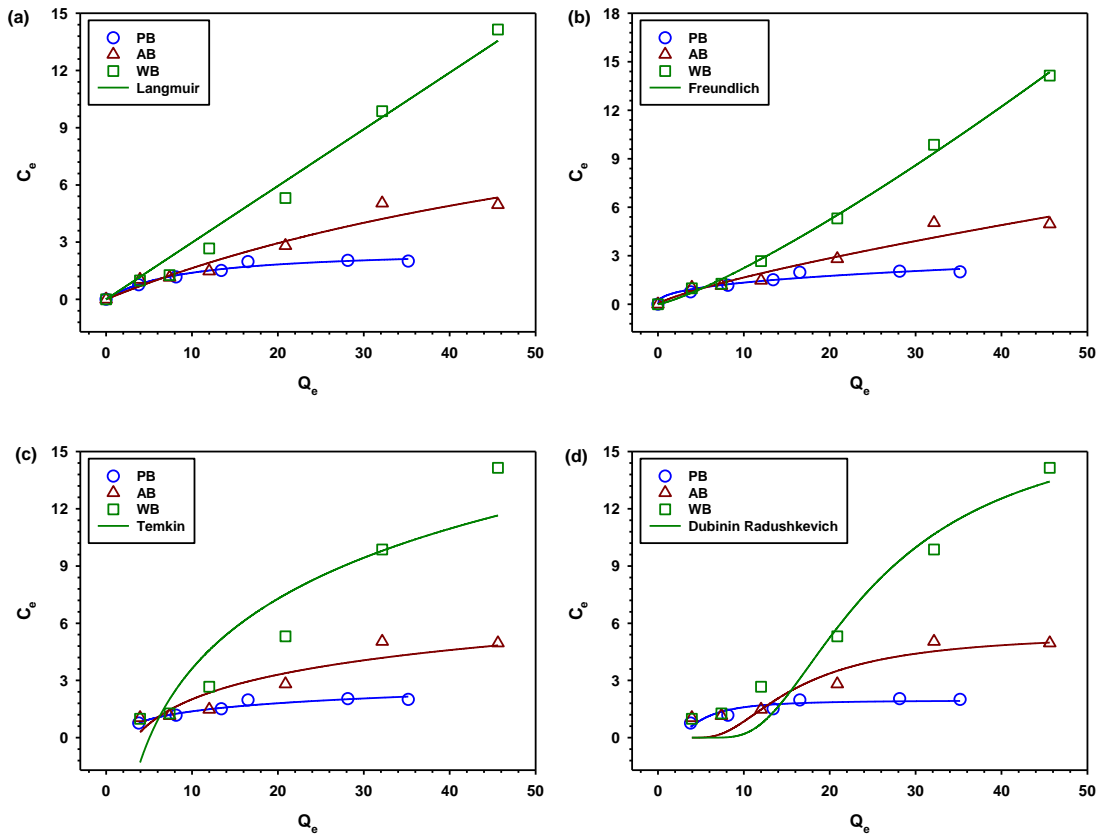


Fig. 3.6: Non-linear fittings of the (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Dubinin Radushkevich models to the adsorption isotherms of diclofenac sodium. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

In Dubinin–Radushkevich model (D-R), the R^2 values for PB, AB and WB biochars were 0.844, 0.842 and 0.945. The E parameter in D-R model presents mean sorption energy that tells information regarding the physical or chemical aspects of the adsorption process. E values below 8 kJ/mol signify physical adsorption, while E between 8 and 16 kJ/mol hints at dominant ion-exchange. E exceeding 16 kJ/mol suggests primary influence of particle diffusion in adsorption (Sathishkumar *et al.*, 2015).

In our dataset, the E values were consistently below 8 for all biochars, indicating a physical adsorption mechanism. The model predicted the highest QD value of 16.93 mg g⁻¹ for WB.

Table 3.3: Parameters calculated by the isothermal models for diclofenac sodium adsorption onto different biochars. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively

	Langmuir			Freundlich			Temkin			Dubinin Radushkevich		
	R ²	Q _{max} (mg g ⁻¹)	K _L (L g ⁻¹)	R ²	n	K _F (mg g ⁻¹)	R ²	B (J mol ⁻¹)	A (L g ⁻¹)	R ²	Q _D (mg g ⁻¹)	E (kJ g ⁻¹)
PB	0.974	2.666	0.109	0.948	0.389	0.547	0.918	1749	0.939	0.844	1.959	7.372
AB	0.949	14.67	0.013	0.944	0.782	0.274	0.855	578.5	0.295	0.842	5.489	2.454
WB	0.982	13641	2.181x10 ⁻⁵	0.997	1.224	0.134	0.853	203.2	0.198	0.945	16.93	1.587

Based on the values of R^2 , Langmuir and Freundlich isotherm models best defined the adsorption of DCF onto the modified biochars. These findings suggested that the heterogeneous surfaces of the modified biochars underwent monolayer to multilayer DCF adsorption. The Langmuir model predicted Q_{\max} of 13641 mg g^{-1} for WB indicating the biochars' greater adsorption potential. Both Langmuir and Freundlich isotherms were able to explain DCF adsorption by modified biochars as shown by other adsorption isotherm studies (Mojiri *et al.*, 2019). It is worth mentioning that a number of adsorption mechanisms may be involved in the removal due to the multivariate properties of biochar (Murad *et al.*, 2022).

3.2.1.4 Adsorption Kinetics of DCF

Important information about the underlying mechanisms including chemical reaction process and mass transport and information about physical as well as chemical properties of the biochar is revealed by adsorption kinetics data. Kinetic experiments for the adsorption of DCF were conducted from water using three modified biochars.

The outcome of contact time on adsorption of DCF by modified biochars is shown in Fig. 3.7. As the contact time was increased, the removal percentage of DCF also increased. The highest removal percentage was obtained by WB followed by AB and PB during 24 h. Equilibrium was not attained until 24 h for all the modified biochars as indicated by the slow upsurge in the adsorbed amount with time. It demonstrated the biochar's heterogeneous nature where active sites differ and impede in reaching adsorption equilibrium.

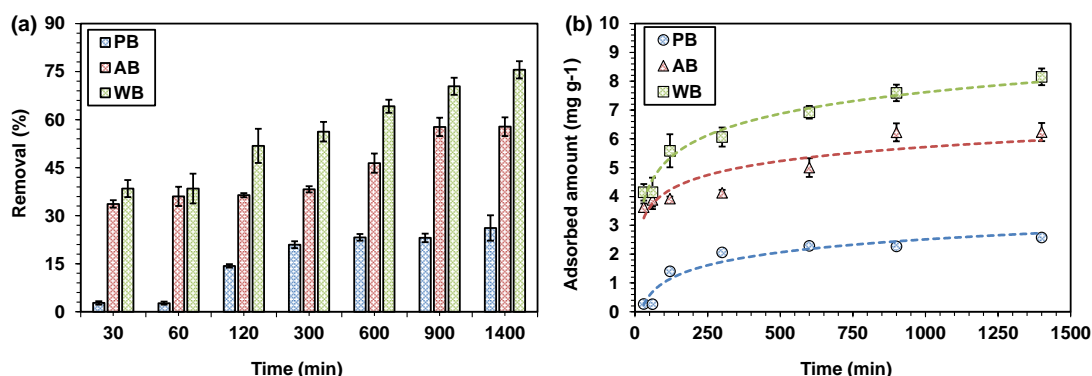


Fig. 3.7: Effect of contact time on (a) removal and (b) adsorption of diclofenac sodium. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

Amongst the modified biochars, greater adsorption was exhibited by WB at all time intervals compared to PB and AB which can be attributed to the participation of diverse functional groups in DCF adsorption. The maximum adsorption capacities of all the modified biochars were in following order WB (8.15 mg/g) > AB (6.23 mg/g) > PB (2.58 mg/g) at 24h.

3.2.1.5 Application of Kinetic Models

Adsorption equilibrium analysis is an excellent method for understanding adsorption efficiency and its mechanisms. It determines the adsorbent equilibrium time. Chemical reactions, possible rate limiting steps and the particle diffusion mechanism of DCF onto the biochar can all be predicted using adsorption kinetic models. Different models were employed as biochar is not homogenous because of involved chemical reactions and experimental inseparability of transport phenomena (Tam *et al.*, 2020). Four different kinetic models i.e. the pseudo-second order kinetic model, power function, Elovich model and the intra-particle diffusion model were employed in current study to investigate the underlying adsorption mechanisms. Equations of the four kinetic models are given below (Eq. 11) to (Eq. 14) respectively (Ahmad *et al.* 2013). The rate controlling mechanism depends on the physico-chemical interactions between adsorbate and adsorbent's surface groups according to pseudo-second order kinetic model (Antunes *et al.*, 2012). Elovich equation can be used to examine the chemisorption behavior between the adsorbate and adsorbent. Weber and Morris proposed the intraparticle diffusion model to determine the role of diffusion in the process of adsorption. The power function equation can be used to explain the relationship between adsorbate mass per unit adsorbent mass (Ahmad *et al.*, 2013).

The expressions for the models applied on experimental data are given as:

The Pseudo second-order kinetic model:

$$t/Q_t = (1/k_2Q_e^2) + t/Q_e \dots\dots\dots (Eq. 11)$$

Elovich kinetic model:

$$Q_t = 1/\beta_E \ln (\alpha_E\beta_E) + 1/\beta_E \ln (t) \dots\dots\dots (Eq. 12)$$

The intraparticle diffusion model:

$$Q_t = K_{diff} t^{1/2} + C \dots\dots\dots (Eq. 13)$$

The power function model:

$$\ln Q_t = \ln b + kf (\ln t) \dots\dots\dots (Eq. 14)$$

where Q_t (mg/g) is the adsorption capacity at time interval (t) represented by k_2 (min^{-1}) and adsorption capacity at equilibrium by Q_e (mg/g), the adsorption rate is α (g/mg/min) and β is the desorption constant.

K_{diff} denotes the intraparticle transport rate constant (g/mg/min), with C representing the intercept. The adsorbent's sorbed pollutant amount at time (t) is Q_t . The rate coefficient ($\text{mg g}^{-1} \text{min}^{-1}$) is kf , and b signifies the rate constant.

Fitting curves are presented in Fig. 3.8 and the constant parameters derived from the kinetic models are outlined in Table 3.4.

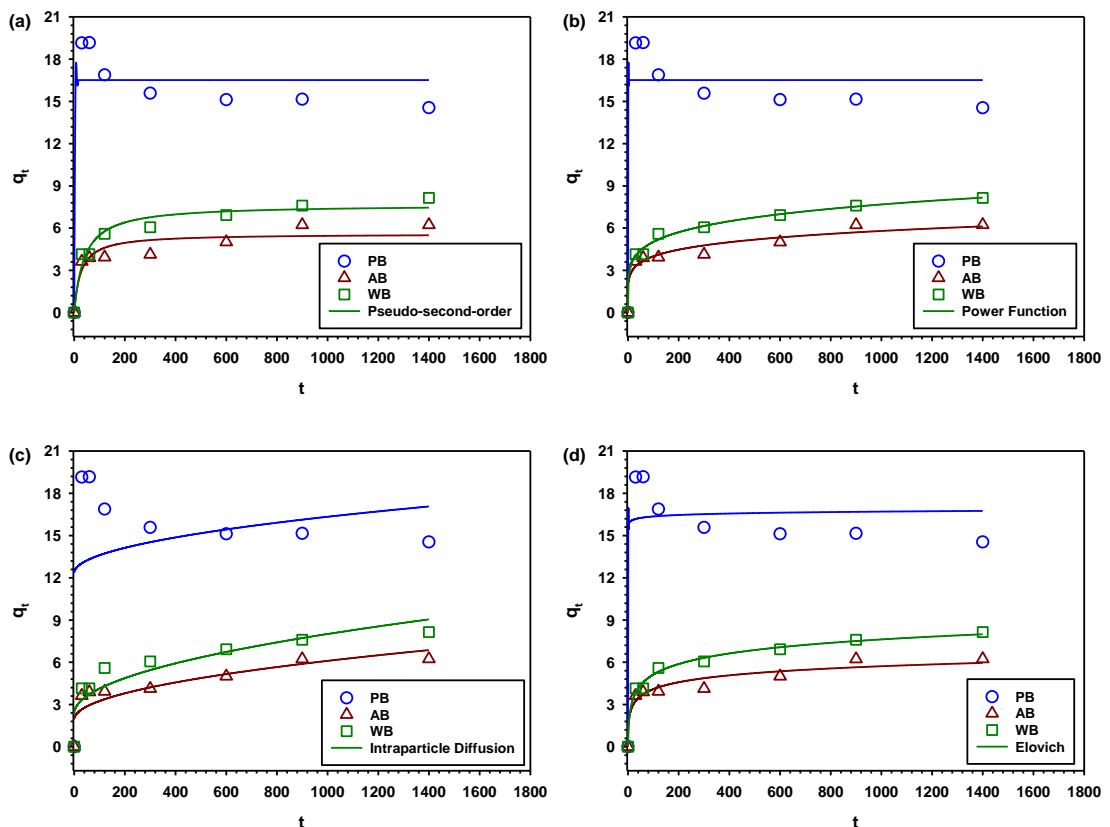


Fig. 3.8: Non-linear fittings of the (a) pseudo-second-order, (b) power function, (c) intra-particle diffusion, and (d) Elovich models to the kinetics adsorption of diclofenac sodium. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

For the pseudo-second-order model, the R^2 values were 0.913 (PB), 0.882 (AB), and 0.956 (WB). The model projected maximum adsorption capacities (Q_e) of 16.51 mg g⁻¹ (PB), 5.589 mg g⁻¹ (AB), and 7.657 mg g⁻¹ (WB).

R^2 values of 0.913 (PB), 0.963 (AB), and 0.992 (WB) were observed for the power function model. Similar to alternative kinetic models, the power function model revealed the highest predicted adsorption rate (k_f) for PB biochar, specifically 16.51 mg g⁻¹ min⁻¹ for DCF, followed by 5.589 mg g⁻¹ min⁻¹ for AB and 7.659 mg g⁻¹ min⁻¹ for WB. The Elovich model gave R^2 values as 0.893, 0.950 and 0.990 for the different biochars (PB, AB and WB), respectively. It made prediction about the rate of DCF adsorption (α) onto PB, AB and WB as 1.048×10^{43} , 2.323 and 1.198 mg g⁻¹ min⁻¹. The experimental sorption kinetics data were not well-fitted by the intra-particle diffusion model.

Additionally, the power function model exhibited R^2 values that effectively described the kinetics of adsorption data, with the Elovich and pseudo-second-order models following suit. The good fitting of the experimental DCF adsorption data to the pseudo-second-order and Elovich models explains the adsorption process was controlled by chemical interactions between biochar and DCF implying that chemisorption was the underlying mechanism. Such chemical interactions are typically caused by strong bonding amidst the surface functional groups of the adsorbent and the adsorbate.

3.2.1.6 Effect of pH on DCF Removal

Since adsorption is a surface-controlled process, the effect of pH on adsorption is a crucial parameter to investigate (Lonappan *et al.*, 2017). These experiments were performed keeping the remaining parameters constant like adsorbent dose 2 g/L, contact time 24 hours and initial concentration 20 mg/L. The effect of pH on the removal rate and adsorption capacity of DCF is shown in Fig. 3.9 (a) and (b) respectively. Maximum removal was shown by all the modified biochars in moderately acidic pH. The maximum removal percentage was achieved at pH 5 by WB (62.98 %) followed by AB (59.72 %) and PB (31.73 %). Bagheri *et al.* (2020) also reported highest removal efficiency of DCF at pH 5 by modified moringa seed powder biochar. Contrarily, the adsorption capacity of DCF decreased as the pH value increased from 5 to 9, suggesting that the solution's pH has a significant impact on the adsorption

capacity (Sulaiman & Al-jabari, 2021). All the modified biochars exhibited maximum adsorption capacity at solution pH of 5.0.

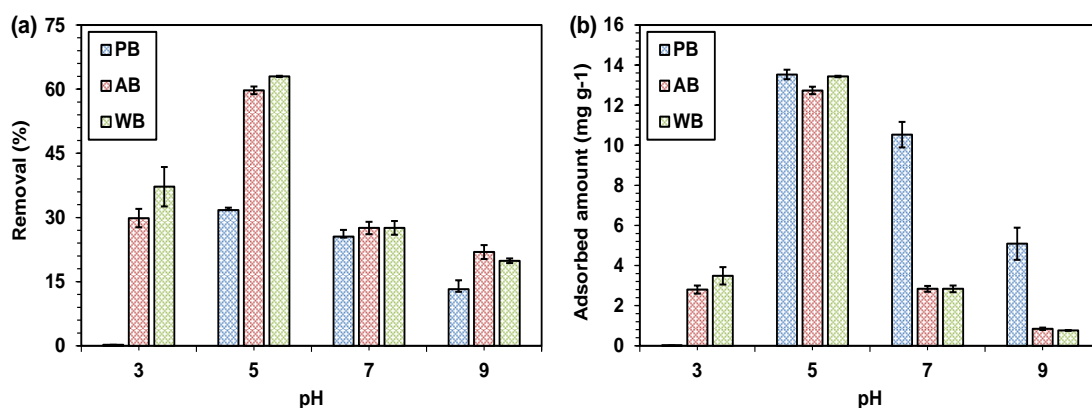


Fig. 3.9: Effect of solution pH on (a) removal and (b) adsorption of diclofenac sodium. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

3.2.2 Removal of Ibuprofen

3.2.2.1 Effect of Biochar Dose on IBU removal

Figure 3.10 illustrates the influence of varying biochar dosages on the removal of IBU from water. Removal of IBU was increased as dosage of modified biochars was increased. As the dosage was increased, removal efficiency increases while adsorption capacity decreases (Pap *et al.*, 2021). Similar trend was stated by Halder *et al.* (2018).

The highest removal rate of 75.97% was achieved using PB biochar at the maximum dose of 5 g L⁻¹. Costa *et al.* (2021) reported 70.53 % removal at maximum dose of 0.15g using murumuru endocarp, chemically activated with ZnCl₂. AB and WB biochar showed maximum removal of 48.73% and 41.84% at 5 g L⁻¹.

Concurrent decreases in the adsorption capacities (2.34 to 1.82 mg g⁻¹ for PB, 5.01 to 1.28 mg g⁻¹ for AB and 4.79 to 1.10 mg g⁻¹ for WB) were observed with increasing biochar dose due to increased diffusive resistance and decreased active surface area caused by aggregation of adsorption sites. Alternative explanation for this could be the low IBU concentration (10 mg/L) as sorption sites of the biochar are completely filled in this condition (Costa *et al.*, 2021).

Table 3.4: Parameters calculated by the kinetic models for diclofenac sodium adsorption onto different biochars. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

	Pseudo-second-order			Power function			Intra-particle diffusion			Elovich		
	R ²	Q _e (mg g ⁻¹)	K ₂ (g mg ⁻¹ min ⁻¹)	R ²	K (mg g ⁻¹)	v	R ²	K _d (mg g ⁻¹)	C (L g ⁻¹)	R ²	α (mg g ⁻¹ min ⁻¹)	β (mg g ⁻¹ min ⁻¹)
PB	0.913	16.51	3.68x10 ⁶	0.913	16.51	3.04x10 ⁻¹⁷	0.072	-	-	0.893	1.048x10 ⁴³	6.458
AB	0.882	5.589	0.007	0.963	1.895	0.162	0.763	0.132	1.932	0.950	2.323	1.416
WB	0.956	7.657	0.003	0.992	2.147	0.1844	0.805	0.180	2.334	0.990	1.198	0.919

Available adsorption sites are limited at lower IBU dose which results in larger adsorption capacity. Additional active sites are introduced as the adsorbent dosage is raised, which in turn enhances removal efficiency while overall adsorption is lowered (Zhang *et al.*, 2019b).

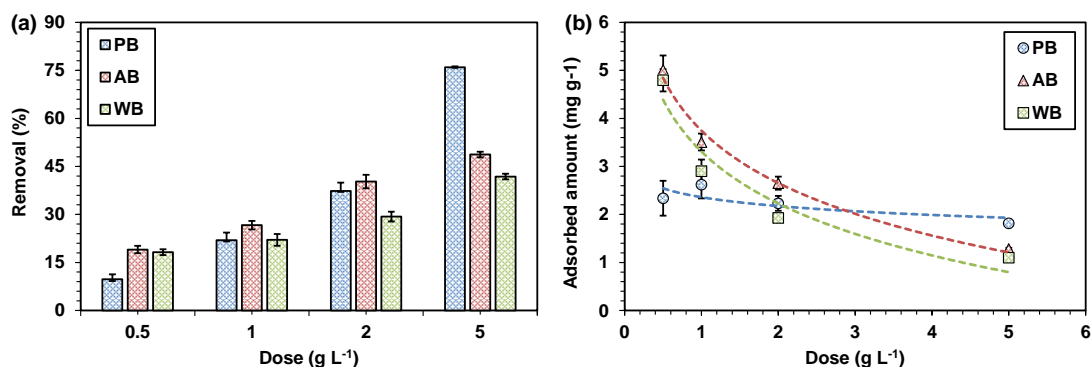


Fig. 3.10: Effect of biochar dose on (a) removal and (b) adsorption of ibuprofen. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

3.2.2.2 Effect of Initial Concentrations on IBU removal

The results of initial concentration on adsorption of IBU by modified biochars are shown in Fig. 3.11. Removal percentage of IBU decreased with increase in concentration of IBU in PB following the general trend. However, in case of AB and WB the removal percentages decreased initially with increasing concentration, but both showed an increase at 20 mg/L until it finally exhibited reduction in removal percentage as maximum concentration was reached.

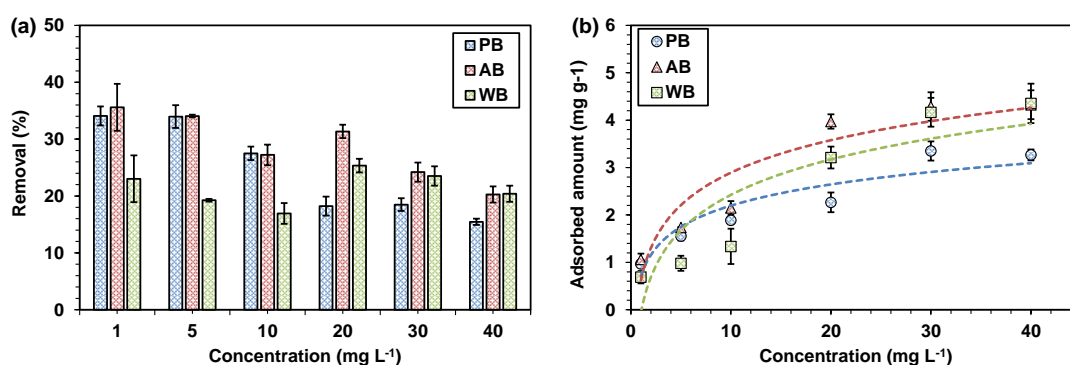


Fig. 3.11: Effect of initial concentration on (a) removal and (b) adsorption of ibuprofen. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

This phenomenon may be attributed to the saturation of active sites on the adsorbents by neighboring IBU molecules, resulting in a restriction of available active sites on the adsorbent surface (Chakraborty *et al.*, 2018). Highest removal % was achieved at 1 mg/L for all biochars i.e. 34.07 % for PB, 35.59% for AB and 23.03% for WB. As we know a general trend follows, when concentration is increased, the adsorption capacity is increased due to saturation of active sites. The adsorption capacities of modified biochars at maximum concentration (40 mg/L) were 3.27 mg g⁻¹ for PB, 4.33 mg g⁻¹ for AB and 4.35 mg g⁻¹ for WB.

3.2.2.3 Application of Adsorption Isotherm Models

In this study, four adsorption models were employed to analyze the IBU adsorption data using modified biochars. The most suitable model was determined based on the R² values. The values of Q_e and modeling curves for IBU adsorption are given in Fig. 3.12. The values of R² and constant parameters and for various models are given in Table 3.5.

The values of R² values of Langmuir model for PB, AB and WB were 0.977, 0.972 and 0.971 respectively. The Maximum adsorption capacity (Q_{max}) was 81 mg g⁻¹ for WB while Q_{max} for PB was 5.273 mg g⁻¹ and 9.144 mg g⁻¹ for AB. Q_{max} reported by Show *et al.*, (2020) for IBU were 8.635 mg/g and 10.570 mg/g respectively by raw and chemically modified tamarind biochar. In the Freundlich model, the values of R² were 0.981, 0.961 and 0.972 for PB, AB and WB. The constant n describes the adsorption system, which indicates intensity of adsorption as well as heterogeneity of the surfaces. When the obtained value of n is > 1, the adsorbate and adsorbent simply interact which indicates the high capacity of the adsorbent to remove the pollutants (Pap *et al.* 2021). The value of n for PB and AB was <1, which indicated normal adsorption. The n value greater than 1 indicates cooperative adsorption in WB. Value of n near to 0 in PB and AB indicate surface heterogeneity and are likely related to the existence of several surface functional groups (Costa *et al.*, 2021). The K_F value was highest for PB i.e., 0.409 mg/g which suggests higher affinity of PB as compared to AB and WB. In Temkin isotherm model, values of R² obtained for PB was 0.951, 0.947 for AB and 0.913 for WB. The value of B was highest for PB (936.5 J mol⁻¹) followed by AB (581 J mol⁻¹) and WB (517.3 J mol⁻¹). In D-R model, the R² values were 0.821, 0.878 and 0.930 for PB, AB and WB, respectively. The value of E was less than 8 in all the

modified biochars depicting that physisorption occurs in all. The highest Q_D value was observed for WB (5.073 mg g⁻¹).

Based on the R^2 values, it can be said that the Langmuir isotherm model along with Freundlich isotherm model as well as Temkin isotherm model fitted well to our experimental sorption data of IBU. Langmuir suggests monolayer to multilayer adsorption while Freundlich assumes heterogeneous surfaces. Hence it showed that adsorption on the heterogeneous surface was in monolayers and multilayers.

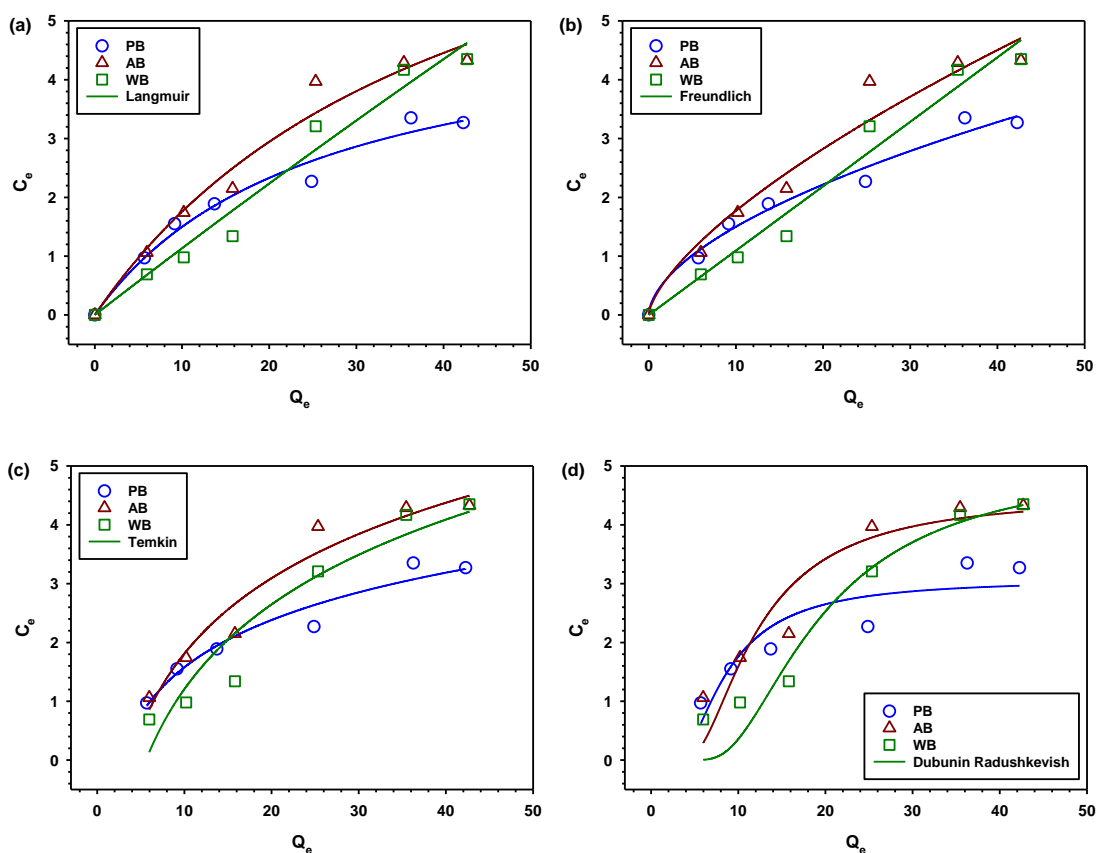


Fig. 3.12: Non-linear fittings of the (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) Dubinin Radushkevich models to the adsorption isotherms of ibuprofen. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

Table 3.5: Parameters calculated by the isothermal models for ibuprofen adsorption onto different biochars. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

	Langmuir			Freundlich			Temkin			Dibinin Radushkevich		
	R^2	Q_{\max} (mg g^{-1})	K_L (L g^{-1})	R^2	n	K_F (mg g^{-1})	R^2	B (J mol^{-1})	A (L g^{-1})	R^2	Q_D (mg g^{-1})	E (kJ g^{-1})
PB	0.977	5.273	0.040	0.981	0.564	0.409	0.951	936.5	0.389	0.821	3.065	4.499
AB	0.972	9.144	0.024	0.961	0.673	0.376	0.947	581.3	0.266	0.878	4.491	3.293
WB	0.971	81.39	0.001	0.971	1.001	0.109	0.913	517.3	0.179	0.930	5.073	2.059

3.2.2.4 Adsorption Kinetics of IBU

The results of kinetic adsorption experiments conducted for IBU are shown in Fig. 3.13. The results revealed that biochars' adsorption capacities increased with increase in time interval. This observation is consistent with other studies conducted for IBU removal using pinewood biochar (Essandoh *et al.*, 2015). For the experiment of contact time, the removal percentage increased from 5.27 to 21.34% for PB, 16.81 to 29.11% for AB, 14.40 to 33.67% for WB. The increase in adsorption capacity i.e. 0.58 to 2.34 mg/g for PB, 1.85 to 3.20 mg/g for AB and 1.58 to 3.70 mg/g for WB with passage of time indicates that equilibrium did not achieved until 24 h, probably due to the biochar's heterogeneous nature. Pap *et al.* (2021) also reported a steady increase during the entire tested time period. The maximum adsorption capacities for the three modified biochars were in the following order: WB (3.70 mg/g) > AB (3.20 mg/g) > PB (2.34 mg/g) after 24 h.

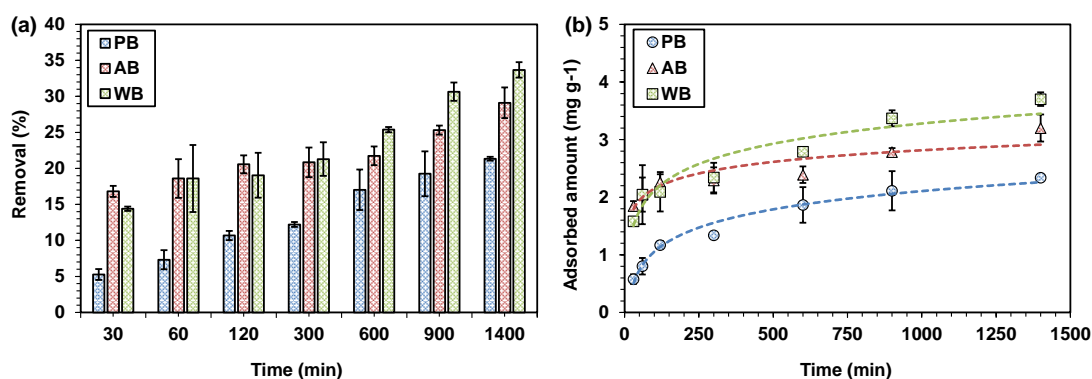


Fig. 3.13: Effect of contact time on (a) removal and (b) adsorption of ibuprofen. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

3.2.2.5 Application of Kinetic Models

The rate of pollutant removal is quantified in order to model adsorption and determine the contact time required to achieve a desired pollutant removal in water treatment processes (Ndoun *et al.*, 2021). The R^2 values along the kinetic parameters of the applied kinetic models to the adsorption data of IBU on the three modified biochars are given in Table 3.6. The R^2 values for the pseudo-second-order model were 0.966 (PB), 0.929 (AB), and 0.908 (WB), indicating that the sorption process's rate-limiting step could be chemisorption. This implies the potential involvement or exchange of

electrons through valency forces between IBU molecules and the adsorbent. The R^2 values for power function kinetic model was 0.991 for PB, 0.974 for AB and 0.982 for WB. The kinetic data was well suited to this model, as evidenced by the constant value of v which was <1 for all biochars. Elovich is based on the assumption that adsorbent's surface possesses diverse energy levels, resulting in the presence of varying activation energies (Pap *et al.*, 2021), R^2 values predicted by this model were 0.990, 0.969 and 0.968 for PB, AB and WB, confirming that chemisorption was the dominant mechanism during adsorption. Intra-particle diffusion model's R^2 values for PB, AB and WB were 0.959, 0.689 and 0.860, respectively. So, the results showed that the three models i.e. power function, Elovich and pseudo-second order kinetic model defined the adsorption data very well.

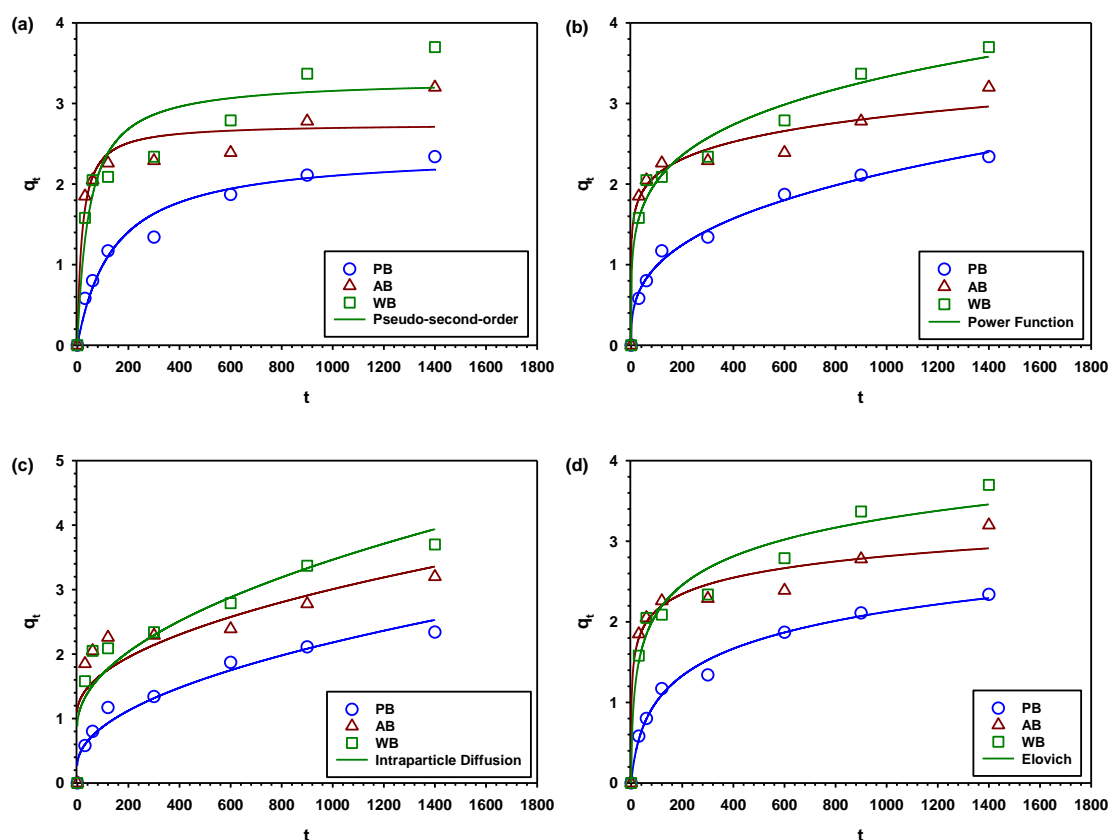


Fig. 3.14: Non-linear fittings of the (a) pseudo-second-order, (b) power function, (c) intra-particle diffusion, and (d) Elovich models to the kinetics adsorption of ibuprofen. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

Table 3.6: Parameters calculated by the kinetic models for ibuprofen adsorption onto different biochars. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively

	Pseudo-second-order			Power function			Intra-particle diffusion			Elovich		
	R ²	Q _e (mg g ⁻¹)	K ₂ (g mg ⁻¹ min ⁻¹)	R ²	K (mg g ⁻¹)	v	R ²	K _d (mg g ⁻¹)	C (L g ⁻¹)	R ²	α (mg g ⁻¹ min ⁻¹)	β (mg g ⁻¹ min ⁻¹)
PB	0.966	2.400	0.003	0.991	0.208	0.337	0.959	0.061	0.266	0.990	0.032	1.947
AB	0.929	2.747	0.019	0.974	1.174	0.128	0.689	0.061	1.093	0.969	4.669	3.440
WB	0.908	3.302	0.007	0.982	0.757	0.215	0.860	0.082	0.876	0.968	0.299	1.938

Among the three kinetic models, power function was the best suited model to the experimental data of IBU based on its R^2 values followed by Elovich model and pseudo-second order kinetic models. So, the fitting of different kinetic models reveals that various mechanisms are involved in the adsorption of IBU onto biochars.

3.2.2.6 Effect of pH on Ibuprofen removal

The initial solution pH had a substantial impact on the adsorption of IBU by affecting the surface characteristics of the modified biochars as well as changing the speciation of IBU (Patel *et al.*, 2022). The experimental conditions for IBU were same as DCF. Contrasting trends were followed by each modified biochar at different pH levels as shown in the Fig. 3.15. AB and WB showed maximum IBU removal at pH 5 with 52.83% and 12.67% removal while PB biochar performed better at pH 3 with 31.41% removal. Also, increase in pH caused decrease in adsorption capacity of the biochars. The highest adsorption capacity was achieved by PB (13.81 mg/g) greater than 2.28 mg/g attained by $ZnCl_2$ activated carbon reported by Costa *et al.* (2021), followed by AB (6.13 mg/g) and WB (3.51 mg/g). The maximum removal % of IBU was reported at pH 3 by Essandoh *et al.* (2015) and at pH 2 by Yang *et al.* (2022), Show *et al.* (2020) and Mondal *et al.* (2016). Furthermore, Chakraborty *et al.* (2018) observed that when pH was raised from 2 to 6, the IBU adsorption decreased from 36 to 5% and 26 to 10% by simple and activated wood apple biochars, respectively. In both cases, the maximum percentage removal of IBU was obtained at about pH 2.5.

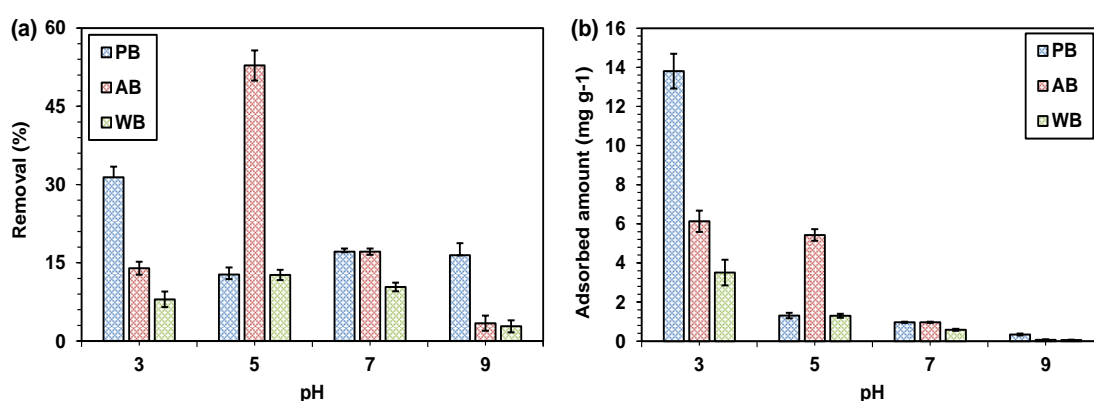


Fig. 3.15: Effect of solution pH on (a) removal and (b) adsorption of ibuprofen. PB, AB and WB are modified biochars derived from pine cone, apricot shell and walnut shell, respectively.

3.2.3 Possible Mechanism(s) of NSAIDs Adsorption onto Modified Biochars

Adsorption mechanism is an imperative study that relates to the sorbate's adherence phenomena onto the sorbent, which can be attributed for the success of a sorption process (Chakraborty, 2020c). In this study, ZnCl₂ modified (AB) and FeCl₃ modified (AB & WB) biochars were employed for the removal of diclofenac and ibuprofen from water. The contaminant is adsorbed on the surface of the adsorbent in two different ways, i.e., (i) Chemisorption and (ii) physisorption. Chemisorption occurs through mechanisms such as covalent bonding, coordination, and attraction between opposite or coulombic ions. It is a gradual process that forms a monolayer on the adsorbent surface. On the other hand, physisorption involves attachment to the adsorbent surface through weak forces like electrostatic attraction and Van der Waals forces, resulting in the creation of a multilayer structure. (Sandoval-González *et al.*, 2022). The three primarily reported adsorption interactions observed for NSAIDs with carbonaceous adsorbents are electrostatic attraction (or repulsion), π - π and n- π EDA (electron donor acceptor) forces, hydrophobic interaction and H-bonding. Electrostatic interactions are primarily determined by surface charge, which is determined by solution pH, pKa of the adsorbate and pH_{PZC} of the adsorbent.

IBU and DCF both have one step of acid dissociation. Both consist of hydrophilic and hydrophobic components. The presence of aromatic rings causes their hydrophobic behavior, whilst the H of the carboxylic group causes their hydrophilic (acidic) nature, which at pH levels higher than pKa become ionisable. These NSAIDs experience a resonance structure transition and gradually become negatively charged when the pH of the solution increases. Due to electrostatic repulsion that is predicted to result from this, their adsorption becomes unfavorable, however, alternative interactions including H-bonding, EDA, and hydrophobic interactions may remain present (Pap *et al.*, 2021).

The sorption potential of DCF and IBU on the modified biochars is likely influenced by the diverse functional groups present on their surfaces. Notably, aromatic rings, which develop during the high-temperature biochar production, constitute a predominant surface feature of the material (Liyanaage *et al.*, 2020). The oxygen-containing functional groups, such as C=O, C-O and OH, may have a favorable effect on the adsorption of some organic compounds (Shirani *et al.*, 2020). These oxygenated functional groups on surfaces of biochar increase after the acidic treatment (Patel *et al.*,

2022). Moreover, the tailored porous structure and rough surface of the biochars permitted for more active sites, that might have been advantageous for NSAIDs adsorption.

3.2.3.1 Diclofenac

It is necessary to investigate how solution pH and pH_{PZC} affect the adsorption performance of DCF. The pH_{PZC} of the modified biochars are given in Table 3.1. When pH is greater than pH_{PZC} ($pH > pH_{PZC}$), the biochar surface is negatively charged. On the other hand, it is positively charged when pH is less than pH_{PZC} ($pH < pH_{PZC}$). DCF has a pK_a value of 4.15. It exists in an un-dissociated form when $pH < 4.15$. When the pH surpasses the pK_a value, DCF molecules acquire a negative charge. With the solution pH rising beyond both the pH_{PZC} and pK_a , both the adsorbent and adsorbate carry negative charges, leading to reduced interactions and consequently lower DCF removal (De Luna *et al.*, 2017). High adsorption is anticipated at lower pH where the neutral form of DCF predominates (Czech *et al.*, 2021).

Moreover, when $pH > pK_a$, the modified biochars have a positive net charge until pH 6 (pH_{PZC} of PB=6.3, AB & WB=6). Thus, the strong electrostatic attraction between the DCF and the modified biochars account for the high adsorption capacity at low pH values (< 7.0) (Sulaiman & Al-jabari, 2021). The biochar surfaces are negative when $pH > pH_{PZC}$, and DCF likewise has a negative charge. So, adsorption becomes progressively unfavorable at higher pH values due to rising electrostatic repulsions (Phasuphan *et al.*, 2019; Shirani *et al.*, 2020).

The uptake at high pH values despite the negatively charged surface suggests the contribution of other interactions responsible for adsorption, such as hydrogen bond formation between -COOH and C-O groups from biochar and DCF, dispersive interactions between π -electrons of biochar and π -electrons of the aromatic ring of DCF and hydrophobic interactions between DCF and biochar surfaces. On the other hand, pore filling mechanism can take part in the adsorption of DCF (Alvear-Daza *et al.*, 2022). Additionally, according to Shirani *et al.*, (2020), Lewis acid-base interaction may be the cause of the adsorption of DCF onto the adsorbent where the O-containing groups of adsorbent act as Lewis acids and the amino groups of DCF molecules perform as Lewis bases.

The drastic reduction in removal efficiency was relatively low in PB. Regardless of pH, existence of oxygen-containing functional groups, such as carboxylic acids, may have assisted in adsorption through hydrogen bonding. Furthermore, The electron-attracting effect of polar functional groups, such as hydroxyl and amine groups, may occur at basic pH levels, and as a result, these groups can interact with aromatic rings (π electron acceptors) in PB (Lonappan *et al.*, 2017).

3.2.3.2 Ibuprofen

The pH of the system affects the stability of IBU. The two variables influencing pH phenomena are pKa value of IBU and surface charge of adsorbents (pH_{PZC}). IBU has a pKa value of 4.9. Above 4 pH, anionic IBU is the dominating species while at lower value, it is primarily present in its molecular form. IBU can quickly bind to the H^+ ions and become adsorbed at lower pH levels. In acidic conditions, where protonated IBU is predominant in solution, the strong interfaces between protonated form of IBU and biochar surfaces appear to maximize removal (Chakraborty *et al.*, 2018). On the other hand, IBU begins to change into its anionic form at pH levels over 4. It is possible to have weak interaction between the biochar and deprotonated IBU given the decrease in quantity adsorbed at basic solution pH. IBU is neutral at pH 3 and the surface charge of the biochars is primarily positive, the removal efficiency was increased by dominant dispersive interactions.

Additionally, pH changes also have an impact on the adsorbent's surface chemistry because of the dissociation of the functional groups (Mondal *et al.*, 2016). Biochar surfaces display a positive charge when the pH is lower than their pH_{PZC} , and a negative charge when the pH exceeds the pH_{PZC} . The positive charge on biochar surfaces results in minimal electrostatic interactions between the adsorbate and adsorbent below pH 4. However, these interactions intensify as the pH increases, primarily because IBU takes on an anionic form above its pKa. (Show *et al.*, 2020). Furthermore, at $pH > pH_{PZC}$ electrostatic repulsion between the negative biochar surfaces and carboxylate anions intensify, resulting in decreased removal efficiency. Even when the interactions are repulsive, IBU is adsorbed on the biochars, demonstrating that π -acceptor interactions drive the adsorption pathway (Ocampo-Perez *et al.*, 2019).

According to several researchers, pore filling, hydrogen bonding, Van der Waals, π - π , n- π and electron donor-acceptor interactions, may all be involved in IBU adsorption (Naima *et al.*, 2022). The phenolic, hydroxyl, and carboxylic groups on the surface of pine wood biochar were responsible for facilitating the adsorption of IBU, as per Essandoh *et al.* (2015).

CONCLUSION

Pine cones, apricot shells and walnut shells were pyrolyzed at 500 °C and 800 °C and impregnated with ZnCl₂ and FeCl₃ to improve their properties in order to influence their sorption capabilities towards diclofenac and ibuprofen. Results showed ZnCl₂ modified pinecone biochar (PB) performed better in removal of ibuprofen while FeCl₃ modified walnut biochar (WB) performed better in removal of diclofenac from water, indicating greater adsorption potential towards diclofenac than ibuprofen. Langmuir and Freundlich models best represented the adsorption process of diclofenac and ibuprofen. Adsorption kinetics data for diclofenac and ibuprofen fitted well to the power function, Elovich, and pseudo-second-order models suggesting their adsorption onto biochars is the result of a number of mechanisms. DCF and IBU removal from water involves electrostatic interaction, hydrogen bonding, chemical bonding, Van der Waals forces and π - π interaction mechanisms. It is evident from the study that the modification of biochar can effectively adsorb ibuprofen and diclofenac from water and can be set in for effective research in future.

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