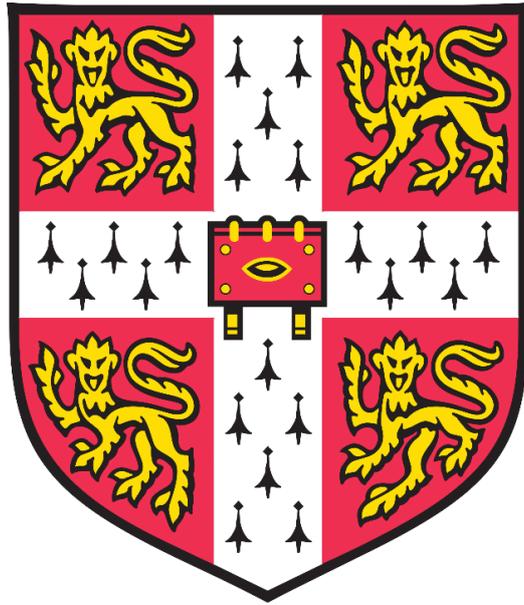


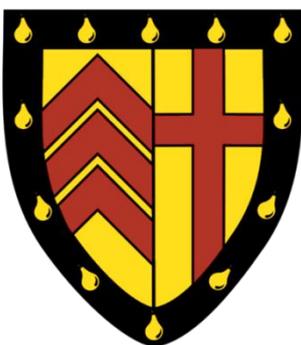
Characteristics and mechanisms of atrazine sorption to biochar for land remediation



*This dissertation is submitted for the degree of Doctor of Philosophy
in the Department of Engineering at the University of Cambridge*

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March 2018



Declaration

I hereby declare that this dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text.

In accordance with the Department of Engineering guidelines, this thesis does not exceed 65,000 words, inclusive of appendices, footnotes, tables and equations and it does not contain more than 150 figures.

Oliver McMillan

Cambridge, March 2018

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This work would not have been possible without the love and support of a village around me. I can never repay the assistance that I've received over the past few years nor fit the names of everyone that has guided me onto this small page.

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*E kore au e ngaro,
he kākano i ruia mai i Rangitātea.*

Abstract

Contaminated land is a widespread, global issue affecting millions of people. Atrazine is a commonly used herbicide which often contaminates groundwater and drinking water supplies and is associated with adverse health outcomes. Biochar is the solid product of pyrolysis and is associated with several environmental benefits. It may be an effective remediation tool when used as a soil amendment. This thesis investigates the mechanisms through which biochar can immobilise atrazine, and the implications of the mechanisms for remediating contaminated land.

Nine biochar samples were obtained from the United Kingdom Biochar Research Centre, which were produced from softwood pellets (SWP), wheat straw pellets (WSP), miscanthus straw pellets (MSP), rice husk (RH) and oil seed rape (OSR) each at pyrolysis temperatures of 550°C and 700°C (excluding OSR at 700°C). The sorption mechanisms controlling atrazine sorption to these biochars were determined through various characterisation methods and batch sorption experiments. The sorption tests showed that sorption to each of the standard biochars occurs via multiple simultaneously occurring mechanisms, which are each promoted under certain conditions. Studies investigating sorption kinetics, isotherms and interactions with humic acids showed that for all biochars in this study, pore filling was a significant process through which atrazine is transported to adsorption sites, although poor intraparticle diffusion for softwood and oil seed rape biochars can prevent efficient transport. Wheat straw and rice husk biochars showed effective pore diffusion, resulting in high sorption capacities. Partitioning was associated with poor remediation outcomes and was significant to softwood biochars, although adsorption dominated overall sorption for all other biochars.

pH was shown to significantly influence the occurrence of various sorption mechanisms. At low pH values, most biochars showed evidence of electrostatic repulsion between positive atrazine species and the positively charged biochar surface. At intermediate pH values, all biochars showed strong hydrogen bonding between H⁺ groups on the surface of the biochar and atrazine. A meta-analysis of previous relevant studies provided further evidence for hydrogen bonding of atrazine to biochar and showed that hydrophobic effects likely play little role in adsorption after accounting for the effects of surface area. Varying contributions

of π - π EDA interactions, hydrogen bonding involving biochar O⁻ groups, and interactions with ash minerals resulted in different sorption profiles for each biochar at high pH values.

In order to further determine the mechanisms controlling sorption at high pH, surface compositions of SWP550, RH700 and OSR550 biochars were modified using hydrofluoric acid. Modification with hydrofluoric acid successfully removed the ash contents of rice husk and oil seed rape biochars and reduced atrazine removal at high pH values. This suggested that the ash fraction increases atrazine removal at high pH through complexation or catalytic hydrolysis. The roles of the various mechanisms are related to remediation outcomes in a novel manner allowing for the improved design of biochar for environmental remediation.

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List of symbols and abbreviations

Standard biochars

SWP	<i>softwood pellets</i>
WSP	<i>wheat straw pellets</i>
MSP	<i>miscanthus straw pellets</i>
RH	<i>rice husk</i>
OSR	<i>oil seed rape</i>

Symbols

$1/N$	<i>Freundlich sorption linearity</i>
$\text{abs}_{n, x}$	<i>absorbance at wavelength n due to compound x</i>
b	<i>Langmuir fitting parameter</i>
C_{aq}	<i>aqueous concentration</i>
C_i	<i>initial aqueous concentration</i>
C_e	<i>aqueous concentration at equilibrium</i>
C_t	<i>aqueous concentration at time t</i>
k_n	<i>model fitting parameter n</i>
K_F	<i>Freundlich fitting parameter</i>
m	<i>mass</i>
q_a	<i>sorption due to adsorption</i>
q_e	<i>sorption at equilibrium</i>
q_p	<i>sorption due to partitioning</i>
q_t	<i>sorption at time t</i>
Q_{max}	<i>Langmuir adsorption capacity</i>
V	<i>solution volume</i>

Abbreviations

Ar C=C	<i>aromatic carbon-carbon double bond</i>
ATR	<i>atrazine</i>
BC x	<i>biochar produced at a highest treatment temperature of x °C</i>
BET	<i>Brunauer–Emmett–Teller</i>
CAHB	<i>charge-assisted hydrogen bond</i>
CaCO ₃	<i>calcium carbonate</i>

CaO	<i>calcium oxide</i>
CEC	<i>cation exchange capacity</i>
DALY	<i>disability-adjusted life year</i>
EE2	<i>ethinylestradiol</i>
FTIR	<i>Fourier-transformed infrared spectroscopy</i>
HCl	<i>Hydrochloric acid</i>
HF	<i>Hydrofluoric acid</i>
HI	<i>hysteresis index</i>
HOC	<i>hydrophobic organic compound</i>
HTT	<i>highest treatment temperature</i>
MTBE	<i>methyl tert-butyl ether</i>
NOM	<i>natural organic matter</i>
PAH	<i>polyaromatic hydrocarbon</i>
pH _{pzc}	<i>pH point of zero charge</i>
SEM	<i>scanning electron microscopy/microscope</i>
SGV	<i>soil guideline value</i>
SiO ₂	<i>silicon dioxide</i>
SOM	<i>soil organic matter</i>
SSA	<i>specific surface area</i>
TGA	<i>thermogravimetric analysis</i>
UKBRC	<i>United Kingdom Biochar Research Centre</i>
UNDP	<i>United Nations Development Program</i>
XRD	<i>x-ray diffraction crystallography</i>
XPS	<i>x-ray photoelectron spectroscopy</i>
π - π EDA	<i>π-π electron donor-acceptor</i>

Chapter 1: Background and introduction

The contamination of soil and groundwater is a widespread issue that can adversely affect human health and ecosystems. While methods exist to remediate and control these contaminations, recent attention is being directed towards the development of lower cost and more sustainable remediation options. This thesis investigates the use of biochar as an effective remediation tool for organic contaminants in soil, with a particular focus on the sorption of atrazine. Chapter 1 provides the relevant background on soil contamination and why it is important to remediate it, as well as a background on biochar and how it may be useful in remediating contaminated soil.

1.1 Soil and groundwater contamination

Soil and groundwater can become contaminated through many pathways ^{1,2} including local contaminations such as spills and leakages from mining activities, oil processing, and landfills, or through diffused sources such as waste application, incomplete combustion (such as in motor vehicles), contaminated waterways, and agricultural application of herbicides or pesticides. Soil contamination is widespread, both in terms of its global relevance and its prevalence within countries. The global number of sites that are contaminated and requiring remediation is difficult to estimate, although is likely to be in the hundreds of thousands ³. Soil contamination is a global issue that is likely to require long-term and diverse solutions.

Soil contaminants may exist in various forms, including organic (carbonaceous), heavy metal, nutrients, radioactive substances and organo-metallic compounds. The types of contaminants present in a given contamination will depend on the activities present at the site. Common organic contaminants include herbicides and pesticides which have leached into groundwater or become attached to soil, polychlorinated biphenyls (PCBs) from historical uses in electrical and plastic equipment and polyaromatic hydrocarbons (PAHs) from combustion processes. The toxicity, mobility and degradability of organic contaminants can vary widely, so it is important to properly characterise the contaminants present on a site.

Exposure to soil contaminants can result in severe adverse health effects for humans and ecosystems, including skin cancers, neurological defects, nervous system damage, impaired sexual development and embryonic development defects. Globally, toxic waste sites may result in the loss of approximately 800,000 disability adjusted life years (DALYs),

comparable to that of Malaria (725,000) ⁴, with as many as 200 million people being directly affected by them ⁵. The widespread nature, occurrence and effects of contaminated land mean that they require diverse, cost-effective and sustainable treatment solutions.

1.2 Atrazine background

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) is a triazine herbicide widely used throughout USA and Australia to control broadleaf weeds and grass, particularly on corn and sorghum crops. Investigations have found atrazine in groundwater and drinking water supplies near areas where it is applied, where it can remain persistent for decades. Its molecular structure is shown in Figure 1-1, and demonstrates a number of functional groups as well as an aromatic ring. These varied properties make atrazine a useful indicator contaminant for determining the interactions with other organic molecules. Atrazine is a useful contaminant to study due to its risks in the environment and the transferability of its chemical interactions to other organic molecules.

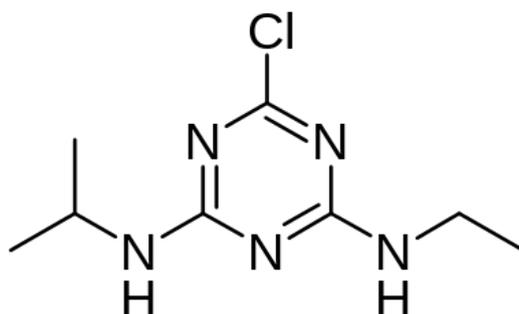


Figure 1-1: Molecular composition of atrazine

Atrazine may have harmful effects on human and animal health. Laboratory studies have suggested that atrazine may turn frogs hermaphroditic ⁶ or otherwise adversely affect their sexual health ⁷, and reduce survival rates of red drum fish larvae ⁸, though these studies have been criticised for a lack of reproducibility ⁹⁻¹¹. While its impacts on human health are not clear, it has been found in the urine of farmers who apply it ¹² and residents who live near to application areas ¹³, and its use has been correlated with incidences of breast cancer ¹⁴, reduced male fertility ^{13,15}, and birth defects ¹⁶. As a result of atrazine's potential harmful effects in the environment and its high likelihood of contaminating groundwater and drinking water supplies, methods of preventing the spread of atrazine into groundwater and surface water supplies have received increasing attention in recent years.

1.3 Soil and groundwater remediation

A range of treatment technologies exists to remediate contaminated sites using various physical, chemical and biological methods. Commonly used treatment technologies include soil vapour extraction, bioremediation, phytoremediation, containment, and excavation to landfill¹⁷⁻¹⁹. The work in this thesis primarily relates to using biochar as a soil amendment to adsorb contaminants; however soil amendments may also be combined with other technologies such as permeable reactive barriers or phytoremediation. Recent research has focused on developing sustainable treatment methods, including in-situ remediation technologies to reduce impacts of remediation such as cost, energy consumption, and handling of contaminated material²⁰. In-situ treatment can be more effective than ex-situ methods due to their cost-effectiveness, low resource intensity, and lower likelihood of secondary pollutions.

1.4 Biochar and its properties

Biochar, shown in Figure 1-2, is the solid carbon-rich product of heating biomass to high temperatures (250 – 700°C) in oxygen-limited conditions – a process known as pyrolysis. The production and application to soil of biochar results in several environmental benefits, such as the re-use of waste products, the sequestration of carbon, and improvements in soil health and plant growth. Biochar may be made from many different initial feedstocks, such as the husk or straw of rice plants, wheat straws, wood products, food waste, sewage sludge or animal manure. The feedstock and pyrolysis conditions both have significant effects on the properties of a given biochar. Recent research has demonstrated that biochar is an effective adsorbent of organic and heavy metal contaminants in soil and water. Due to its high surface area, high alkalinity, high cation exchange capacity and complex pore network, contaminants strongly bind to the surface of biochar, resulting in them being immobilised in the soil profile or removed from aqueous solutions. However, there are a number of uncertainties around the use of biochar in environmental remediation. In particular, the mechanisms through which the contaminants are immobilised and how these are likely to behave in the soil profile over the long term are not thoroughly understood.



Figure 1-2: Biochar produced from softwood pellets

1.5 Aims and objectives

The aim of this thesis is to further understand the role of biochar as an effective tool for immobilising organic contaminants in soil. Though the research will primarily focus on atrazine, it is intended that the results are transferable to other organic contaminants. The primary objectives are therefore as follows:

- to identify the processes through which atrazine is transported to sorption sites on biochar;
- to identify the adsorption mechanisms of atrazine to biochar; and
- to determine the role of the ash fraction in the removal of atrazine using biochar.

1.6 Thesis structure

This thesis is comprised of seven chapters as follows:

Chapter 1: Background and introduction

Chapter 1 provides a background to soil contamination, biochar and its use in soil remediation. It also sets out the aim, objectives and structure of the thesis.

Chapter 2: Literature review

Chapter 2 reviews existing literature on biochar for the sorption of organic contaminants, as well as the influence of soil and ageing on biochar sorption. It identifies research gaps and contradictions, and areas for further research.

Chapter 3: Materials and methods

Chapter 3 provides details of the materials used, and the methodologies for all laboratory experiments and analyses carried out.

Chapter 4: Partitioning and intraparticle transport of atrazine to standard biochars

Chapter 4 investigates the roles of pore filling and partitioning in the sorption of atrazine by biochar. It gives the results of batch sorption studies investigating the sorption kinetics, isotherms and interactions with humic acids of the nine standard biochars.

Chapter 5: Adsorption mechanisms of atrazine to standard biochars

Chapter 5 investigates the roles of hydrogen bonding and hydrophobic interactions in the sorption of atrazine. It details the results of pH-dependency sorption tests of atrazine to the standard biochars. It then relates the sorption capacities to the properties for the nine standard biochars, and for all previous studies investigating the sorption of atrazine to biochar.

Chapter 6: Biochar de-ashing and its influence on the adsorption mechanisms of atrazine

Chapter 6 investigates the role of ash in the removal of atrazine from solution using biochar. It details the characterisation of hydrofluoric acid-modified biochar samples, and the removal of atrazine using raw, modified and ash samples as a function of pH to isolate the role of the ash components.

Chapter 7: Conclusions and recommendations

Chapter 7 summarises the key findings of the thesis, and provides recommendations for future work. It also acknowledges the limitations of the research and suggests follow-up studies that may be able to provide further insights.

Chapter 2: Literature review

The results of previous studies are critical in determining academic consensus, uncertainties and knowledge gaps. Chapter 2 provides a comprehensive analysis of the literature to date relevant to the remediation of organic contaminants from soil using biochar. It first gives a background on land contamination and remediation methods, and then discusses the production and properties of biochar, including previous studies on the biochar set used throughout this thesis. Next, it investigates the use of biochar for the sorption of organic contaminants, including the roles that the different sorption mechanisms play in the laboratory and uses these results to predict their expected influence in the soil profile. It then relates these results to the sorption of atrazine to biochar, and the expected remediation outcomes of using biochar for its immobilisation. Finally, it summarises the major research gaps and how these feed into further study throughout this thesis.

2.1 Land contamination

Soil and groundwater contamination can come from a range of different sources and results in significant adverse effects on humans and ecosystems. This section provides a brief background on the sources, extent and effects of soil contamination, as well as a background on atrazine's use and potential adverse effects.

2.1.1 Sources and extent

Land can become contaminated through many different pathways, and is typically a result of industrial and agricultural activity. The main sources of land contamination are activities such as oil processing, timber processing, mining, landfilling, and the application of pesticides and herbicides²¹⁻²³. Leaks, spills and intentional releases from these activities results in the release of significant quantities of contaminants into the environment every year, as shown in Figure 2-1²¹. In England, the major activities that lead to contaminated sites are waste management (31% of sites), the energy industry (24%), timber processing (16%), and the metal industry (13%) with the remaining contaminations caused by other activities such as ash deposits and chemical and mineral processing²³. Abandoned mines may also present significant risks of further contamination to surface and groundwater bodies in England and Wales²². The source of the contamination will influence the concentrations, types and extent of the contaminants throughout the soil and groundwater profile.

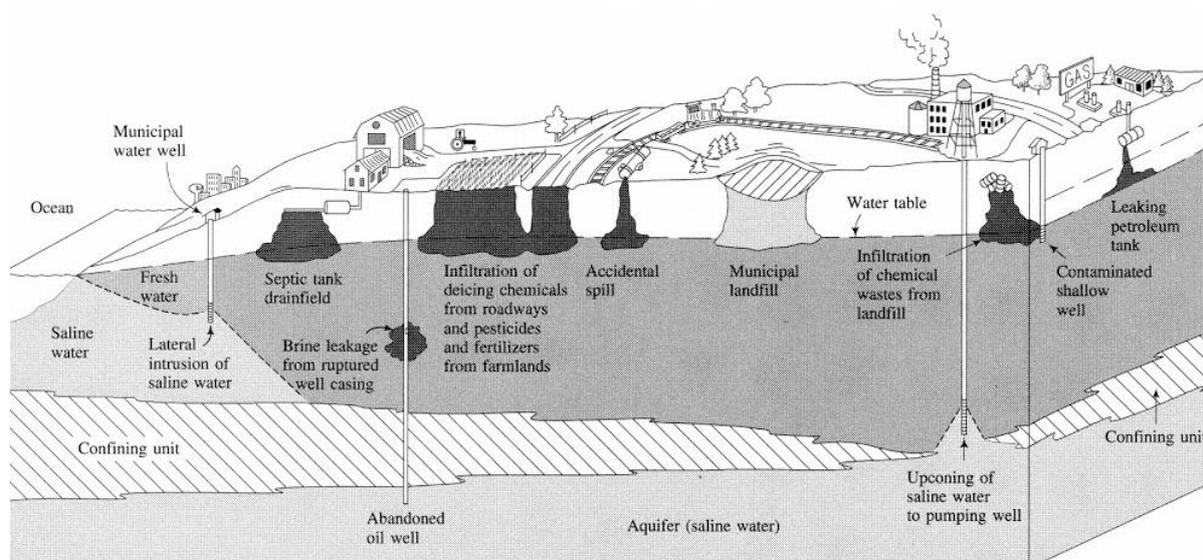


Figure 2-1: Pathways through which chemicals can contaminate groundwater. Reproduced from Fetter et al.²¹

Contaminated sites are widespread, resulting in huge numbers and areas of land posing significant environmental risks. Table 2-1 shows the number of contaminated sites in various countries, and shows that major industrial nations such as the UK, France and USA can have hundreds of thousands of contaminated sites. While various definitions are included in these figures, they provide a useful reference for the scale of land contamination globally. In China, a detailed investigation covering over 70% of the country's land area found that 16% of soil samples exceed environmental quality standards, including 19% of agricultural soils². In the United States, it has been estimated that approximately 9 million hectares of land is contaminated across 500,000 sites, including 1,186 'Superfund' sites which are 'seriously contaminated' as at February 2018²⁴. Further, a 2006 US investigation found pesticides in approximately 60% of the groundwater from urban and agricultural areas^{25,26}. In addition to these sites, the amount and severity of contaminated land is often understated due to underreporting and inadequate characterisation of old sites^{3,27}. The varied nature and vast quantity of contaminated sites results in the need for diverse and sustainable remediation methods.

Table 2-1: Estimated number of contaminated sites in various countries and regions. Data from European Environment Agency (2015)²⁸, Plant et al. (2015)²⁹ and United States Environmental Protection Agency (2018)³⁰ (by the author)

Country	No. contaminated sites
European Union ⁸³	2,917,289
United Kingdom ⁸³	3,145,650 *
France ⁸³	3,093,179 *
USA ⁸⁴	530,000
Belgium (Flanders) ⁸³	236,409
Australia ⁸⁵	150,000
Finland ⁸³	109,516
Switzerland ⁸³	36,000
Lithuania ⁸³	25,916
Slovakia ⁸³	9,240
Hungary ⁸³	8,818
Austria ⁸³	6,141
Malta ⁸³	484

* Value represents 'potentially contaminated sites' as defined by the European Environment Agency

2.1.2 Types of contaminants

There are many different types of contaminants that may be present at a contaminated site. Different contaminant types vary in mobility, degradability, solubility and toxicity. Contaminants can exist in organic (carbonaceous) forms such as pesticides, herbicides, polyaromatic hydrocarbons (PAHs), and volatile organic compounds (VOCs), as well as inorganic forms such as heavy metals, radioactive waste, and nutrients. Examples of selected contaminant types and their sources are given in Table 2-2. This thesis will primarily focus on organic compounds; however sites often contain mixtures of various contaminant types, so it is useful to be aware of how these may behave and interact with each other.

Table 2-2: Contaminant types, and examples of contaminants and their sources (by the author)

Contaminant Type	Contaminant	Source(s)
Total petroleum hydrocarbons	Fluorene	Oil spills, oil processing, crude oil extraction
	Hexane	
	Benzene	
Pesticides and herbicides	Atrazine	Herbicide used for grasses and broadleaf weeds ⁵⁵
	Imidacloprid	Insecticide used to prevent insects eating corn ^{86,87}
	Carbofuran	Insecticide used to control ground-dwelling insects ^{88,89}
Polyaromatic hydrocarbons	Naphthalene	Atmospheric deposition after incomplete combustion ⁹⁰
	Benzo[a]pyrene	
Volatile organic compounds	Benzene	Oil spills ⁹¹ , vehicle combustion ⁹²
	Toluene	Oil spills ⁹³
	Trichloroethylene	Plastic production ⁹⁴ , metal degreasing ⁹⁵
Heavy metal	Arsenic	Gold mining ^{96,97} , timber treatment ⁹⁶ , advanced weathering of rocks ^{96,98,99}
	Lead	Biosolids application ¹⁰⁰ , lead ore mining ¹⁰⁰ , leaded petrol ¹⁰¹ , fertilizer application ¹⁰⁰
	Mercury	Chlor-alkali plants ¹⁰² , fossil fuel combustion ¹⁰² , waste incineration ¹⁰² , contaminated seafood via bioaccumulation ¹⁰³ , gold mining ^{104,105}
	Nickel	Metal plating, electroplating, nickel mining ¹⁰⁰

The composition of contaminants on a given site depends on the nature and source of the contamination. Heavy metals are common contaminants from mining sites, such as arsenic in gold mines or lead and nickel from their respective mines. Organic contaminants can also come from a range of sources. For example, PAHs can reach high concentrations in soils through processes such as incomplete combustion in cars and industrial activities. The volatile organic compound methyl *tert*-butyl ether (MTBE) is used as a fuel additive and often contaminates groundwater via the leaking of underground storage tanks. The intentional application to land of various products can also result in the soil or groundwater being contaminated, such as in the application of biosolids, which can result in lead contamination,

or pesticides and herbicides which can leach into groundwater³¹. These different contaminant types present different risks to the environment and to receptors.

2.1.3 Effects of land contamination

Land contamination results in adverse social, environmental, economic and cultural outcomes on humans, while also resulting in significant damage to ecosystems and wildlife. A 2005 report estimated that the annual costs of remediation globally are between US\$12 billion and \$35 billion³. Further, toxic waste sites may directly affect as many as 200 million people⁵ and result in the loss of approximately 800,000 disability adjusted life years (DALYs),⁴. In general, the importance of soil quality in promoting ecosystem health, biodiversity and food production is well understood and accepted. Goal 15 of the United Nations Development Program (UNDP) Sustainable Development Goals aims to ‘protect, restore, and promote sustainable use of terrestrial ecosystems’³², including soil; a goal that applies to all countries and all peoples³³. Contaminants in soil can reach receptors (e.g. humans, animals or plants) through three major mechanisms³⁴:

- **oral intake:** direct ingestion of contaminated soil (e.g. through dirt on hands) or water, or ingestion through eating contaminated produce or produce with contaminated soil attached;
- **inhalation:** breathing of volatilised contaminants from soil or perched groundwater, or contaminants attached to dust particles;
- **topical or dermal exposure:** contact of the contaminant with skin or a cut.

The health effects of an exposure will depend on the receptor, the properties of the contaminant, the method of exposure and the quantity of the exposure (dosage). For example, heavy metal compounds can accumulate in the body through chronic exposures and result in neurological and birth defects, kidney damage and nervous system damage. In contrast, acute doses of organic compounds such as dioxins and trichloroethylene can result in short- and long-term dizziness and headaches, impaired embryonic development, cancers, and cardiovascular disease. The adverse health outcomes from contaminated soil and groundwater can therefore have devastating effects on communities.

2.1.4 Atrazine use and contamination

Atrazine is a widely applied herbicide used on corn and sorghum crops, however its high mobility and persistence can result in contamination of groundwaters³⁵. From 1992-2004, approximately 35,000 metric tons were applied each year in the USA, although its use has since declined slightly^{36,37}. In 2004, its use was banned in the European Union due to concerns that it, or its degradation products, widely contaminate groundwater³⁸. Irrigation or rainfall may cause atrazine to move through the soil profile, causing contamination of sediments and groundwater^{39,40}, and it can reach high concentrations in waterways immediately after periods of heavy rainfall. A 2015 study suggested that it is the most common pesticide in groundwaters in the USA³⁶, while similar findings have been demonstrated in Australia⁴¹, Brazil⁴² and China^{43,44}. An analysis carried out in the USA⁴⁵ found that 16 of 20 watersheds tested had average atrazine concentrations above 1 part per billion (ppb), and nearly half of these watersheds had peak concentrations above 50 ppb, as shown in Figure 2-2. Once in soil, atrazine is persistent, and can potentially last for decades⁴⁶ – it is still the most common herbicide in groundwater in Germany, despite being banned in 1991⁴⁷. The mobility and persistence of atrazine in the soil profile suggests that it can spread widely into groundwater and drinking water supplies where applied.

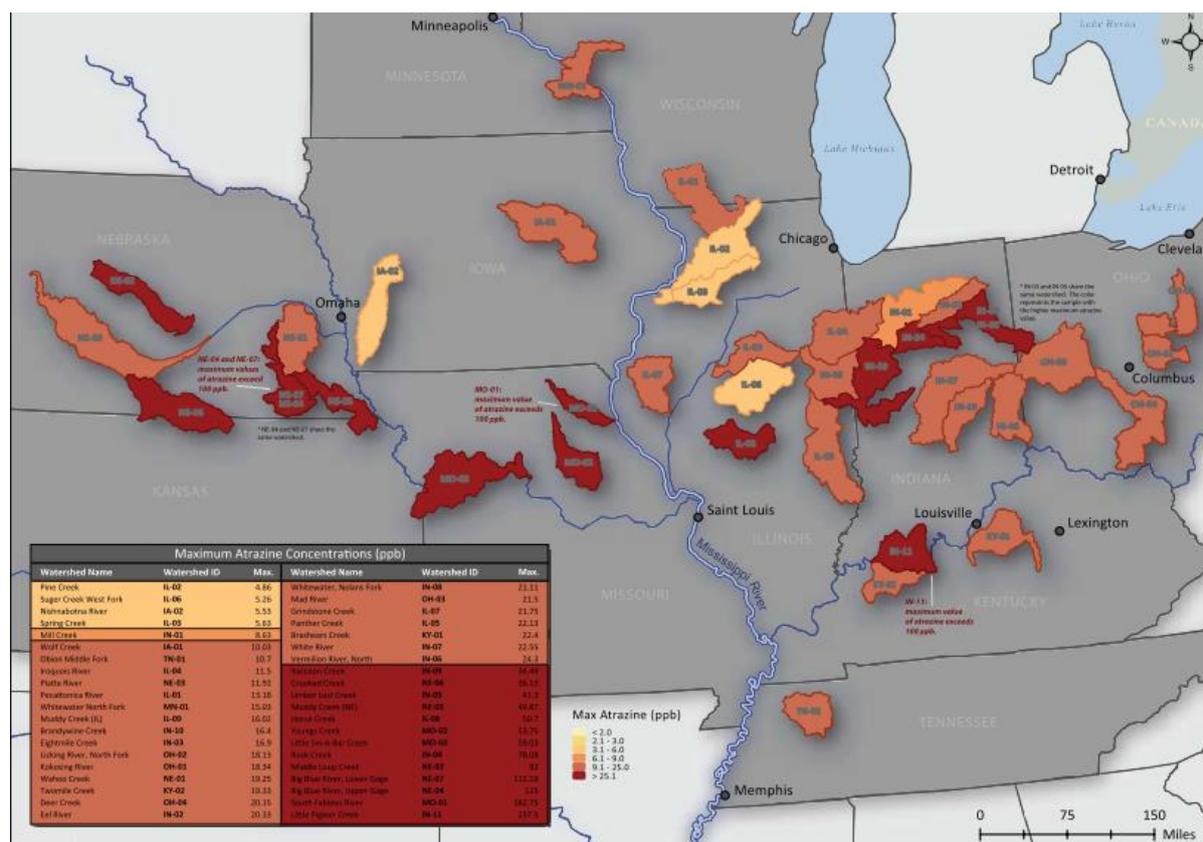


Figure 2-2: Maximum measured atrazine concentrations in American water catchment in 2009. Dark red areas represent catchments with atrazine concentrations measured above 25ppb. Reproduced from Wu et al.³⁷

Atrazine may have harmful effects on human and animal health, although the significance of adverse health effects of atrazine is a controversial topic. A series of studies in the early 2000's by Tyrone Hayes found that atrazine can induce hermaphroditism and impaired sexual development in frogs^{48,49}, although some, including *Syngenta*, the manufacturers of atrazine, dispute the authenticity of these results¹¹. Follow-up studies have found conflicting results, with some finding harmful effects on the sexual health of freshwater fish and frog species⁷, while others have found no clear effect^{9,10}. Its use has been correlated with adverse health effects on humans, including abdominal wall defects¹⁶ and reduced semen quality¹³. However, a 2011 review produced for the WHO found that atrazine does not have adverse effects on human sexual health⁵⁰, and further 2014 review found no causal link between atrazine exposure and adverse pregnancy outcomes⁵¹. However, these studies, as well as others with similar findings, have been criticised for receiving funding from *Syngenta*⁵². Adverse effects of atrazine on human and animal health are therefore disputed. Social, economic and political factors are likely preventing the determination of scientifically objective outcomes. It is not within the scope of this thesis to make a judgement on the validity of each of these studies. However, the fact that a number of studies have

demonstrated harmful effects, combined with its common occurrence in groundwater and drinking water, suggest that the ability to immobilise atrazine is likely to be of environmental benefit.

2.2 Soil and groundwater remediation

Various techniques exist to remediate contaminated soil and groundwater by removing, immobilising, degrading or rendering inert the contaminants. This section provides a brief overview of existing remediation technologies and their applications, as well as background on the use of soil amendments in contaminated soil which are relevant to the remainder of this thesis.

2.2.1 Existing remediation techniques

A range of technologies exist to remediate contaminated soil and groundwater. In the UK, remediation aims to remove either the *source*, *pathway*, or *receptor* of the contamination⁵³. This thesis deals primarily with the use of soil amendments for environmental remediation, which block the *pathway* through which the contaminant may travel. An overview of existing remediation technologies is given in

Table 2-3¹⁷⁻¹⁹ and highlights the range of options available to design engineers at present. The optimal technology for any given site will depend on many factors including the nature and extent of the contamination, the soil properties, the acceptable treatment time and quality, the anticipated end use of the site, the budget, and any physical, political or social constraints. Typically, several methods are combined on a given site to achieve optimum outcomes.

Table 2-3: Overview of technologies available for treating contaminated soil and groundwater (by the author)

Treatment Method	Description
Soil washing	The soil is excavated and washed with water or a treatment solution and returned to the site
Air sparging	Air flow is passed through the groundwater to promote the volatilisation and capture of contaminants
Soil vapour extraction	Air flow is passed through unsaturated soil to promote the volatilisation and capture of contaminants
Bioremediation	Selected bacteria are added to the site to degrade the contaminants
Stabilisation/solidification	A reactive agent (e.g. binder) is added to the soil to solidify the soil and prevent contaminant leaching
Soil amendment	A material or nutrient is mixed into the soil to alter the properties of the soil, enhance degradation, or interact with the contaminants
Incineration	The soil is heated to high temperatures to thermally decompose the contaminants
Phytoremediation	Selected plants are promoted at the site which either uptake or degrade the contaminants
Permeable reactive barrier	A permeable barrier is constructed which reacts with the contaminants to treat them as the groundwater passes through
Containment	An impermeable barrier or cap is constructed to prevent groundwater flow or other spreading of contaminants from the site
Excavation to landfill	The contaminated soil is removed from the site and disposed of in a controlled landfill

While technologies may be combined in order to fully remediate a given site, the most commonly used technology to date has been landfilling. According to a 2007 report on contaminated land in England and Wales, over 90% of all sites are expected to be treated through excavation of the contaminated soil to landfills ²³, although a follow-up report published in 2016 ⁵⁴ suggests that the number has fallen to approximately 65%. This may partially be due to improved legislation, such as the CL:aire Code of Practice for hazardous waste, which allows for more flexible on-site remediation practices. In the USA, an annual

report published in 2017 by the US Environmental Protection Agency ⁵⁵ showed that approximately 50% of remediation projects have involved off-site disposal. Landfilling has been shown to be one of the most unsustainable remediation technologies due to its risks to human health and the local environment, and high use of energy and materials ⁵⁶⁻⁵⁸. For example, Chen et al. ⁵⁸ used multi-criteria analysis to investigate four remediation options for four contaminated sites in New Zealand. They found that landfilling had the worst performance on all sites for four different weightings of human health and safety, local environment, stakeholder concern, land use, and the global environment. However, landfilling is often preferred due to its short timescales and completeness of contaminants removed from the site. In general, the excavation, handling and transport involved in ex-situ remediation presents a number of environmental risks ⁵⁸. Recent research into contaminated land remediation has therefore focused on sustainable in-situ remediation techniques.

2.2.2 Soil amendments for remediation

Soil amendment is a remediation technique that uses an adsorbent, compost or mineral compound to enhance degradation or immobilise contaminants and improve soil fertility. Common materials used as adsorbents include biochar, activated carbon, and minerals such as zeolite, while compost and lime can aid revegetation thereby increasing the overall stability of the site. Soil amendments are particularly useful when the major hazards of a contamination are the contaminant bioavailability or the poor soil health. Soil amendment has the potential to be an effective method for the sustainable and affordable in-situ remediation of contaminated land.

Soil amendments can be applied in various ways depending on the mobility, solubility and extent of the contamination. They are most commonly prepared as sludge and tilled into the upper layer of soil. This allows for simultaneous or delayed planting of vegetation on the amended areas for stabilisation or phytoremediation. They may also be tilled deeper into soil in trial pits to address contamination ‘hotspots’ and prevent deeper leaching of attached molecules ⁵⁹. Finally, they may be constructed into a *permeable reactive barrier*, to adsorb dissolved contaminants as groundwater flows through the amended soil ^{60,61}. A significant advantage of biochar is that it aids revegetation, as discussed in Section 2.3, and is therefore most commonly applied to the top layer of the soil where plants may be grown. However, the method of application will be dependent on the nature of the contamination and the remediation objectives. The reduced resource and transport requirements make soil

amendment a favourable remediation technology^{56,58,62}. Soil amendment therefore represents a potentially sustainable and versatile method of remediating contaminated land.

2.3 Biochar, its production and properties

Biochar is the solid, carbon-rich product of heating biomass under oxygen-limited conditions (pyrolysis). The production of biochar and its application to soil results in several environmental benefits, including the sequestration of carbon, improvements in soil health and plant growth, the re-use of waste products, and the immobilisation of contaminants. Production parameters such as the feedstock used, the pyrolysis temperature and the heating rate will each influence the properties of the final biochar product. This section outlines the key production parameters and the major properties of biochar relevant to its use as a soil amendment.

Definitions of biochar can vary, so terminology used between published studies is not always consistent. The International Biochar Initiative (IBI) defines biochar as ‘a *solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment*’⁶³, and suggests uses such as soil improvement, land remediation/protection, and greenhouse gas sequestration (in addition to various chemical benchmarks). Lehmann et al.⁶⁴ defines biochar by the intention to add the product to soil. Charcoal is also the solid product produced during pyrolysis and is often referred to interchangeably with biochar^{65,66}, particularly when being used as an adsorbent. However, charcoal typically refers to a product used in either water filtration or as a fuel source. Many studies also use the terms *black carbon* and *biochar* interchangeably^{67,68}, with black carbon represent carbonised organic matter that occurs naturally through events such as forest fires. Finally, activated carbon also represents a carbonised organic adsorbent, however refers to one which has been activated at high temperatures or thoroughly treated with activating chemicals in order to increase its surface area. It is therefore important to check the details of each study to determine what material is being used and how it relates to biochar, however, in general the terms ‘biochar’, ‘black carbon’ and ‘charcoal’ may be used interchangeably when referring to studies which have investigated adsorption properties.

2.3.1 Biochar production

The pyrolysis process used to produce biochar involves heating biomass to high temperatures (approximately 200 - 700°C) in the presence of zero or limited oxygen. It results in three

products, each of which may be captured separately for further use: a gaseous syn-gas, a liquid bio-oil, and a solid biochar, as demonstrated in Figure 2-3. Pyrolysis may be carried out in batch units such as kilns or earth pits, or continuous production units, as demonstrated by the units shown in Figure 2-4. Other similar processes, such as gasification, are intended for the production of syn-gas or bio-oil however can also result in appreciable amounts of solid biochar. The selection of the biomass (feedstock), the highest treatment temperature (HTT) and the heating rate are the conditions which will have the greatest influence on the final biochar properties, however other parameters such as the use of an inert gas may also play a role.

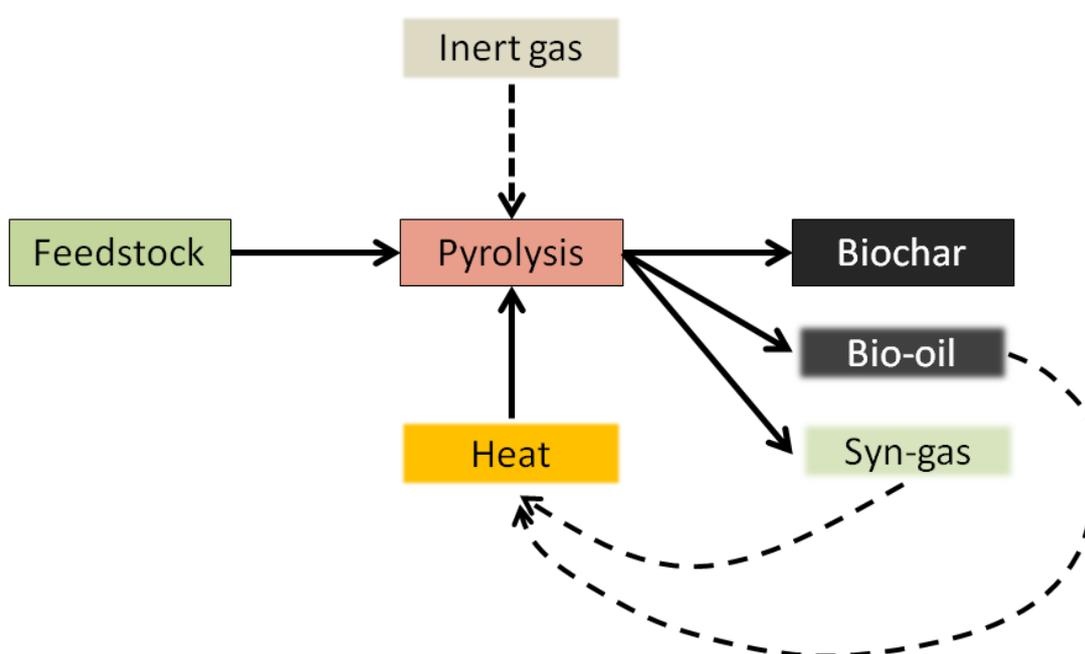


Figure 2-3: Schematic of pyrolysis process. Dashed lines indicate processes that are not always included (by the author)

A wide range of feedstocks have been used to produce biochar, each resulting in products with different properties. Plant-based products such as rice-husk, softwoods, wheat straw and maple wood chars have been commonly reported to produce biochars with high surface areas and well developed pore networks^{69,70}. In contrast, animal products such as swine manure, poultry litter or bonemeal have also been used, resulting in nutrient rich biochars with high ash contents, and a less thoroughly developed pore structure^{71,72}. Waste products such as food waste^{73,74} have also been shown to provide environmental benefits while meaningfully re-using products that would otherwise be disposed of. The selection of a suitable feedstock will depend on the desired biochar properties, the pyrolysis conditions, and the local or commercial availability of the different materials.

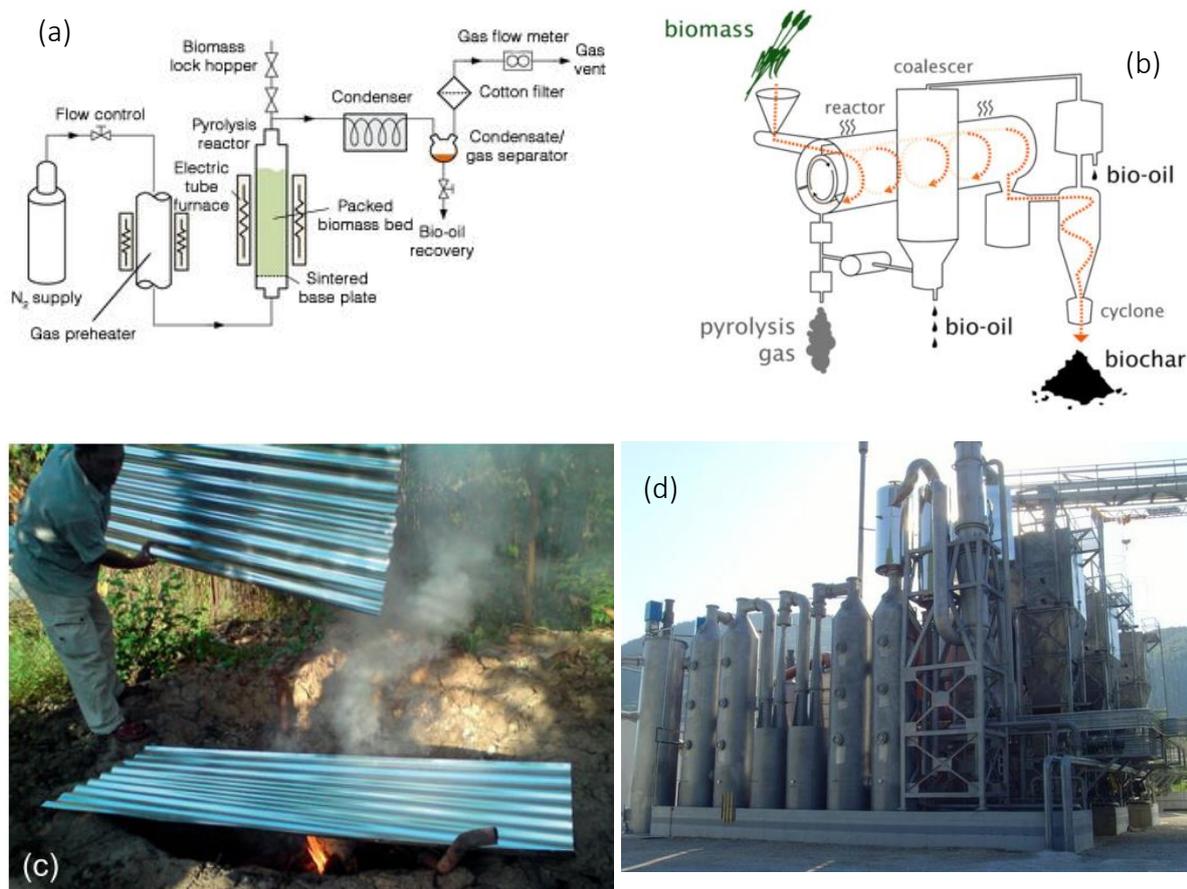


Figure 2-4: Schematics and photographs of pyrolysis systems. (a) schematic of slow pyrolysis unit for batch production of biochar⁷⁵; (b) schematic of a centrifuge reactor for continuous fast pyrolysis⁷⁶; (c) traditional Malaysian earth pit producing palm frond biochar⁷⁷; (d) a biomass gasification plant in Bulgaria⁷⁸

The treatment temperature also significantly affects biochars properties. Biomass components such as lignin and cellulose are degraded at approximately 350°C, while volatile organic components are also removed or carbonised at high temperatures, as shown in Figure 2-5a. Oxygen groups are removed from the carbonised phase resulting in greater aromaticity. The removal of these components also increases the pore space, resulting in greater meso- and micro-pore volumes; however the exact nature of the pore network will still depend on the initial feedstock. The ash content also tends to increase at higher pyrolysis temperatures as it is mostly retained while other organic components are removed, resulting in an overall increase in its relative proportion, as shown in Figure 2-5b. High temperature biochars are therefore typically highly carbonised, with little amorphous material.

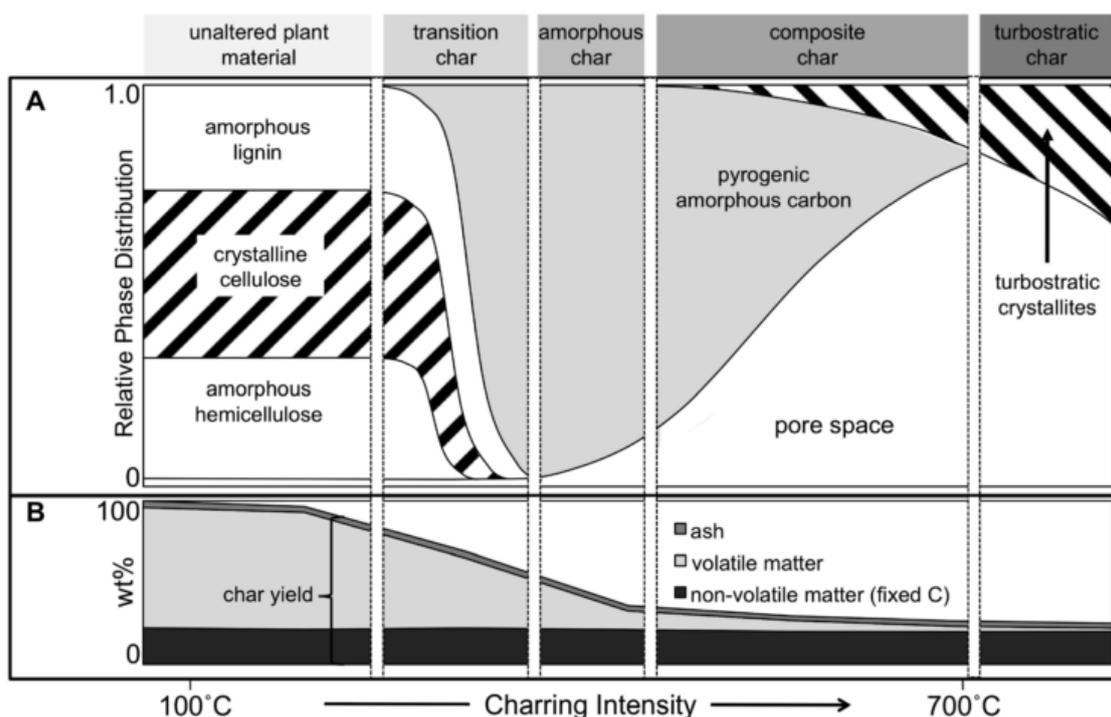


Figure 2-5: Changes in biochar structure as a function of pyrolysis temperature in terms of (a) crystalline phases and (b) physical components. Reproduced from Keiluweit et al.⁶⁸

The heating rate, referring to the rate of temperature change prior to reaching the HTT, can also have a significant effect on the properties of biochar. Biochar is typically produced under either fast pyrolysis (heating rate $>\sim 500$ °C/min) or slow pyrolysis (heating rate $<\sim 20$ °C/min)⁷⁹. Cetin et al.⁸⁰ found that biochars produced at a lower heating rate have a better developed pore network than those produced at high heating rates, as the high heating rates can cause plastic deformation of the biochar resulting in a macroporous pore network. Angin⁸¹ found that biochars produced at higher heating rates had similar elemental properties to those produced at lower heating rates, but had lower surface areas and micropore volumes. The optimal heating rate for a given biochar will therefore depend on its application and the desired net environmental outcomes.

2.3.2 Biochar environmental benefits

Biochar is an environmentally sustainable technology and its production and application results in several environmental benefits. These benefits include the sequestration and long-term storage of carbon, improvements in soil health and associated increased plant growth, the re-use of products that would otherwise go to waste, and the immobilisation of contaminants in soil, as illustrated in Figure 2-6. The following paragraphs provide a short background on each of these benefits.

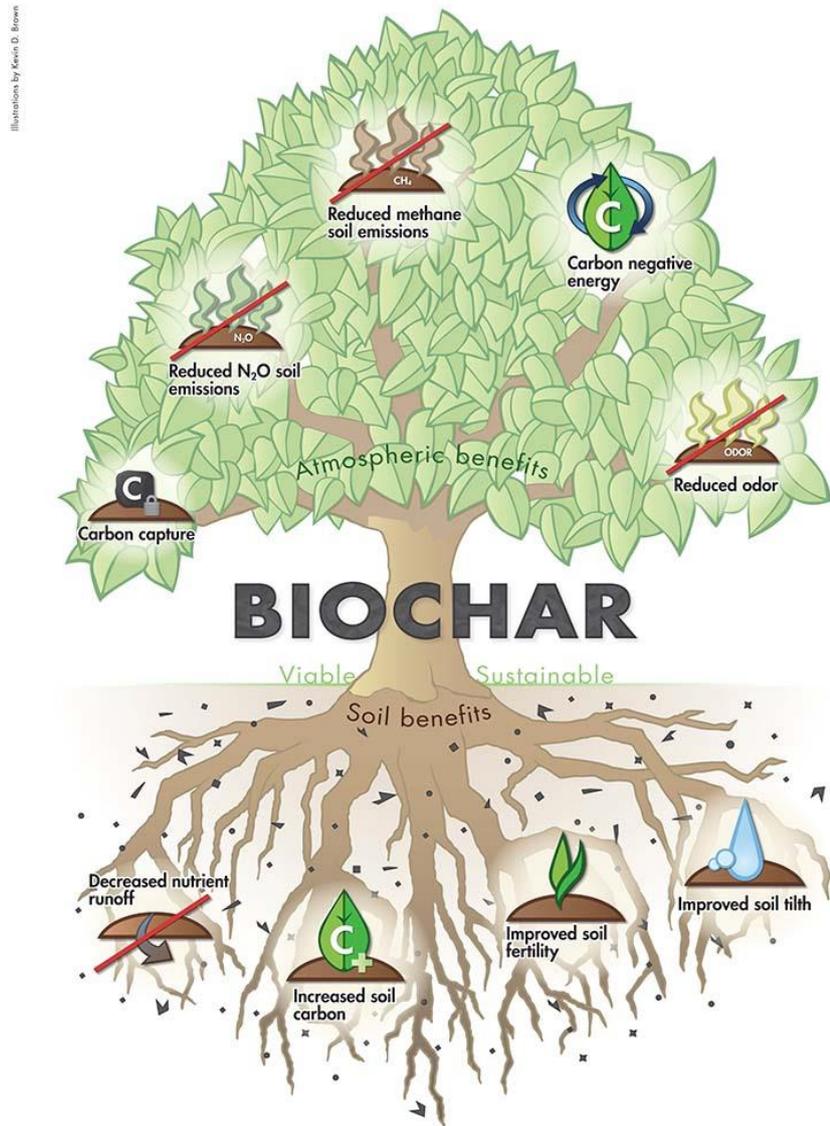


Figure 2-6: Environmental benefits of biochar technology. Reproduced from International Biochar Initiative ⁶³

A significant environmental benefit of using biochar is that its production is typically a net carbon negative process ⁸², which can mitigate the effects of climate change. The carbon abatement is the result of a number of processes, including the offsetting of power to the power grid, agricultural benefits, and the long-term storage of stable carbon. Hammond et al. ⁸³ demonstrated that while coal systems emit approximately 0.50 t-CO₂/MWh of energy produced, and conventional bioenergy systems emit 0.05-0.30 t-CO₂/MWh, pyrolysis systems for producing biochar in the UK will *abate* approximately 1.4-1.9 t-CO₂/MWh of electricity they generate. The relative significance of these processes will depend on many factors such as the biomass used, where the biochar is applied, and which power source is being offset by the excess generation.

Biochar can provide multiple agricultural benefits, improving soil health and crop yields. For example, it can increase the pH of acidic soils resulting in increased crop yields due to a liming effect⁸⁴, with these increased pH values correlating with increased plant growth⁸⁵. It can also increase the water holding capacity of a soil⁸⁶, increasing the efficiency through which plants can obtain nutrients. Finally, the labile organic component of the biochar itself provides nutrients to the soil, increasing the total nutrient availability. Indirectly, these benefits can also result in reduced reliance on fertilizers and herbicides^{87,88}. The majority of biochar uses to date have been application to soil for improved soil health and crop yield, as shown in Figure 2-7 for a trial plot of corn in plain soil. The combined benefits of liming, increased water holding capacity and increased nutrient availability make biochar a promising tool for further uses as a soil amendment in a range of applications.



Figure 2-7: Growth of corn in a trial plot (left) with biochar, and (right) without biochar⁸⁹

Biochar production can also convert materials that would otherwise have little value into valuable soil amendments. Many different feedstocks have been investigated. Food produce such as peanut shells, orange peels and corn cobs have been used to make biochar, suggesting its widespread use can reduce waste from food products. However, the suitability of a feedstock may depend on what materials are locally available. For example, many studies in China have investigated the use of locally abundant materials from rice farming such as the husks and straw of the rice plant. Further, many studies have made biochar from the manure of swine, cattle and poultry, highlighting the wide range of feedstocks that are possible. The

use of these waste products as biochar feedstock highlights the low resource consumption and high sustainability of the material.

Finally, recent research has demonstrated that biochar can be an effective adsorbent of contaminants in soil and water. This is often attributed to its high surface area, high pH, micropore network, heterogeneous composition, complex aromatic structure and high cation-exchange capacity. The adsorption properties are comparable to those of other carbonised adsorbents such as charcoal and activated carbon; however the interactions in soil will also play a significant role. The detailed mechanisms controlling sorption are discussed throughout this thesis. It is intended that through the combined benefits of carbon sequestration, improved soil stability, and immobilisation of contaminants in soil, biochar can represent a sustainable and effective method of stabilising and remediating contaminated land.

2.3.3 Biochar properties

The physicochemical properties of a biochar play an important role in determining its effects in the soil profile. These properties are related to the initial feedstock used and the pyrolysis conditions under which it was prepared. Physical properties include the relative abundances and compositions of the three primary physical components (carbonised fraction, amorphous fraction and ash fraction) and pore network, while chemical properties include aromaticity and polarity of the carbonised fraction and the mineral composition of the ash fraction.

Physical properties

Biochar consists of three main components, as illustrated in Figure 2-8: the carbonised fraction, the amorphous fraction, and the ash fraction. In addition, the carbonised fraction typically contains an extensive pore network which significantly influences overall physical parameters such as pore volume and specific surface area (SSA). These three components together determine the overall physical and chemical properties of a given biochar sample.

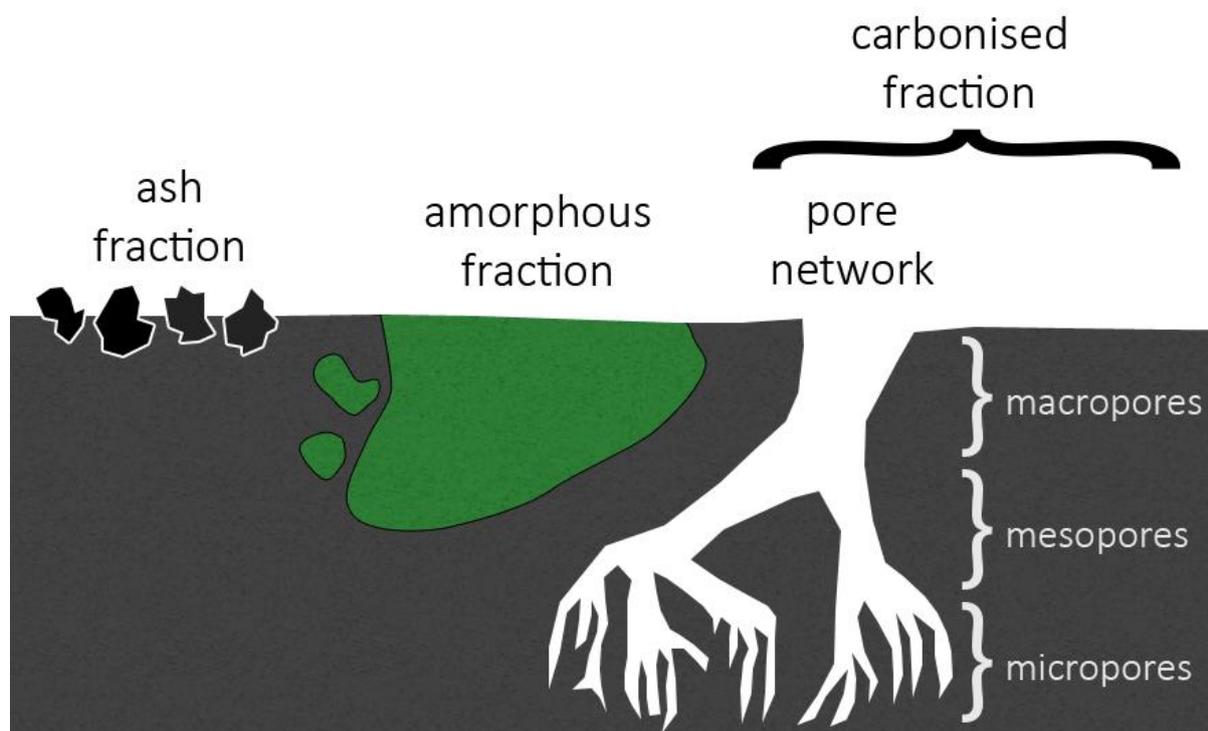


Figure 2-8: Physical components on the surface of a typical biochar particle (by the author)

The amorphous, labile, ‘rubbery’ fraction consists of organic components such as cellulose, hemicellulose and lignin from the initial feedstock. In contrast, the carbonised ‘glassy’ fraction consists of imperfect carbonised, aromatic sheets and includes a complex pore network, which results in high surface areas with which bacteria or molecules may interact. The ash phase consists of mineral components such as quartz and calcite, which exist due to reactions involving minerals in the initial feedstock. The chemical compositions of these three components are discussed in further depth in the following section. These three components each have significant influences on the capacity of biochar to provide environmental benefits.

A complex pore network exists within the carbonised fraction, which has a significant influence on the physical properties of biochar such as surface area and micropore volume. The pore network consists of macropores ($> 50\text{nm}$), mesopores ($20\text{nm} < d < 50\text{nm}$) and micropores ($< 20\text{nm}$) and contributes to the high SSA of biochar, which can range from approximately $1 \text{ m}^2/\text{g}$ to $1,500 \text{ m}^2/\text{g}$ ⁹⁰. The pore size distribution represents the relative abundance of these three pores, and depends on the initial feedstock (as shown in Figure 2-9) and the pyrolysis conditions. In particular, micropores have been shown to have a significant influence on the total available surface area of a biochar, however the presence of mesopores and macropores allows for efficient transport of molecules to this available area. Further, the

presence of amorphous and ash components can block these pore networks, reducing the overall available area. Therefore the carbonised fraction is the most significant determinant of the pore distribution and surface area of a biochar; however the amorphous and ash fractions can also have significant influences.

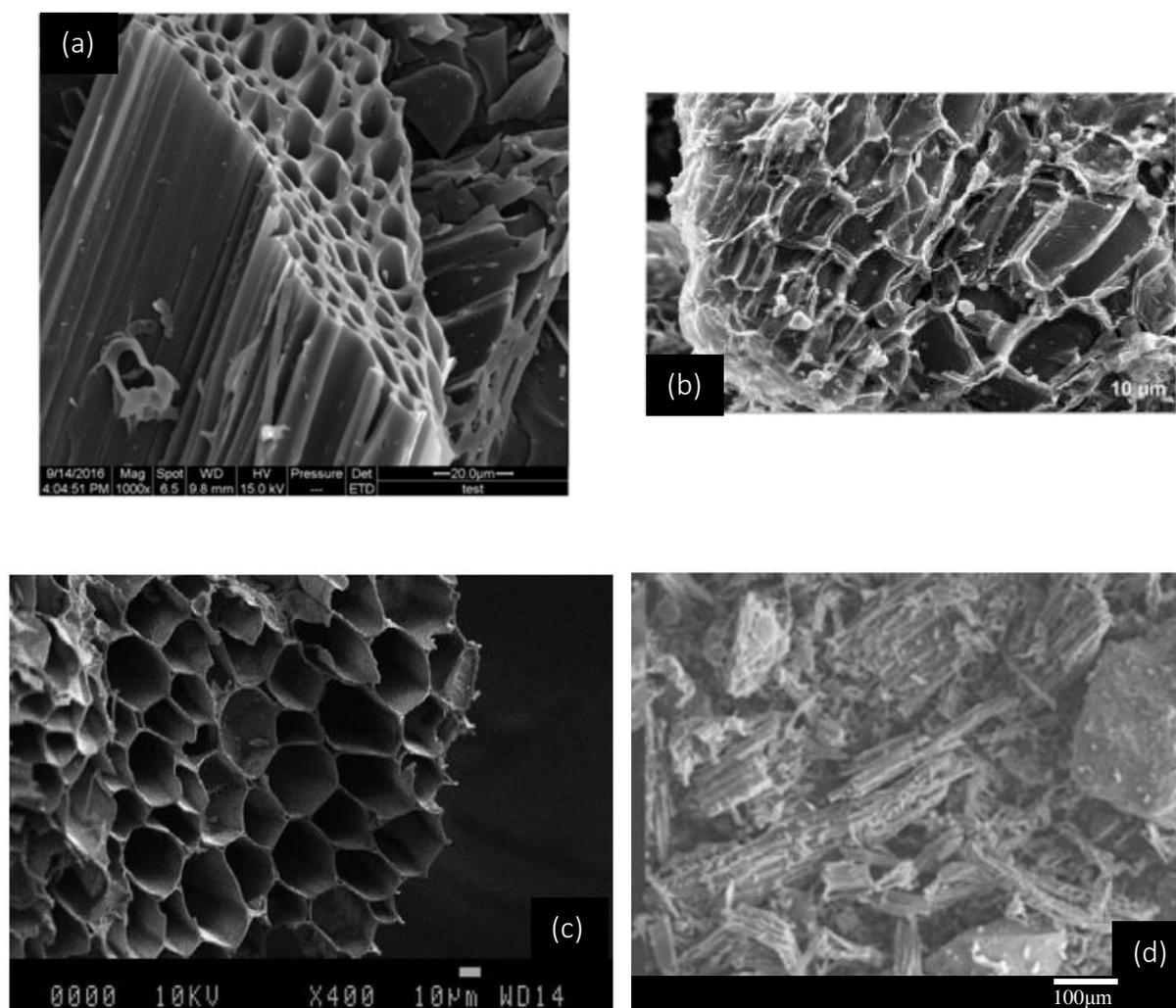


Figure 2-9: Scanning electron microscopy images of (a) corn straw biochar⁹¹ (b) cassava waste biochar⁹², (c) palm frond biochar⁷⁷ and (d) dairy manure biochar⁸⁶

It is worth noting that care should be taken when directly comparing SSA values between different papers. A number of studies have demonstrated that N₂-BET analysis fails to appropriately characterise the microporous regions of carbonised materials^{93–95}. This is primarily due to the low temperature used for N₂ physisorption which reduces the flexibility of the molecule to enter the micropores. This is not significant for CO₂ which is carried out at higher temperatures. Jin et al.⁹⁶ measured the surface area of wheat straw biochar using both N₂ and CO₂ and found that the measured areas can vary by up to one order of magnitude,

highlighting the role of micropores in determining overall surface area. Further, methodologies used to determine surface area, even when using N₂ can vary and influence the results, as highlighted by Sigmund et al.⁹⁷. Regardless, N₂ physisorption is still the most commonly used method to determine SSA and pore size distribution. While it is still useful to compare surface areas across different studies, it is important to note the methods used to ensure they are directly compatible.

Chemical properties

The chemical properties of biochar are typically characterised by high pH, high cation exchange capacity (CEC), and high aromaticity, while polarity and functionality can vary. The three components of biochar (carbonised fraction, amorphous fraction, and ash fraction) each have different chemical structures and therefore have different influences over the chemical properties. The carbonised fraction consists of graphite-like aromatic carbon sheets, while the amorphous fraction consists of various aliphatic carbon chains, and the ash fraction consists of various minerals such as silicon or calcium-based compounds. The overall chemical behaviour of a given biochar will be dependent on the relative abundances and compositions of these three components, with the chemical properties of the carbonised phase typically playing the greatest role.

The carbonised fraction is composed of fused polyaromatic sheets of carbon with functional groups at the edges, as shown in Figure 2-10⁹⁸. At higher HTTs, more volatile components are removed or converted to aromatic rings, and therefore the abundance and size of these rings increases with increasing HTT⁹⁹. The graphitic sheets also become more ordered, as the chemical structure approaches that of graphite¹⁰⁰, as illustrated in Figure 2-11. Oxygen- and nitrogen-containing functional groups can exist at the edge of these aromatic rings and increase the overall polarity of the biochar (as measured by the elemental ratios O/C or (O+N)/C). The carbonised component is the most relevant to the sorption of organic compounds due to its high surface area and hydrophobic nature, and therefore most of the discussion within this thesis will focus on the carbonised fraction.

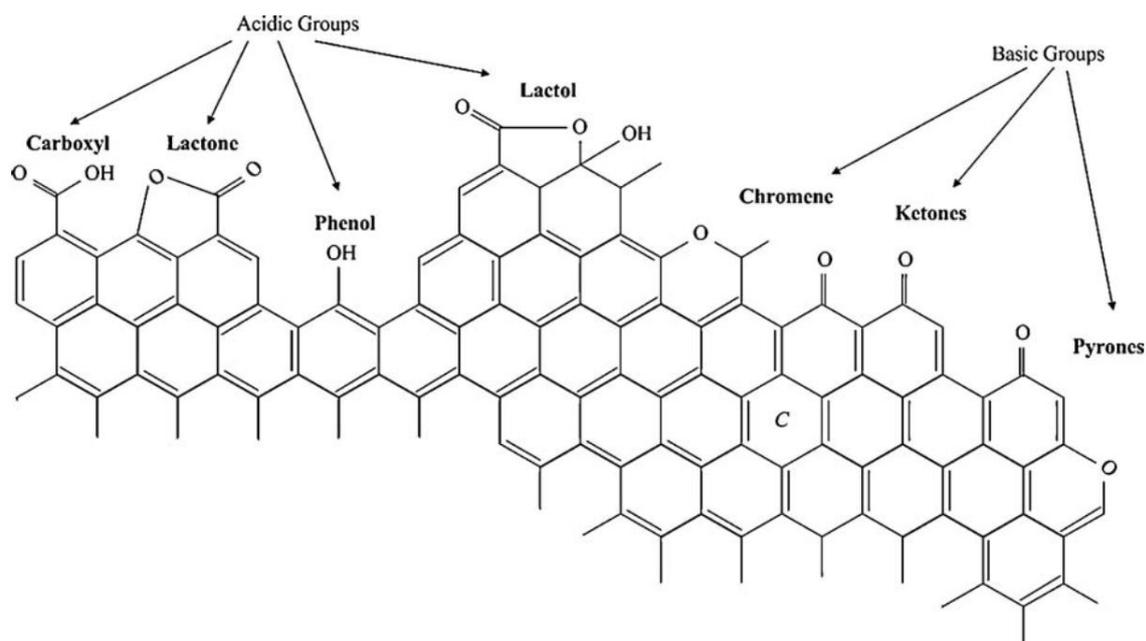


Figure 2-10: Acidic and basic functional groups in the carbonised phase of biochar. Reproduced from Shafeeyan et al.⁹⁸

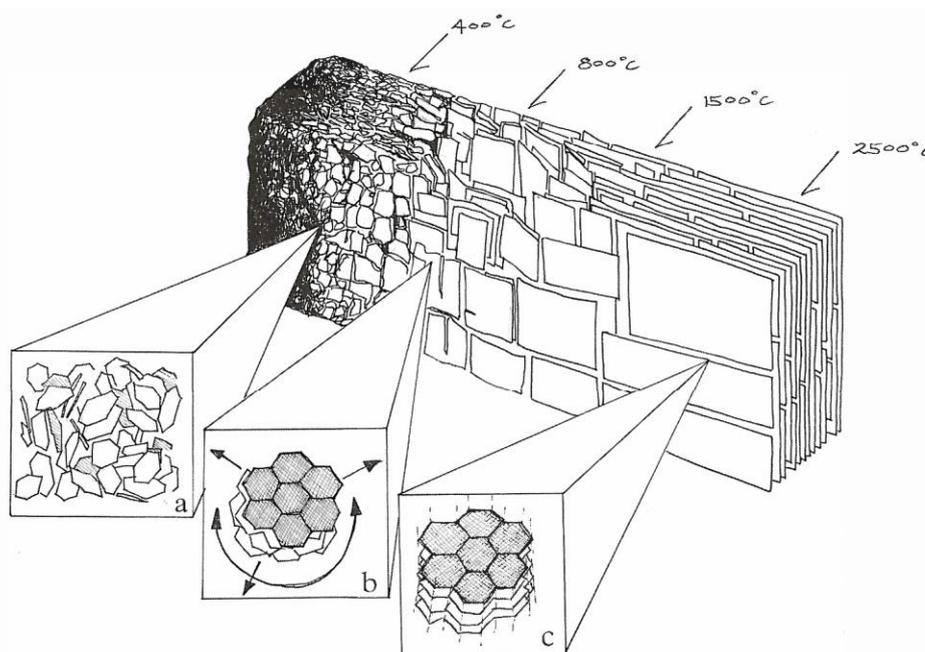


Figure 2-11: Changes in molecular structure of biomass as pyrolysis temperature increases. Replicated from Downie et al.⁹⁰

The amorphous phase consists of aliphatic carbon, such as lignin, cellulose and hemicellulose. The relative abundance of these components will depend on the initial feedstock^{68,101}. The amorphous fraction generally has relatively high oxygen and nitrogen contents compared to the carbonised fraction and will therefore increase bulk polarity. The

functional groups of the amorphous phase can be clearly seen in Fourier-transformed infrared (FTIR) imaging, such as in Figure 2-12, where CH_2 , $-\text{OH}$, ester $\text{C}=\text{O}$, and $\text{C}-\text{O}-\text{C}$ functional groups are all removed at HTTs greater than 300°C ¹⁰². This sharp change from biochar produced at 300°C to 400°C is largely due to the volatilisation of lignin and hemicellulose at approximately 350°C ^{68,77,102}. The chemical composition of the amorphous phase will depend largely on the relative compositions of lignin, cellulose and hemicellulose; however its composition is not regularly discussed in depth with reference to the sorption of organic compounds.

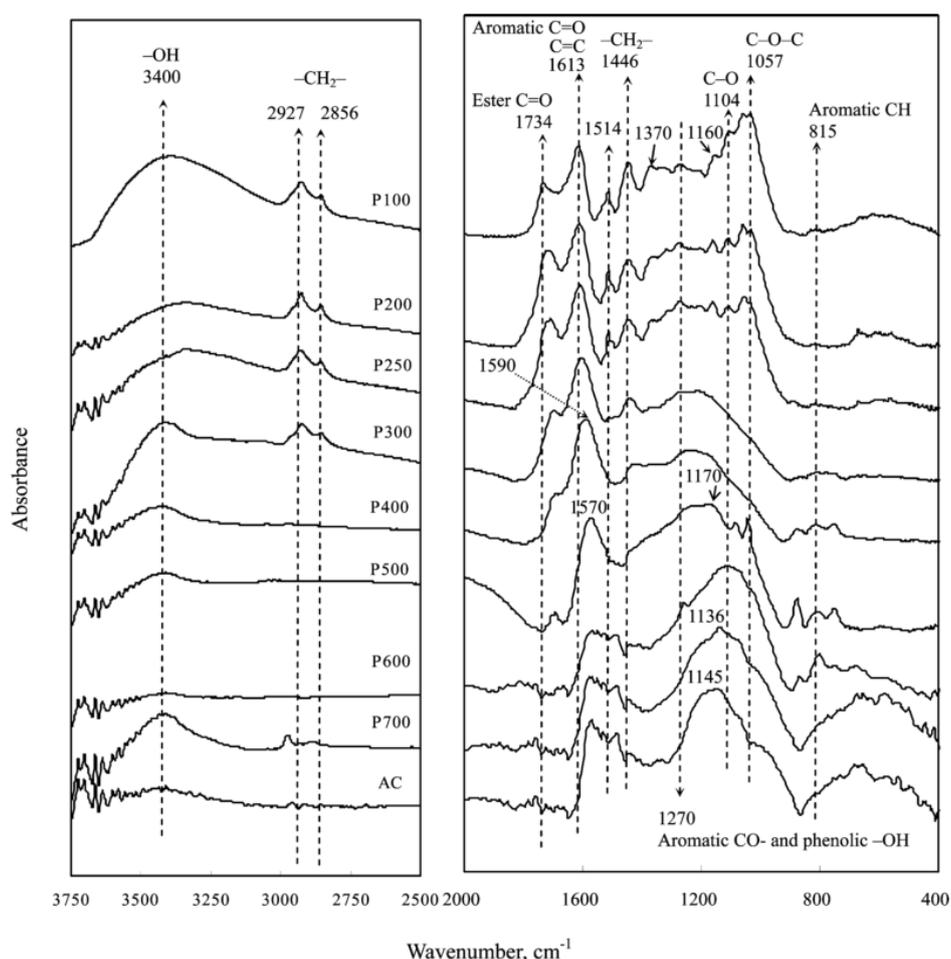


Figure 2-12: FTIR imaging of pine needle biochar at increasing treatment temperatures. Replicated from Chen *et al.*¹⁰²

The ash phase consists of various inorganic components. The types of inorganic compounds present depend on the minerals present in the initial feedstock, and can contribute significantly to the high pH value and cation exchange capacity of biochar. In general, the ash component is mostly SiO_2 ^{103,104}, though may also include other minerals such as oxides, hydroxides or nitrates of Mg, Ca, K and Na. These products may exist in various crystalline

phases, such as quartz, calcite, or sylvite. These minerals can increase the pH of the biochar due to the liming effect of minerals such as calcite^{105,106}. However, these crystal phases can also block the pores of the carbonised organic phase, reducing overall surface area and pore volume. The ash component can therefore play a significant role in soil through increasing soil pH; however it can be undesirable for certain applications due to its blockage of micropore spaces.

2.3.4 Biochar ageing in soil

The properties of biochar can change over time in the soil profile due to various ageing processes. These processes include biological processes such as degradation of the amorphous component, physical processes such as the blocking of pores by soil organic matter, and chemical processes such as oxidation of the biochars surface, as illustrated in Figure 2-13. Other factors will also influence the ageing of biochar but are not discussed in detail here, such as the physical break-up of biochar particles¹⁰⁷, and fungal and bacterial growth on the surface of biochar¹⁰⁸. The combined effects of these ageing processes will influence the long-term behaviour of biochar in the soil profile.

The long-term stability of each of the physical components of biochar (amorphous phase, carbonised phase, ash phase) varies significantly. The carbonised phase is extremely recalcitrant in the environment, and is expected to remain in the soil for hundreds to thousands of years, resulting in biochar being an effective way to sequester and store carbon. However, it may still undergo chemical changes during this time as discussed in the following paragraphs. In contrast, the amorphous phase is expected to be degraded in a matter of weeks to months, with degradation experiments typically showing a two-part model corresponding to early rapid degradation followed by stabilisation of the carbonised fraction^{109,110}. The role of the ash content in long-term stability has rarely been assessed¹¹⁰ and is therefore difficult to determine, although it is unlikely to be the determining factor in a long-term properties of biochar. The long-term properties of the biochar in soil are therefore mostly dependent on the carbonised phase.

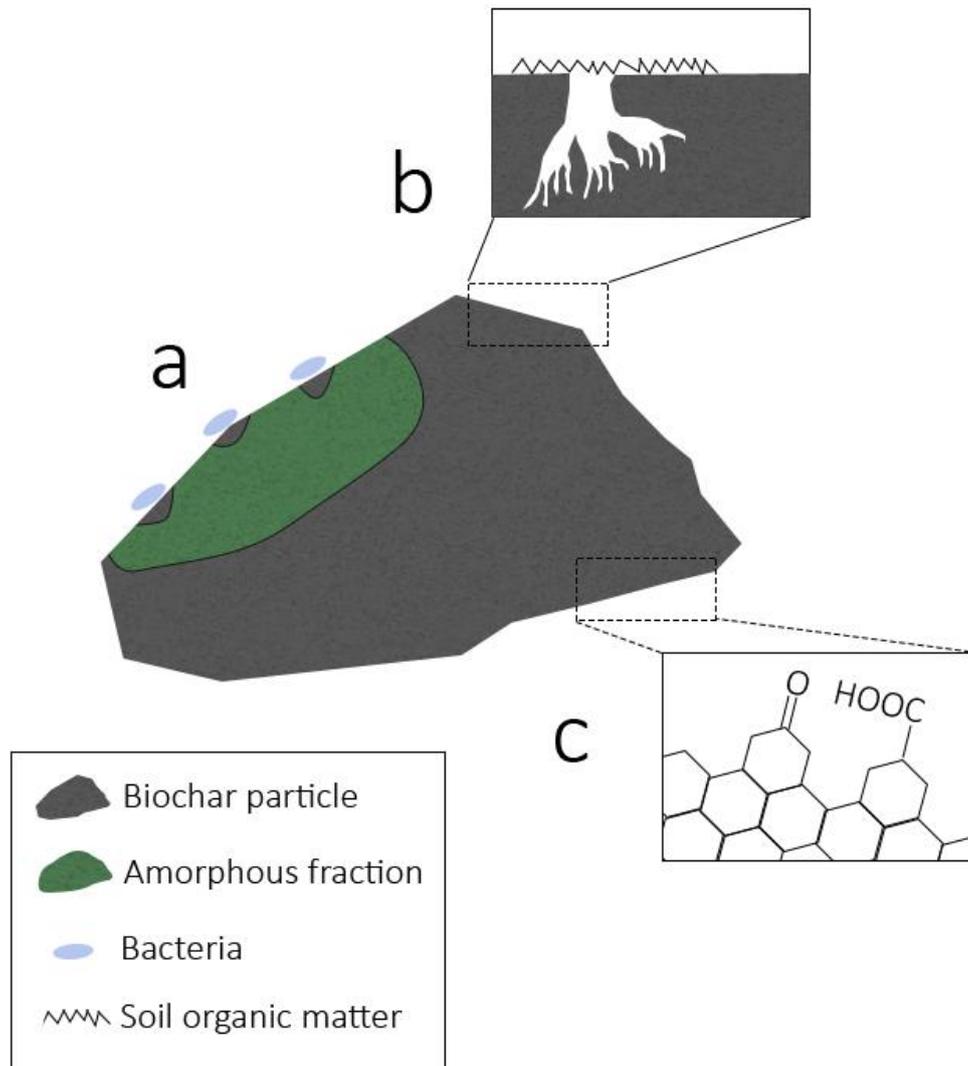


Figure 2-13: Ageing processes on a biochar particle (a) degradation of amorphous component by bacteria; (b) pore blockage by soil organic matter; (c) surface oxidation (by the author)

Long-term field trials investigating the changing properties of biochar over time are uncommon, and therefore various laboratory methods are used to simulate ageing processes. For example, Hale et al.¹⁰⁷ simulated long-term physical, biological and chemical ageing in the laboratory by subjecting biochar to freeze-thaw cycles, nutrients and microorganisms, and elevated temperatures respectively. One study that closely approximates long-term ageing was carried out by Cheng et al.¹¹¹ who compared charcoal samples obtained from soil near an old furnace with fresh samples prepared using similar methods. They found that the aged samples had significantly reduced surface areas and increased oxygen contents, which are in line with laboratory and field results. While laboratory simulations of aging cannot always accurately represent field conditions¹¹², they are a practical method of approximating the long-term ageing process.

The pores of biochar may be blocked by long-chain molecules of soil organic matter (SOM) reducing access to the microporous regions. This can reduce the surface area of the biochar, as well as access to micropore spaces. For example, Kwon & Pignatello^{67,94} incubated a maple wood char with both organic extracts from soil samples⁶⁷ and a representative vegetable oil⁹⁴ to simulate the influence of soil humic and fulvic acids on black carbon. In both cases, they observed reduced surface area after incubation and reduced sorption of benzene and phenanthrene, which they attributed to pore blockage by long-chain SOM molecules. Cheng et al. compared freshly produced charcoal with that found near a historical blast furnace, and found significant amounts of organic matter on the surface which reduced pore accessibility, as shown in Figure 2-14¹¹¹. The blockage of micropores can also reduce sorption capacity of organic compounds through reduced access to sorption sites. Zhang et al.¹¹³ incubated biochar samples with soil for 28 days prior to sorption tests with pyrene, and observed reduced sorption against control samples of approximately 30%. Zhou et al.¹¹⁴ observed a reduction in the sorption of atrazine to a sludge-derived biochar in the presence of humic acids, and confirmed this by demonstrating an associated reduction in surface area. The blockage of pores is likely to be more significant for soils with high organic matter, such as many agricultural soils. These studies provide evidence that SOM can reduce access to the microporous regions of biochar, which should be considered when designing biochar for field application.

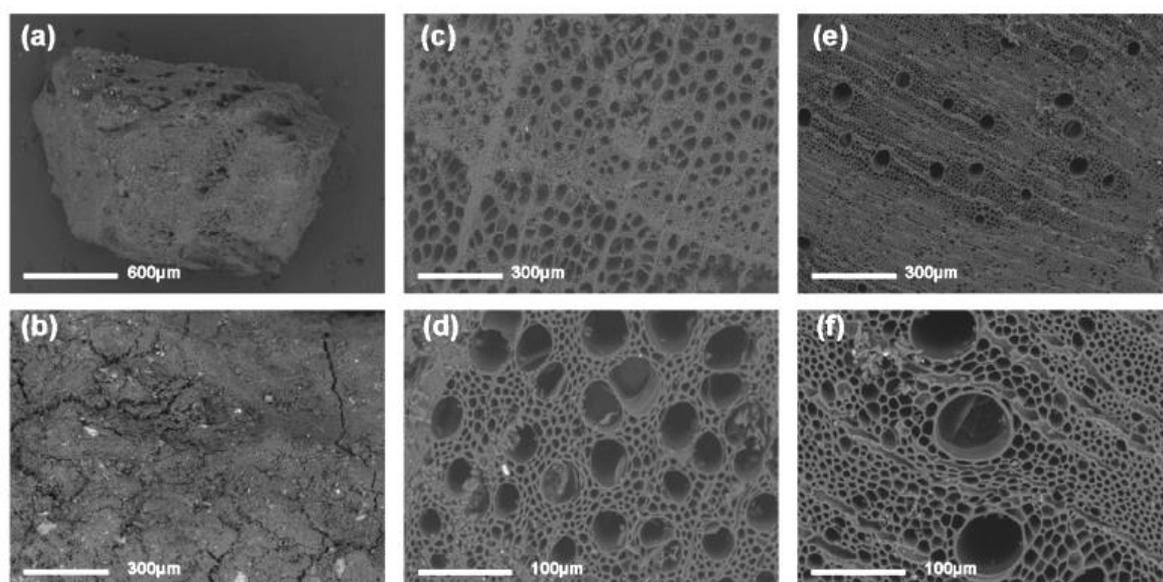


Figure 2-14: Scanning electron microscopy images of a wood charcoal (a-d) after aging in the environment for approximately 100 years, (e-f) fresh charcoal samples. Reproduced from Cheng et al.¹¹¹

The surface of biochar is likely to be oxidised over time in the soil, due to a combination of biological and chemical processes ¹¹⁵. This increases the overall polarity of the biochar, as well as the role of oxygen-containing functional groups. For example, Ren et al. ¹¹⁶ cultured a pig manure biochar with wheat for three months and observed an increased oxygen content, which was attributed to both biotic and abiotic processes. Similarly, Bian et al. ¹¹⁷ observed an increase in C-O groups in a wheat straw biochar after amendment in soil for three years, which was attributed to microbial oxidation. Cheng et al. ¹¹⁵ further investigated the role of oxidation in black carbon by incubating charcoal from black locust bark for four months with each microbial inoculation, manure or nutrient additions. They observed significant increases in both oxygen content and CEC, attributed to increases in carboxylic acid functional groups. Mukherjee et al. ¹¹⁸ observed similar effects after ageing a wood and grass biochar in soil for 15 months by demonstrating increased anion (AEC) and cation (CEC) exchange capacities to four biochars, as shown in Figure 2-15. Some studies have found reduced oxygen content over time in soil, suggesting that long-term oxidation may not always be the case. Dong et al. ¹¹⁹ measured the changes in biochar 5 years after field application and observed *decreased* oxygen content and no chemical structural differences, which is contrary to the above discussion. However, this may be a result of the decreased amorphous component of the biochar, which will have an oxygen content greater than the carbonised phase, and its removal would therefore decrease oxygen content. This is supported by their observation that carbon content increased, which is in line with increased relative abundance of the aromatic phase. Regardless, this study highlights that neither biochar nor soil ageing are homogenous and therefore care should be taken when predicting long-term effects of biochar. These studies suggest that the biochar surface is likely to become more oxidised over time, which will influence its polarity, hydrophobicity and functional groups.

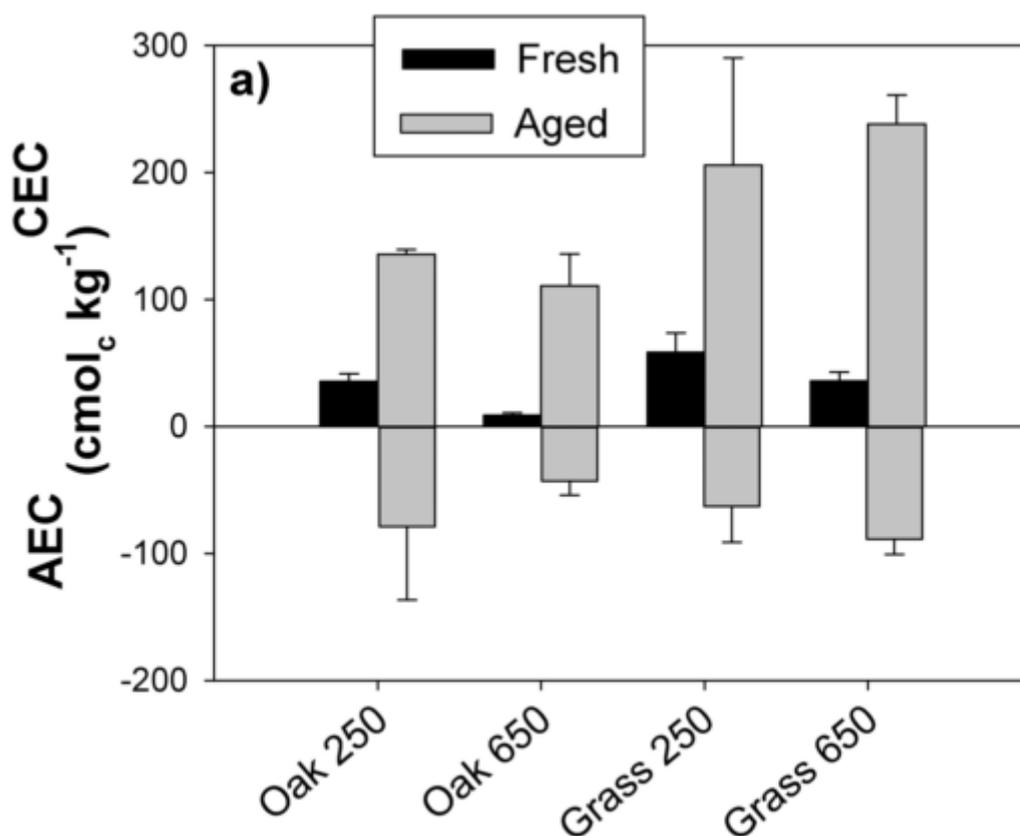


Figure 2-15: Changes in cation exchange capacity (CEC) and anion exchange capacity (AEC) to four biochars after aging in soil for 15 months. Adapted from Mukherjee et al.¹¹⁸

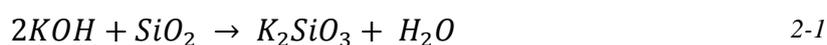
It is useful to consider the effects of biochar ageing, as the processes involved are important in determining the effectiveness of biochar as a soil remediation method in practice. Very few papers relate the results of their adsorption tests to the implications of the use of biochar in soil remediation or water treatment, and so it is important to note that a high adsorption capacity alone does not mean that a biochar will be useful in soil remediation. For example, Cheng et al.¹¹¹ found that the sorption of two organic contaminants to a wood char decreased after ageing, however the sorption of Cu^{2+} increased, suggesting that the ageing process can affect different contaminants in different ways. Further, Ren et al.¹¹⁶ found that ageing increased sorption of low temperature biochars, yet decreased sorption of high temperature biochars, highlighting that the net result also depends on the properties of biochar. By considering the effects of ageing it is possible to get a more accurate representation of the usefulness of biochar as a soil remediation tool.

2.3.5 Chemical modification for de-ashing of biochar

Chemical modification of biochar may alter the physical and chemical properties of an adsorbent, allowing for targeted study of specific components. This thesis primarily focuses

on the removal of the ash fraction in order to better understand its role. This section provides a background on methods of de-ashing that have been carried out to date, and the role that these have on the properties of biochar and its adsorption of various compounds. De-ashing of biochar may be carried out using either a strong base such as potassium hydroxide (KOH), or an acid such as hydrofluoric acid (HF).

Modification using basic compounds has been shown to remove non-carbonised matter, and is often used to activate adsorbents. For example, potassium hydroxide (KOH) is often used in the preparation of activated carbons. Liu et al.¹⁰³ demonstrated that similar results were possible for biochar by using KOH to reduce the ash content of a rice husk biochar from 42.2% to 3.5%. They proposed the reaction shown in Equation 2-1 to describe the mechanism forming potassium silicate.



This removal of the ash component also resulted in increased sorption of tetracycline due to the increased surface area of the modified biochar. Ding et al.¹²⁰ also observed a reduction in silicon content after modifying a hickory biochar with NaOH, suggesting that Na⁺ may also be effective in removing ash components. Together, these studies suggest that modification using basic compounds may be effective in removing the ash component of biochars.

HF has also been shown to effectively remove the ash content. Zhang et al.¹²¹ reduced the ash content of a rice husk biochar from approximately 15.96% to 0.94% through treatment with HF, and also showed that this greatly increased the surface area and micropore volume of the carbonised phase. Sun et al.¹²² also demonstrated the deashing of a range of biochars using HF by showing a reduction in Si of approximately 75%, and corresponding increases in carbon contents. HF treatment therefore may represent an effective method of de-ashing biochars for further study.

2.3.6 Use of biochar in soil remediation

The high surface area, micropore volume, pH and CEC values of biochar make it an effective adsorbent of organic and heavy metal contaminants. Together with improved soil health associated with liming and increased water holding capacity, biochar amendment may represent a holistic method of site restoration. Remediation using biochar involves the

application of biochar to soil with the intention of immobilising contaminants through sorption, thus reducing leaching into groundwater or surface water supplies, as shown in Figure 2-16¹²³. Sorption also reduces the overall biotoxicity of contaminants and prevents them from being transported to humans or ecosystems. While insights into the adsorption properties of biochar in soil can be drawn from studies investigating charcoal and activated carbon filters, these results do not immediately transfer to soil remediation due to biochar-soil interactions and the need to either degrade attached contaminants or hold them for the long term. Biochar therefore represents a potentially low cost, sustainable adsorbent, resulting in the more sustainable remediation of contaminated sites; although one that requires further study before full scale application.

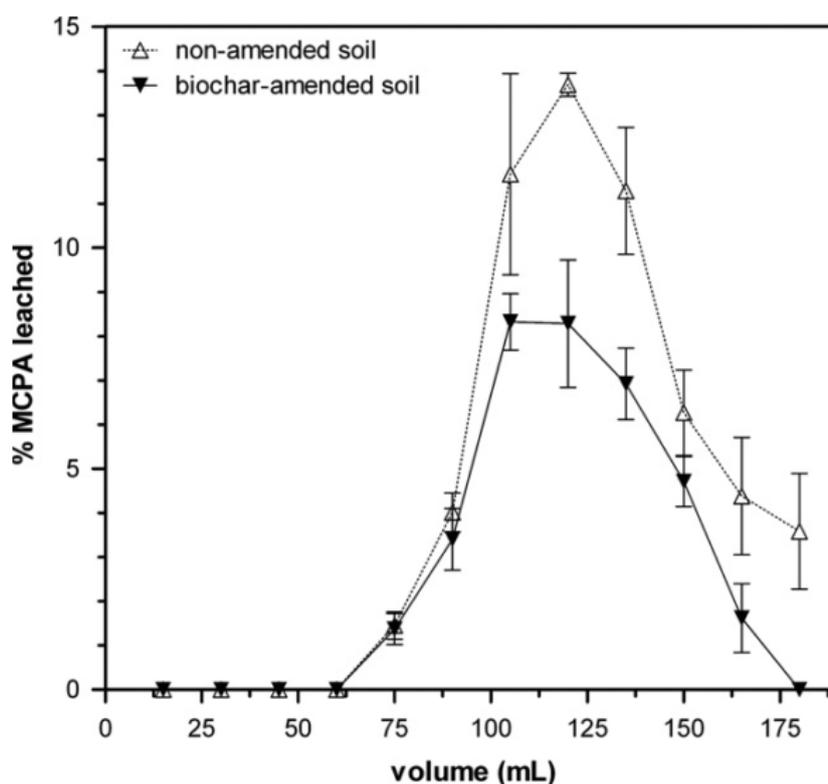


Figure 2-16: Reduced leaching of the herbicide (4-chloro-2-methylphenoxy)acetic acid (MCPA) in soil amended with biochar. Reproduced from Tatarková et al.¹²³

Despite many studies investigating the sorption properties of biochar, it is worth noting that very few discuss application methods. Previous reviews into the use of biochar in soil remediation have commented on a lack of previous field trials^{124,125}, meaning that little data is available on how biochar would be applied to contaminated sites in practice. When applied for the purpose of improving the health of clean soil, biochar is traditionally spread onto the surface of an agricultural site before harrowing it into the soil⁸⁸. This method is likely to be

realistic for site-wide biochar application, however is likely to only reach contaminants close to the surface. Shen et al. ⁵⁹ carried out a long-term field trial by excavating 1m x 1m trial plots of 2m depth, and refilling with combined soil, biochar and compost. This method may be effective in immobilising contamination ‘hotspots’ but is unlikely to be feasible for site-wide application. Recent studies have also investigated the use of biochar in permeable reactive barriers ^{60,61}, which would be effective in treating contaminated groundwater. While a range of application methods are possible, few studies have investigated the performance of biochar under these scenarios, particularly in the long-term.

2.3.7 UKBRC Standard Biochars

The United Kingdom Biochar Research Centre (UKBRC) has produced a set of ten standard biochars to standardise production procedures and allow for accurate comparisons between feedstocks and pyrolysis conditions. In addition to UKBRC’s own characterisation, a number of studies have been published to date which have characterised the physicochemical structures of these biochars and their sorption properties for a number of compounds. The feedstocks and standard biochars are shown in Figure 2-17 ¹²⁶ and comprise softwood pellets (SWP), wheat straw pellets (WSP), miscanthus straw pellets (MSP), rice husk (RH) and oil seed rape (OSR) each produced at HTT values of 550°C and 700°C.



Figure 2-17: Standard biochar feedstocks and biochars; (a) softwood pellets, (b) wheat straw pellets, (c) miscanthus straw pellets, (d) rice husk, and (e) oil seed rape¹²⁶

A list of the studies that have utilised the standard biochars is given in Table 2-4, as well as the adsorbate investigated, where applicable. The published studies to date have generally focused on either (a) the sorption capacity of the standard biochars for heavy metals, such as nickel, copper and zinc, or (b) the health risks of the biochars themselves, and in particular the native polyaromatic hydrocarbon (PAH) component. The studies have also preferentially investigated SWP and MSP biochars, while no published studies to date were found which have investigated the OSR standard biochars. Table 2-4 also suggests that the sorption properties of the standard biochars for organic contaminants have not been thoroughly investigated to date, if at all.

Table 2-4: Published studies to date which have used the UKBRC standard biochars (by the author)

Reference	Adsorbate(s)	SWP		WSP		MSP		RH		OSR	
		550	700	550	700	550	700	550	700	550	700
Sigmund et al. (2018) ¹²⁷	PAHs					✓					
Bielská et al. (2017) ¹²⁸	Pyrene					✓					
Shen et al. (2017) ¹²⁹	Pb ²⁺				✓						
Shen et al. (2017) ¹³⁰	Cd ²⁺ , Cu ²⁺ , Pb ²⁺				✓						
Lisowski et al. (2017) ¹³¹	None	✓	✓			✓	✓				
Shen et al. (2017) ¹³²	Pb ²⁺	✓			✓				✓		
Shen et al. (2017) ¹³³	Ni ²⁺ , Cu ²⁺ , Pb ²⁺	✓	✓			✓	✓				
Shen et al. (2017) ¹³⁴	Ni ²⁺			✓	✓			✓	✓		
Sigmund et al. (2017) ¹³⁵	None	✓				✓	✓				
Singh et al. (2017) ¹³⁶	None	✓	✓	✓	✓	✓	✓	✓	✓		
Shen et al. (2016) ¹³⁷	Ni ²⁺ , Cu ²⁺ , Pb ²⁺	✓	✓	✓	✓	✓	✓	✓	✓		

2.4 Sorption of organic contaminants to biochar

Biochar effectively adsorbs a range of organic compounds, suggesting that it may effectively immobilise contaminants in the soil profile. This high adsorption is typically attributed to its high surface area, high micropore volume, and high aromaticity, which together result in organic contaminants being tightly bound to its surface. The specific sorption properties that occur will be dependent on the physicochemical properties of the biochar used, as well as the properties of the adsorbate molecule. It is therefore important to thoroughly understand the role that each of these components plays in order to suitably design biochar and predict its behaviour towards given contaminants. This section summarises knowledge to date of the key sorption characteristics of biochar towards organic contaminants. It then investigates the different sorption mechanisms that occur and the likely role they will have in soil remediation. Finally, it investigates the role of the ash content in sorption and remediation.

2.4.1 Sorption characteristics of organic contaminants to biochar

Biochar adsorbs organic contaminants to a much greater extent and a more non-linear fashion than soils and the initial feedstock used for pyrolysis. Laboratory sorption measurements are typically carried out as batch sorption tests, which determine the total sorption to biochar from solution in a closed vessel in a fixed amount of time. Batch sorption tests can investigate the sorption kinetics, isotherm, or pH dependency of one or more contaminants in solution, and are useful for providing insights into likely behaviour in soil.

Adsorption theory

Sorption describes the physical and chemical process of one molecule, an adsorbate, becoming attached to another, the adsorbent. As further discussed in 2.4.2, for the purposes of this research, *sorption* is used to refer to the combined effects of specific chemical interactions known as *adsorption*, and non-specific interactions, referred to as *partitioning* (sometimes known as *absorption*). Sorption processes can be modelled and investigated in many ways, and can represent a useful process in soil remediation by immobilising contaminants in the soil profile.

Sorption kinetics are an important characteristic which provide information on the sorption rate of a given system, as well as insights into the sorption processes taking place. Various models exist to model the kinetic profile, each with different assumptions. The accuracy of

the fit of each of these models provides evidence towards their assumptions being accurate, and therefore given sorption processes occurring. The pseudo-first order model assumes that sorption is proportional to the difference between the sorption capacity and the current adsorbed concentration. The pseudo-second order model is based on theories of surface reactions, and assumes that the sorption capacity is driven by an equilibrium state controlled by intraparticle diffusion. The Elovich model assumes a heterogeneous surface with negligible desorption of adsorbed molecules or interactions between adsorbed and aqueous molecules. The film diffusion model uses Boyd Plots, which determine whether sorption is dominated by intraparticle diffusion or whether other interactions are also significant. The intraparticle diffusion model assumes that the sorption rate is controlled by an early rapid chemisorption phase, and slow intraparticle diffusion phase.

The sorption isotherm is also an important sorption characteristic. The sorption isotherm describes the adsorption capacity of an adsorbent over different aqueous adsorbate concentrations at a constant mixing temperature. Two different models are overwhelmingly the most common used to model isotherms of aqueous adsorbate-adsorbent systems: Freundlich and Langmuir. The Freundlich model assumes multi-layered adsorption to a heterogeneous surface, while the Langmuir model assumes monolayer adsorption to homogenous surface sites. The relative fits of these two models can therefore provide useful insights into the state of adsorbed molecules at equilibrium.

Other characterisation tests and models exist to demonstrate different sorption mechanisms under given conditions, although kinetics and isotherms are the most common. The combined results of these tests and models are a common and useful way of determining key sorption characteristics.

Sorption characteristics to biochar

Biochar effectively adsorbs both organic and heavy metal contaminants in laboratory tests^{124,125}, as measured by sorption capacity. In general, the adsorption of organic contaminants to biochar is significantly higher than non-pyrogenic material or soils¹²⁴ and strongly binding. The sorption of organic contaminants to biochar is typically dependent on the SSA and pore size distribution⁷³, while for heavy metals sorption is dependent on CEC¹³⁸, though other properties such as biochar polarity and functionality, ash content and composition, and pH will also have an influence. Sorption to biochar may be one to three orders of magnitude

higher than typical soils¹³⁹ and the original feedstock material¹⁴⁰. This sorption increase is illustrated in Figure 2-18, showing isotherms for the sorption of diuron to various adsorbents (biochar in this case is denoted as *ash*, though it contains the char component). Many papers have reported biochar as having a high sorption capacity for a range of polar and non-polar organic compounds.

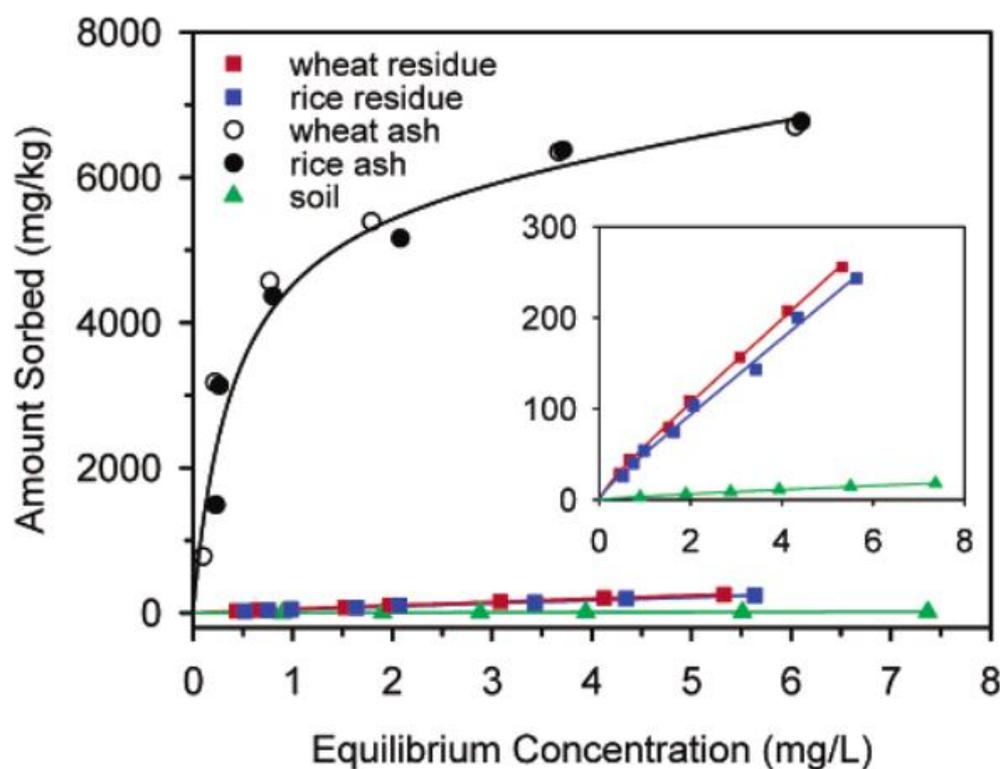


Figure 2-18: Sorption isotherms of diuron to soil, wheat and rice feedstocks, and wheat and rice biochars. Reproduced from Yang and Sheng¹⁴¹

Sorption linearity is another key property influencing the sorption behaviour of biochar. Sorption linearity refers to the relationship between the equilibrium aqueous concentration, C_e , and the equilibrium sorbed concentration, C_s , and can be measured using the fitting parameter $1/N$ from the Freundlich model, where a low $1/N$ value ($< \approx 0.5$) represents high non-linearity. Sorption non-linearity represents high sorption at low aqueous concentrations, and suggests strong interactions between the adsorbent and adsorbate. Biochar typically adsorbs molecules in a non-linear fashion^{73,102,140}, as indicated in Figure 2-18. For example, Sun et al.¹⁴² showed that the sorption of the herbicides fluridone and norflurazon to various biochars and a black carbons had lower $1/N$ values than non-carbonised adsorbents such as humic acid and non-hydrolysable carbon. This sorption non-linearity can significantly reduce the efficiency of biochar at high contaminant concentrations.

2.4.2 Sorption processes of organic contaminants to biochar

The sorption of organic contaminants to biochar is controlled by multiple processes occurring simultaneously, as demonstrated in Figure 2-19. Partitioning describes the distribution of a contaminant molecule between the aqueous and solid phases, and contributes to total sorption is not a form of *adsorption*. Pore filling is not a form of sorption, but rather a process through which adsorbate molecules are transported to sorption sites. The three adsorption mechanisms considered in this thesis are π - π electron donor-acceptor (π - π EDA) interactions, hydrophobic effects (or *condensation*), and hydrogen bonding. These five processes have been consistently identified in the literature; however those which are found to dominate sorption are often inconsistent between papers. Further, the relevance of these processes to actual remediation outcomes has received very little attention. This literature review will therefore first determine the extent to which each of these mechanisms occur in the sorption of organic contaminants to biochar, and subsequently determine their role in remediation by considering their responses to biochar ageing in the soil profile. It is of note that while a particular mechanism may not be an effective method of remediating organic compounds, it is still useful to study as it may be effective in certain scenarios or contribute negatively to environmental outcomes.

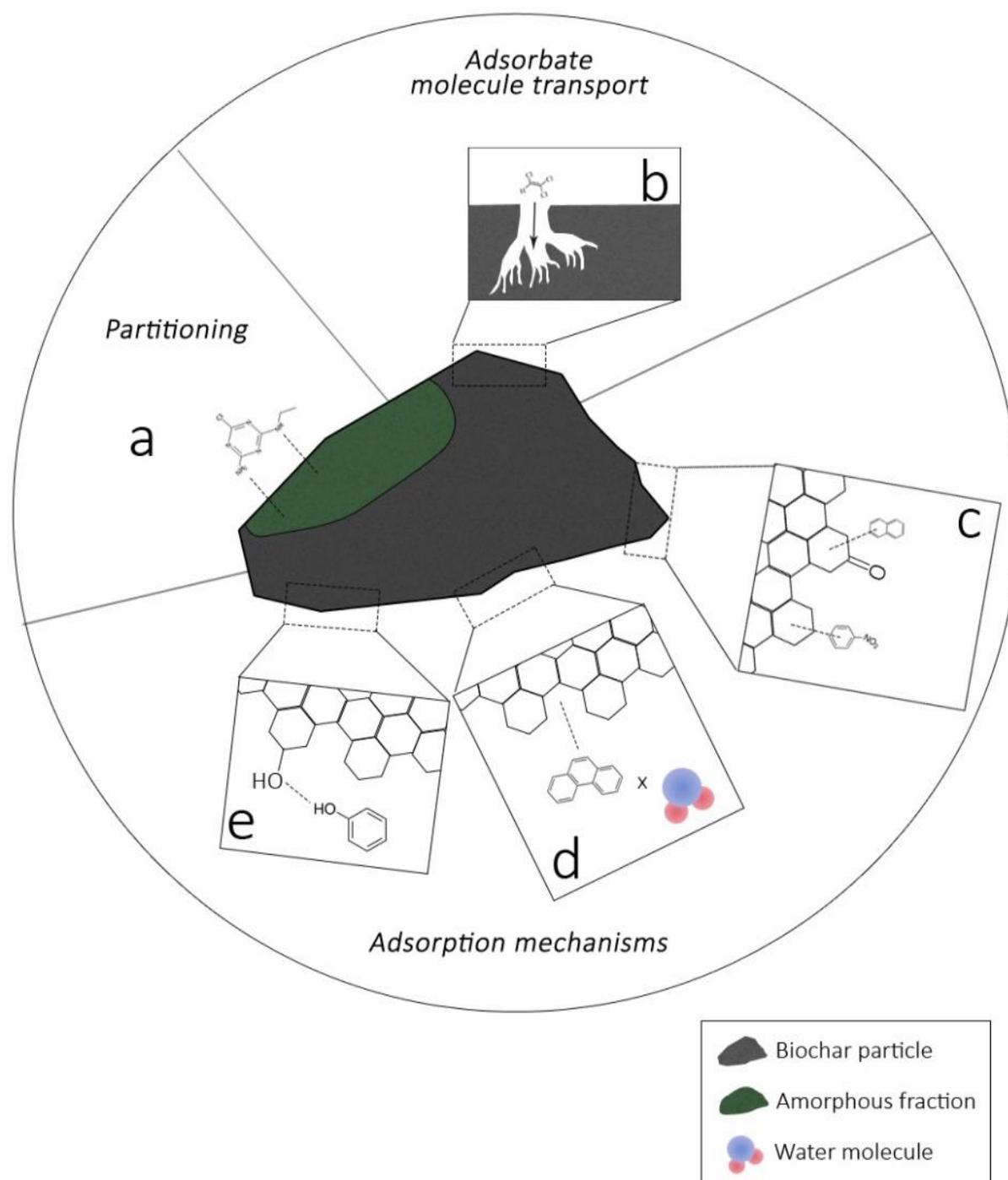


Figure 2-19: Schematic of the sorption processes of organic contaminants to biochar; (a) partitioning to the amorphous phase; (b) pore diffusion; (c) π - π EDA interactions; (d) hydrophobic effects; (e) hydrogen bonding (by the author)

Partitioning

Partitioning refers to the sorption of organic compounds to the amorphous, organic phase of biochar^{73,102,140,143,144}. It is therefore the dominant form of sorption to low temperature biochars, where the amorphous phase exists in high proportions, and to non-carbonised

materials¹⁴⁵. Partitioning is distinct from all other mechanisms discussed in this thesis, in that it is not technically a form of adsorption – it is therefore necessary to use the term *sorption* to refer to the combined effects of *adsorption* and *partitioning*. It typically occurs linearly with respect to aqueous concentration, in contrast to adsorption which is highly non-linear^{102,143,145,146}. Partitioning is commonly identified as a mechanism in the sorption of organic contaminants to biochar; however its role is rarely discussed in depth.

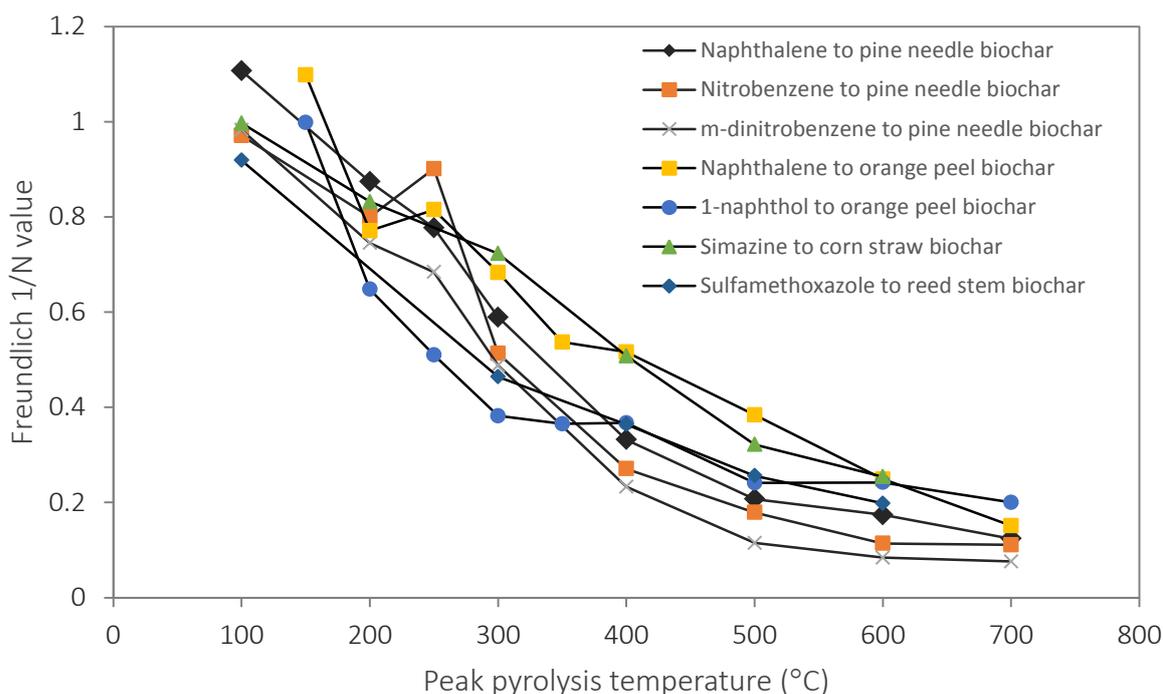


Figure 2-20: Relationship between pyrolysis temperature and Freundlich 1/N value for a range of biochars and contaminants. Based on data from: Chen *et al.*¹⁰² for pine needle biochars; Chen *et al.*⁷³ for orange peels; Zhang *et al.*¹⁴³ for corn straw biochar; and Zheng *et al.*¹⁴⁰ for reed stem biochar (by the author)

The extent to which partitioning occurs is dependent on the relative proportion of the amorphous phase in the biochar. The amorphous phase is typically most significant in low temperature biochars, while for high temperature biochars the carbonised phase is more prominent^{70,102}. The sorption therefore changes from partitioning to adsorption as HTT increases, resulting in changing sorption properties¹⁰². A number of studies have reported increasing non-linearity of isotherms as the HTT increases for a temperature series of biochars, as shown in Figure 2-20 for a range of biochar feedstocks and contaminants. This increase in non-linearity is correlated with the removal of the amorphous phase and an increasing prevalence of adsorption over partitioning at increased pyrolysis temperatures.

The extent of partitioning may be measured using a partitioning coefficient, K_p . K_p describes the linear relationship between the amount of an adsorbate partitioned to a solid phase, and its aqueous concentration ¹⁴⁷. The partitioning component can be mathematically separated from the isotherm using methods such as the dual-mode sorption model ¹⁴⁸, as shown in Figure 2-21 for the sorption of nitrobenzene to a straw ash charcoal. The dual-mode sorption model assumes that there is negligible increase in adsorption at high concentrations, and therefore the slope of the isotherm at high concentrations represents K_p . The dual-mode sorption model therefore allows for the determination of separate partitioning and adsorption isotherms.

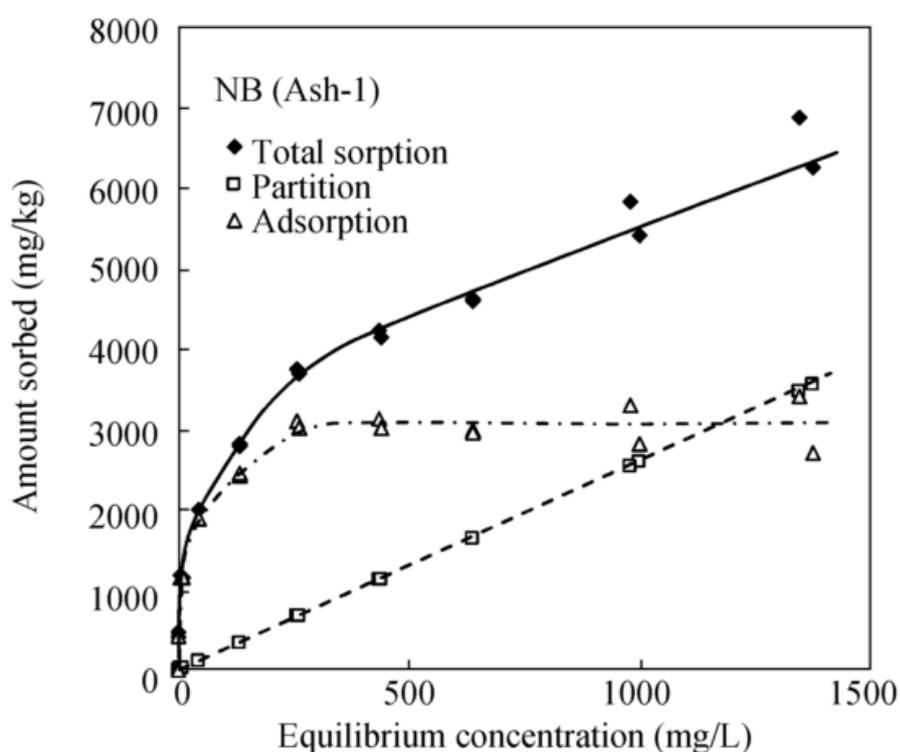


Figure 2-21: Separation of partitioning and adsorption for the sorption of nitrobenzene to a straw ash charcoal. Replicated from Huang and Chen ¹⁴⁸

While many papers have noted the significance of partitioning to the sorption of organic compounds, very few have considered its implications for remediation in depth. The significance of partitioning will depend on its contribution to sorption at environmentally relevant concentrations, its reversibility, and the long-term stability of the amorphous phase. The following paragraphs examine these three factors, and together suggest that partitioning will have a relatively small contribution to the remediation of organic contaminants using biochar.

Partitioning is unlikely to be present in significant quantities at realistic environmental concentrations due its high linearity. The high linearity of partitioning relative to other mechanisms means that it contributes relatively little to total sorption at low concentrations, though its contribution increases at higher concentrations. However, at realistic soil concentrations partitioning is likely to have very little contribution to total sorption. For example, the soil guideline value (SGV) for naphthalene in the UK is between 7 and 1,400 mg/kg, depending on the land use¹⁴⁹. Even at the highest of these limits, partitioning is likely to be an insignificant contributor to the overall sorption. Huang and Chen¹⁴⁸ showed that at a sorbed concentration of 1,400 mg/kg of naphthalene, partitioning comprises <1% of the total sorption to a straw ash charcoal. Other papers have reported much higher adsorption capacities of naphthalene including 80,000 mg/kg⁷³, 136,800 mg/kg^{102,150} and 187,800 mg/kg¹⁵¹ (based on Freundlich isotherm at $C_e = C_{\text{saturation}}$), to which partitioning is likely to be even less significant at low concentrations. This relationship is also true for other contaminants⁶⁻⁸. Li et al.¹⁵² characterised the relative influences of partitioning and adsorption for the sorption of atrazine to a range of softwood and hardwood biochars (Figure 2-22), and showed that adsorption contributes over 85% of sorption at pore water concentrations less than approximately 10 $\mu\text{mol/L}$ (2.2 mg/L), a concentration well above both water quality guidelines¹⁵³ and previous reported environmental concentrations⁴⁵. The high non-linearity of other previous isotherms, also suggests that partitioning is unlikely to play a significant role at low concentrations. Therefore partitioning is expected to represent a small component of total sorption of organic contaminants in soil and will therefore play a relatively small role.

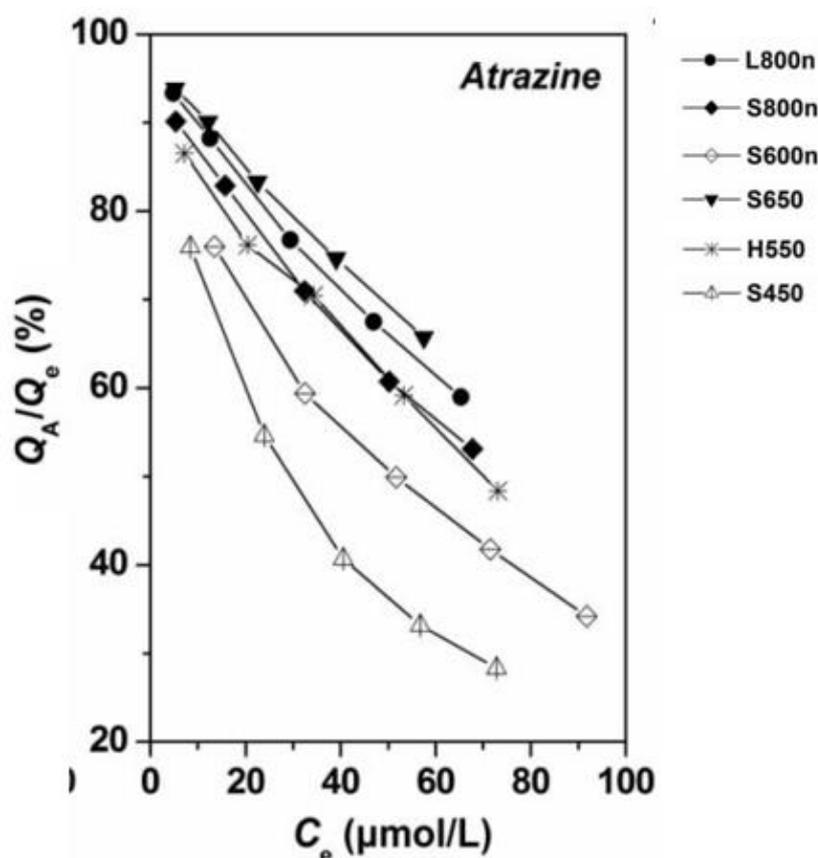


Figure 2-22: Relative contribution of adsorption, Q_A , to total sorption, Q_e , of atrazine by a number of biochars. L: lignin; S: softwood; H: hardwood; number refers to highest treatment temperature; n refers to nitrogen atmosphere during pyrolysis. Adapted from Li et al.¹⁵²

The influence of partitioning will also depend on the reversibility of contaminants immobilised through this mechanism. Partitioning describes the phase-distribution of an organic molecule between the aqueous and solid phases, and can therefore be reversed under conditions where the aqueous phase reduces (e.g. rainfall, groundwater flow). Sorption-desorption tests at a range of initial concentrations may provide further insights into this relationship for a given biochar, as the different contributions of partitioning and adsorption will likely result in different amounts of desorption. Similarly, sorption-desorption tests with and without an adsorption inhibitor, such as *p*-nitrophenol¹⁴⁴, may also provide insights into the reversibility when partitioning is the dominant form of sorption. However, these results provide evidence that the partitioning mechanism may be highly reversible in soil.

Finally, contaminants immobilised through partitioning are likely to be released when the amorphous component of biochar degrades in soil, resulting in little long-term immobilisation through partitioning. As discussed in 2.3.4, the amorphous phase of biochar is likely to degrade in a matter of weeks to months^{76,110}. The net result of this is that partitioning will not

have a significant effect in the long-term, and may actually result in the release of some contaminants, although this has not been thoroughly studied.

The combined results of the relative contribution to sorption, the reversibility of partitioning, and the stability of the amorphous phase suggest that partitioning is likely to play a negligible role in the remediation of contaminated soil using biochar. Partitioning may contribute significantly to the overall sorption while providing little actual environmental benefit, and therefore should be separated from an isotherm using a tool such as the dual-mode sorption model^{143,145,148} for a more accurate representation of the capacity of a biochar for remediation in soil.

Pore filling

Pore filling describes the diffusion of contaminants into the pores of the carbonised phase of the biochar to adsorption sites. Pore filling is therefore not a mechanism of *adsorption* but rather a transport process. *Pore diffusion* can also be used to more generally refer to the transport of adsorbate molecules within an adsorbent. It is a result of the microporous nature of biochar and its extent will depend on the pore structure of the carbonised phase. It has been thoroughly investigated for the sorption of organic compounds to activated carbon^{154,155}, and this knowledge has been used previously to infer insights into how it behaves in biochar. Its relative role in determining total adsorption is a product of the contaminant molecule's size and the physical structure of the biochar, while its long-term role will depend largely on pore accessibility in the presence of soil organic matter.

Pore filling is a significant process contributing to the sorption of many organic contaminants. It is often described as one of the most significant sorption processes for biochar, with Zhang et al.¹⁵⁶ suggesting that pore filling dominates sorption of pesticides to biochars at low concentrations and Lattao et al.⁹⁵ demonstrating that its hindrance can affect sorption by approximately one order of magnitude. Lattao et al.⁹⁵ also correlated sorption of three organic compounds to a temperature series of maple wood chars, and found that the best fit was a model based only on pore volume, suggesting that the presence of pore filling may be the most significant factor controlling sorption of small organic compounds. It is therefore likely that pore filling will contribute significantly to the immobilisation of organic contaminants.

Pore filling typically results in highly non-linear sorption profiles, suggesting that it will play a significant role in sorption at low concentrations. A number of papers have highlighted the highly non-linear profile of adsorption which is controlled by pore filling^{143,157}, due to the combined result of two processes. First, pore filling occurs primarily into micropores (< 20 nm), due to these pore sizes being comparable to those of contaminant molecules which allows for interactions (such as hydrophobic effects, hydrogen bonding or π - π EDA interactions) with both walls of the pore^{151,158,159}. At low contaminant concentrations, the high energy micropores are preferentially filled by contaminant molecules^{140,151,160}. Second, at higher contaminant concentrations these micropores become saturated with adsorbed compounds, after which no further adsorption can occur at these sites. Together, these two processes result in high adsorption at low concentrations but little further adsorption as the aqueous concentration increases, and therefore non-linear adsorption.

The configuration of the pore network can also influence the effectiveness of pore filling. Though micropores contribute the most to total sorption and to the total number of sorption sites^{66,90}, a number of studies have also demonstrated the significance of mesopores to the transport of adsorbate molecules. For example, Latta et al.⁹⁵ demonstrated that the best predictor of sorption for benzene, naphthalene and 1,4-dinitrobenzene to a range of wood chars was a weighted sum of the volumes of micropores and mesopores. Ahmad et al.¹⁶¹ suggested that trichloroethylene is held within the mesopores of pine needle biochar, then adsorbed into micropores through capillary forces. These results, together with similar discussions for activated carbons^{162,163}, suggests that diffusion from mesopores into micropores is necessary for the pore filling mechanism to occur. Therefore while adsorption generally correlates with micropore volume, an overall well-developed pore network is also significant in order to make these adsorption sites accessible.

The extent of pore filling may be reduced for large contaminant molecules due to the size exclusion effect. The size exclusion effect (also called *steric hindrance*) describes the process of bulky adsorbate molecules such as tetracycline¹⁶⁰ and humic acids¹⁶⁴ being unable to access a fraction of the micropores. Figure 2-23 shows the pore size distribution of a red gum biochar produced at 850°C¹⁶⁵ and highlights that effectively all of the pores are available to small compounds like atrazine, while for larger compounds like tetracycline and humic acids up to 80 and 95% respectively of the pore space may be inaccessible. This effect can result in the sorption of large molecules being significantly lower than would be expected based on

other properties of the molecule and the SSA of the biochar^{151,166}. For example, Nguyen et al.¹⁵¹ found that the sorption of 1,2-dichlorobenzene, 1,2,4-trichlorobenzene and 1,4-dichlorobenzene, each having comparable functional-group properties, increased in the order of decreasing molecular diameter, suggesting that steric effects were playing a significant role in controlling the sorption of these compounds. Similarly, Sun et al.¹⁶⁷ found differences in the sorption of PAHs, even after normalising for hydrophobic effects, which were attributed to steric effects during pore filling. Similar effects have also been proposed for the sorption of heavy metals to biochar¹⁶⁸. Together, these studies show that pore filling occurs more appreciably for smaller contaminant molecules than larger ones, and therefore may only be significant for contaminants with small molecular diameters.

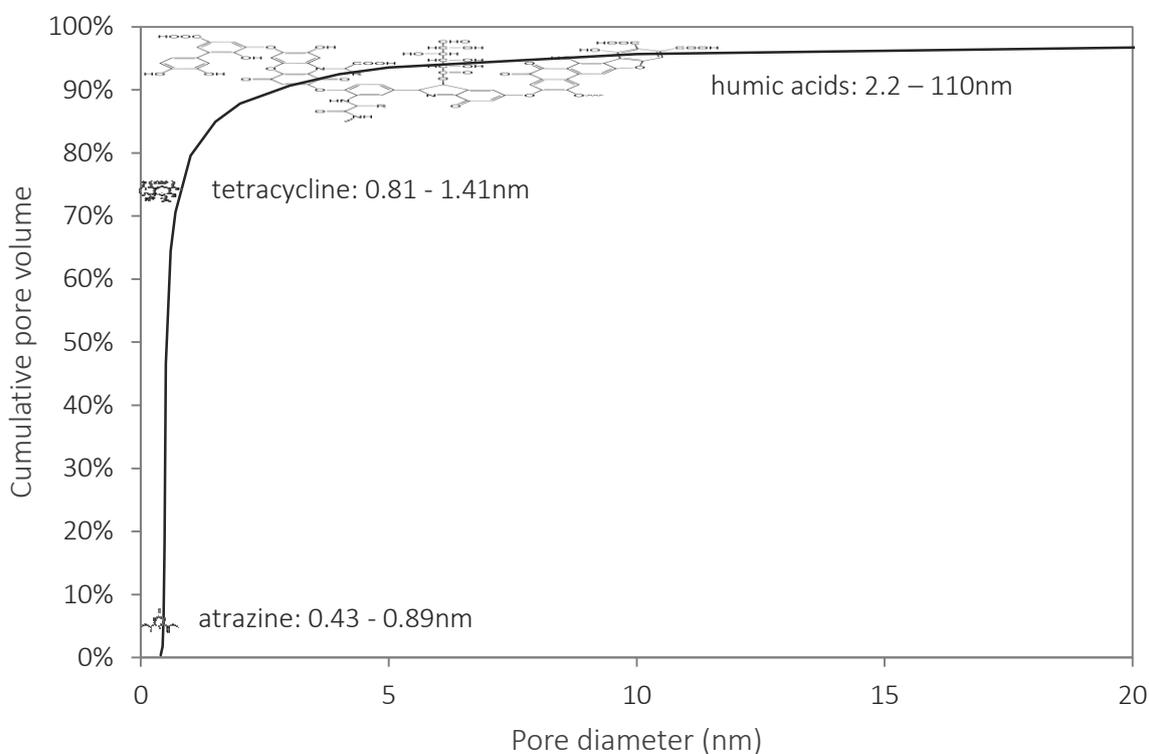


Figure 2-23: Pore size distribution of a red gum biochar, with the molecular size of selected organic compounds within the micropore range. Molecules are unable to adsorb into pores that are smaller than their molecular size. Pore distribution data from Bornemann et al.¹⁶⁵

While pore filling contributes highly to overall sorption at equilibrium, the rate at which pore filling occurs will also be an important design consideration. In order to compare papers discussing adsorption kinetics to pores, it is necessary to make an important distinction, highlighted in Figure 2-24. As the *contact time* increases, adsorbent molecules will first enter the macropore or mesopore region, and then diffuse into the micropores^{95,161,169} which will influence the kinetics of any given adsorption tests. However, as *contaminant concentration*

increases, adsorbent molecules will preferentially occupy the high energy micropore regions (at equilibrium) before adsorbing in the mesopore or macropore regions after the micropores have been filled. Therefore, the process of contaminant molecules entering micropores occurs slowly but in appreciable amounts at low contaminant concentrations, while the process of molecules entering the large pores occurs rapidly but adsorption primarily happens at high concentrations¹⁷⁰. A number of papers are ambiguous on this point when referring the ‘adsorption rates’ or which mechanism occurs ‘first’^{70,102,170} and therefore care should be taken when attempting to draw insights into *adsorption kinetics* from previous studies, as opposed to the *distribution of adsorbed molecules at equilibrium*.

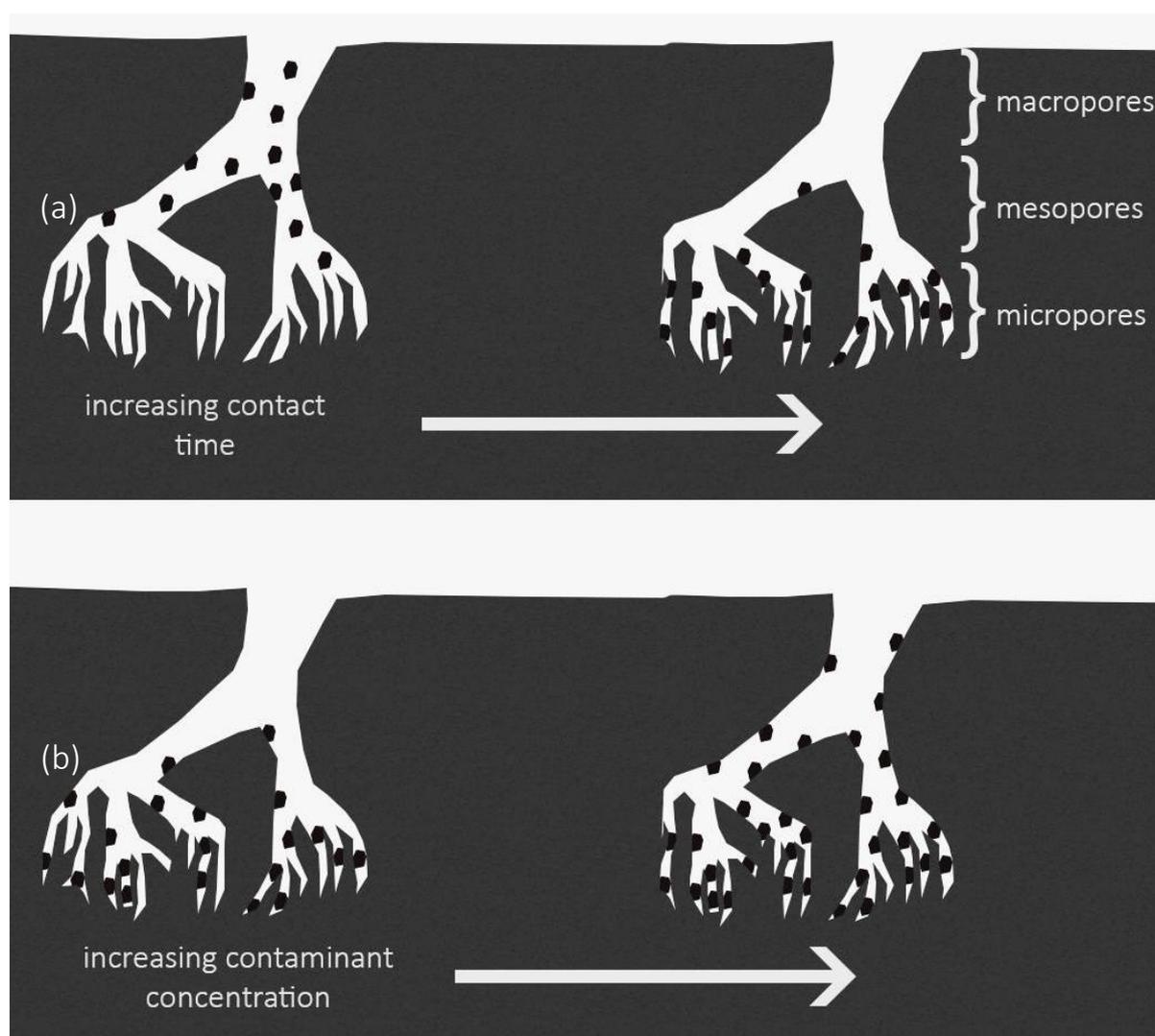


Figure 2-24: Contaminant molecule distributions within pores as (a) contact time and (b) concentration increase in the context of transport via pore diffusion (by the author)

Previous studies have provided conflicting results on the rate of pore filling. In a review of the sorption mechanisms of organic contaminants to biochar, Inyang et al.¹⁷¹ claimed that

‘sorption kinetics for pore filling processes is fast in most instances’. However, the authors do not cite a reference for this claim. Limited studies exist discussing the adsorption rate or kinetics of pore filling to biochar, so it is necessary to refer to studies involving activated carbon. Pelekani et al.¹⁵⁴ claimed that the time for atrazine and methylene blue to reach equilibrium to activated carbons will increase as pore size decreases, suggesting that pore filling is slow to primarily microporous adsorbents. Similarly, Hameed et al.¹⁶⁹ stated that the diffusion of molecules from macropores to micropores and subsequent adsorption to an adsorbent’s surface requires a ‘relatively long contact time’. Moreno-Castilla¹⁶² and Branton et al.¹⁷⁰ both independently suggest that diffusion from macropores to micropores is the rate limiting step for granular, carbonised adsorbents. While these studies suggest that pore diffusion is a process that may take some time, it is difficult to draw conclusions into what contact times will be sufficient to successfully immobilise contaminants in soil, as this may vary significantly from the time determined in a batch aqueous sorption tests. Further, this also suggests that pore diffusion may reduce the effectiveness of biochar for highly mobile contaminants, such as MTBE or other hydrophilic (polar) organic compounds. Shorter equilibrium sorption times are often reported in batch sorption tests than in field studies¹⁷², and therefore sorption is likely to be much slower in practice. Regardless, these results suggest that pore filling will take some time to have a significant effect in soils and may therefore result in some leaching of contaminants in the short term.

The reversibility of adsorption through pore filling will also have a significant influence on its role in remediating contaminants from soil. As with pore filling kinetics, it is necessary to refer to studies on activated carbon for information on the reversibility of the pore filling mechanism. Some studies have shown that activated carbons with more macropores and mesopores will desorb more attached molecules^{154,173}, suggesting reversibility from large pores but not micropores, which in turn suggests that those adsorbed via pore filling are effectively immobilised. Braida et al.¹⁷⁴ has suggested that sorption hysteresis can occur due to deformation of micropores which can lead to the entrapment of attached particles. Similarly, Li et al.¹⁶³ suggested that pore blockage by natural organic matter (NOM) on a powdered activated carbon resulted in reversible sorption, suggesting that those transported to micropores were more tightly bound. Diffusion of adsorbate molecules into micropore spaces results in strong interactions due to the proximity of the adsorbate molecule to two walls of a micropore^{151,158,159}, implying that desorption would also be less significant under these conditions. However, studies typically only refer to the effects of this interaction on sorption

capacity, rather than binding strength and so these implications have not been widely discussed. Regardless, the combined results of activated carbon studies to date and the mechanistic process of pore filling together suggest that pore filling may be effective in irreversibly immobilising organic contaminants in soil, though limited studies are available which discuss this effect specifically for biochar.

Pore blockages by SOM are likely to significantly reduce the extent of pore filling in the soil profile. As described in Section 2.3.4, long chain SOM molecules can adsorb to the surface of biochar and prevent access to microporous regions. Wang et al.¹⁷⁵ carried out sorption tests on a range of soils amended with a pine sawdust biochar. In control tests with no biochar, soils with the highest SOM exhibited the greatest sorption of terbuthylazine; however this sequence was reversed after amendment with biochar. This reversal suggests that SOM has a higher sorption capacity than the mineral content of soil, however interferes with the biochar when biochar is present, which dominates sorption even at low dosage rates. Wang et al.¹⁷⁵ also suggested that these pore blockages can reach saturation within 24 hours of incubation, so is therefore likely to occur before significant amounts of pore filling can take place. Zhang et al.¹¹³ also observed the greatest reduction in sorption of phenanthrene after incubation with soils containing the highest organic contents. Ren et al.¹¹⁶ investigated the sorption of atrazine and phenanthrene to three pig-manure biochars after incubation in sand and cropping with wheat straw, and found that the high temperature biochar had by far the greatest reduction in sorption, which was attributed to blockages of the micropores. The significant decreases in sorption due to competition with SOM highlight the significance of SSA and the role of pore filling in overall sorption. While no known studies have analysed the pore size distribution after incubation with SOM, it is likely that access to micro- and mesopores will be significantly reduced. These studies together suggest that the influence of pore filling may be significantly reduced in the soil profile.

Overall, the literature to date suggests that pore filling may be a significant process influencing the immobilisation of contaminants in soil, due to its high binding strength and low reversibility. However, its effects in influencing remediation may be limited due to the significant reduction in the adsorption of molecules greater than approximately 1 nm, its potentially slow diffusion rate into micropores, reliance on the biochar having both micropores and mesopores, and these pores potentially being blocked by SOM. In particular, high temperature, highly microporous biochars are likely to adsorb contaminants via pore

filling, although these biochars may result in some leaching in the short-term due to the slow diffusion of contaminants into the micropores.

π - π interactions

π - π interactions refer to chemical interactions between the π electrons on the aromatic surface of the carbonised component of biochar and the π electrons of an aromatic adsorbate compound^{95,176}. These are discussed in this thesis as π - π electron donor-acceptor (EDA) interactions, in which one of the aromatic rings acts as an electron donor while the other acts as an electron acceptor, as illustrated in Figure 2-25¹⁶⁶. Biochar can act as a π -electron donor and a π -electron acceptor simultaneously^{166,177}, while aromatic organic contaminants are typically either an acceptor or a donor. Few papers discuss in depth the role of π - π EDA interactions in remediation using biochar. Its overall contribution will depend on the chemical properties of the adsorbent and adsorbate, while its long-term stability will be influenced by the oxidation of biochar in soil during ageing.

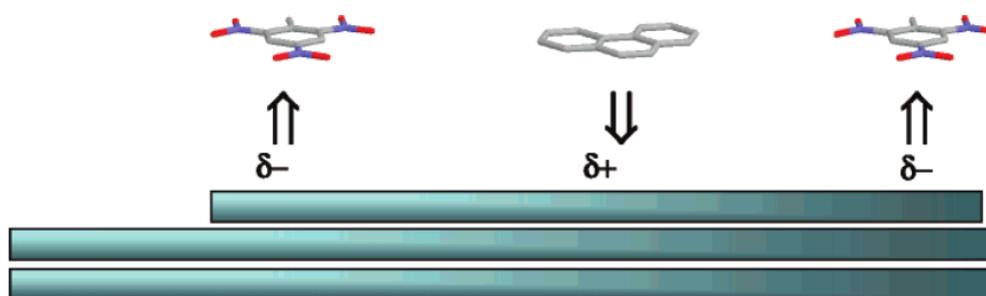


Figure 2-25: Schematic of π - π EDA interactions between a graphitic sheet of charcoal, acting as a π -donor with π -acceptor molecules (e.g. trinitrotoluene) and as a π -acceptor with π -donor molecules (e.g. phenanthrene)¹⁶⁶

The capacity of an adsorbate to donate or accept π electrons depends on the compound's molecular structure. A compound is a π -acceptor if it has an electron withdrawing group, such as $-\text{OH}$, $-\text{NH}_2$, $=\text{O}$, or $-\text{Cl}$, which has a higher electronegativity than C and H and therefore attracts electrons away from the aromatic ring¹⁷⁸, as shown in Figure 2-26. This attraction away from the aromatic ring results in the π -electron groups, which are perpendicular to the aromatic ring, having a slight electron deficiency and therefore a capacity to accept electrons from other sources. Conversely, a compound is a π -donor if no electron withdrawing group is present, such as in PAHs, resulting in a π -electron rich aromatic ring and therefore the capacity to donate electrons to nearby molecules¹⁶⁶. The strength of a π -donor is proportional to the number of carbon atoms in the aromatic system,

while the strength of a π -acceptor is proportional to the electronegativity of the electron withdrawing group¹⁷⁸. It has also been suggested that this effect is more prominent for adsorbate molecules which are more planar¹⁷⁹. Therefore, π - π EDA effects are expected to be the strongest for large PAHs, such as benzo[a]pyrene, and planar aromatic compounds containing highly electronegative groups, such as nitrobenzene, as indicated by the polarisability parameters for selected organic compounds in Table 2-5.

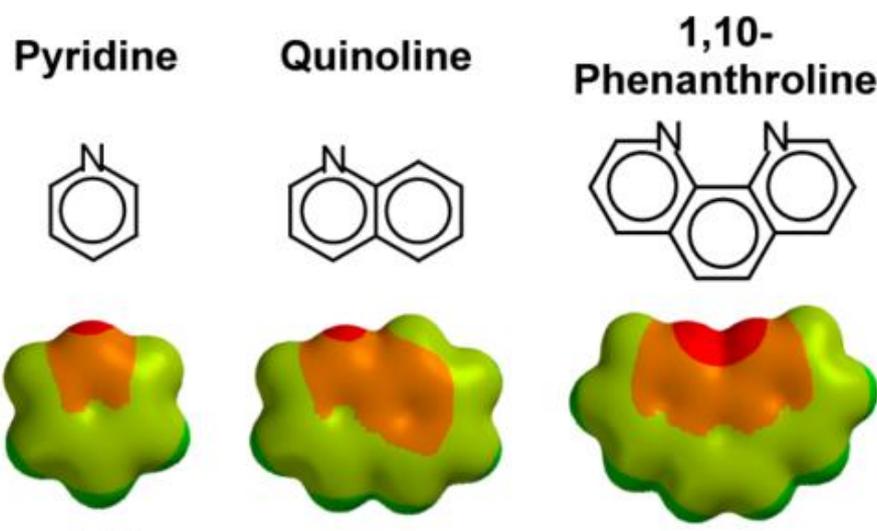


Figure 2-26: Electron density of three π -acceptor compounds. Red represents electron-rich regions while green/blue represents electron-poor regions. Adapted from Xiao et al.¹⁸⁰

For large PAHs some of the pores may be inaccessible due to the size exclusion effect, suggesting that strong influences of pore filling and π -acceptance are unlikely to occur simultaneously. For example, benzo[a]pyrene has a molecular size of approximately 4-9 nm, therefore Figure 2-23 suggests that approximately 90% of the pores will be inaccessible. This suggests that for large PAHs, adsorption through π - π EDA forces in the mesopore and macropore regions may dominate the overall adsorption. In contrast, small compounds with nitrogen or chlorine groups are expected to adsorb strongly to biochar due to the combined effects of pore filling and π - π EDA interactions.

Table 2-5: Polarisability parameters of selected π -electron donors and acceptors (by the author)

	Compound	π^* ^d
π-donors	Benzene ^a	0.59
	Naphthalene ^a	0.70
	Phenanthrene ^a	0.81
π-acceptors	Toluene ^b	0.54
	Chlorobenzene ^b	0.71
	Nitrobenzene ^b	1.01
	Atrazine ^c	1.24

^a data from Hickey et al (1991). ¹⁸¹

^b data from Marcus (1991) ¹⁸²

^c data from Japertas et al. (2007) ¹⁸³

^d polarisability parameter; used as an indicator for π -donor/acceptor strength

The significance of π - π EDA interactions for the sorption of a given contaminant will also depend on the aromaticity and polarity of a biochar ^{177,184}. Sun et al. ¹⁷⁷ suggests that the adsorption of π -electron donors will be promoted in low temperature biochars, due to the high polarity and abundance of electron withdrawing groups in low temperature chars. Similarly, high temperature biochars will promote the adsorbance of π -electron acceptors due to the increasing degree of aromatisation and reduction in polarity, resulting in biochar acting as a π -donor ^{73,102,140,185}. For example, Zheng et al. ¹⁴⁰ investigated the sorption of sulfamethoxazole, a strong π -electron acceptor, to various biochars and attributed the increase in sorption to high temperature chars in part to the increased π -donor capacity of the more aromatic surfaces. Though few other papers discuss these details in depth, some have qualitatively related π - π EDA interactions to the aromaticity and polarity of biochar suggesting that these two factors have the greatest influence ^{179,184,186}. For example, Jin et al. ¹⁷⁹ investigated the sorption of phenanthrene (a π -donor) and dibutyl phthalate (a π -acceptor) to a range of biochars, and found that the biochars with higher polarity exhibited significantly higher π - π EDA effects towards phenanthrene, while the effects were less clear to dibutyl phthalate due to its non-planar structure. A highly aromatic biochar will therefore promote π - π EDA interactions, as the planar surface promotes sorption of π -acceptor compounds while edge-functional groups promote the sorption of π -donor compounds.

The significance of π - π forces in determining adsorption to biochar has been noted several times ^{167,178,187-189}. Sander & Pignatello ¹⁸⁸ and Zhu et al. ¹⁶⁶ demonstrated that increased

adsorption of several aromatic compounds could only be attributed to π - π interactions and proposed an electron-donor acceptor mechanism. The method has since been noted several times. Sun et al.¹⁶⁷ noted their significance for the sorption of PAHs to various pine sawdust charcoals, while Qiu et al.¹⁸⁶ demonstrated their effectiveness for the sorption of two organic dyes to a straw biochar. Yang et al.¹⁹⁰ suggested that they comprise approximately 10-30% of the sorption of a range of aromatic compounds to a bamboo biochar. π - π EDA interactions are therefore likely to exist in significant quantities for the sorption of aromatic compounds to various biochars.

The long-term role of π - π EDA interactions will be influenced by surface changes of biochar over time. The surface of the biochar is expected to be oxidised over time due to biological and chemical processes in the soil, resulting in an increased presence of O-groups. These O-groups draw electrons away from the carbonised sheets, resulting in them being π -electron deficient and increasing the capacity of biochar to act as a π -acceptor, resulting in increased sorption of π -donor molecules and decreased sorption of π -acceptor molecules. This therefore suggests that the long-term role of π - π EDA interactions will be dependent on the properties of the adsorbate molecule; however no papers to this author's knowledge have directly addressed the influence of biochar ageing on π - π EDA effects.

Little data is available on the reversibility of π - π EDA interactions. Keiluweit et al.¹⁷⁶ demonstrated that π - π EDA bonding is generally stronger than hydrogen bonding and therefore suggested that this will enhance the remediation of aromatic contaminants in the environment. However, they also noted the difficulties in comparing values across multiple studies due to the variations in experimental approaches and sorption systems. Conversely, Zhang et al.¹¹³ observed varying results for the sorption reversibility of phenanthrene, a π -donor compound, in soil amended with *pinus radiata* derived biochar as demonstrated in Table 2-6. All biochar amendments significantly increased the sorption of phenanthrene, though amendment with BC700 at 0.5% w/w increased the overall reversibility of sorption as measured by the hysteresis index (HI). Though the authors do not offer a discussion for this anomaly, this result is consistent with stronger sorption of π donor contaminants to low temperature biochars due to π - π EDA interactions. However, this does not explain the significant differences in the HI values between amendments of 0.1% and 0.5%, which may be due to interactions between the soil and the biochar. Regardless, the results discussed above suggest that adsorption through π - π EDA interactions, particularly with biochar acting

as a π -acceptor, tightly binds contaminants and therefore may be effective at immobilising contaminants in soils.

Table 2-6: Adsorbed concentrations of phenanthrene to pinus radiata biochar in soil during sorption and desorption. Data from Zhang et al. (2010) ¹¹³

	$q_{e,s}$	$q_{e,d}$	HI ^a
Soil	160	220	0.38
BC350 @ 0.1%	330	520	0.58
BC350 @ 0.5%	1,400	2,400	0.72
BC700 @ 0.1%	1,000	1,600	0.60
BC700 @ 0.5%	7,300	9,700	0.33

$q_{e,s}$: equilibrium adsorbed concentration during sorption at $C_e = 1 \mu\text{g/L}$

$q_{e,d}$: equilibrium adsorbed concentration during desorption at $C_e = 1 \mu\text{g/L}$

^a Hysteresis Index; a measure of hysteresis where 0 indicates complete reversibility

Recent research has also shown that π - π interactions can occur as π^+ - π interactions, which occur between biochar and cationic aromatic compounds such as sulfamethazine ¹⁹¹ or aromatic amine cations ¹⁸⁰, including many herbicides. In these cases, π - π EDA interactions occur simultaneously with a charge-assisted hydrogen bond (CAHB), which is particularly prevalent at low pH values where zwitterionic compounds exist largely as cations. The presence of π^+ - π EDA interactions suggests that π - π interactions for cationic or zwitterionic compounds are unlikely to desorb if the environmental pH levels decrease, although this should be confirmed experimentally in each case

Overall, the literature to date suggests that π - π EDA interactions are likely to be significant for the sorption of aromatic compounds to biochar. In particular, biochars with highly carbonised and aromatic biochars will promote these interactions, while oxygen groups will increase the capacity of biochar to act as a π -acceptor. π - π EDA interactions will be particularly effective for polar contaminants to high temperature biochars, and for large PAHs to low temperature biochars, though interactions with the pore filling mechanism should also be considered. However, few studies have considered the role of biochar π - π EDA interactions in the long-term soil profile, although the effects of ageing suggests that the sorption of π -acceptor molecules may decrease while the sorption of π -donor molecules will increase.

Hydrophobic effects

Hydrophobic effects refer to the non-specific adsorption of a hydrophobic organic compound (HOC) to the hydrophobic surface of an adsorbate¹⁷¹. While functionally similar to partitioning in many ways¹⁹², this section discusses it in the context of adsorption to the aromatic component of biochar. It is primarily driven by the adsorbate molecule's aversion to dissolving in water¹⁶², although is ultimately a function of the properties of both the adsorbent and adsorbate^{175,193,194}; both adsorbate molecules and biochar may exhibit hydrophobicity. Its relevance in soil remediation will depend on its total contribution to sorption to given biochar, while its long-term significance will depend on the effects of biochar oxidation in soil.

The hydrophobicity of biochar is commonly described as one of its properties most favourable to adsorption, and many studies have noted the significance of hydrophobic effects in immobilising organic contaminants. Typically, high temperature biochars have low polarities (i.e., low O:C ratios) and therefore demonstrate greater hydrophobic effects. Liao et al.¹⁹⁴ investigated the sorption of two dyes to a series of bamboo charcoals before and after microwave modification, and found that the sorption of each dye correlated with biochar hydrophobicity, suggesting that hydrophobic effects may be significant in adsorbing these compounds. Hydrophobic effects are most prevalent to biochars with high aromaticities (i.e., low H:C ratios) and low polarities.

The properties of the adsorbate molecule will also determine the extent of hydrophobic effects. In particular, hydrophobic effects are expected to be significant for HOCs such as PAHs^{167,190,195}. Zhou et al.¹⁹⁶ demonstrated that the sorption of phenanthrene, ethinylestradiol (EE2) and atrazine to peanut shell and wheat straw biochars followed the order of their respective hydrophobicities (octanol-water partition coefficient, K_{ow}), suggesting this property was significant in their sorption. Jin et al.⁹⁶ observed similar results for the sorption of imidacloprid, isoproturon and atrazine to various biochars in soils, suggesting that this effect holds in the soil matrix. Hydrophobic effects are therefore most relevant for contaminants with low K_{ow} values, which typically applies to non-polar organic molecules.

Hydrophobic effects can be partially normalised by considering the partitioning coefficient of the adsorbate molecule between two solvents. The extent of hydrophobic effects will depend

on the hydrophobicity of each molecule, typically measured using the octanol-water partitioning coefficient, K_{ow} , which describes the ratio between which an organic compound preferentially dissolves into octanol and water solutions^{147,197}. n-hexadecane-water and benzene-water partition coefficients are also sometimes used^{188,197}, as these compounds do not participate in hydrogen bonding, while aqueous solubility is also sometimes used. 'Hydrophobicity-normalised' isotherms are therefore presented by dividing the sorption by the solubility of a compound, in an attempt to normalise for these effects^{95,167,194,198}. A number of papers have analysed these hydrophobicity-normalised isotherms, or regular isotherms of a range of contaminants in order to draw insights into the relative significance of hydrogen bonding and hydrophobic effects including: various dyes to biochar¹⁹⁴; various organic compounds to carbon nanotubes¹⁹⁷; various herbicides to biochar-amended soil⁹⁶; and various organic contaminants to biochar¹⁹⁶. While these studies demonstrate that sorption can correlate with hydrophobicity, particularly to low polarity adsorbents, in general they have noted that this correlation does not fully describe the sorption occurring and that other mechanisms, such as hydrogen bonding and π - π EDA are also playing significant roles.

The role of hydrophobic effects in remediating contaminated soil will depend largely on the likelihood of these hydrophobic interactions reducing over time. Some studies have suggested that molecules which are primarily immobilised through hydrophobic interactions may be released under certain conditions. Lima et al.¹⁹⁹ found higher amounts of desorption from non-polar adsorbents, suggesting that hydrophobic effects may be more likely to release contaminants than other mechanisms. Similarly, Pan & Xing¹⁹⁷ observed little sorption hysteresis for the sorption of organic contaminants to carbon nanotubes, which would be primarily driven by hydrophobic effects, suggesting that these effects are highly reversible. This suggests that contaminants which are bound by hydrophobic effects may pose a risk of being de-sorbed in the soil profile, which could pose a risk to the surrounding environment.

The long-term role of hydrophobic effects will also depend on changes to the properties of biochar over time; in particular, surface oxidation of biochar in soil may reduce their influence. Many studies^{115,116} have noted that biochar is likely to be oxidised in the soil over the long-term, which will increase polarity. While this author is not aware of any studies that have investigated the presence of hydrophobic effects after biochar ageing, many have commented on the role of polarity in determining hydrophobicity of a biochar, as previously

noted. Therefore it is expected that the increased oxidation will reduce the presence of hydrophobic effects.

It is also worth considering the molecules for which hydrophobic effects will be the most significant. Hydrophobic effects are most significant for HOCs; these compounds have very low solubility and are therefore unlikely to be highly mobile in a typical soil profile. For example, the risk of PAHs leaching in a contaminated soil in the Niger delta was found to be insignificant²⁰⁰. The use of biochar to immobilise HOCs in this context therefore may not be entirely relevant (however, the use of biochar to revegetate and stabilise the soil may still be highly relevant to remediation and should be considered¹²⁵). Therefore, the compounds for which hydrophobic effects are most significant may be those for which remediation through immobilisation to biochar may not be an effective treatment method.

The role of hydrophobic effects on the long-term immobilisation of contaminants is therefore not entirely clear. While many studies have discussed the importance of hydrophobic effects in adsorbing organic contaminants (the hydrophobicity of biochar's aromatic surface is regularly cited as one of its key properties for adsorption), a closer look at the results of previous studies suggests that it has a number of downsides. It may result in long-term leaching due to sorption reversing and changing biochar properties. While these effects will be less severe for HOCs, these compounds are likely to be relatively immobile even without the presence of biochar, suggesting that biochar amendment may not be an effective method of remediation for these compounds. Therefore, while hydrophobic effects may contribute significantly to the sorption of many contaminants, care should be taken when attempting to control contaminants in the environment based predominantly on the influence of hydrophobic effects.

Hydrogen bonding

Hydrogen bonding occurs between an O or N atom on one molecule and a H atom which is bonded to an O or N atom on the other molecule^{116,186,201,202}, as demonstrated in Figure 2-27²⁰³. Several studies have suggested that hydrogen bonding may occur between a contaminant molecule and phenol or carboxyl groups in the biochar^{196,204,205}, resulting in contaminants being tightly bound. The role of hydrogen bonding in soil remediation will depend on its overall contribution to sorption, the influence of water molecules, and the effects of biochar oxidation in soil.

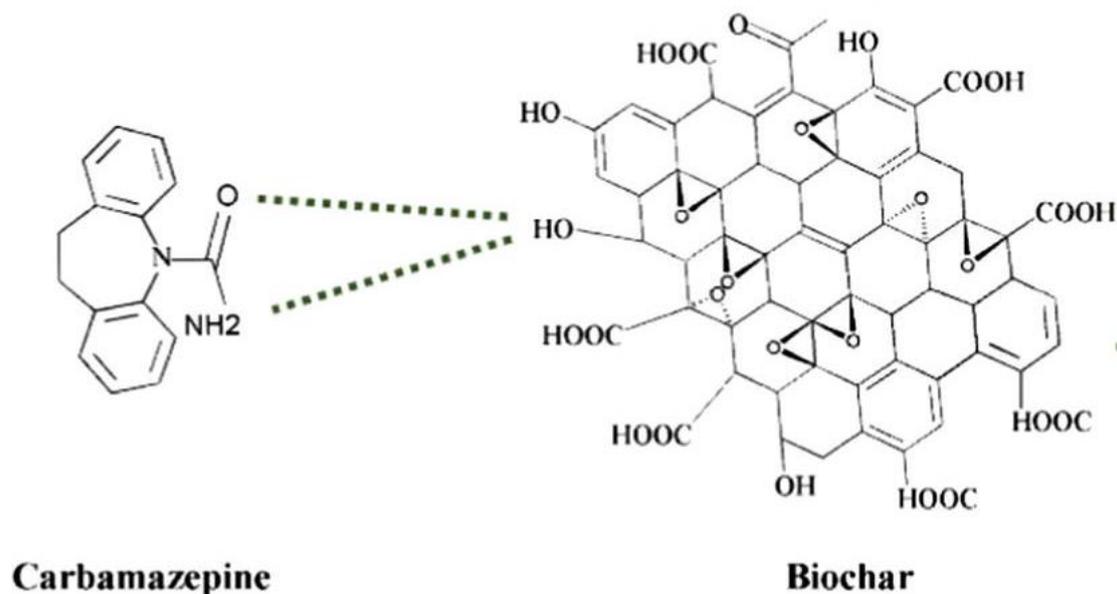


Figure 2-27: Hydrogen bonding schematic for the sorption of carbamazepine to biochar. Adapted from Naghdi et al.²⁰³

Hydrogen bonding is likely to be a significant mechanism controlling the sorption of organic contaminants to biochar, particularly for polar organic compounds. Jung et al.¹⁴⁷ measured the sorption of various endocrine disrupting compounds to activated biochars and observed a positive relationship between adsorbent polarity and the sorption of many compounds, suggesting that hydrogen bonding may be significant in controlling the fate of antibiotics. Ahmed et al.²⁰⁶ investigated the sorption of chloramphenicol to functionalised biochar and found that hydrogen bonding was a significant mechanism, particularly above pH 7, a likely pH range for biochar-amended soil. Similarly, Essandoh et al.²⁰⁷ showed that hydrogen bonding was significant for the sorption of the herbicide metribuzin to biochar, however its extent is dependent on the protonation state of both the adsorbate molecule and the biochar functional groups. Liu et al.²⁰⁸ provided further evidence of atrazine forming hydrogen bonds with biochar by showing an increase in –OH bonds in FTIR after sorption of atrazine to agricultural waste biochars. Qiu et al.¹⁸⁶ observed similar effects on FTIR analysis after the sorption of the dye *brilliant blue* to a straw based biochar, further providing evidence for the significance of hydrogen bonding in a range of contexts. Hydrogen bonding is also likely to tightly bind contaminants, stronger than hydrophobic effects in particular. For example, Lima et al.¹⁹⁹ found that atrazine was less likely to desorb from polar adsorbents, suggesting that hydrogen bonding releases contaminants less readily than hydrophobic effects. Together

these studies show that hydrogen bonding is significant in a range of cases, and therefore should be considered when designing biochar for environmental remediation.

The influence of competition with water may be significant in determining the influence of hydrogen bonding in practice. Water molecules can also form hydrogen bonds with the polar surface of biochar, and therefore may compete for sorption sites with contaminant molecules. For example, Zhu and Pignatello¹⁶⁶ found that oxidation of a wood charcoal decreased the sorption of both polar and non-polar contaminants due to the increased competition with water. Pan and Xing¹⁹⁷ found similar effects for the oxidation of a carbon nanotube, which was initially highly hydrophobic due to the near-completely aromatic surface. Moreno-Castilla¹⁶² suggested that reduced hydrophobicity can increase the adsorption of water molecules, reducing the number of sorption sites available to contaminant molecules and making it difficult to determine what the direct impact is on contaminant-biochar interactions. Wang et al.²⁰⁹ suggested that the sorption of water can decrease the sorption of organic compounds through competing for sorption sites, as well as reducing the overall surface hydrophobicity of the biochar, allowing for a lesser extent of hydrophobic interactions. However, Sander & Pignatello¹⁸⁸ suggested that adsorption can actively displace adsorbed water molecules, and so this effect may be less significant for molecules with high adsorption energies. However, these molecules are not the ones which will be of the greatest concern in the environment, due to their high adsorption energies resulting in generally low mobility in the soil profile. These results suggest that competition with water molecules may be a significant factor in determining the extent of hydrogen bonds in the environment. While this effect is difficult to appropriately characterise, care should be taken when working with polar contaminants to ensure that this effect is captured if attempting to optimise highly polar adsorbents for their removal from the soil.

The influence of hydrogen bonding is likely to increase over time in the soil due to increased surface oxidation of the biochar. As previously noted, the biochar surface is likely to be oxidised in the soil, resulting in an increased number of O-groups and therefore a greater capacity for hydrogen bonding. However no known studies have discussed the role of ageing on the long term significance of hydrogen bonding, though many have noted increased hydrogen bonding after artificially increasing the oxygen content. For example, Franz et al.²¹⁰ noted increased sorption of a number of aromatic compounds to an activated carbon after increasing oxygen content, particularly in cyclohexane where the influence of water is

removed. However many papers have also noted decreased sorption after increasing the oxygen content, even for molecules capable of forming hydrogen bonds, due to interactions with water molecules. The long-term significance of hydrogen bonding will therefore be dependent on the relative sorption properties of the given contaminant and water molecules, and may result in either increased or decreased adsorption.

The role of hydrogen bonding in determining long-term remediation outcomes is therefore likely to be significant. Due to its high contribution to overall sorption and strong binding strength, it is likely to effectively immobilise polar organic contaminants. However, the increased abundance of oxygen-containing functional groups on the surface of biochar over time will promote hydrogen bonding with both contaminant and water molecules, and it is not trivial to determine the net effect of these for a given contaminant.

2.4.3 Role of ash content in remediation

The influence of the ash content in determining the sorption of organic compounds has been investigated several times; however the discussion is often not thorough enough to suitably identify the role of the mineral component. The ash content in biochar comes from the crystallisation of various minerals during pyrolysis, and may exist in various forms such as quartz^{179,211}, calcite^{106,212}, sylvite^{213,214} or hematite^{106,215}. The presence of this ash component may result in contaminants interacting with various ions such as K^+ , Ca^{2+} or Si^{2+} which may influence their sorption on the surface of a biochar or their behaviour in solution, particularly in batch sorption tests. The alkali ash minerals also result in biochars having a high pH value, which is thought to be significant for the comprehensive remediation and revegetation of a site^{59,125}, and so this factor should be considered when selecting a biochar for a suitable application. This component is known to be important for the sorption of heavy metals to biochar, as the ash fraction provides sites for cation exchange resulting in the attachment of heavy metal ions to biochar^{138,216}. However, its role in the sorption of organic compounds is less clear.

The presence of ash may decrease overall sorption of organic contaminants due to obstruction of the carbonised phase, which has a much higher sorption capacity per unit area. A number of papers have reported an increase in sorption capacity after the removal of ash, which is typically attributed to improved pore access^{103,122,148,156}. For example, Liu et al.¹⁰³ showed that the modification of a rice husk biochar using potassium hydroxide removed the ash

content and subsequently increased the surface area of the biochar and the sorption of tetracycline. Conversely, Zheng et al.¹⁴⁰ observed temperature-dependent effects on the sorption of sulfamethoxazole after de-ashing of a reed stem biochar due to the different properties of the remaining inorganic fractions after de-ashing. Zheng et al.¹⁴⁰ also determined that the sorption to the ash component itself was significantly higher than to any of the raw or modified biochars, which would not be expected if its presence hindered sorption, as implied by the other studies. This result suggests that specific contaminant-ash interactions may be significant in determining remediation outcomes. Regardless, the interactions of organic contaminants with the ash fraction of the biochar are likely to depend both on the composition of the ash, and the properties of the contaminant compound.

In general, studies investigating the sorption of organic contaminants to biochar do not thoroughly characterise the ash fraction, even those which investigate the influence of de-ashing. Zheng et al.¹⁴⁰ gives the biochar composition in terms of carbon, nitrogen, oxygen and hydrogen, however this does not give any information on the mineral composition of the ash. Amonette et al.¹⁰⁴ gives elemental compositions of a wide range of feedstocks, however it is not trivial to convert these into an ash composition of biochar, as some of these components will break down during pyrolysis. For example, *meat and bonemeal* comprises approximately 26% calcium, however only 10.4% ash, suggesting that some or all of the calcium breaks down during heating. Few papers have characterised the properties of the ash and mineral contents in depth, making it difficult to draw conclusions about their role in sorption.

Insights into the role of the ash fraction on the sorption of organic contaminants can be gained from de-ashing studies, as well as those which have thoroughly characterised their ash through a combination of x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and elemental analysis. De-ashing may be carried out using hydrofluoric acid¹⁴¹, steam activation²¹⁷, potassium hydroxide¹⁰³ or other chemical activation methods. However, it should be noted that these will also influence other properties of the adsorbent – for example, steam activation will also remove the amorphous phase and significantly increase the surface area of a carbonised material^{218,219}. Table 2-7 outlines the studies to date which have investigated the influence of de-ashing on the sorption of organic compounds. It highlights how poor the characterisation of the ash fraction has been in these studies, meaning that the conclusions cannot be immediately applied to other biochars or contaminants which may

have different interactions with the ash fraction. Overall these studies suggest that the removal of the ash content increases sorption of organic compounds by (a) increasing the surface area and allowing for greater interaction with pore networks, and (b) increasing access to hydrophobic sites on the surface of biochars.

It is also useful to address the different influences of the different crystalline phases that may be present in a given biochar sample. Yuan et al.²¹³ thoroughly characterised the mineral components of biochars produced from various crop residues, and demonstrated that the crystalline phases are dependent on both the feedstock and the pyrolysis conditions. For example, corn straw biochar showed negligible crystalline content in XRD analysis when produced at 300 °C, however at 500 °C, calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and sylvite (KCl) were all present, as shown in Figure 2-28. These different minerals will influence the sorption and remediation capacity of biochar samples and should therefore be relevant for designing biochar remediation systems. In particular, many compounds exhibit pH-dependent sorption, which will be influenced by the presence and structure of these ash components. While studies exist discussing the sorption of organic contaminants to different minerals (e.g. Clausen et al.²²¹), few studies have thoroughly characterised the ash component (including crystalline forms) of a biochar and discussed its role in the sorption of organic contaminants. This suggests that this area may be understudied, which may present opportunities for new insights, particularly for some biochars which can have ash contents of up to 40%²¹². One study that has thoroughly characterised the influence of the ash content was carried out by Li et al.²²⁰, who showed that the removal of oxalate and carbonate minerals from agricultural waste increased the sorption of bisphenol A. This increase was attributed to the increased access to pore spaces, as previously described. The varied results obtained to date after the removal of ash suggest that suitable characterisation of the ash content may help to explain these results.

Table 2-7: Summary of papers investigating influence of de-ashing on sorption of organic contaminants (by the author)

Reference	Feedstock(s)	Adsorbate(s)	Ash composition	Influence on sorption
Liu et al. 103	Rice husk	Tetracycline	Only referred to in terms of SiO ₂	Increased sorption due to increased surface area after removal of ash minerals
Sun et al. 122	Rice straw, wheat straw, maize stalk, chicken manure, swine manure, cow manure	Phenanthrene	Referred to only as 'minerals', although authors note drop in Si content after de-ashing	Sorption increased in most instances due to increased presence of surface hydrophobic sites allowing for hydrophobic interactions. K _{OC} values correlated differently for plant-based biochar compared with manure-based biochars, suggesting that the different ash compositions influence interactions with the carbon surface
Zhang et al. 156	Pig manure	Atrazine; carbaryl	Not discussed, however elemental composition shows presence of (in decreasing quantities) P, Si, Al and S	Adsorption of both compounds increased due to increase surface area after removal of minerals. However, presence of minerals can aid hydrolysis at high pH values
Huang et al. 148	Rice straw	<i>p</i> -nitrotoluene; <i>m</i> -dinitrobenzene; nitrobenzene, naphthalene	Assumed mostly silica	Increased sorption due to enrichment of the charcoal component (both adsorption and partitioning)
Zheng et al. 140	Reed stems	Sulfamethoxazole	Assumed mostly SiO ₂	Sorption decreased after de-ashing to low temperature chars, but increased to high temperature chars; attributed to different compositions of ash in different temperature biochars
Yang et al. 141	Wheat and rice residues	Diuron	Carbonates and silica	Increased sorption due to increased char content
Li et al. 220	Corn cob, pomelo peel, eucalyptus globulus and silkworm excrement	Bisphenol A	Oxalates, CaCO ₃ , KCl	Increased sorption due to increased access to pore spaces

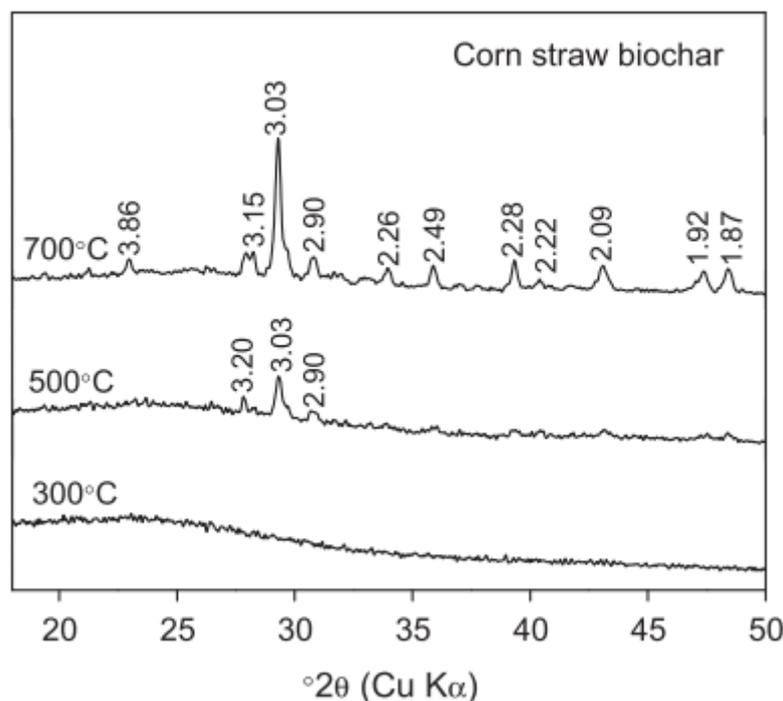


Figure 2-28: Increasing mineral content in a corn straw biochar with increasing pyrolysis temperature, as demonstrated using x-ray diffraction. Adapted from Yuan et al.²¹³

Ash may also influence the removal of contaminants through degradation or complexation of organic molecules. Zhang et al.¹⁵⁶ demonstrated that release of ions from the ash component of a manure biochar catalysed the hydrolysis of the herbicides atrazine and carbaryl, though this effect was aided in the presence of the biochar surface. This effect may be beneficial or harmful, depending on the environmental conditions and the nature of the degradation products, which may be more harmful than the original contaminants⁸. Bessac et al.²²² also showed that atrazine can form a complex with Ca^{2+} ions in the presence of an adsorbent surface, which can also result in the sorption of atrazine due to interactions with the ash fractions. While few studies have followed up on these results, it suggests that it is important to characterise the mineral component of a biochar in order to fully capture the interactions that will govern the remediation of contaminants in practice.

Therefore results to date suggest that the ash content will generally have a relatively low, or even negative, impact on the sorption capacity of a biochar for organic contaminants. However, this may be significantly influenced by the contaminant and the composition and crystalline phase of the ash component. The minerals may also affect the degradation or complexation of attached and dissolved organic molecules, which may be beneficial or harmful in the environment, so should be noted during the design phase when using biochar

as a remediation tool. However, in general its role has been under-studied and its structure poorly characterised making it difficult to infer strong conclusions about its role in remediation.

2.5 Sorption of atrazine to biochar

Atrazine is a widely used organic pesticide that has been found to contaminate groundwater and drinking water supplies, and may have harmful effects on human and animal health. Biochar may be a useful soil amendment to immobilise it in the soil profile. Further, by thoroughly understanding the immobilisation of atrazine, it is possible to gain insights into the control of other herbicides and organic contaminants. Atrazine has a range of chemical properties, including an aromatic ring, amine groups and an overall small molecular size, meaning that it can take part in many chemical and physical interactions. It therefore acts as a useful indicator molecule for analysing the role of each of these chemical interactions on other compounds. Insights into the sorption of atrazine will therefore aid the development of biochar as a useful tool for immobilising contaminants in soil.

A number of studies have been carried out investigating the sorption of atrazine to soils, biochars and activated carbons. In particular, studies exist investigating the sorption of atrazine to different soil types^{223,224}, due to the high risk of atrazine in the soil profile. In a review of atrazine transport in soil, Mudhoo et al.²²⁴ notes that atrazine has been found to adsorb more strongly to soils with high organic contents, however can still remain highly mobile in the soil profile. Correia et al.²²⁵ suggested that atrazine leaching in a tropical Brazilian soil was greatest after two days, suggesting that early rapid capture by adsorption may be an effective method of immobilising atrazine in practice. Therefore the immobilisation of atrazine through biochar may be an effective way to control its adverse environmental effects.

Results from studies investigating sorption to soil do not necessarily translate directly to implications for sorption to biochar, due to the different physical and chemical properties of biochar and soil. Several papers have demonstrated the significance of partitioning in sorption to low-temperature biochars^{196,226}, as also demonstrated for other organic contaminants¹⁰². However, as discussed in Section 2.4.2, partitioning is likely to have little influence on the remediation of a given site and therefore the following discussion focuses primarily on adsorption mechanisms. While pore filling is expected to be a major mechanism

for the adsorption of atrazine, there are inconsistencies reported around its behaviour in π - π EDA interactions, whether hydrogen bonding or hydrophobic effects are favoured, how its sorption is influenced by pH, and factors influencing its sorption kinetics. The following sections therefore draw on available literature data to determine the roles of these mechanisms on the sorption of atrazine.

2.5.1 Role of pore filling in atrazine sorption

Pore filling is likely to be a significant process controlling the sorption of atrazine. Due to its relatively small molecular diameter, atrazine is able to access microporous regions of the biochar and therefore can interact with a high number of sorption sites, however, the diffusion process to these sorption sites will be significant. A number of studies have demonstrated the significance of pore filling in the adsorption of atrazine to biochar. For example, Zhang et al.¹⁵⁶ demonstrated that atrazine exhibited higher normalised sorption than carbaryl to pig manure-derived biochars, which was attributed to its smaller molecular size. Zhao et al.²²⁷ observed increased sorption of atrazine to corn straw biochar after pre-treatment with ammonium dihydrogen phosphate, which resulted in increased surface area and pore volume but negligible changes in aromaticity or polarity, suggesting that the difference was predominantly caused by increased pore availability. Further, Ren et al.¹¹⁶ observed decreased sorption after ageing to high-temperature biochars, for which pore filling is expected to be the dominant mechanism⁹⁵, suggesting it was an important factor in adsorption in this case. These studies indicate that pore filling is likely to play a key role in the sorption of atrazine to biochar, resulting in relatively strong and irreversible adsorption.

2.5.1 Role of π - π EDA effects in atrazine sorption

π - π electron donor-acceptor (π - π EDA) interactions are present in biochar-atrazine systems, due to the presence of an aromatic ring within the atrazine molecule¹⁸³, however previous studies have reported conflicting results on its precise role. Several studies have noted the presence of these effects in the sorption of atrazine to biochar. For example, Xiao et al.¹⁵⁸ suggested that differences in chemical interactions between triazine herbicides and a series of maple wood biochars were dominated by π - π EDA interactions. Similarly, Yang et al.²²⁸ suggested that π - π EDA interactions were significant between atrazine and nitrogen-functionalised biochars, while Deng et al.⁹² suggested they were important in the sorption of atrazine to a high temperature wheat straw biochar. However, atrazine's role in these interactions is not entirely clear.

Notably, previous studies are not in agreement about whether atrazine is a π -donor or π -acceptor molecule. This is an important property determining atrazine's role in π - π EDA interactions. P. Zhang et al.¹⁵⁶ suggested that the presence of the chlorine atom in the atrazine molecule acts as an electron withdrawing group, resulting in atrazine being a π -acceptor. Similarly, Jung et al.¹⁴⁷ and W. Zhang²⁰⁴ demonstrate evidence of atrazine acting a π -electron acceptor due to its increased hydrophobic-normalised sorption to low-polarity biochars. In contrast, Yang et al.²²⁸ demonstrated increased sorption to nitrogen-functionalised biochars, which was attributed to increased π - π EDA interactions with atrazine acting as the π -donor. However, it is not clear how the authors separated these effects from hydrogen bonding. Similarly, a number of other papers have also claimed that atrazine acts as a π -donor^{92,143,205}. As atrazine only has one aromatic ring, unlike biochar, it is not possible for it to act as both a π -donor and π -acceptor simultaneously. Therefore one of these cases must be false. Xiao et al.^{158,180} claimed that triazine herbicides can participate in π^+ - π EDA interactions, which represent a combination of π - π EDA and cation- π interactions (with atrazine acting as the π -acceptor). This may partially explain the lack of clarity on π - π EDA interactions involving atrazine. Insights into the likely role of atrazine in π - π EDA interactions can be gained from considering its molecular structure.

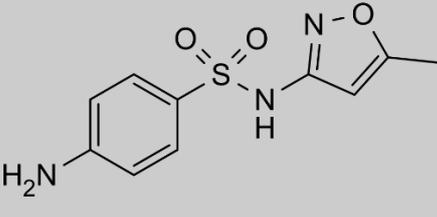
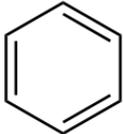
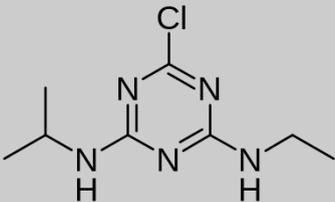
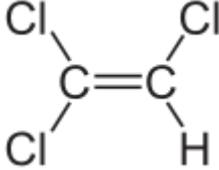
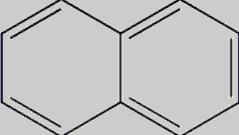
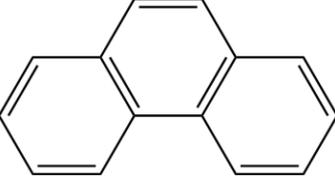
Mechanistically, atrazine is not a typical aromatic compound; due to the presence of nitrogen atoms within the aromatic ring (it is therefore considered a *triazine* compound). However, the presence of chlorine (electronegativity = 3.16) and nitrogen (electronegativity = 3.04) attached to carbon atoms (electronegativity = 2.55) in the aromatic ring suggest that atrazine is most likely to act as a π -acceptor²²⁹. Xiao et al.¹⁸⁰ demonstrated this by showing the presence of π - π EDA effects to non-functionalised graphite, which would not be present if atrazine were acting as a π -donor. Therefore, for the purposes of this thesis, atrazine is assumed to act as a π -acceptor molecule, and is likely to play a significant role in sorption, particularly to highly carbonised biochars.

2.5.2 Role of hydrogen bonding and hydrophobic effects in atrazine sorption

Several studies have discussed the relevance of hydrogen bonding and hydrophobic effects on the adsorption of atrazine. Atrazine is often referred to as a HOC^{156,204,224}, suggesting that hydrophobic effects would dominate its sorption to biochar; however, it is also capable of readily forming hydrogen bonds due to the presence of N groups^{196,205}. As a result, there are papers which have concluded that hydrogen bonding controls atrazine sorption, while others

have concluded that hydrophobic effects control atrazine sorption. For reference, the hydrophobicity of atrazine, as measured by $\log K_{ow}$, is compared with that of other organic compounds in Table 2-8, and shows that atrazine has a hydrophobicity comparable to benzene, though much lower than PAHs such as naphthalene and phenanthrene. The balance between hydrophobic effects and hydrogen bonding is important to understand, as it is a reflection of whether a highly aromatic, non-polar biochar (favouring hydrophobic effects) or a functional group-rich, polar biochar (favouring hydrogen bonding) is optimal in immobilising atrazine. This balance will influence the biochar design as well as the predictions of atrazine's long-term fate due to biochar oxidation in soil. Several studies have shown hydrophobic effects to be important for the sorption of atrazine. Ren et al.¹¹⁶ suggested that hydrophobic effects (together with pore-filling) may be the primary mechanism in the adsorption of atrazine to high temperature biochars. Similarly, Zhou et al.¹⁹⁶ suggested that hydrophobic effects dominate the sorption of organic compounds to biochar and to soil, while Zheng et al.²³⁶ suggested that hydrophobic interactions between atrazine and greenwaste biochar occur quickly, implying that they may be useful in rapidly immobilising atrazine under field conditions. Results from studies investigating other adsorbents can also provide insights into the sorption mechanisms of atrazine. For example, Sun et al.²⁰⁵ suggested that sorption of atrazine to SOM was governed by hydrophobic interactions, due correlations of sorption with aryl carbon on four SOM components. Together these studies suggest that hydrophobic effects are significant in immobilising atrazine by biochar.

Table 2-8: Hydrophobicity of atrazine and other organic contaminants (by the author)

Compound	Chemical structure	log K_{ow}
Sulfamethoxazole ¹⁴⁷		0.79
Benzene ^{184,230}		2.13-2.2
Atrazine ^{96,116,147,196,231}		2.18 – 2.70 ^a
Trichloroethylene ^{232,233}		2.61
Naphthalene ^{184,230,234,235}		3.29 – 3.5
Phenanthrene ^{184,230,234,235}		4.46 – 4.7

Notes: ^a Hale et al. ¹⁸⁴ lists the log K_{ow} value of atrazine as 1.5

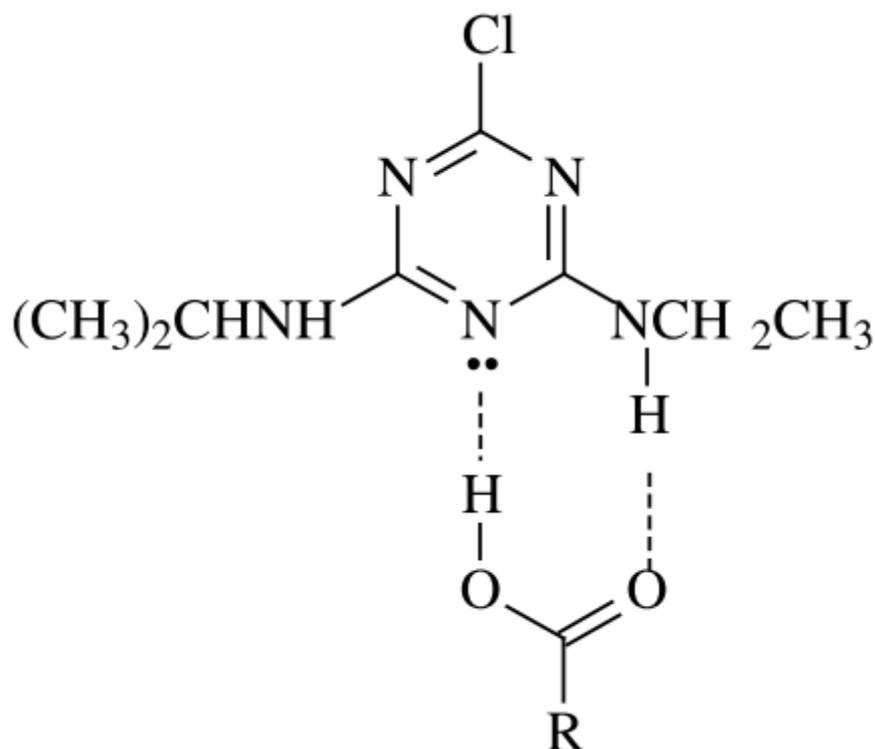


Figure 2-29: Diagram of mechanism for atrazine molecule acting simultaneously as a hydrogen bond donor and acceptor. Replicated from Xing et al.¹⁵⁹

Conversely, several studies have also shown the hydrogen bonding is important in immobilising atrazine to biochar. Zhang et al.²⁰⁴ suggested that hydrogen bonding of atrazine to a temperature series of sludge-derived biochars was most prominent to biochars produced at $\sim 400^{\circ}\text{C}$, due to the destruction of oxygen-containing functional groups at temperatures above this value. Zhou et al.¹⁹⁶ also showed that atrazine can form hydrogen bonds with -O and -OH groups on biochar, acting as both a H^+ bond donor and H^+ acceptor²⁰⁵. They also suggested that the wheat straw biochar used would form more hydrogen bonds than the peanut shell biochar, due to its higher polarity and greater abundance of functional groups. Xing et al.¹⁵⁹ even demonstrated that atrazine can act as a hydrogen bond donor and acceptor simultaneously in the presence of bifunctional molecules, such as multiple functional groups in a carbonised biochar ring, as demonstrated in Figure 2-29. Zhang et al.²⁰⁴ provided further evidence for the significance of hydrogen bonding by demonstrating that atrazine sorption decreased with increasing ionic concentration in solution, which is consistent with hydrogen bonding. Liu et al.²⁰⁸ also demonstrated an increase in -OH bonds on FTIR of an agricultural waste biochar after adsorption of atrazine, suggesting that hydrogen bonds were present. Finally, positive correlations between atrazine sorption and the polarity of humic substances²⁰⁹ and SOM²⁰⁵ provide further evidence for the interaction of atrazine with O-containing

functional groups. Together these studies suggest that hydrogen bonding is significant for the sorption of many organic contaminants to biochars and other carbonised adsorbents.

Some studies have explicitly demonstrated that hydrogen bonding is more significant than hydrophobic effects for the sorption of atrazine to biochar. This is likely due to atrazine's strong capacity to participate in hydrogen bonding. For example, Zhang et al.²⁰⁴ observed less sorption of atrazine to low-polarity sludge-derived biochars (i.e., controlled by hydrophobic effects) than to high-polarity biochars (i.e., controlled by hydrogen bonding), while Lima et al.¹⁹⁹ observed similar results for atrazine to various organic amendments. Mudhoo et al.²²⁴ observed greater de-sorption of atrazine from soil organic matter than from montmorillonite, suggesting that hydrophobic effects are more reversible than hydrogen bonding and Lima et al.¹⁹⁹ observed similar results in various organic amendments. Jin et al.⁹⁶ correlated hydrophobicity of various organic contaminants to various biochars and determined that hydrophobic effects for atrazine were less significant than the other compounds tested. Contrasting plots of sorption of atrazine with aromaticity (as aryl carbon) and polarity (as O+N:C ratio) are shown in Figure 2-30. These studies suggest that while hydrophobic effects may be significant in a number of contexts, it is more likely that hydrogen bonding will control the immobilisation of atrazine in practice.

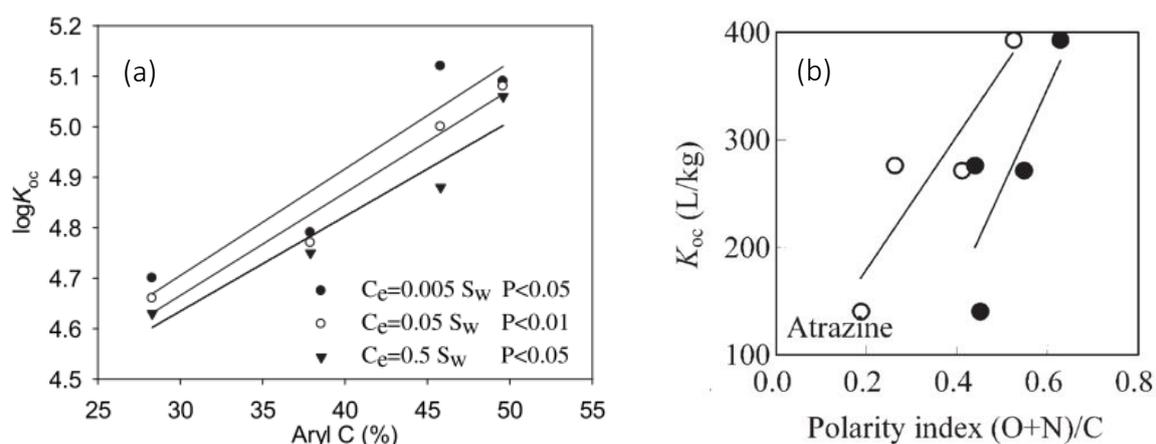


Figure 2-30: Sorption of atrazine to organic substances correlating positively with (a) aryl carbon, suggesting the dominance of hydrophobic effects²⁰⁵ and (b) polarity, suggesting the dominance of hydrogen bonding²⁰⁹

The contrasting results from these previous studies suggest that further investigation into the role of hydrophobic effects and hydrogen bonding is necessary. For example, it is not entirely clear whether oxygen-containing functional groups on the carbonised fraction are beneficial for sorption as they promote hydrogen bonding, or whether they are hindering sorption due to

the attraction of water and the loss of hydrophobic sites. A study using a range of biochars and determining their sorption of atrazine, or a comprehensive review of all available literature may provide insights into the roles of the different biochar properties.

2.5.3 Influence of solution pH on atrazine sorption and hydrolysis

Insights into the sorption mechanisms of atrazine can also be drawn from the relationships observed between atrazine sorption and pH. Atrazine is a weakly basic compound, with a pKa of approximately 1.7¹⁹⁹. It therefore exists as a neutral compound at high and neutral pH levels, however can become protonated in very acidic conditions. Conversely, biochar has a range of functional groups, and pH_{pzc} values for biochar are generally in the range of 6-9^{103,237}. Therefore, biochar can become predominantly protonated at low pH values, or have a primarily negatively charged surface in very basic conditions. Atrazine is capable of forming hydrogen bonds as both the H⁺ donor and acceptor¹⁹⁶ and these two mechanisms will respond differently to changes in pH, resulting in variations in the sorption capacity of biochars for atrazine over pH. The approximate speciations of atrazine and a representative biochar surface are shown in Figure 2-31, based on the ionisation implied by the Henderson-Hasselbalch equation. It shows both atrazine and biochar being positively charged at very low pH values¹⁶². As pH increases, the neutral form of atrazine dominates, while biochar becomes increasingly neutral first, and then increasingly negatively charged. The relative abundance of these species will affect how the compounds behave relative to each other. Note that for the biochar shown, a pH_{pzc} value of 8.5 was assumed; this value will vary for each biochar and therefore the relative abundances of functional groups at a given pH value will change accordingly. The speciations of the atrazine molecule and the biochar functional groups will both influence the sorptive interactions.

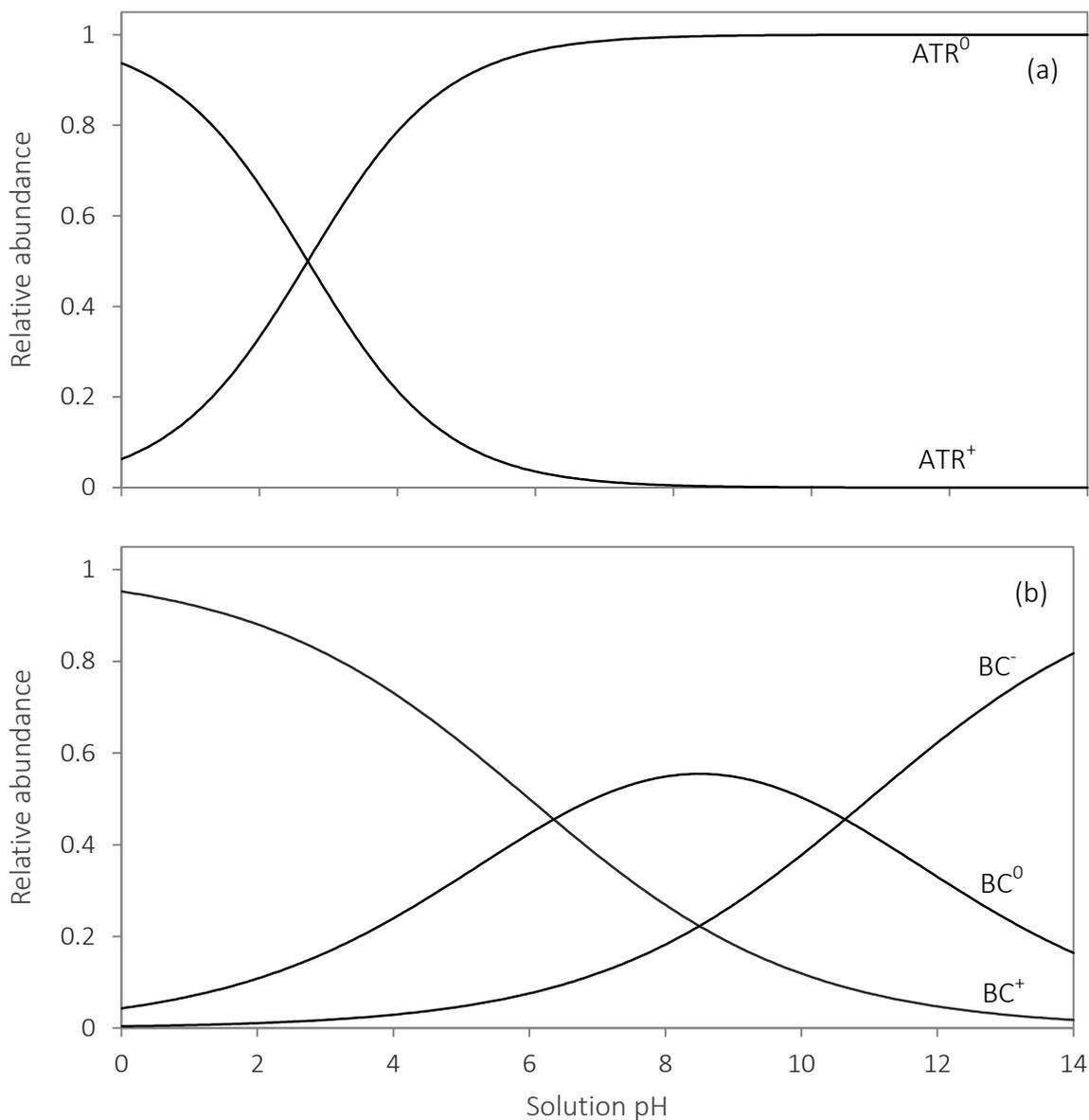


Figure 2-31: Approximate speciations of (a) atrazine and (b) a representative biochar as a function of pH (by the author)

Published studies to date investigating the influence of pH on atrazine sorption have found varying results. Some have found higher sorption at higher pH values while others have found reduced sorption. Liu et al.²⁰⁸ observed a positive correlation between biochar pH and atrazine sorption capacity for a range of biochars, although this may not be directly applicable to the effects of solution pH on any one of the biochars tested. Wang et al.²⁰² observed decreased sorption of atrazine to wheat straw biochar at low solution pH due to repulsion between the positively charged atrazine molecules and biochar surface. Zhao et al.²²⁷ also observed decreasing sorption with increasing pH for corn straw biochar, which was attributed to H^+ ions on the surface of the biochar being able to form hydrogen bonds with the

atrazine molecule at low pH values, suggesting that atrazine more readily forms hydrogen bonds as an H^+ acceptor than as a H^+ donor. In contrast, Zhang et al.²⁰⁴ observed little change in sorption to sewage sludge biochars when the pH values were adjusted to values greater than 4, and significantly reduced sorption at lower pH values. Reduced sorption at very low pH values is expected, as both the atrazine and the biochar surface would be positively charged, as evidenced in Figure 2-31, resulting in repulsive electrostatic forces. For Zhang et al.²⁰⁴, the small change in sorption above pH 4 suggests that sorption of the neutral form of atrazine is not significantly affected by the surface charge of the biochar. The varying results from these studies suggest that the influence of pH on atrazine sorption depends on other factors, such as the properties of the biochar.

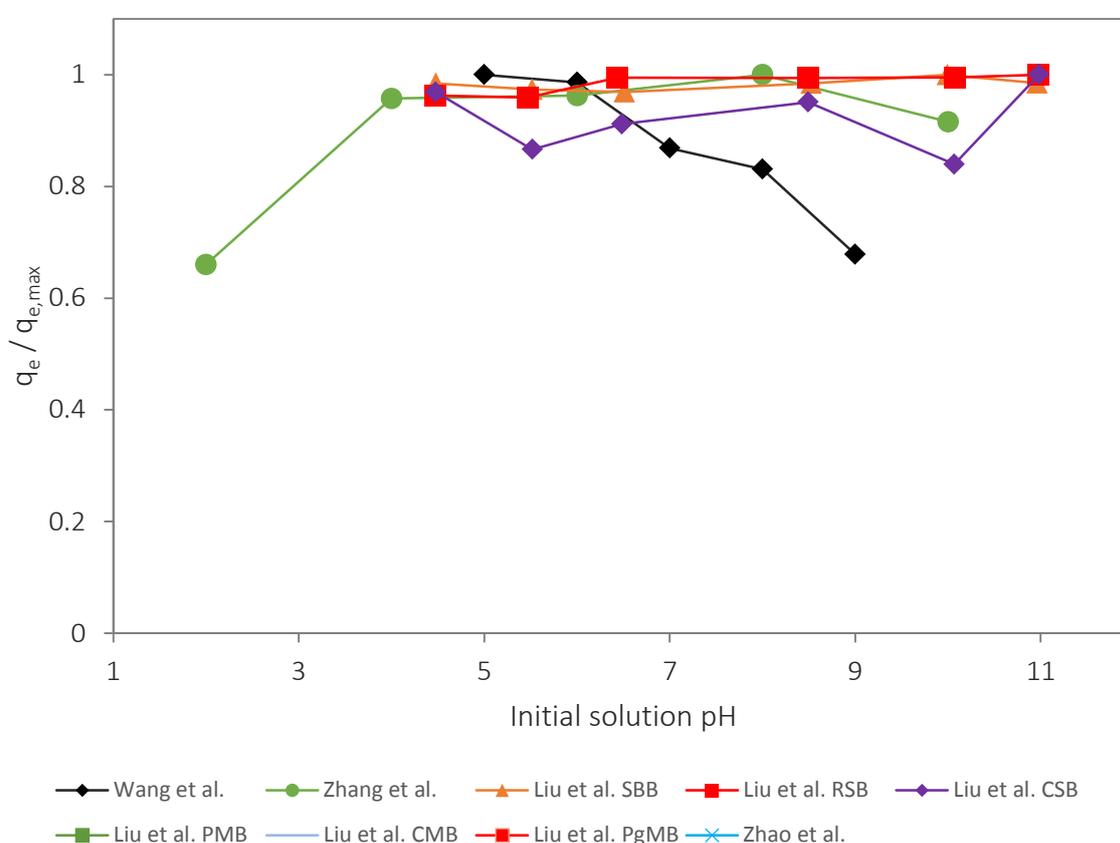


Figure 2-32: Adsorption capacity for atrazine vs. initial pH for a range of biochars (by the author)

It is useful to compare the effects of pH on atrazine sorption over all published studies to date. A combined plot of the adsorbed quantity of atrazine to the biochars (normalised by maximum adsorption capacity) from these studies is given in Figure 2-32, and shows that the effect of solution pH on biochars sorption capacities for biochar varies significantly by biochar. A number, such as pig manure (PgMB) and poultry manure biochars (PMB) used by

Liu et al. ²⁰⁸ show clear increases in the pH range of 5 to 11. Others, such as wheat straw biochar from Wang et al. ²⁰² and corn straw biochar from Zhao et al. ²²⁷ show clear decreases in sorption capacity in the same pH range. Others, such as sewage sludge biochar used by Zhang et al. ²⁰⁴ and corn straw biochar (CSB) used by Liu et al. ²⁰⁸ show intermittent decreases and increases as pH increases, while other biochars show no significant effects with respect to pH. These varying trends suggest that the influence of pH on the sorption of atrazine is dependent on the particular biochar. Selected biochar properties are shown alongside the effect of increased pH on atrazine sorption in Table 2-9. The different pH_{pzc} values of the different biochars suggests that they will each have different net surface charges at any given pH value. A qualitative comparison of the effects of pH on biochars based on their properties will be useful in determining the factors influencing sorption.

Table 2-9: Selected biochar properties and effect of increased pH on sorption of atrazine in previous studies (by the author)

Reference	Feedstock	HTT ^a (°C)	pH_{pzc}	$q_{e,max}$ (mg/g)	Ash (%)	Effect of pH increase on sorption
Wang et al. ²⁰²	Wheat straw	750	8.3	33.5	Not given	Decrease
Zhang et al. ²⁰⁴	Sewage sludge	400	8.2	17.5	Not given	Increase (pH < 4); no effect (pH >4)
Liu et al. ²⁰⁸	Soy beans	450	9.2	1.4	17.69	No effect
	Corn stalk	450	8.7	0.9	15.21	No clear effect ^b
	Rice stalk	450	8.8	1.2	27.12	No effect
	Poultry manure	450	8.3	1.0	37.92	Increase
	Cattle manure	450	8.7	1.1	22.37	No effect
	Pig manure	450	8.6	0.7	42.35	Increase
Zhao et al. ²²⁷	Corn straw	450	6.0	0.9	9.03	Decrease

^a highest treatment temperature during pyrolysis

^b Corn stalk biochar used in Liu et al. shows ranges of increasing and decreasing sorption as a function of pH, however there is not enough evidence to distinguish these from random fluctuations.

The only biochars to show an increase in sorption as pH increases are those derived from sewage or manure, suggesting that a property of these biochars is influencing sorption differently to plant-derived biochars. Manure biochars have the highest ash contents of those reported, as is expected for sludge-derived biochars ¹²². It is therefore possible that the ash component of biochar is influencing the relationship between atrazine and pH. This may be

due to catalytic hydrolysis or complexation of atrazine in the presence of ash minerals, as discussed in Section 2.4.3. Regardless, the combined results of these studies clearly suggest that the presence of ash results in higher removal of atrazine at high pH values.

The reason for decreasing sorption in plant-derived biochars at high pH values is not entirely clear, although may represent changing influences of hydrogen bonding. Decreased sorption was observed to corn straw biochar (ash content of 9%) and wheat straw biochar as pH increased; the ash content of the wheat straw is not given, however other studies investigating wheat straw biochar have reported ash contents of 1.6-2.8%⁷⁶ and 7.8-13.4%⁹⁶. It is therefore likely that the ash content of the wheat straw used by Wang et al.²⁰² is much lower than those of the sludge-derived biochars in Table 2-9. If this were the case, then it may also be possible that biochars with low ash contents observe decreases in sorption as pH increases. This is therefore likely reflective of interactions between the carbonized char structure and the atrazine molecule. As pH increases, the surface of biochar becomes increasingly negatively charged which will reduce the capacity of biochar to donate H⁺ ions, while increasing its capacity for accepting H⁺ ions and donating π -electrons. Decreased sorption with increasing pH may therefore suggest that the combined effects of decreased sorption via hydrogen bonding with atrazine as the H⁺ acceptor outweigh the effects of increased sorption through π - π EDA interactions with atrazine as the π -acceptor and hydrogen bonding with atrazine as the H⁺ donor. This is consistent with computational analysis which suggests that atrazine has five sites which are capable of accepting an H-bond, but only two sites capable of donating an hydrogen bond²³⁸. These results therefore suggest that at high pH values, atrazine has a lesser capacity for forming hydrogen bonds as the H⁺ acceptor, which strongly influences overall sorption.

A schematic summarising the pH ranges at which different effects are the most significant, based on the discussion carried out here, is given in Figure 2-33. The schematic highlights the range of different mechanisms occurring at different pH values. It demonstrates the shift from biochar acting as H⁺ donor at low pH values due to its positively charged surface, and transitioning to an H⁺ acceptor at high pH values due to its negatively charged surface. Similarly, biochar shifts from a prevalence towards π -acceptance at low pH values due to its positive surface charge, and towards π -donor at high pH values due to an abundance of π -electrons. Note that these mechanisms do not necessarily occur exclusively inside these pH ranges; the figure simply indicates that they are promoted within the regions specified. The

exact pH range of each mechanism will also be dependent on the pH_{pzc} of the biochar being used, as this will influence its surface charge at any given pH value. The schematic highlights the wide range of factors that influence the sorption of atrazine to biochar and how the dominant forces can change based on solution pH.

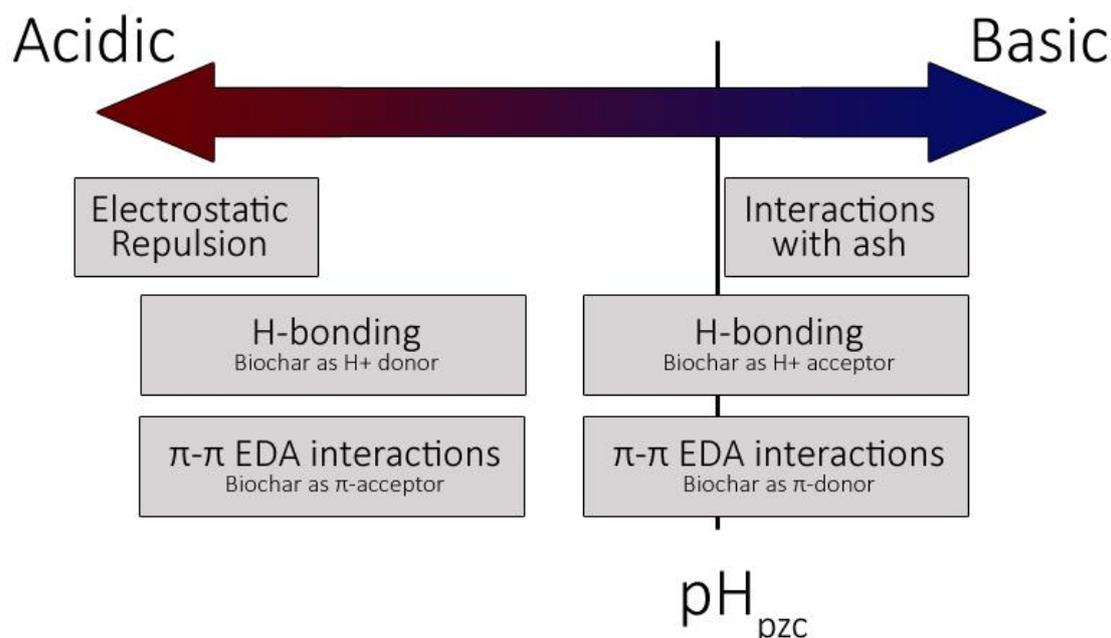


Figure 2-33: Range of pH values at which various mechanisms of atrazine interaction with biochar are promoted (by the author)

2.5.4 Adsorption kinetics of atrazine

The sorption rate and kinetic profile reflect the sorption mechanisms occurring between atrazine and biochar. Different studies have used a wide range of equilibrium times for determining the sorption of atrazine to biochar in batch sorption studies, suggesting that the sorption rate is highly dependent on the biochar properties. The times used are given in Table 2-10, and show equilibrium times varying from 60 minutes to ten days, even amongst studies which conducted kinetic tests. For example, Alam et al.²³⁹ demonstrated 92% removal of atrazine (from initial concentration of 4 mg/L) after 60 minutes to a wood charcoal, while data from Liu et al.²⁰⁸ suggests that equilibrium was not clearly reached to several biochars after 250 hours of mixing. The reasons for such a discrepancy are not clear, and may be influenced by experimental variables such as the magnitude and frequency of shaking, mixing temperature and solid-to-liquid ratio. However, it is unlikely that these factors would play such a significant role (when within reasonable ranges) and the equilibrium times are also likely affected by the sorption mechanisms occurring, and pore filling in particular.

Table 2-10: Equilibrium mixing times used for sorption of atrazine to biochar (by the author)

Reference	Equilibrium time (days)	Kinetic tests
Alam et al. (2000) ²³⁹	60 min	Yes
Soni et al. (2015) ²⁴⁰	0.5	No
Spokas et al. (2009) ²⁴¹	0.5	No
Mandal et al. (2017) ²⁴²	1	Yes
Clay et al. (2016) ²⁴³	1	No
Zheng et al. (2010) ²³⁶	1	Yes
Cheng et al. (2014) ¹¹¹	1	Stated; not shown ^a
Zhang et al. (2013) ¹⁵⁶	1	Stated; not shown ^a
Martin et al. (2012) ²⁴⁴	1	Stated; not shown ^a
Clay and Malo (2012) ¹³⁹	1	No
Zhang et al. (2015) ²⁰⁴	1.5	Yes
Jin et al. (2016) ⁹⁶	2	Stated; not shown ^a
Ren et al. (2016) ¹¹⁶	3 or 7 ^b	No
Wang et al. (2016) ²⁰²	4	Yes
Cao et al. (2009) ²²⁶	4	Stated; not given ^a
Zhou et al. (2016) ¹⁹⁶	7	Stated; not given ^a
Liu et al. (2015) ²⁰⁸	10	Yes
Zhao et al. (2013) ²²⁷	N/A ^c	No ^c

^a equilibrium time is based on preliminary tests, however this data is not provided
^b mixing time is not clear from methodology section
^c data given in referenced paper which is not accessible

Six studies have investigated the kinetic sorption profile of atrazine to biochar. Details of the studies that have carried out kinetic sorption studies are given in Table 2-11. These studies also found a wide range of equilibrium sorption times, ranging from 1 hour to 196 hours. No clear relationships exist between equilibrium sorption time and initial atrazine concentrations, solid-to-liquid ratios, mixing frequencies, pyrolysis temperature, particle size or sorption capacities. Liu et al.²⁰⁸ found relatively consistent equilibrium times of approximately 196 hours for a range of feedstocks, suggesting that feedstock alone is unlikely have such an influence. Zheng et al.²³⁶ investigated the influence of particle size on the kinetics of atrazine sorption to greenwaste biochar, and found that smaller particles reached equilibrium faster and had higher sorption capacities despite similar SSA values. This was attributed to the biochars with smaller particle sizes allowing for increased access to micropore regions. While this may be partially attributable, it does not fully explain the trends observed over multiple studies, suggesting that particle size alone is not the primary influence for such great differences in sorption time. The reason for the different reported equilibrium times is

therefore not entirely clear, however cannot be entirely attributed to feedstock, mixing conditions, initial atrazine concentration or particle size.

The sorption kinetics are also influenced by the sorption mechanisms taking place (which are in turn a function of the biochar properties). An analysis of the reported sorption mechanisms may therefore provide insights into the reasons for particular kinetic profiles. Chen et al.¹⁴⁶ compared the adsorption rates of naphthalene to a temperature series of pine needle biochars and observed slow sorption to medium temperature biochars but fast sorption to low and high temperature biochars. This trend was attributed to a number of simultaneous effects. First, for low temperature biochars partitioning to the organic fraction dominates the sorption, which occurs rapidly. As HTT increases, the biochar becomes less polar and the organic phase becomes more condensed, resulting in reduced access and hydrophobic effects, which slow the partitioning rate. However, for biochars produced at $\text{HTT} > \sim 400^\circ\text{C}$ partitioning is no longer significant, and the pores are further developed, allowing for faster sorption. It is also possible that π - π EDA effects were significant for high-temperature chars, which may also increase the sorption rate. The implications for atrazine suggest that the sorption rate may be controlled by a number of simultaneously occurring effects. Relatively low equilibrium times in studies investigating the sorption of atrazine to fungi (5 hours²⁴⁵), biomass (12 hours²⁴⁶) and soil (24 hours^{247,248}), to which rapid partitioning would be the major mechanism, provide evidence that similar effects may occur for atrazine. However, such discrepancies between seemingly comparable studies as shown in Table 2-11 suggest that it is not trivial to estimate the equilibrium sorption time. It is therefore recommended that kinetic sorption studies are carried out for atrazine in order to determine suitable equilibrium mixing times before carrying out batch equilibrium investigations.

Table 2-11: Equilibrium times and selected parameters for studies investigating the sorption kinetics of atrazine to biochar (by the author)

Reference	Adsorbent	C _i (mg/L)	Solid-liquid ratio (g/L)	Mixing frequency (RPM)	Max Particle size (µm)	q _e (mg/g)	Equilibrium time (hours)
Alam et al. (2000)	Wood charcoal	4	10	150	300	0.37	1
Mandal et al. (2017) ²⁴²	Various biochars at 600°C	1	1	Not given	150	0.5 - 0.9	24
Zheng et al. (2010) ²³⁶	Greenwaste biochar at 450°C	10	10	180	53 – 250	0.6 – 0.9	24 – 120 ^a
Zhang et al. (2015)	Sewage sludge biochar at 400°C	12.5 and 25	1	120	250	8 - 16	36
Wang et al. (2016)	Wheat straw biochar at 750°C	5.8	N/A	70	841	32	80
Liu et al. (2015)	Various biochars at 450°C	5, 10, 15, 25 and 35	10	115	600	0.4 – 3	196

^a Zheng et al. found that sorption equilibrium time was dependent on particle size

2.6 Research gaps and scheme of thesis

This literature review has highlighted a number of knowledge gaps, inconsistencies, and trends that have received little attention to date. While biochar has received increasing attention in recent years¹³⁷, a number of uncertainties still remain around its use as an adsorbent for organic contaminants in soil. The following paragraphs summarise the most significant findings on the use of biochar, the mechanisms through which it adsorbs organic contaminants, and its potential interactions with atrazine.

The production and application of biochar can result in several environmental benefits, and it may also be useful in remediating contaminated soil and groundwater. Biochar promotes the re-use of waste materials, carbon sequestration and improved soil health. Its high surface area, hydrophobicity and varied functionality may aid the immobilisation of heavy metal and organic contaminants in soil.

However, **while the mechanisms through which biochar immobilises organic contaminants have been investigated many times, their roles in long-term remediation outcomes in particular has rarely been addressed.** Studies typically determine the suitability of biochar for use in remediation based on sorption capacity from laboratory studies alone. It is important to further understand the role and behaviour of these mechanisms before biochar is widely used as a soil amendment on contaminated land. This review therefore considered the role of the different mechanisms in determining real-world remediation outcomes.

The partitioning mechanism is often present in significant quantities in batch sorption tests, yet **partitioning to the amorphous phase is likely to have little influence on remediation outcomes** for a given contaminant. This is a combined result of the rapid degradation of the amorphous component in soil, the reversibility of partitioning, and its low contribution to sorption at environmental concentrations. For this reason, it is recommended that partitioning is separated from *adsorption* where possible to more accurately reflect the capacity of a biochar to immobilise contaminants in the soil in the long-term.

Pore filling is likely to be a significant process controlling the mobility of contaminants in the environment for certain contaminants, however is vulnerable to competition with soil organic matter. Pore filling facilitates the efficient movement of organic molecules to

adsorption sites and results in tightly bound contaminants, making them unlikely to be leached into the environment. However, its influence can be reduced by 30-90% in the presence of soil organic matter. Care should therefore be taken when designing biochar for remediation, particularly in soils with high organic contents which may largely negate the benefits of biochar.

While studies often refer to the hydrophobic nature of biochar as a benefit for its remediation capacity, results to date suggest that **hydrogen bonding is likely to be more effective than hydrophobic effects at immobilising contaminants in the long term**. This is due to the strength of hydrogen bonding in retaining adsorbed compounds, while hydrophobic effects are likely to be more reversible. The hydrophobic nature of the biochars surface will oxidise over time due to biotic and abiotic processes, which will promote the presence of hydrogen bonds and reduce available sites for hydrophobic condensation. Contaminants best suited to being immobilised through hydrophobic effects, such as PAHs, are also generally the least mobile and are therefore less suitable for being remediated through sorption. While the presence of hydrogen bonding can be significantly reduced due to competition with water molecules, these results suggest that biochar may be more effective at remediating contaminants which favour hydrogen bonding in the environment.

The role of the ash content has not been thoroughly discussed in previous studies, but may have significant influence over the remediation capacity of a biochar. Its influence on pH (ash generally raises the pH of biochar) can influence contaminant mobility, and its release of minerals can influence contaminant hydrolysis and complexation. The forms of ash, including ionic availability and crystalline form will influence these properties, and are therefore relevant for remediation outcomes. In particular, many biochars which have been shown to be effective adsorbents, such as those produced from manure or rice husk, have ash contents of 30-50% and so this component may interact closely with the carbonised phase and influence remediation outcomes.

Atrazine is a widely used herbicide which contaminates soil and groundwater and may be effectively immobilised by biochar, although the precise mechanisms are not fully understood. Atrazine has been found to contaminate drinking water supplies in the USA, while also exhibiting harmful effects on aquatic life, particularly amphibians. Its effects on human health are not clear. Atrazine is a highly mobile contaminant which may make biochar amendment an effective tool for immobilising it in the environment.

Pore filling is likely to be significant in determining the immobilisation of atrazine.

Studies investigating the sorption of atrazine have shown close relationships between pore availability and sorption capacity, suggesting that pore filling is a key component of its sorption. Further, those which have studied interactions with SOM have shown significant decreases in its sorption when pores are blocked, which is consistent with this outcome. This is also consistent with atrazine's small molecular size, which allows for access to a large amount of pore space.

The relative roles of hydrogen bonding and hydrophobic effects are not clear, and previous papers have shown conflicting evidence for which plays a greater role.

Previous studies have shown that both hydrogen bonding and hydrophobic effects dominate the sorption of atrazine to biochar, however this is not possible due to the different conditions that favour each of the two.

The net effect of environmental pH on the sorption of atrazine is not clear,

which may influence its long-term binding of the contaminant. Studies have shown a range of results for the sorption of atrazine to biochar over a pH range. Different studies have reported increasing sorption with pH, decreasing sorption with pH, and multiple effects over a relevant pH range. The factors influencing these processes are not entirely clear, and are likely to depend on a number of properties of the biochar.

Chemical modification of biochar may be an effective method of elucidating the sorption mechanisms taking place. Modification of biochar using potassium hydroxide or hydrofluoric acid can remove the ash fraction of the biochar, which has been shown to increase sorption in some cases, or to isolate the role of the ash fraction.

This research gaps addressed in this thesis are therefore as follows: (a) determining the relative significance of pore filling and partitioning in the sorption of atrazine to biochar, and their likely roles in the soil profile; (b) determining the relative significance of the different adsorption mechanisms on the sorption of atrazine to biochar, and their likely roles in the soil profile; and (c) determining the influence of pH on biochar sorption, and the contribution of the ash component to this effect. These research gaps form the basis of Chapters 4, 5 and 6 respectively, as outlined in the schematic in Figure 2-34.

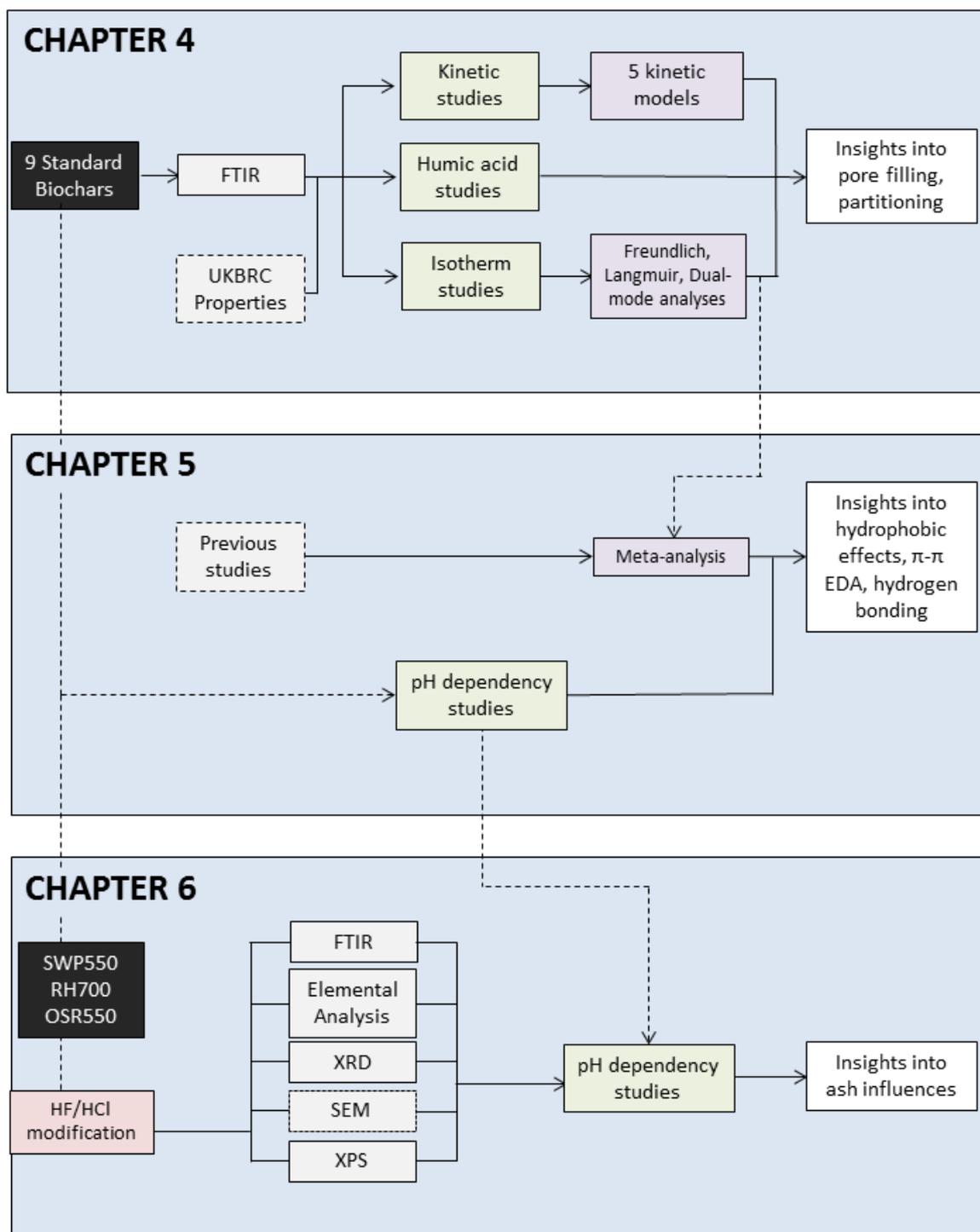


Figure 2-34: Schematic of work carried out for Chapters 4, 5 and 6 of the thesis. Dashed boxes indicate where some or all of the data has been drawn on from previous studies

Chapter 3: Materials and methods

3.1 Materials

3.1.1 Biochars

Nine standard biochars were prepared by collaborators at the UKBRC at the University of Edinburgh^{132,134} to be used in experiments described throughout Chapters 4, 5 and 6 of this thesis. Biochars were produced at 550°C and 700°C from five feedstocks: softwood pellets (SWP), wheat straw pellets (WSP), miscanthus straw pellets (MSP), rice husk (RH) and oil seed rape (OSR). In each case the number used after the feedstock refers to the highest treatment temperature (HTT); for example, *RH700* refers to rice husk biochar produced at 700°C. It was not possible to obtain OSR700, and therefore nine biochars were used in this study: SWP550, SWP700, WSP550, WSP700, MSP550, MSP700, RH550, RH700 and OSR550. The biochars were dried overnight at 80°C, then ground and sieved to a particle size of less than 0.15 mm before further analysis.

UKBRC have characterised many physicochemical properties of the standard biochars, including the C, O, H and N contents, pH and SSA. The properties of the standard biochars as determined by UKBRC are shown in Table 3-1. The biochars' properties vary widely, though all have high pH values (>7.9) and high carbon contents (>47%). Notably, SWP700 has a significantly higher surface area than the others, while the RH biochars have very high ash contents. These properties will influence their sorption characteristics and behaviour in the soil profile.

Biochar ash was obtained to be used in experiments described in Chapter 6 by heating the samples to 800°C in air for four hours, and is referred to throughout this thesis with the suffix '-ash'. For example, *RH700-ash* refers to the ash from rice husk biochar initially produced at 700°C.

Table 3-1: Selected physicochemical properties of the standard biochars as determined by UKBRC. SWP: softwood pellets; WSP: wheat straw pellets; MSP: miscanthus straw pellets; RH: rice husk; OSR: oil seed rape. Suffix refers to highest heating temperature during pyrolysis

		SWP550	SWP700	WSP550	WSP700	MSP550	MSP700	RH550	RH700	OSR550
SSA ^a	m ² /g	26.4	162.3	26.4	23.2	33.6	37.2	20.1	42.0	7.3
pH		7.91	8.44	9.94	10.03	9.77	9.72	9.71	9.81	9.78
Ash	%	1.25	1.89	21.25	23.82	12.15	11.55	47.93	47.93	19.50
C	%	85.52	90.21	68.26	69.04	75.41	79.18	48.69	47.32	68.85
H	%	2.77	1.83	2.10	1.18	2.42	1.26	1.24	0.63	1.82
O ^b	%	10.36	6.02	6.92	5.30	9.24	6.99	2.47	2.06	8.91
N	%	< 0.10	< 0.10	1.39	1.32	0.78	1.03	1.04	0.85	1.59
O:C		0.091	0.050	0.076	0.058	0.091	0.066	0.038	0.033	0.097
H:C		0.39	0.24	0.37	0.20	0.38	0.19	0.28	0.16	0.32

^a BET surface area measured using N₂

^b calculated by difference based on 100% - (C + H + N + ash)

3.1.2 Chemicals and equipment

Calcium chloride hexahydrate (analytical grade), hydrochloric acid (37%), and NaOH (general purpose grade) were purchased from Fisher Scientific. Atrazine (analytical standard) was purchased from Sigma Aldrich. Sodium azide and humic acid (in sodium salt; 45-70% as humic acid) were purchased from Across Organics. Hydrofluoric acid (40%) was purchased from MERCK.

pH was measured using an Accumet AP85 pH meter and calibrated with buffer solutions prior to each use. 1.5mL semi-micro UV-cuvettes were used in the UV-vis spectrophotometer for measuring atrazine concentration.

3.2 Experimental methods and procedures

3.2.1 Biochar modification

Modification of the biochar samples was carried out as described in Chapter 6 in order to alter the physical and chemical properties of the adsorbents. Modification was carried out using a solution containing 1M hydrofluoric acid and 10% hydrochloric acid together (HF/HCl). Approximately 5g of biochar was mixed with 50 mL of solution for 3 hours at room temperature. The samples were first centrifuged at 3000 RPM for 10 minutes, and the liquid phase decanted and replaced with deionised water. This centrifuge process was

repeated for a total of three times, and then samples were dried overnight at 105°C. Samples were then rinsed with deionised water and vacuum filtered through Whatman Cat 1001 125 11µm filter paper three times, and dried overnight at 105°C and stored for further analysis.

3.2.2 Biochar characterisation

Fourier-transformed infrared spectroscopy

The raw and modified biochars were further analysed using Fourier-transformed infrared (FTIR) spectroscopy as described in Chapters 4 and 5 in order to determine the presence of functional groups. FTIR analysis determines the presence of surface functional groups on a material based on their absorbance (or transmittance) of infrared light at various wavelengths. Note that FTIR results in this thesis are plotted by transmittance, and downwards curve therefore represents an absorbance 'peak'. FTIR analysis was performed on dry samples with a Perkin Elmer Spectrum Two FT-IR Spectrometer in the range 4000 cm⁻¹ to 450 cm⁻¹ at a resolution of 1 cm⁻¹.

pH point of zero charge

The pH point of zero charge (pH_{pzc}) was determined using the pH drift method in the presence of atrazine. pH_{pzc} describes the pH at which the positive and neutral groups on an adsorbent are equal, resulting in net zero charge. 20mL solutions containing 0.05M CaCl₂ and 200 mg/L NaN₃ were prepared at initial pH values of approximately 3, 4, 5, 6, 7, 8, 9 and 10 using 1M HCl and 1M NaOH solutions, and mixed with 0.1 g of biochar for 72 hours. The pH of the final solution was then measured. The pH_{pzc} is the point at which the final pH is equal to the initial pH, as demonstrated in Figure 3-1²⁴⁹.

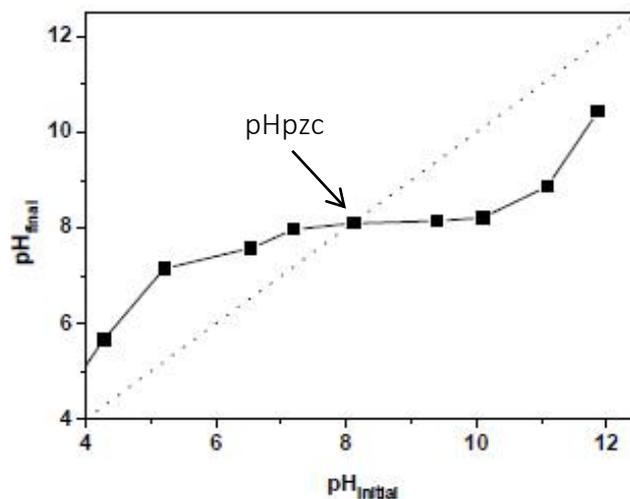


Figure 3-1: Determination of pH point of zero charge using the pH drift method. Figure adapted from Schimmel et al.²⁴⁹

X-ray diffraction

Selected raw and modified biochars were further analysed using x-ray diffraction (XRD) crystallography as described in Chapter 6 in order to determine the crystalline phases in the samples. XRD determines the presence of crystalline components based on their resonance in the presence of X-rays at varying incidence angles. The dry samples were mounted on a flat holder and examined by a Siemens D500 X-ray diffractometer, as shown in Figure 3-2, with a CuK α source operating at 30mA and 40kV, emitting radiation at a wavelength of 1.5405 Å. The scanning was carried out between 2θ values of 10-60 ° at a rate of 0.6 s/step and a step size of 0.03°.



Figure 3-2: Siemens D500 X-ray diffractometer. Reproduced from Shen et al.¹³⁷

Scanning electron microscopy

Selected raw and modified biochars were further analysed using Scanning Electron Microscopy (SEM) as described in Chapter 6 in order to determine their physical structures. SEM uses high powered microscopes to give an image of surface characteristics. The biochar samples were coated with gold, and surface morphologies examined by a Phenom Pro desktop Scanning Electron Microscope at 5 kV, with images being taken at 500, 1,000 and 2,500x magnifications.



Figure 3-3: Equipment used for scanning electron microscopy; (a) Phenom Pro desktop scanning electron microscope; (b) FEI Quanta 200 FEI system. Adapted from Shen et al. (2016)¹³⁷

Elemental and ash compositions

C, H and N fractions were determined using an Exeter Analytical CE-440 Elemental Analyser. Approximately 1.5 mg of sample was weighed into a platinum boat and burnt in pure oxygen at 975°C. The resulting water, carbon dioxide and nitrogen contents were measured using thermal conductivity detectors against known standards. The ash fraction was determined by calculating the proportion of solid-phase sample remaining after heating to 800°C in air for four hours. Oxygen was determined on an ash-free basis using Equation 3-1.

$$O(\%) = 100\% - C(\%) - H(\%) - N(\%) - Ash(\%) \quad 3-1$$

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was carried out on the raw and modified biochars to determine surface Si content and carbon composition, as described in Chapter 6. XPS analyses the surface elemental and functional compositions by measuring the electrons which escape under a focused beam of x-rays. XPS was carried out using an ESCALAB250Xi x-ray photospectrometer, as shown in Figure 3-4, at approximately 13,500V. For each biochar, a survey scan was carried out between 1350 and 0eV at a step interval of 1eV, and a detailed scan of the C1s spectra was carried out between 300 and 281 eV at a step interval of 0.1eV. The survey data was analysed using Avantage analysis software and the C1s data was analysed by fitting a least-squares fit of Gaussian curves after background removal.

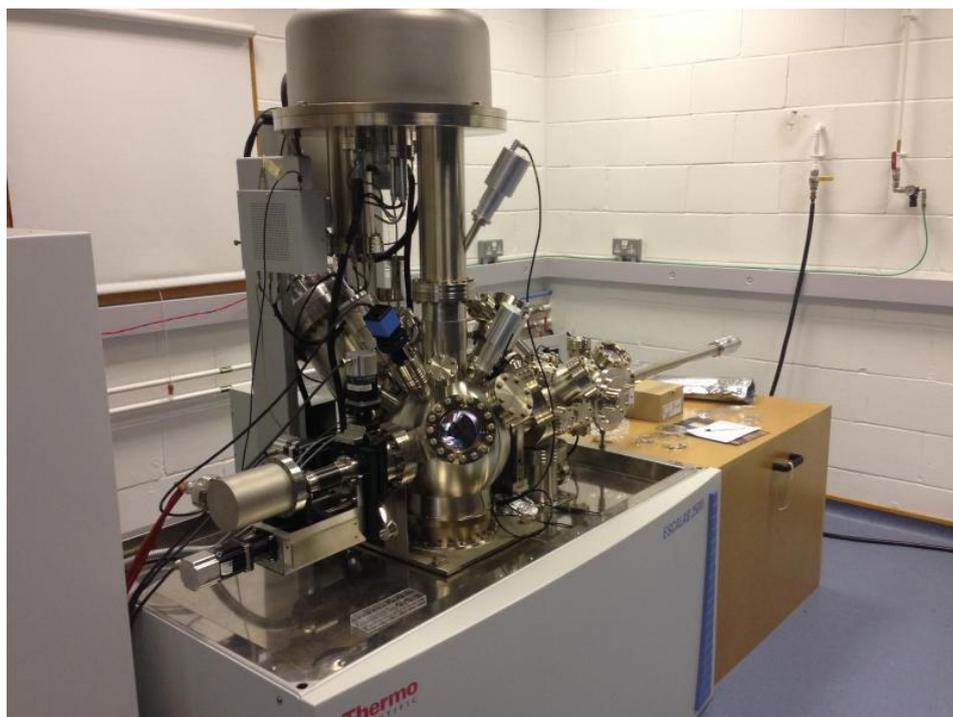


Figure 3-4: Thermo Scientific ESCALAB 250Xi x-ray photospectrometer used for XPS analysis. Photo courtesy Chris Amey

3.2.3 Sorption tests

All sorption tests described in Chapters 4 and 5 were carried out in 30 mL amber glass bottles, in solutions containing 0.05 mol/L CaCl_2 , to maintain constant ionic strength in solution^{250,251} and 200 mg/L NaN_3 , to inhibit microbial activity^{113,252}. Atrazine was spiked as required from a stock solution of 3,000 mg/L in methanol, ensuring that the solution remained < 1% methanol v/v so that co-solvent effects could be neglected^{96,156}. A schematic of the methodology for the kinetic, isotherm, pH-dependency and humic acid studies is given in Figure 3-5, and the purposes of the tests are summarised in Table 3-2.

Solutions were made up immediately prior to beginning the test and measured immediately after removal from the shaker to reduce the influence of sodium azide reacting with atrazine, which can be significant after periods of approximately 14 days²⁵². Blank tests investigating the loss of atrazine through sorption to empty bottles or volatilisation resulted in negligible losses of atrazine. All sorption tests were carried out in duplicate unless stated otherwise and standard deviations are shown on all figures where applicable.

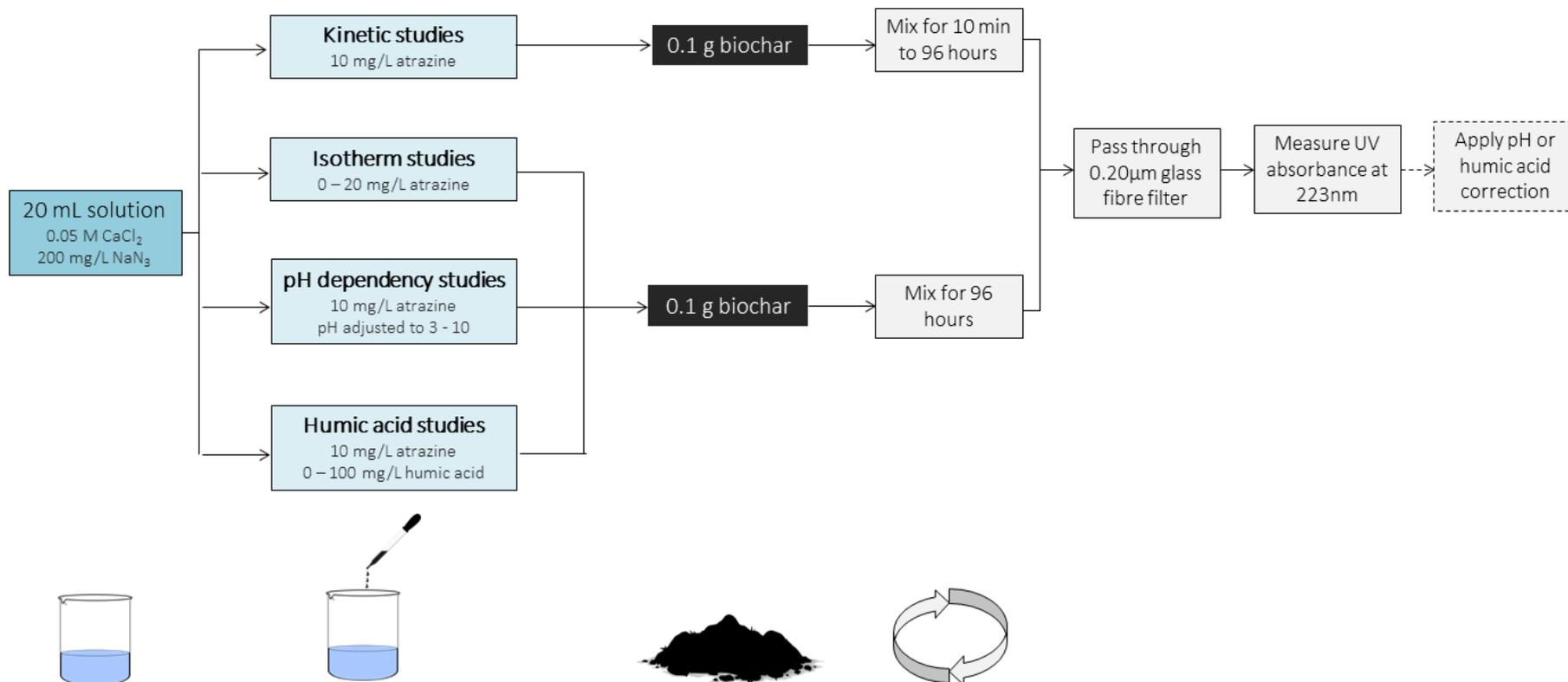


Figure 3-5: Schematic of methodology for kinetic, isotherm, pH-dependency, and humic acid sorption studies

Table 3-2: Summary of batch sorption tests carried out and their purposes

Test	Description	Models	Insights
Kinetic	Sorption profile of atrazine to biochar samples over time	<ul style="list-style-type: none"> • Pseudo-first order • Pseudo-second order • Elovich • Film diffusion • Intraparticle diffusion 	<ul style="list-style-type: none"> • Determination of sorption rate • Determination of intraparticle diffusion influence • Determination of total chemical sorption
Isotherm	Sorption of atrazine at equilibrium under increasing aqueous concentration	<ul style="list-style-type: none"> • Freundlich • Langmuir • Dual-mode 	<ul style="list-style-type: none"> • Determination of sorption capacity • Determination of sorption linearity • Determination of partitioning extent • Determining of total adsorption
Humic acid	Sorption of atrazine under increasing humic acid concentration	N/A	<ul style="list-style-type: none"> • Determination of extent of pore filling • Insights into efficiency of micropore structure
pH-dependency	Sorption of atrazine under changing solution pH	N/A	<ul style="list-style-type: none"> • Determination of pH_{pzc} • Determination of extents of hydrogen bonding, π-π interactions and electrostatic repulsion

Kinetic sorption studies

Adsorption kinetics were analysed as described in Chapter 4 for the nine standard biochars. Solutions containing 10 mg/L atrazine were prepared and mixed with approximately 0.1 g of biochar for between 10 minutes and 100 hours. Based on the results of the kinetic studies, equilibrium was assumed to have been reached after 96 hours of mixing for further experiments.

Five models were fitted to the data in order to compare their respective fits: pseudo-first order model, pseudo-second order model, Elovich, intraparticle diffusion, and film diffusion. The assumptions of each of these models were described previously in Section 2.4.1. The equations for these models are given in Table 3-3, where q_t represents sorption at time, t ; q_e represents sorption at equilibrium; and k_1 , k_2 , α , β , k_i and C_i are fitting parameters of the respective models. The film diffusion model consists of plotting the Boyd Number, B_t , against time, t .

Table 3-3: Models and equations fitted to kinetic sorption data

Model	Equation
Pseudo-first order	$q_t = q_e[1 - e^{-k_1 t}]$
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$
Elovich	$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$
Intraparticle diffusion	$q_t = k_{id} \sqrt{t} + C_i$
Film diffusion	$B_t = -\ln\left(1 - \frac{q_t}{q_e}\right) - 0.4977$

Intraparticle diffusion plots were generated by fitting a two-step linear model to a plot of q_t vs. \sqrt{t} . The first step describes the initial rapid chemical sorption phase, while the second step describes the slower, intraparticle diffusion phase. The two lines were fitted by minimising the squares of the errors between the observed values and the fitted model.

Boyd plots were generated for the film diffusion model by fitting B_t , as calculated using the equation in Table 3-3, against t . 95% confidence intervals for the y-intercept were determined using the ANOVA regression analysis package in Excel.

Isotherm studies

Isotherms were determined for the nine standard biochars as described in Chapter 4. Ten data points were obtained by preparing 20 mL solutions containing between 0 and 20 mg/L atrazine and mixed with approximately 0.1 g of biochar for 96 hours. For RH biochars, the sorption was too high to accurately measure atrazine concentration, and therefore approximately 0.025g of biochar was added.

Two linearised models were fitted to the isotherm data in order to compare their respective fits: Freundlich and Langmuir. These two models are commonly used to model the profile of sorption isotherms and were described previously in Section 2.4.1. The equations for these models are given in Table 3-4, where q_e represents adsorbed equilibrium concentration; C_e represents aqueous equilibrium concentration; K_F and $1/n$ represent the fitting parameters for the Freundlich model; and Q_{max} and b represent the fitting parameters for the Langmuir model.

Table 3-4: Models and equations fitted to isotherm data

Model	Equation	Linearised equation
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$
Langmuir	$q_e = \frac{Q_{max} b C_e}{1 + b C_e}$	$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max} b} \frac{1}{C_e}$

The fitting parameters of the Freundlich model were determined by plotting $\ln(q_e)$ vs. $\ln(C_e)$ and determining the linear line of best fit. K_F and $1/n$ were then determined using equations 3-2 and 3-3 respectively, where c represents the y-intercept, and m represents the gradient of the line of best fit.

$$K_F = e^c \quad 3-2$$

$$\frac{1}{n} = e^m \quad 3-3$$

The fitting parameters of the Langmuir model were determined by plotting $1/q_e$ vs. $1/C_e$ and determining the linear line of best fit. Q_{max} and b were then determined using equations 3-4 and 3-5 respectively, where c represents the y-intercept, and m represents the gradient of the line of best fit.

$$Q_{max} = \frac{1}{c} \quad 3-4$$

$$b = \frac{1}{Q_{max} \cdot m} \quad 3-5$$

The dual-mode sorption model was also used to analyse isotherms. The dual-mode sorption model assumes that the isotherm can be separated into a linear partitioning and a non-linear adsorption component. The dual-mode model may be represented as per Equations 3-6 to 3-8, where: q_e represents the sorbed concentration; q_p represents the partitioned concentration; q_a represents the adsorbed concentration; K_P represents the partitioning coefficient; C_e represents the aqueous concentration; $Q_{a,max}$ represents the Langmuir maximum adsorption capacity; and b_a is the Langmuir fitting coefficient.

$$q_e = q_p + q_a \quad 3-6$$

$$q_p = K_P C_e \quad 3-7$$

$$q_a = \frac{Q_{a,max} b_a C_e}{1 + b_a C_e} \quad 3-8$$

K_P was calculated using the slope of the isotherm at $C_e = 10$ mg/L, and the Langmuir model was fit to the residual q_a values to determine the Langmuir adsorption model coefficients.

pH dependency studies

pH dependent sorption was determined for the nine standard biochars as described in Chapter 5 and for the modified biochars and ash fractions as described in Chapter 6. Eight data points were obtained by preparing 20 mL solutions containing 10 mg/L atrazine with pH values of between 3 and 10 using 1M HCl and 1M NaOH solutions. pH was measured before and after mixing in order to determine the influence of the buffering effect of the biochar. Samples were shaken for 96 hours before further analysis. Blank solutions with no biochar showed no significant losses or measurable degradation over the entire pH range tested. pH dependency

sorption profiles of atrazine sorption to RH700-HF and OSR550-ash were determined using one sample for each data point due to limited availability of the adsorbents.

Humic acid studies

The sorption of atrazine in the presence of humic acid was determined as described in Chapter 4. 20 mL solutions containing 10 mg/L atrazine were prepared. Humic acid was also added in concentrations of 0 to 100 mg/L. Samples were then shaken for 96 hours before further analysis. In order to provide a fixed comparison, the estimated sorption capacity of the standard biochars in the presence of 75 mg/L humic acid was determined based in interpolating the sorption capacities of the two most similar measurements.

3.2.4 Atrazine analysis

Sample preparation

After shaking, samples were filtered through a Thermo Scientific Chromacol 0.20 μm glass fibre filter before analysis with UV-vis photo spectroscopy. Preliminary investigations showed that approximately 10% of atrazine can be removed by the filter, although this reduction was negligible after three passes through the filter. Each solution was therefore filtered three times back into itself before the sample was taken in order to equilibrate the filter.

Measurement of atrazine concentration in unaltered pH solutions

Atrazine concentration was measured using Perkin Elmer Lambda 35 UV-vis spectrophotometer. Preliminary investigations showed that maximum atrazine adsorption occurs at 223 nm, based on the peak of its spectrum as observed in Figure 3-6. The calibration curve was therefore determined based on the relationship between atrazine concentration and the absorbance of UV light at 223 nm, as given in Figure 3-7. The calibration showed a good linear fit ($R^2 = 0.9977$) and was checked periodically to ensure it remained accurate over time. The limit of detection (LOD) was calculated as 0.1 mg/L, and therefore readings below this value were not included in modelling and calculation steps.

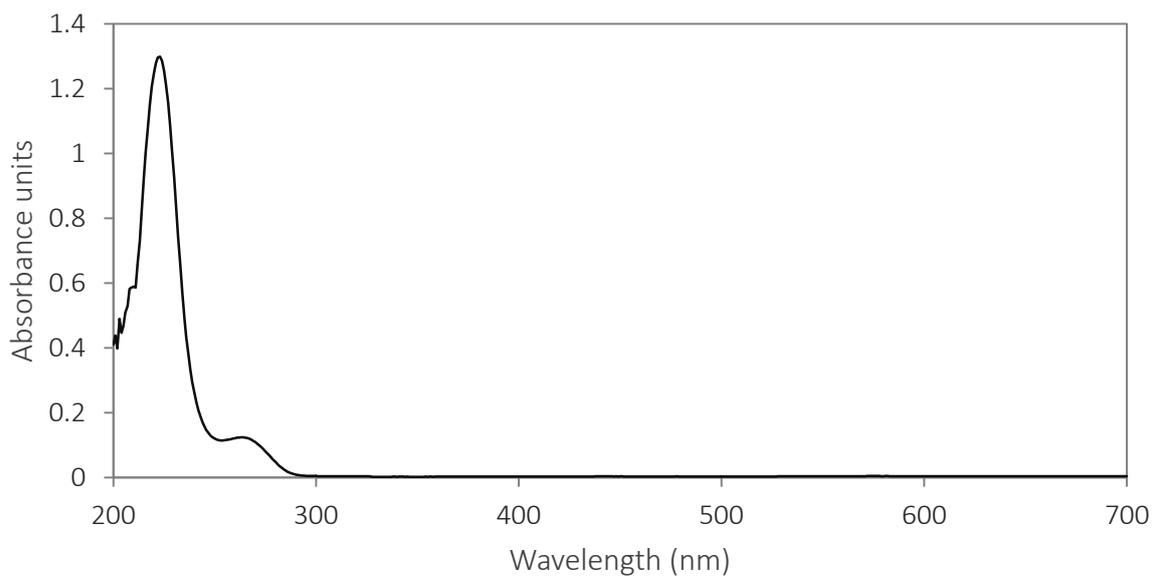


Figure 3-6: UV-vis absorbance spectrum of atrazine at 20 mg/L in solution

The concentration of atrazine adsorbed to biochar, C_s , was calculated using Equation 3-9, where C_i is the initial atrazine concentration in solution, C_{aq} is the final atrazine concentration in solution, V is the solution volume, and m is the mass of the adsorbent.

$$C_s = \frac{(C_i - C_{aq}) \cdot V}{m} \quad 3-9$$

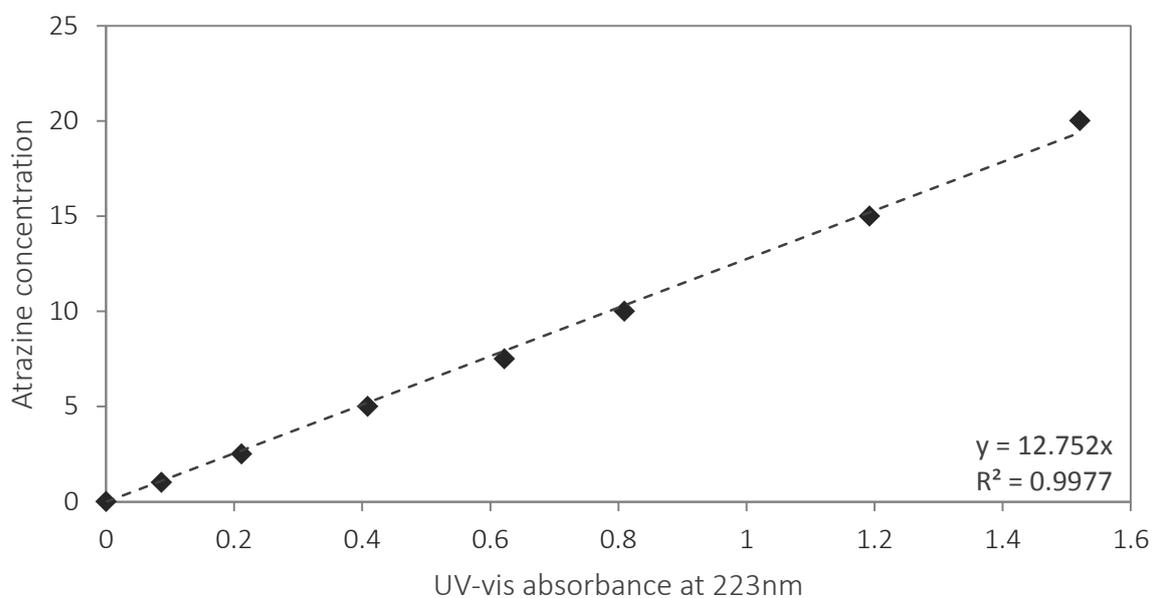


Figure 3-7: Calibration curve for atrazine at 223 nm

Measurement of atrazine in altered pH solutions

Further calibration was necessary in order to accurately measure atrazine at low pH values, as the pH was found to influence absorbance readings at 223 nm. Figure 3-8 shows the change in absorbance of the blank solution from that with no pH adjustment (pH 6.69). Equation 3-10 was fitted to the data ($R^2 = 0.984$) in order to represent the *s*-shaped curve, where Δabs represents the change in absorbance at 223 nm. k_1 , k_2 and k_3 were found to be -0.85, -9.5 and -2 respectively. Measurements with atrazine at 10 ppm showed no significant differences in UV absorption at 223 nm after correcting for discrepancies using the model.

$$\Delta abs = \frac{k_1}{1 + e^{k_2 - k_3 \cdot pH}} \quad 3-10$$

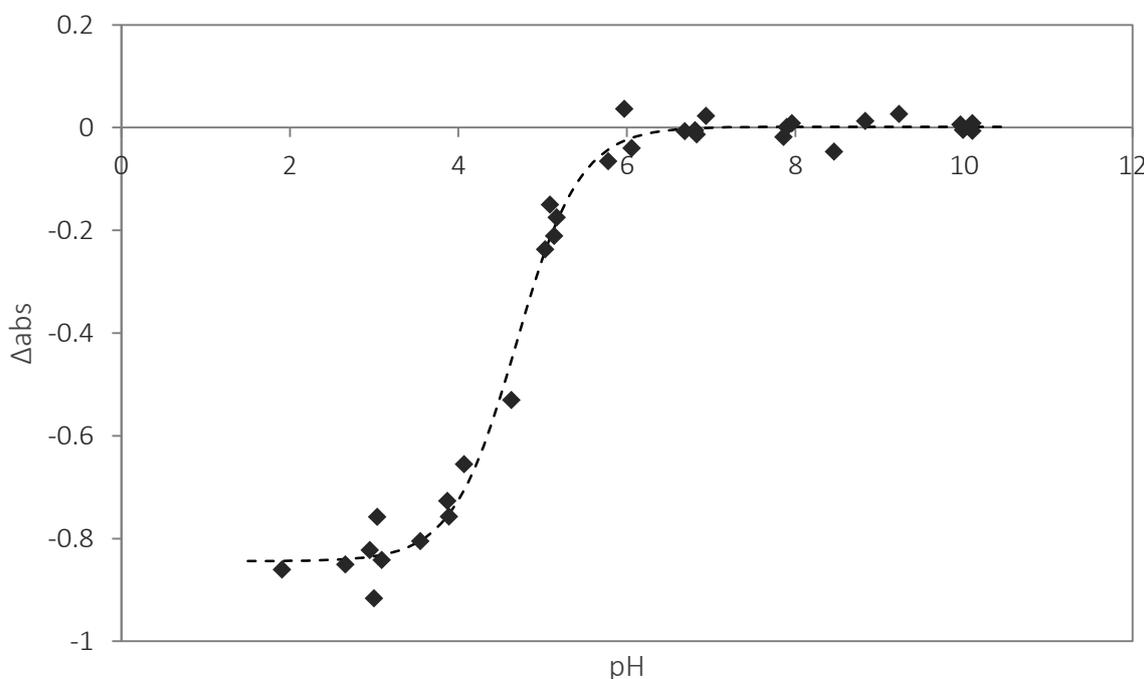


Figure 3-8: Discrepancy in absorbance of $\text{CaCl}_2/\text{NaN}_3$ solution at 223 nm from absorbance with no pH adjustment (pH = 6.8)

Simultaneous measurement of atrazine and humic acid

In order to determine the influence of competitive sorption between atrazine and humic acids (HA) to the biochars, as discussed in Chapter 4, it was necessary to measure the concentrations of both chemicals in solution simultaneously. The absorbance spectra of atrazine and HA are shown in Figure 3-9, and suggests that there is interaction between 200 and 290nm, however only HA shows significant absorbance at wavelengths greater than

290nm. Therefore, the concentration of humic acid was determined at 300nm, and the absorbance at 223nm attributable to the presence of humic acid was subtracted from the spectrum in order to determine the absorbance (and subsequently, concentration) of atrazine at 223nm.

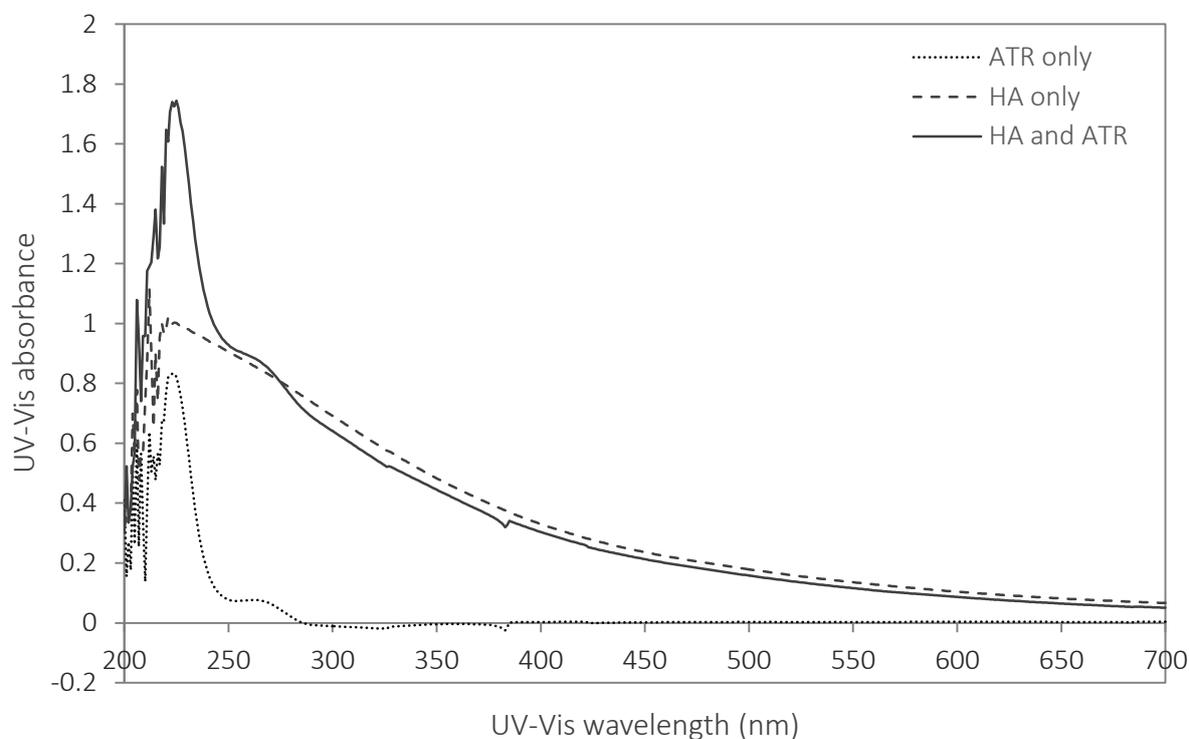


Figure 3-9: UV-Vis spectra of atrazine, humic acid, and atrazine and humic acid together. Atrazine concentration = 10 mg/L; Humic acid concentration = 100 mg/L

This process may be expressed as the Equations 3-11 to 3-13, where: C_{HA} is the concentration of humic acids in the solution; abs_{300} is the measured absorbance at 300nm; $abs_{223,atr}$ is the absorbance at 223nm due to the presence of atrazine; abs_{223} is the measured absorbance at 223nm; C_{atr} is the concentration of atrazine in solution; and k_1 , k_2 , and k_3 are fitting constants. k_1 , k_2 and k_3 were determined by calibration using a range of samples and were found to be 148.33, 102.14 and 12.765 respectively.

$$C_{HA} = k_1 \cdot abs_{300} \quad 3-11$$

$$abs_{223,atr} = abs_{223} - \frac{C_{HA}}{k_2} \quad 3-12$$

$$C_{atr} = k_3 \cdot abs_{223,atr} \quad 3-13$$

Measurement of atrazine after mixing with HF modified biochars

It was not possible to measure atrazine after mixing with HF-modified biochars based on the methods previously described, due to interference from dissolved compounds. In order to measure the atrazine peak, the background concentration of dissolved ions from a blank solution was therefore subtracted from the measured peak prior to the calculation of atrazine concentration.

3.3 Regression and meta-analyses

A meta-analysis of previous studies investigating the sorption of atrazine was carried out as described in Chapter 5 by compiling all accessible published studies investigating the sorption of atrazine to biochar. The atomic compositions of C, H, O and N were recorded, as well as the SSA values. Elemental H:C and O:C ratios were then calculated. Sorption capacity was determined at an aqueous concentration of 2.5 mg/L based on the reported Freundlich isotherm parameters. Studies which did not investigate sorption up to 2.5mg/L, did not investigate isotherms of atrazine to raw biochar, or which contained values significantly different to other studies were discarded.

Chapter 4: Partitioning and intraparticle transport of atrazine to standard biochars

Partitioning and intraparticle diffusion are two important processes for describing the interactions of atrazine with biochar, as they will both have significant implications for the effectiveness of the adsorbents as remediation tools. As outlined in Chapter 2, partitioning represents the component of sorption which does not translate to realistic remediation outcomes, yet can contribute significantly to overall sorption. It is therefore important to understand its role in order to gain a true understanding of the effectiveness of a given biochar. Similarly, pore filling does not necessarily directly translate to remediation outcomes but is an important process in allowing strong adsorption to occur. Its role is therefore an important factor in determining the suitability of a biochar for use in remediation. Chapter 4 therefore discusses the characterisation of the standard biochar samples and the results of various batch sorption tests to determine the extent of these sorption processes. It then discusses the implications of these results for using biochar to remediate atrazine and other organic contaminants in the soil profile. Preliminary results described in this chapter were presented in McMillan et al. (2016)²⁵³.

First, FTIR analysis is carried out on the nine standard biochar samples, which complements further characterisation by UKBRC¹²⁶ and allows for a determination of the functional groups that are present in each sample. Batch sorption tests are then carried out in order to investigate the kinetic profiles, interactions with humic acids and isotherms of the nine standard biochar samples, allowing for determination of the mechanisms controlling the distribution of atrazine molecules within biochar particles. The combined results from these studies provide novel insights into the roles of partitioning and pore filling, which allows for accurate determinations of adsorption mechanisms as described in Chapters 5 and 6. An understanding of these processes therefore allows for the effective design of a biochar for immobilising atrazine in the environment.

4.1 Biochar characterisation

The properties of biochar samples provide insights into potential sorption characteristics and mechanisms and are important factors controlling the sorption of organic compounds. The standard biochars have been partially characterised by UKBRC¹²⁶ and this data was presented previously in Table 3-1. Further characterisation was carried out for Chapter 4 of

this thesis in order to determine the functionalities and surface structures of the adsorbents. This section details the outcomes of FTIR tests, and combines the data with that provided by UKBRC to give insights into the physicochemical properties of the standard biochars.

4.1.1 FTIR analysis of standard biochars

Fourier-transformed infrared (FTIR) spectroscopy analysis investigates the presence of functional groups in a material based on their transmittance of infrared light at various wavelengths. FTIR analysis was carried out on the nine standard biochars and the spectra are shown in Figure 4-1 to Figure 4-5. No biochars showed any peaks or trends at wave numbers greater than approximately 2000 cm^{-1} and therefore the spectra are presented only for the range 2500 to 400 cm^{-1} in order to more clearly show this region. The FTIR results suggest that the feedstock and pyrolysis temperature each have a significant effect on the chemical and functional composition of the biochars. All biochars showed aromatic C=C groups, confirming the aromatic nature of the biochars, while a number showed a significant ash component in the form of SiO_2 . Softwood biochars showed different functionalities to other biochars due to the absence of a significant ash content, while the ash and oxygen components of biochar produced from oil seed rape may exist in different forms to other biochars investigated in this study.

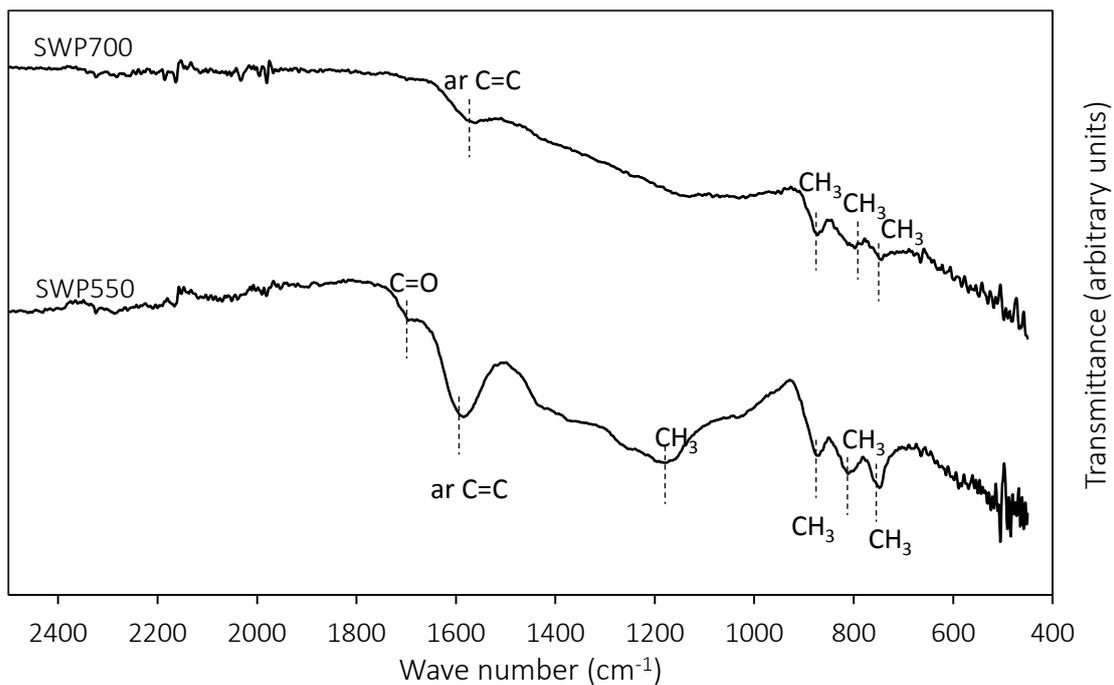


Figure 4-1: FTIR spectra of SWP550 and SWP700 biochars

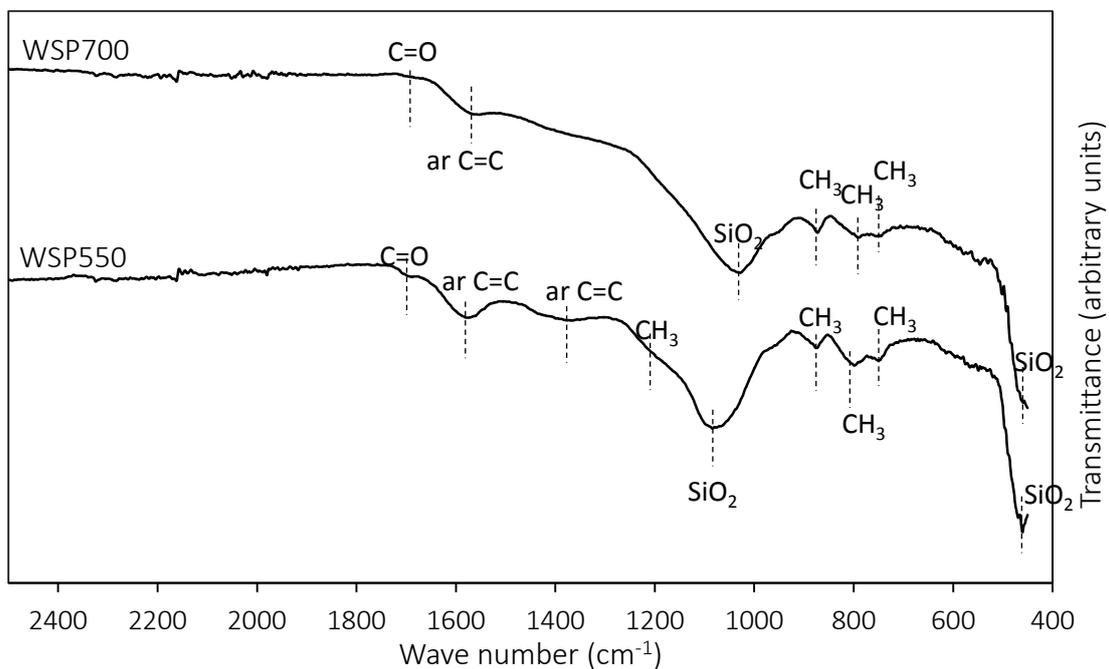


Figure 4-2: FTIR spectra of WSP550 and WSP700 biochars

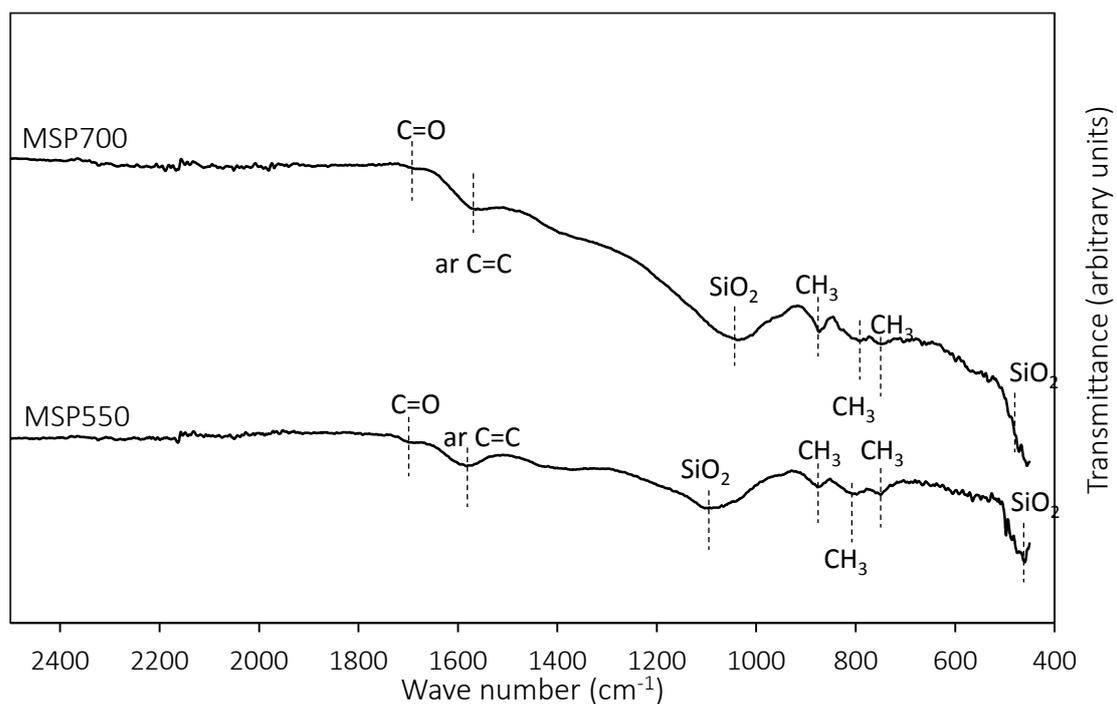


Figure 4-3: FTIR spectra of MSP550 and MSP700 biochars

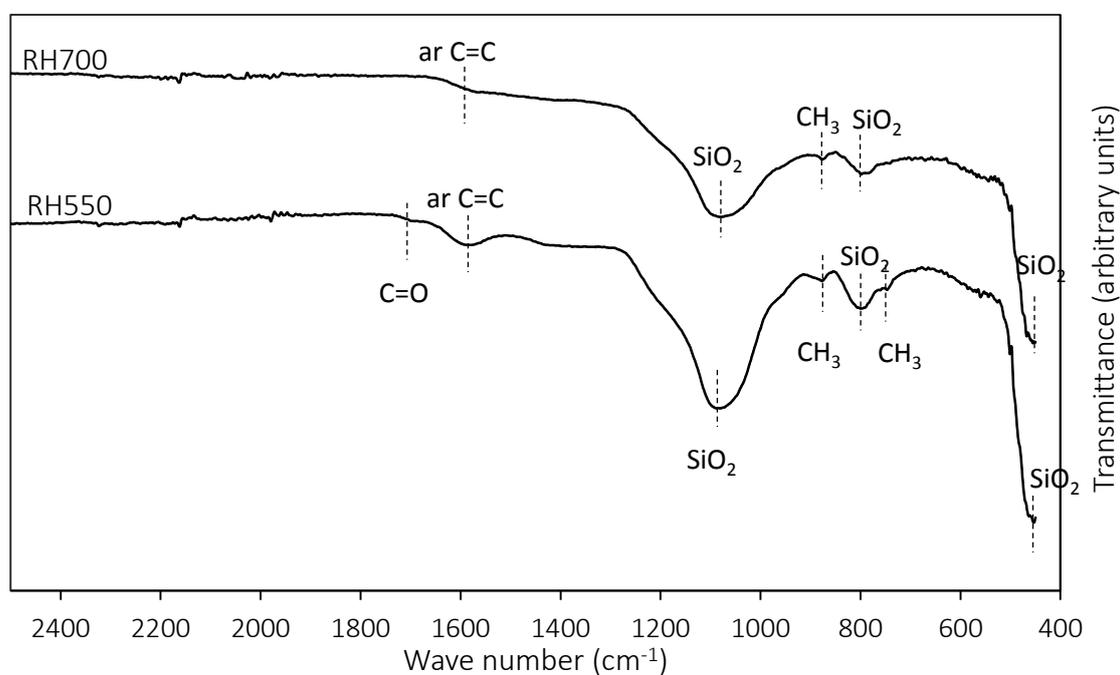


Figure 4-4: FTIR spectra of RH550 and RH700 biochars

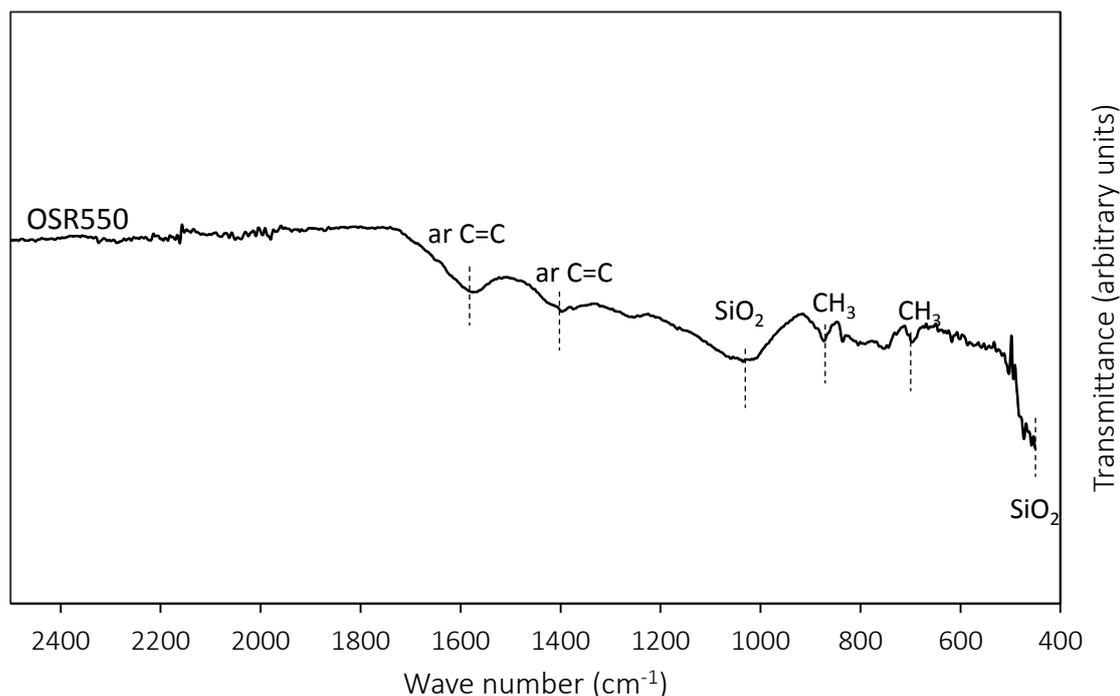


Figure 4-5: FTIR spectrum of OSR550 biochar

The FTIR spectra confirm the aromatic nature of the biochars. All standard biochars show a characteristic aromatic C=C peak at approximately 1590 cm^{-1} , as well as out of plane aromatic $-\text{CH}_3$ bending peaks at 880 , 815 and 750 cm^{-1} . This result is consistent with previous FTIR analysis of biochars^{229,254–257}, and with the high carbon contents of the biochars determined by UKBRC (Table 3-1). The absence of aliphatic C-C or $-\text{CH}_2$ functional groups also suggests that the majority of the carbon in the standard biochars exists within the carbonised phase. The aromatic nature of the biochars highlights the important role of the carbonised component in the overall chemical properties of biochar.

The FTIR analysis confirms the presence of ash in rice husk and wheat straw biochars, and suggests that this component is primarily SiO_2 . Biochars produced from rice husk and wheat straw contained a large, clear peak from approximately 920 cm^{-1} to 1250 cm^{-1} , with the maximum absorbance at approximately 1080 cm^{-1} . Together with peaks at approximately 800 cm^{-1} and 450 cm^{-1} , these peaks suggest the presence of Si-O-Si bonds¹⁰³ which correspond to ash in the form of SiO_2 . This result is in line with the proximate analysis of the biochars carried out by UKBRC which showed that these two feedstocks resulted in biochars with the highest ash contents (approximately 41% and 22% for rice husk and wheat straw biochars respectively), the majority of which is likely exist as SiO_2 ^{148,212,258}. MSP and OSR biochars also showed similar peaks, although to a lesser extent, again in line with what is expected

from the ash contents of the different biochars (approximately 12% and 19% for MSP and OSR biochars respectively). The much smaller peak at 800 cm^{-1} for OSR550 compared with WSP550, despite similar ash contents, suggests that the ash of OSR550 may contain significant components of other minerals. Sattar et al.²⁵⁹ produced biochar from rapeseed via steam gasification and found high mineral contents of Ca and K, suggesting that these may form a significant part of the ash of OSR550. SWP biochars showed no evidence of SiO_2 , which would be expected from their ash contents of approximately 1.5-2%. These three peaks provide clear evidence for the presence of SiO_2 in WSP, MSP, RH and OSR biochars; however can also obscure the presence of other functional groups appearing between approximately 900 cm^{-1} and 1250 cm^{-1} .

Several biochars contained peaks corresponding to oxygen-containing functional groups, although not all biochars showed evidence of these groups. SWP550, WSP550, WSP700, MSP550, MSP700 and RH550 each have a small peak at approximately 1700 cm^{-1} , which is most likely due to C=O bonds, either as part of carbonyl groups^{257,260-262} or lactone groups^{102,263}. In SWP and RH biochars, this peak is no longer present in the higher temperature biochar, confirming previous results that these groups are removed at higher pyrolysis temperatures^{98,257}. Notably, although no other oxygen-containing functional groups are apparent from the FTIR spectra, the presence of this group does not directly relate to the oxygen contents of the biochars. For example, OSR550 has the highest polarity of all of the standard biochars tested (O:C = 0.097) and does not exhibit these carboxyl peaks, while WSP700 (O:C = 0.058) and RH550 (O:C = 0.038) have much lower polarity yet do exhibit them. This suggests that the oxygen groups in OSR550 are either: (a) not clearly identifiable by FTIR, e.g. aliphatic C-O groups at approximately 1050 cm^{-1} would be difficult to distinguish from the nearby peak corresponding to SiO_2 ; or (b) are contained within the internal structure of the biochar, resulting in a high bulk oxygen content but low surface functionality. Angin et al.²⁶⁴ characterised biochar from rapeseed at various temperatures and found that C-O groups were removed at approximately $500\text{ }^\circ\text{C}$, suggesting that the latter option is more likely to be true. Therefore, although the elemental analysis shows that the bulk polarity of OSR550 is relatively high, the oxygen groups may have a relatively small role in its sorption mechanisms. Conversely, the ketone groups may play a role in the sorption of compounds to SWP, WSP and MSP biochars, despite lower bulk oxygen contents.

None of the biochars analysed showed evidence of –OH functional groups, which normally appear as a broad peak at approximately 3500 to 3200 cm^{-1} ^{229,265,266} (range not shown). The absence of this peak suggests that the majority of these groups are removed at temperatures lower than 550 °C for the feedstocks tested. The removal of –OH groups has been demonstrated to occur between 350 and 500 °C for cottonseed hull ²⁶⁰, and between 500 and 600 °C for pine needles ¹⁰², while a thermal gravimetric analysis (TGA) of oil seed rape ²⁶⁷ showed significant weight loss between 300 and 350 °C, suggesting this is where most of the volatiles are removed. It should also be noted that some biochars in previous studies have shown an increase in –OH groups with increasing pyrolysis temperature ^{265,266} – this is most likely due to the introduction of trace oxygen into the pyrolysis process, which may cause partial oxidation of the biochar. This is unlikely to have occurred for the standard biochars due to the careful control exhibited over the pyrolysis conditions. The absence of –OH groups is significant for the sorption properties of an adsorbent because these are the groups most readily able to form hydrogen bonds ^{186,201}. Carbonyl and ketone groups may participate in hydrogen bonding, however the exclusive presence of these groups suggests that the biochars in this study will only be able to act as H-acceptor compounds, and will therefore only readily form hydrogen bonds with H-donor molecules. While atrazine can readily form hydrogen bonds, as discussed in Chapter 2, computational analysis ^{196,238} suggests that it has a greater number of sites which can accept a hydrogen bond. Therefore it can be expected that its sorption capacity will be decreased to the standard biochars compared to other biochars of comparable surface area and pore volume.

Therefore, the FTIR analysis confirms the functionalised aromatic structure of the biochars, with all displaying clear aromatic C=C peaks, and many displaying C=O ketone groups. FTIR also confirms the significant presence of ash, particularly in the RH and WSP biochars, and that this ash portion exists predominantly as SiO₂. The analysis suggests that the biochars contain little or no –OH groups, most likely as a result of their relatively high production temperatures. The absence of these –OH groups may reduce the capacity for hydrogen bonding with atrazine, which is thought to be one of its major mechanisms of sorption.

4.2 Sorption characteristics of standard biochars

Batch sorption tests are a useful tool for simulating sorption processes in a controlled laboratory environment. Various parameters may be controlled in the laboratory which can provide insights into the behaviour and mechanisms that may occur in the soil profile. Three

tests were carried out for Chapter 4 as set out previously in Table 3-2, which each investigate different characteristics of atrazine sorption to the nine standard biochar samples. First, kinetic sorption tests were carried out to investigate the sorption of atrazine to biochar over time, and the results were interpreted using five different mathematical models. These tests provide information on the sorption rate of atrazine, the ways in which the molecule diffuses onto the surface or into the pore space of the biochars. Next, sorption tests investigating interaction with humic acid molecules allowed for a more in-depth insight into the roles of pore filling, and potential behaviours that can be expected from each adsorbent in the soil profile. Finally, isotherm studies were carried out to determine the relationship between aqueous concentration and adsorbed concentration. Isotherms allow for insights into the sorption efficiency of various biochars, as well as determination of the relative contributions of adsorption and partitioning using the dual-mode sorption model. Together, these tests provide insights into processes controlling the transport of atrazine to adsorption sites in the standard biochar samples.

4.2.1 Kinetic sorption studies

Kinetic studies determine the sorption of a compound over time, and provide insights into the transport of adsorbate molecules to sorption sites and the adsorbent's likely behaviour in the environment. The sorption rate gives an indication of the likely short-term immobilisation that will occur in the soil profile; biochars which can rapidly adsorb atrazine are likely to be more effective in reducing short-term leaching. The kinetic profile also provides insights into the way that the atrazine molecule diffuses onto the biochar surface, and whether film diffusion or intraparticle diffusion is more likely to be the rate-limiting step. Kinetic sorption studies were carried out by mixing each of the nine standard biochars in a 10 mg/L solution of atrazine for up to 96 hours and taking periodic measurements of atrazine concentration. The kinetic profile was modelled using five mathematical equations. First, the suitability of the pseudo-first order, pseudo-second order and Elovich models are discussed, and then the relevance of film diffusion and intraparticle diffusion models are determined.

Pseudo-first order, pseudo-second order and Elovich models

The kinetic sorption profiles for the nine standard biochars are shown in Figure 4-6 to Figure 4-10 together with the fits of the pseudo-first order, pseudo-second order and Elovich models. The fitting parameters for these three models are given in Table 4-1. All biochars showed rapid increases in sorption in the first 30 minutes to 24 hours, before the adsorption rates

slowed and then reached zero or near-zero after 100 hours. This is consistent with a three-phase adsorption process observed by previous studies²⁰⁸, which is attributable to the rapid chemical interactions to macropores, slow diffusion of adsorption sites, and the gradual saturation of adsorption sites over time. However, the saturation of adsorption sites is not clearly observed in most cases. The results show generally poor fits for the pseudo-first order (R^2 values 0.185 - 0.721) and the pseudo-second order (R^2 values 0.399 – 0.821) models, and reasonable fits for the Elovich model (R^2 values 0.692 – 0.924). For all biochars tested the R^2 values followed the order Elovich \geq pseudo-second order $>$ pseudo-first order.

Sorption kinetics may be controlled by a number of processes, including the transport of the adsorbate molecules, film diffusion through boundary layers, intraparticle diffusion and chemisorption²⁶⁸. The pseudo-first order model assumes that the sorption rate is proportional to the difference between sorption capacity and the current adsorbed concentration^{269,270}, and is rarely the best fit for the sorption of organic compounds to carbonized absorbents^{270,271}. The pseudo-second order model is based on theories of surface reactions²⁷² and is closely related to the Langmuir isotherm model^{269,273}. It assumes that the sorption capacity of a compound is driven by an equilibrium state, which is primarily controlled by intraparticle diffusion.

The pseudo-first order and pseudo-second order models showed significantly wide ranges of rate constants (variations of approximately 500x). However, these values are not a fair reflection of the actual sorption rates due to the poor fit of the models. A visual assessment of the kinetic profiles suggests that while there is variation in sorption rates between the biochars, variations of this magnitude are not present. Similarly, the calculated equilibrium sorption capacity values for all of the biochars do not match the experimental data, suggesting that the models are not suitably capturing the kinetic profile. The relatively low R^2 values for these models over all of the biochars investigated also suggest that they are not an accurate representation of the kinetic profile. The pseudo-first order and pseudo-second order models are therefore not considered accurate models in this case, and the rate constants associated with each are not applicable for further analysis.

Table 4-1: Kinetic model fitting parameters for the pseudo-first order, pseudo-second order and Elovich models to the standard biochars

Biochar	Pseudo-first order			Pseudo-second order			Elovich		
	q_e	k_1	R^2	q_e	k_2	R^2	α	β	R^2
SWP550	0.223	0.341	0.616	0.247	1.689	0.657	0.394	25.13	0.727
SWP700	0.255	1.101	0.527	0.266	7.226	0.718	5.015	30.85	0.718
WSP550	1.003	0.649	0.721	1.069	0.836	0.821	4.656	6.619	0.923
WSP700	0.924	0.651	0.677	0.983	0.936	0.789	4.738	7.302	0.924
MSP550	0.663	6.676	0.185	0.698	11.22	0.399	851.9	17.73	0.757
MSP700	0.594	5.302	0.252	0.627	10.07	0.403	241.9	17.84	0.692
RH550	0.915	1.309	0.414	0.968	1.958	0.617	16.59	8.505	0.903
RH700	1.226	1.709	0.320	1.305	1.738	0.522	27.43	6.388	0.842
OSR550	1.376	0.150	0.799	1.510	0.154	0.871	0.973	3.667	0.948

The Elovich model assumes a heterogeneous adsorbent surface, with negligible desorption of adsorbed particles and interactions between adsorbed and aqueous molecules^{261,268}. While initially developed to model the sorption of gases to heterogeneous surfaces, it has been found to accurately represent aqueous sorption to carbonised materials²⁷⁴. The relatively good fits of the Elovich model, together with relatively poor fits of the pseudo-first and -second order models, suggest that a range of sorption sites exist on the biochar samples, and that the atrazine is tightly bound by the biochar and is therefore likely to effectively immobilise atrazine in the environment.

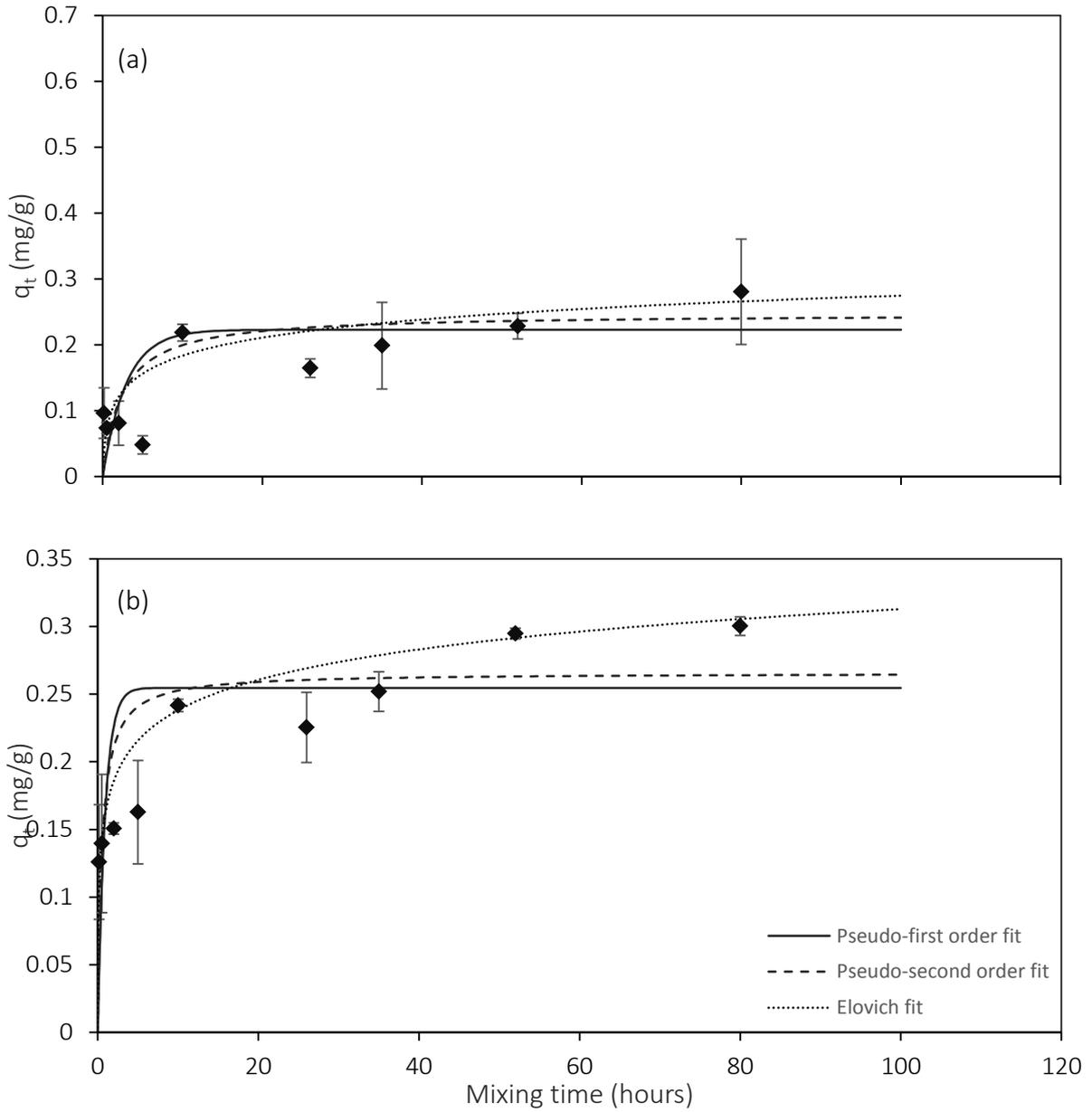


Figure 4-6: Kinetic sorption plots of (a) SWP550 and (b) SWP700 biochars with pseudo-first order, pseudo-second order and Elovich model fits

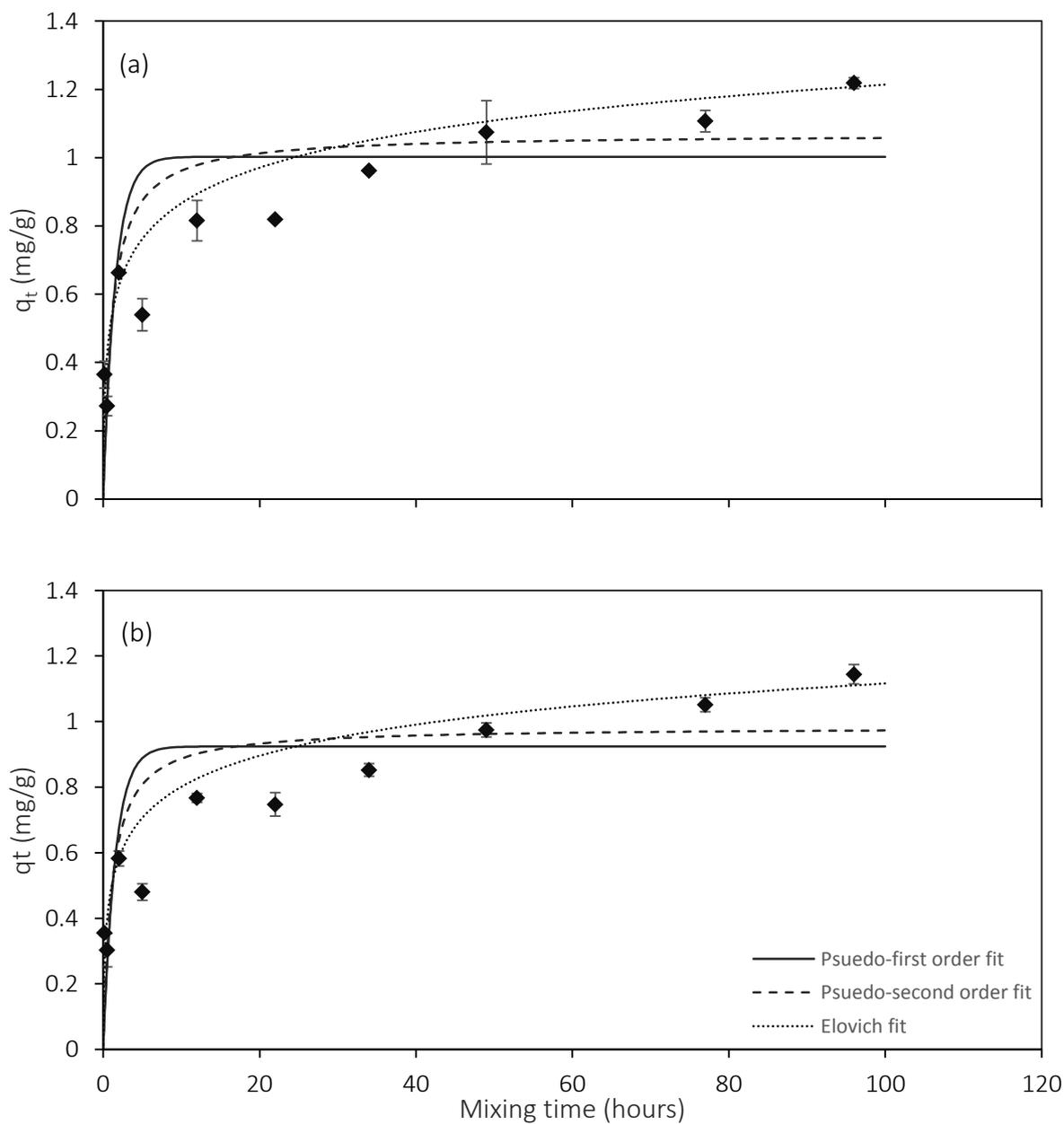


Figure 4-7: Kinetic sorption plots of (a) WSP550 and (b) WSP700 biochars with pseudo-first order, pseudo-second order and Elovich model fits

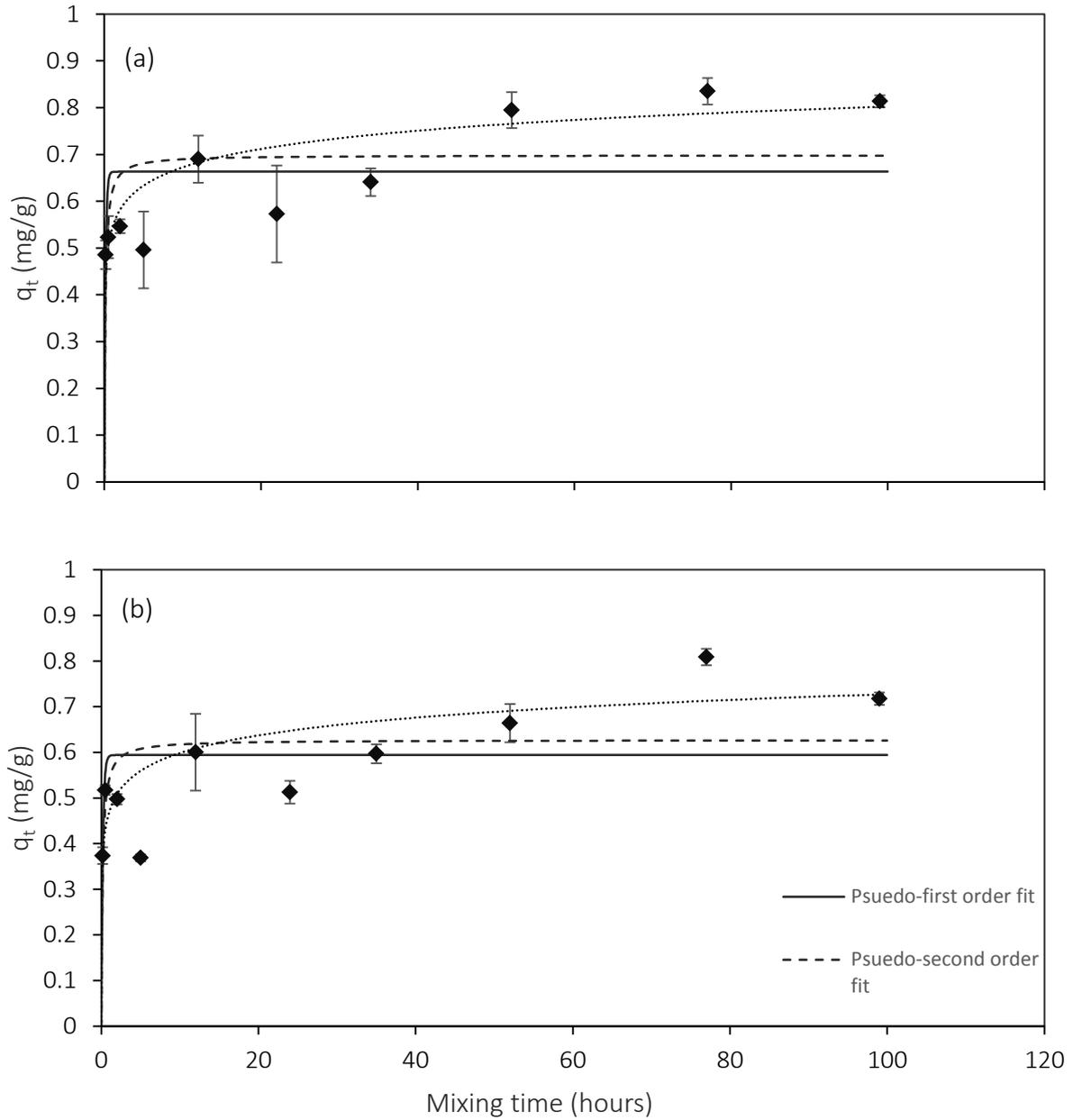


Figure 4-8: Kinetic sorption profiles for (a) MSP550 and (b) MSP700 biochars with pseudo-first order, pseudo-second order and Elovich model fits

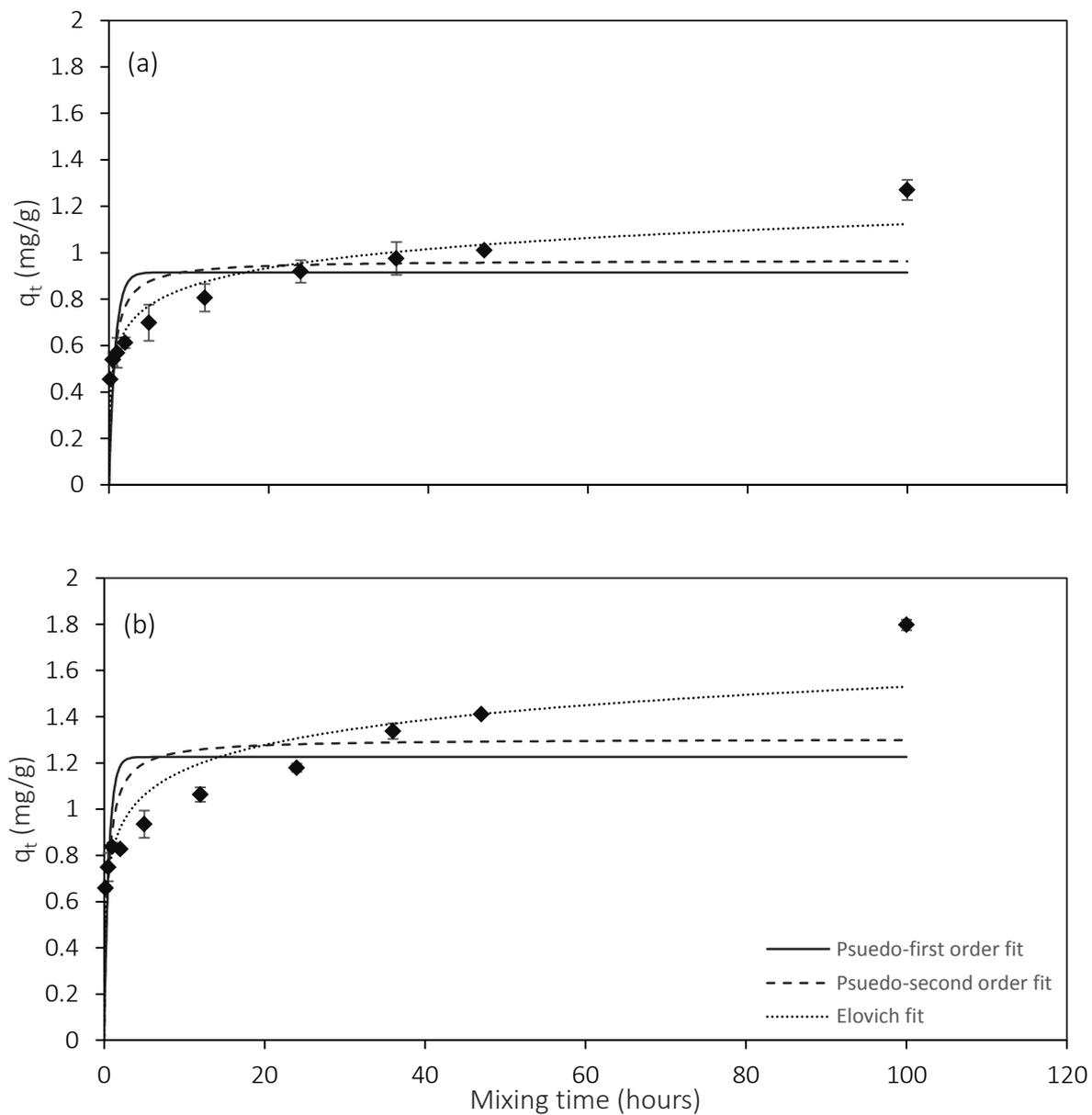


Figure 4-9: Kinetic sorption profiles for (a) RH550 and (b) RH700 biochars with pseudo-first order, pseudo-second order and Elovich model fits

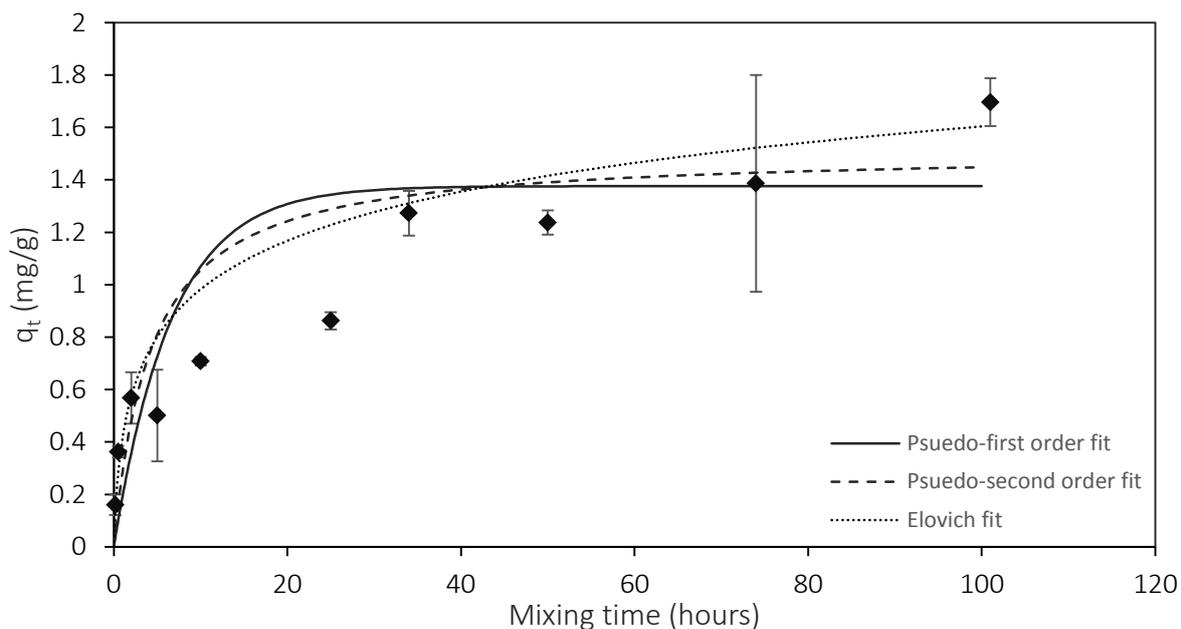


Figure 4-10: Kinetic sorption profile of OSR550 with pseudo-first order, pseudo-second order and Elovich model fits

The kinetic sorption results suggest that while sorption may not have reached completion after 100 hours, the sorption rate slowed enough within this time period (except potentially SWP biochars) for use in equilibrium studies. An equilibrium time should be chosen to fairly reflect the maximum sorption capacity of a given biochar, however should be as small as feasible in order to reduce effects of degradation, which for atrazine in the presence of NaN_3 can be significant after approximately six days²⁵². A short mixing time therefore justifies the assumption that all of the atrazine removal is due to sorption to biochar. For this reason, mixing times of 96 hours will be used in all further tests for all biochars. This time is well within the range of equilibrium values used previously for the sorption of atrazine to biochar (Table 2-10), which shows that previous studies investigating the sorption of atrazine to biochar have found equilibrium times between 30 minutes and 192 hours.

In general, the kinetic sorption plots suggest that the sorption rate of atrazine to the standard biochars is primarily controlled by pore filling, particularly for WSP and RH and OSR biochars. SWP biochars demonstrated that sorption may be controlled by a combination of physical and rapid chemical interactions, while MSP biochars may be more predominantly controlled by rapid chemical in the macroporous regions. The different sorption profiles of each biochar are likely a result of their different chemical and physical properties. The film diffusion and intraparticle diffusion models are better able to distinguish between these effects.

Film diffusion and intraparticle diffusion models

In order to further investigate the influence of intraparticle diffusion, the kinetic sorption data was fitted to film diffusion and intraparticle diffusion models. If sorption rate is controlled by film diffusion, it suggests that interactions at the sorption sites are the rate limiting step. In contrast, if sorption rate is controlled by intraparticle diffusion it suggests that the time taken for atrazine to reach these adsorption sites is the rate limiting step. These two processes are demonstrated in Figure 4-11. The film diffusion model uses Boyd plots^{261,275} to determine the relative influences of film diffusion and intraparticle diffusion. A trend passing through the origin suggests that sorption is controlled by intraparticle diffusion, while deviations from this suggest that film diffusion and intraparticle diffusion are both significant²⁷⁶. The intraparticle diffusion model uses a multi-stage linear model of q_e vs. \sqrt{t} . The graphs are shown fitted with a two-part linear model of best fit, which correspond respectively to the early rapid sorption phase and a slow intraparticle diffusion phase²¹⁹.

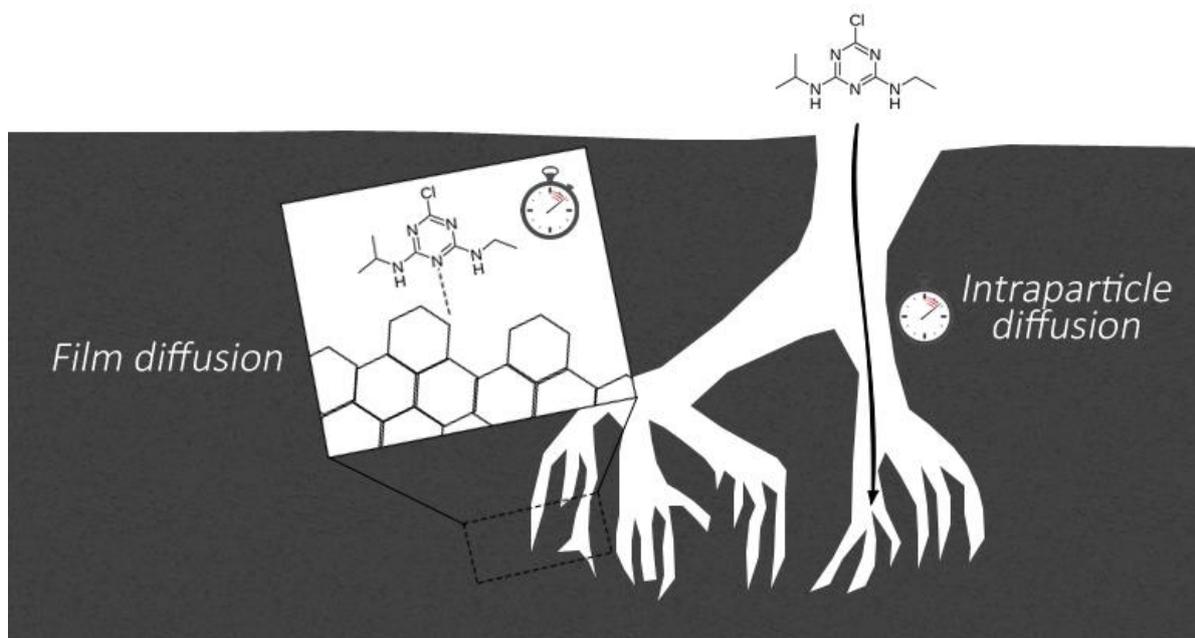


Figure 4-11: Schematic of sorption rate controlled by film diffusion vs. intraparticle diffusion

The Boyd plots for the sorption of atrazine to the standard biochars are shown in Figure 4-12, and the p values and confidence intervals are given in Table 4-2. SWP550, SWP700, MSP700, RH700 and OSR550 have p values less than 0.05, suggesting that the Boyd plot does not pass through zero for these biochars, and film diffusion effects are therefore significant. Conversely, this suggests that for WSP550, WS700, MSP550 and RH550 biochars the regression does pass through the origin, suggesting that intraparticle diffusion is

most important for these biochars. This difference highlights the fact that different processes control the sorption to biochars of different feedstocks. For RH700, the origin is outside of the 95% confidence interval, however a visual assessment of the plot suggests that the linear regression does not fully capture the trend, and it may in fact pass through the origin. Similarly, the confidence interval for MSP550 includes the origin largely because it is very wide due to high variability in the high sorption values. A cluster of values near the y axis that are not at the origin suggests that the linear regression does not fully capture this trend, and that it is unlikely the regression passes through the origin. Therefore, for RH and WSP biochars, the film diffusion model suggests that intraparticle diffusion is a determining factor controlling the diffusion of atrazine, and therefore the sorption is likely driven by sorption to meso- and micropores. In contrast, for SWP, MSP and OSR550 biochars, film diffusion is likely to also play a role, and sorption to the meso- and macropore regions and chemical interactions are both likely to be significant.

Table 4-2: *p* values and 95% confidence intervals for the y-intercept of the Boyd plots. A *p*-value less than 0.05 provides significant evidence against the null hypothesis of the y-intercept being equal to zero

Biochar	p value	Lower 95% CI	Upper 95% CI
SWP550	0.001	-0.420	-0.155
SWP700	0.003	-0.258	-0.081
WSP550	0.587	-0.171	0.279
WSP700	0.796	-0.186	0.234
MSP550	0.058	-0.021	0.894
MSP700	0.033	0.035	0.591
RH550	0.071	-0.011	0.214
RH700	0.040	0.004	0.133
OSR550	0.032	-0.369	-0.022

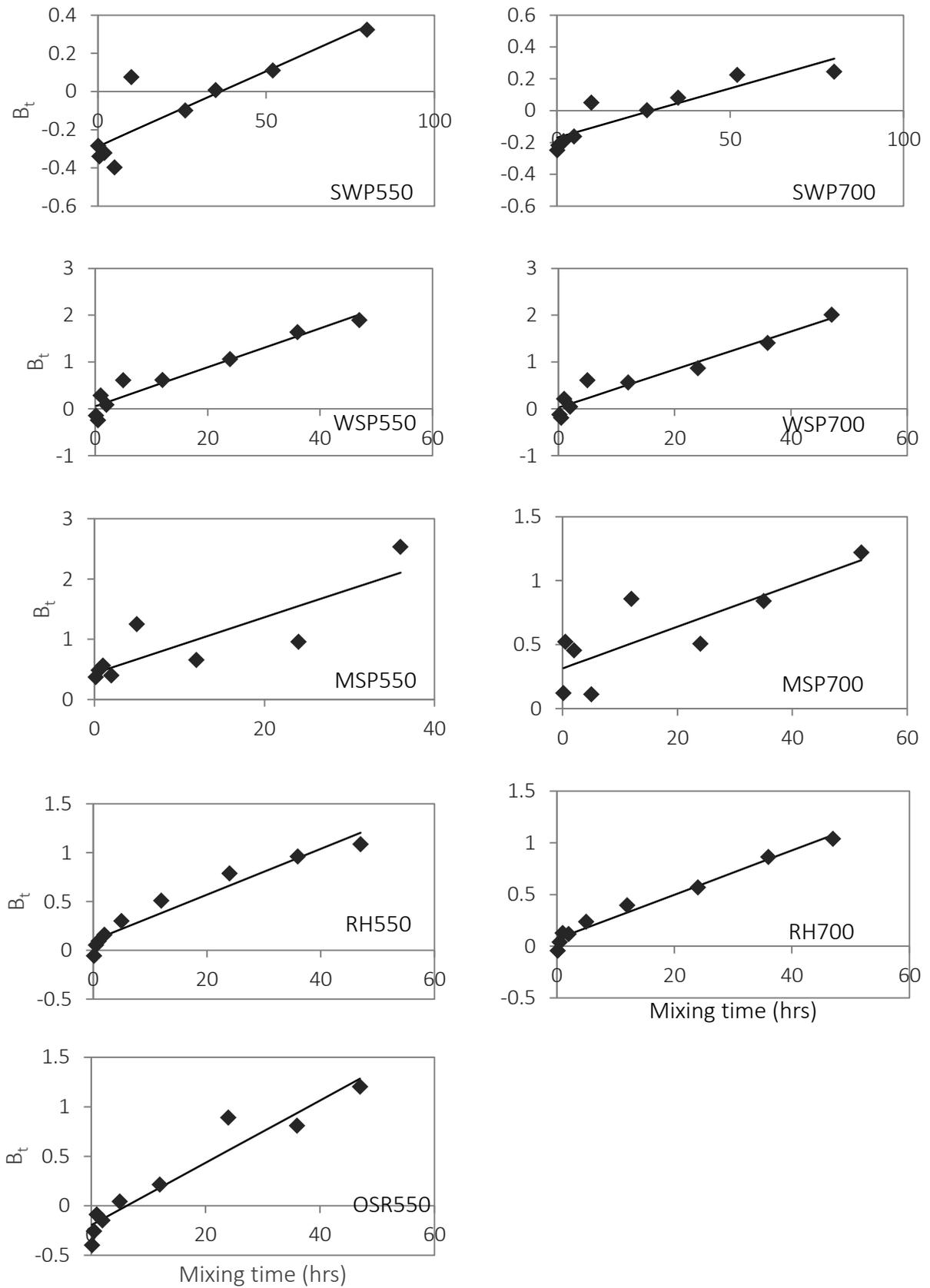


Figure 4-12: Boyd kinetic plots for the nine standard biochars

Intraparticle diffusion plots showing q_e vs. \sqrt{t} are given in Figure 4-13 to Figure 4-19. In general, the biochars show clear distinctions between two different phases of sorption, as the final equilibrium phase is not clearly reached in most cases. The good fits of the intraparticle diffusion model suggest that the microporous regions are generally playing a significant role in the sorption of atrazine, which would be expected due to the highly microporous nature of the biochars and the small particle size of atrazine.

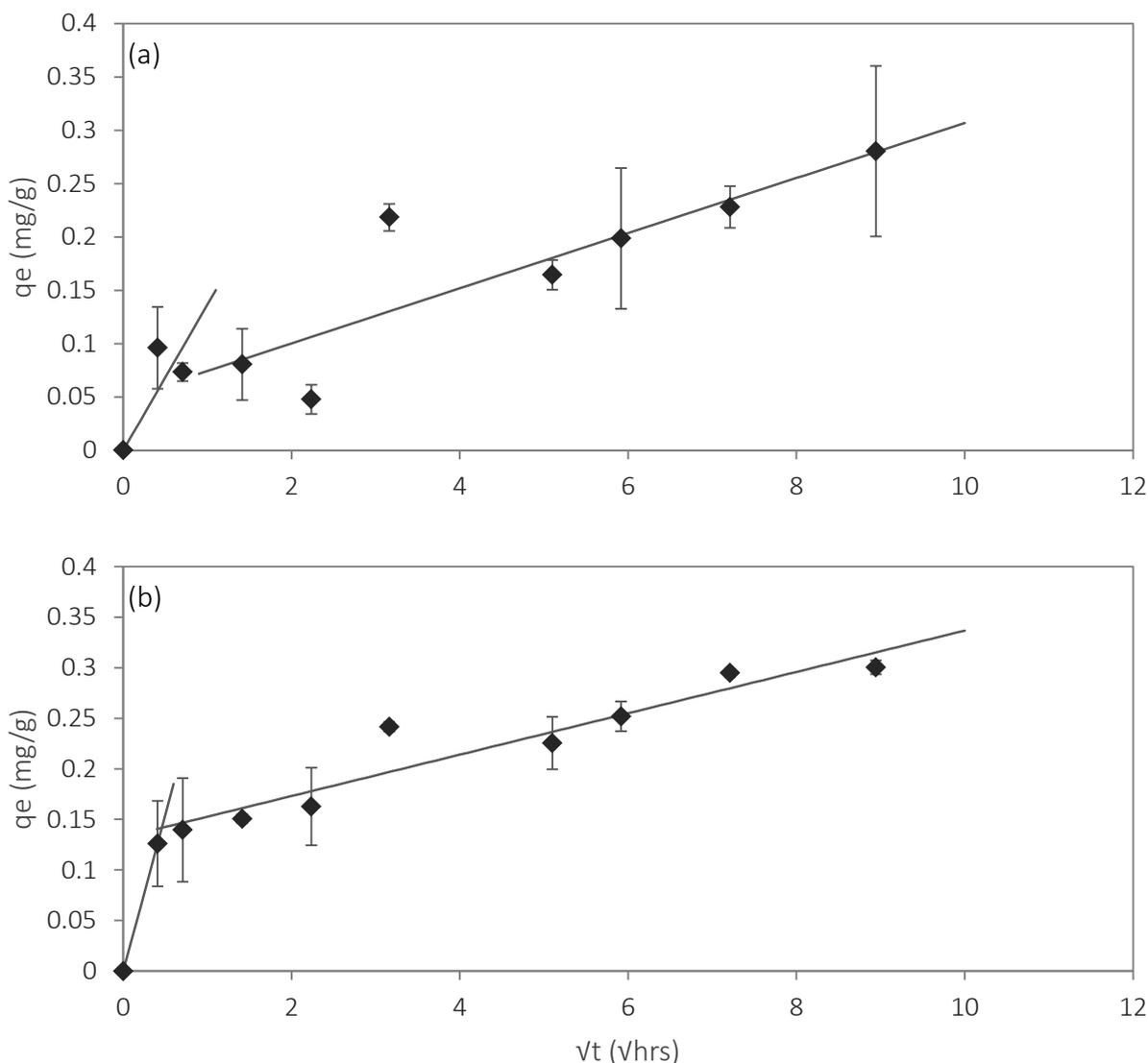


Figure 4-13: Intraparticle diffusion plots for (a) SWP550 and (b) SWP700 biochars

SWP550 shows relatively poor agreement with the intraparticle diffusion model, however this does not necessarily mean that intraparticle diffusion is not relevant. In particular, the initial rapid adsorption phase is much less clear than for many other biochars tested, which suggests that rapid chemical interactions may play little role in the sorption of atrazine to SWP550. However, there is a clear slow diffusion phase from $\sqrt{t} \approx 4$ to 9 $\sqrt{\text{hours}}$, which may

suggest that intraparticle diffusion does play a role. In contrast, SWP700 shows a relatively good fit to the intraparticle diffusion model, with an initial rapid adsorption phase (though a relatively small contribution to the total sorption), followed by a long and steady intraparticle diffusion phase.

These results do not appear to fit closely with the elemental, FTIR and Boyd plot analyses. The high polarity values of the SWP biochars suggest that SWP biochars would be capable of forming hydrogen bonds with atrazine, and adsorption would therefore occur through hydrogen bonding, in addition to pore filling in the microporous structure of the softwood biochars¹³². The sorption profile would therefore be expected to have a significant amount of early, rapid sorption associated with the chemical interactions, followed by a period of slower sorption representing diffusion into the micropores. However, SWP550 shows little to no early rapid sorption, while SWP700 shows only a very small amount, particularly compared to other less polar biochars such as RH550 and RH700. This discrepancy may be caused by a number of factors, such as: (a) the form of oxygen present not participating in hydrogen bonding; (b) the oxygen groups existing within the pore network and therefore not allowing for rapid sorption; (c) chemical interactions being suppressed by competition with water molecules; (d) the oxygen existing within the amorphous phase, not the carbonised phase; or (e) a poorly developed macro- and mesopore network preventing rapid access to the oxygen groups.

First, the form of oxygen present in the biochars may not be capable of forming hydrogen bonds with the atrazine. While this is unlikely due to atrazine's ability to form hydrogen bonds as both an H-donor and H-acceptor, the presence of oxygen only as C=O groups demonstrated in the FTIR may suggest that SWP biochars have a lower capacity for hydrogen bonding than biochars featuring predominantly –OH groups. However, this explanation does not fit with the results observed for MSP biochars presented later in this section, which show a large contribution of chemical interactions attributable to interactions with the O-groups. Further, SWP700 does not contain C=O groups according to FTIR analysis, yet shows a greater initial sorption than SWP550. Therefore the type of oxygen groups present cannot fully explain the lack of chemical interactions with SWP biochars.

Second, the oxygen groups may exist inside the pore networks of the char, which would make them inaccessible in the short term, therefore preventing rapid sorption. This may occur as a result of the carbonisation during the pyrolysis process not allowing for complete

removal of volatile components from the microporous regions, or through some oxidation of the pore spaces. This presence of oxygen in the pore space would in turn result in the biochar having a high oxygen content (and subsequent O:C ratio), however these oxygen groups are not available to interact with adsorbents in the short term. However, this explanation again contradicts the FTIR analysis, which is only able to detect surface functionalities^{207,277}. For example, the FTIR results for OSR550 did not show O-containing functional groups despite a high O-content, suggesting that these groups exist within the internal or pore structure of the biochar. Therefore, this explanation may partially explain the lack of chemical interactions for SWP700, which does not show C=O groups in FTIR analysis, but cannot explain the lack of chemical interactions with SWP550.

Third, the chemical interactions may be suppressed by competition with water molecules for hydrogen bonding sites on the biochars' surfaces. This would reduce the amount of rapid sorption of atrazine, resulting in pore diffusion being more significant. However, this effect is not observed for other biochars with high polarity, such as OSR550 and MSP biochars, which makes this explanation less likely. However, not all biochars will experience reduced sorption due to high oxidation, and further insights into this effect should be obtained from the pH-dependency studies in Chapter 5.

Fourth, the oxygen may exist in the amorphous phase, in which case it would not form hydrogen bonds as readily as the functionalised aromatic phase, resulting in slower and lesser amounts of sorption. The sorption to the amorphous phase is likely to be significantly less than to the carbonised phase due to the reduced surface area and hydrophobicity¹⁵². The presence of these oxygen groups in aliphatic chains in the amorphous component are therefore likely to exhibit relatively low sorption compared with oxygen-containing functional groups in the carbonised phase. However, this explanation is unlikely as (a) FTIR analysis confirmed the carbonised structure of the SWP biochars, and (b) the high pyrolysis temperatures used mean that it is unlikely there is a significant amorphous fraction remaining in the SWP biochars, particularly for SWP700.

Finally, pore macro- and meso-pore networks may result in significant amounts of the biochars' surface areas being inaccessible in the short term, resulting in little or no early rapid sorption to SWP biochars. The pore size distribution of SWP chars was characterised by Sigmund et al.⁹⁷ who demonstrated that both SWP biochars have significant mesopore volume. These biochars should therefore be able to effectively transport atrazine to

microporous adsorption sites. Shen et al.¹³⁷ carried out SEM imaging of SWP550, and showed that it consisted of plant fibres, with pores ($\approx 5 \mu\text{m}$ diameter) parallel to the fibres, as shown in Figure 4-14. Therefore, a lack of mesopore and macropore space, or any other explanation considered here, cannot fully explain the poor intraparticle diffusion of atrazine through SWP biochars.

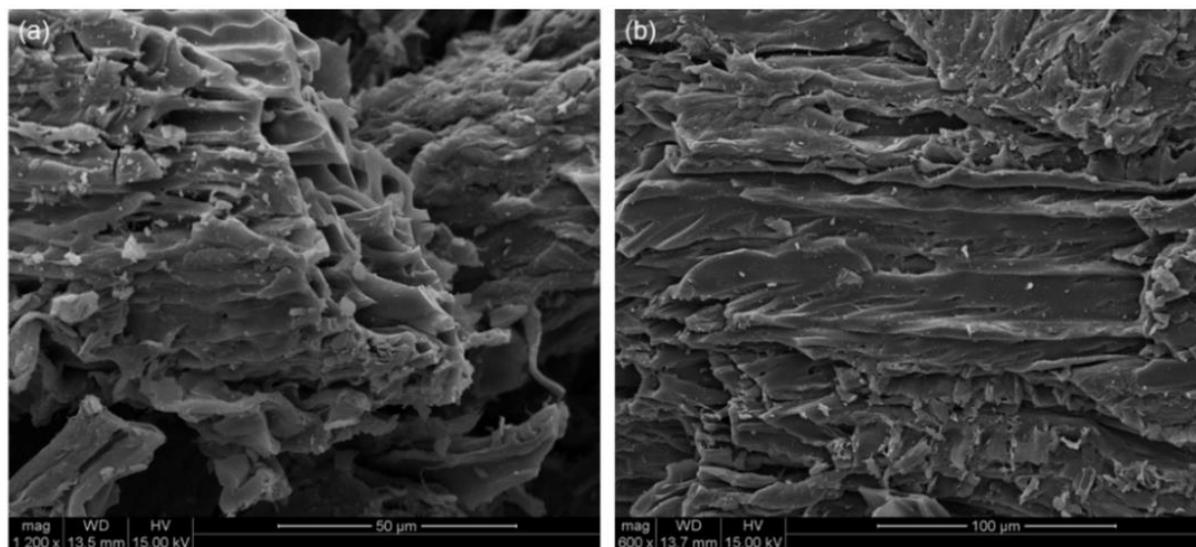


Figure 4-14: SEM images of SWP700 biochar (a) parallel to fibre direction; and (b) perpendicular to fibre direction. Reproduced from Shen et al.¹³⁷

WSP biochars show good fits to the intraparticle diffusion model, with clear rapid sorption and intraparticle diffusion phases. This clearly suggests that the sorption of atrazine to WSP biochars is initially controlled by chemical interactions, followed by slow diffusion through the pores. However, the early rapid sorption represents only a minor component (<30%) of the total sorption, suggesting that most of the atrazine undergoes intraparticle diffusion. These results are consistent with SEM images of WSP700 taken by Shen et al.¹³⁷ shown in Figure 4-16, which show a range of pore sizes, suggesting atrazine molecules can effectively diffuse through the biochar particles.

The combined results of the kinetic models therefore suggest that sorption of atrazine to wheat straw biochar is dominated by pore diffusion, although chemical interactions do also contribute. The good fit of the Elovich model for both WSP550 and WSP700 suggests that the biochars are tightly binding the atrazine. Similarly, the Boyd plot passes through the origin which suggests that the sorption kinetics are controlled by intraparticle diffusion, not film diffusion. Finally, the intraparticle diffusion model shows clear phases of rapid early sorption followed by steady diffusion of atrazine into the micropores. These results are

consistent with the proximate analysis of the wheat straw biochars which show that they both have medium-high polarities and medium-high surface areas, suggesting that they are capable of both hydrogen bonding and pore filling. Further tests such isotherm and pH analyses are necessary in order to more accurately determine the nature of the chemical interactions.

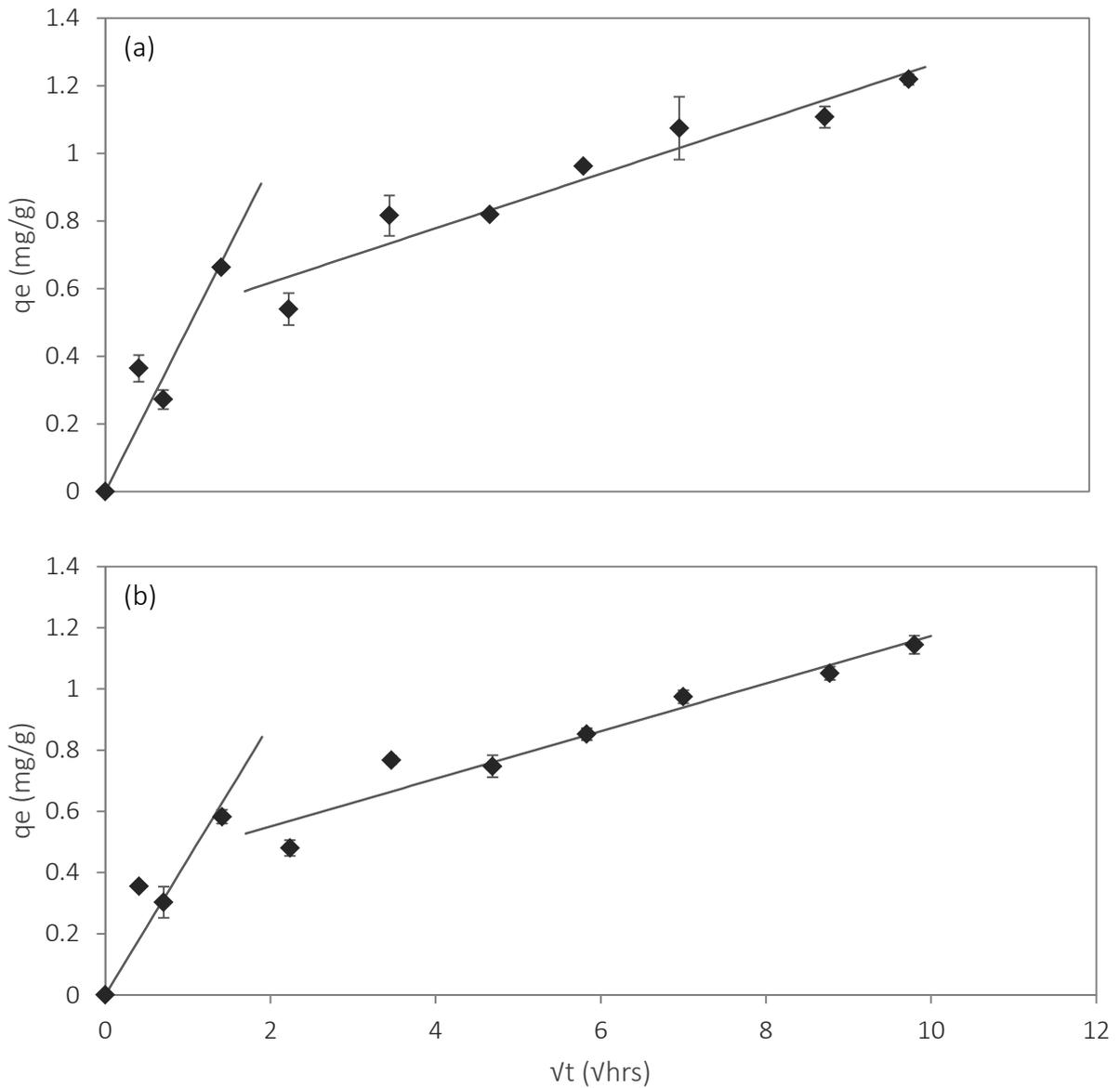


Figure 4-15: Intraparticle diffusion plots for (a) WSP550 and (b) WSP700 biochars

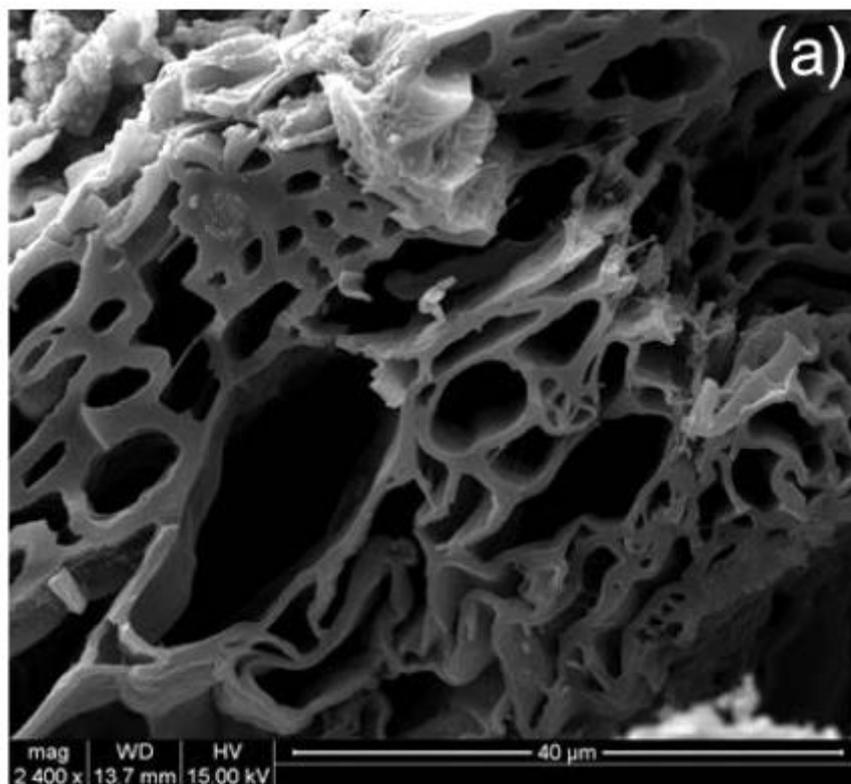


Figure 4-16: SEM image of WSP700. Adapted from Shen et al.¹³⁷

MSP biochars show good fits to the intraparticle diffusion model. Notably, both biochars show large amounts of early rapid sorption, suggesting the presence of significant chemical effects. This is then followed by a slow, longer period corresponding to intraparticle diffusion. The high contribution of initial chemical interactions is consistent with the relatively high polarities of each of the MSP biochars, which suggest that the biochars may participate in hydrogen bonding. The FTIR analysis confirmed that both MSP biochars contained C=O groups, which may therefore act as H⁺ acceptors in hydrogen bonding. While the presence of these groups suggest that the chemisorption is associated with hydrogen bonding, further isotherm and pH-dependency tests are necessary in order to more accurately determine the nature of the chemical interactions. Shen et al.¹³⁷ found that sorption of various heavy metals to MSP700 biochar was dominated by chemisorption, which is consistent with these results suggesting that MSP biochars have abundant and available sites for chemical interactions with adsorbate molecules. These results are consistent with the results from the film diffusion model, which suggested that both film diffusion (associated with chemisorption) and intraparticle diffusion play roles in the sorption of atrazine to MSP biochars. The sorption kinetic profiles therefore resemble initial rapid chemisorption,

followed by a slower intraparticle diffusion phase, suggesting pore filling is playing an important role in the sorption to MSP biochars.

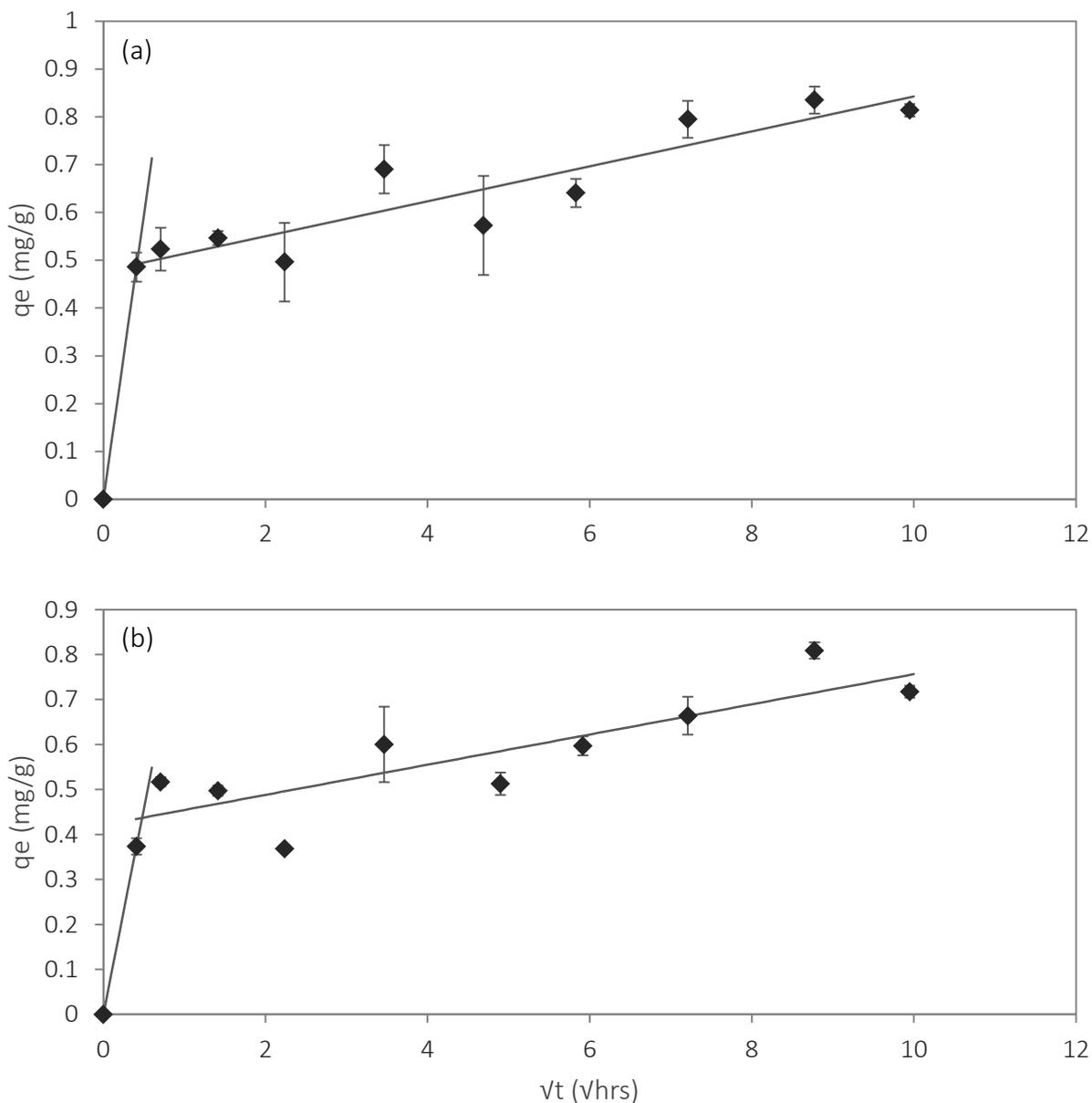


Figure 4-17: Intraparticle diffusion plots for (a) MSP550 and (b) MSP700 biochars

RH biochars show good fits to the intraparticle diffusion model, with a clear period of a rapid early sorption and a long, slower phase representing intraparticle diffusion. However the sorption profile is clearly most influenced by the intraparticle diffusion phase, which does not appear to slow after 100 hours of sorption, suggesting an abundance of micropores and good access to sorption sites. This result is consistent with the Boyd plots, which suggest that intraparticle diffusion dominates sorption to RH biochars, and with the low polarity and high aromaticity observed in elemental analysis. Notably however, the SSA values for RH

biochars are not outstanding, and the value for RH550 is relatively low compared to other biochars, which would suggest that RH biochars do not contain abundant sorption sites or microporous regions. However, this is most likely due to the N₂-BET method used to determine SSA by UKBRC, which has been previously shown to understate the SSA of materials with significant microporous regions^{94,185}.

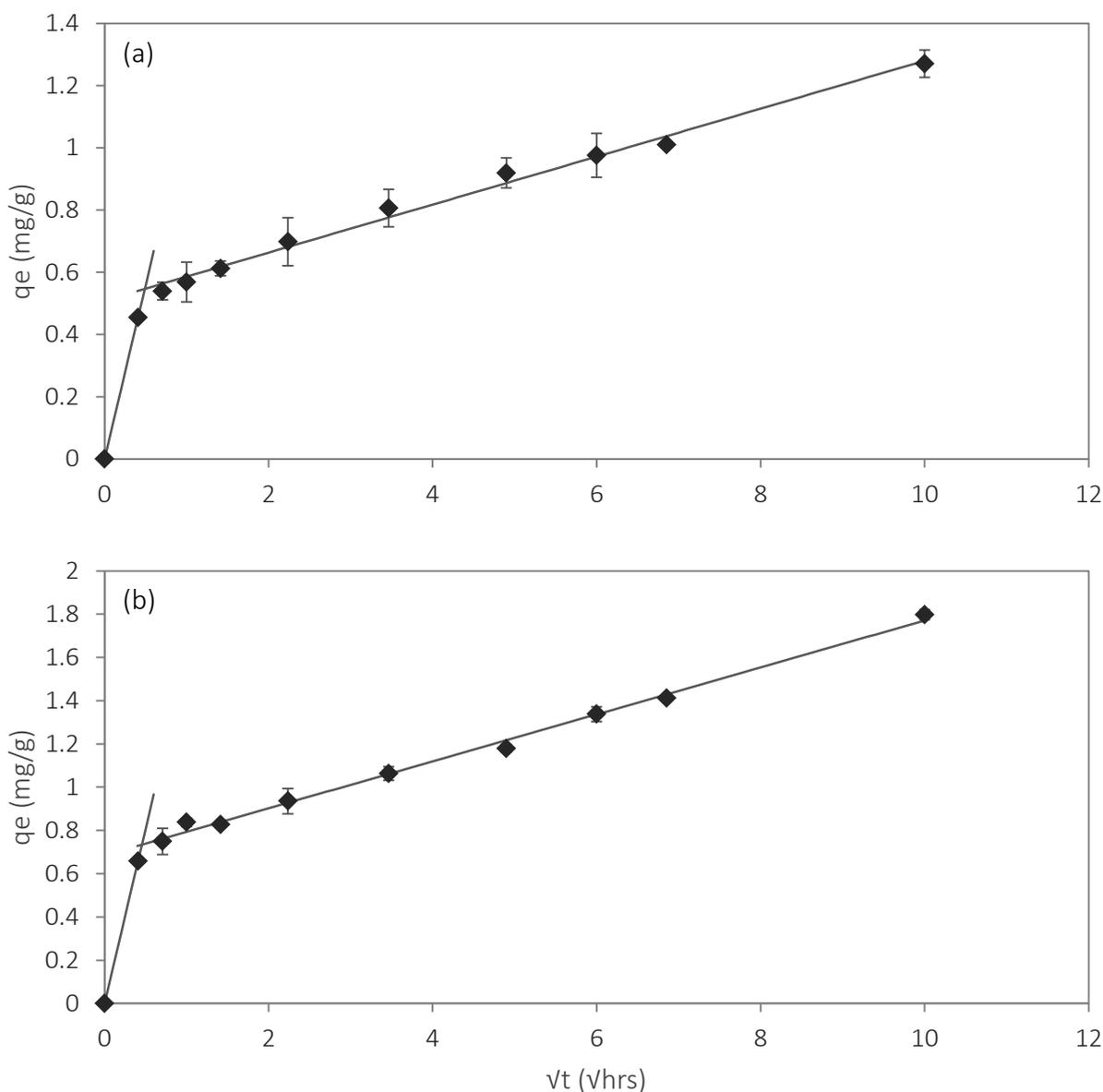


Figure 4-18: Intraparticle diffusion plots for (a) RH550 and (b) RH700 biochars

The combined results for rice husk biochars therefore suggest that intraparticle diffusion and film diffusion both play significant roles in the sorption of atrazine, although pore filling contributes to a greater extent. The kinetic plots show good fits to the Elovich model, suggesting that rice husk biochar is tightly binding the atrazine molecules. However,

equilibrium is not clearly reached after 100 hours, suggesting that slow intraparticle diffusion may be limiting the sorption rate. The outcomes from the film diffusion model are not clear, and it is likely that film diffusion and intraparticle diffusion are both significant influences. This is confirmed by the intraparticle diffusion model, which shows a significant period of early rapid sorption as well as an extended period of intraparticle diffusion. Therefore, short-term sorption is controlled by rapid chemical sorption to macro and mesopores, while at higher mixing times pore filling becomes dominant. Further isotherm and pH-dependency tests can determine the nature of the adsorption mechanisms, while investigations into the interactions with humic acids can provide insights into the role of pore filling.

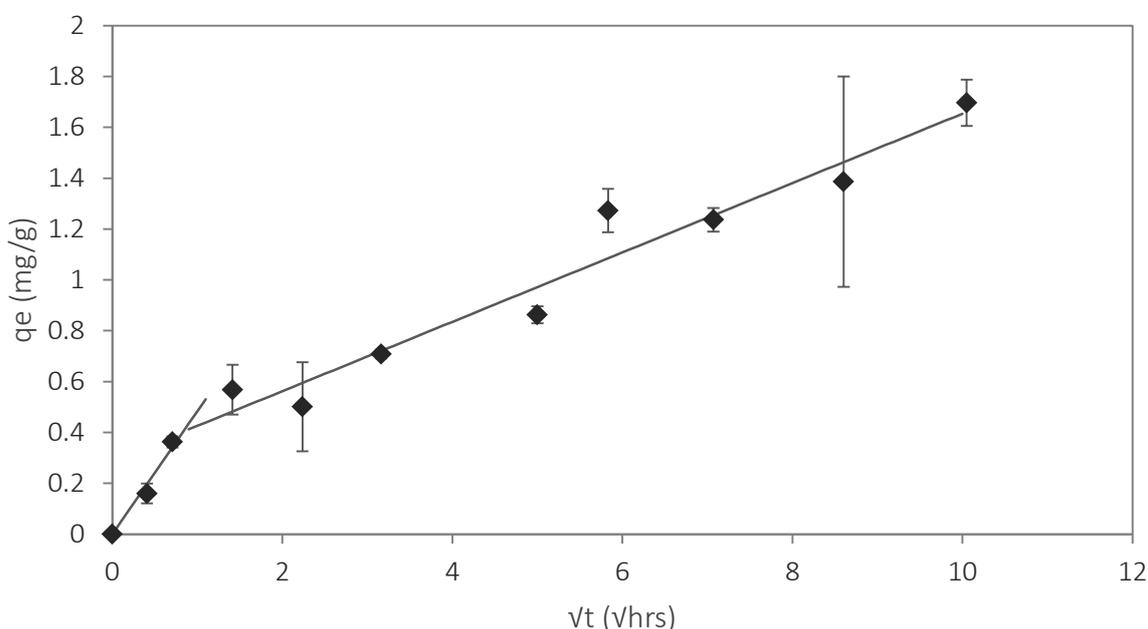


Figure 4-19: Intraparticle diffusion plot for OSR550 biochar

OSR550 shows a reasonable fit to the intraparticle diffusion model. While the sorption profile initially shows a period of early rapid sorption, followed by slow intraparticle diffusion, the later sorption shows what appears to be an increase in the rate of intraparticle diffusion, which would not be consistent with the steady saturation of available sorption sites over time. This multi-phase trend may correspond to different phases of atrazine molecules diffusing into the micropores of OSR550; for example, it may represent a poorly developed mesoporous network, resulting in the slow (but significant in terms of quantity) sorption to the micropores. This result is consistent with the discrepancy between the elemental analysis and the FTIR results, which respectively show an abundance of elemental oxygen yet little oxygen-containing surface functional groups. This may suggest that the oxygen groups exist

inside the pore network of OSR550, which would result in high sorption once intraparticle diffusion has taken place.

The kinetic sorption studies therefore suggest that for OSR550 both chemisorption and intraparticle diffusion contribute to sorption. The good fit of the Elovich model suggest that the molecules are being tightly bound. The film diffusion model suggests that both chemical interactions and pore diffusion are significant, while the intraparticle diffusion model shows the presence of some rapid chemical interactions to macropores followed by steady, slow intraparticle diffusion. Sorption kinetics are therefore mostly controlled by intraparticle diffusion, although chemical interactions are also significant. Further isotherm and pH-dependency tests can determine the nature of these chemical interactions.

Summary of kinetic sorption mechanisms

The kinetic sorption tests indicate that sorption to the standard biochars is predominantly controlled by intraparticle diffusion processes, although film diffusion relating to rapid chemical adsorption is also significant for several biochars. The generally good fits to the Elovich model suggests that the biochars are tightly binding the atrazine, and therefore may be useful at immobilising the contaminant in soil. The film diffusion and intraparticle diffusion models show good agreement, except for SWP550 which can largely be attributed to the high influence of random errors in measurement in this case. Together, these two models allow for the clear elucidation of the presence of chemical and physical effects in the different biochars.

The kinetic models therefore suggest that the biochars are tightly binding the atrazine molecules through a combination of intraparticle diffusion (i.e., pore filling) and chemisorption (i.e., hydrogen bonding, hydrophobic effects, and π - π interactions). Intraparticle diffusion plays a larger role for WSP and RH biochars, chemisorption is more significant for MSP biochars, while other factors inhibit efficient kinetic interactions involving SWP and OSR biochars.

4.2.1 Interaction with humic acids

Humic acids may block the pore networks of biochars, inhibiting the influence of pore filling^{67,107,111,116}. Batch sorption tests investigating the interactions with absorbent molecules to biochar in the presence of humic acids were therefore carried out in order to confirm the roles

of pore filling to the different standard biochars. These tests provide useful insights into (a) the role of pore filling in the adsorption process; (b) the efficiency of the meso- and micropore network to transport adsorbate molecules; and (c) the likely behaviour in the soil profile in the presence of soil organic matter.

The sorption capacities of the nine standard biochars in the presence of increasing humic acid concentration are shown in Figure 4-20. All biochars showed decreased sorption in the presence of humic acids, suggesting that pore access is a contributing factor to the sorption to these adsorbents, and therefore providing further evidence for the role of pore filling. In some cases, sorption capacity was reduced by up to 64%. While unrealistically high concentrations were used in this study, the reduction in sorption in the presence of potential molecules in the soil mechanistically demonstrates that the pores may be blocked reducing the significance of pore filling to these biochars.

The interpolated reduction in sorption in the presence of 75 mg/L humic acids is shown in Figure 4-21 in order to provide a more even comparison against all biochars. The greatest reductions were observed to the biochars produced at 550°C; particularly those produced from softwood and oil seed rape. This provides further evidence for the theory that these biochars have poorly developed pore networks, as they are not able to effectively adsorb atrazine when the micropores are blocked. The reductions in sorption in the presence of humic acid are therefore likely to be primarily associated with reduced pore access, although reduced access to adsorption sites may also contribute in some cases.

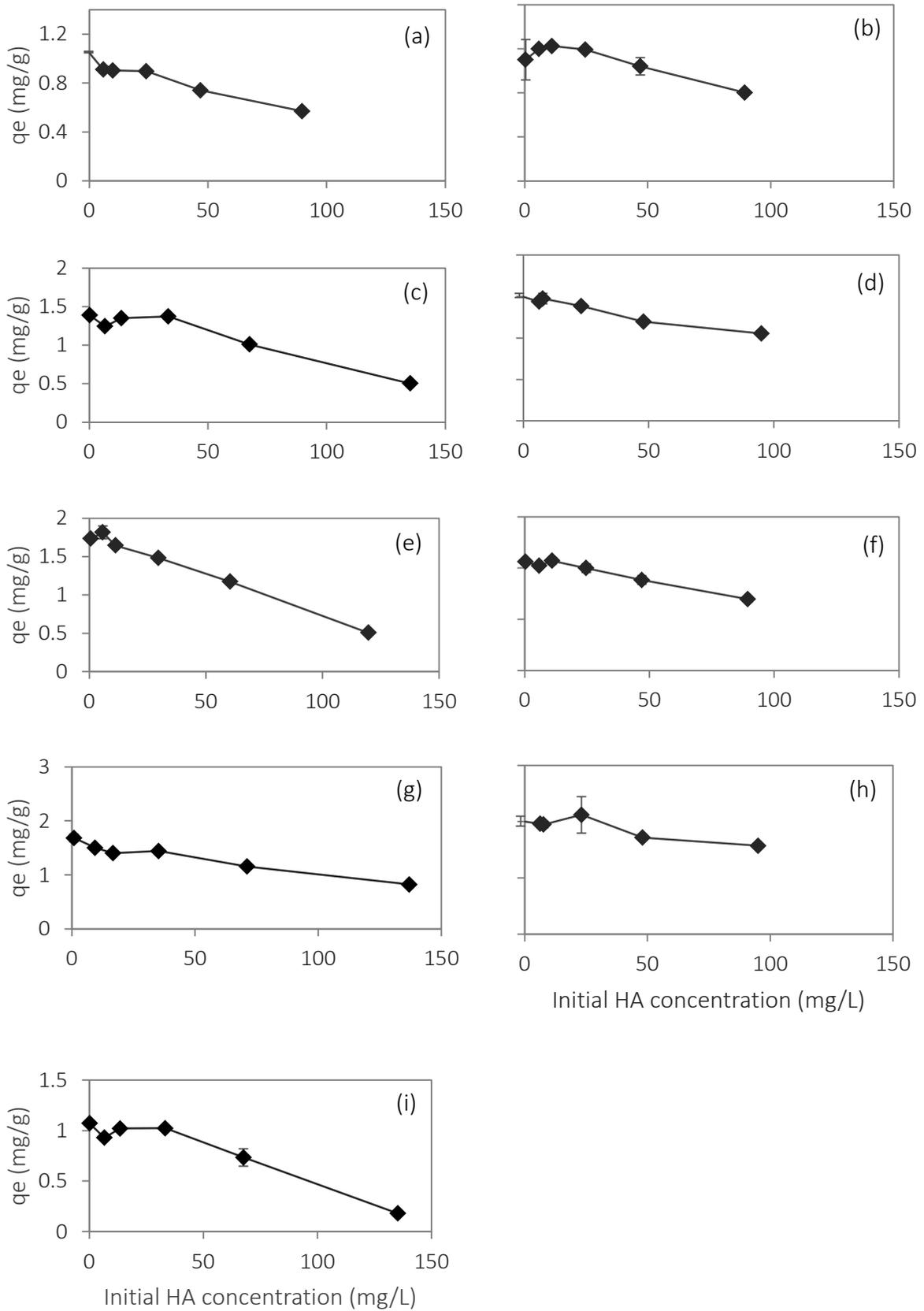


Figure 4-20: Influence of humic acid on sorption of atrazine to (a) SWP550; (b) SWP700; (c) WSP550; (d) WSP700; (e) MSP550; (f) MSP700; (g) RH550; (h) RH700; and (i) OSR550. Initial atrazine conc = 10 mg/L.

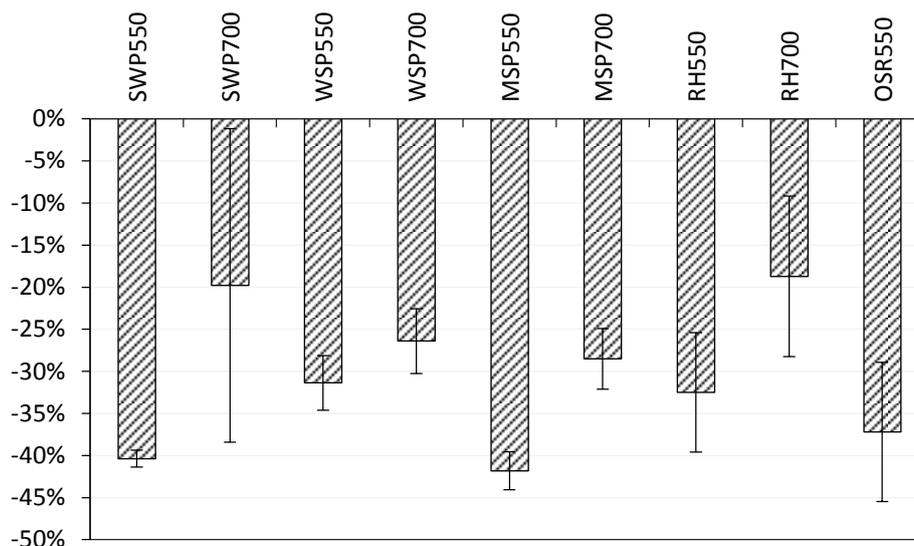


Figure 4-21: Reduction in sorption capacity of standard biochars in the presence of 75mg/L humic acids

The humic acid tests therefore provide a range of insights into the sorption mechanisms of atrazine to the standard biochars. First, they highlight the role of pore filling in controlling the immobilisation of atrazine. The significant reductions in sorption, sometimes up to 60%, provide evidence that reducing micropore access significantly reduces availability of sorption sites and therefore decreases the ability of biochar to immobilise the adsorbate molecules. Second, they show that biochars with well-developed pore networks, such as RH700, are better able to adsorb atrazine when some become blocked than those with less-developed pores, such as SWP550 and OSR550. Finally, they suggest that the efficiency of the biochars will likely be significantly reduced in soils due to interaction with soil organic matter. Whether that influences the feasibility of biochar as a useful remediation option will depend on the desired outcomes and design parameters, however is important for design engineers to consider these effects.

4.2.2 Isotherm studies

Isotherm studies are used to determine the relationship between solid and aqueous concentrations in an adsorption system. They are one of the most common methods of characterising the sorption properties of a given system, as they provide useful information on the sorption capacity under high loading, while the shape of the curve itself suggests the presence of partitioning which is important to account for before determining potential environmental benefits, as outlined in Chapter 2. The isotherm data is first fitted to the Freundlich and Langmuir models, the two most common models for characterising isotherms.

The partitioning and adsorption components of sorption are then separated using the dual-mode sorption model, which allows for a more accurate representation of the true long-term immobilisation potential of the biochars.

Freundlich and Langmuir models

Isotherm tests were carried out on the nine standard biochars and the data was fitted with the Freundlich and Langmuir models. The results are shown in Figure 4-22 to Figure 4-26 and the fitting parameters are shown in Table 4-3. The Freundlich model assumes multi-layered adsorption to a heterogeneous adsorbent, while the Langmuir model assumes monolayer adsorption to homogenous surface sites. Therefore, the relative fit of these two models can provide insights into the nature of the sorption sites controlling sorption.

Table 4-3: Fitting parameters for Freundlich and Langmuir models to standard biochar isotherms. K_F and $1/N$ are Freundlich fitting parameters; Q_{max} and b are Langmuir fitting parameters

Biochar	Freundlich Model			Langmuir Model		
	K_F	$1/N$	R^2	Q_{max}	b	R^2
SWP550	0.314	0.520	0.778	1.384	0.284	0.730
SWP700	1.007	0.263	0.944	1.637	2.118	0.851
WSP550	2.205	0.289	0.997	1.853	49.169	0.891
WSP700	1.422	0.352	0.980	1.684	7.910	0.801
MSP550	1.080	0.302	0.997	1.587	4.521	0.944
MSP700	1.071	0.341	0.993	1.872	2.169	0.968
RH550	2.188	0.376	0.943	5.033	0.902	0.866
RH700	2.834	0.370	0.959	5.940	1.243	0.890
OSR550	1.612	0.298	0.935	1.426	32.452	0.628

The isotherms show that all of the biochars exhibited highly non-linear sorption (Freundlich $1/N$ values were between 0.29 and 0.52), suggesting that they exhibit high sorption at low concentrations, while sorption efficiency decreases at high concentrations. The Freundlich and Langmuir models both exhibited good fits to the standard biochars ($R^2 > 0.8$), with the exceptions of both models to SWP550 and the Langmuir model to OSR550. The poor fits to SWP550 are likely due to the high influence of random variation in measurements due to its low sorption capacity ($Q_{max} = 1.38$ mg/g). In all cases, the Freundlich model was a better fit than the Langmuir model, suggesting that the heterogeneity of the biochars plays a significant role in the sorption. For high temperature chars, the Langmuir model is generally a better fit due to the highly carbonized surface^{102,148}, however the Freundlich model more accurately reflects the simultaneous sorption to carbonised and uncarbonised phases in the biochars

^{102,250}. Previous studies investigating the sorption of atrazine, even to high temperature chars, have also found that the Freundlich model accurately describes its behaviour ^{92,228}.

It should also be noted that the majority of the isotherms presented here do not reach completion (e.g. levelling off or reaching a linear state at high concentrations), due to the low solubility of atrazine. Isotherm tests were carried out using initial concentrations of up to 20 mg/L (atrazine solubility = 33 mg/L), as preliminary tests showed solubility effects were significant above this value. The influence of the Langmuir analysis is therefore limited, as this model assumes that the sorption approaches a maximum sorption capacity, and is therefore less appropriate when this value is not reached (or approached to a meaningful extent). However, the behaviour of the isotherm at low concentrations is the most important for considering its behaviour in the environment, due to environmentally relevant concentrations of atrazine typically being < 0.1 mg/L ²⁰⁴.

The isotherms for SWP550 and SWP700 are given in Figure 4-22 and show that SWP700 demonstrated higher sorption than SWP550, likely due to the higher degree of carbonisation and pore spaces produced at higher pyrolysis temperatures ⁶⁶. SWP550 showed slightly better fits to the Freundlich than Langmuir models ($R^2 = 0.78$ and 0.73 respectively), suggesting that neither model fully captures the sorption processes. SWP700 showed a better fit by the Freundlich model ($R^2 = 0.94$ and 0.85), suggesting that multi-layered adsorption may be the dominant mechanism. SWP700 also showed high and more non-linear sorption than SWP550, which may suggest that further carbonisation occurred at the increased pyrolysis temperature. This result is consistent with elemental and FTIR analyses for SWP biochars.

The relatively high sorption linearity of SWP550 may also indicate the pore filling is not dominating sorption. This is consistent with the kinetic sorption studies which suggested that SWP550 cannot efficiently transport atrazine molecules to adsorption sites. Sorption is therefore likely to be controlled by other processes such as adsorption to macroporous regions or partitioning. The dual-mode sorption model will be useful in determining the overall extent of partitioning to SWP550. In contrast, SWP700 shows greater non-linearity and therefore is better able to transport atrazine to adsorption sites. This is again consistent with the results from the kinetic studies which showed clearer pore filling for SWP700 than for SWP550. Therefore the sorption of atrazine to SWP550 is likely to be controlled by partitioning to the amorphous phase, while sorption to SWP700 has a greater influence of pore filling and chemical adsorption mechanisms.

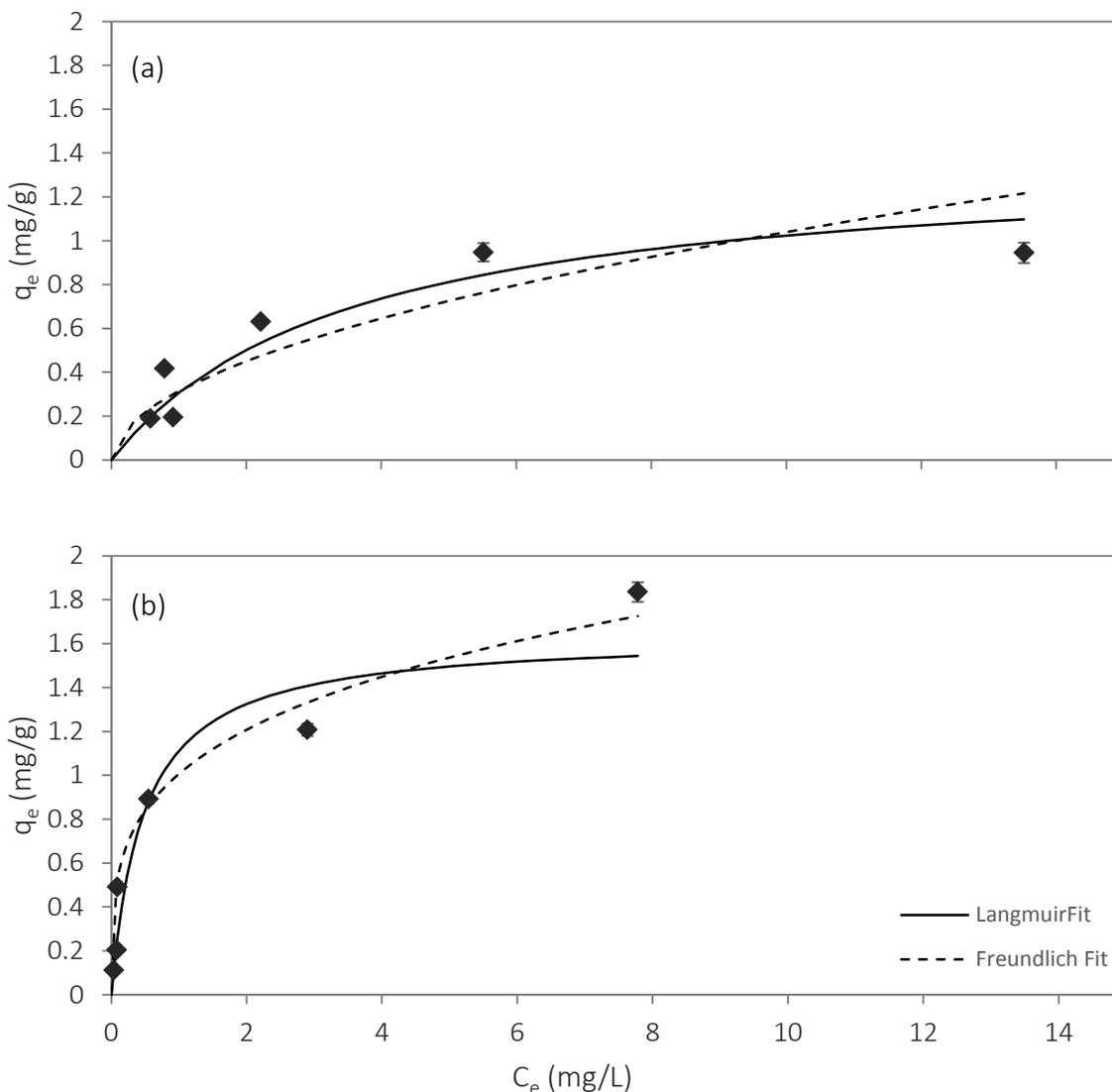


Figure 4-22: Sorption isotherms of (a) SWP550 and (b) SWP700 biochars

The isotherms for WSP550 and WSP700 biochars are shown in Figure 4-23, and show good fits to the Freundlich model ($R^2 = 0.997$ and 0.980 respectively). Notably, the sorption to WSP550 was greater than to WSP700. This is consistent with the measured SSA values, which suggests that surface area may play a major role in the sorption to WSP biochars. This may also suggest that the pore networks of wheat straw biochars may collapse at higher temperatures, resulting in reduced surface area and a reduced number of sorption sites, as previously found for high temperature biochars⁶⁹. It may also represent the significance of polar interactions, as the greater polarity of WSP550 may allow for increased chemical sorption mechanisms.

The high non-linearity of the isotherms is consistent with the results of the kinetic studies, which suggested that the sorption to the WSP biochars is dominated by pore filling. Further, the decrease in sorption due to the collapsed pores reducing available surface area also confirms that the sorption is primarily controlled by surface area associated with micropores. Sorption tests investigating interactions with humic acids will also be useful in determining the likelihood that sorption to WSP biochars will be reduced in soil due to interactions with SOM.

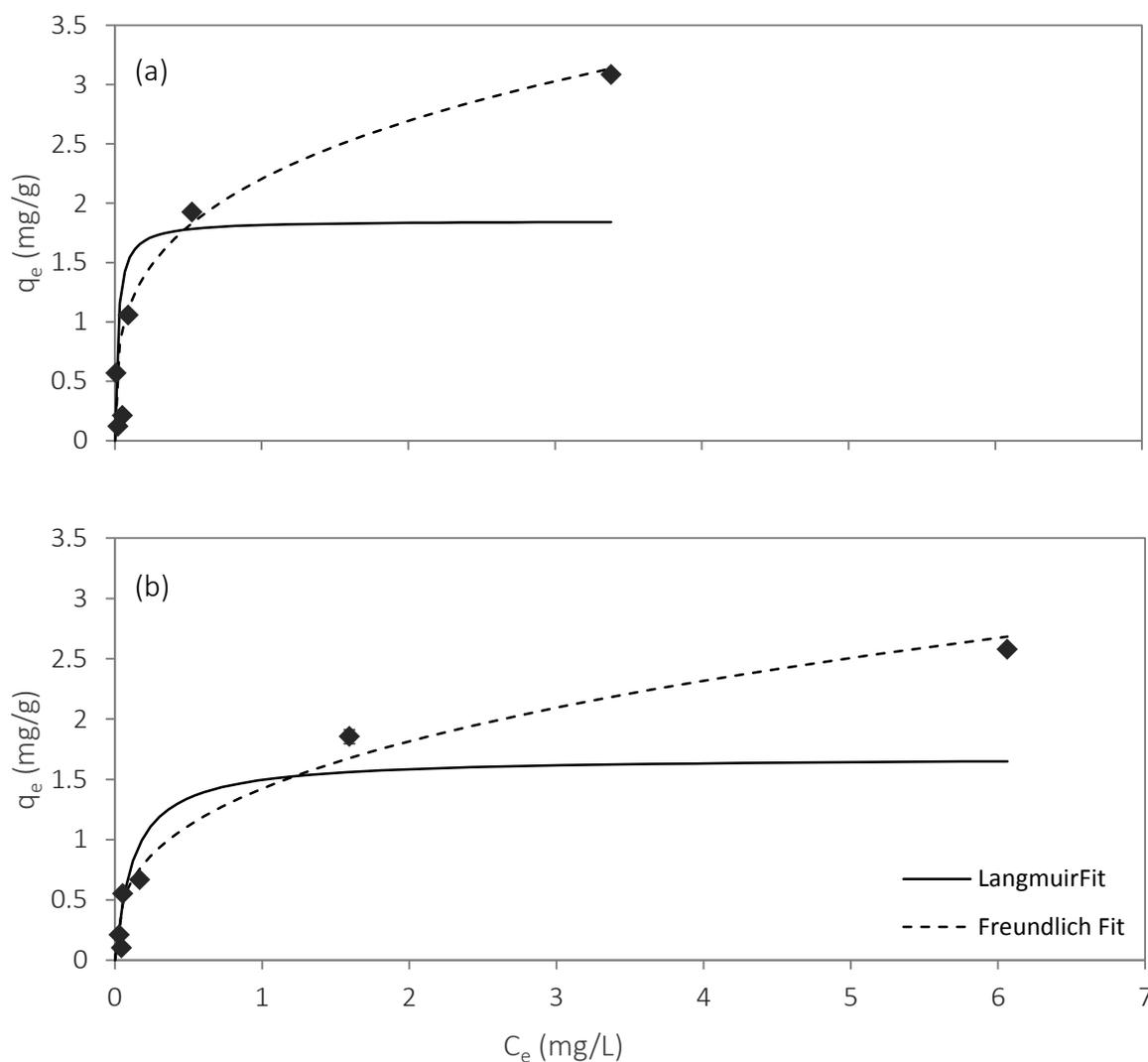


Figure 4-23: Sorption isotherms of (a) WSP550 and (b) WSP700 biochars

The isotherms for MSP550 and MSP700 are shown in Figure 4-24. MSP550 and MSP700 showed very similar sorption profiles, suggesting that pyrolysis of miscanthus straw above 550 °C does not significantly change its relevant properties. This is consistent with its measured SSA values, which are relatively similar (33.6 vs. 37.2). However, the oxygen

content, polarity and aromaticity values were different between the two biochars. A negligible change in sorption capacity suggests that either: (a) these properties are not important in controlling the sorption of atrazine to these biochars; or (b) a number of simultaneous changes cancelled out to produce no net effect. The first explanation is unlikely, as the kinetic studies suggest that chemical sorption mechanisms are highly significant for the sorption of atrazine to miscanthus straw biochars. It is therefore likely that the small change reflects the changing influence of chemical interactions. For example, a reduction in polarity for MSP700 may increase hydrogen bonding while also increasing interaction with water molecules. The results from the pH-dependency tests will be useful in determining the nature of these chemical interactions.

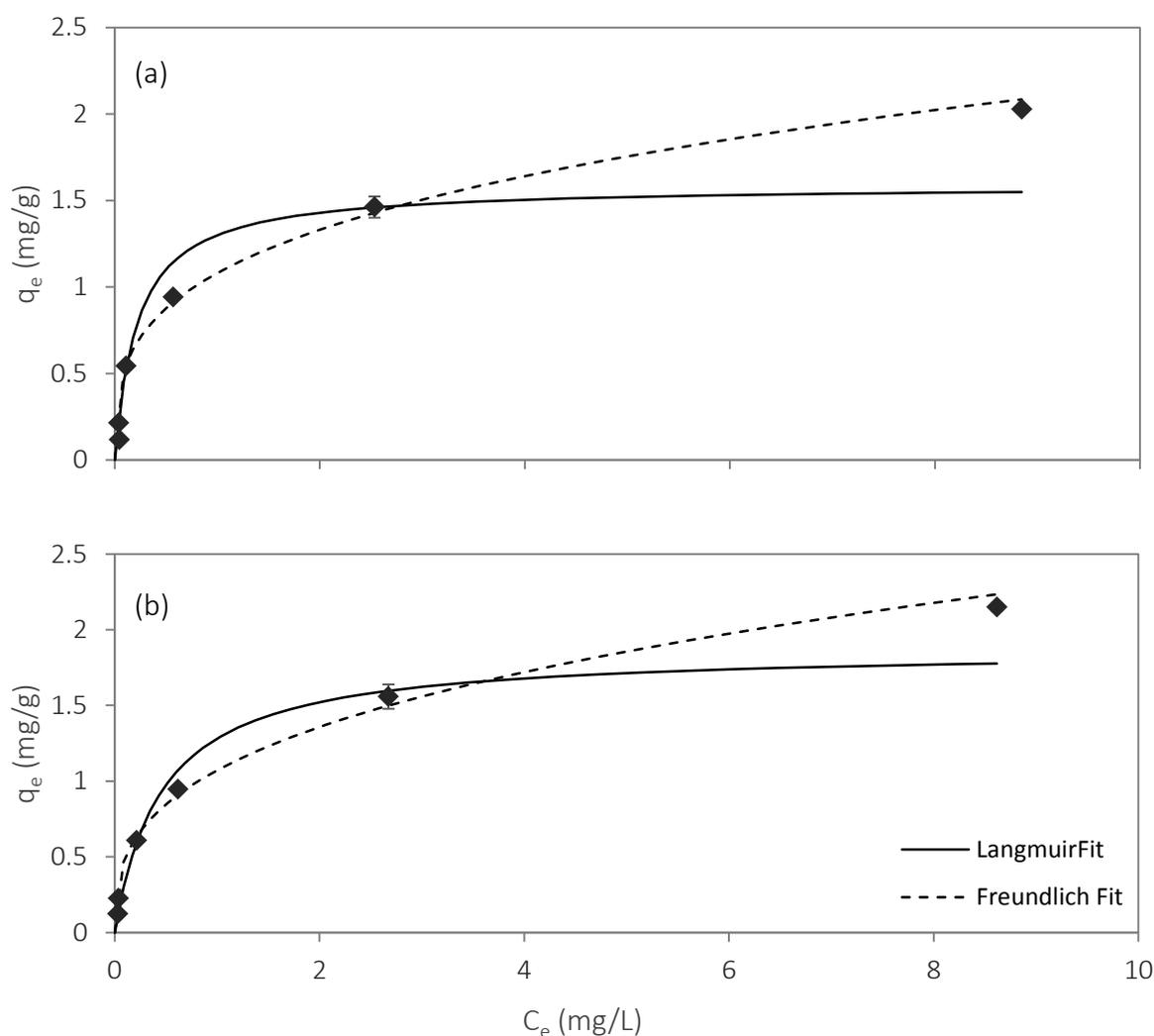


Figure 4-24: Sorption isotherms of (a) MSP550 and (b) MSP700 biochars

The isotherms for RH550 and RH700 are shown in Figure 4-25. RH550 and RH700 showed by far the highest sorption of all biochars tested (maximum measured sorption of 6.9 mg/g

and 8.2 mg/g respectively), suggesting that they may be useful for immobilising contaminants in the environment. Both biochars showed good fits to the Freundlich model ($R^2 > 0.94$), and clearly did not reach a maximum adsorption capacity suggesting that its true capacity may be much higher. A visual assessment of both shows that the Langmuir fit is not appropriate, as the calculated Q_{\max} values are significantly lower than the measured maximum q_e values.

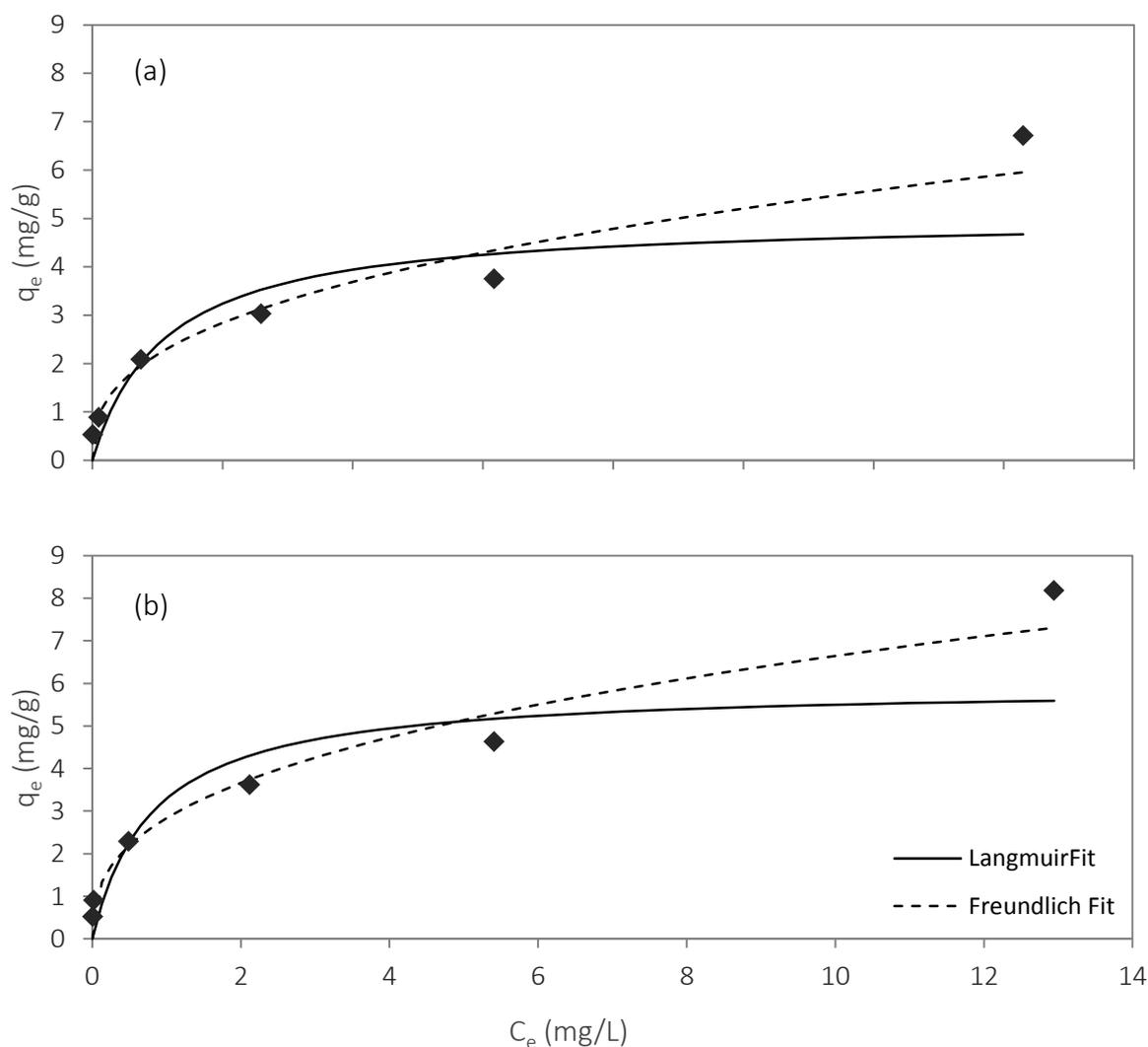


Figure 4-25: Sorption isotherms of (a) RH550 and (b) RH700 biochars

The sorption of atrazine to rice husk biochars is significantly higher than other biochars considered in this thesis. The reasons for this are not yet entirely clear. The SSA of the rice husk biochars are not the highest among the standard biochars, although it may still have more micropore space. The kinetic studies suggest that pore filling dominates sorption to RH biochars, which provides evidence towards a high micropore space. The high ash content of the rice husk biochars (> 40%) may also play a role; Chapter 5 of this thesis primarily

investigates the role of the ash content in sorption to the standard biochars. However, based on the results of the kinetic and isotherm studies, the high sorption capacity of the rice husk biochars is most likely attributable to a high micropore volume that is not fully captured by N₂-BET analysis.

The isotherm for OSR550 is shown in Figure 4-26. OSR550 showed a good fit to the Freundlich model ($R^2 = 0.94$). Notably, OSR550 had the highest K_F of all biochars produced at 550 °C, except for RH550 despite having by far the lowest measured SSA. This suggests that while SSA may be useful predictor of sorption for a given feedstock (e.g. WSP and MSP), it may not accurately capture sorption when considering different feedstocks. OSR550 had relatively high polarity and low aromaticity compared to the other biochars, which may have played a role in its high sorption capacity.

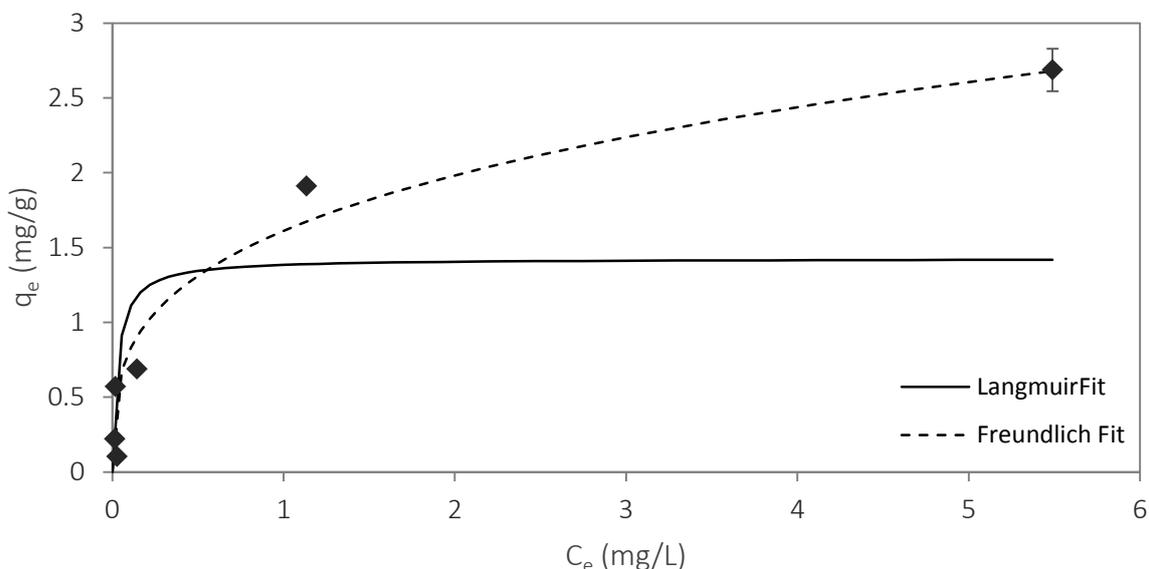


Figure 4-26: Sorption isotherm of OSR550 biochar

The profiles of the isotherms overall show highly non-linear sorption, and confirm the results of the kinetic sorption studies. Pore filling is a significant mechanism for WSP and RH biochars, while partitioning is likely to be more significant for SWP biochars. In order to further determine the relative influence of these mechanisms, it is necessary to use the dual-mode sorption model to separate adsorption and partitioning.

Dual-mode sorption model

The isotherms were further analysed using the dual-mode sorption model in order to determine the relative influences of partitioning and adsorption. As discussed in Chapter 2:, partitioning contributes significantly to overall sorption, but is likely to represent little long-term remediation benefit. Adsorption is therefore a more useful measure of the ability of biochar to immobilise contaminants in soil. The dual-mode sorption model assumes that the partitioning component of sorption is linear, and can therefore be separated from the non-linear adsorption component.

Dual-mode sorption isotherms for the sorption of atrazine are shown in Figure 4-27 to Figure 4-31, and indicate the contributions of partitioning and adsorption to the total sorption. The calculated partitioning coefficients (K_p), and comparisons of the Langmuir model fits for the sorption and adsorption profiles are given in Table 4-4. The dual-mode model appeared to separate partitioning and adsorption contributions successfully, as evidenced by the increase in R^2 values for all fits to the Langmuir model, except for SWP550, and a visual assessment of the separated isotherms.

The dual-mode sorption model shows that partitioning is significant for SWP biochars, particularly for SWP550 where it contributes nearly 50% of total sorption at high concentrations. The high volatile fraction of SWP550 as measured by UKBRC (14.2%)¹²⁶ likely represents the residual lignin, cellulose and hemicellulose components to which linear partitioning occurs. In contrast, the volatile fraction of SWP700 is significantly lower (6.7%)¹²⁶, and therefore a significantly lower contribution of partitioning is expected. However, the relative contribution of partitioning to SWP700 is still significantly higher than other biochars tested here. The high contributions of partitioning to the softwood biochars suggest that they may not be ideally suited to remediating atrazine from contaminated soil and groundwater.

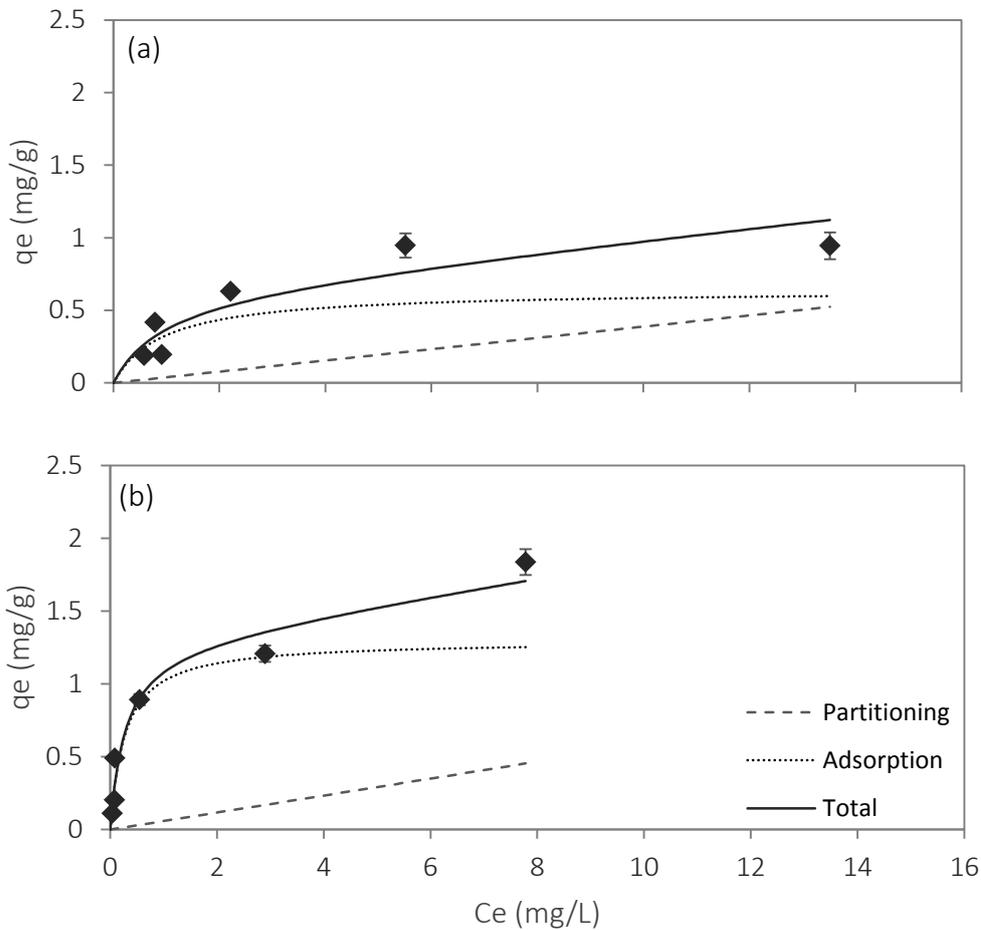


Figure 4-27: Dual-mode separated sorption isotherms for (a) SWP550 and (b) SWP700

The high influence of partitioning to SWP despite low amounts of chemisorption in the kinetic studies provides further evidence towards a poorly developed micropore network in the SWP biochars. An incomplete pore network does not allow for the rapid movement of atrazine through the biochar molecule, preventing rapid partitioning from occurring. This may be a similar effect to that observed by Braida et al.¹⁷⁴, who found that partitioning of benzene to charcoal particles is influenced by the structure of the pore network. The high influence of partitioning is therefore not inconsistent with the kinetic sorption studies, and provides further evidence towards the importance of the pore network to the sorption of atrazine.

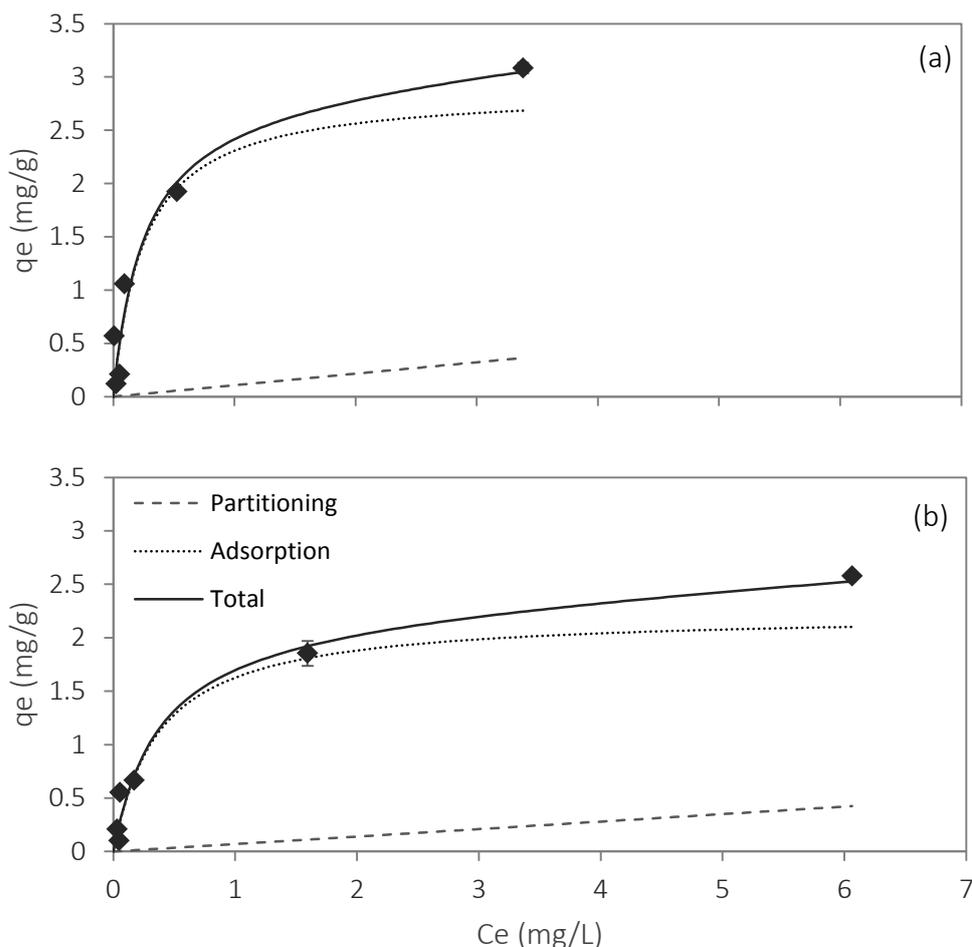


Figure 4-28: Dual-mode separated sorption isotherms for (a) WSP550 and (b) WSP700

The relative contribution of partitioning to the wheat straw biochars is low, suggesting that strong adsorption is dominating sorption. The volatile fractions of the wheat straw biochars are intermediate to high (10.55% and 7.38% for WSP550 and WSP700 respectively)¹²⁶, suggesting that the carbonised fraction is dominating sorption. The high contribution of adsorption is consistent with the results from the kinetic studies, which suggested that intraparticle diffusion is significant for the sorption of atrazine to wheat straw biochars. These combined results therefore suggest that non-linear pore filling dominates sorption of atrazine to biochar. As discussed in Chapter 2, pore filling is an effective method of immobilising contaminants in the environment due to the strong and irreversible nature of the interactions. However, the presence of pore filling effects can be further determined by investigating the interactions with humic acids, which can significantly reduce the influence of this mechanism in practice.

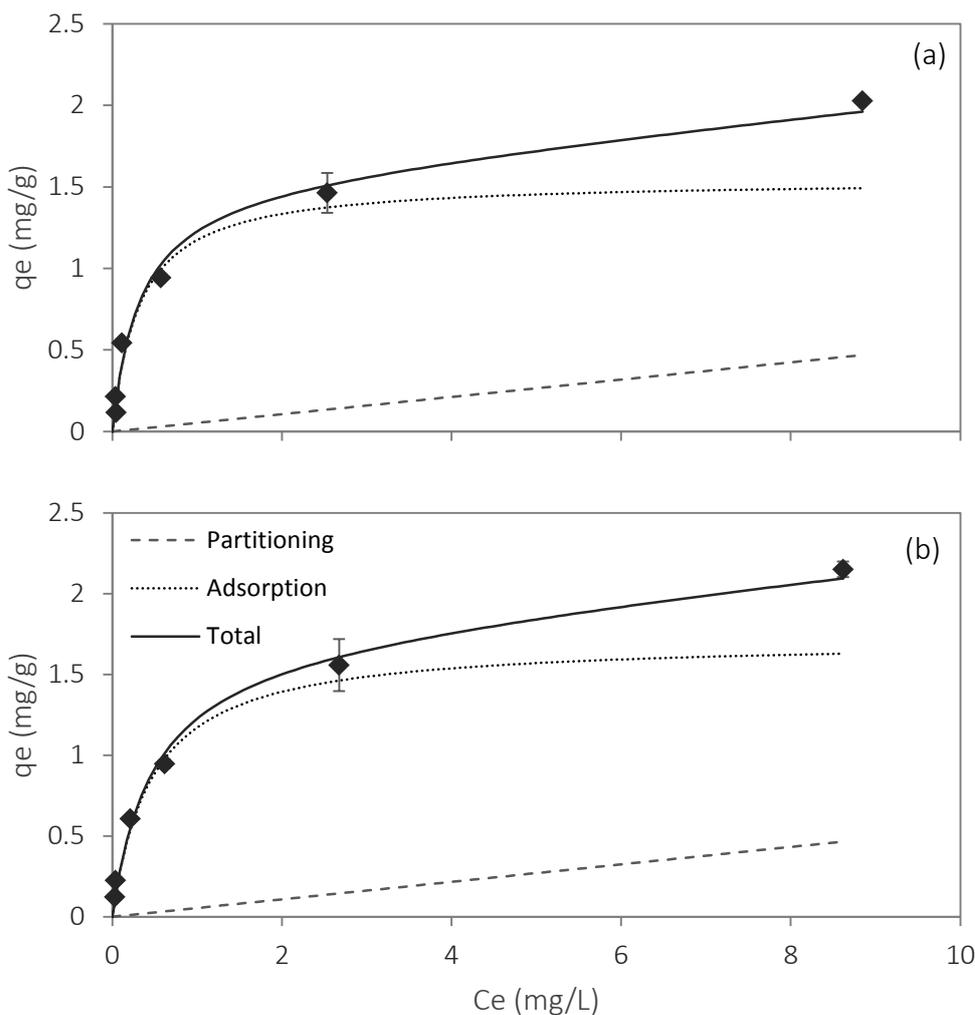


Figure 4-29: Dual-mode separated sorption isotherms for (a) MSP550 and (b) MSP700

There is some evidence of partitioning of atrazine to miscanthus straw biochars, although adsorption still dominates total sorption. The presence of partitioning may partially explain the rapid chemisorption observed in the kinetic tests, as partitioning would contribute to these rapid interactions¹⁴⁶. The intermediate to high volatile fractions (11.62% and 7.71% for MSP550 and MSP700 respectively)¹²⁶ suggest that amorphous components such as lignin, cellulose and hemicellulose are present, which provides sites to which partitioning may occur. However, the extent of rapid interactions observed in the kinetic studies is significantly higher than the extent of partitioning; suggesting that other mechanisms such as hydrogen bonding, π - π EDA interactions or hydrophobic effects may be present. Further pH-dependency tests can provide information on the presence of these mechanisms.

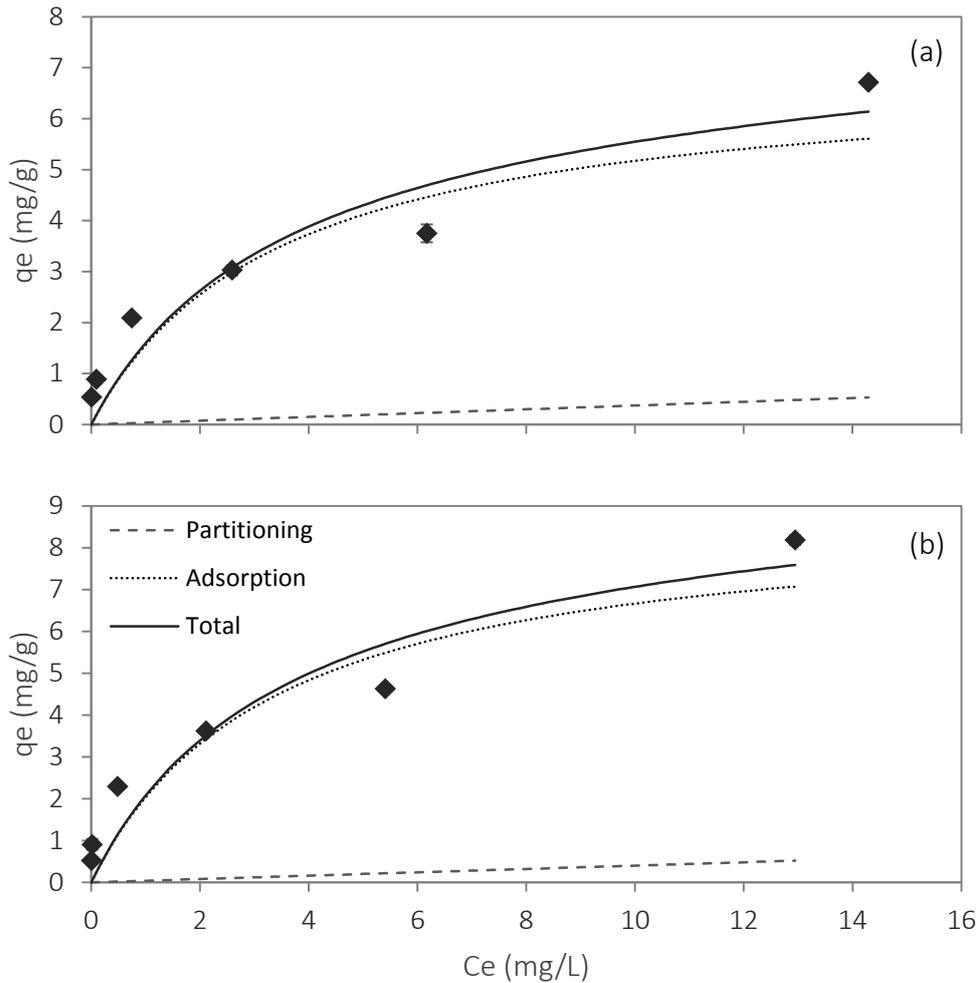


Figure 4-30: Dual-mode separated sorption isotherms for (a) RH550 and (b) RH700

The relative contribution of partitioning to the rice husk biochars was very low, suggesting that adsorption processes are dominating sorption. The kinetics studies suggested that adsorption mechanisms play a large role in the sorption of atrazine to RH biochars. The volatile components of the rice husk biochars are relatively low (7.48% and 4.99% for RH550 and RH700 respectively), suggesting that there is relatively little space available for amorphous partitioning. Notably, the high ash fractions of the rice husk biochars do not result in partitioning, suggesting that this component either does not participate in sorption or interacts in a different way with atrazine. The high overall contribution of adsorption and high adsorption capacity makes rice husk biochars well-suited to application in soil remediation.

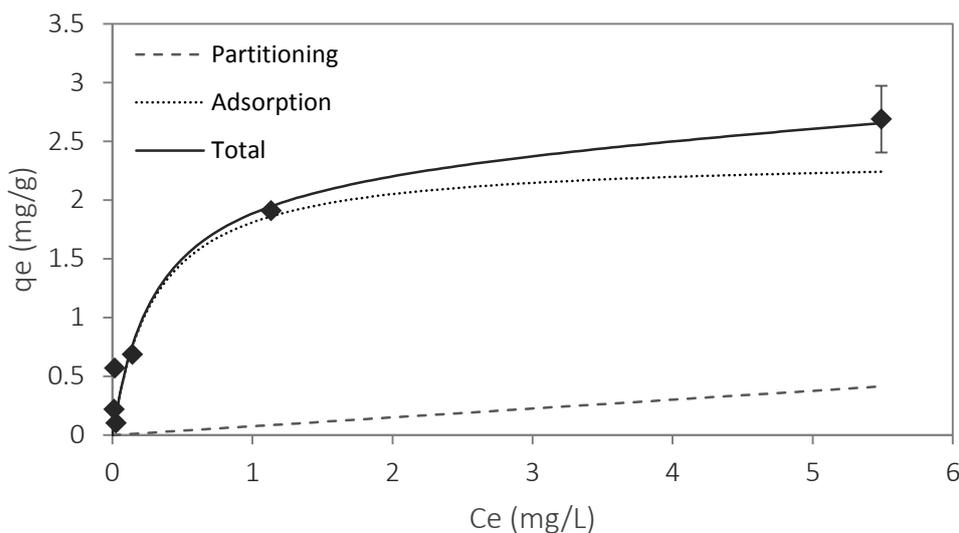


Figure 4-31: Dual-mode separated sorption isotherm for OSR550

Some partitioning of atrazine occurred to OSR550, although sorption was still dominated by adsorption mechanisms. A high adsorption component is consistent with the kinetic studies which showed that non-linear pore filling contributed highly to overall sorption at equilibrium. Partitioning to OSR550 is expected due to its high volatile fraction (16.38%), however the relative contribution was much lower than softwood biochars, which have comparable (although lower) volatile components. Notably, this partitioning fraction also does not fully account for the rapid interactions observed in the kinetic studies, suggesting that adsorption mechanisms such as hydrogen bonding, π - π EDA interactions or hydrophobic effects are also significant. Further tests investigating pH may be able to identify the nature of these interactions.

Table 4-4: Fitting parameters and summary of dual-mode sorption model

Biochar	Sorption Langmuir R^2	Adsorption Langmuir R^2	K_P (L/g)	Q_{max} (mg/g)
SWP550	0.730	0.700	0.038	0.640
SWP700	0.851	0.940	0.058	1.296
WSP550	0.891	0.923	0.108	2.882
WSP700	0.801	0.973	0.070	2.231
MSP550	0.944	0.978	0.053	1.545
MSP700	0.968	0.989	0.054	1.716
RH550	0.866	0.877	0.037	6.965
RH700	0.890	0.890	0.040	8.919
OSR550	0.628	0.946	0.075	2.366

The relative contributions of adsorption to the overall sorption to each of the nine biochars are shown in Figure 4-32. The relative contributions show that for all feedstocks, adsorption played a greater role in sorption to the higher temperature biochar than to the lower temperature biochar, confirming previous results²⁷⁸. It also confirms that for all biochars, even those produced from SWP, adsorption contributed more than 90% of the total sorption at low, environmentally relevant concentrations, confirming the important role that it will play in immobilising contaminants in the environment. Notably, adsorption to RH biochars comprised over 90% of sorption even at high concentrations, suggesting a high number of sorption sites to these chars.

These results are generally in agreement with previous studies which have used the dual-mode sorption model for the sorption of organic compounds to biochar. Li et al.¹⁵² found that the sorption of atrazine to a series of lignin, softwood and hardwood biochars comprised adsorption for most of the biochars up to $C_e \approx 50 \mu\text{mol/L}$ (10.784 mg/L). Similarly, they also found that those produced from softwood and at lower temperatures had the lowest overall contributions of adsorption. These results therefore confirm the unsuitability of low-temperature softwood biochars for remediating atrazine in the environment. The high relative fractions of adsorption to the other biochars provides evidence that they will be effective at immobilising atrazine in the environment, although this is subject to the nature of the chemical interactions occurring. Insights into these interactions may be gained by investigating the influence of solution pH on sorption.

The limitations of the dual-mode model should also be acknowledged. The sorption isotherms did not reach clear stages of being dominated by linear partitioning, and therefore

the K_p values represent an approximation only. Similarly, as for the initial fitting of the Langmuir model, which assumed that sorption approaches a value corresponding to adsorption capacity, this value is also not clearly reached after accounting for partitioning. The adsorption capacities generated from the Langmuir model, while still useful for further analysis, should be confirmed by carrying out tests with adsorption inhibitors prior to real-world application.

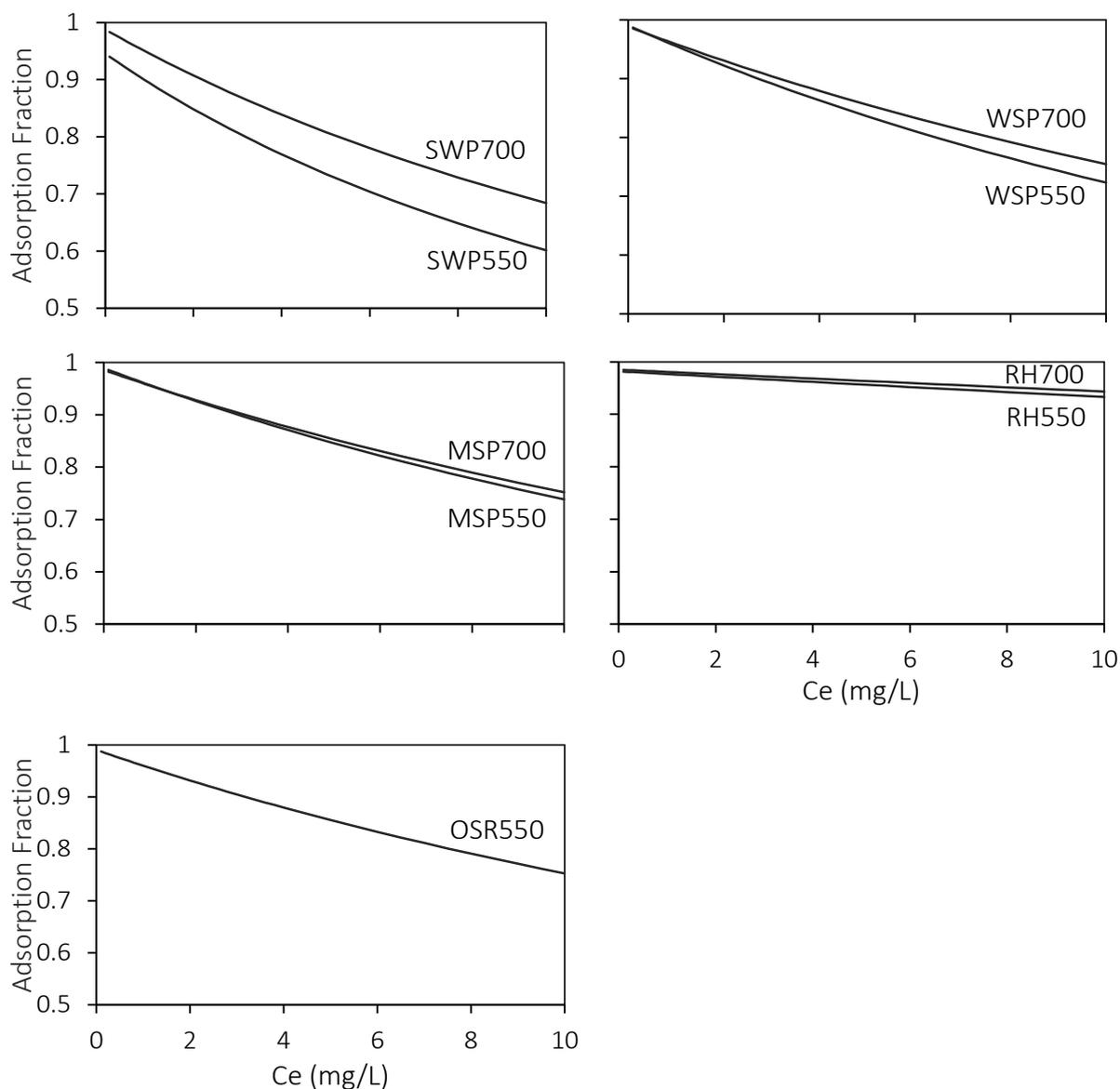


Figure 4-32: Relative contributions of adsorption to the overall sorption of the nine standard biochars, as a function of aqueous concentration

Partitioning appeared to have a significant effect on the sorption of atrazine to SWP and MSP biochars, a small effect on OSR550, and little effect on WSP and RH biochars. This suggests that WSP and RH biochars may be the most effective in remediating atrazine in soil. Notably, this is in agreement with the findings of Shen et al.¹³⁷ who found that WSP biochars were the

most successful at remediating heavy metals from soils. Further, for SWP biochars it suggests that sorption is largely controlled by partitioning, which would explain the relatively low sorption despite the high oxygen contents. Partitioning to the amorphous phase is expected to be much weaker than adsorption to the functionalised carbonised phase, which would explain the low sorption to these biochars, as well as the high influence of partitioning in overall sorption.

Summary of isotherm results

The isotherm studies showed that the sorption of atrazine to the standard biochars is highly non-linear and dominated by pore filling and adsorption. The isotherms showed good fits to the Freundlich model, suggesting that the heterogeneity of the biochars is significant in determining the sorption characteristics. In particular, the dual-mode separation model confirmed that the sorption of atrazine to the rice husk and wheat straw biochars is dominated by pore filling to adsorption sites, suggesting that these biochars can tightly and irreversibly bind atrazine in the environment. The influence of partitioning to softwood biochars was relatively high, suggesting that they may have little long-term relevance. The isotherm results also suggested that partitioning cannot fully explain the rapid interactions to the miscanthus and oil seed rape biochars, and therefore further investigations are necessary in order to determine their nature.

4.3 Summary and conclusions

The batch sorption studies have indicated that pore filling is a significant process in the immobilisation of atrazine to most of the standard biochars, while the influence of partitioning varies. Sorption to some biochars, such as SWP biochars, may consist of nearly 50% partitioning, while sorption to others, such as RH biochars, is dominated by adsorption mechanisms, even at high concentrations. Partitioning was shown in Chapter 2 to have little correlation with long-term remediation outcomes, while pore filling may effectively contribute to immobilisation method depending on the environmental conditions. The results therefore suggest that suitability of the standard biochars for use in remediation varies significantly. Detailed discussions of mechanisms and suitabilities for using each biochar in practice are given in Section 6.4.

Sorption to SWP biochars was low, and was controlled by partitioning, particularly for SWP550, while the extent and effectiveness of pore filling is greater for SWP700. Pore

diffusion was poor for both biochars, particularly SWP550, which could not be explained. The high influence of partitioning and vulnerability to the blocking of pore spaces suggests that SWP biochars are not well suited to the remediation of organic contaminants, although the adsorption mechanisms should also be considered.

The sorption of atrazine to WSP biochars is dominated by pore filling processes, with partitioning playing a relatively small role. This is in part attributable to the range of pore sizes available in WSP molecules, which allow for the efficient transport of atrazine to adsorption sites. However, these pores were blocked in the presence of humic acids, suggesting that sorption capacity may be reduced in soil. Further, some rapid chemical interactions were observed, suggesting that adsorption to macropores or mesopores may also be significant and should be further investigated. These results suggest that WSP may be a feasible option for remediating organic contaminants in practice, although the nature of the chemical interactions should first be understood.

Sorption to MSP biochars is highly influenced by pore filling, however the presence of chemical interactions was higher than for other biochars. Some partitioning was observed in isotherm plots; however the high influence of rapid chemical adsorption suggests that adsorption mechanisms are significant for the sorption of atrazine to MSP biochars. The suitability of MSP biochar for remediating organic contaminants in practice will therefore depend on the nature of these chemical interactions.

Sorption to RH biochars was significantly higher than to other biochars. The reasons for this are not fully understood, however effective pore filling is likely to contribute. Similarly, the role of partitioning was very low, suggesting that RH biochars may effectively immobilise atrazine in the long-term. Further analysis of the chemical mechanisms is necessary in order to more accurately determine their suitability in practice.

Sorption to OSR550 was heavily influenced by inefficient pore diffusion, as the kinetic studies suggested that atrazine may not move efficiently through the biochar molecule. This was highlighted by the large reduction in sorption in the presence of humic acids. The results also suggested the presence of strong chemical interactions, however these were also potentially hindered by the poorly developed pore structure.

Overall, the results suggested that biochars with a well-developed pore structure can facilitate rapid chemical interactions and provide resistance to blockage of pores by soil organic matter. Designers should therefore prioritise the use of feedstocks which are capable of developing these pore networks. However, the extent and nature of the adsorption mechanisms will significantly influence the long-term feasibility of using biochar and therefore requires further investigation.

Chapter 5: Adsorption mechanisms of atrazine to standard biochars

The adsorption mechanisms of atrazine to biochar will have a significant influence on the long-term remediation outcomes. It is important to understand how atrazine is bound in order to accurately predict the risks involved with changing environment pH, heavy rainfall, biological processes, or other unforeseen conditions. Chapter 4 highlighted the way in which atrazine was transported to adsorption sites, and the potential influence of partitioning in overall sorption. This chapter therefore investigates the sorption mechanisms that occur at these sorption sites, which will directly affect long-term remediation outcomes using biochar. It determines these effects through investigating the influence of pH on atrazine sorption which promotes the presence of various mechanisms in different ranges. It then determines the relationships between the properties of the biochars and their sorption capacities as determined in Chapter 4, before combining the data with previous studies available in the literature into a meta-analysis of the role of different biochar properties.

5.1 pH dependent behaviour of standard biochars

Measuring the influence of pH on the sorption of organic compounds is a useful way to isolate sorption mechanisms that may change their behaviour based on the pH of the solution. Atrazine is a weakly basic compound ($pK_a = 1.7$) and will therefore exist as a cation at very low pH values. Conversely, the measured pH values of the biochars were between 7.91 and 10.03 (Figure 5-1), suggesting that its surface charge and electron availability may be pH dependent. The influence of pH may be significant for predicting the long-term efficiency of adsorbents in the environment, as the pH of the soil can change due to processes such as chemical oxidation of the soil, the presence of other contaminants, or acidic rainfall. It is therefore important to understand how pH may influence the mobility of adsorbed contaminants.

5.1.1 Buffering capacities

The buffering properties of the nine standard biochars are shown in Figure 5-2, and allow for determination of the pH_{pzc} as given in Figure 5-1. In general, the biochars showed strong abilities to buffer solutions towards pH values of approximately 10, suggesting that the presence of biochar may allow the soil matrix to resist small changes of pH in the

environment. These plots also suggest that the surfaces of the biochars are positively charged at low to neutral pH values, and negatively charged only under very alkaline conditions. The buffering effect is the result of the release of alkaline mineral components of the biochars, resulting in high solution pH values^{213,279} together with alkaline functional groups on the biochar surface such as ketones.

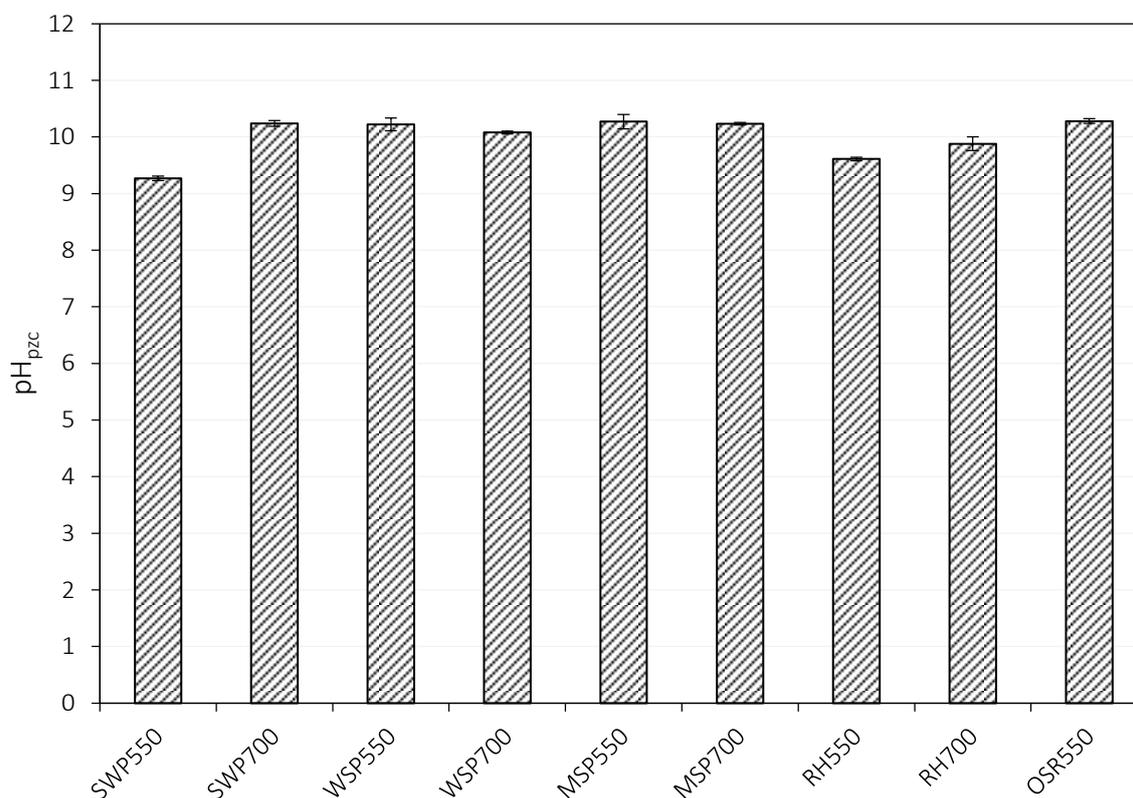


Figure 5-1: pH point of zero charge values for the standard biochars in the presence of atrazine

Biochars of different feedstocks showed different buffering capacities, which can be attributed to influences of ash and the functional groups. SWP biochars showed relatively little buffering, particularly SWP550 which did not significantly change the solution pH at all below pH4. This is consistent with the low ash fractions of the SWP biochars and the low pH values measured by UKBRC. Conversely, WSP, MSP and OSR biochars showed very good buffering, even at low pH values. This is consistent with their relatively high ash contents, and suggests that they have enough inorganic alkaline components to neutralise small additions of HCl. Notably, these biochars also had better buffering capacities than RH biochars, despite RH biochars having by far the highest ash contents of all of the standard biochars. While RH biochars did demonstrate reasonable buffering capacities, the extent of this suggests that the ash fraction of the RH biochars may comprise different minerals or

crystalline structures to WSP, MSP and OSR biochars. The precise compositions of these fractions, and how these could change over time, may represent important factors in the use of these biochars in remediating organic compounds.

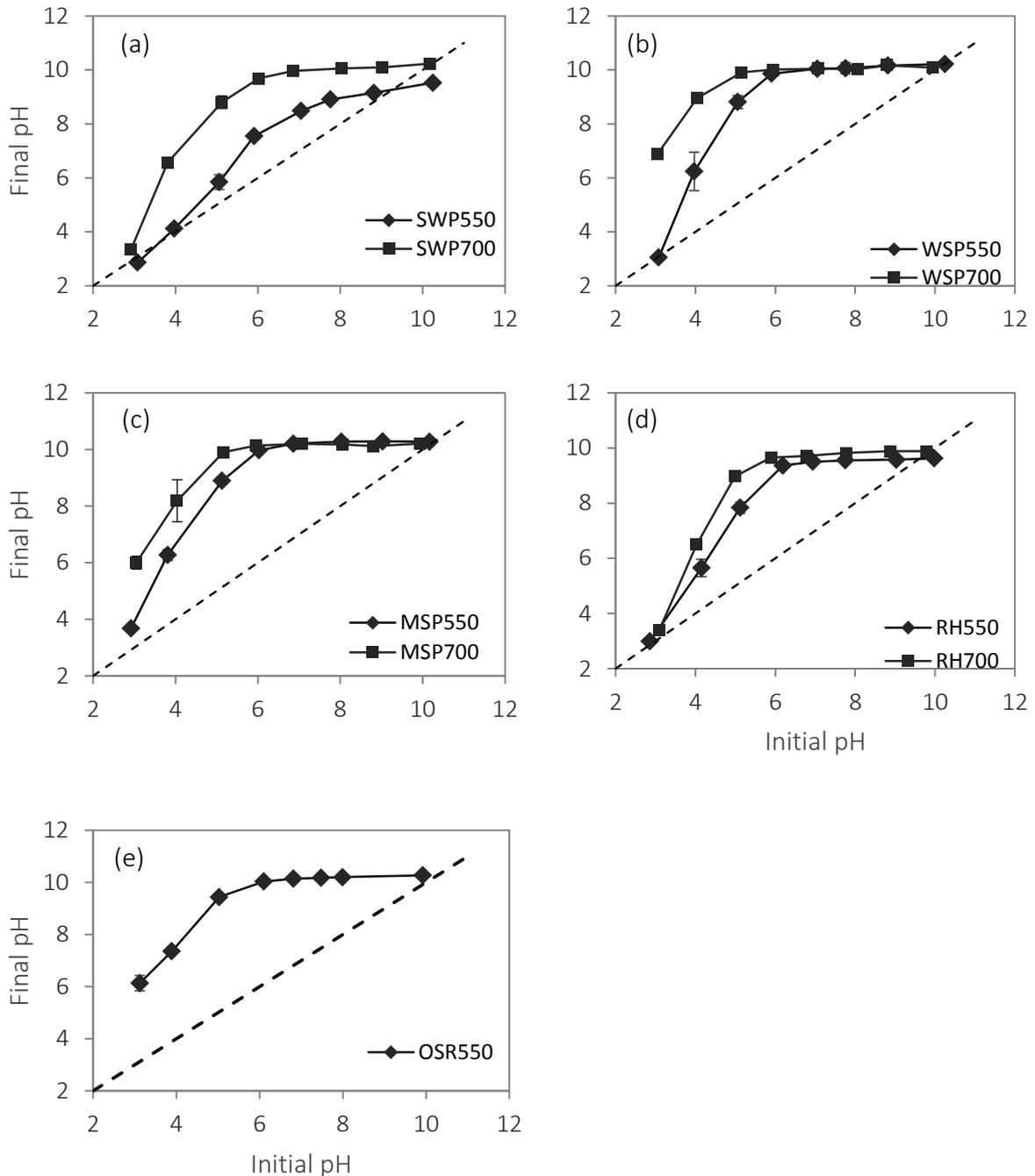


Figure 5-2: Initial and final pH values in solution in the presence of 10 mg/L atrazine by (a) SWP biochars; (b) WSP biochars; (c) MSP biochars; (d) RH biochars; and (e) OSR550 biochar

Other studies have also discussed the buffering effect of biochar and the role of this on atrazine sorption, although do not discuss the implications in detail. Zhao et al.²²⁷ noted the buffering effect of corn straw biochar in the presence of atrazine, although did not suggest a

reason for why it occurs. Wang et al.²⁰² observed the same effect for a wheat straw biochar and suggested that the presence of oxygen-containing functional groups can neutralise H^+ and OH^- ions in solution. Other studies which investigate buffering in general have discussed the effect of the ash content releasing soluble ions, resulting in a buffering effect^{105,106}. The buffering effect is therefore likely influenced by both the presence of oxygen-containing functional groups and the presence of the ash content. This effect is discussed further in the context of de-ashed biochars in Chapter 6.

5.1.2 Influence of solution pH on atrazine sorption to standard biochars

The sorbed amounts of atrazine (initial concentration = 10 mg/L) by initial and final solution pH values are given in Figure 5-3 to Figure 5-8. Blank tests showed negligible sorption of atrazine across all pH values. All biochars showed pH-dependent sorption of atrazine, suggesting that different mechanisms occur at different pH values to all biochar surfaces. It is necessary to show the sorption with respect to both initial and final solution pH, as both of these parameters are useful for explaining the mechanisms present.

Softwood pellet biochars

SWP biochars both demonstrated low sorption at very low pH values ($pH < 4$). This can be attributed to electrostatic repulsion between the positively charged atrazine molecule and the positively biochar surfaces in this range, as shown in Figure 5-4. This effect is also highlighted by the poor buffering effect of the SWP biochars meaning that the low pH values are not changed during the mixing process, as highlighted in Figure 5-3 (b) and (d).

At intermediate pH ranges ($4 < \text{final pH} < 8$), both biochars exhibited high sorption of atrazine. This can be attributed to the presence of hydrogen bonding, with biochar acting as the H^+ donor. At these values, the presence of the cationic atrazine molecule is negligible (see Figure 2-31), and the biochar surface is positively charged, as evidenced by the solution pH values being less than the pH_{pzc} values determined in Figure 5-2. This therefore allows for hydrogen bonding between the atrazine molecule and H^+ ions on the surface of the biochar, resulting in high sorption in this range. The presence of hydrogen bonds is consistent with the elemental and FTIR analysis for SWP550, which showed significant oxygen content as well as the presence of oxygen-containing functional groups respectively. However, the oxygen content of SWP700 is relatively low, and the FTIR analysis did not indicate the presence of oxygen-containing functional groups. Therefore, the presence of changing sorption due to

hydrogen bonding determined here suggests that the oxygen is contained within the pores of the biochar, and therefore does not contribute to surface functionality. This is also consistent with the relatively small contribution of rapid interactions determined by the kinetic analysis – as the oxygen groups are largely contained within the pores, they do not contribute to rapid chemisorption. Therefore the influence of hydrogen bonding is significant for both SWP550 and SWP700 biochars at intermediate pH ranges.

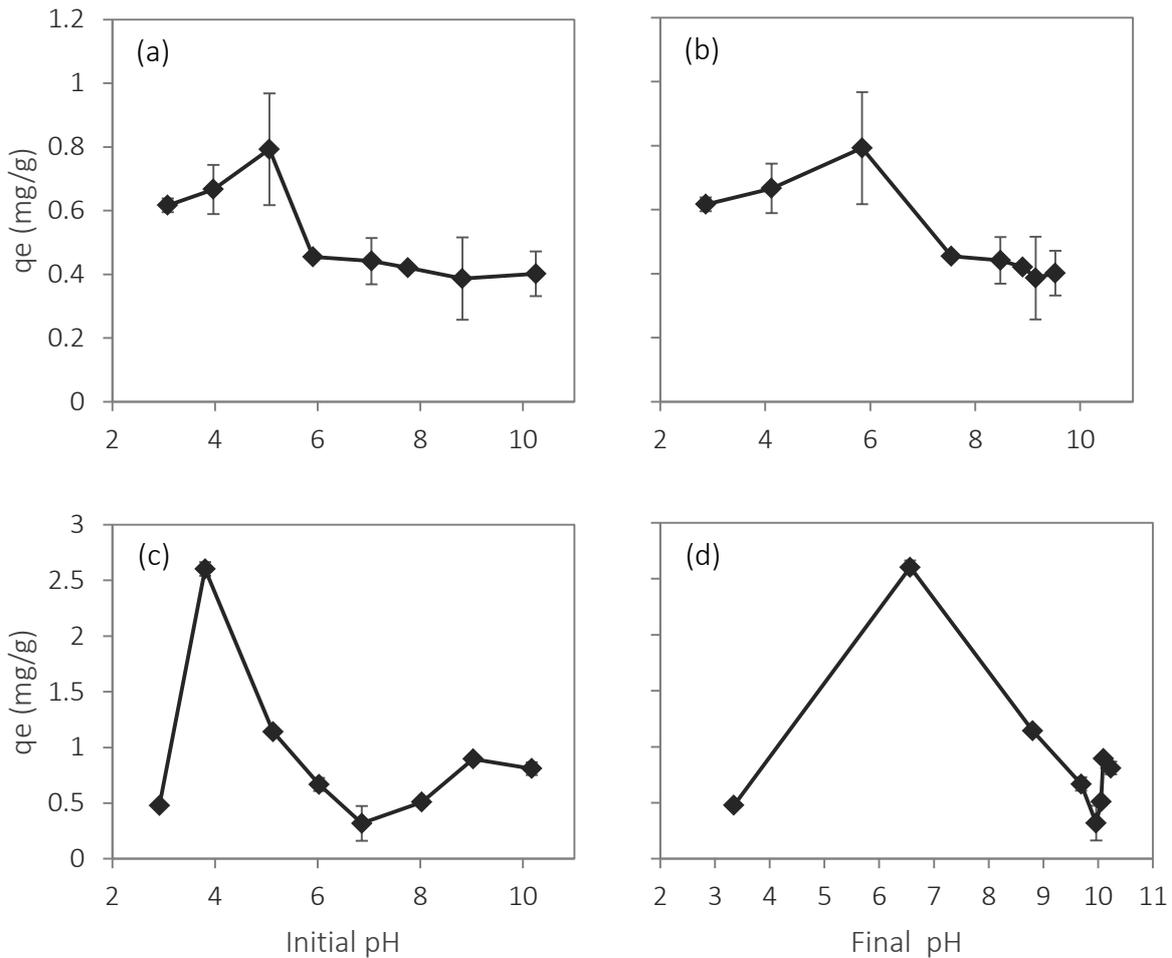


Figure 5-3: Sorption of atrazine by SWP biochars as a function of solution pH. (a) SWP550 by initial pH; (b) SWP550 by final pH; (c) SWP700 by initial pH; (d) SWP700 by final pH. Initial atrazine concentration = 10 mg/L; biochar mass = 0.1 g; solution contained 20 mL of 0.05 M CaCl_2 and 200 mg/L NaN_3 ; mixing time = 96 hours

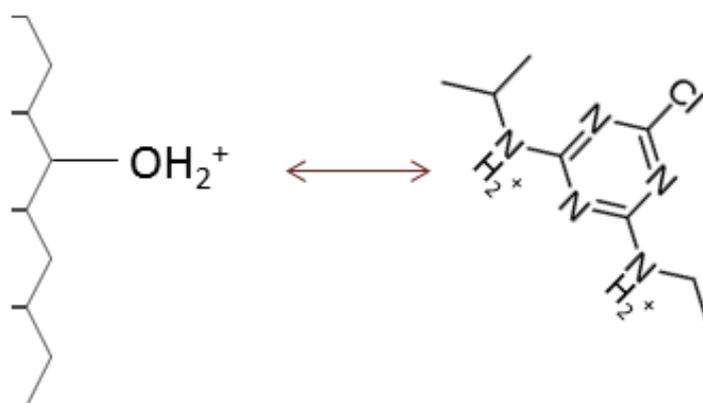


Figure 5-4: Electrostatic repulsion between biochar and atrazine at low pH values

At high pH ranges, the sorption of SWP550 is low, while SWP700 decreases sharply before rising for very high final pH values. This effect is likely due to the different contributions of π - π EDA effects between the two biochars. SWP550 has a relatively high O:C ratio and a high H:C ratio, while SWP700 has a relatively low O:C ratio and low H:C. This difference means that SWP700 has a more graphite-like structure, more electron-dense regions, and therefore a greater capacity to act as a π -electron donor and therefore experiencing increased sorption at high pH values. Conversely, SWP550 has a relatively high oxygen content and is therefore unable to act as a π -electron donor. The decrease at high pH values for SWP550 suggests that little hydrogen bonding is occurring where atrazine is donating the H^+ ion, resulting in decreasing sorption at high pH values. This is consistent with the results determined in Chapter 2, which suggested that atrazine more readily takes part in hydrogen bonding as a H^+ acceptor than a H^+ donor. This is also consistent with the isotherm analysis, which suggested that SWP700 was more condensed than SWP550 due to the higher sorption non-linearity. The pH-dependency tests therefore suggest that both hydrogen bonding is significant for both SWP550 and SWP700, while π - π EDA interactions are also significant for SWP700.

The prevalence of hydrogen bonding at intermediate pH values but not at high pH values is consistent with the chemical properties of atrazine. Atrazine has five sites capable of accepting H^+ ions but only two capable of donating H^+ ions²³⁸, and is therefore more prominent when the surface of biochar is positively charged and has an abundance of H^+ . As the surface pH of biochar increases the abundance of H^+ ions decrease while the abundance

of negatively-charged functional groups (such as $-O^-$) increase, and therefore sorption will decrease unless this difference is accounted for by a different mechanism.

Wheat straw pellet biochars

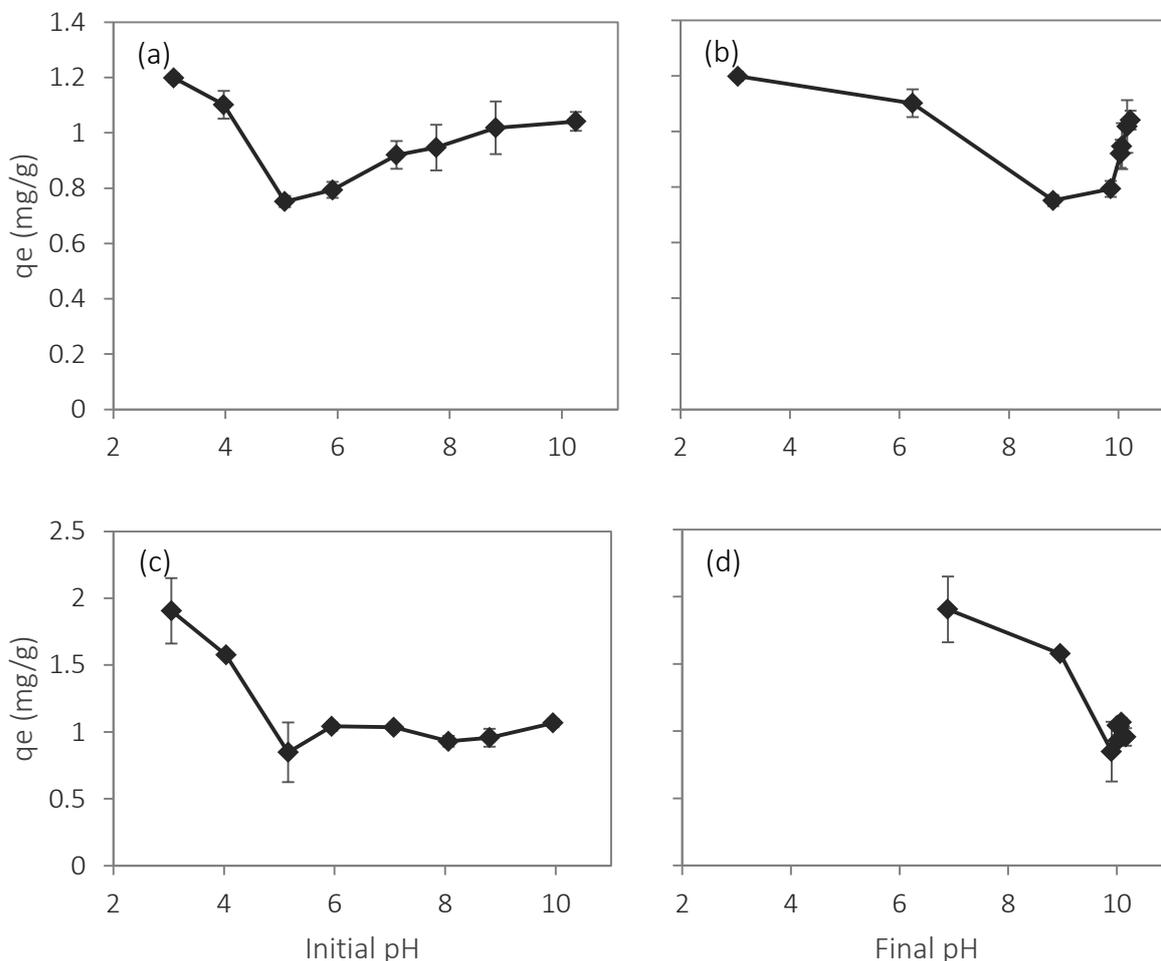


Figure 5-5: Sorption of atrazine by WSP biochars as a function of solution pH. (a) WSP550 by initial pH; (b) WSP550 by final pH; (c) WSP700 by initial pH; (d) WSP700 by final pH. Initial atrazine concentration = 10 mg/L; biochar mass = 0.1 g; solution contained 20 mL of 0.05 M $CaCl_2$ and 200 mg/L NaN_3 ; mixing time = 96 hours

WSP biochars showed similar pH dependent effects to each other across the entire pH range. Electrostatic repulsion effects at very low pH values were not present for WSP700 due to strong buffering effects. However, it is notable that WSP550 demonstrated high sorption at very low pH values, suggesting that electrostatic repulsion effects did not dominate sorption in this range. Possible explanations for this are that the high polarity of WSP550 allowed for strong hydrogen bonding in this range, which may outweigh the presence of repulsion effects. However, this effect was not observed for other biochars with high polarity values, such as SWP biochars. Another explanation is that the surface charge of WSP550 may not match that of the solution pH, or that a range of surface charges exist and there were still sufficient

neutral or negative groups to attract the neutral or cationic phase of atrazine. However, the trends in sorption at high pH values may also help to explain these effects.

Both WSP biochars showed high sorption at low-intermediate pH values ($4 < \text{final pH} < 7$) due to strong hydrogen bonding, with WSP biochars donating the H^+ ion. Both biochars then demonstrated greatly reduced sorption in the range $7 < \text{pH} < 9.5$, due to the reduction of this hydrogen bonding due to the removal of these H^+ groups as pH approaches pH_{pzc} . However, both WSP biochars then demonstrated increased sorption at very high pH values. As highlighted in Chapter 2, increased sorption at high pH values can be caused by three factors: (a) increased π - π EDA interactions with the highly negative surface of biochar; (b) increased hydrogen bonding with the negative biochar surface accepting an H^+ ion; or (c) hydrolysis or complexation involving the ash fraction. The increase is not likely to be due to π - π EDA interactions, as the increase is greater for WSP550 than for WSP700, despite its lower degree of carbonisation and higher abundance of oxygen groups. Similarly, interactions with the ash fraction would also be expected to be greater for WSP700 than for WSP550 due to the more abundant ash fraction. However, it is also possible that the crystalline form of the ash phase can influence the extent of hydrolysis¹⁵⁶, and more soluble forms produced at lower pyrolysis temperatures may be better able to catalyse the degradation of atrazine. However, the most likely explanation is that WSP biochars, and particularly WSP550 readily participate in hydrogen bonding. The greater magnitude of increase in WSP550 than WSP700 can therefore be explained by the greater abundance of oxygen groups on WSP550. This may also partially explain the lack of decreased sorption of very low pH values, due to the ability of WSP550 to readily form hydrogen bonds, as well as the greater absolute sorption of WSP550 than WSP700. Further analysis of the types of the oxygen groups present in WSP550 may confirm this analysis.

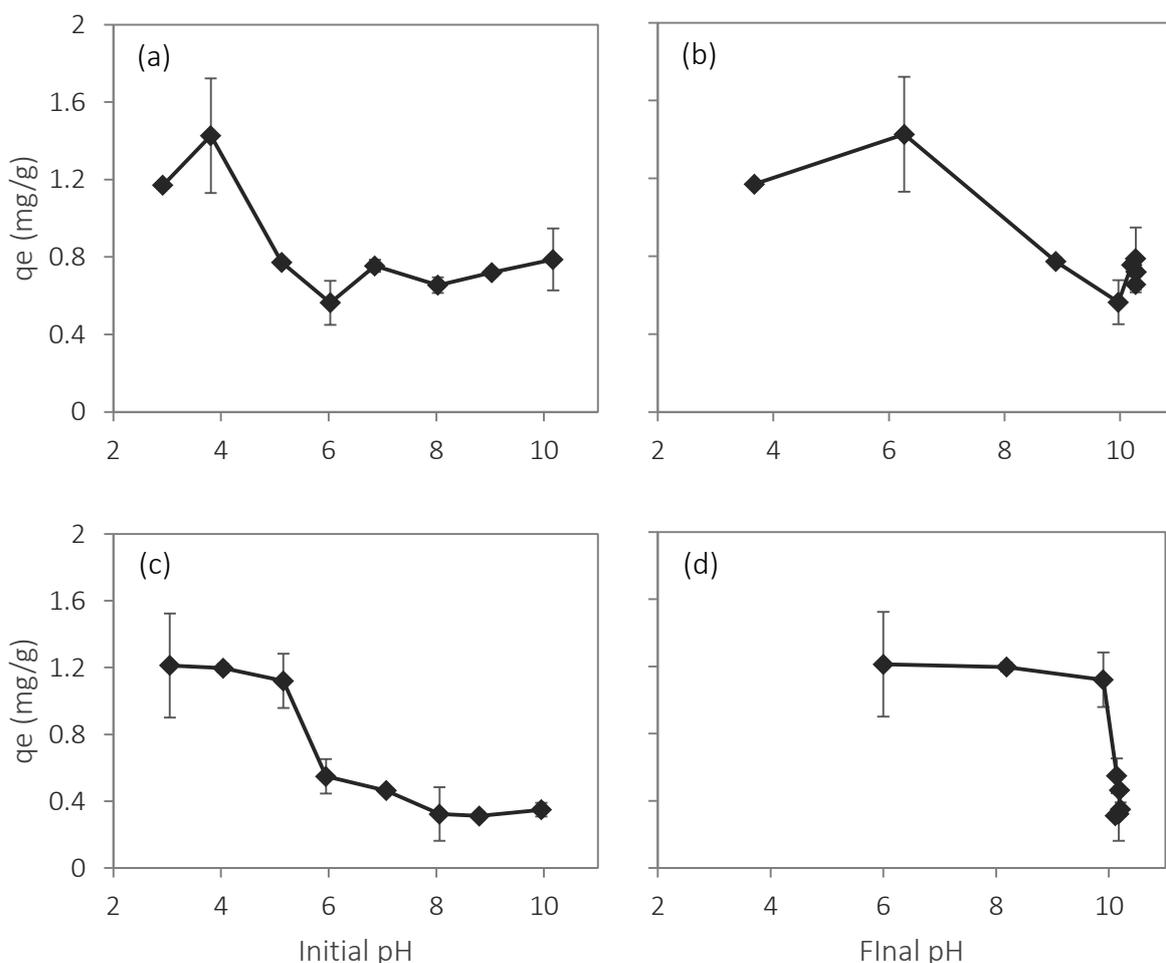
Miscanthus straw pellet biochars

Figure 5-6: Sorption of atrazine by MSP biochars as a function of solution pH. (a) MSP550 by initial pH; (b) MSP550 by final pH; (c) MSP700 by initial pH; (d) MSP700 by final pH. Initial atrazine concentration = 10 mg/L; biochar mass = 0.1 g; solution contained 20 mL of 0.05 M CaCl_2 and 200 mg/L NaN_3 ; mixing time = 96 hours

MSP biochars showed similar pH dependent effects to each other at low and medium pH values. MSP550 showed reduced sorption at very low pH values ($\text{pH} < 4$), due to electrostatic repulsion between the positively charged atrazine molecule and biochar surface. This effect was not present for MSP700, as its strong buffering ability increased the solution pH above this level. Both MSP550 and MSP700 showed high sorption at intermediate pH ranges ($4 < \text{final pH} < 9.5$), due to the presence of hydrogen bonding between H^+ molecules on the positively charged biochar surface and the atrazine molecule.

However, the two biochars showed different effects at very high pH values – MSP550 showed a sharp increase, while MSP700 showed a sharp decrease at pH values approaching 10. One possible reason for this discrepancy is the higher O content of MSP550 allowing for hydrogen bonding with MSP550 as the H^+ acceptor at high pH values. This also suggests

that, in contrast, MSP700 is not able to form hydrogen bonds as an H^+ acceptor due to its lower oxygen content. However, FTIR analysis of MSP700 does suggest the presence of $C=O$ groups, which may form hydrogen bonds. Further, the more carbonised structure of MSP700 should allow for π - π EDA effects at high pH values, as occurs for SWP700. The contrast between these results suggests that the sorption of atrazine to MSP biochars is predominantly controlled by hydrogen bonding, with MSP550 more readily able to form hydrogen bonds as a H^+ acceptor than MSP700. The difference between these results and those observed for SWP biochars highlights the differences between biochars with seemingly similar functional properties and difficulties in accurately characterising different biochars.

Rice husk biochars

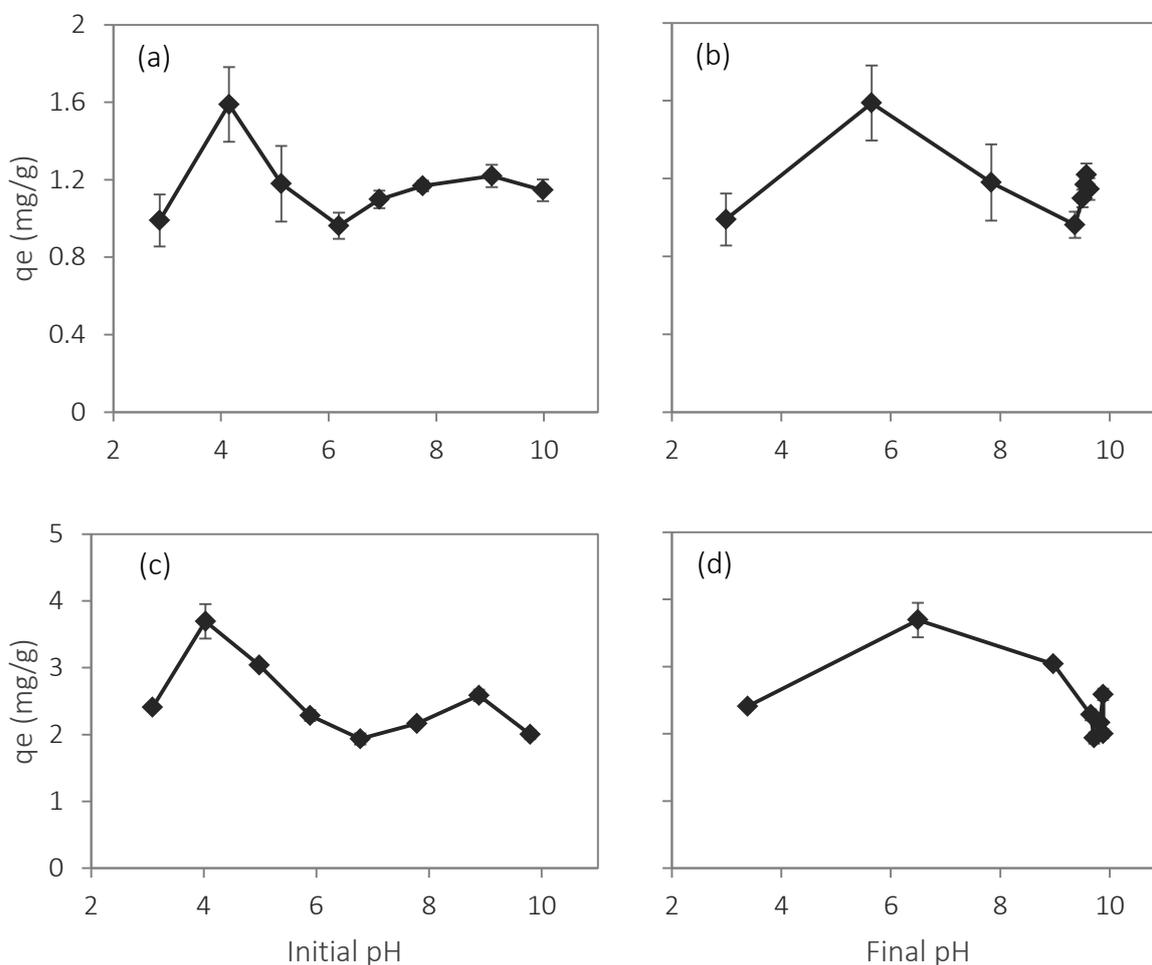


Figure 5-7: Sorption of atrazine by RH biochars as a function of solution pH. (a) RH550 by initial pH; (b) RH550 by final pH; (c) RH700 by initial pH; (d) RH700 by final pH. Initial atrazine concentration = 10 mg/L; biochar mass = 0.1 g; solution contained 20 mL of 0.05 M $CaCl_2$ and 200 mg/L NaN_3 ; mixing time = 96 hours

RH biochars show low sorption at very low pH values (final pH < 4) due to electrostatic repulsion between the cationic atrazine molecule and the positively charged form of atrazine.

This effect is particularly notable due to the poor buffering capacity of RH biochars at very low pH values. However, both RH biochars exhibit high sorption at intermediate pH values ($4 < \text{pH} < 9$), due to the presence of hydrogen bonding with the RH biochars acting as H^+ donors.

Both RH biochars also show sharp increases in sorption at very high final pH values. This effect can be attributed to either the interactions with the ash fraction¹⁵⁶ or the presence of π - π EDA effects with RH biochars acting as the π -donor. The low polarity values of the RH chars, and lack of $\text{C}=\text{O}$ groups in RH700 suggest that these biochars are not capable of forming hydrogen bonds as H^+ acceptors, meaning that this sharp increase is not attributable to hydrogen bonds. The high ash content and the low polarity and high aromaticity (low H:C ratio) mean that ash effects and π - π EDA bonding to the negatively charged biochar surface are both possible explanations for this sharp increase. Further investigation of the carbonised phase and the ash fraction are necessary in order to determine the cause of this effect.

Oil seed rape biochar

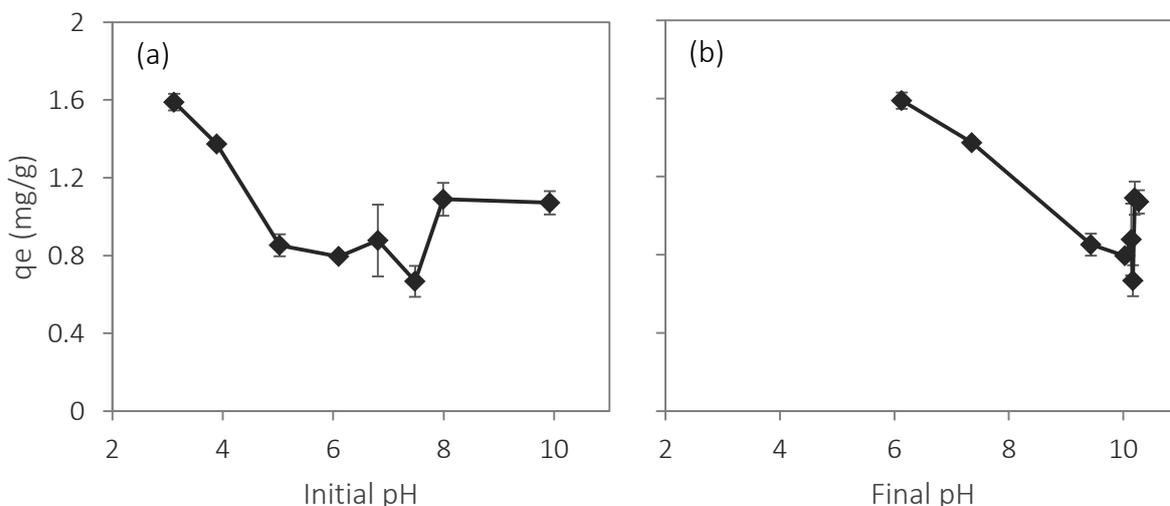


Figure 5-8: Sorption of atrazine by OSR550 biochars as a function of solution pH. (a) by initial pH; (b) by final pH. Initial atrazine concentration = 10 mg/L; biochar mass = 0.1 g; solution contained 20 mL of 0.05 M CaCl_2 and 200 mg/L NaN_3 ; mixing time = 96 hours

OSR550 showed similar pH effects to WSP biochars. Electrostatic repulsion at very low pH values was not present due to the strong buffering effect of OSR550. It showed high sorption at low-intermediate pH ranges, attributed to the presence of hydrogen bonding with oxygen-containing functional groups on the surface of the biochar. Sorption then decreased as pH increased due to the removal of these H^+ donor sites, before increasing sharply as pH reached pH_{pzc} . As with RH biochars, it is not possible to distinguish the effects occurring at high pH

values, which may represent a combination of hydrogen bonding, ash interactions and π - π EDA interactions to the carbonised fraction.

5.1.3 Discussion

Overall, the standard biochars showed similar pH effects across low-intermediate pH ranges, but different effects at high pH levels. All biochars that did not exhibit strong buffering at very low pH values demonstrated low sorption due to electrostatic repulsion between the positive atrazine molecule and the positive biochar surface, except for WSP550. All biochars then showed high sorption in the intermediate pH range, due to the presence of hydrogen bonding between atrazine and H^+ groups on the surface of biochar. Sorption then decreased for all biochars as pH approached pH_{pzc} and these H^+ groups were removed. Varying effects were then observed at $pH \approx pH_{pzc}$ or $pH > pH_{pzc}$, including π - π EDA effects due to the abundance of π electrons, hydrogen bonding with biochar acting as the H^+ acceptor, and interactions with the ash fraction.

Notably, it is these different mechanisms at high pH values that are likely to be the most significant in practice, as the buffering effect of the biochars will increase pH values to these levels. For example, strong hydrogen bonding with hydrogen acting as the H^+ donor for OSR550 will only be significant if the initial environmental pH is less than approximately 4, which is unlikely to be common in practice. Further, the range of mechanisms show that a small decrease in environmental pH may result in sharp increases or decreases in sorption, depending on the biochar used. However, a significant decrease in environmental pH is likely to result in increased sorption due to the increased extent of hydrogen bonding, while decreases necessary to result in electrostatic repulsion effects are unlikely to occur in practice.

The findings from these pH-dependency tests, when combined with the biochar characterisation, kinetic and isotherm studies provide novel insights into the contributing mechanisms over changing pH. In particular, the changing of the dominant mechanism from hydrogen bonding with abundant H^+ groups on the biochar surface in the range $4 \leq pH \leq 9$ to π - π EDA interactions at $pH > pH_{pzc}$ have not been thoroughly investigated before. Further, the absolute quantities and the high number of biochars that exhibit hydrogen bonding highlight the significance of the mechanism in immobilising atrazine. It is therefore not relevant to suggest a single dominant mechanism, but rather a changing dominant mechanism

from electrostatic repulsion to hydrogen bonding to other interactions based on environmental pH.

For RH and OSR biochars it was not possible to determine the processes resulting in the increased removal of atrazine at high pH values, due to competing influences of π - π EDA interactions and interactions with the ash fractions, as demonstrated in Figure 5-9. In order to isolate the effects of the ash fraction, it is useful to modify the RH and OSR biochars in order to remove the ash fraction and investigate the changing sorption processes. This is the basis of Chapter 6 of this thesis. Further, the tests so far have not provided insights into the relevance of hydrophobic effects. In order to determine the relevance of hydrophobic effects it is necessary to analyse the sorption capacities and properties of the biochar set as a whole. The following section details this analysis for the standard biochars and for all biochars used previously in the literature.

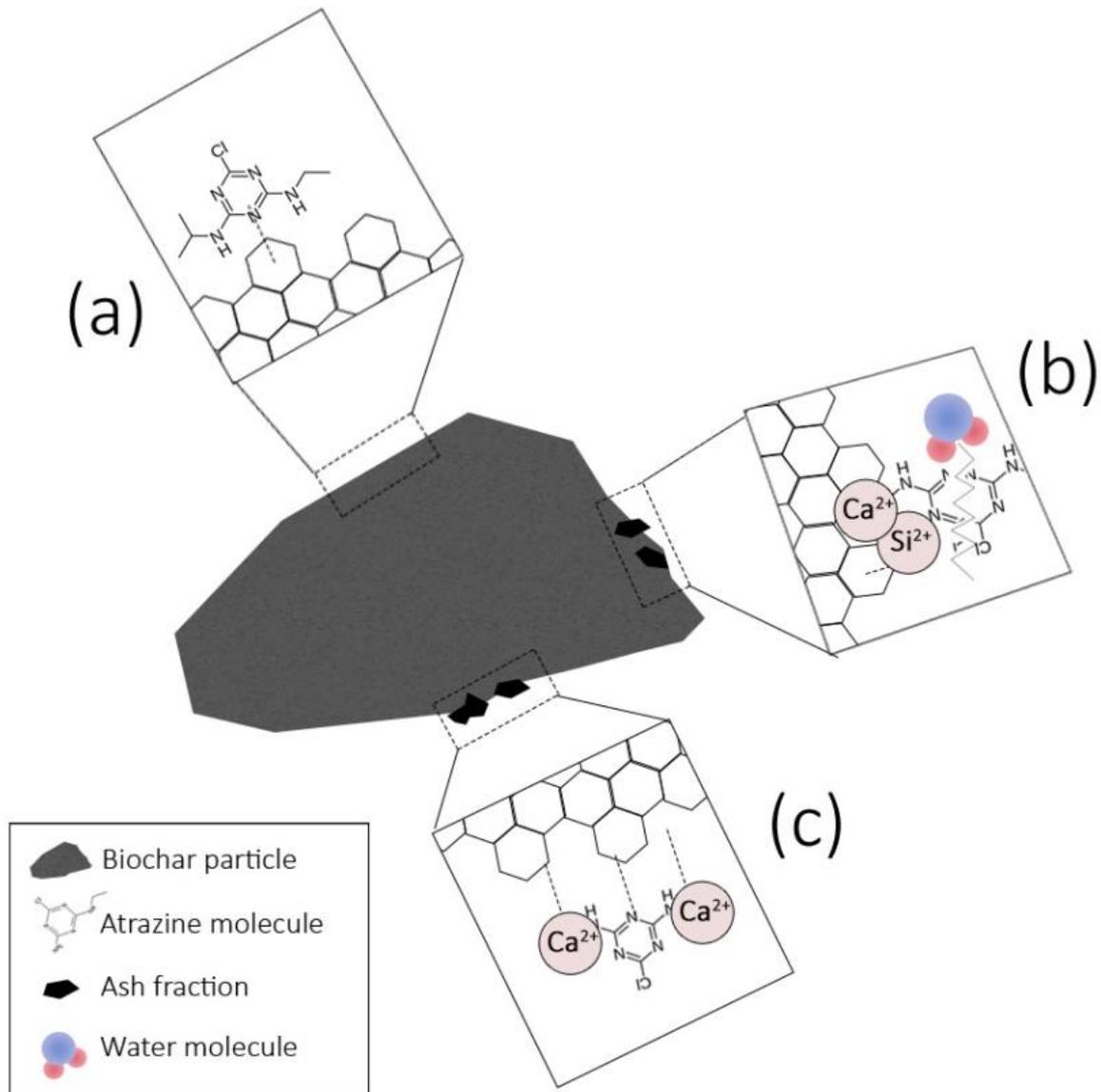


Figure 5-9: Factors influencing the increased removal of atrazine at high pH to RH and OSR biochars; (a) π - π EDA interactions with biochar acting as a π -donor; (b) catalytic hydrolysis of atrazine molecules in the presence of dissolved minerals; (c) complexation of atrazine in the presence of the ash fraction

5.2 Role of biochar characteristics on sorption mechanisms

In order to assess the role of different biochar characteristics on the sorption of atrazine, it is useful to look at the relationships between various biochar properties and sorption parameters. Previous studies have noted the significance of factors such as surface area, hydrophobicity, polarity, and carbon content to the sorption of various organic compounds. However, the precise role of each of these in immobilising atrazine is not entirely clear, with previous studies finding conflicting relationships between these parameters. This section

therefore addresses the overall properties of the standard biochars by comparing their respective properties with measures of partitioning and adsorption capacity. It then combines the data obtained in this study with that available in the literature to determine wider relationships between biochar properties and sorption parameters, and in particular the role of hydrogen bonding and hydrophobic effects.

5.2.1 Role of biochar characteristics on partitioning

The relationship between partitioning contributions and biochar properties depends on the relative abundance of the amorphous phase. Partitioning can contribute to total sorption but is unlikely to result in successful remediation outcomes, as outlined in Chapter 2, and it is therefore important to understand which biochar properties determine its significance. This section relates various biochar properties such as volatile fraction and oxygen content with partitioning in order to determine the factors controlling its influence.

The influence of biochar volatile fraction and oxygen fraction (as determined by UKBRC) on each of K_p and the percentage of total sorption controlled by adsorption (Q_A/Q_T) at $C_e = 10$ mg/L (as determined in Chapter 4) is shown in Figure 5-10. These two parameters are indicators of the total contribution of partitioning to total sorption. As discussed in Chapter 2, partitioning is likely to have little influence on overall remediation outcomes, and therefore biochars with low contributions of partitioning should be favoured where suitable. Correlations with K_p show weak trends ($R^2 < 0.1$), suggesting that partitioning cannot be fully explained by the presence of oxygen or of volatile components. This may be in part due to some contribution of adsorption to sorption linearity, particularly for the biochars where the isotherm did not suitably level off at high concentrations. Therefore, the percentage of sorption controlled by adsorption showed better fits with the volatile component and the oxygen content. Both the volatile component ($R^2 = 0.30$) and the oxygen content ($R^2 = 0.74$) show negative trends with adsorption contribution, suggesting that an increase in each of these variables increases the relative contribution of partitioning. These correlations therefore suggest that biochars with low volatile fractions and low oxygen contents are likely to adsorb atrazine more strongly. This is generally in agreement with previous studies, which have shown that as pyrolysis temperature increases, volatile and oxygen components are removed and sorption becomes stronger and more adsorption-dominated^{95,102}.

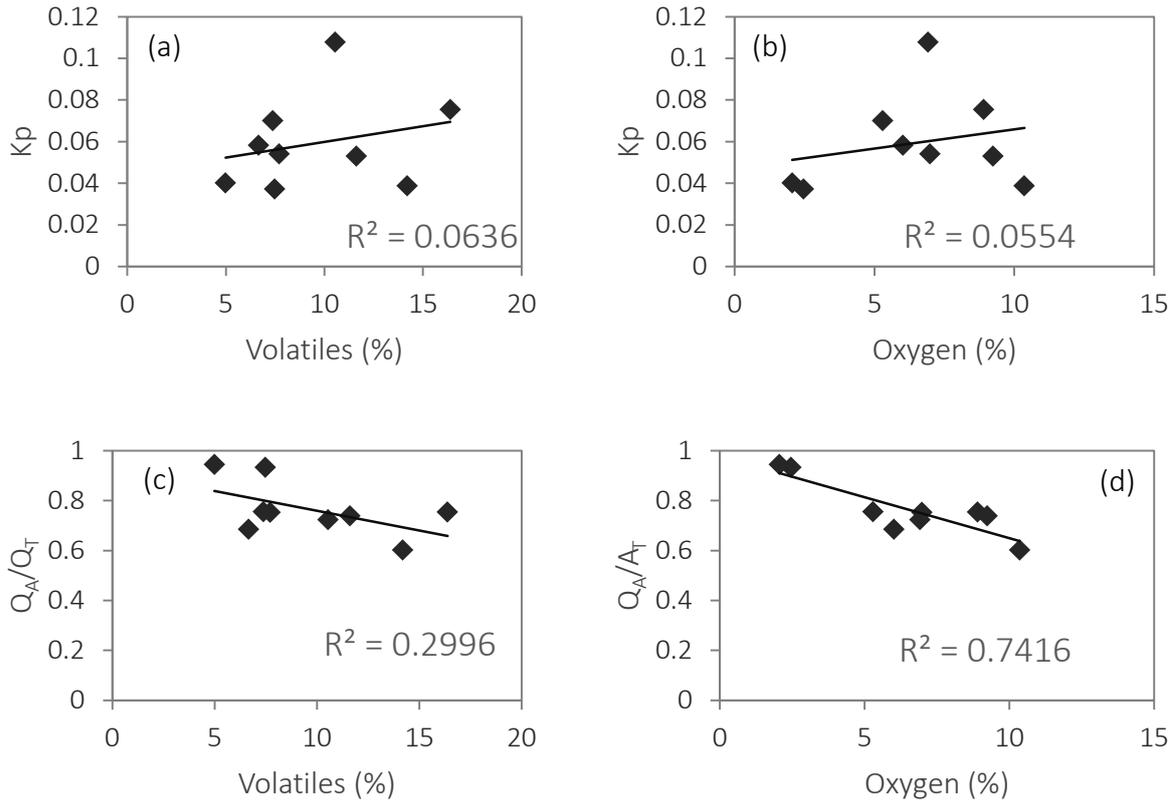


Figure 5-10: Correlations of partitioning coefficient with (a) biochar volatile fraction and (b) biochar oxygen content; and the percentage of sorption attributable to adsorption at $C_e = 10\text{mg/L}$ with (c) biochar volatile fraction and (d) biochar oxygen content

In order to further determine the biochar properties that contribute to partitioning, a predictive model of Q_A/Q_T was constructed based on the biochar properties. As the different properties such as O content and volatiles. The weightings of C, H, O, N and ash fractions were optimised for predictive accuracy of Q_A/Q_T by linear regression. The scatter plot is shown in Figure 5-11 and the predictive model is given as Equation 5-1. The predictive model suggests that carbon, oxygen and ash fractions contribute positively to adsorption, while hydrogen and nitrogen fractions contribute negatively (i.e., favour partitioning). The strong fit of the linear regression ($R^2 = 0.94$) suggests strong predictive power of the model.

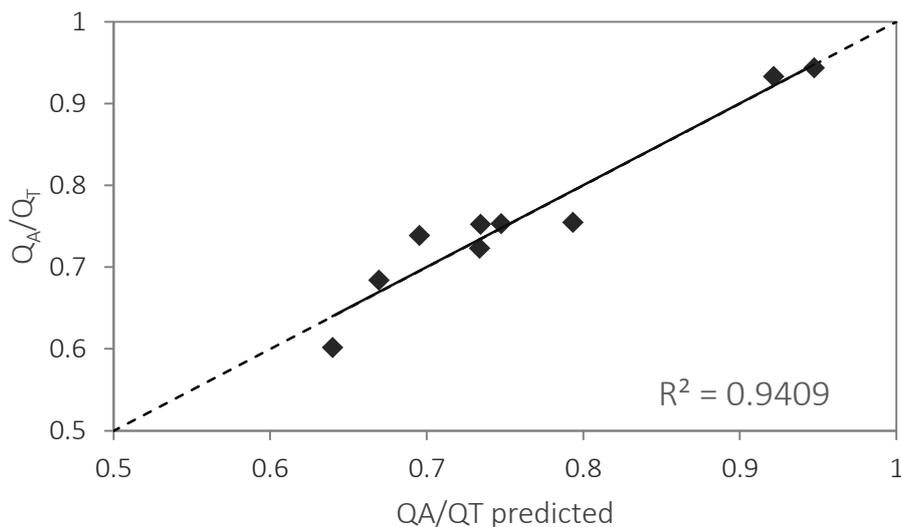


Figure 5-11: Scatter plot of a weighted product of C, H, O and N and ash contents against the relative contribution of adsorption at $C_e = 10$ mg/L

$$\frac{Q_A}{Q_T} = 0.004C - 0.05H + 0.009O - 0.02N + 0.01Ash + 0.342 \quad 5-1$$

The model suggests that hydrogen and nitrogen fractions are biggest contributors to partitioning. This is consistent with previous results, as a high hydrogen content suggests low aromaticity, and subsequently a high relative fraction of the amorphous phase to which partitioning may occur. Similarly, nitrogen exists primarily in the amorphous phase, and is therefore a useful indicator of the fraction of the biochar that is available for this mechanism. Conversely, a high carbon fraction promotes adsorption. This is as expected, as a high carbon fraction suggests high degree of carbonisation and aromaticity, providing sites for non-linear adsorption mechanisms such as pore filling. However, the positive contribution of oxygen suggests that the oxygen fractions in the standard biochars are primarily associated with oxidised functional groups in the aromatic phase promoting adsorption mechanisms such as hydrogen bonding and π - π EDA interactions. Further, the positive contribution of the ash phase is unexpected, as the presence of ash has previously been shown to decrease adsorption of organic compounds. This suggests that hydrolysis or complexation effects may be having large effects. The model therefore provides insights into ways to predict the relative contribution of adsorption and partitioning based on easily determined properties of biochar.

Relationships such as this between the partitioning of organic contaminants and biochar properties have not been carried out before to this author's knowledge. This is in part due to the shortage of papers that address the role of partitioning in depth, even among those which

have found it to be significant, and also due to the lack of discussion about its practical role in remediation.

5.2.2 Role of biochar properties on adsorption capacity

The role of biochar properties in determining adsorption capacity is important in determining the suitability of a biochar for use in immobilising contaminants in soil. The ability to suitably predict both the adsorption capacity and the long-term remediation outcomes will significantly aid developments of biochar as a useful amendment for contaminated soil. Further, the results from these models will provide relevant insights into the mechanisms occurring, as the significance of properties such as aromaticity, polarity and specific surface area suggest occurrences of hydrogen bonding, hydrophobic effects or pore filling. The following sections outline correlations of properties with adsorption capacity (note difference from *sorption capacity*; the role of partitioning is excluded), and the development of a predictive model for adsorption capacity based on the biochar properties.

Figure 5-12 shows correlations between a number of biochar properties and adsorption capacities for atrazine among the standard biochars. SSA shows effectively no correlation ($R^2 = 0.04$) with sorption capacity, which is most likely due to the inability of N_2 -BET analysis to effectively capture micropore area⁹⁴, and therefore SSA as measured by UKBRC is not a fair reflection of the available sorption sites for atrazine. Notably however, H:C ratio showed a negative correlation ($R^2 = 0.17$) with adsorption capacity, as did O:C ratio ($R^2 = 0.53$). These trends suggest that the sorption of atrazine is being controlled by hydrophobic effects, and not hydrogen bonding as suggested by previous analysis. The reason for the discrepancy between these results is likely due to the influence of pore structure on the sorption of atrazine, particularly SWP and WSP biochars, which is not fully captured by the elemental ratios or SSA values. Mandal et al.²⁴² similarly correlated a range of biochar properties with atrazine sorption and found increasing sorption with increasing O:C and H:C ratios, suggesting that a single study may not be a reliable indicator for such analyses.

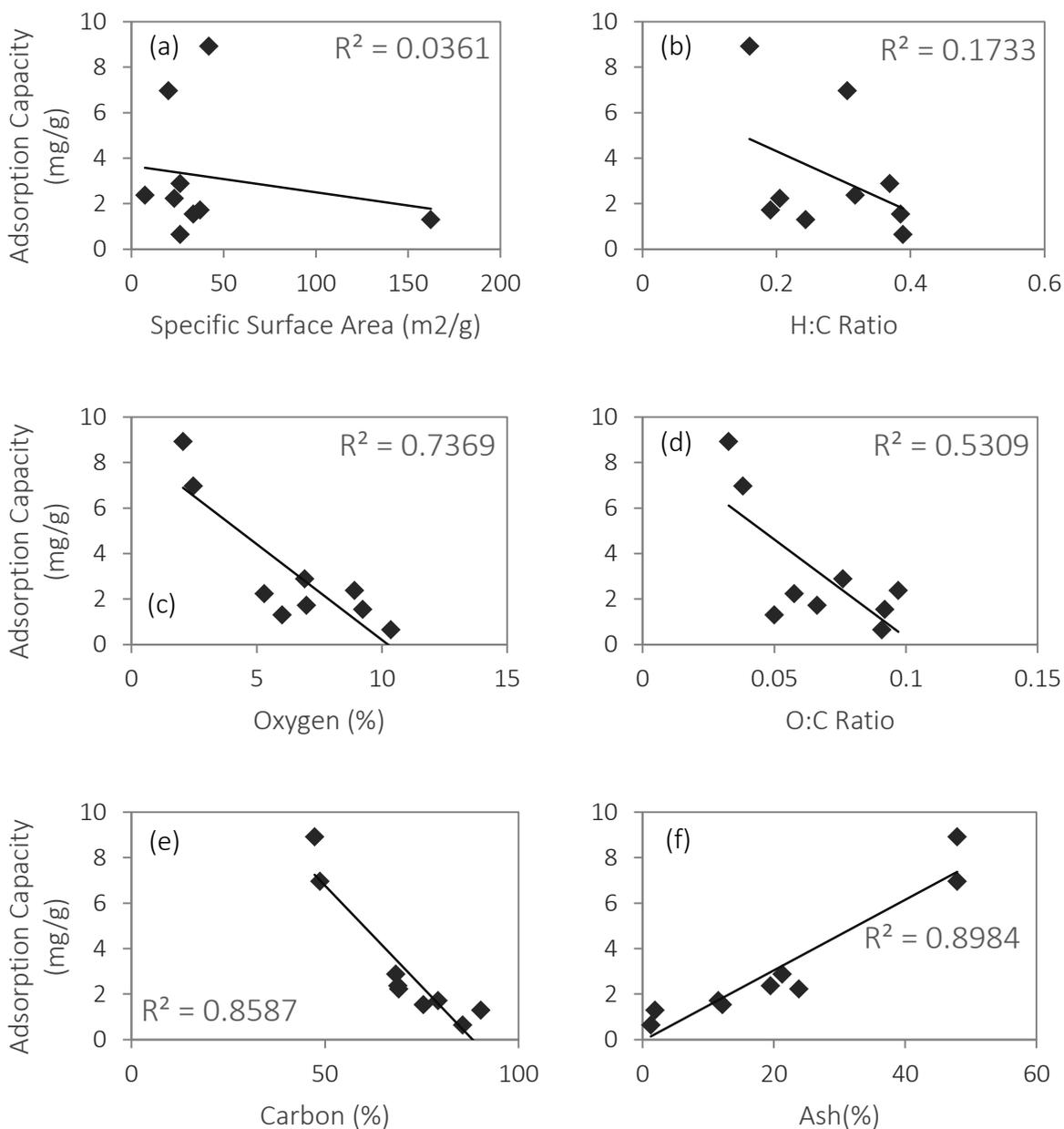


Figure 5-12: Correlations of adsorption capacity with (a) specific surface area, (b) H:C ratio, (c) oxygen content, (d) O:C ratio, (e) carbon content and (f) ash content

There was also a strong positive correlation between ash content and adsorption capacity. As noted in Chapter 2, many studies have suggested that the removal of ash increases sorption, and therefore this result appears counter-intuitive. There are several reasons for why a positive correlation of adsorption capacity with ash content may have been observed here. First, the ash itself may have a higher sorption capacity than the carbon component of the biochar, resulting in biochars with high ash contents displaying high adsorption. This is very unlikely, as numerous previous studies have shown that the ash fraction has a very low sorption capacity for organic compounds^{122,148,280}, including atrazine¹⁵⁶. Second, the ash

content may be contributing to the hydrolysis of atrazine, increasing apparent adsorption. This effect has been demonstrated before¹⁵⁶, as the release of minerals from the ash can catalyse reactions with atrazine when interacting with the surface of biochar. Finally, the presence of SiO₂ may correlate with well-structured pore networks, resulting in high amounts of pore filling to biochars with high ash contents, despite the ash content itself playing little role. Without further investigation of the ash component, it is not possible to distinguish between these explanations.

In order to better understand the role of the biochar properties on adsorption capacity, a predictive model was constructed. The model predicts the adsorption capacity of a biochar based on C, H, O, N, and ash contents, and well as SSA. The scatter plot of the model is given in Figure 5-13 and the model is given by Equation 5-2. The model shows a good fit ($R^2 = 0.98$) indicating that it is useful predictor of adsorption capacity. The coefficients of the optimised model suggest that oxygen, ash and surface area contribute positively to adsorption, while carbon, hydrogen and nitrogen contribute negatively.

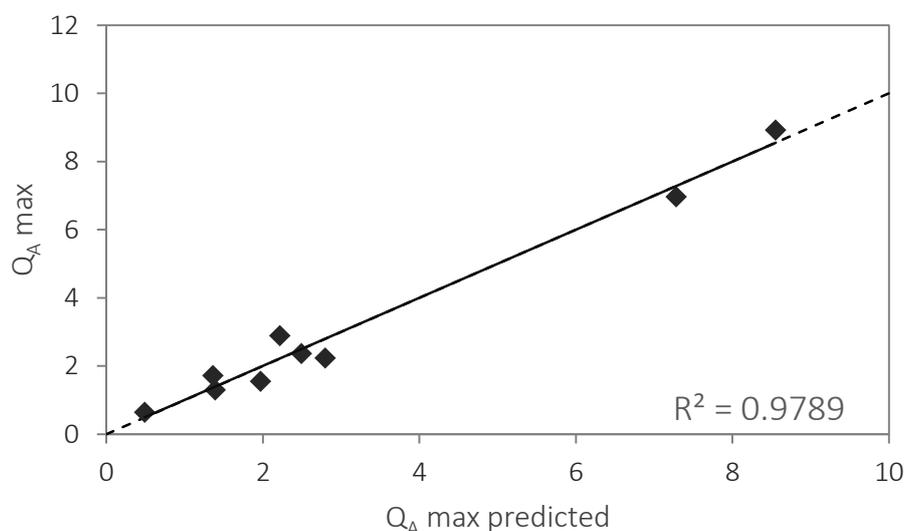


Figure 5-13: Scatter plot of predicted and actual adsorption capacities of the standard biochars based on a regression model

$$Q_{A,max} = -0.03 \cdot C - 0.91 \cdot H + 0.50 \cdot O - 1.42 \cdot N + 0.21 \cdot Ash + 0.016 \cdot SSA \quad 5-2$$

The reasons for hydrogen and nitrogen contributing negatively to adsorption are likely similar to those for why they contribute positively to partitioning: that they primarily comprise the amorphous phase and therefore do not partake in adsorption. Further, the positive

contribution of oxygen suggests that it provides sites for adsorption to occur, suggesting that either hydrogen bonding or π - π EDA interactions are significant for the sorption of atrazine to the standard biochars. This is in contrast to the results from simple correlations of biochar properties, which suggested that hydrophobic effects are more significant.

This analysis provides new insights into the role of hydrophobic effects in the sorption of atrazine to biochar. In particular, it suggests that hydrophobic effects do not significantly contribute to sorption after accounting for other variables such as surface area. As biochar hydrophobicity is also often correlated with higher surface areas, due to its relationship with pyrolysis temperature, hydrophobicity may correlate with high sorption capacity while having relatively little overall effect.

The model therefore provides a useful method of determining the role of biochar characteristics in the sorption of atrazine. However, the precise role of oxygen is still not entirely clear. Further, a number of studies have claimed that hydrophobic effects dominate the sorption of atrazine to biochar, while others have suggested that interaction with water molecules can reduce sorption to biochars with high oxygen contents. Both of these effects would result in oxygen having a negative effect on total adsorption. It is therefore necessary to further investigate the role of polarity (and conversely, aromaticity) in the sorption of atrazine to biochar.

5.2.3 Meta-analysis on role of biochar parameters on atrazine sorption

In order to provide a more comprehensive view on the roles of polarity and hydrophobicity on the sorption of atrazine to biochar, a meta-analysis of previous studies was carried out. This analysis can provide useful insights into the relative roles of hydrogen bonding and hydrophobic effects, for which previous studies have provided conflicting results. The sorption of atrazine at an equilibrium aqueous concentration of 2.5 mg/L was correlated with biochar properties in relevant previous studies. This concentration was determined in order to prevent extrapolating the sorption capacities of studies which investigated sorption at low concentrations, instead allowing for interpolation within the range which was studied. 39 biochars were analysed from 12 different studies, including the present study, which have conducted isotherms of atrazine to at least one biochar sample. The studies included in the analysis are given in Table 5-1. Several studies were also considered but not included in the analysis, as given in Table 5-2.

Table 5-1: Summary of studies and biochar properties used for meta-analysis of sorption characteristics

Study	Feedstock	HTT ^a	C (%)	H (%)	O (%)	SSA ^b (m ² /g)
Mandal et al. (2017) ²⁴²	Bamboo Chip	600	81.2	2.83	8.27	246.7
	Corn Cob	600	79.1	2.87	8.86	242.1
	Eucalyptus Bark	600	79.1	3.3	12.17	188.2
	Rice Husk	600	57.2	2.28	7.13	159.1
	Rice Straw	600	49.5	2.56	9.24	220.2
Ren et al. (2016) ¹¹⁶	Pig Manure	300	62.2	6.53	27.3	2.89
	Pig Manure	500	73	4.26	19	7.19
	Pig Manure	700	75.7	2.75	18.4	94
Zhou et al. (2016) ¹⁹⁶	Wheat Straw	550	85.6	3.75	6.93	8.8
	Peanut Shell ^c	550	88.4	2.59	6.99	19.7
Jin et al. (2016) ⁹⁶	Wheat Straw	300	63.3	4.4	24	2.59
	Wheat Straw	500	70.2	4.28	12.8	3.012
Liu et al. (2015) ²⁰⁸	Soybean	450	57.52	2.63	17.64	17.5
	Corn stalk	450	62.2	2.99	16.16	19.6
	Rice stalk	450	52.4	2.77	15.18	25.8
	Poultry manure	450	43.84	2.36	12.78	15.4
	Cattle manure	450	55.55	2.94	14.93	13.5
	Pig manure	450	41.24	2.02	11.65	13.4
Tan et al. (2016) ²²⁹	Corn Straw	500	42.328	1.17	14.23	32.85
Zhang et al. (2015) ²⁰⁴	Sewage Sludge	300	13.6	2.2	*	7.9
	Sewage Sludge	400	10.3	1.16	*	14.1
	Sewage Sludge	400	10.5	1.13	*	23.7
	Sewage Sludge	500	9.87	1.40	*	17.2
	Sewage Sludge	500	10	1.46	*	20.1
	Sewage Sludge	600	9.61	0.46	*	13.2
	Sewage Sludge	600	9.69	0.44	*	16
Cheng et al. (2014) ¹¹¹	Wood Charcoal	*	90.8	2.2	6.8	122
Zhang et al. (2013) ¹⁵⁶	Pig Manure	350	31.58	2.36	16.93	23.8
	Pig Manure	700	25.16	1.12	4.83	32.6
Zhao et al. (2013) ²²⁷	Corn Straw	450	75.17	3.25	20.6	44.97
Zheng et al. (2010) ²³⁶	Greenwaste	450	70.66	2.91	13.59	7.29
Present study	Softwood	550	85.52	2.77	10.36	26.4
	Softwood	700	90.21	1.83	6.02	162.3
	Wheat Straw	550	68.26	2.1	6.92	26.4
	Wheat Straw	700	69.04	1.18	5.3	23.2
	Miscanthus Straw	550	75.41	2.42	9.24	33.6
	Miscanthus	700	79.18	1.26	6.99	37.2

	Straw					
	Rice Husk	550	48.69	1.24	2.47	20.1
	Rice Husk	700	47.32	0.63	2.06	42
	Oil Seed Rape	550	68.85	1.82	8.91	7.3

* Value not supplied

^a highest treatment temperature during pyrolysis

^b specific surface area

^c Biochar was excluded due to extremely high sorption capacity

Table 5-2: Studies excluded from meta-analysis and reasons for exclusion

Study	Feedstock(s)	Reason for exclusion
Li et al. (2015) 152	Lignin, softwood, hardwood	Sorption capacities approximately 10x other studies
Cao et al. (2009) 226	Dairy manure	Biochars had very low carbon contents
Martin et al. (2012) ²⁴⁴	Poultry litter, papermill sludge	Hydrogen and oxygen contents not provided
Clay et al. (2016) 243	Maize, switchgrass, ponderosa pine	Methodology not clear
Wang et al. (2016) ²⁰²	Wheat straw	
Alam et al. (2000) ²³⁹	Charcoal	
Yang et al. (2017) ²²⁸	Wheat straw	
Deng et al. (2017) ⁹²	Cassava waste	
Spokas et al. (2009) ²⁴¹	Woodchips	Isotherms include soil
Ouyang et al. (2016) ²⁸¹	Corn cob, corn stalk, soybean straw, rice straw, corn stalk	No isotherms presented
Ouyang et al. (2016) ²⁸²	Corn straw	
Soni et al. (2015) 240	Pine wood chips	
Delwiche et al. (2014) ²⁸³	Pine chips	
Clay and Malo (2012) ¹³⁹	Maize stover	
Cao et al. (2011) 250	Dairy manure	
Nag et al. (2011)	Wheat straw	

Figure 5-14a shows the relationship between aromaticity (H:C ratio, where a low ratio represents high aromaticity) and atrazine sorption over the relevant studies, while Figure 5-14b shows the relationship between polarity (O:C ratio) and atrazine sorption over the relevant studies. Some positive correlation exists between sorption capacity and H:C ratio ($R^2 = 0.10$), while a weak negative correlation exists between sorption capacity and O:C ratio ($R^2 = 0.17$). However, in the case of H:C ratio, the positive correlation is heavily influenced by the high H:C ratios and sorption capacities determined by Zhang et al. (2015)²⁰⁴. Excluding these studies results in a weakly negative correlation ($R^2 = 0.10$; data not shown), suggesting that there is not a strong link between H:C ratio and sorption. However, both plots show relatively weak correlations, and further analysis is necessary in order to determine a meaningful relationship. These plots suggest that neither aromaticity nor polarity alone can accurately predict the sorption of atrazine by biochar.

The biochars used across the studies were produced from a range of feedstocks and under many different pyrolysis conditions, and therefore the H:C and O:C ratios do not move in isolation from other properties which also influence sorption. For example, biochars produced at high temperatures typically have low H:C ratios, low O:C ratios and high surface areas. High sorption at low H:C ratios may therefore also reflect the influence of surface area on sorption. The relationships between pyrolysis temperature and H:C ratio, O:C ratio and SSA for the biochars used in this analysis are shown in Figure 5-15. These plots for H:C ratio and O:C ratio show some correlations ($R^2 \approx 0.4 - 0.6$), suggesting that higher temperature biochars are more aromatic (i.e., have lower H:C ratios) and are less polar (i.e., have lower O:C ratios), confirming previous well-established results^{90,104}. It is therefore useful to normalise sorption by surface area to more accurately reflect the chemical interactions taking place.

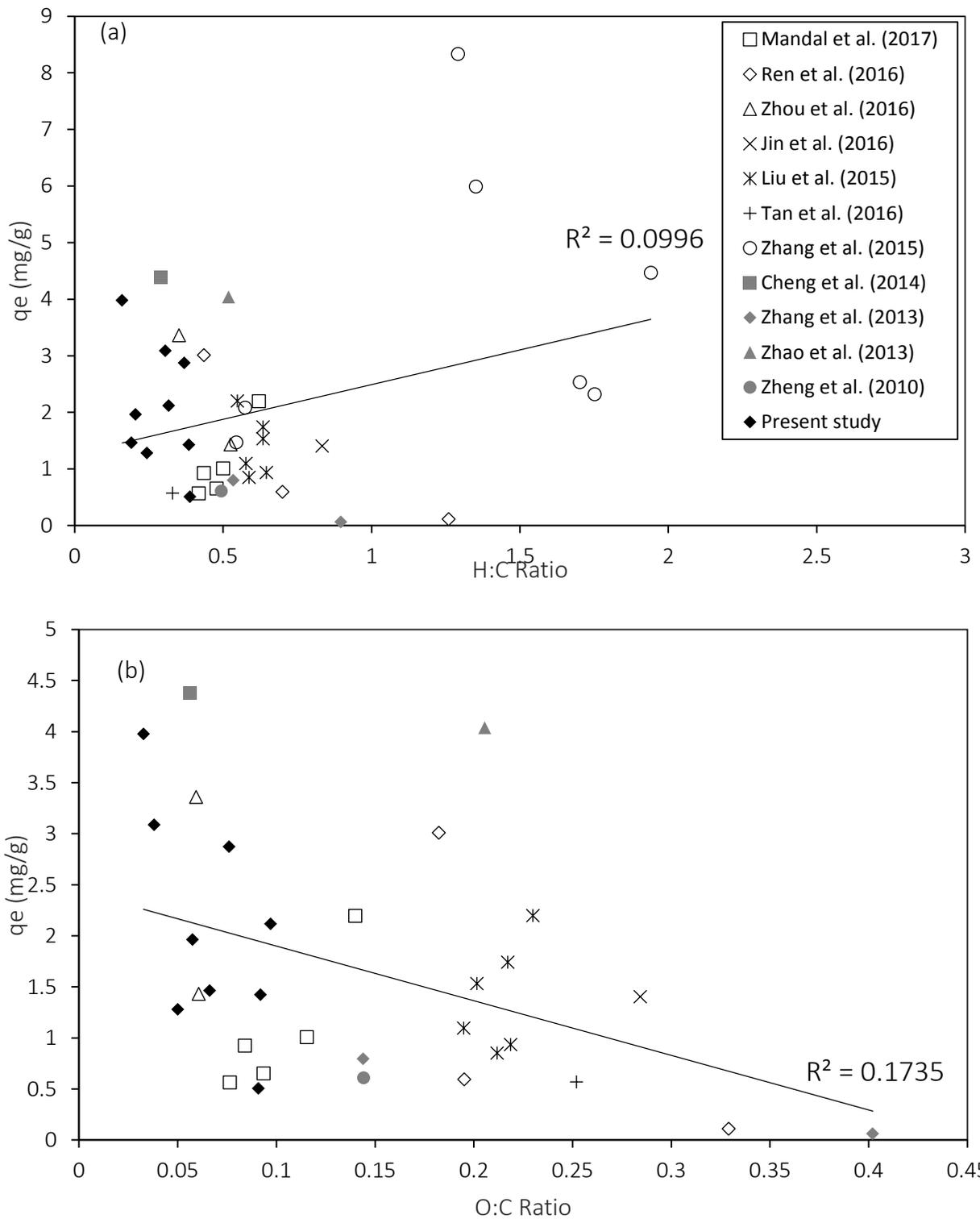


Figure 5-14: Relationship between sorption of atrazine at $C_e = 2.5\text{mg/L}$ and (a) biochar H:C ratio and (b) biochar polarity over reporting studies

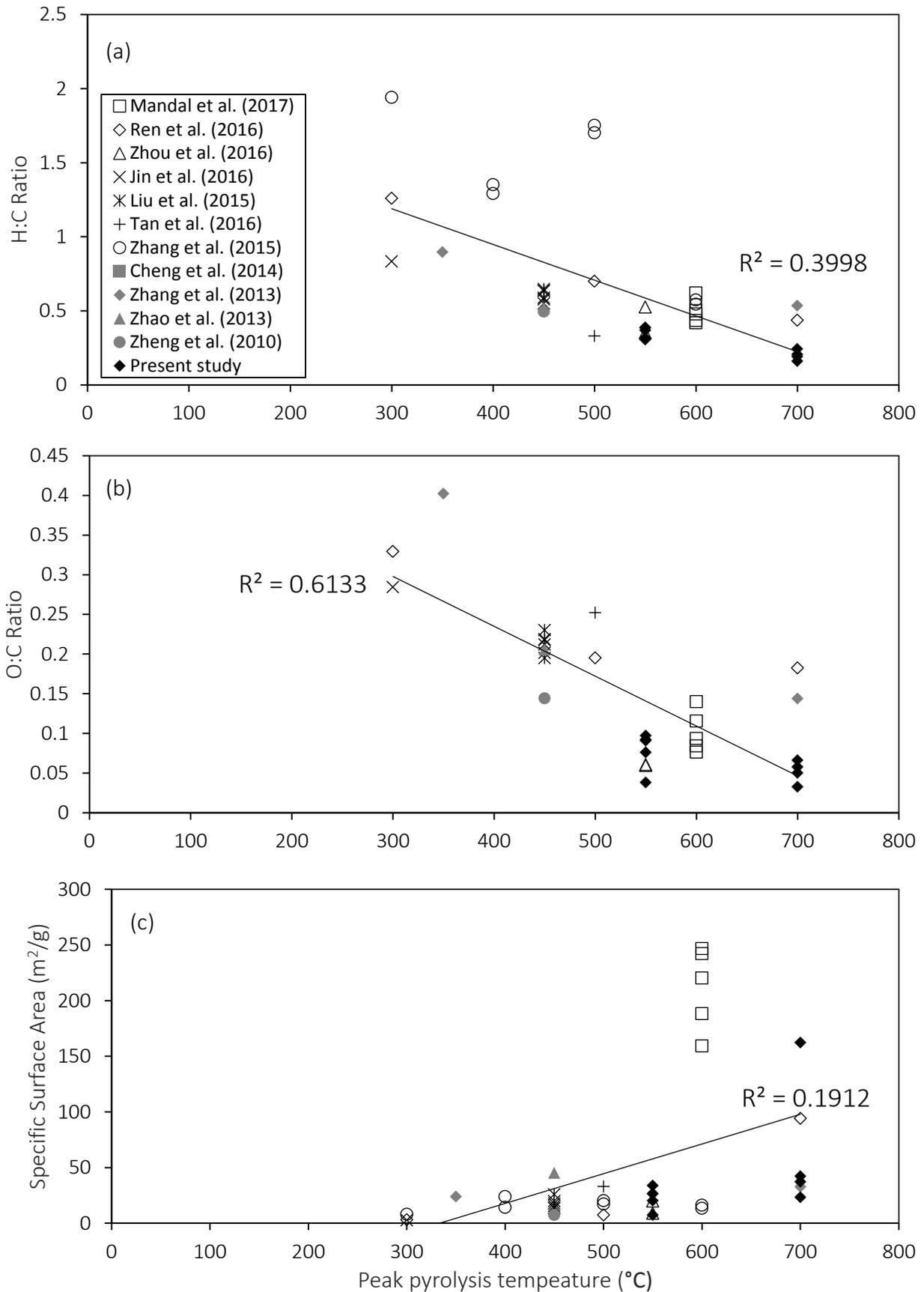


Figure 5-15: Correlations between highest treatment temperature and (a) H:C ratio, (b) O:C ratio and (c) specific surface area for biochars used to determine atrazine sorption

Sorption was normalised by surface area and correlated with aromaticity and polarity, in order to investigate the sorption of atrazine per unit area to various chemical structures. These correlations are shown in Figure 5-16. There is some evidence ($R^2 = 0.29$) that biochars with higher H:C ratios have higher surface-area normalised sorption, while there is no clear relationship ($R^2 = 0.01$) between polarity and surface-area normalised sorption. The positive relationship between H:C ratio and surface-area normalised sorption suggests hydrophobic effects are not dominating the sorption of atrazine, as more aromatic biochars showed lower sorption per unit area. The poor relationship between polarity and surface-area normalised sorption may suggest that the form of oxygen may also have a significant effect on sorption which is not captured by this analysis. For example, phenol groups will be able to donate H^+ ions in a hydrogen bond, and may therefore be more effective than carbonyl groups, which cannot. Cheng et al.¹¹¹ observed higher sorption per unit area to a wood charcoal after long-term exposure in soil, which was attributed to the oxidation processes increasing the availability of hydrogen bonding. This result may provide more directly comparable results than the present study, which will also be influenced by the different production parameters, feedstocks and sorption methodology. Few studies have investigated the influence of biochar oxidation on the sorption of atrazine, as detailed in Chapter 2, and therefore this meta-analysis provides the most widely applicable results available to date.

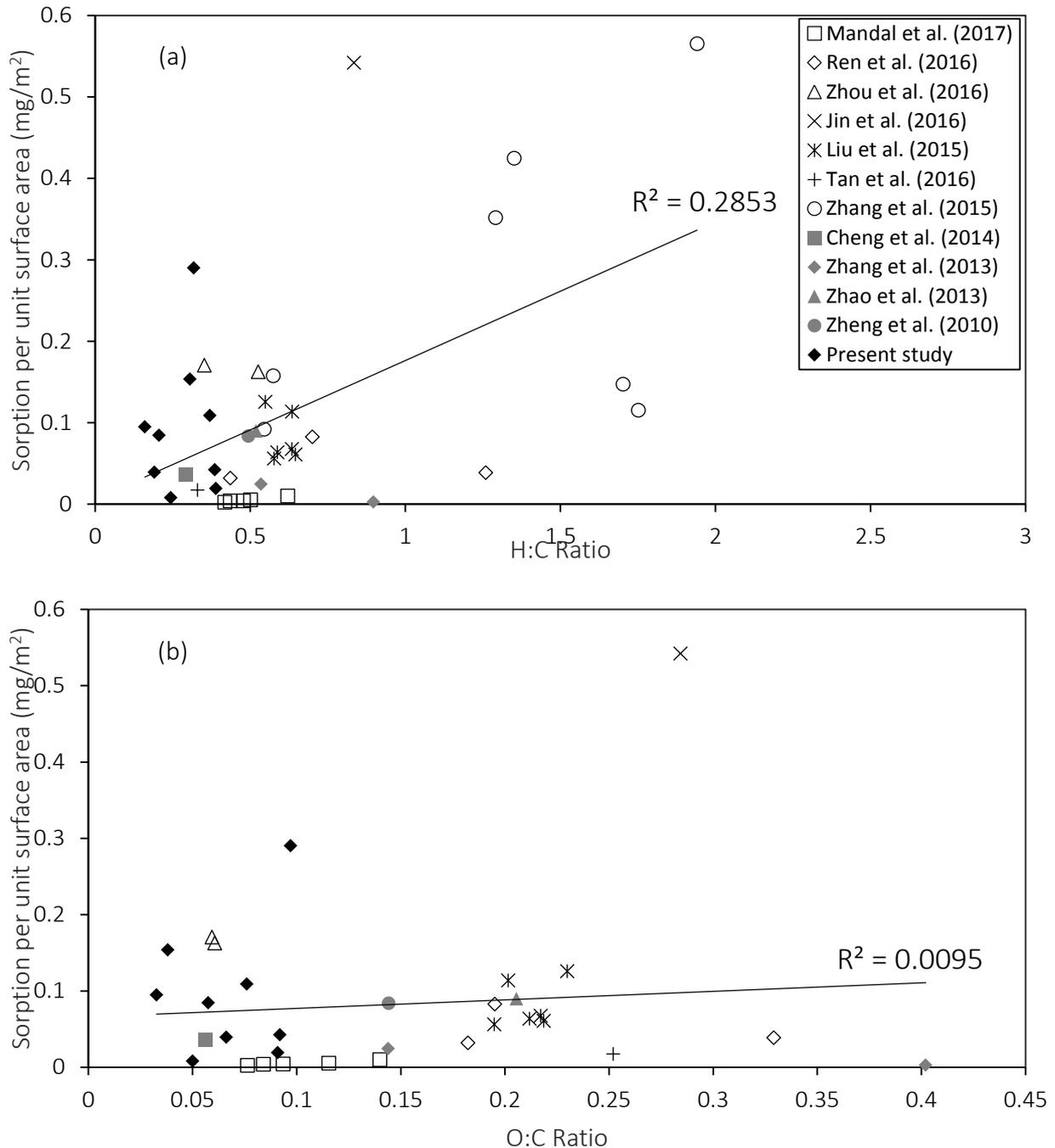


Figure 5-16: Atrazine sorption per unit area as a function of (a) biochar H:C ratio and (b) biochar O:C ratio from literature data

The meta-analysis therefore confirms that the sorption of atrazine to biochar is not primarily a result of hydrophobic interactions, and while it does not provide strong evidence for the role of hydrogen bonding, the failure of hydrophobic effects to show a strong correlation with sorption capacity implies that hydrogen bonding is playing a greater role. This result is in agreement with the models developed using the standard biochars, and provides new evidence on the role of the oxygen fraction, particularly the component that exists within the carbonised phase of the biochar. While atrazine can behave as a hydrophobic organic

compound, this evidence suggests that its polarity and capacity for hydrogen bonding contribute more to its adsorption and subsequent immobilisation in the environment.

5.3 Summary and conclusions

Chapter 5 has investigated the roles of the adsorption mechanisms of atrazine to biochar through first analysing the influence of pH on sorption, and second analysing the relationship between biochar properties and sorption capacity in the present study and in the literature. The results generally suggest that hydrogen bonding is more significant than hydrophobic effects, and that the significance of hydrophobic effects may be overstated due to their correlation with other properties beneficial to sorption.

The pH-dependency sorption tests revealed a number of sorption mechanisms to the different biochars, including electrostatic repulsion, hydrogen bonding, π - π EDA interactions, and interactions with the ash fraction. At low pH values, all biochars except for those produced from miscanthus straw demonstrated reduced sorption, which was attributed to electrostatic repulsion between the positively charged biochar surface and the positively charged atrazine molecule. At intermediate pH ranges, all biochars showed increased sorption which was attributed to atrazine forming hydrogen bonds with the positively charged biochar surface in this range. However, at high pH values, which likely reflect more realistic environmental levels, the mechanisms varied significantly suggesting chemical interactions may significantly influence sorption capacity in the environment. A more detailed discussion of the applicability of the biochars is given in Section 6.4.

SWP700 demonstrated greatly increased sorption at high pH values, while SWP550 did not. This difference was attributed to π - π EDA interactions to the more carbonised SWP700 biochar. Conversely, MSP and WSP biochars demonstrated increased sorption at high pH values, particularly for those produced at 550°C from each feedstock, suggesting that polar groups and hydrogen bonding are dominating sorption in this range. Hydrogen bonding is likely to be a more effective method of immobilising contaminants in the long-term due to the increased oxidation of biochar in soil over time.

The mechanisms determining the sorption of atrazine to RH and OSR biochar at high pH values was not clear. It was not possible to distinguish between competing influences of hydrogen bonding, π - π EDA interactions, and the influence of the ash fraction. Further

investigation is necessary in order to determine the dominant effects to these biochars, particularly the influence of the ash component.

An overall analysis of the standard biochar data found that sorption is overall controlled by surface area and oxygen contents, suggesting that as a whole, pore filling and hydrogen bonding are the mechanisms which contribute the most to sorption capacity. However, oxygen was also associated with partitioning which is not expected to be significant for remediation, suggesting that more detailed characterisation is necessary.

A meta-analysis of all available literature data, including the present study, confirmed the role of surface area in the sorption of atrazine, and also suggested that hydrophobic effects were not likely to be significant for the sorption of atrazine. The significance of hydrogen bonding was not clear, which was most likely attributable to the various forms in which it can exist. These results suggest that oxygen content alone cannot predict hydrogen bonding potential.

The overall results presented in this chapter suggest that biochar may be efficient at irreversibly immobilising atrazine in the long-term. The reductions in sorption at very low pH values ($\text{pH} < 3$) are unlikely to occur in practice and therefore the environmental significance of the electrostatic repulsion effects will be relatively low. Conversely, the strong influence of hydrogen bonding, particularly to WSP and MSP biochars, suggests that the binding of atrazine is likely to become stronger over time and the atrazine will therefore be effectively retained. However, the effects at high pH values should be considered more closely, particularly for RH and OSR chars, as the precise interactions will significantly influence the outcomes of their applications.

Chapter 6: Biochar de-ashing and its influence on the adsorption mechanisms of atrazine

The results of Chapters 4 and 5 suggest that the sorption of atrazine to the standard biochar samples is controlled by the pore networks, surface functional groups, and ash content. However, it is not entirely clear what role each of these components play. Chapter 6 investigates the modification of the standard biochar samples, in order to better understand the influences of the functional groups and ash fractions, and their likely contributions to remediation in the soil profile. Finally, the implications of the findings from Chapters 4 and 5 for the use of biochar in remediation contaminated land are addressed. Preliminary results from this chapter were presented in McMillan et al. (2017)²⁸⁴.

This chapter focuses on three of the standard biochars: SWP550, RH700 and OSR550. In Chapter 4 and 5 it was not possible to determine the mechanisms controlling sorption to RH700 and OSR550, particularly at high pH values. It was hypothesised that this was due to interactions with the ash fractions, although the form of oxygen may also have played a role. SWP550 had the lowest ash fraction, and therefore represents a useful control biochar to determine the influence of modification on the carbonised component. Several characterisation methods are carried out in order to accurately assess the role of the modification on both the carbonised and ash fractions of the biochars. This chapter therefore removes the ash component of the biochars in order to isolate its role in the removal of atrazine.

6.1 De-ashing of standard biochars

Modification of selected biochars was carried out using hydrofluoric acid and hydrochloric acid together in order to isolate the role of the ash fraction on the sorption of atrazine. HF has previously been shown to remove the ash component of biochar^{122,148,156}. HF modification was carried out on SWP550 (ash content 1.25%), RH700 (47.93%) and OSR550 (19.50%). Characterisation of the raw and modified biochars was then carried out using FTIR, elemental analysis, XRD, XPS and SEM. These tests provide insights into the functional groups, mineral fractions, surface chemistry, and surface structures respectively. The results from these tests are important in determining the outcome of the modifications, as well as the subsequent sorption mechanisms of the modified biochar samples.

SWP550, RH700 and OSR550 were modified using a HCl/HF solution, producing SWP550-HF, RH700-HF and OSR550-HF respectively. Ash samples were also obtained for these three biochars. In Chapter 5, it was not possible to determine the sorption mechanisms occurring to RH700 and OSR550 biochars due to potential interactions with the ash fraction. In this chapter, the biochars are de-ashed in order to isolate the effects of the ash fraction. Characterisation of the isolated ash components was also carried out, in order to further isolate the role of the ash component. The inclusion of SWP550, which has very low ash content, is used effectively as a control to determine the influence of HF modification on the carbonised component of the biochar. However, it was not possible to isolate SWP550-ash due to its low content.

6.1.1 FTIR of raw, modified and ash biochar fractions

Fourier transformed infrared (FTIR) spectroscopy analysis of the raw, modified and ash fractions were carried out in order to determine their surface functionality. The detailed FTIR spectra of the raw biochars were previously discussed in Chapter 4, and this section therefore primarily discusses them comparatively. FTIR spectra of the raw biochar, ash component, and HF-modified biochars are shown in Figure 6-1 for SWP550, Figure 6-2 for RH700 and Figure 6-3 for OSR550. FTIR characterisation of the raw, de-ashed and ash samples provide insights into the effectiveness of the modification procedure and the role of the ash phase in determining functionality.

SWP550 showed no significant differences in FTIR analysis after modification with HF. The oxygen-containing functional groups were still present in the same forms, as were the $-CH_3$ groups and the aromatic C=C groups. The lack of change in SWP550 after HF modification suggests that it has negligible influence on the carbonised biochar component. Therefore, changes in RH700 and OSR550 after modification can be attributed to interactions between HF and the ash component of these biochars.

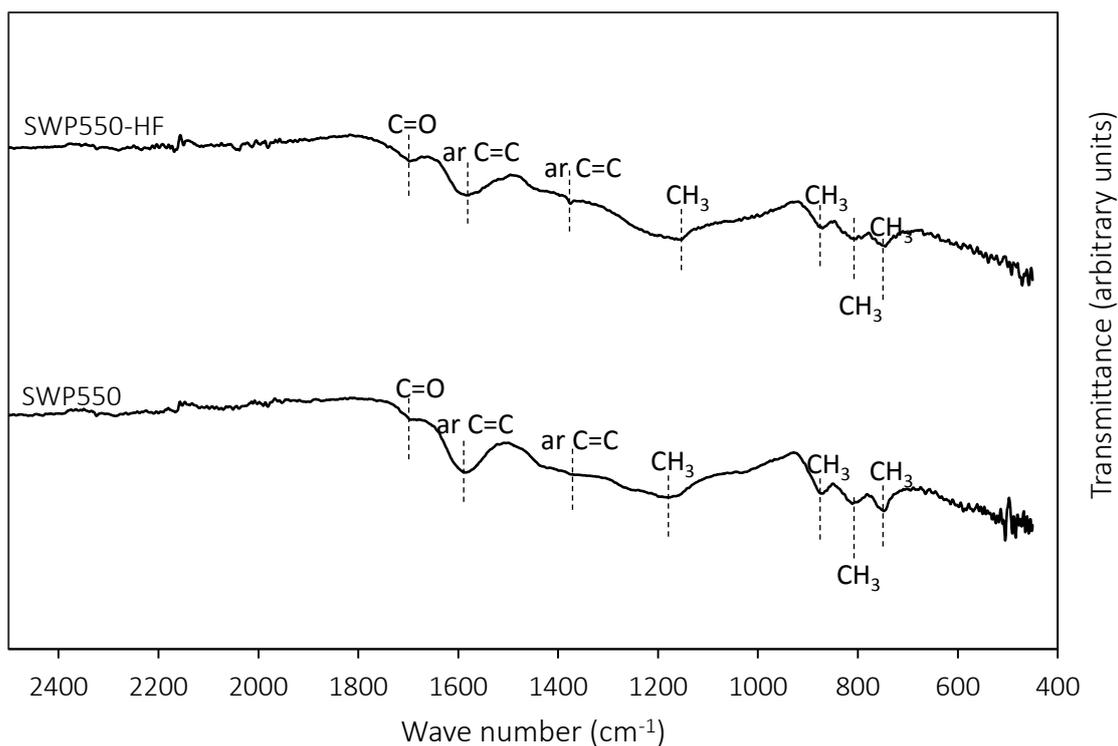


Figure 6-1: FTIR plot of SWP550 and SWP550-HF biochars

RH700 showed significant changes after modification with HF. RH700-HF had a much smaller peak at approximately 1090 cm^{-1} than RH700, corresponding to a reduction in the presence of SiO_2 , a major component of typical biochar ash phases. This is confirmed by similar reductions in the peaks at approximately 800 cm^{-1} and 450 cm^{-1} , which also correspond to SiO_2 . RH700-HF showed relatively little other differences from RH700; it retained the aromatic structure evidenced by peaks at approximately 1600 cm^{-1} and 800 cm^{-1} .

The FTIR analysis also revealed that RH700-ash had a notably different structure than that of RH700. It did not contain peaks corresponding to $\text{C}=\text{C}$ or $-\text{CH}_3$ groups, instead comprising entirely of three peaks corresponding to SiO_2 . These peaks also correspond closely to the peaks removed from RH700 by HF modification, confirming that it was the ash content removed by HF modification. The FTIR analysis therefore confirms that RH700-ash comprises primarily SiO_2 , which was successfully removed from RH700 by HF modification.

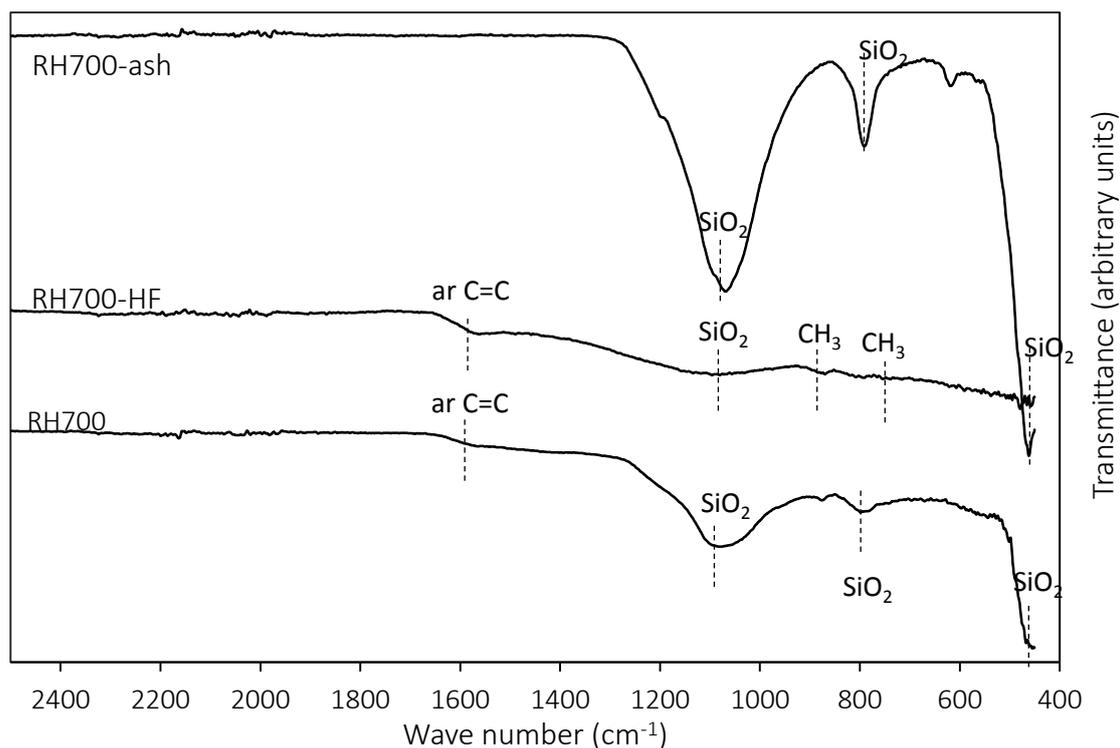


Figure 6-2: FTIR plot of RH700 and RH700-HF biochars, and RH700-ash

OSR550 also showed the removal of peaks at 1050 cm^{-1} and 450 cm^{-1} corresponding to SiO_2 after modification with HF. It otherwise showed very little change in functionality after modification, which is in line with the results of RH700. One small change was a slight increase in C=O groups at approximately 1690 cm^{-1} , which may be due to the acidification of the surface by the HF/HCl solution.

OSR550-ash showed the characteristic peaks of SiO_2 at 1100 cm^{-1} , 800 cm^{-1} and 450 cm^{-1} , confirming that the ash component of OSR550 primarily consists of SiO_2 . However it also contained other peaks at approximately 950 cm^{-1} and 600 cm^{-1} which are not present in RH700-ash. While it is not possible to determine what these are from the FTIR plots alone, it suggests that OSR550-ash may contain minerals other than SiO_2 , which may influence its behaviour in solution, such as Ca^{2+} or Mg^{2+} .

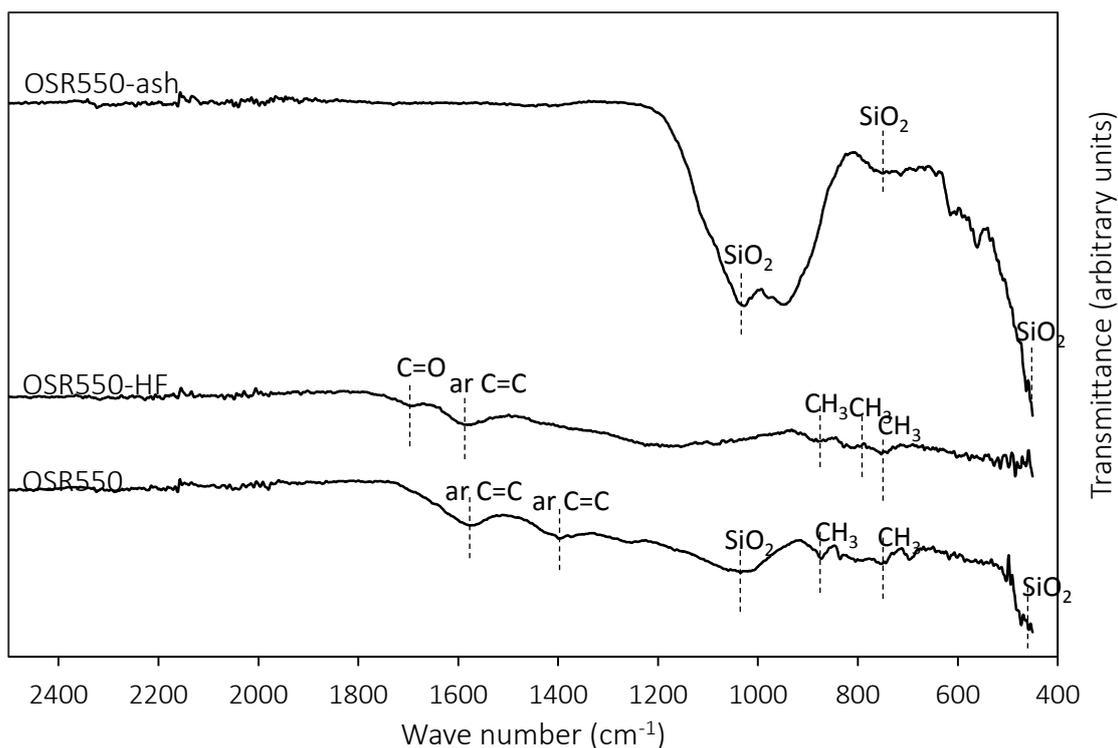


Figure 6-3: FTIR plots of OSR550 and OSR550-HF biochars, and OSR550-ash

FTIR characterisation of the HF-modified chars confirms that the modification has relatively little influence on the properties of the carbonised component of SWP550, RH700 and OSR550. However, it successfully removed the SiO_2 components of RH700 and OSR550, which was confirmed by alignment of the removed peaks shown in RH700-ash and OSR550-ash respectively.

6.1.2 Elemental analysis of raw and modified biochars

The bulk C, H, N, O and ash fractions of the raw and modified biochars were determined through analysing the products of high-temperature combustion. The relative proportions of these components provide further information on the overall outcomes of the modification procedure, and are shown in Table 6-1. Overall, the elemental analysis results confirm that the modification using HF successfully removed the majority of the ash component.

Table 6-1: Elemental composition of raw and hydrogen fluoride-modified biochars, and ash fractions

Biochar	C (%)	H (%)	N (%)	O(%) ^a	Ash (%)	O:C	H:C
SWP550	82.62	2.81	0.04	13.29	1.25 ^b	0.121	0.407
SWP550-HF	83.00	2.81	0.05	13.51	0.63	0.122	0.406
RH700	43.64	0.76	0.47	7.20	47.93 ^b	0.124	0.209
RH700-HF	85.51	1.23	1.40	10.22	2.02	0.090	0.172
RH700-Ash	0.14	0.00	0.00	- ^c	- ^c	- ^c	- ^c
OSR550	67.77	2.24	0.85	9.65	19.50 ^b	0.107	0.396
OSR550-HF	79.90	2.42	1.03	14.36	2.30	0.135	0.363
OSR550-Ash	0.33	0.04	0.00	- ^c	- ^c	- ^c	- ^c
^a oxygen calculated by difference on an ash-free basis							
^b as determined by UKBRC							
^c not determined							

SWP550 showed very little change after modification with HF, most likely due to its low initial ash content. The ash content reduced from 1.25% to 0.63%, resulting in corresponding small increases in carbon (82.62% to 83.00%) and oxygen (13.29% to 13.51%). The elemental analyses of SWP550 biochars therefore provide further evidence that the HF modification did not significantly influence the carbon component of SWP550. In contrast, RH700 and OSR550 biochars showed significant changes after HF modification; notably, there were near-complete reductions in ash contents (47.93% to 2.02% for RH700, and 19.50% to 2.30% for OSR550) and large increases in carbon and oxygen contents. These changes suggest that the HF modification successfully removed the ash fractions, resulting in corresponding increases in carbon content. RH700-HF and OSR550-HF also showed slight decreases in H:C ratios, suggesting the overall proportion of the highly aromatic carbonised component increased. The increased oxygen contents for RH700-HF and OSR550-HF also suggest that some oxidation of the carbonised component may have occurred during modification, although XPS analysis may be able to more accurately determine its extent. Overall, the results show that HF modification successfully removed the ash components of the three biochars, with little significant effect on the carbonised fractions.

6.1.3 XRD analysis of standard biochars, ash and modified biochars

The HF-modified biochars (including the raw and ash samples) were further characterised using x-ray diffraction (XRD) in order to better understand the mineral phases present. XRD spectra of the biochars (and their derivatives) are shown in Figure 6-4 for SWP550, Figure 6-5 for RH700 and Figure 6-6 for OSR550. The XRD plots show a number of crystalline components in the RH, OSR and ash samples.

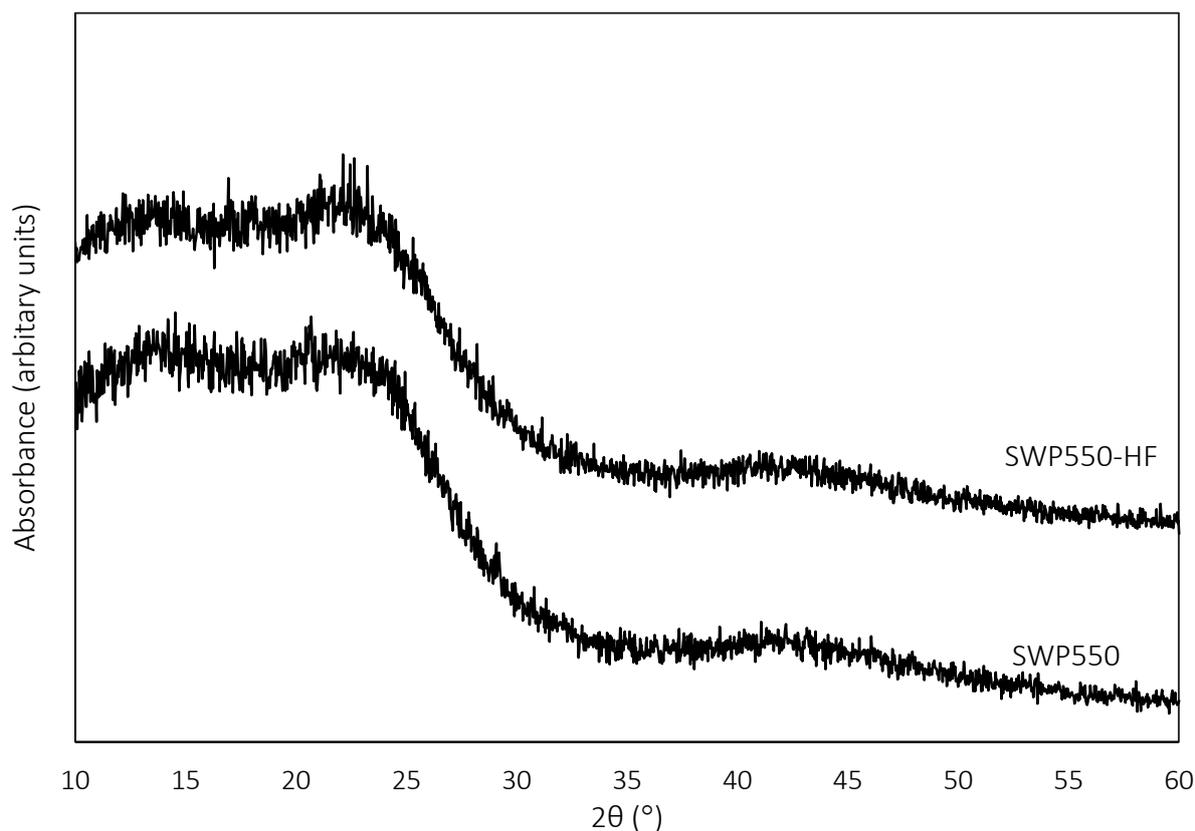


Figure 6-4: XRD plot for SWP550 and SWP550-HF biochars

The XRD spectra for SWP550 and SWP550-HF show no significant differences, which is in line with the results of the FTIR analysis. The spectra both show broad peaks from approximately 20° to 30°, corresponding to aromatic carbon, as well as a smaller broad peak from approximately 40° to 45° corresponding to amorphous carbon. No other peaks are present in SWP550 or SWP550-HF, which suggests an absence of mineral components in line with the low ash contents and lack of SiO₂ in the FTIR spectra.

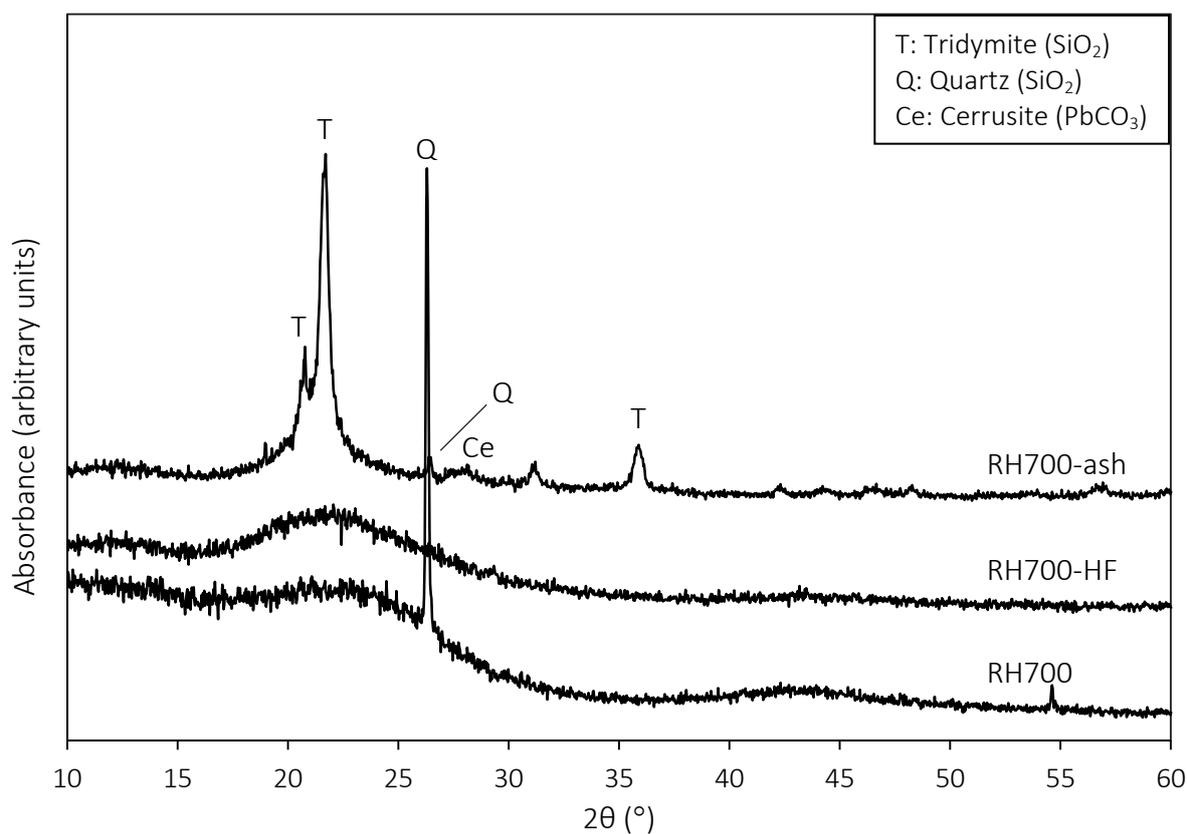


Figure 6-5: XRD plot for RH700 and RH700-HF biochars, and RH700-ash

The XRD spectra for RH700 and its derivatives reveal the presence of a number of mineral groups. RH700 and RH700-HF showed similar broad peaks between 20° and 30° corresponding to the presence of aromatic carbon. RH700 showed a large peak at approximately 27° , corresponding to the presence of quartz, which is in line with the strong peaks of SiO_2 present in the FTIR spectrum. This peak was not present in RH700-HF, suggesting that the quartz was removed by the HF modification; this result again is in line with the removal of the ash component by HF as suggested by the FTIR analysis.

The XRD spectrum for RH700-ash was noticeably different from RH700 and RH700-HF. First, the broad peak between 20° and 30° was no longer present, confirming the absence of carbon from the combusted ash phase. A small peak was present at approximately 27° , corresponding to the quartz as present in RH700. However, the most significant peaks were at approximately 20.5° and 21° , corresponding to tridymite, a different phase of SiO_2 . This suggests that the combustion itself can alter the crystalline structure of the ash component, and therefore the isolated ash sample may not fairly represent the phases present in the raw biochar sample.

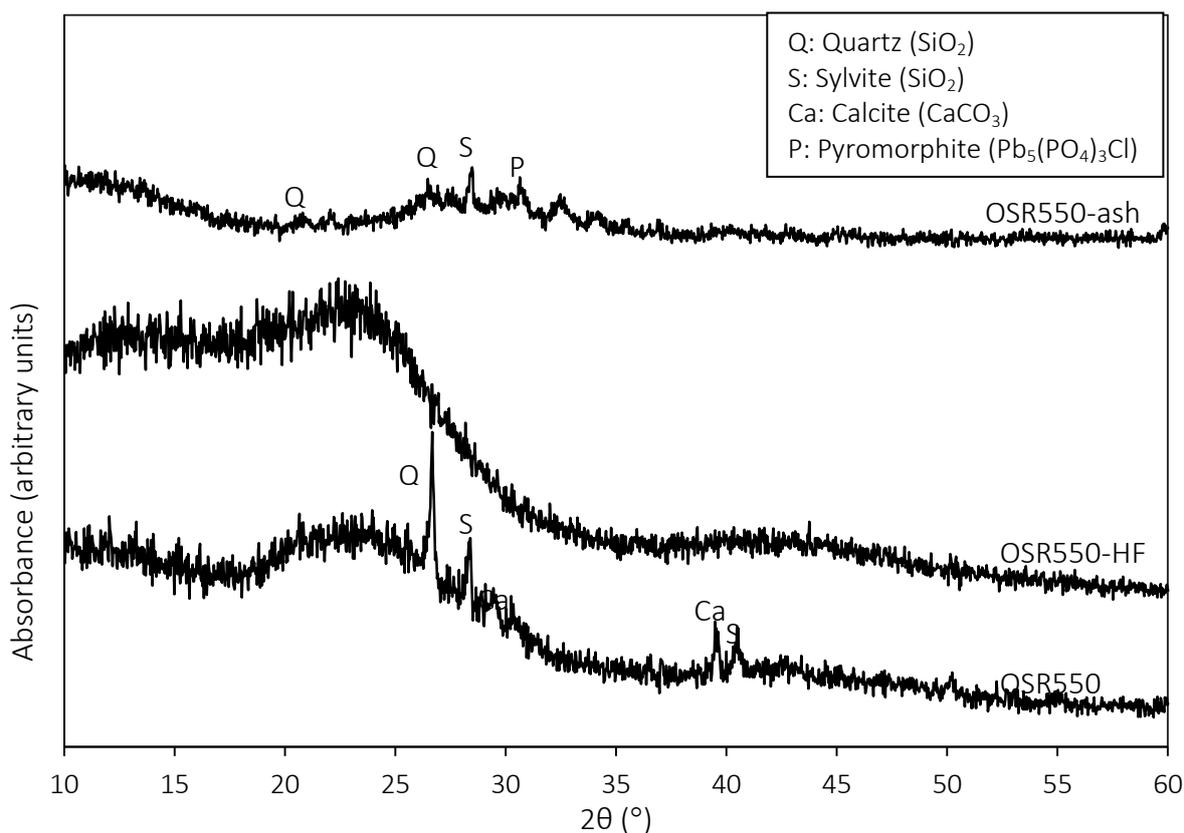


Figure 6-6: XRD plot of OSR550 and OSR550-HF biochars, and OSR550-ash

OSR550 also showed noticeable differences after modification with HF. OSR550 showed a clear broad peak between 20° and 30° corresponding to aromatic carbon, as was also present in SWP550 and RH700. It also showed characteristic peaks of quartz and sylvite, two different forms of SiO₂, confirming the presence of SiO₂ indicated in the FTIR analysis. However, OSR550 also showed peaks corresponding to calcite (CaCO₃), suggesting that Ca was present in the biochar. A small peak was also present at approximately 30°, which may indicate the presence of pyromorphite, a form of lead chlorophosphate (Pb₅(PO₄)₃Cl), which would correspond to the presence of lead in OSR550. The presence of calcite and pyromorphite confirm the FTIR results that OSR550 contains mineral forms beyond SiO₂.

While the characteristic aromatic carbon curve was retained in OSR550-HF, all mineral components were removed suggesting that the HF modification was successful. OSR550-ash noticeably did not show significant amounts of mineral content, despite theoretically comprising purely mineral phases. Small amounts of quartz and sylvite were present, suggesting that SiO₂ phases are maintained after combustion. However, calcite and

pyromorphite were no longer apparent, as these phases are removed at approximately 750°C²⁸⁵.

The XRD results therefore confirm the FTIR and elemental analysis results. They show that SWP550 had negligible crystalline components and was not significantly affected by HF modification. In contrast, RH700 comprised significant quantities of quartz, which were removed by HF modification. OSR550 contained quartz and , sylvite and calcite which were removed by HF modification.

6.1.4 SEM imaging of modified biochars

Scanning electron microscopy (SEM) images were taken of the modified biochars in order to determine their surface structures. SEM images of SWP550 and RH700 were taken by Shen (2016)¹³⁷, while images of OSR550, RH700-HF and OSR550-HF were taken for the present study. Images of SWP550-HF were not taken due to the high cost and low availability of SEM and the lack of evidence that it differed significantly from SWP550. The SEM images reveal insights into the pore structure of the raw and modified biochars.

The SEM images of SWP550 are shown in Figure 6-7 and show that the pore structure of SWP550 is largely determined by the fibrous nature of the initial feedstock. Long, narrow pores of approximately 5µm diameter exist¹³⁷ which are exposed on the outer edge of a particle in Figure 6-7a, while the closely clustered entrances to the deeper micropore space is visible in Figure 6-7b. Components are visible in the upper-left corner of Figure 6-7b which may represent some inorganic ash components, however the overall quantity of this phase is relatively low, as consistent with the measured ash content.

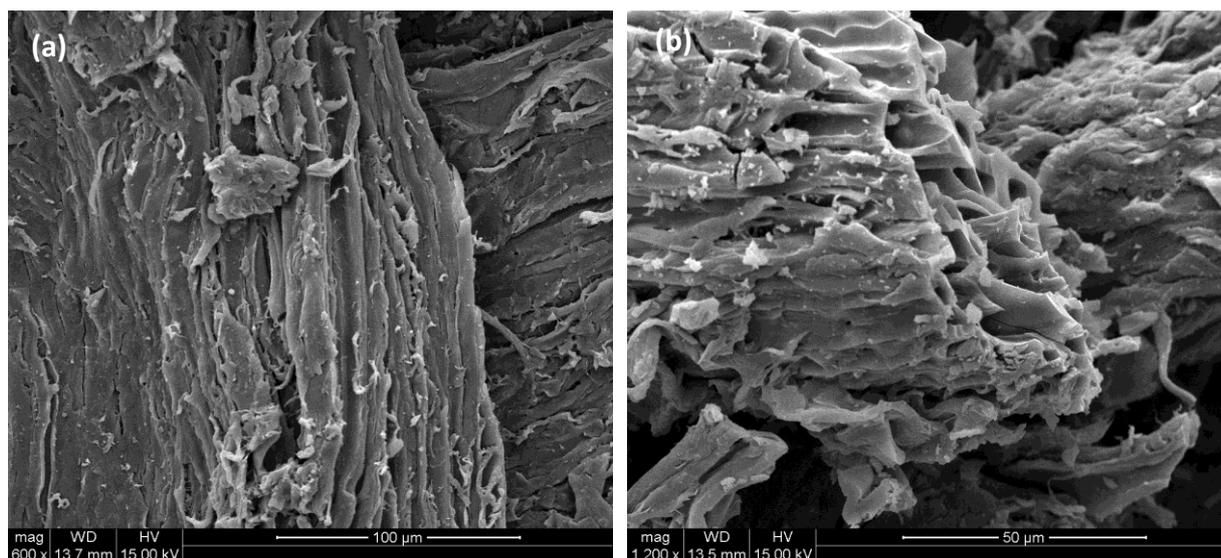


Figure 6-7: Scanning electron microscopy images of SWP550 biochar. Based on work by Shen (2016)¹³⁷

SEM images of RH700 are shown in Figure 6-8a-b, together with SEM images of RH700-HF in Figure 6-8c-d and show large ($\approx 20\mu\text{m}$), honeycomb-shaped pores. The large pores likely represent the entrance to a wider network of meso- and micropore spaces, allowing for atrazine molecules to efficiently diffuse through the RH700 particles. It is not possible to distinguish between carbonised material and inorganic material using SEM, so insights into the distribution of the ash phase cannot be gained from these images. After HF modification, the honeycomb-like pores are still visible in Figure 6-8c. The fact that the pore structure was mostly retained suggests that the modification did not significantly influence the physical characteristics of the carbonised fraction and was therefore successful in selectively altering the ash fraction.

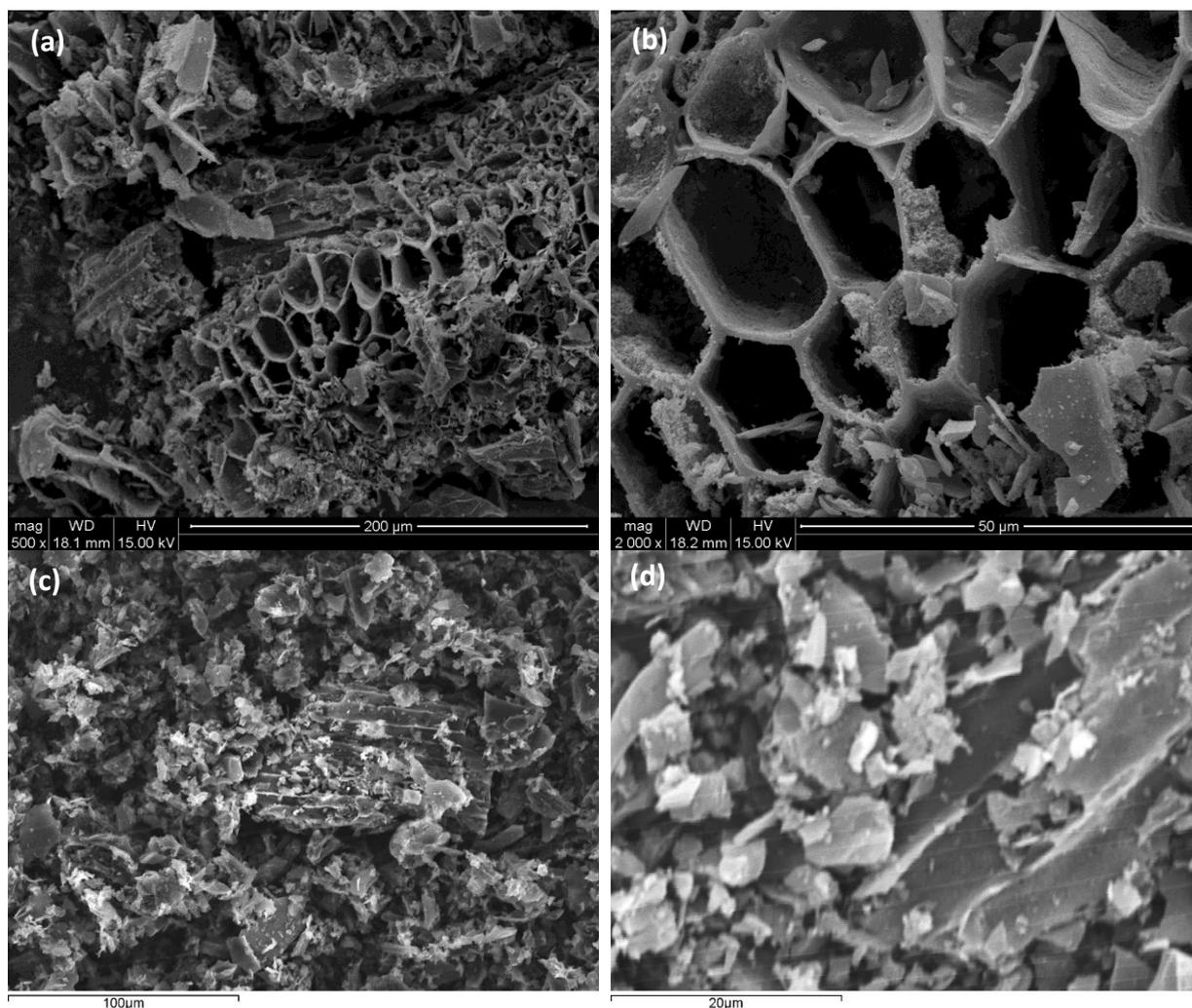


Figure 6-8: Scanning electron microscopy images of (a-b) RH700 and (c-d) RH700-HF biochars

SEM images of OSR550 are shown in Figure 6-9a-b together with OSR550-HF in Figure 6-9c-d, and show similar fibrous-natured pores to softwood biochars. After modification, there is no clear difference to the overall pore structure, suggesting that the modification successfully altered the ash fraction without significantly altering the carbonised fraction.

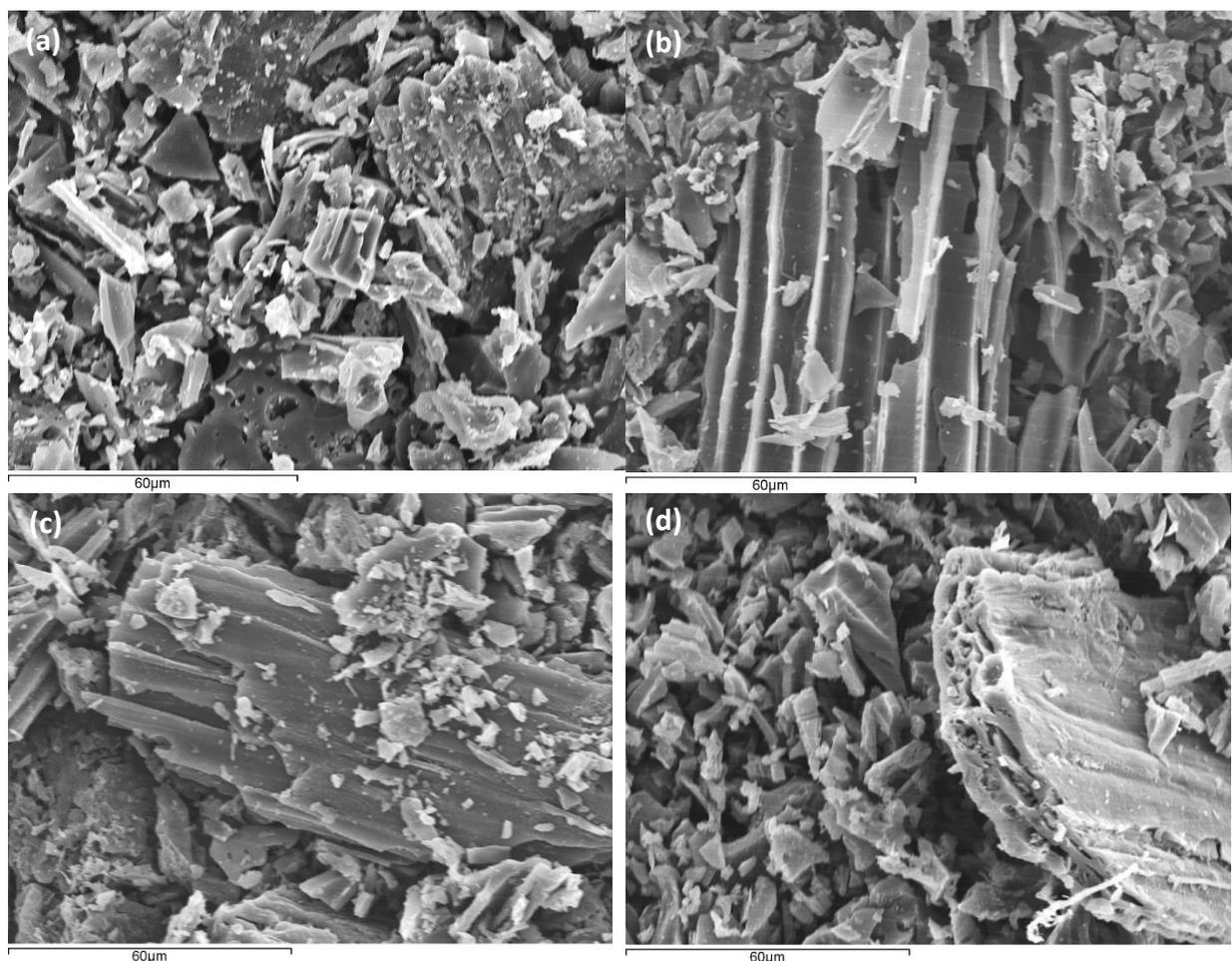


Figure 6-9: Scanning electron microscopy images of (a-b) OSR550 and (c-d) OSR550-HF biochars

Overall, the SEM images confirm the porous natures of the biochars, and that these pores are retained, and sometimes even enhanced, after modification with HF. However, the SEM images were not able to identify the ash fraction so insights into this component can only be gained from other characterisation methods.

6.1.5 XPS of modified biochars

X-ray photoelectron spectroscopy (XPS) analysis was carried out on the raw and modified biochars in order to determine their surface elemental composition, and the forms of carbon present. A survey scan was used to determine the surface elemental ratios, as given in Table 6-2 and Figure 6-10 to Figure 6-12, and detailed C_{1s} scans were carried out to determine the forms of the carbon groups.

Table 6-2: Surface elemental ratios of the raw and HF-modified biochars as determined by XPS

	SWP550	SWP550-HF	RH700	RH700-HF	OSR550	OSR550-HF
C (%)	83.04	83.11	68.49	89.65	72.35	76.24
O^a (%)	14.76	13.85	16.81	6.86	19.85	15.00
O^b (%)	12.42	13.47	1.80	6.26	12.26	11.19
N (%)			1.21	1.18	bdl	1.26
P (%)	bdl				bdl	
F (%)		2.72		0.80		4.28
Cl (%)	0.23	0.23		1.00	1.28	bdl
Si (%)	0.44		12.07	0.52	3.81	0.56
Ca (%)	1.53	0.32	1.05		2.71	2.65
Na (%)			0.37			
B (%)	bdl				bdl	
Mg (%)				bdl		
Al (%)					bdl	
Sr (%)					bdl	
Fe (%)						bdl

^a total detected oxygen

^b excluding oxygen in SiO₂ and CaCO₃ minerals

bdl element detected but not quantified

Empty cell indicates element was not detected

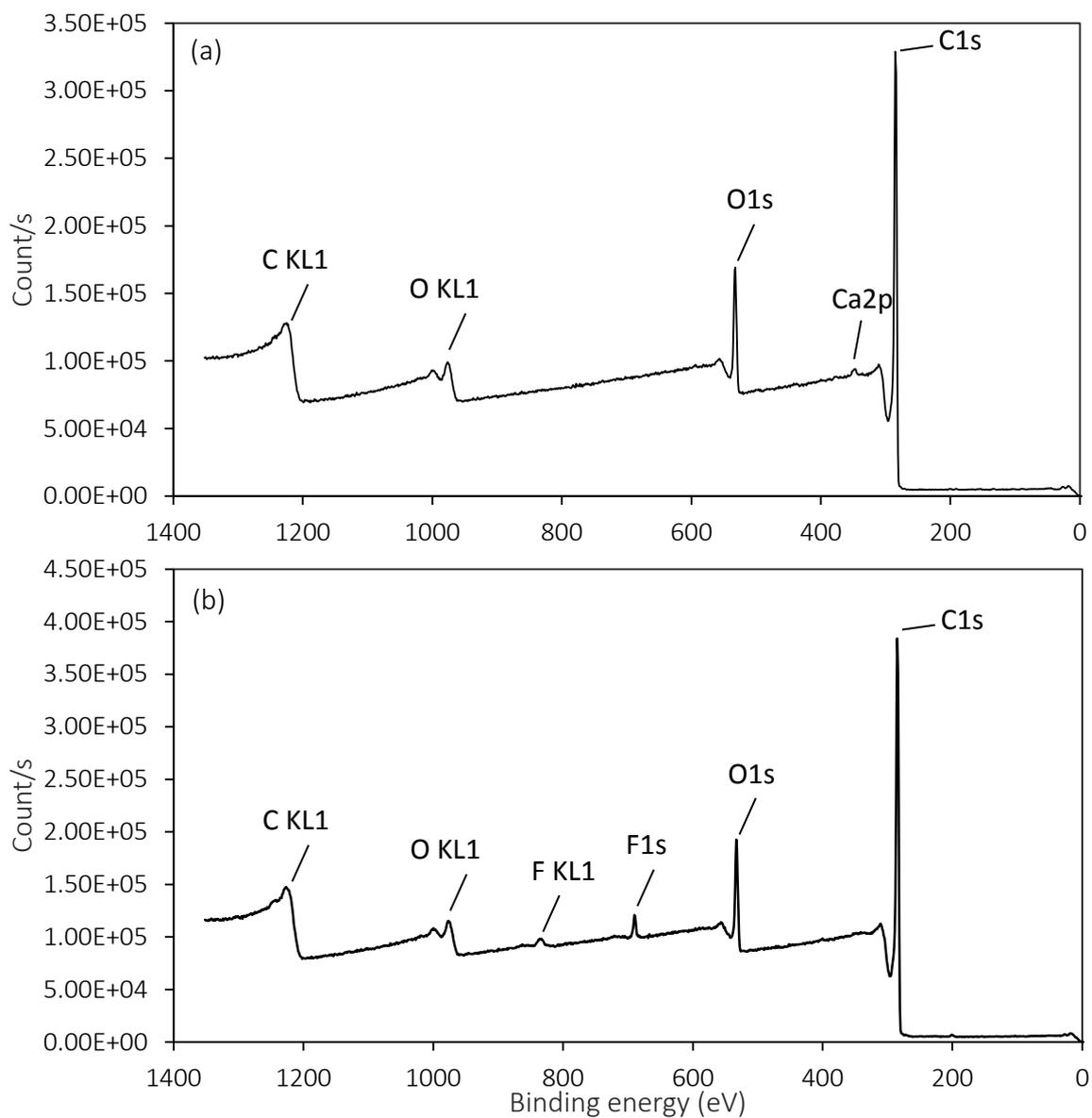


Figure 6-10: XPS survey scans of (a) SWP550 and (b) SWP550-HF biochars

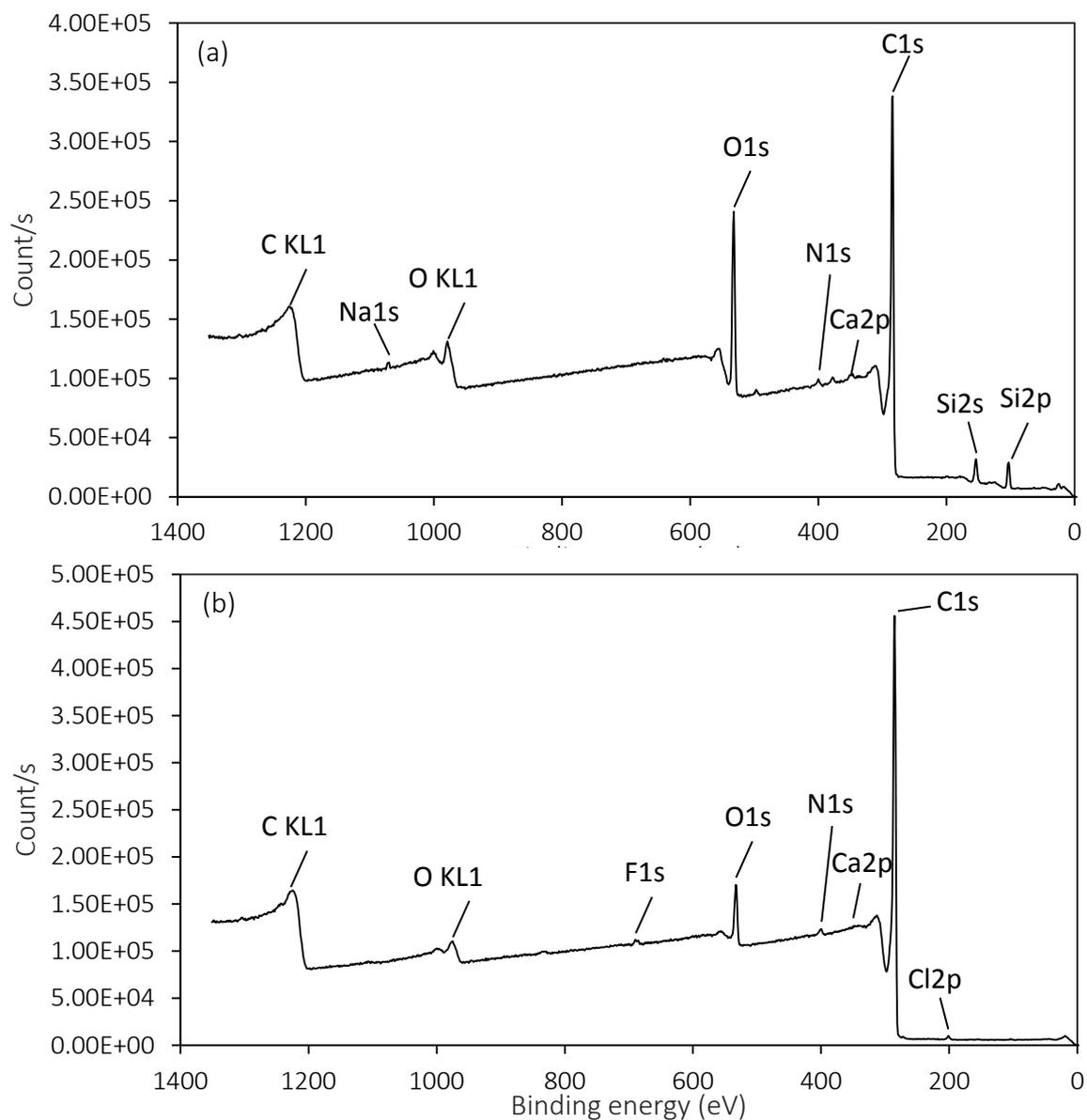


Figure 6-11: XPS survey scans of (a) RH700 and (b) RH700-HF biochars

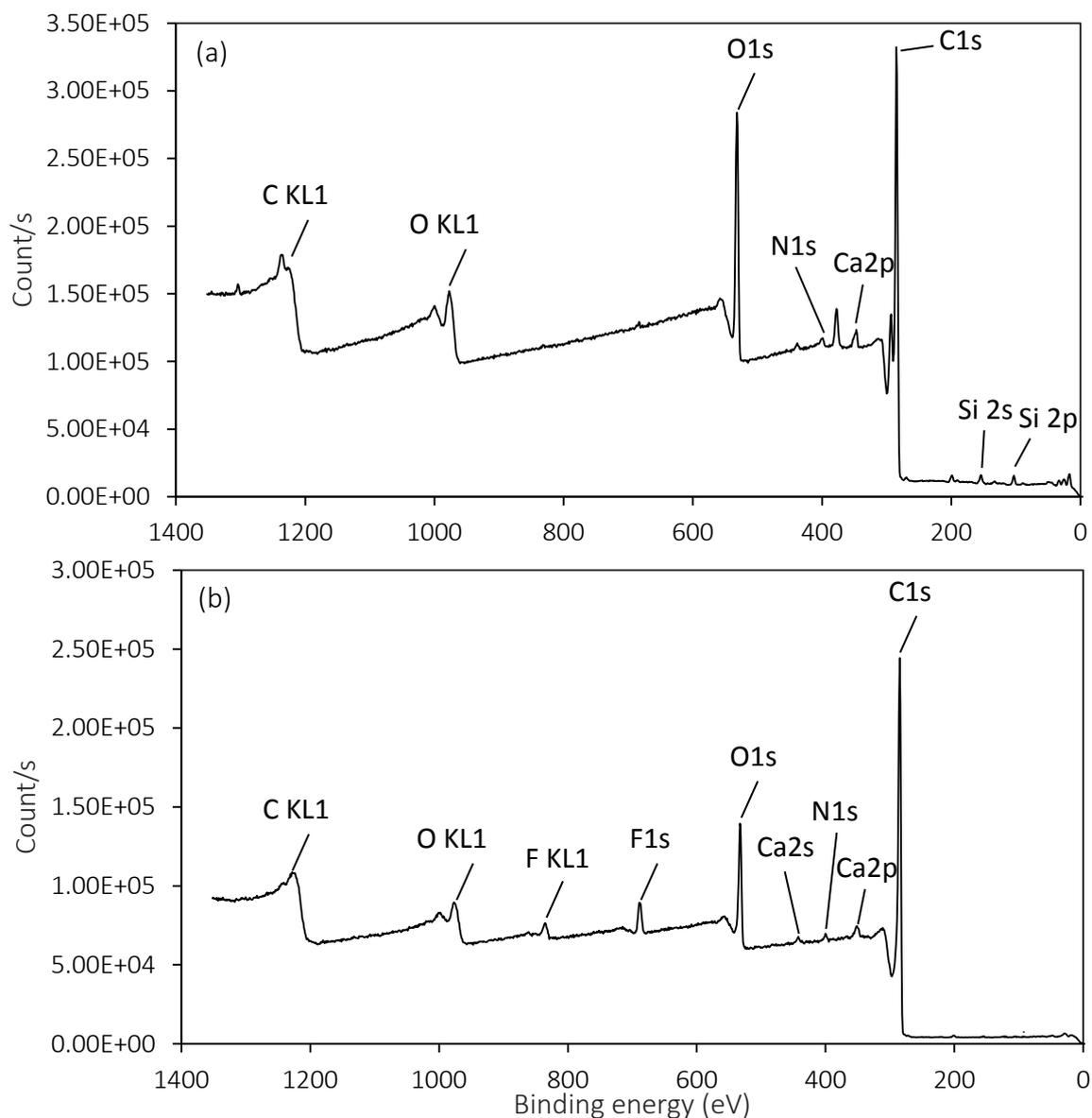


Figure 6-12: XPS survey scans of (a) OSR550 and (b) OSR550-HF biochars

The surface elemental compositions confirm that mineral contents reduced after HF modification. Surface Si reduced from 0.44% to below detectable levels for SWP550, 12.07% to 0.52% for RH700, and 3.81% to 0.56% for OSR550, confirming that the de-ashing was successful. Calcium also reduced significantly for SWP550 and RH700, although was not affected in OSR550, suggesting it may exist in a different form in OSR550 than the other biochars. Other minerals such as Na, B and Mg were detected in some of the biochars, but are unlikely to significantly influence sorption properties.

Notably, all biochars showed increases in F content after modification, suggesting the fluorine may have formed mineral deposits on the biochar surfaces. These minerals were not

detected on XRD scans, suggesting that they are not in crystalline forms, or are present in too small quantities. It is possible that the addition of these groups may result in some slight acidification of the biochars, particularly if they are attached to organic forms of carbon. However, as no significant functional peaks were observed corresponding to F groups on FTIR, nor any new crystalline phases determined using XRD, these groups are considered unlikely to significantly influence the properties of the modified biochars.

The effects of HF modification on the surface oxygen groups varied. There was a slight decrease in the total oxygen content of SWP after modification, from 14.76% to 13.85%. However, after accounting for the removal of oxygen which exists in silicates (i.e., two O atoms for each atom of Si) and carbonates (three O atoms for each atom of Ca), the oxygen content actually slightly increases from 12.42% to 13.47%. This suggests that there was some oxidation of the carbonised component of SWP550 after HF modification. A similar effect was observed for RH700, which showed an increase in surface organic oxygen from 1.80% to 6.26%. Conversely, OSR550 had decreased surface oxygen content, even after accounting for inorganic components, from 12.26% to 11.19%, suggesting that there was no significant oxidation of OSR550.

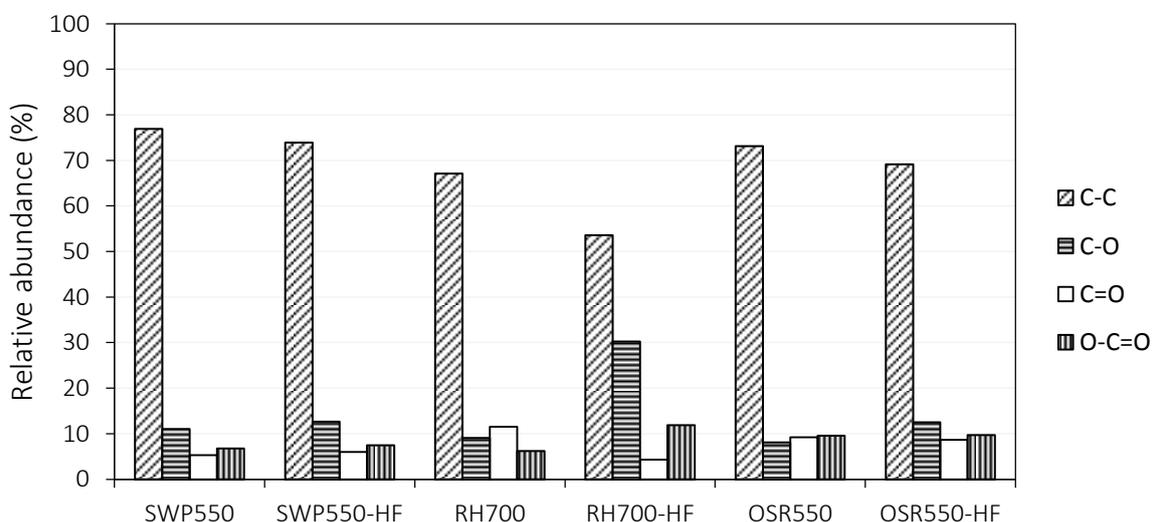


Figure 6-13: Surface organic functional groups of raw and modified biochars as determined by detailed XPS spectra

In order to better understand the different compositions of the organic surface oxygen groups, detailed C1s scans were carried out on each of the raw and modified biochars. The surface compositions of organic functional groups are given in Figure 6-13 and the detailed scans are given in Figure 6-14 to Figure 6-16. The scans highlight the different ranges of functional

groups present. All biochars showed a strong peak at approximately 284.7 eV which was attributed to graphitic and aliphatic C-C groups. Three smaller peaks were also detected among all of the biochars: the peaks at 285.5-286.2 eV were attributed to C-O groups in phenols, alcohols and ester groups^{202,280,286,287}; the peaks at 287.1-287.7 eV were attributed to C=O carbonyl groups²⁸⁷; and the peaks at 289.6-289.8eV were attributed to O-C=O groups in carboxylic or ester groups²⁰⁸. RH700 and OSR550 also contained a peak at approximately 293.4 eV, while OSR550 also contained a peak at 296.1 eV. These are not directly attributable to other peaks demonstrated previously. The detailed XPS analysis demonstrated a wider range of functional groups than FTIR analysis, suggesting that FTIR may not be able to fully capture the functional composition of the standard biochars. However, the detailed C1s scan results were largely in agreement with the survey scan and with elemental analysis results.

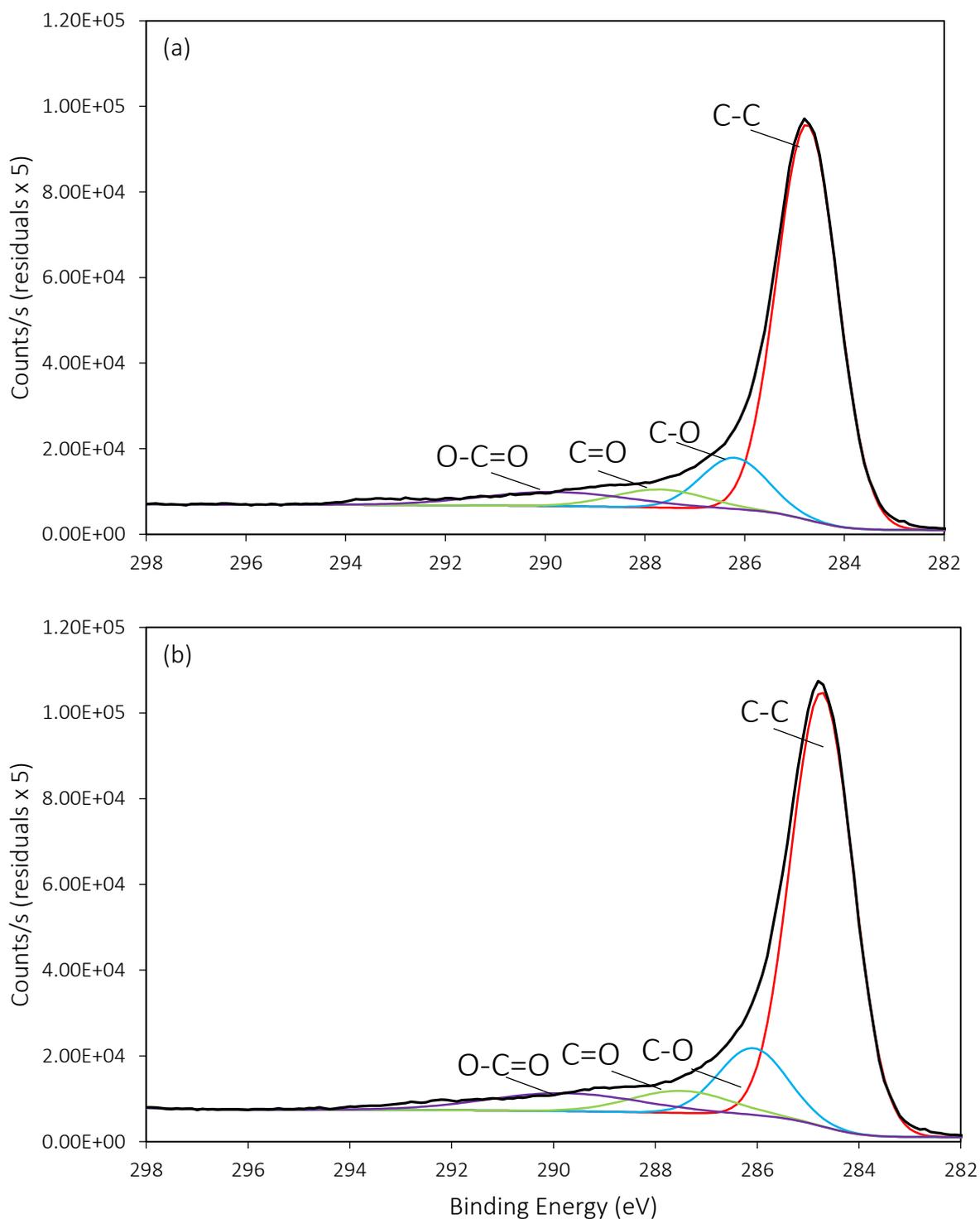


Figure 6-14: Detailed XPS C1s spectra of (a) SWP550 and (b) SWP550-HF

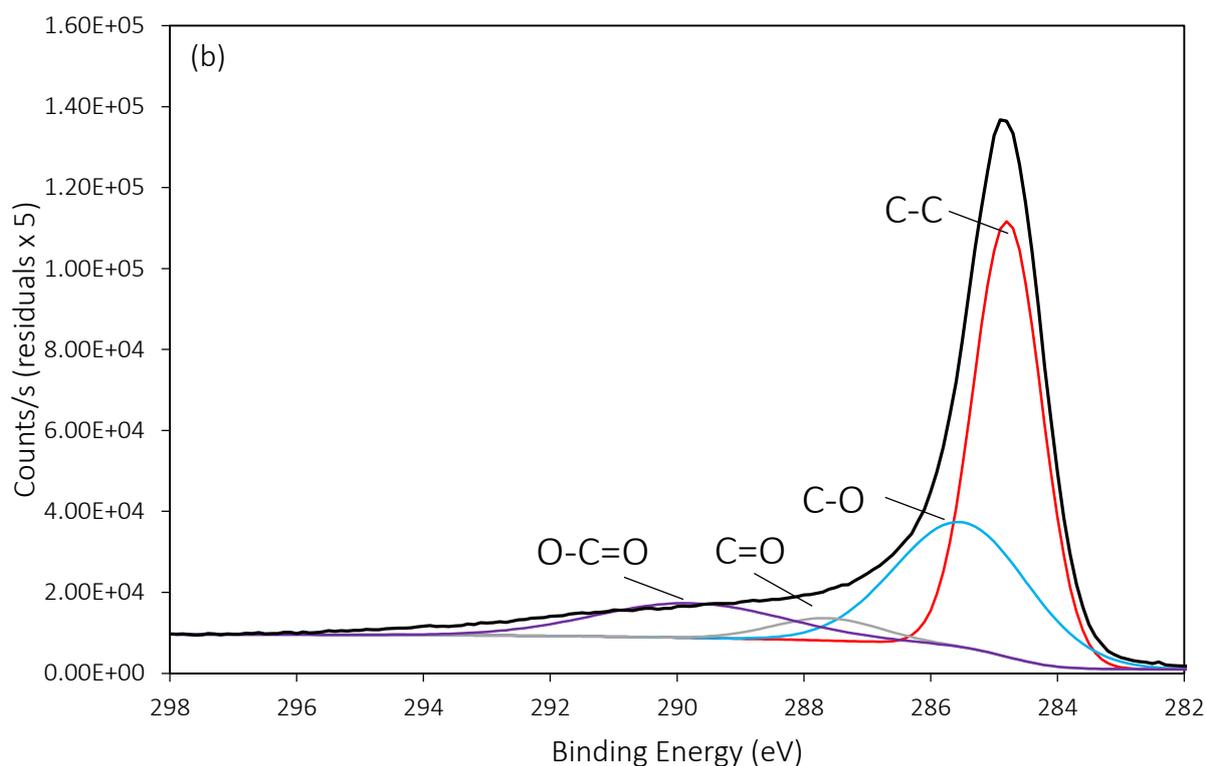
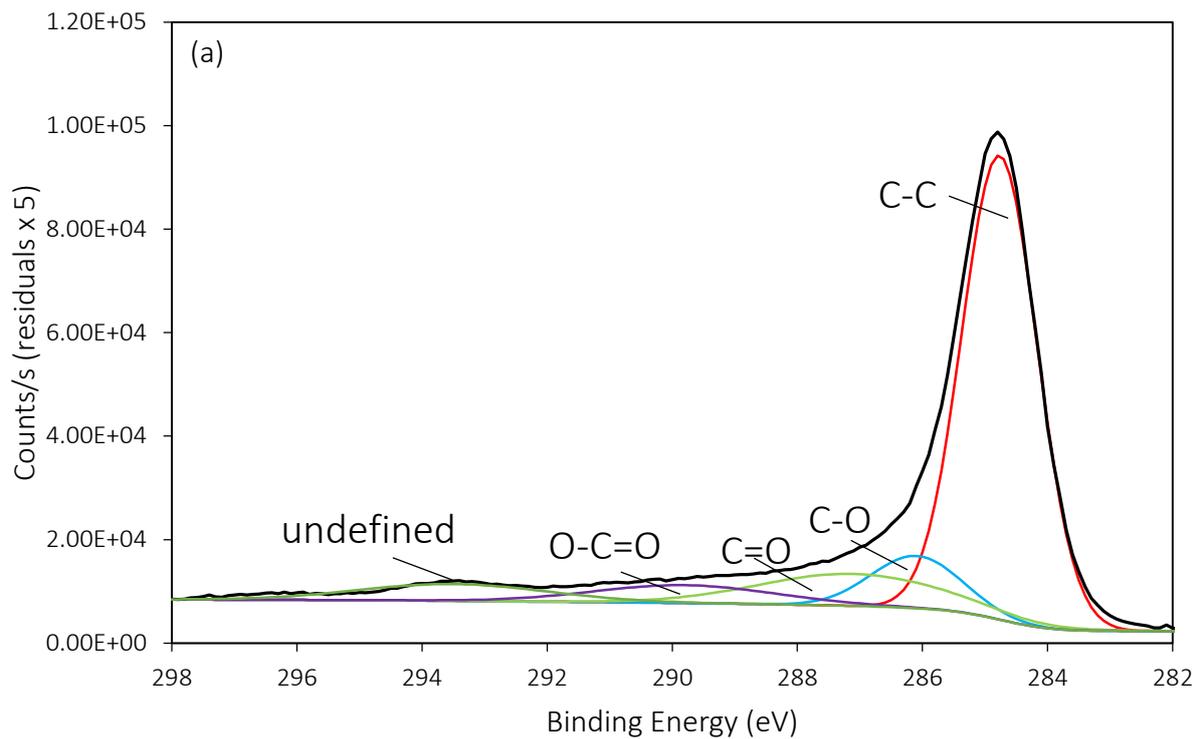


Figure 6-15: Detailed XPS C1s spectra of (a) RH700 and (b) RH700-HF

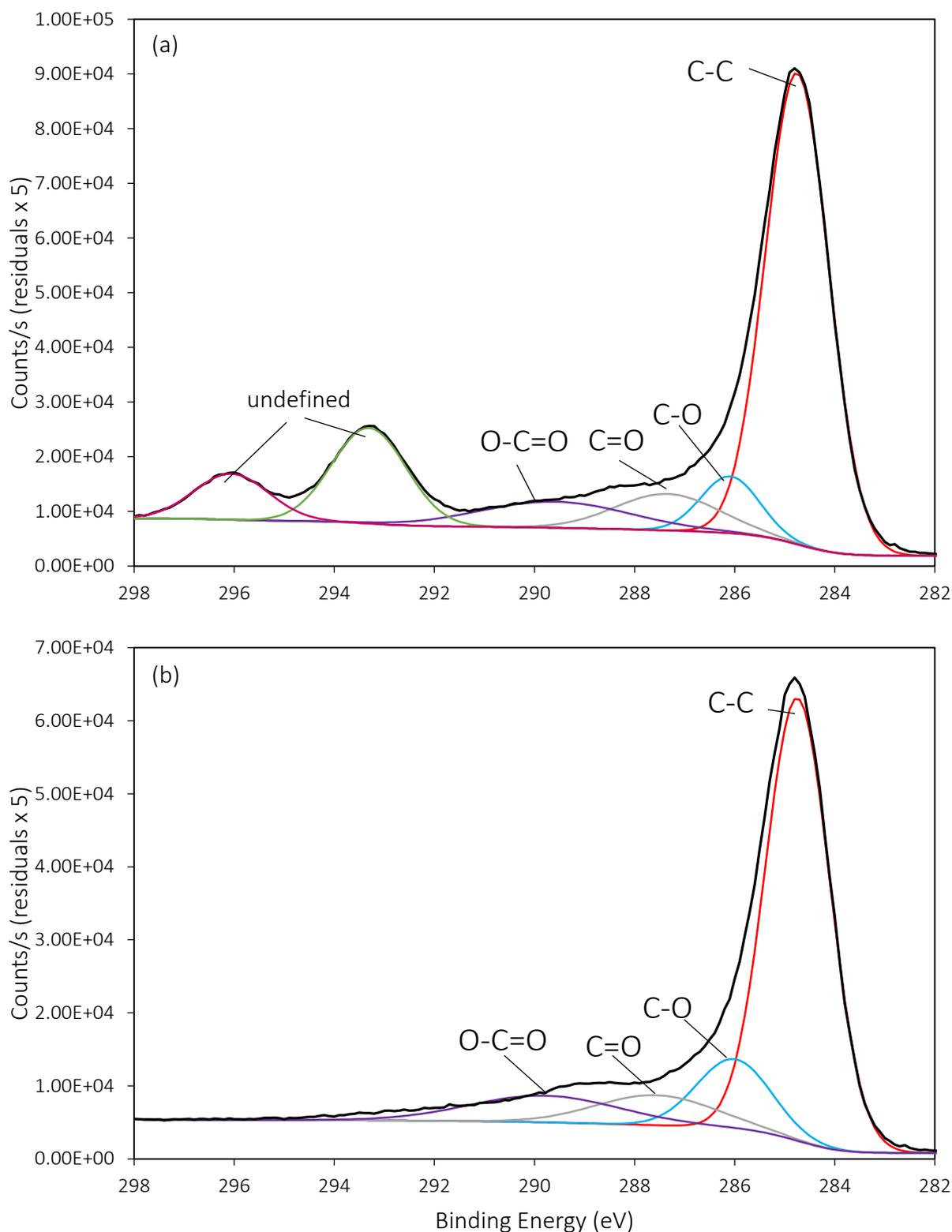


Figure 6-16: Detailed XPS scans of C1s spectra of (a) OSR550 and (b) OSR550-HF

All biochars showed a decrease in C-C groups after HF treatment, which implies that some surface oxidation occurred during modification. The decrease in C-C groups for SWP550 was relatively small (76.91% to 73.90%), and was mostly accounted for by a corresponding increase in C-O groups. The addition of these acidic functional groups suggests that the acidity of SWP550 may have increased after modification. RH700 showed a significant decrease in C-C and C=O ketone groups after modification, which was accounted for by an increase in C-O and O-C=O groups. This is consistent with the survey scans which suggested that the amount of organic oxygen had increased significantly, and suggests that the acidity of the biochars is likely to increase significantly due to (a) the removal of alkaline ash minerals, (b) the removal of basic C=O groups, and (c) the addition of acidic C-O and O-C=O groups. OSR550 showed relatively similar effects to SWP550, with a small decrease in C-C groups (73.10% to 69.11%) mostly accounted for by a corresponding increase in C-O groups, suggesting surface acidity may have increased.

6.2 Influence of solution pH on atrazine sorption to raw, modified and ash fractions of standard biochars

The sorption of atrazine to the raw, modified and ash fractions of SWP550, RH700 and OSR550 (except for SWP550-ash) as a function of solution pH was determined. The results for the raw biochars were presented previously in Chapter 4. The sorption tests were carried out as a function of pH, as these provided the greatest indication of the chemical sorption mechanisms occurring in Chapter 4 and also suggested that the ash content may be contributing to the removal of atrazine in the presence of biochar. The pH-dependent sorption of raw and modified biochars therefore provides important insights into the likely behaviour of biochar in the soil over the long-term under changing pH conditions and therefore the appropriate design of biochar as a soil amendment.

6.2.1 Buffering capacity

The buffering capacity of the raw, modified and ash fractions of SWP550, RH700 and OSR550 were determined by comparing the initial and final solution pH values. This also allows for the determination of the pH_{pzc} which provides insights into the surface charges of the functional groups. The buffering capacity is an important property of biochar when applied to soil, however it also has a significant influence over the adsorption mechanisms which occur in solution.

The pH_{pzc} values of the raw, modified and ash fractions of the biochars are shown in Figure 6-17. All three biochars show significant decreases in pH_{pzc} after modification with HF, suggesting that the biochars have been acidified. This may be a result of the removal of inorganic basic components such as CaCO_3 , as suggested by XRD analysis, the removal of basic functional groups such as carbonyl groups, or the addition of acidic groups as indicated by XPS analysis. The large decrease for SWP550 suggests that the decrease is not attributable to the removal of ash alone, as SWP550 has very low ash content and its removal would therefore not have such a great impact. The XPS analysis confirmed an increase in acidic functional groups for all three biochars, which likely contributes to their increased acidities. This may partially explain why the decrease in pH for OSR550 was greater than that for RH700. However, XRD also showed the presence of calcite on OSR550 which was removed by HF modification, which would also reduce alkalinity. Notably, OSR550-ash has a greater pH_{pzc} value than RH700-ash, despite RH700 having a higher pH_{pzc} than OSR550. This is most likely due to the greater overall contribution of calcite to the pH of OSR550-ash, which exists in smaller quantities in OSR550 and is not as significant in RH700 or RH700-ash. The HF modifications therefore reduced the pH_{pzc} values of the biochars by adding the presence of acidic functional groups and removing the presence of basic functional to all three biochars, while also removal alkaline components of OSR550.

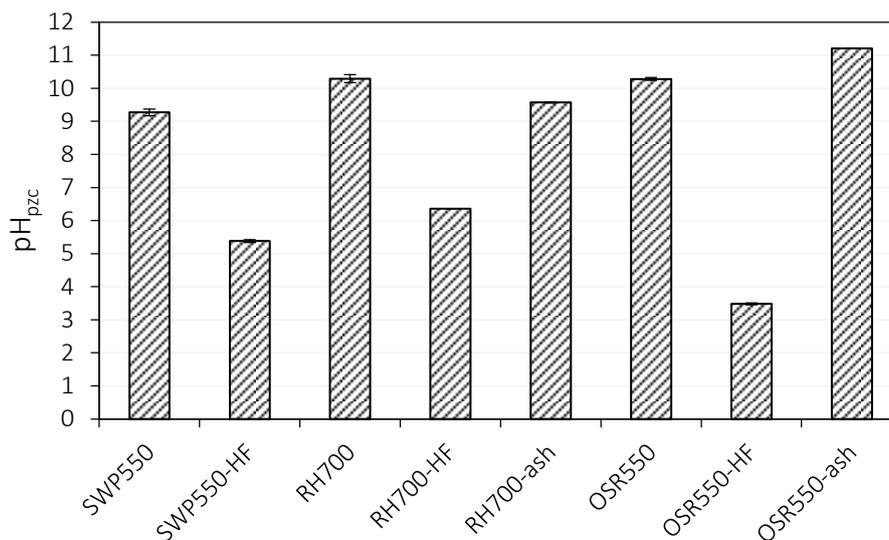


Figure 6-17: pH point of zero charge values for the raw, modified and ash fractions of the standard biochars

The buffering properties of SWP550 and SWP550-HF are shown in Figure 6-18, and confirm that the HF modification altered the acidity of the biochar. At low pH values (pH < 5), the final pH values were approximately equal. However, as the initial solution pH increased further, SWP550 increased the solution pH to approximately 8, while SWP550-HF decreased the solution pH to approximately 5.

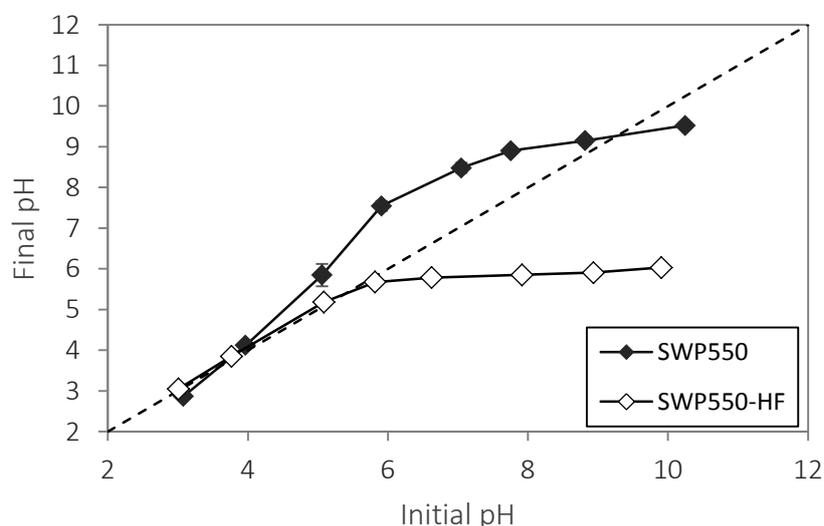


Figure 6-18: Buffering capacities of SWP550 and SWP550-HF biochars in the presence of atrazine

The buffering properties of RH700, RH700-HF and RH700-ash are shown in Figure 6-19. They show that the buffering capacity of RH700-ash is slightly lower than RH700, while RH700-HF has significantly reduced pH, as was the case for SWP550-HF. The lower

buffering capacity of RH700-ash than RH700 suggests that the high buffering capacity of RH700 is not due to the contribution of inorganic minerals alone, and is also attributable in part to the surface chemistry of the carbonised fraction.

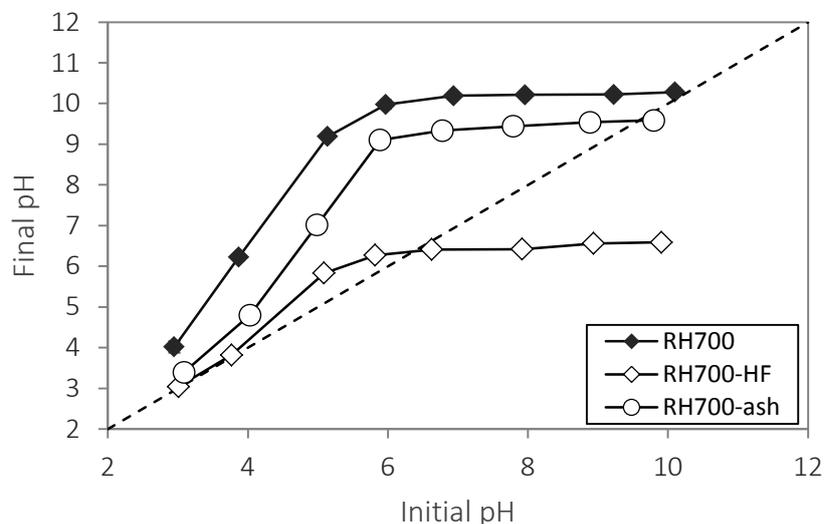


Figure 6-19: Buffering capacities of RH700, RH700-HF and RH700-ash biochars in the presence of atrazine

The buffering properties of OSR550, OSR550-HF and OSR550-ash are given in Figure 6-20. OSR550-HF shows a similar profile to SWP550-HF and RH550-HF, which is most likely attributable to the presence of acidic functional groups. Notably, RH700-ash shows a greater buffering potential than RH700, which is likely due to the presence of alkaline minerals such as calcite.

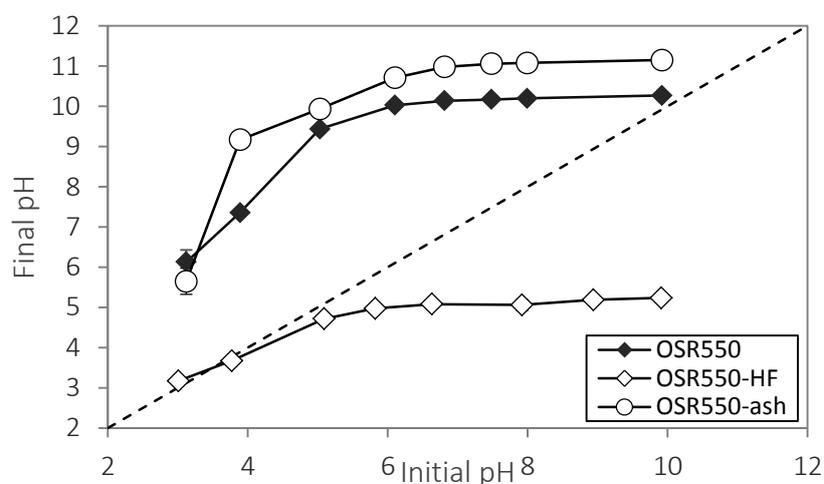


Figure 6-20: Buffering capacities of OSR550, OSR550-HF and OSR550-ash biochars

Overall, the buffering capacities of the raw and modified biochars show that HF increased the acidity of the biochars dependent on their ash contents. RH700, which is rich in silica-based ash components showed a lesser decrease in pH_{pzc} than OSR550, which contains calcium-based ash components. These results were also in line with the buffering results of the pure ash fractions, in which OSR550-ash showed higher alkalinity than both OSR550 and RH700-ash. These results suggest that the composition of the ash fraction has a significant influence on the buffering capacity of the biochars and therefore the sorption mechanisms that take place. Due to the generally poor characterisation of the ash fraction, this is a novel finding which has received very little discussion in the literature to date. The following section provides further information on how the different compositions of ash fractions can influence the significance of different sorption mechanisms.

6.2.2 pH-dependency of sorption capacity

The relationship between solution pH and the sorption of atrazine to the raw, modified and ash fractions of SWP550, RH700 and OSR550 were determined. The three different fractions allow for the determination of novel insights into the role of each of the carbonised component, the ash fraction, and the interactions between these two. This section will first analyse the overall changes in sorption of the modified and ash fractions for the raw biochars, and then assess the different mechanisms causing these differences.

Changes in absolute sorption capacity

The relative sorption capacities of the raw, modified and ash fractions of SWP550, RH700 and OSR550 biochars are given in Figure 6-21, and allow for comparisons of sorption capacities between the three fractions. Previous studies have generally demonstrated increased sorption of organic compounds after de-ashing, as highlighted in Chapter 2, however the results from this study suggest that this is not always the case and that the net result depends on both the physical structure of the carbonised fraction and the composition of the ash fraction.

The HF-modified biochars and ash components showed different changes in sorption over the different feedstocks. SWP550 showed very little change in sorption after modification with HF, which is in line with the characterisation suggesting the modification did not significantly affect the chemical properties of the biochar. In contrast, RH700-HF showed slightly increased sorption compared with RH700 at some pH values, and no significant

changes at others, while OSR550-HF clearly showed greater sorption at the entire pH range tested except for pH3. RH700-ash and OSR550-ash both showed significantly lower sorption than the biochars from which they were produced, which is in line with previous studies showing that they have low sorption capacities due to a lack of carbon, micropore structure and low surface areas. However, the different changes in sorption for RH700 and OSR550 after de-ashing suggest that the original ash compositions had different influences on the overall sorption properties.

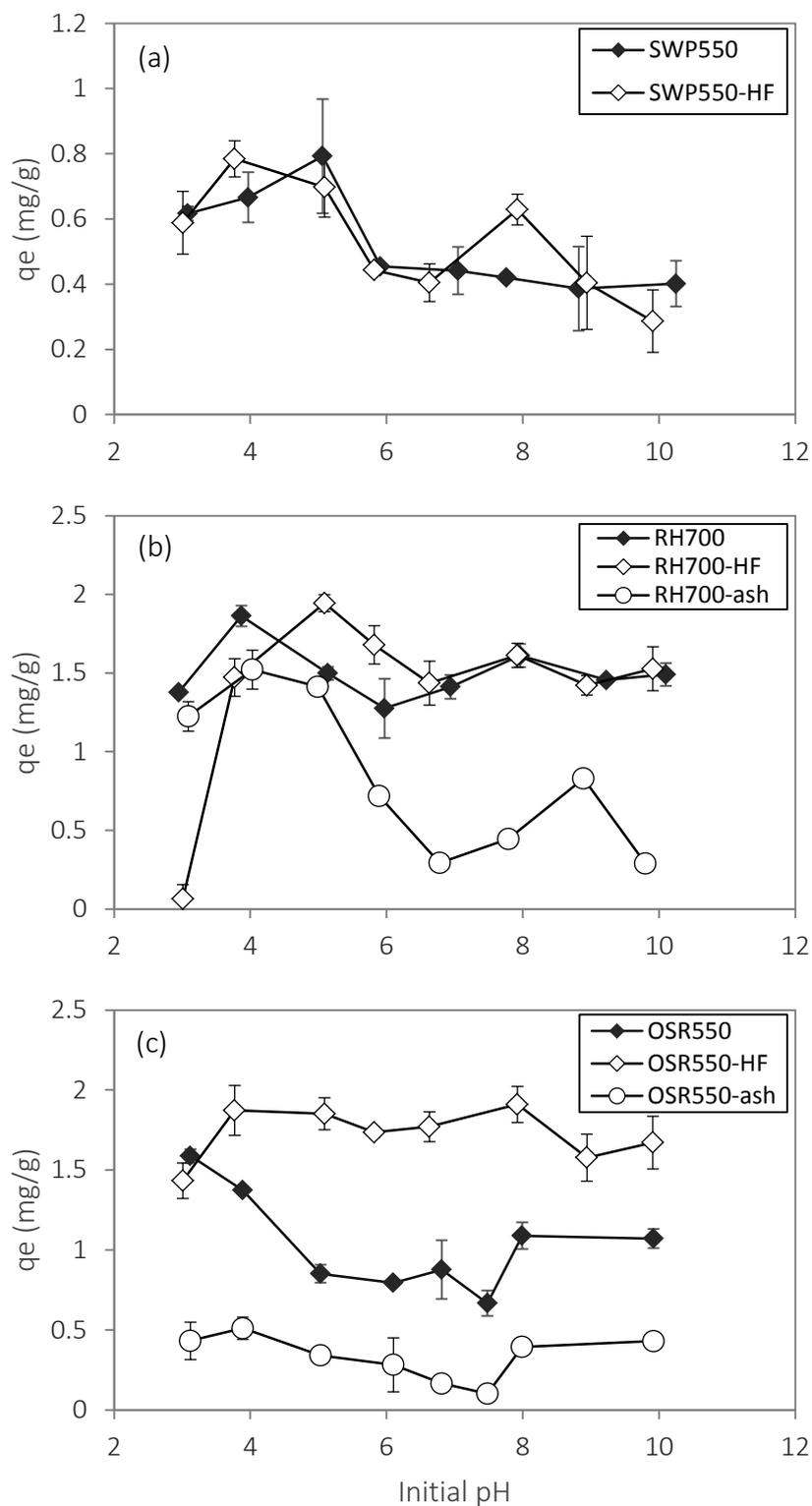


Figure 6-21: Sorption capacity against initial solution pH for raw, modified and ash fractions of (a) SWP550, (b) RH700 and (c) OSR550

The absolute change in sorption after de-ashing may be partially attributed to an increase in surface area. As outlined in Chapter 2, ash can block access to microporous regions of the biochars reducing access to sorption sites, and de-ashing can therefore increase access to

these sorption sites. SEM images provide some evidence that this has occurred for RH700 and OSR550, however without measuring surface area it is not possible to make a conclusion. Unfortunately, despite repeated attempts, BET analysis was not able to be carried out on the HF-modified biochars. In order to better determine the sorption mechanisms occurring, it is therefore useful to look at the relative changes in sorption, after accounting for buffering effects. The following sections therefore outline the sorption mechanisms as a function of final pH and change in pH in order to determine the different mechanisms controlling sorption to the raw, modified and ash samples.

Changes in mechanisms of atrazine sorption to SWP550

The sorption capacities of atrazine over final solution pH to SWP550 and SWP550-HF biochars are shown in Figure 6-22, and show similar sorption profiles after accounting for the influences of buffering. Both biochars show reduced sorption at very low pH values, which can be attributed to electrostatic repulsion between the positively charged biochar surface and the partially positively charged atrazine molecules, as described in Chapter 4. Both biochars then show sharp increases in sorption, which is attributed to increased hydrogen bonding between atrazine and abundant H^+ ions on the surface of the biochars, as described previously in Chapter 4. Both biochars then show sharp decreases as pH approaches pH_{pzc} , which is attributed to the reduced quantity of H^+ ions on the surface of each sample as pH increases. SWP550 shows the greatest sorption in the range $pH \approx 6$, while SWP550-HF shows the greatest sorption when $pH \approx 4$. SWP550-HF shows continued reductions in sorption when $pH > pH_{pzc}$, while the pH range considered does not significantly exceed pH_{pzc} for SWP550. These differences primarily represent differences due to the different buffering capacities of the two biochars.

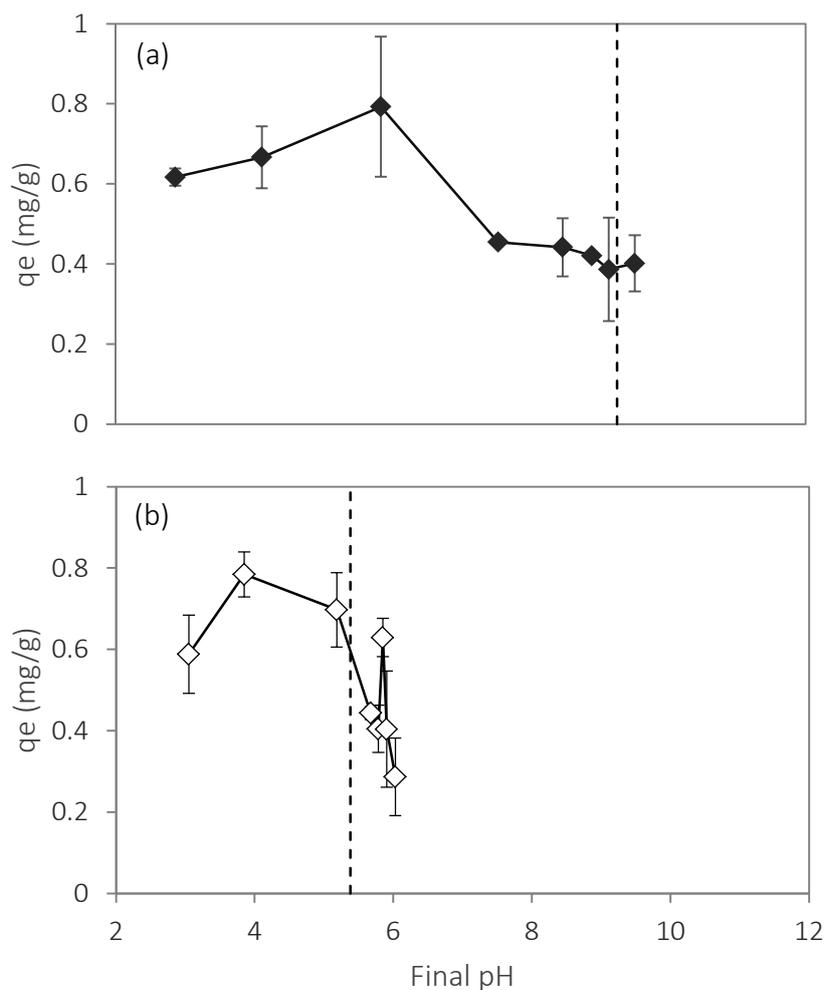


Figure 6-22: pH dependent sorption profiles of (a) SWP550 and (b) SWP550-HF. Dashed lines indicate the pH point of zero charge

The significant decreases in both SWP biochars at $pH > pH_{pzc}$ provides insights into several different mechanisms occurring. As highlighted in Chapter 2, the mechanisms promoted at very high pH values are typically driven by the negative surface charge of the biochar, and are: (a) π - π EDA interactions where biochar is acting as the π -donor; (b) hydrogen bonding where biochar acts as the H^+ acceptor; and (c) catalytic hydrolysis in the presence of dissolved minerals. Catalytic hydrolysis for SWP550 is highly unlikely due to the very low ash content, resulting in very low quantities of dissolved minerals. The lack of π - π EDA interactions suggests that SWP550 is not carbonised to a high enough degree to allow these effects to occur in significant quantities, while the lack of hydrogen bonding suggests that SWP550 biochars do not possess oxygen-containing functional groups which can act as H^+ acceptors.

These results are largely in line with the results of Chapter 4, which suggested that sorption of atrazine to SWP biochars is largely controlled by physical sorption (i.e., pore filling), although partitioning is also significant, and hydrogen bonding (where biochar acts as the H⁺ donor) can also contribute at intermediate pH ranges. The HF modifications of SWP550 therefore provided a relatively successful control by showing that there were few significant changes in sorption profile to a biochar with very low ash content. While the acidity and buffering properties of SWP550 did change significantly, the sorption capacity values did not change significantly and the sorption profiles and mechanisms were very similar after accounting for buffering effects.

Changes in mechanisms of atrazine sorption to RH700

The sorption capacities of atrazine to RH700, RH700-HF and RH700-ash as a function of final solution pH are given in Figure 6-23, and show very different profiles for all three adsorbents. All three show reduced sorption at very low pH values, attributable to electrostatic repulsion, as discussed for SWP550. All three then show sharp increases in sorption when $\text{pH} \approx 5$. The increased sorption to RH700 and RH700-HF can be attributed to increased hydrogen bonding in this range, as discussed for SWP550. However, the increased sorption to RH700-ash in this range is notable, as the carbon content is very low (0.14%) and hydrogen bonding would therefore be unable to occur. RH700 then shows a sharp spike above pH_{pzc} , while RH700-HF shows no clear change or a slight decrease, while the sorption to RH700-ash generally decreases.

The sorption profiles therefore vary particularly at high pH values (i.e., $\text{pH} \approx \text{pH}_{\text{pzc}}$ or $\text{pH} > \text{pH}_{\text{pzc}}$ for each adsorbent), and the influences in this range therefore provide important insights into the mechanisms occurring. In Chapter 5, it was determined that it was not possible to distinguish the mechanisms occurring to RH700 at high pH values due to competing influences of hydrogen bonding, π - π EDA interactions, and interactions with ash minerals. The low ash content from RH700-HF, greater degree of oxygen-containing functional group characterisation, and isolated ash component therefore allow for isolation of each of these competing effects.

The lack of increase in RH700-HF at high pH values confirms that the increase in RH700 is not due to increased hydrogen bonding, due to the greater hydrogen bonding capacity of RH700-HF. XPS analysis showed that RH700-HF has more groups which are capable of

forming hydrogen bonds, particularly those which can accept H^+ ions at high pH values such as phenol and carboxylic acid groups. If the strong increase was due to increased hydrogen bonding, then a *greater* increase would be expected at high pH values for RH700-HF than RH700. This is not observed, and therefore it is unlikely that strong hydrogen bonding is dominating the sorption of atrazine to RH700 at high pH values.

It is therefore assumed that the sharp increase in sorption to RH700 at high pH values is caused by either increased π - π EDA interactions or interactions with the ash fraction. Both of these are possible: RH700-HF had increased oxygen-containing functional groups in the carbonised phase, and would therefore have a reduced capacity to donate π -electrons at high pH which may explain the lack of increase for RH700-HF. Similarly, RH700-HF has a very low ash content, and interactions with minerals are therefore unlikely. However, OSR550 was not significantly oxidised by the HF modification. In order to determine this effect, it is therefore necessary to further investigate the effects on OSR550 after modification.

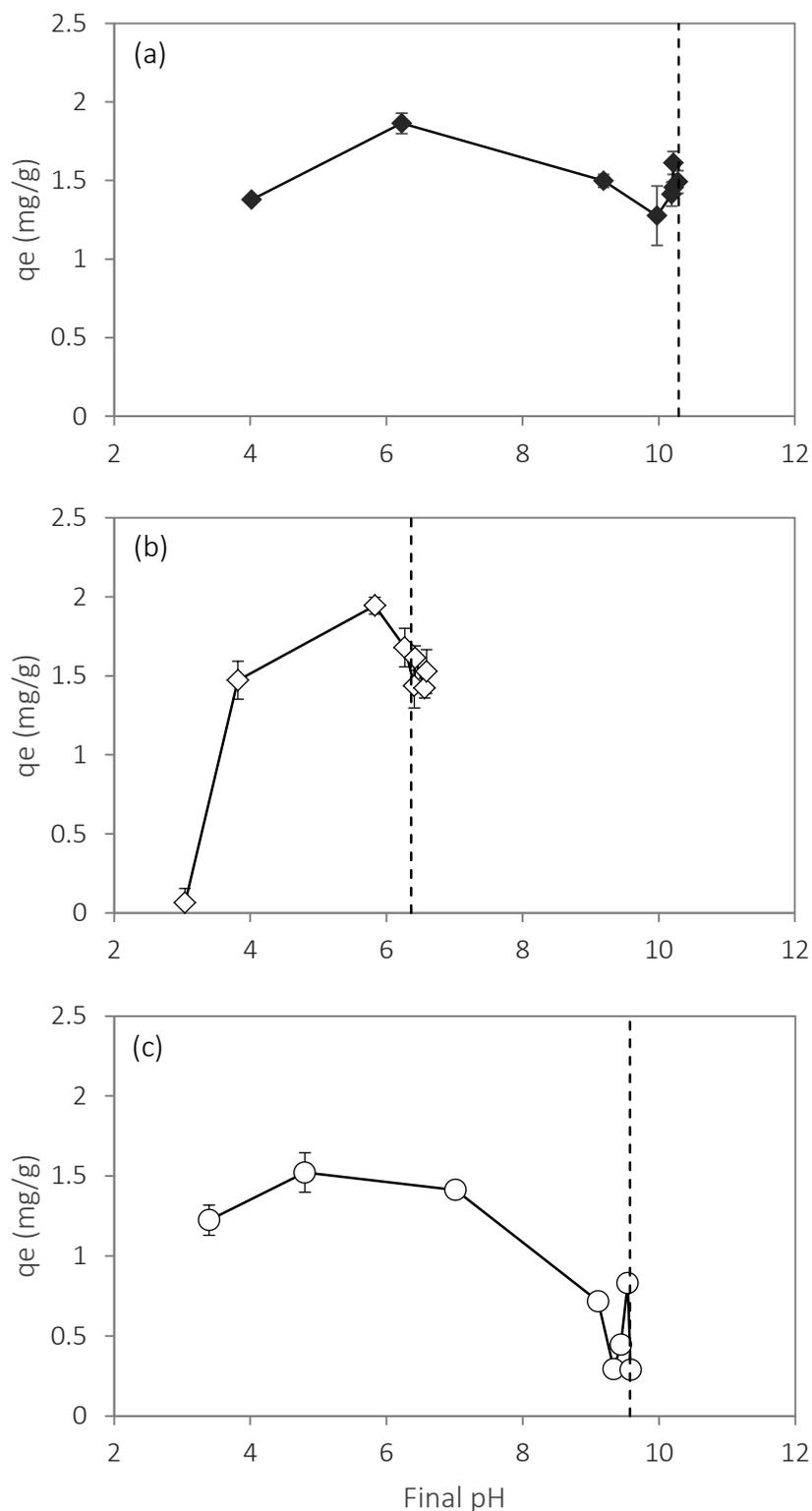


Figure 6-23: pH-dependent sorption profiles of (a) RH700; (b) RH700-HF; and (c) RH700-ash. The dashed lines indicate the pH points of zero charge

Changes in mechanisms of atrazine sorption to OSR550

The sorption profiles of OSR550, OSR550-HF and OSR550-ash are shown in Figure 6-24, and appear to show similar profiles to those of RH700-based adsorbents. OSR550-HF and

OSR550-ash show low sorption at very low pH values, while the buffering capacity of OSR550 raises pH levels above this range. All three adsorbents show high sorption at intermediate pH ranges, and decreased sorption at values tending towards pH_{pzc} . At $\text{pH} \approx \text{pH}_{\text{pzc}}$, the trends in sorption capacities for the three biochars vary significantly, which can give insights into the mechanisms occurring. Note that the pH_{pzc} of OSR550-HF may not accurately reflect the true point of zero charge. Based on the data presented previously in this thesis, a more accurate pH_{pzc} value may be approximately 4.8. The anomaly may be in part to the high sensitivity in the pH measurements for determining the pH_{pzc} for HF-modified biochars. As indicated in Figure 6-20, a small measurement error can significantly alter the pH_{pzc} . The value marked on the graph should therefore be treated as a guide only.

At high pH values, the sorption of atrazine to OSR550 sharply increases, while sorption decreases to OSR550-HF and there is no clear trend for OSR550-ash. These different trends suggest that different mechanisms are controlling sorption in this range to the three adsorbents. As previously described for RH700, it is unlikely that the difference between OSR550 and OSR550-HF is due to hydrogen bonding due to the more favourable conditions for hydrogen bonding at high pH values for OSR550-HF than OSR550. Therefore the difference for OSR550 biochars must also be due to differences in π - π EDA interactions or influences from the ash composition.

It is unlikely that the differences in sorption at high pH values to OSR biochars are caused by π - π EDA interactions. XPS scans of OSR550-HF showed only a slight decrease in C-C groups, and a slight overall decrease in surface organic oxygen. The conditions for π - π EDA interactions at high pH (i.e., a highly carbonised, non-polar surface) are therefore not significantly changed, and are potentially even slightly improved. It is therefore unlikely that such a small change in sorption properties would shift sorption from sharply increasing to sharply decreasing in this range. The spike in sorption to OSR550 is therefore not attributable to π - π EDA interactions.

The spike in sorption to OSR550 is therefore most likely due to interactions with the ash fraction. The elemental, XRD and XPS analyses all showed that the HF modification successfully removed SiO_2 and CaCO_3 fractions, and therefore interactions with ash would not be as significant to OSR550-HF. However, the sharp spike in sorption at high pH values is not observed for the raw OSR550-ash fraction. This suggests that the spike is due to some interactions involving the carbonised biochar as well as ash fractions. This conclusion also

suggests that similar reasons are the most likely explanation for the similar effects happening to RH700 biochars.

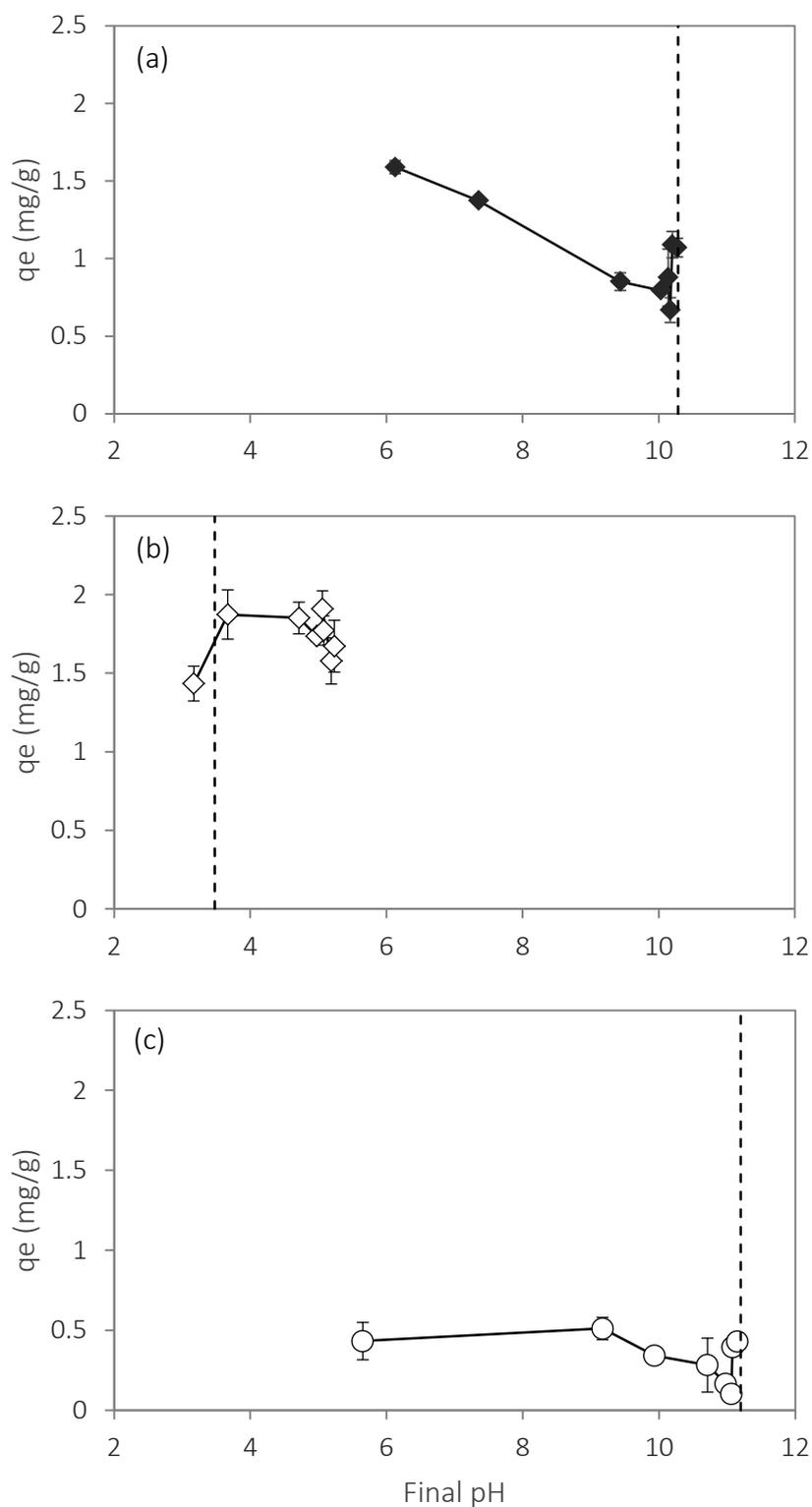


Figure 6-24: pH-dependent sorption profiles of (a) OSR550; (b) OSR550-HF; and (c) OSR550-ash. The dashed lines indicate the pH points of zero charge

6.2.3 Discussion of role of ash on sorption mechanisms of atrazine

De-ashing using HF had relatively little influence on the sorption of atrazine to SWP550 biochar, however for RH700 and OSR550 it changed the trend of increasing sorption at high pH values to a decreasing trend. The explanation for this was not attributable to hydrogen bonding or π - π EDA interactions, and is considered most likely to be the result of interactions of atrazine with the mineral fractions of the biochars. The potential mechanisms for this include catalytic hydrolysis of atrazine or the formation of complex ions.

The catalytic hydrolysis of atrazine may represent the cause of the increased removal of atrazine at high pH values. As discussed in Chapter 2, previous studies have suggested dissolved ions can facilitate the degradation of atrazine, particularly at high pH values, which would result in an increase in apparent sorption. Zhang et al.¹⁵⁶ demonstrated that the presence of dissolved minerals can facilitate the hydrolysis of atrazine, either through the formation of a complex or through promoting nucleophilic attack. This effect may be present here, as the removal of Si, Ca and Na minerals from RH700 and OSR550 will remove the necessary components for this mechanism. However, this mechanism may be unlikely as no degradation products were observed during UV-vis analysis of the solutions after mixing with the standard biochars (data not presented). Further studies investigating the presence of these minerals may be able to confirm the effect.

The formation of complexes may also result in the increased sorption of atrazine. Bessac et al.²²² demonstrated that atrazine-(Ca²⁺)₂ complexes can form on the surface of an adsorbent. The high Ca composition of RH700 and , in particular, OSR550 may facilitate this effect. However, XPS analysis of OSR550-HF showed a similar Ca content to OSR550, suggesting that it is still present. It is possible that the Ca in OSR550-HF existed primarily as the insoluble CaF₂, which is consistent with the approximate elemental ratios observed. While no peak was observed corresponding to CaF₂ on XRD analysis, no peak was observed corresponding to *any* form of calcium, suggesting that it may not be present in great enough quantities or not able to be detected by XRD. These reasons suggest that the formation of atrazine-(Ca²⁺)₂ complexes may be a potential mechanism for the increased removal of atrazine.

6.3 Summary of biochar modification and role on ash interactions

Chapter 6 has investigated the modification of biochar and its influence on the sorption mechanisms of atrazine. Modifications of SWP550, RH700 and OSR550 were carried out using a HF/HCl solution in order to remove the ash components. Samples were then characterised using FTIR, elemental analysis, XRD analysis, XPS analysis and SEM imaging in order to accurately determine the effects of the modifications on the surface elements, chemical compositions and physical structures. The pH-dependency of the sorption of the HF-modified samples, together with the raw and ash fractions was then investigated and the dominant mechanisms discussed.

HF-modification successfully removed the ash contents of RH700 (SiO_2) and OSR550 (SiO_2 and CaCO_3), while having little effect on SWP550 due to its low ash content. RH700-HF and OSR550-HF therefore had greater carbon contents than their respective initial biochars. Some acidic functional groups had been added to RH700-HF, as determined by detailed XPS scans of the C1s spectra, although this effect was small for SWP550-HF and OSR550-HF. SEM imaging did not clearly show the removal of ash, however confirmed that the pore structures were not significantly altered by the modification.

All three modified biochars had significantly reduced pH_{pzc} values, which was attributed to the acidification of functional groups and removal of alkaline inorganic components during modification. pH-dependent sorption effects to SWP550-HF was similar to SWP550, after accounting for buffering effects, as predicted by the small changes to its composition. RH700-HF and OSR550-HF biochars were similar to their original biochars at low and intermediate pH ranges, however the effects at high pH values varied. The variation in sorption at high pH was attributed to the removal of ash components in RH700 and OSR550 biochars, which may influence either the catalytic degradation of atrazine or the formation of complexes. The results suggest that the presence and composition of the ash fraction can significantly influence the removal of atrazine from pore waters, particularly in high pH ranges which are likely to represent realistic environmental levels.

6.4 Summary of atrazine removal processes and biochar suitability for application in remediation

The sorption tests and characterisation methods used throughout Chapters 4, 5 and 6 of this thesis have revealed a number of insights into the transport, partitioning and adsorption of atrazine to the standard biochars. They have also showed that many different mechanisms occur to the different biochars depending on the environmental conditions. The following paragraphs summarise the key results for each feedstock considered in this thesis and their subsequent utility for remediating atrazine in practice.

6.4.1 Softwood pellet biochars

Sorption of atrazine to SWP biochars is controlled by a number of mechanisms depending on the particular conditions, as demonstrated in Figure 6-25, although the sorption capacities were low. Partitioning is significant to both SWP biochars as evidenced by the comparatively high linearities of their isotherms, and can comprise nearly 50% of sorption to SWP550 at high atrazine concentrations. Pore filling is present in significant quantities to the SWP biochars, although inefficient pore diffusion may contribute to the low sorption capacities. pH-dependency studies showed that electrostatic repulsion between positively charged atrazine molecules and biochar surface functionalities can hinder sorption at low pH values. However, hydrogen bonding can significantly increase sorption at intermediate pH values, while π - π EDA interactions are present at high pH values for SWP700 due to its greater degree of carbonisation.

The mechanisms and extent of atrazine sorption to the softwood biochars suggest that they are not suitable for use in remediating atrazine. SWP biochars had the lowest sorption capacities of all feedstocks tested, and a significant component of total sorption was due to partitioning which may be reversed over time in the soil. Further, increased sorption to SWP700 at high pH values was attributed to π - π EDA interactions, which are also unstable in the long term due to the increased oxidation of the aromatic sheets over time. These results suggest that SWP biochars will be inefficient at removing atrazine in soil, and may result in significant quantities of attached contaminants being leached over time.

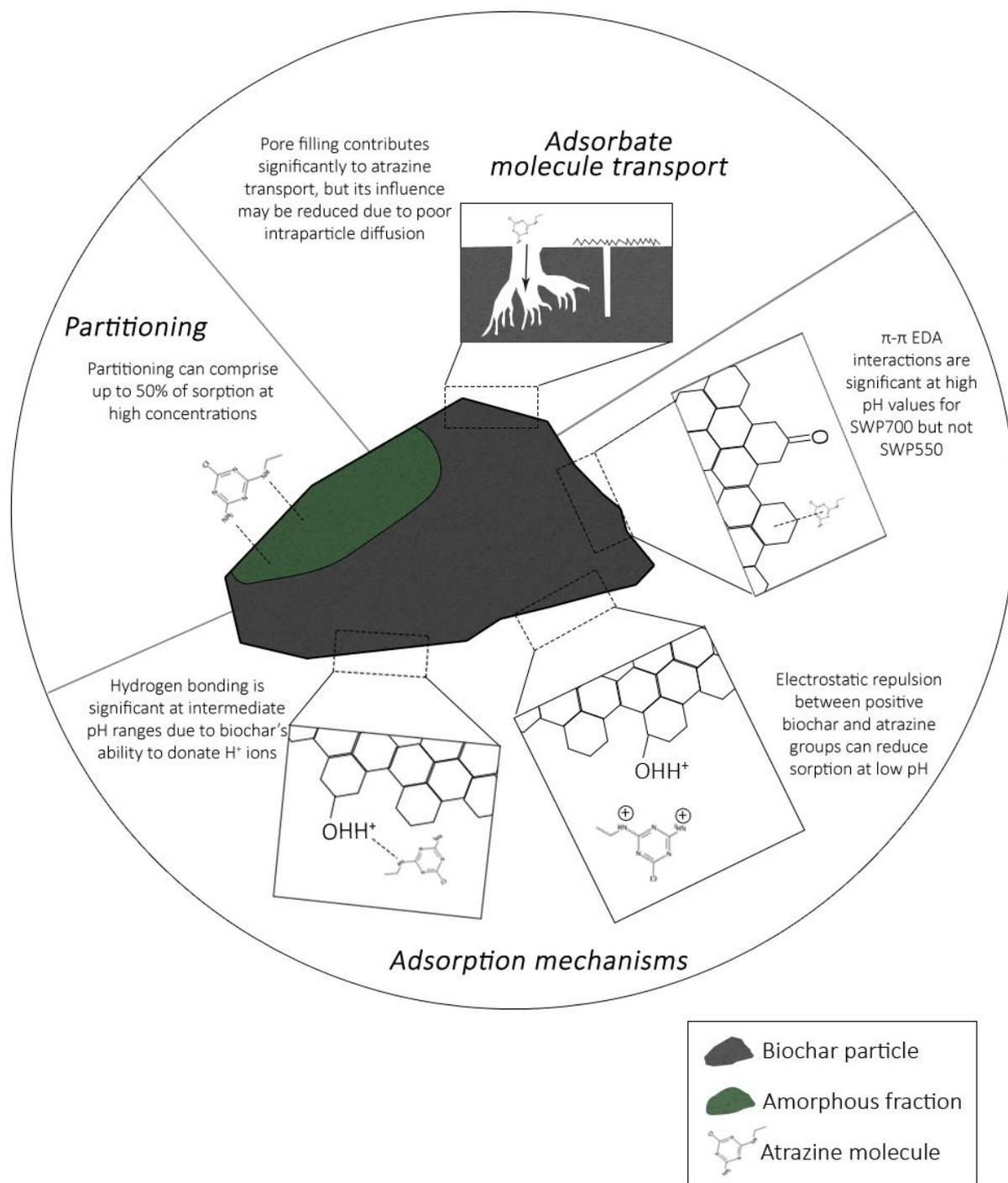


Figure 6-25: Schematic of sorption mechanisms determining atrazine sorption to SWP standard biochars

6.4.2 Wheat straw biochars

Sorption of atrazine to wheat straw biochar is captured by pore filling processes leading atrazine to sites for hydrogen bonding as demonstrated in Figure 6-26. The significance of pore filling is evidenced by the good fit of the intraparticle diffusion model, and the film diffusion model suggesting that film diffusion is not significant in determining kinetic

sorption. WSP700 has a slightly lower sorption capacity and surface area than WSP550, which may be attributable to strong hydrogen bonding on WSP550, even at low pH values. However, WSP700 had a lesser reduction in sorption in the presence of humic acids, suggesting that it may still be better able to transport atrazine through the biochar particle. The dual-mode sorption model confirmed the high influence of adsorption to total sorption. The pH-dependency studies showed the significance of hydrogen bonding across all pH ranges, captured by biochar donating H^+ ions at low pH values, and accepting H^+ ions at high pH ranges.

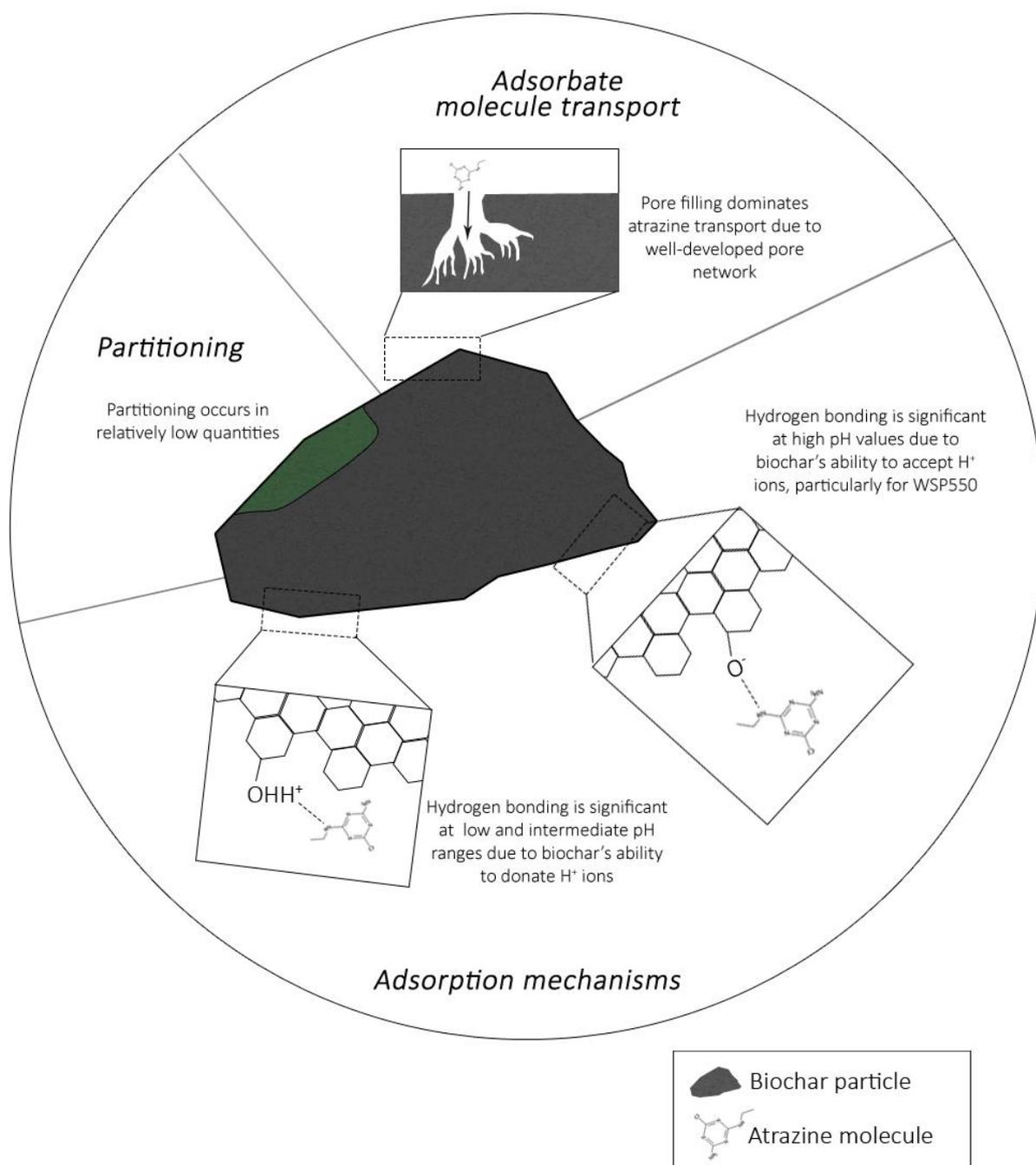


Figure 6-26: Schematic of mechanisms controlling sorption of atrazine to WSP biochars

The results suggest that WSP550 is better suited for use in remediating atrazine than WSP700, due to its strong influences of hydrogen bonding and greater stability at high pH values. The high overall influence of adsorption suggests that WSP biochars will tightly bind atrazine in the environment. Further, as both biochars are dominated by hydrogen bonding, these effects will become stronger over time meaning that atrazine is effectively immobilised. WSP550 is likely to be more suitable due to its higher sorption capacity and greater extent of

hydrogen bonding, although WSP700 may be better suited in soils with high organic contents as it demonstrated lower reductions in the presence of humic acids.

6.4.3 Miscanthus straw biochars

The sorption of atrazine to miscanthus straw biochars is largely controlled by strong interactions of hydrogen bonding, although partitioning can also have a significant role, as demonstrated in Figure 6-27. The kinetic studies showed a large quantity of rapid early sorption, suggesting strong chemical interactions and effective access to macroporous sorption sites. The strong chemical interactions are confirmed by the high sorption of MSP550 at low pH values, which is significant enough to negate the influence of electrostatic repulsion between positively charged atrazine and biochar functional groups. However, the isotherms contained a significant linear component, suggesting that partitioning is a contributing factor to overall sorption.

The results suggest that the suitability of MSP for remediating atrazine is feasible, although the high influence of partitioning, large sorption reductions in the presence of organic matter, and decreases in sorption to MSP700 at high pH may make them unsuitable for some applications. Partitioning could contribute up to 30% of sorption to MSP550 at high concentrations, which may result in some leaching of atrazine over time. MSP550 in particular showed strong hydrogen bonding across a wide pH ranges, suggesting it can effectively mitigate changes in soil conditions. In contrast, sorption to MSP700 reduced sharply under high pH, which suggests that it cannot form either hydrogen bonds as an H⁺ acceptor nor exhibit π - π EDA interactions.

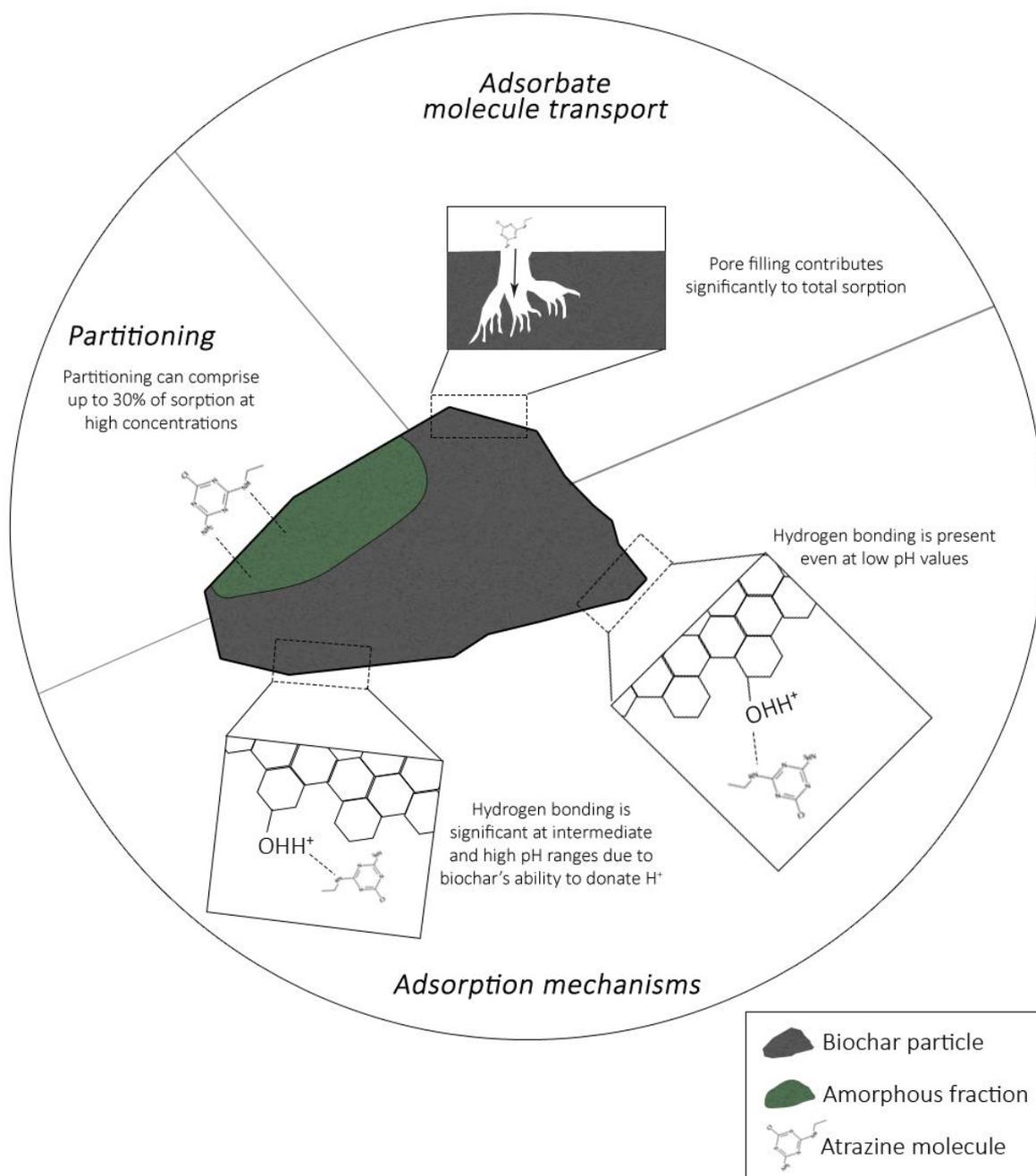


Figure 6-27: Schematic of mechanisms controlling sorption of atrazine to MSP biochars

6.4.4 Rice husk biochars

Rice husk biochars displayed by far the highest sorption of all of the standard biochars, attributable to effective pore filling processes and interactions with the ash fraction. The kinetic models suggested that intraparticle diffusion occurs steadily and in high quantities to RH biochars, highlighting the significance of pore filling. Further, the isotherms were highly non-linear and dominated by adsorption. RH550 had greatly reduced sorption in the presence of humic acids, while the decrease for RH700 was much lower; suggesting that pore filling

was playing a significant role and is influenced by the development of the pore network. pH-dependency tests suggested that hydrogen bonding occurs at intermediate pH values, while the increased sorption at high pH values were attributed to strong interactions with the ash fraction, as demonstrated in Figure 6-28.

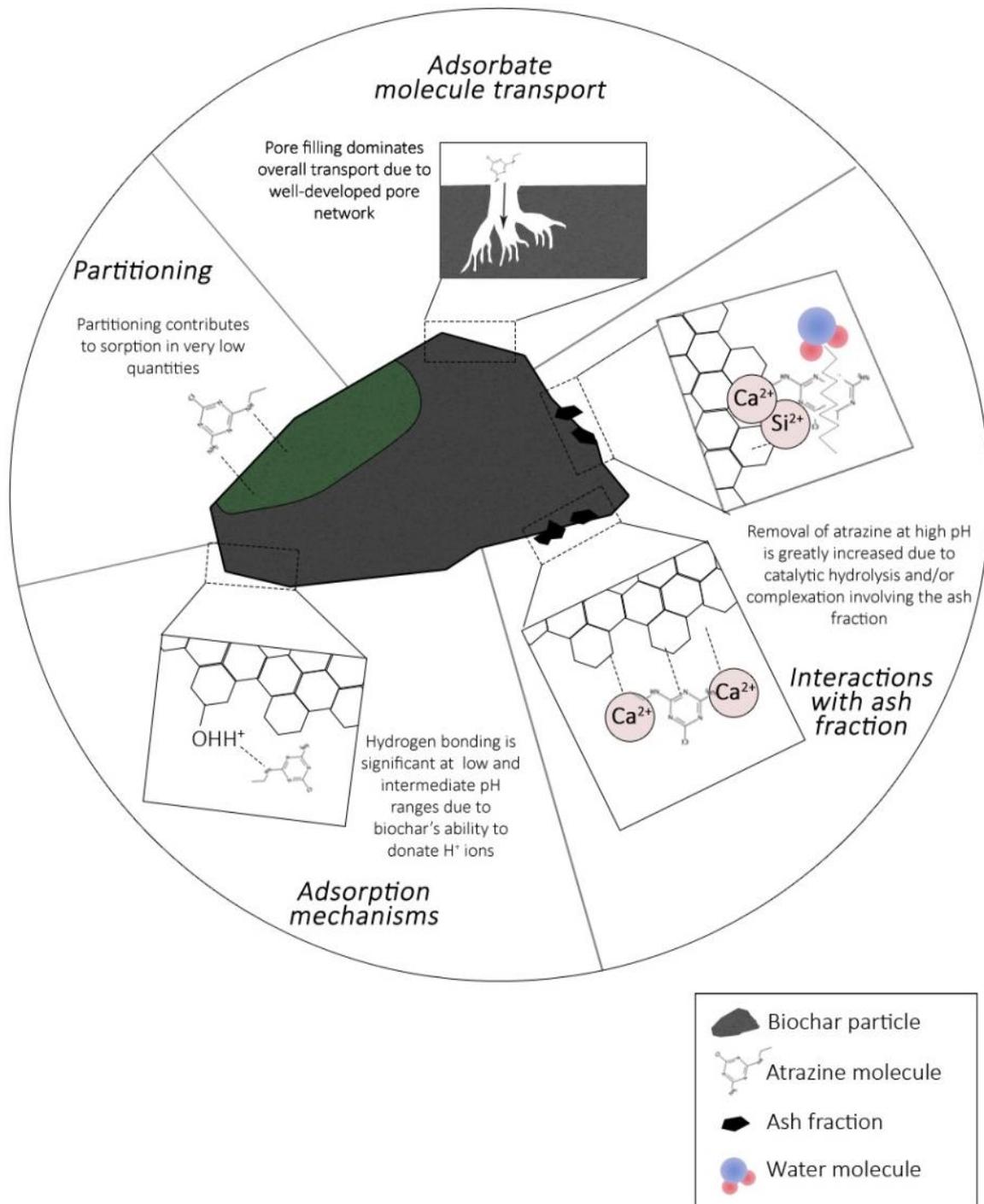


Figure 6-28: Schematic of mechanisms of sorption to RH biochars as determined by physical and chemical sorption tests

The high sorption capacities of the rice husk biochars suggest that they may be the best suited for the remediation of atrazine, although the interactions with the ash fraction should be better understood. The low contributions of partitioning and the high contributions of hydrogen bonding suggest that RH biochars are likely to strongly bind atrazine. However, the mechanism through which the ash fraction influences atrazine removal should be better understood before widespread application. If catalytic hydrolysis is causing the increased removal, then the toxicity, mobility and stability of the products should be better understood. Conversely, if complexation is significant then the strength and stability of this bond should be investigated.

6.4.5 Oil seed rape biochar

The sorption of atrazine to OSR550 was controlled by several processes, as demonstrated in Figure 6-29, with pore filling playing a significant role in transporting molecules into the more polar micropore regions. Kinetic studies showed that the initial rapid sorption was much slower than other biochars, suggesting poor access to sites for chemical interactions. Further evidence was provided for this poorly developed micropore network which showed OSR550 had relatively high sorption despite having by far the lowest surface area, suggesting it comprises primarily micropores that were not detectable by N₂-BET. Further, the humic acid studies showed a large decrease, suggesting that these pores are easily blocked. pH-dependency studies showed that the chemical interactions included hydrogen bonding at intermediate pH levels, while interactions with the ash fraction can increase atrazine removal in highly alkaline conditions.

As for RH biochars, the suitability of OSR biochars for application in remediation is largely dependent on the precise role of the ash fraction. Removal of atrazine at high pH was largely attributable to interactions with the ash fraction, and therefore the products and stability of this interaction should be better understood before widespread application. However, partitioning was also present in significant quantities to OSR550, which could potentially result in leaching of atrazine in the long-term. It is therefore recommended that OSR550 should not be used to remediate atrazine before further study.

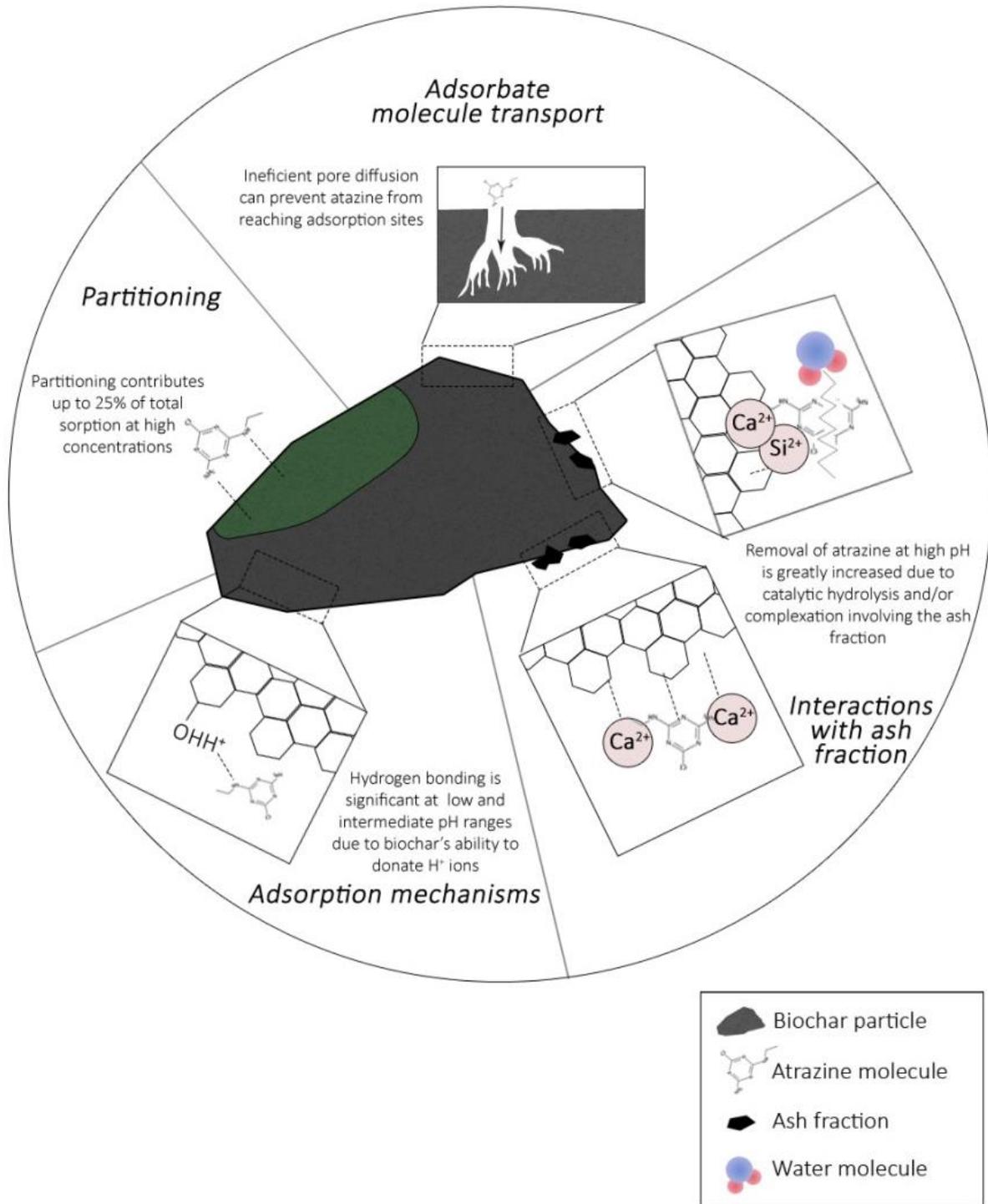


Figure 6-29: Schematic of mechanisms of sorption to OSR550 biochar as determined by physical and chemical sorption tests

Chapter 7: Conclusions and recommendations

7.1 Conclusions and outcomes

This thesis has investigated the sorption of atrazine to biochar, using a wide range of samples and techniques to isolate the significance of various sorption mechanisms. It has highlighted the role of pore filling, hydrogen bonding and interactions with the ash component, while suggesting that hydrophobic effects play little role and partitioning may have negative environmental outcomes. The environmental implications of these results require close attention, as they may have varied effects depending on particular conditions.

Chapter 2 investigated previous research into the use of biochar for remediating organic contaminants, and highlighted a number of inconsistencies and gaps in the efforts to date. In particular it highlighted that the role of the sorption mechanisms of organic contaminants in determining long-term remediation has received little attention to date, while the characteristics and mechanisms of atrazine sorption are not fully understood.

The literature review showed that there has been extensive research to date into the sources and extent of soil contamination, as well as the types of contaminants present in the environment. The quantity and extent of contaminated land presents a wide range of challenges for design engineers. However, many studies have also noted that the total reported number of contaminated sites is likely much higher than estimated due to underreporting. For example, a 2015 report by the European Environment Agency (EEA)²⁸ found approximately 5.7 contaminated sites per 10,000 habitants across the EU, but over seven times as many *potentially contaminated sites*, suggesting that the extent of the problem outlined in Chapter 2 is potentially an underestimate. The need for diverse, sustainable and affordable remediation techniques is therefore of critical importance.

The literature review also highlighted the many studies which have investigated the sorption mechanisms of organic contaminants to biochar. Sorption is controlled by a number of simultaneously occurring mechanisms, which for the purposes of this thesis were categorised as (a) partitioning, (b) pore filling, (c) π - π interactions, (d) hydrophobic effects, and (e) hydrogen bonding. Other mechanisms are occasionally present (as the results chapters would subsequently highlight), such as electrostatic attraction and repulsion, and the formation of

complexes. Many studies have reported on the significance and favourable conditions for these mechanisms for a range of contaminants.

However, it was noted that discussion on the practical significance of these mechanisms has received little attention to date. While the presence of these mechanisms has been clearly demonstrated, very few studies have gone on to discuss what the implications of these mechanisms are for remediation outcomes using biochar. Many simply recommend a biochar for use in the soil based on adsorption capacity alone, without regard for how it may change over time or under changing conditions. Chapter 2 therefore drew on available knowledge to determine the roles that each of the mechanisms will likely play in practice, which can assist engineers in designing biochar appropriate for the given objectives.

The review found that partitioning is likely to have very little long-term environmental relevance. This is due to (a) the rapid degradation of the amorphous component in the soil profile, (b) the reversibility of partitioned molecules, and (c) the small role that it plays at low, environmentally relevant concentrations. This finding suggests that the amorphous phase is not beneficial for maximising adsorption, which was already understood, but also that it may actually result in negative overall outcomes. The true remediation capability of some biochars may be misrepresented, as partitioning can contribute significantly to sorption capacity in batch sorption studies. Further molecules immobilised through partitioning may desorb once within soil and can represent an environmental risk if not accounted for. It is therefore recommended that studies report *adsorption capacity*, which excludes partitioning, rather than *sorption capacity*, in order to more accurately represent the usefulness of a given biochar. This can be achieved through desorption studies, the dual-mode sorption model, or through investigating sorption in the presence of adsorption blocking compounds.

The review found that pore filling is likely to play a large role in remediation, although can be significantly reduced under certain conditions. Previous studies have shown that soil organic matter can become attached to the biochar surface, reducing access to adsorption sites and therefore reducing sorption. This can significantly reduce the overall sorption capacity, particularly in soils with high organic contents, such as agricultural soils. Further, it also noted that a well-developed pore network consisting of macropores, mesopores and micropores is necessary for the effective diffusion of adsorbate molecules to sorption sites. This cannot always be captured by simple surface area techniques, particularly N₂-BET analysis.

The review also found that hydrogen bonding is likely to play a greater role than hydrophobic effects in practice, due to its increasing strength over time in soil. Hydrogen bonding is driven by interactions involving oxygen-containing functional groups on the surface of biochar, while hydrophobic effects require a condensed aromatic surface. Due to the long-term oxidation of biochar in soil over time, it is expected that the strength of hydrogen bonding will increase over time, while the strength of hydrophobic effects will decrease. This suggests that molecules which adsorb through hydrogen bonding may represent those which are best suited to remediation using biochar.

The review found that all of the mechanisms investigated have been found to be significant for the immobilisation of atrazine, with pore filling and hydrogen bonding likely to play the greatest roles. Due to atrazine's small molecule size, it is capable of accessing microporous sorption sites, while its ability to both donate and accept H⁺ ions means it can participate in hydrogen bonding in a wide range of conditions. However, several studies have also noted the role of hydrophobic effects over hydrogen bonding, while there was some disagreement on the role of π - π EDA interactions. For these reasons, it was necessary to further investigate the role of these sorption mechanisms on the immobilisation of atrazine using biochar.

Chapter 4 investigated the role of partitioning and pore filling on atrazine sorption. It utilised previous characterisation by UKBRC and previous studies on standard biochars, together with FTIR analysis, to determine adsorption kinetics, isotherms and interactions with humic acids. The results suggested that partitioning was significant for SWP and, to a lesser extent, MSP biochars. Pore filling contributed to sorption in all biochars although its efficiency varied.

FTIR analysis confirmed the aromatic nature of the biochars and showed relatively little oxygen-group functionality, while suggesting the presence of ash may be significant in some biochars. WSP, MSP, RH and OSR biochars all showed evidence of SiO₂ groups, suggesting the presence of quartz or other forms of silicon dioxide. Many of the biochars, particularly those produced at 550°C showed C=O bonds, which most likely corresponds to ketone groups. The FTIR characterisation was largely in line with the elemental analysis carried out by UKBRC in terms of the ash and oxygen groups it revealed.

Kinetic sorption studies suggested that intraparticle diffusion was the rate determining step for most of the biochars, although film diffusion also contributed in some cases which

corresponds to significant chemical effects. SWP and OSR biochars showed relatively poor intraparticle diffusion, suggesting that these biochars had pore structures which could not efficiently transport atrazine molecules. In contrast, WSP and RH biochars showed effective pore filling, which was confirmed by previous SEM images which showed well-developed and accessible pores in these samples. MSP showed significant early sorption, suggesting that rapid chemical interactions to the macropores may be significant. The kinetic studies therefore revealed the importance of the pore structure in adsorbing atrazine, and the importance of selecting a suitable feedstock for achieving the optimal outcomes.

Studies investigating the interactions with humic acid largely confirmed the roles of pore filling to each of the samples. All biochars showed significant reductions in sorption due to humic acids, up to nearly 50% in some cases, which was attributed to the blockage of micropore sites. All biochars showed greater reductions when produced at lower temperatures, which suggests that the higher temperature chars had better developed pore structure, or that the humic acid can also interfere with polar adsorption sites. SWP and OSR biochars in particular showed large decreases, further suggesting that they cannot efficiently transport atrazine to microporous sites. These results highlight the importance of accounting for the presence of soil organic matter when determining adsorption capacity.

Isotherm studies highlighted the role of linear partitioning and confirmed the contributions of highly non-linear adsorption mechanisms to several biochars. SWP biochars in particular had high overall contributions of partitioning, as determined using the dual-mode sorption model, suggesting that these are unlikely to be effective for remediation in practice. In contrast, RH and WSP biochars had relatively low influences of partitioning, suggesting that these may more effectively immobilise atrazine in the environment. The isotherms also demonstrated that RH biochars had by far the highest sorption capacities of all of the biochars, despite their relatively low measured surface areas and carbon contents, suggesting that other properties may be contributing to total sorption.

The results of Chapter 4 therefore suggested that pore filling dominates sorption to many biochars, although its influence may be vulnerable to environmental effects, while partitioning can also increase the apparent remediation capacity, particularly for low-temperature biochars. It also suggested that biochars produced from materials such as rice husks and wheat straws are better suited to remediating atrazine than softwood or oil seed

rape. The availability, cost and sustainability of these materials at a given site will also significantly influence their applicability in remediation.

Chapter 5 investigated the adsorption mechanisms of atrazine to biochar, focusing in particular on the relative roles of hydrogen bonding and hydrophobic effects. The contributions of these effects are important as they will determine the responses of sorption in the long-term as biochar oxidises in the soil, which could potentially result in leaching over time if the mechanisms are reversed. Chapter 5 therefore analysed these effects through pH-dependency sorption tests, together with a meta-analysis of the results from Chapter 4 and previous literature data.

pH-dependent sorption tests showed that sorption changed significantly over pH, which was attributed to changing contributions of several mechanisms. Most biochars showed significantly reduced sorption at very low pH values, which was attributed to electrostatic repulsion between the cationic atrazine molecule and the positively charged biochar surface in this range. Notably, electrostatic repulsion was not observed for WSP700, MSP700 and OSR550 biochars due to strong buffering effects preventing very low pH values from occurring, and for MSP550 which was attributed to strong hydrogen bonding in this range. While these extremely low pH values are unlikely to occur in practice, these tests demonstrate the electrostatic repulsion effects can be important for ionisable compounds to biochar.

The pH-dependent sorption tests also showed significantly increased sorption at intermediate pH values ($5 \leq \text{pH} \leq 9$), which was attributed to strengthened hydrogen bonding. In this range, the biochar surface was positively charged ($\text{pH} < \text{pH}_{\text{pzc}}$), while the atrazine molecule was in a neutral state, and therefore biochar was able to donate H^+ ions to form hydrogen bonds. All biochars demonstrated this effect, suggesting that it is the result of strong effects involving the atrazine molecule. These increased sorption rates at intermediate pH values suggest that small changes in pH may greatly increase atrazine sorption, suggesting that the biochars may be able to effectively mitigate the effects of some increased soil acidity.

At high pH values, the biochars showed greatly different sorption profiles, which is attributable to hydrogen bonding, π - π EDA interactions and interactions with the ash phase. SWP550 showed no significant increase at high pH, while SWP700 showed a sharp increase which was attributed to the stronger carbonised phase allowing for greater π - π EDA

interactions. In contrast, WSP550 showed a sharp increase at high pH which was not observed for WSP700, and was subsequently attributed to the increased oxygen content of WSP550 allowing for stronger hydrogen bonding in this range. MSP biochar demonstrated the same effects. The mechanisms of sorption at high pH to RH and OSR biochars were not able to be determined due to possible interactions with the ash component, and they were therefore used for further analysis to be carried out in Chapter 6.

An analysis of the relationship between standard biochar properties and adsorption capacities, as determined in Chapter 4, further highlighted the overall role of hydrogen bonding in the sorption of atrazine. A predictive model of sorption capacity found that oxygen content and ash content contributed the most to total sorption, suggesting that hydrogen bonding and interactions with the ash component had strong influences on the removal of atrazine. The mechanisms through which the ash contributes to sorption are not fully understood and were investigated further in Chapter 6.

A meta-analysis of all relevant previous studies of atrazine sorption to biochar confirmed that hydrophobic effects are unlikely to dominate the sorption of atrazine, although was not able to confirm the role of hydrogen bonding. After accounting for surface area, there was a weakly negative correlation between sorption capacity and aromaticity, and no correlation between sorption capacity and polarity. These suggest that hydrophobic effects are not greatly contributing to sorption. The role of hydrogen bonding may be better determined by accounting for the specific state of the oxygen-containing functional groups.

The results from Chapter 5 therefore highlight the role of hydrogen bonding over that of hydrophobic effects, which is generally beneficial for remediation. However, they contrast with those from Chapter 4, which demonstrated the significance of pore filling, as these mechanisms are unlikely to complement each other due to their presences to biochars of different production temperatures. Due to the oxidation of biochar in the soil over time, high temperature biochars will experience increased hydrogen bonding strength and may therefore effectively immobilise atrazine in both the short- and long-terms.

Chapter 6 investigated the modification of biochar using hydrofluoric acid and its effects on the biochar composition and the mechanisms of atrazine removal. The modifications successfully de-ashed RH700 and OSR550 biochars without significantly altering SWP550.

The results suggested that the mechanisms governing sorption at high pH values to RH700 and OSR550 were influenced by both the biochar surface and the presence of the ash fraction.

Modification with a hydrofluoric acid/hydrochloric acid mixture successfully removed the majority of the ash contents of RH700 and OSR550, which had high ash contents, while having little effect on the low-ash SWP550 sample. This was confirmed through FTIR, elemental, XRD and XPS analyses, which showed the removal of SiO₂ groups on RH700, and SiO₂ and CaCO₃ groups on OSR550. The modifications resulted in de-ashed samples which allowed for a useful comparison of raw and ash-free biochars for which the sorption mechanisms may be isolated.

The XPS analysis, in particular, provided in-depth insights into the presence of various oxygen-containing functional groups. The detailed C1s scans suggested that some oxidation of the carbonised fractions had occurred during modification, confirming results from the spectra scan and the elemental analysis. They showed that for RH700, in particular, basic groups such as C=O bonds were reduced after modification, while acidic C-O and O-C=O groups were increased. Further, the XPS analyses also revealed the presence of various functional groups which were not detected by FTIR, confirming the results from Chapter 5 which suggested that many biochars can act as both H⁺ donors and H⁺ acceptors in various conditions. The XPS analyses therefore confirmed the various functional groups present on the biochars, and suggested that some acidic oxidation had occurred to the carbonised fractions.

pH dependency tests with the raw and modified biochar confirmed the role of the ash fraction in affecting sorption to RH700 and OSR550 biochars at high pH values. All modified biochars showed similar sorption trends across pH at low and intermediate pH ranges, however the effects at high pH values varied. This variation was not attributable to hydrogen bonding or π - π EDA interactions, and was therefore attributed to interactions with the ash fraction. Possible mechanisms for this increased removal of atrazine include the formation of complexes with Ca²⁺ ions, or the catalytic hydrolysis of atrazine molecules in the presence of dissolved ions. The environmental implications of this mechanism are important, as they have the potential to result in increased sorption at high, environmentally relevant pH values, or the potential formation of harmful by-products.

This thesis has therefore identified the mechanisms through which atrazine is removed from solution to a wide range of biochars, allowing for novel insights into the ways in which atrazine may behave under various conditions. Further, it has discussed in depth for the first time the implications of these removal methods for real-world remediation outcomes, and recommended biochars for application based on parameters other than simple sorption capacity, which does not always reflect suitability for soil application. These results can therefore be used to better predict the long-term fate of atrazine and other organic contaminants in biochar-amended soil and to better design a biochar for the effective immobilisation of atrazine.

7.2 Future outlook

This thesis has highlighted the significance of various sorption mechanisms, and provided novel insights into the roles of partitioning, pore filling, π - π EDA interactions, hydrophobic effects and hydrogen bonding. Future research directions should seek to validate the role of these mechanisms in determining remediation outcomes by considering the effects of long-term de-sorption and degradation of atrazine, as well as comparing the results to other organic contaminants.

Much of this thesis has been based on conclusions drawn from various literature studies, particularly on the long-term roles of the different mechanisms. Future studies should confirm these effects. For example, studies investigating de-sorption of attached molecules (including those which can and cannot participate in hydrogen bonding) in the presence of oxidation or changing pH would provide insights into the likely behaviour of biochar in the long-term. Long-term de-sorption does not necessarily invalidate biochar as a remediation tool – the slow release of attached contaminants may reduce harmful concentrations to allowable levels – however it is necessary to understand its role in order to accurately predict long-term outcomes.

Further research is necessary to identify the specific mechanism or mechanisms through which ash influences the removal of atrazine at high pH values. While this study has suggested that Si^{2+} and Ca^{2+} ions influence outcomes, the results did not closely match those from other previous studies. Further, the effect was not observed for WSP and MSP biochars, despite their significant ash fractions. These interactions are important, as many biochar samples have ash fractions of 40% or greater and the interactions observed occur at realistic

environmental levels. It should first be determined whether degradation of atrazine is occurring, and second what the mobility, stability and toxicity of the degradation products are. If atrazine complexes are formed, the strength of the mechanisms controlling their sorption should be determined in order to assess their stability. This may be determined through artificially adding soluble or insoluble ash deposits onto the surfaces of various biochars or by investigating the long or medium-term stability of atrazine in the presence of biochars with different ash compositions.

The tests in this study have also been carried out under carefully controlled laboratory conditions. To date, few field trials have been carried out investigating the use of atrazine in contaminated land, and in particular comparing different application methods. For the control of atrazine, the most realistic application options would be as a surface layer to intercept surface runoff or as a permeable reactive barrier to treat contaminated groundwater. However, few studies have investigated the transferability of laboratory studies to remediation outcomes in these environments. While these are time consuming and expensive to carry out, they are necessary in order to validate the expected behaviour of biochar in remediation.

This thesis has investigated the modification of biochar in order to isolate specific sorption mechanisms only, although many studies have modified biochar to explicitly improve sorption capacity. These studies should carefully consider the net advantages of purchasing, handling and disposing of these chemicals, as they can potentially reverse many of the environmental advantages of using biochar or introduce new contamination risks. In particular, HF is unlikely to be sustainable to use in high quantities for the on-site production of de-ashed biochar. The use of other chemical modifiers such as hydrogen peroxide, methanol or hydrochloric acid may also reduce the overall environmental sustainability of biochar application. Studies such as life cycle analysis or other decision making tools should be considered in these cases in order to determine net benefits.

Finally, it is important to be aware of the potential for biochar to introduce contaminants into the soil profile. Both rice husk and oil seed rape biochars showed evidence of lead products on their surface, which is not necessarily a trivial hazard, while many previous studies have noted the risks of native biochar PAH components. It is necessary to trade-off the significant environmental advantages of biochar with these risks.

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