

Synthesis and Application of Recycled Carbon Fibre-Based Adsorbents for the Removal of Antibiotics from Freshwater Aquaculture Environments

A thesis submitted for the degree of Doctor of Philosophy

by

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Abstract

The growing environmental impact of end-of-life carbon fibre composites and the rising use of antibiotics in aquaculture present two critical sustainability challenges. Carbon fibre reinforced polymers, widely used in aerospace and automotive industries, generate significant waste. While aquaculture is a major source of pharmaceutical pollution. Antibiotics such as ciprofloxacin and oxytetracycline are commonly used in fish farming and have been linked to the emergence of antimicrobial resistance in aquatic environments.

This research aimed to develop high-performance, sustainable carbon-based adsorbents using recycled carbon fibres recovered from Carbon fibre reinforced polymer waste, and to optimise their use for the removal of ciprofloxacin and oxytetracycline from water. A systematic approach was applied to optimise each stage of the adsorbent development process including chemical activation, surface modification, adsorption, and regeneration. Design of Experiments techniques were used to identify optimum process parameters.

Initial testing with sodium hydroxide-activated recycled carbon fibres yielded low adsorption capacities (16.84 mg/g for methylene blue), indicating incomplete activation. Process optimisation employing potassium hydroxide significantly improved adsorbent performance. The optimum conditions were identified as an activation temperature of 670 °C, impregnation ratio of 1:10 (CF:KOH) and hold time of 0.5 h, achieving methylene blue adsorption capacities above 450 mg/g and yields exceeding 70%. Surface-modified samples utilising 10 M nitirc acid, 16 h contact time at 28 °C, resulted in increased acidity and mesoporosity. However, it was found that additional modification was not essential to maintain high antibiotic removal. Optimised adsorption conditions were identified to be an adsorbent dose of 0.8 g/L, pH of 2 and initial concentration of 2 mg/L, which resulted in removal efficiencies above 95% for both CIP and OTC. Regeneration studies using 0.1 M potassium hydroxide demonstrated strong reusability, with regeneration efficiencies remaining above 75% over seven cycles.

The results confirm that recycled carbon fibre-derived adsorbents are effective, reusable, and environmentally sustainable materials for removing antibiotic contaminants from aquaculture wastewater.

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Peer-Reviewed Journal Publications and Conference Proceedings

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Declaration

I declare that the content presented within this thesis are entirely my own original work, which have not been submitted for the fulfilment of any other academic award. During my time as a research degree candidate at Brunel University London, I have not been registered in any other program at Brunel or any other academic institution. Furthermore, I declare that I have completed all necessary coursework and requirements related to my research degree registration.

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Rest in Peace

10.06.1964-18.06.2022

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Peter John Taylor 24 April 1958 – 7 March 2025

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List of Abbreviations

AC	Activated carbon
ANOVA	Analysis of variance
BBD	Box-Behnken design
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CA	Carbonaceous adsorbent
CCD	Central composite design
CF	Carbon fibre
CFRP	Carbon fibre reinforced polymer
CIP	Ciprofloxacin
СМС	Critical micelle concentration
CVD	Chemical vapour deposition
СХ	Carbon xerogel
DoE	Design of experiment
DOM	Dissolved organic matter
EDS	Energy dispersive x-ray spectroscopy
EoL	End of life
FQ	Fluoroquinolone
FTIR	Fourier transform infrared spectroscopy
HT	Hold time
НТС	Hydrothermal carbonisation
IR	Impregnation ratio
IUPAC	International union of pure and applied chemistry
MTZ	Mass transfer zone
MW	Microwave
OFAT	One factor at a time
ОТС	Oxytetracycline
PAC	Powdered activated carbon
PAN	Polyacrylonitrile

PFO	Pseudo-first order
PSO	Pseudo-second order
RAS	Recirculating aquaculture system
RSM	Response surface methodology
SBS	Sodium benzenesulfonate
SEM	Scanning electron microscopy
SPE	Solid-phase extraction
SSA	Specific surface area
SSE	Sum of square errors
тс	Tetracycline
UV	Ultraviolet
VOC	Volatile organic compounds

List of Samples

rCF	Recycled carbon fibre
vCF	Virgin carbon fibre
ACF	Activated carbon fibre
ArCF	Activated recycled carbon fibre
Na-ACF	Sodium hydroxide activated carbon fibre
K-ACF(-Opt)	Potassium hydroxide activated carbon fibre (Optimum sample using
	dual optimisation)
mCF(-Opt)	Modified carbon fibre (Optimum sample using dual optimisation)
C-mrCF-Opt	Modified carbon fibre (Optimum sample using individual optimisation
	toward CIP)
O-mrCF-Opt	Modified carbon fibre (Optimum sample using individual optimisation
	toward OTC)
mrCF-Opt	Madified earbon fibro (Ontinum completucing Toguchi)
(Taguchi)	Modified carbon fibre (Optimum sample using Taguchi)
%-mrCF-Opt	Dual-optimised mrCF (max. % removal for CIP & OTC)
%-K-ArCF-Opt	Dual-optimised K-ArCF (max. % removal for CIP & OTC)
%-mrCF-CIP-Opt	CIP-specific % removal-optimised mrCF
%-mrCF-OTC-Opt	OTC-specific % removal-optimised mrCF
q _e -mrCF-Opt	Dual-optimised mrCF (max. adsorption capacity)
q _e -mrCF-CIP-Opt	CIP-specific qe-optimised mrCF
q _e -mrCF-OTC-Opt	OTC-specific qe-optimised mrCF
0.1K-mrCF	mrCF regenerated with 0.1 M KOH
0.25K-mrCF	mrCF regenerated with 0.25 M KOH
0.1Na-mrCF	mrCF regenerated with 0.1 M NaOH
0.25Na-mrCF	mrCF regenerated with 0.25 M NaOH

Nomenclature

C ₀	Initial concentration (mg/L)
Ce	Equilibrium concentration (mg/L)
Log K _{ow}	Octanol-water partition coefficient
pH _{PZC}	Point of zero charge
q _e	Equilibrium adsorption capacity (mg/g)
q _{max}	maximum adsorption capacity (mg/g)
KL	Langmuir constant (L/mg)
K _F	Freundlich constant (mg/g)(L/mg) ^{1/n}
n	Correction factor for adsorption intensity
Κ _τ	Temkin isotherm constant (L/g)
A _T	Temkin equilibrium binding constant (J/mol)
R	Universal gas constant (J/mol·K)
т	Temperature (K or °C)
q _t	Cumulative amount adsorbed at time t (mg/g)
K _x	Rate constant (1/min or g/mg·min)
ΔG	Gibbs free energy (kJ/mol)
ΔH	Heat of adsorption (kJ/mol)
ΔS	Entropy change (J/mol·K)
k _d	Distribution coefficient (L/g)
DE(%)	Degeneration efficiency (%)
M _{AA}	Mass of the adsorbent after adsorption cycle (g)
M _{BA}	Mass of the adsorbent before an adsorption cycle (g)
M _{VA}	Mass of the virgin adsorbent (g)
MB _N	Methylene blue number (mg/g)
RE(%)	Regeneration efficiency (%)
q _{reg}	Adsorption capacities of the regenerated and original CA (mg/g)
q orig	Adsorption capacities of the regenerated and original CA (mg/g)
θ	n _a /n _m
p/p ⁰	Relative pressure

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n _a	Specific amount adsorbed (cm ³ /g) at the relative pressure, p/p ⁰
n _m	Specific monolayer capacity (cm ³ /g)
γ	Surface tension (J/m ²)
V _m	Molar volume (m ³ /mol)
r	Radius of the meniscus formed within a mesopore (m)
A	Absorbance
3	Molar absorption coefficient (M ⁻¹ cm ⁻¹)
с	Concentration (M)
λ_{max}	Wavelength of maximum absorption (nm)
Μ	Mass (g)
V	Volume (L)
n _{csf}	Number of moles of surface groups per gram of adsorbent (mol/g)
n _{hci}	Moles of hydrochloric acid used (mol)
n _B	Moles of base used (mol)

1. Introduction

With the ever-increasing human population, comes the need to produce increasing amounts of nutrient dense foods, such as fish. At present, fish consumption accounts for 17% of animal protein consumed within the human diet and is increasing annually [1]. For this reason, traditional fishing methods cannot sustainably meet the global demand for fish, causing natural resources to become depleted and consequently having a negative impact on predator – prey relationships, affecting the whole food chain [2]. The World Wildlife Fund (WWF) has estimated that a third of the world's oceans are already exceeding their biological limits as a result of overfishing [3]. Additionally, traditional fishing practices such as trawling disrupt surface sediments, effecting benthic communities and causing contaminants to become remobilised into the water column [2]. Therefore, alternative solutions had to be implemented to prevent mass extinction of wild fish populations and irreversible damage to natural and marine environments, the solution being aquaculture.





Aquaculture is a form of farming and is widely considered to be the most rapidly growing food industry globally, expanding on average 7 – 10% per annum, for the last 30 years, surpassing the total production for capture fisheries in 2013 (Figure 1.1) [1,4,5]. Total production of several species of fish including crustaceans, fish and molluscs have seen the largest annual growth by approximately 7% per annum between 1950 – 2020 (Figure 1.2) [6].



Figure 1.2: Types of species farmed within the global aquaculture production, between 1950 – 2020. Data taken from FishStatJ (FAO).

A major challenge within intensive fish farming is the growth and spread of pathogens, parasites and pests (PPP), due to large populations living in proximity. Many approaches have been taken to reduce or prevent the spread of PPP, such as improving management practices (e.g. stocking density, species rotation and filtration), selective breeding for disease resistance and multivalent vaccines [7]. However, these methods require large investments meaning they are not accessible to everyone, particularly within developing countries. Therefore, therapeutics such as antimicrobials, pesticides, nutrients and more are still common practice within many aquaculture settings to reduce or prevent the spread of PPP. However, the rapid expansion of the industry is quickly becoming unsustainable due to environmental contamination, habitat destruction and eutrophication as a result of the widespread use of therapeutics [8]. This thesis will focus on the application and management of antibiotics within the industry.

Antibiotic administration in aquaculture varies globally; however, comprehensive data on the quantities and nature of their use is sparse due to the lack of regulation and reporting in some areas of the world. Antibiotics can be administered using several treatment methods, namely, therapeutic – treating only the exposed animals, metaphylactic – treating the group when a disease is identified or prophylactic – using treatment to prevent disease outbreaks. In Europe, antibiotics are generally administered therapeutically in the form of an injection.

Whereas, in Asia and other developing countries antibiotics are administered as a prophylactic treatment in the feed, leading to direct environmental contamination. This has led to significant differences in antibiotic consumption for aquaculture globally, ranging from approximately 1 g/t of live fish in Norway, to over 700 g/t in Vietnam [9]. In 2017, four countries within the Asia-Pacific region contributed the largest share of antimicrobial consumption, including: China (57.9%), India (11.3%), Indonesia (8.6%), and Vietnam (5%) [1]. It has been predicted that by 2030 the aformentioned countries will remain the largest consumers of antimicrobials (Figure 1.3). Antibiotics are a major concern in natural waters due to their low biodegradability, potential for long range transport and the ability to bioaccumulate [9].



Figure 1.3: Antimicrobial consumption in aquaculture in 2017 and 2030 [1].

Sapkota et al. compiled data about the antibiotics applied in the top 15 aquacultureproducing countries, which account for 95% of aquaculture production, globally [10]. Fluoroquinolones (FQ) and tetracyclines (TC) were identified as two of the most prolifically applied antibiotics in the aquaculture industry; in veterinary medicine, approximately 44.0 t and 22.42 t of TCs and FQs, respectively, were applied in Portugal in 2011 [11]. Within aquaculture, many of these antibiotic classes are poorly metabolised meaning up to 80% of the antibiotics consumed enter the environment in a biologically active form [12,13].

As previously mentioned, there is a lack of information regarding the quantities of antibiotics administered globally within aquaculture. However, an insight into antibiotic use within aquaculture can be found within literature. Ciprofloxacin (CIP) and oxytetracycline (OTC), of the FQ and TC antibiotic classes, respectively, are consistently the most commonly cited antibiotics within literature, as shown in Figure 1.4A and 1.4B. The increased research surrounding the antibiotics CIP and OTC can be attributed to the detection antibiotic residues and resistant genes in close-proximity to aquaculture settings [14–16] For this reason there will be a particular focus toward CIP and OTC throughout this thesis.



Figure 1.4: Scopus indexed publications per annum for fluoroquinolone (A) and tetracycline (B) antibiotics, between 2000 – 2022.

Due to the rapid growth of the industry, aquaculture has become widely recognised as one of the main sources of antibiotics being found within the aquatic environment [17]. There are serious ecological impacts associated with the release of antibiotics into aquatic environments because of their persistence within sediments, surface waters, ground waters and biota. Many organisations including The World Health Organisation (WHO) and many national governments have highlighted the potential risks associated with irresponsible use
of antibiotics within the aquaculture industry; due to the emergence of antimicrobial resistance (AMR) [5].

AMR arises and is maintained over time due to genetic mutations or horizontal gene transfer mechanisms including: the uptake of free DNA *via* transformation, conjugation with other bacteria and transduction with bacteriophages; however, this is accelerated by the presence of antimicrobials causing selective pressures within the environment [10]. This is a serious concern for both human and environmental health since AMR does not respect geographical or phylogenetic borders, having the capability to spread from aquatic bacteria to human and animal pathogens (or vice versa) [18].

The WHO has declared AMR as one of the top 10 global public health threats of our generation, because it reduces the effectiveness of many drugs used to treat common infections. Resistant bacteria have been shown to double probability of developing a severe health issues and triple the chances of patient mortality having contributed to an estimated 25,000 deaths annually, in Europe [19–21]. AMR presents a significant cost to national economies and health systems because patients often require prolonged hospital stays with more intensive and expensive care; America has reported in excess of \$20 billion in spending each year, due to the prolonged hospital stays combined with the potential need for intensive care units and/or patient isolation to prevent transmission [20,21]. However, the full impact of AMR globally is unknown because epidemiological data are sparse in many areas of the world.

Elevated levels of AMR resistance have been reported in close proximity to aquaculture sites, which can be attributed to overuse and misuse of antimicrobials. It has been well documented that exposed aquatic bacteria develop and readily spread AMR genes, creating a global environmental and human health concern because many aquatic bacteria can facilitate the transfer of AMR genes to fish, human and animal pathogens [10,14,22–24]. This can be attributed to the phylogenetic relationship between aquatic bacteria and human pathogens, increasing the likelihood of horizontal gene transfer. One example has been shown in *E. coli*, where several aquatic bacteria have facilitated the transfer of multi-resistance plasmids including *Aeromonas salmonicida*, *Aeromonas hydrophila*, *Edwardsiella tarda*, *Citrobacter*

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freundii, Photobacterium damselae subsp. piscicida, Vibrio anguillarum, and Vibrio salmonicida [5,10,22,23].

In order to limit antibiotic consumption within aquaculture, research is ongoing to find alternative treatments such as vaccines, probiotics, bacteriophages, medicinal plants and more [18]. However, these alternatives are not currently cost-effective, particularly for low-value fish species, or within developing countries, meaning antibiotic use is still seen as a necessity to prevent the spread of bacterial infections. It has been widely reported that the presence of pharmaceutical compounds such as antibiotics, significantly degrade the quality of surrounding waterways or environments [25]. Therefore, cost-effective water treatment techniques must be implemented to reduce or prevent the release of antibiotics into the wider environment.

Many techniques have been applied to remediate pollutants in aqueous media, such as: biodegradation, coagulation, flocculation, flotation, ion exchange, ozonation, reverse osmosis, solvent extraction, ultrafiltration and more [26–28]. Adsorption processes remain at the forefront in remediation technologies, owing to their simplicity in operation and design, and the relatively lower cost overall. Common adsorbent categories include carbon-based materials, zeolites, oxygen-containing compounds and polymer-based compounds; owing to their high specific surface area (SSA), distinct pore structure, high thermal stability and abrasion resistance.

Some key considerations for adsorbent precursors are material availability and cost, making waste or recycled materials promising candidates for adsorbent synthesis [13]. Recycled carbon fibres (rCFs) in particular are a promising candidate for adsorbent synthesis due to the surplus of available material when carbon fibre reinforced polymer (CFRP) products reach their end-of-life, (EoL), as discussed below.

CFRPs use is increasing rapidly across a range of industries including aviation, automotive, wind turbine, infrastructure, sports equipment and more, with the first two industries being the biggest contributors (Figure 1.5) [29,30]. Polyacrylonitrile-based (PAN-based) carbon fibres (CFs) are most commonly applied within the aforementioned industries owing to their

excellent tensile strength, durability, low weight, chemical resistance and temperature tolerance [31–33].



Figure 1.5: Percentage of CFRP use within major industrial sectors [34].

Carbon fibre (CF) production has seen an 180% growth between 2006 – 2018 from 28,000 t to 78,500 t, which is largely attributed to the rapid expansion of the CFRP industry [31,35,36]. Recent studies have projected a global growth rate of 11% per annum between now and 2030 [29,37]. However, EoL products and offcuts within the CFRP industry present a major environmental challenge, with waste projected to reach 20 kt annually, by 2025. Therefore alternative, sustainable pathways must be found for EoL CFRP waste.

At present, CFRPs can be recycled mechanically or by applying fibre reclamation techniques such as thermal and chemical recycling. Mechanical recycling involves the crushing, milling or shredding of CFRP which can then be separated into the fibrous and non-fibrous fractions *via* sieving. Thermal recycling (i.e. pyrolysis) involves the thermal decomposition of the resin by heating (450 - 700 °C) in an inert atmosphere (commonly N₂). The polymeric matrix is volatilised into lower-weight molecules and char, while the inert CFs remain largely unchanged. Chemical recycling breaks down the CFRP matrix by employing a reactive medium such as supercritical fluids, catalysts, and solvents, at low temperature (< 350 °C) [35,38].

A major drawback of current recycling processes is the destruction of the CF form (in the case of mechanical recycling) or degradation to the mechanical stability of the CFs (during thermal or chemical recycling), creating a lack of trust in the properties of recycled product, meaning they are not readily reused within their former industries. This can be attributed to the lack of legal standards to regulate the use of rCFs within major industrial sectors. In recent years, research has turned to investigate the methods to enhance characteristics (e.g. tensile and flexural strength) of rCF-based CFRPs *via* the introduction of various coatings such as nanoparticles or polymers. However, there is still a lack of understanding around the degradation conditions (i.e. temperature, pH, moisture, exposure to seawater etc.) of these rCF-based products, preventing their use within the major industrial sectors discussed previously. Without an appropriate market, recycling is not profitable leading to waste going to landfill. Therefore, suitable applications within alternate industries must be identified to create a circular economy for CFRP waste [36].

Gen2Carbon (formerly ELG Carbon Fibre Ltd.) is a UK-based company which specialises in the recycling of CFRPs on an industrial-scale. They are capable of processing up to 5 t of waste per day, using a continuous pyrolysis process. However, rCFs are short in length and fluffy with a approximately a 10% reduction in mechanical strength, meaning they cannot be substituted for virgin carbon fibres (vCFs) in many sectors. Instead, rCFs are viewed as a new product, requiring different processes and designs. Previously, ELG had started a project with the aim to establish a closed-loop recycling process for EoL aircraft CFRPs, by developing a new product using the rCF material.

Adsorbent synthesis could offer an ideal pathway to create a high-value product from rCFs. Many carbonaceous adsorbents (CAs) including activated and modified virgin CFs (vCFs) have already been applied to successfully remove a range of pollutants from both aqueous and gaseous media [39–42]. However, at present there is little research into the activation, modification and application of their rCF counterpart [31,34,43]

CAs are attractive adsorbents in both aqueous and gaseous phase applications, owing to their high surface area (> 400 m²/g), low cost, tuneable porosity and surface functionalisation, and improved sustainability when using waste or recycled materials. For aqueous phase adsorption mesoporosity or hierarchical porosity is favoured due to the enhanced diffusion of pollutants into the porous network, which is often the rate limiting step [13,44,45]. Furthermore, surface functionalisation is of high importance since it determines the

mechanism of adsorption (e.g. physisorption or chemisorption). Physisorption consists of physical interactions such as Van der Walls forces, hydrogen bonding and hydrophobic interactions. Whereas chemisorption involves the formation of chemical bonds (i.e. ionic or covalent), between functional groups. Adsorption of antibiotics onto CAs can occur *via* physisorption or chemisorption, due to their chemical structure which typically consists of hydrocarbons in the form of aromatic or cyclic structures with heteroatoms or functional groups substituted within the structure.

This project aims to focus on the two global issues discussed above, namely, the environmental contamination caused by the aquaculture industry and the surplus of waste generated by the CFRP industry. This will be achieved by synthesising activated and modified CFs which will be applied as adsorbents for the *in-situ* remediation of antibiotics from freshwater aquaculture settings. Process optimisation applying design of experiment (DoE) techniques, will be carried out throughout the activation, modification and adsorption campaigns to enhance the adsorbent characteristics and adsorbate-adsorbent interactions, with an aim to improve the adsorption capacity toward target antibiotics (CIP and OTC).

2. Literature Review

2.1. The Aquaculture Industry

Aquaculture dates back to approximately 1000 BCE with evidence being found in Ancient China and Egypt [46]. However, it didn't take on it's modern, industrialised form until artificial granulated fish food was developed in the mid-20th century. Since then, aquaculture has become one of the most rapidly expanding food industries globally, which can be attributed to the rapid expansion across Asia (Figure 2.1A). China has experienced the most substantial growth, now accounting for almost 60% of all aquaculture production globally (Figure 2.1B). As of 2020, the top 15 aquaculture producing countries accounted for over 90% of global production, with only four of the top producers being located outside of Asia, namely Brazil, Chile, Egypt and Norway [47].



Figure 2.1: Total aquaculture production by continent (A) and the percentage of aquaculture production within the top 15 aquaculture producing countries (B), data generated *via* FAO software (FishStatJ v4.04.00) [47].

The total number of commercially farmed aquaculture species has also seen a 31.9% increase. Between 2006 – 2018, the number of species farmed increased from 472 – 622, with the most farmed species of fish being crustaceans and molluscs (Table 2.1) [47]. In comparison, terrestrial agriculture only consists of approximately 38 species of livestock and 173 species of crop, giving an indication of the scale and diversity of aquaculture practices [46].

Table 2.1: Aquaculture production statistics, data generated via FAO software (FishStatJv4.04.00) [47].

Species Group	Number of countries farming species group	Global aquaculture production
Carps, barbels and other cyprinids	95	29,789,359
Marine shrimps and prawns	62	6,555,315
Catfishes	86	6,264,326
Tilapias and other cichlids	124	6,194,760
Oysters	46	6,125,606
Clams, cockles, shellfish	22	5,522,876
Salmons, trout, smelts	83	3,855,434

Overall, aquaculture is widely viewed as an invaluable farming technique to providing economic, social and food security, by creating a range of jobs and improving access to low-cost protein sources (Figure 2.2). However, a major hurdle faced by the industry is the destruction of ecosystems due to unsustainable aquaculture practices creating a human and environmental health concern. One of the leading concerns within the industry is degradation of the water quality, due to the multiple waste sources within aquaculture. Typically, aquaculture waste can be separated into two types of waste, namely, solid (feed, faeces etc.) and dissolved (chemicals, pathogens etc.), each presenting their own environmental challenges [48].

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The "chemical cocktail" employed to maintain fish heath and water quality on an industrial scale is of particular concern, having a negative impact on surrounding ecosystems. The chemicals employed within aquaculture consist of antibiotics, hormones, nutrients, chemical treatments and more. The environmental fate of these pollutants is complex, with many degradation pathways being reported [49,50].



Figure 2.2: Social and economic impacts of aquaculture.

Excess antibiotic consumption within the industry presents major challenges, being widely viewed as a necessity to prevent mass stock losses; however, many studies have highlighted the link between aquaculture and rising AMR across the globe [50–52], and the need for efficient techniques to manage aquaculture effluents, consequently antibiotic remediation has been selected as the focus for this thesis. The following sub-sections which will provide a summary of the types of aquaculture, antibiotic pollution generated by aquaculture, environmental impacts and the current treatment techniques.

2.1.1. Types of Aquaculture

Aquaculture is diverse and can be practiced in a range on environmental conditions (e.g. freshwater, marine or brackish water), from artic oceans to tropical rice fields. Furthermore, intensity of the practices can vary from highly intensive to small-scale family-owned businesses. Small-scale aquaculture typically has low fish stocking densities, where water quality can be maintained *via* natural processes such as plankton [53].

Human and environmental concerns arise with increasing intensification of the industry. Higher stocking densities, result in increased degradation of water quality, due to the amplified demand for feed, treatments to prevent spread of PPP and nutrients to promote growth (Section 2.1.2).

Aquaculture methods can also be classified into high-risk systems and low-risk systems (Table 2.2). High-risk systems utilise open-net pens (or cages) and ponds, and are commonly highly intensive, containing thousands to hundreds of thousands of fish [54]. These systems benefit from having low initial investment costs due to their utilisation of natural environments. However, the open nature of these systems presents major environmental challenges due to waste discharge and the introduction of non-native species, diseases and parasites into surrounding environments (Section 2.1.3).

Low-risk systems are typically physically contained or treated to prevent or reduce contamination of surrounding environments and the release of non-native species and PPP. This is achieved by closely monitoring and managing water quality, which subsequently increases fish health and reduces the growth and spread of PPP. However, these farming techniques often have complex operational procedures and require high initial investment and maintenance costs.

	System	Species Farmed	Advantages	Disadvantages
High-risk	Open-net pens	Salmon, trout, bass, sea bream, tuna, cod and others	Cost-effective Natural environment utilisation Industrial scalability Little/no land requirement Ease of Monitoring and Management	Waste discharge Disease and parasite control Invasive species Introduction of invasive species
	Ponds	Carp, tilapia, catfish, milkfish, shrimp & prawns and others	Natural environment utilisation Industrial scalability Environmental integration	Waste discharge Habitat destruction Disease and parasite control Resource intensity
Low-risk	Closed	Salmon, tilapia, catfish, bass, perch, sturgeon and others	Environmental control Resource efficiency Increased product quality	High initial investment Complex operation High energy consumption System failures
	Recirculation	Salmon, tilapia, catfish, bass, perch, sturgeon	Environmental control	High initial investment

Table 2.2: Summary of the different types of aquaculture.

	System	Species Farmed	Advantages	Disadvantages
		shrimp & prawns and	Resource efficiency	Complex operation
		others	Increased product quality	High energy consumption
			Space efficiency	System failures
			Renewable energy sources	Market and economic factors
				High feed and nutrient costs
	Sal		Efficient water use	High initial investment
		Salmon, tilapia, catfish,	Ease of monitoring and management	Water supply
	Raceways	bass, carp, sturgeon and	High stocking density	High energy consumption
	others	others	Environmental control	Disease spread
			Scalability	Environmental impact
			Low environmental impact	High initial investment
		Bivalves, seaweed,	Improved water quality	Increased exposure to elements
Su	Suspended		Reduced predation	Maintenance
			Space efficiency	Biofouling
			Increased growth rates	Regulatory and Spatial Competition

Despite all the advantages presented by the aquaculture industry, there are a number of concerns relating to the environmental impact of aquaculture practices, such as the depletion of natural ecosystems, chemical contamination and changes in the pH of soil and water [55]. This thesis will focus on low-risk, intensive aquaculture with a particular emphasis on freshwater, closed and recirculating aquaculture systems (RAS).

The waste generated by intensive aquaculture consists of matter such as excess feed, faeces, chemical treatments, therapeutics and more resulting in a reduction in water quality. This is signified by detectable changes to various water quality parameters such as the dissolved and insoluble organic matter, nutrient content (i.e. nitrogen and phosphorus), biological oxygen demand and pH of the wastewater.

Despite RAS reducing wastewater discharge by 10 - 100 times, the pollution concentration is approximately 10 - 100 times higher [56]. This presents a major obstacle to make RAS economically and environmentally justifiable. Therefore, simple and effective waste purification techniques are required (Section 2.1.3).

2.1.2. Antibiotic use in Aquaculture, A Human and Environmental Health Concern

The use of antibiotics in foodstuffs (e.g. animal products) has caused widespread concern over food safety and due to the growth and spread of AMR. Not only does AMR reduce the effectiveness of treatments within aquaculture; resistance genes can also be transferred from aquatic bacteria to human or animal pathogens constituting a human and environmental health risk. It was estimated that AMR contributed to an estimated 1.27 million deaths in 2019, globally; this number is projected to reach 10 million by 2050 [57].

As mentioned in Chapter 1, antibiotic use within aquaculture is of particular concern, being one of the leading sources of antibiotics within aquatic environments. A number of studies have identified a correlation between antibiotic use in aquaculture and the development of AMR genes [5,23,49–52,58].

This section will address antibiotic pollution arising from aquaculture practices, with a particular focus on the selected antibiotics, CIP and OTC, and their respective classes, FQs and TCs. These compounds were chosen due to their widespread use in aquaculture and other areas of veterinary medicine.

It is well known that aquaculture conditions promote the growth and spread of PPP and therefore, antibiotic application is widely viewed as a necessity to prevent mortalities within farmed fish populations. As a result, antibiotics have become one of the most widely applied chemicals in aquaculture. It is estimated that China loses between 10 - 25 billion GBP of income per annum due to disease outbreaks within aquaculture, with over half of infections being bacterial [59]. This has led aquaculture to become widely recognised as a "genetic hotspot" for resistance gene transfer, as discussed in Chapter 1 [17,50].

Antibiotic consumption is not evenly distributed globally, which can be accredited to the varied treatment techniques (e.g. therapeutic, metaphylactic or prophylactic). At present, there are no databases globally to provide information regarding the quantities of antibiotics consumed within aquaculture. However, several review articles have compiled data regarding the antibiotic classes and quantities consumed reporting that antibiotic consumption within aquaculture, increased globally between 1990 – 2018, which was largely attributed to the prophylactic use of antibiotics within China, Vietnam and Chile [10,60]. Up to 67 different antibiotic compounds from eight antibiotic classes are utilised in 11 of the 15 major producing countries (Figure 2.1). It has been widely reported in literature that Southeast Asia and South America are the largest consumers. Despite an overall increase in antibiotic consumption globally, a number of countries such as Japan, Norway, Thailand, UK and USA, have strived to reduce antibiotic use *via* improved therapeutic administration techniques (i.e. injection and probiotics) [10,60].

Due to the rapid growth of the aquaculture industry, there are serious ecological impacts associated with the release of antibiotics into aquatic environments because of their ability to accumulate in sediments, surface waters, ground waters and biota. To date, numerous antibiotic-resistant strains have been detected within fin-and-shellfish aquaculture environments, globally. Hossain et al. compiled data regarding antibiotic use and AMR bacteria within the top 15 aquaculture producing countries globally and found that quinolone (QN) type and TC type antibiotics were some of the most prolifically applied antibiotics [50]. Meanwhile, the most frequently isolated resistant bacteria were found to be *Aeromonas* spp., *Bacillus* spp., *Enterobacteriaceae*, *Exiguobacterium* spp., *Pseudomonas* spp., *Streptococcus* spp., and *Vibrio* spp.

In 2020, China accounted for over 60% of aquaculture production globally. Furthermore, China is also the largest antibiotic producer worldwide, consuming approximately 162,000 tonnes in 2013, with over half of antibiotic consumption being attributed to veterinary medicine [59]. Within China, over 234 cases of antibiotic residues were reported within aquaculture products, across 24 species of fish; CIP, norfloxacin and sulfisoxazole being the most regularly detected.

Both FQs and TCs are poorly absorbed and metabolised by both humans and animals, meaning up to 70% and 90% of FQs and TCs, respectively, are excreted unchanged into the surrounding environment, leading to their detection in surface waters, sediments and ground waters. Both antibiotic classes have low octanol partition coefficients between -2.876 and 1.283, indicating high water solubility [17]. However, the drugs possess the ability to form divalent cationic complexes with Ca²⁺ and Mg²⁺, meaning they are also adsorbed to sediments and soils leading to persistence within the environment.



Figure 2.3: Structure of (A) fluoroquinolones and (B) tetracyclines.

OTC is a large molecule with three environmentally relevant pK_a values ranging between pH 4 - 8. Generally, at the pH of natural waters (~ 8.2), OTC exists in zwitterionic form with a negative charge on the hydroxyl group and a positive charge on the tertiary amine group (Figure 2.3). The negative log K_{ow} of OTC (-2.876) indicates that hydrophobic exclusion does not play a role in sorption into sediments. Instead, a combination of electrostatic attraction, ion-exchange and complexation reactions occur. Studies have suggested that OTC is adsorbed to marine sediments *via* binding to divalent ions as mentioned above. When dispersed in surface water, OTC is susceptible to hydrolysis and photolysis, due to its ability to absorb light in the 200 – 400 nm region. The presence of Ca²⁺ hinders hydrolysis processes but accelerates

photolysis, indicating that photolysis is likely to be the primary pathway for degradation in marine environments [61].

The presence of FQs and TCs in the environment is a major concern because they are wide spectrum antibiotics, meaning they readily target both Gram-positive and Gram-negative bacteria and consequently causing disruption to many natural processes within the aquatic environment which involve bacteria. An example of where natural processes are being impacted, is the nitrification process (Figure 2.4). Gram-negative bacteria (*Nitrosomonas sp.* and *Nitrobacter sp.*) are responsible for converting ammonium to nitrite and finally nitrate. However, the antibiotics cause a significant reduction in the numbers of these bacteria leading to excess ammonia within the environment, which is extremely toxic to fish.



Figure 2.4: The nitrification process.

As can be seen from the discussions in this section, the utilisation of FQs and TCs within aquaculture is a necessity for aquaculture to be economically viable by preventing mortalities within the industry; however, antibiotic pollution as a result of their prolific use is a major concern, contributing to the development and spread of AMR, and negatively impacting natural processes. Therefore, effective treatment techniques are required to limit the impacts of antibiotics in aquaculture wastewater, as discussed in the following section.

2.1.3. Current Treatment Techniques

This section will discuss the current water treatment techniques available to treat antibiotics within low-risk aquaculture wastewaters. Typically, wastewater treatment can be loosely classified into three categories, namely physical, chemical and biological. Physical methods include adsorption, sedimentation, flocculation and filtration. Chemical treatments consist of ozonation, chlorination and Fenton's oxidation. Finally biological treatments utilise living organisms to degrade antibiotics. Table 2.3 summarises the advantages and disadvantages of some of these treatment processes.

Table 2.3: Summary of the advantages and disadvantages associated with water treatmenttechniques, taken from [13].

Process	Advantages	Disadvantages	
Adsorption	Cheap and simple	Regeneration can be expensive	
	High removal capacities	and reduces adsorption capacity	
	Fast reaction kinetics	Non-selective/limited selectivity	
	Low energy	pH sensitive	
	Applicable to batch and	Competitive adsorption	
	continuous flow		
	Non-selective		
Biological	Rapid (aerobic digestion)	High energy input	
Treatment	High efficiency	Large amounts of bio-waste	
	Natural breakdown of	Potential ecological damage	
	pollutants yield cleaner	Unreliable	
	waste effluent	Slow (anaerobic digestion)	
Photodegradation	Low cost	Incomplete degradation	
	Durability	(potentially toxic or biologically	
	Industrial scalability	active products)	
	Potential renewable energy use	Limited efficiency in turbid or	
		coloureu waters.	
		Energy Consumption (where	
		renewables aren't available)	

Biological treatments have proven to be successful at removing, reducing or converting antibiotics into their degradation products *via* biological processes. Five types of biological treatment exist within aquaculture, namely, trickling filter, fluidised bed reactor, rotating biological contactor and constructed wetlands. The process relies upon plants and microorganisms such as algae or heterotrophic bacteria to immobilise non-living organic matter within their cells. The utilisation of plants aquatic plants for the purification of aquaculture wastewater is particularly advantageous due to the production of oxygen *via* photosynthesis, which alleviates the risks of oxygen depletion and reduces the need for traditional aeration. However, there is a lack of literature regarding the safety of biological treatments in aquaculture, since the artificial introduction of active organisms into aquatic environments may result in disruption of the ecological balance, causing long term damage [62,63]. Furthermore, large amounts of hazardous biowaste is generated resulting in increased disposal costs.

Photodegradation in aquaculture commonly employs solar energy to oxidise or reduce antibiotics into their degradation products via photolysis, which can occur directly or indirectly. Direct photolysis occurs when chromophores absorb light at wavelengths present in sunlight. Whereas indirect photolysis utilises a photosensitiser to induce chemical transformation. Photocatalytic degradation is an example of indirect photolysis which has been utilised within aquaculture [62,64]. The technique employs ultraviolet (UV)/visible/infrared (IR) light to activate a photocatalytic material (i.e. semiconductor), which results in the excitation of electrons from the valance band to the conduction band, generating photo-induced electron and hole pairs [64]. The electron and hole pairs possess the ability to react with oxygen, water and hydroxyl groups, producing reactive oxygen species (i.e. free radicals). Free radicals subsequently interact with pollutant molecules resulting in the complete or partial degradation. However, photocatalytic degradation of antibiotics within aquaculture presents some challenges, since the type of light, presence of ions and/or dissolved organic matter (DOM), temperature, pH and salinity may hinder the degradation of antibiotics [61,64]. Furthermore, the partial degradation of antibiotics within aquaculture presents major issues, since antibiotic fragments may still be biologically active and therefore, contributing to AMR.

Adsorption processes remain at the forefront in industrial remediation technologies owing to its simplicity in operation and design and the relatively low operational costs. Common adsorbent categories for the adsorption of antibiotic compounds include carbon-based materials, oxygen-containing compounds and polymer-based compounds, owing to their high specific surface area (SSA), distinct pore structure, high thermal stability and abrasion resistance. Adsorption is becoming an increasingly promising technology for the remediation of antibiotics within aquaculture due to the aforementioned advantages [65,66]. Furthermore, adsorption has the ability to operate as a standalone technology, or be incorporated into existing infrastructure, such as RAS. A number of studies have utilised various adsorbents including CAs to remediate antibiotics from wastewater; however, at present, there is a lack of literature regarding the competitive adsorption between antibiotics and other components within aquaculture waste streams (Section 2.4.2.2). Therefore, further research is required to gain a better understanding of the adsorption behaviours within the system, in order to make the technology industrially viable.

2.2. End of Life Carbon Fibre Reinforced Polymers and Carbon Fibre Recycling

The following section relates to the choice of precursor for adsorbent synthesis, namely rCFs. The International Union of Pure and Applied Chemistry (IUPAC) defines CFs as fibres, filaments, lines or reels with a diameter of approximately $5 - 10 \mu m$, containing at least 92 wt.% carbon, in a non-graphitic (i.e. amorphous) state [67,68]. CFs are produced using spinning processes (dry, melt and wet), which are applied to organic precursors such as PAN, pitches (coal-tar and petroleum), phenolic resins and natural sources (cellulosic biomass) [33]. Once a fibrous form is achieved, the CFs are thermally stabilised in air, followed by carbonisation in an inert atmosphere, at elevated temperatures.

Thermal stabilisation is an important step which involves the cross-linking of carbon chains to form a ladder-like structure (Figure 2.5). The process consists of heating the fibres to 200 - 400 °C in air and holding for 30 - 120 minutes, introducing oxygen onto the fibre surface, and subsequently causing a rearrangement of the structure. Stabilisation produces a structure that can withstand high temperatures during later processing stages, such as the carbonisation step. The method increases carbon yield by preventing melting or fusion of the fibres and therefore, avoiding excessive removal of volatile carbon atoms [69].

Carbonisation involves heating CFs in an inert atmosphere, commonly N₂, to increase the carbon content *via* the release of moisture and volatile organic compounds (VOCs) from the starting material. This is achieved by removing any volatile gases present in the structure, in the form of CO₂, CO and H₂O or any condensed liquids. The process involves several physiochemical changes including dehydrogenation, cyclisation, polymerisation and aromatisation [33]. Carbonisation improves several properties of the CFs such as: thermal and chemical resistance, conductivity and stability.

2.2.1. Polyacrylonitrile Based Carbon Fibres

The performance of CFs is largely dependent on the precursor which should have the following qualities: high carbon content, high molecular weight and high degree of molecular orientations. PAN meets all the above requirements which has led to approximately 90% of all CFs being produced using PAN as the precursor [68].

PAN is a semi-crystalline, thermoplastic polymer with the chemical formula $(C_3H_3N)_n$ [33]. During the spinning process, acrylonitrile plastic powder is combined with another plastic such as methyl acrylate or methyl methacrylate [68]. The polymerisation process is initiated using a catalyst to form a final product of PAN [68]. The polymer is then spun into fibres, washed and finally stretched until the desired diameter is achieved. Stretching additionally helps to align the molecules within the fibre.

During synthesis, PAN-CFs undergo preliminary cyclisation and thermo-oxidative dehydrogenation to form an amorphous graphitizable carbon with a sp² hexagonal structure (Figure 2.5) [70,71]. Operating conditions such as temperature and hold time are selected to be below the transition temperature of the fibre to prevent structural alterations and/or damage. Typically for PAN based fibres stabilisation and carbonisation, temperatures range between 250 - 350 °C and 700 - 1500 °C, respectively [71].



Figure 2.5: Synthesis of PAN-based carbon fibres.

2.2.2. Applications of Carbon Fibre Reinforced Polymers

The first wave of CFRP use was seen in the 1990s where prepregs were utilised within the primary airframe structure of the Boeing 777 [72]. Since then, CFRP production has increased at a compound annual growth rate of 12.5%, with the aviation and automotive industries being the biggest contributors (Figure 2.6) [29,30]. The development of PAN-based fibres aided the rapid growth of the CFRP industry, being more economical and yielding more

attractive properties such as higher carbon content and improved tensile strength, chemical resistance and temperature tolerance, when compared to their pitch-based or cellulosic-based counterparts [31–33,72].



Figure 2.6: The development of carbon fibre application with time, taken from . Copyright 2021, Mitsubishi Materials [73].

The modern aviation industry is an example of the environmental challenges presented by EoL CFRP products. Many vehicles including the Boeing 787 and Airbus A350 typically consist of up to 50 wt% CFRP. In some ways this widely improves the environmental impact of the aviation industry, owing to their light weight in comparison to the traditional metal structures [35,74]. However, sustainability issues arise when the vehicles reach their end of life (EoL), typically after 25 – 30 years, with over 16,000 commercial aircraft having been retired in the last 35 years [75]. This issue was amplified due to the coronavirus pandemic, with many airlines either going bankrupt or announcing they are bringing forward fleet retirement programmes [75]. Current waste management processes include moving vehicles to landfill, incineration or recycling (Section 2.2.3), the former being the lowest cost, with many vehicles being abandoned in the desert. This highlights the need for to improve EoL pathways for CFRP products.

2.2.3. Carbon Fibre Recycling Processes

CFRPs can be recycled mechanically or by applying fibre reclamation techniques such as pyrolysis or chemical recycling, which can be further sub-divided into hydrolysis and solvolysis. The widespread adoption of recycled CFRPs is currently hindered by the absence of established EoL recycling processes. This limitation stems primarily from industry scepticism regarding the performance reliability of recycled materials, compounded by the lack of standardised regulatory frameworks governing their use across major industrial sectors. Without a suitable market, recycling is not profitable leading to waste going to landfill; therefore, suitable applications within alternate industries must be identified to create a circular economy for CFRP waste [36].

Mechanical recycling involves crushing, milling or shredding to break down CFRPs. Initially the material would be broken down into pieces approximately 50 - 100 mm in size, using cutting or shredding processes, followed by milling to achieve the final product typically ranging in sizes between $50 \ \mu\text{m} - 10 \ \text{mm}$ [76]. The resulting powder can be separated by sieving into powdered (resin-rich) and fibrous (fibre-rich) products. Mechanical recycling has several advantages, being the fastest and cheapest method to reclaim fibres, while not producing hazardous materials. However, this is an aggressive method which destroys the fibre meaning they can only be reapplied in low value applications for instance as fillers and reinforcements in the construction industry [35].

Chemical recycling breaks down the CFRP matrix by employing a reactive medium such as supercritical fluids, catalysts and solvents, under low temperature (< 350 °C) [35,38]. The CFs remain intact with little degradation in mechanical properties due to their excellent chemical and thermal stability; although, some defects such as char, residual matrix, pitting and degradation of strength have been reported, particularly at longer gauge lengths. The method does suffer several drawbacks including limited industrial scalability, reduced adhesion to polymeric resins and low contamination tolerance. Degradation of the resin can be achieved using either solvolysis or hydrolysis, where the chemicals/solvents applied are selected based on the nature of the polymer matrix. Solid composites in particular, may require an initial mechanical grinding stage to increase the surface area. Solvolysis involves the use of

concentrated chemicals to depolymerise the composite; however, many chemicals involved are hazardous, creating major environmental impacts when carried out at large scales.

Pyrolysis is readily industrially scalable and leaves the valuable CFs intact, making it one of the most widespread processes for recycling CFRPs [77,78]. It involves thermal decomposition of the resin by heating (450 - 700 °C) in an inert atmosphere (commonly N₂). The polymeric matrix is volatilised into lower-weight molecules and char, while the inert CFs remain largely unchanged. The method can recover relatively long fibres retaining a high proportion (\leq 90%) of their mechanical properties [35,79]. However, the remnant char within the structure can prevent the proper adhesion of the reclaimed CFs with new resins meaning a controlled post-treatment is required to remove any residual char without further degrading the fibres during combustion [80]. Additionally, the method produces complex mixtures of hazardous materials in the chemical feedstock, consisting of nitrogenous, oxygenated and sulphur-containing organic compounds mixed with water and off-gases such as carbon monoxide and dioxide, hydrogen and low molecular weight hydrocarbons. Studies have suggested that the gases generated could have applications as an alternative fuel; however, this does not compensate for the problem generated by the liquid waste.

As outlined earlier, Gen2Carbon operates at an industrial scale, processing substantial quantities of PAN-based CFRPs originating from diverse sectors. Accordingly, the rCFs utilised in this study can be considered representative of the variability inherent to PAN-based rCFs recovered from mixed-source waste streams.

2.2.4. Applications of Recycled Carbon Fibres

At present, despite the availability of recycling processes for CFs, they are not economically viable due to the somewhat limited industrial applications. Therefore, in recent decades research has sought to improve the characteristics of rCFs for the incorporation back into CFRP products. This has been achieved by introducing coatings such as polymers and nanoparticles to enhance flexural and tensile strength amongst other characteristics [81–85]. For example, silica nanoparticles (3 wt%) have been incorporated into rCFs resulting in an improvement in tensile and flexural strength by 20% and 36%, respectively. Despite the promising research in this area, there is a lack of understanding around the degrading

conditions of rCF-based products (i.e. temperature, pH, moisture, exposure to seawater and etc.). As of 2022, few studies had been conducted regarding the degradation conditions of rCFs; however, it has been suggested that the previously mentioned conditions could lead to a decline in mechanical strength, thermal stability, and fatigue resistance [86]. Consequently, more research is needed on the degradation characteristics of rCF-based CFRPs before they can be broadly reintroduced into the major industrial sectors discussed earlier.

An alternative, promising technology for rCFs could be the development of CAs. A number of studies have utilised virgin CFs (vCFs) for the development of adsorbents for applications in both aqueous and gaseous media. However, there is a gap in the research regarding the application of rCFs as adsorbents. Nahil and Williams investigated the thermal activation of rCFs by heating to 850 °C (ramp rate 5 °C/min) under nitrogen, once the desired temperature was reached, the gas was switched to steam and held for 5 h [31]. The subsequent activated rCFs (ArCFs) were mostly microporous with a surface area of 802 m²/g; however, the material was not applied as an adsorbent within this study. Nevertheless, the characteristics of the ArCFs in the aforementioned study are promising for adsorbent production.

2.3. Synthesis of Carbonaceous Adsorbents

The following section will discuss the preparation of adsorbents from carbonaceous precursors, using physical or chemical activation and/or modification techniques. At present, there is a lack of research regarding the synthesis of PAN-based rCF adsorbents and therefore, virgin PAN-based CFs and other forms of CA have been discussed below. A comprehensive review of methodologies used within current literature has been undertaken, followed by an in-depth discussion regarding the mechanisms.

2.3.1. Activation of Carbon Fibres

Activation is a vital stage for the synthesis of CAs, responsible for the development of the porous network and the consequent increased surface area and pore volume which is fundamental to adsorption processes. The techniques applied to activate CAs are well-established and often consist of applying an activation agent (physical or chemical) and elevated temperatures (<350 °C). Subsequently, the process burns off non-carbonised regions of the carbonaceous framework, releasing volatiles (i.e. CO₂, CO, H₂O and low molecular

weight hydrocarbons) and ejecting pore-blocking tar, from the CA framework, which is continuously removed from the reactor in the gas flow.

Correct selection of the activation methodology is of high importance, since different approaches result in different physical and chemical characteristics (i.e. surface area, pore size distribution and surface functionalisation), which play a significant role in the selectivity of adsorbents. Within aqueous phase adsorption, high surface area (> 700 m²/g) along with ordered mesoporosity or hierarchical porosity are preferred. High surface areas enable a greater number of molecules to interact with the adsorbent's surface, whilst mesopores (and to some extent, macropores) facilitate the diffusion of pollutants into the internal porous structure, which is commonly the rate limiting step.

According to IUPAC definition, micropores have diameters less than 2 nm, mesopores are between 2 – 50 nm and macropores are larger than 50 nm. Microporous adsorbents often exhibit limited adsorption capacities for high molecular weight compounds, such as antibiotics, due to molecular size exclusion, where the adsorbate is too large to access the internal pore structure [87].

Surface functionalisation is a critical factor in determining the adsorption mechanism (e.g. physisorption or chemisorption), as functional groups serve as active sites for adsorbate interaction. In particular, oxygen-containing functional groups have been shown to significantly enhance the adsorption of antibiotics such as CIP and OTC, as detailed in [88,89].

From the above information, this section will discuss the activation techniques employed to produce adsorbents with high surface areas, mesoporosity, and the presence of oxygen-containing functional groups.

2.3.1.1. Physical Activation

Physical activation is a well-established technique which has been commonly applied to increase the SSA and porosity of carbonaceous precursors by exposing them to high temperatures (> 700 °C) in the presence of a gaseous activation agent. Physical activation benefits from being industrially scalable, simple and low cost, due to the lack of chemical agents and time consuming washing steps which result in secondary pollution. However, higher temperatures and hold times are required leading to increased energy consumption,

to produce CAs with lower surface area, porosity and yields, when compared to the chemically activated counterpart. Additionally, during the activation process, valuable heteroatoms and surface groups may be eliminated from the structure due to intense heating. Therefore, additional modification steps may be required to introduce new surface groups.

It has been suggested that the physical activation mechanism occurs *via* a two-step process, where firstly disorganised carbon (i.e. amorphous) is emitted from the structure, resulting in a 10-20 wt% reduction. Gaseous activation agents then enter the internal network of the carbonaceous structure by means of diffusion resulting in the widening of inaccessible pores [76–78].

The most commonly cited physical activation agents are carbon dioxide or steam, since the mechanism of activation is endothermic making the process more readily controlled [90]. The former method begins with the Boudouard reaction, where CO₂ interacts with the carbonaceous framework *via* dissociative chemisorption. This interaction leads to the formation of surface oxides and the subsequent release of CO, which contributes to the development of the porous network (Figure 2.7) [91,92]. Notably, the production of CO in the Boudouard reaction is only favoured at temperatures above 700 °C.

Steam activation involves the reaction between water and the carbon surface to form CO and hydrogen. Subsequently, the CO can participate in carbon gasification and the water gas shift reaction where the full degree of porosity is developed. The CO₂ produced during the water gas shift reaction then has the capability to further enhance the activation of the surface. However, the H₂ produced may hinder steam gasification by deactivating active sites on the carbon surface through dissociative adsorption of hydrogen, reverse oxygen exchange or scavenging of surface oxides; a phenomenon introduced by Hermann and Hüttinger [92–94].

Higher adsorption capacities are typically observed at elevated temperatures and longer hold times due to the increased burn off of carbon, volatile materials and tar, creating a greater SSA and a better developed pore structure [95]. However, increased burn-off causes a decrease in yield and therefore, a compromise is required between adsorption capacity and carbon yield.

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Figure 2.7: A comparison of the physical activation mechanisms of steam and CO_2 , where C_f represents carbon atoms that are not bonded to surface complexes and are thus available to react with oxygen molecules, while C(O) refers to surface oxygen complexes, taken from [13].

Choi et al. investigated the physical activation of PAN-based carbon fibre using a steam activation agent [96]. Prior to activation the PAN-fibres were oxidised at 230 °C for 4 h, then carbonised at 900 °C. A range of temperatures (700 – 900 °C) and hold times (30 – 360 min) were studied. Initially the PAN-CFs were heated at a rate of 5 °C/min under N₂ (200 mL/min) until the desired temperature was reached, after which the supply was switched to steam at a rate of 200 mL/min. Figure 2.8a and Figure 2.8b show the influence of temperature and hold time on the yield and surface area, respectively. The surface area was enhanced by higher activation temperatures and hold times due to the enhanced development of microporous structures *via* the decomposition of blocked channels. Contrastingly, lower temperatures and hold times resulted in reduced surface area; however, an improvement in mesoporosity was conducted for gas-phase applications and therefore, concluded that higher temperatures with extended hold times may be more advantageous, as this could promote the formation of the desirable mesoporous structure [13].



Figure 2.8: The yield variation as a function of time and temperature during physical activation (a), and the correlation between activation temperature/time and S_{BET} (b) [96].

Similarly, the influence of activation temperature on the adsorption characteristics of PANbased CFs has been investigated using CO₂ as the activation agent [97]. Firstly, the CFs were carbonised at 1000 °C for 2 h, in an inert atmosphere. The CFs were then activated at temperatures of 700, 800, 900 and 1000 °C for 2 h in CO₂ (30 mL/min). Increasing activation temperature resulted in higher specific surface areas, up to 900 °C, after which a small decline was observed (Figure 2.9), which can be attributed to the destruction of micropores due to pore wall collapse.



Figure 2.9: The correlation between perentage burn-off on the specific surface area of PANbased ACFs [97].

Precursor	Activation Agent/ Flow rate (mL/min)	Activation Temp (°C)	Heating atmosphere/ Flow rate (mL/min)	Activation Time (h)	S _{BET} (m²/g)	V _{micro} /V _{tot} (cm³/g)	Ref
PAN-rCF	Steam	850	N ₂	5	800	-	[31]
PAN-CF	Steam/200	850	-	0.75	1041.9	0.42/0.49	[96]
PAN-CF	CO ₂ /30	900	-	2	576	0.34	[97]
PAN-CF	Steam	850	N ₂	-	1241	0.45/-	[98]
	Air	850	N ₂	-	527	0.160/-	-
Polyethylene-CF	Steam/0.5	900	N ₂ /300	0.66	1750	0.60/0.99	[99]
Bamboo-CF	Steam/8	850	N_2	0.67	2024	0.57/0.99	[100]
Biomass-CF	Steam	800	N ₂	-	840	-	[101]
Biomass-CF	Steam/80	600		3.33	615	0.02/0.16	[102]

Table 2.4: Summary of physical activation techniques in literature and the subsequent properties of CAs.

Precursor	Activation Agent/ Flow rate (mL/min)	Activation Temp (°C)	Heating atmosphere/ Flow rate (mL/min)	Activation Time (h)	S _{BET} (m ² /g)	V _{micro} /V _{tot} (cm³/g)	Ref
Pitch-CF	CO ₂	890	N ₂ /100	22.5	2487	0.86	[103]
Pitch- CF	Steam	900	N ₂ /100	-	1900	-	[104]
MWCNTs	Steam/800	800	N ₂ /100	-	85.8	-	_
MWCNTs	CO ₂	800	N ₂ /100	-	144.0	-	_
Oil palm-AC	CO ₂ /100	900	N ₂	0.50	1366		[105]

2.3.1.2. Chemical Activation

Chemical activation consists of heating the precursor in the presence of a chemical activation agent. The technique offers several advantages over physical activation, including controlled and improved development of surface area, porosity and yields at lower activation temperatures and hold times [90,106–110]. Additionally, carbonisation and surface functionalisation can occur *simultaneously* during chemical activation processes. However, there are also several disadvantages associated with the method, such as the requirements for expensive chemical agents and a washing/drying step which leads to the generation of a secondary waste in the process.

A number of parameters must be considered for chemical activation processes. These include chemical agent, impregnation ratio (IR), mixing method, activation temperature, hold time, atmospheric conditions (i.e. type of gas and flow rate) and ramp rate. The selection of chemical agents is particularly important because this strongly effects the ultimate surface morphology, functionalities and overall crystallinity. Chemical agents are generally categorised based on their acidity or alkalinity. The most common alkali activation agents include potassium hydroxide (KOH), sodium hydroxide (NaOH) and potassium carbonate (K_2CO_3), whilst acidic activation agents include phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4) and zinc chloride (ZnCl₂) [93].

2.3.1.2.1. Acidic Activation

As mentioned above, H_3PO_4 and H_2SO_4 are the most utilised acidic activation agents; although, other activation agents such as H_2SO_4 , HNO_3 and hypochlorites have also been applied less frequently. Of the acidic activation agents, H_3PO_4 is particularly attractive, producing CAs with the highest surface areas up to 1550 m²/g, whilst sustaining high yields (Table 2.6), and therefore, will be the focus of this sub-section [111].

The mechanism of H_3PO_4 is temperature dependent, at temperatures below 400 °C, H_3PO_4 is dehydrated, resulting in the expulsion of water (Reaction 2.1) [112]. At temperatures between 400 – 700 °C, H_3PO_4 is converted to P_4O_{10} (Reaction 2.2). The carbon surface is then etched *via* two parallel reactions between P_4O_{10} and the carbon surface, resulting in pore formation and widening whilst simultaneously expelling CO_2 and CO (Reactions 2.3 and 2.4).

At elevated temperatures (> 700 °C), the CO₂ and CO produced can further physically activate the surface via the Boudouard reaction and water gas shift reaction, discussed in Section 2.3.1.1.

$$\begin{array}{lll} 2H_{3}PO_{4} \rightarrow H_{4}P_{2}O_{7} + H_{2}O & \Delta H_{R} = -418.5 \ \text{kJ/mol} & \text{Reaction 2.1} \\ \\ 2H_{4}P_{2}O_{7} \rightarrow P_{4}O_{10} + 4H_{2}O & \Delta H_{R} = +1304.6 \ \text{kJ/mol} & \text{Reaction 2.2} \\ \\ P_{4}O_{10} + 2C \rightarrow P_{4}O_{6} + CO_{2} & \Delta H_{R} = +477.1 \ \text{kJ/mol} & \text{Reaction 2.3} \\ \\ P_{4}O_{10} \ or \ P_{4}O_{6} + CH_{x} \rightarrow PH_{3} + CO_{2} \ or \ CO & \text{Reaction 2.4} \\ \\ C + CO_{2} \rightarrow 2CO & \Delta H_{R} = +172.5 \ \text{kJ/mol} & \text{Reaction 2.5} \end{array}$$

Table 2.5: Surface areas and porosity characteristics and maximum CIP adsorption capacity of AC, AC-SBS [113].

Sample	S _{bet}	V _{mic}	V_{tot}	q _{max}	
	(m²/g)	(cm³/g)	(cm³/g)	(mg/g)	
AC	1050	0.268	1.050	250	
AC-SBS	738	0.159	0.925	286	

Wang et al. investigated the production of ACs using H_3PO_4 and sodium benzenesulfonate (SBS) for the adsorption of CIP. The precursor was combined with H_3PO_4 (40 wt%) in a 1:2 ratio (AC, g:H_3PO_4, g), in the presence or absence of SBS (8 mmol), which were denoted AC-SBS and AC, respectively. The subsequent mixture was heated to 450 °C for 1 h, after which the ACs were washed with hot distilled water until a neutral pH was achieved. Finally, the samples were dried at 105 °C for 8 h. The textural characteristics were assessed using N₂ adsorption isotherms. Activation without SBS resulted in higher surface areas and pore volumes, as shown in Table 2.5. Both AC and AC-SBS achieved high CIP adsorption capacity greater than 250 mg/g. Despite the high adsorption capacity, from an industrial scalability

perspective, working with highly concentrated acids such as H₃PO₄ is costly and presents health and safety hazards (e.g. corrosive, decomposition products etc.). Lower concentrations or alternative chemical activation agents could be applied to limit these issues.

2.3.1.2.2. Alkali Activation

Alkali activation agents such as hydroxides and carbonates have proven to be attractive candidates for the production of CAs achieving higher surface areas up to 3388 m²/g (Table 2.6), whilst being less costly and corrosive when compared to CAs produced using aforementioned acidic agents [114]. Furthermore, studies employing alkali activation agents have produced CAs with high mesoporosity, narrow pore size distribution and oxygen-containing surface moieties, resulting in enhanced adsorption towards target antibiotics.

At present, there are gaps in knowledge of the mechanisms that takes place during activation. Lillo-Ródenas et al. studied the mechanism in detail and hypothesised three possible reactions [110]. It is widely agreed that the first step of the mechanism consists of overlapping redox reactions between the hydroxide (Reactions 2.6 and 2.7). Next, K_2CO_3 and carbon are reduced to K, K_2O , CO and CO_2 in accordance with Reactions 2.9 – 2.13. Subsequently, the products of these reactions may further aid the development of porosity *via* enhanced etching of the surface. Furthermore, alkali metals (Na⁺ and K⁺) possess the ability to intercalate between graphene sheets of a carbonaceous structure increasing the spacing between the sheets and subsequently the specific surface area and pore volume, as discussed in more depth in Chapter 4 [106,115,116].

$6KOH + 2C \leftrightarrow 2K + 3H_2 + 2K_2CO_3$	ΔH_R = +248.0 kJ/mol	Reaction 2.6
$4KOH + C \iff 4K + CO_2 + 2H_2O$	Δ H _R = +733.7 kJ/mol	Reaction 2.7
$2KOH \to K_2O + H_2O$	ΔH_R = +200.4 kJ/mol	Reaction 2.8
$K_2CO_3 + C \rightarrow K_2O + 2CO$	ΔH_R = +566.0 kJ/mol	Reaction 2.9
$C + H_2 O \rightarrow CO + H_2$	ΔH_R = +175.3 kJ/mol	Reaction 2.10
$K_2O + C \to 2K + CO$	Δ H _R = +252.6 kJ/mol	Reaction 2.11

$$CO + H_2O \rightarrow H_2 + CO_2$$
 $\Delta H_R = +2.9 \text{ kJ/mol}$ Reaction 2.12

PAN-based CFs have been activated by combining the precursor with KOH and water in a 1:1 – 1:3 ratio (CF:KOH). The slurry was then treated at 120 °C for 12 h under N₂, to allow for the impregnation of KOH into the CFs, after which the temperature was increased to 600 – 800 °C under N₂ (1 L/min). The samples were then washed and dried at 110 °C in a vacuum oven. It was found that higher IR and temperatures resulted in increased development of mesoporosity (Figure 2.10). Two samples achieved promising characteristics for adsorption of antibiotics, namely the samples activated at 700 °C and 800 °C in a 1:3 ratio, achieving surface areas of 3388 and 3034 m²/g and mesopore volumes of 0.547 and 1.098 cm³/g, respectively.



Figure 2.10: Impact of temperature and impregnation ratio on meso and micropore volume [114].

Alkathiri et al. conducted a similar procedure to activate PAN-based CF; however, prior to activation the CFs were stabilised at 250 °C for 7 h under air, followed by carbonisation at 850 °C for 2 h under N₂ (135 mL/min) [115]. The carbonised fibres were then activated by mixing with KOH in a 1:3 ratio (CF:KOH), heating to 950 °C (10 °C/min) and held for 1 h achieving a surface area and pore volume of 2889 m²/g and 2.39 cm³/g, respectively.

In some cases, a pre-oxidation step is recommended to optimise the surface area and porosity (Figure 2.11c - f) [117]. For example, the chemical activation of PAN-based CFs using KOH, was investigated with and without pre-oxidation. The pre-oxidation consisted of heating the

sample at 500 °C in air. The samples were subsequently impregnated with KOH activation agent using an IR of 1:2 (CF:KOH), then activated by heating to 850 °C at a ramp rate of 5 °C/min under a continuous N₂ flow (50 mL/min) and maintained at the target temperature for 1 hour. The resulting samples were then washed and dried. The pre-oxidation step resulted in a significant improvement in surface area and pore volume from 780 m²/g and 1.16 cm³/g to 2231 m²/g and 0.39 cm³/g, respectively, which was further confirmed using SEM (Figure 2.11). Despite the improvement in surface area when using pre-oxidation, within this study, other studies have achieved similar surface areas without the need for an additional processing step [115,118]. From an industrial-scalability and economic perspective, additional processing steps should be avoided where possible.



Figure 2.11: SEM images of PAN-ACF prepared by direct carbonisation (a, b), chemical activation using KOH (c, d) and pre-oxidation followed by chemical activation using KOH [117].

Okman et al. conducted a study to compare the impact of two chemical activation agents (KOH and K_2CO_3) for the synthesis of ACs from grape seeds [119]. The biomass was impregnated with either activation agent at IR ranging between 0.25:1 - 1:1 (chemical:AC) for 24 h, then dried at 105 °C. The impregnated material was then activated at 600 – 800 °C for 1

h under N₂ with a flow rate of 30 mL/min. After activation, the subsequent samples were refluxed in concentrated HCl, followed by washing with deionised water until chloride ions were not detected. Finally, the samples were dried at 105 °C for 24 h. The highest S_{BET} was observed when activating the samples at 800 °C with K₂CO₃ (IR 0.5:1, Figure 2.12). The highest surface area for KOH activation was obtained at an activation temperature and IR of 800 °C and 0.25:1, respectively; due to the increased etching effect of KOH which causes destruction of the pore walls at higher IR. The 600 °C KOH activation data appear to be less robust and potentially unreliable, as the trend observed showing 50 wt.% having the lowest S_{BET} is counterintuitive and inconsistent with expected behaviour. Typically, increased KOH loading enhances activation and porosity development up to a point, before causing structural collapse at very high ratios. The observed surface area trend does not follow this established pattern, suggesting that the 600 °C KOH data may be influenced by experimental variability, incomplete activation, or other uncontrolled factors. This inconsistency calls into question the reproducibility and reliability of the 600 °C KOH results.



Figure 2.12: BET surface areas of ACs derived from the chemical activation (either K_2CO_3 or KOH) of grape seeds in relation to carbonisation temperature [119].
	Precursor	Activation Agent/ IR (CA:Chemical)	Activation Temp (°C)	Activation Time (h)	Gas/Flow rate (mL/min)	S _{BET} (m²/g)	V _{micro} /V _{tot} (cm³/g)	Ref
	Watermelon rind-AC	H ₂ SO ₄ /1:1	150	24	-	0.357	-	[120]
Agents	Acacia erioloba seed-AC	H ₂ SO ₄ /10%	600	1	-	129.83	0.05/-	[121]
	Macadamia nutshell-AC	H ₂ SO ₄ /1:1	650	0.75	-	426.3	0.19/0.21	[122]
		K ₂ CO ₃ /1:1	650	1	-	459.8	0.21/0.23	
	Kesambi wood biomass- AC	H ₂ SO ₄ /96%	400	0.5	-	179.05	0.00/2.17	[123]
Acidio	Eucalyptus residue-AC	H ₃ PO ₄ /1:2.5	400	3	N ₂	1545.44	0.04//1.70	[124]
	Sisal hemp pulp-CF	H ₃ PO ₄ /1:1.25	450	1	-	1801	-/1.02	[125]
	Kenaf stem-CF	H ₃ PO ₄ /1:3	600	0.5	N ₂	1570	0.54/1.82	[126]
	Oil palm shell-AC	H ₃ PO ₄ /1:2	700 (W)	0.083	-	854.42	-/0.74	[127]
	Agricultural waste-AC	H ₃ PO ₄ /60%	200 (W)	0.067	N ₂ /200	-	-	[128]

Table 2.6: Review of chemical activation techniques for CAs, adapted from [13].

	Precursor	Activation Agent/ IR (CA:Chemical)	Activation Temp (°C)	Activation Time (h)	Gas/Flow rate (mL/min)	S _{BET} (m²/g)	V _{micro} /V _{tot} (cm³/g)	Ref
	Cherry stone	NaOH dry	600	0.33	-	704	0.32/-	[129]
Agents		NaOH impreg 24 h	600	0.33	-	788	0.36/-	_
	Non-woven biomass flax	КОН	800	0-3	N ₂	1051	0.411/0.533	[130]
	fibre	K ₂ CO ₃	800	0-3	N ₂	1007	0.399/0.516	_
		KOH (vac)	800	0-3	N ₂	1197	0.460/0.589	_
Basic	PAN-CF	KOH/8:1	750	1	-	891	-/0.39	[131]
		NaOH/8:1	750	1		855	-/0.37	_
	PAN-CF	KOH/2:1	850	1	N ₂ /50	780.17	0.35/0.39	[117]
			Pre-ox: 500	1				_
		KOH/2:1	850		N ₂ /50	2231.24	0.76/1.16	_
		-	850	1	N ₂ /50	0.24	-	

Precursor	Activation Agent/ IR (CA:Chemical)	Activation Temp (°C)	Activation Time (h)	Gas/Flow rate (mL/min)	S _{BET} (m²/g)	V _{micro} /V _{tot} (cm ³ /g)	Ref
PAN-CF	KOH/3:1	950	1	N ₂ /150	2889	2.39/1.87	[115]
	-	950	1	CO _{2/} 250	774	-	
PAN-CF		Pre-treat: 120	12	N ₂		V _{meso}	[114]
	KOH/3:1	700	0.5	N ₂ /1000	3388	0.547	
		800			3034	1.098	
	Steam	800	4	N ₂ /1000	670	0.031	_
PAN-CF	KOH/1:3	850	1	N ₂	3220	0.655/1.204	[118]
Pitch based	KOH/8:1	750	1	N ₂	2420	0.94	[90]
	NaOH/8:1	750	1	N ₂	3033	1.02	_
		890	22.5	CO ₂ /100	2487		_
MWCNTs	KOH/1:5	800	-	N ₂ /500	1184	0.50	[109]

2.3.2. Modification of Carbon Fibres

Surface modification is a powerful technique that enhances the surface characteristics of a CA by introducing or removing specific functional groups. This process can tailor the surface to be either more hydrophilic or hydrophobic, thereby increasing the adsorbent's affinity for target pollutants and improving its adsorption capacity. Beyond surface area and pore volume, adsorbent modification could be considered one of the most important aspects of adsorbent synthesis since functional groups can act as active sites for adsorption.

Similarly to activation, modification is typically categorised into physical or chemical techniques. Physical modification involves heating a CA to expel heteroatoms from the surface, which subsequently increases the hydrophobicity of the adsorbent surface. Whereas chemical modification often involves the application of acidic or basic agents to introduce heteroatoms such as oxygen, nitrogen, phosphorous and sulphur into the carbonaceous matrix [13]. In recent decades attention has turned to more energy efficient techniques such as microwave, plasma, or ozone treatments; however, these techniques often require large amounts of capital investment which can be prohibitive.

Due to the aromatic characteristics of CAs, it is widely recognised that when functionalised, their chemical properties would resemble those of their aromatic hydrocarbon equivalents and subsequently have the ability to readily generate reactive acidic or basic surfaces due to the presence of delocalised electrons (Figure 2.13) [132]. Acidic and basic functional groups increase the hydrophilicity of a surface which is advantageous for applications in aqueous media.

Despite the advantages, modification techniques also come with certain drawbacks. For instance, the introduction of additional surface functionalities can lead to pore blockage and subsequently a reduced surface area. Regardless of this phenomenon, it is important to recognise that the relationship between adsorption capacity and factors such as surface area, pore size distribution, or volume is not linear, owing to the diverse range of interactions that occur during adsorption. In some cases, the increased surface functionalities can enhance the adsorption capacity, due to the enhanced active sites for adsorption.



Figure 2.13: Acidic and basic surface groups of CAs [19].

The selection of functional groups is critical, as bulkier groups can significantly contribute to pore blocking. Moreover, if the modification agent is not carefully chosen, repulsive interactions may arise, leading to a reduction in adsorption capacity. Therefore, it is essential to first consider the specific characteristics of the adsorption system. For instance, pH can greatly influence the speciation of both pollutants and the surface functionalities of the adsorbent. The functionalities must be compatible with one another, either through physical or chemical interactions, under the targeted experimental conditions. In aqueous-phase applications, oxygen-containing functional groups such as carboxyl, carbonyl, phenolic, lactone, and quinone groups are particularly effective for pollutant uptake [88,89].

2.3.2.1. Thermal Modification

Thermal modification enhances the hydrophobicity of a surface by expelling heteroatoms (e.g. nitrogen, oxygen, phosphorous and sulphur etc) from the structure *via* high temperature treatments. Lach et al. investigated the modification of commercial ACs employing two heating techniques [133]. The first method involved heating the AC to 400 °C in a rotary kiln under a constant flow of either steam, CO₂ or air. The second method employed an SEOW

joule heating stand for the modification which utilises the ACs as a semiconductor. The same modification conditions as the previous experiments were employed. For both techniques modification in air led to the highest surface areas and total acidity and basicity, resulting in the highest adsorption capacity toward OTC. Modification in the kiln and SEOW heating stand using air exhibited comparable OTC adsorption capacities of 89.50 and 89.65 mg/g, respectively. However, the former method was found to be much less energy intensive and therefore, was found to be the most promising technique.

Similarly, coconut shell-based powdered ACs (PACs) have been thermally modified to enhance the adsorption of TCs [134]. Prior to modification, the PACs were washed with 1% HCl, then deionised water until a pH of 7 was reached. The PACs were then dried at 105 °C overnight. The thermal modification consisted of heating the ACs in a tube furnace to temperatures of 500 - 900 °C (rate of 5 °C/min) and held for 2 h under Ar flow (50 mL/min). It was found that increasing the temperature by 300 °C to 800 °C resulted in a 39% increase in the adsorption capacity toward TCs (Figure 2.14). By further increasing the temperature to 900 °C, a 25% decrease in adsorption capacity was detected which was attributed to the destruction of pore walls, resulting in a reduction in surface area. When compared to the nonmodified sample, a 44% improvement in adsorption capacity was observed which was attributed to the enhanced surface area and π - π interactions.





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2.3.2.2. Chemical Modification

Chemical modification can be further subdivided into acidic, basic or impregnation treatments. Acidic treatment is utilised to oxidise the porous CA surfaces, enhancing the acidic properties and hydrophilic nature of the adsorbent; with the most widely applied acidic agents being HNO₃ and H₂SO₄. In contrast, basic treatments create CAs with a positively charged surface, typically using amines. Impregnation techniques are utilised to introduce metals such as silver, copper, aluminium and iron into the CA structure.

ACFs have been chemically modified by HNO₃, comparing the effects of several heating methods, namely, water bath heating, microwave-assisted and sonication-assisted, which were denoted N₀-ACFF, N_M-ACFF and N_s-ACFF, respectively [135]. The impacts of HNO₃ concentration (22-68%), dosage (10 – 30 mL), treatment time (1 – 3 h) and temperature (30 – 60 °C) were investigated on the uptake capacity for Cu²⁺. The study was optimised using a one-factor-at-a-time (OFAT) approach, identifying the optimum conditions for the oxidation of ACFs as a HNO₃ concentration, dosage, treatment time and temperature of 68%, 20 mL, 2 h and 60 °C, achieving a maximum removal capacity of 23.13 mg/g for N_M-ACFF. It is not recommended to use an OFAT approach for optimising processes with > 2 factors since this may lead to the inaccurate identification of the optimum point (Section 2.6). Treatment using a water bath resulted in a reduced surface area and pore volume in comparison to the ACF precursor, whilst sonication and microwave treatment resulted in an increase in the aforementioned characteristics (Table 2.7). However, N₀-ACFF resulted in the highest percentage of heteroatoms which play an active role in the adsorption of antibiotics.

One study used a two-step process which combined impregnation and basic modification treatments to produce functionalised ACs for the adsorption of CIP and NOR [136]. Firstly, the AC was soaked with a solution containing FeSO₄ (0.25 mol/L) and FeCl₃ (0.50 mol/L) for 2 h under N₂ (60 mL/min). Afterward, NH₃·H₂O (10 mL) was added to the vessel, and the temperature was increased to 70 °C at a rate of 5 °C/min and held for 4 h. the resulting ACs were then washed and dried at 90 °C for 4 h. The Fe₃O₄ loaded BAC were then reacted with epichlorohydrin (10 mL) and N,N-dimethylformamide (10 mL) at 90 °C for 2 h under stirring. The modified ACs achieved a maximum removal capacity of 131.6 and 293.2 mg/g for CIP and

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NOR, respectively, in comparison to the activated counterpart which only achieved adsorption capacities of 131.6 and 173.3 mg/g for CIP and NOR, respectively.

Table 2.7: Surface structure and elemental composition of ACFs before and after oxidation,

Adsorbent	BET surface area	Total pore volume	Micropore volume (cm ³ /g)	Ultra- micropore volume	Super- micropore	Mesopore volume (cm ³ /g)	Elemental composition (%)		
(m²/g)		(cm ³ /g)	(0 / 8/	(cm³/g)		(0 / 8/	С	Ν	0
ACFF ₀	1083.4	0.423	0.4108	0.3403	0.0705	0.0121	87.8	1.2	11.0
No-ACFF	971.63	0.3902	0.3759	0.2704	0.1055	0.0142	81.8	2.5	15.7
Ns-ACFF	1219.4	0.519	0.5014	0.3776	0.1238	0.0175	84.4	1.9	13.7
N _M -ACFF	1171.8	0.4549	0.4436	0.3954	0.0482	0.0112	81.7	1.8	16.5

taken from [135].

Precursor	Modification	Modification Temperatu Time		S _{bet} (S _{BET} (m ² /g) V _{micro} /V _{to}		ot (cm ³ /g) pH _{PZC}		Functional re	ref	
	Concentration (M)	1e (C)	(11)	СА	m-CA	CA	m-CA	CA	m-CA	introduced	
PAN-ACF cloth	HNO₃/3	50	24	1123.3	1209.3	0.55/0.7 4	0.50/0.6 9	8.2	2.2		[137]
Phenol- based ACFs	HNO ₃ /0.1	20	1	1670	1550.0	0.64/0.6 8	0.62/0.6 5			Hydroxyl, carboxyl	[138]
ACF felt	HNO ₃ /3.65	-	2	835.26	1104.5	0.26/-	0.32/-			carboxyl, hydroxyl and carbonyl	[41]
GAC	HNO ₃ /10	90	12	1392	48.0	-/0.93	-/0.4	5.8			[139]
AC	HNO₃/15	90	2	1399	738.1	0.55/0.6 8	0.29/0.4 0	3.6	2.8	lactonic, phenolic, and carboxylic	[140]
MWCNT	H2SO4/18 HNO3/14	120	0.5							Carboxylic, carbonyl	[141]

Table 2.8: Review of the modification techniques for CAs

Modification	Temperatu	Time	S _{BET} (m²/g)	V _{micro} /V _{to}	_{ot} (cm³/g)	pl	HPZC	Functional	ref
agent/ Concentration (M)	re (°C)	(n)	СА	m-CA	CA	m-CA	СА	m-CA	Groups	
3:1 vol/vol										
H ₃ PO ₄	1. 180	1. 0.7		1230.6		0.50/0.6		4.1		[142]
	2. 500	5				2				
		2. 1								
H ₂ O ₂	Ambient	3	1223	1202	0.45/0.5	0.45/0.5			Pyridinic,	[143]
					8	7			pyrrolic	
									quaternary-N	
Thermal	500	0.55	1267	2121	0.46/0.6	0.68/0.9				[144]
					0	0				
HF/4	50	24	1239	979	0.42/0.4	0.21/0.3			Carboxylic	[145]
					3	1			hydroxyl	
NaOCI/0.13	700	24	1910	1946	0.75/0.7	0.76/0.8	8.40	7.80	Carbonyl	[146]
Thermal		1			9	0			phenolic	
O ₂ plasma	300 (W)	3	2121	1615	0.82/1.2	0.63/0.8			Phenolic,	[147]
					2	9			carboxylic	
	Modification agent/ Concentration (M) 3:1 vol/vol H ₃ PO ₄ H ₂ O ₂ H ₂ O ₂ NaOCl/0.13 Thermal O ₂ plasma	Modification agent/ Concentration (M)Temperatu re (°C)3:1 vol/volH3PO41. 180 2. 500H2O2AmbientThermal500HF/450NaOCl/0.13700Thermal20O2 plasma300 (W)	Modification agent/ concentration (M) Temperatu re (°C) Time (h) 3:1 vol/vol 1. 180 1. 0.7 H ₃ PO ₄ 1. 180 1. 0.7 2. 500 2. 10 H ₂ O ₂ Ambient 3 Thermal 500 0.55 NaOCl/0.13 700 24 Thermal 300 (W) 3	Modification agent/ Concentration (M) Temperatu re (°C) Time (h) SBET (CA 3:1 vol/vol .	Modification agent/ Concentration (M) Temperatu re (°C) Time (h) $S_{BET}(m^2/g)$ $3:1$ vol/vol L m -CA $3:1$ vol/vol $1.\ 180$ $1.\ 0.7$ 1230.6 H_3PO_4 $1.\ 180$ $1.\ 0.7$ 1230.6 $2.\ 500$ 5 12 1230.6 H_2O_2 Ambient 3 1223 1202 H_2O_2 Ambient 3 1267 2121 $HF/4$ 500 0.55 1267 2121 $NaOCI/0.13$ 700 24 1910 1946 $Thermal$ 300 (W) 3 2121 1615	$\begin{array}{c c c c c c } \mbox{Modification} & \mbox{Tene (°C)} & \mbox{Imperatu} & \mbox{Time} & \mbox{Set} (\mbox{Mod}) & \mbox{Mod} & \mbox$	Modification agent/ Concentration (M) Temperatu re (°C) Time (h) $S_{BET}(m^2/g)$ $V_{micr}/V \cup (m^3/g)$ CA m-CA CA CA CA M-CA $3:1 vol/vol$ 1. 1.0.7 1230.6 0.50/0.6 H_3PO_4 1. 1.0.7 1230.6 0.50/0.6 2.500 5 1223 1230.6 0.50/0.6 H_2O_2 Ambient 3 1223 1202 0.45/0.5 H_2O_2 Ambient 3 1267 2121 0.46/0.6 0.68/0.9 $MF/4$ 50 24 1239 979 0.42/0.4 0.21/0.3 NaOCl/0.13 700 24 1910 1946 0.75/0.7 0.76/0.8 M_2 300 (W) 3 2121 1615 0.82/1.2 0.63/0.8	$ \begin{array}{c c c c c c } \begin{tabular}{ c c c } & \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	$ \begin{array}{c c c c c } \begin{tabular}{ c c c } & Impervance & $	$\begin{array}{c c c c c } \begin{tabular}{ c c c } \begin{tabular}{ c c c c c c } \begin{tabular}{ c c c c c c c } \begin{tabular}{ c c c c c c c } \begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

Precursor	Modification	Temperatu	Time	S _{BET} (r	m²/g)	V _{micro} /V _t	ot (cm³/g)	pł	H PZC	Functional	ref
	agent/ Concentration (M)	re (C) (n) (M)	(n)	СА	m-CA	CA	m-CA	CA	m-CA	Groups introduced	
Lyocell fibres	N₂ plasma	120 (W)	0.17	1003	1040	0.39/0.5 1	0.37/0.5 3			Pyridinic, pyrrolic quaternary-N	[148]
MWCNT	HNO ₃ /3 H ₂ SO ₄ /1	85	3	435	330	-/0.91	-/0.48			Acidic	[149]
MWCNT	HNO ₃	85	3	435	256	-/0.91	-/0.35			Acidic	[149]
MWCNT	KMnO ₄	85	3	435	283	-/0.91	-/0.37			Acidic	[149]
MWCNT	NaClO	85	3	435	297	-/0.91	-/0.38			Acidic	[149]

2.4. Adsorption of Antibiotics in Aquaculture

Traditional adsorption techniques have been widely applied to remove a range of pollutants including antibiotics, heavy metals and dyes [28,150–153]. The method has several advantages over other remediation techniques including being simple, industrially scalable, environmentally friendly and efficient. CAs such as AC, ACFs and carbon nanotubes (CNTs) are a popular choice of adsorbent due to their high SSA, abundant pore structures and tuneable surface functionalities which increase adsorption capacities.

However, adsorption of antibiotics can be complex due to the vast range of chemical characteristics within antibiotic classes. In general, antibiotic adsorption is particularly dependent on adsorbate-adsorbent interactions which have been reported to be both physical and chemical in nature, depending on environmental conditions [154].

Over recent decades, studies have applied various adsorbents such as CAs, zeolites and clays to remediate antibiotics. This section will provide an in-depth discussion about single and multi-component adsorption mechanisms and modelling followed by comprehensive review of the current literature regarding the application of CAs to adsorb FQ and TC antibiotics within aquaculture, with a particular focus on CIP and OTC.

2.4.1. Adsorption Mechanisms

Adsorption involves the mass transfer of pollutants from liquid (or gaseous) phase to a solid adsorbent surface. The process consists of three steps namely, external diffusion, internal diffusion and adsorption onto active sites (i.e. chemisorption), as depicted in Figure 2.15. External diffusion involves the migration of adsorbates through the liquid film surrounding the adsorbent; this phenomenon is influenced by the concentration gradient between the bulk solution and the surface of the adsorbent. The second step is internal diffusion which involves the movement of adsorbates through the porous structure. Finally, the third step involves the adsorption of the molecule onto an active site, as described below.



Figure 2.15: Schematic of the adsorption mass transfer steps.

Different pollutants interact with the carbon surface *via* different mechanisms (i.e. physisorption or chemisorption, Figure 2.16). Physical attraction is the process of adsorption *via* weak bonds such as Van der Waals forces (i.e. Keesom, Debye, London), hydrogen bonding or hydrophobic interactions, forming in a multilayer on the surface. Chemisorption is an irreversible process involving the formation of chemical bonds (i.e. ionic or covalent) between functional groups on the adsorbate and adsorbent surface, in a monolayer. The process is specific in nature and requires a certain energy level for the chemical bonds to form. The rate of both physisorption and chemisorption increases with increasing temperatures, due to the increased kinetic energy of adsorbate molecules and enhanced diffusion rate among other factors.



Figure 2.16: Depiction of physisorption (A) and chemisorption (B).

Two important phenomena to consider within adsorption are the activation and binding energies. Activation energy (E_a, kJ/mol) refers to the minimum energy required to allow a reaction or process to proceed (i.e. for a molecule to be adsorbed) and typically provides an understanding on the reaction kinetics and adsorption dynamics. Whereas binding energy describes the strength of the interaction between the adsorbent and adsorbate, giving an indication of the stability of the system.

2.4.1.1. Physisorption

Physisorption is the weakest form of adsorption with binding energies typically ranging between 0.01 - 0.5 eV [155]. The process is simple and cost effective as it doesn't require surface functionalisation of the adsorbate and involves little conformational change of the pollutants. Additionally, the process is readily reversible which is beneficial for adsorbent regeneration [156]. Physisorption occurs when the attractive forces between the adsorbent and adsorbate are greater than those between the adsorbate and solute. The phenomenon involves non-localised, weak intermolecular forces such as hydrogen bonding, Van der Waals forces, π - π interactions and hydrophobic effects between the adsorbent and adsorbate, forming a multilayer on the adsorbate surface [154].

Hydrogen bonding is an intermolecular force that arises from a dipole-dipole interaction between a hydrogen covalently bonded to a highly electronegative atom (N, O or F) and another highly electronegative atom (Figure 2.17A).

Van der Waals forces occur due to the transient polarisability of adjacent molecules creating a weak temporary attractive or repulsive interaction. Van der Waals forces can be further subcategorised to Keesom, Debye and London forces based upon the molecules involved in the interaction (Figure 2.17B) [157]. Keesom forces involve the interaction of two molecules with a permanent dipole due to the difference in charge distribution. Debye forces involve the redistribution of charge within a molecule with no dipole moment when in close proximity to a molecule with a permanent dipole (i.e. induction). Thirdly, London forces occur between two molecules with no dipole moment due to fluctuations in the electron cloud which induces a charge redistribution in neighbouring molecules. π - π interactions arise between molecules with π -systems (i.e. cyclic systems with conjugated carbon double bonds), resulting in strong attractive forces between molecules [158].

Hydrophobic effects are a short-range attraction occurring between non-polar molecules in aqueous solution due to their tendency to self-aggregate in aqueous solution, subsequently reducing the surface area of non-polar molecules exposed to aqueous molecules (Figure 2.17D) [159].



Figure 2.17: Schematic representation of hydrogen bonding (A), the three types of Van der Waals forces (B), π - π interactions (C) and hydrophobic interactions (D).

2.4.1.2. Chemisorption

Conversely, chemisorption is more selective and irreversible, involving the formation of new chemical bonds between an adsorbate and functional groups on an adsorbent surface. The bonds are typically ionic or covalent in nature with binding energies greater than 0.5 eV per bond [155]. The presence of functional moieties on the adsorbent surface is paramount to allow the exchange or sharing of electrons between functional groups of the adsorbent and adsorbate [160].



Figure 2.18: Schematic representation of covalent bonding (A) and ionic bonding (B).

A number of studies have identified oxygen-containing surface groups such as carboxylic acids, phenols and carbonyls to play a key role in the chemisorption of antibiotics. This has been further confirmed by the number of studies were the data best fits to the Langmuir adsorption isotherm and pseudo-second order kinetic model, indicating that adsorption is chemical in nature (Table 2.12:).

2.4.1.3. Adsorption Isotherms

Adsorption isotherms are fundamental to describe the equilibrium within an adsorption system and provide insights on the interactions between adsorbents and adsorbate molecules. There are numerous adsorption isotherms cited in literature (both theoretical and empirical) which are typically divided depending on type of surface coverage (monolayer vs multilayer), whether adsorbates are mobile or localised, surface homogeneity and the number of model parameters employed. The most commonly cited isotherms for liquid adsorption are Langmuir, Freundlich and Temkin isotherms, which are discussed below.

The Langmuir adsorption isotherm (Equation 2.1) was one of the first proposed theoretical models and typically describes chemisorption phenomenon [161]. The isotherm is based on several assumptions; adsorption occurs in a monolayer only, the surface of the adsorbent is homogeneous, and all sites are energetically equivalent, adsorption is irreversible, each active site only interacts with one adsorbent molecule and adsorbent molecules are localised, meaning there is no lateral interactions between adsorbent molecules.

$$q_e = \frac{q_{max}K_LC_e}{1 + K_LC_e}$$
 Equation 2.1

Where, q_e (mg/g) is the equilibrium adsorption capacity, q_{max} is the maximum adsorption capacity (mg/g), K_L (L/mg) is the Langmuir constant, relating to rate of adsorption, and C_e (mg/L) is the concentration at equilibrium.

The Freundlich isotherm is an empirical adsorption model, which developed upon Langmuir's equation. The Freundlich model typically describes physisorption, meaning the reaction is reversible. Freundlich's assumptions allow for multilayer adsorption on a surface with asymmetric energy distribution, a decreasing adsorption energy as more molecules are adsorbed, and accounts for surface heterogeneity. The Freundlich equation can be described using the following Equation:

$$q_e = K_F C_e^{1/n}$$
 Equation 2.2

Where, K_F (L/mg) is the Freundlich constant, and n is a correction factor for adsorption intensity. One disadvantages of the Freundlich isotherm is the fact that it cannot predict the equilibrium uptake capacity; however, researchers have often employed the parameters K_F and 1/n to draw conclusions, where the former constant is the partition coefficient, which provides an indication of the adsorption capacity. Whilst n is the correction factor, which indicates whether a process is favourable. Due to the empirical nature of the Freundlich isotherm, there is a lack of theoretical basis, meaning the constants may not reflect the fundamental adsorption mechanisms. Furthermore, since K_F is not a true equilibrium constant and therefore does not provide meaningful information when applied to calculate thermodynamic parameters. The Temkin isotherm is another empirical isotherm (Equation 2.3) which accounts for chemisorption. The isotherm is best suited to intermediate adsorbate concentrations. Due to adsorbate-adsorbent interactions, it is assumed that the heat of adsorption (ΔH_{ads}) of all adsorbate molecules within a layer decrease linearly as adsorption capacity increases.

$$q_e = \frac{RT}{A_T} ln K_T C_e$$
 Equation 2.3

Where, K_T is the Temkin isotherm constant (L/mg), A_T is the Temkin equilibrium binding constant (J/mol), R is the universal gas constant (8.314 J/mol·K) and T is the temperature (K). A number of other isotherm models have also been utilised to describe adsorption processes. A summary of these isotherm models is presented in (Table 2.9).

Model	Equation	Assumptions	Ref
Toth	$q_e = \frac{K_T C_e}{\left(a_T + C_e\right)^{1/t}}$	 Surface heterogeneity Non uniform adsorption energies Monolayer coverage Adsorption site independence 	[162]
Sips	$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	 Surface heterogeneity Finite adsorption capacity Monolayer coverage Adsorption site independence 	[163]
Redlich- Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	Surface heterogeneityFinite adsorption capacityMonolayer coverage	[164]

Table 2.9: Summa	y of adsorption	isotherm models,	adapted from	[13].
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Flory- Huggins $\frac{\theta}{C_0} = K_{FH}(1-\theta)^{n_{FH}}$ • Surface coverage by large [165,166] moleculesHuggins $\frac{\theta}{C_0} = K_{FH}(1-\theta)^{n_{FH}}$ • Lattice model of adsorption • Non-ideal interactions • Entropy of mixingHill $q_e = \frac{K_{SH}C_e^{n_H}}{K_D + C_e^{n_H}}$ • Cooperative binding • Surface homogeneity • Fractional saturationBET q_e $= \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)]\binom{C_e}{C_s}}$ • Surface homogeneity • Uniform adsorption energies for each layer • Multi-layer coverage • No lateral interactions • Dynamic equilibrium hetween layers	Model	Equation	Assumptions Ref
$Hill = \frac{K_{S_H}C_e^{n_H}}{K_D + C_e^{n_H}}$ $= \frac{q_s C_{BET}C_e}{(C_s - C_e)[1 + (C_{BET} - 1)](C_e/C_s)}$ $Iagger = Lattice model of adsorption = 0 ext{ Non-ideal interactions}}$ $Iagger = Lattice model of adsorption = 0 ext{ Non-ideal interactions}}$ $Iagger = Lattice model of adsorption = 0 ext{ Non-ideal interactions}}$ $Iagger = Lattice model of adsorption = 0 ext{ Non-ideal interactions}}$ $Iagger = Lattice model of adsorption = 0 ext{ Non-ideal interactions}}$ $Iagger = Lattice model of adsorption = 0 ext{ Non-ideal interactions}}$	Flory- Huggins	$\frac{\theta}{C_0} = K_{FH} (1-\theta)^{n_{FH}}$	 Surface coverage by large [165,166] molecules
Hill $q_e = \frac{K_{s_H} C_e^{n_H}}{K_D + C_e^{n_H}}$ Cooperative binding[167]BET $q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)] (C_e/C_s)}$ • Surface homogeneity[168]• Surface homogeneity• Surface homogeneity[168]• Multi-layer coverage• Multi-layer coverage• No lateral interactions• Dynamicequilibrium• Dynamicequilibrium			Lattice model of adsorption
Hill $q_e = \frac{K_{S_H} C_e^{n_H}}{K_D + C_e^{n_H}}$ • Cooperative binding[167]BET q_e • Surface homogeneity• Fractional saturation BET q_e • Surface homogeneity[168] $= \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)] (C_e/C_s)}$ • Uniform adsorption energies for each layer• Multi-layer coverage• No lateral interactions• Dynamic equilibrium between layers• Dynamic equilibrium			Non-ideal interactions
Hill $q_e = \frac{K_{s_H} C_e^{n_H}}{K_D + C_e^{n_H}}$ • Cooperative binding[167]• Surface homogeneity• Surface homogeneity• Fractional saturationBET q_e • Surface homogeneity[168] $= \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)] (C_e/C_s)}$ • Uniform adsorption energies for each layer• Multi-layer coverage• No lateral interactions• Dynamic equilibrium between layers• Dynamic equilibrium			Entropy of mixing
$q_e = \frac{1}{K_D + C_e^{n_H}}$ • Surface homogeneity • Fractional saturation BET q_e $= \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)]\binom{C_e}{C_s}}$ • Surface homogeneity [168] • Uniform adsorption energies for each layer • Multi-layer coverage • No lateral interactions • Dynamic equilibrium between layers	Hill	$K_{s_H}C_e^{n_H}$	Cooperative binding [167]
• Fractional saturation BET q_e $= \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)](C_e/C_s)}$ • Surface homogeneity [168] • Uniform adsorption energies for each layer • Multi-layer coverage • No lateral interactions • Dynamic equilibrium between layers		$q_e = \frac{1}{K_D + C_e^{n_H}}$	Surface homogeneity
BET q_e $= \frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)](C_e/C_s)}$ • Surface homogeneity [168] • Uniform adsorption energies for each layer • Multi-layer coverage • No lateral interactions • Dynamic equilibrium between layers			Fractional saturation
$= \frac{q_s c_{BET} c_e}{(c_s - c_e)[1 + (c_{BET} - 1)] \binom{c_e}{c_s}} $ • Uniform adsorption energies for each layer • Multi-layer coverage • No lateral interactions • Dynamic equilibrium between layers	BET	q _e	• Surface homogeneity [168]
 Multi-layer coverage No lateral interactions Dynamic equilibrium between layers 		$=\frac{q_s C_{BET} C_e}{(C_s - C_e)[1 + (C_{BET} - 1)] \left(\frac{C_e}{C_s}\right)}$	 Uniform adsorption energies for each layer
 No lateral interactions Dynamic equilibrium between layers 			Multi-layer coverage
Dynamic equilibrium between layers			No lateral interactions
between ayers			 Dynamic equilibrium between layers

Overall, adsorption isotherms are essential for understanding the interactions between adsorbates and adsorbents. In many cases, the adsorption of antibiotics onto CAs is well described by the Langmuir isotherm model, indicating that chemisorption is likely the dominant adsorption mechanism.

2.4.1.4. Kinetic Models

Adsorption kinetic models are utilised to determine the rate of adsorption and understand adsorbent performance which is essential for the design of adsorption systems. The process is governed by factors such as pH, adsorbate concentration, flow rate, adsorbent dose, surface morphology, and surface functionalisation. The most common kinetic models are the pseudo-first order (PFO), pseudo-second order (PSO), Elovich and intraparticle diffusion (IPD) models which are described by Equation 2.4 - 2.7, respectively. The kinetic models can be

manipulated into both linear and non-linear forms; however, many studies have reported that linearisation of the process may cause inaccurate estimations of parameters [169]. Therefore, non-linear forms are being more widely applied across literature.

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$
Equation 2.4
$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$
Equation 2.5

$$\frac{dq_t}{dt} = \alpha exp^{-\beta q_t}$$
 Equation 2.6

$$t = \left(\frac{q_t - C}{K_p}\right)^2$$
 Equation 2.7

Where q_e is the amount adsorbed at equilibrium (mg/g), q_t is the cumulative amount adsorbed at time t (mg/g) and k_1 (1/min), k_2 (g/mg·min) and k_p (mg/g·min^{0.5}) are the PFO, PSO and IPD rate constants, respectively. α is the initial adsorption rate (when $q_t = 0$, mg/g·min) and β is a constant related to surface coverage and activation energy for chemisorption (g/mg).

In addition, there are a number of other kinetic models that have been reported (although less frequently) in the literature. These models have been summarised in Table 2.10.

Model	Equation
Mixed order	$\frac{dq_t}{dt} = k_1(q_e - q_t) + k_2(q_e - q_t)^2$
Ritchie's	$\frac{d\theta}{dt} = \alpha (1-\theta)^n$
Ritchie's second order	$q_t = \frac{\alpha q_\infty t}{1 + \alpha t}$

Table 2.10: Summary of kinetic models, taken from [13].

Model	Equation
Pseudo n th order	$\frac{dq_t}{dt} = k_n (q_e - q_t)^n$
Boyd's external diffusion	$F = 1 - \frac{1}{\pi^2} \sum_{1}^{\infty} \left(\frac{1}{n^2}\right) \exp(-n^2 B_t)$
	$B_t = -0.497 - \ln(1-F)$. $F = \frac{q_t}{q_{\infty}}$
Frusawa and Smith (F&S)	$\frac{C_t}{C_0} = \frac{1}{1 + m_x K} + \frac{m_s K}{1 + m_s K} e^{-\frac{1 + m_s K}{m_s K} K_{F\&S} St}$
Mathews and Weber (M&W)	$K_{M\&W} = \frac{r_0 \rho (1-\varepsilon)}{3m_s} \cdot \frac{\ln \left(\frac{C_0}{C_t}\right)}{t}$
Phenomenological external mass transfer (EMT)	$\frac{dq_t}{dt} = k_{ext} \left(C_0 - \frac{mq_t}{V} - \frac{q_t}{q_{max}K_L - q_tK_L} \right)$
Boyd's intraparticle diffusion	$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 Bt}$
Pore volume and surface diffusion (PVSD)	$V\frac{dC_t}{dt} = -mS_pk_F(C_t - C_{tr} \mid r=r_0)$
Langmuir kinetics	$\frac{dq_t}{dt} = k_a C_t (q_e - q_t) - k_d q_t$
Phenomenological AAS	$\frac{dq_t}{dt} = k_a \left(C_0 - \frac{mq_t}{V} \right) \left(q_{max} - q_t \right) - \frac{k_a}{k_L} q_t$

Previous literature suggests that the PFO model tends to best fit adsorption data during the initial stages of the process, particularly under conditions of high initial adsorbate concentrations. In such cases, mass transfer is primarily governed by both internal and external diffusion, and the adsorbent possesses a limited number of active sites for adsorption [170]. While PSO models are typically more applicable during the later stages of the adsorbent process, particularly when high initial concentrations of adsorbent are used and active sites are plentiful.

2.4.1.5. Adsorption Thermodynamics

Adsorption thermodynamics are another key analysis technique to determine whether a process is favourable. This is determined using the Gibbs free energy of adsorption (ΔG_{ads}). For an adsorption process to be considered spontaneous ΔG_{ads} must be negative. The simple form of the equation can be expressed as follows:

$$\Delta G_{ads} = \Delta G_{non-electrostatic} + \Delta G_{electrostatic}$$
Equation 2.8

Where $\Delta G_{electrostatic}$ denotes to the energy of columbic interactions (i.e. attractive or repulsive forces between two similar or dissimilar charges) and $\Delta G_{non-electrostatic}$ signifies all other interactions (i.e. Van der Waals forces, hydrophobic interactions and hydrogen bonding – which are always attractive). Experimentally, the ΔG_{ads} can be determined using Equation 2.9 – 2.12. The distribution coefficient (K_d) can be calculated using Equation 2.9:

$$K_d = \frac{q_{eq}}{C_{eq}}$$
 Equation 2.9

Where, K_d signifies a dimensionless constant (L/g). Often, isotherm constants can be substituted for K_d , for example the Langmuir constant can be expressed in L/mol units; therefore, the value can be expressed as a dimensionless constant by multiplying it by the number of moles of water in a litre of solution (55.5 mol/L). Subsequently, the true Δ G value can be calculated using Equation 2.10.

$$\Delta G^0 = -RT ln K_d \qquad \qquad \text{Equation 2.10}$$

Where ΔG^0 (kJ/mol) is the Gibbs free energy at standard conditions (i.e. 25 °C, 1 M, 1 atm), R is the universal gas constant (kJ/mol·K).

Equation 2.11 expresses the relationship between ΔG^0 , enthalpy/heat of adsorption (ΔH^0 , kJ/mol) and entropy change (ΔS^0 , kJ/mol·K) under standard conditions:

$$\Delta G^{0} = \Delta H^{0} - T \Delta S^{0}$$
 Equation 2.11

By substituting Equation 2.10 into Equation 2.11, the following linear equation is generated:

$$lnK_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$
 Equation 2.12

Therefore, by plotting InK_d against the inverse temperature, ΔH^0 and ΔS^0 can be determined from the slope and intercept, respectively.

When expressed as ΔG , ΔH and ΔS , this refers to the Gibbs free energy, heat of adsorption and entropy change under real world conditions (i.e. any condition).

In addition to adsorption isotherms, thermodynamic calculations offer an insight into an adsorption mechanism. ΔH^0 can provide a host of information; for example, positive ΔH^0 values indicate an endothermic process and negative values indicate exothermic processes. Additionally, the magnitude of ΔH^0 indicates the adsorption mechanism with physisorption typically ranging between 2.1 – 20.9 kJ/mol and chemisorption ranging between 21 – 200 kJ/mol [171]. Unfortunately, this technique is only accurate if K_d has been calculated accurately, which is highly dependent on the adsorption system which has been discussed in depth elsewhere [171,172].

2.4.2. Adsorption of Antibiotics

2.4.2.1. Single-component Adsorption

Batch Adsorption is a dynamic technique, utilised to identify the influence of various factors (i.e. pH, initial concentration, adsorbent dose, temperature etc.) on the adsorption capacity and gain an insight into adsorption mechanisms *via* the application of adsorption isotherms and kinetics. Many studies have employed batch adsorption to gain an understanding of how CAs interact with and adsorb various antibiotics including CIP and OTC.

Hayrera et al. investigated the adsorption of OTC using hierarchical ACs via batch adsorption processes to determine the impacts of pH [173]. ACs were contacted with an OTC solution (10 -600 mg/L) for 4 h and shaken in a water bath at temperatures between 25 -45 °C, using an adsorbent dose of 0.625 g/L. After which the samples were filtered through a 0.45 μ m polyvinylidene fluoride filter, and then the concentration of OTC concentration was determined using a UV–visible spectrophotometer (λ_{max} = 358 nm). At pH \leq 7, there was no notable decrease in adsorption capacity (Figure 2.19A). However, a significant decrease in adsorption capacity was observed at pH above 8. This phenomenon was attributed to the interactive/repulsive effects between the AC and OTC. The point of zero charge (pH_{PZC}) of the AC was identified as 3.9, therefore, at pH < 3.9, the AC surface is positively charged, whilst OTC dominantly exists in its negatively charged form, resulting in interactive effects (Figure 2.19B). The data suggests that OTC adsorption is also significantly influenced by π - π interactions and hydrophobic effects between the pH of 3.9 – 8, because OTC exists in its most hydrophobic state with zero charge, where it readily accepts π -electrons from the conjugated structures within the AC. Finally at pH > 8, repulsive effects occur between the negatively charged adsorbent surface and OTC molecules resulting in a notable decrease in adsorption capacity. The adsorption isotherms and kinetics were also investigated, with the best fitting models being Langmuir (R² = 0.9990) and Elovich (R² = 0.9964), respectively, suggesting that adsorption is governed by a combination of bulk and surface diffusion and chemisorption on energetically heterogenous surfaces.



Figure 2.19: (A) The influence of pH on the adsorption of OTC onto ACs and (B) the zeta potential of AC with the speciation of OTC, taken from [173].

Lanthium modified carbon nanotubes (CNTs) have been applied for the removal of TC antibiotics. For example, Yu et al. synthesised lanthium modified multi-walled CNTs to remove OTC from a simulated aquaculture solution [174]. The CNTs were then contacted with the OTC solution for 1 h and shaken at a rate of 150 rpm. The optimum conditions were found to be an adsorbent dosage of 0.03 g/L, OTC concentration of 20 mg/L, contact time of 1.5 h, and pH of 7, achieving a maximum equilibrium adsorption capacity of 108.46 mg/L. Within a different article the research group conducted the same study for the adsorption of TC [175], finding the optimum conditions to be the same as above; however, a lower maximum equilibrium adsorption was both physical and chemical in nature, identifying Van der Waals forces, π - π interactions, and electrostatic interactions as the main mechanisms.

Carabineiro et al. employed three types of commercial CAs, specifically, ACs, polymer-based carbon xerogel (CX) and CNTs, to determine the adsorption isotherms and kinetics for the adsorption of CIP [176]. The CAs were modified via three techniques, namely nitric acid modification which was denoted CA_a. CA_b and CA_c were produced by thermally treating the CA_a samples at 350 or 900 °C, respectively, to further modify their surface chemistry. Finally, gas phase activation was also employed on CX to generate oxygen groups on the surface by heating to 400 °C. The CAs (CA, CA_a, CA_b, CA_c and CA_d) were combined with a CIP solution (initial concentration 3 – 30 mg/L) using an adsorbent dose of 50 mg/L, for 72 h under shaking, with the temperature and pH being maintained at 25 °C and 5, respectively. For the kinetics, aliquots were removed at allotted time intervals throughout the duration of the experiment, whereas for the isotherms, only the final concentrations were measured. The concentration was determined using UV-vis at a wavelength of 270 nm. The data were found to fit best to the PSO kinetic model (R² > 0.9290) and Langmuir adsorption isotherm (R² > 0.9840). The high temperature, thermally treated CAs performed the best for AC_c and CX_c, whereas the acid modified samples (AC_a and CX_a) performed the worst suggesting that CIP adsorbs best on a less acidic surfaces *via* π - π interactions at pH 5 (Figure 2.20).



Figure 2.20: q_{max} of CA samples for the adsorption of CIP, taken from [176].

Tran et al. employed mangosteen peel-derived ACs to investigate the adsorption of CIP, employing an OFAT approach [177]. Five experimental factors were studied, namely, pH, contact time, adsorbent dose, initial concentration and temperature. The pH of the CIP solution was adjusted using 1 M NaOH and 0.1 M HCl. A prescribed amount of adsorbent was added to a 100 mL Erlenmeyer flask and combined with CIP and shaken at the required conditions, as described in Table 2.11. Post adsorption, the CIP concentration was determined using UV-vis, scanning wavelengths in the region of 190 – 1100 nm. The optimal conditions were found to be a pH, contact time, CA adsorbent dose, initial concentration and temperature of 6, 60 min, 3 g/L, 400 mg/L and 45 °C, respectively. Similarly to OTC, a decline in pH was observed at pH > 6 due to the repulsive interactions between the negatively charged surface of the AC and CIP⁻. When the pH was between 5.3 (pH_{PZC}) and 6, the AC surface possesses a positive charge whilst CIP exists predominantly in its negatively charge form, resulting in attractive interactions and subsequently an enhanced adsorption capacity. The data were also fit to adsorption isotherms (Langmuir, Freundlich, Temkin, Elovich and Redlich-Peterson) and kinetic models (PFO and PSO), and the activation energy and thermodynamic parameters were determined. The adsorption data best fit the Langmuir isotherm and PSO kinetic model, with R² values of 0.9986 and 0.9999, respectively. The activation energy was calculated to be < 0.17 eV suggesting that the adsorption of CIP was dominated by external diffusion. Finally, the thermodynamic parameters were calculated to be a ΔG^0 between -0.845 and -5.329 kJ/mol (temperature dependent), a ΔH^0 of 66.957 kJ/mol and a ΔS^0 of 0.223 kJ/mol, indicating that the adsorption of CIP onto AC was spontaneous.

	Experimental conditions				
Parameters	рН	Time (min)	CA mass (g/L)	Initial CIP concentration (mg/L)	Temperature (°C)
Effect of pH	3 - 10	60	3.0	50	25
Effect of contact time	6	15 – 120	3.0	50	25
Effect of adsorbent dose	6	60	1.2 - 8.0	50	25
Effect of initial concentration	6	60	3.0	50 - 400	25
Effect of temperature	6	60	3.0	50	25 – 45

Table 2.11: Parameters of the experiments and experimental conditions, taken from [177].

As can be seen above, there are a range of parameters that significantly influence the adsorption of antibiotics onto CAs, with pH, contact time, adsorbent dose, initial concentration and temperature often having the strongest influence. Current literature provides an insight into influence of these parameters on the adsorption of CIP and OTC and the potential adsorption mechanisms. However, it is recommended that these parameters are evaluated on a case-by-case basis for each material, due to the range of physiochemical characteristics of CAs. DoE is a promising approach to optimise adsorption of antibiotics on CAs, whilst simultaneously allowing the researcher to gain an insight into potential interaction mechanisms between parameters and their subsequent influence on adsorption capacity, as discussed in Section 2.6.2.2.

Sample	S _{BET} (m²/g)	V _{micro} /V _{tot} (cm³/g)	Pollutant	C₀ (mg/L)	q _{e -} (mg/g)	Optimum pH	Adsorption isotherm/R ²	Kinetic model/ R ²	Ref
AC	852	-/0.67	Ciprofloxacin		101.7	8.5	Langmuir/0.999	PSO/0.998	[178]
AC	852	-/0.67	Norfloxcin		99.71	4.5	Langmuir/0.999	PSO/0.998	[178]
AC	852	-/0.67	Levofloxcin		104.76	8.5	Langmuir/0.999	PSO/0.999	[178]
m-AC (Thermal)	1013	0.34/0.66	Ciprofloxacin	20	300	7	Langmuir/0.995	PSO/0.981	[179]
m-AC (H₃PO₄)	-	-	Ciprofloxacin	50	49.75	8	Langmuir/0.982	PSO/0.999	[172]
CNTs (Thermal)	456	0/2.13	Ciprofloxacin	20	60	7	Langmuir/0.998	PSO/0.980	[179]
AC	1524	0.65/0.83	Tetracycline	500	369.4	3	Temkin/0.980	Elovich/0.990	[180]
m-AC (H ₂ O ₂)	117.05	-/0.10	Tetracycline	500	42.45	9	Langmuir/0.991	PSO/0.947	[181]
ACF	1007.69	0.34/0.49	Tetracycline		249.02	2	Freundlich/0.999	PSO/0.999	[182]
ACF	1007.69	0.34/0.49	Oxytetracycline		249.00	2	Langmuir/0.998	PSO/0.999	[182]
AC	-	-	Oxytetracycline	10	17.99	9	Freundlich/0.980	PSO/0.990	[183]

Table 2.12: – Review of carbonaceous adsorbents to remediate aquaculture pollutants.

2.4.2.2. Competitive Adsorption

Competitive adsorption is one of the main limiting factors, when considering adsorption in natural waters, whether between target pollutants themselves or external factors such as salinity and dissolved organic matter (DOM). Since this thesis is focusing on low-risk freshwater aquaculture systems, this section will largely focus on competitive adsorption between antibiotics and the latter factor since multiple antibiotics are not commonly applied simultaneously.

The natural prevalence of DOM originates from a wide range of sources such as leaching from animal faeces, rocks, crops and more. For this reason, DOM has diverse chemical structures, containing a range of functional groups and molecular sizes, with humic-like, fulvic-like and tyrosine-like being identified as some of the most common forms of DOM in aquaculture [184,185]. For this reason, a range of interaction mechanisms between CAs and DOM have been identified in literature, some frequent examples being complexation, covalent bonding, π - π interactions, electrostatic interactions and Van der Waals forces. Numerous studies have identified direct site competition and pore blockage as the leading interference mechanisms of DOM, when considering the adsorption of pollutants onto carbonaceous materials [186–189].

The competitive adsorption between pharmaceutical compounds (i.e. binary, tertiary solutions), utilising CAs has been studied in recent years [190–193]. However, there is a significant gap in literature regarding the competitive adsorption of pharmaceuticals in the presence of natural matter such as DOM. Some studies have suggested that there is a significant decrease in the adsorption capacity of CAs towards target pharmaceuticals in the presence of DOM. For example, Sousa et al. employed ACs to study the competitive adsorption behaviour of three antibiotics, namely, sulfamethoxazole (SMX), trimethoprim (TMP) and CIP, in single, binary or tertiary system, utilising ultra-pure water or treated wastewater effluents as the adsorption medium [194]. Wastewater was collected from a municipal wastewater treatment plant of Aveiro (Portugal) and characterised by measuring conductivity, pH, and DOM, where the respective results were identified to be 6.8 mS/cm, 8.0, and 13.3 mg/L. A decrease in adsorption capacity was observed in binary and tertiary systems when compared to single-component systems due to the enhanced competition for active sites (Figure 2.21).

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Figure 2.21: Percentage of adsorption of SMX, TMP and CIP onto ACs from ultrapure (left), and wastewater (right)), in single, binary and ternary solutions, C_0 : 10 µmol/L, contact time: 24h, DOM: 13.3 mg/L), taken from [194].

Choi et al. investigated the adsorption of TC antibiotics onto coal and coconut based ACs in the presence and absence of DOM [195]. The DOM water was collected from a pilot plant, treating river water, the pH, alkalinity DOM content and turbidity were found to be 8.1, 65 mg/L, 3.12 mg/L and 15.3 NTU, respectively. Prior to adsorption, both the DOM water and DI water were dosed with TCs to achieve an initial concentration of 10 μ g/L and the pH was adjusted to 7. The coal or coconut ACs were then contacted with the TC solutions for 24 h at temperature of 25 °C and adsorbent dose of 0.7 mg/L. The ACs were then removed *via* filtration and the antibiotic concentration was determined using UV-vis. Organic interference was found to have a negative influence on the removal capacity of the TCs, resulting in a 22 – 78% reduction depending on antibiotic type (Figure 2.22).

Due to the significant lack of literature utilising CAs, gaining an understanding of the competitive adsorption between antibiotics and DOM onto non-carbonaceous adsorbents and soils can be useful to gain an insight into the major influencing factors and adsorption mechanisms involved. Studies have investigated the competitive adsorption of TCs onto soils, finding that factors such as cation exchange capacity and iron oxide and surface texture content play a significant role on the adsorption of TCs in the presence of DOM [196].

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Figure 2.22: Comparison of the removal of TCs from the deionised and DOC water by ACs (C_0 : 10 μ g/L, contact time: 24h, DOC: 0.8 mg/L), taken from [195]. Where MNC, DXC, MCC, CTC, DMC are minocycline-HCl, doxycycline-hyclate, meclocycline-sulfosalicylate, chlortetracycline-

HCl and democycline-HCl, respectively.

Conde-Cid et al. investigated the competitive adsorption of TC antibiotics and DOM onto six types of soil (denoted 3AL, 19 AL, 50 AL, 6S, 51S and 71S) from two agricultural areas in Spain [197]. The DOM content of the soils was determined and ranged between 1.1 - 10.9% carbon content. The DOM content of the soils in decreasing order was 50AL > 71S > 3AL > 6S > 51S > 19 AL. It was observed that soil samples with a higher DOM content resulted in increased adsorption capacities of TC type antibiotics, having the largest influence on OTC, which was attributed to the enhanced interactions between the different reactive functional groups within the DOM and antibiotic compounds.

Furthermore, adsorbent pore size distribution plays a vital role when considering competitive adsorption between organic pollutants and DOM. DOM consists of molecules typically ranging from 1 - 450 nm in size [189], and therefore, microporous or smaller mesoporous carbon materials typically showed a greater affinity to smaller organic molecule over DOM, which can be attributed to pore size exclusion. However, DOM still could adsorb to the carbon surfaces *via* π - π stacking interactions and Van der Waals forces, resulting in the blockage of some pore

entrances. When the pore size distribution is sufficiently increased, direct competition for sites becomes the most important mechanism for adsorption, since DOM can enter the larger pores, ultimately reducing the adsorption capacity for target pollutants.

The impact of common aquaculture ions on the adsorption of TC antibiotics using commercial and lanthanum-modified zeolites have also been investigated [198]. Prior to competitive adsorption, the impacts of La modification concentration (0 – 0.6 mol/L), adsorbent dose (0.01 – 0.06 g), chlortetracycline (CTC) initial concentration (5 – 30 mg/L), reaction time (5 – 30 min) and pH (5 – 10) were investigated, with the optimum conditions found to be 0.2 mol/L, 0.03 g, 10 mg/L, 20 min and 7, respectively. The competitive batch adsorption experiments consisted of introducing 100 mg/L of the individual ions (Na⁺, NO₂⁻, H₂PO₄⁻ and NH₄⁺) into the adsorption system at the optimum conditions. Na⁺, NO₂⁻ and NH₄⁺, were found to have little effect on the adsorption capacity of CTC, achieving removal efficiencies above 80% (Figure 2.23). Whereas a small decrease was observed for H₂PO₄⁻, which was attributed to the ligand exchange between lanthanum and H₂PO₄⁻ to form insoluble phosphate.



Figure 2.23: The effects of interference ions on the adsorption of CTC [198].

As can be seen above, there is a significant lack of research utilising CAs to gain an understanding of the competitive adsorption behaviour of antibiotics in the presence of natural matrices. In order for CAs to become industrially *via*ble in an aquaculture setting, significant research is required within this area.

2.5. Adsorbent Regeneration

Adsorbent regeneration is a critical factor in improving the recyclability and long-term usability of an adsorbent, both of which are essential for developing a high-performance, industrially viable material. The regeneration process involves removing adsorbed pollutants from the surface, typically through physical, chemical, or biological methods, while preserving the integrity of the adsorbent's porous structure. The advantages and disadvantages of the regeneration methods are summarised in Table 2.13.

Regeneration Technique	Method	Advantages	Disadvantages
Thermal	Pyrolysis at high temperature to thermally desorb or decompose adsorbates. RE increases with temperature.	Simple operation. High RE. Industrial scalability. Suitable for adsorbents loaded with a heterogenous mixture of adsorbates.	Reduction in S _{BET} due to decomposition. High energy consumption.
Solvent	Vary pH, temperature and/or ionic strength of solvent to desorb adsorbates.	Can be coupled with other degradation processes such including Fenton	RE is dependent on the solubility of the adsorbate within the solvent.
	Can be conducted at supercritical or subcritical conditions.	degradation. Useful for organics with high concentrations and low boiling points. Simple operation. High RE.	Residual solvent may cause pore blocking. Hazardous waste stream. Solvents need to be recycled. Limited scalability.

Table 2.13: Comparison between regeneration technologies, taken from [13]

Regeneration Technique	Method	Advantages	Disadvantages		
Electro- chemical	Application of an	Simple operation.	Lack of knowledge –		
	electrical current for electrochemical oxidation of adsorbates.	Suitable for both inorganic and organic adsorbates.	new technology. Mass transfer limitations between		
		Low adsorbent fouling.	electrodes can cause		
		Low energy consumption.	the cathode.		
		Quick.			
		High RE.			
Microwave	Apply MW irradiation to thermally desorb or decompose adsorbate.	Enhanced homogeneity of desorption.	Expensive. Better suited to fluidised be systems.		
		Can increase pore size and surface area.	Pore-blocking from decomposition products.		
		Quick.			
		Low energy consumption.			
		High RE.			
Ultrasonic	Provide sonicating power to cause desorption <i>via</i> physical phenomena (i.e. micro- streaming/turbulence).	Low energy consumption.	Only effective for physisorption [199].		
		Simple operation.	Low RE.		
		No attrition of adsorbent.			
		No secondary pollution.			
Ozonation	Supply adsorbent with a continuous flow of an ozone-oxygen mixture, to remove adsorbates <i>via</i> ozonation or interactions with free radicals.	Readily degrades organic adsorbates.	Modification of adsorbent surface.		
		Little degradation to SBET.	Doesn't react with all molecules.		
		Can improve adsorption capacity of adsorbent.	Requires calcination of adsorbent before reuse.		

Regeneration Technique	Method	Advantages	Disadvantages
Biological	Application of microbials for biodegradation of adsorbates.	Converts toxic pollutants into small non-toxic molecules.	Limited scalability. Fouling due to regeneration by- products.
			More effective for chemically activated adsorbents than thermally activated [200].

The efficiency of a regeneration technique is commonly determined using desorption efficiency (DE, %) and regeneration efficiency (RE, %). DE – otherwise known as cumulative heel – is described as the percentage of adsorbate desorbed with respect to total amount adsorbed within an exhausted structure. DE is generally measured by comparing differences in weight of a CA, between the adsorption cycles (Equation 2.13) [201,202]. RE involves evaluating the adsorption capacities of the original CA with the regenerated CA and can be determined using Equation 2.14 [67].

$$DE(\%) = \frac{M_{AA} - M_{BA}}{M_{VA}} \times 100$$
 Equation 2.13

Where, M_{BA} and M_{AA} (g) are the masses of the adsorbent before and after an adsorption cycle, respectively. M_{VA} is the mass of the virgin adsorbent.

$$RE(\%) = \frac{q_{reg}}{q_{orig}} \times 100$$
 Equation 2.14

Where, q_{reg} and q_{orig} (mg/L), are the adsorption capacities of the regenerated and original CA, respectively.

2.5.1. Thermal Regeneration

Thermal regeneration involves heating the exhausted CAs to supply a sufficient amount of thermal energy to break adsorbent-adsorbate interactions. This typically involves heating to temperatures up to 600 °C, in order to remove the retained adsorbate.

De Carvalho Costa et al. investigated the influence of temperature on the regeneration of TC saturated ACs [77]. ACs were heated to temperatures of 200 °C (TTM1) or 400 °C (TTM2) at a rate of 10 °C/min and held for 2 h under atmospheric conditions[77]. After one cycle a RE of 100% and 87% was reported for TTM1 and TTM2, respectively. The study then assessed the adsorbent regeneration for 13 cycles, applying method TTM1, finding that a high RE (> 90%) was maintained until the sixth cycle before a more impactful decline was observed (Figure 2.24). This decline in RE was attributed to the deposition of pollutants as impurities on the adsorbent surface, resulting in pore blocking.

ACs saturated with CIP were subjected to thermal treatment at 600 °C for 1 h in an oxygen depleted atmosphere which resulted in poor a RE of 54% after one cycle [203]. The results correlated with a reduction in surface area by almost half, from 332 to 170 m²/g, when comparting the fresh AC to the thermally regenerated.

Alkathiri et al. regenerated PAN-ACFs using both thermal (heating to 400 - 600 °C for 1 h under N₂ flow) and chemical techniques (20 mL of n-hexane or ethanol for 10 min inside sealed flasks) [115]. The study concluded that thermal regeneration was the most effective with an efficiency of 83.9% after the first cycle, and 77.5% after the second.




2.5.2. Chemical Regeneration

Chemical regeneration employs a chemical agent which alters the speciation of an adsorbed compound *via* acid-base or redox reactions, subsequently disturbing the equilibrium of the adsorption process. Regenerants can be divided into inorganic and organic solvents, from which they can be further subdivided based on properties such as pH, polarity, molecular weight and toxicity [204].

pH plays a particularly important role in the chemical regeneration of adsorbents, impacting the speciation of both the adsorbent surface and the adsorbed contaminant, resulting in interactive or repulsive effects. The influence of pH is highly dependent on several factors such as the pH_{PZC} of the CA and the pKa of the adsorbate. Solvent polarity also has a crucial influence on adsorbent regeneration, since polar solvents aid the desorption of polar contaminants via dipole-dipole interactions and hydrogen bonding. Whereas non-polar solvents rely on physical interactions such as hydrophobic effects and London dispersion forces. Since CAs often possess a degree of non-polarity, polar solvents are often considered to be advantageous for regeneration since they are unlikely to be adsorbed significantly onto the CA surface and are readily removed after the regeneration process by washing with deionised water. Low molecular weight solvents are favoured since it allows for enhanced diffusion into the porous network of the CA, facilitating the displacement of the adsorbed molecules. Finally, toxicity of the solvent must be constrained to limit adsorbent contamination and hazardous waste streams. Chemical regeneration presents a number of advantages over physical regeneration, particularly for aqueous phase applications, for example simple operation, energy efficiency and the lack of requirement for high temperature apparatus.

Various regeneration solvents have been applied in the regeneration of CAs, exhausted with FQ or TC type antibiotics. As discussed in Section 2.4.1, adsorption of these antibiotic classes is often favoured at acidic pH (< 5). Therefore, hydroxides such as NaOH or KOH, make attractive candidates as regeneration solvents, due to the significant shift in pH which alters the speciation of the antibiotics and the CA surface charge resulting in repulsive forces and subsequently desorption [89,205].

For example, Chandrasekaran et al. utilised NaOH to regenerate pre-adsorbed CIP from ACs. The ACs were contacted with 0.1 M NaOH for 24 h, after which the recovered solid was washed

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thoroughly with deionised water before being used in subsequent adsorption-desorption cycles [89]. The RE after the first cycle was 99%; however, after the fourth cycle, the RE had dropped to 48%. The reduced efficiency was attributed to morphological disruption of active sites and pore blocking due to the formation of sodium salts. Similar studies have investigated the regeneration of ACs exhausted with ciprofloxacin using higher concentration NaOH (0.25 M), achieving regeneration rates of up to 90% after one cycle [206]. The reduction in RE when utilising higher concentration solvents could be attributed to increased pore blocking due to the formation solvents could be attributed to increased pore blocking due to the formation of Additionally, a higher hydroxide concentration results in a higher number of OH⁻ groups being retained on the surface.

TC-loaded ferromagnetic ACs were regenerated using 0.1 M NaOH and shaking for 3 h, as above, the adsorbents were washed prior to reuse [205]. A high RE (<70%) was retained after 4 regeneration cycles (Figure 2.25).



Figure 2.25: Effect of the number of regeneration cycles on TC adsorption by FAC [205].

Li et al. utilised electro-assisted desorption techniques [207], applying several regeneration agents, namely 20% HNO₃ 20% HCl and deionised water, to determine which solvent had the performed the best for the regeneration of norfloxacin-laden ACF felts, finding that HNO₃ significantly outperformed the other solvents, achieving an RE of 96%, after six cycles, in comparison to HCl and deionised water which had RE of 89% and 71%, respectively.

2.6. Design of Experiment & Statistical Analysis

2.6.1. Design of Experiment Techniques

In order to gain an understanding of the relationships between key process variables, it is important to explore a range of conditions. A common but inefficient approach is one-factorat-a-time (OFAT) testing, where, as the name implies, one factor is varied, whilst all other factors are kept constant. Whilst this technique may provide some valuable information about a process, it is widely agreed that it is largely dependent on guesswork, experience, and intuition for success, since a large area of the design space is left unexplored which could lead to the inaccurate identification of the optimum point (Figure 2.26). Furthermore, OFAT designs are unable to evaluate the interaction effects between factors which may have a considerable impact on the optimum conditions.



Figure 2.26: Examples of different experimental designs.

Design of experiment (DoE) is a powerful statistical tool to identify relationships between multiple input variable (i.e. factors) and the subsequent output variable(s) (i.e. response). DoE is commonly divided into three categories, namely, space filling, factorial and response surface methodology (RSM) designs. Space filling designs are useful in the early stages of research where there is little knowledge around the system. Since the processes in this thesis are well-

established with a range of literature to refer to, these designs are scarce. Factorial designs are typically applied for screening and refinement of a process. Finally, RSM is used for the optimisation of a process and to determine interaction effects between factors.

Factorial designs can be divided into full factorial or fractional factorial designs (Figure 2.26). Full factorial designs consist of testing all possible combinations of all factors and levels and are useful in the early stages of research, particularly when working with a small number of factors (\leq 4) and a limited number of levels per factor. Full factorial designs present several advantages over OFAT designs, such as increased efficiency since they can test multiple factors and interactions in fewer experimental runs. However, when compared to other DoE techniques they are considered to be inefficient and costly, since the number of runs increases exponentially with increasing numbers of factors. For example, considering a full factorial design, a 3 level, 3 factor design requires 27 (3³) experimental runs, while a three level, five factor design requires 243 (3⁵) experimental runs.

A more time and resource efficient method is fractional factorial design which is a type of orthogonal array design used to study the main effects and interaction effects in the minimum number of experimental runs; however, there is a trade-off between resolution and efficiency within these designs. Fractional factorial designs are commonly presented in the form 2(k-p) where k is the number of factors and 1/2p represents the fraction of the full factorial (2k).

RSM is useful for the optimisation of processes and the identification of interaction effects between factors. Common RSM techniques include central composite design (CCD) and Box-Behnken design (BBD). These techniques are especially attractive because they allow for the estimation of curvature within a design space, which cannot be portrayed by a simple linear model. This is achieved by fitting a second order (or above) polynomial model.

CCD can be described as a form of factorial design with centre points and axial points (Figure 2.26). The technique is particularly attractive for sequential experiments since they can build upon previous factorial experiments by introducing axial and centre points. However, CCD requires a higher number of experiments when compared to BBD, increasing the time, resources and expenses of an experimental campaign. Furthermore, CCD results in extreme operating conditions, in the case if circumscribed (CCC) designs, which may result in loss of data points or be hazardous to the operator (i.e. when utilising at high temperature, pressure or

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concentrations). Whereas the application of face centred (CCF), and inscribed designs (CCI) result in a reduction in the area of the design space, which may be unfavourable (Figure 2.27).

In contrast, BBD does not contain embedded factorial designs meaning they are not readily built upon previous factorial experiments. Instead, BBD operates at the midpoints on the edges of an experimental design space (Figure 2.26), which is advantageous because it avoids extreme and potentially hazardous experimental conditions. Furthermore, they are more cost-effective and time-efficient than CCD, since they require fewer experimental runs.

After the completion of a *designed* experimental campaign, the gathered data needs to be evaluated statistically to understand the significance and/or interactions of the factors investigated. The most prominent analysis techniques include analysis of variance (ANOVA) and RSM.



Figure 2.27: The three types of CCD.

ANOVA is a popular technique allowing for the simultaneous evaluation of multiple factors (\geq 3 factors) at several levels (\geq 3 levels) to determine their statistical significance. This is achieved by evaluating and separating the variation associated with the main effects in the design space by applying a least squares method [95,208]. A couple of assumptions must be fulfilled for ANOVA to be applicable, namely: all replicates must be independent of each other, and experimental runs must be randomised. Furthermore, a normality test should be conducted prior to ANOVA to determine whether the results follow a normal distribution [209]. ANOVA outputs include a range of data with the most important information being the p-value and F-value. The p-value measures the probability that any observed difference could have arisen by random chance. It could also be viewed as the probability of achieving results close to the actual/representative of the experimental data. In order for an input variable to be considered statistically significant, the p-value must be sufficiently small (typically \leq 0.05), meaning the null hypothesis can be rejected with a 95% confidence level. F-values determine the variation between or within the samples in a data set, where larger values indicate higher variation between sample means.

RSM is utilised with CCD or BBD to establish an empirical statistical model which can approximate the relationship between a set of input variables (x_i) and a response variable (y_i) [210]. RSM is particularly useful to graphically visualise the impacts various parameters may have on a given response. In order to generate a 3D response surface plot or 2D contour plot, each factor must be measured on a minimum of three levels, since this accounts for the presence of curvature within a design space. Typically, ANOVA is applied prior to RSM, to identify the statistically significant factors and therefore, only produce contour plots of these factors.

2.6.2. Design of Experiments for the Synthesis and Application of Carbonaceous Adsorbents

A number of DoE techniques have been applied in literature for the activation, modification and adsorption processes of CAs. The following sub-sections summarise where DoE techniques have been applied to optimise the synthesis and adsorption of aqueous phase CAs.

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2.6.2.1. Optimisation of Adsorbent Synthesis

Screening techniques such as full factorial designs have occasionally been applied as a screening process for the activation of CAs [211,212]. For example, Lim et al. applied a three-factor, three-level design, investigating the effects of activation time (5.68 – 69.32 min), activation temperature (379.29 – 520.71 °C) and IR (1:0.28 – 1:3.47, AC:H₃PO₄) on the responses, iodine number and yield of ACs derived from oil palm trunk [211]. The optimum synthesis parameters were found to be an activation time, activation temperature and IR of 6 minutes, 450 °C and 1:2.29, respectively.

More commonly RSM approaches have been applied to optimise the synthesis procedure such as CCD [213,214], and BBD [215,216]. The production of ACs from waste tyres has been optimised by employing a four-factor, three-level CCD [214]. The impacts of activation temperature (550 – 750 °C), activation time (15 – 75 min), CO_2 flow rate (200 – 400 mL/min) and impregnation ratio (1:0.75 – 1:3.75 KOH:AC), on yield and specific surface area were investigated. Activation temperature was found to have the largest influence on the yield which can be attributed to the increased carbon burn-off, in the form of VOCs. All parameters were found to be statistically significant on the specific surface area, with activation temperature having the largest impact. The study identified an optimum point for each response, which for S_{BET} was found to be an activation temperature, activation time, CO₂ flow rate and impregnation ratio of 745.15 °C, 45.09 min, 221.40 mL/min and 1.66 achieving a maximum SBET of 928.86 m²/g; however, a low yield of 13.06% was observed. Whereas to optimise yield, lower activation temperatures (554.06 °C) and times (33.80 min), and increased CO₂ flow rates (318.91 mL/min) and IR (1:3.44) were favourable achieving a maximum yield and S_{BET} of 47.15% and 378.08 m²/g, respectively. This study could be improved by optimising both responses simultaneously and therefore, identifying one optimum point with sufficient SBET and yield.

The synthesis of AC/iron oxide composites for the adsorption of Acetylsalicylic acid has been optimised using BBD [215]. The impacts of impregnation ratio $(1:1 - 1:3, \text{ precursor:FeCl}_3)$, activation temperature (600 - 800 °C), and activation time (60 - 180 min) on yield and adsorption capacity were investigated. As each independent variable was increased, a decrease in yield was observed due to the expulsion on carbon and VOCs during pore formation. The reverse trend was observed for adsorption capacity since increased burn-off results in higher surface area and pore volume. The optimum conditions were identified as an IR of 2.62:1,

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activation temperature of 727.09 °C, and activation time of 129.26 min to simultaneously achieve an overall yield of 60.44% and adsorption capacity of 69.09 mg/g.

2.6.2.2. Optimisation of Adsorption Process

DoE has also been applied to optimise the adsorption of various antibiotics. Most commonly, an RSM approach has been applied, investigating the impacts of parameters such as pH, contact time, initial concentration, adsorbent dose, temperature and more.

The adsorption of CIP using rice husk-derived ACs has been optimised, employing a four-factor CCD-RSM design [217]. The impacts of contact time (20 - 420 min), adsorbent dose (0.4 - 0.8 g/L), CIP concentration (150 - 350 mg/L) and pH (3 - 9), on the adsorption capacity were investigated. All factors were found to be statistically significant with p values ≤ 0.0001 . The optimum values for the variables contact time, adsorbent dosage, CPX concentration and solution pH were defined as 306.86 min, 0.40 g/L, 314.79 mg/L and 7.92, respectively, achieving a maximum removal efficiency of 454.68 mg/g.

Similarly, CCD-RSM has been applied to optimise the biosorption of OTC and Cd²⁺ [218] Adsorbent dosage (2 – 4 g/L), OTC concentration (175 – 275 µmol/L), Cd(II) concentration (400– 800 µmol/L), pH (4–8), and contact time (12–24 h) were evaluated to determine the optimum sorption conditions (removal %). A number of factors were identified as statistically significant for the adsorption of OTC, including the independent effects of adsorbent dose, OTC concentration and contact time were, the squared effects of adsorbent dose, OTC concentration and the interaction effects of OTC concentration and pH. The optimal conditions were found to be an adsorbent dose of 4.19 g/L, OTC concentration of 165.54 µmol/L, Cd²⁺ concentration of 362.16 µmol/L, pH of 6, and contact time of 25.14 h, achieving a maximum OTC removal % of 63.66%. A higher removal % for OTC was observed at pH 6 (Figure 2.28), when OTC exists in its zwitterionic form, therefore, the adsorption mechanisms were attributed to the attraction of OTC cationic groups (R-N+) onto the negative surface of BBR, and/or π - π stacking interactions.



Figure 2.28: Response surface plots for combined effect of (a1) pH and reaction time(F1 = 4.1892 g L-1; F2 = 165.54 μ M; F3 = 362.16 μ M; T = 20 ± 1 °C); (a2) adsorbent mass and reaction time (F2 = 165.54 μ M; F3 = 362.16 μ M; F4 = 6; T = 20 ± 1 °C); (a3) OTC and Cd(II) concentrations, on biosorption efficiency of OTC and Cd(II) (F1 = 4.1892 g L-1; F4 = 6; F5 = 25.135 h; T = 20 ± 1 °C) [218].

Tran et al. applied an OFAT approach to investigate the adsorption of CIP onto ACs [177]. Five factors were studied, namely pH (3 – 10), contact time (15 – 120 min), adsorbent dose (0.3 – 0.2 g/L), initial concentration (50 – 400 mg/L) and temperature (30 – 50 °C). The optimum conditions were found to be a pH, contact time, adsorbent dose, initial concentration and temperature of 6, 60 min, 3 g/L, 400 mg/L and 50 °C, achieving a maximum adsorption capacity of 29.76 mg/g. Despite identifying an optimum point, employing an OFAT design presents major drawbacks, since a large portion of the design space is left unexplored and the interaction effects cannot be determined, resulting in a low adsorption capacity when compared to other studies.

2.7. Characterisation Techniques

The following section provides an overview of the theoretical principles and practical applications of the analytical techniques used to characterise the physical and chemical properties of the carbon fibres (CFs) and adsorbate solutions throughout this thesis.

2.7.1. Surface Area Analysis

2.7.1.1. Physical Surface Analysis Techniques

Surface analysis *via* physical gas adsorption is arguably the most important and widely applied characterisation technique for CAs, providing valuable information on the surface area and pore size distribution. This section will discuss the most common methods to characterise the

texture of porous adsorbents *via* physisorption processes, the most common technique being cryogenic N₂ adsorption/desorption isotherms at 77 K [219,220].

Nitrogen possesses several characteristics making it ideal for physical surface analysis, being a linear, diatomic molecule, with a quadrupole moment. This typically results in localised, monolayer adsorption; however, the phenomenon is highly dependent on the surface chemistry of an adsorbent and is particularly applicable for polar surfaces [221]. Adsorption isotherms (aimed for surface area analysis) are acquired at the *normal* boiling temperature (i.e. 1 atm), which for nitrogen is 77 K. However, at this low temperature, the diffusion into ultramicropores (< 0.7 nm) is restricted due to the quadrupole moment of N₂ which can interact with surface functional groups, changing the orientation of the N₂ molecule and subsequently the micropore filling pressure. Therefore, other adsorbates such as Argon or carbon dioxide may be required. Prior to analysis the samples are degassed at elevated temperatures to expel any adsorbed species (e.g. CO₂, water vapour etc.) from the adsorbent surface. The degassing temperature is dictated by the adsorbent type.

Adsorption isotherms are used to determine the amount of adsorbate present on the adsorbent surface at a given pressure or concentration, when subjected to a fixed temperature. Traditionally the IUPAC recommends that physisorption isotherms are grouped into six categories (Figure 2.29).



Relative Pressure (p/p⁰)

Figure 2.29: Types of physisorption isotherm, adapted from [222].

Each of the six isotherm categories provide valuable information on surface structure, adsorbent type and adsorbate-adsorbent interactions (Table 2.14) [222]. However, in reality, many materials may fit into several categories.

Isotherm	Surface Characteristics	Surface Interactions
Туре І	Microporous with small external surfaces. Common for CAs, porous oxides, molecular sieve zeolites.	Monolayer adsorption, pores fill at low relative pressure due to considerable adsorbent adsorbate interactions
Туре II	Macroporous or non-porous	Reversible mono-and-multilayer adsorption, where multilayer adsorption begins at point B
Type III	Macroporous or non-porous	Weak adsorbent-adsorbate interactions, no monolayer formation
Type IV	Mesoporous	monolayer-and-multilayer adsorption, capillary condensation
Type V	Hydrophobic surface, microporous and mesoporous.	Water adsorption
Type VI	Uniform nonporous surface, typical of graphitised carbon blacks.	characteristic of stepwise multilayer adsorption

Table 2.14: Summary of the information provided by physisorption isotherms.

Hysteresis is a common phenomenon observed in Type IV and V adsorption isotherms, arising from the pore size distribution, geometry and connectivity of a porous material. The phenomenon is commonly observed in mesoporous materials, as a result of capillary condensation due to adsorption metastability and/or network effects [223]. The shape of hysteresis loops varies due to differences in pore structure and can be classified as $H_1 - H_4$, as per the IUPAC definition (Figure 2.30). H_1 hysteresis loops are typical of porous materials with distinct, cylindrical pore channels or agglomerates with uniform spheres. Disordered materials, with a complex, interconnected network of narrow pores exhibit H_2 hysteresis. H_3 hysteresis loops arise from the desorption of non-polar gases at low P/P₀ values (in the relative pressure range from 0.4 to 0.45) and are common of aggregated, pliable, plate-like particles such as clays. H_4 hysteresis loops are associated with narrow slit pores.



Relative Pressure, P/P₀

Figure 2.30: The four types of hysteresis loops identified by IUPAC, adapted from [222].

The most widely applied method for the determination of surface area is the Brunauer-Emmet-Teller surface area (S_{BET}), which aims to describe the physisorption of gas molecules on a solid surface. BET theory relies on several assumptions, namely, multilayer adsorption, interactions between adjacent layers only (i.e. lateral interactions are negligible), and a decrease in enthalpy of adsorption as layers are formed further from the adsorbent surface. The BET equation is derived from the Langmuir theory (Equation 2.15) however, the equation is commonly employed in a linear form, as shown in Equation 2.16.

$$\theta = \frac{Cp}{(1 - p/p_0)(p_0 + p(C - 1))}$$
Equation 2.15
$$\frac{p/p_0}{n_a(1 - p/p_0)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C}(p/p^0)$$
Equation 2.16

Where ϑ is n_a/n_m , n_a is the specific amount adsorbed (cm³/g) at the relative pressure, p/p^0 and n_m is the specific monolayer capacity (cm³/g) [222]. *C* is the BET constant which provides information on the energy of adsorption in the first adsorbed layer. *C* is calculated from the intercept and gradient of the linear BET plot.

Traditionally, the Barrett-Joyner-Halenda (BJH) method has been applied to determine the pore size distribution and pore volume of a porous material, particularly within the larger mesopore and smaller macropore (1.7-300 nm) range. BJH theory is based upon two assumptions; pores are cylindrical in shape and the amount adsorbed is a result of a combination of physisorption on pore walls and capillary condensation within mesopores. The method is derived from the Kelvin equation (Equation 2.17) and relates the volume of adsorbed/desorbed species at a given pressure to the pore radius that becomes occupied/unoccupied at the same pressure [224]. This is achieved by calculating the change in the thickness of an adsorbed film as a result of decreasing relative pressure, by determination of the ascending and descending boundary curves of sorption isotherms [224]. Each reduction in pressure results in the evacuation of adsorbed species from the capillary condensate and subsequently a decrease in depth of the physically adsorbed layer.

$$ln\frac{p}{p_0} = \frac{2\gamma V_m}{rRT}$$
 Equation 2.17

Where, γ is the surface tension (J/m²), V_m is the molar volume (m³/mol), r is the radius of the meniscus formed within a mesopore (m), R is the universal gas constant (J/mol·K) and T is the temperature (K).

A major drawback of the BJH method is the inaccuracies when measuring micropores and smaller mesopores due to the physical effects during practical adsorption such as pore network effects and tensile strength. Despite widespread agreement regarding the inaccuracy of the BJH theory it is still the most widely applied method in literature.

Another consideration for the analysis of pore size and volume is the presence of hysteresis loops, which arise from mesoporous, narrow slit or bottle necked pores, resulting in differences between the adsorption and desorption branches. Typically, the desorption branch is analysed for H₁ materials with uniform, cylindrical pores [225]. Whereas, for materials with an interconnected network and/or broad pore size distribution, displaying H₂ hysteresis, the

adsorption branch is commonly analysed since the shape of the desorption branch is determined by network effects.

2.7.1.2. Chemical Surface Analysis Techniques

This section will discuss the chemical surface analysis techniques for CAs, with a focus on the determination of mesoporosity, net surface charge and surface acidity and basicity. The latter two techniques were determined using an automated titrator (SI analytics TitroLine 5000).

2.7.1.2.1. Methylene Blue Number

Methylene blue number (MB_N) is a tool that is commonly applied to determine the mesoporosity of porous materials, which is a fundamental characteristic of aqueous-phase adsorbents. This method is attributed to the molecular dimensions of methylene blue (MB). Adsorption becomes favourable when the pore size is approximately 1.7 times larger than the 2nd largest dimension of the molecule. Since MB has dimensions of 1.7, 0.76 and 0.33 nm (Figure 2.31), a significant amount of MB would be adsorbed by mesopores, whilst a small amount may be adsorbed by larger micropores or smaller macropores [226,227].



Figure 2.31: Dimensions of MB [34].

2.7.1.2.2. Point of Zero Charge

pH_{PZC} is defined as the pH where the net surface charge of a material is zero. Aside from surface area analysis, pH_{PZC} is one of the most important characterisation techniques for aqueous-phase CAs, since an acidic, basic or neutral surface can impact the adsorption behaviour. When the pH is equal to pH_{PZC} the surface charge of a CA is neutral, the surface becomes negatively

charged when the pH is above (i.e. more basic) the pH_{PZC}, and a positively charged surface is observed when the pH is below (i.e. more acidic) than the pH_{PZC}. Therefore, determination of pH_{PZC} allows the researcher to hypothesise the interactions that may occur at various pH within an adsorbent-adsorbate system, such as electrostatic attraction or repulsion, cation bridging, ligand exchange and covalent bonding [228].

2.7.1.2.3. Boehm Titrations

Boehm titrations are a useful technique to identify and quantify the types of oxygen-containing groups (e.g. carboxylic acids, lactones, phenols and basic groups) on the surface of a CA. The method relies upon the well-known acid-base reactions of carboxylic acids, lactones and phenols, and is achieved by applying three reaction bases: NaOH, Na₂CO₃ and NaHCO₃. The first base has the ability to react with all oxygen-containing functional groups, whilst Na₂CO₃ reacts with carboxylic acids and lactones, whereas NaHCO₃ only reacts with carboxylic acids (Figure 2.32).



Figure 2.32: Reactions of NaOH, Na₂CO₃ and NaHCO₃ with carboxylic acids, lactones and phenols.

The method was first proposed by Bohem in 1966; however, a major drawback was the lack of standardisation, meaning that a range of techniques were applied over time, leading to inconsistencies in results. More recently, Goertzen and Oickle et al. have published several articles aiming to standardise the methodology by assessing various experimental factors such as the expulsion of CO₂ from solutions, the end-point determination during titration, the method of agitation, the effect of filtering and the application of lower concentration titrants [229,230].

The studies found that dissolved CO₂ has a significant impact on the quantification of surface groups by Boehm titration [229,230], and therefore, it was suggested that CO₂ is expelled from the reaction bases by bubbling N₂ or Ar for 2 h through the solution, prior to titration. With regards to end point determination, there was no significant difference between using potentiometric or colour indication methods. The best method of agitation was found to be shaking, when compared to stirring or sonication, since the later methods cause a change in the macroscopic surface of carbon particles. However, the agitation time needs to be determined on a case-by-case basis and the surface structure of CAs must be considered. Where possible, shorter agitation times should be used since longer durations could alter or damage the carbon surface; however, shorter times may result in incomplete reactions with the bases. Typically, higher surface area, microporous adsorbents require longer agitation times to allow diffusion into the porous network and therefore, complete reaction to take place. Similar results were observed for all titrant concentrations; however, a larger standard deviation was observed at lower concentration, which was attributed to the influence of dissolved CO₂.

2.7.2. Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray Spectroscopy (EDS)

SEM-EDS is a valuable tool used to study surface morphology and determine the average elemental composition of a surface. The technique relies upon several key components, namely, the electron source, anode, electromagnetic lenses, scanning coils and electron detectors (Figure 2.33). The electron source is responsible for producing a small electron beam with a large, stable current; however, the stability of the beam is highly dependent on the type of electron gun, with the newer field-emission or LaB₆ guns out-performing the traditional thermionic or tungsten type guns. The SEM-EDS applied in this research utilised a field emission gun, which provides improved spatial resolution images when compared to other electron guns [231,232]. The anode consists of a positively charged metal plate which attracts the electrons from the beam and guides the flow towards the lenses. The electromagnetic lenses and apertures reduce the beam diameter, with the final lens focusing the beam on the sample. The beam diameters in SEM typically range between <1 to 20 nm. The scanning coils control the position of the electron beam on the sample. The sample is mounted on a stage within a chamber, under vacuum (5 – 10 Pa absolute). The vacuum is used to produce a consistent

electron beam since scattering occurs in the presence of gases. Additionally, a vacuum prevents electrical discharge within the electron gun.



Figure 2.33: Schematic of SEM-EDS apparatus.

Several detectors exist within the SEM apparatus to detect the range of electron signals that are generated when the electron beam interacts with a sample. The extent in which the beam penetrates the sample is highly dependent on the accelerating voltage and the density of the material, with lower density samples typically having a tear-drop shaped interaction volume. The most commonly generated electron signals within SEM are secondary electrons (SE), backscattered electrons (BSE) and characteristic x-rays (Figure 2.34) [233]. Accelerating voltage has a large impact on the types of electrons emitted and therefore the resolution. Lower acceleration voltages (<10 ekV) result in the emissions of SE allowing for the observation of clear surface structures, however a reduction in resolution. Whereas high acceleration voltages (>10 ekV) result in a greater number of BSE resulting in better resolution, but loss in clarity of surface structures.

SE are low energy electrons (<50 eV), emitted from the k-orbital of an atom as a result of inelastic scattering. SE are generated from the surface of a sample and are typically used for producing topographical images. SE emission is mostly impacted by surface curvature with a larger number of SEs emitting from prominent surfaces when compared to pores or sunken areas . BSE are high energy electrons, which are generated *via* elastic scattering. The quantity of BSE detected is directly proportional to the average atomic number, and therefore, BSE can provide information on surface composition. Finally, characteristic X-rays are emitted when an excited electron relaxes to ground state, emitting X-ray energy which Is characteristic of a specific element.



Figure 2.34: Electron signal types generated during SEM-EDS.

2.7.3. Spectroscopic Analysis

This section will discuss the spectroscopic techniques applied throughout the experimental campaigns. Many characterisation techniques utilise electromagnetic radiation to determine how it interacts with, or emits from, different matter. Electromagnetic radiation can interact with samples in a variety of ways including reflection, scattering, absorbance, fluorescence, phosphorescence and photochemical reactions. The type of characterisation technique and type of interaction is dependent on the wavelength of the electromagnetic radiation applied, such as infrared (IR), visible light or ultraviolet (UV).

2.7.3.1. Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is a characterisation technique which is used for identifying (surface) functional groups of a solid, liquid or gas. The technique relies upon the molecular vibrations which occur as a result of transitions between quantised vibrational energy states, when a molecule is subjected to IR radiation. These vibrational modes can vary being either an

(a)symmetrical, bend or stretch (Figure 2.35). Each molecule has unique vibrational modes since different atoms possess characteristic vibrational frequencies (v_i). Molecules with N atoms possess 3N degrees of freedom (i.e. the number of vibrational modes of a molecule), therefore, there can be a significant range in the complexity of the spectra produced, ranging from the simple vibrational modes of a diatomic molecule to the much more complex motion of a polyfunctional molecule [234].



Figure 2.35: Common molecular vibrations of FTIR, where (-) and (+) signify in-plane and outof-plane bending, respectively [34].

IR spectroscopy was revolutionised when FTIR was introduced allowing a wide range of wavelengths to be assessed rapidly *via* the application of interferometry, by taking advantage of the interactions of electromagnetic waves, which can either result in constructive or destructive interference (Figure 2.36).



Figure 2.36: Illistration of constructive and destructive interference.

The FTIR design is important to the above phenomenon, consisting of an IR source, beamsplitter, fixed and moving mirrors and a detector (Figure 2.37). The beamsplitter splits and directs the IR source to the two mirrors, where they are reflected, recombined and directed through the sample to the detector. The moving mirror causes the IR beams to travel different distances causing variation in the phases of the waves when they recombine, resulting in the constructive or destructive interference, as discussed above. Each interference pattern produces a different wavelength of IR to be present within the beam, allowing for the quick analysis of a range of wavelengths, which typically range between 400-4000 cm⁻¹.



Figure 2.37: Diagram of FTIR apparatus.

Traditionally, transmission methodologies such as the KBr method have been employed for FTIR analysis, which consists of applying a "carrier" for a given sample, by creating a mixture and compressing it into a self-sustaining disk. KBr is particularly attractive carrier since it does not exhibit any absorption bands above 400 cm⁻¹. However, the technique is known to induce changes in crystallinity, hydration state or polymorphism in some samples. Additionally, KBr is extremely hygroscopic and therefore, is prone to introducing large O-H bands if not treated properly prior to analysis (i.e. by heating to temperatures above 100 °C).

In recent decades the attenuated total reflectance (ATR) method has become increasingly popular, owing to the lack of need for pre-preparation of a sample. The technique employs an ATR crystal which allows for the total internal reflection to generate an evanescent wave at the reflection points (or nodes), which penetrates and interacts with the sample, providing information about the functional groups present within a structure [235]. The most common ATR crystals are diamond and germanium, since they possess two important characteristics required for ATR, the first being optical transparency to the energy frequency (i.e. the material absorbs little or no IR radiation). Secondly the material must have a refraction index which is higher than the surrounding media, hence, acting as a wave guide by reflecting the light energy internally.

Penetration depth is a highly important consideration for ATR methods since penetration depth acts as the path length. A greater path length (i.e. increased penetration) results in more prominent peaks during data acquisition. The depth of penetration is dependent on two factors, the wavenumber and the refractive index of the crystal and the sample [235]. An increased penetration depth is observed as wavenumber is decreased (Figure 2.38). Whereas the refractive index is dependent on the type of crystal used. For example, a geranium crystal with a refractive index of approximately 4 would have a lower sample penetration than diamond which has a refractive index of approximately 2.4.

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Figure 2.38: Impact of wavenumber on sample penetration depth.

ATR has a range of advantages over traditional transmission techniques, such as increased detail in the fingerprint region, real-time measurement and being non-destructive. Highly pure or graphitised CAs exhibit strong absorption of infrared radiation due to their dark colour and extended conjugated carbon structures. This results in reduced reflectance or transmittance of the infrared source and shortened effective path lengths, often leading to poor-quality spectra in conventional FTIR analysis. Therefore, many CAs may still require traditional transmission techniques in order to gain insightful spectra, since KBr "dilutes" the black CA allowing more IR radiation to reach the detector.

FTIR is particularly useful for the analysis of carbonaceous adsorbents such as activated carbon fibres, having been widely applied in literature [172,207,236,237]. The technique is particularly useful for detecting surface functional groups which commonly play an active role in adsorption, as well as being able to gain insights into adsorption mechanisms, particularly for chemisorption processes, involving the formation of new bonds. The most commonly assigned peaks for CAs have been summarised previously by Taylor and Masoudi Soltani[13].

2.7.3.2. Raman Spectroscopy

Raman spectroscopy is a widely applied technique for the characterisation of carbonaceous adsorbents. Similarly to FTIR, Raman is utilised to determine vibrational modes of a molecule and gain insights into the molecular structure but in contrast to FTIR, Raman identifies the changes in the polarisability of a molecular bond. The Raman effect is a result of the inelastic scattering of light and was first identified in the work of Raman and Krishnan in 1928. However, Raman spectroscopy did not become an established technique until monochromatic light sources (i.e. lasers) were implemented in 1966 [238]. The technique has since become an important, non-destructive procedure for the analysis of carbonaceous materials.

Fundamentally, Raman techniques rely upon light scattering phenomenon. When a material is subjected to a monochromatic light source (i.e. incident beam), the electron cloud becomes polarised, causing excitation to a higher energy level state; most commonly a virtual energy state. The molecular energy then decays back to ground state, resulting in the scattering of radiation.

Figure 2.39 shows the types of radiation that may be scattered when a molecule is subjected to a monochromatic light source. When the scattered radiation is of the same frequency as the incident beam, elastic scattering occurs (Rayleigh scattering). Whereas, if the radiation is of a different frequency, inelastic scattering occurs (Raman scattering). When sufficient energy is supplied by an incident beam, the electron may be promoted to a real electronic state; this phenomenon is known as resonance and can significantly improve signal intensity [239].

Raman spectroscopy is particularly useful for identifying non-polar bonds such as C-C and C=C, since symmetrical vibrations have a large change in polarisability during vibration, whereas polar molecules with asymmetrical vibrations exhibit a small change in polarisability during vibration leading to weaker signals.



Figure 2.39: Jablonski energy diagram showing the transitions involved during infrared absorption, Rayleigh, Raman Stokes, anti-Stokes, and resonance Raman scattering.

Raman spectroscopy is the one of few analytical techniques that can distinguish between the types of carbon present within a structure due to the shapes and position of bands within the spectrum, making the technique particularly attractive for CAs with some degree of disorder (i.e. amorphous carbons) since it is sensitive to both crystalline and amorphous structures, unlike other techniques such as X-ray diffraction [240]. This is because Raman spectroscopy has the ability to excite both the π and σ states, leading to the generation of several characteristic bands. The most important and usually the most intense bands being the D and G bands which are observed at 1350 and 1597 cm⁻¹. The D band, also known as the disorder induced band, is representative of amorphous, sp³ hybridised carbon, whist the G band represents crystalline sp² hybridised carbon. The disorder of a carbonaceous material can then be quantified by determining the ratio between the D and G band intensities (I_D/I_G).

Another key band is the 2D band (also known as the G' band) which is observed at 2600 cm⁻¹; however, this is usually present in the Raman spectra of graphene. The 2D band is the second order of the D band as a result of two phonon vibrations [241]. Unlike the D band, the 2D band doesn't signify defects. The band is particularly useful for determining the thickness of

graphene layers since there are noticeable changes in size and shape as the number of layers are increased.

Another advantage of Raman over FTIR is the fact that water is a weak Raman scatterer due to its polarity meaning that adsorbed moisture is absent from the produced spectra, unlike FTIR which can produce broad O-H peaks when moisture is present.

2.7.3.3. UV-Vis Spectrophotometry

UV-vis is a versatile, non-destructive and inexpensive technique used for the analysis of solutions. The technique utilises the ultraviolet (UV) and visible radiation of the electromagnetic spectrum to measure the absorbance of energy by various compounds. This is achieved by illuminating the sample with a light source within the wavelengths of 190-900 nm, from which the instrument measures the light absorbed, transmitted or reflected by the sample at a given wavelength. The instrument is calibrated with a reference/ blank sample (i.e. the solvent) to provide a baseline measurement.



Figure 2.40: Diagram of UV-vis spectrophotometer apparatus.

In this thesis, UV-vis was used to quantify the concentration of various pollutants. Quantification of known pollutants relies upon the Beer-Lambert law (Equation 2.18) since the amount of light absorbed is directly proportional to the quantity of absorbing molecules in which the light passes through.

$$A = \varepsilon lc$$
 Equation 2.18

Where, A is the absorbance, ε is the molar absorption coefficient (M⁻¹cm⁻¹), *l* is the optical path length (cm) and *c* is the molar concentration (M). The standard path length for an optical cell is 1 cm.

In order to quantify concentrations effectively, the wavelength of maximum absorption must be identified, which is known as the lambda max (λ_{max}) and is dependent on the chromophore(s) present within a molecule.

2.7.4. Compositional Analysis

Ultimate analysis, also known as CHN analysis, is a tool for the rapid, indirect determination of bulk carbon, nitrogen and hydrogen compositions *via* the quantification of their combustion products of CO₂, H₂O and N₂, respectively. It is particularly useful when combined with other quantitative analysis techniques such as EDS (Section 2.7.2) and proximate analysis. CHN analysis is a destructive technique involving the heating of a sample to high temperatures (>900 °C) in an oxygen atmosphere, which results in combustion of the sample. The gaseous mixture is then swept out of the combustion chamber by an inert carrier gas such as helium and subjected to several purification steps. Firstly, the gaseous mixture is passed over high purity, heated copper (~600 °C) to eliminate excess oxygen and reduce nitrogen oxides, followed by passing through absorbent traps, to ensure only CO₂, H₂O and N₂ remain [242]. The subsequent gaseous mixture is then separated and quantified using gas chromatography (GC) coupled with thermal conductivity detection, or a series of IR and thermal conductivity cells for the detection of individual components.

Ultimate analysis applies high purity standards (>99.9%) to establish single calibration factors for each element (C, H and N), by analysing weighed portions of the calibration standard and comparing the results to the theoretical elemental composition, which is derived from the molecular formula and expressed as mass fractions.

Proximate analysis is a destructive, bulk analysis technique, used to quantify the amount of fixed carbon, VOC, moisture and ash content within a given sample. The process involves several stages of heating in various atmospheric conditions to evolve gases and/or combust the sample, emitting the former three components, whist the remnant mass is the ash content.

The VOC and moisture content are determined by the change in mass. The ash is determined using the residual mass and the fixed carbon is determined by subtracting the mass of all other constituents from the initial sample mass, as described in section 3.6.7.

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2.8. Research Gap

The research gap addressed in this thesis centres on two key areas, namely, the precursor material of rCFs and the competitive adsorption between antibiotics and DOM. The production of rCFs is rising with the ever-increasing waste stream of CFRP bases products, however, at present there is a lack of uses for the recycled products. rCFs are a promising precursor to produce CAs owing to their high carbon content, low weight, temperature and chemical tolerance, and more. Furthermore, vCFs have already proven to be attractive candidates to produce CAs for aqueous phase applications. Despite this, currently there are very few studies that investigate the production of CAs from rCF precursors. Therefore, this thesis sought to determine whether rCFs were feasible candidates for the production of CAs *via* preliminary investigations. The author then sought to optimise each processing step for the synthesis and application (i.e. activation, modification and adsorption) of rCF-based CAs, to achieve the desired adsorbent characteristics and maximise the removal efficiency of target pollutants (CIP and OTC).

Another research gap lies in the application of the application of the adsorbent within the aquaculture industry. Several current review articles have identified aquaculture as one of the leading causes for antibiotics being found within natural waters. Furthermore, they have highlighted adsorption as a promising separation technology for the removal of aquaculture contaminants.

2.9. Research Aims and Objectives

This research aims to find a novel, sustainable and renewable solution to remediate pollutants generated by the aquaculture industry, using rCFs as the adsorbent precursor. The objectives to achieve the stated aim comprise:

- To optimise the activation and modification of rCFs in order to improve porous structure and uptake capacity;
- 2. To characterise industrial-grade precursor, activated and modified rCF and vCF *via* a range of analytical techniques;

- To conduct single-component batch adsorption/desorption experiments, applying DoE to gain an understanding of the impacts of various experimental conditions on the removal capacity of specific pollutants;
- 4. To investigate equilibrium isotherms and kinetic models of antibiotic adsorption on optimum samples.

2.10. Thesis Outline

The following chapter provides an overview regarding current aquaculture practices with particular focus on antibiotic use and its subsequent environmental fate. This is followed by a comprehensive review of the literature regarding water purification techniques with a particular focus on adsorbent synthesis and applications in aqueous media. Chapter 3 describes the methodologies applied throughout this thesis. Chapters 4 and 5 discuss the optimisation of the synthesis of rCF-based adsorbents using activation and modification techniques, respectively. Chapter 6 features the single-component adsorption of the antibiotics, CIP and OTC, applying optimisation techniques. Chapter 7 addresses the chemical regeneration of the spent adsorbents. Chapter 8 provides a summary and detailed comparison of the results and their significance within an aquaculture setting. Finally, Chapter 9 presents the conclusions and future work for this project.

3. Experimental Methodology and Analytical Techniques

This chapter provides detailed information on the chemicals and reagents used throughout the course of this study. It also presents comprehensive descriptions of the experimental methodologies employed for the synthesis and application of CF-based adsorbents for the removal of antibiotics from aqueous media. Furthermore, the chapter outlines the analytical techniques utilised to characterise the physical, chemical, and morphological properties of the CFs, as well as the methods used to determine the concentrations of adsorbates in solution.

3.1. Materials and Reagents

The precursor rCFs in this study were G-TEX M (200 gsm), obtained from Gen2Carbon Ltd. (West Midlands, UK), which was recovered from CFRPs using a modified pyrolysis process.

The vCFs were purchased to have similar characteristics to the rCFs for comparative purposes, therefore PAN-based Toray T300 1k CFs with a fibre diameter of 7 μ m were purchased form easy composites. The diameter was selected based on the diameters of the rCFs observed using SEM in Chapter 4.

All other chemical reagents were purchased from Fisher Scientific (UK), (Table 3.1). The precursors and chemicals were used as received, without further purification.

Chemical	Formula	Molecular Weight	Purity (%)
Sodium hydroxide	NaOH	40.00	≥98.0
Potassium hydroxide	КОН	56.11	≥85.0
Nitric Acid	HNO ₃	63.01	≥70.0
Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	331.35	≥98.0
Oxytetracycline dihydrate	$C_{22}H_{24}N_2O_9 \cdot 2H_2O$	496.46	≥95.0
Hydrochloric acid	HCI	36.46	≤37.0
Sodium carbonate	Na ₂ CO ₃	105.99	98.0

Table	3.1:	Chemical	l reagents.
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Chemical	Formula	Molecular Weight	Purity (%)
Sodium bicarbonate	NaHCO ₃	84.01	99.7
Sodium nitrate	NaNO ₃	84.99	98.0
Potassium bromide	KBr	119.02	99.9
Potassium hydrogen phthalate	КНР	204.22	100.0
Oakton buffer solution (pH 4.01, 7.00 and 10.01)	-	-	

3.2. Preparation of Activated Carbon Fibre

ArCFs were prepared by combining rCFs (100 mg) with a specified quantity of two different hydroxides (used as the activating agent) to produce a wet mixture. The subsequent amalgam was transferred into an aluminosilicate crucible, which in turn was placed into the centre of an Inconel tube (Figure 3.1). The furnace was supplied with N₂ gas (100 mL/min). All other parameters, such as activation temperature, hold time, and IR, were determined by either the BBD design (Table 3.2) or the preliminary experiments which are described in Section 4.2.2. After activation, the furnace was allowed to cool to temperatures below 200 °C, at which point the N₂ flow was reduced to 10 mL/min. The samples were recovered from the tube when the temperature was below 50 °C and washed with DI 80 °C water until a neutral pH was achieved. The ACFs were then dried overnight at 60 °C in an oven. ACFs activated using NaOH and KOH were denoted as Na-ArCF (or Na-AvCF) and K-ArCF (or K-AvCF), respectively. Whilst r and v denote the recycled and virgin-based materials, respectively.



Figure 3.1: Schematic of chemical activation apparatus, taken from [34].

3.2.1.1. Preliminary Experiments

Due to the lack of research regarding the chemical activation of rCFs, preliminary investigations were conducted to determine whether hydroxide activation was a suitable technique to employ for further optimisation.

The initial experiment consisted of combining rCFs (100 mg) with NaOH in a 1:1 ratio and heating to 700 °C (5 °C/min) for one hour [34], after which the ArCFs were washed and dried using the method described above. The resulting Na-ArCF were applied to the adsorption of MB. The Na-ArCFs were combined with MB (20 mg/L) in a sealed container and placed on a Fisherbrand multi-platform shaker plate (200 rpm) for 24 h. After which the MB concentration was determined using the method described in Section 3.6.5.3. The rCF precursor and ArCFs were also analysed using SEM-EDS.

Based upon the results of the preliminary investigation (Section 4.2.1), it was decided to proceed with hydroxide activation; however, the stronger KOH activation agent was selected, due to the superior surface areas achieved with these methods (Table 2.6). Further investigations were then employed at the harshest experimental conditions to determine the maximum limits before total burn-off/loss of the sample was observed.

3.2.1.2. Optimisation of Chemical Activation Process

After the preliminary investigations, RSM was employed to optimise the activation process; opting for BBD, thereby avoiding the most extreme conditions and subsequently preventing the complete burn-off of the K-ACFs, as discussed in the previous section. Additionally, BBD is more cost-effective, requiring fewer experimental runs when compared to CCD, while still providing valuable data for effective optimisation of the process.

Experiments were conducted to investigate the effects of three parameters (Table 3.2): activation temperature (x_1 , 670 – 830 °C), activation time (x_2 , 0.5 – 3 h) and IR (x_3 , 1:1 – 1:10) on the response variables of yield (y_1 , %) and MB adsorption capacity (y_2 , q_e , mg/L), which were calculated using Equation 3.1 and Equation 3.2, respectively. The selection of parameters and their ranges were based upon current literature (Table 2.6), where activation temperature, hold time and IR are regularly identified as the most significant factors for the activation of CAs using KOH [215–217].

Parameter	Code	Range
Activation Temperature (°C)	X 1	670 – 830
IR (CF:KOH)	X ₂	1:1 – 1:10
Hold Time (h)	X ₃	0.5 - 3

Table 3.2: Parameters, codes and ranges of the BBD design [34].

$$Yield (y_1) = \frac{M_{final}}{M_{initial}} \times 100$$
 Equation 3.1

Where, *M*_{initial} and *M*_{final} are the mass of the CF (g) before and after activation, respectively.

$$q_e(y_2) = \frac{(C_0 - C_e)V}{M}$$
 Equation 3.2

Where, V is the volume of MB solution (L), M is the mass of adsorbent (g) and C_0 and C_e are the initial concentrations and the equilibrium concentration of MB (mg/L), respectively.

After completing the experimental campaign, the data set was analysed with ANOVA to determine statistically significant parameters and their combined effects. RSM was then utilised to identify the optimum conditions and visualise the interaction effects between factors and their impacts on the responses.

The optimum samples (K-ArCF-Opt) were subsequently subjected to comprehensive characterisation to evaluate their physical and chemical properties, following the methodologies outlined in Section 3.6. The S_{BET} and pore size distribution of the K-ACFs were determined through N₂ adsorption–desorption isotherms. MB_N was additionally employed as a complementary method to further estimate the mesoporosity [53,54]. The morphological and compositional properties of the precursor, activated, and spent materials were further characterised using SEM/EDS, FTIR, and Raman spectroscopy.

3.3. Preparation of Modified Carbon Fibre

3.3.1. Preparation of Modified Carbon Fibre via Experimental Design

The precursor material used in this study was the optimum activated sample (K-ArCF-Opt), synthesised following the procedure outlined in Section 3.2. Prior to modification, HNO₃ was heated to the desired temperature using a heating mantle and air-cooled condenser (findenser, 400 mm) reflux system, where the temperature was monitored using an internal thermometer (Figure 3.2). Once the desired temperature was achieved, ArCFs were modified by introducing the required amount of precursor (0.001 w/v%) into the reflux system under magnetic stirring (200 rpm). The HNO₃ concentration, hold time and reaction temperature were specified as, per the screening (i.e. Taguchi) and DoE designs shown in Table 3.3 and Table 3.4, respectively. After modification, the mrCFs were separated *via* vacuum filtration, washed with deionised water until a neutral pH (~7) was achieved and dried in an oven (60 °C) overnight. Once dried, the mrCFs were applied to adsorb antibiotics CIP and OTC using the method described in Section 3.3.2.



Figure 3.2: Schematic of apparatus used during chemical modification.

3.3.1.1. Screening of Modification Procedure via Taguchi

Taguchi orthogonal arrays were employed to screen the effects of three parameters (Table 3.3), on the response variables of CIP and OTC adsorption capacity (y_i , q_e , mg/L), which were calculated using Equation 3.2. Current literature for the modification of other CAs for aqueous phase applications was assessed (Table 2.8) to select the parameters and determine the boundaries of the design space which are summarised in Table 3.3.

Parameter	Code	Range
HNO ₃ Concentration (M)	X 1	1-10
Hold Time (h)	X2	1-10
Temperature (°C)	X3	20 – 90

Table 3.3: Parameters, codes and ranges of the Taguchi modification design.

3.3.1.2. Optimisation of Modification Procedure via RSM

After initial screening, it was sought to optimise the modification procedure *via* RSM. BBD was selected as the experimental design method because it is more economical, requiring lower number of experimental runs when compared to other RSM techniques (i.e. CCD) and avoiding the harshest and most hazardous operating conditions (i.e. high concentration HNO₃ or temperatures), while making little compromise on the quality of the data generated.

Based upon the results of the Taguchi screening design (Section 3.3.1.1), the same three factors were optimised; however, the design space was changed with the upper limits (+1) for HNO₃ concentration and temperature being reduced to 6 M and 60 °C, respectively. The hold time was extended to 16 - 24 h.

Experiments were organised to investigate the effects of three parameters (Table 3.2), namely, HNO₃ Concentration (x_1 , 1 – 6 M), hold time (x_2 , 16 – 24 h) and temperature, (x_3 , 20 – 40 °C) on the response variables of CIP and OTC adsorption capacity (y_i , q_e , mg/L).

Parameter	Code	Range
HNO₃ Concentration (M)	X 1	1-6
Hold Time (h)	X ₂	16 – 24
Temperature (°C)	X 3	20 – 60

Table 3.4: Parameters, codes and ranges of the BBD modification design.

Upon the completion of the experimental campaign, the data set was analysed using ANOVA, to identify the statistically significant parameters and their combined effects. RSM was employed to optimise the activation process and visualise the interaction effects between factors, on a given response.

3.3.2. Antibiotic Adsorption

Batch adsorption experiments were conducted to determine the uptake capacity of CIP and OTC. The mrCFs were contacted with the antibiotic solution (2 mg/L) on a shaker plate (200 rpm) for 24 h using an adsorbent dose of 0.1 g/L. The pH of the solution was not adjusted and was measured to be ~5.5 and the temperature was kept at 20 °C. Once the adsorption experiments were completed, the mrCFs were separated *via* decantation and the solutions were analysed using UV-vis with a wavelength of 273 nm for CIP and 354 nm for OTC. The equilibrium adsorption capacity was then calculated using Equation 3.2. The antibiotic batch adsorption experiments were also conducted using the K-ACF-Opt produced in Chapter 4, for comparative purposes.

Modified and spent materials were characterised (Section 3.6) for surface, structural, and compositional properties using N₂ isotherms, MB_N, SEM/EDS, FTIR, and Raman spectroscopy.

3.4. Optimisation of Adsorption Process

Antibiotic solutions were prepared volumetrically and adjusted to the required pH, using 0.1 M HCl or NaOH. The pH was measured using a pH probe (Oakton 700) which was calibrated using three Oakton pH buffer solutions (4.01, 7.00 and 10.01). Solutions were stored in a cool dark cupboard and unused solutions discarded after one week to avoid degradation of the antibiotic solutions. A one-week period was considered acceptable based on UV-vis measurements, with

degradation deemed significant when the concentration reached 97% of the original stock solution.

Batch adsorption experiments were conducted to determine the uptake capacity of CIP and OTC. A known amount of mCF-Opt was combined with a solution of each antibiotic at concentrations ranging between 0.5 – 2 mg/L and shaken for 24 h at 200 rpm, as determined by the BBD design (Table 3.5). After adsorption, the mCFs were separated *via* decantation and the solutions were analysed using UV-vis with a wavelength of 273 nm for CIP and 354 nm for OTC. The equilibrium adsorption capacity was then calculated using Equation 3.2, whilst the removal percentage was calculated using Equation 3.3.

Removal (%) =
$$\frac{(C_0 - C_e)}{C_0} \times 100$$
 Equation 3.3

3.4.1.1. Optimisation of Adsorption Procedure employing RSM

Experiments were organised to investigate the effects of three parameters (Table 3.5), namely, adsorbent dose (x_1 , 0.1 – 0.9 g/L), pH (x_2 , 2 – 8) and initial concentration, (x_3 , 0.5 – 2 mg/L). Two pairs of response variables were studied, namely the removal percentage of CIP and OTC (y_i , %), with the aim to maximise the amount of antibiotics removed for the solution. Additionally, CIP and OTC adsorption capacities (y_i , q_e , mg/L) were investigated, to maximise the loading capacity of the adsorbent.

Parameter	Code	Range
Adsorbent Dose (g/L)	X 1	0.1-0.9
рН	X2	2 – 8
Initial Concentration (mg/L)	X ₃	0.5 – 2

Table 3.5: Parameters, codes and ranges of the BBD adsorption design.

Upon the completion of the experimental campaign, the data set was analysed using ANOVA, to identify the statistically significant parameters and their combined effects. RSM was employed to optimise the adsorption process and visualise the interaction effects between factors, on a given response.
3.4.1.2. Adsorption Isotherms and Kinetics

Data was also acquired to fit adsorption isotherms and kinetics models. An adsorbent dose of 0.8 g/L and pH of 2 was employed based upon the optimum point of the BBD design. The adsorption isotherms were conducted at initial concentrations of 1, 2, 5, 10, 15, 25, 37 and 50 mg/L and temperatures of 20, 30 and 40 °C which was achieved by placing the shaker plate in an oven and allowing the temperature to equilibrate prior to introducing the adsorbents.

The kinetic data was collected at initial concentrations of 2 and 5 mg/L. Aliquots were taken at specific time intervals (5, 10, 15, 30, 45, 60, 120, 240, 480, 1440, 2880 and 4320 min) throughout the adsorption process and the absorbance. Post adsorption, the solution was separated and analysed using the method described above.Properties of the spent materials were investigated using FTIR using the methods described in Section 3.6.

3.5. Regeneration

3.5.1. Antibiotic Adsorption and Desorption

Antibiotic solutions were prepared, and the pH adjusted according to the procedure outlined in Section 6.2.2. Adsorption experiments were performed under the optimal conditions for %mrCF-Opt as established in the previous chapter.

Following adsorption, the antibiotic-laden samples were washed with deionised water until a neutral pH was reached and then dried overnight in an oven at 60 °C. To account for sample loss during the washing and drying processes, the samples were reweighed before each adsorption cycle, and the volume of antibiotic solution was adjusted to maintain an adsorbent dose of 0.8 mg/L.

After drying, the antibiotic laden mrCFs were placed in the regenerant solutions (0.1 M NaOH, 0.1 M KOH, 0.25 M NaOH, 0.25 M KOH) for 4 h and shaken at 200 rpm. After regeneration, the samples were washed and dried using the method described above. The RE was then determined using Equation 2.14.

3.6. Characterisation

3.6.1. Surface Area Analysis

The surface area of the materials was evaluated using both physical and chemical methods. N_2 adsorption isotherms were performed at 77 K using a Micromeritics ASAP 2020 analyser, over

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a relative pressure range of $3 \times 10^{-8} - 1.00$ to determine the specific surface area and pore volume.

To further investigate the mesoporosity of the material MB_N analysis was conducted. MB_N is defined as the maximum amount of dye adsorbed per gram of adsorbent and was determined by contacting 5 mg of ACFs with MB at a range of concentrations (25, 50, 100, 150, 200, 500 and 1000 mg/L) and shaking for 24 h (200 rpm). The initial and equilibrium concentrations were determined using UV-vis spectroscopy *via* the method described in Section 3.6.5.3. The equilibrium adsorption capacity was calculated using Equation 3.2. From this information, MB_N (mg/L) was then determined using a linearised form of the Langmuir isotherm (Equation 3.4) [227]. MB_N is equivalent to q_{max} and is determined by dividing 1/slope of the graph.

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}}$$
 Equation 3.4

Where q_e is the equilibrium adsorption capacity (mg/g), C_0 and C_e are the equilibrium capacity (mg/L), V represents the total volume of solution contacted with the adsorbent (L), M is the mass of the adsorbent (g) and q_{max} is the maximum adsorption capacity (mg/g). b is the Langmuir constant related to the affinity of the binding sites (L/mg).

3.6.2. Point of Zero Charge

For CAs, pH_{PZC} is most commonly determined using either mass titrations or potentiometric titrations. The most frequently cited method for mass titrations was proposed by Noh and Schwartz [243]. This method involves combining CAs (0.05, 0.1, 0.5, 1, 5 and 10 wt.%) with three solutions of varied pH, which are commonly adjusted by adding HCl or NaOH, dropwise. The solutions are then agitated for 24 h to allow equilibration, after which the final pH is measured. The pH_{PZC} is determined by plotting the mass fraction (wt.%) against the measured pH. As the mass fraction (wt.%) increases, the points should begin to converge. The point where all points converge is considered to be the pH_{PZC} (Figure 3.3a). Mass titrations benefit from being simple and inexpensive, leading to their widespread application in literature; however, the method is very sensitive to traces of acids or bases, leading to inaccuracies [244].

Due to the inaccuracies of mass titrations, potentiometric titrations were applied within this thesis since they offer higher accuracy for the determination of pH_{PZC}. The method consisted of combining CAs with NaNO₃ and allowing the solution to equilibrate for 24 h under agitation

(200 rpm). NaOH was then titrated with the CA-containing solution, measuring the pH after each addition. The equivalence point represents the pH_{PZC} , which is determined by plotting the volume of titrant vs pH (Figure 3.3b).



Figure 3.3: Illustrations of PZC determination *via* mass titration (a), potentiometric titration (b).

3.6.3. Boehm Titrations

Prior to conducting the Boehm titrations, both sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions were standardised. Sodium hydroxide was standardised by titrating a known concentration of potassium hydrogen phthalate (KHP) solution, with the endpoint determined potentiometrically. Subsequently, the standardised NaOH solution was used to standardise the HCl solution by reverse titration.

For the Boehm titration, 20 mg of either ACF or mCF was combined with 50 mL of one of four 0.05 M solutions: HCl, NaOH, Na₂CO₃, or NaHCO₃. The mixtures were agitated for 24 hours to allow sufficient interaction between the carbon material and the titrants. After agitation, 10 mL aliquots were withdrawn for titration. Aliquots containing basic reagents (NaOH, Na₂CO₃, NaHCO₃) were titrated spiked with 10 mL of 0.05 M HCl and back titrated with NaOH. Whereas the acidic aliquot (HCl) was titrated directly with 0.05 M NaOH. Titrations were performed using an automated titrator, with endpoints determined potentiometrically. The number of moles of surface functional groups neutralised by the titrant, n_{CSF} (mol), was calculated using either Equation 3.5 or Equation 3.6 for acidified and non-acidified equations, respectively. Finally, the

number of moles of surface groups per gram of adsorbent, η_{CSF} (mol/g), can be calculated using Equation 3.7.

$$n_{CSF} = \frac{n_{HCl}}{n_B} [B] V_B - ([HCl] V_{HCl} - [NaOH] V_{NaOH}) \frac{V_B}{V_a}$$
 Equation 3.5

$$n_{CSF} = [B]V_B - [HCl]V_{HCl}\frac{V_B}{V_a}$$
 Equation 3.6

$$\eta_{CSF} = \frac{n_{CSF}}{M_C}$$
 Equation 3.7

Where, n_{HCI} and n_B , represent the number of moles of HCl and base, respectively (mol). [B], [HCl] and [NaOH] denote the concentrations of the base, HCl, and NaOH solutions, respectively (mol/L). V_B , V_{HCl} and V_{NaOH} correspond to the volumes of the respective solutions (L). Finally M_C represents the mass of carbon used (g).

3.6.4. Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray Spectroscopy (EDS)

In this thesis, a Supra 35VP with a field emission gun was applied for SEM-EDS analysis. Due to the high conductivity of CFs, the materials did not require sputter coating prior to analysis. Low-magnification images were obtained using a secondary electron detector at a working distance of 4.5 mm and an accelerating voltage of 10 ekV. For high-magnification imaging an inlense detector was used with a decreased working distance of 3.5 and an increased accelerating voltage of 20 ekV. Backscattered electron detectors were employed for EDS analysis with an accelerating voltage of 20 ekV. Copper tape was applied as the adhesive, rather than the more common carbon adhesive to avoid misinterpretation of the sample elements, particularly carbon, and the background.

3.6.5. Spectroscopic Analysis

3.6.5.1. Fourier-Transform Infrared Spectroscopy (FTIR)

In this thesis transmission FTIR was applied using KBr, due to the high absorbance of CFs. Prior to preparation, KBr was dried for a minimum of 48 h in an oven at 100 °C. The CF samples were then combined with KBr in a 1:300 ratio (CF:KBr) and ground with a pestle and mortar until a homogenous mixture was achieved. The ratio of 1:300 (CF:KBr) was determined by detrimentally reducing the amount of CF, whilst maintaining the quantity of KBr until a clear

spectrum was obtained. The mixture was then transferred into a pellet-forming die, to which a 10-tonne force was applied for 5 minutes. The resultant pellet was used for FTIR analysis in the region of 4000-500 cm⁻¹ for 20 scans at a resolution of 4 cm⁻¹.

3.6.5.2. Raman Spectroscopy

In this thesis, analysis was conducted using a Reinshaw inVia Raman microscope with a 532 nm laser. Crystalline silicon was used as an x-axis calibration standard, to enable the conversion of wavelength to Raman shift, since a sharp peak is produced at 520 cm⁻¹. The CFs were ground to a fine powder with a pestle and mortar prior to analysis. Raman analysis was conducted in the region of 600-2400 cm⁻¹ for 20 scans.

3.6.5.3. UV-Vis Spectrophotometry

In order to quantify concentrations effectively, the wavelength of maximum absorption must be identified, which is known as the lambda max (λ_{max}) and is dependent on the chromophore(s) present within a molecule. The λ_{max} in this work, and for each pollutant studied in this thesis was determined using a Shimadzu UV-1800, UV-vis spectrophotometer, scanning between the wavelengths of 250 – 700 nm. The λ_{max} for CIP, OTC and MB were identified to be 273, 357 and 664 nm, respectively; these values were cross-checked with existing literature for further confirmation of λ_{max} .

Calibration curves are required in UV-vis to quantify solutions of unknown concentration. In this thesis the calibration curves were produced by preparing a minimum of 5solutions of known concentration, measuring the absorbance at the λ_{max} and creating a plot of concentration vs absorbance. The resulting plot creates a linear graph and should have an R² value greater than 0.97, as shown in Figure 3.4. Unknown concentrations can then be calculated from the linear equation, y=mx+C.





When analysing MB_N with UV-vis, all solutions were diluted with water at a 1:5 ratio (MB:H₂O) in order to maintain an absorbance value of less than 2 AU, since values above this result in less than 1% of the light source reaching the detector. Due to the logarithmic nature of UV-vis, once absorbance reaches 3 AU, less than 0.1% of light would reach the detector, leading to inaccurate readings. For the antibiotics, CIP and OTC, individual calibration curves were produced for the various solution pH (e.g. non-adjusted, pH 2, 5 and 8).

3.6.6. Ultimate Analysis

The most commonly applied standard for CHN analysis is acetanilide which has a theoretical mass fraction of 71.088, 6.712, 10.363 and 11.837% for C, H, N and O, respectively.

The analyses method for CAs are often specified by governmental standard procedures such as ATSM D3176-15, where the results are presented as percent mass fractions [245]. In this thesis, all ultimate analysis was conducted using a Thermo Scientific Flash 2000 Organic Elemental Analyser.

3.6.7. Proximate Analysis

The method employed in this thesis follows the ASTM D7582, using a Mettler Toledo TGA 2, thermogravimetric analyser. The method involves firstly heating the sample to 107 °C under N₂ with a gas flow rate of 22 mL/min and holding these conditions for 1 h, to determine the moisture content. The VOC content was then determined by ramping the temperature to 950 °C at a rate of 30 °C/min; these conditions were held for 7 min. The sample was then cooled to 600 °C to enable the atmosphere to be changed to an oxidising gas (in this study, air). Finally, the material was heated to 950 °C with a ramp rate of 6 °C/min and maintained for 3 h to expel the fixed carbon under ambient air.



Figure 3.5: Temperature profile of proximate analysis, adapted from [31].

The moisture and VOC content are determined by the change in mass (Equation 3.8 and Equation 3.9). The ash is determined using the residual mass (M_{ash}, Equation 3.11) and the fixed carbon is determined by subtracting the mass of all other constituents from the initial sample mass (Equation 3.10).

Moisture Content (%) =
$$\left(\frac{M_0 - M_1}{M_0}\right) \times 100$$
 Equation 3.8

VOC content (%) =
$$\left(\frac{M_1 - M_2}{M_0}\right) \times 100$$
 Equation 3.9

Carbon Content (%) =
$$\left(\frac{M_0 - (M_1 + M_2 + M_{ash})}{M_0}\right) \times 100$$
 Equation 3.10

Ash Content (%) =
$$\left(\frac{M_0 - M_{ash}}{M_0}\right)$$
 Equation 3.11

Where, M_0 is the initial sample mass (mg), $M_1 - M_3$ are the sample masses (mg) after the heating phases 1 – 3 shown in Figure 3.5.

4. Activation of Carbonaceous Adsorbents for Aqueous-phase Applications

4.1. Introduction

The increasing application of CFRP-based products is presenting a major environmental challenge when products reach their EoL. Despite the range of available recycling technologies for CFRPs, a review article on the recycling of CFs, published by Verma et al. concluded that rCFs are not currently economically viable and in some cases may be more expensive to produce than vCFs, highlighting the need for new, high-value applications for rCFs [247].

As of 2021, global CF production reached approximately 181 kt [248]. Assuming that scrap, waste or EoL material accounts for 10% of annual CF production, up to 18.1 kt tonnes of surplus waste could be generated annually. Studies have valued the average price of rCFs as £9/kg [249,250]. Therefore, up to £163 million worth of rCFs could be introduced into the market, by transitioning to recycling CFs over traditional disposal techniques such as landfill or incineration. Additionally, further research into new applications of rCFs, such as adsorption, could create value added products.

From an environmental standpoint, rCFs production has a significantly lower energy demand (2-30 MJ/kg) and reduced CO₂ emissions of 5.4-11 kg/kg of CO₂, when compared to the production of PAN-vCFs which produce up to 31 kg/kg CO₂ [251–253]. While traditional disposal practises such as incineration offer lower CO₂ emissions (2.2-3 kg/kg) when compared to recycling process, their energy demand is much greater (32-34 MJ/kg) and result in the destruction of a potentially high value product [254,255].

Currently, articles investigating the conversion of rCFs to adsorbents using activation processes are scarce, particularly those derived *via* chemical activation methods [31]. Despite the limited publications in this area, current research is promising to produce ACFs from rCFs, which can be attributed to the structural changes that occur during the recycling process. It has been reported that thermal treatment results in increased interlayer spacing of the internal graphene layers, subsequently leading to a larger surface area prior to activation (Figure 4.1) [256].



Figure 4.1: Comparison between the interlayer distance of vCFs vs rCFs [34].

Furthermore, thermal recycling processes can introduce surface oxygen-containing surface groups, such as carboxyl, hydroxyl, and ketones that act as active sites for adsorption [13]. Consequently, rCFs already have the essential physiochemical properties that make them promising candidates for use as aqueous-phase adsorbents. However, as a novel adsorbent precursor, extensive research and process optimisation is essential to improve the material's characteristics.

MB was employed in this study as a cost-effective, conventional, and reliable method to estimate the mesoporosity of a large number of samples through the determination of the methylene blue number (MB_N), as outlined in Section 3.6.1. MB was chosen due to its well-defined molecular size and strong affinity for porous surfaces, enabling a straightforward and accurate estimation of the accessible surface area, particularly within mesoporous structures.

While dye adsorption is often employed as a model for surface area analysis, large-scale dye removal remains critically important due to significant human and environmental health risks. Globally, an estimated 10,000 tonnes of dyes are used annually, primarily in the textile industry,

with MB among the most widely applied [257]. However, the extensive use of MB raises serious concerns, as it is toxic, carcinogenic, and non-biodegradable owing to the stability of its aromatic ring structure (Figure 4.2). Exposure to MB has been linked to various adverse health effects, including respiratory distress, hypertension, neurological disorders, anaemia, gastrointestinal pain, and nausea [258–260]. Furthermore, its degradation products contain aromatic components which are carcinogenic and mutagenic.



Figure 4.2: Structure of MB.

MB is highly water-soluble and can be released into the environment in substantial quantities through industrial discharges and effluents, posing an environmental concern [257]. Furthermore, the intense colour and high molar absorption coefficient (8.4 x 10⁴ L/mol) of MB, even at low concentrations, results in reduced sunlight transmittance in natural waterbodies, diminishing the photosynthetic activity of aquatic plants and subsequently lowering the chemical and biological oxygen demand, thereby creating anoxic conditions that limit aquatic biodiversity.

Similarly to antibiotic adsorption, MB can be adsorbed *via* physical (i.e. hydrogen bonding, hydrophobic effects etc.) or chemical mechanisms where oxygen-containing groups have been shown to aid the electrostatic attraction of cationic MB dyes. Meaning ArCFs could have promising value for the adsorption of alternative aqueous phase pollutants.

The focus of this chapter is to firstly determine whether rCFs are suitable precursors for the production of aqueous-phase adsorbents. Thereafter, the author strived to optimise the physiochemical characteristics of the adsorbent by employing DoE techniques, specifically BBD, to study the activation process. The effects of several factors were investigated, namely, activation temperature, activation time and IR on the responses yield and MB adsorption capacity. Furthermore, the precursor, activated and spent materials are thoroughly characterised to assess the physical and chemical properties.

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4.2. Results and Discussion

4.2.1. Preliminary Studies

4.2.1.1. Sodium Hydroxide Activation

Both Na-ACFs demonstrated similar maximum experimental adsorption capacities exceeding 5.75 mg/L, which is consistent with values reported in the literature [261], highlighting the potential of rCFs as effective adsorbent materials. However, these values are lower than those observed when using DoE methods [258], suggesting that further optimisation of experimental parameters is needed in the next phase of the study. Notably, both ArCF and AvCF exhibited comparable MB adsorption capacities, reinforcing the promising potential of rCFs as efficient adsorbents.

Sample	Absorbance	Ce	\mathbf{q}_{e}	Removal	Ref
		(mg/l)	(mg/g)	(%)	
MB	2.70	-	-	-	-
ArCF	2.36	16.84	5.76	21.80	-
AvCF	2.36	16.83	5.77	21.83	-
ACF	-	-	23.75	-	[258]
AC	-	-	454.20	-	[262]
AC	-	-	4.80	-	[261]

Table 4.1: UV-vis absorbance of Na-AvCF and Na-ArCF at 664 nm.

Figure 4.3A and B depict the surface morphology of Na-AvCF and Na-ArCF, respectively. Both Na-ACFs presented a smooth fibrous structure with no visible surface defects (Figure 4.3). aligning with the appearance of chemically activated PAN-based CFs reported in current literature [258]. However, Na-ArCFs had more visible impurities on the surface in contrast to its virgin counterpart which had a largely clean surface. EDS was employed to confirm the

increased impurities, where higher levels of Na, Mg, and other impurities such as Si, K, and Ca were identified with in the rCF-based sample (Table 4.2).



Figure 4.3: SEM images of Na-AvCF (A) and Na-ArCF (B), adapted from [43].

Notably, Na-ArCFs had a higher average fibre diameter of 7.75 \pm 0.14 µm when compared to Na-AvCF (7.26 \pm 0.06 µm) which can be explained *via* a couple of interconnected phenomena. Firstly, the CF thermal recycling process results in an increased interlayer distance between the graphene sheets, therefore, rCFs already possessed a marginally higher surface diameter prior to activation, which is consistent with the EDS data. Furthermore, Na-ArCF possesses significantly higher quantities of Na⁺ (Table 4.2), which are able to intercalate between graphene sheets resulting in an increased fibre diameter.

Flomont	Composition (wt%)			
Liement	Na-AvCF	Na-ArCF		
С	24.13	22.72		
0	69.76	65.78		
Na	0.14	2.35		
Mg	0.03	0.15		
Others	5.94	9.00		

Table 4.2: Percentage composition of Na-AvCF and Na-ArCF, adapted from [43].

4.2.1.2. Selection of DoE Parameters and Ranges

Oxygen-containing moieties play a crucial role in the adsorption of many aqueous-phase adsorbents including MB and the target aquaculture antibiotics, CIP and OTC. Current literature has reported that higher IR results in enhanced oxidation of CA surfaces. Furthermore, a low and slow activation approach (i.e. low temperature and long hold times) has been reported to enhance the development of mesoporosity [126]. Consequently, investigating high IR and long hold times were of interest resulting in the selection of a maximum IR of 1:10 and hold time of 3 h. Whilst the lower limits were based on current literature (Table 2.6).

Since all experimental runs within a DoE design require a sample to be produced in order to assess a given response, the minimum temperature at which complete carbon burn-off occurs was investigated. This was achieved by progressively decreasing the temperature from 900 °C, whilst IR and hold time were set at their maximum values until a minimum yield of 25% was achieved. This yield was necessary to ensure there was sufficient adsorbent material for subsequent adsorption experiments and material characterisation. The threshold temperature was found to be 830 °C (Figure 4.4). Consequently, the final DoE ranges were set as follows: activation temperature of 670 - 830 °C, IR of 1:1 - 1:10, and hold time of 0.5 - 3 hours.



Figure 4.4: Impact of temperature on yield when IR and hold time were set to 1:10 and 3 h, respectively.

4.2.2. Optimisation of Chemical Activation Process

To optimise the production conditions of ACFs from rCF precursors, a three-factor BBD was employed. The experimental conditions assayed are detailed in Table 4.3 and the run order was randomised to minimise systematic error. Regression coefficients were derived from data obtained in experiments 1-12, while experiments 13-15 were replicates at the central point to ensure repeatability [263].

The highest yield (104.80%) was observed for Run 5, which was attributed to the intercalation of K⁺ ions, introduction oxygen-containing moieties on the CA surface and the presence of aluminosilicates due to slight corrosion of the combustion boat, as discussed further in Section 4.2.3.2. In this run, the activation temperature and time were set to their minimum values of 670 °C and 0.5 hours, respectively, with the IR was set at the centre point (1:5.5), resulting in a reduction in the burn-off of carbon, when compared to other runs with harsher experimental conditions.

Run	Activ Temp (vation erature °C)	ا (CF:	R KOH)	Hold T	ime (h)	Yield (%)	q _e (mg/g)
	X 1	Code	X ₂	Code	X ₃	Code	Уı	¥2
1	670	-1	1.75	0	1:1	-1	99.40	5.97
2	830	+1	1.75	0	1:1	-1	52.35	6.07
3	670	-1	1.75	0	1:10	+1	46.35	55.19
4	830	+1	1.75	0	1:10	+1	3.79	58.74
5	670	-1	0.5	-1	1:5.5	0	104.80	18.96
6	830	+1	0.5	-1	1:5.5	0	58.18	11.49
7	670	-1	3	+1	1:5.5	0	87.51	11.88
8	830	+1	3	+1	1:5.5	0	24.65	7.86

Table 4.3: BBD matrix with real and coded values of three factors studied, and responses yield and q_e of each run performed, taken from [34].

Run	Activ Temp (vation erature °C)	l (CF:	R KOH)	Hold T	ime (h)	Yield (%)	q _e (mg/g)
	X 1	Code	X 2	Code	X3	Code	y 1	¥2
9	750	0	0.5	-1	1:1	-1	86.13	0.91
10	750	0	0.5	-1	1:10	+1	38.19	49.40
11	750	0	3	+1	1:1	-1	72.29	4.56
12	750	0	3	+1	1:10	+1	23.43	55.13
13	750	0	1.75	0	1:5.5	0	55.36	16.42
14	750	0	1.75	0	1:5.5	0	69.30	45.22
15	750	0	1.75	0	1:5.5	0	43.91	57.72

ANOVA was conducted to evaluate the statistical significance of the overall model and to determine the impact of individual factors on both yield and MB adsorption capacity responses. The comprehensive ANOVA results are presented in Appendix A. The model's predictive capability was assessed through regression coefficients (R^2), adjusted regression coefficients (R^2_{adj}) and predictive regression coefficients (R^2_{pred}), as summarised in Table 4.4.

Initial analysis revealed high R² values (>95%) for both responses, though the lower R²_{pred} values suggested potential limitations in the model's predictive accuracy. Through systematic elimination of statistically insignificant terms based on the ANOVA results, the model was refined. While this optimisation led to a marginal decrease in R² values, the overall statistical significance remained robust. Notably, the refined model demonstrated improved R²_{adj} values from 89.72% to 92.57% for yield, and from 97.27% to 98.08% for adsorption capacity, indicating better overall model fit. Most significantly, the R²_{pred} values showed substantial improvement, increasing from 78.57% to 89.03% for yield and from 84.41% to 96.08% for adsorption capacity, indicating

	R ²	\mathbf{R}^2_{adj}	R ² pred
Yield	95.23	92.57	89.03
Adsorption capacity	98.76	98.08	96.08

Table 4.4: Refined regression coefficient and adjusted and predicted regression coefficientsfor the responses in this study i.e. yield and adsorption capacity.

The ANOVA results for yield and MB adsorption capacity are shown in Table 4.5. The p-value was used to assess the significance of the factors and their interaction effects at a 95% confidence level (p-value < 0.05).

For yield, all three primary process variables were statistically significant, with p-values of 0.000, 0.000, and 0.006, for temperature, IR and hold time, respectively. These results suggest a largely linear relationship between the variables and yield across the design space. Additionally, the squared effects of IR (p = 0.037) were also significant, indicating some curvature in the model.

In contrast, for MB adsorption capacity, only IR and its squared term were statistically significant both having p values of 0.000, suggesting that MB adsorption is predominantly influenced by changes in IR, including non-linear effects. Neither temperature nor hold time had significant impacts on this response. Nevertheless, the linear terms for temperature and hold time were retained in the model to maintain hierarchy and ensure the statistical validity of the quadratic and interaction terms. These findings are visually supported by the Pareto charts in Figure 4.5, which highlight the standardised effects of each factor and their relative contributions to both responses.

It is important to note that the ANOVA results presented in Table 4.5 reflect a reduced model, where non-significant terms were removed for clarity and model refinement. The complete ANOVA including all interaction terms and non-significant variables is provided in Appendix A for reference.

Source	Code	Yield	d (%)	MB adsorption capacity (mg/g)	
		F-Value	P-Value	F-Value	P-Value
Model	-	35.90	0.000	143.87	0.000
Linear	-	56.26	0.000	209.64	0.000
Temperature	x ₁	78.42	0.000	1.61	0.236
IR	X2	77.89	0.000	627.08	0.000
Hold Time	X3	12.48	0.006	0.23	0.643
Square	-	5.35	0.029	45.21	0.000
IR*IR	x ₂ ²	5.95	0.037	78.16	0.000
Hold Time*Hold Time	x ₃ ²	4.01	0.076	8.19	0.019

Table 4.5: ANOVA results for the refined model of the chemical activation campaign, whenconsidering the responses yield and MB adsorption capacity.

The 3D contour plots (Figure 4.5) illustrate the impacts of the three factors on the responses. As expected, an inverse relationship exists between yield and MB number. When increasing parameters to their maximum value (+1), there is a distinct antagonistic effect on the yield with activation temperature and IR having the largest impacts (Figure 4.5A – C). Whereas a synergistic effect was observed for MB adsorption capacity with IR and the squared effect of IR being most impactful (Figure 4.5D – F). Figure 4.5D and 4.5F depict the dramatic impact of IR, with higher adsorption capacities being observed when IR is set to the maximum value.



Figure 4.5: 3D response surface plots for combined effects of temperature and IR (A, D), temperature and hold time, (B, E) IR and hold time (C, F), on the responses yield (A – C) and MB adsorption capacity (D – F).

The significant impact of activation temperature on the yield can be credited to the enhanced etching of the carbon surface at temperatures above 600 °C, resulting in the expulsion of carbon in the form of CO_2 and CO, and tar in the form of VOCs, thus increasing the surface area and porous network but decreasing yield [13]. The evolved gases can then physically activate the surface *via* the mechanisms discussed in Chapter 2 (Figure 2.7).

The impact of IR on MB adsorption capacity can be described *via* several phenomena. Firstly, higher IR results in enhanced development of porosity at due to increased etching of the carbon surface, by the chemical activation agent. Additionally, intercalation of alkali metals such as K⁺

results in increased spacing between graphene sheets, subsequently enhancing specific surface area and pore volume (Figure 4.6). Finally, a higher hydroxide ratio leads to an increased abundance of oxygen-containing moieties on the carbon-surface which act as active sites for adsorption, which have the capability to interact with aqueous phase pollutants such as methylene blue *via* physical interactions such as hydrogen bonding, or chemical interactions (i.e. ionic or covalent bonding).



Figure 4.6: Intercalation of K⁺ between graphene sheets, taken from [34].

4.2.2.1. Optimum Point Validation and Comparison with Virgin Carbon Fibres

Yield and MB adsorption were optimised *via* an equally weighted dual-response optimisation in order to validate the model. The optimum point was identified at an activation temperature, IR and hold time of 670 °C, 1:10 and 0.5 h, respectively. The optimum samples were denoted as K-ACF-Opt, where r and v correspond to the recycled and virgin samples. K-ArCF-Opt was found to have a yield of 70.14% and MB adsorption capacity of 19.04 mg/L. However, the response surface graphs suggest that further increasing the IR could result in improved MB adsorption, whilst yield could be enhanced by reducing each factor beyond the design space of this study. Therefore, a compromise was necessary when selecting the optimal conditions to maximise both yield and adsorption capacity.

The second order polynomial equations for yield and MB adsorption capacity are presented in Equation 4.1 and Equation 4.2, respectively, where x_i represent the influence of the independent variables on a response y_i (i.e. yield or MB adsorption capacity) and $(x_i)^2$ represent the quadratic terms indicating that there is curvature present within the design space.

$$y_1 = 337.3 - 0.311x_1 - 0.050x_2 - 26.440x_3 - 0.497(x_2)^2 + 5.280(x_3)^2$$
 Equation 4.1

$$y_2 = 10.5 - 0.016x_1 - 1.511x_2 + 1.190x_3 + 0.653(x_2)^2 - 2.738(x_3)^2$$
 Equation 4.2

From Equation 4.1, it is evident that hold time (x_3)has the most substantial influence on yield, with a pronounced negative linear coefficient of -26.440, , though its positive quadratic term suggests some recovery at longer durations as observed in Figure 4.5B and C. Temperature and IR show smaller negative impacts. In contrast, Equation 4.2 shows weaker overall effects on adsorption capacity, with all coefficients below \pm 3. Here, hold time has a small positive linear impact, while its negative quadratic term suggests reduced capacity at extended durations, consistent with the trend observed Figure 4.5E. IR has a mixed influence, with a negative linear and a positive quadratic effect, indicating a potential optimal range, however this was not identified within the investigated design space.

Overall, the regression models highlight that yield is more sensitive to variations in the process parameters, particularly hold time, while MB adsorption capacity is influenced to a lesser extent, with more balanced effects from the input variables. These findings can guide optimisation strategies by identifying parameter ranges that maximise both yield and adsorption performance.

4.2.2.1.1. Yield and Impact of Scale-up

The parity plot depicting the actual yield vs the predicted yield based on Equation 4.1 is shown in Figure 4.7. The reasonable R² value of 0.89 indicates that Equation 4.1 is a suitable model for predicting and comparing experimental and modelled values. A lower yield was observed for K-ArCF-Opt, when compared to Runs 1, 5, 7, 9 and 11; however, this is expected , as the selected conditions reflect a deliberate compromise between maximising yield and enhancing MB adsorption capacity.



Figure 4.7: Parity plot of the actual yield vs predicted yield, where (•) is the optimum point, and (•) are the replicates at the centre point, adapted from [34].

The effect of scale-up on the yield was also investigated for both K-ArCF-Opt and K-AvCF-Opt, by increasing the quantity of precursor by up to 8 times (Figure 4.8). Despite some variation, scale up had little to no effect on the yield of K-AvCF-Opt, maintaining values greater than 70% up to a precursor mass of 0.8 g. Conversely, scale-up had a negative impact on the yield of K-ArCF-Opt, with a decrease in yield of 27.7% when scaling up from 0.1 g – 0.8 g of rCF. Despite the initial decrease, the trend appears to plateau just above 40% when the precursor mass is greater than 0.6 g, which is promising for industrial scalability. Nevertheless, to truly determine industrial scalability, future studies should investigate larger precursor masses.



Figure 4.8: Impact of scale up on yield, taken from [34].

4.2.2.1.2. Methylene Blue Adsorption

Figure 4.9 depicts the parity plot for actual vs predicted MB adsorption capacity. A strong correlation is evident between the values, with an R² value of 0.99, indicating that the model (Equation 4.2) can accurately predict the experimental results.





The surface characteristics of the adsorbent were then assessed by employing N₂ adsorption isotherms to determine the S_{BET} and pore volume (Section 4.2.3.1) and MB_N to determine the mesoporosity of the adsorbent *via* the methods described in Chapter 3. Comparable S_{BET} of 428 and 415 m²/g were observed for K-ArCF-Opt and AvCF-Opt, respectively. Despite this, the MB_N of K-ArCF-Opt was notably higher when compared to K-AvCF-Opt (Table 4.7), which was attributed to higher content of oxygen-containing functional groups on the K-ArCF-Opt surface. These functional groups are known to facilitate chemisorption, thereby enhancing the adsorbent's interaction with MB molecules and contributing to the improved adsorption performance observed for K-ArCF-Opt.

To contextualise these results, the adsorption performance of the optimum samples were compared with data reported in the literature. Although several previously reported ACFs exhibit significantly higher S_{BET} values of 1975 m²/g and 1801 m²/g with corresponding q_{max} values of 729.00 and 478.50 mg/g, respectively [125,264]. K-ArCF-Opt sample achieved a q_{max} of 454.55 mg/g, demonstrating competitive performance despite its lower surface area.

Moreover, this sample surpassed the adsorption capacity of an ACF with 1614 m²/g, which reported an uptake of 325.83 mg/g [265].

Both samples developed in this study also outperformed various ACs reported in the literature, such as those with S_{BET} values of 1172, 708, and 594 m²/g, which exhibited significantly lower adsorption capacities of 162.54, 241.30, and 180.00 mg/g, respectively [258,266,267]. These comparisons underscore the efficiency of the activation method employed, suggesting that surface chemistry and pore structure, particularly mesoporosity and the presence of functional groups, play a more critical role than surface area alone in governing MB adsorption. Consequently, the materials developed in this work show strong potential for application in advanced water treatment technologies.

A key advantage of the rCFs used in this study is that they bypass the need for a separate carbonisation step prior to activation. Due to their high carbon content and pre-existing graphitic structure, meaning they are already thermally stable and structurally suited for direct chemical activation. This not only simplifies the synthesis process but also lowers energy demands and enhances the overall efficiency and scalability of the material preparation.

In contrast, many activation methods reported in the literature involve more complex and resource-intensive procedures. Additionally, many reported methods rely on aggressive chemical agents such as concentrated phosphoric acid or ammonium phosphate salts, which are both corrosive and environmentally hazardous (Table 4.6).

For instance, the preparation of ACFs in [264] required a prolonged 12-hour impregnation with phosphoric acid followed by sequential thermal treatments up to 500 °C. Similarly, the protocol described in [265] employed high-temperature water activation at 900 °C with a substantial gas flow rate (125 m³/h), presenting scalability and operational safety challenges.

The approach developed in this work, by contrast, is significantly faster, more straightforward, and avoids the use of such hazardous reagents. The brief KOH impregnation (only 5 minutes) and short activation time at moderate temperature (670 °C for 30 minutes) under nitrogen represent a minimalist yet highly effective methodology. This results in reduced thermal and chemical loads, making the process more sustainable and industrially attractive.

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CA	Activation Method	S _{BET} (m²/g)	q _{max} (mg/g)	Ref
٨٢	Impregnate: 85% KOH (1:10), 0.08 h	128	151 55	This
	Activate: N ₂ 100 ml/min, 670 °C, 0.5 h	420	434.33	work
٨٢	Impregnate: 85% KOH (1:10), 0.08 h	/15	344 83	This
ACI	Activate: N ₂ 100 ml/min, 670 °C, 0.5 h	415	544.85	work
	Carbonise: 200 °C, 4 h			
ACF	Impregnate: 85% H ₃ PO ₄ , 60 °C, 12 h	1975	729.00	[264]
	Activate: N ₂ 100 ml/min, 300 °C, 2 h, 500 °C,			
	1 h			
	Impregnate: 7.5% (NH ₄) ₂ HPO ₄ , 1 h, dry 110 °C			
ACF	Carbonise: 300 °C, 30 min, 800 °C, 5 min	1614	325.83	[265]
	Activate: H_2O 125 m ³ /h, 900 °C, 7 min			
٨٢	Impregnate: 15% H ₃ PO ₄ , 12 h	1801	<i>4</i> 78 50	[125]
	Activate: 450 °C, 1 h	1001	478.50	[123]
A.C.	Impregnate: NaOH 80 g/L, dry 100 °C, 24 h	1170	162 54	[250]
AC	Activate: Ar 100 ml/min, 400 °C, 3 h	11/2	102.54	[236]
	Impregnate: H ₃ PO ₄ (1:1)	2422	222.20	[250]
AC	Activate: N ₂ 120 ml/min, 400 °C, 3 h	2132	333.30	[259]
	Impregnate: H ₃ PO ₄ (1:2), dry 100 °C overnight	709	241.20	
AL	Activate: N ₂ , 700 °C, 1 h	708	241.30	[266]
	Impregnate: 45% H ₃ PO ₄ (1:2), 10 h	E04	180.00	[267]
AC	Activate: 550 °C, 0.83 h	594	180.00	[207]

Table 4.6: Comparison of S_{BET} and q_{max} for K-ArCF-Opt, K-AvCF-Opt and other CAs.

4.2.3. Material Characterisation

This section will discuss the physicochemical characteristics of the precursor, optimum and spent ACF samples.

4.2.3.1. Surface Analysis

4.2.3.1.1. Physical Surface Analysis

The S_{BET} , pore volume and pore size were measured and calculated for both K-ArCF-Opt and K-AvCF-Opt (

Table 4.7). Similar S_{BET} were observed for both ACFs and precursor materials. The precursors were shown to have a low surface area (<50 m²/g), whereas a significant improvement was observed after activation with surface areas exceeding 410 m²/g.

To evaluate the statistical significance of the differences between recycled and virgin fibres, both before and after activation, t-tests were conducted. For the precursor materials, a t-statistic of 2.13 and a P-value of 0.0001 indicated a highly significant difference between recycled and virgin CFs. Similarly, for the activated materials, a t-statistic of 2.44 and P-value of 0.04 confirmed a significant difference, with the recycled variant (K-ArCF-Opt) showing superior physical surface properties.

The higher surface area of K-ArCF-Opt was attributed to the reduced mechanical strength after recycling, as a result, the carbonaceous framework is more readily etched away by the activation agent, leading to an increase in surface area. Furthermore, K-ArCF-Opt had a higher total pore volume, despite having a smaller micropore volume, indicating a higher volume of meso-and-macropores, which are attractive for aqueous-phase adsorbents.

Sample	S _{BET} (m²/g)	V _{micro} (cm³/g)	V _{total} (cm³/g)	Average Pore size (nm)	MB _N (mg/g)
rCF	48.95 ± 5.34	-	0.07	-	-
vCF	27.62 ± 3.86	-	0.04	-	-
K-ArCF-Opt	427.63 ± 15.12	0.02	0.35	4.08	714.29
K-AvCF-Opt	414.88 ± 6.30	0.04	0.33	4.20	400.00

Table 4.7: Textural properties of ArCF and AvCF based upon the N₂ adsorption isotherms and MB adsorption, taken from [34].

The S_{BET} physisorption isotherms for both K-ArCF-Opt and K-AvCF-Opt are presented in Figure 4.10. Both K-ACFs exhibit a Type IV isotherms, which are characteristic of mesoporous materials. The initial steep increase in the quantity of N₂ adsorbed at lower relative pressures is indicative of monolayer surface adsorption. Whilst the gradual rise at higher relative pressures represents multilayer adsorption. Additionally, both isotherms display a H₄ type hysteresis loop, which is commonly associated micro-and-mesoporous materials with narrow slit pores; this phenomenon is attributed to capillary condensation within the mesopores.



Figure 4.10: BET physisorption isotherm of (A) K-ArCF-Opt and (B) K-AvCF-Opt.

The BJH data in Figure 4.11 further supports this interpretation, revealing that a significant portion of the cumulative pore volume is concentrated within the smaller mesopore and micropore range, between 1.8 and 5.7 nm. Moreover, it is evident that K-ArCF-Opt possesses a notably higher pore volume in the micropore to small mesopore region, contributing to its higher S_{BET}, when compared to K-AvCF-Opt.



Figure 4.11: BJH Pore size distribution plot of K-ArCF-Opt and K-AvCF-Opt.

4.2.3.1.2. Chemical Surface analysis

Boehm titrations were applied to determine the total acidity and basicity of the samples using the method described in Chapter 3. K-ArCF-Opt samples were found to possess substantially higher levels of all oxygen-containing surface groups when compared to K-AvCF-Opt, particularly for carboxyl and basic groups (Table 4.8).

Table 4.8: Chemical surface analysis of K-ArCF-Opt and K-AvCF-Opt based on Boehm titrations

Sample	Quantity of surface groups mmol/g					
	Carboxyl	Phenol	Lactone	Basic		
K-ArCF-Opt	2.41	0.29	0.31	2.32		
K-AvCF-Opt	0.07	0.07	0.11	0.03		

[34].

4.2.3.2. SEM-EDS

SEM images of the recycled and virgin carbon fibre precursors are presented in Figure 4.12, whilst the activated samples are shown in Figure 4.13. Figure 4.12A and B show the non-activated CFs at a magnification or 20,000x, displaying a smooth fibrous form with some striations on the surface. A comparable image was depicted for the activated samples in Figure 4.13A and B, with some evident surface defects.



Figure 4.12: SEM imaging of rCF (A), vCF (B) at 20,000x magnification, working distance 3.4, accelerating voltage 5 ekV [34].

When increasing the magnification to 150,000x, the external porous structure becomes apparent (Figure 4.13B and D). Both K-ACFs displayed a heterogeneous surface structure

characterised by a combination of meso- and macropores, with average pore sizes ranging from 11.88 to 59.40 nm, as determined using the SEM's built-in measurement tool. These observations align with the S_{BET} data, which further confirmed a substantial meso- and macropore volume exceeding 0.31 cm³/g. Notably, the porous structure appeared to be angular in shape for K-ArCF-Opt, whereas the K-AvCF-Opt displayed an orbicular porous network. Due to limited resolution the microporous structure couldn't be imaged, therefore, further research could include alternative techniques such as TEM to view the microporous network. However, the applicability of this technique is highly dependent on the crystallinity of the material and would not be useful for highly amorphous samples.



Figure 4.13: SEM imaging of K-ArCF-Opt (A), K-AvCF-Opt (C) at 20,000x magnification working distance 3.4, accelerating voltage 5 ekV and K-ArCF-Opt (B), K-AvCF-Opt (D) at 150,000x magnification working distance 3.5, accelerating voltage 3 ekV [34].

The EDS results indicated a high carbon content up to 100% for the precursor materials Figure 4.14A); however, this is likely an overestimation since EDS is not a sensitive technique, particularly for very light, or trace elements. Furthermore, some known elements within the CF

structure (i.e. nitrogen and hydrogen) cannot inherently be identified using EDS. Nitrogen cannot be detected due to its low Z number which overlaps with the carbon and oxygen K-alpha. Meanwhile, hydrogen, having only a 1s¹ electron configuration, does not emit x-rays since core electrons can't be removed. In some areas, small amounts of oxygen and potassium were identified which was ascribed as oxygen-containing moieties and impurities introduced during the CF recycling process.



Figure 4.14: EDS spectra of rCF (A) and ArCF (B), [34].

Following activation, there was a distinct reduction in the carbon content of both K-ACF-Opt due to the expulsion of carbon in the form of VOCs during activation, combined with the incorporation of oxygen containing functional groups and potassium into the K-ArCF-Opt structure, which in turn may have decreased the amount of carbon in percentage terms (Figure 4.14B). The reduction in carbon content was more pronounced for K-ArCF-Opt to which had a carbon content below 73%, whilst K-AvCF maintained a carbon content above 84%. This can be attributed to the reduced mechanical strength of rCFs which allow the surface to be more readily etched during activation, therefore expelling greater quantities of carbon.

The elevated K content was attributed to the intercalation of K⁺ ions between the graphene sheets of the carbonaceous structure; a recognised activation mechanism when applying alkali activation agents [13]. The intercalation of K⁺ was further evidenced by the notable increase in fibre diameter, with the average diameter of rCF and vCF increasing by 13.95% and 0.67%, respectively (Table 4.9).

Sample	Diameter (µm)
rCF	7.22 ± 0.09
vCF	7.02 ± 0.05
K-ArCF-Opt	8.23 ± 0.41
K-AvCF-Opt	7.07 ± 0.10

Table 4.9: Mean fibre diameters of recycled and virgin CFs determined by SEM Analysis

Post-activation, several crystalline impurities were observed on the surface, which was attributed to corrosion of the aluminosilicate crucible by the KOH activation agent, leaving residues on the CF surface. This was confirmed using EDS analysis of the crystalline deposits which revealed small amounts of AI and Si of 1.51% and 1.77%, respectively (Figure 4.14B). Additionally, traces of copper were found, which were linked to the use of copper adhesive tape during the SEM-EDS analysis and thus excluded from the weight percentage calculations.

4.2.3.3. Elemental Analysis

Table 4.10 shows the elemental (ultimate) analysis results of the rCF and vCF before and after activation. Both precursor materials exhibited a high carbon content above 90%, in accordance with the IUPAC definition for CF. Additionally, a nitrogen content above 3% was observed for both CFs, typical of PAN-based CFs. Furthermore, rCFs possessed an oxygen content of almost double that of vCFs due to oxidation during recycling processes.

Post-activation there was a considerable reduction in carbon content to less than 80% which can be attributed to the burn-off of fixed carbon and expulsion of VOCs and other decomposition products during activation, which is in agreement with the EDS data.

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Additionally, the nitrogen content of both ACFs almost halved following the activation process due to the cleaving of C-N bonds at elevated temperatures. As anticipated, there is a significant increase in oxygen content after the activation, due to the application of alkali activation agents which introduce oxygen-containing groups such as lactone, carboxyl, phenol, lactol, pyrone, ketone and chromene groups (Figure 2.13), into the carbonaceous framework *via* overlapping redox reactions (Reactions 2.6 and 2.7).

Sample	C (%)	H (%)	N (%)	O (%)
rCF	93.87	0.28	4.07	1.78
vCF	95.32	0.43	3.32	0.93
K-ArCF-Opt	78.19	0.53	2.34	18.94
K-AvCF-Opt	78.20	0.53	1.88	19.39

Table 4.10: Elemental analysis of precursor and activated carbon fibres [34].

4.2.3.4. Proximate analysis

The amount of fixed carbon, VOCs, water and ash were quantified using proximate analysis (Table 4.11). Similarly to the above, a significant decrease in fixed carbon content was observed after activation. Moreover, there was a noteworthy increase in VOC, water and ash content. The rise in VOC content after activation is uncharacteristic for carbonaceous adsorbents, since VOCs are typically released during activation. However, the observed increase in VOC percentage may be inflated due to the considerable reduction in carbon content (due to decomposition), which consequently doubled the percentage of ash content. The ash content might have also risen due to the presence of intercalated potassium species used during activation as well as the corrosion of the aluminosilicate crucible discussed above. Finally, the increased water content was likely due to the adsorption of atmospheric moisture due to the increased hydrophilicity of the adsorbent surface after activation.

Table 4.11: Proximate analysis of rCF, vCF, ArCF and AvCF [34].

Sample	C (%)	VOC (%)	Water (%)	Ash (%)
--------	-------	---------	-----------	---------

rCF	93.21	2.84	0.00	3.95
vCF	92.80	4.82	0.00	2.38
ArCF	75.30	15.27	1.88	7.55
AvCF	73.66	13.67	4.70	7.97

4.2.3.5. Fourier-Transform Infrared Spectroscopy (FTIR)

Both precursors showed characteristic spectra of PAN-based CFs (Figure 4.15). The broad peaks at 3696 and 3650 cm⁻¹ were ascribed as O-H stretching vibrations due to the hygroscopic nature of KBr. The peak at 3580 cm⁻¹ was credited to N-H stretching vibrations [268]. The peaks arising in the range of 2947 – 2844 cm⁻¹ are characteristic of C-H bonds (CH, CH₂ and CH₃) [268]. Nitrile groups (C=N) within the PAN chain led to the peak at 2310 cm⁻¹ [268,269]. The presence of aromatic benzene rings give rise to the peak at 1532 cm⁻¹. Finally, the peaks at 1242 – 1191 cm⁻¹ are representative of C-N bending vibrations [270].



Figure 4.15: Infrared spectra of rCF (top) and vCF (bottom).

After activation, there were some noteworthy changes to the functional groups present (Figure 4.17). Specifically, the introduction of peaks in 1725, 1351 and 1223 cm⁻¹, which were associated with the introduction of C=O, O-H and C-O groups, respectively [269]. Furthermore, the absence of the C=N peak at 2310 cm⁻¹, suggesting the cleavage of bonds during the high temperature activation process.



Figure 4.16: Infrared spectra of K-ArCF-Opt and K-AvCF-Opt, taken from [34].

FTIR is a particularly valuable technique for detecting changes in chemical bonds following adsorption, offering insights into the formation of chemisorptive interactions during the process. In this study, significant alterations in the bonding environments of both ACF samples were observed after adsorption, further supporting the occurrence of chemisorption mechanisms (Figure 4.17). The peaks in the range of 3664 – 3380 cm⁻¹ are associated with O-H stretching vibrations [271]. The peak at 2913 cm⁻¹ corresponds to intramolecular stretching vibrations of C-H and N-H. Notably, a new peak was introduced at 2433 cm⁻¹, indicative of S-H stretching vibrations typical of thiols, suggesting that the sulphur group in MB may play a role in adsorption *via* interactions with oxygen-containing surface groups. As observed in non-activated samples, peaks at 1558 cm⁻¹, characteristic of aromatic benzene structures, are

present. Additionally, peaks at 1381 and 1236 cm⁻¹ are linked to O-H and N-H bending vibrations [271]. Peaks at 1000 – 989 cm⁻¹ correspond to C=C bending vibrations, while the peak at 773 cm⁻¹ represents the C-H bending vibration of monosubstituted benzene derivatives [235].



Figure 4.17: Infrared spectra of K-ArCF-Opt (top) and K-AvCF-Opt (bottom) after adsorption of MB, taken from [34].

4.2.3.6. Raman Spectroscopy

Raman spectroscopy is a powerful technique for analysing CAs due the ability to distinguish between ordered and disordered carbonaceous structures *via* the D and G bands, both of which are present in the Raman spectra for the precursor and activated samples, at approximately 1370 cm⁻¹ and 1590 cm⁻¹, respectively (Figure 4.18). The D band is an A_{1g} breathing mode symmetry, representative of disordered sp³ hybridised carbon bond stretching [272]. While the G band is of E_{2g} mode symmetry which is characteristic of the C-C in-plane stretch of sp² hybridised carbon, found in graphitic materials [272]. In addition to the D and G bands, both samples exhibit several other peaks. The peaks at around 815 and 905 cm⁻¹ were ascribed to the ring breathing of piperidine and C-N-C stretch of secondary amines, respectively [273]. While the sharp peak at 2350 cm⁻¹ was attributed to N=C=O pseudo-antisymmetric stretching [273].

For the activated samples, some additional peaks were present, with the most interesting being the D₄ band at 1246 cm⁻¹, which is characteristic of both A_{1g} symmetry and the presence of ionic impurities; a further indication of the intercalation of K⁺ into the CF structure [274]. Finally, the peaks at 1052, 1114, 1286 and 1552 cm⁻¹ were attributed to ortho-disubstituted benzene stretch, N=N stretch, NO₂ stretch and antisymmetric NO₂ stretch, respectively [273].



Figure 4.18: Raman spectra of rCF (top) and K-ArCF-Opt (bottom), taken from [34].

Interestingly, the peak intensity for the ACFs is significantly higher when compared to the precursor. An increase in intensity of the D band can be an indication of successful functionalisation, since there is a positive linear correlation between D band intensity and surface functionalisation, up to approximately 6 groups attached per 1000 carbon atoms, providing further evidence with regards to the oxidation of the ACFs [275,276]. This can be calculated by integrating the area of the peak.
4.3. Conclusion

This chapter investigated the chemical activation of rCFs using hydroxides. Preliminary investigations revealed that hydroxides were a promising activation agent for the production of CAs, however, the activation conditions were not harsh enough, hindering the development of the porous network and subsequently resulting in low MB adsorption capacities of 5.75 mg/g.

Based on the preliminary investigations the author then sought to optimise the activation procedure by employing BBD-RSM to evaluate the effects of various factors on the response variables, namely yield and MB adsorption capacity. The optimal conditions were determined to be an activation temperature of 670 °C, an IR of 1:10 and a hold time of 0.5 hours. All factors had a statistically significant effect on the yield, with activation temperature and IR having the most considerable impact. In contrast, for MB adsorption capacity, only the linear and squared effects of IR were statistically significant, with higher ratios being more advantageous due to increased surface etching and oxidation, enhancing the active site for adsorption.

K-ArCF-Opt achieved a maximum MB equilibrium adsorption capacity of 454.55 mg/g, surpassing the 344.83 mg/g capacity K-AvCF-Opt. This phenomenon was attributed to the reduced mechanical strength of the rCF precursor, allowing for more extensive surface etching to occur during activation, resulting in an increased surface area. Additionally, K-ArCF-Opt had a higher quantity of oxygen-containing groups, enhancing their adsorption capabilities.

The activation method developed in this study is notable for its simplicity and efficiency. Unlike more complex procedures reported in the literature, many of which involve multi-step treatments, extended soaking times, or corrosive chemical agents, this method relies on brief KOH impregnation (only 5 minutes) and a short activation time at moderate temperature (670 °C for 30 minutes). This minimalist yet highly effective approach reduces both thermal and chemical loads, making the process more sustainable, scalable, and industrially attractive.

However, further research is required to assess the commercial viability of rCFs as aqueousphase adsorbents. Moving forward studies should focus optimisation of the modification and adsorption processes to further enhance the adsorption capacity ArCFs toward the target antibiotics CIP and OTC as discussed in Chapters 5 and 6.

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5. Modification of Carbonaceous Adsorbents for Aqueous-phase Applications

5.1. Introduction

A number of studies have highlighted that the adsorption of CIP and OTC can be physical (i.e. physisorption) or chemical (i.e. chemisorption) in nature depending on the environmental conditions (i.e. pH, salinity etc.) [277]. Physisorption of antibiotics often occurs when antibiotics exist in their zwitterionic form and may arise due to Van der Waals forces or hydrogen bonding, although hydrophobic effects and π - π interactions are more commonly reported. Whereas chemisorption occurs when there are opposing charges between the adsorbent surface and antibiotics leading to interactive effects (i.e. ionic or covalent bonding). A number of studies have identified that oxygen-containing functionalities on adsorbent surfaces play a key role in the adsorption of antibiotics such as CIP and OTC, and therefore, developing adsorbents with these characteristics is promising [88,89].

Post-synthesis adsorbent modification is a promising technique to alter the surface functional groups, enhancing the selectivity toward target pollutants, subsequently improving the adsorption capacity. However, adsorbent modification presents some drawbacks such as reduced surface area due to pore blocking. Additionally, the characteristics of the adsorbent system must be considered prior to selection of the modification agents to prevent or limit repulsive interactions.

Acidic modification has commonly been employed to oxidise CA surfaces, with the most common acidic agents being HNO₃ and H₂SO₄ [41,137–139]. The former method is particularly attractive for aqueous phase applications, having been shown to enhance the oxygen-containing surface moieties and promote the formation of mesoporous structures [15]. Due to the aromatic nature of CAs, it is widely accepted that when functionalised, their chemical properties would be alike that of their aromatic hydrocarbon counterparts and subsequently have the ability to readily generate reactive acidic or basic surfaces due to the presence of delocalised electrons [132].

The focus of this chapter is to optimise the modification of recycled carbon fibre-based adsorbents with the aim to improve their adsorption capacity towards target antibiotics in this research, i.e. CIP and OTC. This was achieved *via* the initial screening of the process using a

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Taguchi orthogonal array design of experiments. Based upon the results, the procedure was then optimised using BBD-RSM.

5.2. Results and Discussion

5.2.1. Optimisation of Modification Process

5.2.1.1. Screening of Modification Process

Prior to optimisation, the modification process was screened using a randomised, three factor, three level, L^9 Taguchi orthogonal array matrix to investigate the impacts of HNO₃ concentration, hold time and temperature on the adsorption of antibiotics (CIP and OTC), as shown in Table 5.1.

Run	HN Concentr	HNO ₃ Hold Time (h) Temperature (°C) ntration (M)		q _{e,} CIP (mg/g)	q _{e,} OTC (mg/g)			
	X 1	Code	X2	Code	X ₃	Code	Уı	¥2
1	1	-1	1	-1	20	-1	9.80	4.55
2	1	-1	5.5	0	55	0	10.42	4.38
3	1	-1	10	+1	90	+1	8.94	5.09
4	5.5	0	1	-1	55	0	9.11	5.19
5	5.5	0	5.5	0	90	+1	9.33	4.40
6	5.5	0	10	+1	20	-1	10.69	8.36
7	10	+1	1	-1	90	+1	7.42	2.06
8	10	+1	5.5	0	20	-1	7.62	9.35
9	10	+1	10	+1	55	0	10.67	6.31

Table 5.1: Taguchi matrix with real and coded values of three factors studied, and responses yield and q_e of each run performed.

ANOVA was employed to assess the impact of the factors on the responses i.e. CIP and OTC adsorption capacity, achieving R² values of 89.26% and 94.32%, respectively (Table 5.2). These values are below the commonly sought-after threshold 95%; however, it is essential to realise the complexity of the system under study and the limitations of the Taguchi design in capturing all possible interactions and non-linear effects. Furthermore, the R²_{pred} was found to be zero indicating that the predictive performance of the regression model is poor.

Table 5.2: Regression coefficient and predicted regression coefficients of the refined modelfor the responses in this study, i.e. CIP and OTC adsorption capacity.

	R ²	R^2_{adj}	R^2_{pred}
q _e , CIP (mg/g)	89.26	57.03	0.00
q _e , OTC (mg/g)	94.32	77.26	0.00

Due to the low R² values, residual analysis was conducted to determine whether the data is normally distributed (Figure 5.1). Overall, the residual analysis suggested that the model provides a reasonable fit; however, there are some indications of non-linearity and nonnormality within the residuals. The deviations observed in the normal probability plot and the uniform distribution in the Histogram suggest that the model may benefit by investigating quadratic or interaction terms. Consequently, BBD-RSM was conducted to explore these additional terms and address potential non-linear effects, thereby, aiming to improve the robustness and accuracy of the model.



Figure 5.1: Residual analysis for model fit: (A) probability plot (Q-Q Plot) for normality, (B) residuals vs. fitted values plot, (C) histogram of residuals, (D) residuals vs. observation.

ANOVA was also employed to assess the statistical significance of the regression model and factors. In the case of CIP adsorption capacity, neither the model nor the factors were found to be statistically significant. Whereas, for OTC the regression model and the impacts of hold time and temperature were found to be statistically significant with p-values of 0.027, 0.042 and 0.015, respectively.

	q _{e,} CIP	(mg/g)	q _e , OTC (mg/g)			
Factors	F-value	p-value	F-value	p-value		
Regression	1.50	0.322	7.41	0.027		
HNO ₃ Concentration (M)	1.60	0.262	1.59	0.263		
Hold Time (h)	2.11	0.206	7.34	0.042		
Temperature (°C)	0.79	0.416	13.30	0.015		

Table 5.3: ANOVA results for the Taguchi screening modification campaign, for the responses CIP and OTC adsorption capacity.

The S/N ratio serves as an indicator of process robustness, measuring how resistant the model is to variations in input parameters. Since the objective of this experimental campaign was to maximise the adsorption capacity towards target antibiotics, the "larger is better" approach was selected for analysing the S/N ratios, as expressed in Equation 5.1.

$$\frac{S}{N} = -10 \cdot \log\left(\sum \left(\frac{1}{y^2}\right) / n\right)$$
 Equation 5.1

Where, *y* represents the response variable derived from a particular parameter-level combination, and *n* denotes the number of such responses for that specific parameter-level combination.



Figure 5.2: The S/N ratio for the evaluated L9 array when considering CIP (A) and OTC (B) adsorption capacity as the response.

Based on Figure 5.2, it is evident that all three factors exert a significant influence on the S/N ratio for OTC adsorption capacity, while their effects on CIP adsorption capacity are comparatively less pronounced, with HNO₃ concentration exhibiting the most notable impact. Increasing the hold time was found to have a strong positive effect on the adsorption capacity for both antibiotics. Moreover, the data suggest that the true maxima of the responses may occur at hold times beyond the upper limit of the design space explored in this study.

Differing trends are observed for the effects of HNO_3 and temperature on the S/N ratio of the responses. In the case of CIP adsorption capacity, low to moderate HNO_3 concentrations of 1 - 5.5 M are favoured. Above this, a notable decline in the S/N ratio occurs, likely due to over-oxidation inhibiting the interaction between CIP and the CA surface. In contrast the highest S/N ratio for OTC is observed at the centre point, suggesting that there is non-linearity within the design space. Finally, the figure indicates that OTC adsorption is favoured at lower temperatures, whereas the maximum S/N ratio for CIP is at the centre point, again indicating that there is non-linearity within the design space.

5.2.1.2. Optimisation of Modification Procedure via Box Behnken Design

Based upon the results of the Taguchi screening design, a three-factor BBD was undertaken to optimise the modification of ACFs in order to improve the adsorption of antibiotics. The set of experimental conditions assessed are shown in Table 5.4. In order to interpret the results without the influence of systematic errors, the sequence for the experimental work was randomised. Experimental data from Runs 1 to 12 were used to calculate the regression

coefficients, while Runs 13 to 15, which were replicates at the central point, served to evaluate experimental repeatability [263]. From the data, it can be observed that the highest adsorption capacities for CIP and OTC were achieved during Runs 9 and 11, respectively.

Table 5.4: BBD matrix with real and coded values of three factors studied, and responses, CIPand OTC adsorption capacity, of each run performed.

Run	HN Concentr	IO₃ ation (M)	Hold T	īme (h)	Temperature (°C)		q _{e,} CIP (mg/g)	q _{e,} OTC (mg/g)
	X 1	Code	X2	Code	X3	Code	¥1	¥2
1	1	-1	16	0	40	-1	6.17	4.89
2	6	+1	16	0	40	-1	6.88	4.02
3	1	-1	24	0	40	+1	6.05	3.25
4	6	+1	24	0	40	+1	6.69	4.19
5	1	-1	20	-1	20	0	5.93	3.69
6	6	+1	20	-1	20	0	6.20	3.95
7	1	-1	20	+1	60	0	6.36	4.63
8	6	+1	20	+1	60	0	6.62	4.28
9	3.5	0	16	-1	20	-1	15.12	2.28
10	3.5	0	24	-1	20	+1	4.68	3.66
11	3.5	0	16	+1	60	-1	7.73	5.39
12	3.5	0	24	+1	60	+1	9.04	3.33
13	3.5	0	20	0	40	0	5.95	3.10
14	3.5	0	20	0	40	0	6.28	4.11
15	3.5	0	20	0	40	0	6.87	3.81

The model was analysed using ANOVA to determine the statistically significant factors and/or interaction effects and their subsequent effect on the responses CIP and OTC adsorption capacity. Full statistical outputs, including insignificant terms, are provided in Appendix B, while the regression coefficients for the refined model are summarised in Table 5.5. The R² values for CIP and OTC adsorption capacity were found to be 83.86% and 87.70%, respectively, indicating good overall fit.

Notably the model for OTC demonstrated stronger predictive capability ($R^2_{pred} = 62.08\%$) than that for CIP ($R^2_{pred} = 19.11\%$). Nevertheless, both models were statistically significant (p < 0.01, Table 5.7), and key factors and interactions were found to influence adsorption performance. While these models are consistent with literature benchmarks for similar RSM studies and are suitable for identifying trends and guiding further experimentation [278], the low R^2_{adj} and particularly low R^2_{pred} for CIP (19.11%) suggest limited reliability for predictive purposes. Therefore, caution is advised when applying the CIP model for predicting new data points.

Table 5.5: Refined regression coefficient and adjusted and predicted regression coefficients for the responses in this study i.e. CIP and OTC adsorption capacity .

	R ²	R^2_{adj}	R ² _{pred}
q _e CIP (mg/g)	83.86	74.90	19.11
qe OTC (mg/g)	87.70	78.47	62.08

The statistical analysis revealed distinct patterns in the adsorption behaviour of CIP and OTC. Hold time demonstrated a significant linear effect on CIP adsorption (p = 0.022), while temperature emerged as the dominant linear factor influencing OTC adsorption (p = 0.004). Additionally, OTC adsorption exhibited significant quadratic effects with respect to hold time (p = 0.041). Additionally, the interaction between HNO₃ concentration and hold time significantly impacted OTC adsorption (p = 0.034). Most notably, the interaction between hold time and temperature proved to be a critical factor, strongly influencing the adsorption of both antibiotics with highly significant p-values (p < 0.0002, Table 5.7). The relative importance of these effects are illustrated through Pareto charts in Figure 5.3.

	Code	q _e , CIP (y ₁)		q _e , OTC (y ₂)	
Source	-	F-Value	P-Value	F-Value	P-Value
Model	-	7.32	0.006	9.51	0.003
Linear		3.73	0.072	7.00	0.013
HNO ₃	x ₁	0.13	0.730	0.00	0.983
Hold time	X2	7.61	0.022	4.59	0.064
Temp	X3	0.38	0.555	16.40	0.004
Square	-	4.81	0.034	5.90	0.041
HNO3*HNO3	X1 ²	4.55	0.065	-	-
Hold time*Hold time	x ₂ ²	5.10	0.054	5.90	0.041
Temp*Temp	X ₃ ²	3.98	0.081	-	-
2-Way Interaction	-	22.02	0.002	15.07	0.002
HNO ₃ *Hold time	X1X2	-	-	6.50	0.034
Hold time*Temp	X ₂ X ₃	22.02	0.002	23.65	0.001

Table 5.6: ANOVA results for the refined model of the chemical modification campaign, whenconsidering the responses CIP and OTC adsorption capacity.



Figure 5.3: Pareto charts showing the standardised effects of variables and interactions on (A) CIP and (B) OTC adsorption capacity.

The impacts of the hold time and temperature are shown in the 3D contour plots (Figure 5.4A and B). Interestingly, inverse trends are observed when considering the adsorption capacity of CIP and OTC. At low temperatures, lower hold times favour higher adsorption capacity toward CIP, whilst at higher temperatures, longer hold times are favoured. Whereas, to increase OTC adsorption capacities longer hold times are favoured at lower temperatures. Meanwhile the impact of hold time at higher temperatures is significantly more pronounced with lower hold times being favoured. This phenomenon could be attributed to the types of functional groups introduced at various temperatures and their subsequent interactions with CIP and OTC, as discussed in Section 5.2.1.3.

The effect of HNO₃ concentration and hold time on OTC adsorption capacity is depicted in Figure 5.4C. A non-linear trend is evident, where intermediate values of HNO₃ concentration and hold time result in the lowest adsorption capacity. In contrast, higher adsorption of OTC is observed at both low and high HNO₃ concentrations when combined with extended hold times. This curvature suggests a complex interaction between acid strength and exposure duration, potentially influencing the surface chemistry of the adsorbent and the types or density of oxygen-containing functional groups.

At low temperatures and hold times, the degree of oxidation would be significantly lower than when factors are set to their maximum values. The trends for the adsorption capacity of CIP suggest the adsorption process can be driven by both physisorption and chemisorption, since the adsorption capacity remains high at both the lowest and harshest conditions. Whereas the trends observed for OTC suggest the adsorption process is largely driven by chemisorption since a higher degree of oxidation is favoured. The decline in OTC adsorption capacity at the harshest conditions can be attributed to over-oxidation which results in pore blocking and subsequently reduced surface areas. Since OTC is a larger molecule than CIP it is more susceptible to pore size exclusion due to reduced pore sizes.

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Equation 5.2 represents the refined model for CIP adsorption. HNO₃ concentration has a negative linear and quadratic effect, while hold time shows a positive quadratic effect. Temperature has a mild positive impact, whilst the only significant interaction, between hold time and temperature, positively influences adsorption.

In contrast, Equation 5.3 shows that OTC adsorption is mainly influenced by a strong negative linear effect of HNO_3 concentration. Other terms, including interactions, have minimal effects, indicating that acid strength is the dominant factor in OTC uptake. Although model robustness improved following refinement, both models still exhibit limited predictive strength ($R^2_{pred} < 0.90$), indicating the need for further studies to enhance understanding of the system.

$$y_{1} = 6.367 - 1.179(x_{1}) - (x_{2}) + 1.179(x_{3}) - 1.391(x_{1})^{2}$$

$$+ 1.473 (x_{2})^{2} + 1.301(x_{3})^{2} + 2.940 (x_{2}x_{3})$$
Equation 5.2
$$y_{2} = 3.668 - 1.401(x_{1}) + 0.205(x_{2}) + 0.240(x_{3}) + 0.071(x_{1})^{2}$$

$$+ 0.045(x_{1}x_{2}) - 0.012(x_{2}x_{3})$$
Equation 5.3

5.2.1.3. Optimum Point Validation and Comparison with Activated Carbon Fibres

The model was validated using a combination of optimisation and experimental confirmation strategies. Initially, an equally weighted dual-response optimisation was conducted to maximise the adsorption capacities for both antibiotics, resulting in the optimised sample referred to as mrCF-Opt. To further verify the accuracy of the predictive model, individual optimisations were also carried out for CIP and OTC, yielding the samples C-mrCF-Opt and O-mrCF-Opt, respectively. The optimised synthesis conditions and corresponding adsorption capacities are presented in Table 5.7.

Among all tested configurations, the dual-response optimisation yielded the highest adsorption capacities for both antibiotics. Statistical analysis confirmed that the performance of mrCF-Opt was significantly superior to that of the individually optimised counterparts, C-mrCF-Opt (t = 2.76, p = 0.01) and O-mrCF-Opt (t = 4.01, p = 0.002). Based on these results, mrCF-Opt was selected for all subsequent analyses.

From a practical perspective, the synthesis of a single adsorbent with high performance across multiple contaminants is advantageous for large-scale or industrial applications. Therefore, the use of mrCF-Opt not only reflects the optimal balance of adsorption efficiency for CIP and OTC but also aligns with the overarching aim of developing a versatile and scalable adsorbent. Accordingly, mrCF-Opt was employed in all further characterisation and application-based studies presented throughout this thesis.

Following surface modification, the adsorption capacity for OTC increased by 20.75%, a difference that was found to be statistically significant when compared to K-ArCF-Opt (t = -2.83, p = 0.01), thereby confirming the beneficial effect of modification on OTC uptake. In contrast, a 6.79% decrease in adsorption capacity was observed for CIP; however, statistical analysis revealed that this difference was not significant (t = 0.80, p = 0.48). These findings suggest that, under the current experimental conditions, surface modification had no appreciable impact on the adsorption capacity of CIP.

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Nonetheless, the absence of statistical significance does not negate the potential value of surface modification, particularly given the complex and dynamic nature of aqueous-phase adsorption systems. Therefore, to more accurately assess the effect of HNO₃ treatment on CIP removal, further optimisation of the adsorption process is required, as discussed in detail in Chapter 6.

Sample	Optimum conditions		ons	q _e (CIP, mg/g)	q _e (OTC, mg/g)
	[HNO₃] (M)	Hold time (h)	Temp (°C)		
mrCF-Opt	10	16	28	9.633 ± 1.101	7.716 ± 1.180
mvCF-Opt	10	16	28	8.108 ± 1.447	6.597 ± 0.862
C-mrCF-Opt	3.73	16	20	7.632 ± 1.491	-
O-mrCF- Opt	1	16	60	-	6.184 ± 0.531
mrCF-Opt (Taguchi)	5.5	10	20	7.605 ± 1.296	6.782 ± 1.058
mvCF-Opt (Taguchi)	5.5	10	20	8.995 ± 1.242	6.836 ± 0.681
K-ArCF-Opt	-	-	-	10.013 ± 1.634	6.390 ± 0.792
K-AvCF-Opt	-	-	-	9.267 ± 1.609	5.910 ± 0.439

Table 5.7: Dual and independent response optimisation for the modification of K-ArCF-Opt, and the subsequent adsorption capacities toward CIP and OTC.

To better understand the efficiency of mrCF-Opt, its adsorption capacity was compared with values reported in the literature (Table 5.8). While some materials, such as m-ACs and m-CNTs, report higher q_{max} values, often exceeding 300 mg/g [176,180], these were typically obtained using much higher initial concentrations (up to 500 mg/L) and more intensive thermal or multistep treatments. In contrast, mrCF-Opt was prepared using a single-step nitric acid modification process (10 M HNO₃, 28 °C, 16 h), achieving competitive uptake capacities for both CIP

(9.63 mg/g) and OTC (7.72 mg/g), using an initial concentration of 2 mg/L. Although the method involves a strong acid, it avoids high-temperature treatment or multi-reagent systems, offering a more streamlined and potentially scalable route to produce efficient adsorbents for water treatment. However, for a true comparison with literature values, q_{max} must be determined through isotherm modelling, which is addressed in the following chapter.

Table 5.8: Comparison of modification methods and subsequent antibiotic adsorption capacities of optimised rCF samples and various CAs reported in the literature.

Sample	Modification Method	Pollutant	C ₀ (mg/L)	q _{e -} (mg/g)	Optimum pH	Ref
mrCF- Opt	10 M HNO₃, 16 h, 28 °C	CIP	2	9.633	-	This work
mvCF- Opt	10 M HNO₃, 16 h, 28 °C	CIP	2	8.108	-	This work
ArCF- Opt	10 M HNO₃, 16 h, 28 °C	CIP	2	10.013	-	This work
AvCF- Opt	10 M HNO₃, 16 h, 28 °C	CIP	2	9.267	-	This work
mrCF- Opt	10 M HNO₃, 16 h, 28 °C	ОТС	2	7.716	-	This work
mvCF- Opt	10 M HNO₃, 16 h, 28 °C	отс	2	6.597	-	This work
ArCF- Opt	10 M HNO₃, 16 h, 28 °C	отс	2	6.390	-	This work
AvCF- Opt	10 M HNO₃, 16 h, 28 °C	отс	2	5.910	-	This work
AC	0.8 g/g K ₂ CO ₃ , MW 540 W, 8 min	CIP		101.7	8.5	[178]
m-AC	N ₂ 100 ml/min, 900 °C, 1h	CIP	20	300	7	[176]
m-AC	5 M HNO ₃ , 3 h, 130 °C	CIP	20	200	7	[176]
CNTs	N ₂ 100 ml/min, 350 °C, 1h	CIP	20	150	7	[176]
m-CNT	7 M HNO ₃ , 3 h, 130 °C	CIP	20	150	7	[176]

Sample	Modification Method	Pollutant	C₀ (mg/L)	q _{e -} (mg/g)	Optimum pH	Ref
m-AC	0.3 M H ₃ PO ₄ , 3 h, 250 °C	CIP	50	49.75	8	[172]
AC	NaOH (3:1), 4 h, 130 °C	ТС	500	369.4	3	[180]
m-AC	30% H ₂ O ₂ , 24 h, 25 °C	ТС	500	42.45	9	[181]
ACF	MW, 600 °C, 0.25 h	OTC		249.00	2	[182]
AC	85% H ₃ PO ₄ , 4 h, 150 °C	OTC	10	17.99	9	[183]

5.2.2. Material Characterisation

This section will discuss the physicochemical characteristics of mCF-Opt and the antibiotic laden samples. Additionally, comparisons will be undertaken between the precursor, ACF-Opt, mrCF-Opt and the antibiotic laden materials.

5.2.2.1. Surface Analysis

5.2.2.1.1. Physical Surface Analysis

The S_{BET} , pore volume and pore size were measured and calculated for both mrCF-Opt and mvCF-Opt (Table 5.9). To determine the statistical relevance of the observed differences, t-tests were conducted. A comparison between the activated and modified samples revealed a statistically significant difference in surface area, (t = 5.63, P = 0.004), confirming the enhanced porosity of the recycled sample.

Although a slight reduction in S_{BET} and pore volume was observed for mvCF-Opt, compared to its activated counterpart, this difference was not statistically significant (t = 0.68, P = 0.55). These marginal changes are likely attributable to pore-blocking effects introduced by newly formed surface functional groups—a well-documented phenomenon in surface chemistry.

Interestingly mrCF-Opt exhibited a notable increase in both S_{BET} and V_{micro} relative to K-ArCF-Opt, which was statistically validated (t = -3.55, P = 0.02). While such enhancement post-modification is less frequently reported, similar outcomes have been documented in the literature and are typically attributed to the leaching of impurities and intercalated K⁺ ions through a combination of synergistic mechanisms [41,140]. For instance, NO₃⁻ ions can react with K⁺ to form soluble KNO₃ (Reaction 5.3), while HNO₃ can dissolve metal oxides or

hydroxides (e.g., Al, Ca, Fe) via acid-metal reactions (Reaction 5.2). These resulting salts are often removed during the post-treatment washing process. Additionally, HNO₃ is known to etch the carbon matrix and remove residual tar that clogs pores, further contributing to an increase in accessible surface area.

$$K^+_{(aq)} + NO_3^-_{(aq)} \leftrightarrow KNO_3$$
 Reaction 5.1

$$M_2O_3 + 6HNO_3 \leftrightarrow 2M(NO_3)_3 + 3H_2O$$
 Reaction 5.2

Sample	S _{BET} (m²/g)	V _{micro} (cm ³ /g)	V _{total} (cm³/g)	Pore size (nm)
mrCF-Opt	448.10 ± 16.24	0.19	0.36	3.07
mvCF-Opt	410.69 ± 7.83	0.03	0.31	3.39
K-ArCF-Opt	427.63 ± 15.12	0.02	0.35	4.08
K-AvCF-Opt	414.88 ± 6.30	0.04	0.33	4.20

Table 5.9: Textural properties of mrCF-Opt and mvCF-Opt based upon the N₂ adsorption isotherms.

Figure 5.5 shows the S_{BET} physisorption isotherms for mrCF-Opt and mvCF-Opt. Similarly to the K-ACFs, both mCFs exhibit IUPAC's Type IV isotherms which are typical of mesoporous materials. The monolayer adsorption is indicated by the initial steep increase in the quantity of N₂ adsorbed at low relative pressures up to 0.05 - 0.3, since in this range the adsorbent surface has not reached saturation, so adsorption is mostly governed by surface interactions. Whereas multilayer adsorption is indicated by the gradual rise in N₂ adsorption at higher relative pressures (0.3 - 0.95), where the monolayer is fully formed, and adsorption occurs due to intermolecular forces between adsorbed molecules. The sudden steep rise on the adsorption isotherm at relative pressures > 0.95 is driven by capillary condensation within meso-and macropores.

mvCF-Opt displays H4 hysteresis, similar to its AvCF-Opt counterpart, which is representative of mesoporous materials with narrow slit pores (Figure 4.10). Intriguingly, mrCF-Opt now

displays H1 hysteresis, suggesting changes in the pore structure from narrow slit pores to cylindrical pore channels. This could be attributed to etching and restructuring of the carbon surface by nitric acid, resulting in the formation of new pores and the conversion of narrow slit pores to cylindrical channels.



Figure 5.5: BET physisorption isotherm of (A) mrCF-Opt and (B) mvCF-Opt.

Figure 5.6A and B depict the BJH data for for the activated and modified samples, respectively. Both modifed samples display a similar pore size distribution to their activated counterparts (Figure 4.11) showing that a significant portion of the cumulative pore volume is concentrated in the smaller mesopore and micropore range, specifically between 1.8 and 5.7 nm.

However, subtle differences are evident, for example mrCF-Opt displays a narrower, more intense peak centred near 3.1 nm, compared to the broader distribution of K-ArCF-Opt peaking closer to 4.1 nm. This shift suggests acid modification promoted pore refinement through the removal of ash or residual inorganics. Similarly, mvCF-Opt exhibits a slightly narrower and more sharply defined distribution than K-AvCF-Opt, with a lower total pore volume and less pronounced tailing into the macropore region.

These observations suggest that acid modification primarily alters surface chemistry and partially refines pore geometry, particularly for rCF-based adsorbents, without fundamentally disrupting the mesoporous framework. The enhancement in microporosity for mrCF-Opt, reflected by the sharper peak and higher intensity at lower diameters, also corresponds with the increase in V_{micro} reported in Table 5.9.



Figure 5.6: BJH Pore size distribution plot of mrCF-Opt and mvCF-Opt.

5.2.2.1.2. Chemical Surface Analysis

Boehm titrations were applied to determine the total acidity and basicity of the samples using the method described in Chapter 3. mrCF-Opt samples were found to possess substantially higher levels of all oxygen-containing surface groups, except phenols, when compared to mvCF-Opt, this is particularly apparent for lactone and basic groups (Table 5.10).

Sample	Quanti	pH _{PZC}			
	Carboxyl	Phenol	Lactone	Basic	-
mrCF-Opt	2.69	0.24	2.04	2.31	3.25
mvCF-Opt	2.61	0.27	0.14	0.33	3.17

At present there is a lack of understanding around the mechanisms for the oxidation of CA surfaces using HNO₃. However, the reactions of CA surfaces have often been likened to those of benzene derivatives. Therefore, likely reactions that could occur are the nitration of phenols (Reaction 5.3 and 5.4), the esterification of benzoic acid (Reaction 5.5), the hydrolysis of quinones (Reaction 5.6), oxidation of polyaromatic hydrocarbons (Reaction 5.7) or the oxidation of aniline (Reaction 5.8), all of which result in significant oxidation of the carbon

surface. The surface modification reactions depicted in Reactions 5.3–5.8 involve the use of concentrated and dilute nitric acid and acidic alcohols, all of which present significant hazards including strong oxidising potential, corrosivity, and the risk of exothermic reactions, necessitating careful control of reaction conditions and appropriate safety measures.



The pH_{PZC} mrCF-Opt was also determined potentiometrically. Post-modification, the pH_{PZC} was found to be 3.25, this is slightly below the value of 3.95 observed for K-ArCF-Opt, which can be

attributed to the enhanced acidity of the modified sample due to the significant increase in lactone groups.

5.2.2.2. SEM-EDS

SEM images of the mCF samples are presented in Figure 5.7. Similarly to the ACFs in Chapter 4 (Figure 4.13), at low magnification the mCFs display a smooth fibrous form with some surface defects and striations (Figure 5.7A and B). However, when increasing the magnification to 150,000x, some post-modification morphological differences can be observed (Figure 5.7C and D). mrCF presents a heterogenous surface consisting of cylindrical meso- and macropores which supports the H1 hysteresis displayed in Figure 5.5A. Contrastingly, mvCF-opt exhibits a flaky surface with narrow pore structures, consistent with the H4 hysteresis presented in Figure 5.5B.



Figure 5.7: SEM imaging of mrCF-Opt (A), mvCF-Opt (C) at 20,000x magnification and mCF-Opt (B), mvCF-Opt (D) at 150,000x magnification.

The EDS results are shown in Figure 5.8. Due to equipment failures a different electron microscope was used for EDS analysis. Therefore, new spectra were acquired for K-ArCF-Opt

for comparative purposes. Post-modification, a decline in carbon, potassium, chlorine, and other species was observed, whilst an increase in oxygen and nitrogen content was observed, although these effects are more pronounced for mrCF when compared to mvCF. The decrease in metal ions and chlorine confirms the suggestion that impurities were leached from the CA structure during chemical modification, resulting in the increased surface areas. Furthermore, the increased oxygen and nitrogen content suggest successful oxidation and/or nitration of the surface.



Figure 5.8: EDS spectra of K-ArCF-Opt (A), mrCF-Opt (B) and mvCF-Opt (C).

5.2.2.3. Elemental Analysis

The elemental analysis of mrCF-Opt and mvCF-Opt is shown in Table 5.11. Interestingly both samples show an increase in carbon content and a corresponding decrease in oxygen content relative to their activated counterparts. This apparent trend can be attributed to changes in mass proportion rather than an absolute loss of oxygen functionalities. During modification, some oxygen-containing moieties may decompose or be replaced by more stable carbon-rich structures, which could increase the relative percentage of carbon. However, this does not necessarily indicate a reduction in surface oxygen functionality. It is important to note that elemental analysis is a bulk technique, whereas methods such as Boehm titration and EDS specifically probe surface chemistry. The higher surface acidity observed by those methods confirms the successful introduction of oxygen-containing functional groups, despite the relative decrease in oxygen observed in the bulk composition.

Sample	C (%)	Н (%)	N (%)	O (%)
mrCF-Opt	81.56	0.97	2.47	15.00
mvCF-Opt	81.39	0.28	2.92	15.41
K-ArCF-Opt	78.19	0.53	2.34	18.94
K-AvCF-Opt	78.20	0.53	1.88	19.39

Table 5.11: Elemental analysis of precursor and activated carbon fibres.

5.2.2.4. Proximate Analysis

The amount of fixed carbon, volatile organic compounds (VOCs), water and ash were quantified using proximate analysis (Table 5.12). After modification, an increase in carbon and water content was observed for both samples, although this was more pronounced for mvCF-Opt, whilst a decrease in VOC and ash content was observed. The increased carbon content may be inflated (in percentage terms) due to the considerable reduction in ash and VOC content postmodification. The reduction in ash content can be attributed to the leaching of ash-based impurities during the modification process, whilst VOCs are removed from the structure *via* oxidation processes. Finally, the increased water content was likely due to the enhanced adsorption of atmospheric moisture due to the increased hydrophilicity of the material, as confirmed by the Bohem titrations.

Sample	C (%)	VOC (%)	Water (%)	Ash (%)
mrCF-Opt	81.62	10.67	4.17	3.54
mvCF-Opt	78.57	10.49	7.03	3.88
K-ArCF-Opt	75.30	15.27	1.88	7.55
K-AvCF-Opt	73.66	13.67	4.70	7.97

Table 5.12: Proximate analysis of mrCF-Opt and mvCF-Opt.

5.2.2.5. Fourier-Transform Infrared Spectroscopy (FTIR)

Both mCFs showed similar peaks which are representative of HNO_3 modified CFs (Figure 5.9). The spectra show some similarities to the precursor materials and ACF samples discussed in Chapter 4 (Figure 4.15 Figure 4.16), such as the peaks present at 2919 and 2841 cm⁻¹ which can be attributed to the aliphatic stretching vibrations of C-H bonds (CH, CH₂ and CH₃) [268]. Furthermore, the characteristic C=C stretching vibrations of benzene and the broad O-H stretching peaks remain present at 1532 cm⁻¹ and 3200 – 3600 cm⁻¹, respectively [268,269].

However, some new peaks have also been introduced, such as the peaks at 1113 and 1207 cm⁻¹, which are representative of the C-O stretching vibrations carboxylic acids and phenols [279]. The peak at 1384 cm⁻¹ can be attributed to NO₂ symmetric stretching vibrations indicating the introduction of nitro groups during HNO₃ modification. Finally, the peak at 3117 cm⁻¹ can be attributed to the C-H stretching vibrations, characteristic of aromatic structures [279].



Figure 5.9: Infrared spectra of mrCF-Opt (top) and mvCF-Opt (bottom).

5.2.2.6. Raman Spectroscopy

Raman spectroscopy is a powerful tool for characterising CAs due to its ability to distinguish between ordered and disordered carbon structures, as discussed in Chapter 4. Similarly to the precursor and activated samples, the mrCF-Opt sample exhibits characteristic D and G bands at approximately 1370 cm⁻¹ and 1560 cm⁻¹, respectively (Figure 5.10) [272]. Notably, the G band in mrCF-Opt is slightly shifted to a lower wavenumber, with an increased D/G intensity ratio indicating a higher degree of structural disorder, consistent with the increase in oxygen-containing functional groups such as carbonyl and carboxyl groups. This supports previous reports showing a positive correlation between D band intensity and surface functionalisation up to approximately six groups per 1000 carbon atoms [275,276,280,281].

In contrast to the precursor and K-ArCF-Opt samples, mrCF-Opt also displays a distinct D' band with a prominent shoulder, typically associated with amorphous or highly disordered carbon structures. This feature further supports the conclusion of extensive surface oxidation, which disrupts the graphitic lattice. Broad peaks observed between 700 and 1100 cm⁻¹ are attributed

to vibrational modes of oxygen-containing functionalities such as C–O, C=O, and C–O–C. Additionally, peaks around 815 and 905 cm⁻¹ correspond to the ring breathing of piperidine and the C–N–C stretch of secondary amines, respectively. The sharp band near 2350 cm⁻¹ remains visible, attributed to N=C=O pseudo-antisymmetric stretching.

Although these features confirm extensive functionalisation, the overall Raman signal intensity for mrCF-Opt appears lower than that of the precursor and activated samples. This may result from increased surface disorder, reduced π -conjugation, or non-resonant scattering effects caused by extensive oxidation, all of which diminish Raman signal enhancement [275,276,280,281].



Figure 5.10: Raman spectra of rCF (top), K-ArCF-Opt (middle) and mrCF-Opt (bottom).

5.3. Conclusion

This chapter investigated the HNO₃ surface modification of ACFs by employing screening and optimisation processes. The Taguchi screening design yielded low R^2 factors (<90%) and lack of significant factors for the adsorption of CIP suggesting that non-linear relationships may exist between factors, suggesting a more complex design such as RSM design may be more appropriate to model the system effectively.

Based on the outcomes of the Taguchi screening design, BBD-RSM was subsequently applied to further investigate and optimise the surface modification process, evaluating the influence of various factors on CIP and OTC adsorption capacities. The optimal conditions identified were a HNO₃ concentration of 10 M, a hold time of 16 hours, and a temperature of 28 °C. However, due to relatively low model strength, with R² values below 90%, additional studies are recommended to achieve more robust optimisation of the modification process.

Under optimum conditions, a 21% increase in adsorption capacity was observed for OTC achieving a maximum adsorption capacity of 7.71 mg/L. This increase was statistically significant compared to the unmodified K-ArCF-Opt (t = -2.83, p = 0.01), confirming the positive effect of surface modification on OTC uptake. However, a 7% decrease in adsorption capacity toward CIP was observed achieving an equilibrium adsorption capacity of 9.63 mg/g. However, this difference was not statistically significant (t = 0.80, p = 0.48), indicating that modification had no appreciable effect on CIP adsorption under the tested conditions. Despite this, aqueous phase adsorption systems are complex, and therefore, to determine whether adsorbent modification is beneficial for the adsorption of CIP, the adsorption system must be studied and optimised, as discussed in the following chapter.

Additionally, statistical comparison of optimised samples demonstrated that dual-response optimisation yielded the highest overall performance, with mrCF-Opt significantly outperforming individually optimised samples C-mrCF-Opt (t = 2.76, p = 0.01) and O-mrCF-Opt (t = 4.01, p = 0.002). Accordingly, mrCF-Opt was selected for all subsequent material characterisation and application-based studies in this thesis.

After modification both mCF-Opt exhibited an increase in oxygen and nitrogen functionalities, suggesting successful oxidation of the CA surface. Notably an increase in surface area was observed for mrCF-Opt, post-modification, which was attributed to the leaching of impurities and tar during the modification process.

Further research is required to assess the commercial viability of rCF-based adsorbents for aqueous-phase applications. Moving forward studies should focus optimisation adsorption processes to further enhance the adsorption capacity of mrCF-Opt toward the target antibiotics CIP and OTC as discussed in Chapters 6.

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6. Single-Component Adsorption of Antibiotics onto Carbonaceous Adsorbents

6.1. Introduction

Aqueous phase adsorption systems are complex, involving a range of physical and chemical interactions such as Van der Waals forces or hydrogen bonding, hydrophobic effects, π - π interactions, electrostatic interactions and more [88,277,282,283]. In the previous chapter, it was noted that oxygen-containing functionalities play a key role in the adsorption of CIP and OTC; however, this is highly dependent on the environmental conditions (i.e. temperature, pH and concentration) which have a great influence on the speciation (i.e. overall charge) of the antibiotics and adsorbent surface, subsequently impacting the adsorption mechanisms.

At present the mechanisms governing antibiotic adsorption are not well understood and many past studies have employed an OFAT approach to investigate the impacts of pH, temperature, adsorbent dose and initial concentration [173,176,179,284]. This approach has led to a significant lack of understanding around the adsorption system, particularly regarding the interaction effects between the factors.

The focus of this chapter was to optimise the adsorption process of mrCF-Opt with the aim to enhance their adsorption capacity toward target antibiotics, CIP and OTC, whilst gaining valuable insights into the adsorption mechanisms. This was achieved by employing BBD-RSM to investigate the effects of several factors, namely, adsorbent dose, pH and initial antibiotic concentration on the responses: CIP and OTC removal percentage (or adsorption capacity). The optimum conditions were then applied to investigate the adsorption isotherms and kinetics to determine the maximum adsorption capacity and better understand the adsorption behaviour.

6.2. Results and Discussion

6.2.1. Optimisation of Antibiotic Adsorption Process

In this work, a three-factor BBD was applied to investigate and optimise the adsorption of CIP and OTC by investigating the effects of adsorbent dose, pH and antibiotic concentration. The set of experimental conditions assayed are presented in Table 4.3. Similarly to Chapters 4 and 5, the experimental campaign was randomised to minimise the influence of systematic errors. Data from experiments 1 to 12 were used to calculate the regression coefficients, while experiments 13 to 15, were replicates at the central point, which were utilised to evaluate

experimental repeatability [263]. This approach allows for efficient evaluation of multiple variables while ensuring the reliability of the results. All experiments were conducted in triplicate, with mean values used for optimisation. The minimal time investment required for repeated measurements allowed for improved statistical reliability through increased data points.

Analysis of the data presented in Table 6.1 reveals distinct optimal conditions for different performance metrics. For CIP, maximum removal efficiency was achieved in Run 11, while Run 2 yielded the highest removal for OTC. Peak adsorption capacities were observed in Run 1 for CIP and Run 3 for OTC. However, the response surface analysis (Figure 6.2 and Figure 6.3) suggests that true optimal conditions may lie outside the investigated design space, as no clear maxima were identified.

The divergence in optimal conditions can be explained by the underlying adsorption mechanisms. Runs 11 and 2, characterised by high adsorbent dosages and initial concentrations, favoured enhanced removal efficiency. Conversely, the lower adsorbent dosages in Runs 1 and 3 promoted higher adsorbent saturation, resulting in superior adsorption capacities. These relationships are explored in detail in subsequent sections.

Table 6.1. BBD matrix with real and coded values of three factors studied, and responses yield and q_e of each run performed.

Dum	Adsobent dose				Antibiotic		Removal (%)		q _e (mg/L)	
KUN	(g	/L)		рп	(mg/L)		CIP	отс	CIP	отс
	X 1	Code	X2	Code	X ₃	code	y 1	y 2	Уз	Y 4
1	0.1	-1	2	0	1.25	-1	70.43	59.17	19.83	9.12
2	0.9	+1	2	0	1.25	-1	97.97	99.99	2.42	1.49
3	0.5	-1	8	0	1.25	+1	55.83	44.74	20.38	10.33
4	0.5	+1	8	0	1.25	+1	48.02	81.58	2.24	0.89
5	0.5	-1	5	-1	0.50	0	33.45	78.57	21.04	7.40

Duna	Adsobent dose				Antibiotic		Removal (%)		q _e (mg/L)	
KUN	(g,	/L)		рн (mg		/L)	CIP OTC		CIP	отс
	X 1	Code	X 2	Code	X ₃	code	y 1	¥2	Уз	y 4
6	0.5	+1	5	-1	0.50	0	36.29	83.33	2.34	0.28
7	0.5	-1	5	+1	2.00	0	61.02	28.57	18.96	9.40
8	0.5	+1	5	+1	2.00	0	77.24	92.86	2.19	0.39
9	0.5	0	2	-1	0.50	-1	83.15	100	4.42	1.12
10	0.1	0	8	-1	0.50	+1	45.49	84.21	4.10	0.56
11	0.9	0	2	+1	2.00	-1	98.73	91.19	4.13	2.67
12	0.5	0	8	+1	2.00	+1	93.48	76.32	4.05	4.14
13	0.5	0	5	0	1.25	0	72.24	69.05	3.89	0.40
14	0.5	0	5	0	1.25	0	54.02	52.38	3.93	1.78
15	0.5	0	5	0	1.25	0	61.31	21.43	3.73	2.74

6.2.1.1. Optimisation When Considering Removal Percentage as the Response Variables

The RSM model was statistically analysed using ANOVA to determine the statistically significant factors and/or interaction effects and their subsequent effect on the responses removal percentage of CIP (y_1) and OTC (y_2). Initial analysis revealed R² values of 96.36% and 88.18% for CIP and OTC adsorption capacity, respectively (Appendix C). Following model refinement through the removal of insignificant terms, the R² value for CIP adsorption remained constant at 96.36%, while a slight decrease was observed for OTC adsorption (86.71%, Table 6.2). The high R² value for CIP adsorption exceeds the threshold for statistical significance, indicating strong model fit to the experimental data.

Importantly, model refinement led to substantial improvements in both the adjusted and predicted R² values. The R²_{adj} values increased from 89.80% to 91.41% for CIP adsorption and from 66.91% to 76.75% for OTC adsorption. Similarly, the R²_{pred} values showed marked improvement, increasing from 78.35% to 84.86% for CIP and from 65.62% to 72.03% for OTC. These improvements suggest reduced model overfitting and enhanced predictive capability for both systems.

Although model refinement improved the overall statistical parameters, the R² values for OTC removal remained below the threshold for statistical significance, with R²_{adj} and R²_{pred} values under 80%. This relatively weaker model fit can be attributed to the inherent complexity of OTC adsorption, as OTC is a larger molecule than CIP with multiple functional groups and exists in various ionised forms (Figure 6.1). However, it should be noted that other RSM optimisation studies have reported similar R² values and deemed them acceptable [278]. To further enhance model robustness and develop more comprehensive insights into the system behaviour, additional optimisation iterations exploring an expanded design space would be beneficial.

Table 6.2: Refined re	egression coefficie	ent, and adjus	ted and predict	ed regression	coefficients

	R ²	R^2_{adj}	R ² pred
Removal (%), CIP (mg/g)	96.36	91.41	84.86
Removal (%), OTC (mg/g)	86.71	76.75	72.03

for the responses CIP and OTC removal percentage.

Both the linear and quadratic models were found to be statistically significant for the removal % of both antibiotics, achieving p-values below 0.01 (Table 6.3). For CIP removal, multiple factors showed statistical significance including the independent effects of pH (p = 0.001) and initial concentration (p < 0.001), quadratic effects of pH (p = 0.002) and adsorbent dose (p = 0.012), as well as interaction effects between adsorbent dose and pH (p = 0.030) and between pH and initial concentration (p = 0.040). While the OTC removal process revealed fewer significant parameters, specifically the independent effects of adsorbent dose (p = 0.003) and pH (p = 0.042), along with their respective quadratic effects (pH: p = 0.009; adsorbent dose: p = 0.018).

Table 6.3: ANOVA results for the refined model of the adsorption campaign when considering removal percentage as the responses.

Source	Code	Removal	Removal %, CIP (y ₁)		%, OTC (y₂)	
Source		F-Value	P-Value	F-Value	P-Value	
Model	-	19.61	0.001	8.70	0.004	
Linear	-	32.82	0.000	9.25	0.006	
Adsorbent dose	X1	4.86	0.070	18.09	0.003	
рН	X2	37.29	0.001	5.87	0.042	
Initial Conc.	X ₃	56.32	0.000	3.80	0.087	
Square	-	21.22	0.002	9.66	0.007	
Adsorbent dose*	X1 ²	12.47	0.012	_	_	
Adsorbent dose	×1					
рН*рН	x ₂ ²	27.12	0.002	11.91	0.009	
Initial Conc.*	X3 ²	_	_	8.77	0.018	
Initial Conc.	5					
2-Way Interaction	-	5.33	0.040	5.14	0.053	
Adsorbent dose*pH	x ₁ x ₂	8.07	0.030	-	-	
Adsorbent dose*Initial Conc.	x ₁ x ₃	1.16	0.324	5.14	0.053	
pH*Initial Conc.	X ₂ X ₃	6.78	0.040	_	_	



Figure 6.1: Chemical structure of CIP (A) and OTC (B), and speciation diagrams for CIP (C) and OTC (D).

The impacts of the factors are evident from the 3D contour plots in Figure 6.2. Generally, it can be observed that increasing adsorbent dose and initial concentration results in improved removal percentage of both antibiotics, although this effect is significantly more pronounced for CIP. The improved removal of antibiotics at high dosage and concentrations can be attributed to the higher availability of surface area and active sites combined with the enhanced diffusion and mass transfer of pollutants into the porous network at higher concentrations.

Whereas the impacts of pH can be explained by the speciation of CIP and OTC (Figure 6.1). At pH 2 and 5, CIP predominantly exists in its cationic form, whereas at pH 8 the primary species is the zwitterionic form, where the lowest removal percentages are observed, which may suggest that the adsorption process is driven by electrostatic interactions. A similar trend was observed for OTC where the lowest removal percentages were observed at pH where the predominant OTC species is zwitterionic. This pH-dependent behaviour aligns with previous studies where it has been demonstrated that electrostatic interactions between the adsorbent surface and antibiotic species play a crucial role in the adsorption mechanism [173,174,176].



Figure 6.2: 3D response surface plots for combined effects of adsorbent dose and pH (A, D), adsorbent dose and initial concentration, (B, E) and pH and initial concentration (C, F), on the responses CIP (A – C) and OTC (D – F) removal percentage.

Both equations indicate significant linear, quadratic and interaction effects, demonstrated by the large coefficients. The removal of insignificant terms has clarified the dominant factors influencing each response, enhancing the interpretability and reliability of the models. In the case of y_1 , strong linear effects from x_1 and x_2 , as well as a substantial quadratic effect from $(x_1)^2$, remain evident. Similarly, for y_2 , significant contributions arise from linear effects of x_2 and x_3 , along with pronounced quadratic effects from $(x_2)^2$ and $(x_3)^2$.

Of particular interest are the retained interaction terms, specifically x_1x_3 , which exhibits contrasting influences across the two models, exerting a positive effect on y_2 , while
contributing negatively to y_1 . This divergence suggests a potential conflict between the optimisation of the two responses, where improving one outcome may adversely affect the other. As such, these findings underscore the necessity for a multi-objective optimisation strategy that accounts for trade-offs between competing responses.

$$y_{1} = 91.8 + 106.30(x_{1}) - 23.98(x_{2}) - 1.56(x_{3}) - 71.30(x_{1})^{2}$$

$$+ 1.87 (x_{2})^{2} - 7.36(x_{1}x_{2}) + 11.10(x_{1}x_{3}) + 3.60 (x_{2}x_{3})$$

$$y_{2} = 210.8 - 12.70(x_{1}) - 29.87(x_{2}) - 126.05(x_{3}) + 2.61 (x_{2})^{2}$$

$$+ 35.9(x_{3})^{2} + 49.6(x_{1}x_{3})$$

Equation 6.2

6.2.1.2. Optimisation When Considering qe as the Response Variable

Alike above, ANOVA was employed to statistically analyse the model, this time considering adsorption capacity of both antibiotics as the responses. Significant improvements in R² values were observed for both antibiotics although the improvement was more pronounced for OTC (Table 6.4). Both models exhibited high R² values, above 95%, and this level of significance was maintained for the adjusted and predicted R² values when considering the adsorption capacity of CIP, indicating a highly robust model at predicting responses for new observations. Although marginal decreases were observed in the adjusted and predicted R² values and predicted R² values for OTC adsorption capacity, their retention above 90% reinforced the model's statistical robustness and predictive reliability.

	R ²	R^2_{adj}	R^{2}_{pred}
q _e , CIP (mg/g)	99.89	99.83	99.61
q _e , OTC (mg/g)	96.22	94.12	90.18

Table 6.4: Refined regression coefficient and adjusted and predicted regression coefficientsfor the responses CIP and OTC adsorption capacity.

Table 6.5 presents the ANOVA analysis when considering q_e as the response. Interestingly, the set of statistically significant factors differed from those identified when removal percentage was used, with fewer variables found to have a significant impact. The model, and linear and

quadratic effects found to be statistically significant for the adsorption capacity of both antibiotics. Adsorbent dose was found to be particularly impactful with the independent and quadratic effects being statistically significant for CIP and OTC. Finally, the interaction effects between and adsorbent dose and initial concentration were statistically significant for the adsorption capacity towards CIP, whilst the interactions between pH and initial concentration were statistically significant for OTC adsorption capacity.

The response surface plots (Figure 6.3) illustrate the effects of the three factors on the responses. The dramatic impact of adsorbent dose can be observed in Figure 6.3A, B, D and E, where a significant improvement is observed when adsorbent dose is set to the minimum value. At low adsorbent dose, there is limited accessible surface area and availability of active sites, combined with increased competition for adsorption sites, resulting in increased adsorbent saturation and subsequently enhanced adsorption capacity. Consequently, the system achieves greater efficiency in adsorption at reduced adsorbent doses.

The impact of pH is less pronounced when considering adsorption capacity as the response. However, similarly to the previous section the lowest adsorption capacities are observed when the antibiotics exist predominantly in their zwitterionic form, further supporting the idea that the adsorption process is driven by chemisorption and electrostatic interactions.

Table 6.5: ANOVA results for the refined model of the adsorption campaign when considering q_e as the responses.

Sourco	Codo	q _e , Cl	Р (уз)	q _e , OTC (y ₄)		
Source	Code	F-Value	P-Value	F-Value	P-Value	
Model	-	844.72	0.000	25.40	0.001	
Linear	-	1944.33	0.000	60.01	0.000	
Adsorbent dose	X1	5825.31	0.000	171.51	0.000	
рН	X2	0.00	0.973	0.36	0.576	
Initial Concentration	X3	7.68	0.039	8.16	0.036	
Square	-	586.48	0.000	15.06	0.006	

Source	Codo	q _e , Cl	Р (уз)	q _e , OTC (y ₄)		
Source	Coue	F-Value	P-Value	F-Value	P-Value	
Adsorbent dose* Adsorbent dose	X1 ²	1749.63	0.000	42.23	0.001	
рН*рН	x ₂ ²	1.42	0.287	2.82	0.154	
Initial Conc.* Initial Conc.	X ₃ ²	0.49	0.513	0.42	0.544	
2-Way Interaction	-	3.34	0.114	1.13	0.420	
Adsorbent dose* pH	X ₁ X ₂	1.26	0.313	1.02	0.358	
Adsorbent dose* Initial Conc.	X1X3	8.61	0.032	1.10	0.342	
pH*Initial Conc.	X ₂ X ₃	0.14	0.719	16.44	0.010	



Figure 6.3: 3D response surface plots for combined effects of adsorbent dose and pH (A, D), adsorbent dose and initial concentration, (B, E) and pH and initial concentration (C, F), on the responses CIP (A – C) and OTC (D – F) adsorption capacity.

The refined regression models for CIP (y_3) and OTC (y_4) adsorption capacity, provide further insights into the influence of the process variables. As with the earlier models, statistically insignificant terms have been removed, leaving only those predictors with meaningful effects on the responses. This refinement enhances model clarity and supports a more targeted approach to process understanding and optimisation. Equation 6.3 andEquation 6.4 highlight the dominant influence of x_1 , and its quadratic term $(x_1)^2$ on both responses. In both models, x_1 exhibits a strong negative linear effect, accompanied by a large positive quadratic coefficient, indicating a clear curvature within the design space, as shown in Figure 6.3. This trend is consistent across both responses, reinforcing the importance of carefully controlling this factor during process optimisation.

For y_3 , the response is predominantly influenced by the linear and quadratic effects of x_1 , as well as its interaction with x_3 (Equation 6.3). The strong negative linear coefficient for x_1 and the substantial positive coefficient for $(x_1)^2$ indicate that there is an optimal region for x_1 where the response is maximised.

Additional effects in the model for y_3 include a significant interaction between x_1 and x_3 , further emphasising the need to consider variable interactions. For y_4 , modest contributions from x_2 , x_3 , and a mild quadratic effect from $(x_2)^2$ are also observed, though their impact is less pronounced. The presence of significant interaction and curvature terms in both models further suggests that a simple linear optimisation would be insufficient; rather, a more nuanced, response surface optimisation approach is warranted.

$$y_3 = 27.84 - 68.83(x_1) - 0.0014(x_2) - 1.235(x_3) + 44.62(x_1)^2$$
 Equation 6.3
+ 1.609(x_1x_3)

$$y_4 = 11.83 - 29.46(x_1) - 0.833(x_2) + 1.206(x_3) + 19.09(x_1)^2$$
Equation 6.4
$$+ 0.0896(x_2)^2$$

6.2.1.3. Optimum Point Validation and Comparison with Activated Carbon Fibres

Both models were validated using an equally weighted dual-response optimisation, to optimise the removal percentage, denoted %-mCF-Opt or adsorption capacity (q_e-mCF-Opt) of both antibiotics. Similarly to the previous chapter, the model was then validated for the individual responses, CIP and OTC removal percentage or adsorption capacity, which were denoted as %-mrCF-AB-Opt and q_e-mrCF-AB-Opt, respectively, where AB is CIP or OTC. The optimum conditions and corresponding removal percentages and antibiotic adsorption capacities are presented in Table 6.6.

Sample	Optim	ium co	nditions	q _e (n	ng/g)	Removal (%)		
	Adsorbent dose (g/L)	рН	Initial conc (mg/L)	CIP	отс	CIP	отс	
%-mrCF-Opt	0.8	2	2.0	2.361 ± 0.06	2.423 ± 0.08	96.47 ± 2.04	97.72 ± 3.36	
%-K-ArCF- Opt	0.8	2	2.0	2.274 ± 0.22	2.435 ± 0.20	94.66 ± 9.02	91.12 ± 7.74	
%-mrCF-CIP- Opt	0.8	2	2.0	2.355 ± 0.07	2.405 ± 0.11	96.24 ± 2.39	96.99 ± 4.59	
%-mrCF- OTC-Opt	0.9	2	2.0	2.073 ± 0.09	2.113 ± 0.08	93.30 ± 4.31	92.58 ± 3.36	
%-mvCF-Opt	0.8	2	2.0	2.406 ± 0.05	2.406 ± 0.12	99.86 ± 2.45	96.26 ± 5.83	
%-K-AvCF- Opt	0.8	2	2.0	2.411 ± 0.06	2.248 ± 0.21	99.18 ± 2.96	90.38 ± 8.90	
q _e -mrCF-Opt	0.1	8	1.3	9.058 ± 0.45	5.685 ± 1.88	79.57 ± 3.59	42.45 ± 16.93	
q _e -mrCF-CIP- Opt	0.1	8	0.5	16.716 ± 1.48	19.433 ± 1.17	81.94 ± 5.04	89.56 ± 7.65	
q _e -mrCF- OTC-Opt	0.1	8	2.0	15.940 ± 0.44	16.266 ± 2.40	79.72 ± 4.23	83.26 ± 11.20	
q _e -mvCF-Opt	0.1	8	1.3	11.060 ± 0.35	5.855 ± 2.22	89.26 ± 1.92	45.84 ± 18.85	

Table 6.6: Dual and independent response optimisation for the adsorption of CIP and OTC on K-ArCF-Opt and mrCF-Opt.

The highest removal percentages for both antibiotics onto activated and modified CFs were observed under the conditions identified for %-mrCF-Opt. Whereas the highest equilibrium adsorption capacities for CIP and OTC were observed under the conditions identified for q_e-mrCF-CIP-Opt. The high removal percentages achieved for %-mrCF-Opt can be attributed to several factors, including a higher adsorbent dose and initial concentration. These conditions

offer a larger surface area, more available active sites for adsorption, and a greater driving force for the diffusion and mass transfer of antibiotics into the porous network. Additionally, the low pH enhances interactions between the cationic antibiotics and the adsorbent surface as discussed in Section 6.2.1.1. Conversely, the high adsorption capacities observed for qe-mrCF-CIP-Opt are driven by the lower adsorbent dose, which leads to increased competition for active sites and, consequently, higher saturation of the adsorbent.

Furthermore, the removal percentages observed for %-K-ArCF-Opt and %-mrCF-Opt were comparable suggesting that the extra modification processing step utilising corrosive chemicals is not necessary to maintain high removal percentages towards CIP and OTC. However, it is recommended to proceed with competitive adsorption studies using this material to determine if it offers any significant advantages over the activated samples, such as enhanced selectivity.

From a practical perspective within a RAS aquaculture system, maximising removal percentage is more critical than maximising adsorption capacity, as maintaining high water quality is the priority. Since %-mrCF-Opt achieved the highest removal percentages across both antibiotics, and considering the industrial appeal of a versatile "one-size-fits-all" approach, the conditions identified for %-mrCF-Opt were selected for further analysis and characterisation.

To statistically validate the observed trends, the data were further analysed to determine whether the differences in removal percentage (%) and equilibrium adsorption capacity between the activated and modified CF samples were significant (Table 6.7). When comparing the samples optimised for removal percentage (%-mCF-Opt) to the optimum modified sample (mCF-Opt) developed in the previous chapter, a statistically significant increase in OTC removal and a significant decrease in CIP removal were observed for both recycled and virgin CFs, with p-values \leq 0.0003. Additionally, CIP removal was found to be significantly higher for q_e-mrCF-Opt compared to q_e-mvCF-Opt (p = 0.03), indicating that recycled CFs outperformed virgin CFs in this regard. All other comparisons between activated and modified rCFs and vCFs were not statistically significant (p > 0.05), suggesting broadly comparable performance across these samples.

Table 6.7: Summary of independent t-test results comparing the percentage removal (%R) and equilibrium adsorption capacity (q_e) for CIP and OTC between modified and unmodified carbon fibre samples. Statistical significance is indicated by "ss" (significant) or "nss" (not significant) based on a threshold of p < 0.05.

. .	C	CIP	C	тс	Significance	
Comparison	t-stat	p-value	t-stat	p-value	Significance	
%-mrCF-Opt vs. %-mvCF-Opt	-1.85	0.14	0.38	0.73	nss	
%-mrCF-Opt vs. %-K-ArCF-Opt	0.34	0.77	1.36	0.27	nss	
mrCF-Opt vs. %-mrCF	3.02	0.02	-6.00	0.0001	SS	
%-mvCF-Opt vs. %-K-AvCF-Opt	0.31	0.77	0.96	0.41	nss	
q _e -mrCF-Opt vs. q _e -mvCF-Opt	-4.12	0.03	-0.23	0.83	ss (CIP), nss (OTC)	
mvCF-Opt vs. %-mvCF-Opt	-4.13	0.003	-6.65	0.0003	SS	

6.2.2. Adsorption Studies: Equilibrium, Kinetic and Thermodynamic Analyses

This section will discuss the equilibrium, kinetic and thermodynamic analyses for the adsorption of CIP and OTC on %-K-ArCF-Opt and %-mrCF-Opt.

6.2.2.1. Adsorption Isotherms

%-K-ArCF-Opt and %-mrCF-Opt were further analysed to determine the best fitting equilibrium adsorption isotherm models for the adsorption of CIP and OTC, to gain insights into the mechanism of adsorption. The data were fitted to the Langmuir, Freundlich, Temkin, Toth and Redlich-Peterson models; the calculated regression coefficients and equilibrium adsorption data are presented in Table 6.8, while the adsorption isotherm plots for CIP and OTC are depicted in Figure 6.4 and Figure 6.5, respectively.

Overall, the Toth isotherm demonstrated the best fit across the data, with the exception of CIP adsorption onto mrCF-Opt at 20 °C, where the Langmuir isotherm provided a superior fit. Although this deviation from the general trend was observed, all adsorption experiments were

conducted in triplicate, and the data exhibited low variability (standard deviation $\pm 2 \text{ mg/g}$), suggesting the result is reliable. Nevertheless, to further validate this observation, future studies should incorporate additional concentration data points at 20 °C or investigate intermediate temperatures (e.g., 15 °C or 25 °C) to assess the continuity of the trend.



Figure 6.4: K-ArCF-Opt (A) and mrCF-Opt (B) adsorption isotherm and experimental data for the adsorption of CIP.



Figure 6.5: K-ArCF-Opt (A) and mrCF-Opt (B) adsorption isotherm and experimental data for the adsorption of OTC.

The Toth isotherm is useful to describe systems that deviate from ideal behaviour, particularly those with heterogeneous surfaces where the adsorption energy distribution is not uniform. The calculated K_T values are comparable those reported in literature for the adsorption of CIP and OTC on CAs, suggesting a good binding affinity between the adsorbate and adsorbent [133,285]. Furthermore, many of the calculated t values are greater than 1, which can be indicative of cooperative adsorption effects or other complex interactions between adsorbate molecules.

Sample	Temp		Тс	oth			Redlich-Peterson		1	Langmuir Temkin				Freundlich				
	(°C)	R ²	q _{max}	Kτ	t	R ²	K _R	a _R	g	R ²	q _{max}	ΚL	R ²	Kτ	b	R ²	K _F	n
%-K-ArCF-	20	0.879	19.83	0.69	1.12	0.879	15.12	0.74	1.00	0.879	20.25	0.75	0.853	3.35	14.34	0.824	8.07	3.53
Opt-CIP	30	0.962	47.38	1.07	129.72	0.955	60.98	0.75	1.17	0.944	56.62	1.37	0.840	7.98	44.51	0.836	25.69	2.94
	40	0.964	53.21	1.27	2.04	0.959	75.45	0.86	1.20	0.948	61.02	1.56	0.933	12.21	17.14	0.810	28.26	2.66
%-mrCF-	20	0.884	36.81	0.42	0.89	0.886	16.55	0.64	0.90	0.983	26.41	0.64	0.899	3.83	329.57	0.864	9.77	2.39
Ορι-CIP	30	0.940	41.66	0.44	49.18	0.917	20.56	0.19	1.29	0.895	51.22	0.50	0.903	4.21	215.59	0.775	15.49	2.46
	40	0.985	52.78	0.94	0.81	0.986	47.12	1.15	0.93	0.983	43.40	0.81	0.833	50.93	410.37	0.927	18.84	3.03
%-K-ArCF-	20	0.981	220.66	0.10	0.30	0.981	6.927	0.81	0.61	0.975	44.59	0.06	0.904	2.32	399.45	0.978	4.49	1.85
Ορτ-ΟΤΟ	30	0.939	41.09	0.47	1.08	0.939	20.24	0.48	1.00	0.939	42.22	0.48	0.952	5.06	282.34	0.874	12.43	2.42
	40	0.991	34.09	0.71	1.97	0.989	27.90	0.484	1.16	0.961	37.36	0.96	0.928	13.30	372.61	0.815	15.03	3.28
%-mrCF-	20	0.975	10.32	0.35	1.47	0.973	4.56	0.34	1.06	0.971	10.96	0.48	0.943	7.05	1256.9	0.86	4.05	3.55
Opt-OTC	30	0.979	50.99	0.20	1.22	0.978	10.77	0.15	1.08	0.978	56.66	0.20	0.968	2.99	230.18	0.944	10.36	1.84
	40	0.962	46.99	1.51	2.09	0.955	93.28	1.63	1.06	0.910	49.69	2.47	0.770	152.39	439.77	0.870	23.88	3.42

Table 6.8: K-ArCF-Opt and mrCF-Opt equilibrium adsorption data for the adsorption of CIP and OTC at 20, 30 and 40 °C.

6.2.2.2. Adsorption Kinetics

Kinetic models were applied to assess the adsorption rate and to gain an understanding of the adsorbent performance and mass transfer mechanisms. The kinetic data were fitted to PFO, PSO, Elovich, intraparticle diffusion and Avrami kinetic models, finding the latter model to be the best fit, having the highest R² values (Table 6.10). This was further supported by the similarity between the experimental q_e values and those calculated using the Avrami model. Figure 6.6 depicts the experimental data and fitted Avrami kinetic model for the adsorption of CIP onto %-K-ArCF-Opt and %-mrCF-Opt, whilst Figure 6.7 depicts the kinetic models for OTC adsorption.



Figure 6.6: K-ArCF-Opt (A) and mrCF-Opt (B) kinetic model and experimental data for the

adsorption of CIP.



Figure 6.7: K-ArCF-Opt (A) and mrCF-Opt (B) kinetic model and experimental data for the adsorption of OTC.

Although less commonly applied, the Avrami model has been applied within literature to describe the adsorption of antibiotics such as CIP, OTC and other pharmaceuticals [286,287]. The Avrami model is a fractional kinetic model which has commonly been utilized to describe phase transformations in materials and is particularly useful for describing adsorption processes with non-linear kinetics. The model has several assumptions, namely heterogeneous adsorption and nucleation, time-dependent nucleation, where adsorption is influenced by surface coverage and interaction effects and growth of adsorbed clusters. The Avrami model is presented below, in Equation 6.5.

$$q_t = q_e \cdot \{1 - exp[-(k_{AV} \cdot t]^{n_{AV}}\}$$
 Equation 6.5

Where, q_e is the amount adsorbed at equilibrium (mg/g), q_t is the cumulative amount adsorbed (mg/g), at time t (min), and k_{AV} is the Avrami rate constant (min⁻¹). The Avrami exponent, nAV, is a factionary number, associated with the possible variations in the adsorption mechanism during the adsorption process. Rather than adhering to a single integer-kinetic order, the adsorption mechanism can exhibit multiple kinetic orders that change during the interaction between the adsorbate and the adsorbent.

The calculated rate constants and Avrami exponents are presented in Table 6.10. The values achieved for k_{AV} are comparable or in many cases exceed those reported in literature for the adsorption of pharmaceuticals indicating a fast rate of adsorption [286–288]. Meanwhile the fractional values for n_{AV} suggest the adsorption mechanism is complex with potentially multiple adsorption mechanisms occurring at different stages of the process. A fractional n_{AV} value can also indicate slow nucleation with complex growth or transformation processes.

It is well known that many organic molecules such as antibiotics possess the ability to agglomerate/self-aggregate under certain conditions (i.e. temperature, pH, salinity, agitation etc), due to physical interactions such as π - π bonding, hydrophobic effects and hydrogen bonding, which is consistent with the observed fractional n_{AV} values. These aggregates are not highly ordered structures but rather loose, reversible molecular clusters whose formation is influenced by factors such as temperature, pH, ionic strength, and agitation.

However, at present, there is a lack of understanding of the aggregation behaviour of CIP and OTC under the specific conditions used in this study. Further investigation using techniques such as dynamic light scattering (DLS), UV-visible spectroscopy, or nuclear magnetic

resonance (NMR) could provide valuable insights into how aggregation affects adsorption performance and the underlying mechanisms of interaction with carbon-based adsorbents. Understanding this behaviour is essential for accurately interpreting adsorption kinetics and capacities, particularly in concentrated or environmentally relevant systems.

Based upon the data produced from the Avrami model, interpolations were made to determine the time (min) required to reach 50 and 95% of the equilibrium adsorption capacity which were denoted as $t_{0.5}$ and $t_{0.95}$, respectively. From the data presented in Table 6.9, it can be observed that %-K-ArCF-Opt has a high initial affinity toward CIP, particularly at increased concentrations as indicated by the quick times to reach $t_{0.5}$ (Table 6.9). However, at low concentrations the time taken to reach $t_{0.5}$ is very slow suggesting that the adsorption process is limited by slower diffusion into the porous network, or repulsive interactions as adsorption sites become occupied. After modification, there is a reduction in initial affinity towards CIP as indicated by the longer times to reach $t_{0.5}$, which can be attributed to the reduced accessibility due the reduction in pore size after modification. Furthermore, the enhanced oxidation of %-mrCF-Opt creates a more complex surface chemistry which may require longer times to equilibrate.

	Initial Concentration (mg/L)							
		2	5					
Sample	t 0.5	t 0.95	t 0.5	t 0.95				
%-K-ArCF-Opt-CIP	1.57	538.92	0.05	120.18				
%-mrCF-Opt-CIP	5.58	101.60	1.94	54.37				
%-K-ArCF-Opt-OTC	6.06	264.66	2.50	158.15				
%-mrCF-Opt-OTC	4.17	90.29	0.87	97.23				

Table 6.9: Calculated $t_{0.5}$ (min) and $t_{0.95}$ (min) values from the interpolation of the Avrami kinetic model data.

In the case of %-K-ArCF-Opt, the time to reach t_{0.5} for OTC adsorption is significantly slower than the time required for the adsorption of CIP. This can be attributed to the slower external and internal diffusion, due to the larger molecular size of OTC. Interestingly at lower concentration %-K-ArCF-Opt reaches t_{0.95} quicker for OTC than CIP, suggesting that OTC may have a greater affinity towards binding sites leading to a more efficient adsorption process. After modification, significant improvements are observed in the time taken to reach t_{0.5} and t_{0.95} for OTC adsorption, suggesting that the surface groups introduced during modification have a high affinity towards OTC.

Sample	Conc		Avra	ami			PSO			Elov	ich			PFO			IPD	
	(mg/L)	R ²	q _e	K _A	n	R ²	q _e	K ₂	R ²	β	α	С	R ²	q _e	K ₁	R ²	Kp	С
%-ArCF-	2	0.966	2.02	0.62	0.25	0.934	1.89	0.13	0.956	8.55	1.8e ⁺³	0.12	0.863	1.82	0.14	0.360	0.02	1.28
Opt-CIP	5	0.992	3.72	1.21	0.19	0.989	3.61	0.21	0.976	6.48	6.1e ⁺⁶	0.15	0.939	3.45	4.85	0.188	0.02	2.82
%-mrCF-	2	0.962	1.64	0.29	0.50	0.947	1.54	0.096	0.889	8.85	202.53	0.11	0.907	1.59	0.09	0.333	0.03	1.03
Opt-CIP	5	0.986	3.57	0.52	0.44	0.981	3.57	0.095	0.936	6.63	2.8e ⁺⁶	0.15	0.949	3.48	0.17	0.213	0.02	2.58
%-ArCF-	2	0.973	1.23	0.35	0.39	0.971	1.19	0.11	0.942	10.30	24.09	0.10	0.919	1.13	0.09	0.437	0.01	0.73
Ορτ-ΟΤΟ	5	0.993	3.24	0.50	0.35	0.978	3.15	0.07	0.955	5.39	5.8e ⁺³	0.19	0.923	3.03	0.135	0.304	0.02	2.18
%-mrCF-	2	0.972	1.15	0.35	0.48	0.979	1.15	0.17	0.928	13.14	314.10	0.08	0.948	1.09	0.12	0.347	0.009	0.76
Upt-01C	5	0.981	3.20	0.72	0.31	0.978	0.13	3.15	0.954	7.52	3.4e ⁺⁶	0.13	0.955	3.04	0.21	0.214	0.02	2.34

Table 6.10: K-ArCF-Opt and mrCF-Opt kinetic models for the adsorption of CIP and OTC at initial concentrations of 2 and 5 mg/L.

6.2.2.3. Adsorption Thermodynamics

 Δ H and Δ S were determined using the linear form of the Van't Hoff equation (Equation 2.12). In K_T was plotted against 1/t. where the slope represents (- Δ H/R) and the intercept is Δ S/R. Δ G was then determined using the Gibbs free energy equation (Equation 2.10).

The thermodynamic data are presented in Table 6.11. From the data, it is evident that the adsorption process is endothermic for both antibiotics indicated by the positive ΔH values, which is consistent with the increased adsorption capacities at higher temperatures. Furthermore, a small increase in entropy (i.e. disorder) was observed, indicated by the positive ΔS values, aligning with the predictions from the Avrami adsorption isotherm model, which suggests that adsorption is a complex, heterogeneous process and may involve the formation of antibiotic clusters or agglomerates on/with the adsorbent surface. Finally, the adsorption process was found to be spontaneous at all temperatures as indicated by the negative ΔG values. Furthermore, it was observed that ΔG gradually decreases as temperature is increased, indicating that the degree of spontaneity of the reaction increases, at higher temperatures, further supporting the statement that the process is endothermic.

Although similar values have been reported in literature for the adsorption of CIP and OTC onto CAs [287,289], a number of studies have highlighted the limitations in utilising isotherm data to calculate thermodynamic data, particularly within complex adsorption systems alike those discussed within this chapter, therefore the data should be interpreted with caution [171,172].

Sample	ΔH	ΔS (J/mol)	ΔG (kJ/mol)				
	(KJ/MOI)	_	20 °C	30 °C	40 °C		
%-K-ArCF-Opt-CIP	+21.01	+2.18	-23.13	-24.86	-26.13		
%-mrCF-Opt-CIP	+28.65	+2.48	-21.86	-22.72	-25.32		
%-K-ArCF-Opt-OTC	+101.46	+5.87	-16.76	-5.86	-24.78		
%-mrCF-Opt-OTC	+37.11	+2.84	-21.28	-20.73	-25.32		

Table 6.11: Thermodynamic data for the adsorption of CIP and OTC onto K-ArCF-Opt and

mrCF-Opt.

6.2.3. Fourier-Transform Infrared Spectroscopy (FTIR)

The spent %-mCF-Opt samples showed the same peaks as the mrCFs prior to adsorption. Notably, there were some changes in peak intensity for some of the peaks, particularly for the O-H, $C=C_{(aromatic)}$, O-N=O and C-O/C-N peaks at 3200 – 3600, 1532, 1384 cm⁻¹and 1113 cm⁻¹, respectively [268,269]. Since the KBr disks were prepared quantitatively, increases in peak intensity suggest a higher concentration of corresponding functional groups, indicating successful incorporation of the antibiotics into the CA structure, given that these groups are inherent to the antibiotic molecules. However, for more accurate quantification, the area under each peak should be integrated, as it is directly proportional to the number of vibrating dipoles (i.e. bonds) according to the Beer–Lambert Law in infrared spectroscopy.



Figure 6.8: Infrared spectra of mrCF-Opt (top) and mvCF-Opt (bottom).

6.3. Conclusion

This chapter investigated the adsorption of CIP and OTC onto mCF-Opt and K-ACF-Opt, with the aim to optimise the adsorption process and gain insights into the adsorption mechanisms. The data were optimised to maximise the removal percentage and adsorption capacity of both antibiotics.

High coefficients of determination ($R^2 > 88\%$) were achieved for both antibiotics, with OTC exhibiting lower model fit due to increased system complexity. Within the investigated design space, optimal conditions for maximising removal percentages were established at 0.8 g/L adsorbent dose, pH 2, and 2 mg/L initial concentration. These conditions achieved removal efficiencies exceeding 90% with equilibrium adsorption capacities ranging from 2.3 to 2.5 mg/g. However, the absence of clear maxima within the design space suggests that true optimal conditions may exist beyond the investigated parameters.

For maximising adsorption capacity, optimal conditions were identified at 0.1 g/L adsorbent dose, pH 8, and 2 mg/L initial concentration. These parameters yielded substantially improved adsorption capacities of over 9 mg/g for CIP and 5 mg/g for OTC. The enhanced performance under these conditions can be attributed to increased competition for active sites at lower adsorbent doses, leading to higher adsorbent saturation. However, this resulted in reduced removal percentages as the adsorbent reached saturation before complete removal could be achieved. As with removal efficiency, the absence of clear maxima suggests potential for further optimisation beyond the current design space.

Given the importance of maintaining water quality in aquaculture applications, the conditions optimised for maximum removal percentage (%-mrCF-Opt) were selected for subsequent analyses, despite the lower adsorption capacities. This decision prioritises practical application effectiveness over theoretical maximum capacity.

The adsorption isotherms, kinetic models and adsorption thermodynamics were assessed. The best fitting isotherm and kinetic models were found to be Toth and Avrami, respectively, achieving high R² values (above 0.95). Overall, the data indicated that the adsorption of both antibiotics is complex and likely involves both physical and chemical interactions. Furthermore, the adsorption process may involve the formation of heterogenous agglomerates or clusters of adsorbent molecules on the adsorbate surface.

To gain further insights into the adsorption mechanisms of CIP and OTC, it is suggested that further research is conducted at a wider range of pH values to understand the interactions that may occur, for example at pH ~4 where the antibiotics are largely cationic and the adsorbent surfaces are anionic, which could result in enhanced electrostatic interactions. Furthermore, research should be conducted to understand the impacts of concentration, pH and temperature on the agglomeration behaviour of both antibiotics.

Finally, from an industrial scalability perspective for applications in RAS aquaculture systems, research should be conducted to determine the recyclability and reusability of the adsorbent by investigating adsorbent regeneration, as discussed in the following chapter.

7. Regeneration of Antibiotic-laden Activated Carbon Fibre Adsorbents

7.1. Introduction

Adsorbent regeneration is a crucial factor in enhancing the recyclability and reusability of adsorbent materials, making them more suitable for industrial applications. Adsorbents with high regeneration efficiency offer numerous advantages, such as cost reduction, improved environmental sustainability through reduced waste generation, greater process efficiency, and decreased secondary pollution [13].

Traditional regeneration methods, such as thermal swing adsorption/desorption, often require expensive equipment and consume significant energy. To maintain a more cost-effective and practical approach in aquaculture, the less conventional chemical regeneration or pH swing regeneration method was utilised. This approach leverages changes in the chemical speciation of both the adsorbent surface and antibiotics at different pH levels to create repulsive interactions that facilitate the desorption of antibiotics [89,205].

This chapter focuses on investigating the regeneration of antibiotic-laden mrCF-Opt using chemical regeneration techniques. Four regenerant solutions were examined, namely NaOH (0.1 M and 0.25 M) and KOH (0.1 M and 0.25 M), with regeneration efficiency evaluated over seven cycles, including the initial adsorption cycle (C_0).

7.2. Results and Discussion

7.2.1. Adsorbent Regeneration

Figure 7.1A and B show the regeneration efficiency of %-mrCF-Opt over 7 cycles for CIP and OTC, respectively. Similar trends are observed for the regeneration efficiency of mrCF towards both antibiotics. Initially a slight increase in adsorption efficiency is observed with all samples achieving a regeneration efficiency above 100%. This was attributed to the leaching of residual impurities from the activation process such as aluminosilicate and ash *via* Reactions 7.1 and 7.2. The removal of these impurities could result in higher surface areas and subsequently improved adsorption capacities.

 $2MOH + SiO_2 \rightarrow M_2SiO_3 + H_2O$ Reaction 7.1 $2MOH + Al_2O_3 + 3H_2O \rightarrow M_2Al(OH)_4 + H_2O$ Reaction 7.2

However, after the 2nd cycle a significant decline in regeneration efficiency to approximately 70-80% is observed for both antibiotics across all regenerant solutions. Throughout the rest of the cycles the regeneration efficiency stabilises indicating promising reusability for the adsorbents.





The regeneration data was analysed using ANOVA to assess whether significant differences existed between the regenerant solutions across successive regeneration cycles (Table 7.1). With the exception of Cycle 2, no significant differences were observed between the regenerants until after the fifth regeneration cycle. From Cycle 5 onwards, the P-values dropped below 0.05, indicating statistically significant differences in performance between the regenerant solutions. This suggests that while initial regeneration efficiencies were comparable, prolonged reuse may impact the effectiveness of certain regenerants.

	Courses	E) (alua	D. Value		
	regenerants	solutions acros	ss 7 cycles.		
Table 7.1: ANOVA result	s for difference	es observed in	regeneration e	fficiency between	four

Source	F-Value	P-Value
C ₁	1.07	0.42
C ₂	8.29	0.01
C ₃	0.37	0.77
C ₄	2.99	0.10
C5	5.49	0.02
C ₆	5.15	0.03
C ₇	6.21	0.01

A t-test was performed to evaluate whether the concentration of KOH (0.1 M vs. 0.25 M) had a significant effect on regeneration efficiency after seven cycles. The results yielded a tstatistic of -0.58 and a p-value of 0.30, indicating no statistically significant difference in performance between the two concentrations

Base	lonic radius (nm)	Heat of Hydration (kJ/mol)
NaOH	0.133	-932
КОН	0.102	-847

Table 7.2: Chemical properties of Na⁺ and K⁺ [290].

The data clearly indicate that stronger bases, such as KOH, were more effective in regenerating the adsorbent surface. This enhanced performance is likely due to the lower heat of hydration of K⁺ compared to Na⁺, which may facilitate greater interaction with the adsorbent surface. However, statistical analysis revealed that increasing the KOH concentration had no significant effect on regeneration efficiency. Therefore, from an

economic, environmental, and safety standpoint, the use of 0.1 M KOH is recommended as the optimal regeneration concentration.

Following the cycle-based analysis and statistical evaluation, it is important to contextualise the performance of %-mrCF-Opt against previously reported regeneration methods for similar adsorbents. Table 7.3 compares the regeneration efficiencies of %-mrCF-Opt with various conventional CAs used for adsorbing different aqueous phase pollutants.

In this study, %-mrCF-Opt regenerated with both 0.1 M and 0.25 M KOH exhibited consistently high regeneration efficiencies for CIP and OTC. For CIP, 0.1 M KOH achieved 108.93% efficiency at C1 and 75.45% at C7, while 0.25 M KOH produced comparable values (107.08% at C1 and 76.38% at C7). OTC regeneration followed similar trends, reaching 109.76% (C1) and 74.18% (C7) with 0.1 M KOH, and 103.25% (C1) and 78.91% (C7) with 0.25 M KOH. These results highlight not only the effective desorption of antibiotics from %-mrCF-Opt but also its efficiency over multiple reuse cycles.

When compared to AC regenerated with 0.1 M NaOH (99% at C1, 48% at C4) [89], %-mrCF-Opt clearly demonstrates superior long-term regeneration performance. Fe-AC used for TC regeneration achieved slightly lower retention, after fewer cycles (95% at C1, 73% at C4) [205].

More energy-intensive techniques such as thermal regeneration at 200 °C offered good initial recovery (100% at C1), but performance dropped to 65% by C13 [77]. Non-thermal alternatives such as ultrasonic and methanol regeneration were less effective, with efficiencies below 60% by C7 [77].

High-temperature regeneration (600 °C) of PAN-ACF achieved relatively strong performance (83.9% at C1, 77.5% at C2) for ρ -cresol [115], but such methods may be impractical due to operational costs and thermal degradation risks.

In contrast, the mild alkaline regeneration employed in this study avoids these limitations while delivering high and consistent efficiencies across different pollutants. Overall, confirming that %-mrCF-Opt, regenerated under ambient conditions with low-concentration KOH, provides a sustainable and high-performance alternative to conventional (i.e. thermal) regeneration strategies.

Sample	Pollutant	Regenerant	Regeneration efficiency (%)	Ref
%-mrCF-Opt	CIP	0.1 M KOH	C1 – 108.93 C7 – 75.45	This work
%-mrCF-Opt	CIP	0.25 M KOH	C1 – 107.08 C7 – 76.38	This work
%-mrCF-Opt	отс	0.1 M KOH	C1 –109.76 C7 – 74.18	This work
%-mrCF-Opt	отс	0.25 M KOH	C1 – 103.25 C7 – 78.91	This work
AC	CIP	0.1 M NaOH	C1 – 99 C4 – 48	[89]
Fe-AC	тс	0.1 M NaOH	C1 – 95 C4 - 73	[205]
AC	тс	Thermal 200 °C	C1 – 100 C13 – 65	[77]
AC	тс	Ultrasonic	C1 – C7 < 60	[77]
AC	тс	100% methanol	C1 – C6 < 60	[77]
ACF-felt	NOR	20% HNO ₃		[207]
PAN-ACF	ρ-cresol	Thermal 600 °C	C1 - 83.9 C2 - 77.5	[115].
PAN-ACF	p-cresol	n-hexane	C1 – 78.6 C2 – 54.4	[115].

Table 7.3: Comparison of regeneration methods and efficiencies for various CAs and Pollutants

7.3. Conclusion

This chapter investigated the regeneration performance of %-mrCF-Opt for CIP and OTC using mild alkaline treatments. Regeneration efficiencies initially exceeded 100%, likely due to the removal of residual impurities from the activation process. Although a decline was observed after the second cycle, efficiencies stabilised between 70–80% over subsequent cycles, indicating strong reusability.

ANOVA and t-test results confirmed no significant difference between 0.1 M and 0.25 M KOH, making the lower concentration the more practical choice. Compared with conventional ACs and other regeneration methods from the literature, %-mrCF-Opt demonstrated superior multi-cycle performance under ambient conditions. This efficacy is likely due to the stronger basic nature of KOH, which enhances the regeneration of the adsorbent surface by breaking adsorbate-adsorbent interactions more effectively. Additionally, the lower heat of hydration of K⁺ compared to Na⁺ contributes to its greater availability for interaction with the adsorbent surface. These results highlight %-mrCF-Opt as a cost-effective, sustainable adsorbent suitable for repeated use in the removal of pharmaceutical contaminants from water.

8. Discussion and Future Works

This chapter summarises the key findings of the thesis, with a focus on their relevance to freshwater aquaculture. Each stage of adsorbent development – from precursor selection and treatment (i.e. activation and modification) to adsorption and regeneration – was systematically optimised using DoE techniques. The results demonstrate the potential of rCFs as sustainable precursors for CAs and emphasise the importance of process optimisation to enhance responses such as surface area, yield, adsorption performance and reusability.

8.1. Process optimisation and Parameter selection

Table 8.1 below consolidates the experimental variables studied at each stage and outlines the corresponding optimum conditions to maximise desired properties, derived through statistical modelling and experimental validation. During activation, a lower activation temperature (670 °C), short hold time (0.5 h), and high IR (1:10 CF:KOH) were found to produce the most effective adsorbents. This combination maximised surface development while minimising surface degradation or excessive burn-off. For surface modification, the optimum treatment involved 6 M nitric acid at 28 °C for 16 hours, effectively enhancing surface functionality without compromising pore structure.

Adsorption optimisation revealed contrasting conditions depending on the performance metric. When optimising for removal efficiency (%), acidic pH conditions (pH 2) and a higher adsorbent dose (0.8 g/L) were preferred, supporting stronger electrostatic attraction between the adsorbent surface and the ionised antibiotic molecules. In contrast, when optimising for adsorption capacity, basic pH conditions (pH 8) and lower adsorbent doses were favoured. This difference does not indicate a change in adsorption mechanism but rather reflects how solution conditions influence the amount of contaminant removed per gram of adsorbent.

For regeneration, 0.1 M KOH was identified as the most effective regenerant. It provided high regeneration efficiency across multiple cycles while avoiding the use of more aggressive or energy-intensive methods.

These process optimisations provided the foundation for developing materials with enhanced surface properties, as explored in the following section.

Table 8.1: Summary of optimised processes and corresponding conditions for activation	,
modification, adsorption, and regeneration of rCF-based adsorbents.	

Process	Sample	DoE parameters	Optimum Conditions
		Temp – 670 – 830 °C	Temp – 670 °C
Activation	K-ArCF-Opt	Hold time – 0.5 – 3 h	Hold time – 0.5 h
		IR – 1:1 – 1:10 (CF:KOH)	IR – 1:10 (CF:KOH)
		HNO_3 conc – 1 – 6 M	HNO₃ conc – 6 M
Modification	m-rCF-Opt	Hold time – 16 h	Hold time – 16 h
		Temp – 28 °C	Temp – 28 °C
	%-K-ArCE-Opt	Adsorbent dose – 0.1 – 0.9 g/L	Adsorbent dose – 0.8 g/L
Adsorption (%)	%-m-rCE-Opt	pH – 2 – 8	pH - 2
	<i>ж</i> -ш-ст-орс	' Initial conc – 0.5 – 2 mg/L	Initial conc – 2 mg/L
		Adsorbent dose – 0.1 –	Adsorbent dose – 0.1 g/L
Adsorption (q _e)	q _e -K-ArCF-Opt	0.9 g/L	pH - 8
	q _e -m-rCF-Opt	pH – 2 – 8	Initial conc – 1.3 mg/l
		Initial conc – 0.5 – 2 mg/L	
		0.1 M NaOH or KOH	
Regeneration	0.25K-mrCF-Opt	0.25 M NaOH or KOH	0.25 М КОН
		Contact time – 4 h	

8.2. Surface Property Enhancements and Composition

Analysis of the physical and chemical surface properties of the precursor (rCFs and vCFs) and the treated (i.e. activated and modified) products provided key insights into the effectiveness of the chemical treatment strategies (Table 8.2). The raw CF materials initially exhibited low surface areas (< 50 m²/g), highlighting their limited adsorption potential in their untreated form. However, chemical activation using KOH proved highly effective, exhibiting substantial enhancements in surface area, increasing by 773.78% and 1429.23% for K-ArCF-Opt and K-AvCF-Opt, respectively. Furthermore, K-ArCF-Opt exhibited a significantly higher surface area than K-AvCF-Opt (t = 2.44, P = 0.04), supporting the conclusion that recycled carbon fibres are more amenable to pore development during activation. This is likely due to reduced mechanical strength and structural disorder introduced during the recycling process, which renders the carbonaceous framework more susceptible to etching by the activating agent. K-ArCF-Opt also exhibited higher total pore volume than K-AvCF-Opt, despite a slightly smaller micropore volume, suggesting a shift towards more accessible meso- and macropores, which are particularly beneficial in aqueous-phase adsorption.

In addition to increased surface area, both samples demonstrated markedly improved mesoporosity, as evidenced by Type IV nitrogen adsorption isotherms with H4 or H1 hysteresis loops; features typically associated with mesoporous structures. These characteristics suggest enhanced adsorbate accessibility and diffusion in aqueous environments, which are critical for effective adsorption performance.

Moreover, K-ArCF-Opt exhibited significantly higher total acidity and basicity, along with a lower point of pH_{PZC} compared to K-AvCF-Opt. These results indicate more extensive surface oxidation of the rCF precursor, which could enhance interactions with a broader range of contaminants through acid-base and electrostatic mechanisms.

Post-modification, mrCF-Opt retained a higher surface area than mvCF-Opt, and the difference between these two modified materials was statistically significant (t = 5.63, P = 0.004). This further supports the superior porosity of the rCF-based adsorbents even after chemical oxidation. In contrast, although mvCF-Opt showed a slight reduction in surface area and pore volume compared to its activated counterpart (K-AvCF-Opt), although the difference was not statistically significant (t = 0.68, P = 0.55). This was attributed to minor pore-blocking effects from the introduction of new surface functional groups, a well-documented phenomenon in surface chemistry. Furthermore, acidic treatment resulted in increased acidity and further reductions in pH_{PZC} for both recycled and virgin materials, indicating successful oxidation of the CF surface.

Table 8.2: Physical and chemical surface properties of CF-based adsorbents based on BET N₂ adsorption isotherm at 77K, Boehm titrations and potentiometric titrations.

Sample	S _{BET} (m²/g)	V _{micro} (cm³/g)	V _{total} (cm ³ /g)	N₂ isotherm (Hystersis)	Total acidity (mmol/g)	Total Basicity (mmol/g)	рН _{РZC}
rCF	48.94	-	0.07	Type (III)	-	-	-
vCF	27.13	-	0.04	Type (III)	-	-	-
K-ArCF-Opt	427.63	0.02	0.35	Type IV (H4)	3.01	2.32	3.95
K-AvCF-Opt	414.88	0.04	0.33	Type IV (H4)	0.25	0.03	4.34
mrCF-Opt	448.10	0.19	0.36	Type IV (H1)	4.97	2.31	3.25
mvCF-Opt	410.69	0.03	0.31	Type IV (H4)	3.02	0.33	3.17

Table 8.3 presents the elemental and proximate analysis results, offering insights into the composition of both precursor, activated and modified materials. These findings provide additional evidence of porosity development and the successful incorporation of surface functional groups during activation and modification processes.

Post-activation a reduction of reduced carbon and nitrogen levels and increased oxygen content (~19%) was observed, further confirming successful incorporation of oxygenated functional groups. Proximate analysis showed decreased fixed carbon and increased VOC, ash, and water content which was attributed to carbon burn-off, expulsion of potassium residues, and moisture adsorption.

Modification further improved material properties, reducing ash and volatile matter and increasing carbon and water content. The rise in water content suggests enhanced hydrophilicity, which can facilitate interaction with hydrophilic aqueous-phase contaminants. These changes support the broader goal of developing adsorbents suitable for water treatment applications.

Sample	Ul	timate An	alysis, (wt	%)	Proximate Analysis, (wt%)			
oumpie	С	Н	Ν	0	С	VOC	Water	Ash
rCF	93.87	0.28	4.07	1.78	93.21	2.84	0.00	3.95
vCF	95.32	0.43	3.32	0.93	92.80	4.82	0.00	2.38
K-ArCF- Opt	78.19	0.53	2.34	18.94	75.30	15.27	1.88	7.55
K-AvCF- Opt	78.20	0.53	1.88	19.39	73.66	13.67	4.70	7.97
mrCF- Opt	81.56	0.97	2.47	15.00	81.62	10.67	4.17	3.54
mvCF- Opt	81.39	0.28	2.92	15.41	78.57	10.49	7.03	3.88

Table 8.3: Composition of precursors and the activated and modified CF-based adsorbents.

8.3. Adsorption Performance

The adsorption performance of the developed materials was assessed both in terms of removal efficiency and adsorption capacity. Table 8.4 illustrates the significant improvement following activation and modification. The activation process was demonstrably effective, as indicated by the substantial enhancement in adsorption performance, where CIP removal increased from 5.85% to 96.47%, and OTC from 0.00% to 97.72%.

Following optimisation of the adsorption process, %-mrCF-Opt and %-K-ArCF-Opt demonstrated comparable adsorption performance for both CIP and OTC, with no statistically significant differences observed (CIP: p = 0.77; OTC: p = 0.27). This suggests that additional surface modification may not be essential for improving antibiotic adsorption under the conditions tested. However, further evaluation under more complex scenarios, such as competitive adsorption in the presence of dissolved organic matter (DOM), is recommended

to determine whether functionalisation enhances selectivity and performance in realistic environmental settings.

In addition, %-mrCF-Opt exhibited similar adsorption capacities to its vCF counterpart, with differences in CIP and OTC removal found to be statistically insignificant (CIP: p = 0.14; OTC: p = 0.73). These findings highlight the viability of rCF-derived materials as sustainable and effective adsorbents.

Table 8.4: Dual and independent response optimisation for the adsorption of CIP and OTC on K-ArCF-Opt and mrCF-Opt.

Sample	Optim	ium con	ditions	q _e (mg/g)		Removal (%)	
	Adsorbent dose (g/L)	рН	Initial conc (mg/L)	CIP	отс	CIP	отс
%-mrCF-Opt	0.8	2	2.0	2.361	2.423	96.47	97.72
%-K-ArCF-Opt	0.8	2	2.0	2.274	2.435	94.66	91.12
%-mvCF-Opt	0.8	2	2.0	2.406	2.406	99.86	96.26
%-K-AvCF-Opt	0.8	2	2.0	2.411	2.248	99.18	90.38
rCF-Opt	0.8	2	2	0.483	0.642	5.01	3.62
rCF	0.2	~5.5	2	0.583	0.000	5.85	0.00
mrCF-Opt	0.2	~5.5	2	9.633	7.716	89.96	76.71
mvCF-Opt	0.2	~5.5	2	8.108	6.597	81.93	66.15
q _e -mrCF-Opt	0.1	8	1.3	9.058	5.685	79.57	42.45
q _e -mrCF-CIP-Opt	0.1	8	0.5	16.716	19.433	81.94	89.56
q _e -mrCF-OTC-Opt	0.1	8	2.0	15.940	16.266	79.72	83.26
q _e -mvCF-Opt	0.1	8	1.3	11.060	5.855	89.26	45.84

Table 8.5 provides a summary of the key findings related to adsorption isotherms, kinetic modelling, and thermodynamic analysis. For CIP, both K-ArCF-Opt and mrCF-Opt exhibited increasing adsorption capacities with rising temperature, indicative of endothermic adsorption behaviour. However, adsorption performance varied between the two adsorbents

depending on temperature. At 20 °C, mrCF-Opt-CIP achieved the highest adsorption capacity (36.81 mg/g), outperforming K-ArCF-Opt-CIP (19.83 mg/g). However, at elevated temperatures (30 °C and 40 °C), K-ArCF-Opt-CIP outperformed its modified counterpart, reaching capacities of 47.38 and 53.21 mg/g, respectively, compared to 41.66 and 52.78 mg/g for mrCF-Opt-CIP.

Notably, mrCF-Opt-CIP exhibited the highest calculated heat of adsorption (+28.65 kJ/mol), suggesting stronger binding interactions with CIP at lower temperatures. This may explain its superior performance at 20 °C. Interestingly, while the Toth isotherm generally provided the best fit across all systems, the Langmuir model better described the equilibrium data for mrCF-Opt-CIP at 20 °C. This supports the presence of monolayer adsorption under these specific conditions and may also contribute to the observed shift in performance trends as temperature increases. Additionally, adsorption kinetics for both adsorbents followed the Avrami model, indicating complex, multi-step adsorption behaviour likely governed by a combination of surface diffusion and site heterogeneity.

Comula	q _e (mg/L)			Mode	el	Heat of	Regeneration Efficiency (%)	
Sample	20 °C	30 °C	40 °C	Equilibrium	Kinetic	(kJ/mol)	7 cycles 0.25 M KOH	
K-ArCF- Opt-CIP	19.83	47.38	53.21	Toth	Avrami	+21.01	-	
mrCF- Opt-CIP	36.81	41.66	52.78	Toth (Langmuir @ 20 °C)	Avrami	+28.65	76.38	
K-ArCF- Opt-OTC	220.66	41.09	34.09	Toth	Avrami	+101.46	-	
mrCF - Opt-OTC	10.32	50.99	46.99	Toth	Avrami	+37.11	78.91	

Table 8.5: Antibiotic adsorption behaviour.

For OTC, both adsorbents again followed the Toth isotherm and the Avrami kinetic model, consistent with a heterogeneous surface and complex adsorption kinetics. K-ArCF-OTC-Opt

demonstrated an exceptionally high adsorption capacity at 20 °C (220.66 mg/g), though its performance declined at elevated temperatures, possibly due to partial desorption or thermal sensitivity of the adsorbent–adsorbate complex. In contrast, mrCF-OTC-Opt showed a more stable adsorption profile across the temperature range and a higher heat of adsorption (+37.11 kJ/mol), indicating stronger and more thermally stable interactions with OTC.

8.4. Regeneration and Reusability

Although less commonly applied, chemical regeneration was utilised due to its applicability within an aquaculture setting, where the flow within an adsorption column could be diverted to a secondary tank containing the regenerant solution. Importantly, regeneration studies showed promising reusability, with mrCF-based adsorbents maintaining regeneration efficiencies of approximately 75% after seven cycles, when using 0.1 M KOH (Table 8.6. These findings support the potential of rCF-based adsorbents for sustainable, repeated use in water treatment applications.

Sample	Pollutant	Regenerant	Regeneration efficiency (%)	Ref
%-mrCF-Opt	CIP	0.1 М КОН	C1 – 108.93 C7 – 75.45	This work
%-mrCF-Opt	CIP	0.25 M KOH	C1 – 107.08 C7 – 76.38	This work
%-mrCF-Opt	отс	0.1 М КОН	C1 –109.76 C7 – 74.18	This work
%-mrCF-Opt	ОТС	0.25 M KOH	C1 – 103.25 C7 – 78.91	This work

Table 8.6: Summary of regeneration methods and efficiencies.

8.5. Implications for Aquaculture and Future Works

The findings of this study have clear implications for the development of practical, sustainable water treatment solutions within freshwater aquaculture systems. The optimised rCF-based adsorbents not only demonstrated strong performance in removing antibiotics such as CIP

and OTC, but also showed consistent reusability using mild, low-cost regeneration methods. These attributes make them highly suitable for integration into RAS, where water quality must be maintained without frequent water exchange.

Incorporating adsorption units into existing aquaculture infrastructure would allow for the passive and targeted removal of residual pharmaceuticals that accumulate in closed-loop systems. One feasible strategy is the retrofitting of adsorption columns within the water circulation loop, using modular filter beds packed with rCF-based adsorbents. The use of materials regenerated with mild reagents such as 0.1 M KOH also aligns well with on-site water treatment practices in aquaculture, where regenerant solutions could be stored and used in controlled cycles, minimising operational complexity and chemical hazards.

To ensure practical deployment, several design and operational factors must be considered. These include designing column dimensions to match the scale of water throughput, optimising the flow rate to ensure sufficient contact time and ensuring chemical compatibility of the adsorbents with typical RAS water chemistry, which may include high levels of organic matter or salts. The relatively low regeneration temperature requirements of the developed adsorbents also make them ideal for remote or low-energy settings, where access to advanced regeneration infrastructure is limited.

While the lab-scale performance of the adsorbents was robust under controlled conditions, real-world aquaculture environments present more complex challenges. Natural waters contain competing ions, DOM, and fluctuating pH and temperature conditions, all of which can influence adsorption performance. As such, future research should explore the performance of these adsorbents in multi-component systems, where competitive adsorption may occur, and assess their long-term stability and fouling resistance under continuous flow conditions.

Additional investigations into continuous adsorption systems (i.e. fixed-bed reactors), are essential for scaling up this technology. Understanding breakthrough behaviour, mass transfer limitations, and bed saturation dynamics will be critical for informing reactor design and operation schedules. Incorporating real-time monitoring and automated regeneration cycles may further improve operational efficiency and reduce maintenance burdens in commercial settings.

From a sustainability perspective, further studies should also examine the end-of-life handling of spent adsorbents. While regeneration extends material lifespan, eventual saturation or fouling may require disposal or alternative reuse strategies. Options such as carbon recovery, catalytic conversion, or integration into composite building materials could be explored as part of a circular economy approach.

In summary, this research supports the development of sustainable adsorption-based technologies for pharmaceutical removal in aquaculture. With further optimisation and pilot-scale validation, rCF-derived adsorbents have the potential to improve water quality, reduce chemical discharge, and enhance the environmental performance of fish farming operations.

9. Conclusion

Aquaculture is the fastest-growing food production industry globally and is increasingly recognised as a major contributor to the spread of AMR genes in aquatic environments. The World Health Organisation has identified AMR as one of the top ten global health threats. At the same time, the CFRP industry continues to expand, generating significant EoL waste with limited reuse infrastructure. In 2020, the UK reported that 35% of EoL carbon fibres were landfilled, 20% were recycled, and only 2% were reused, highlighting the environmental impact of inadequate disposal practices.

This research aimed to provide a novel, sustainable, and renewable solution to both of these challenges by developing high-performance adsorbents from rCFs for the removal of antibiotics used in aquaculture. A structured experimental approach was applied to optimise each stage of adsorbent development, and all four research objectives were successfully achieved.

The first objective, which focused on optimising the activation and modification of rCFs to enhance porosity and adsorption potential, was met through the application of DoE. Initial trials using sodium hydroxide produced limited porosity and low adsorption capacity, indicating incomplete activation. Subsequent optimisation using potassium hydroxide, at 670 °C with a CF:KOH ratio of 1:10 and a 0.5 h hold time, led to a significant increase in MB adsorption capacity (454.55 mg/g) while maintaining a reasonable yield (70.14%). Surface modification using nitric acid further introduced oxygen-containing functional groups and, in some cases, increased surface area due to the removal of impurities.

The second objective, involving characterisation of precursor, activated, modified, and spent materials, was fulfilled through a range of analytical techniques. Nitrogen adsorption isotherms, elemental and proximate analysis, SEM-EDS, FTIR, and Raman spectroscopy confirmed that chemical treatment significantly altered surface structure, composition, and functionality, thereby supporting enhanced adsorption capacity.

The third objective was achieved by conducting single-component batch adsorption and desorption experiments using CIP and OTC. DoE was applied to assess the influence of pH, adsorbent dose, and initial concentration, where high removal efficiencies above 95% were achieved under optimised conditions. Interestingly, additional surface modification did not
significantly enhance removal performance in most cases, suggesting that activation alone may be sufficient under simplified conditions.

The fourth objective was addressed through adsorption modelling. Both K-ArCF-Opt and mrCF-Opt were best described by the Toth isotherm and Avrami kinetic models, indicating heterogeneous surface adsorption and complex kinetic behaviour, possibly involving multilayer adsorption and adsorbate clustering. These insights were consistent with the material properties observed during characterisation.

The developed adsorbents also demonstrated strong reusability. Chemical regeneration using 0.1 M potassium hydroxide retained approximately 75% efficiency after seven cycles for both antibiotics, highlighting the materials' stability and practical potential for repeated use.

While the results are promising, there are limitations to consider. All adsorption and regeneration tests were conducted under controlled laboratory conditions using single-component systems. In real aquaculture environments, factors such as DOM, varying ionic strength and pH fluctuations may influence performance. Additionally, regeneration was evaluated in batch mode, and its effectiveness under continuous flow conditions remains to be investigated.

Despite these limitations, this study contributes meaningfully to both waste valorisation and water treatment. It demonstrates that industrial carbon fibre waste can be transformed into a reusable, high-efficiency adsorbent with relatively low chemical and energy input. The use of rCFs not only reduces material waste but also provides a practical solution for pharmaceutical removal from aquaculture wastewater, supporting more sustainable and circular practices.

Future research should investigate the behaviour of these adsorbents in multi-contaminant systems and assess their resistance to fouling in the presence of DOM. Further exploration of surface modification processes, particularly the effects of acid concentration, hold time, and temperature, may improve control over functional group formation. Additionally, understanding the aggregation behaviour of CIP and OTC under varying conditions could refine adsorption modelling and system design. Finally, optimising the regeneration process—including regenerant concentration, contact time, and temperature—will be key to ensuring long-term performance in practical applications.

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References

- Schar D, Klein EY, Laxminarayan R, Gilbert M, Van Boeckel TP. Global trends in antimicrobial use in aquaculture. Sci Rep [Internet]. 2020 Dec 14 [cited 2021 Feb 23];10(1):21878. Available from: https://doi.org/10.1038/s41598-020-78849-3
- Kaiser MJ, Jennings S, Collie JS, Hall SJ, Poiner IR, Kaiser MJ, et al. Impacts of fishing gear on marine benthic habitats . [cited 2021 Aug 2]; Available from: https://www.researchgate.net/publication/230659975
- What is Overfishing? Facts, Effects and Overfishing Solutions [Internet]. [cited 2024 Mar 17]. Available from: https://www.worldwildlife.org/threats/overfishing
- Boyd CE, McNevin AA. Aquaculture, Resource Use, and the Environment. Vol. 9780470959, Aquaculture, Resource Use, and the Environment. Wiley Blackwell; 2015. 1–337 p.
- Organisation WH. Antimicrobial Use in Aquaculture and Antimicrobial Resistance [Internet]. 2006. Available from: https://www.who.int/topics/foodborne_diseases/aquaculture_rep_13_16june2006 .pdf
- 6. Romero J, Feijoó CG, Navarrete P. 6 Antibiotics in Aquaculture-Use, Abuse and Alternatives [Internet]. [cited 2021 Apr 7]. Available from: www.intechopen.com
- Naylor RL, Hardy RW, Buschmann AH, Bush SR, Cao L, Klinger DH, et al. A 20-year retrospective review of global aquaculture. Nature 2021 591:7851 [Internet]. 2021 Mar 24 [cited 2024 Feb 15];591(7851):551–63. Available from: https://www.nature.com/articles/s41586-021-03308-6
- Buschmann AH, Tomova A, López A, Maldonado MA, Henríquez LA, Ivanova L, et al. Salmon Aquaculture and Antimicrobial Resistance in the Marine Environment. PLoS One [Internet]. 2012 Aug 8 [cited 2021 Aug 20];7(8):e42724. Available from: https://journals.plos.org/plosone/article?id=10.1371/journal.pone.0042724
- 9. Miranda CD, Godoy FA, Lee MR. Current status of the use of antibiotics and the antimicrobial resistance in the chilean salmon farms [Internet]. Vol. 9, Frontiers in

Microbiology. Frontiers Media S.A.; 2018 [cited 2021 Jun 8]. p. 1284. Available from: www.frontiersin.org

- Sapkota A, Sapkota AR, Kucharski M, Burke J, McKenzie S, Walker P, et al. Aquaculture practices and potential human health risks: Current knowledge and future priorities. Environ Int. 2008 Nov 1;34(8):1215–26.
- Van Doorslaer X, Dewulf J, Van Langenhove H, Demeestere K. Fluoroquinolone antibiotics: An emerging class of environmental micropollutants. Science of The Total Environment. 2014 Dec 1;500–501:250–69.
- Sun R, Chen J, Pan C, Sun Y, Mai B, Li QX. Antibiotics and food safety in aquaculture. J Agric Food Chem [Internet]. 2020 Oct 28 [cited 2022 Dec 12];68(43):11908–19. Available from: https://pubs.acs.org/doi/pdf/10.1021/acs.jafc.0c03996
- Taylor JH, Masoudi Soltani S. Carbonaceous adsorbents in the removal of aquaculture pollutants: A technical review of methods and mechanisms. Ecotoxicol Environ Saf [Internet]. 2023 Nov 1 [cited 2023 Oct 11];266:115552. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0147651323010564
- Kerry J, Coyne R, Gilroy D, Hiney M, Smith P. Spatial distribution of oxytetracycline and elevated frequencies of oxytetracycline resistance in sediments beneath a marine salmon farm following oxytetracycline therapy. Aquaculture. 1996 Oct 15;145(1– 4):31–9.
- 15. Björklund H V., Råbergh CMI, Bylund G. Residues of oxolinic acid and oxytetracycline in fish and sediments from fish farms. Aquaculture. 1991 Sep 1;97(1):85–96.
- Leal JF, Santos EBH, Esteves VI. Oxytetracycline in intensive aquaculture: water quality during and after its administration, environmental fate, toxicity and bacterial resistance. Rev Aquac [Internet]. 2019 Nov 1 [cited 2021 Aug 11];11(4):1176–94. Available from: https://onlinelibrary.wiley.com/doi/full/10.1111/raq.12286
- 17. Pereira AMPT, Silva LJG, Meisel LM, Pena A. Fluoroquinolones and Tetracycline Antibiotics in a Portuguese Aquaculture System and Aquatic Surroundings: Occurrence and Environmental Impact. Journal of Toxicology and Environmental Health - Part A:

Current Issues [Internet]. 2015 Aug 3 [cited 2021 Apr 8];78(15):959–75. Available from: http://www.tandfonline.com/doi/full/10.1080/15287394.2015.1036185

- Bondad-Reantaso MG, MacKinnon B, Karunasagar I, Fridman S, Alday-Sanz V, Brun E, et al. Review of alternatives to antibiotic use in aquaculture. Rev Aquac [Internet]. 2023 Sep 1 [cited 2024 Feb 19];15(4):1421–51. Available from: https://onlinelibrary.wiley.com/doi/full/10.1111/rag.12786
- 19. Antimicrobial resistance [Internet]. [cited 2021 Sep 29]. Available from: https://www.who.int/news-room/fact-sheets/detail/antimicrobial-resistance
- 20. 'Marston H 'Dixon, D 'Knisely, J. Antimicrobial Resistance. JAMA. 2016;
- Dadgostar P. Antimicrobial resistance: implications and costs. Infect Drug Resist [Internet]. 2019 [cited 2024 May 8];12:3903–10. Available from: https://www.tandfonline.com/action/journalInformation?journalCode=didr20
- 22. Naviner M, Gordon L, Giraud E, Denis M, Mangion C, Le Bris H, et al. Antimicrobial resistance of Aeromonas spp. isolated from the growth pond to the commercial product in a rainbow trout farm following a flumequine treatment. Aquaculture. 2011 May 21;315(3–4):236–41.
- 23. Gordon L, Giraud E, Ganière J-P, Armand F, Bouju-Albert A, Cotte ND La, et al. Antimicrobial resistance survey in a river receiving effluents from freshwater fish farms. J Appl Microbiol [Internet]. 2007 Apr 1 [cited 2021 Aug 10];102(4):1167–76. Available from: https://sfamjournals.onlinelibrary.wiley.com/doi/full/10.1111/j.1365-2672.2006.03138.x
- Tendencia EA, De La Peña LD. Antibiotic resistance of bacteria from shrimp ponds.
 Aquaculture. 2001 Apr 16;195(3–4):193–204.
- Ahmad AL, Chin JY, Mohd Harun MHZ, Low SC. Environmental impacts and imperative technologies towards sustainable treatment of aquaculture wastewater: A review. Journal of Water Process Engineering. 2022 Apr 1;46:102553.
- 26. Chai WS, Cheun JY, Kumar PS, Mubashir M, Majeed Z, Banat F, et al. A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application. J Clean Prod. 2021 May 10;296:126589.

- Chakraborty R, Asthana A, Singh AK, Jain B, Susan ABH. Adsorption of heavy metal ions by various low-cost adsorbents: a review. https://doi.org/101080/0306731920201722811 [Internet]. 2020 [cited 2021 Aug 19]; Available from: https://www.tandfonline.com/doi/abs/10.1080/03067319.2020.1722811
- 28. Aljeboree AM, Alshirifi AN. Adsorption of Pharmaceuticals as emerging contaminants from aqueous solutions on to friendly surfaces such as activated carbon: A review.
- 29. Zhang J, Chevali VS, Wang H, Wang CH. Current status of carbon fibre and carbon fibre composites recycling. Compos B Eng. 2020 Jul 15;193:108053.
- Karuppannan Gopalraj S, Kärki T. A review on the recycling of waste carbon fibre/glass fibre-reinforced composites: fibre recovery, properties and life-cycle analysis. SN Applied Sciences 2020 2:3 [Internet]. 2020 Feb 18 [cited 2021 Jul 30];2(3):1–21. Available from: https://link.springer.com/article/10.1007/s42452-020-2195-4
- 31. Nahil MA, Williams PT. Recycling of carbon fibre reinforced polymeric waste for the production of activated carbon fibres. J Anal Appl Pyrolysis. 2011 May 1;91(1):67–75.
- Chen JY. Activated Carbon Fibre and Textiles [Internet]. Activated Carbon Fiber and Textiles. Elsevier Science & Technology; 2016 [cited 2021 Jul 31]. 08–25 p. Available from: https://ebookcentral.proquest.com/lib/brunelu/detail.action?docID=4627945
- Hassan MF, Sabri MA, Fazal H, Hafeez A, Shezad N, Hussain M. Recent trends in activated carbon fibers production from various precursors and applications—A comparative review. Vol. 145, Journal of Analytical and Applied Pyrolysis. Elsevier B.V.; 2020. p. 104715.
- 34. Taylor JH, Troisi G, Masoudi Soltani S. Application of chemically-activated recycled carbon fibres for aqueous-phase adsorptions part I: Optimisation of activation process. Chemical Engineering Journal Advances. 2024 May 15;18:100591.
- 35. Pimenta S, Pinho ST. Recycling carbon fibre reinforced polymers for structural applications: Technology review and market outlook. Waste Management. 2011 Feb 1;31(2):378–92.

- Bledzki AK, Seidlitz H, Goracy K, Urbaniak M, Rösch JJ. Recycling of Carbon Fiber Reinforced Composite Polymers—Review—Part 1: Volume of Production, Recycling Technologies, Legislative Aspects. Polymers 2021, Vol 13, Page 300 [Internet]. 2021 Jan 19 [cited 2021 Aug 12];13(2):300. Available from: https://www.mdpi.com/2073-4360/13/2/300/htm
- Pakdel E, Kashi S, Varley R, Wang X. Recent progress in recycling carbon fibre reinforced composites and dry carbon fibre wastes. Resour Conserv Recycl. 2021 Mar 1;166:105340.
- 38. Vieira DR, Vieira RK, Chain MC. Strategy and management for the recycling of carbon fiber-reinforced polymers (CFRPs) in the aircraft industry: a critical review. http://dx.doi.org/101080/1350450920161204371 [Internet]. 2016 May 4 [cited 2021 Aug 12];24(3):214–23. Available from: https://www.tandfonline.com/doi/abs/10.1080/13504509.2016.1204371
- Wang J, Zhao F, Hu Y, Zhao R, Liu R. Modification of Activated Carbon Fiber by Loading Metals and Their Performance on SO2 Removal. Chin J Chem Eng. 2006 Aug 1;14(4):478–85.
- Ge Y, Cheng B, Wang X, Zhao T. Rapid Preparation of Activated Carbon Fiber Felt under Microwaves: Pore Structures, Adsorption of Tetracycline in Water, and Mechanism. Ind Eng Chem Res [Internet]. 2020 Jan 8 [cited 2022 Nov 19];59(1):146–53. Available from: https://pubs.acs.org/doi/full/10.1021/acs.iecr.9b04259
- Zhao X, Jia B, Sun Q, Jiao G, Liu L, She D. Removal of Cr6+ ions from water by electrosorption on modified activated carbon fibre felt. R Soc Open Sci [Internet]. 2018
 Sep 1 [cited 2022 Nov 21];5(9). Available from: https://royalsocietypublishing.org/doi/10.1098/rsos.180472
- Wang S, Li X, Zhao H, Quan X, Chen S, Yu H. Enhanced adsorption of ionizable antibiotics on activated carbon fiber under electrochemical assistance in continuous-flow modes. Water Res. 2018 May 1;134:162–9.
- 43. Taylor J, Babamohammadi S, Troisi G, Masoudi Soltani S. Chemical Activation of Recycled Carbon Fibres for Application as Porous Adsorbents in Aqueous Media

[Internet]. [cited 2022 Nov 17]. Available from: https://ieeexplore.ieee.org/stamp/stamp.jsp?tp=&arnumber=9928646

- Ighalo JO, Iwuozor KO, Igwegbe CA, Adeniyi AG. Verification of pore size effect on aqueous-phase adsorption kinetics: A case study of methylene blue. Colloids Surf A Physicochem Eng Asp. 2021 Oct 5;626:127119.
- Gang D, Uddin Ahmad Z, Lian Q, Yao L, Zappi ME. A review of adsorptive remediation of environmental pollutants from aqueous phase by ordered mesoporous carbon. Chemical Engineering Journal. 2021 Jan 1;403:126286.
- 46. Food and Agriculture Organisation of the United Nations. History of aquaculture
 [Internet]. [cited 2024 Jun 19]. Available from: https://www.fao.org/4/ag158e/AG158E02.htm
- 47. FAO. Fisheries and Aquaculture Global Statistical Collections. Rome: FishStatJ (v4.04.00); 2020.
- Ahmad AL, Chin JY, Mohd Harun MHZ, Low SC. Environmental impacts and imperative technologies towards sustainable treatment of aquaculture wastewater: A review. Journal of Water Process Engineering. 2022 Apr 1;46:102553.
- 49. Shah SQA, Cabello FC, L'Abée-Lund TM, Tomova A, Godfrey HP, Buschmann AH, et al. Antimicrobial resistance and antimicrobial resistance genes in marine bacteria from salmon aquaculture and non-aquaculture sites. Environ Microbiol [Internet]. 2014 May 1 [cited 2021 Aug 20];16(5):1310–20. Available from: https://sfamjournals.onlinelibrary.wiley.com/doi/full/10.1111/1462-2920.12421
- Hossain A, Habibullah-Al-Mamun M, Nagano I, Masunaga S, Kitazawa D, Matsuda H. Antibiotics, antibiotic-resistant bacteria, and resistance genes in aquaculture: risks, current concern, and future thinking. Environmental Science and Pollution Research [Internet]. 2022 Feb 1 [cited 2024 Mar 27];29(8):11054–75. Available from: https://link.springer.com/article/10.1007/s11356-021-17825-4
- 51. Reverter M, Sarter S, Caruso D, Avarre JC, Combe M, Pepey E, et al. Aquaculture at the crossroads of global warming and antimicrobial resistance. Nature Communications

2020 11:1 [Internet]. 2020 Apr 20 [cited 2022 Jun 9];11(1):1–8. Available from: https://www.nature.com/articles/s41467-020-15735-6

- Watts JEM, Schreier HJ, Lanska L, Hale MS. The Rising Tide of Antimicrobial Resistance in Aquaculture: Sources, Sinks and Solutions. Mar Drugs [Internet]. 2017 Jun 1 [cited 2022 Aug 1];15(6). Available from: /pmc/articles/PMC5484108/
- 53. Romano N. Husbandry of aquatic animals in closed aquaculture systems. Aquaculture Health Management: Design and Operation Approaches. 2020 Jan 1;17–73.
- 54. Sievers M, Korsøen Ø, Warren-Myers F, Oppedal F, Macaulay G, Folkedal O, et al. Submerged cage aquaculture of marine fish: A review of the biological challenges and opportunities. Rev Aquac [Internet]. 2022 Jan 1 [cited 2024 Jun 15];14(1):106–19. Available from: https://onlinelibrary.wiley.com/doi/full/10.1111/raq.12587
- 55. Cherian T, Ragavendran C, Vijayan S, Kurien S, Peijnenburg WJGM. A review on the fate, human health and environmental impacts, as well as regulation of antibiotics used in aquaculture. Environmental Advances. 2023 Oct 1;13:100411.
- Mongirdas V, Žibienė G, Žibas A. WASTE AND ITS CHARACTERIZATION IN CLOSED RECIRCULATING AQUACULTURE SYSTEMS-A REVIEW. Journal of Water Security. 2017;3:2017002.
- Naghavi M, Vollset SE, Ikuta KS, Swetschinski LR, Gray AP, Wool EE, et al. Global burden of bacterial antimicrobial resistance 1990–2021: a systematic analysis with forecasts to 2050. The Lancet [Internet]. 2024 Sep 28 [cited 2025 Jan 5];404(10459):1199–226. Available from: http://www.thelancet.com/article/S0140673624018671/fulltext
- 58. Cabello FC, Godfrey HP, Buschmann AH, Dölz HJ. Aquaculture as yet another environmental gateway to the development and globalisation of antimicrobial resistance. Lancet Infect Dis. 2016 Jul 1;16(7):e127–33.
- 59. Liu X, Steele JC, Meng XZ. Usage, residue, and human health risk of antibiotics in Chinese aquaculture: A review. Environmental Pollution. 2017 Apr 1;223:161–9.
- 60. Lulijwa R, Rupia EJ, Alfaro AC. Antibiotic use in aquaculture, policies and regulation, health and environmental risks: a review of the top 15 major producers. Rev Aquac

[Internet]. 2020 May 1 [cited 2022 Dec 12];12(2):640–63. Available from: https://onlinelibrary.wiley.com/doi/full/10.1111/raq.12344

- Richeng X, Arisi L, Wang Q, Yates SR, Biswas KC. Hydrolysis and photolysis of oxytetracycline in aqueous solution. Journal of Environmental Science and Health Part B. 2010;45:73–81.
- Yang X, Chen Z, Zhao W, Liu C, Qian X, Zhang M, et al. Recent advances in photodegradation of antibiotic residues in water. Chemical Engineering Journal. 2021 Feb 1;405:126806.
- Han P, Lu Q, Fan L, Zhou W. A Review on the Use of Microalgae for Sustainable Aquaculture. Applied Sciences 2019, Vol 9, Page 2377 [Internet]. 2019 Jun 11 [cited 2024 Jun 28];9(11):2377. Available from: https://www.mdpi.com/2076-3417/9/11/2377/htm
- Silva CP, Louros V, Silva V, Otero M, Lima DLD. Antibiotics in Aquaculture Wastewater: Is It Feasible to Use a Photodegradation-Based Treatment for Their Removal? Toxics 2021, Vol 9, Page 194 [Internet]. 2021 Aug 21 [cited 2024 Jul 3];9(8):194. Available from: https://www.mdpi.com/2305-6304/9/8/194/htm
- Ahmad AL, Chin JY, Mohd Harun MHZ, Low SC. Environmental impacts and imperative technologies towards sustainable treatment of aquaculture wastewater: A review. Journal of Water Process Engineering. 2022 Apr 1;46:102553.
- 66. Wan Mahari WA, Waiho K, Azwar E, Fazhan H, Peng W, Ishak SD, et al. A state-of-theart review on producing engineered biochar from shellfish waste and its application in aquaculture wastewater treatment. Chemosphere. 2022 Feb 1;288:132559.
- McNaught A, Wilkinson A. IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). [Internet]. 2nd ed. The IUPAC Compendium of Chemical Terminology. Research Triangle Park, NC: Blackwell Scientific Publications,; 1997 [cited 2021 Jul 31]. Available from: https://goldbook.iupac.org/terms/view/C00831
- Bhatt P, Goe A. Carbon Fibres: Production, Properties and Potential Use. Material Science Research India. 2017 Jun 28;14(1):52–7.

- Yusof N, Ismail AF. Post spinning and pyrolysis processes of polyacrylonitrile (PAN)based carbon fiber and activated carbon fiber: A review. J Anal Appl Pyrolysis. 2012 Jan 1;93:1–13.
- Ryu Z, Rong H, Zheng J, Wang M, Zhang B. Microstructure and chemical analysis of PANbased activated carbon fibers prepared by different activation methods. Vol. 40, Carbon. Elsevier Ltd; 2002. p. 1144–7.
- Perepelkin KE. Carbon Fibres with Specific Physical and Physicochemical Properties Based on Hydrated Cellulose and Polyacrylonitrile Precursors. A Review. Fibre Chemistry 2002 34:4 [Internet]. 2002 [cited 2021 Aug 1];34(4):271–80. Available from: https://link.springer.com/article/10.1023/A:1021097032162
- Zhang J, Lin G, Vaidya U, Wang H. Past, present and future prospective of global carbon fibre composite developments and applications. Compos B Eng. 2023 Feb 1;250:110463.
- 73. Changing the World with New Materials. A Half-Century History of CFRP. Revista MMC
 | MITSUBISHI MATERIALS CORPORATION [Internet]. [cited 2024 Jul 17]. Available from: https://www.mmc-carbide.com/mx/download/magazine/vol05/tec_vol05
- 74. O'Malley C. Life Cycle Analysis of the Airbus A350 to Identify Opportunities to Improve Aircraft SustainabilityNo Title. 2018;
- 75. IATA Aircraft Decommissioning [Internet]. [cited 2021 Jul 31]. Available from: https://www.iata.org/en/programs/environment/aircraft-decommissioning/
- 76. Pickering SJ. Recycling technologies for thermoset composite materials—current status. Compos Part A Appl Sci Manuf. 2006 Aug 1;37(8):1206–15.
- de Carvalho Costa LR, de Moraes Ribeiro L, Hidalgo GEN, Féris LA. Evaluation of efficiency and capacity of thermal, chemical and ultrasonic regeneration of tetracycline exhausted activated carbon. Environ Technol [Internet]. 2022 Mar 8 [cited 2023 Dec 19];43(6):907–17. Available from: https://www.tandfonline.com/doi/abs/10.1080/09593330.2020.1811391

- 78. Naqvi SR, Prabhakara HM, Bramer EA, Dierkes W, Akkerman R, Brem G. A critical review on recycling of end-of-life carbon fibre/glass fibre reinforced composites waste using pyrolysis towards a circular economy. Resour Conserv Recycl. 2018 Sep 1;136:118–29.
- 79. Perry N, Bernard A, Laroche F, Pompidou S. Improving design for recycling Application to composites. CIRP Annals. 2012 Jan 1;61(1):151–4.
- Lopez-Urionabarrenechea A, Gastelu N, Acha E, Caballero BM, Orue A, Jiménez-Suárez
 A, et al. Reclamation of carbon fibers and added-value gases in a pyrolysis-based composites recycling process. J Clean Prod. 2020 Nov 10;273:123173.
- Alsaadi M, Bulut M, Erkliğ A, Jabbar A. Nano-silica inclusion effects on mechanical and dynamic behavior of fiber reinforced carbon/Kevlar with epoxy resin hybrid composites. Compos B Eng. 2018 Nov 1;152:169–79.
- Dass K, Chauhan SR, Gaur B. Study on the effects of nano-aluminum-oxide particulates on mechanical and tribological characteristics of chopped carbon fiber reinforced epoxy composites. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications [Internet]. 2017 Jun 1 [cited 2024 Jan 5];231(4):403–22. Available from: https://journals.sagepub.com/doi/10.1177/1464420715598798
- Singh SK, Kumar A, Jain A. Effect of nanoparticles dispersion on viscoelastic properties of epoxy–zirconia polymer nanocomposites. IOP Conf Ser Mater Sci Eng [Internet].
 2018 Mar 1 [cited 2024 Jan 5];330(1):012001. Available from: https://iopscience.iop.org/article/10.1088/1757-899X/330/1/012001
- 84. Effect of nanoparticles dispersion on viscoelastic properties of epoxy-zirconia polymer nanocomposites.
- 85. Suresh.J. S, Devi DrMP, Sasidhar Dr. M. Effect on Mechanical Properties of Epoxy Hybrid Composites Modified with Titanium Oxide (TiO2) and Silicon Carbide (SiC). 2017;
- Isa A, Nosbi N, Che Ismail M, Md Akil H, Wan Ali WFF, Omar MF. A Review on Recycling of Carbon Fibres: Methods to Reinforce and Expected Fibre Composite Degradations. Materials 2022, Vol 15, Page 4991 [Internet]. 2022 Jul 18 [cited 2024 Jan 5];15(14):4991. Available from: https://www.mdpi.com/1996-1944/15/14/4991/htm

- Tamai H, Yoshida T, Sasaki M, Yasuda H. Dye adsorption on mesoporous activated carbon fiber obtained from pitch containing yttrium complex. Carbon N Y. 1999 Jan 1;37(6):983–9.
- Ajala OA, Akinnawo SO, Bamisaye A, Adedipe DT, Adesina MO, Okon-Akan OA, et al. Adsorptive removal of antibiotic pollutants from wastewater using biomass/biocharbased adsorbents. RSC Adv [Internet]. 2023 Jan 1 [cited 2024 Mar 30];13(7):4678. Available from: /pmc/articles/PMC9897205/
- 89. Chandrasekaran A, Patra C, Narayanasamy S, Subbiah S. Adsorptive removal of Ciprofloxacin and Amoxicillin from single and binary aqueous systems using acidactivated carbon from Prosopis juliflora. Environ Res. 2020 Sep 1;188:109825.
- Maciá-Agulló JA, Moore BC, Cazorla-Amorós D, Linares-Solano A. Activation of coal tar pitch carbon fibres: Physical activation vs. chemical activation. In: Carbon. Elsevier Ltd; 2004. p. 1367–70.
- 91. Marsh H, Rodríguez-Reinoso F. Activation Processes (Thermal or Physical). Activated Carbon. 2006 Jan 1;243–321.
- Sajjadi B, Chen WY, Egiebor NO. A comprehensive review on physical activation of biochar for energy and environmental applications. Reviews in Chemical Engineering [Internet]. 2019 Aug 1 [cited 2023 Jan 25];35(6):735–76. Available from: https://www.degruyter.com/document/doi/10.1515/revce-2017-0113/html
- 93. Ruiz-Fernández M, Alexandre-Franco M, Fernández-González C, Gómez-Serrano V. Development of activated carbon from vine shoots by physical and chemical activation methods. Some insight into activation mechanisms. Adsorption [Internet]. 2011 Jun 4 [cited 2023 Jan 25];17(3):621–9. Available from: https://link.springer.com/article/10.1007/s10450-011-9347-1
- 94. Hermann G, HÜttinger KJ. Mechanism of water vapour gasification of carbon-A new model. Carbon N Y. 1986;24(6):705–13.
- Gorbounov M, Taylor J, Petrovic B, Masoudi Soltani S. To DoE or not to DoE? A Technical Review on & Roadmap for Optimisation of Carbonaceous Adsorbents and Adsorption Processes. S Afr J Chem Eng. 2022 Jul 1;41:111–28.

- 96. Choi YJ, Kim JH, Lee KB, Lee YS, Im JS. Correlation verification of process factors and harmful gas adsorption properties for optimization of physical activation parameters of PAN-based carbon fibers. Journal of Industrial and Engineering Chemistry. 2019 Dec 25;80:152–9.
- 97. Park S-J, Kim K-D. Influence of activation temperature on adsorption characteristics of activated carbon fiber composites. Carbon N Y. 2001;39:1741–6.
- Ryu Z, Zheng J, Wang M, Zhang B. Nitrogen Adsorption Studies of PAN-Based Activated Carbon Fibers Prepared by Different Activation Methods. J Colloid Interface Sci. 2000 Oct 15;230(2):312–9.
- 99. Kim K-W, Lee H-M, Kang S-H, Kim B-J. Synthesis and Characterization of Activated Carbon Fibers Derived from Linear Low-Density Polyethylene Fibers Stabilized at a Low Temperature. Polymers (Basel). 2021 Nov 12;13(3918).
- Ma X, Yang H, Yu L, Chen Y, Li Y. Preparation, Surface and Pore Structure of High Surface Area Activated Carbon Fibers from Bamboo by Steam Activation. Materials 2014, Vol 7, Pages 4431-4441 [Internet]. 2014 Jun 12 [cited 2024 Jul 18];7(6):4431–41. Available from: https://www.mdpi.com/1996-1944/7/6/4431/htm
- 101. Williams PT, Reed AR. Development of activated carbon pore structure via physical and chemical activation of biomass fibre waste. Biomass Bioenergy. 2006 Feb 1;30(2):144–52.
- 102. Ncibi MC, Jeanne-Rose V, Mahjoub B, Jean-Marius C, Lambert J, Ehrhardt JJ, et al. Preparation and characterisation of raw chars and physically activated carbons derived from marine Posidonia oceanica (L.) fibres. J Hazard Mater. 2009 Jun 15;165(1–3):240– 9.
- Maciá-Agulló JA, Moore BC, Cazorla-Amorós D, Linares-Solano A. Activation of coal tar pitch carbon fibres: Physical activation vs. chemical activation. Carbon N Y. 2004 Jan 1;42(7):1367–70.
- 104. Zhao N, He C, Jiang Z, Li J, Li Y. Physical activation and characterization of multi-walled carbon nanotubes catalytically synthesized from methane. Mater Lett. 2007 Feb 1;61(3):681–5.

- Aik Chong Lua, Guo J. Preparation and characterization of activated carbons from oilpalm stones for gas-phase adsorption. Colloids Surf A Physicochem Eng Asp. 2001 Jan 30;179(2–3):151–62.
- 106. Marsh H, Rodríguez-Reinoso F. Activation Processes (Chemical). Activated Carbon.2006 Jan 1;322–65.
- 107. Rio S, Faur-Brasquet C, Coq L Le, Courcoux P, Cloirec P Le. Experimental design methodology for the preparation of carbonaceous sorbents from sewage sludge by chemical activation—application to air and water treatments. Chemosphere. 2005 Jan 1;58(4):423–37.
- 108. Hoseinzadeh Hesas R, Arami-Niya A, Wan Daud WMA, Sahu JN. Preparation of granular activated carbon from oil palm shell by microwave-induced chemical activation: Optimisation using surface response methodology. Chemical Engineering Research and Design. 2013 Dec 1;91(12):2447–56.
- 109. Jorda M. High surface area carbon nanotubes prepared by chemical activation. 2002;
- 110. Lillo-Ródenas MA, Cazorla-Amorós D, Linares-Solano A. Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism. Carbon N Y. 2003 Feb 1;41(2):267–75.
- 111. Din M, Ashraf S, progress AI-S, 2017 undefined. Comparative study of different activation treatments for the preparation of activated carbon: a mini-review. journals.sagepub.com [Internet]. 2017 Sep 1 [cited 2023 Jan 26];100(3):299–312. Available from: https://journals.sagepub.com/doi/pdf/10.3184/003685017X14967570531606
- 112. Neme I, Gonfa G, Masi C. Activated carbon from biomass precursors using phosphoric acid: A review. Heliyon. 2022 Dec 1;8(12):e11940.
- 113. Wang M, Li G, Huang L, Xue J, Liu Q, Bao N, et al. Study of ciprofloxacin adsorption and regeneration of activated carbon prepared from Enteromorpha prolifera impregnated with H3PO4 and sodium benzenesulfonate. Ecotoxicol Environ Saf. 2017 May 1;139:36–42.

- Martín-Gullón I, Andrews R, Jagtoyen M, Derbyshire F. PAN-based activated carbon fiber composites for sulfur dioxide conversion: Influence of fiber activation method. Fuel. 2001 May 1;80(7):969–77.
- 115. Alkathiri DSS, Sabri MA, Ibrahim TH, ElSayed YA, Jumean F. Development of activated carbon fibers for removal of organic contaminants. International Journal of Environmental Science and Technology [Internet]. 2020 Dec 1 [cited 2021 Mar 3];17(12):4841–52. Available from: https://doi.org/10.1007/s13762-020-02808-8
- 116. Gao Y, Yue Q, Gao B, Li A. Insight into activated carbon from different kinds of chemical activating agents: A review. Science of The Total Environment. 2020 Dec 1;746:141094.
- 117. Shen W, Zhang S, He Y, Li J, Fan W. Hierarchical porous polyacrylonitrile-based activated carbon fibers for CO2 capture. J Mater Chem [Internet]. 2011 Sep 28 [cited 2021 Mar 4];21(36):14036–40. Available from: www.rsc.org/materials
- 118. Lu AH, Zheng JT. Study of microstructure of high-surface-area polyacrylonitrile activated carbon fibers. J Colloid Interface Sci. 2001 Apr 15;236(2):369–74.
- Okman I, Karagöz S, Tay T, Erdem M. Activated Carbons From Grape Seeds By Chemical Activation With Potassium Carbonate And Potassium Hydroxide. Appl Surf Sci. 2014 Feb 28;293:138–42.
- 120. Jawad AH, Razuan R, Appaturi JN, Wilson LD. Adsorption and mechanism study for methylene blue dye removal with carbonized watermelon (Citrullus lanatus) rind prepared via one-step liquid phase H2SO4 activation. Surfaces and Interfaces. 2019 Sep 1;16:76–84.
- 121. Rahman A, Hango HJ, Daniel LS, Uahengo V, Jaime SJ, Bhaskaruni SVHS, et al. Chemical preparation of activated carbon from Acacia erioloba seed pods using H2SO4 as impregnating agent for water treatment: An environmentally benevolent approach. J Clean Prod. 2019 Nov 10;237:117689.
- 122. Dao TM, Le Luu T. Synthesis of activated carbon from macadamia nutshells activated by H2SO4 and K2CO3 for methylene blue removal in water. Bioresour Technol Rep. 2020 Dec 1;12:100583.

- 123. Neolaka YAB, Lawa Y, Naat J, Riwu AAP, Darmokoesoemo H, Widyaningrum BA, et al. Indonesian Kesambi wood (Schleichera oleosa) activated with pyrolysis and H2SO4 combination methods to produce mesoporous activated carbon for Pb(II) adsorption from aqueous solution. Environ Technol Innov. 2021 Nov 1;24:101997.
- 124. Han Q, Wang J, Goodman BA, Xie J, Liu Z. High adsorption of methylene blue by activated carbon prepared from phosphoric acid treated eucalyptus residue. Powder Technol. 2020 Apr 15;366:239–48.
- 125. Liu B, Du C, Chen JJ, Zhai JY, Wang Y, Li HL. Preparation of well-developed mesoporous activated carbon fibers from plant pulp fibers and its adsorption of methylene blue from solution. Chem Phys Lett. 2021 May 16;771:138535.
- 126. Baek J, Lee HM, An KH, Kim BJ. Preparation and characterization of highly mesoporous activated short carbon fibers from kenaf precursors. Carbon Letters [Internet]. 2019
 Aug 1 [cited 2023 Apr 9];29(4):393–9. Available from: https://link.springer.com/article/10.1007/s42823-019-00042-y
- 127. Tan IAW, Chan JC, Hameed BH, Lim LLP. Adsorption behavior of cadmium ions onto phosphoric acid-impregnated microwave-induced mesoporous activated carbon. Journal of Water Process Engineering. 2016 Dec 1;14:60–70.
- 128. Canales-Flores RA, Prieto-García F. Taguchi optimization for production of activated carbon from phosphoric acid impregnated agricultural waste by microwave heating for the removal of methylene blue. Diam Relat Mater. 2020 Nov 1;109:108027.
- 129. Pietrzak R, Nowicki P, Kaźmierczak J, Kuszyńska I, Goscianska J, Przepiórski J. Comparison of the effects of different chemical activation methods on properties of carbonaceous adsorbents obtained from cherry stones. Chemical Engineering Research and Design. 2014 Jun 1;92(6):1187–91.
- 130. Illingworth JM, Rand B, Williams PT. Understanding the mechanism of two-step, pyrolysis-alkali chemical activation of fibrous biomass for the production of activated carbon fibre matting. Fuel Processing Technology. 2022 Oct 1;235:107348.

- Maciá-Agulló JA, Moore BC, Cazorla-Amorós D, Linares-Solano A. Influence of carbon fibres crystallinities on their chemical activation by KOH and NaOH. Microporous and Mesoporous Materials. 2007 Apr 20;101(3):397–405.
- 132. Rehman A, Park M, Park S-J. Current Progress on the Surface Chemical Modification of Carbonaceous Materials. 2019; Available from: www.mdpi.com/journal/coatings
- Lach J, Ociepa-Kubicka A, Mrowiec M. Oxytetracycline Adsorption from Aqueous Solutions on Commercial and High-Temperature Modified Activated Carbons. Energies 2021, Vol 14, Page 3481 [Internet]. 2021 Jun 11 [cited 2024 Jul 24];14(12):3481. Available from: https://www.mdpi.com/1996-1073/14/12/3481/htm
- 134. Kim DG, Boldbaatar S, Ko SO. Enhanced Adsorption of Tetracycline by Thermal Modification of Coconut Shell-Based Activated Carbon. Int J Environ Res Public Health [Internet]. 2022 Nov 1 [cited 2024 Jul 2];19(21):13741. Available from: https://www.mdpi.com/1660-4601/19/21/13741/htm
- 135. Yu J, Chi C, Zhu B, Qiao K, Cai X, Cheng Y, et al. High adsorptivity and recycling performance activated carbon fibers for Cu(II) adsorption. Science of The Total Environment. 2020 Jan 15;700:134412.
- 136. Peng X, Hu F, Zhang T, Qiu F, Dai H. Amine-functionalized magnetic bamboo-based activated carbon adsorptive removal of ciprofloxacin and norfloxacin: A batch and fixed-bed column study. Bioresour Technol. 2018 Feb 1;249:924–34.
- 137. Huang CC, Su YJ. Removal of copper ions from wastewater by adsorption/electrosorption on modified activated carbon cloths. J Hazard Mater. 2010 Mar 15;175(1–3):477–83.
- 138. Oda H, Yamashita A, Minoura S, Okamoto M, Morimoto T. Modification of the oxygencontaining functional group on activated carbon fiber in electrodes of an electric double-layer capacitor. J Power Sources. 2006 Aug 25;158(2):1510–6.
- 139. Qin Q, Wu X, Chen L, Jiang Z, Xu Y. Simultaneous removal of tetracycline and Cu(II) by adsorption and coadsorption using oxidized activated carbon. RSC Adv [Internet]. 2018 Jan 5 [cited 2022 Mar 24];8(4):1744–52. Available from: https://pubs.rsc.org/en/content/articlehtml/2018/ra/c7ra12402c

- 140. Demiral İ, Samdan C, Demiral H. Enrichment of the surface functional groups of activated carbon by modification method. Surfaces and Interfaces. 2021 Feb 1;22:100873.
- 141. Khan I, Huang S, Wu C, Yarlagadda V, Lin G, Chong Y, et al. Acid modified multiwalled carbon nanotubes condition by reflux. Mater Res Express [Internet]. 2019 [cited 2022 Nov 22];6:115003. Available from: https://doi.org/10.1088/2053-1591/ab4396
- 142. Turk Sekulic M, Boskovic N, Slavkovic A, Garunovic J, Kolakovic S, Pap S. Surface functionalised adsorbent for emerging pharmaceutical removal: Adsorption performance and mechanisms. Process Safety and Environmental Protection. 2019 May 1;125:50–63.
- 143. Yang H, Liu H, Zhou K, Yan ZQ, Zhao R, Liu ZH, et al. Oxidation path analysis of NO in the adsorption and removal process using activated carbon fibers. Journal of Fuel Chemistry and Technology. 2012 Aug 1;40(8):1002–8.
- 144. Rong H, Ryu Z, Zheng J, Zhang Y. Influence of heat treatment of rayon-based activated carbon fibers on the adsorption of formaldehyde. J Colloid Interface Sci [Internet]. 2003
 May 15 [cited 2023 Apr 10];261(2):207–12. Available from: https://pubmed.ncbi.nlm.nih.gov/16256524/
- Bai BC, Kim EA, Lee CW, Lee YS, Im JS. Effects of surface chemical properties of activated carbon fibers modified by liquid oxidation for CO2 adsorption. Appl Surf Sci. 2015 Oct 30;353:158–64.
- 146. Guedidi H, Reinert L, Soneda Y, Bellakhal N, Duclaux L. Adsorption of ibuprofen from aqueous solution on chemically surface-modified activated carbon cloths. Arabian Journal of Chemistry. 2017 May 1;10:S3584–94.
- 147. Park SJ, Kim BJ. Influence of oxygen plasma treatment on hydrogen chloride removal of activated carbon fibers. J Colloid Interface Sci. 2004 Jul 15;275(2):590–5.
- 148. Bai BC, Lee HU, Lee CW, Lee YS, Im JS. N2 plasma treatment on activated carbon fibers for toxic gas removal: Mechanism study by electrochemical investigation. Chemical Engineering Journal. 2016 Dec 15;306:260–8.

- 149. Lu C, Chiu H. Chemical modification of multiwalled carbon nanotubes for sorption of Zn2+ from aqueous solution. Chemical Engineering Journal. 2008 Jun 15;139(3):462–8.
- Xiang Y, Xu Z, Wei Y, Zhou Y, Yang X, Yang Y, et al. Carbon-based materials as adsorbent for antibiotics removal: Mechanisms and influencing factors. J Environ Manage. 2019 May 1;237:128–38.
- 151. Rivera-Utrilla J, Gómez-Pacheco C V., Sánchez-Polo M, López-Peñalver JJ, Ocampo-Pérez R. Tetracycline removal from water by adsorption/bioadsorption on activated carbons and sludge-derived adsorbents. J Environ Manage. 2013 Dec 15;131:16–24.
- 152. Bajpai' AK, Rajpoot M. Adsorption Techniques A Review. J Sci Ind Res (India). 1999;1:844–60.
- 153. Barakat MA. New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry. 2011 Oct 1;4(4):361–77.
- 154. Kern M, Škulj S, Rožman M. Adsorption of a wide variety of antibiotics on graphenebased nanomaterials: A modelling study. Chemosphere. 2022 Jun 1;296:134010.
- 155. Spanjaard D, Desjonquères MC. Electronic Theory of Chemisorption. Interaction of Atoms and Molecules with Solid Surfaces [Internet]. 1990 [cited 2024 Jul 2];255–323. Available from: https://link.springer.com/chapter/10.1007/978-1-4684-8777-0_9
- 156. Sandhyarani N. Surface modification methods for electrochemical biosensors. Electrochemical Biosensors. 2019 Jan 1;45–75.
- Hadjittofis E, Das SC, Zhang GGZ, Heng JYY. Interfacial Phenomena. Developing Solid Oral Dosage Forms: Pharmaceutical Theory and Practice: Second Edition. 2017 Jan 1;225–52.
- 158. West A. Intermolecular Forces and Solvation. Interface Science and Technology. 2018 Jan 1;21:49–130.
- 159. Schaeffer L. The Role of Functional Groups in Drug–Receptor Interactions. The Practice of Medicinal Chemistry: Fourth Edition. 2008 Jan 1;359–78.
- Spanjaard D, Desjonqueres MC. Electronic Theory of Chemisorption. In: Interaction of Atoms and Molecules with Solid Surfaces. Springer; 1990. p. 255–323.

- 161. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc [Internet]. 1918 Sep 1 [cited 2022 Nov 28];40(9):1361–403. Available from: https://pubs.acs.org/doi/abs/10.1021/ja02242a004
- 162. Tóth J. Uniform interpretation of gas/solid adsorption. Adv Colloid Interface Sci. 1995 Mar 1;55(C):1–239.
- 163. Sips R. On the Structure of a Catalyst Surface. J Chem Phys [Internet]. 2004 Dec 22 [cited 2023 Apr 12];16(5):490. Available from: https://aip.scitation.org/doi/abs/10.1063/1.1746922
- 164. Redlich O, Peterson DL. A useful adsorption isotherm. J Phys Chem [Internet]. 1959 Jun
 1 [cited 2023 Apr 12];63(6):1024–1024. Available from: https://typeset.io/papers/a-useful-adsorption-isotherm-2y2dkn79q5
- 165. Flory PJ. Thermodynamics of High Polymer Solutions. J Chem Phys [Internet]. 1942 Dec
 22 [cited 2023 Apr 12];10(1):51. Available from: https://aip.scitation.org/doi/abs/10.1063/1.1723621
- 166. Huggins ML. Theory of Solutions of High Polymers. J Am Chem Soc [Internet]. 1942 Jul
 1 [cited 2023 Apr 12];64(7):1712–9. Available from: https://pubs.acs.org/doi/pdf/10.1021/ja01259a068
- 167. Hill TL. Theory of Physical Adsorption. Advances in Catalysis. 1952 Jan 1;4(C):211–58.
- 168. Brunauer S, Emmett PH, Teller E. Adsorption of Gases in Multimolecular Layers. J Am Chem Soc [Internet]. 1938 Feb 1 [cited 2023 Apr 12];60(2):309–19. Available from: https://pubs.acs.org/doi/abs/10.1021/ja01269a023
- 169. William Kajjumba G, Emik S, Öngen A, Kurtulus Özcan H, Aydın S. Modelling of Adsorption Kinetic Processes—Errors, Theory and Application. Advanced Sorption Process Applications. 2019 Feb 20;
- 170. Adsorption kinetic models_ Physical meanings, applications, and solving methods [Internet]. [cited 2021 Sep 20]. Available from: https://reader.elsevier.com/reader/sd/pii/S0304389420301448?token=E5237854C83 BA5E99AFE9220B81B06C4276FAD21486A97151CF50E38E9C1486677663D12FC77D1 1EFD00D44BA06C8429&originRegion=eu-west-1&originCreation=20210917133111

- 171. Liu Y. Is the Free Energy Change of Adsorption Correctly Calculated? J Chem Eng Data [Internet]. 2009 Jul 9 [cited 2022 Nov 30];54(7):1981–5. Available from: https://pubs.acs.org/doi/full/10.1021/je800661q
- Agboola OS, Olugbenga &, Bello S. Enhanced adsorption of ciprofloxacin from aqueous solutions using functionalized banana stalk. [cited 2022 Nov 30]; Available from: https://doi.org/10.1007/s13399-020-01038-9
- 173. Hayrera FO, Kim DG, Ko SO. Effects of Chemical Activation Conditions on Hierarchical Porous Carbon via Oxytetracycline Adsorption. Water (Switzerland) [Internet]. 2023 Sep 1 [cited 2024 Jan 19];15(17):3146. Available from: https://www.mdpi.com/2073-4441/15/17/3146/htm
- 174. Yu R, Yu X, Xue B, Liao J, Zhu W, Fu J. Adsorption of oxytetracycline from aquaculture wastewater by modified carbon nanotubes: kinetics, isotherms and thermodynamics. Fullerenes, Nanotubes and Carbon Nanostructures [Internet]. 2021 [cited 2024 Mar 30];29(1):28–38. Available from: https://www.tandfonline.com/doi/abs/10.1080/1536383X.2020.1806248
- 175. Yang H, Yu X, Liu J, Wang L, Guo M. Preparation of Magnetic Fe3O4/Activated Carbon Fiber and a Study of the Tetracycline Adsorption in Aquaculture Wastewater. Materials and technology. 2019;53(4):505–10.
- Carabineiro SAC, Thavorn-Amornsri T, Pereira MFR, Figueiredo JL. Adsorption of ciprofloxacin on surface-modified carbon materials. Water Res. 2011 Oct 1;45(15):4583–91.
- 177. Tran QT, Do TH, Ha XL, Nguyen HP, Nguyen AT, Ngo TCQ, et al. Study of the Ciprofloxacin Adsorption of Activated Carbon Prepared from Mangosteen Peel. Applied Sciences 2022, Vol 12, Page 8770 [Internet]. 2022 Aug 31 [cited 2024 Jun 13];12(17):8770. Available from: https://www.mdpi.com/2076-3417/12/17/8770/htm
- 178. Abbas AS, Ahmed MJ, Darweesh TM. Adsorption of Fluoroquinolones Antibiotics on Activated Carbon by K2CO3 with Microwave Assisted Activation. Iraqi Journal of Chemical and Petroleum Engineering [Internet]. 2016 Jun 2016 [cited 2021 Feb 24];17(2):15–23. Available from: https://ijcpe.uobaghdad.edu.iq/index.php/ijcpe/article/view/78/74

- 179. 'Carabineiro SAC 'Thavorn-AT 'Oereura, MFR 'Figueiredo, J L'. Adsorption of ciprofloxacin on surface-modified carbon materials. Water Res. 2011;45(15):4583–91.
- 180. Martins AC, Pezoti O, Cazetta AL, Bedin KC, Yamazaki DAS, Bandoch GFG, et al. Removal of tetracycline by NaOH-activated carbon produced from macadamia nut shells: Kinetic and equilibrium studies. Chemical Engineering Journal. 2015 Jan 15;260:291–9.
- 181. Tan Z, Zhang X, Wang L, Gao B, Luo J, Fang R, et al. Sorption of tetracycline on H2O2-modified biochar derived from rape stalk. https://doi.org/101080/2639594020191607779 [Internet]. 2019 Jan 1 [cited 2023 Feb 2];31(1):198–207. Available from: https://www.tandfonline.com/doi/abs/10.1080/26395940.2019.1607779
- 182. 'Huang L 'Zhang, B 'Niu, S 'Gao, B. Characterization of Activated Carbon Fiber by Microwave Heating and the Adsorption of Tetracycline Antibiotics. Separation Science and Technology . 2013;48(19).
- 183. 'Nayeri D 'Mousavi, SA 'Mehrabi, A. Oxytetracycline removal from aqueous solutions using activated carbon prepared from corn stalks. Journal of Applied Research in Water and Wastewater. 2019;11.
- 184. Nimptsch J, Woelfl S, Osorio S, Valenzuela J, Ebersbach P, von Tuempling W, et al. Tracing dissolved organic matter (DOM) from land-based aquaculture systems in North Patagonian streams. Science of The Total Environment. 2015 Dec 15;537:129–38.
- 185. Kamjunke N, Nimptsch J, Harir M, Herzsprung P, Schmitt-Kopplin P, Neu TR, et al. Landbased salmon aquacultures change the quality and bacterial degradation of riverine dissolved organic matter. Scientific Reports 2017 7:1 [Internet]. 2017 Mar 3 [cited 2023 Jan 23];7(1):1–15. Available from: https://www.nature.com/articles/srep43739
- 186. Gbadegesin LA, Tang X, Liu C, Cheng J. Transport of Veterinary Antibiotics in Farmland Soil: Effects of Dissolved Organic Matter. Int J Environ Res Public Health [Internet]. 2022 Feb 1 [cited 2022 Dec 7];19(3):1702. Available from: https://www.mdpi.com/1660-4601/19/3/1702/htm
- 187. Wang Q, Mitchell RL, Hofman R, Yu J, Yang M, Rietveld LC, et al. How properties of low molecular weight model competitors impact organic micropollutant adsorption onto

activated carbon at realistically asymmetric concentrations. Water Res. 2021 Sep 1;202:117443.

- 188. Ebie K, Li F, Azuma Y, Yuasa A, Hagishita T. Pore distribution effect of activated carbon in adsorbing organic micropollutants from natural water. Water Res. 2001 Jan 1;35(1):167–79.
- 189. Guillossou R, Le Roux J, Mailler R, Pereira-Derome CS, Varrault G, Bressy A, et al. Influence of dissolved organic matter on the removal of 12 organic micropollutants from wastewater effluent by powdered activated carbon adsorption. Water Res. 2020 Apr 1;172:115487.
- Cela-Dablanca R, Conde-Cid M, Ferreira-Coelho G, Arias-Estévez M, Fernández-Calviño D, Núñez-Delgado A, et al. Adsorption of Tetracycline and Sulfadiazine onto Three Different Bioadsorbents in Binary Competitive Systems. Processes 2021, Vol 9, Page 28 [Internet]. 2020 Dec 24 [cited 2024 Jul 3];9(1):28. Available from: https://www.mdpi.com/2227-9717/9/1/28/htm
- 191. Bo L, Gao N, Liu J, Gao B. The competitive adsorption of pharmaceuticals on granular activated carbon in secondary effluent. Desalination Water Treat [Internet]. 2016 Aug
 1 [cited 2024 Jul 3];57(36):17023–9. Available from: https://www.tandfonline.com/doi/abs/10.1080/19443994.2015.1082942
- 192. Yadav MSP, Sanjeev NO, Vallabha MS, Sekar A, Valsan AE, Varghese GK. Competitive adsorption analysis of antibiotics removal from multi-component systems using chemically activated spent tea waste: effect of operational parameters, kinetics, and equilibrium study. Environmental Science and Pollution Research [Internet]. 2023 Mar 1 [cited 2024 Jul 3];30(15):42697–712. Available from: https://link.springer.com/article/10.1007/s11356-022-22323-2
- 193. Ahmed MB, Zhou JL, Ngo HH, Guo W, Johir MAH, Sornalingam K. Single and competitive sorption properties and mechanism of functionalized biochar for removing sulfonamide antibiotics from water. Chemical Engineering Journal. 2017 Mar 1;311:348–58.

- 194. Sousa ÉML, Otero M, Gil M V., Ferreira P, Esteves VI, Calisto V. Insights into matrix and competitive effects on antibiotics removal from wastewater by activated carbon produced from brewery residues. Environ Technol Innov. 2023 May 1;30:103074.
- 195. Choi KJ, Kim SG, Kim SH. REMOVAL OF TETRACYCLINE AND SULFONAMIDE CLASSES OF ANTIBIOTIC COMPOUND BY POWDERED ACTIVATED CARBON. Environ Technol [Internet]. 2008 [cited 2024 Jul 3];29(3):333–42. Available from: https://www.tandfonline.com/doi/abs/10.1080/09593330802102223
- Jones AD, Bruland GL, Agrawal SG, Vasudevan D. Factors influencing the sorption of oxytetracycline to soils. Environ Toxicol Chem [Internet]. 2005 Apr [cited 2024 Jul 3];24(4):761–70. Available from: https://pubmed.ncbi.nlm.nih.gov/15839547/
- 197. Conde-Cid M, Ferreira-Coelho G, Núñez-Delgado A, Fernández-Calviño D, Arias-Estévez M, Álvarez-Rodríguez E, et al. Competitive adsorption of tetracycline, oxytetracycline and chlortetracycline on soils with different pH value and organic matter content. Environ Res. 2019 Nov 1;178:108669.
- 198. Yu R, Yu X, Xue B, Liao J, Zhu W, Tian S. Adsorption of chlortetracycline from aquaculture wastewater using modified zeolites. Journal of Environmental Science and Health, Part A [Internet]. 2020 Apr 15 [cited 2024 Jul 3];55(5):573–84. Available from: https://www.tandfonline.com/doi/abs/10.1080/10934529.2020.1717275
- 199. Yu J, Meng Z, Chi C, Gao X, Chen B, Zhu B, et al. Low temperature pickling regeneration process for remarkable enhancement in Cu(II) adsorptivity over spent activated carbon fiber. Chemosphere [Internet]. 2021 Oct 1 [cited 2022 Mar 25];281. Available from: https://doi.org/10.1016/j.chemosphere.2021.130868
- 200. Omorogie MO, Babalola JO, Unuabonah EI. Regeneration strategies for spent solid matrices used in adsorption of organic pollutants from surface water: a critical review. New pub: Balaban [Internet]. 2014 Jan 8 [cited 2023 Apr 12];57(2):518–44. Available from: https://www.tandfonline.com/doi/abs/10.1080/19443994.2014.967726
- 201. Dutta T, Kim T, Vellingiri K, Tsang DCW, Shon JR, Kim KH, et al. Recycling and regeneration of carbonaceous and porous materials through thermal or solvent treatment. Chemical Engineering Journal. 2019 May 15;364:514–29.

- 202. Jahandar Lashaki M, Atkinson JD, Hashisho Z, Phillips JH, Anderson JE, Nichols M. The role of beaded activated carbon's pore size distribution on heel formation during cyclic adsorption/desorption of organic vapors. J Hazard Mater. 2016 Sep 5;315:42–51.
- 203. do Nascimento RA, Novaes N dos R de O, Morilla DP, da Luz PTS, Costa CML, Faria LJG de. Removal of Ciprofloxacin and Norfloxacin from Aqueous Solution with Activated Carbon from Cupuaçu (Theobroma grandiflorum) Bark. Molecules [Internet]. 2024 Dec 1 [cited 2025 May 10];29(24):5853. Available from: https://pmc.ncbi.nlm.nih.gov/articles/PMC11676745/
- 204. Larasati A, Fowler GD, Graham NJD. Insights into chemical regeneration of activated carbon for water treatment. J Environ Chem Eng. 2021 Aug 1;9(4):105555.
- Khenniche L, Chemache Z, Saidou-Souleymane M, Aissani-Benissad F. Elimination of antibiotics by adsorption on ferromagnetic carbon from aqueous media: regeneration of the spent carbon. International Journal of Environmental Science and Technology [Internet]. 2022 Oct 1 [cited 2023 Dec 18];19(10):9571–86. Available from: https://link.springer.com/article/10.1007/s13762-021-03808-y
- 206. Wang M, Li G, Huang L, Xue J, Liu Q, Bao N, et al. Study of ciprofloxacin adsorption and regeneration of activated carbon prepared from Enteromorpha prolifera impregnated with H3PO4 and sodium benzenesulfonate. Ecotoxicol Environ Saf. 2017 May 1;139:36–42.
- 207. Li X, Hu Y, She D, Shen WB. Modified Activated Carbon Fiber Felt for the Electrosorption of Norfloxacin in Aqueous Solution. Sustainability 2020, Vol 12, Page 3986 [Internet].
 2020 May 13 [cited 2023 Dec 7];12(10):3986. Available from: https://www.mdpi.com/2071-1050/12/10/3986/htm
- 208. Montgomery D. Design and Analysis of Experiments [Internet]. 8th ed. John Wiley & Sons, Incorporated; 2017 [cited 2021 May 17]. Available from: https://www.google.co.uk/books/edition/Design_and_Analysis_of_Experiments/Py7 bDgAAQBAJ?hl=en&gbpv=0
- 209. Ghasemi A, Zahediasl S. Normality tests for statistical analysis: A guide for non-statisticians. Int J Endocrinol Metab [Internet]. 2012 Apr [cited 2021 Jun 30];10(2):486–9. Available from: /pmc/articles/PMC3693611/

210. Khuri A, Mukhopadhyay S. Response Surface Experiments and Designs. In: Dean A, Morris M, Stufken J, Bingham D, editors. Handbook of Design and Analysis of Experiments [Internet]. 1st ed. CRC Press LLC; 2015 [cited 2021 May 17]. p. 198–235. Available

https://ebookcentral.proquest.com/lib/brunelu/reader.action?docID=4087696

- 211. Lim A, Chew JJ, Ngu LH, Ismadji S, Khaerudini DS, Sunarso J. Synthesis, Characterization, Adsorption Isotherm, and Kinetic Study of Oil Palm Trunk-Derived Activated Carbon for Tannin Removal from Aqueous Solution. ACS Omega [Internet]. 2020 Nov 10 [cited 2021 Feb 10];5(44):28673–83. Available from: http://pubs.acs.org/journal/acsodf
- 212. Alam MZ, Ameem ES, Muyibi SA, Kabbashi NA. The factors affecting the performance of activated carbon prepared from oil palm empty fruit bunches for adsorption of phenol. Chemical Engineering Journal. 2009 Dec 1;155(1–2):191–8.
- 213. O. Basheer A, M. Hanafiah M, Abdulhakim Alsaadi M, Al-Douri Y, Malek MA, Mohammed Aljumaily M, et al. Synthesis and Characterization of Natural Extracted Precursor Date Palm Fibre-Based Activated Carbon for Aluminum Removal by RSM Optimization. Processes [Internet]. 2019 Apr 28 [cited 2021 Feb 10];7(5):249. Available from: https://www.mdpi.com/2227-9717/7/5/249
- 214. Mozaffarian M, Soleimani M, Bajgiran MA. A simple novel route for porous carbon production from waste tyre. Environmental Science and Pollution Research [Internet].
 2019 Oct 1 [cited 2021 Feb 10];26(30):31038–54. Available from: https://doi.org/10.1007/s11356-019-06080-3
- 215. Jung KW, Choi BH, Song KG, Choi JW. Statistical optimization of preparing marine macroalgae derived activated carbon/iron oxide magnetic composites for sequestering acetylsalicylic acid from aqueous media using response surface methodologys. Chemosphere. 2019 Jan 1;215:432–43.
- 216. Pereira Da Silva C, Da Guarda Souza MO, Dos Santos WNL, Oliveira Bastos Silva L. Optimization of the Production Parameters of Composites from Sugarcane Bagasse and Iron Salts for Use in Dye Adsorption. Scientific World Journal. 2019;2019.

- 217. Zhang B, Han X, Gu P, Fang S, Bai J. Response surface methodology approach for optimization of ciprofloxacin adsorption using activated carbon derived from the residue of desilicated rice husk. J Mol Liq. 2017 Jul 1;238:316–25.
- 218. Karoui S, Ben Arfi R, Fernández-Sanjurjo MJ, Nuñez-Delgado A, Ghorbal A, Álvarez-Rodríguez E. Optimization of synergistic biosorption of oxytetracycline and cadmium from binary mixtures on reed-based beads: modeling study using Brouers-Sotolongo models. Environmental Science and Pollution Research [Internet]. 2021 Sep 1 [cited 2024 Sep 30];28(34):46431–47. Available from: https://link.springer.com/article/10.1007/s11356-020-09493-7
- Mozaffari Majd M, Kordzadeh-Kermani V, Ghalandari V, Askari A, Sillanpää M. Adsorption isotherm models: A comprehensive and systematic review (2010–2020). Science of The Total Environment. 2022 Mar 15;812:151334.
- 220. Foo KY, Hameed BH. Insights into the modeling of adsorption isotherm systems.Chemical Engineering Journal. 2010 Jan 1;156(1):2–10.
- 221. Kaldenhoven RG, Hill JM. Determining the pore structure of activated carbon by nitrogen gas adsorption. Catalysis [Internet]. 2018 [cited 2024 Jan 16];30:41–63.
 Available from: https://books.rsc.org/books/edited-volume/1507/chapter/956177/Determining-the-pore-structure-of-activated-carbon
- 222. Thommes M, Kaneko K, Neimark A V., Olivier JP, Rodriguez-Reinoso F, Rouquerol J, et al. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure and Applied Chemistry [Internet]. 2015 Oct 1 [cited 2024 Jan 15];87(9–10):1051–69. Available from: https://www.researchgate.net/publication/282624978_Physisorption_of_gases_with _special_reference_to_the_evaluation_of_surface_area_and_pore_size_distribution [IUPAC_Technical_Report]
- 223. Sing KSW, Williams RT. Review Physisorption Hysteresis Loops and the Characterization of Nanoporous Materials.
- 224. Bardestani R, Patience GS, Kaliaguine S. Experimental methods in chemical engineering: specific surface area and pore size distribution measurements—BET, BJH,

and DFT. Can J Chem Eng [Internet]. 2019 Nov 1 [cited 2023 Feb 14];97(11):2781–91. Available from: https://onlinelibrary.wiley.com/doi/full/10.1002/cjce.23632

- 225. Rouquerol F, Rouquerol J, Sing K. Assessment of Mesoporosity. Adsorption by Powders and Porous Solids. 1999 Jan 1;191–217.
- 226. Nunes CA, Guerreiro MC. Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers. Quim Nova [Internet]. 2011 [cited 2022 Feb 9];34(3):472–6. Available from: http://www.scielo.br/j/qn/a/VY5JpTFcqRhbzSFZc9xqd3J/?lang=en
- 227. Raposo F, De La Rubia MA, Borja R. Methylene blue number as useful indicator to evaluate the adsorptive capacity of granular activated carbon in batch mode: influence of adsorbate/adsorbent mass ratio and particle size. J Hazard Mater [Internet]. 2009 Jun 15 [cited 2023 Dec 26];165(1–3):291–9. Available from: https://pubmed.ncbi.nlm.nih.gov/19013717/
- Kah M, Sigmund G, Xiao F, Hofmann T. Sorption of ionizable and ionic organic compounds to biochar, activated carbon and other carbonaceous materials. Water Res. 2017 Nov 1;124:673–92.
- Goertzen SL, Thériault KD, Oickle AM, Tarasuk AC, Andreas HA. Standardization of the Boehm titration. Part I. CO2 expulsion and endpoint determination. Carbon N Y. 2010 Apr 1;48(4):1252–61.
- 230. Oickle AM, Goertzen SL, Hopper KR, Abdalla YO, Andreas HA. Standardization of the Boehm titration: Part II. Method of agitation, effect of filtering and dilute titrant. Carbon N Y. 2010 Oct 1;48(12):3313–22.
- 231. Warkick T. FEG-SEM | Field Emission Gun | Scanning Electron Microscopy [Internet].
 2021 [cited 2024 Jan 31]. Available from: https://blue-scientific.com/why-use-feg-sem/
- 232. Singh AK. Experimental Methodologies for the Characterization of Nanoparticles. Engineered Nanoparticles. 2016 Jan 1;125–70.
- 233. Reed SJB. Scanning electron microscopy. Electron Microprobe Analysis and Scanning Electron Microscopy in Geology [Internet]. 2005 Aug 25 [cited 2024 Jan 31];41–75.

Available from: https://www.cambridge.org/core/books/electron-microprobeanalysis-and-scanning-electron-microscopy-in-geology/scanning-electronmicroscopy/A533157B3B97FF542CFA8B1C582C3865

- 234. Griffiths P. Introduction to the Theory and Instrumentation for Vibrational Spectroscopy. In: Chalmers J, Peter G, editors. Handbook of Vibrational Spectroscopy.
 5th ed. Chichester: John Wiley & Sons, Ltd; 2010. p. 1–16.
- 235. Mettler Toledo. ATR-FTIR Spectroscopy Fundamentals of Attenuated Total Reflectance (ATR). 2023.
- 236. Silva TL, Cazetta AL, Souza PSC, Zhang T, Asefa T, Almeida VC. Mesoporous activated carbon fibers synthesized from denim fabric waste: Efficient adsorbents for removal of textile dye from aqueous solutions. J Clean Prod. 2018 Jan 10;171:482–90.
- 237. El-Shafey EI, Ali SNF, Al-Busafi S, Al-Lawati HAJ. Preparation and characterization of surface functionalized activated carbons from date palm leaflets and application for methylene blue removal. J Environ Chem Eng. 2016 Sep 1;4(3):2713–24.
- 238. Discover 50 years of Raman innovation by HORIBA [Internet]. [cited 2024 Jan 31]. Available from: https://www.horiba.com/pol/scientific/technologies/raman-imagingand-spectroscopy/history-of-raman-spectroscopy/
- 239. Orlando A, Franceschini F, Muscas C, Pidkova S, Bartoli M, Rovere M, et al. A Comprehensive Review on Raman Spectroscopy Applications. Chemosensors 2021, Vol 9, Page 262 [Internet]. 2021 Sep 13 [cited 2024 Jan 10];9(9):262. Available from: https://www.mdpi.com/2227-9040/9/9/262/htm
- 240. Li Z, Deng L, Kinloch IA, Young RJ. Raman spectroscopy of carbon materials and their composites: Graphene, nanotubes and fibres. Prog Mater Sci. 2023 Jun 1;135:101089.
- 241. Fisher Scientific T. Characterizing graphene with Raman spectroscopy. 2019;
- 242. CHNS Elemental Analysers. 2008 [cited 2024 Jan 15]; Available from: www.rsc.org/amc
- 243. Noh JS, Schwarz JA. Effect of HNO3 treatment on the surface acidity of activated carbons. Carbon N Y. 1990 Jan 1;28(5):675–82.
- 244. Mahmood T, Saddique MT, Naeem A, Westerhoff P, Mustafa S, Alum A. Comparison of Different Methods for the Point of Zero Charge Determination of NiO. Ind Eng Chem

Res [Internet]. 2011 Sep 7 [cited 2023 Feb 13];50(17):10017–23. Available from: https://pubs.acs.org/doi/abs/10.1021/ie200271d

- 245. ASTM D3176-15 Standard Practice for Ultimate Analysis of Coal and Coke [Internet].
 [cited 2024 Jan 18]. Available from: https://standards.iteh.ai/catalog/standards/astm/6a80ff89-80ee-473e-bf3d-3b641b606103/astm-d3176-15
- 246. Gorbounov M. VALORISATION OF BIOMASS COMBUSTION ASH IN PREPARATION AND APPLICATION OF ACTIVATED CARBON FOR CO2 ADSORPTION. [London]: Brunel University; 2024.
- 247. Verma S, Balasubramaniam B, Gupta RK. Recycling, reclamation and re-manufacturing of carbon fibres. Curr Opin Green Sustain Chem. 2018 Oct 1;13:86–90.
- Zhang J, Lin G, Vaidya U, Wang H. Past, present and future prospective of global carbon fibre composite developments and applications. Compos B Eng. 2023 Feb 1;250:110463.
- 249. Giorgini L, Benelli T, Brancolini G, Mazzocchetti L. Recycling of carbon fiber reinforced composite waste to close their life cycle in a cradle-to-cradle approach. Curr Opin Green Sustain Chem. 2020 Dec 1;26:100368.
- McConnell VP. Launching the carbon fibre recycling industry. Reinforced Plastics. 2010 Mar 1;54(2):33–7.
- 251. Das S. Life cycle assessment of carbon fiber-reinforced polymer composites. The International Journal of Life Cycle Assessment 2011 16:3 [Internet]. 2011 Feb 22 [cited 2021 Aug 12];16(3):268–82. Available from: https://link.springer.com/article/10.1007/s11367-011-0264-z
- 252. Witik RA, Teuscher R, Michaud V, Ludwig C, Månson JAE. Carbon fibre reinforced composite waste: An environmental assessment of recycling, energy recovery and landfilling. Compos Part A Appl Sci Manuf. 2013 Jun 1;49:89–99.
- 253. Puri P, Compston P, Pantano V. Life cycle assessment of Australian automotive door skins. International Journal of Life Cycle Assessment [Internet]. 2009 Jul 21 [cited 2024

Jan 5];14(5):420–8. Available from: https://link.springer.com/article/10.1007/s11367-009-0103-7

- 254. Tapper RJ, Longana ML, Norton A, Potter KD, Hamerton I. An evaluation of life cycle assessment and its application to the closed-loop recycling of carbon fibre reinforced polymers. Compos B Eng. 2020 Mar 1;184:107665.
- 255. Li X, Bai R, McKechnie J. Environmental and financial performance of mechanical recycling of carbon fibre reinforced polymers and comparison with conventional disposal routes. J Clean Prod. 2016 Jul 20;127:451–60.
- 256. He D, Soo VK, Stojcevski F, Lipiński W, Henderson LC, Compston P, et al. The effect of sizing and surface oxidation on the surface properties and tensile behaviour of recycled carbon fibre: An end-of-life perspective. Compos Part A Appl Sci Manuf. 2020 Nov 1;138:106072.
- 257. Oladoye PO, Ajiboye TO, Omotola EO, Oyewola OJ. Methylene blue dye: Toxicity and potential elimination technology from wastewater. Results in Engineering. 2022 Dec 1;16:100678.
- 258. Maia LS, da Silva AIC, Carneiro ES, Monticelli FM, Pinhati FR, Mulinari DR. Activated Carbon From Palm Fibres Used as an Adsorbent for Methylene Blue Removal. J Polym Environ [Internet]. 2021 Apr 1 [cited 2022 Feb 19];29(4):1162–75. Available from: https://link.springer.com/article/10.1007/s10924-020-01951-0
- 259. Joshi S, Shrestha RG, Pradhananga RR, Ariga K, Shrestha LK. High Surface Area Nanoporous Activated Carbons Materials from Areca catechu Nut with Excellent Iodine and Methylene Blue Adsorption. C 2022, Vol 8, Page 2 [Internet]. 2021 Dec 27 [cited 2023 May 26];8(1):2. Available from: https://www.mdpi.com/2311-5629/8/1/2/htm
- 260. Khan I, Saeed K, Zekker I, Zhang B, Hendi AH, Ahmad A, et al. Review on Methylene Blue: Its Properties, Uses, Toxicity and Photodegradation. Water 2022, Vol 14, Page 242 [Internet]. 2022 Jan 14 [cited 2023 Oct 22];14(2):242. Available from: https://www.mdpi.com/2073-4441/14/2/242/htm
- 261. Ahmadi A, Ignatova S, Ketabchi MR, Clough P, Soltani SM, Ahmadi (A, et al. Commercial waste wood in the removal of methylene blue from aqueous media. Desalination and

Water Treatment [Internet]. 2020 [cited 2022 Mar 17];407–21. Available from: www.deswater.com

- Hameed BH, Din ATM, Ahmad AL. Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. J Hazard Mater. 2007 Mar 22;141(3):819–25.
- Devesa-Rey R, Bustos G, Cruz JM, Moldes AB. Optimisation of entrapped activated carbon conditions to remove coloured compounds from winery wastewaters. Bioresour Technol. 2011 Jun 1;102(11):6437–42.
- 264. Silva MC, Spessato L, Silva TL, Lopes GKP, Zanella HG, Yokoyama JTC, et al. H3PO4– activated carbon fibers of high surface area from banana tree pseudo-stem fibers: Adsorption studies of methylene blue dye in batch and fixed bed systems. J Mol Liq. 2021 Feb 15;324:114771.
- 265. Liu QX, Zhou YR, Wang M, Zhang Q, Ji T, Chen TY, et al. Adsorption of methylene blue from aqueous solution onto viscose-based activated carbon fiber felts: Kinetics and equilibrium studies. Adsorption Science and Technology [Internet]. 2019 May 1 [cited 2023 Aug 11];37(3–4):312–32. Available from: https://journals.sagepub.com/doi/full/10.1177/0263617419827437
- 266. Jawad AH, Mohd Firdaus Hum NN, Abdulhameed AS, Mohd Ishak MA. Mesoporous activated carbon from grass waste via H3PO4-activation for methylene blue dye removal: modelling, optimisation, and mechanism study. Int J Environ Anal Chem [Internet]. 2020 [cited 2023 Jan 26]; Available from: https://www.tandfonline.com/doi/abs/10.1080/03067319.2020.1807529
- 267. Cheng C, Zhang J, Mu Y, Gao J, Feng Y, Liu H, et al. Preparation and evaluation of activated carbon with different polycondensed phosphorus oxyacids (H3PO4, H4P 2O7, H6P4O13 and C 6H18O24P6) activation employing mushroom roots as precursor. J Anal Appl Pyrolysis [Internet]. 2014 [cited 2023 Aug 11];108:41–6. Available from: https://www.researchgate.net/publication/262937843_Preparation_and_evaluation _of_activated_carbon_with_different_polycondensed_phosphorus_oxyacids_H3PO4 _H4P2O7_H6P4O13_and_C6H18O24P6_activation_employing_mushroom_roots_as_ precursor

- 268. Jing M, Wang C guo, Wang Q, Bai Y jun, Zhu B. Chemical structure evolution and mechanism during pre-carbonization of PAN-based stabilized fiber in the temperature range of 350–600 °C. Polym Degrad Stab. 2007 Sep 1;92(9):1737–42.
- 269. Shim JW, Park SJ, Ryu SK. Effect of modification with HNO3 and NaOH on metal adsorption by pitch-based activated carbon fibers. Carbon N Y. 2001 Sep 1;39(11):1635–42.
- 270. Shen W, Wang H, Guan R, Li Z. Surface modification of activated carbon fiber and its adsorption for vitamin B1 and folic acid. Colloids Surf A Physicochem Eng Asp. 2008 Dec 31;331(3):263–7.
- Liu M, Li X, Du Y, Han R. Adsorption of methyl blue from solution using walnut shell and reuse in a secondary adsorption for Congo red. Bioresour Technol Rep. 2019 Feb 1;5:238–42.
- 272. Katz S, Pevzner A, Shepelev V, Marx S, Rotter H, Amitay-Rosen T, et al. Activated carbon aging processes characterization by Raman spectroscopy. MRS Adv [Internet]. 2022 Apr
 1 [cited 2023 Oct 22];7(12):245–8. Available from: https://link.springer.com/article/10.1557/s43580-021-00189-9
- 273. Socrates G. Infrared and Raman characteristic group frequencies. Tables and charts. Journal of Raman Spectroscopy [Internet]. 2001 [cited 2024 Aug 12];347. Available from: https://www.wiley.com/enus/Infrared+and+Raman+Characteristic+Group+Frequencies%3A+Tables+and+Charts %2C+3rd+Edition-p-9780470093078
- 274. Sadezky A, Muckenhuber H, Grothe H, Niessner R, Pöschl U. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. Carbon N Y. 2005 Jul 1;43(8):1731–42.
- 275. Graupner R. Raman spectroscopy of covalently functionalized single-wall carbon nanotubes. Journal of Raman Spectroscopy [Internet]. 2007 Jun 1 [cited 2023 Oct 22];38(6):673–83. Available from: https://onlinelibrary.wiley.com/doi/full/10.1002/jrs.1694

- 276. Strano MS, Dyke CA, Usrey ML, Barone PW, Allen MJ, Shan H, et al. Electronic structure control of single-walled carbon nanotube functionalization. Science [Internet]. 2003
 Sep 12 [cited 2023 Oct 22];301(5639):1519–22. Available from: https://pubmed.ncbi.nlm.nih.gov/12970561/
- 277. Xia M, Li A, Zhu Z, Zhou Q, Yang W. Factors influencing antibiotics adsorption onto engineered adsorbents. Journal of Environmental Sciences. 2013 Jul 1;25(7):1291–9.
- 278. Salman MS, Yazdi SK, Hosseini S, Gargari MK. Effect of nitric acid modification on porous characteristics of mesoporous char synthesized from the pyrolysis of used cigarette filter. J Environ Chem Eng. 2014 Sep 1;2(3):1301–8.
- 279. Smith B. Infrared spectral interpretation: A systematic approach. Infrared Spectral Interpretation: A Systematic Approach [Internet]. 2018 Feb 6 [cited 2024 Aug 27];1–304. Available from: https://www.taylorfrancis.com/books/mono/10.1201/9780203750841/infrared-spectral-interpretation-brian-smith
- 280. Eckmann A, Felten A, Mishchenko A, Britnell L, Krupke R, Novoselov KS, et al. Probing the nature of defects in graphene by Raman spectroscopy. Nano Lett [Internet]. 2012
 Aug 8 [cited 2024 Aug 27];12(8):3925–30. Available from: https://pubmed.ncbi.nlm.nih.gov/22764888/
- Ferrari AC, Robertson J. Raman spectroscopy of amorphous, nanostructured, diamond–like carbon, and nanodiamond. Philosophical Transactions of the Royal Society of London Series A: Mathematical, Physical and Engineering Sciences [Internet].
 2004 Nov 15 [cited 2024 Aug 27];362(1824):2477–512. Available from: https://royalsocietypublishing.org/doi/10.1098/rsta.2004.1452
- 282. Eniola JO, Kumar R, Barakat MA. Adsorptive removal of antibiotics from water over natural and modified adsorbents. Environmental Science and Pollution Research [Internet]. 2019 Dec 1 [cited 2024 Jul 4];26(34):34775–88. Available from: https://link.springer.com/article/10.1007/s11356-019-06641-6
- 283. Yu F, Li Y, Han S, Ma J. Adsorptive removal of antibiotics from aqueous solution using carbon materials. Chemosphere. 2016 Jun 1;153:365–85.

- 284. Oleszczuk P, Pan B, Xing B. Adsorption and desorption of oxytetracycline and carbamazepine by multiwalled carbon nanotubes. Environ Sci Technol [Internet]. 2009 Dec 15 [cited 2024 Jan 19];43(24):9167–73. Available from: https://pubs.acs.org/doi/full/10.1021/es901928q
- 285. Meseguer VF, Ortuño JF, Aguilar MI, Lloréns M, Pérez-Marín AB, Fuentes E. Ciprofloxacin Uptake from an Aqueous Solution via Adsorption with K2CO3-Activated Biochar Derived from Brewing Industry Bagasse. Processes [Internet]. 2024 Jan 1 [cited 2024 Sep 11];12(1):199. Available from: https://www.mdpi.com/2227-9717/12/1/199/htm
- 286. Babaei AA, Lima EC, Takdastan A, Alavi N, Goudarzi G, Vosoughi M, et al. Removal of tetracycline antibiotic from contaminated water media by multi-walled carbon nanotubes: operational variables, kinetics, and equilibrium studies. Water Sci Technol [Internet]. 2016 Sep 1 [cited 2024 Sep 9];74(5):1202–16. Available from: https://pubmed.ncbi.nlm.nih.gov/27642840/
- 287. de Oliveira Carvalho C, Costa Rodrigues DL, Lima ÉC, Santanna Umpierres C, Caicedo Chaguezac DF, Machado Machado F. Kinetic, equilibrium, and thermodynamic studies on the adsorption of ciprofloxacin by activated carbon produced from Jerivá (Syagrus romanzoffiana). Environmental Science and Pollution Research [Internet]. 2019 Feb 20 [cited 2024 Sep 10];26(5):4690–702. Available from: https://link.springer.com/article/10.1007/s11356-018-3954-2
- 288. Rodrigues DLC, Machado FM, Osório AG, de Azevedo CF, Lima EC, da Silva RS, et al. Adsorption of amoxicillin onto high surface area–activated carbons based on olive biomass: kinetic and equilibrium studies. Environmental Science and Pollution Research [Internet]. 2020 Nov 1 [cited 2024 Sep 10];27(33):41394–404. Available from: https://link.springer.com/article/10.1007/s11356-020-09583-6
- Yu R, Yu X, Xue B, Liao J, Zhu W, Fu J. Adsorption of oxytetracycline from aquaculture wastewater by modified carbon nanotubes: kinetics, isotherms and thermodynamics. Fullerenes, Nanotubes and Carbon Nanostructures [Internet]. 2021 [cited 2024 Jul 4];29(1):28–38. Available from: https://www.tandfonline.com/doi/abs/10.1080/1536383X.2020.1806248

290. NIST Chemistry WebBook [Internet]. [cited 2024 Sep 13]. Available from: https://webbook.nist.gov/chemistry/
Appendix A: Activation Chapter Raw Experimental Data

Absorbance	Actual concentration (mg/L)	
0.041	20.400	
0.089	44.400	
0.208	103.900	
0.306	152.900	
0.418	208.900	
0.895	447.400	
1.982	990.900	
	Absorbance 0.041 0.089 0.208 0.306 0.418 0.895 1.982	

Table A.1: MB Calibration Curve

Table A.2: MB Adsorption on K-ArCF-Opt, where indicates outliers.

	Mass CF	Abs	Ce	q e	Mean	St Dev
	0.0052	0.008	2.611	64.103		
_	0.0053	0.012	4.833	52.411	•	
ng/I	0.0048	0.004	0.389	81.019	42 720	22 420
25 n	0.0053	0.025	12.056	18.344	43.720	32.430
	0.0051	0.031	15.389	2.723		
	0.0053	0.037	18.722	-13.103		
	0.0053	0.035	17.611	138.889		
_	0.0049	0.051	26.500	104.875		
/gu	0.0051	0.052	27.056	98.039	76 201	21.880
50 r	0.0047	0.086	45.944	5.910	- /6.281	
	0.0047	0.060	31.500	82.742		
	0.0051	0.078	41.500	27.233		
	0.0049	0.147	79.833	138.889		
<	0.0052	0.108	58.167	235.043		
mg/	0.005	0.118	63.722	216.667	110 5/	01 97
8	0.0048	0.197	107.611	-2.894	119.34	91.07
Н	0.0047	0.199	108.722	-8.865		
	0.0047	0.197	107.611	-2.955		
	0.005	0.129	134.278	19.444		
<	0.0053	0.146	133.722	22.676		
mg/	0.0047	0.197	123.722	75.231	221 01	112 02
20	0.005	0.245	143.722	-16.745	221.91	112.95
-	0.0049	0.244	97.056	214.120		
	0.0048	0.226	108.722	141.560		
l/g	0.0048	0.178	175.944	147.392		
ш 0	0.0052	0.199	178.167	141.844	277.31	85.44
20	0.0048	0.306	172.056	157.585		

	Mass CF	Abs	Ce	q e	Mean	St Dev
	0.0049	0.320	193.167	55.031		
	0.0047	0.324	124.833	390.691		
	0.0052	0.313	148.167	277.778		
	0.0053	0.351	460.944	315.904		
-	0.0047	0.228	470.389	269.608		80.29
mg/	0.0051	0.270	431.500	489.005	205 70	
8	0.0051	0.412	469.833	272.331	205.76	
ы	0.0051	0.833	492.611	160.675		
	0.0051	0.850	480.944	222.222		
	0.0048	0.780	929.278	372.340		
<	0.0051	0.849	961.500	178.197		
mg	0.0051	0.791	909.833	447.222	666 40	245 24
000	0.0050	0.805	959.278	188.679	666.40	245.34
1(0.0052	0.776	985.389	69.444		
	0.0047	1.676	959.833	201.247	-	

Table A.3: MB Adsorption on K-AvCF-Opt, where indicates outliers.

	Mass CF	Abs	Ce	q e	Mean	St Dev
	0.0049	0.015	7.40	66.33	58.96	15.03
_	0.0049	0.014	6.90	68.88	•	
l/gr	0.0048	0.025	12.40	41.67		
25 n	0.0051	0.011	5.40	73.53	-	
	0.0050	0.023	11.40	45.00		
	0.0049	0.021	10.40	51.02	-	
	0.0051	0.070	34.90	46.57	63.23	31.10
_	0.0048	0.057	28.40	83.33		
/gu	0.0051	0.046	22.90	105.39		
50 r	0.005	0.069	34.40	50.00		
	0.0049	0.078	38.90	28.06		
	0.0053	0.061	30.40	66.04		
	0.0048	0.175	87.40	85.94	81.35	40.94
	0.005	0.194	96.90	35.00		
<	0.0053	0.196	97.90	28.30		
mg/	0.0053	0.167	83.40	96.70		
8	0.0047	0.154	76.90	143.62		
-	0.0052	0.155	77.40	127.40		
	0.0049	0.179	89.40	73.98		
	0.0048	0.185	92.40	59.90		
02 7	0.0053	0.251	125.40	129.72	112.02	50.41
Ξi i	0.0051	0.243	121.40	154.41		

	Mass	Abs	Се	q e	Mean	St Dev
	CF					
	0.005	0.230	114.90	190.00		
	0.0049	0.275	137.40	79.08		
	0.0053	0.272	135.90	80.19		
	0.0047	0.265	132.40	109.04	-	
	0.0051	0.289	144.40	41.67		
	0.0051	0.373	186.40	110.29	161.19	158.27
_	0.0053	0.325	162.40	219.34	•	
/gu	0.005	0.237	118.40	452.50	•	
8	0.0053	0.389	194.40	68.40	•	
8	0.0049	0.414	206.90	10.20	•	
	0.0047	0.378	188.90	106.38	•	
	0.0052	0.932	465.90	-88.94	126.53	98.66
	0.0048	0.841	420.40	140.63	•	
g/I	0.0049	0.845	422.40	127.55	•	
Ĩ	0.0047	0.853	426.40	111.70	•	
500	0.0049	0.845	422.40	127.55	•	
	0.0051	0.814	406.90	198.53	•	
	0.0047	0.875	437.40	53.19	•	
	0.0048	1.798	898.90	479.17	528.18	277.74
=	0.0052	1.710	854.90	653.85	•	
mg	0.0049	1.805	902.40	451.53	•	
00	0.0049	1.962	980.90	51.02		
10	0.0051	1.969	984.40	31.86		
	0.0047	1.992	995.90	0.00		

Table A.4: Regression coefficient and adjusted and predicted regression coefficients for theresponses in this study i.e. yield and adsorption capacity, taken from [34].

	R ²	R^2_{adj}	R^{2}_{pred}
Yield	96.33	89.72	78.57
Adsorption capacity	99.03	97.27	84.41

Source	Code	Yield	Yield (%)		ion capacity g/g)
		F-Value	P-Value	F-Value	P-Value
Model	-	14.57	0.004	56.45	0.000
Linear	-	40.63	0.001	147.67	0.000
Temperature	X 1	56.63	0.001	1.14	0.335
IR	X2	56.25	0.001	441.71	0.000
Hold Time	X3	9.01	0.030	0.16	0.704
Square	-	2.81	0.148	21.42	0.003
Temperature*Temperature	x ₁ ²	0.69	0.445	0.58	0.479
IR*IR	x ₂ ²	4.01	0.102	53.86	0.001
Hold Time*Hold Time	x ₃ ²	3.10	0.139	6.02	0.058
2-Way Interaction	-	0.27	0.844	0.25	0.857
Temperature*IR	X ₁ X ₂	0.06	0.820	0.04	0.847
Temperature*Hold Time	X1X3	0.75	0.425	0.25	0.636
IR*Hold Time	X ₂ X ₃	0.00	0.963	0.46	0.527

Table A.5: ANOVA results for the chemical activation campaign, for the responses yield and MB adsorption capacity adapted from [34].

Equations A.1 and A.2 show the full polynomial models for the optimisation of the activation process prior to removing insignificant terms. Where, y_1 is yield, y_2 is MB adsorption capacity, x_1 is temperature, x_2 is IR and x_3 is hold time.

$$y_1 = 649 + 1.2x_1 - 2.5x_2 + 3.6x_3 - 0.00063(x_1)^2 - 0.48(x_2)^2 + 5.48(x_3)^2$$
 Equation A.1
+0.0031(x_1x_2) - 0.041(x_1x_3) - 0.041(x_2x_3)

$$y_2 = -92 + 0.28x_1 - 2.5x_2 + 1.8x_3 - 0.00021(x_1)^2 + 0.65(x_2)^2 -$$
Equation A.2
$$0.28(x_3)^2 + 0.00097(x_1x_2) + 0.0086(x_1x_3) + 0.21(x_2x_3)$$

Appendix B: Modification Chapter Raw Experimental Data

	StdOrder	Sample name	[HNO₃]	Hold time	Temp	Mass CF	Mass mrCF	Yield (%)
ninary sts	High point	mrCF-HP	6 (+1)	24 (+1)	60 (+1)	0.0604	0.0420	69.54
Prelir te	Low point	mrCF-LP	1 (-1)	16 (-1)	20 (-1)	0.0601	0.0490	81.53
	1	mrCF-1	1	16	40	0.1000	0.0875	87.50
	2	mrCF-2	6	16	40	0.1001	0.0630	62.94
	3	mrCF-3	1	24	40	0.1003	0.0812	80.96
	4	mrCF-4	6	24	40	0.1000	0.0812	81.20
	5	mrCF-5	1	20	20	0.1001	0.0711	71.03
	6	mrCF-6	6	20	20	0.1000	0.0850	85.00
	7	mrCF-7	1	20	60	0.1004	0.0843	83.96
	8	mrCF-8	6	20	60	0.1000	0.0839	83.90
	9	mrCF-9	3.5	16	20	0.1001	0.0874	87.31
	10	mrCF-10	3.5	24	20	0.1001	0.0887	88.61
	11	mrCF-11	3.5	16	60	0.1002	0.0876	87.43
	12	mrCF-12	3.5	24	60	0.1002	0.0905	90.32
	13	mrCF-13	3.5	20	60	0.1002	0.0823	82.14
	14	mrCF-14	3.5	20	40	0.1003	0.0738	73.58
	15	mrCF-15	3.5	20	40	0.1004	0.0390	38.84

Table B.1: Modification BBD raw data.

Table B.2: CIP adsorption experiments conducted at 20 °C.

Sample	Mass CF	Abs	Final conc	Qe	Mean	St dev
	0.0050	0.012	0.2378	6.8089		
mrCF-1	0.0051	0.060	0.7256	4.2842	6.1706	1.6619
	0.0050	0.000	0.1159	7.4187		
	0.0052	0.000	0.1159	7.1334		
mrCF-2	0.0047	-0.029	-0.1789	9.4599	6.8792	2.7167
	0.0049	0.068	0.8069	4.0443		
	0.0051	0.059	0.7154	4.3341		
mrCF-3	0.0053	0.010	0.2175	6.5194	6.0548	1.5418
	0.0049	0.005	0.1667	7.3109		
	0.0048	0.019	0.3089	6.7221		
mrCF-4	0.0052	0.02	0.3191	6.1562	6.6893	0.5174
	0.0047	0.013	0.2480	7.1895		
mrCF-5	0.0049	0.043	0.5528	5.3406	5.9306	0.5132

Sample	Mass CF	Abs	Final conc	Qe	Mean	St dev
	0.0049	0.025	0.3699	6.2739		
	0.0051	0.022	0.3394	6.1773		
	0.005	0.067	0.7967	4.0142		
mrCF-6	0.0049	0.011	0.2276	6.9998	6.2012	1.9168
	0.0047	0.0056	0.1728	7.5895		
	0.0053	0.007	0.1870	6.6632		
mrCF-7	0.0051	-0.001	0.1057	7.3231	7.0087	0.3310
	0.0048	0.013	0.2480	7.0397		
	0.0051	0.05	0.6240	4.7824		1 7711
mrCF-8	0.0047	-0.003	0.0854	8.0544	6.0268	1.//11
	0.0047	0.049	0.6138	5.2435		
	0.0053	-0.045	-0.3415	9.1559		
mrCF-9	0.0048	0.0017	0.1331	7.6378	15.1214	11.6719
	0.0053	-0.45	-4.4573	28.5703		
	0.0049	0.077	0.8984	3.5777	4.6762	
mrCF-10	0.0051	0.01	0.2175	6.7751		1.8183
	0.0047	0.078	0.9085	3.6758		
	0.005	-0.015	-0.0366	8.1809		0.4138
mrCF-11	0.0051	-0.002	0.0955	7.3729	7.7252	
	0.0051	-0.007	0.0447	7.6220		
	0.0053	0.002	0.1362	6.9029		
mrCF-12	0.0047	-0.025	-0.1382	9.2436	8.0463	1.1713
	0.0048	-0.005	0.0650	7.9925		
	0.0051	0.002	0.1362	7.1736		
mrCF-13	0.0052	0.042	0.5427	5.0813	5.9516	1.0896
	0.0049	0.038	0.5020	5.5998		
	0.0051	0.09	1.0305	2.7897		
mrCF-14	0.0049	-0.025	-0.1382	8.8664	6.2822	3.1385
	0.0053	-0.004	0.0752	7.1905		
	0.0051	-0.002	0.0955	7.3729		
mrCF-15	0.0053	0.025	0.3699	5.8004	6.8666	0.9238
	0.0052	-0.006	0.0549	7.4265		

Table B.3: adsorption experiments conducted at 20 °C.

Sample	Mass CF	Abs	Final	Qe	Mean	St dev
	0.0051	0.003	0.6553	4.5670		
mrCF-1	0.0047	0.002	0.6242	5.1209	4.8856	0.2862
	0.005	0.001	0.5932	4.9689		
mrCF-2	0.0048	0.01	0.8727	3.7202	4 0102	0 4 4 2 6
	0.0048	0.005	0.7174	4.5290	4.0193	0.4436

Sample	Mass CF	Abs	Final conc	Qe	Mean	St dev
	0.0053	0.007	0.7795	3.8087		
	0.0051	0.000	0.5621	5.0237		
mrCF-3	0.005	0.013	0.9658	3.1056	3.2489	1.7076
	0.0048	0.023	1.2764	1.6175	•	
	0.0047	0.003	0.6553	4.9557		
mrCF-4	0.0048	0.010	0.8727	3.7202	4.1860	0.6715
	0.0052	0.007	0.7795	3.8820	•	
	0.0049	0.018	1.1211	2.3767		
mrCF-5	0.005	0.007	0.7795	4.0373	3.6908	1.1796
	0.005	0.003	0.6553	4.6584	•	
	0.0053	0.004	0.6863	4.2482		
mrCF-6	0.0052	0.007	0.7795	3.8820	3.9523	0.2678
	0.005	0.009	0.8416	3.7267	•	
	0.005	-0.001	0.5311	5.2795		
mrCF-7	0.0051	0.019	1.1522	2.1313	3.6850	1.5745
	0.0049	0.010	0.8727	3.6443	•	
	0.0052	0.005	0.7174	4.1806	4.0039	0.5223
mrCF-8	0.005	0.011	0.9037	3.4161		
	0.0051	0.004	0.6863	4.4148		
	0.0053	0.014	0.9969	2.7833	2.2757	0.5021
mrCF-9	0.0048	0.019	1.1522	2.2645		
	0.0048	0.022	1.2453	1.7792		
	0.0053	0.008	0.8106	3.6623		0.1418
mrCF-10	0.0053	0.009	0.8416	3.5158	3.6591	
	0.0047	0.010	0.8727	3.7994	-	
	0.0050	-0.002	0.5000	5.4348		
mrCF-11	0.0048	0.000	0.5621	5.3377	5.3866	0.0485
	0.0049	-0.001	0.5311	5.3872	-	
	0.0052	0.010	0.8727	3.4341		
mrCF-12	0.0048	0.017	1.0901	2.5880	3.3289	0.6943
	0.0047	0.009	0.8416	3.9646		
	0.0050	0.005	0.7174	4.3478		
mrCF-13	0.0052	0.016	1.0590	2.5382	3.1041	1.0786
	0.0048	0.018	1.1211	2.4262		
	0.0048	0.004	0.6863	4.6907		
mrCF-14	0.0049	0.014	0.9969	3.0105	4.1099	0.9526
	0.0052	0.002	0.6242	4.6285	•	
	0.0051	0.006	0.7484	4.1103		
mrCF-15	0.0052	0.005	0.7174	4.1806	3.8088	0.5842
	0.0052	0.012	0.9348	3.1355		

Table B.4: Regression coefficient and adjusted and predicted regression coefficients for theresponses in this study i.e. yield and adsorption capacity.

	R ²	\mathbf{R}^2_{adj}	R ² pred
q _{e,} CIP (mg/g)	85.13	58.38	0.00
q _e , OTC (mg/g)	88.94	63.03	13.08

Table B.B.5: ANOVA results for the chemical activation campaign, for the responses yieldand MB adsorption capacity adapted from.

	Code	q _e ,	CIP (y1)	q _e ,	OTC (y₂)
Source	-	F-Value	P-Value	F-Value	P-Value
Model	-	3.18	0.108	4.47	0.057
Linear	-	1.67	0.287	4.86	0.061
HNO ₃	x ₁	0.18	0.688	0.00	0.986
Hold time	X2	4.59	0.085	3.19	0.134
Тетр	X3	0.25	0.641	11.40	0.020
Square	-	3.12	0.126	1.38	0.351
HNO ₃ *HNO ₃	X1 ²	2.95	0.147	4.04	0.101
Hold time*Hold time	x ₂ ²	3.30	0.129	0.02	0.887
Temp*Temp	x ₃ ²	2.58	0.169	0.01	0.927
2-Way Interaction	-	4.75	0.063	7.16	0.029
HNO ₃ *Hold time	X1X2	0.00	0.982	4.52	0.087
HNO₃*Temp	X1X3	0.00	0.998	0.53	0.501
Hold time*Temp	X ₂ X ₃	14.26	0.013	16.44	0.010

Equations B.1 and B.2 show the full polynomial models for the optimisation of the modification process prior to removing insignificant terms. Where, y_1 and y_2 are CIP and OTC adsorption capacity, respectively. x_1 is HNO₃ concentration, x_2 is hold time and x_3 is temperature.

$$y_1 = 81.0 + 1.69x_1 + 5.44x_2 - 1.0094x_3 - 0.223(x_1)^2 - 0.0920(x_2)^2$$
Equation B.1
+0.00325(x_3)^2 - 0.0019(x_1x_2) - 0.00(x_1x_3) - 0.03675(x_2x_3)
$$y_2 = -1.74 - 1.277x_1 + 0.288x_2 + 0.2469x_3 + 0.0710(x_1)^2 - 0.021(x_2)^2$$
Equation B.2

 $+0.000053(x_3)^2 + 0.0451(x_1x_2) + 0.00308(x_1x_3) + 0.01075(x_2x_3)$

Table	C.1: CIP a	dsorptio	on optimum p	oint studies	s, where	denot	es experin	nents cond	ucted with	n vCF-based	adsorben	ts.
Sample	Dose (g/L)	рН	Initial conc (mg/L)	Mass CF (g)	Abs	Final conc (mg/L)	Qe	Mean	St dev	Removal %	mean	St dev
				0.0203	0.008	0.0299	2.4262	_		98.5054		
%-mrCF-Opt	0.8	2	2	0.0204	0.014	0.1114	2.3144	2.3607	0.0583	94.4293	96.4674	2.0380
				0.0206	0.011	0.0707	2.3414			96.4674		
% mrCE CID				0.0203	0.008	0.0299	2.4262	_		98.5054		
0nt	0.8	2	2	0.0204	0.015	0.1250	2.2978	2.3552	0.0653	93.7500	96.2409	2.3858
				0.0206	0.011	0.0707	2.3414			96.4674		
% mrCE OTC				0.0224	0.023	0.2337	1.9713	_		88.3152		
%-IIICF-OTC-	0.9	2	2	0.0226	0.012	0.0842	2.1192	2.0730	0.0882	95.7880	93.2971	4.3144
				0.0225	0.012	0.0842	2.1286			95.7880		
				0.0203	0.006	0.0027	2.4597	_		99.8641		
%-K-ArCF-Opt	0.8	2	2	0.0204	0.029	0.3152	2.0647	2.3161	0.2185	84.2391	94.6558	9.0211
				0.0206	0.006	0.0027	2.4239			99.8641		
				0.0205	0.005	-0.0109	2.4523	_		100.5435		
%-mvCF-Opt	0.8	2	2	0.0204	0.003	-0.0380	2.4976	2.4476	0.0526	101.9022	99.8641	2.4494
				0.0203	0.010	0.0571	2.3928	-		97.1467		
				0.0204	0.012	0.0842	2.3477	_		95.7880		
%-K-AvCF-Opt	0.8	2	2	0.0207	0.005	-0.0109	2.4286	2.4111	0.0566	100.5435	99.1848	2.9612
				0.0206	0.004	-0.0245	2.4569			101.2228		
				0.0026	0.008	0.3036	9.4847	_		75.7124		
ae-mrCF-Opt	0.1	8	1.29	0.0026	0.015	0.3968	8.5884	9.0579	0.4496	80.1598	79.5650	3.5924
	0.1	0	1.29	0.0026	0.011	0.3435	9.1006			82.8229		

Appendix C: Antibiotic Adsorption Chapter Raw Experimental Data

Sample	Dose (g/L)	рН	Initial conc (mg/L)	Mass CF (g)	Abs	Final conc (mg/L)	Qe	Mean	St dev	Removal %	mean	St dev
				0.0023	0.003	0.2370	11.4455	_		88.1491		
qe-mvCF-Opt	0.1	8	1.29	0.0024	0.003	0.2370	10.9686	11.0597	0.3493	88.1491	89.2588	1.9219
			0.0026	-0.002	0.1704	10.7650			91.4780			
				0.0022	0.021	0.4767	17.3103			76.1651		
qe-mrCF-CIP-	0.1 8	8	2	0.0024	0.007	0.2903	17.8096	16.7158	1.4832	85.4860	81.9352	5.0412
				0.0028	0.009	0.3169	15.0276			84.1545		
				0.0024	0.023	0.5033	15.5903			74.8336		
qe-mrCF-OTC-	0.1	8	2	0.0026	0.012	0.3569	15.7994	15.9404	0.4379	82.1571	79.7159	4.2283
Opt				0.0025	0.012	0.3569	16.4314			82.1571		

Table C.2: OTC adsorption optimum point studies, where

denotes experiments conducted with vCF-based adsorbents.

Sample	Dose (g/L)	рН	Initial conc (mg/L)	Mass CF (g)	Abs	Final conc (mg/L)	Qe	Mean	St dev	Removal %	mean	St dev															
				0.0203	0.000	-0.0132	2.4793			100.6608																	
%-mrCF-Opt	0.8	2	2	0.0200	0.001	0.0308	2.4615	2.3607	0.0583	98.4581	97.7239	3.3646															
			0.0202	0.003	0.1189	2.3280			94.0529																		
				0.0203	0.000	-0.0132	2.4793			100.6608																	
%-mrCF-CIP-	0.8	2	2	0.0200	0.001	0.0308	2.4615	2.3552	0.0653	98.4581	96.9897	4.5852															
Ομί				0.0202	0.004	0.1630	2.2735			91.8502																	
				0.0224	0.002	0.0749	2.1486			96.2555																	
%-mrCF-UTC-	0.9	2	2	0.0226	0.005	0.2070	1.9834	2.0730	0.0882	89.6476	92.5844	3.3646															
000				0.0224	0.004	0.1630	2.0502			91.8502																	
				0.0199	0.001	0.0308	2.4738			98.4581																	
%-K-ArCF-Opt	0.8	0.8 2	2 2	0.0202	0.004	0.1630	2.2735	2.3161	0.2185	91.8502	91.1160	7.7354															
				0.8	μι υ.ο															0.0200	0.008	0.3392	2.0760			83.0396	

Sample	Dose (g/L)	рН	Initial conc (mg/L)	Mass CF (g)	Abs	Final conc (mg/L)	Qe	Mean	St dev	Removal %	mean	St dev
				0.0200	0.001	0.0308	2.4615			98.4581		
%-mvCE-Ont	0.8	2	2	0.0198	0.005	0.2070	2.2638	2.4476	0.0526	89.6476	96.2555	5.8276
70-mvci-Opt	0.0	2	Z	0.0202	0.000	-0.0132	2.4916			100.6608		
				0.0201	0.004	0.1630	2.2848			91.8502		
%-K-AvCF-Opt	0.8	2	2	0.0202	0.001	0.0308	2.4371	2.4111	0.0566	98.4581	90.3818	8.9019
				0.0200	0.009	0.3833	2.0209			80.8370		
				0.0025	0.025	0.7424	5.4764			42.4529		
qe-mrCF-Opt	0.1	8	1.29	0.0021	0.030	0.9607	3.9203	9.0579	0.4496	25.5272	42.4529	16.9256
				0.0025	0.020	0.5240	7.6598			59.3785		
				0.0024	0.030	0.9610	3.4303			97.8166		
qe-mvCF-Opt	0.1	8	1.29	0.0026	0.019	0.4800	7.7854	5.855	0.3493	82.5328	89.9563	18.848
				0.0025	0.023	0.6550	6.3501			89.5197		
	0.1	0	2	0.0026	0.009	0.0440	18.8112	_		97.82		
qe-mrCF-CIP-	0.1	8	Z	0.0023	0.010	0.0870	20.7900	19.443	1.168	82.53	89.956	7.651
Ομί				0.0026	0.002	0.0520	18.7275	-		89.52		
				0.0026	0.010	0.0873	18.3910			95.6332		
qe-mrCF-UIC-	0.1	8	2	0.0024	0.017	0.3930	16.7394	16.7158	1.4832	80.3493	83.2606	11.2044
Opt				0.0027	0.020	0.5240	13.6665			73.7991		

Table C.3: Regression coefficient and adjusted and predicted regression coefficients for theresponses CIP and OTC removal percentage.

	R ²	R^2_{adj}	R ² _{pred}
Removal (%), CIP (mg/g)	96.36	89.80	78.35
Removal (%), OTC (mg/g)	88.18	66.91	65.62

Table C.4: ANOVA results for the adsorption campaign when considering removal percentage as the responses.

Source	Code	Remova (y	al %, CIP ₂₁)	Removal %, OTC (y ₂)		
		F-Value	P-Value	F-Value	P-Value	
Model	-	14.69	0.004	4.14	0.066	
Linear	-	27.64	0.002	6.50	0.035	
Adsorbent dose	X 1	4.09	0.099	12.71	0.016	
рН	X2	31.41	0.002	4.12	0.098	
Initial Conc.	X 3	47.43	0.001	2.67	0.163	
Square	-	11.93	0.010	4.56	0.068	
Adsorbent dose*Adsorbent dose	x ₁ ²	10.32	0.024	0.12	0.743	
рН*рН	x ₂ ²	22.87	0.005	8.47	0.033	
Initial Conc.*Initial Conc.	x ₃ ²	0.05	0.827	6.26	0.054	
2-Way Interaction	-	4.49	0.070	1.37	0.353	
Adsorbent dose*pH	X1X2	6.79	0.048	0.24	0.648	
Adsorbent dose*Initial Conc.	X 1 X 3	0.97	0.369	3.61	0.116	
pH*Initial Conc.	x ₂ x ₃	5.71	0.062	0.26	0.629	

Equation C.1 and Equation C.2 show the full polynomial models for the optimisation of the adsorption process prior to removing insignificant terms. Where, y_1 and y_2 are the removal percentage of CIP and OTC, respectively. x_1 is adsorbent dose, x_2 is pH and x_3 is initial concentration.

$$y_{1} = 93.8 + 105.9(x_{1}) - 24.05(x_{2}) - 5.2(x_{3}) - 70.9(x_{1})^{2}$$
Equation C.1
+ 1.875 (x₂)² + 1.45(x₃)² - 7.36(x₁x₂) + 11.1(x₁x₃)
+ 3.60 (x₂x₃)
$$y_{2} = 218.0 - 14.5(x_{1}) - 30.8(x_{2}) - 136.4(x_{3}) + 17.7(x_{1})^{2}$$
Equation C.2

+ 2.636
$$(x_2)^2$$
 + 36.2 $(x_3)^2$ - 3.17 (x_1x_2) + 49.6 (x_1x_3)
+ 1.79 (x_2x_3)

Table C.5: Regression coefficient and predicted regression coefficients for the responses CIPand OTC removal percentage.

	R ²	R^2_{adj}	R^{2}_{pred}
Removal (%), CIP (mg/g)	99.93	99.82	98.99
Removal (%), OTC (mg/g)	97.86	94.01	85.95

Equation C.1 and Equation C.2 show the full polynomial models for the optimisation of the adsorption process prior to removing insignificant terms. Where, y_1 and y_2 are CIP and OTC adsorption capacity, respectively. x_1 is adsorbent dose, x_2 is pH and x_3 is initial concentration.

$$y_3 = 28.381 - 68.20(x_1) - 0.186(x_2) - 1.909(x_3) + 44.77(x_1)^2$$
Equation C.3
+ 0.0227 (x₂)² + 0.214(x₃)² - 0.154 (x₁x₂)
+ 1.609(x₁x₃) + 0.0278 (x₂x₃)

$$y_4 = 10.55 - 25.46(x_1) - 0.899(x_2) + 2.21(x_3) + 18.94(x_1)^2$$
Equation C.4
+ 0.0870 (x₂)² - 0.539(x₃)² - 0.378(x_1x_2)
- 1.57(x_1x_3) + 0.225 (x_2x_3)

	Code	q _e ,	CIP (y₃)	q _e ,	ОТС (у4)
Source		F-Value	P-Value	F-Value	P-Value
Model	-	844.72	0.000	25.40	0.001
Linear	-	1944.33	0.000	60.01	0.000
Adsorbent dose	X 1	5825.31	0.000	171.51	0.000
рН	X2	0.00	0.973	0.36	0.576
Initial Concentration	X ₃	7.68	0.039	8.16	0.036
Square	-	586.48	0.000	15.06	0.006
Adsorbent dose*Adsorbent dose	x1 ²	1749.63	0.000	42.23	0.001
pH*pH	x ₂ ²	1.42	0.287	2.82	0.154
Initial Conc.*Initial Conc.	x ₃ ²	0.49	0.513	0.42	0.544
2-Way Interaction	-	3.34	0.114	1.13	0.420
Adsorbent dose*pH	X 1 X 2	1.26	0.313	1.02	0.358
Adsorbent dose*Initial Conc.	x ₁ x ₃	8.61	0.032	1.10	0.342
pH*Initial Conc.	X ₂ X ₃	0.14	0.719	16.44	0.010

Table C.6: ANOVA results for the adsorption campaign when considering $q_{e}\,as$ the responses.

Appendix D: Regeneration Chapter Raw Experimental Data

Degenerant	Conc	Dum				q _e (n	ng/L)			
Regenerant	(M)	Kun	C0	C1	C2	С3	C4	C5	C6	C7
		1	2.36	1.81	1.83	1.77	1.79	1.73	1.56	1.46
NaOH	0.1	2	2.32	2.54	1.82	1.85	1.70	1.74	1.78	1.76
NaOn	0.1	3	2.33	2.52	1.84	1.79	1.81	1.75	1.60	1.62
		Mean	2.33	2.29	1.83	1.80	1.77	1.74	1.65	1.62
		1	2.34	2.54	1.81	1.74	1.83	1.84	1.83	1.81
кон	0 1	2	2.36	2.61	1.82	1.80	1.86	1.75	1.74	1.80
	0.1	3	2.28	2.55	1.86	1.81	1.86	1.81	1.79	1.72
		Mean	2.33	2.57	1.83	1.78	1.85	1.80	1.79	1.78
		1	2.31	2.54	1.78	1.81	1.82	1.66	1.59	1.57
NaOH	0.25	2	2.24	2.55	1.70	1.79	1.70	1.71	1.73	1.72
NaOn	0.25	3	2.35	2.54	1.78	1.70	1.76	1.53	1.61	1.65
		Mean	2.30	2.54	1.75	1.77	1.76	1.63	1.64	1.65
		1	2.39	2.51	1.84	1.81	1.83	1.86	1.79	1.77
KOH	0.25	2	2.34	2.48	1.90	1.78	1.83	1.83	1.78	1.85
КОП	0.25	3	2.30	2.58	1.87	1.78	1.81	1.74	1.72	1.78
	-	Mean	2.34	2.52	1.87	1.79	1.82	1.81	1.76	1.80

Table D.1: Regeneration of CIP-laden mrCF-Opt.

Table D.2: Regeneration of OTC-laden mrCF-Opt.

Paganarant	Conc	Bun				q _e (n	ng/L)			
Regenerant	(M)	Kun	C0	C1	C2	С3	C4	C5	C6	C7
		1	2.36	1.81	1.83	1.77	1.79	1.73	1.56	1.46
NaOH	0.1	2	2.32	2.54	1.82	1.85	1.70	1.74	1.78	1.76
NaOn	0.1	3	2.33	2.52	1.84	1.79	1.81	1.75	1.60	1.62
		Mean	2.33	2.29	1.83	1.80	1.77	1.74	1.65	1.62
		1	2.34	2.54	1.81	1.74	1.83	1.84	1.83	1.81
кон	0.1	2	2.36	2.61	1.82	1.80	1.86	1.75	1.74	1.80
		3	2.28	2.55	1.86	1.81	1.86	1.81	1.79	1.72
		Mean	2.33	2.57	1.83	1.78	1.85	1.80	1.79	1.78
		1	2.31	2.54	1.78	1.81	1.82	1.66	1.59	1.57
NaOH	0.25	2	2.24	2.55	1.70	1.79	1.70	1.71	1.73	1.72
NaOn	0.25	3	2.35	2.54	1.78	1.70	1.76	1.53	1.61	1.65
		Mean	2.30	2.54	1.75	1.77	1.76	1.63	1.64	1.65
		1	2.39	2.51	1.84	1.81	1.83	1.86	1.79	1.77
КОН	0.25	2	2.34	2.48	1.90	1.78	1.83	1.83	1.78	1.85
КОН	0.23	3	2.30	2.58	1.87	1.78	1.81	1.74	1.72	1.78
		Mean	2.34	2.52	1.87	1.79	1.82	1.81	1.76	1.80