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Magnetic pine sawdust biochar: Synthesis, characterisation and mechanistic studies of the removal of sulfamethoxazole in aqueous media

Febelyn Tria Reguyal

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Abstract

Global concern on the occurrence of pharmaceuticals such as antibiotics in aquatic environment has been increasing due to the potential development of drug-resistant microorganisms. Biochar, a carbonaceous waste-derived material produced via pyrolysis of biomass, could be a cheaper alternative adsorbent to activated carbon. The pine sawdust biochar was magnetised by forming Fe₃O₄ nanoparticles on its surface and was used to adsorb one of the most frequently detected antibiotics in surface water, sulfamethoxazole (SMX). Several characterisation techniques were used in this study namely elemental analysis, Brunauer-Emmet-Teller (BET) surface area analysis, Barrett-Joyner-Halenda (BJH) pore size and volume analysis, X-ray diffraction (XRD), Scanning Electron Microscopy – Elemental Dispersive Spectroscopy (SEM-EDS), X-ray Photoelectron Spectroscopy (XPS), Physical Property Measure System Vibrating Sample Magnetometer (PPMS-VSM).

The synthesised magnetic pine sawdust biochar (MPSB) had a high saturation magnetisation of 47.8 A.m²/kg, but it was only stable within solution pH of 4 to 9. The highest sorption of SMX was observed at pH = 4 where it had a maximum adsorption capacity of 13.8 mg/g. MPSB exhibited fast sorption of SMX and closely followed pseudo-second order kinetic model for low concentrations. Thermodynamic parameters, ΔG°, ΔH° and ΔS° implied that the adsorption of SMX onto MPSB was spontaneous and exothermic. Five adsorbents with different amount of Fe₃O₄ per mass of adsorbent (0%, 25%, 50%, 75% and 100%) were used to adsorb SMX. Surface area and sorption capacity had a strong negative linear relationship with the amount of Fe₃O₄ per mass of adsorbent while the pore volume and saturation magnetisation of the adsorbent increased with increasing percentage of Fe₃O₄. The results of the approximate site energy distribution analysis based on the Redlich-Peterson model showed that the addition of Fe₃O₄ on biochar reduced the area under the frequency distribution curve of sorption site energies leading to the reduction of the sorption sites available for SMX. Moreover, pH, ionic strength and presence of natural organic matter (NOM) and a competing compound, 17α-ethinylestradiol (EE2) on the sorption of SMX onto magnetic biochar were evaluated. Among these parameters, EE2 had the strongest inhibition on the sorption of SMX on MPSB where the sorption mechanisms of these compounds could due to the π-π electron donor-acceptor and hydrophobic interaction.
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Finally, I sincerely thank God for the immeasurable guidance and love.
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**Synthesis of magnetic biochar from pine sawdust via oxidative hydrolysis of FeCl2 for the removal of sulfamethoxazole from aqueous solution**

| Nature of contribution by PhD candidate | Performed experiments, data analysis and manuscript writing |
| Extent of contribution by PhD candidate (%) | 80 |

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Removal of sulfamethoxazole by magnetic biochar: Effects of environmental conditions and competition with 17β-ethinylestradiol

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List of Symbols and Abbreviations

$A$ competitive strength ($\%$)

$A_{RP}$ Redlich–Peterson model constant (L/mg)

$A_T$ Temkin isotherm constant (L/g)

$B_D$ Dubinin–Radushkevich model constant (mol$^2$/kJ$^2$)

$C$ constant describing the thickness of boundary layer

$C_o$ initial concentration of the adsorbate

$C_e$ equilibrium concentration of the adsorbate; equilibrium concentration of sorbate in liquid phase (mg/L)

$C_s$ solute solubility in the solvent (mg/L)

$E_s$ lowest physically realisable sorption energy (J/mol)

$E^*$ difference of sorption energy at $C_e$ and $C_s$

$F(E^*)$ site energy frequency distribution over a range of sites with homogeneous energies between the solute and solvent for a given sorption site (mol-mg/J-g)

$k_1$ pseudo-first order rate constant

$k_2$ pseudo-second order rate constant

$K_d$ distribution coefficient; sorption coefficients for the primary solute in the single-solute (L/g)

$K_d'$ sorption coefficients for the primary solute in the single-solute and bi-solute systems (L/g)

$K_{DR}$ Dubinin–Radushkevich model constant (mg/g)

$K_F$ Freundlich isotherm constant

$k_i$ intra-particle diffusion constant

$K_L$ Langmuir isotherm constant (L/mg)

$K_{ow}$ octanol-water partition coefficient

$K_{RP}$ Redlich–Peterson model isotherm constant (L/g)
\( m \) mass of the adsorbent

\( M \) molar mass of the adsorbate

MPSB magnetic pine sawdust biochar

\( N_A \) Avogadro’s number

\( pH_{pzc} \) point of zero charge

\( q \) amount adsorbed per mass of adsorbent (mg/g)

\( q_{e,\text{calc}} \) calculated equilibrium capacity obtained from the isotherm model (mg/g)

\( q_{e,\text{exp}} \) experimental equilibrium capacity (mg/g)

\( q_{\exp} \) experimental sorption capacity

\( q_e(C_e) \) total sorption of solute to the sorbent (mg/g)

\( (q_{\exp})_{\text{ave}} \) experimental average \( q \)

\( q_b(E, C_e) \) isotherm over local sorption sites with sorption energy \( E \) (mg/g)

\( q_m \) maximum monolayer adsorption capacity (mg/g)

\( Q_{\text{max}} \) theoretical maximum surface coverage (mg/g)

\( (q_{\text{pred}})_i \) predicted sorption capacity for the \( i^{th} \) term

\( q_t \) amount of SMX adsorbed onto the adsorbent at time \( t \)

PSB pine sawdust biochar

\( R \) gas constant (8.314 J/mol-K)

\( R_L \) dimensionless equilibrium parameter of Langmuir isotherm

\( RSS \) residual sum of squared errors

\( S_{\text{BET}} \) BET surface area of the adsorbent (m²/g)
\( t \) adsorption time

\( T \) absolute temperature (K)

\( TSS \) total sum of squared errors

\( V \) volume of adsorbate

\( \beta_{RP} \) Redlich–Peterson model exponent

\( \beta_T \) Temkin constant related to heat of sorption (J/mol)

\( \Delta G^o \) change in Gibbs free energy (J/mol)

\( \Delta H^o \) change of enthalpy (J/mol)

\( \Delta S^o \) change of entropy (J/mol-K)

\( \varepsilon_D \) Polanyi potential

\( \rho \) adsorbate density (g/cm\(^3\))

\( \sigma \) surface area occupied by one molecule (Å/molecule)
CHAPTER 1: Introduction
Chapter 1: Introduction

1.1 Motivation

Pharmaceuticals and their metabolites have been widely detected in surface water (Pal et al., 2010; Silva et al., 2011; Vaicunas et al., 2013; Zou et al., 2011), groundwater (Jurado et al., 2012; Lapworth et al., 2012) and sediments (Hu et al., 2012; Silva et al., 2011) usually in trace concentrations. However, their occurrences in the environment have been raising environmental and public concerns due to their indirect negative effects to human health e.g. the potential development of drug-resistant microorganisms (Manaia et al., 2012). Due to lack of legislation, the current water treatment technologies mostly do not remove the pharmaceuticals in the primary and secondary stages of water treatment. Among the pharmaceuticals, 39% of the most widely detected pharmaceuticals in surface water are antibiotics (Hughes et al., 2013). The presence of antibiotics in the aquatic environment may result in the development of antibiotic resistance of microorganism (Baquero et al., 2008; Schwartz et al., 2003). One of the frequently detected antibiotics in aquatic environment is sulfamethoxazole (SMX), which belongs to the sulfonamide group and is used in the treatment of diseases in human and livestock. After consumption, majority of the antibiotics is excreted unchanged or as metabolite in the faeces and urine and end up in wastewater treatment plant. Sewage treatment plants are not optimised to remove the trace amounts of antibiotics residues and thus they find their ways into the receiving aquatic bodies. SMX has also been found to be toxic to various aquatic organisms like fish and crustaceans at high concentrations (Isidori et al., 2005; Kim et al., 2007). Hence, it is important to develop technologies that could minimise to within acceptable levels of SMX and other pharmaceuticals in water treatment facilities.

Adsorption is one of the post treatment technologies commonly employed in water treatment due to its effectiveness and simplicity of operation. However, one of the
drawbacks of adsorption technique is the high cost of the adsorbent. For the past decades, cheaper alternative adsorbents have been studied and one of these is biochar. Biochar is carbonaceous waste-derived material produced from the pyrolysis of agricultural, forest and animal wastes (Ahmad et al., 2014; Duku et al., 2011; Mohan et al., 2014a). Biochar has been mainly used for agricultural applications but numerous studies have shown that biochar could be an effective adsorbent for both inorganic and organic contaminants, including emerging organic contaminants (Mohan et al., 2014a; Tan et al., 2015). It has been considered to be an alternative for the expensive and most widely used adsorbent, activated carbon. Its attractiveness as adsorbent is due to its (i) porous structure; (ii) relatively high surface area and pore volume; (iii) surface functionalities; and (iv) stability (Reddy and Lee, 2014). However, currently, it is applied in powder form, which results in the difficulty of the biochar separation after treatment. To address this, one of the methods considered is the magnetisation of biochar.

The application of magnetic particle technology to improve the recovery of the adsorbent is one of the emerging methods to make adsorption process more economical. The most commonly used method to magnetise the adsorbent is via physical and/or chemical integration of magnetic iron oxides (Fe₃O₄ and γ-Fe₂O₃) in the adsorbent. Moreover, iron oxide has the ability to adsorb inorganic and organic contaminants and degrade organic contaminants (Xu et al., 2012). Several studies have demonstrated the fast recovery of the magnetic carbonaceous adsorbent after treatment using a permanent magnet or application of external magnetic field (Wang et al., 2014a; Zhang et al., 2013). However, the incorporation of iron oxides in the carbonaceous adsorbents have resulted disadvantages such as reduction in surface area (Chen et al., 2011; Mohan et al., 2011a; Oliveira et al., 2002a) and lower sorption capacity compared to the carbonaceous adsorbent (Chen et al., 2011; Mohan et al., 2014b; Oliveira et al., 2002). On the contrary, few studies have
demonstrated that magnetisation of adsorbents also increased the surface area, enhanced the adsorption performance and resulted in stable composites (Devi and Saroha, 2014; Zhu et al., 2014). Furthermore, the adsorption can be improved regardless of the adsorbent used by altering the properties of the matrix such as pH, temperature, ionic strength, contact time and other parameters. Hence, developing a novel magnetic biochar may potentially be a solution to reduce the cost of the adsorption process in water treatment.

1.2 Research objectives

The overarching aim of this thesis was to develop a novel magnetic biochar to remove SMX from aqueous solution. The specific objectives of this study were to:

1. Develop, synthesise and characterise a magnetic biochar derived from pine sawdust, which is one of New Zealand’s major wood wastes, for the removal of SMX in aqueous solution;

2. Identify the effects of Fe$_3$O$_4$ nanoparticles on biochar on its physico-chemical properties and sorption properties using site energy distribution analysis;

3. Determine the effects of different environmental factors namely pH, time, ionic strength, presence of natural organic matter (NOM) and a competing compound, 17$α$-ethinylestradiol (EE2); and

4. To provide new insights on the sorption mechanism of SMX onto magnetic biochar in aqueous solution.


1.3 **Thesis framework**

This thesis consists of 6 chapters where 2 chapters were published in *Journal of Hazardous Materials* (Chapter 3) and *Environmental Pollution* (Chapter 4). Chapter 5 was accepted in *Science of the Total Environment*. As a result, some of the materials are repetitious particularly the materials and methods section. In addition, due to the word, figure and table limitations of the journal, brevity in the chapters (Chapter 3, 4 and 5) may be observed. In this manuscript, the thesis was presented in the following outline and a thesis framework of the research is illustrated in Figure 1.1.

Chapter 1 briefly introduces the motivation, overarching aim and specific research objectives and thesis framework.

Chapter 2 presents the current and past literature focusing on the sources, pathways and occurrence of human antibiotics in the environment. It also presents the physical and chemical properties of SMX and its adverse effects on different organisms. This chapter also demonstrates the potential of magnetic carbonaceous adsorbent particularly magnetic biochar as a cheaper sorbent and its limitations for water treatment. Physico-chemical properties and applications, particularly in water remediation, of the two major components of the magnetic biochar, iron oxide and biochar, are also discussed. Moreover, it discusses the current status of the synthesis, sorption applications and challenges of magnetisation of carbonaceous adsorbents.

Chapter 3 discusses the synthesis, characterisation, sorption application of magnetic biochar on the removal of SMX in aqueous media and its regeneration. The sorption mechanism of SMX onto magnetic biochar is also proposed in this chapter.

Chapter 4 presents the discussion of the effects of Fe₃O₄ nanoparticles on the
physical and chemical properties of biochar as well as its sorption properties. The effects of Fe$_3$O$_4$ on the sorption capacity and behaviour of SMX on magnetic biochar are explained using the concept of site energy distribution analysis.

Chapter 5 discusses the effects of different environmental conditions namely pH, ionic strength, time, natural organic matter and a competitive pharmaceutical compound, EE2, an endocrine disrupting compound. This chapter also explains the stronger affinity of magnetic biochar with the EE2 compared to SMX.

Chapter 6 summarises the major findings of the study and provides recommendations for future research.
Figure 1.1. Thesis framework
CHAPTER 2: Literature review
2.1 Sources and occurrence of antibiotics

Generally, the major sources of antibiotics in the environment are humans and animals because of their incomplete absorption and metabolism after an antibiotic is administered in the body. They are excreted through their faeces and urine. The excretion rates of these compounds and their metabolites depend on the type of antibiotics and vary from traces up to 95% (Whitacre, 2010). For example, SMX, which is one of the most commonly detected antibiotics in different environmental matrices, has a reported excretion rate of 57% (Johnson and Williams, 2004). The reported sources of antibiotics are sewage treatment plants (STP), pharmaceutical manufacturing industries wastewater treatment plants (WWTP) and agricultural farms applying animal manure in soil as fertilizer (Kemper, 2008; Kemper et al., 2008). From these sources, the residual pharmaceuticals are transported to aquatic environment via different routes. Figure 2.1 illustrates the transport of antibiotics to various receptors.
Figure 2.1. Sources, pathways and receptors of antibiotics (Farré et al., 2008; Heberer, 2002; Kümmerer, 2010; Pal et al., 2010; Stuart et al., 2012)

2.2 Properties, ecotoxicity and occurrence of SMX in surface water

SMX has been detected in various environmental matrices. The highest concentration of SMX recorded in surface water is 940 ng/L detected in Baiyangdian Lake, China (Li et al., 2012). However, compared to the concentrations of SMX detected in STP and WWTP, these concentrations are relatively low. In addition, SMX has also been detected in groundwater and drinking water (Perret et al., 2006). Some of the applications and physicochemical properties of SMX are shown in Table 2.1. Ecotoxicological assessments have been done for SMX. These studies have been conducted in different organism namely fish, rotifer, bacteria, crustaceans, cnidarian and algae with different toxicological endpoint
tests such as fertilization rate, mortality, immobilization or population growth inhibition as shown in Table 2.2 based on the Lowest Observed Effect Concentration (LOEC), No Observed Effect Concentration (NOEC), Lethal Concentration (LC50) and Effect Concentration (EC50).

Table 2.1. Some of the applications and physicochemical properties of SMX

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Sulfonamide antibiotics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class</td>
<td>Sulfonamide antibiotics</td>
</tr>
<tr>
<td>Selected applications</td>
<td>Treatment of urinary tract infection; growth promoter of animals</td>
</tr>
<tr>
<td>Molar mass, g/mol</td>
<td>253.30</td>
</tr>
<tr>
<td>Chemical Structure (Chemspider)</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in alcohol; Very slightly soluble in H2O</td>
</tr>
<tr>
<td>pKa</td>
<td>1.6; 5.7 (Boreen et al., 2004)</td>
</tr>
</tbody>
</table>

2.3 Current methods on SMX removal in aqueous solution

Various treatment methods have been used in the removal and degradation of SMX in aqueous solution. Some of these methods are ozonation (Garoma et al., 2010), oxidation by chlorine, ozone and permanganate (Gao et al., 2014), conductive diamond electrochemical oxidation (de Vidales et al., 2012), membrane bioreactor under anoxic and aerobic conditions (Hai et al., 2011), photocatalytic degradation using TiO2 (Abellán et al., 2007) and sorption using biochar (Zheng et al., 2013) and functionalised carbon nanotubes (Zhang et al., 2011a).
Table 2.2. Ecotoxicity of SMX

<table>
<thead>
<tr>
<th>Organism</th>
<th>Species</th>
<th>Toxicological endpoint</th>
<th>Ecotoxicity data (mg/l)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacteria</td>
<td><em>V. fischeri</em></td>
<td>EC50 (5 min)</td>
<td>74.2</td>
<td>Kim et al., 2007</td>
</tr>
<tr>
<td>Bacteria</td>
<td><em>V. fischeri</em></td>
<td>EC50 (15 min)</td>
<td>78.1</td>
<td></td>
</tr>
<tr>
<td>Crustacean</td>
<td><em>D. magna</em></td>
<td>EC50 (48 h)</td>
<td>189.2</td>
<td></td>
</tr>
<tr>
<td>Crustacean</td>
<td><em>D. magna</em></td>
<td>EC50 (96 h)</td>
<td>145.6-208.9</td>
<td></td>
</tr>
<tr>
<td>Fish</td>
<td><em>O. latipes</em></td>
<td>LC50 (48 h)</td>
<td>&gt;750</td>
<td></td>
</tr>
<tr>
<td>Fish</td>
<td><em>O. latipes</em></td>
<td>LC50 (96 h)</td>
<td>562.5</td>
<td></td>
</tr>
<tr>
<td>Cnidarian</td>
<td><em>H. attenuate</em></td>
<td>LC50 (96 h)</td>
<td>&gt;100</td>
<td>Quinn et al., 2008</td>
</tr>
<tr>
<td>Cnidarian</td>
<td><em>H. attenuate</em></td>
<td>LOEC (96 h)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cnidarian</td>
<td><em>H. attenuate</em></td>
<td>NOEC (96 h)</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Bacteria</td>
<td><em>V. fischeri</em></td>
<td>EC50 (30 min)</td>
<td>23.3</td>
<td>Isidori et al., 2005</td>
</tr>
<tr>
<td>Rotifer</td>
<td><em>B. calyctilorus</em></td>
<td>LC50 (24 h)</td>
<td>26.27</td>
<td></td>
</tr>
<tr>
<td>Rotifer</td>
<td><em>B. calyctilorus</em></td>
<td>EC50 (48 h)</td>
<td>9.63</td>
<td></td>
</tr>
<tr>
<td>Crustacean</td>
<td><em>T. platyurus</em></td>
<td>LC50 (24 h)</td>
<td>35.36</td>
<td></td>
</tr>
<tr>
<td>Crustacean</td>
<td><em>D. magna</em></td>
<td>EC50 (24 h)</td>
<td>25.2</td>
<td></td>
</tr>
<tr>
<td>Crustacean</td>
<td><em>C. dubia</em></td>
<td>EC50 (24 h)</td>
<td>15.51</td>
<td></td>
</tr>
<tr>
<td>Crustacean</td>
<td><em>C. dubia</em></td>
<td>EC50 (7 d)</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Algae</td>
<td><em>P. subcapitata</em></td>
<td>EC50 (72 h)</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>Algae</td>
<td><em>S. capricornutum</em></td>
<td>EC50</td>
<td>1.53</td>
<td>Eguchi et al., 2004</td>
</tr>
</tbody>
</table>

2.4 Biochar

Biochar is a solid carbonaceous product generated when organic biomass is heated in the absence or under limited amount of oxygen at 350-500°C (Lehmann and Joseph, 2015). Biochar can be produced via pyrolysis (fast, intermediate and slow) and gasification. Ahmad et al. (2014) summarised the operating temperature, residence time and percentage distribution of products generated during the production of biochar as shown in Table 2.3. The properties of biochar depend on many factors namely pyrolysis temperature, residence time and feedstock (Ahmad et al., 2014).
Table 2.3. Biochar production processes (Ahmad et al., 2014).

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature (°C)</th>
<th>Residence time</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Liquid (bio-oil)</td>
</tr>
<tr>
<td>Fast pyrolysis</td>
<td>300–1000</td>
<td>Short (&lt;2 s)</td>
<td>75 (75%)</td>
</tr>
<tr>
<td>Intermediate</td>
<td>~500</td>
<td>Moderate (10–20 s)</td>
<td>50 (50%)</td>
</tr>
<tr>
<td>Slow pyrolysis</td>
<td>100–1000</td>
<td>Long (5–30 min)</td>
<td>30 (30%)</td>
</tr>
<tr>
<td>Gasification</td>
<td>&gt;800</td>
<td>Moderate (10–20 s)</td>
<td>5 (5%)</td>
</tr>
</tbody>
</table>

Biochar has been utilised for several applications such as soil amendment, waste management, energy production, climate change mitigation and pollutant (organic and inorganic) remediation as illustrated in Figure 2.2 (Ahmad et al., 2014; Lehmann and Joseph, 2015). Besides the 5 major areas which have been a major focus of the application of biochar, in recent times, biochar has also been used as a filler material in wood plastic composites (DeVallance et al., 2016), construction materials (Zhao et al., 2014). The use of biochar as a soil amendment was mainly driven by the concept of Amazonian Indian’s use of charcoal (terra preta or black earth) as a form for rich and fertile soil for agricultural productivity due to its high organic carbon content, water retention capacity and nutrient retention ability (Glaser et al., 2002; Sohi et al., 2010). Generally, biochar has alkaline pH enabling it to increase the pH of acidic soil resulting in higher crop productivity (Glaser et al., 2002). Moreover, some biochar can increase the microbial activity in soil (Steinbeiss et al., 2009; Van Zwieten et al., 2010).
Biochar can also be used for waste management since the feedstock used for its production could be derived from plant and animal wastes. Some of the biochar feedstock studied are sawdust, grass, wheat straw, peanut shell, cow manure, pig manure, shrimp hull, bone dregs, wastewater sludge, waste paper, chlorella, and waterweeds (Zhao et al., 2013). In addition, the use of waste biomass in the production of biochar can also be one of the ways to mitigate climate change by sequestering C in soil due to its long-term stability (Lehmann and Joseph, 2015). In addition, bioenergy is produced during pyrolysis of biomass and can reduce the consumption of fossil fuels. Roberts et al. (2010) performed life cycle assessment of biochar and found that the net energy of biochar can reach up to 4899 MJ/ton of dry switchgrass feedstock. In addition, production of biochar from stover and yard waste has negative greenhouse gas (GHG) emissions of -864 and -885 kg CO$_2$e per tonne of dry feedstock, respectively (Roberts et al., 2010). In the last few years, application of biochar has been in the pollutant remediation and several researchers around the world have used
range of biochar to remove a variety of organic and inorganic contaminants from environmental media such as soil and water. Biochar has been found to be a promising adsorbent that could potentially replace activated carbon due to the similarities in their properties. The application of biochar in water pollution remediation is further discussed in section 2.5.2.

2.5 Magnetic biochar

The difficulty of the separation of powdered carbonaceous adsorbents like activated carbon, charcoal and biochar has led to the application of magnetic technology to produce magnetic adsorbents that could easily be separated from the aqueous solution after use (Oliveira et al., 2002; Zhang et al., 2013). Magnetic adsorbent generated through the combine utilisation of the properties of iron oxide and biochar has aided the removal of a variety of inorganic and organic contaminants in water. Figure 2.3 below shows the potential use of magnetic biochar after combining the iron oxide and biochar and application in diverse areas.
2.5.1. Iron oxide in water remediation

Iron oxide exists in different forms such as magnetite ($\text{Fe}_3\text{O}_4$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematit ($\alpha\text{-Fe}_2\text{O}_3$). In the comprehensive review published by Xu et al. (2012), iron oxide has been used in water treatment, which could be used in the removal of organic and inorganic contaminants, due to its (i) extremely small size, (ii) high surface-area-to-volume ratio, (iii) surface modifiability, (iv) excellent magnetic properties and (v) great biocompatibility (Xu et al., 2012). Some of the contaminants that can be adsorbed by iron oxide are arsenic (Cheng et al., 2016), chromium (Jiang et al., 2013), phosphate (Yoon et al., 2014), methylene blue and cresol red dyes (Zhang and Kong, 2011).
One intrinsic property of iron oxide, which makes it attractive in water treatment application, is its magnetism. The magnetic property of the adsorbent allows the iron oxide adsorbent to be easily recovered after treatment using a magnet or application of magnetic field. On the other hand, the application of iron oxide nanoparticles in water treatment has been limited by its aggregation in aqueous media. Numerous studies have been conducted to stabilise iron nanoparticles in water by modifying its properties using stabilisers such as surfactants and polymers (Laurent et al., 2008). Surface enhanced iron oxide has also been used for the removal of organic contaminants such as polyacrylic acid-bound iron oxide magnetic nanoparticles (Mak and Chen, 2004) and magneticFe$_3$O$_4$/C core-shell for the removal of organic dyes (methylene blue and cresol red) in aqueous solutions (Zhang and Kong, 2011). Depending on the preparation method and surface coating used, its properties vary in size, surface morphology, magnetic property, surface chemistry and sorption properties. Hence, the properties of iron oxide could be tailored depending on its application as well as target contaminants (Xu et al., 2012).

2.5.2 Biochar in water remediation

One of the environmental applications of biochar is in water remediation for the removal of inorganic and organic contaminants and has been found to be effective (Ahmad et al., 2014; Mohan et al., 2014a). Biochar properties depend on the type of feedstock used for production, pyrolysis temperature and production method (Kloss et al., 2012; Sun et al., 2014). It is considered as one of the alternative adsorbents that could potentially replace activated carbon as the major adsorbent because it is low cost, renewable and sustainable (Mohan et al., 2014a). Biochar is produced in a similar way as activated carbon except that the pyrolysed biomass does not undergo further treatment to activate its surfaces.
Sorption abilities of biochars derived from different feedstock and produced at different temperatures for the removal of heavy metals (Cr, Hg, Cd, Ni, Pb, Cu, Zn, U and Co) have been critically reviewed by Inyang and co-workers in 2016. In addition, the sorption of heavy metals onto biochar could be explained by multiple sorption mechanisms namely precipitation, complexation, ion exchange, electrostatic attraction and physical sorption (Inyang et al., 2016). Biochar has also been used as an effective adsorbent in the removal of nutrients such as nitrates, phosphates and the sorption of organic contaminants like dyes, phenols, pesticides, polynuclear aromatics and solvents (Hale et al., 2013; Mohan et al., 2014a; Wang et al., 2015a). Generally, biochar produced at high temperature has been found to be effective on sorbing organic contaminants due to its higher surface area, high aromaticity and low polarity (Ahmad et al., 2012; Uchimiya et al., 2010).

2.5.3 Preparation of magnetic biochar

There are two types of methods that are commonly used in the synthesis of magnetic biochar. The first one involves saturation of the biomass in iron precursors followed by heating either by pyrolysis or microwave technique. In a study conducted by Chen et al. (2011), magnetic biochar derived from orange peel was initially saturated in FeCl$_2$ and FeCl$_3$ solution (1:1 ratio) for 30 min followed by co-precipitation using NaOH added dropwise until the solution pH is 10. Following this, it was pyrolysed at different temperatures (250, 400 and 700°C). The magnetic property of the adsorbent was confirmed by TEM, SAD, XRD and by applying magnet to separate the magnetic adsorbent after sorption (Chen et al., 2011). A magnetic biochar was also produced by initially immersing the cottonwood in FeCl$_3$ for 2h and then dried at 80°C for 2h under air. Then, the FeCl$_3$ saturated and air-dried biomass was pyrolysed at 600°C for 1 h in N$_2$ environment. The
magnetic biochar produced is 74.3% $\gamma$-Fe$_2$O$_3$ with saturation magnetisation of 69.2 emu/g (Zhang et al., 2013). Similarly, Mubarak et al. (2014) also used FeCl$_3$ to saturate the palm oil empty fruit brunch (0.5:1 ratio) and then used microwave heating technique to a high surface area magnetic adsorbent (890 m$^2$/g) (Mubarak et al., 2014). On the other hand, a naturally occurring hematite was used as iron precursor for the production of magnetic biochar from pinewood. Initially, the hematite mineral with traces of kaolinite and quartz was crushed and sonicated for 30 min in deionised water. Then, the pinewood was vigorously mixed with the solution of hematite for 2 h and was oven-dried at 80°C. The hematite-rich pinewood was then pyrolysed at 600°C in the presence of N$_2$ (Wang et al., 2015b).

The second method is the chemical co-precipitation of biochar with the iron precursor. This method is more commonly used in the production of magnetic biochar compared to the first method. In this method, the biochar is saturated in Fe$^{3+}$/Fe$^{2+}$ precursor followed by the addition of a base, usually NaOH, until the solution pH reaches 10 to 11 as shown in the chemical reaction below. The synthesis is followed by washing of excess reagents and drying of the magnetic adsorbent (Laurent et al., 2008).

$$\text{Fe}^{2+} + \text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$$ (eq. 2.1)

However, magnetite is not very stable and may undergo oxidation. Fe$_3$O$_4$ may transform to another form of iron oxide, which is $\gamma$-Fe$_2$O$_3$. It is also magnetic but less magnetic than Fe$_3$O$_4$. The following reaction may occur in the presence of oxygen (Laurent et al., 2008):

$$\text{Fe}_3\text{O}_4 + 2\text{H}^+ \rightarrow \gamma - \text{Fe}_2\text{O}_3 + \text{Fe}^{2+} + \text{H}_2\text{O}$$ (eq. 2.2)

Corn stover biochar (500°C), commercial wood chip biochar (500°C) and eucalyptus leaf residue biochar (400°C) were used in FeCl$_3$ and FeSO$_4$ as iron precursor (Han et al.,
Chapter 2: Literature review

2015; Mohan et al., 2014c; Wang et al., 2015c). Sun et al. (2015) used corn stalk biochar produced at 400°C saturated in FeCl₃ and FeCl₂ solution at 80°C followed by dropwise addition of NaOH (Sun et al., 2015). Solution of FeSO₄ and Fe₂(SO₄)₃ was used to magnetise oak bark and oak wood biochars (400 and 450°C) followed by pH adjustment until 10-11 using NaOH. On the other hand, Ren et al., (2015) used a packed column to produce magnetic granulated biochar (350°C) from corn stalks. The column was packed with granulated biochar, followed by FeCl₃ preloading onto the biochar by pumping it through the column. Then, in situ precipitation was done by rinsing the column with 0.5 M NaOH (Ren et al., 2015). Baig et al. (2014) compared the two methods in terms of the physical characteristics of the magnetic biochars and their adsorption capacities. The one-step synthesis of the magnetic biochar from Kan grass (500°C) was found to produce magnetic biochar of better quality in terms of Fe₃O₄ loading, thermal stability and saturation magnetisation and As (III, V) sorption capacity. The BET surface area of all the adsorbents produced did not have a significant difference which ranged from 27.90 – 38.22 m²/g (Baig et al., 2014). A schematic diagram of the synthesis of magnetic biochar is presented in Figure 2.4.
2.5.4 Removal of organic contaminants using magnetic biochar

The amount of studies in the application of magnetic biochar in organic contaminants is less than the studies in inorganic contaminants. In addition, most of these studies synthesised and used magnetic biochar in the removal of organic dyes and emerging contaminants. A high surface area palm oil empty fruit bunch (890 m²/g) magnetised by impregnating FeCl₃ by single stage microwave heating technique was used to adsorb methylene blue in aqueous solution. Highly porous magnetic biochar was produced at 900W in 20 min radiation with 1:2 FeCl₂ and biomass ratio. The magnetic adsorbent exhibited a maximum adsorption capacity for methylene blue of 265 mg/g (Mubarak et al., 2014). The similar adsorbent was used to adsorb methylene blue and orange-G from wastewater. The effects of pH, adsorbent dosage, agitation speed and contact time in the sorption of these contaminants were investigated.
dyes were optimised using Design Expert Software v.6.0.8. The optimum pH condition for the sorption of methylene blue was found to be pH 2 and 10. At pH 2, the hydrogen ions on the surface of the magnetic biochar were replaced by the cationic methylene blue. The high sorption at pH 10 was due to the lowering of the electrostatic repulsion between the cationic dye and the magnetic adsorbent. On the other hand, anionic orange-G had highest sorption at pH 2 due to the protonation of magnetic adsorbent at low pH. However, the optimum dosage, agitation speed and contact time for the sorption process were 1.0 g, 125 rpm and 120 rpm for both dyes, respectively. Langmuir model best described the sorption isotherm of methylene blue and orange-G on magnetic adsorbent with maximum sorption capacity of 31.25 and 32.36 mg/g, respectively. Additionally, the fast sorption of methylene blue on the magnetic adsorbent and orange blue was best described by pseudo-second order.

Equilibrium concentration of methylene blue at pH 2, 6 and 10 was achieved at 160 min, 160 min and 60 min, respectively. It was observed that orange-G reached the equilibrium in 50 min in all pH values studied (Mubarak et al., 2015).

In a study conducted by Sun et al. (2015), it was observed that acid-treated biochar from corn stalks when coated with Fe$_3$O$_4$ nanoparticles via chemical co-precipitation efficiently removed crystal violet with maximum sorption capacity of 349 mg/g at initial concentration of 400 mg/L, pH 6.0 and temperature of 40$^\circ$C. The authors reported that Langmuir model best described the sorption of crystal violet onto Fe$_3$O$_4$-coated biochar, while thermodynamic analysis showed the sorption of crystal violet onto Fe$_3$O$_4$-coated biochar was spontaneous, endothermic and increased the entropy. The magnetic biochar gave a saturation magnetisation value of 61.48 emu/g. The coating of Fe$_3$O$_4$ onto acid treated biochar resulted in an increase of sorption capacity from 80.36 mg/g to 99.38 mg/g. This increase was associated with the introduction of Fe$_3$O$_4$ on the surface of biochar which widened the average pore radius of the biochar (Sun et al., 2015). This could be attributed
to the reduction of the zeta potential from -22.7 to -41.07 mV enhancing the electrostatic attraction of the cationic crystal violet onto Fe₃O₄-coated biochar. Pseudo-second order kinetic model best described the sorption on crystal violet onto the Fe₃O₄-coated biochar. Sun et al. (2015) proposed a mass transfer mechanism of crystal violet onto Fe₃O₄-coated biochar using Weber model. Crystal violet molecules diffused from the external layer of the adsorbent followed by internal diffusion in the pores and lastly, adsorption of crystal violet. Reusability of the adsorbent was studied using mixing crystal violet saturated adsorbent with absolute ethyl alcohol twice where the sorption capacity of 99.19 mg/g was reduced to 73.31 mg/g which may be due to incomplete desorption of crystal violet onto the adsorbent (Sun et al., 2015).

Magnetic biochar composite (MBC) was used to remove effluent organic matter in aqueous solution (Wei et al., 2016). MBC has a BET surface area of 359.7 m²/g. Its functional groups were N-H at 3130 cm⁻¹, C=O at 1630 cm⁻¹ and C-OH at 1400 cm⁻¹, Fe-O at 579 cm⁻¹ and C-H at 880 cm⁻¹. Positively charged effluent organic matter is most likely adsorbed in the adsorbent since it is negatively charged at pH > 5 as demonstrated by its zeta potential. Pseudo-second order kinetic model best represented the sorption of effluent organic matter in MBC. Langmuir isotherm best described the sorption isotherm. In their study, Wei et al. (2016) used a combination of excitation–emission matrix (EEM), parallel factor analysis (PARAFAC), synchronous fluorescence, two-dimensional correlation spectroscopy (2D-COS), and molecular weight distribution to understand the interaction of effluent organic matter and MBC. EEM analysis demonstrated that MBC had higher affinity for non-biodegradable component of the effluent organic matter compared to its biodegradable component. On the other hand, PARAFAC analysis demonstrated that humic-like and fulvic-like substances were easier to adsorb compared to protein-like substances. Synchronous fluorescence and 2D-COS also confirmed the results of the EEM-PARAFAC.
MBC also had a highest removal (77%) for substances with 492 Da molecular weight (Wei et al., 2016).

Peng et al. (2014) synthesised an iron-impregnated biochar derived from microalgae via hydrothermal treatment was used to adsorb tetracycline from aqueous system (Peng et al., 2014). Its isotherm data was best fitted by Langmuir isotherm and has a maximum monolayer sorption capacity of 95.86 mg/g, which is higher than the sorption capacity of biochar. The effects of iron on the physico-chemical properties of biochar were evaluated where BET surface area and pore volume generally increased as the amount of iron increased. Iron impregnation changed the morphology of the biochar form sheets to particles as the amount of iron impregnated increased. At low amount of iron salt, the biochar from microalgae formed biochar nanosheets. Excessive addition of iron salt resulted in the formation of particle magnetic biochar i.e. 3.0 g of dried microalgae mixed with 6 and 9 mmol of iron salt (NH_4)_2SO_4.FeSO_4.6H_2O. Maximum sorption capacity increases as the amount of iron in the biochar increase but further increase resulted in a slight reduction. Regeneration using 0.10 M NaOH with 3 cycles of adsorption and desorption was performed on the iron impregnated biochar, where the adsorption capacity is 93%, 99 % and 96% in each stage of regeneration, respectively. Three factors were considered that cause the high sorption of iron-impregnated biochar which are due to higher surface area, more hydrogen bonding and bridging effect of the structural Fe for tetracycline (Peng et al., 2014).

On the other hand, Wang et al. (2017) simultaneously carbonised, magnetised and activated corn stalks, reed stalks, and willow branches, which produced high surface area activated magnetic biochars (AMB) (760.7, 777.5 and 856.8 m^2/g, respectively). The iron oxides on AMB were magnetic γ-Fe_2O_3 and traces of α-Fe_2O_3. AMB has been found to be positively charged between pH 2-10. Norfloxacin had strong affinity for AMB and was best
described by Langmuir isotherm where the maximum monolayer sorption capacities of corn stalk AMB, reed stalk AMB and willow branches AMB were 7.2469, 3.5139 and 6.2587 mg/g, respectively. Norfloxacin adsorption on AMB could also be best described by pseudo-second order kinetic model. Thermodynamic analysis demonstrated that the sorption of norfloxacin on AMB was spontaneous and endothermic. Moreover, solution pH did not have an effect on the sorption of norfloxacin on AMB (Wang et al., 2017).

In the study of Shan et al. (2016), iron and iron oxide were ball milled with biochar produced from coconut, pinenut and walnut shells at 500°C. The biochar/Fe₃O₄ (365 m²/g) was used to adsorb carbamazepine and tetracycline, where the maximum sorption capacity is 62.7 mg/g and 94.2 mg/g, respectively. On the other hand, the sorption of carbamazepine and tetracycline on biochar/Fe₃O₄ could be better described by Freundlich model compared to Langmuir model. Solution pH did not affect the sorption of carbamazepine, but the sorption of tetracycline slightly decreased as the pH was increased from 4.0 to 9.0. This was due to the different pKa of the carbamazepine (2.3 and 13.9) and tetracycline (3.3, 7.7, 9.7, 12). Sorption of carbamazepine and tetracycline were associated with the surface complexation of Fe₃O₄ with the amide and hydroxyl functional groups of the two compounds. In addition, hydrophobic interaction and π-π interaction could also be involved due to the carbonaceous component of the adsorbent. After the sorption process, the saturated biochar/Fe₃O₄ underwent ball milling to degrade the sorbed carbamazepine and tetracycline. Almost half (46.2%) of sorbed carbamazepine was degraded after 6h of ball milling. The degradation was enhanced by the addition of 0.3 g SiO₂ per gram of biochar/Fe₃O₄ during ball milling resulting in 98.4% degradation. On the contrary, ~99% of sorbed tetracycline was degraded with 3h of ball milling, faster than carbamazepine degradation, due to its larger pore size preventing it from diffusing in the micropores (Shan et al., 2016). Recently, Tan et al. (2016) reviewed the sorption mechanisms of magnetic
biochar in organic contaminants removal. The sorption mechanisms are hydrogen bond, π-π interaction, electrostatic attraction and hydrophobic interaction (Tan et al., 2016).

2.6 Summary

SMX has been frequently detected in the aquatic environment and though the concentration of SMX detected is low, one of its potential harmful effects is the development of antibiotic-resistant organisms. Additionally, SMX, at high concentrations, has been found to be toxic in different organisms such as fish and crustaceans. Currently, there are various treatment methods used to remove SMX from aqueous solution and one of these is the removal of SMX using biomass-derived biochar. Biochar has the potential to replace activated carbon in the future. Its production cost is estimated to be US $246 per tonne (McCarl et al., 2009) while activated carbon costs US$ 1500-8900 per tonne (Klasson et al., 2009). The cost production of biochar may be low, but its cost-effectiveness will require the life cycle analysis of the system where biochar is applied. Biochar has been used in the sorption of organic and inorganic contaminants and most studies have focussed on the laboratory batch sorption studies under varied environmental conditions. However, one of the drawbacks of the biochar application in sorption processes is the difficulty of its separation after treatment. To address this, magnetisation of biochar using iron oxide has been done to easily separate the powdered magnetic biochar using a magnet or application of the external magnetic field. Both biochar and iron oxide can adsorb organic and inorganic contaminants and have been used in the removal of contaminants from aqueous solution. Since biochar and iron oxide differ in physical and chemical properties, the sorption behaviour of various contaminants is also different. The combination of biochar and iron oxide can potentially produce a novel magnetic biochar that can adsorb SMX and be easily separated after treatment.
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CHAPTER 3: Synthesis of magnetic biochar from pine sawdust via oxidative hydrolysis of FeCl₂ for the removal of sulfamethoxazole from aqueous solution

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Chapter Abstract

Magnetisation of carbonaceous adsorbent using iron oxide (Fe₃O₄) has potential to decrease the recovery cost of spent adsorbent because it could be separated magnetically. However, formation of various phases of FeₓOᵧ and iron hydroxide (Feₓ(OH)y) during synthesis, particularly the non-magnetic phases are difficult to control and could significantly reduce the magnetic saturation of the adsorbent. Hence, formation of the most magnetic Fe₃O₄, Fe₃O₄, on biochar via oxidative hydrolysis of FeCl₂ under alkaline media was performed to synthesise magnetic adsorbent using pine sawdust (magnetic pine sawdust biochar: MPSB). The Fe₃O₄ nanoparticles on the surface of biochar contributed to high saturation magnetisation of MPSB, 47.8A.m²/kg, enabling it to be separated from aqueous solution using a magnet. MPSB was examined physically and chemically using various techniques. Sorbent-stability, parametric, kinetics, isotherm, thermodynamic and sorbent-regeneration studies were performed to comprehend the potential of MPSB as adsorbent to remove an emerging contaminant, sulfamethoxazole (SMX) from aqueous solution. Results showed that MPSB was stable within solution pH 4 to 9. Adsorption of SMX onto MPSB was favourable at low pH, fast and best described by Redlich-Peterson model. Adsorption was exothermic with physisorption possibly due to hydrophobic interaction and spent adsorbent could be regenerated by non-polar solvents.
3.1 Introduction

Over the last decade, there has been an increasing global concern regarding the occurrence, and distribution of trace level residues of several human pharmaceuticals as well as veterinary antibiotics in surface water (Kasprzyk-Hordern et al., 2008), groundwater (Fram and Belitz, 2011), sediments (Silva et al., 2011) and soil (Thiele-Bruhn, 2003). Although the detected concentrations are usually at trace level (ng/L to µg/L), their occurrence may have negative effects on human health due to their accumulation and the potential development of drug-resistant microorganisms, which may lead to lack of alternative treatments (Manaia et al., 2012). Sulfamethoxazole (SMX) is one of the most frequently detected antibiotics in surface water (Kasprzyk-Hordern et al., 2008) and groundwater (Fram and Belitz, 2011) due to its inefficient removal in the sewage treatment plants and high persistence in the environment. At high concentration, SMX could be toxic to various aquatic organisms like fish and crustaceans (Isidori et al., 2005; Kim et al., 2007). Therefore treatment of SMX and similar emerging contaminants is of significance due to its possible harmful effects in the environment and in humans.

Biochar, a carbonaceous biomass-derived material, has been receiving increasing attention because of its several potential environmental applications such as soil amendment, carbon sequestration and contaminant remediation (Lehmann and Joseph, 2009; Mohan et al., 2014a). It is produced via pyrolysis of biomass such as wood waste, and various agricultural crop residues like pitch pine (Kim et al., 2012), corn cobs (Mullen et al., 2010) and corn stover (Mullen et al., 2010), as well as animal waste such as dairy manure (Cao et al., 2009), poultry litter (Sun et al., 2011) and swine solids (Sun et al., 2011). It has also been utilised as precursor to produce activated carbon and has been recognised for its ability to adsorb various organic and inorganic contaminants in soil and water systems (Cao et al.,
2009; Chen and Chen, 2009; Mohan et al., 2011b; Sun et al., 2011; Yao et al., 2011). The use of biochar as low-cost adsorbent has been well demonstrated in the scientific literature and a number of reviews are available (Ahmad et al., 2014; Mohan et al., 2014a). However, one of the drawbacks of using powder form adsorbent is the difficulty of recovering or separating the material after its use (Wu et al., 2005). Recently, there has been much interest in the development of magnetic biochar to make the material readily recoverable following the adsorption treatment to remove a particular contaminant of interest (Liu et al., 2010; Oliveira et al., 2002). For example, activated carbon/iron oxide composite has been found to possess high adsorption capacity for chloroform, phenol, chlorobenzene and drimaren red dye. It could easily be recovered after treatment because of its magnetic property from loading of γ-Fe₂O₃ and Fe₃O₄ on activated carbon (Oliveira et al., 2002). Furthermore, the magnetisation of carbonaceous adsorbents also increases the adsorption capacity of non-magnetic adsorbent (Chen et al., 2011).

Two common methods are used to synthesise magnetic carbonaceous adsorbents like magnetic biochar i.e. pre-saturation of biomass in iron precursor followed by pyrolysis at high temperature (Chen et al., 2011; Zhang et al., 2013) and chemical co-precipitation of biochar in Fe³⁺/Fe²⁺ solution upon addition of NaOH until the pH reaches 10-11 (Mohan et al., 2014b). Several techniques have also been used to physically and chemically characterise magnetic biochar such as X-ray Diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to determine the crystalline formation of iron oxide (Chen et al., 2011; Mohan et al., 2014b; Zhang et al., 2013); and vibrating sample magnetometer (VSM) (Mohan et al., 2014b) and physical property measurement system (PPMS) (Mohan et al., 2014b) to measure the magnetic properties. Earlier studies used synthesised magnetic carbonaceous adsorbents which were composed of different phases of iron oxides (Fe₃O₄)
and iron hydroxides (Fe₅(OH)₇) including the non-magnetic phases (Chen et al., 2011; Faulconer et al., 2012; Ma et al., 2013; Mohan et al., 2011a; Mohan et al., 2014c; Oliveira et al., 2002; Zhang et al., 2013). In the synthesis of magnetic powdered activated carbon, three phases of Fe₅O₇ were identified namely γ-Fe₂O₃, Fe₃O₄ and α-Fe₂O₃ (Faulconer et al., 2012). Both γ-Fe₂O₃ and Fe₃O₄ are magnetic iron oxides, however, α-Fe₂O₃ is a non-magnetic iron oxide. Similarly, in magnetic activated carbon from almond shells, non-magnetic Fe₅(OH)₇, Fe(OH)₂ and Fe(OH)₃ were detected (Mohan et al., 2011a). Although different synthesis methods were used, the presence of non-magnetic iron oxides/hydroxides could decrease the magnetic saturation of the magnetic adsorbent which could be more difficult to recover after treatment compared to magnetic adsorbent composed only of magnetic Fe₅O₇ particularly the most magnetic Fe₅O₇, Fe₃O₄ (Cornell and Schwertmann, 2006).

Therefore, the overarching aim was to develop a strong magnetic adsorbent by controlling the formation of nano-sized Fe₃O₄ on pine sawdust biochar (PSB) via oxidative hydrolysis of FeCl₂ under alkaline media that prevented the formation of other Fe₅O₇ and Fe₅(OH)₇. Magnetic pine sawdust biochar (MPSB) was characterised using an array of techniques for physico-chemical properties. The specific objectives were to determine the adsorbent stability in aqueous solution and determine the effect of pH, time, concentration and temperature to understand the SMX sorption and mechanisms onto MPSB. Additionally, the potential of sorbent-regeneration using nine solvents was performed.
3.2 Materials and methods

3.2.1 Materials

PSB was produced from *Pinus radiata* sawdust by slow pyrolysis using a full-scale continuous steam gasification slow pyrolysis process. The process involves delivery of up to 2 tonne/h of feedstock from a hopper into a spiral heat exchanger which is heated counter currently with hot boiler gasses. The feedstock residence time in the heat exchanger is 8–10 min with a highest heat treatment temperature (HTT) of 700 °C, which was monitored with a thermocouple placed on the body of the pyrolysis unit. The pyrolysed char was separated gravitationally from the hot gasses which were condensed in an air condenser. Biochar was ground and sieved in the size range of 75-300μm. Following this, PSB was washed once with 0.01M NaOH and dried prior to its application in the synthesis process. SMX and FeCl₂.4H₂O were purchased from Sigma-Aldrich. KOH, NaOH, concentrated HNO₃, formic acid, KNO₃, HCl , methanol, ethanol, 2- propanol, acetonitrile, acetone, dichloromethane, chloroform and tetrahydrofuran were analytical grade and were used as received. The N₂ gas used in the synthesis of MPSB was purchased from BOC, New Zealand.

3.2.2 Synthesis of MPSB

Synthesis of MPSB described here is a modified method for the synthesis of Fe₃O₄ via oxidative hydrolysis of FeSO₄ in alkaline media (Cornell and Schwertmann, 2006). All deionised water used during the process of synthesis was degassed for 2h with N₂. PSB was saturated in 200ml of 0.3M FeCl₂ with continued stirring at 500rpm for 24h in a glass
reactor. The mixture was then degassed with N₂ and heated to 90°C in a water bath. The reactor was continuously degassed with N₂ and the temperature was kept at 90°C during the operation. Eighty millilitres of 3.33M KOH and 0.27M KNO₃ solution was then added dropwise to the mixture containing PSB and FeCl₂ for the reaction to take place for an additional hour. The mixture was sealed, cooled overnight and centrifuged at 4000rpm. The supernatant was decanted and the particles were washed with deionised water for five times. The solid particles were vacuum dried at 40°C for 48h.

3.2.3 MPSB characterisation

The C, H and N of washed PSB and MPSB were analysed at the Campbell Microanalytical Laboratory, New Zealand. The ash content, using ASTM D 1506-99 method, of washed PSB was not detected and the ash content of MPSB was not measured due to the residuals of iron oxide after combustion. Micromeritics Tristar 3000 instrument was used in N₂ gas adsorption/desorption isotherm test under liquid nitrogen (-196°C). From adsorption/desorption isotherm data, specific surface areas, and cumulative pore volumes and pore diameters were determined according to the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Prior to the N₂ adsorption, samples were degassed for 2h at 350°C under N₂ gas. The crystal structure of the adsorbents was determined using -XRD (Bruker D2 Phaser) with CuKα radiation (λ=1.5406Å). Data were recorded over 2Θ range of 15–90 with a step increment of 0.02 and an interval time of 0.008s per step. The magnetic property was measured at external magnetic fields ranging between ±7.16MA/m using PPMS)under VSM option. Surface morphology and iron distribution on the surface were visualised and determined using Scanning Electron Microscopy–Energy
Dispersive X-ray Spectroscopy (SEM-EDS, Philips XL30S Field Emission Gun with Silicon Lithium detector). The point of zero charge ($pH_{pzc}$) was measured via potentiometric mass titration (Bourikas *et al.*, 2003) using an automatic titrator (848 Titrino plus). The total iron content of MPSB was measured by acid digestion using concentrated HNO$_3$. Leaching tests were also carried out to determine the stability of iron oxide at different pH. After acid digestion and equilibrium adsorption at different pH values, the samples were filtered using 0.45µm regenerated cellulose membrane and acidified using concentrated HNO$_3$. Following this, the filtrate was analysed using Atomic Absorption Spectroscopy (AAS) to measure iron content at 248.3nm wavelength.

### 3.2.4 Batch adsorption

Batch adsorption experiments were carried out in 125ml Erlenmeyer flasks with 25ml of SMX solution and 0.05g MPSB on a temperature controlled shaking water bath at 80 rpm and 25°C unless stated otherwise. The optimum initial pH was identified by carrying out the 24h-batch adsorption at two concentrations: 5.3 and 20.3mg/L SMX between pH range of 2 to 10 which was adjusted with 0.1M NaOH and 0.1M HCl. The pH at which the sorption was highest without leaching of iron was considered as optimum and was used in subsequent experiments. Batch isotherms were constructed using initial equilibrium SMX concentration of 1-66.2mg/L. For the kinetic studies, SMX concentrations used ranged from 1-20.5mg/L with sorption contact time ranging from 30s to 24h. Thermodynamics studies were performed using 20.1mg/L SMX at 25°C, 35°C, 45°C and 55°C. All batch sorption experiments of SMX using MPSB were done using at least 2 replicates.
3.2.5 Regeneration of spent MPSB

Five hundred millilitres of 20.8mg/L SMX solution was added to 0.5g MPSB. The solution was mixed using an orbital mixer for 24h at 80rpm followed by magnetic separation of the spent MPSB from the solution. The spent MPSB was vacuum dried at 40°C for 24h. Approximately 0.02g of dried spent MPSB was added to 20mL solvents (deionised water, methanol, ethanol, 2- propanol, acetonitrile, acetone, dichloromethane, chloroform and tetrahydrofuran) in glass centrifuge tubes. The tubes were sealed and placed in an end-over-end shaker to desorb the SMX on spent MPSB for 24h. Concentrations of SMX before adsorption, after adsorption and after solvent desorption were measured and mass balance was performed to determine the % SMX desorbed. The regeneration studies were performed in duplicates.

3.2.6 Analysis of SMX

All samples were filtered through 0.45µm regenerated cellulose membranes, and concentration of SMX was measured with HPLC equipped with ultraviolet detector using Phenomenex Kinetex column (5µm, C18, 150x4.6mm). The UV wavelength used is 270nm. The mobile phase was a mixture of 0.1% formic acid and acetonitrile with 1:1 volume ratio and the injection volume was 10µL. The runtime was 4.5min with SMX retention time of 2.25min. The amount of SMX adsorbed, \( q \), was calculated as follows:

\[
q = (C_o - C_e) \times \frac{V}{m} \tag{eq. 3. 1}
\]

where, \( C_o \) and \( C_e \) are the initial and equilibrium concentrations of SMX, \( m \) is the mass of the adsorbent and \( V \) is the volume of SMX solution.
3.2.7 Data Analysis

Kinetic data were fitted to three kinetic models: the pseudo-first order, pseudo-second order and intra-particle diffusion using eq. (3.2), (3.3) and (3.4), respectively.

\[ q_t = q_e (1 - e^{-k_1 t}) \]  

(eq. 3.2)

\[ q_t = \frac{q_e^2 k_2 t}{1+q_e k_2 t} \]  

(eq. 3.3)

\[ q_t = k_i t^{1/2} + C \]  

(eq. 3.4)

where \( t \) is the adsorption time, \( q_t \) is the amount of SMX adsorbed onto MPSB at time \( t \), \( q_e \) is the amount of SMX adsorbed at equilibrium, \( k_1, k_2 \) and \( k_i \) are rate constants of pseudo-first, pseudo-second and intra-particle diffusion and \( C \) is a constant describing the thickness of boundary layer.

Isotherm experimental data were fitted in five isotherm models namely Langmuir, Freundlich, Temkin, Redlich-Peterson and Dubinin-Radushkevich as illustrated in eq. (3.5)-(3.9), respectively.

\[ q_e = \frac{q_m K_l C_e}{1+K_l C_e} \]  

(eq. 3.5)

\[ q_e = K_F C_e^n \]  

(eq. 3.6)

\[ q_e = \frac{RT}{B_T} \ln(A_T C_e) \]  

(eq. 3.7)

\[ q_e = \frac{K_R P C_e}{1+A_R P C_e B_R P} \]  

(eq. 3.8)

\[ q_e = K_D R e^{\exp(-B_D e_D^2)} \]  

where \( e_D = RT \ln \left(1 + \frac{1}{C_e}\right) \)  

(eq. 3.9)
where $q_e$ is the amount adsorbed per mass of adsorbent (mg/g); $q_m$ is the maximum monolayer adsorption capacity (mg/g); $K_L$ is the Langmuir isotherm constant (L/mg); $C_e$ is the equilibrium concentration; $n$ is a measure of adsorption linearity; $K_F$ is the Freundlich isotherm constant; $\beta_T$ is the Temkin constant related to heat of sorption (J/mol); $A_T$ is the Temkin isotherm constant (L/g); $R$ is the gas constant (8.314 J/mol K); $T$ is the absolute temperature (K); $K_{RP}$ is the Redlich–Peterson model isotherm constant (L/g), $A_{RP}$ is the Redlich–Peterson model constant (L/mg); $\beta_{RP}$ the Redlich–Peterson model exponent; $K_{DR}$ is the Dubinin–Radushkevich model constant (mg/g); $B_D$ is the Dubinin–Radushkevich model constant (mol²/kJ²); and $\varepsilon_D$ is the Polanyi potential.

The errors of parameter estimation are minimised by maximising the non-linear regression coefficient calculated using eq. (3.10), (3.11) and (3.12).

$$R^2 = 1 - \frac{RSS}{TSS} \quad \text{(eq. 3.10)}$$

$$RSS = \sum_{i=1}^{n} (q_{pred_i} - q_{exp})^2 \quad \text{(eq. 3.11)}$$

$$TSS = \sum_{i=1}^{n} (q_{pred_i} - (q_{exp})_{ave})^2 \quad \text{(eq. 3.12)}$$

where $RSS$ is the residual sum of squared errors, $TSS$ is the total sum of squared errors, $(q_{pred_i})$ is the predicted sorption capacity for the $i^{th}$ term, $q_{exp}$ is the experimental sorption capacity and $(q_{exp})_{ave}$ is the experimental average $q$. 

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3.3 Results and discussion

3.3.1 Physico-chemical properties of MPSB

Some of the physical and chemical properties of PSB, MPSB and Fe₃O₄ are listed in Table 3.1. The %C and %H are highest in PSB followed by MSPB and not detected in Fe₃O₄. On the other hand, the %Fe measured using acid digestion in PSB is negligible while MPSB and Fe₃O₄ have %Fe of 28.76% and 70.63%, respectively. The %Fe based on EDS results (Figure 3.1a and Figure 3.1b) of PSB (0.18%) and MPSB (23.22%) are almost similar to the measured total iron content. The lower %Fe of MPSB in the EDS result is because EDS could only measure the iron content on the surface of MPSB. Additionally, the theoretical %Fe of Fe₃O₄ (72.36%) and %Fe measured for synthesised Fe₃O₄ (70.63%) have only 2.4 % difference. The results of %C, %H and %Fe are expected since PSB could be the only source of C and H in the adsorbent and Fe₃O₄ could be the main source of Fe. Additionally, the %N for all adsorbents is very low (<0.7%) which means both components of MPSB do not contain significant amount of nitrogen.

Table 3.1. Physico-chemical properties of PSB, MPSB and Fe₃O₄

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%Fe</th>
<th>BET surface area (m²/g)</th>
<th>BJH cumulative pore volume (cm³/g)*</th>
<th>BJH average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSB</td>
<td>86.82</td>
<td>1.57</td>
<td>&lt;0.3</td>
<td>n.d.</td>
<td>297.8</td>
<td>0.08</td>
<td>3.67</td>
</tr>
<tr>
<td>MPSB</td>
<td>55.77</td>
<td>0.82</td>
<td>&lt;0.5</td>
<td>28.76</td>
<td>125.8</td>
<td>0.14</td>
<td>9.60</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.7</td>
<td>70.63</td>
<td>19.4</td>
<td>0.21</td>
<td>38.40</td>
</tr>
</tbody>
</table>

*between 1.70 to 300.0 nm diameter
**Theoretical percent iron in Fe₃O₄ is 72.36%.
It is also notable that PSB has a high surface area of 297.8m$^2$/g. Fe$_3$O$_4$, which was produced by the same synthesis method for the synthesis of MPSB, has a surface area of 19.4m$^2$/g, which is in agreement with other synthesised Fe$_3$O$_4$ reported earlier (Cornell and Schwertmann, 2006). MPSB has a lower surface area (125.8m$^2$/g) compared to PSB (297.8m$^2$/g). The lower surface area of magnetic composite compared to activated carbon and biochar has also been observed in several past studies (Chen et al., 2011; Mohan et al., 2011a; Oliveira et al., 2002). However, the reduction in the BET surface area is expected because the magnetic composite is composed of a high surface area carbonaceous material and a low surface area Fe$_x$O$_y$ (Oliveira et al., 2002). In addition, it is conceivable that the nano-sized Fe$_3$O$_4$ may have blocked some of the pores of the PSB which is likely to have resulted in the reduced surface area.
Chapter 3: Synthesis of magnetic biochar from pine sawdust via oxidative hydrolysis of FeCl₂ for the removal of sulfamethoxazole from aqueous solution

<table>
<thead>
<tr>
<th>Element</th>
<th>% Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>94.67</td>
</tr>
<tr>
<td>O</td>
<td>4.2</td>
</tr>
<tr>
<td>K</td>
<td>0.47</td>
</tr>
<tr>
<td>Ca</td>
<td>0.47</td>
</tr>
<tr>
<td>Fe</td>
<td>0.18</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>% Mass</th>
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<td>C</td>
<td>67.46</td>
</tr>
<tr>
<td>O</td>
<td>8.3</td>
</tr>
<tr>
<td>K</td>
<td>0.88</td>
</tr>
<tr>
<td>Ca</td>
<td>0.14</td>
</tr>
<tr>
<td>Fe</td>
<td>23.22</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 3.1. Energy Dispersive X-ray Spectroscopy data for (a) PSB; and (b) MPSB
MPSB was synthesised via oxidative hydrolysis of FeCl$_2$ saturated onto PSB under alkaline condition with a controlled temperature of 90°C. During the process of synthesis, the mixture was continuously degassed with N$_2$ to prevent any formation of Fe$_x$O$_y$ and Fe$_x$(OH)$_y$ other than Fe$_3$O$_4$. The XRD patterns of PSB and MPSB are shown in Figure 3.2 and it can be observed that the diffraction pattern of PSB does not show any crystalline peak indicating its amorphous nature (Figure 3.2a). The diffraction pattern of MPSB confirmed the presence of Fe$_3$O$_4$ on MPSB as shown in Figure 3.2b. Strong and sharp peaks of Fe$_3$O$_4$ (2$\theta$=30.1, 35.5, 37.3, 43.1, 53.4, 57.0 and 62.5) as marked by their indices in Figure 3.2 suggest that the Fe$_3$O$_4$ is highly crystalline. There were no traces of other phases of Fe$_x$O$_y$ detected except the magnetic Fe$_3$O$_4$. Similarly, no peaks of impurities were detected which suggest the washing carried out on MPSB was sufficient to remove all the excess reagents and impurities. Additionally, there was no carbon peak observed on the MPSB, which is similar to the XRD patterns of PSB indicating that PSB remained amorphous after the synthesis. Reported studies on synthesised magnetic carbonaceous adsorbents consisted of different phases of Fe$_x$O$_y$ and Fe$_x$(OH)$_y$ including the non-magnetic ones (Ma et al., 2013; Mohan et al., 2011; Oliveira et al., 2002). The presence of non-magnetic iron oxides/hydroxides could reduce the magnetic saturation of the magnetic adsorbent, thereby making it more difficult to be recovered after treatment. On the other hand, Zhang et al. (2013) synthesised a magnetic biochar with uniformly dispersed single phase iron oxide (γ-Fe$_2$O$_3$) via chemical co-precipitation and subsequent pyrolysis (Zhang et al., 2013). Generally, γ-Fe$_2$O$_3$ (46 emu/g) is less magnetic than Fe$_3$O$_4$ (Kang et al., 1996; Cornell and Schwertmann, 2006). Hence, theoretically, at the same iron oxide and biochar mass ratio, biochar magnetised with Fe$_3$O$_4$ would be more magnetic. In this work, biochar was magnetised using single phase Fe$_3$O$_4$, which would have better magnetic property compared
to other magnetic carbonaceous adsorbents with mixed phases of iron oxide or with single phase $\gamma$-$Fe_2O_3$ reported assuming that the ratio of iron oxides/hydroxides and carbonaceous material is the same for both adsorbents.

Figure 3.2. X-Ray Diffraction analysis of (a) PSB; and (b) MPSB

The magnetisation of MPSB was measured using PPMS under VSM option. Magnetic hysteresis cycle of MPSB shows the synthesised adsorbent achieved a saturation magnetisation of 47.8A.m$^2$/kg or emu/g (Figure 3.3a). This is indicative of the magnetic strength of the adsorbent implying that the use of magnet or application of external magnetic field could recover the MPSB after treatment. The saturation magnetisation value obtained for MPSB is less than the earlier reported saturation magnetisation of $Fe_3O_4$ which is
67.8emu/g (Panda et al., 2001) and 53.8-66.0emu/g (Han et al., 1994). The lower value compared to pure magnetite (89.9A.m²/kg) is likely due to the non-magnetic PSB in the composite. The magnetic separation ability of MPSB was also tested by placing a magnet on the side of the glass bottle (Figure 3.3b).

Figure 3.3. Magnetic properties: (a) Magnetic hysteresis cycles of MPSB; (b) Magnetic separation of MPSB after adsorption of SMX from aqueous solutions

The surface morphologies of PSB and MPSB show that PSB has a honeycomb-like structure as illustrated in Figure 3.4a and 3.4e. The honeycomb-like structure was also made of pores which can be additional active sites for the sorption of SMX. The honeycomb-like structure of PSB was preserved after magnetisation and the nano-particles on the surface of PSB are Fe₃O₄. Fe₃O₄ is not uniformly distributed on the surface of PSB, which can be
advantageous because PSB has a significantly higher affinity for SMX sorption as compared to Fe₃O₄. Uniform dispersion of magnetite on the surface of PSB could significantly decrease the sorption capacity of the composite. The EDS elemental mapping results as illustrated in Figures 3.4b-d and 3.4f-h provide further insights on the elemental distribution of C, O and Fe on PSB and MPSB and provides evidence of the non-uniform dispersion of Fe₃O₄ on the surface of PSB. The figures clearly show the significant difference between the PSB and MPSB. Element map of C in PSB is denser than MPSB since the %C of PSB is higher than MPSB. On the other hand, the element maps of O and Fe are more intense in MPSB due to the presence of Fe₃O₄ on the surface of PSB.
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Figure 3.4. SEM images of PSB and elemental maps of PSB and MPSB (a) PSB x2500; (b) PSB - C map; (c) PSB - O map; (d) PSB - Fe map; (e) MPSB x2500; (f) MPSB - C map; (g) MSPB - O map; (h) MPSB - Fe map
3.3.2 Effect of pH on the adsorption of SMX onto MPSB

For ionisable compounds, solution pH is an important parameter affecting the sorbate-speciation and could change the properties of the adsorbent. To determine the influence of solution pH on the adsorption of SMX onto MPSB, a preliminary experiment was undertaken to identify the optimum pH for the sorption of SMX onto MPSB. Figure 3.5 illustrates the % removal of SMX adsorbed at initial solution pH range of 2 to 10. It can be observed that the highest SMX removal was achieved at pH 2 and 3 which resulted in the complete removal of SMX. However, at pH 2 and 3, there was leaching of iron which implies that the iron content of the MPSB is not stable at pH ≤ 4. Additionally, iron was also detected at pH 10. Fe₃O₄ stability varies with pH and supporting materials could influence its stability. The leaching of iron in weakly acidic and weakly basic solutions was also observed in other magnetic adsorbents (Ai et al., 2011; Wang et al., 2010). Thus, the material is only stable at pH 4 to 9 and therefore, pH 4 was considered as the optimum pH for the sorption studies conducted using SMX onto MPSB.
Figure 3.5. Effect of pH on the sorption of SMX onto MPSB

### 3.3.2 Adsorption kinetics

The amount of SMX adsorbed per gram of adsorbent ($q$) after adsorption onto MPSB as a function of time is shown in Figure 3.6. The adsorption of SMX occurred rapidly which may be due to the abundant availability of active sites. Apparent equilibrium was reached in less than 30min at low concentration, evidence of the high affinity of SMX onto MPSB. As the initial concentration of SMX decreases, the adsorption becomes faster. The ability of MPSB to adsorb SMX fast implies that MPSB would be a good adsorbent to be used in water treatment but this would require further testing for other compounds.

The kinetic parameters for the adsorption of SMX onto MPSB are shown in Table 3.2.
Among the kinetic models used, the pseudo-second order model described the experimental data best at low concentrations, 1 and 5.1 mg/L. However, at SMX concentration of 20.5 mg/L, the pseudo-first order best described the kinetic data. The lower rate constant associated with higher SMX concentration can be attributed to the fast uptake of active sites leaving other molecules to have difficulty finding active sites causing the slow sorption. The amount of SMX is higher but the rate at which the molecules are adsorbed is slower. Furthermore, the calculated $q_e$ has good agreement with the experimental $q_e$ values (Table 3.2). Since the fitting of kinetic data in pseudo-first and pseudo-second order kinetic models could not provide a definite sorption mechanism, the kinetic data were also fitted using intraparticle diffusion model. However, it failed to demonstrate a good agreement with the experimental data since the non-linear regression coefficient ($R^2$) is significantly lower compared to pseudo-first order and pseudo-second order kinetic models. Thus, intraparticle diffusion is unlikely to be the rate controlling step in the sorption of SMX onto MPSB.
Table 3.2. Kinetic parameters for pseudo-first order, pseudo-second order, and intra-particle diffusion mechanism of SMX onto MPSB [pH=4; Temperature=25°C]

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>qₑ,exp (mg/g)</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Intra-particle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>k₁ (L/min)</td>
<td>qₑ,calc (mg/g)</td>
<td>R²</td>
</tr>
<tr>
<td>1</td>
<td>0.5171</td>
<td>0.2632</td>
<td>0.5171</td>
<td>0.9798</td>
</tr>
<tr>
<td>5.1</td>
<td>2.4938</td>
<td>0.3849</td>
<td>2.4938</td>
<td>0.9940</td>
</tr>
<tr>
<td>20.5</td>
<td>8.7373</td>
<td>0.2531</td>
<td>7.5534</td>
<td>0.9239</td>
</tr>
</tbody>
</table>
Figure 3.6. Adsorption kinetics of SMX onto MPSB [pH=4; Temperature=25°C]

3.3.3 Adsorption isotherm

The equilibrium concentration data obtained from the adsorption of SMX onto MPSB for initial concentrations ranging from 1-66.2mg/L are correlated using five models namely Langmuir, Freundlich, Temkin, Redlich-Peterson and Dubinin-Radushkevich isotherms. The isotherm parameters for the adsorption of SMX onto MPSB are shown in Table 3.3. Based on the Langmuir parameters, the $q_m$ of MPSB for SMX is 13.83mg/g, which is lower compared to the $q_m$ of PSB (17.49mg/g), based on our preliminary studies. This may be attributed to the formation of Fe$_3$O$_4$ on the surface of MPSB since we initially found out that Fe$_3$O$_4$ has almost no sorption affinity for SMX. The reduction in the sorption
capacity may be also due to the lower surface area of MPSB compared to PSB. Although MPSB has lower sorption capacity compared to PSB, MPSB can easily be recovered by a magnet or application of external magnetic field to be recovered after treatment which could significantly reduce the treatment cost.

Table 3.3. Adsorption isotherm parameters of SMX onto MPSB [pH=4; Temperature=25°C]

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameters</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$ (mg/g)</td>
<td>13.83</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9108</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$ (mg/g(L/mg)$^{1/n}$)</td>
<td>4.96</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9636</td>
</tr>
<tr>
<td>Temkin</td>
<td>$A_T$ (L/g)</td>
<td>280.4</td>
</tr>
<tr>
<td></td>
<td>$\beta_T$ (J/mol)</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.7974</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>$K_{RP}$</td>
<td>2044.3</td>
</tr>
<tr>
<td></td>
<td>$A_{RP}$ (L/g)</td>
<td>409.5</td>
</tr>
<tr>
<td></td>
<td>$\beta_{RP}$</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9637</td>
</tr>
<tr>
<td>Dubinin-Raduskevich</td>
<td>$K_{DR}$ (mol$^2$/KJ$^2$)</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>$Q_{DR}$ (mg/g)</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>$E$ (KJ/mol)</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.7877</td>
</tr>
</tbody>
</table>

The essential feature of the Langmuir isotherm can be expressed in terms of the dimensionless equilibrium parameter $R_L$, which is defined as

$$R_L = \frac{1}{1+K_LC_o} \quad (\text{eq. 3.13})$$

where $C_o$ is the initial adsorbate concentration and $K_L$ is the Langmuir constant. The $R_L$ value implies that the type of the isotherm to be unfavourable ($R_L>1$), favourable ($0<R_L<1$),
linear ($R_L=1$), or irreversible ($R_L=0$) (Hall et al., 1966). Based on the computed values of $R_L$, which range between 0.028–0.667, the adsorption of SMX onto MPSB is favourable at conditions used in this study.

Among the isotherm models used in this study, the adsorption of SMX onto MPSB using Redlich-Peterson isotherm best fit the experimental data based on the non-linear regression coefficient ($R^2$) as shown in Figure 3.7. Redlich-Peterson isotherm combines the features of Langmuir and Freundlich isotherm in one model. This implies that the heterogeneity of the surface of the adsorbents plays a role on the sorption of SMX onto MPSB.
Figure 3.7. SMX adsorption isotherms in aqueous solution using MPSB at pH 4 and 25°C fitted in isotherm models: (a) Langmuir; (b) Freundlich; (c) Temkin; (d) Redlich-Peterson and (e) Dubinin-Radushkevich
3.3.4 Thermodynamic studies

Batch adsorption experiments from 25 to 55°C were performed to determine the effect of temperature on the sorption of SMX onto MPSB and its thermodynamic parameters. The $K_d$ values and thermodynamic parameters listed in Table 3.4 were obtained using the following equations:

$$K_d = \frac{c_s}{c_e}$$  \hspace{1cm} (eq. 3.14)

$$\Delta G^o = -RT\ln K_d$$  \hspace{1cm} (eq. 3.15)

$$\Delta G^o = \Delta H^o - T\Delta S^o$$  \hspace{1cm} (eq. 3.16)

$$\ln K_d = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$  \hspace{1cm} (eq. 3.17)

where $\Delta G^o$ is the change in Gibbs free energy, $R$ is the gas constant, $T$ is the absolute temperature, $K_d$ is the distribution coefficient, $\Delta H^o$ is the change of enthalpy and $\Delta S^o$ is the change of entropy. The values of $\Delta H^o$ and $\Delta S^o$ were determined by plotting $\ln K_d$ with respect to $1/T$.

The slope and y-intercept of the resulting graph were used to compute $\Delta H^o$ and $\Delta S^o$. The negative $\Delta G^o$ for all temperatures indicate that the SMX sorption onto MPSB is spontaneous and favourable. In addition, as the sorption temperature increases, the magnitude of $\Delta G^o$ also decreases, which suggests that the sorption becomes less spontaneous and sorption is more favourable at lower temperature. All computed $\Delta G^o$ are within the range of -20000 to 0 J/mol which implies that the sorption of SMX onto MPSB is due to physical adsorption (Jaycock and Parfitt, 1981). In addition, as the temperature increases, lower $K_d$ values are generally observed for organic compounds because solubility also increases (Delle Site, 2001). The negative value of $\Delta H^o$ denotes that the sorption is exothermic. The
negative value of $\Delta S^o$ indicates that as the amount of SMX adsorbed on the surface of MPSB increases, the SMX solid-liquid interactions with the synthesised MPSB becomes less random.

Table 3.4. Thermodynamic parameters for the adsorption of SMX (20.1 mg/L) onto MPSB [pH=4; Temperature=25°C]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_d$</th>
<th>$\Delta G^o$</th>
<th>$\Delta H^o$</th>
<th>$\Delta S^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.8306</td>
<td>-1498.06</td>
<td>-2089.56</td>
<td>-2.05</td>
</tr>
<tr>
<td>35</td>
<td>1.7593</td>
<td>-1446.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>1.7006</td>
<td>-1403.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>1.7007</td>
<td>-1448.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3.5 Regeneration of spent MPSB

The regeneration of SMX saturated MPSB using water and 8 organic solvents is plotted in Figure 3.8. The x-axis is arranged by decreasing relative polarity i.e. the deionised water (0.998) < methanol (0.762) < ethanol (0.654) < 2-propanol (0.546) < acetonitrile (0.460) < acetone (0.355) < dichloromethane (0.309) < chloroform (0.259) < tetrahydrofuran (0.207) (Linstrom and Mallard). The use of polar solvent, water, has been found to be unfavourable since % SMX desorption is very low (<4%). The use of relatively less polar organic solvents to regenerate the SMX saturated MPSB has been found to be significantly higher than the use of deionised water. The % SMX desorbed ranges from ~45 to ~67%. This clearly shows that the polarity of the solvent used in regeneration plays a role in the regeneration process. As mentioned in previous section, the sorption has been found to be
physiosorption. Hence, a longer desorption process could lead to higher regeneration efficiency. Other regeneration process such as thermal and chemical regeneration could be better options in desorbing SMX onto spent MPSB, which could be a focus of future studies.

![Figure 3.8. Regeneration of SMX saturated MPSB using 9 solvents.](image)

### 3.3.6 Plausible sorption mechanism of SMX onto MPSB

SMX is an amphoteric compound and exists in the environment as negative, neutral and positive species depending on the pH of the solution. SMX has two $pK_a$ values: 1.6 and 5.7 (Boreen et al., 2004). The $pH_{pzc}$ of MPSB was identified using potentiometric mass titration. The $pH_{pzc}$ plays an important role in identifying if electrostatic attraction occurs
between the adsorbent and the adsorbate. MPSB has a \( pH_{pzc} \) of 9.46, which implies that MPSB is positively charged at pH lower than 9.46 and negatively charged at pH greater than 9.46. At pH 4, MPSB is positively charged and SMX is neutral. Furthermore, at solution pH greater than \( pK_{a2} = 5.7 \) (Boreen et al., 2004), SMX negative species are more dominant and has lower affinity to MPSB. Thus, the high adsorption of SMX at low pH and low adsorption at high pH are not likely due to electrostatic attraction of SMX and MPSB.

The solubility of SMX, which is also dependent on temperature and pH, can influence the adsorption behaviour of SMX onto MPSB. SMX has an octanol-water partition coefficient (\( K_{ow} \)) of 3.02 (log \( K_{ow} = 0.48 \)) (Machatha and Yalkowsky, 2005). It is least soluble in water at pH 3.22, with a solubility value of 28.1±0.2mg/100ml at 25°C, however, its solubility slightly increased to 38.0±0.2, 29.0±0.3 and 39.1±0.5mg/100ml at pH 2.08, 3.94 and 5.41, respectively. SMX is highly soluble at basic and very acidic media with solubility reaching up to 3480±61.5mg/100ml and 620.7±9.3mg/100 ml at 25°C, respectively (Dahlan et al., 1987). Figure 3.5 shows that the sorption of SMX onto MPSB is negatively affected by increase in pH, therefore, SMX sorption onto MPSB is also negatively affected by SMX solubility. Hence, hydrophobic interaction could possibly explain this sorption behaviour since it is also a physical sorption associated with the sorption of SMX onto MPSB. Hydrophobic interaction was also found on the sorption of SMX onto functionalised carbon nanotube due to the pH influence on SMX solubility resulting in less sorption of SMX at pH where the solubility of SMX is low (Zhang et al., 2010). This finding is also supported by the result of the regeneration studies using polar deionised water and non-polar organic solvents. Generally, non-polar solvents are hydrophobic thus the hydrophobic SMX was dissolved or desorbed by the non-polar organic solvents during regeneration of the spent adsorbent.
As mentioned earlier, SMX has no sorption affinity for the synthesised Fe$_3$O$_4$; hence the sorption of SMX onto MPSB could be only due to PSB component. Based on the results of the elemental analysis, PSB is highly carbonised as reflected by its low hydrogen and high carbon composition (H/C ratio = 0.018). At this very low, H/C ratio, the highest possible (O+N)/C is 0.13, which is indicative that PSB has a very low polarity and hydrophilicity substantiating that PSB is a hydrophobic biochar. Biochar produced at very high temperature have hydrophobic surfaces due to high degree of carbonisation and low (O+N)/C ratio (Zhang et al., 2011a). On the other hand, SMX has hydrophobic functional group, which is the methyl group. The methyl group attaches to the hydrophobic surface of MPSB. Figure 3.9 shows how SMX behaves on PSB, Fe$_3$O$_4$ and MPSB. SMX methyl group attaches on the hydrophobic surface of PSB. On the other hand, SMX is not sorbed on Fe$_3$O$_4$. Lastly, the methyl group of SMX attached on the PSB surface of MPSB but not on the Fe$_3$O$_4$ dispersed on the surface of PSB.
Figure 3.9. Sorption behaviour of SMX onto (a) PSB; (b) Fe$_3$O$_4$ and (c) MPSB

In summary, successful synthesis of a novel magnetic adsorbent by forming single phase iron oxide (Fe$_3$O$_4$) nanoparticles on the surface of PSB was demonstrated. Fe$_3$O$_4$ reduced the BET specific surface area of PSB and its SMX adsorption capacity, however, it can easily be recovered after adsorption by a magnet due to its high saturation magnetisation of 47.8A.m$^2$/kg. MPSB was found to be stable at pH 4 to 9 due to the leaching of iron at extreme solution pH conditions. At pH 4, the adsorption of SMX onto MPSB was rapid, exothermic due to physisorption, favourable and the isotherm was best described by Freundlich model. Non-polar organic solvents could regenerate the SMX saturated MPSB. Hydrophobic interaction could be the possible sorption mechanism involved in SMX sorption onto MPSB.
3.4 Environmental Relevance and Significance

The utilisation of wood waste, pine sawdust, to produce effective adsorbent could potentially be seen as having two positive environmental effects: the waste minimisation and reuse of waste to mitigate contaminants in aquatic environment. Moreover, the magnetisation of biochar derived from pine sawdust has shown promising results, which could be applied to other waste-derived adsorbents. However, one of the biggest challenges of using any adsorption technology is the regeneration of the spent adsorbent and the scalability from laboratory to pilot-scale and eventually at commercial level to make the technology a viable option. For example, most lab-scale sorption studies are carried out under optimum operating conditions and various parameters are optimised (e.g. initial concentrations, contact time, temperature etc.). In order to determine the feasibility of the technology at commercial level, factors such as contaminant loading, concentration and contact time used in lab-scale adsorption studies may need to be altered. Thus, though the use of magnetic adsorbents has become popular in recent times, no commercial application is underway at present. An adsorbent with low production cost yet with high adsorption efficiency for a variety of pollutants should be considered. Additional studies should be undertaken to expand the list of test contaminants and to optimize the adsorbent and support media ratio with regards to flow and sorption parameters.
CHAPTER 4: Site energy distribution analysis and influence of Fe$_3$O$_4$ nanoparticles on sulfamethoxazole sorption by magnetic biochar

Published in Environmental Pollution
Chapter Abstract

Magnetisation of carbonaceous adsorbents using iron oxides has been found to be one of the potential solutions for easy recovery of adsorbent after use. We evaluated the effects of Fe$_3$O$_4$ nanoparticle addition on the physico-chemical properties of biochar and its sorption properties. Five adsorbents with varying amount of Fe$_3$O$_4$ per mass of adsorbent (0%, 25%, 50%, 75% and 100%) were used to adsorb sulfamethoxazole (SMX), an emerging micropollutant. Five isotherm models were used to evaluate the sorption behaviour of SMX onto the adsorbents where Redlich-Peterson model was found to best describe the data. Based on this model, the approximate site energy distribution for each adsorbent was determined. Surface area and sorption capacity had strong negative linear relationship with the amount of Fe$_3$O$_4$ per mass of adsorbent while the pore volume and saturation magnetisation of the adsorbent increased with increasing percentage of Fe$_3$O$_4$. The results of the approximate site energy distribution analysis showed that the addition of Fe$_3$O$_4$ on biochar reduced the area under the frequency distribution curve of sorption site energies leading to the lowering of the sorption sites available for SMX. This could be attributed to the blockage of the hydrophobic surface of biochar reducing the hydrophobic interaction between SMX and biochar.
4.1 Introduction

In recent years, there has been an increasing interest on the application of magnetic adsorbents to ease the separation of carbonaceous adsorbents to make the whole adsorption process more cost-effective. Some of the most frequently used carbonaceous adsorbents have been commonly derived from agricultural waste. Carbonaceous adsorbents such as activated carbon, biochar, charcoal and char have demonstrated good sorptive ability for a variety of inorganic and organic contaminants (Babel and Kurniawan, 2003; Crini, 2006; Dias et al., 2007; Pollard et al., 1992). Thus, the magnetisation of these materials became popular and could be a possible practical solution to separate and recover non-magnetic adsorbents. (Rajapaksha et al., 2016).

Sorption mechanisms of various contaminants on magnetic adsorbents are usually explained using isotherm parameters. However, this alone has not been sufficient to fully understand the underlying mechanism on the sorption of contaminants on magnetic carbonaceous materials. In general, sorption isotherm for a contaminant is a common approach to describe a great diversity of retention and release phenomena. Sorption isotherms provide and quantify the overall interaction between the sorbate and the sorbent. However, sorption isotherms does not specify the type of interactions or reactions between the sorbate and the sorbent (Sposito, 1984). For instance, the retention can be either due to surface retention without creating 3-dimensional structure or to precipitation of a new solid phase (McBride, 1994). Thus, knowledge on sorption isotherm purely explains the macroscopic or microscopic data and does not reveal anything on the complicated mechanisms involved (Limousin et al., 2007). Therefore approaches such as approximate site energy distribution analysis has been used to explain the mechanisms of sorption of organic chemicals in soils.
The working principle behind site energy distribution is such that in most theoretical treatments of adsorption on heterogeneous solids, the adsorbent surface is assumed to have a continuous distribution of adsorption sites with respect to adsorption energy. Isotherm models are derived based on the assumptions of site energy distribution (Shen et al., 2015). The changes in the site energy distribution on the surfaces of the adsorbents are reflected by the isotherm parameters. Understanding the energy distribution on the surface of the adsorbents could provide more information on the interaction between the adsorbate and the adsorbent and can help understand the mechanisms involved.

In the past, the site energy distribution analysis has been used to explain the heterogeneous sorption site distribution of activated carbon and soil organic matter (Carter et al., 1995; Yuan and Xing, 1999). For instance, site energy distribution analysis was used to explain the sorption mechanism of naphthalene, lindane and atrazine on ten types of carbonaceous materials where oxygen content was found to decrease the average sorption energy resulting in the reduction of adsorbent’s sorption capacity (Shen et al., 2015). The authors reported that surface area has been found to have significantly greater influence on the sorptive ability of the adsorbents compared to the introduction of oxygen-containing functional groups. An earlier study used site energy distribution analysis to explain the effect of preloading of 1,2,4-trichlorobenzene on activated carbon and sorption of trichloroethylene (Carter et al., 1995). The authors observed that surface heterogeneity of activated carbon was reduced due to the preloading and the loss of higher energy sites was more dominant compared to low energy sites. Similarly, site energy distribution analysis was also used to investigate the displacement mechanism of pyrene by phenanthrene from soils and sediments wherein pyrene displacement had significant stronger energy reduction effect on high energy sites compared to low energy sites (Wang et al., 2005).
The study conducted by Yuan and Xing (1999) revealed that prometon competed with atrazine resulting in the sorption energy reduction of atrazine in Cheshire soil. In addition, Pahokee peat soil and its organic matter fractions (humin and humic acid) exhibited different sorption energies in 1,2-dichlorobenzene. However, cations (Ca$^{2+}$ and Al$^{3+}$) did not significantly affect the sorption energy between Michigan humic acid and naphthalene. Hence, site energy distribution analysis has been useful in understanding the sorption mechanisms of different sorbate-sorbent systems. This could be also used to understand the sorption behaviour of organic contaminants on magnetic adsorbent, however, no studies have been reported so far which used sorbents that are magnetic in nature.

For the past few years, emerging micropollutants (EMs) such as several antibiotics have been detected in surface water (Pal et al., 2010; Silva et al., 2011; Vaicunas et al., 2013; Zou et al., 2011), groundwater (Jurado et al., 2012; Lapworth et al., 2012) and sediments (Hu et al., 2012; Silva et al., 2011) at trace levels, usually in ng/L to µg/L. Given their ubiquitous presence in the aquatic environment in many parts of the world together with their indirect negative effects to human health such as the potential development of drug-resistant microorganisms, EMs have become an environmental and public concern (Jordan et al., 2010; Manaia et al., 2012). Among various pharmaceutical drugs, sulfamethoxazole (SMX) is one of the frequently detected drugs in the aquatic environment. In the previous chapter, the sorption of SMX onto magnetic biochar was investigated showing that hydrophobic interaction could be the dominant sorption mechanism (Reguyal et al., 2017). However, the influence of Fe$_3$O$_4$ nanoparticles on sorption of organic pollutants onto magnetic biochar is not well understood due to paucity of information in the literature. Fe$_3$O$_4$ generally requires modification to improve its affinity for organic pollutants. We hypothesise that the addition of Fe$_3$O$_4$ on biochar may decrease the sorption affinity of biochar for organic pollutants.
The overarching objectives of this study were to evaluate the influence of the varying amount of Fe$_3$O$_4$ nanoparticles onto magnetic biochar, testing both in its physico-chemical properties and sorptive ability for SMX using site energy distribution analysis. Given the importance of sorption isotherm parameters corresponding to specific site energy distribution, we utilised several isotherm models to determine sorption parameters and selected the best model to discuss the interaction between sorbent and sorbate.

### 4.2 Materials and methods

#### 4.2.1 Materials

The pine sawdust biochar (PSB), which was produced at 700°C, was obtained from Lakeland Steel Ltd., New Zealand. Initially, PSB was ground and sieved where 75 µm to 300 µm particles were used. The biochar was then washed with 0.01 M NaOH and dried at 105°C overnight. SMX and ferrous chloride tetrahydrate (FeCl$_2$.4H$_2$O) were purchased from Sigma-Aldrich. High Performance Liquid Chromatography (HPLC) grade methanol and acetonitrile were purchased from Merck for the preparation of SMX stock solution and HPLC organic mobile phase, respectively. Potassium hydroxide (KOH), sodium hydroxide (NaOH), nitric acid (HNO$_3$) and formic acid were acquired from Univar. Potassium nitrate (KNO$_3$) and hydrochloric acid (HCl) were purchased from Labchem and Macron Fine Chemicals, respectively. All chemicals were used as received. The nitrogen (N$_2$) gas was purchased from BOC, New Zealand.

#### 4.2.2 Preparation of magnetic pine sawdust biochar (MPSB)

The preparation of MPSB described here is a modified method for the synthesis of
Fe$_3$O$_4$ developed by Schwertmann and Cornell (Cornell and Schwertmann, 2006). All deionised water and solution were degassed using N$_2$ for 2 h. The ratio of the Fe$_3$O$_4$ with the biochar in the composite was varied. Five magnetic adsorbents prepared and used in this study were named 0-MPSB, 25-MPSB, 50-MPSB, 75-MPSB and 100-MPSB; where the numbers 0, 25, 50, 75 and 100 indicate the theoretical percentage of Fe$_3$O$_4$ on magnetic adsorbent. Initially, PSB was saturated in 0.3 M FeCl$_2$ with continuous stirring (500 rpm) for 24 h in an airtight container. The mixture was then degassed with N$_2$ and heated to 90°C in a water bath. Throughout the synthesis, the N$_2$ was used to degas the mixture and the temperature of the mixture was maintained at 90°C followed by dropwise addition of a solution of 3.33 M KOH and 0.27 M KNO$_3$ to the mixture. After addition of KOH and KNO$_3$ solution, the reaction was undertaken for another hour; the mixture was sealed and cooled to room temperature. The ratio of PSB with FeCl$_2$ and KOH/KNO$_3$ solution was varied depending on the desired percentage of Fe$_3$O$_4$ in magnetic biochar. KOH/KNO$_3$ solution was added in excess to complete the reaction. The magnetic adsorbent was recovered from the mixture via centrifugation at 4000 rpm, washed five times with deionised water and dried in a vacuum oven at 40°C for at least 48 h.

4.2.3 Characterisation of adsorbents

The proximate analysis was performed to identify the %C, %H and %N of the adsorbents (Campbell Microanalytical Laboratory, Dunedin, New Zealand). The total iron content of MPSB was measured by acid digestion using concentrated HNO$_3$ followed by Atomic Absorption Spectroscopy (AAS). The adsorbents were digested in HNO$_3$ for 24 h then filtered using 0.45 µm regenerated cellulose membrane. The filtrate was then analysed using AAS at 248.3 nm. Micromeritics Tristar 3000 instrument was used in N$_2$ gas
adsorption/desorption isotherm at -196°C using liquid N₂. Specific surface areas and cumulative pore volumes were determined according to the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively using the N₂ adsorption/desorption isotherm data. Prior to the N₂ adsorption/desorption, samples were degassed for 2 h at 350°C under N₂ gas. The crystalline structure of the adsorbents was determined using X-Ray Diffraction (XRD, Bruker D2 Phaser) with CuKα radiation (λ=1.5406 Å). Data were recorded over the 2θ range of 15–90° with a step increment of 0.02° and an interval time of 0.008 s per step. The magnetic property was measured at external magnetic fields ranging between ±90 kOe using Physical Property Measurement System (Quantum Design) under Vibrating Sample Magnetometer (VSM) option. Surface morphologies of the adsorbents were captured using Scanning Electron Microscopy (SEM, FEI Quanta 200 FEG, USA). Composition and speciation of surface elements were identified using X-ray Photoelectron Spectroscopy (Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer, Kratos Analytical, Manchester, United Kingdom) equipped with a hemispherical electron energy analyser. The spectra were excited using monochromatic Al Kα X-rays (1486.69 eV) with the X-ray source operating at 150 W. CasaXPS software was used for data analysis while Shirley backgrounds were used in peak fitting. Survey quantification was performed using relative sensitive factors from the instrument.

4.2.4 Batch sorption experiments

All equilibrium batch sorption experiments were performed in Kimax glass centrifuge tubes with Teflon-lined screw caps. A background electrolyte solution of 0.01 M NaCl was used. All adsorbates were prepared from stock solution of SMX prepared in
methanol. An aliquot of 30 mL were added to pre-weighed magnetic adsorbent. The solid to solution ratio used throughout this study was 1:200. The methanol was kept below 0.1% v/v to eliminate the co-solvent effect. The solution pH was adjusted to 7 ± 0.10 using 0.01 M NaOH and 0.01 M HCl solutions to eliminate the effect of pH on the sorption unless otherwise stated. The actual initial solution concentrations were measured and used in the calculations. The apparent equilibrium time of 24 h was taken as the contact time which was based from our preliminary kinetic studies and average values were reported.

4.2.5 Analysis of SMX concentration

All samples were filtered using 0.2 µm regenerated cellulose membranes. Analyte concentrations were measured using HPLC (Shimadzu, LC 2030) with ultraviolet detector using Phenomenex Kinetex column (5µm, C18, 150 x 4.6 mm). A 20µL of sample was injected and analysed in broad range of wavelength (300 – 800 nm) where the wavelength that provided the highest signal for SMX was 270 nm. The samples were eluted at 1 mL/min flowrate composed of a mixture of 0.1% formic acid and acetonitrile with 1:1 volume ratio for 5 min where the retention time of SMX was ~2.2 min. The amount of analyte adsorbed in apparent equilibrium, \( q_e \), was calculated as follows:

\[
q_e = (C_o - C_e) \times \frac{V}{m}
\]

(eq. 4. 1)

where \( C_o \) and \( C_e \) are the initial and equilibrium concentrations of adsorbate (mg/L), \( m \) is the mass of the adsorbent (g) and \( V \) is the volume of solution (L).
4.2.6 Sorption isotherm models

Five isotherm models, Langmuir, Freundlich, Redlich-Peterson, Temkin and Dubinin-Radushkevich were used to fit the experimental data of SMX sorption onto the adsorbents. The equations describing Langmuir, Freundlich, Redlich-Peterson, Temkin and Dubinin-Radushkevich (Foo and Hameed, 2010) models are given in eq. (4.2)-(4.6).

\[
q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad \text{(eq. 4.2)}
\]

\[
q_e = K_F C_e^N \quad \text{(eq. 4.3)}
\]

\[
q_e = \frac{K_R P C_e}{1 + \alpha R P C_e^{\beta R P}} \quad \text{(eq. 4.4)}
\]

\[
q_e = \frac{R T}{b_T} \ln(A_T C_e) \quad \text{(eq. 4.5)}
\]

\[
q_e = q_s e x p\left(-k_{ad} \epsilon D^2\right) \quad \text{where} \quad \epsilon D = \frac{R T}{c_e} \ln\left(1 + \frac{1}{c_e}\right) \quad \text{(eq. 4.6)}
\]

In above equations, \( q_e \) is the amount adsorbed per mass of adsorbent (mg/g); \( q_m \) is the maximum monolayer adsorption capacity (mg/g); \( K_L \) is the Langmuir isotherm constant (L/mg); \( C_e \) is the equilibrium concentration (mg/L); \( N \) is a measure of adsorption intensity; \( K_F \) is the Freundlich isotherm constant (mg/g (L/mg)\(^N\)); \( K_R P \) is the Redlich–Peterson model isotherm constant (L/g), \( \alpha R P \) is the Redlich–Peterson model constant (L/mg); \( \beta R P \) is the Redlich–Peterson isotherm exponent; \( b_T \) is the Temkin isotherm constant; \( A_T \) is the Temkin isotherm equilibrium binding constant (L/g); \( R \) is the gas constant (8.314 J/mol-K); \( T \) is the absolute temperature (K); \( q_s \) is the theoretical isotherm saturation capacity (mg/g); \( k_{ad} \) is the Dubinin–Radushkevich model constant (mol\(^2\)/kJ\(^2\)); and \( \epsilon D \) is Dubinin–Radushkevich isotherm constant. The data were fitted in the isotherm models by using non-linear chi-
square ($\chi^2$) test where $\chi^2$ was minimised using eq. (7) (Ho et al., 2005).

$$\chi^2 = \sum_{i=1}^{N} \left( \frac{q_{e,\text{exp}} - q_{e,\text{calc}}}{q_{e,\text{calc}}} \right)^2$$  \hspace{1cm} (eq. 4. 7)

In eq. (4.7), $q_{e,\text{calc}}$ is the calculated equilibrium capacity obtained from the isotherm model (mg/g), and $q_{e,\text{exp}}$ is experimental equilibrium capacity (mg/g).

4.2.7 Estimating approximate site-energy distribution

One of the assumptions of isotherm models is based on the distribution of sorption site energies which can be determined from the theoretical isotherm representing the measured equilibrium data. The general integral equation for the sorption of organic compounds onto adsorbent can be written as:

$$q_e(C_e) = \int_{-\infty}^{+\infty} q_h(E, C_e) F(E) \, dE$$ \hspace{1cm} (eq. 4. 8)

or

$$F(E^*) = \frac{-d q_e(E^*)}{d E^*}$$ \hspace{1cm} (eq. 4. 9)

where $C_e$ is the equilibrium concentration of sorbate in liquid phase (mg/L), $q_e(C_e)$ is the total sorption of solute to the sorbent (mg/g), $q_h (E, C_e)$ is the isotherm over local sorption sites with sorption energy $E$ (mg/g), and $F(E^*)$ is the site energy frequency distribution over a range of sites with homogeneous energies between the solute and solvent for a given sorption site (mol-mg/J-g) (Carter et al., 1995). The range of the energies is assumed to be from 0 to infinity ($\infty$) since the value of negative infinity ($-\infty$) will not have any physical
meaning. Due to difficulty in solving this equation, and given there is no general analytical solution for eq. (4.8), simplification using condensation approximation or asymptotically correct approximation proposed by Cerofolini as shown in eq. (4.10) was used (Cerofolini, 1974). This method was used to derive the approximate site energy distribution based on various isotherm models such as Freundlich, Langmuir, Langmuir-Freundlich, Sips, Redlich-Peterson and Dubinin-Ashtaknov isotherm models

\[
C_e = C_s e^{-\frac{E-E_s}{RT}} = C_s e^{-\frac{E^*}{RT}} \quad \text{(eq. 4.10)}
\]

where \(C_s\) is the solute solubility in the solvent (mg/L), \(E_s\) is the lowest physically realisable sorption energy (J/mol), \(R\) is the universal gas constant (J/mol-K), \(T\) is the absolute temperature (K) and \(E^*\) is the difference of sorption energy at \(C_e\) and \(C_s\) (J/mol) (Carter et al., 1995; Cerofolini, 1974; Shen et al., 2015).

4.3 Results and discussion

4.3.1 Properties of magnetic adsorbent

The elemental compositions, BET-N\(_2\) specific surface areas, BJH pore volumes, BJH surface area of pores and saturation magnetisations of the adsorbents are summarised in Table 4.1. PSB could be the only source of the elemental C, H and N of the magnetic adsorbent. The Fe content could only come from the Fe\(_3\)O\(_4\) synthesised together with PSB since no Fe was detected in the PSB. However, the O content could potentially come either from PSB, Fe\(_3\)O\(_4\) or both. As expected, the percentages of C and H decreased as the amount of Fe\(_3\)O\(_4\) per mass of the adsorbent increased. Likewise, the O and Fe content increased as more Fe\(_3\)O\(_4\) was present per mass of the adsorbent. The ash content of washed PSB was
found to be negligible and could not be detected. Moreover, the ash content of the magnetic adsorbents was not measured due to the residuals of iron oxide after combustion in magnetic adsorbents which would have resulted in significant errors.

The results of the N₂ sorption/desorption also showed that the BET surface area decreases as the amount of Fe₃O₄ in the adsorbent increases. Previous studies have shown that the addition of iron oxide resulted in the surface area reduction of activated carbon, hydrochar and biochar (Chen et al., 2011b; Do et al., 2011; Liu et al., 2010; Mohan et al., 2011a; Oliveira et al., 2002). However, the effect of Fe₃O₄ on the BET surface area of the adsorbent has not been clear. Furthermore, in earlier studies, synthesised magnetic adsorbents were produced from different forms of iron oxide including the non-magnetic iron oxide phases (Faulconer et al., 2012; Mohan et al., 2011a; Oliveira et al., 2002). Since only Fe₃O₄ was formed after magnetisation, the change in the BET surface area could only be attributed to the magnetisation of the adsorbent due to Fe₃O₄. The BJH pore volume of the adsorbents between 1.7 and 300 nm increased with increased in the amount of Fe₃O₄ per mass of the adsorbent.

Figure 4.1 shows the linear relationship between the adsorbents and their BET surface area and BJH pore volume with $R^2$ of 0.99 and 0.92, respectively. The reduction of the BET surface area could be attributed to the addition of a low surface area Fe₃O₄ on a high surface area biochar and the blockage of the pores. Although the adsorbents with higher Fe₃O₄ have higher pore volume compared to adsorbent with less percentage of Fe₃O₄, it may have less number of pores particularly smaller than 1.7 nm. Table 4.1 also shows the BJH surface area of pores accounting for pores between 1.7 nm and 300 nm. It is clear BET surface area is significantly higher than BJH surface area of pores. On the contrary, 100-
MPSB has shown that the BJH surface area of pores is higher than the BET surface area both in m²/g implying that this adsorbent has no or few pores less than 1.7 nm.

Moreover, the saturation magnetisation of the material has a linear relationship with the amount of Fe₃O₄ per mass of adsorbent as shown in Figure 4.1 with $R^2 = 0.99$. This would be expected since the amount Fe₃O₄ provides the magnetic property on biochar so as its Fe₃O₄ percentage increases, its saturation magnetisation would also increase. Figure 4.1 provides a good indication that the properties of magnetic biochar such as the BET surface area and the saturation magnetisation could be controlled since these parameters would play a crucial role in the adsorption and recovery efficiency of the adsorbents, respectively.
Table 4.1. Physical and chemical properties of the adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% O&lt;sup&gt;a&lt;/sup&gt;</th>
<th>%Fe</th>
<th>%Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Saturation magnetisation, (A.m&lt;sup&gt;2&lt;/sup&gt;/kg)</th>
<th>BET surface area, m&lt;sup&gt;2&lt;/sup&gt;/g</th>
<th>BJH surface area of pores&lt;sup&gt;c&lt;/sup&gt;, m&lt;sup&gt;2&lt;/sup&gt;/g</th>
<th>BJH pore volume&lt;sup&gt;c&lt;/sup&gt;, cm&lt;sup&gt;3&lt;/sup&gt;/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-MPSB</td>
<td>86.82</td>
<td>1.57</td>
<td>&lt;0.3</td>
<td>11.31</td>
<td>0</td>
<td>0</td>
<td>0.3</td>
<td>297.77</td>
<td>88.34</td>
<td>0.08</td>
</tr>
<tr>
<td>25-MPSB</td>
<td>64.51</td>
<td>1.11</td>
<td>&lt;0.3</td>
<td>-</td>
<td>19.63</td>
<td>27.12</td>
<td>16.2</td>
<td>252.14</td>
<td>89.62</td>
<td>0.11</td>
</tr>
<tr>
<td>50-MPSB</td>
<td>55.77</td>
<td>0.82</td>
<td>&lt;0.3</td>
<td>-</td>
<td>31.97</td>
<td>44.16</td>
<td>42.1</td>
<td>157.94</td>
<td>55.19</td>
<td>0.12</td>
</tr>
<tr>
<td>75-MPSB</td>
<td>23.53</td>
<td>0.37</td>
<td>&lt;0.3</td>
<td>-</td>
<td>52.40</td>
<td>72.38</td>
<td>59.4</td>
<td>97.41</td>
<td>47.75</td>
<td>0.15</td>
</tr>
<tr>
<td>100-MPSB</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>-</td>
<td>70.66</td>
<td>97.6</td>
<td>89.9</td>
<td>19.43</td>
<td>21.81</td>
<td>0.21</td>
</tr>
</tbody>
</table>

<sup>a</sup>%O for magnetic adsorbents could not be obtained by mass difference  
<sup>b</sup>Assumption: All total iron have completely formed into Fe<sub>3</sub>O<sub>4</sub>.  
<sup>c</sup>between 1.7 and 300.0 nm diameter
4.3.2 Sorption isotherm modelling

The distributions of SMX between the liquid phase and the solid phase when the SMX uptake had reached equilibrium were fitted using Langmuir, Freundlich, Redlich-Peterson, Temkin and Dubinin-Raduskevich isotherm models. The calculated isotherm parameters using non-linear chi-square test are summarised in Table 4.2. Among the isotherm models, Redlich-Peterson gave the best fit for the sorption of SMX onto 0-MPSB,
25-MPSB, 50-MPSB and 75-MPSB based on the calculated $\chi^2$. An examination of the sorption isotherms of all the adsorbents fitted with Redlich-Peterson isotherm model revealed that SMX was not sorbed onto 100-MPSB or Fe$_3$O$_4$ (Figure 4.2). The non-sorption of SMX onto 100-MPSB implies that the sorption for magnetic adsorbents could only be attributed to the PSB component of the adsorbent. Additionally, all isotherms for the sorption of SMX for 0-MPSB, 25-MPSB, 50-MPSB and 75-MPSB are concave downwards indicating that the sorbate initially occupies the surface then eventually saturates the surface.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$K_L$</th>
<th>$q_m$</th>
<th>$\chi^2$</th>
<th>$K_F$</th>
<th>$N$</th>
<th>$\chi^2$</th>
<th>$K_{RP}$</th>
<th>$\alpha_{RP}$</th>
<th>$\beta_{RP}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-MPSB</td>
<td>10.28</td>
<td>18.95</td>
<td>9.10</td>
<td>10.70</td>
<td>0.21</td>
<td>6.76</td>
<td>1117.69</td>
<td>84.60</td>
<td>0.86</td>
<td>1.91</td>
</tr>
<tr>
<td>25-MPSB</td>
<td>87.91</td>
<td>12.56</td>
<td>5.95</td>
<td>9.16</td>
<td>0.17</td>
<td>7.54</td>
<td>2074.43</td>
<td>182.03</td>
<td>0.91</td>
<td>1.28</td>
</tr>
<tr>
<td>50-MPSB</td>
<td>51.54</td>
<td>9.90</td>
<td>4.40</td>
<td>7.28</td>
<td>0.15</td>
<td>7.85</td>
<td>924.31</td>
<td>103.10</td>
<td>0.93</td>
<td>3.20</td>
</tr>
<tr>
<td>75-MPSB</td>
<td>51.77</td>
<td>5.19</td>
<td>2.73</td>
<td>4.17</td>
<td>0.13</td>
<td>1.61</td>
<td>1602.82</td>
<td>356.00</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>100-MPSB</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.2. Isotherm parameters of the sorption of SMX onto different adsorbents
Redlich-Peterson model is a hybrid of Langmuir and Freundlich models that describe the sorption behaviour on homogenous and heterogeneous surfaces. For $\beta_{RP} = 1$, Redlich-Peterson equation is reduced to Langmuir isotherm model (Foo and Hameed, 2010). However, all adsorbents have $\beta_{RP} = 0.86-0.93$, which indicates that the SMX were adsorbed on heterogeneous surfaces. In addition, $K_F$ and $N$ in Freundlich model decreased at higher amount of $\text{Fe}_3\text{O}_4$ in the adsorbent. Similarly, the calculated $q_m$ in Langmuir isotherm and $q_s$ in Dubinin-Raduskevich isotherm linearly decreased as the amount of $\text{Fe}_3\text{O}_4$ increased, a clear indication that the addition of $\text{Fe}_3\text{O}_4$ on PSB had strong influence on the maximum monolayer sorption capacity and theoretical isotherm saturation capacity of the adsorbents.
for SMX, respectively (see Figure 4.3). This could also be attributed to the reduction of BET surface area as the amount of Fe$_3$O$_4$ increased as discussed in section 4.3.1. Hence, the addition of Fe$_3$O$_4$ or magnetisation of biochar resulted in the reduction of the BET surface area leading to the reduction of $q_m$ and $q_s$. Although, there have been a few studies where the reduction of the BET surface area and the subsequent sorption capacity have been found, the influence of the amount of Fe$_3$O$_4$ has not been established. Additionally, in several earlier studies, most magnetic adsorbents used were composed of different phases of iron oxide, Fe$_x$O$_y$ and Fe$_x$(OH)$_y$ (Ma et al., 2013; Mohan et al., 2011a; Oliveira et al., 2002). Therefore, the relationship between the Fe$_3$O$_4$ and sorption parameters ($q_m$ and $q_s$) may not hold true in the overall sorption capacity of the sorbent.

Figure 4.3. Effect of Fe$_3$O$_4$ on the $q_m$ (○) and $q_s$ (□) of magnetic adsorbent for sorbing SMX.

\[ y = -0.1811x + 18.371 \quad R^2 = 0.9877 \]

\[ y = -0.1719x + 17.806 \quad R^2 = 0.9924 \]
4.3.3 Redlich-Peterson approximate site energy distribution

Site energy distribution analysis has been found to be useful in explaining the sorption mechanisms of different sorbate-sorbent systems (Carter et al., 1995; Shen et al., 2015; Wang et al., 2005; Yuan and Xing, 1999). As mentioned in previous section, Redlich-Peterson isotherm model gave the best fit for the sorption of SMX onto the adsorbents. To understand the influence of Fe₃O₄ on the sorption behaviour of biochar, Redlich-Peterson site energy distribution analysis was used. The approximate site energy distribution function for Redlich-Peterson model was derived using eq. (4.4), (4.8) – (4.10) as follows:

Substituting eq. (4.10) to eq. (4.4),

\[ q_e = \frac{K_{RP}C_se^{-E^*/RT}}{1+\alpha_{RP}(C_se^{-E^*/RT})^{\beta_{RP}}} \]  \hspace{1cm} (eq. 4.11)

Substituting eq. (11) to eq. (9),

\[ F(E) = -\frac{d}{dE^*} \frac{K_{RP}C_se^{-E^*/RT}}{1+\alpha_{RP}(C_se^{-E^*/RT})^{\beta_{RP}}} \]  \hspace{1cm} (eq. 4.12)

Factoring out \( K_{RP}C_s \) and expanding the denominator,

\[ F(E) = -K_{RP}C_s \frac{d}{dE^*} \frac{e^{-E^*/RT}}{1+\alpha_{RP}C_s^{\beta_{RP}}(e^{-\beta_{RP}E^*/RT})} \]  \hspace{1cm} (eq. 4.13)

Getting the partial derivative with respect to \( E^* \).
$F(E) = -K_{RP}C_s \left[ \frac{1+\alpha_{RP}C_s^\beta_{RP} \left( e^{-\beta_{RP}E^*/RT} \right) \left( \frac{-E^*}{RT} \right) \left( 1+\alpha_{RP}C_s^\beta_{RP} \left( e^{-\beta_{RP}E^*/RT} \right) \right) \left( \frac{-\beta_{RP}}{RT} \right) \left[ 1+\alpha_{RP}C_s^\beta_{RP} \left( e^{-\beta_{RP}E^*/RT} \right) \right]^2 \right] \right] \quad \text{(eq. 4.14)}$

Factoring out $(-1/RT)(e^{-E^*/RT})$,}

$$F(E) = \frac{K_{RP}C_s}{RT} \left( e^{-E^*/RT} \right) \left[ \frac{\beta_{RP} \left( I_{RP}C_s^\beta_{RP} \left( e^{-\beta_{RP}E^*/RT} \right) \right) \left[ 1+\alpha_{RP}C_s^\beta_{RP} \left( e^{-\beta_{RP}E^*/RT} \right) \right]^2 \right] \right] \quad \text{(eq. 4.15)}$$

Rearranging,

$$F(E) = \frac{K_{RP}C_s}{RT} \left( e^{-E^*/RT} \right) \left[ \frac{1+\beta_{RP} \left( I_{RP}C_s^\beta_{RP} \left( e^{-\beta_{RP}E^*/RT} \right) \right) \left[ 1+\alpha_{RP}C_s^\beta_{RP} \left( e^{-\beta_{RP}E^*/RT} \right) \right]^2 \right] \quad \text{(eq. 4.16)}$$

Eq. (4.16) is the approximate site energy distribution function based on Redlich-Peterson model and was used for the sorption of SMX onto the magnetic biochar with different ratio of Fe$_3$O$_4$ and PSB as shown in Figure 4.4. The 100-MPSB has no frequency distribution at all sorption site energy values studied because SMX did not exhibit any sorption affinity for 100-MPSB within the experimental sorption site energy values which ranged from ~3,000 to ~32,000 J/mol. Additionally, the area under the curve of $F(E^*)$ versus sorption site energy reveals the number of the available sorption sites in a specific energy range as represented by eq. (4.8) (Cerofolini, 1974), implying there is no available sorption sites for SMX onto 100-MPSB. Since SMX had no sorption affinity for 100-MPSB, for the rest of the discussion, 100-MPSB would not be included. On the other hand, the frequency distributions of sorption site energies of other adsorbents are all non-symmetrical unimodal.
shapes. Initially, at low sorption site energies (<~8000 J/mol), the frequency distributions are exponentially increasing followed by exponential decrease after reaching the highest frequency. Then, at high site energy values (> ~18,000 J/mol), frequency distributions started to slowly decrease and converge to ~0 mol-mg/J-g. Although their distribution functions are of the same shapes, the areas under the curve of different adsorbents are significantly different. Additionally, the difference among adsorbents are more significant at low energy sites than as they approach the high energy sites. At higher energy sites, the sorption site frequency is similar regardless of the amount of Fe₃O₄ in the adsorbent and physico-chemical properties affected due to the addition of Fe₃O₄ in PSB. Hence, Fe₃O₄ has no significant effect at high energy sites but it has significant effect at low site energy values.

Figure 4.4. Redlich-Peterson model based site energy distributions of magnetic pine sawdust biochar. Broken lines represent the predicted data outside the experimental data range.
Figure 4.4 clearly shows that as the amount of Fe$_3$O$_4$ is increased, the area under the distribution function decreased which indicates that the available sorption sites are also reduced. This has been consistent with the effect of increasing Fe$_3$O$_4$ in $q_m$ and $q_s$. Additionally, the sorption energy with the highest frequency in the adsorbents varies within the range of ~7,000 to ~12,000 J/mol among the adsorbents. This could indicate the change in the surface heterogeneity of the biochar due to the addition of Fe$_3$O$_4$. Furthermore, among the adsorbents, 0-MPSB has the highest frequency of low sorption site energies. On the contrary, 25-MPSB has the highest frequency of intermediate sorption site energy values. It is possible that Fe$_3$O$_4$ could have reduced the frequency of the low sorption site energies but increase the frequency of the higher sorption site energies.

The prepared adsorbents also have different calculated Redlich-Peterson parameters. To determine the influence of these parameters on the site energy distribution, changes on the parameters using one of the adsorbents (75-MPSB) were depicted in Figure 4.5 with the effect of $K_{RP}$ on the site energy distribution curves in Figure 4.5a. The unimodal shape and width of the curves remained the same but the area under the curve increased as $K_{RP}$ increased. This suggests that at higher $K_{RP}$, the adsorbent has higher number of available sorption sites. On the contrary, at higher $\alpha_{RP}$, the area under the curve of the distribution was reduced but its shape was not affected (Figure 4.5b). Additionally, the sorption site energy with the highest frequency shifted to the left or lower sorption site energy when $\alpha_{RP}$ increased. Both $K_{RP}$ and $\alpha_{RP}$ are related to the number of available sorption sites due to the change in the area under the distribution function. Figure 4.c shows the effect of $\beta_{RP}$, on the frequency distribution. At $\beta_{RP}$=1.0, Redlich-Peterson is reduced to Langmuir isotherm model. Langmuir isotherm distribution function has symmetrical unimodal shape (Carter et al., 1995). When $\beta_{RP}$ is reduced, the distribution became unsymmetrical where low energy
sites have higher energy frequency than high energy sites (see Figure 4.5c). Further decrease in $\beta_{RP}$ resulted in exponential decrease of frequency distribution from the low energy sites to high energy sites. $\beta_{RP}$ reflects the surface heterogeneity of the adsorbent where at lower value, the adsorbent surface is more heterogeneous and the distribution of sorption energies become unsymmetrical.
Figure 4.5. Effect of the variation of Redlich-Peterson parameters in the site energy distribution function of 75-MPSB: (a) Changes in $K_{RP}$, (b) Changes in $\alpha_{RP}$, (c) Changes in $\beta_{RP}$. Broken lines are predicted values.
4.3.4 Influence of Fe$_3$O$_4$ on surface heterogeneity of biochar (PSB)

A visual examination of SEM images presented in Figure 4.a-d reveals the surface morphologies of all the adsorbents with the surface of each adsorbent changed as the amount of Fe$_3$O$_4$ increased. Figure 4.6a illustrates the surface morphology of 0-MPSB or PSB which shows its surfaces and pores, which are potential adsorption sites for SMX. On the contrary, Figure 4.6b-d (25-MPSB, 50-MPSB and 75-MPSB) illustrate that the pores on the PSB are blocked by the Fe$_3$O$_4$. The non-uniform formation of Fe$_3$O$_4$ on the surface of PSB and blockage of pores resulted in the reduction of the BET surface area of the adsorbents since BET surface area decreased as the amount of Fe$_3$O$_4$ in the adsorbent increased. This resulted in lower sorption capacity of magnetic PSBs (25-MPSB, 50-MPSB and 75-MPSB) compared to non-magnetic PSB. Additionally, Fe$_3$O$_4$ has no affinity for SMX thereby reducing the sorption capacity of the PSB upon its addition. Although magnetisation decreased the sorption capacity of PSB, magnetic biochar could easily be recovered after sorption process due to its magnetic properties. The reduction of the SMX sorption capacity of the adsorbent upon addition of Fe$_3$O$_4$ on biochar may not be applicable to other sorbate especially when the sorbate has sorption affinity for Fe$_3$O$_4$. 
To gain more quantitative information, further surface analysis of the adsorbents was performed using XPS. There are 3 major peaks, which are the C1s, O1s and Fe2p as shown in Figure 4.7. The surface elemental compositions of the adsorbents are not consistent with the bulk elemental composition listed in Table 4.1 which is expected for these types of analysis. Generally, the O and Fe content of magnetic PSBs are higher compared to PSB alone. The surface of 0-MPSB is composed only of C and O while the magnetic PSBs (25-
MPSB, 50-MPSB and 75-MPSB) have C, O and Fe. In the Fe2p region, no peak appeared in the 0-MPSB or PSB since it does not have any Fe content which was also confirmed by its elemental composition analysis (see Table 4.1). On the other hand, two peaks were observed at 710.26 – 710.63 eV assigned to Fe2p^{3/2} and 723.56 – 723.81 eV assigned to Fe2p^{1/2} which confirmed the presence of iron oxide in 25-MPSB, 50-MPSB and 75-MPSB (Yamashita and Hayes, 2008). The C1s and O1s were deconvoluted as shown in Figure 4.8 and the atomic concentration of each peak is listed in Table 4.3. The deconvolution of C1s peak of 0-MPSB has 3 peaks with binding energy 282.23 eV, 284.28 eV and 285.63 eV. These binding energies were assigned to carbide, graphite and C-O, respectively (Puziy et al., 2008; Terzyk, 2001). All four adsorbents; 0-MPSB, 25-MPSB, 50-MPSB and 75-MPSB have PSB component in them and only differ with the amount of Fe3O4. In 0-MPSB, carbide is assigned to 282.83 eV, however, this peak shifted to lower binding energy (282.25 - 282.49 eV) in magnetic PSBs (25-MPSB, 50-MPSB and 75-MPSB). Recently, Hu et al. (2015) also observed the consistency of having similar C1s peaks between the pristine biochar and iron-impregnated biochar. However, they observed more C1s peaks which were C-H, graphite C, C-O, C=O and C=O/O-C=O since the surface functional groups of the biochar they used were different from the biochar we used in this study (Hu et al., 2015).
Figure 4.7. XPS survey spectra of the adsorbents

Table 4.3. Deconvolution of C1s and O1s of the adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>0-MPSB</th>
<th>25-MPSB</th>
<th>50-MPSB</th>
<th>75-MPSB</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>Carbide</td>
<td>282.83</td>
<td>5.7</td>
<td>282.49</td>
</tr>
<tr>
<td></td>
<td>Graphitic</td>
<td>284.28</td>
<td>86.29</td>
<td>284.31</td>
</tr>
<tr>
<td></td>
<td>C-O</td>
<td>285.63</td>
<td>8.01</td>
<td>285.77</td>
</tr>
<tr>
<td>O 1s</td>
<td>Fe-O</td>
<td>-</td>
<td>-</td>
<td>527.99</td>
</tr>
<tr>
<td></td>
<td>C-O</td>
<td>530.36</td>
<td>49.12</td>
<td>529.93</td>
</tr>
<tr>
<td></td>
<td>H-O</td>
<td>532.51</td>
<td>50.88</td>
<td>531.75</td>
</tr>
</tbody>
</table>
Figure 4.8. Deconvolution of C1s and O1s of the adsorbents of magnetic adsorbents.
The deconvolution of O1s peak of 0-MPSB revealed two peaks at 530.36 eV and 532.51 eV, which were attributed to C-O and O-H, respectively. The C-O peak could be associated with the C-O peak in C1s. The O-H could be due to the presence of adsorbed water or moisture in the sample (Rosenthal et al., 2010). Similar peaks could be observed in 25-MPSB, 50-MPSB and 75-MPSB. However, an additional peak at lower binding energy (527.67 eV to 527.99 eV) appeared which could be assigned to the lattice oxygen ($O_2^-$) in the metal oxide (Fe-O) due to presence of Fe$_3$O$_4$ on the surface of these adsorbents (Cheng et al., 2005). This is the only additional peak after the addition of Fe$_3$O$_4$ in PSB. The presence of Fe$_3$O$_4$ on 25-MPSB, 50-MPSB and 75-MPSB was confirmed by the XRD results. XPS results of the adsorbents have shown the influence of Fe$_3$O$_4$ on the change of the surface elemental composition of PSB. The changes in the surface elemental composition of PSB due to the addition of Fe$_3$O$_4$ could have also influenced its sorption ability. This could only be one of the factors since BET surface area could have greater influence on decreasing sorption capacity of adsorbents with high amount of Fe$_3$O$_4$.

### 4.3.5 Effects of Fe$_3$O$_4$ on the sorption behaviour of SMX

In this study, the addition of Fe$_3$O$_4$ on PSB has generally resulted in a decrease in the frequency distribution of sorption site energies for SMX. Hence, the sorption capacity of the adsorbent decreased as the Fe$_3$O$_4$ percentage in the adsorbent increased. Given SMX has no sorption affinity for Fe$_3$O$_4$, the sorption of SMX in the adsorbents could only be attributed to the PSB component of the adsorbent. Elemental analysis of 0-MPSB or PSB has revealed that the adsorbent is highly carbonised (% C = 86.82) and has H/C molar ratio of 0.0.22. Due to very low H/C of the PSB, the adsorbent has low polarity and high...
hydrophobicity (Zhang et al., 2011b), which further lends support to the fact that 0-MPSB or PSB is hydrophobic. Similarly, biochar produced at 700°C to adsorb sulfamethazine had less number of O-containing functional groups and highly aromaticised resulting in its lower surface interaction with water molecules (Rajapaksha et al., 2014; Rajapaksha et al., 2015; Vithanage et al., 2014). It was proposed that the sorption of SMX onto magnetic biochar is due to the hydrophobic interaction between the hydrophobic biochar component of the magnetic adsorbent and the hydrophobic methyl functional group of SMX (Reguyal et al., 2017). The addition of Fe₃O₄ could have reduced the hydrophobicity of the adsorbent due to the Fe₃O₄ on the surface of the biochar reducing the accessibility of the hydrophobic surface; hence, the available sorption sites for SMX have been reduced. The increase in bulk and surface oxygen content due to the presence of O-containing functionalities has been found to significantly decrease the average energy of effective sorption site and site heterogeneity of 10 carbonaceous adsorbents for naphthalene, lindane and atrazine (Shen et al., 2015). In their study, Shen et al. (2015) found that due to these O-containing functional groups, the hydrophilicity of the adsorbents was enhanced resulting in the reduction of the interaction between the sorbate and the hydrophobic portion of the adsorbent (Shen et al., 2015). However, in the present study, the increase in the bulk and surface oxygen due to the formation of Fe₃O₄, a metal oxide, on the surface of PSB has not facilitated any increase in the sorption capacity of Fe₃O₄ containing adsorbents (25-MPSB, 50-MPSB and 75-MPSB), resulting in decrease in the sorption capacity.

4.4 Conclusions

In this study we have demonstrated that the magnetisation of PSB using Fe₃O₄
clearly impacts the physico-chemical properties and subsequently the sorption capacity of the PSB for SMX taken as model compound. We further conclude that BET surface area, $q_m$ and $q_s$, have been found to linearly decrease with the increase in Fe$_3$O$_4$ per mass of the adsorbent. The BJH pore volume and saturation magnetisation of the adsorbents increased with increasing percentage of Fe$_3$O$_4$ in the adsorbent. Another observation is that the addition of Fe$_3$O$_4$ in PSB reduced the low sorption site energies but not the high sorption site energies. The application of site energy distribution analysis showed that the frequency of the site energies was found to generally decrease with increasing Fe$_3$O$_4$ in the adsorbent resulting in smaller area under the curve of the distribution function; hence, sorption site energies for SMX were reduced by the addition of Fe$_3$O$_4$. We finally conclude that the inaccessibility of the hydrophobic surface of PSB for SMX due to the Fe$_3$O$_4$ presence on the PSB surface lowered the hydrophobic interaction between SMX and PSB. The findings reported in this study are critical for better understanding of the sorption mechanisms of SMX and other organic pollutants to magnetised adsorbents.
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CHAPTER 5: Adsorption of sulfamethoxazole by magnetic biochar: Effects of pH, ionic strength, natural organic matter and 17α-ethinylestradiol

Accepted in Science of the Total Environment
Recent studies have shown the widespread occurrence of pharmaceuticals in the aquatic environment leading to increasing global concern on their potential adverse effects in the environment and public health. In this study, we evaluated the use of magnetic biochar derived from pine sawdust, one of New Zealand's major wood wastes, to remove an emerging contaminant, sulfamethoxazole (SMX), at different pH, ionic strength, natural organic matter (NOM) and a competing compound, 17α-ethinylestradiol (EE2). In single-solute system, the sorption of SMX onto magnetic biochar was found to be highly pH-dependent and slightly increased with increase in ionic strength. However, the effects of pH, ionic strength and NOM were relatively insignificant compared to the sorption inhibition caused by EE2 in binary-solute system. Both SMX and EE2 sorption onto the highly carbonised biochar in magnetic biochar were postulated to be due to the π-π electron donor acceptor and hydrophobic interaction. EE2 is more hydrophobic than SMX. Hence, strong competition between these compounds was identified where EE2 markedly inhibited the sorption of SMX onto magnetic biochar in all artificial environmental conditions studied.
5.1. Introduction

Pharmaceutical substances such as antibiotics have been detected in the aquatic environment such as surface water and ground water (Kasprzyk-Hordern et al., 2008; Komori et al., 2013; Lapworth et al., 2012). These compounds and their metabolites can find their ways from households, hospitals, industries, animals and landfills into the receiving water bodies (Kümmerer, 2009; Lapworth et al., 2012). Most of these compounds enter in the environment in trace levels, but some of them are in substantial amounts and found to have potential toxic effects on human and wildlife. Although their concentrations are usually very low, concerns have arisen because biologically active compounds have been found to have effects on organisms such as fish and crustaceans. The accumulation of antibiotics in the environment may lead to the development of antibacterial resistance that could cause difficulties in treating diseases and imbalance of microbial ecosystems (Aris et al., 2014; Hernando et al., 2006; Kümmerer, 2009).

Various treatment methods are available to remove the contaminants that are monitored and regulated by the government or regulating bodies. Among these treatment methods such as oxidation process, membrane filtration, reverse osmosis, adsorption has been one of the simplest and most effective methods. Most commercial adsorption treatment technologies use activated carbon, which is expensive (Worch, 2012). Recently, the use of biochar in water remediation has been gaining interest due to its lower production cost (US $246 per tonne) (McCarl et al., 2009) compared to activated carbon (US$ 1500-8900 per tonne) (Klasson et al., 2009). Biochar is a solid carbonaceous material produced via pyrolysis of biomass such as agricultural crop residues, animal manure and sewage sludge (Agrafioti et al., 2013; Cao and Harris, 2010; Mullen et al., 2010). Several studies have demonstrated the potential of biochar in water remediation and its ability to remove various
contaminants such as heavy metals (Cao et al., 2009; Liu and Zhang, 2009), oxyanions (Yao et al., 2011) and organic compounds (Chen and Chen, 2009; Sun et al., 2011). However, biochar is applied in powder form resulting in difficulty of its separation after the adsorption process. Adsorbent separation after treatment has been one of the drawbacks of using powder form adsorbent (Wu et al., 2005). To improve this, magnetisation of biochar using iron oxide has been done in a few studies via co-precipitation of biochar on iron precursor (Mohan et al., 2014b) and saturation of biomass in iron precursor followed by pyrolysis at high temperature (Chen et al., 2011; Zhang et al., 2013). Magnetisation of biochar using iron oxide has been found to be effective in separating the magnetic adsorbent after use and could potentially reduce the recovery cost of adsorbent. In addition, few magnetic carbonaceous adsorbents have been found to exhibit higher sorption compared to the non-magnetic carbonaceous adsorbent (Chen et al., 2011). This implies that magnetisation of carbonaceous adsorbents can also improve the sorption properties of the carbonaceous adsorbents particularly if the adsorbate has strong affinity for both the compound giving magnetic property and the carbonaceous component. Furthermore, factors such as adsorbent and adsorbate properties could also influence the sorption behaviour.

In this study, magnetic biochar was used to adsorb sulfamethoxazole (SMX), one of the most frequently detected pharmaceutical compounds in surface water and groundwater. SMX is an antibiotic that belongs to the sulfonamide group used in the treatment of human and animal diseases and its widespread occurrence in the environment could potentially lead to antibiotic resistance. Environmental conditions such as pH, ionic strength, presence of natural organic matter (NOM) and competing compound have been found to influence the sorption behaviour of SMX onto carbonaceous adsorbent (Chen et al., 2014; Ji et al., 2009; Wang et al., 2013). For example, changes in solution pH affected the SMX sorption on
sorbents such as graphene through influencing $\pi-\pi$ electron donor acceptor (EDA) interactions (Chen et al. 2014). Therefore, the above environmental conditions could also influence the sorption behaviour of SMX onto magnetic biochar, which has a carbonaceous component, biochar. However, effects of the above environmental parameters, presence of co-contaminant and NOM in water have not been explored in the literature. Hence, the overarching aim of this study was to determine the effects of pH, ionic strength, presence of NOM and competing compound. 17α-ethinylestradiol was used as a competing compound, which is an endocrine disrupting compound and has also been frequently detected in environmental matrices. Furthermore, the competitive sorption between SMX and EE2 onto magnetic biochar was evaluated in different environmental conditions.

5.2. Materials and methods

5.2.1. Materials

The magnetic biochar used in this study was synthesised and characterised as reported in an earlier work (Reguyal et al., 2017). Briefly, the pine sawdust biochar was stirred in 200 ml of 0.30 M FeCl$_2$ at 500 rpm for 24 h. The mixture was then degassed using N$_2$ and heated to 90°C water bath. These environmental conditions were maintained throughout the synthesis process. The solution of 3.33 M KOH and 0.27 M KNO$_3$ was added dropwise stirred continuously for an additional hour of mixing was done. Then, the mixture was cooled overnight in an airtight glass reactor. Finally, the magnetic biochar was centrifuged, washed and dried in vacuum oven at 40°C for 48 h. Table 5.1 shows the physico-chemical properties of the magnetic biochar. SMX and EE2 were purchased from Sigma-Aldrich. Methanol and acetonitrile were high-performance liquid chromatography (HPLC)
grade purchased from Merck. Formic acid (CH$_2$O$_2$), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were analytical grade and were used as received. Suwanee River NOM was purchased from International Humic Substances Society (Minnesota, USA). X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos Axis Ultra DLD XPS (Kratos Analytical, Manchester, UK) using monochromatic Al Kα X-rays (1486.69 eV) with the X-ray source operating at 150 W.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Biochar</th>
<th>Magnetic biochar</th>
</tr>
</thead>
<tbody>
<tr>
<td>%C</td>
<td>86.8±0.2</td>
<td>55.8±0.3</td>
</tr>
<tr>
<td>%H</td>
<td>1.57±0.03</td>
<td>0.82±0.08</td>
</tr>
<tr>
<td>%N</td>
<td>&lt;0.30</td>
<td>&lt;0.30</td>
</tr>
<tr>
<td>%O*</td>
<td>11.3±0.2</td>
<td>14.2±2.2</td>
</tr>
<tr>
<td>%Fe**</td>
<td>n.d.</td>
<td>28.8±1.7</td>
</tr>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>297.8</td>
<td>125.8</td>
</tr>
<tr>
<td>BJH cumulative pore volume (cm$^3$/g)**</td>
<td>0.08</td>
<td>0.14</td>
</tr>
<tr>
<td>BJH average pore diameter (nm)</td>
<td>3.67</td>
<td>9.6</td>
</tr>
<tr>
<td>Saturation magnetisation (A.m$^2$/kg)</td>
<td>0.3</td>
<td>48.7</td>
</tr>
</tbody>
</table>

*By difference
**Theoretical percent iron in Fe$_3$O$_4$ is 72.36%.
***between 1.70 to 300.0 nm diameter

5.2.2. Characterisation

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos Axis Ultra DLD XPS (Kratos Analytical, Manchester, UK) using monochromatic Al Kα X-rays (1486.69 eV) with the X-ray source operating at 150 W.
5.2.3. Batch sorption

All SMX and EE2 stock solutions were prepared in methanol. Batch adsorption experiments were carried out in glass centrifuge tubes with Teflon-lined screw caps. A solution of 30 ml adsorbate was added to 6 mg magnetic biochar. The concentrations of methanol in all prepared solutions were less than 0.1% to avoid the co-solvent effect. The glass centrifuge tubes were then sealed and placed in an end-over-end shaker in a dark room with a controlled temperature of 25°C for 24 h. Our preliminary studies showed that apparent equilibrium for SMX was achieved in less than 6 h. To investigate the effect of pH on sorption of SMX (~4m/L) onto the magnetic biochar, the solution pH was adjusted using 0.01 N NaOH and 0.01 N HCl by drop wise. The pH range used in the study was 4.5 to 8.5 because the magnetic biochar was found to be only stable within this pH range as evaluated in our previous study (Reguyal et al., 2017).

In the competitive sorption experiment between SMX and EE2, batch isotherms were constructed using multiple SMX concentrations ranging from 0.5 to 10 mg/L in the presence of EE2 (0.5, 1.8 and 3.9 mg/L). Similarly, the multiple concentrations of EE2 ranging from 0.1 to 4 mg/L in the presence of SMX (0.5, 3.5, 9.1 mg/L) were used in the study. The kinetics study was performed at pH=6.5, ionic strength of 0.01 M NaCl at SMX and EE2 concentration of ~4 mg/L. In addition, the concentrations of NaCl (0–1 mol/L) and NOM (0 – 20 mg-C/L) were varied to determine the influence of ionic strength and NOM on the sorption of SMX (~4mg/L) and EE2 (~4mg/L) onto magnetic biochar at pH=6.5. Actual initial concentrations of the solution were measured, reported and used in all calculations. The solution of SMX together with NOM was covered and mixed for 24 h at 500 rpm prior to the addition of magnetic biochar to equilibrate the solution. The highest concentrations used in the isotherm studies were below the reported solubility of the adsorbates in water.
All batch sorption experiments including blanks were done in duplicates.

5.2.4. Analytical methods

Prior to the analysis of the samples by high-performance liquid chromatography (HPLC), samples were filtered using 0.2 µm regenerated cellulose membranes. The size of magnetic biochar prepared was greater than the membrane size and therefore passing of the solid material could not have been possible. Filtration was done to avoid the clogging of the guard columns used in the HPLC analysis. SMX and EE2 concentrations were measured using HPLC (Shimadzu, LC 20AD) coupled with ultraviolet and fluorescent detectors using Phenomenex Luna column (5µm, C18, 150 x 4.6 mm). The samples were analysed in a broad range of wavelength (300 – 800 nm) using diode array detector (Shimadzu, SPD-M20A) where the wavelength that provided the highest signal for SMX was 270 nm. EE2 concentration was analysed using a fluorescent detector with an excitation wavelength of 200 nm and an emission wavelength of 310 nm (Shimadzu, RF 20A XS). The mobile phase was a mixture of 0.1% formic acid and acetonitrile (Merck) with a volume ratio of 1:1 and an isocratic flowrate of 1 ml/min. Total run times for each analysis was 8 min, with a retention time of 2.2 min and 3.9 min for SMX and EE2, respectively. The amount of adsorbed adsorbate, \( q \), was calculated as follows:

\[
q = (C_o - C_e) \times \frac{V}{m} \quad (5.1)
\]

where \( C_o \) and \( C_e \) are the initial and equilibrium concentrations of adsorbate (mg/L), \( m \) is the mass of the adsorbent (g) and \( V \) is the volume of solution (L).

Stock solution of NOM was prepared in deionised water and NOM concentrations
were determined using total organic carbon (TOC-5000A, Shimadzu) analyser.

5.2.5. Sorption modelling and data analysis

There were 3 isotherm models used to fit the experimental data of SMX sorption onto magnetic biochar namely Langmuir, Freundlich and Redlich-Peterson. The equations describing Langmuir, Freundlich and Redlich-Peterson (Foo and Hameed, 2010) models are given in eq. (5.2)-(5.4).

\[ q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \]  
\[ q_e = K_F C_e^N \]  
\[ q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^\beta_{RP}} \]

In above equations, \( q_e \) is the amount adsorbed per mass of adsorbent (mg/g); \( q_m \) is the maximum monolayer adsorption capacity (mg/g); \( K_L \) is the Langmuir isotherm constant (L/mg); \( C_e \) is the equilibrium concentration (mg/L); \( N \) is a measure of adsorption intensity; \( K_F \) is the Freundlich isotherm constant (mg/g (L/mg)^N); \( K_{RP} \) is the Redlich–Peterson model isotherm constant (L/g), \( \alpha_{RP} \) is the Redlich–Peterson model constant (L/mg); and \( \beta_{RP} \) is the Redlich–Peterson isotherm exponent. The measured data were fitted to the isotherm models by using non-linear chi-square (\( \chi^2 \)) test where (\( \chi^2 \)) was minimised using eq. (5.5) (Ho et al., 2005).

\[ \chi^2 = \sum_{i=1}^{n} \left( \frac{q_{e,exp} - q_{e,calc}}{q_{e,calc}} \right)^2 \]
where, \( q_{e,\text{calc}} \) is the calculated equilibrium capacity obtained from the isotherm model (mg/g), and \( q_{e,\text{exp}} \) is experimental equilibrium capacity (mg/g).

### 5.2.6. Sorption modelling and data analysis

The competitive strength between SMX and EE2 were determined using the following equation.

\[
A = \frac{(K_d - K_{d'})}{K_d} \times 100\% \tag{5.6}
\]

where \( A \) is the competitive strength (%), \( K_d \) and \( K_{d'} \) are the sorption coefficients for the primary solute in the single-solute and bi-solute systems (L/g), respectively (Wang et al., 2014b).

In addition, the theoretical maximum coverage of the magnetic biochar for SMX and EE2 was determined using the following equation (Haghseresht and Lu, 1998):

\[
Q_{\text{max}} = \frac{S_{\text{BET}} M \times 10^{23}}{N_A \sigma} \tag{5.7}
\]

where, \( Q_{\text{max}} \) (mg/g) is theoretical maximum surface coverage, \( S_{\text{BET}} \) is the BET surface area of the adsorbent (m\(^2\)/g); \( M \) is the molar mass of the adsorbate; \( N_A \) is the Avogadro’s number (6.02x10\(^{23}\)); \( \sigma \) is the surface area occupied by one molecule (Å/molecule) calculated using the following equation proposed McClellan and Harnsberger.

\[
\sigma(\text{Å/molecule}) = 1.091 \times 10^{16} \left( \frac{M}{\rho N_A} \right)^{2/3} \tag{5.8}
\]

where, \( \rho \) is the adsorbate density (g/cm\(^3\)) (McClellan and Harnsberger, 1967).
5.3. Results and discussion

5.3.1. Sorption of SMX in single-solute system

The sorption isotherms of SMX onto magnetic biochar were investigated in the single-solute system at 3 different pH conditions (~4.5, ~6.5 and ~8.5). Table 5.2 summarises the sorption parameters fitted to 3 isotherm models with Redlich-Peterson model describing the best fit for SMX with lowest $\chi^2$ values (0.01-0.28) with the pH range studied. Redlich-Peterson model describes combined sorption in homogeneous and heterogeneous surfaces. Based on the calculated $q_m$, SMX had the highest $q_m$ at pH~4.5 and lowest at pH~8.5. Generally, the sorption of SMX significantly decreased as the pH was increased. SMX is an ionisable compound where the distribution between organic and aqueous phases depends on its degree of ionisation which in turn is dependent on the solution pH and $pK_a$. SMX has a $pK_a$ of 1.25 and 5.29 (Wu et al., 2013). In SMX sorption, the electrostatic attraction could be one of the sorption mechanisms involved since its sorption was affected by the change in solution pH.

Table 5.2. Isotherm parameters of the sorption of SMX onto magnetic biochar at different pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>$L/mg$</th>
<th>$mg/g$</th>
<th>$K^2$</th>
<th>$L/mg$</th>
<th>$mg/g$</th>
<th>$N$</th>
<th>$K^2$</th>
<th>$L/mg$</th>
<th>$mg/g$</th>
<th>$B_{RP}$</th>
<th>$pK_a$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>22.6</td>
<td>19.1</td>
<td>1.82</td>
<td>13.7</td>
<td>0.26</td>
<td>0.57</td>
<td>9.28x10^2</td>
<td>6.04x10^4</td>
<td>0.82</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>23.2</td>
<td>12.9</td>
<td>2.65</td>
<td>10.1</td>
<td>0.20</td>
<td>0.03</td>
<td>1.71x10^4</td>
<td>1.67x10^3</td>
<td>0.81</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>5.64</td>
<td>9.42</td>
<td>2.01</td>
<td>6.35</td>
<td>0.23</td>
<td>0.28</td>
<td>1.25x10^5</td>
<td>1.97x10^4</td>
<td>0.77</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To evaluate if the electrostatic attraction is one of the sorption mechanisms between SMX and magnetic biochar, the influence of ionic strength on the sorption of SMX was
Chapter 5: Adsorption of sulfamethoxazole by magnetic biochar: Effects of pH, ionic strength, natural organic matter and 17α-ethinylestradiol

evaluated. The effect of ionic strength on the SMX sorption was studied at pH~6.5 where the charges of SMX ($pK_a < $ solution pH) and magnetic biochar ($pH_{pzc} = 9.46 > $ solution pH) are mostly oppositely charged. Theoretically, an increase in ionic strength results in a decrease in adsorption capacity of the adsorbent when the adsorbate has attractive electrostatic forces on the adsorbent. Conversely, an increase in ionic strength results in increased adsorption capacity of the adsorbent when the adsorbate has repulsive electrostatic forces on the adsorbent (Al-Degs et al., 2008). However, although the adsorbent and adsorbate were oppositely charged based on the solution pH and $pH_{pzc}$ of the magnetic biochar, the sorption of SMX onto magnetic biochar generally increased with the increasing ionic strength. The increase in the sorption capacity at higher ionic strength implies that electrostatic sorption mechanism could be repulsive or not involved. Additionally, SMX sorption on magnetic biochar was highest at pH where SMX was dominant in neutral species. On the other hand, the increase in ionic strength resulting in higher sorption of SMX onto magnetic biochar can also be due to the ‘salting-out’ effect. This phenomenon has been observed in several studies where high concentration of salt ions affect the activity coefficient of the solute in question by modifying the structure of water and/or by direct ion-dipole) interaction with the solute (Essington, 2003).

5.3.2. Effect of EE2 on SMX sorption

As mentioned in section 5.3.1, SMX sorption decreased when the pH of the solution increased. On the contrary, the sorption of the competitor, EE2, was not significantly affected by the solution pH based on our preliminary studies as shown in Figure 5.1. The effect of EE2 on the sorption of SMX onto magnetic biochar was evaluated at pH~6.5.
Figure 5.1. Effect of pH on the sorption SMX and EE2 onto magnetic biochar [T=25°C; µ=0.01 M NaCl].

Figure 5.2 shows that the sorption of SMX decreased in the presence of EE2. At low concentration of EE2 (~ 0.5 mg/L), SMX sorption was significantly reduced. The presence of EE2 decreased the SMX sorption affinity on magnetic biochar. EE2 inhibition in SMX sorption was stronger at higher EE2 concentration. However, a further increase of EE2 concentration from 1.8 mg/L to 3.9 mg/L did not make a significant difference on the sorption isotherm of SMX. The concentration of EE2 could not be further increased due to its low aqueous solubility of 4.8 mg/L (Fredj et al., 2015).
Figure 5.2. Effect of (a) EE2 on SMX (4 mg/L) sorption and (b) SMX on EE2 (4 mg/L) sorption [pH~6.5; T=25°C; µ=0.01 M NaCl].

On the other hand, EE2 isotherm trend was not significantly affected by the presence of SMX even at a concentration twice the highest concentration of EE2 used. This implies that the magnetic biochar has higher sorption affinity for EE2. It is interesting to note that SMX sorption is affected by EE2 even at low concentrations. SMX and EE2 probably share the similar adsorption sites. Both compounds have an affinity for biochar component only, however, our preliminary studies showed that iron oxide had negligible sorption affinity for SMX and EE2 as illustrated in Figure 5.3.
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A single-point $K_d$ was used to determine the competitive strength using eq. (5.6). At 4.1 mg/L SMX initial concentration in the presence of 0.5 mg/L and 4.1 mg/L EE2, the competitive strength is 93.2% and 71.3%, respectively. The higher competition strength of EE2 at a lower concentration of SMX indicates that the sorption potential of EE2 is higher at low SMX concentration. This finding is similar to the carbamazepine sorption competition with SMX on activated carbon and single-walled carbon nanotubes (Wang et al., 2014b).

Using eq. (5.7) and eq. (5.8), the calculated $Q_{\text{max}}$ for SMX and EE2 sorption on magnetic biochar are 111.2 mg/g and 103.4 mg/g, respectively. These calculated $Q_{\text{max}}$ for both adsorbates are higher than $q_m$, which means that the surface of the magnetic biochar

Figure 5.3. Sorption of SMX and EE2 on Fe$_3$O$_4$ [pH~6.5; T=25°C; $\mu$=0.01 M NaCl].
was not completely covered by SMX and EE2. BET surface area measured by N\textsubscript{2} sorption/desorption could not all be available to the adsorbate. The sorption affinity of SMX and EE2 on each component was determined and was found that both adsorbates had stronger sorption affinity for biochar compared to magnetic biochar because SMX and EE2 did not have sorption affinity for iron oxide. This means that SMX and EE2 had sorption interaction with the biochar component of the magnetic biochar only. However, the surface area measured accounted for the whole component of the magnetic biochar. Magnetic biochar in this study was only ~60\% biochar. Hence, although the surface area is 125.8 m\textsuperscript{2}/g, not all surfaces of magnetic biochar had sorption affinity and were not available for both adsorbates. Lastly, sorption conditions for both adsorbates might not be at its optimum.

To determine the SMX and EE2 uptake of magnetic biochar, the sorption kinetics both in single and binary-solute systems were compared as shown in Figure 5.4. The sorption of EE2 was not markedly affected by SMX while EE2 significantly reduced the uptake of magnetic biochar for SMX. Additionally, the rate of EE2 uptake of magnetic biochar was faster compared to SMX. Both EE2 and SMX in single-solute system reached the equilibrium within 6 h. However, in the binary-solute system, EE2 reached the equilibrium within 3 h, which is shorter than in single-solute system. Similarly, SMX reached the equilibrium in the binary-solute system in less than 1 h. In early contact with SMX and EE2 with the adsorbent, SMX could compete with EE2 in the sorption sites. However, EE2 inhibition of SMX sorption became stronger as both adsorbates became in contact with the magnetic biochar. The shorter period to reach the sorption equilibrium for both compounds was due to the greater amount of the adsorbate present that would compete for the sorption sites. It was also found that the sorption of the more hydrophobic compound on biochar would have steady and faster sorption by occupying the active pore sites to inhibit
the sorption of less hydrophobic or ionisable compound (Jung et al., 2013).

Figure 5.4. Sorption kinetics of SMX without EE2 (○) and with EE2 (□) onto magnetic biochar in single and binary solute systems [T=25°C; µ=0.01 M NaCl].

The effect of ionic strength on the sorption of SMX onto magnetic biochar in the presence of EE2 was also evaluated with varying ionic strength (0, 0.01, 0.05, 0.1, 0.5 and 1.0 mol/L NaCl) to investigate the influence of ionic strength on the sorption on magnetic biochar. Similar concentrations of SMX and EE2 both in single and binary solute systems were used in the study. As shown in Figure 5.5, the sorption of SMX in the single-solute system generally increased with an increase in ionic strength. However, in the presence of EE2, the sorption of SMX was significantly reduced but was not significantly affected by
the ionic strength. The presence of a competing organic compound, EE2, in the solution resulted in the decrease of sorption capacity of SMX which is significantly stronger compared to the increase in ionic strength. This finding is consistent with the results in the previous sections that magnetic biochar has a stronger affinity for EE2 compared to SMX.

Figure 5.5. Effect of ionic strength on SMX (~4 mg/L) sorption in the presence of EE2 [T=25°C; pH=6.5].

5.3.3. Effect of EE2 and NOM in SMX sorption

NOM, which is a complex mixture formed due to the degradation of biological materials in the environment, is ubiquitous in natural water sources and can impact the water treatment facilities. NOM has been found to reduce the sorption capacity and efficiency of
activated carbon in drinking water treatment (Newcombe et al., 1993). NOM competes with the organic compounds and blocks the micropores of the black carbon (Pignatello et al., 2006). Hence, this study evaluated the effect of NOM on the sorption of SMX and EE2 in single and binary solute system as shown in Figure 5.6. There was no marked effect of NOM on the sorption of SMX and EE2. However, the presence of EE2 in the solution caused a stronger inhibition on SMX sorption onto magnetic biochar compared to NOM even at high concentrations (20 mg-C/L), which is five times the concentration of EE2 (~4 mg/L) used. In the presence of NOM, EE2 strongly inhibited the sorption of SMX onto magnetic biochar which implies that EE2 is a stronger competitor for sorption sites than NOM.

Figure 5.6. Effect of NOM concentration on the sorption of SMX (~4 mg/L) without EE2 and with EE2 (~4 mg/L) onto magnetic biochar [T=25°C; μ=0.01 M NaCl].
5.3.4. Sorption behaviour of SMX and EE2

Surface analysis on magnetic biochar was performed using XPS survey as shown in Figure 5.7 and peak deconvolution as shown in Figure 5.8. Biochar did not exhibit any Fe 2p peak which implies that it has negligible Fe content on its surface. Two peaks were observed at 710.58 eV and 723.81 eV assigned to Fe2p\(^{3/2}\) and Fe2p\(^{1/2}\), respectively which confirmed the presence of iron oxide (Yamashita and Hayes, 2008). The deconvolution of C1s peak resulted in 3 peaks with binding energies of 282.25-282.83 eV, 284.28-284.33 eV and 285.63-285.95 eV for both adsorbents which were assigned to carbide, graphitic carbon and C-O, respectively (Puziy et al., 2008; Terzyk, 2001). In O1s peak deconvolution of biochar, 2 peaks at 530.36 eV and 532.51 eV were observed and assigned to C-O and O-H, respectively. The C-O peak in O1s deconvolution could be associated with the C-O peak in C 1s. The presence of adsorbed water or moisture in the sample is associated with the O-H peak (Rosenthal et al., 2010). These peaks were also observed in magnetic biochar (529.98 eV and 532.09 eV), but an additional peak at 527.79 eV was assigned to (Fe-O) due to the presence of iron oxide on magnetic biochar surfaces (Cheng et al., 2005). The lack of Fe 2p peak of biochar means that its surfaces were available to SMX and EE2. On the contrary, the presence of iron oxide on the surface of the magnetic biochar implied that the magnetisation of the biochar reduced accessibility of SMX and EE2 on the biochar surfaces of the adsorbent (Reguyal and Sarmah, 2018).
Figure 5.7. XPS spectrum of magnetic biochar.

The sorption of SMX onto magnetic biochar is highly pH-dependent. However, the electrostatic attraction between SMX and magnetic biochar was disregarded due to the effect of ionic strength on the sorption of SMX onto magnetic biochar where at high ionic strength; the sorption capacity of magnetic biochar is higher compared at low ionic strength. SMX consists of an aromatic benzene ring and an aromatic heterocyclic group which could interact with the aromatic rings on the surface of the highly carbonised biochar surface of the magnetic biochar via π-π electron coupling (Ji et al., 2009). SMX has also been found to have a strong interaction with the graphitic surfaces of biochar produced from shreds of red pine via π-π EDA interaction (Xie et al., 2014). Similarly, EE2 has an aromatic benzene ring
which could also interact with the graphitic surfaces of the magnetic biochar via \( \pi-\pi \) EDA interaction. Jung et al. (2013) concluded that the graphitic part of biochar and powder activated carbon had stronger \( \pi-\pi \) interaction with EE2 compared to SMX due to higher sorption capacity of a more hydrophobic compound, EE2 (Jung et al., 2013).

Figure 5.8. Deconvolution of (a) C1s of biochar; (b) O1s of biochar; (c) C1s of magnetic biochar; and (d) O1s of magnetic biochar.
Hydrophobic interaction has been one of the sorption mechanisms considered for the pH dependence of SMX sorption on carbonaceous adsorbent such as graphene (Chen et al., 2014), carbon nanotubes (Zhang et al., 2010), and magnetic biochar (Reguyal et al., 2017) due to the changes in SMX dissolution based on the solution pH. At pH 3.22 (25°C), SMX reaches the minimum water solubility, 281 mg/L, and is dominated by neutral species but at high pH value (pH=7.83), SMX solubility in water increased to 34802 mg/L (Dahlan et al., 1987). The water solubility of SMX is pH-dependent wherein at low pH it is less soluble compared at high pH resulting in higher sorption on hydrophobic biochar surfaces of magnetic biochar. The sorption of SMX onto magnetic biochar can thus be attributed to the hydrophobic interaction between SMX and the hydrophobic surface of biochar. On the contrary, EE2 (log $K_{OW} =4.2$) is more hydrophobic compared with SMX (log $K_{OW} =0.9$) resulting in significant reduction of SMX sorption even at low EE2 concentrations (Fredj et al., 2015; Wu et al., 2013). EE2 also did not have sorption affinity for iron oxide and it only competed with the biochar component of magnetic biochar. Lastly, EE2 had stronger inhibition on SMX sorption onto magnetic biochar compared with NOM as depicted in a schematic representation in Figure 5.9.
Figure 5.9. Schematic representation of the effect of EE2 and NOM on the sorption of SMX onto magnetic biochar.
5.4. Conclusions and future focus

Sorption of SMX onto magnetic biochar and the influence of environmental conditions namely pH, ionic strength, the presence of competing compound (EE2) and NOM were evaluated. SMX sorption onto magnetic biochar was highly pH-dependent wherein the sorption at lower pH was more favourable than at high pH. The SMX sorption onto magnetic biochar slightly increased with increase in ionic strength and decreased with increase in NOM concentration. In the single-solute system, the sorption of SMX could be due to the $\pi$-$\pi$ EDA interaction and hydrophobic interaction of SMX on the carbonaceous component of magnetic biochar. But the interaction between SMX and graphitic surfaces of the magnetic biochar was strongly inhibited by EE2 in all the environmental conditions studied even at low concentration due to its stronger $\pi$-$\pi$ EDA interaction and hydrophobic interaction on the biochar surfaces of the magnetic biochar.

From an environmental implication point of view, one can envisage that magnetic biochar would be suitable for sorbing hydrophobic organic contaminants in water. Other potential environmental benefits of using magnetic biochar synthesised in this study are (1) minimisation of wood waste since biochar used is derived from pine sawdust; and (2) reuse of waste material for water remediation. For non-magnetic adsorbents such as waste-derived biochar, the magnetic modification does provide an alternative solution for easy recovery of materials. However, the pilot-scale demonstration is still lacking. It is imperative that through proper examination of a magnetic adsorbent such as the one developed in this study would pave the way to realise the full potential of the economic feasibility of this technology.
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CHAPTER 6: Summary, conclusions, and recommendations for future work
6.1. Summary

Chapters 3, 4 and 5 provide details of the major contributions of this thesis. Chapter 3 is focused on the synthesis, characterisation and application of MPSB in the removal of SMX from aqueous solution. The biochar used in this study was from pine sawdust, one of New Zealand’s major wood wastes, produced at 700°C. The magnetisation of biochar was performed via oxidative hydrolysis of FeCl₂, where the formation of single-phase Fe₃O₄ nanoparticles was successfully carried out on the surface of biochar. PSB, MPSB and Fe₃O₄ were characterised using several techniques namely elemental analysis, N₂ gas adsorption/desorption isotherm test under liquid nitrogen to measure the surface area and pore characteristics of the adsorbent, XRD to determine the crystalline structure of the adsorbents, SEM-EDS to visualise the surface morphology and elemental distribution on the surface of the biochar and PPMS under VSM option to measure the magnetic property of the adsorbent. MPSB had a high saturation magnetisation of 47.8 A.m²/kg, which enabled MPSB to be separated by a magnet after the sorption equilibrium was reached. The stability of MPSB was also evaluated due to the presence of Fe₃O₄, which could result in leaching of iron at certain pH range. In this study, MPSB was found to be stable within solution pH 4 to 9 since iron leaching was observed outside this pH range. At pH = 4, the highest sorption capacity of MPSB was observed, which was 13.8 mg/g. Additionally, MPSB exhibited fast sorption of SMX, where it closely followed the pseudo-second order kinetic model for low concentrations. In Chapter 3, the thermodynamic studies were also performed, where ΔG°, ΔH° and ΔS° imply that the adsorption of SMX onto MPSB was spontaneous and exothermic. Regeneration of MPSB using organic solvents were also done but were only able to desorb ~45 to 67% of SMX.

Chapter 4 was focused on the influence of Fe₃O₄ nanoparticles on the physico-
chemical properties and sorption properties of PSB. The amount of Fe$_3$O$_4$ nanoparticles was varied with 0%, 25%, 50%, 75% and 100% per mass of magnetic adsorbent. Each adsorbent was characterised by the same techniques used in Chapter 3. In addition, XPS analysis for each adsorbent was performed to provide more information on the physico-chemical properties of the adsorbents. The addition of Fe$_3$O$_4$ nanoparticles on PSB clearly impacted the physical and chemical properties of PSB. BET surface area decreased as the amount of Fe$_3$O$_4$ nanoparticles increased. In contrast, the pore volume and saturation magnetisation increased as the percentage of Fe$_3$O$_4$ increased. The sorption isotherm of SMX onto these synthesised adsorbents was fitted in 5 isotherm models namely Langmuir, Freundlich, Redlich-Peterson, Dubinin-Radushkevich and Temkin. Among these models, Redlich-Peterson was found to best describe the isotherm data of magnetic adsorbents. Using this model, the approximate site energy distribution function was derived and used in the analysis on the influence of Fe$_3$O$_4$ on the sorption properties of magnetic adsorbent. The results of the approximate site energy distribution analysis showed that the addition of Fe$_3$O$_4$ on biochar reduced the area under the frequency distribution curve of sorption site energies leading to the reduction of the sorption sites available for SMX.

In Chapter 5, the sorption of SMX onto MPSB with different environmental conditions namely pH, ionic strength and presence of NOM and EE2 were evaluated. Initially, the sorption of SMX onto MPSB in single-solute system was found to be highly pH-dependent and slightly increased with increase in ionic strength. However, in binary-solute system in the presence of EE2, the effects of these environmental conditions were relatively insignificant compared to the sorption inhibition caused by EE2. Both SMX and EE2 sorption onto the highly carbonised surfaces of the biochar in magnetic biochar were due to the $\pi$-$\pi$ electron donor acceptor and hydrophobic interaction. Hence, strong competition between these compounds was identified where EE2 significantly inhibited the
6.2. Conclusions

This research developed a novel magnetic biochar from pine sawdust and investigated its application on the removal of SMX in aqueous solution. Primarily, this thesis focused on the synthesis and characterisation of magnetic biochar, and studied the sorption mechanism of SMX onto magnetic biochar in aqueous system. The major findings of this study are as follows:

- Synthesis of magnetic biochar was carried out via oxidative hydrolysis of FeCl₂ on pine sawdust biochar forming Fe₃O₄ nanoparticles on the biochar surfaces.
- Fe₃O₄ nanoparticles, confirmed by the XRD and XPS analyses, formed on the surfaces of PSB resulted in the blockage of the pores of biochar. Fe₃O₄ addition generally resulted in the reduction of BET surface area and %C, and increase of %Fe, %O, average pore volume and saturation magnetisation.
- SMX did not have any sorption affinity for Fe₃O₄ nanoparticles. The formation of Fe₃O₄ reduced the accessibility of SMX on the biochar surfaces. Hence, Fe₃O₄ nanoparticles or the magnetisation of biochar resulted in lower sorption capacity of the adsorbent for SMX. This finding was also confirmed by the site energy distribution analysis.
- The sorption of SMX onto magnetic biochar can be best described by Redlich-Peterson isotherm model and had the maximum sorption capacity of 13.8 mg/g at pH = 4. It is also highly pH-dependent, where low pH is more favourable. However, the magnetic biochar is only stable within solution pH 4 to 9 due to the

sorption of SMX onto magnetic biochar in all environmental conditions studied.
leaching of iron outside the pH range. Magnetic biochar has a fast uptake for SMX. Additionally, strong inhibition of EE2 on SMX sorption onto magnetic biochar was observed.

- SMX and EE2 sorption onto magnetic biochar could be due to the π-π EDA and hydrophobic interaction. Both SMX and EE2 had aromatic rings that could interact with the aromatic rings of the highly carbonised biochar surface via π-π coupling. Moreover, the higher sorption of EE2 compared to SMX onto magnetic biochar could be due to its higher hydrophobicity.

6.3. Recommendations for future work

Although the magnetic biochar has shown good potential in the adsorption of SMX, an emerging contaminant, further questions have arisen with regards to its application in water treatment. This thesis would like to recommend the following for future work:

- This study only used 1 type of biochar. However, since hydrophobic interaction has been one of the sorption mechanisms involved, the use of biochar with different hydrophobicity may provide more information on the interaction between SMX and magnetic biochar.

- The study on the sorption of other organic contaminants particularly those with different properties with SMX may help predict the sorption behaviour of different organic contaminants onto magnetic biochar.

- The magnetic biochar could also be used in the sorption of inorganic contaminants and contaminated water with various contaminants.

- The modification or use of different synthesis methods of magnetic biochar could
be done to improve its physico-chemical properties as well as its sorption properties.

- Regeneration of magnetic biochar using thermal and chemical treatment could also be investigated.

- The feasibility of the magnetic biochar for large scale water treatment should also be considered. Usually, studies in the development of novel adsorbents are done in laboratory scale.

- Lastly, although magnetic biochar may reduce the recovery cost of the adsorbent after use, the cost of the magnetisation process should all be accounted. Cost-benefit analysis should be carried out for the application of magnetic biochar in water remediation.
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