Adsorption of Carbamazepine from Water by Hydrothermally Treated and Steam Activated Flax Shives and Oat Hulls

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By

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ABSTRACT

Recently water pollution is one of the many threats that the world population is confronting, which requires immediate consideration. Numerous emerging pharmaceutical pollutants are commonly found in aquatic environments, wastewater, and ground surface because of their extensive uses for human beings and animals. Carbamazepine (CBZ), an antiepileptic drug, is one of the emergent pollutants. The existence of the pollutants turns into a serious health risk to people. In order to control these pollutants in the environment, it is necessary to develop efficient removal methods.

In this thesis, flax shives and oat hulls representing cellulosic materials of agricultural byproducts were used to develop hydrochars and steam activated hydrochar adsorbents. They were used to adsorb CBZ as a model pharmaceutical pollutant from artificially contaminated water. The adsorbents were characterized by surface properties and composition. Hydrothermal carbonization increased the porosity and surface area of raw flax shives and raw oat hulls, which were further significantly enhanced by steam activation. In addition, both hydrothermal carbonization and steam activation increased the carbon content and decreased the oxygen content and ratio of H/C of the flax shive and oat hull adsorbents. These thermal treatments generated aromatic structure and functional groups such as hydroxyls and carbonyls or carboxyls which were important for CBZ adsorption.

CBZ equilibrium adsorption was investigated at various temperatures (20-40°C) and solution pH (2-10). Steam activation significantly enhanced the adsorption capacity of the hydrochars made from either flax shives or oat hulls. However, both the hydrochars with or without steam activation demonstrated effective CBZ adsorption in comparison with numerous reported adsorbents. The achieved adsorption capacities were not significantly affected by solution pH, indicating that the adsorbents developed in this work are applicable to remove CBZ and alike pharmaceutical pollutants from water/wastewater in a wide range of pH values. The results implied that electrostatic interaction between the charged adsorbents and CBZ molecules, and hydrogen bonding may not be the major adsorption mechanisms. The π - π Electron-Donor-Acceptor (EDA) interactions and hydrophobic interaction could play important roles in the adsorption. The CBZ adsorption was effective at room temperature, which was enhanced at a higher temperature, showing the adsorption was endothermic in nature.

In addition, the isotherms of CBZ adsorption by the steam activated hydrochars were experimentally generated at various temperatures (20-40°C), which were successfully simulated by the Sips model. The site energy distribution of CBZ adsorption based on the Sips modeling results was further determined. The higher weighed mean of site energy obtained at 40°C indicated higher adsorption affinity, thus more favorable for adsorption. Furthermore, the thermodynamic parameters of CBZ adsorption were determined. The results again indicated the CBZ adsorption was endothermic and spontaneous.

The experimental CBZ adsorption kinetic data of both hydrochars and steam activated hydrochars were generated and successfully simulated by the pseudo-second-order kinetic model. Because of higher adsorption rate constants and lower activation energy, steam activated hydrochars adsorbed CBZ faster than the hydrochars. Desorption of CBZ from hydrochars and steam activated hydrochars was investigated with different solvents and at various pH levels. The highest desorption efficiency was obtained with organic solvent ethanol. Overall, the results demonstrated that flax shives and oat hulls are promising feedstock's to be made into adsorbents for treatment of wastewater contaminated by CBZ and additional similar pharmaceuticals.

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DEDICATION

I am dedicating this thesis to four beloved people who have meant and continue to mean so much to me.

This thesis is dedicated to my amazing parents, Dr. Hamid Aghababaei and Mrs. Soheila Sabbagh who gave me the greatest gift anyone could give another person. They believe in me in all of the aspects of my life, support, and encourage me to reach all my goals.

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ABBREVIATIONS

BET	Brunner-Emmet-Teller	
CBZ	Carbamazepine	
FE-SEM	Field emission scanning electron microscopy	
HC	Hydrothermal carbonization	
HPLC	High performance liquid chromatography	
HC-H ₃ PO ₄ -6h	Hydrochar thermally treated with H ₃ PO ₄ for 6h	
HC-H ₃ PO ₄ -12h	Hydrochar thermally treated with H ₃ PO ₄ for 12h	
HC-NaOH-6h	Hydrochar thermally treated with NaOH for 6h	
HC-NaOH-12h	Hydrochar thermally treated with NaOH for 12h	
MWCNTs	Multi-walled carbon nanotubes	
MOF	Metal organic framework	
PZNC	Point of zero net charge	
RSS	Residual sum of squares	
SAHC-H ₃ PO ₄ -6h	Steam activated hydrochar thermally treated with H_3PO_4 for 6h	
SAHC-H ₃ PO ₄ -12h	Steam activated hydrochar thermally treated with H_3PO_4 for 12h	
SWCNT	Steam Single-Walled Carbon Nanotube	
SUs	Standard units	

NOMENCLATURE

A	Initial adsorbent weight (g)		
В	Dried adsorbent weight (g)		
b	Adsorption equilibrium constant (L/mg) ⁿ		
C_{0}	Initial concentration of adsorbate (mg/L)		
C_e	Final concentration of adsorbate (mg/L)		
Cs	Maximum solubility of adsorbate in water (mg/L)		
E	Represents the difference of the sorption energies between the solute (adsorbate) and		
	solvent for a given adsorption site (kJ/mol)		
E^*	Difference of adsorption energy at Ce and Cs (kJ/mol)		
$F(E^*)$	Site energy distribution over a range of energies (mg·mol/(g·kJ))		
⊿G°	Standard Gibbs free energy change of adsorption (kJ/mol)		
∆H°	Standard enthalpy change (kJ/mol)		
K_S	Sips isotherm constant (L/mg)		
Кс	Adsorption distribution coefficient (L/mg)		
KL	Langmuir isotherm constant (L/mg)		
K _F	Freundlich isotherm constant (L/mg)		
k_d	Distribution coefficient (L/mg)		
n	Indicator of surface site heterogeneity of the adsorbent (dimensionless)		
pK_{a1}	First acid dissociation constant of CBZ (dimensionless)		
pK_{a2}	Second acid dissociation constant of CBZ (dimensionless)		
qe	Adsorbed amount at equilibrium (mg/g)		
q_m	Maximum adsorption capacity (mg/g)		
R^2	Coefficient of determination (dimensionless)		
R	Universal gas constant (kJ/mol·K)		
⊿S°	Standard entropy change (J/mol·K)		
Τ	Absolute temperature (K)		
V	Volume of solution (mL)		

W_I	Weight of the produced adsorbent (g)	
Wo	Initial mass of the raw precursor before impregnation (g)	

Greek Letters

α	Initial adsorption rate (mg/g·h)	
β	Elovich constant (g/mg)	
μ (E*)	Weighed mean of site energy distribution (kJ/mol)	

CHAPTER 1 INTRODUCTION

1.1. Research Motivation

The demand for clean water is continuously increasing because of the significant growth of the population worldwide. In the meantime, the current sources of water supply are getting more contaminated as economic is being developed (Carpenter et al., 2011). Numerous pollutants of emerging concerns such as pharmaceutical drugs, polycyclic hydrocarbons, endocrine disrupters, surfactants, and so on are increasingly being found in aquatic environments (Kümmerer, 2011), marine sediments and treated wastewaters (Vasquez et al., 2014). Pharmaceuticals were first identified in surface and wastewaters in the United States and Europe in 1960s (Stumm-Zollinger & Fair, 1965). According to literature, it was estimated that the average annual use of pharmaceuticals per person is approximate 15 g around the world and 50-150 g in industrialized countries (Benotti et al., 2009). The existence of pharmaceutical drugs in treated wastewaters (Vasquez et al., 2014) and particularly in drinking water (Mompelat et al., 2009) becomes threats to the environment and human health.

Carbamazepine (CBZ) is an antiepileptic drug which has commonly used to control seizures. It is one of the most usually identified drug deposits in water bodies (Zhang et al., 2008a). The usage of CBZ per year is more than 1000 tons and the release of it into aqueous environment is estimated to be around 30 tons per year. According to research, this pharmaceutical causes harm to aquatic organisms, for examples, crustaceans and cnidarians (Vernouillet et al., 2010; Martin-Diaz et al., 2009; Zhang, et al., 2008). CBZ has a very high persistence and was observed at a concentration more than 10 times that of other micropollutants (Kleywegt et al., 2011). It is taken in by human being if its residues are not successfully removed from drinking water.

In order to remove pharmaceuticals from the contaminated water and wastewaters, various methods such as adsorption (Sing, 2013), advanced oxidation process (Sillanpää et al., 2011), membrane separation (Ravanchi et al., 2009) and bioremediation (Gaspard et al., 2014) are used. However, pharmaceuticals are not effectively removed from waters through these methods because each method has its own limitations. Adsorption is a popular technology in water treatment due to being cost-effective and efficient. However, research on removal of pharmaceuticals by adsorption needs furthermore improvement on enhancing adsorption performance and reducing costs.

Among different kinds of adsorbents, biomass derived chars (biochars) have shown promising potentialities for treatment of antibiotic and additional pharmaceutical contaminated water/wastewater. Using low cost biomasses as feedstock to develop biochar adsorbents may improve cost-effective and eco-friendly aspects of adsorption technology for removal of aqueous contaminates. Flax shives and oat hulls are inexpensive and abundantly available in Canada and worldwide. They mainly contain cellulose, hemicellulose and lignin (Perruzza, 2010) which are potential compounds to be in structure of adsorbent for removal of organics. However, no in-depth research has been done to investigate the capability of adsorbents made from flax shives and oat hulls to remove CBZ and alike pharmaceutical residues from wastewater thus far.

In order to develop biochars suitable for adsorption with reasonably high surface area along with functional groups, activation is necessary. There are various activation methods among which hydrothermal carbonization, chemical impregnation and steam activation attract research and industrial interests. In the recent years use of hydrothermal carbonization (HC) for producing hydrochars has received considerable attention due to its ability to convert biomasses at moderate temperatures (e.g. 180-310°C) with reduced CO₂ emission to produce hydrochars, which have enhanced surface area and functional groups that are used in adsorption (Liu, et al., 2010; Liu and Zhang 2009). HC is an environmentally friendly technology. In addition, it was demonstrated that acid or alkali impregnation of biomasses significantly enhanced porosity and surface area of adsorbent during hydrothermal treatment (Khoshbouy et al., 2018; Zubrik et al., 2017; Wang et al., 2011). Steam activation was demonstrated to be one of the commonly used processes for producing activated carbons with high pore volumes and large porosity (Zbair et al., 2018; Fu et al., 2011) which enhances adsorption performance.

The aim of this research is to develop adsorbents from low-cost, easily available, and highly abundant agriculture by-products such as flax shives and oat hulls to effectively adsorb CBZ as a model of pharmaceutical pollutants from aqueous solution, and to investigate the fundamentals of pharmaceutical adsorption. These agricultural wastes were converted to hydrochars and activated hydrochars using the methods combining different technologies including chemical impregnation, hydrothermal carbonization, and steam activation. They were further characterized for surface physical and chemical properties. The effects of key operation parameters including pH, time, and temperature on CBZ adsorption were investigated. The isotherms of CBZ adsorption were generated experimentally, and the Sips model was used to analyze the equilibrium data.

According to the obtained isotherm modeling results, distribution of site energy was further estimated. CBZ adsorption mechanisms were elucidated. The adsorption kinetics were also investigated experimentally and further analyzed in aid of mathematical modeling. Desorption of adsorbed CBZ and reuse of regenerated adsorbents were investigated. Finally, life cycle assessment of the adsorbent production process was discussed in this work.

1.2. Knowledge Gap

Even though research has been carried on adsorption of pharmaceuticals, the focus of them has been on removing antibiotics from water. Importantly, the fundamentals and mechanisms of adsorption of pharmaceuticals on the surface of adsorbents made from the natural materials are not well understood. Based on the literature review, the following specific areas are identified as the knowledge gaps.

- 1. CBZ is one of the most commonly detected pharmaceutical residues in water bodies. It has not been effectively removed from contaminated water. Adsorption is an alternative technology for water treatment. Whether it is feasible to develop a novel adsorption process to effectively remove CBZ as a model pharmaceutical pollutant from contaminated water is important to know. Such research is at its early stage.
- 2. Among different kinds of adsorbents, biomass derived chars (biochars) have shown promising potentialities for treatment of water/wastewater contaminated by antibiotics and additional pharmaceuticals because of being cost-effective and eco-friendly aspects. Oat hulls and flax shives are generated abundantly as agricultural byproducts in Canada and worldwide. They mainly contain cellulosic components potentially to be in structure

of adsorbent for removal of pharmaceuticals. However, investigation on the capability of adsorbents made from flax shives and oat hulls for removal of pharmaceutical pollutants from wastewater and the adsorption mechanisms are not well understood yet. These agricultural byproducts have not been effectively used for industrial applications which can enhance the revenues of agricultural and related industries.

- 3. Hydrothermal carbonization has numerous advantages compared to pyrolysis such as simplicity, low-cost production, and energy and CO₂ efficiency. The conversion is at moderate temperatures with the reduced CO₂ emission. As well, steam activation is one of the commonly used processes for producing activated carbon with high pore volumes and large porosity. However, whether hydrothermal carbonization and steam activation can effectively convert the above mentioned agricultural byproducts to adsorbents with efficient adsorption performance is limited.
- 4. To understand the fundamentals of pharmaceutical adsorption on the above-mentioned adsorbents, it is important to determine the chemical composition, functional groups, porosity, surface areas and additional properties of the hydrochars and steam activated hydrohars developed in this work. The information on the surface chemical and physical properties of the adsorbents are limited.
- 5. In order to develop a novel CBZ adsorption process, it is essential to understand equilibrium and thermodynamic parameters of the process. Solution pH could be a significant parameter in adsorption of charged species because it affects not only the speciation and degree of ionization of adsorbate but also the surface charge of adsorbent. Temperature is another important parameter affecting the adsorption process. How pH and temperature specifically affect equilibrium of CBZ adsorption by the adsorbents developed from flax shives and oat hulls are yet understood. In addition, the adsorbents have multiple components, surface energetic heterogeneity of which are important to investigate to optimize the adsorption process. Such information is not adequately available.
- 6. Mechanisms of pharmaceuticals adsorption are associated with functional groups on adsorbate and adsorbent, and interaction forces. Investigation in this area contributes to the fundamental adsorption science and engineering. The nature of the groups on CBZ and on the hydrochars and steam activated hydrochars developed in this work responsible

for CBZ adsorption are not well understood. The types of binding forces need to be determined.

- 7. Adsorption of CBZ using flax shive and oat hull based adsorbents is promising and may provide an alternate adsorbent for removal of CBZ and similar pharmaceutical pollutants from water. However, how fast the adsorption speed is, what could be the rate controlling step, and what are the key operation parameters is not known, yet. It is essential to analyze the adsorption kinetics in aid of mathematical modeling.
- 8. To reduce the costs of material processing and adsorption operation, regeneration and reusability of flax shive and oat hull based adsorbents after CBZ adsorption are important. What type of solvents at which conditions can effectively desorb adsorbed CBZ are not well understood.

1.3. Hypothesis

Based on the literature review, the following hypotheses were proposed:

- 1. Oat hulls and flax shives after treated through chemical and thermal treatments have the capability for effective adsorption of CBZ from artificial wastewater.
- 2. The Sips model considering the surface heterogeneity has the potential to describe the equilibrium data in this process. The site energy distribution is a feasible method to describe the surface energy of adsorbent.
- 3. The kinetic data of CBZ adsorption can be effectively incorporated into and analyzed by the selected kinetic models.
- 4. CBZ loaded adsorbents can be desorbed and reused.

1.4. Objectives

To address the knowledge gaps, the following key objectives were proposed.

1. Development and characterization of adsorbents based on flax shives and oat hulls.

1.1. Develop hydrochars and steam activated hydrochars from oat hulls and flax shives through the methods combining of chemical activation, hydrothermal activation and steam activation process.

- **1.2.** Characterize the physical and chemical properties of the raw material and the produced hydrochars and steam activation hydrochars.
- 2. Adsorption of CBZ on hydrochars and steam activated hydrochars developed from flax shives and oat hulls.
 - **2.1** Analyze the equilibrium data of CBZ adsorption at various pH and temperature in aid of isotherm modeling.
 - 2.2 Determine the site energy and its distribution of CBZ adsorption.
 - **2.3** Evaluate the heat of adsorption, and determine thermodynamic parameters.
 - 2.4 Elucidate the mechanisms of CBZ adsorption.
 - **2.5** Analyze the kinetic data of CBZ adsorption in aid of kinetic modeling.

3. Desorption and reuse of the CBZ loaded adsorbents.

- 3.1 Desorb CBZ loaded adsorbents using organic solvents and water
- **3.2** Reuse the generated adsorbents for CBZ adsorption.

1.5. Thesis Layout

This thesis was written in the traditional way. It is composed of 10 chapters reporting the most significant results associated with all the objectives stated in Section 1.4, which is followed by a list of references and appendices. The first chapter is the introduction which presents the background of the research, knowledge gaps, hypotheses, and objectives. Chapter 2 presents the literature review on pharmaceutical pollution, strengths and weakness of the current water treatment methods, advantages and key aspects of pharmaceutical adsorption, important information of production of hydrochars and steam activated hydrochars for adsorption, and the mechanisms considered in pharmaceutical adsorption on activated carbons so far. Chapter 3 describes the materials, methods of developing and characterizing adsorbents, and adsorption and desorption processes. Chapters 4, 5, 6, 7, 8, and 9 covers the research results achieved in this work together with discussion according to the above mentioned objectives. Chapter 10 concludes and summarizes the most significant contributions of this thesis and provides recommendations for future improvement, which is followed by the list of references and appendices.

CHAPTER 2 LITERATURE REVIEW

Contribution of this chapter to overall Ph.D. work

This chapter provides an overview on pharmaceutical pollution, environmental impacts and properties with a focus on CBZ as a model pollutant. It also presents the strengths and weakness of the current water treatment methods and highlights the advantages and key aspects of treating pharmaceuticals by adsorption. Important information is reported on developing adsorbents from biomasses through chemical impregnation, hydrothermal carbonization and steam activation. The current achievements on adsorption equilibrium, site energy and kinetics are reviewed. Finally, mechanisms proposed for pharmaceuticals adsorption are summarized. This chapter provides important information to identify the knowledge gaps and develop the objectives and the methodologies of this thesis to carry out the research work.

2.1. Pharmaceuticals in Waters

2.1.1. Occurrence

Pharmaceuticals are commonly used to diagnose and treat illness of human and animals. Most of them have been synthetically manufactured, therefore are considered xenobiotic. Nowadays pharmaceuticals are being used worldwide, however the usage type and their quantity varies per country (Klaus Kümmerer, 2001). As mentioned earlier, the average annual usage of these compounds per person is around 15 g around the world, which could be up to 50-150 g in industrialized countries (Benotti et al., 2009). The total usage of pharmaceuticals and antibiotics in 2020 was estimated to reach 4.5 trillion doses. Over half of the world's populace expends more than 1 dose per individual per day. In 2020 per capita utilization of medication come to approximately 1.6 standard units (SUs) per individual per day.

Most industrialized countries had utilization over 2 SUs per individual per day and much of the expanded utilization in 2020 was driven by China, India, Brazil and Indonesia.

Carbamazepine (CBZ) is one of the foremost commonly used pharmaceuticals. It is an antiepileptic drug utilized to control seizures, relieve neuralgia, and treat a wide variety of mental disorders. The annual consumption of CBZ was estimated to be more than 1000 tons.

Pharmaceuticals cannot be completely metabolized in human or animal body and significant amounts are discharged with feces and urine. In the case of CBZ, around 72% of orally administered dosage is metabolized, whereas 28% is unchanged and consequently leaves the body with feces (Zhang et al., 2008a). According to the dose, the elimination half-life varies in the range of 25-65 h (Zhang et al., 2008a; Wishart et al., 2006). It was estimated that about 30 ton CBZ release into aqueous environment each year.

The current facilities in sewage treatment cannot effectively and completely remove the pharmaceuticals and their related metabolites, thus, they enter the water streams and even drinking waters. Figure 2.1 shows the detailed pathways for the pharmaceutical pollutants to enter the surface and waters (Figure 2.1).



Figure 2. 1 Pathways of input and distribution of pharmaceuticals in the environment (Kümmerer, 2008). Permission to use was obtained.

As seen in the above figure, these pollutants can enter ground water, sea water, even potable water in addition to soil if without effective treatment.

In general, the used pharmaceuticals by humans end up in domestic wastewater and are transported to wastewater treatment plants (WWTPs) (Kasprzyk-Hordern et al., 2009; Kümmerer, 2001). The conventional WWTPs are normally designed for removing bulk organic matter, nitrogen and phosphorus but most of them are not suitable and designed for pharmaceutical removal. Though some pharmaceuticals are removed during wastewater treatment, most of the pharmaceuticals remain and are discharged with the WWTP effluent (Deblonde et al., 2011; Verlicchi et al., 2012). Therefore, wide ranges of various pharmaceuticals at ng/L up to low μ g/L concentrations have been detected in wastewater effluents and in surface waters (Nikolaou et al., 2007). Even concentrations up to 0.1 μ g/L have been detected in the drinking water sources (de Wilt, 2018). Among the most common pharmaceuticals existing in the WWTP effluent and rivers in North America and Europe is CBZ (Cai and Larese-Casanova 2014; Mohapatra et al., 2012). For instance, the amount of CBZ in the wastewater streams of Canada and Germany was stated to be up to 6.3 μ g/L. In addition, it was up to 1.1 μ g/L in surface waters and up to 30 μ g/L in drinking water (Kosjek et al., 2009). CBZ has a very high persistence. It was observed at a concentration more than 10 times that of other micropollutants (Kleywegt et al., 2011).

2.1.2 Environmental Effects

As mentioned above, the widespread uses of pharmaceuticals from different sources of agricultural and veterinary practices along with human consumption result in pharmaceutical pollution in the environment.

The pharmaceutical pollutants are present in wastewater effluents, surface and ground waters (Yu et al., 2008; Nikolaou et al, 2007; Fent et al., 2006). In addition, irrigation of plants with water containing pharmaceuticals causes an uptake of pharmaceuticals by plants. This results in exposure of pharmaceuticals to food chain. (Barrett 2015). Moreover, the amounts of pharmaceuticals emitted into the environment is world-wide and increases. In the near future this won't have a significant change. Similar to other chemicals which enter the environment, pharmaceuticals change the physiological functions. The pharmaceuticals are designed to help

animals and humans through their disease therefore they are capable to be biologically active to wildlife species (Vasquez et al., 2014). As such, this leads to concern about eco-toxicological effects on organisms.

The existence of pharmaceuticals in the environment with different toxicity has achieved great attention of regulatory organizations because of the existing and potential adverse effects, such as being toxic for aquatic organisms, and developing genes of antibiotic resistance in pathogens (Yu et al., 2008). Figure 2.2 shows the acute toxicity of pharmaceuticals used for humans in various aquatic organisms entities of various trophic levels (Kümmerer, 2009). Among them, CBZ has an acute toxicity less than 100 mg/L. For examples, acute toxicity of CBZ was observed at 17.2 mg/L in Daphnia while 34.4 mg/L in midges. Besides, growth in Daphnia was inhibited at 12.7 mg/L and that in midges was 9.2 mg/L (Thaker, 2005).

In general, CBZ is not biodegradable when its concentration is low. Besides, CBZ degrades very slowly through the sun light (Chen, et al., 2017). Because CBZ has strong persistence in the environment, it can be toxic for additional many aquatic organisms, such as cnidarians and crustaceans in long terms (Vernouillet et al., 2010; Martin-Diaz et al., 2009; Zhang, et al., 2008; Putra et al., 2009).



Figure 2. 2 Acute toxicity of human pharmaceuticals in different aquatic organisms of different trophic levels (Kümmerer, 2009). Permission to use was obtained.

Moreover, it should be noted that most of the polar pharmaceutical compounds dissolve well in water and this leads to a ready dispersion in aquatic environments. The metabolic processes in the human body can change the pharmaceuticals into metabolites before excretion, as shown Figure 2.3. After excretion, additional transformation of the pharmaceuticals or their metabolites can happen in plants of wastewater treatment and in the environment leading in unlimited transformation products. Compared to the original compounds the products which have been formed during the specific water treatment have high toxicity levels (Illés et al., 2014).



Figure 2. 3 Transformation pathways of pharmaceuticals (K. Kümmerer, 2008).

2.1.3 Carbamazepine

As discussed above, carbamazepine (CBZ) as an antiepileptic drug commonly exists in various water bodies (Zhang, et al., 2008). It has a molecular formula of $C_{15}H_{12}N_2O$ with a molecular weight of 236.27 g/mol (Vardanyan & Hruby, 2006). The chemical structure of CBZ together with other properties are presented in Table 2.1. In comparison, chemical–physical properties of selected pharmaceuticals are presented in Table 2.2 (Bottoni et al., 2010).

Similar to many antibiotics, CBZ has benzene rings, which are linked with carbonyl and amide groups. As seen in Table 2.1, CBZ has two acid disassociation constants (pKa), 2.3 and 13.9 corresponding to the above-mentioned carbonyl and amide groups, while most pharmaceuticals have lowers values of pKa as shown in Table 2.2. As such, CBZ exists in a cationic form when solution pH is below 12 while the pharmaceuticals listed in Table 2.2 may have positive or negative charge depending on pH.

Carbamazepine (CBZ)				
Structure, formula	$C_{15}H_{12}N_2O$			
molecular weight	236.27 g/mol			
	H ₂ N O			
Usage	Analgesic, antiepileptic			
Water solubility	125 mg/L (20°C)			
Log K _{ow} (n-octanol- water)	2.45			
Henry's law constant	1.09×10 ⁻⁵ pa m ³ mol ⁻¹ (25°C)			
рКа	2.3, 13.9			
Elimination half life	25-65 h			
Excretion	72% Oral dosage excreted in			
	urine, 28% in feces			
Dosage	Maintenance usually 800-			
	1200 mg daily			

Table 2. 1 Chemical and pharmacological properties of carbamazepine (Yu et al., 2008; Clara et al., 2004).

In addition, CBZ has a solubility of 125 mg/L in water at 20°C which is lower than antibiotics such as levofloxacin and noraflaxcacin. In general, n-octanol/water partition ratio or partition coefficient (log Kow) is useful to evaluate hydrophobicity of a pharmaceutical compound. If the value of Kow is greater than one, the substance is more soluble in fat-like solvents such as n-octanol (hydrophobic), otherwise, it is more soluble in water (hydrophilic). CBZ has a value of log Kow being 2.45, showing it has hydrophobicity. The value is at the intermediate level of the

log Kow values of the pharmaceuticals listed in Table 2.2. This indicates that CBZ could be adsorbed by hydrophobic interaction (Patel et al., 2019; Hodges et al., 2019; Yamamoto et al., 2009). However, how significant the role is in a specific CBZ adsorption system needs be investigated.

Compound	pKa	Log Kow
Clofibric acid	4.20	2.57
Mefenamic acid	9.30	5.12
Amoxycilin	-	0.87
Aspirin	3.50	1.19
Atenolol	9.20	0.16
Carbamazepine	2.3, 13.9	2.45
Benzimidazole	5.48	1.32, 6.20
Carbamazine	13.90	2.25
Cimetidine	6.80	0.40
Ibuprofen	4.91	3.97
Metformin hydrochloride	12.40	-1.43
Oxytetracyline	3.30	-0.90
Allipurinol	9.30	-0.55
Quinine sulfate	5.07	5.40

Table 2. 2 Chemical-physical properties of some selected pharmaceuticals (Bottoni et al., 2010).

2.2. Pharmaceutical Removal Methods

The current methods to remove pharmaceuticals from water or wastewater include adsorption (Sing 2013), advanced oxidation process (Sillanpää et al., 2011), membrane separation (Takht Ravanchi et al., 2009b) and bioremediation (Gaspard et al., 2014). The methods used for removal of these pollutants mostly depends on the chemical characteristics of the pharmaceuticals, concentration of them in effluent and the cost of the processes (Homem and Santos 2011). More details on the current treatment methods are given below.

2.2.1. Advanced Oxidation Process

Advanced oxidation processes (AOPs) were first used in the 1980s for drinking water treatment and later were widely studied for treating different wastewaters. They are mainly used for removal of organic and sometimes inorganic pollutants. In this method, hydroxyl radical and other reactive oxygen species such as counting singlet oxygen, hydrogen peroxide and superoxide anion radical are generated. Then they are used to oxidize the pollutants. These oxidants may also have the potential for biodegradation (Barrett 2015). In AOP, in order to generate intermediate radicals with significantly high reactivity and oxidation potential, additional energy sources or catalysts are provided (Plant et al., 2011). Ozonation, fenton, photolysis, photo-fenton, etc. are some examples of AOPs (Homem and Santos 2011; Le-Minh et al., 2010), among which ozonation is the most popular one. For examples, Huber et al. (2003) investigated the oxidation of pharmaceuticals such as bezafibrate, diazepam, diclofenac, ibuprofen, iopromide and sulfamethoxazole in a conventional ozonation process in drinking water treatment. Coelho et al. (2009) used ozonation to degrade diclofenac existing in aqueous solution. However, AOPs usually cannot completely mineralize pharmaceuticals. In addition, some of the oxidized products such acridine and so on generated in AOPs are still threats to the environment (Kosjek et al., 2009; Wiegman et al., 2003). Moreover, AOP methods require energy and the reagents costs can be high (Andreozzi 1999). Subsequently, they actually need further improvement to offer total mineralization of micropollutants.

2.2.2. Bioremediation

Bioremediation is a method that uses microorganisms to degrade or reduce the concentration of the pollutants through a biological process. This method is widely used in wastewater treatment for removal of toxic organic and inorganic pollutants (Kümmerer et al., 2000). This process mainly uses naturally occurring microorganisms to treat wastewater as their nutrients. It aims to decrease the levels of the pollution to an acceptable range according to the limitations set by regulatory agencies or to totally transform the organic pollutants to carbon dioxide (Kümmerer et al., 2000). Although it is economical and reduces energy consumption (Phapal et al., 2015) bioremediation technique may not be a suitable option for treating
pharmaceutical pollutants with high toxicity as they can be toxic for microorganisms (Homem and Santos 2011). Previous studies revealed that due to persistence of carbamazepine to biodegradation-based conventional treatment, this method is not a suitable method for its removal (Keen et al., 2012).

2.2.3. Membrane Separation

This technique aims to separate fine particles or dissolved species from solution through a membrane functioning as a selective or semipermeable barrier according to the physical or molecular size of particle or solute. If the species are larger than the membrane pore size, they are retained while those smaller can easily pass through the membrane.

Membrane processes are classified as micro-filtration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), dialysis, and electrodialysis (ED). Commercial membranes are mostly made of organic polymers such as polyamides and polysulfone, and of ceramics based on oxides of silicium, zirconium, aluminum, and titanium. Nanofiltration membrane is a separation process used for pharmaceutical removal from wastewater. An effective nano-membrane should be designed in a way that would only reject pharmaceuticals but not ions. As such, there is no need to desalt in wastewater treatment (Röhricht et al., 2009). Due to wide applications and the performance, membrane technology has achieved significant attention, however during the last decade, the percentage of reduction of CBZ in simulated contaminated water through membrane filtration (micro filtration) in a hybrid system with granular activated carbon (MF-GAC) was shown to be low (Shanmuganathan et al., 2015).

2.2.4. Adsorption

Adsorption refers to adhesion of molecules or atoms from a gas or liquid to the surface of an adsorbent, which could be physical and or chemical (Barrett 2015). The adsorption phenomenon in a porous solid structure usually involves the following steps: (1) adsorbate transport in the bulk fluid phase, (2) external mass transfer, (3) intraparticle diffusion, and (4) adsorption of adsorbate on active sites in the porous structure.

This method was reported to be effective and suitable to remove heavy metals and antibiotics from aqueous solution (Nayak et al., 2017; Ncibi and Sillanpaa 2015).

2.3. Adsorbents

One of the most important aspects in an adsorption process are adsorbents. Adsorption efficiency is highly associated with properties of adsorbent. In order to have high efficiency it is important to use adsorbents with high porosity and surface area, and suitable pore size and functional groups for adsorption (Gupta et al., 2009a). Adsorbents which are used for wastewater treatment are mainly categorized into two different groups: inorganic and organic adsorbents. In the previous research on removal of pharmaceuticals from wastewater various inorganic adsorbents have been used such as zeolite, goethite, etc.

Nowadays due to the environmental problems, researchers have focused on developing low-cost adsorbents in order to solve these problems and identified the organic adsorbents such as shells and hulls from fruits, nuts, saw dust, corncob waste and straw (Worch, 2012).

Though there are various types of adsorbents, biochars derived from biomasses are promising in removing antibiotics and additional pharmaceuticals from contaminated water because of their aromatic structure and polar groups hydroxyls, carboxyls, and aminos. This kind of biochars due to their high porosity and large surface area play an important role in high adsorption speed and capacity (Wang et al., 2010; Aghababaei et al., 2017). Using biochars for removal of metal ions have been studied for decades (Subramaniam 1970) and in the past years investigation on their application for removal of pharmaceuticals from aqueous solution has gained interests among researchers.

2.3.1. Organic Adsorbents

Organic adsorbents can be made from various biological materials (also called biomaterials) such as algal, chitinous and wood/forest biomaterials, agricultural by-products, food wastes, and additional sources. Previous research has demonstrated that biosorbents based on plant materials such as peat, moss, water hyacinth, and canola meal were able to adsorb metals (Al-

Asheh and Duvnjak 1999, Volesky 2003; Zhanguang Liu et al., 2013; Nielsen et al., 2014; Naghdi et al., 2016; Chen, et al., 2017). In addition, adsorbents were developed from pomelo peel, rice husk, sugarcane bagasse, corn cobs, banana pith, apple residue, coconut husks, olive mill solid residue, spent grain, peanut skins, wheat straw, tea leaves, and alike plant byproducts. Moreover, biochars and activated carbon were also made from by-products of plants (Movasaghi et al., 2019; Chen, Xie et al., 2017; Zhanguang Liu et al., 2013; Chojnacka 2006; Yuh Shan Ho 2006). Raw biomaterials usually have low surface area and tend to release organic components when in aqueous solution. Thus, a lot of them are converted to biochars for adsorption application. Though numerous types of biomaterials were studied in metal biosorption, research on agricultural by-products based adsorbents for pharmaceutical adsorption is limited. As for CBZ adsorption, the adsorbents developed from agricultural byproducts are also limited, as shown in Table 2.3.

Saskatchewan is one of the key provinces in Canada to produce flax, oat, canola, barley, wheat, and other agricultural products. Abundant by-products are generated during the processing of these crops such as flax shives, oat hulls, canola meal, barley straw and wheat straw. Thus flax shives and oat hulls are readily available at low price, they can be used as biosorbent. They are produced from milling processes and their main part is fibrous sheath (Oat and health 2002). These materials are structurally composed of cellulose, hemicellulose, lignin and protein (Galdeano & Grossmann 2006) as well as several secondary metabolites such as phenols, ketones, aldehydes and carboxylate (Zou et al., 2011). This indicates using oat hulls and flax shives as the raw material for making adsorbents has a potential for removal of pharmaceuticals from wastewater. However, so far oat hulls and flax shives have only been used directly, or as the source of activated carbon preparation, for removal of metals such as arsenic and dye from wastewater, respectively (Banerjee et al., 2016; Chuang et al., 2005). The chemical structure of cellulose, hemicellulose and lignin are presented in Figure 2.4

Adsorbents	Maximum adsorption	References		
	amount (mg/g)			
Rice straw (Agricultural waste)	65.8	(Liu et al., 2013)		
Activated carbon (AC)/Fe ₃ O ₄ (Mixture of	45.3	(Shan et al., 2016)		
Coconut, pine nut and walnut shells)				
Magnetic biochar/Fe ₃ O ₄ (Mixture of	62.7	(Shan et al., 2016)		
Coconut, pine nut and walnut shells)				
Synthesized activated carbons from peach	242	(Álvarez-Torrellas		
stones		et al., 2017)		
Peanut shell-biochars	3.4	(Chu et al., 2017)		
Activated palm kernel shell	170.1	(To et al., 2017)		
Pine-wood nanobiochar	116.0	(Naghdi et al., 2016)		
Biomass (pomelo peel) activated carbon	286.5	(Chen et al., 2017)		
Bleached pulp 800-HCl-H ₃ PO ₄	81.0	(Oliveira et al.,		
		2018)		

Table 2. 3 Adsorbents made from plant materials and agricultural by-products for pharmaceutical CBZ removal.

The listed adsorbents in Table 2.3 either have relatively low uptake or the work lacks systematic investigation. Interaction mechanisms between CBZ and heterogeneous surface are still not clear. The work is still at its early stage and there is a need for further research in this area. In addition, there is no research on using flax shives and oat hulls for carbamazepine removal from wastewater. In the present research, oat hulls and flax shives were investigated to develop cost effective adsorbents for carbamazepine removal. Biomass derived chars (biochars) have shown interesting possibilities for treatment of antibiotic and additional pharmaceutical contaminated water. In order to increase the surface area and porosity and create functional groups which could enhance adsorption, biomasses are converted to biochars utilizing various thermochemical methods, for instance, hydrothermal carbonization and slow pyrolysis.



Figure 2. 4 Chemical structure of cellulose, hemicellulose and lignin (Abutaleb et al., 2020). Permission to use was obtained.

2.4. Development of Adsorbents

Suitable biochars for adsorption need reasonably high surface area along with a large porosity. In other words, adsorbents should have a large quantity of microporous and macroporous, be rich in surface functional groups (e.g. oxygen-containing functional groups), and have low ash content to ensure fast adsorption speed and high capacity (Ahmad et al., 2020; Sharma et al., 2020; Maniscalco et al., 2020; Libra et al., 2011).

For that end, adsorbents need to be activated. Among the reported activation methods, hydrothermal carbonization, chemical impregnation, and steam activation are effective. They are discussed as follows.

2.4.1. Hydrothermal Carbonization (HC) Process

In the past few years the use of hydrothermal carbonization for producing biochars has received considerable attention due to its ability to effectively convert biomass to hydrochars that are used in adsorption (Liu and Zhang 2009; Liu, Zhang, and Wu 2010). The HC process is an environmentally friendly technology, in which biomass is thermally converted into high carbon content material at moderate temperatures (Kruse et al., 2013; Chambukulam et al., 1981). HC of

different biomasses was studied along with water in different percentages and normally the temperature was between (180-250°C) at elevated pressure (2-10 MPa) for several hours (Xiao et al., 2012). Bergius and Specht (1913) were the first people who introduced and used this process. They converted cellulose into high carbon content material. In another study, cellulose mixed with water was thermally treated in a sealed reactor at 210-310°C (Jamari & Howse, 2012). The research over the last decade has demonstrated that hydrothermal carbonization is promising due to its advantage of transforming biomass into products at moderate temperatures (Titirici, et al., 2008; Titirici et al., 2007). Considerable research has investigated the use of brown chars as activated carbon adsorbents for water purification systems or CO_2 sorption (Libra et al., 2011), solid fuels (Parshetti, et al., 2013; Funke and Ziegler 2010; Titirici et al., 2008; Titirici et al., 2007; Yu et al., 2004), sources of bio-oil (Xiao et al., 2012; Akhtar and Amin 2011; Heilmann et al., 2010; Hoekman et al., 2011) and soil amendment to enhancing soil fertility and crop yields (Du et al., 2012; Libra et al., 2011; Rillig et al., 2010). A plan diagram of HC with a number of conceivable applications of hydrochar was proposed by Kang and colleagues (Kang et al., 2012), which is shown in Figure 2.5.



Figure 2. 5 Plan of HC process for possible applications (Kang et al., 2012). Permission to use was obtained.

The hydrothermal process can be classified into two types, namely, direct and catalytic HC. In a direct HC process, catalyst is not used and only a mixture of feed and water is heated in a closed vessel at various temperatures.

On the other hand, in a catalytic HC process, a catalyst is added (Funke & Ziegler, 2010). Reaction time, process temperature, and biomass to water ratio are the main factors which play important roles in this process (Xiao et al., 2012; Heilmann et al., 2011; Berge et al., 2011). The water in this process facilities carbonization and at the same time affects the distribution of product (Funke and Ziegler 2010; Behar et al., 2003; Mok et al., 1992). Thermodynamically, water does not have a high heating value as an totally oxidized substance (Nizamuddin et al., 2017). Therefore, water is an agent of reaction capable of conducting these hydrothermal reactions contrasting to pyrolysis reactions (Ramsurn and Gupta 2012; Akiya and Savage 2002).

2.4.2. Chemical activation

In the hydrothermal carbonization process, it was reported that using water as the sole agent during the hydrothermal process could not effectively develop porous adsorbents for wastewater treatment (Hao et al., 2014). In addition, research has shown that acid or alkali treatment (impregnation) of precursors before thermal treatment significantly enhanced porosity and surface area of adsorbent during thermal treatment (Khoshbouy et al., 2018; Zubrik et al., 2017; Wang et al., 2011). A number of chemicals have been used as activating agents prior to or in concurrence with the hydrothermal process. They usually act as a dehydrating agents, removing oxygen and hydrogen from the lignocellulosic material, leading to an increase in the surface area and porosity (Jain et al., 2014; Hoekman et al., 2011). In recent research, the most commonly used chemical activation agents are H₃PO₄ (Li et al., 2015; Belhaneche_Bensemra et al., 2005), ZnCl₂ (Jain et al., 2014; Belhaneche_Bensemra et al., 2005), strong base (NaOH) (Fu et al., 2018; Li et al., 2015), and H₂O₂ acid (Jain et al., 2015). Among these agents, H₃PO₄ was very effective in creating porosity and functional groups in biochars developed from cellulosic materials such as banana peels (Zhou et al., 2017; Tang et al., 2016), barley straw (Yan, 2017), corn stover, switch grass, hybrid poplar and douglas-fir (Zhang et al., 2007), hemp (Moxley et al., 2008), bermuda grass, reed and rapeseed (Li et al., 2009), and bagasse, wheat, and rice straw (Sathitsuksanoh et al., 2012).

In addition, H₃PO₄ treatment has numerous advantages such low hazard concerns, corrosion, and costs (Chu et al., 2018; Li et al., 2010; Girgis and El-Hendawy, 2002).

2.4.3. Steam Activation

Though it was demonstrated that hydrothermal carbonization enhanced surface area and porosity of adsorbents, the values of which were not adequately high. Recently, more efforts have been made to make adsorbents with highly microporous structure to obtain high adsorption speed and capacity. Steam activation is one of the commonly used processes for that purpose (Zbair et al., 2018; Fu et al., 2011). Activated carbon (AC) is termed to represent the group of carbonaceous materials with high surface area and porosity, which are widely used in treatment of wastewater (Azbar et al., 2004). Nowadays, there are wide and increasing sources of materials used to produce activated carbons. Suitable precursors include low-cost materials with low inorganic and high carbon contents. The precursors are treated via a physical activation method, that is heating in the presence of CO₂, steam, or an inert gas to produce activated carbon at 500 to 1000°C (Kushwaha et al., 2013; Gupta et al., 2009b). It is sometimes combined with chemical impregnation, in which a chemical is added to the precursor before the thermal treatment to enhance the activation process. This combined physico-chemical treatment has been used in converting potato peel (Kyzas & Deliyanni, 2015), date palm leaflets (El-Shafey et al., 2012), mung bean husk (Mondal et al., 2015), raspberry (Dubey et al., 2014) and coconut shell (Yu et al., 2008) to activated carbon. Steam activation along with nitrogen is one of the commonly used processes for producing activated carbon with high micropore volumes, higher microporosity and high surface area (Zbair et al., 2018; Fu et al., 2011) which lead to increase of the diffusion rate of adsorbates. Moreover, steam activation enhances the numbers of functional groups such as hydroxyls and carboxyls in the adsorbents, thus leading to a high adsorption capacity (Maneerung et al., 2016; Bouchelta et al., 2008). For an example, Maneerung et al. (2016) demonstrated that activated carbons prepared by steam activation have higher surface area (microporous materials) and higher adsorption capacity of rhodamine B in comparison with those obtained from CO_2 and N_2 activations.

2.5. Adsorption Equilibrium

2.5.1. Factors Affecting Adsorption in a Batch System

Batch adsorbers are widely used in wastewater treatment industry. They are suitable for adsorbents with small to medium particles size. This kind of adsorbers are beneficial where the adsorption step is not constant; the scale of operation is small; and long contact time is required (Worch 2012; Crini and Badot 2008). There are key factors which play important roles in the adsorption equilibrium such as pH of solution and effect of temperature. These parameters are discussed below. It should be noted that in the following context, when the effect of one specific adsorption parameter is discussed, it is assumed that the rest of the parameters are kept constant in the system.

2.5.1.1. Effect of pH

The pH of solution could be a significant parameter affecting not only speciation of adsorbates but also surface charge of adsorbents (Sun et al., 2016). This parameter also affects the adsorption mechanism of antibiotics through its impact on the charge state of the functional groups of the adsorbents and the degree of ionization of the adsorbates (Ncibi & Sillanpaa, 2015). In common, effect of pH on pharmaceuticals adsorption depends on the characteristics of the adsorbents which is used and speciation of pharmaceuticals in aqueous solution (Wu et al., 2015; Sun et al., 2012). When the adsorbates have net charge opposite to the adsorbents, they can be adsorbed through electric attractoin. Point of zero net charge (PZNC) of an adsorbent is important in determining surface charge at a specific pH, thus affecting adsorption. The PZNC of the adsorbent indicates the pH condition at which the net charge density on the surface is zero. When the other hand, when the pH values are lower than PZNC, the adsorbent surface charge is positive (Sun et al., 2012). At different pH values, the charge of the adsorbate molecules change. Therefore, either pH can be favorable for the adsorption process or may not be based on the impact of pH on both adsorbents and adsorbates (Qin et al., 2014; Wu et al., 2010).

2.5.1.2. Effect of Temperature

Another important factor which plays a significant role in an adsorption equilibrium process, is temperature. The role of this effect (temperature) is associated with adsorption energy, for example whether the process is endothermic or exothermic. Temperature affects equilibrium, spontaneity and randomness of the adsorption processes. The impact of temperature varies with pharmaceuticals in consideration. For example, adsorption of cephalexin by alligator weed activated carbon is endothermic and increasing the temperature slightly increased the adsorption (Miao et al., 2016). Ncibi. (2017) studied the removal of carbamazepine and dorzolamide using mesoporous activated carbons and multi-walled carbon nanotubes and also noted that the equilibrium uptake had an increase by rising the temperature from 15°C to 45°C. However, Khazri et al. (2017) studied the effect of the temperature on the removal of naproxen, ibuprofen and carbamazepine with clay at different temperatures. The results showed that increase of the temperature markedly decreased the adsorption capacity, a nature of being exothermic. They came to the conclusion that the rise of temperature caused destabilization within the physical forces which were involved; therefore, to promote the pharmaceutical adsorption, there was an optimum value of temperature. Kovalova et al. (2013) studied the temperature effect on the adsorption of cytarabine and 5-fluorouracil on commercial adsorbent powdered activated carbon (PAC). The results also showed that lower temperature increased the adsorption uptake. However, temperature does not always have a strong effect on an adsorption process. For instance, temperature did not have any effect on adsorption of cephalexin by loofah sponge activated carbon under the tested conditions (Kong et al., 2016). Kong et al. (2017) also reported that the adsorption of ofloxacin by luffa sponge activated carbon was not significantly affected by temperature. This could be because of the adsorptive forces formed between the pharmaceutical and the functional groups on the surface of the adsorbent and among the close molecules in the adsorbed phase were weak at those tested conditions (Fan et al., 2011). Generally, there are two main ways that temperature affects adsorption equilibrium: changing the molecular movement at the adsorption interface and causing interactions between adsorbate and adsorbent.

Depending on adsorbate and adsorbent in use, an adsorption process can be endothermic or exothermic. Usually, when the process is endothermic, by increasing the temperature the adsorption capacity increases. As for exothermic processes, the impact is opposite. Increase of temperature can decrease solution viscosity which facilitates the diffusion of adsorbate molecules within the external boundary and through the internal pores (Sayğili & Güzel, 2016).

2.5.2. Thermodynamics of Adsorption

thermodynamic feasibility То determine and spontaneity of an adsorption process, it is essential to investigate adsorption thermodynamics. In addition, for elucidating the adsorption mechanisms, it is important to understand the effect of temperature and analyze the thermodynamic parameters such as Gibbs free energy, change 2017). enthalpy, and entropy (El-Araby et al., These thermodynamic parameters are usually estimated by adsorption equilibrium constants regressed by isotherm modeling.

Specifically, standard Gibbs free energy change, ΔG° (kJ/mol), standard entropy change of adsorption, ΔS° (J/mol/K), and standard enthalpy change, ΔH° (kJ/mol) are determined using the following equations.

$$\Delta G^o = -RT \ln K_c \tag{2.1}$$

$$\ln K_c = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$
(2.2)

$$\Delta G^o = \Delta H^o - T \Delta S^o \tag{2.3}$$

where Kc represents the adsorption distribution coefficient, R denotes the universal gas constant (8.314 J/mol.K), and T means the absolute temperature (K). K_C is an important parameter associated with the thermodynamic parameters. Gibbs free energy change shows whether the adsorption process is spontaneous or not (Moreno-Castilla, 2004). If the value is negative, the adsorption process is spontaneous. The greater negative value of this parameter shows that the process is more favorable. If this value is positive, the process does not happen spontaneously (Liu, 2009).

According to the thermodynamic point of view, enthalpy change shows the amount of heat that is necessary for the process and this heat could be released or absorbed. The amount of enthalpy change delivers useful information for understanding the type of adsorption. The sign of this value shows that either an adsorption is physisorption or chemisorption. When the value of enthalpy change is less than 80 kJ/mol, the bonds between adsorbate and adsorbent are weak and physisorption occurs, otherwise if the value of enthalpy change is more than 80 kJ/mol, the bonds between adsorbate and adsorbent become strong indicating chemisorption (El-Araby et al., 2017). The differences between physisorption and chemisorption are listed in Table 2.4.

Property	Physical adsorption	Chemical adsorption
Type of bonding forces	Van der Waals	Similar to a chemical bond
Adsorption heat	Low, 10-80 kJ/mol	High, 80-200 kJ/mol
Reversibility	Fully reversible	Irreversible
Formation of multilayer	Yes	No

Table 2. 4 Characteristics of physical and chemical adsorption (El-Araby et al., 2017).

Another interpretation of enthalpy changes in the system is related to its sign. If the value is negative it shows that the adsorption process is exothermic and heat is released from the system. On the other hand, when this value is positive, it indicates that the system absorbs heat and is endothermic (Soustelle, 2011). Entropy indicates randomness in the system. A positive value of entropy change shows that randomness in the system increases; however, a negative value indicates decrease of randomness.

2.6. Adsorption Kinetics

Kinetic studies deliver significant information related to the adsorption rate. When an adsorbent is selected to be used in wastewater treatment facilities at an industrial scale, high

adsorption rate is an essential characteristic in addition to high adsorption capacity and removal efficiency (Aljeboree et al., 2014).

Time is one of the key parameters in adsorption kinetics. At initial stages of contact time, because of high concentration and high mass transfer driving force of adsorbate in solution, and more active sites available on the surface of adsorbent, adsorption takes place rapidly. As time progresses the surface coverage of the adsorbent is high; adsorption becomes slower;, and finally no net adsorption takes place at which status adsorption reaches steady state (equilibrium) (Wu et al., 2015; Stipp 1999). According to previous studies the pharmaceutical adsorption similarly increases very fast as the contact time increases, however it gradually reaches a more or less constant value.

significant factor which is important in the adsorption kinetics is Another temperature. Based on the Arrhenius equation, increase of reaction temperature increases reaction rate constant thus enhances the rate (Scott Fogler, 1987). It has been reported that for hydrophobic compounds, low temperatures caused in a large decrease in the removal rate of certain pharmaceuticals (Nam et al., 2014). In addition, according to the previous studies on pretreated oat hulls (Movasaghi et al., 2019), increase in temperature from 15°C to 45°C had an increase in the adsorption rate and capacity. Another study of removing ofloxacin by activated carbon derived from luffa sponge also showed increasing temperature from 25°C to 35°C increased adsorption (Kong et al., 2017). In general, with increasing temperature, the molecular activity at the boundary layer increases, thus increasing the adsorbate diffusion rate. Besides, it can decrease solution viscosity which facilitates the diffusion of molecule within the external boundary and through the internal pores (Sayğili & Güzel, 2016). In general, there are four different kinetic models popularly used in pharmaceutical adsorption. They are the pseudo-first-order kinetic model (Demirbas et al., 2004), the pseudosecond-order kinetic model (Ho and McKay, 1999), Elovich (Demirbas et al., 2004) and the intraparticle diffusion models (Aljeboree et al., 2014).

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2.7. Desorption

It is important to desorb adsorbed pollutant and regenerate adsorbent for reuse. Thus, one of the key processes in wastewater treatment is desorption. It has an important effect on the environmental and economic aspects, particularly when adsorbents and treatment processes are expensive (Wang & Chen, 2009). There are different kinds of methods for desorption such as chemical, thermal swing, pH shift, electrochemical, steam, ultrasonication, solvent extraction, and microbiological methods (De Andrade et al., 2018; Kulkarni & Kaware, 2014).

To select a suitable method, it is necessary to consider the type of adsorbent, quality of water/effluent, goals of further treatment, and costs of regeneration (Worch, 2012). Furthermore, reducing the need for fresh adsorbents, desorption of adsorbed pollutants to regenerate adsorbents can mitigate the problems associated with disposal of used adsorbents (Adegoke et al., 2017).

Compared to the above mentioned various methods using chemicals as desorption agents has more advantages. For instance, in this method there is less loss of adsorbent due to the burn off that occurs in thermal regeneration. Besides, additional recovery of adsorbate is achievable by applying extra separation methods such as distillation (David, 1999; Martin & Ng, 1984). In a chemical desorption process, pollutant loaded adsorbents are placed in a solvent containing chemical agents at specific operating conditions such as temperature and pH for a predetermined time. Desorption solvents which are used should be non-destructive for adsorbents, environmental-friendly, efficient, and inexpensive (Wang & Chen, 2009).

In chemical desorption, various solvents can be used including inorganic solvents such as acid or base aqueous solutions (e.g. HCl, HNO₃, H₂SO₄, NaOH), and organic solvents such as ethanol and methanol with or without H₂O, acetonitrile, and methanol/acetic acid (10:1) if the affinity of the adsorbate towards H₂O is relatively low. In another word, if the adsorbate is less hydrophilic and more hydrophobic, organic solvents are suitable desorption agents (Alatalo et al., 2016). Krika et al. (2015) studied the desorption of Cd ²⁺ ions using 0.2 M HCl. With the increase of hydrochloric acid concentration, the desorption efficiency increased. This was because the acid brought in more H⁺ ions which replaced Cd ²⁺ from the active sites on the adsorbent, thus Cd ²⁺ was desorbed. In general, if adsorption is through electrostatic attraction between adsorbate and adsorbent with opposite charges, the adsorbate can be effectively desorbed by adjusting solution pH during desorption. Wu et al. (2013) studied the desorption of ciprofloxacin (CIP, antibiotic) from clay minerals (kaolinite) surfaces in aqueous solution. Solution pH affected the surface

charge of kaolinite and the degree of ionization of CIP. The point of net zero charge of kaolinite is about 4.7-5. Ciprofloxacin hydrochloride is an antibiotic. It has two pKa values of 6.0 and 8.8 with respects to carboxyl and amino groups in the molecule (Osonwa et al., 2017). Thus, desorption of ciprofloxacin from kaolinite is highly pH dependent. Specifically, when solution pH was decreased from 5 to lower values, and increased from 7 to higher values, desorption was enhanced because of the increased electrostatic repulsion between kaolinite surface and CIP charged by same sign.

Alatalo et al. (2016) and Cigdem (2012) investigated the desorption of a less hydrophilic adsorbate, methylene blue, from activated carbons with ethanol and demonstrated that ethanol was efficient in the desorption process. In a study of CBZ removal, ethanol was also used in desorption of CBZ from graphene oxide and a recovery of 93% CBZ was achieved (Cai, 2015). In addition, ethanol was used in desorption of CBZ to investigate the possibility of chemical versus physical adsorption based on that it should easily remove physically adsorbed CBZ due to hydrophobic interaction and higher solubility of CBZ in ethanol (20.8 g/L) (Cai, 2015; Cai and Larese-Casanova, 2014). It was also considered that using organic solvents for desorption are important cost-saving measure in the water treatment applications. However, the area of research needs to be further investigated.

2.8. Mechanisms of Pharmaceutical Pollutants Adsorption from Aqueous Solution by Activated Carbons

Adsorption often takes place by two major mechanisms, namely chemical adsorption and physical adsorption. This classification is based on the binding and strength. In physical adsorption, the forces between adsorbate and solid surface are relatively weak (mostly van der Waals interactions); however, the forces in chemical adsorption are much stronger (Barrett 2015; Liang et al., 2014). Adsorbents such as activated carbons, biochars and hydrochars have diversified applications in the treatment of wastewater. Characteristics of the adsorbents such as surface chemical and physical properties play important roles in the process. In addition, characteristics of the pollutants in water are also important. Both of them control the mechanisms of adsorption (Lladó Valero, 2016).

In general, in an adsorption process dealing with activated carbons as adsorbent and pharmaceutical pollutants as adsorbate in aqueous solution there are three general types of interactions which play important roles on the adsorption: 1) adsorbate-activated carbon, 2) adsorbate-water, and 3) activated carbon-water (Lladó Valero, 2016; Karanfil, 2006). There are described as follows.

2.8.1. Adsorbate-Activated Carbon Interactions

Pharmaceutical pollutants are usually small molecules with a surface area of 1-3 nm² (Lladó Valero, 2016; Okouchi et al., 1992) These small molecules can contact the pores of the adsorbents such as activated carbons and hydrochars. Therefore, the physical adsorption between the adsorbates and the adsorbents can be determined by the pore size distribution and surface area of the adsorbents. In addition, chemical factors such as chemical composition of the adsorbents, functional groups of the pharmaceutical molecules, and the solution chemistry can increase or decrease the adsorption. In the case of steam activated carbons or hydrochars, the main heteroatom in the functional groups which is oxygen plays an important role in adsorbing the pharmaceutical pollutants. In general, it is considered that the important and main interactions between a pharmaceutical adsorbate and an activated carbon and similar adsorbent are: 1) π - π electronacceptor-donor (EDA) dispersion interactions between the aromatic ring of the adsorbate and the basal plane of the steam activated carbon/hydrochars. 2) electrostatic attraction-repulsion interactions, 3) hydrogen bonding between surface functional groups and aromatic pharmaceutical molecules, electron acceptor-donor complex formation mechanism (Franz et al., 2000; Lladó Valero, 2016). In addition, hydrophobic interaction can take place when adsorbate has hydrophobicity.

2.8.1.1. π - π EDA Dispersion Interactions

The π - π EDA dispersion interactions are the attraction formed between electron-deficient (acceptors) and electron-rich (donors), which are polar interactions (Foster & Fyfe, 1966). The interactions were considered in the adsorption of compounds with aromatic structure and carbon based adsorbents. Usually, the π -system polarizability or electron-donating ability of substitutes makes an increase in the donor

strength, and the strength of acceptor is associated with the number and the electronwithdrawing ability of substitutes (Chen et al., 2017). Gao et al. (2012) investigated the removal of tetracycline with graphine oxide, in which π - π interaction and cation- π bonding were proposed as the major mechanisms. In addition, the π - π EDA interactions have been proposed as the main and important mechanism for the adsorption of antibiotics and additional pharmaceuticals (e.g., ofloxacin, norfloxacin, sulfadiazine, sulfamethoxazole, sulfamethazine, cephalexin, amoxicillin. carbamazepine, naphthalene sulphonic acids) on activated carbon (Rivera-Utrilla & Sánchez-Polo, 2011), graphene (Nan Cai, 2015), graphene oxides (Liu et al., 2016), biochar (Peng et al., 2016; Chen et al., 2017), nano biochar (Naghdi et al., 2019) and carbon nanotubes (Wang et al., 2010). Overall, the π - π EDA interactions have been to be one of the predominant mechanisms in the adsorption of considered pharmaceutical compounds on carbon based heterogeneous adsorbents.

2.8.1.2. Electrostatic Interactions (Van der Waals Interaction)

These interactions refer to the attractive or repulsive interactions between objects having electric charges. Pharmaceuticals could be charged through protonation and deprotonation of their functional groups, so could be activated carbons and similar adsorbents. Thus, electrostatic interactions may take place between pharmaceuticals and activated carbons, contributing to adsorption mechanism. However, their specific roles could vary in different adsorption systems.

Solution pH is a parameter which may affect electrostatic interactions in an adsorption process. This key parameter thus may affect the pharmaceutical adsorption by its impact on the charge of functional groups of adsorbent and adsorbate ionization degree (Ncibi & Sillanpaa, 2015). As a result, effect of pH could be used to diagnose the contribution of electrostatic interaction in the pharmaceutical adsorption process. For example, when the effect of pH was significant, electrostatic interactions were considered to be one of the major mechanisms between the adsorbents (activated carbons) and the selected pharmaceuticals (4-Nitrophenol, Sulfamethoxazole, Ibuprofen, Diclofenac) with charges of opposite signs (Chen, et al., 2017; Zhao et al.,

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2016). Peng et al. (2016) also considered that electrostatic interactions had a significant role on the mechanism of adsorption of antibiotics such as β -Lactams, macrolides, sulfonamides and tetracyclines on carbon based adsorbents. However, Yu et al. (2014) studied the adsorption of tetracycline with multi-walled carbon nanotubes containing different oxygen contents.

They considered that electrostatic interactions existed but were insignificant because tetracycline adsorption capacity was not changed significantly at a wide pH range of 2-10. The adsorption had multiple mechanisms, most likely π - π interactions among the carbon nanotubes surface and the benzene rings and double bonds of the tetracycline molecules, electrostatic interactions between tetracycline and carbon nanotubes-3.2%O, and hydrophobic interactions between carbon nanotubes-3.2%O and tetracycline.

2.8.1.3. Hydrogen-bond Interactions

Hydrogen bonding is a specific type of dipole-dipole attraction between molecules. For example, hydrogen bonding can form between functional groups OH, COOH, and NH₂ of aromatic compounds, and activated carbons/hydrochars and biochars (Chen, et al., 2017). Hydrogen bonding have been reported in the adsorption of norfloxacin with carbon nanotubes (Wang et al., 2010) and pretreated barely straw (Yan, 2017). They were also proposed as one of the mechanisms in the adsorption of fluoroquinolones antibiotics on pretreated barley straws (Bei Yan, 2017). Hydrogen bonding is also one of the mechanisms for adsorption of diclofenac by potassium ferrate-activated porous graphitic biochar (Tam, et al., 2020). Solution pH may also affect hydrogen bonding.

2.8.2. Adsorbate – Water Interactions

The interactions adsorbate adsorption. between and water also affect hydrophobic Pharmaceutical compounds have properties which can make the

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compounds pushed to the surface of activated carbon/hydrochar. This tendency is known as solvent-motivated adsorption (Lladó Valero, 2016; Ahlert, 1997). Hydrophobic interaction could have a significant role in pharmaceutical adsorption on activated carbons, which can be predicted by octanol–water distribution coefficient (Kow) of the pharmaceutical. The higher the Kow, the higher the opportunity of hydrophobic interaction (Chen, et al., 2017).

2.8.3. Activated Carbon – Water Interactions

Activated carbons and hydrochars are usually obtained with functional groups containing oxygen and/or nitrogen on the surface. These functional groups can interact with water molecules, leading in increased hydrophilicity of the adsorbents, thus making cluster and blocking the pores. As a result, the pore blockages can slow down the adsorption (Lladó Valero, 2016).

CHAPTER 3 MATERIALS AND METHODS

Contribution of this chapter to overall Ph.D. work

This chapter presents the materials, methods of adsorbent development and characterization, adsorption and desorption experiments, and data analysis, which were used in the overall study of this thesis.

3. Materials and Methods

3.1. Raw Flax shives and Oat hulls and Preparation

Raw flax shives were obtained from SWM Inc. Manitoba, Canada. They were a by-product generated from the flax fibre production process. The raw material contains 53.2% cellulose, 13.6% hemicellulose, 20.5% lignin, 3% protein, 4.3 % moisture, 3.5 wt% ash and 1.9% unknown residues (Ghanbari & Niu, 2018). Raw oat hulls, a by-product of the oat milling process, were provided by Richardson Millings Ltd, Saskatchewan, Canada. According to the data provided by the supplier, the material is composed of 37% cellulose, 35% hemicellulose, 7% lignin, 3.8% moisture and 3.1 wt% ash. The rest are mainly starch residue and small amounts of protein (2-4%) (Thompson et al., 2000). The adsorbent particles with the size range of 0.425-1.18 mm were obtained by sieving the particles using Canadian Standard Sieves Series (Combustion Engineering Canada Inc.) and used for further treatment.

3.2. Preparation of Solution

3.2.1. CBZ solution preparation

Carbamazepine (CBZ) was purchased from Sigma Aldrich (purity > 98%), Canada. Synthetic aqueous solutions of CBZ compound were prepared by dissolving certain amount of the chemical in deionized water. In this research, sulfuric acid (H_2SO_4 , > 98.0% (w/v), E.M Science) and sodium hydroxide (NaOH, > 98.3 wt%, Fisher Scientific and H3PO4 > 85% (w/v), Fisher Scientific) were used to make 0.1 M H₂SO₄ and 0.1 M NaOH aqueous solutions for pH adjustment and 1 M H₂SO₄ and 1 M NaOH for treatment of adsorbents. In addition, hydrated nickel sulfate (NiSO4·6H2O, > 98.9 wt%, Fisher Scientific) was used for co-adsorption experiments (The results are in Appendices.). Moreover, ethanol (CH₃CH₂OH, Sigma Aldrich, Canada) and methanol (CH₃OH, Sigma Aldrich, Canada) have been used for desorption study.

Molecular structure	Molecular weight (g/mol)	Water solubility (mg/ L, 25°C)	pK _{a1}	pK _{a2}	References
H ₂ N O	236.26	125	2.3	13.9	(Punyapalakul and Sitthisorn 2010; Deng et al., 2013; Zhang et al., 2008; Yu et al., 2008)
Cher					

Table 3. 1 The molecular structure and chemical properties of carbamazepine.

In order to verify whether there is degradation of CBZ molecules during adsorption at different concentrations, CBZ aqueous solutions (Ci=5 and Ci=125 mg/L) were prepared and operated at the same experimental conditions as those of the adsorption except that there was no adsorbent for 72 h at 20°C and 40°C. The average difference between the initial and final concentration was 8.8%, showing that degradation of CBZ during the adsorption process was insignificant.

3.2.1.1. Solubility of CBZ

The solubility of CBZ in water at 30 and 40°C was determined by the shake flask method (Larsson, 2009; Mota et al., 2009). According to this method, a fixed amount of CBZ was added to deionized water and shaken at 150 rpm for 24 h at room temperature. The saturated samples were filtered using plastic syringes coupled with polypropylene filters (0.45 μ m). Quantitative analysis of CBZ in the supernatant was then performed using high performance liquid chromatography (HPLC, Agilent Technologies 1260). The solubility was determined by the average of at least two repeated measurements.

3.3. Methods of Adsorbent Treatments

3.3.1. Hydrothermal Carbonization (HC) Process

In the HC treatment, 5 g dry flax shives or oat hulls particles in the size range of 0.425-1.18 mm were impregnated individually with 25 mL acid (1 M H₃PO₄) or base (1 M NaOH) aqueous solution by mixing for 12 h. The choice of H₃PO₄ was because this acid was very effective in creating porosity and functional groups in hydrochars developed from cellulosic materials in comparison with other agents (Zhou et al., 2017; Tang et al., 2016; Yan, 2017). In order to make a comparison, NaOH was also used.

Hydrothermal treatment was then carried out in an autoclave (reaction vessel). The mixture of the flax shives/oat hulls and acid/base solution was completely placed in a 50 mL reaction vessel (model: HC230, COL-INT-TECH). The temperature of the reactor was increased at a constant heating rate 20°C/min to 220°C and maintained at this temperature for a period up to 16h (either nitrogen or oxygen was not provided in the process). Additional experiments were conducted with heating up to 180°C in order to compare the hydrochars yields with those obtained at 220°C during the HC process. After HC, the oven was cooled down. The treated residues were thoroughly washed with deionized water followed by solvent extraction with ethanol and oven dried at 105°C for 24h. The prepared dried hydrochars were weighed to calculate the yield and then stored inside a desiccator for the next step experiments.

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3.3.2. Steam Activation

The selected dried hydrochars produced from the HC process were further treated by steam activation under N_2 flow in a fixed bed reactor at 850°C. The flow of N_2 as the carrier gas into the reactor was controlled by a mass flow controller (Brooks Instrument, 5850S/B) at 138 mL STP/min. About 10 g of the flax shives or oat hulls hydrochar samples were loaded into the reactor (H:72 cm, D:5 cm). The temperature of the furnace was increased at a constant heating rate of 7°C/min to 850°C. Then the steam with a rate of 10.3 mL/h was injected to the reactor for one hour at this temperature. After the furnace was cooled down under the N_2 flow, the samples were collected. More details on the steam activation method can be found elsewhere (Azargohar & Dalai, 2008). The yield of the adsorbents (hydrochars and steam activated hydrochars) were calculated as follows:

Yield (%) =
$$\left(\frac{W_1}{W_0}\right)$$
 X100 (3.1)

where W_I is the dry weight of the produced adsorbent (g) and W_o is the initial dry mass of the raw precursor before impregnation (g).

3.4. Characterization of Adsorbents

3.4.1. Particle Size Distribution

In order to study the effect of chemical, hydrothermal, and steam activation, the particle size distribution of raw and treated flax shives and oat hulls (hydrochars or steam activated hydrochars) were measured using Mastersizer 2000 (Malvern Instruments). First of all, 5 g of the treated or raw samples were dispersed in water and then transferred to the optical bench. Several individual detectors were arranged within the optical bench and each of the detectors captured the light scattering from a specific range of angles. At small angles the larger particles scatter right and on the other side, small particles scatter at large angles. After the angular scattering intensity data was obtained, the Mie theory was used to calculate the size of the particles. The particle size was stated as a volume equivalent sphere diameter.

3.4.2. Surface Area and Pore Size Distribution

Specific surface area and pore size distribution of adsorbents are significant indicators for porous characteristics of adsorbents. They were measured by a pore size analyzer (Micromeritics ASAP 2020, Micromeritics Instrument Corporation, USA) via N_2 adsorption at 77 K. First, the samples (raw flax shives and raw oat hulls, and their hydrochars and activated hydrochars) were degassed at 383.15 K under vacuum of 500 μ Hg for 6h. The Brunauer-Emmett-Teller (BET) surface area was then determined from the relative pressure (P/P_o) ranging from 0.001 to 0.21. The t-plot method was used to determine surface area of micropore.

3.4.3. Determination of Moisture Content

1.0 g of adsorbents was placed in a dried and weighed crucible. The crucible was placed in an oven and dried at 110°C for 4h to achieve constant weight. In order to avoid the moisture absorption, the samples were cooled in desiccators. The moisture content was calculated as follows (ASTM Standard D2867, 2014).

Moisture content (%) =
$$\left(\frac{A-B}{A}\right)$$
X100 (3.2)

where A denotes initial adsorbent weight (g) and B represents dried adsorbent weight (g).

3.4.4. Determination of Ash Content /Volatile Matter

Ash contents of raw materials, hydrochars and steam activated hydrochars were determined by heating each of the samples in the muffler furnace at 650° C for 4h. Specifically, a clean and empty crucible was first placed in the furnace which was then heated up to remove moisture at the desired temperature of 650° C by a constant heating rate of 7°C/min. Then, it was cooled inside a desiccator, and weighed. About 1.0 g of each sample was weighed and placed in the dry crucible. The crucible with the samples

was put in the furnace and the temperature was increased to 650°C at the same heating rate as described above and maintained for 4h. Afterwards, the crucible was moved out from the furnace and cooled down in a desiccator. After reaching room temperature, it was re-weighed. The ash content was calculated using the equation ("ASTM Standard D2866," 2018).

Ash (%) =
$$\frac{\text{Ash Weight}}{\text{Oven dry weight of adsorbent}} X100$$
 (3.3)

For volatile matter determination, 1.0 g of each sample was heated at 950°C in the absence of air for 7 min. The loss in weight was reported as volatile matter. The volatile matter was calculated using the following equation (ASTM Standard D5832, 2014).

Volatile (%) =
$$\frac{\text{Weight of volatile component (g)}}{\text{Oven dry weight of adsorbent (g)}} X100$$
 (3.4)

3.4.5. Elemental Analysis of Adsorbents

To measure the elemental composition of the raw materials (flax shives and oat hulls), hydrochars, and activated hydrochars, the samples were oven dried at 60°C. Afterward, about 2 g of each sample was transferred to the glass vials. In order to measure the contents of carbon, hydrogen, and nitrogen, an elemental analyzer (Vario EL III CHNS, Elementar Americas, Inc., Ronkonkoma, New York, USA) was used. The amount of O is calculated by the total amount minus the content of C, H, N, and S (Borugadda et al., 2020; Aghababaei et al., 2017c; Shahkarami et al., 2015). Finally, the data were reported in average and standard deviation based on duplicated experiments.

3.4.6. FE-SEM Analysis

To visualize the surface structure of the adsorbents, the Field Emission Scanning Electron Microscope (FE-SEM) technique was used in order to minimize the sample charging. They were first coated with 3-6 nm of Pt/Pd coating with a sputter coater. Then variable-pressure FE-SEM (SEM, JSM 6010LV, JEOL) was used to take images in a high vacuum mode with voltage of 2-10 kV, which was applied dependent on extent of sample charging through a secondary electron detector.

3.4.7. Fourier Transform Infrared Spectroscopy

To investigate the functional groups on the adsorbents, FTIR measurements were performed on an Ilumminat IR spectrometer (Smith's Detection, MA) attached to a Renishaw Invia Reflex microscope (Renishaw Inc., Ill.). The finely ground particles of hydrochars and steam activated hydrochars, with CBZ and without CBZ were loaded along with the powder of pure CBZ. Samples were fixed on a borosilicate slide. Then the IR beam was focused on the sample by a 36X diamond ATR objective (NA= ∞ ; Smith's Detection, MA). The adsorbents loaded with pharmaceuticals were collected by filtration, washed with deionized water for three times, and then dried at 50°C. To ensure the quality of the data, the experiments were repeated for three times. The FTIR spectra were scanned for 512 times at room temperature in the range of 4000-650 cm⁻¹ with a resolution of 4 cm⁻¹ and presented in averages.

3.4.8. X-ray Photoelectron Spectra (XPS)

To investigate the functional groups possibly participating in CBZ adsorption, measurement of X-ray Photoelectron Spectroscopy (XPS) was completed with a Kratos (Manchester, UK) AXIS Supra system under UHV conditions at the Saskatchewan Structural Sciences Centre (SSSC). This system combining a hemispherical analyzer (HSA) and a spherical mirror analyzer (SMA) was equipped with a 500 mm Rowland circle monochromated Al K- α (1486.6 eV) source. A spot size of the hybrid used in this analysis was (300 X 700) microns. The survey scan spectra were collected in the binding energy range of 0-1200 eV in 1 eV steps with a pass energy of 160 eV. High-resolution scans were also completed by 0.1eV steps with a pass energy of 20 eV. An emission current of 15 mA and an accelerating voltage of 15 keV were applied for the analysis. These methods are similar to those reported in literature (Shi, 2020; Chand et al., 2019). To fit photoelectron spectra, the Casa XPS (version 2.3.5) and Multipack software were employed.

3.4.9. Near-edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

To analyze the aromatic structures and additional functional groups on the adsorbents, C K NEXAFS spectra of flax shives/oat hulls and steam activated hydrochars were obtained by an 11ID-1 beamline via slew scanning mode on spherical grating monochromator (SGM) beamline at Canadian Light Source (CLS) that was designed for high-resolution soft x-ray spectroscopy. Flax shives, oat hulls and their steam activated hydrochars/ hydrochars were mixed with deionized water (1 - 2 mg/mL) in 1.5 mL Eppendorf vials to acquire a slurry. Further, the vortex mixer was used to uniformly disperse the fine solid particles and wet the slurry. After ensuring the complete mixing, using a pipette, an aliquot of 4 - 6 µL was deposited on gold (Au) coated silica (Si) wafers fixed to the sample plate using double-sided carbon tape and vacuum dried at room temperature to remove the water. The prepared sample plate was placed in a chamber with high vacuum (1.33 e-5 Pa); while recording the spectra, the ring current was filled to 250 mA for every 8 h. The beamline was configured for a resolving power of ca. 7500 at the C K edge, and the photon energy was scanned from 270 to 300 eV with 0.1 eV resolution and a dwell time of 0.5 s. Ten different spots were measured (60 s per spot) on each sample to ensure that the resulting spectra were identical. Total electron yield (TEY) was collected by monitoring the drain current for all the samples at beam spot size 100 µm². Background measurements were collected at the photon energy range of 270 to 300 eV for gold (Au) mesh for normalization. The processed data were averaged for ten scans and divided with Au data to plot against photon energy, and the main transitions $(1s-\pi^*)$ are used to interpret the outcomes of the fine structures.

3.5. Adsorption Experiments

Experiments of CBZ adsorption were operated by a batch process. About 5 mg of dry adsorbent (raw flax shives, raw oat hulls, their hydrochars and steam activated hydrochars described in sections 3.1 and 3.3) and 10 mL CBZ solution with 0 to 250 mg/L CBZ were mixed

in a 50 mL glass vial. The samples were covered to avoid light which may cause degradation. The pH of the mixtures having an original pH value of around 5.8-6 were adjusted to desired values (pH 2-10) by 0.1 M sodium hydroxide solution or 0.1 M hydrochloric acid. The mixtures were then agitated at 220 rpm and a constant temperature ($20 \pm 0.5^{\circ}$ C, 30° C or 40° C) in a shaker until reaching equilibrium. The adsorption experiments were carried out for 2 to 96 h. After the adsorption, the supernatant was taken out by a 1 mL syringe (B-D Syringes) and the solution was filtered by a syringe filter (0.45 µm polypropylene membrane). High performance liquid chromatography (HPLC, Agilent Technologies 1260) was used to measure the CBZ concentration of the supernatant. The mobile phase had a flow rate of 0.75 mL/min and contained 30:70 (v/v) of 0.1% formic acid in deionized water and acetonitrile anhydrous. The retention time of CBZ in the HPLC was 1.22 min.

In addition, the adsorption experiments of CBZ on hydrochars and steam activated hydrochars made from flax shive in the presence of Ni^{2+} were done in a batch mode by mixing 5.0 \pm 0.1 mg hydrochar/steam activated hydrochar with a 10.0 mL CBZ-nickel solution. The CBZ and the nickel molar ratio was (1:1 wt.%). The uptake of CBZ or Ni²⁺ was determined by HPLC or AAS, respectively. The adsorption data obtained in the presence of nickel is presented in Appendix D.

The adsorption uptake of CBZ or Ni²⁺ at equilibrium per unit mass of adsorbent was calculated according to the following equation when the volume of solution was not changed significantly during adsorption.

$$q_t = (C_o - C_e) V/M$$
(3.5)

where C_0 (mg/L) is the initial and Ce (mg/L) the equilibrium CBZ concentration. V (L) represents the total solution volume, and M (g) denotes the dry fresh adsorbent mass. All the experiments were replicated for up to three times. The results were presented in average and standard deviation.

3.6. Desorption Experiments

Regarding the desorption experiments, the CBZ loaded hydrochars and steam activated hydrochars were separated from the aqueous solution after the adsorption reached equilibrium. For

that, the adsorption mixtures (CBZ + adsorbents) were decanted for a period of time and the aqueous solution was taken out by a syringe. Afterwards, deionized water was used to wash the adsorbents quickly to remove the fraction of the CBZ molecules which were not adsorbed. Finally, the adsorbents were dried at 45° C for 6h till constant weight was obtained.

Afterwards, about 2 mg dry adsorbents which were loaded with CBZ were added to 10 ml different solvents (water, methanol, ethanol, 50% water/ 50% methanol or 50% water/ 50% ethanol). For determining the desorption efficiency, syringe filters (0.45 µm polypropylene membrane) were used to filtrate the solutions at the end of desorption. The CBZ concentration of the supernatant after filtration was determined by HPLC in the same method as described in the section of 3.4. All experiments were repeated for three times. Desorption efficiency was determined using the following equation:

Desorption efficiency =
$$\frac{\text{Amount of pharmacutical desorbed}}{\text{Amount of pharmacutical initially loaded}} X100$$
 (3.6)

CHAPTER 4 DEVELOPMENT AND CHARACTERIZATION OF ADSORBENTS

Contribution of this chapter to overall Ph.D. work

This chapter presents the results of successfully developing hydrochars (HC) and steam activated hydrochars (SAHC) from raw flax shives and oat hulls by H_3PO_4 and NaOH impregnation, hydrothermal carbonization, and steam activation process. The key factors including chemicals (acid and base), hydrothermal carbonization time, and temperature were investigated. The influence of these parameters on the surface area, elemental composition, and yield of the obtained adsorbents were determined. In addition, the oat hull and flax shive based adsorbents were characterized on chemical and physical properties by multiple methods, such as particle size distribution, compositions, and scanning electron microscopy (SEM).

4.1. Preparation of Adsorbents

In this work, two agricultural by-products flax shives and oat hulls, representatives of cellulosic materials were used as precursors. As a general guide, good adsorbents must have a reasonable high surface area along with a large porosity for adsorption of pollutants, in other words, the adsorbent must have a good combination of micropores and macropores. According to the IUPAC (International Union of Pure and Applied Chemistry 1991), the pore of a solid material can be categorized into three groups: micropore (< 2 nm), mesopore (2-50 nm), and macropore (> 50 nm). Therefore, the high value of surface area was set as one of the major criteria to optimize the preparation conditions, i.e., the type of chemical agent (acid or base), treatment time and temperature of the hydrothermal process. For that end, the two raw materials were firstly impregnated in two different kinds of chemical aqueous solutions, acid (1 M H₃PO₄) or base (1 M NaOH). Then the samples together with the impregnation solution were treated by hydrothermally treated for 6 and 12 h (HC-H₃PO₄-6h and HC-H₃PO₄-12h), and those impregnated by NaOH and hydrothermally treated for 6 and 12 h (HC-NaOH-6h and HC-NaOH-12h).

Based on the achieved results using flax shives and oat hulls, the hydrochars impregnated with H₃PO₄ and hydrothermally treated for 6 and 12 h (HC-H₃PO₄-6h and HC-H₃PO₄-12h) had higher BET surface area and higher yield of hydrochars. They were selected to be further treated by the second stage of treatment, i.e. steam activation. The products are steam activated hydrochars (SAHC-H₃PO₄-6h and SAHC-H₃PO₄-12h). The aforementioned hydrochars and steam activated hydrochars were characterized as follows.

4.2. Characterization of Adsorbents

4.2.1. Particle Size Distribution

Distribution of particle size was analyzed for the raw materials (flax shives and oat hulls), hydrochars, and steam activated hydrochars. The results summarized in Table 4.1 show that the volume median diameter of the treated flax shives and oat hulls were lower compared to those of the raw materials. It is noteworthy that there was a substantial precursor weight loss during the hydrothermal and steam activation process (yield in Table 4.2) which resulted in a general shift of particle size to smaller values. This shift was smaller in the HC process compared to steam activation process. Such results can be related to several factors which happened during the process such as dehydration, breakage of the fragile bonds, and decomposition of carbon materials, (Sun et al., 2016; Timur et al., 2006). During the steam activation process, the temperature increased to 850°C. The increase of the temperature caused further thermal decomposition of the hydrochars. According to literature, for cellulosic materials the weight loss at 220-315°C is due to hemicellulose decomposition, and that at 315-400°C is related to cellulose pyrolysis. Lignin decomposition usually take place in the range of 160-900°C (Huang, 2019). The results of SEM which has been reported in section (4.2.2) showed that more pores and fragmentation were seen for the steam activated hydrochars.

Hydrochar	median	volume mean	D (V, 0.9)**	D (V, 0.1)*	Hydrochar	median	volume mean	D (V, 0.9)**	D (V, 0.1)* um
	(<u>µm</u>)	dimeter (µm)	(µm)	(<u>um</u>)		(<u>um</u>)	dimeter (µm)	(µm)	
Raw Flax shives	1287	1618.5	2370	635	Raw Oat hulls	890	1236	2236	535
HC-H ₃ PO ₄ -6h	673	879	1461	78	HC-H ₃ PO ₄ -6h	354	546	940	17
HC-H ₃ PO ₄ -12h	248	754.2	968.06	16	HC-H ₃ PO ₄ -12h	253	409	726	12
Steam activated	median	volume mean	D (V, 0.9)	D (V, 0.1)	Steam activated	median	volume mean	D (V, 0.9)	D (V, 0.1) µm
hydrochar	(µm)	dimeter (µm)	(µm)	um	hydrochar	(um)	dimeter (µm)	(µm)	
SAHC-H ₃ PO ₄ -6h	368	556	853	36	SAHC-H ₃ PO ₄ -6h	274	477	800	22
SAHC-H ₃ PO ₄ -12h	382	505	859	34	SAHC-H ₃ PO ₄ -	221	352	712	21
					12h				

Table 4. 1 The particle size distribution of flax shive and oat hull hydrochars and steam activated hydrochars

*D (V,0.1): The portion of particles with diameters smaller than this value is 10%.

**D (V,0.9): The portion of particles with diameters below this value is 90%.

4.2.2. Porous Characteristics of Adsorbents

The porous characteristics of raw and thermochemically treated flax shives and oat hulls are summarized in Table 4.2. The applied thermal and chemical treatments produced hydrochars and steam activated hydrochars with various BET surface areas and pore volumes. It is seen that acid (H₃PO₄), base (NaOH), reaction time, and carbonization temperature played important roles in the HC process. As shown in Table 4.2, the surface areas of the flax shives based hydrochars ($2.0 \pm 0.9 - 16.5 \pm 0.2 \text{ m}^2/\text{g}$) were up to over ten times that of the raw material ($1.30 \pm 0.07 \text{ m}^2/\text{g}$). Similar results were obtained in the case of oat hulls. In addition, impregnation of the raw materials with the H₃PO₄ solution led to higher surface area and pore volume for the respective adsorbents in comparison with impregnation with the NaOH solution. The reason could be that NaOH is one of the strongest bases which could decompose the cellulosic materials easier and collapse most of the pore structure (Kucharska et al., 2018; Zheng et al., 2018). During the reaction, sodium hydroxide is dissociated into sodium ion (Na⁺) and hydroxide ion (OH⁻). Increasing the hydroxide ion concentration results in an increase in the rate of the hydrolysis (Kim et al., 2016; Modenbach, 2013). In the present work, NaOH with a high concentration of 1 M was used. It effectively

breaks the ether and ester bonds in the lignin-carbohydrate complexes, thus cleaves the linkage between lignin and hemicellulose (Kim et al., 2016). In addition, NaOH is effective for splitting the carbon-to-carbon and ester bonds in lignin molecules. It solubilizes hemicellulose and lignin significantly (SJÖSTRÖM, 1993). Thus in this work, the main lignocellulose structure of the materials was broken down in the presence of 1 M NaOH. In the case of 1 M H₃PO₄ solution, it is a weak acid. However, it effectively cleaves the linkage of lignin and hemicellulose along with reducing the cellulose crystallinity, leading in increasing the porosity under relatively mild conditions but without significantly destroying the main cellulosic structure (Siripong et al., 2016; Sathitsuksanoh et al., 2013). In addition, it helps to produce functional groups on the materials such as hydroxyls and carboxyls (Wan et al., 2019).

Though the BET surface areas of the hydrochars $(12.2-28.7 \text{ m}^2/\text{g})$ increased over ten times those of the raw materials $(0.21- 1.30 \text{ m}^2/\text{g})$, they were significantly lower compared with those of the steam activated hydrochars (527-793 m^2/g). The values of the surface area of hydrochars obtained in this work are similar to those reported in literature. For example, surface area of hydrochars prepared from sunflower stem was 21 m²/g, walnut shells 31 m²/g, and olive stone 22 m²/g (Román et al. (2013). In addition, Sevilla (2009) reported the surface area of hydrochars prepared from cellulose to be 30 m²/g. Moreover, the hydrochars developed from pinewood had a surface area of 21 m^2/g (Liu et al., 2010b). The reason could be due to the pore blockage leading to poor transportation of organic matters from the liquid phase during the HC process or the liquid phase compounds transferring to the surface of the hydrochars, as was discussed in the literature (Román et al., 2013). Furthermore, it was observed that the surface area of the hydrochar samples was slightly increased by increasing the reaction time from 6 to 12 h. In general, during a HC process, the longer reaction time can lead to higher pore volume, porosity, and surface area (Nizamuddin et al., 2017). The hydrochars made from flax shives and oat hulls impregnated with H₃PO₄ and thermally treated for 6 and 12 h with high surface areas were selected for further steam activation. The physical properties of steam activated hydrochars are also presented in Table 4.2.

Importantly, it was observed that after steam activation, the hydrochars had significantly higher BET surface area, micropores, and pore volumes. For example, as shown in Table 4.2, the BET surface area, micropores, and pore volume of the flax shives hydrochars impregnated with H_3PO_4 and thermally treated for 6 and 12 h are 12.2 and 16.5 m²/g, 0.1 and 0.2 m²/g, and 0.05 and 0.07 cm³/g, respectively. The respective values increased to 793 and 618 m²/g, 643 and 525 m²/g, and 2.57-2.53 cm³/g after the hydrochars were steam activated at 850°C. Similar results were achieved in the case of oat hulls. Significant amount of micropores were created through steam activation, thus the surface area increased. It is established that chemical impregnation, temperature, and residence time of thermal treatment plays important roles on the yields of hydrochars (Figure 4.1A) and oat hull hydrochars (Figure 4.1B). It was observed that the hydrochars impregnated with H_3PO_4 had higher yields than those impregnated with NaOH. This again could be because NaOH is a very strong base and decomposed the materials to a greater extent and caused more mass loss.



Figure 4. 1 Hydrochar yields of flax shives (A) and oat hulls (B).

Flax shives					Oat Hulls					
Chemical/thermal	BET Surface	Micropore area	Pore	Yield	Chemical/thermal	BET Surface	Micropore area	Pore	Yield	
treatment	area (m²/g)	(m ² /g)	volume	(%)	treatment	area (m ² /g)	(m ² /g)	volume	(%)	
			(cm ³ /g)					(cm ³ /g)		
Raw	$1.30 \pm$	-	-	-	Raw	0.21 ±	-	-	-	
	0.07**					0.09**				
HC-H ₃ PO ₄ -6h	12.2±0.2	0.1±0.1	0.05	61	HC-H ₃ PO ₄ -6h	21.1 ± 0.2	0.5 ± 0.1	0.15	53	
HC-H3PO4 -12h	16.5±0.2	0.2±0.2	0.07	54	HC-H ₃ PO ₄ -12h	28.7 ± 0.3	0.6 ± 0.2	0.18	48	
HC-NaOH-6h	2.0±0.9	-	0.01	16	HC-NaOH-6h	2.41 ± 0.01	-	0.001	9	
HC-NaOH-12h	8.9±0.1	-	0.04	14	HC-NaOH-12h	3.69 ± 0.04	-	0.003	9	
SAHC-H3PO4-6h	793±26	643.6±0.1	2.57	40*	SAHC-H ₃ PO ₄ -6h	527 ± 17	$428.3{\pm}0.2$	0.42	29*	
				(65**)					(54**)	
SAHC-H ₃ PO ₄ -12h	618±20	524.9±0.1	2.53	31*	SAHC-H ₃ PO ₄ -12h	602 ± 20	495.3 ±0.2	0.42	25*	
				(58**)					(51**)	

Table 4. 2 The surface properties and yields of raw and thermally treated flax shives and oat hulls.

Note: HC-H₃PO₄-6h and HC-H₃PO₄-12h: hydrochar (HC) thermally treated with H₃PO₄ for 6 and 12h

HC-NaOH-6h and HC-NaOH-12h: hydrochar thermally treated with NaOH for 6 and 12 h

SAHC-H₃PO₄-6h and SAHC-H₃PO₄-12h: steam-activated hydrochar thermally treated with H₃PO₄ for 6 and 12h

*: Yield for the combination of hydrothermal carbonization and steam-activation. **: Yield for the steam activation only.

** (Ghanbari and Niu, 2018; Ghanbari and Niu, 2019)
In addition, Figure 4.1 shows that the hydrochar yields slightly decreased as the temperature increased from 180 to 220°C. It is also noticeable that the hydrochar yields decreased more significantly in the first 6h, and then slowly decreased afterwards. This trend indicates that the major decomposition and transformation of the material structure took place during the first 6h, and then the structure became relatively stable under the tested conditions. With the increase in reaction time and/or temperature, different kinds of degradation reactions such as decarboxylation, dehydration and aromatization were enhanced, therefore the extent of carbonization of the material (flax shive) increased. This led to decrease in hydrochar yield (Anukam et al., 2015; Reza et al., 2014). Comparing the two precursors, flax shives had a higher yield than oat hulls. This may be associated with the fact that the former has higher cellulose (53%) and lignin (21%) content than the latter (37% and 7% respectively), which is discussed in the next section. It was observed that due to the difference in the carbonization process the yields of hydrochars are obviously higher than those of steam activated hydrochars (HC + steam activation) with a reference to the raw materials, as shown in Table 4.2. During steam activation, additional structures such as oxygen containing groups were further decomposed and aromatic structures were generated. More details can be found in Chapter 7 of this thesis.

4.2.3. FE-SEM Analysis

The FE-SEM images of raw flax shives and oat hulls, their hydrochars and steam activated hydrochars are shown in Figures 4.2-4.4. The results show that the HC and steam activation using different chemical treatments generated hydrochars and steam activated hydrochars with different surface structure. Figure 4.2A and Figure 4.3A show the images of raw flax shives and raw oat hulls which is consistent with that reported in literature showing the dense structure of raw materials containing cellulose, hemicellulose and lignin (Ghanbari & Niu, 2018).

After the flax shives and oat hulls were made into hydrochars, changes were observed on the surface of the hydrochar particles. According to the SEM images

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(Figure 4.2B-E (flax shives) and Figures 4.3B-E (oat hulls)), massive spherical microparticles are observed on the surfaces of all the hydrochars no matter whether they were impregnated with acid or base and thermally treated for 6 or 12h. The formation of these kinds of structure may be due to the decomposition of the materials during the HC process, and precipitation and growth of the residues as spheres. Similar phenomenon and discussion was reported on hydrochars produced from corn stover (Fuertes et al., 2010) and cellulose materials (Sevilla & Fuertes, 2009b).

Figure 4.4. shows the images of steam activated hydrochars made from flax shives and oat hulls impregnated with H₃PO₄. The pore structure of all the steam activated hydrochars is clearly visible and no significant microparticles are seen on the surfaces. By steam activation at 850°C, the microparticles seen on the surface of the hydrochars and additional components such as lignin in the hydrochars were further to well-developed porous degraded, leading structures. particularly micropore structure. Thus, the volume of pore and surface area of the steam activated hydrochars increased, as confirmed by the results shown in Table 4.1. The combination of the chemical and thermal treatment and steam activation developed more pores on the lignocellulose materials as a result of which resulted in further degradation (cellulose, hemicellulose and mainly lignin) (Bartkowiak & Zakrzewski, 2004). Overall, the results of SEM and surface properties shown in Table 4.1 demonstrated that the steam activated hydrochars had well developed porous structures.



Figure 4. 2 SEM images of raw and treated flax shives residues at 220°C (raw flax shives (A), HC-H₃PO₄ -6h (B), HC-H₃PO₄ -12h (C), HC-NaOH-6h (D), HC-NaOH-12h (E)).





Figure 4. 3 SEM images of raw and chemically-treated oat hull residues (hydrochars) at 220°C (raw (A), HC-H₃PO₄-6h (B), HC-H₃PO₄-12h (C), HC-NaOH-6h (D), NaOH-6h (E)).



Figure 4. 4 SEM images of steam activated hydrochars (Flax shives: SAHC-H₃PO₄- 6h (A) and SAHC-SAH₃PO₄ -12h (B); Oat hulls: SAHC-H₃PO₄ -6h (C) and SAHC-H₃PO₄ -12h (D)).

4.2.4. Proximate Analysis

Table 4.3 shows the proximate analysis of raw flax shive and oat hulls and their corresponding hydrochars and steam activated hydrochars. It is seen that raw flax shives and raw oat hulls have high volatile matter (72.2% and 69.6%) and low ash content (3.5% and 3.1%), which indicates that raw flax shive and oat hulls could be

promising materials for preparing carbon adsorbents. Such properties of other types of natural materials were also discussed by other researchers (Yorgun et al., 2009). In addition, it is noticeable that the volatile matter of the hydrochars reduced to the range of 46.6%-53.6%, and fixed carbon contents increased from 20.0-23.5% (raw materials) to 41.2-49.6%, showing that partial volatile matter was decomposed during the HC process at 220°C. However, the amount of volatile matters are still high indicating that the significant amounts of organic compounds such as cellulose, hemicellulose and lignin still remained in the hydrochars. After steam activation at 850°C, the steam activated hydrochars retained a lower volatile matter content at 7.3-8.6% and the main components are fixed carbon. In addition, the increase of percentage ash content in the steam activation at 850°C is related to the increased release of volatile matter and the increased consumption of fixed carbon (Martínez-Mendoza et al., 2020). It was also observed that the flax shives steam activated hydrochars had higher fixed carbon contents than oat hulls steam activated hydrochars, because raw flax shives contain higher amounts of cellulose and lignin. This could also be a reason that the yield of flax shive hydrochars are higher than that of oat hull hydrochars.

Flax shives				Oat hulls					
Chemical/thermal	Moisture	Volatile matter	Ash	Fixed	Chemical/ther	Moisture	Volatile	Ash	Fixed
treatment				carbon	mal treatment		matter		carbon
Raw flax shives	4.3	72.2	3.5	20.0	Raw oat hulls	3.8	69.6	3.1	23.5
HC-H ₃ PO ₄ -6h	2.0	53.6	3.2	41.2	HC-H ₃ PO ₄ -6h	1.6	50.7	2.6	45.1
HC-H ₃ PO ₄ -12h	1.9	51.8	2.6	43.7	HC-H ₃ PO ₄ -12h	1.4	47.5	2.3	48.8
HC-NaOH-6h	1.8	52.5	2.9	42.8	HC-NaOH-6h	1.5	47.1	2.3	49.2
HC-NaOH-12h	1.5	49.1	2.3	47.1	HC-NaOH-12h	1.1	46.6	1.9	49.6
SAHC-H ₃ PO ₄ -6h	3.0	8.6	40.1	48.3	SAHC-H ₃ PO ₄ -6h	1.5	8.3	41.6	43.3
SAHC-H ₃ PO ₄ -12h	2.3	7.3	39.6	50.8	SAHC-H ₃ PO ₄ -12h	1.4	7.8	40.1	46.5

Table 4. 3 The proximate analysis of raw flax shives and oat hulls, hydrochars, and steam activated hydrochars (dry base wt.%).

4.2.5 Contents of C, H, N, and S

The contents of C, H, N, and S of the raw biomasses and their derived hydrochars and steam activated hydrochars are reported in Table 4.4. The results show that carbon is one of the major elements in raw flax shives and oat hulls. The carbon contents of flax shives (46%) and oat hulls (44%) are similar. These values increased in the hydrochars treated with H₃PO₄ to about 68 wt% and 65 wt%, while remained similar in the hydrochars treated with NaOH (about 48 wt% and 45 wt%). Another major element was identified to be oxygen, which was about 47 wt% in raw flax shives and 49 wt% in raw oat hulls. The values decreased to about 27 wt% and 31 wt% in the respective hydrochars treated with H₃PO₄, and again remained constant (about 47 wt% and 49 wt%) in the hydrochars treated with NaOH. It is to note that contents of inorganics often present in regular biomass-derived material were not considered for the contents of oxygen, which were not directly measured by the CHNS/O equipment.

H₃PO₄ was an effective chemical to facilitate carbonization during the HC process. NaOH was a very strong base which may decompose the carbon structure of the materials to a greater

extent and convert them into CO_2 and H_2O , and additional gases. As a result, the carbon content in the hydrochars does not show an obvious increase. This can also be confirmed by the fact that the hydrochars treated with NaOH is very fragile. As a result, they were not chosen to further go through steam activation. In addition, the results in Table 4.4 shows that during the steam activation process, the carbon content of the hydrochars treated with H₃PO₄ further increased to about 94% and 80% for flax shives and oat hulls respectively. Besides, oxygen contents decreased to about 1.1 wt% and 15 wt%, respectively. Steam activation is one of the commonly used processes for producing steam activated carbon with high pore volumes and large porosity (Zbair et al., 2018; Fu et al., 2011). Furthermore, it was noticed that there was a slightly higher carbon content in the case of flax shives. This may be because flax shives contain larger amounts of cellulose (53%) and lignin (21%) than oat hulls (cellulose 37% and lignin 7%).

Sulfur (S) and nitrogen (N) contents were very low in the hydrochars (Table 4.4) as the major components in raw flax shives and raw oat hulls are cellulose, hemicellulose and lignin which do not contain S and N. The low amounts may be from the small amounts of proteins or other components in the raw materials which contain S and N. In the HC process, the contents of S and N further decreased, because nitrogen and sulfur oxides were formed during the hydrothermal process, which were dissolved in the process liquid (Lin et al., 2015; He et al., 2013). It is noted that that the hydrothermal reaction time (6h and 12h) didn't have significant effect on the carbon content during the carbonization. This is because the major carbon conversion occurred within the first 6 h during the HC process.

The atomic molar ratios of H/C were also calculated using the elemental composition data and shown in Table 4.4. The molar ratio of H/C can be an index of aromaticity or carbonization (Bogusz et al., 2015). After HC, the ratio of H/C of the hydrochars was decreased in comparison with that of the raw materials, indicating that hydrochars may contain more aromatic carbon than the raw biomass. This is because dehydration and decarboxylation during the HC process cause formation of aromatic carbon in the product (He et al., 2016). In addition, after steam activation at 850°C, the ratios of H/C of the steam activated hydrochars (SACH-H₃PO₄-6h and SAHC-H₃PO₄-

12h) further decreased, which indicated the formation of a higher degree of carbonaceous and aromatic structure (Heidari et al., 2019).

Adsorbents	Elemental composition (wt %)					Atomic ratio	
Flax shives							
	C (%)	H (%)	N (%)	S (%)	O (%)	H/C	
Raw flax shive	46.57 ± 0.31	5.77 ± 0.56	0.48 ± 0.42	0.28	46.9 ± 0.41	1.48	
HC-H ₃ PO ₄ -6hr	67.66 ± 0.33	3.94 ± 0.69	0.47 ± 0.01	0.04	27.72 ± 0.59	0.65	
HC-H3PO4 -12h	68.13 ± 0.03	3.28 ± 0.76	0.48 ± 0.01	0.04	26.18 ± 0.73	0.71	
HC-NaOH-6h	47.79 ± 0.66	5.95 ± 0.07	0.09 ± 0.07	0.04	46.10 ± 0.58	1.49	
HC-NaOH-6hr	47.50 ± 0.36	5.69 ± 0.23	0.14 ± 0.23	0.10	46.55 ± 0.35	1.43	
SAHC-H ₃ PO ₄ -6h*	94.54 ± 0.11	3.65 ± 0.01	0.41	0.012	1.14	0.45	
SAHC-H ₃ PO ₄ 12h*	94.28 ± 0.37	3.49 ± 0.09	0.44	0.036	1.31	0.42	
		Oa	t hulls				
Raw oat hulls	43.5 ±0.01	5.41 ±0.02	1.47	0.76 ±0.03	48.84 ±0.09	1.49	
			±0.03				
HC-H ₃ PO ₄ -6hr	63.55 ± 0.08	3.92 ±0.01	0.77	0.04	31.70 ±0.09	0.74	
HC-H ₃ PO ₄ -12h	64.58 ± 0.05	4.55 ±0.02	0.66	0.05	30.14 ±0.05	0.84	
HC-NaOH-6hr	44.79 ± 0.08	5.79 ±0.08	0.04	0.04	49.33 ±0.16	1.55	
HC-NaOH-12hr	44.49 ± 0.21	5.64 ±0.02	0.18	0.05	49.62 ±0.24	1.52	
SAHC-H ₃ PO ₄ -6h	80.65 ± 0.24	3.78 ±0.02	0.42	0.58	14.55 ±0.2	0.56	
SAHC-H ₃ PO ₄ -12h	80.15 ± 0.02	3.70 ±0.03	0.48	0.04	15.63 ±0.01	0.55	

* The maximum standard deviation is lower than 0.01 for the data of which standard deviation is not listed in the above table.

4.3. Chapter Summary

In this chapter flax shives and oat hulls representative of agricultural by-products were used to develop hydrochars and steam activated hydrochar adsorbents. The adsorbents were characterized by surface properties and composition.

Hydrothermal carbonization slightly enhanced the surface area of raw flax shives and raw oat hulls. Steam-activation was effective in creating pore structure and generating high internal surface area. Hydrothermal treatment at a relatively low temperature, such as 220°C, slightly increased the carbon content and decreased the ratio of H/C of the flax shive and oat hull based adsorbents while the impact of steam activation in the above mentioned respects is significantly higher. In addition, it is noticeable that chemical impregnation, temperature and residence time of thermal treatment played important roles on the yields of hydrochars. H₃PO₄ was an effective chemical to facilitate carbonization during the HC process. The hydrochars and steam activated hydrochars had different elemental compositions in addition to their difference in surface area, which led in difference in CBZ adsorption capacity that is discussed in the following chapters.

CHAPTER 5 CARBAMAZEPINE ADSORPTION EQUILIBRIUM AND ISOTHERM MODELING

Contribution of this chapter to overall Ph.D. work

In this chapter, flax shive and oat hull based hydrochars and steam activated hydrochars adsorbents were used to adsorb carbamazepine (CBZ) as a model pharmaceutical pollutant from artificially contaminated water. CBZ adsorption equilibrium was investigated at various temperatures (20-40°C) and solution pH (2-10). The adsorption capacity of hydrochars and steam activated hydrochars made from either flax shives or oat hulls were compared with the raw materials and numerous adsorbents reported in the literature. The CBZ adsorption isotherms were generated by experiments and further analyzed by the Sips model. The results and data provided in this chapter are essential for further analysis of energetics, thermodynamics and mechanisms of CBZ adsorption in the following chapters of this thesis.

5.1. Effects of Key Operation Parameters on the Adsorption Capacity of CBZ

5.1.1. Effect of Temperature

5.1.1.1. Hydrochars

In order to determine the effect of temperature (20-40°C) on the capacity of CBZ adsorption by the hydrochars produced from flax shives and oat hulls, adsorption studies were conducted at the pH of 6.0 ± 0.2 with an initial CBZ concentration of 50 mg/L. Figure 5.1 shows the CBZ adsorption capacity achieved at 20, 30, and 40°C. The results demonstrated that adsorption capacity of CBZ by all the hydrochars was noticeably enhanced as the temperature was increased from 20 to 40°C indicating the CBZ adsorption is endothermic. In addition, the hydrochars impregnated with 1 M H₃PO₄ demonstrated higher CBZ adsorption capacity than those impregnated with 1 M NaOH which was a very strong base and may significantly degrade the functional groups such as hydroxyls and carboxyls.



Figure 5. 1 Impact of of temperature on the adsoprtion capacity (qe) of CBZ by hydrochars made from flax shives (A) and oat hulls (B) (concentration 50 mg/L, adsorbent dosage 5.0 ± 0.1 mg, initial pH 6.0 \pm 0.2, 48 h for flax shives and 72 h for oat hulls pretreated with H₃PO₄ and 24 hours for oat hulls pretreated with NaOH hydrochars).

At the tested experimental conditions, the hydrochars obtained by thermal treatment for 6 h shows slightly higher CBZ adsorption capacity than those treated for 12 h. At longer times, a portion of functional groups could be decomposed, indicating 6 h treatment was more suitable.

It is noted that although the BET surface area and total pore volume of the hydrochars were low compared with those of steam activation hydrochars as shown in Figure 5.1, the hydrochars based on either flax shvies or oat hulls demonstrated effective CBZ adsorption capacity up to around 47 mg/g. The results indicated that CBZ adsorption may not be only associated with surface area but also functional groups of the surface of hydrochar. The major adsorption mechanism between the aromatic structures of adsorbents and organic compound was considered to be π - π EDA interaction (Tang et al., 2018).

5.1.1.2. Steam Activated Hydrochars

The effects of temperature (20-40°C) on the adsorption of CBZ by steam activated hydrochars (SAHC-H₃PO₄-6h and SAHC-H₃PO₄-12h) made from flax shive and oat hulls were investigated by operating the CBZ adsorption experiments with an initial concentration of 50 mg/L at pH 6.0 \pm 0.2 for 2 h sufficient for achieving equilibrium. The adsorption capacity of CBZ is shown in Figure 5.2. Importantly, the results show that the steam activated hydrochars had significantly higher values of adsorption capacity than (almost double) the hydrochars without steam activation. In addition, it is noticeable that the adsorption temperature within 20 to 40°C did not have an important effect on CBZ adsorption capacity on steam activated hydrochars in comparison with that on hydrochars at similar test conditions (initial CBZ concentration of 50 mg/L and pH 6.0 \pm 0.2). This result could be important for the technology to be applied in industrial water treatment process.



Figure 5. 2 Impact of temperature on the adsorption capacity of CBZ by steam activated hydrochars developed from (A) flax shives and (B) oat hulls (initial CBZ concentration ~50 mg/L, adsorbent dosage 5.0 ± 0.1 mg, initial pH 6.0 ± 0.2 and 2 h).

However, the result does not provide information on whether temperature has a significant impact on the adsorption capacity at CBZ concentrations other than the current tested one. Thus, investigation of the CBZ adsorption isotherms is essential and presented in later sections of this chapter.

5.1.2. Impact of Solution pH

pH is a significant parameter in ion adsorption from aqueous solution. This parameter may also affect the adsorption mechanism of pharmaceuticals via its effect on ionization degree of pharmaceuticals (adsorbate) and charge of adsorbent functional groups (Aghababaei et al., 2017; Ncibi and Sillanpaa 2015). To investigate the effect of solution pH, the hydrochars treated with H₃PO₄ and their steam activated products demonstrating higher adsorption capacities were selected for the experiments. The CBZ adsorption capacities versus equilibrium pH are presented in Figures 5.3 (flax shives) and 5.4 (oat hulls). It is noticeable that the CBZ adsorption capacity of either the hydrochars or the steam activated hydrochars did not change significantly at the wide pH ranges of 2-10, though it is slightly higher at pH 6. Figure 5.3 shows that at pH6, the hydrochars and the steam activated hydrochars have adsorption capacities up to around 47 and 98 mg/g, respectively. Similarly, the oat hull based hydrochars and steam activated hydrochars had values up to 50 and 99 mg/g, respectively.



Figure 5. 3 Impact of pH on the adsorption capacity of CBZ with flax shive adsorbents, (A) hydrochars (initial CBZ concentration 50 mg/L, adsorbent dosage 5.0 ± 0.1 mg , 48h and 40 ± 2 °C); (B) Steam activated hydrochars (initial CBZ concentration 50 mg/L, adsorbent dosage 5.0 ± 0.1 mg, 2h and 20 ± 2 °C).



Figure 5. 4 Influence of pH on the adsorption capacity of CBZ with oat hulls adsorbents (A) Hydrochars (initial CBZ concentration 50 mg/L, adsorbent dosage 5.0 ± 0.1 mg, 48h and 40 ± 2°C); (B) Steam activated hydrochars (initial CBZ concentration 50 mg/L, adsorbent dosage 5.0 ± 0.1 mg, 2h and 20 ± 2°C).

It is to note that by increasing pH from 2 to 6, the adsorption capacity of CBZ slightly increased then it gradually decreased beyond pH of 6 up to 10. Similar trend was observed on adsorption of CBZ on carbon nanotubes and graphene (Liu et al., 2014), multi-walled carbon nanotubes and mesoporous activated carbons (Ncibi, et al., 2017), pine-wood derived nanobiochar (Naghdi et al., 2016), and activated biochar derived from pomelo peel (Chen et al., 2017).

In this research, although there was a slight change in the adsorption capacity of hydrochars and steam activated hydrochars by changing the pH from 2 to 10, this change was small. This finding suggests that the hydrochars and the steam activated hydrochars developed from flax shives and oat hulls in this work are applicable to treat water or wastewater contaminated by CBZ at a wide range of pH.

5.1.2.1. Determination of Point of Zero Net Charge (PZNC)

It is known that surface charge of solid particles (adsorbent) usually results from deprotonation and protonation of their functional groups, which leads to form an electrical double layer in the solution surrounding the surface (Hunter, 1981). Thus, zeta potential of raw flax shive and oat hull materials, their hydrochars and steam activated hydrochars was measured at pH 2-10 to help understanding the surface charge of the adsorbents. The results are presented in Figures 5.5 and 5.6. The surface charge of the raw flax shives and oat hulls, and their hydrochars and steam activated hydrochars were around zero at pH 3-4. When solution pH is lower than the point of charge (PZNC), adsorbent surface is charged positively with protons. zero net However, when solution pH is higher than the value of PZNC, adsorbent surface has negative charge through deprotonation. Therefore, surface charge of the hydrochars or the steam activated hydrochars was positive at pH < 3, otherwise was negative at pH > 3According to the results shown before, by increasing pH from 2 to 6 the CBZ 4. adsorption capacity slightly increased followed by a slight decrease in the pH range of 6 to 10. Possible adsorption mechanisms are discussed as bellow.

Table 3.1 shows the two pKa values of CBZ, being 2.3 (carbonyl group) and 13.9 (amino group), indicating the compound is in its zwitterionic forms at pH 2-10 (Punyapalakul & Sitthisorn, 2010). When the solution pH is lower than this range (pH2.3-13.9), CBZ is mostly in the form of its cationic, while above the range it is in its anionic form (Punyapalakul & Sitthisorn, 2010). Considering this aspect and the charge state of the adsorbents described above, the following analysis of the pH effect was proposed. When pH was increased from 2 to 6, CBZ molecules exhibited overall positive charge but with a reducing trend, and the charge of the hydrochars changed from positive to negative. As such, electrostatic repulsion reduced and attraction increased, thus CBZ adsorption capacity slightly increased. But when pH was continuously increased from 6-10, more hydroxides existed in the solution, which can compete with the negatively charged adsorbent surface for the positive charged CBZ. As a result, the CBZ adsorption capacity gradually reduced. Overall, it can be said that in the investigated pH range (2 to 10), the electrostatic attraction between CBZ molecules and the charged adsorbents was insignificant because the adsorption capacity of CBZ did not change significantly. This was also observed in other works (Chen et al., 2017; Nghiem et al., 2005). In the present case, the pH effect on adsorption of CBZ under the tested experimental conditions were minor and electrostatic interaction is insignificant. CBZ adsorption by hydrochars and steam activated hydrochars were mostly associated with π - π EDA interactions, hydrophobic attraction, and hydrogen bonding (Chen et al., 2017). More details related to the mechanism is discussed in Chapter 7.



Figure 5. 5 Impact of pH on the zeta potential of selected raw and treated hydrochars (A) and steam activated hydrochars, (B) produced from flax shive.



Figure 5. 6 Impact of pH on the zeta potential of selected raw and treated hydrochars (A) and steam activated hydrochars, (B) produced from oat hull.

5.1.3. Effect of Treatment of Adsorbents

To evaluate the impact of the hydrothermal process and steam activation on CBZ adsorption capacity, isotherms of raw flax shives and raw oat hulls, and their hydrochars treated with H₃PO₄ and their steam activated products were generated. The isotherms are presented in Figure 5.7 (flax shives) and Figure 5.8 (oat hulls). It is noticeable that the hydrochars had an adsorption capacity up to 500% higher than that of either the raw oat hulls or raw flax shives. Besides, the capacity increased up to 1100% in the case of the steam activated hydrochars. This could be a result of significantly enhanced precursor porosity and formation of functional groups on the adsorbents surface through the treatment methods. Similar observation was reported by other researchers who treated lignocellulose raw materials with phosphoric acid and subsequently with heat (Yan and Niu 2017; Sych et al., 2012). Overall, the treatment methods used in this work successfully enhanced the CBZ adsorption capacity.



Figure 5. 7 Adsorption isotherms of CBZ on flax shive hydrochars treated with H_3PO_4 in comparison with raw flax shives. (A) Before steam activation and (B) After steam activation (adsorbent dosage 5.0 ± 0.1 mg, pH 6.0 ± 0.2 , and $40 \pm 2^{\circ}C$ for the HC and $20 \pm 2^{\circ}C$ for the SAHC).



Figure 5. 8 Adsorption isotherms of CBZ on oat hull hydrochars treated with H₃PO₄ in comparison with raw oat hulls. A) Before steam activation and B) After steam activation (adsorbent dosage 5.0 ± 0.1 mg, pH 6.0 ± 0.2 , and $40 \pm 2^{\circ}$ C for the HC and $20 \pm 2^{\circ}$ C for the SAHC).

In addition, it is noticeable that among the adsorbents developed from flax shives, the steam activated hydrochars treated with H_3PO_4 for 6h (SAHC- H_3PO_4 -6h) had the highest adsorption capacity, while in the case of oat hulls the steam activated hydrochars treated with H_3PO_4 for 12h (SAHC- H_3PO_4 -12h) demonstrated the slightly higher adsorption uptake. Therefore, the two adsorbents were selected for further investigation on adsorption isotherm at various temperature and modelling.

5.2. Adsorption Isotherm and Modelling

The equilibrium data of CBZ adsorption on the steam activated hydrochars are experimentally generated at 20-40°C, pH 6.0±0.2, and various CBZ concentrations.

The experimental results are presented in data points in Figure 5.9A for the adsorbents developed from flax shives and in Figure 5.9B for those developed from oat hulls. It can be seen in both cases that CBZ adsorption capacity increased when temperature was increased from 20 to 40°C, again showing the adsorption was endothermic. In addition, the CBZ adsorption capacity gradually increased as equilibrium CBZ concentration in the solution increases till reaching a plateau. Considering the nature of the isotherms and the heterogeneity of the surface of the adsorbents, the Sips model was selected to simulate the isotherms (Do, 1998). The details of the model simulation are presented below.

5.2.1. Sips Model

The Sips model combines Langmuir and Freundlich type isotherms and has been used to describe heterogeneous surfaces such as the adsorption of NOR on reduced graphene oxide (Tang et al., 2013), adsorption of enrofloxacin and ofloxacin on bamboo biochar (Wang et al., 2015), adsorption of sulfamethoxazole on carboxylic-functionalized carbon nanotubes (Lan et al., 2016), adsorption of ciprofloxacin on activated carbon and carbon xerogel (Carabineiro et al., 2012), and adsorption of levofloxacin on adsorbents based on barley straw (Yan & Niu, 2018). The Sips model reduces to the Freundlich isotherm at low adsorbate concentrations and becomes the Langmuir isotherm at high adsorbate concentrations (Ahmed & Dhedan, 2012).

The model is written as follows:

$$q_e = q_m \frac{(K_s C_e)^n}{1 + (K_s C_e)^n}$$
(5.1)

where q_e represents the equilibrium uptake (mg/g), and q_m denotes the maximum adsorption capacity (mg/g). C_e is the equilibrium concentration of the solute in the bulk solution (mg/L), K_S (L/mg) is the equilibrium constant of adsorption and the parameter of n describes the surface heterogeneity. To avoid the asymmetrical errors caused by linearizing the model (Ncibi, 2008), the Sips model in non-linear form was used in this work. As such, the model parameters were determined by non-linear model regression.

The adsorption isotherms simulated by the Sips model are depicted in lines in Figure 5.9 and the modeling results are presented in Table 5.1. The results demonstrated that the Sips model satisfactorily simulated the CBZ adsorption isotherms of both flax shive and oat hull steam activated hydrochars with the coefficients of determination R^2 of 0.92 - 0.96. It is reported that the n value in the Sips model describes the surface site heterogeneity of adsorbent. A value of n lower than 1 indicates that the adsorbent surface is heterogeneous (Ishiguro and Koopal, 2011; Cerofolini and Rudzinski, 1997). The values of n obtained in this work are 0.47 (flax shives) and 0.93 (oat hulls), which are consistent with the fact that the steam activated hydrochars made from the natural material flax shives and oat hulls containing multiple components had heterogeneous surfaces. Since the range of the tested temperatures is relatively small, the q_m and n values were similar at all three temperatures. Similar results were obtained in the work on activated carbon (Yang et al., 2016).

Model parameters	Flax shives			Oat hulls			
	Tem	peratur	e (°C)	Tem	peratur	e (°C)	
	20	30	40	20	30	40	
$q_m (\mathrm{mg/g})$	293.5	293.5	293.5	162.6	162.€	162.6	
K_{S} (L/mg)	0.11	0.50	0.99	0.20	1.28	1.57	
n (-)	0.47	0.47	0.47	0.93	0.93	0.93	
R^2	0.95	0.96	0.92	0.98	0.95	0.98	
$RSS \ ((mg/g)^2)$	993	895	2527	288	821	259	

Table 5. 1 The Sips modelling results of CBZ adsorption on steam activated hydrochars

RSS: Residual sum of squares, calculated as $\Sigma (qe-qcal)^2$

In addition, the value of q_m of the steam activated hydrochars developed from flax shives is much higher than that of the one developed from oat hulls, indicating the former had more adsorption sites. The values of equilibrium constant K_s increased as the temperature increased from 20 to 40°C, again showing an endothermic process of the CBZ adsorption on the steam activated hydrochars. Increase of K_s value at a higher temperature is because of increase in interactions between the adsorbent and the adsorbate (Kapoor & Viraraghavan, 1997). In addition, the values of K_s in the case of flax shives are lower than those in the case of oat hulls, indicating that the interaction between the surface of the former adsorbent and CBZ is weaker. It was considered that antibiotic adsorption by activated carbons or chars could be through π - π interaction which could be enhanced at higher temperature (Yan, 2017). Furthermore, the K_s values (0.11- 0.2) obtained at room temperature in this work are higher than that obtained for levofloxacin adsorption by pretreated barley straw (0.07 L/mg) at similar conditions (Bei Yan, 2017), indicating a slightly stronger binding between the steam activated hydrochars and CBZ.



Figure 5. 9 CBZ adsorption isotherms of steam activated hydrochars at different temperatures, developed (A) from flax shives treated with H₃PO₄ for 6h, (B) from oat hulls treated with H₃PO₄ for 12h (10.0 \pm 0.5 mL CBZ solution, adsorbent dosage 5.0 \pm 0.1 mg, pH 6.0 \pm 0.2). Simulation was done by the Sips model. The dash lines present the model simulation and the symbols present the experimental data points.

5.3. Comparison of CBZ Adsorption Capacity of Various Adsorbents

The maximum CBZ adsorption capacities obtained in this work were compared with those reported in literature. The comparison data are shown in Table 5.2.

Adsorbents	Maximum capacity	Temperature	References
	(mg/g)	(K)	
MWCNTs (10–20 nm outer diameters)	441.4	296	(Oleszczuk et al., 2009)
AC from peach stones	335	303	(Torrellas et al., 2015)
MWCNTs	224.6	318	(Ncibi et al., 2017)
Meso-AC1	191.5	318	(Ncibi et al., 2017)
Magnetic nanocomposite of activated carbon (Fe ₃ O ₄ /C)	182.9	298	(Baghdadi et al., 2016)
Bentonite clay	134.2	291	(Çalişkan et al., 2014)
Single-walled CNT	130	-	(Lerman et al., 2013)
Pine-wood nanobiochar	116	298	(Naghdi et al., 2016)
Synthetic zeolite	100	298	(Martucci et al., 2012)
Amberlite XAD-7 resin	98.6	293	(Domínguez et al., 2011)
Rice straw	65.8	301	(Liu et al., 2013)
Activated carbon (AC)/Fe ₃ O ₄	45.3	303	(Shan et al., 2016)
Expanded graphite	43.5	Room Temp	(Borisova et al., 2013)
MOF-derived magnetic porous carbon	37.9	298	(Chen et al., 2017a)
Sewage sludge/fish waste	37.2	303	(Nielsen, et al., 2015)
Raw flax shives	16.5	313	This work
Flax shive -HC-H ₃ PO ₄ -6h	81.8	313	This work
Flax shive -SAHC-H ₃ PO ₄ -6h	293.5	293-313	This work
Raw oat hulls	14.5	313	This work
Oat hull -HC-H ₃ PO ₄ -12h	75.3	313	This work
Oat hull- SAHC-H ₃ PO ₄ -12h	162.6	293-313	This work

Table 5. 2 Comparative analysis for the removal of CBZ using various adsorbents.

The data shown in Table 5.2 demonstrated that both the hydrochars and activated hydrochars developed from flax shives and oat hulls in this work have higher adsorption capacities than numerous adsorbents reported in literature. Particularly, the steam activated hydrochars developed form both flax shives and oat hulls in this work have adsorption capacities higher than most of the adsorbents listed in Table 5.2 except for Multi-walled Carbon Nanotubes (MWCNTs, 10-20 nm outer diameters), and MWCNTs. In general, the production costs of carbon nanotube are high. The hydrochars and steam activated hydrochars made from flax shives and oat hulls are promising for adsorption of CBZ and similar pharmaceutical pollutants from contaminated water. In addition, in order to assess the capability of the adsorbents to adsorb CBZ at a low concentration, the steam activated hydrochars which had higher adsorption capacity, flax shive-SAHC-H₃PO₄-12h, were selected. The initial CBZ concentration was about 1 ppm chosen based on the detection limit of the HPLC available to this research work.

Table 5. 3 CBZ uptake by flax shive based steam activated hydrochars (SAHC-H₃PO₄-6h and SAHC-H₃PO₄-12h) from 1 ppm CBZ aqueous solution.

Bioadsorbent	2 h	4 h	6 h
SAHC-H ₃ PO ₄ -6h	0.20 (mg/g)	0.26 (mg/g)	0.28 (mg/g)
SAHC-H ₃ PO ₄ -12h	0.55 (mg/g)	0.61 (mg/g)	0.63 (mg/g)



Figure 5. 10 Removal efficiency of carbamazepine onto flax shive steam activated hydrochars (SAHC-H₃PO₄-6h and SAHC-H₃PO₄-12h) (CBZ concentration 1 mg/L, 5.0 ± 0.1 mg adsorbent , pH 5.8-6 and 20°C, rotational speed 220 rpm).

The results are shown in Table 5.3 and Figure 5.10. It can be seen that even the CBZ concentration was lowered to 1 ppm, the adsorbents were able to adsorb CBZ with a removal efficiency up to 32.47% and 14.43% for SAHC-H₃PO₄-12h and SAHC-H₃PO₄-6h, respectively. In addition, the obtained uptake of CBZ was up to 0.63 mg/g, which is still higher than that of mesoporous silica SBA-15 with a maximum adsorption capacity of 0.16 mg/g reported in literature (Bui & Choi, 2009).

In addition, in order to study the effect of different batches on the adsorption uptake, the steam activated hydrochars and hydrochars prepared from flax shives and oat hulls under the same conditions were compared for the CBZ removal. According to the results presented in Table 5.4, the difference of CBZ uptake at the same conditions by either hydrochars or steam activated hydrochars from different batches of same feedstocks was insignificant. More investigation in the regards could be done in the future.

Table 5. 4 CBZ uptake by flax shive and oat hull steam activated hydrochars and hydrochars from different batches (Initial CBZ concentration for both steam activated hydrochars and hydrochars 50 mg/L, adsorben<u>t</u> dosage 5 mg, initial pH 6.0±0.2, 20°C, 2 h for steam activated hydrochars both flax shives and oat hulls, 20°C and 48 h, 72 h for flax shive hydrochars and oat hull hydrochars respectively.).

Bioadsorbent	q _e (mg/g)			
	Flax shives			
Year	2016	2017		
HC-H ₃ PO ₄ -6h	43.96 (mg/g)	46.85 (mg/g)		
SAHC-H ₃ PO ₄ -6h	96.44 (mg/g)	97.94 (mg/g)		
	Oa	t hulls		
Year	2016	2017		
HC-H ₃ PO ₄ -12h	39.17 (mg/g)	40.98 (mg/g)		
SAHC-H ₃ PO ₄ -12h	92.72 (mg/g)	93.14 (mg/g)		

5.4. Chapter Summary

Based on the results obtained from this chapter, the following aspects are summarized.

Both hydrochars and steam-activated hydrochars developed from either flax shives or oat hulls were effective for adsorption of CBZ though their surface areas are significantly different. CBZ adsorption was dependent on not only surface area but also the functional groups on the surface of adsorbents. The steam activated hydrochars treated with H_3PO_4 demonstrated higher CBZ adsorption capacity than the hydrochars and the raw materials under the same tested conditions.

In addition, at room temperature, both the hydrochars and steam-activated hydrochars demonstrated effective CBZ adsorption. This is important for application of the adsorbents in practical water treatment. Furthermore, the CBZ adsorption capacity of steam activated hydrochars increased with an increase of temperature from 20°C to 40°C, indicating the endothermic adsorption.

CBZ adsorption capacity was high at a wide pH range (2-10), though was slightly higher at pH 6. The effect of pH (2-10) was not significant. This is favored in treating water/wastewater at a wide pH range. The results also indicate that the adsorption mechanism is not mainly through electrostatic attraction between oppositely charged CBZ and the adsorbents. Other mechanisms such as π - π interaction, hydrophobic, and hydrogen bonding may play roles in the adsorption. More details on elucidation of the adsorption mechanisms was done in Chapter 7 of this thesis.

The Sips model successfully simulated the CBZ adsorption isotherms of steam activated hydrochars developed from flax shives and oat hulls. The achieved adsorption capacities of hydrochars and steam activated hydrochars at the tested conditions were high compared with numerous adsorbents reported in the literature. In addition, steam activated hydrochars were able adsorb CBZ from a low concentration such as 1 ppm. The uptake was higher than mesoporous silica SBA-15 reported in literature. Adsorption in lower CBZ concentration such as ng/L or $\mu g/L$ observed in water bodies needs to be done in the future research.

CHAPTER 6 ADSORPTION SITE ENERGY DISTRIBUATION AND THERMODYNAMIC PARAMETERS

Contribution of this chapter to overall Ph.D. work

This chapter presents energetic characteristics of CBZ adsorption which are important to understand the fundamentals of the adsorption. Specifically, approximate site energy and its distribution of CBZ adsorption based on the Sips modeling results were determined. The weighed mean of site energy distribution was further calculated to evaluate the effect of adsorption temperature. Moreover, the thermodynamic parameters of CBZ adsorption were determined. The results presented in this chapter provide important information to elucidate the mechanism of CBZ adsorption on the adsorbents.

6.1. Approximate Site Energy and its Distribution

`In general, site energy distribution of an adsorbent with a heterogeneous surface is relevant to equilibrium adsorption. This is described by Eq. (6.1) below (Yan and Niu 2017; Shen et al., 2015;Carter et al., 1995).

$$q_e(C_e) = \int_0^{+\infty} q_h(E, C_e) F(E) dE$$
(6.1)

The above equation shows that the overall equilibrium adsorption of q_e of an adsorbate on a heterogeneous surface is determined by the integral of a local homogeneous isotherm of adsorption represented by $q_h(E, C_e)$ multiplied with the site energy distribution, F(E). Change of sorption energies between the adsorbent and adsorbate is represented by E. According to the literature, the limits of E in the integral is usually set from zero to infinity (Yan & Niu, 2017). The Cerofolini approximation was used considering the complexity of determination of site energy distribution. Accordingly, the relationship between the concentration of the adsorbate in the liquid phase at equilibrium (*Ce*) and the energy of adsorption (*E*) is as follows (Cerofolini, 1974).

$$C_e = C_s exp(-\frac{E-E_s}{RT}) \tag{6.2}$$

Then,

$$C_e = C_s exp(-\frac{E^*}{RT}) \tag{6.3}$$

where $E^* = E - Es$.

Then, it was calculated by the following equation.

$$E^* = -RT\ln(C_e/C_s) \tag{6.4}$$

where *Cs* is solubility of adsorbate in liquid phase. *R* represents the universal gas constant, and T denotes the absolute temperature (K). *Es* shows the adsorption energy when *Ce* equals *Cs*. It is also the lowest sorption energy (Yan and Niu 2017; Derylo-Marczewska et al., 1984). The value of E^* represents the difference of sorption energies between *E* and the point of reference *E_s*. It is calculated by inputting the known values of *C_s* and *C_e* into Eq. (6.3).

When Eq. (6.3) is incorporated into the Sips model Eq. (6.1), $q_e(C_e)$ is presented in terms of E^* , $q_e(E^*)$.

Then the site energy distribution can be obtained by differentiation of the isotherm as shown in Eq. (6.5),

$$F(E^*) = \frac{-dqe(E^*)}{dE}$$
(6.5)

The final equation is obtained as follows:

$$F(E^*) = \frac{q_m \, nb \, c_s^n \, e^{\frac{-nE^*}{RT}}}{RT (1+b \, c_s^n e^{\frac{-nE^*}{RT}})^2} \tag{6.6}$$

where *b* represents Ks^n . Then Eq. (6.6) was used to calculate approximate site energy distribution $F(E^*)$ of CBZ adsorption on the adsorbents. Integration of the distribution represents the maximum adsorption capacity q_m :

$$\int_{0}^{+\infty} F(E^{*}) dE = q_{m} \tag{6.7}$$

It was reported that weighted mean of site energy distribution can depict interaction strength between adsorbate and adsorbent (Carter et al., 1995). In order to obtain the weighed mean of site energy $\mu(E^*)$ of the steam activated hydrochars for CBZ adsorption, the mathematical expression of E^* which is related to the site energy distribution in the range from zero to infinity was determined by the following equation (Shen et al., 2015):

$$\mu(E^*) = \frac{\int_0^{+\infty} E^* \cdot F(E^*) \, dE^*}{\int_0^{+\infty} F(E^*) \, dE^*}$$
(6.8)

Inserting Eqs. (6.6) and (6.7) into Eq. (6.8) and integrating, the weighed mean can be determined (Shen et al., 2015),

$$\mu(E^*) = \frac{RT}{n} \ln(1 + bC_s^n)$$
(6.9)

In addition, the value of $\mu(E^*)$ is a measure of affinity of adsorbent surface for adsorbate. A higher value of weighted mean of site energy indicates higher adsorption affinity and stronger binding (Carter et al., 1995).

First, the site energy E^* values determined by Eq. (6.3) for the steam activated hydrochars made from flax shives is presented as a function of equilibrium CBZ adsorption capacity q_e in Figure 6.1, and those from oat hulls in Figure 6.2. The steam activation hydrochars were selected in this investigation because of their higher CBZ adsorption capacity.

The solubility of the pharmaceutical (CBZ) in water, which was represented by Cs was calculated by the method described in section (3.1.2.1). The solubility of CBZ in water at 20 °C is

125 mg/L (Deng et al., 2013) and those at 30 °C and 40°C were determined in this work to be 156 \pm 2 mg/L and 203 \pm 11 mg/L respectively.

According to the two figures, there was a decrease in E^* as adsorption capacity increased at all the three different temperatures. This shows that when the CBZ concentration is low, the CBZ molecules were first adsorbed on the adsorption sites with higher energy. Afterward, they occupied adsorption sites with lower energy when CBZ concentration increased. This trend was also observed in norfloxacin adsorption by carbon nanotube (Wang et al., 2010) and pretreated barely straw (Yan & Niu, 2018).



Figure 6. 1 Dependence of site energy on CBZ loading on steam activated hydrochars developed from flax shives (SAHC-H₃PO₄-6 h) (10.0 \pm 0.5 mL CBZ solution, 5.0 \pm 0.1 mg steam activated hydrochars treated with H₃PO₄ for 6 h, pH 5.8 \pm 0.03).



Figure 6. 2 Dependence of site energy on CBZ loading on steam activated hydrochars made from oat hulls (SAHC-H₃PO₄-12 h) (10.0 \pm 0.5 mL CBZ solution, 5.0 \pm 0.1 mg steam activated hydrochars treated with H₃PO₄ for 12 h, pH 5.8 \pm 0.03).

The site energy distribution calculated by Eq. 6.6 for CBZ adsorption on steam activated hydrochars developed from flax shives is shown in Figure 6.3 and from oat hulls in Figure 6.4.

It can be seen that the adsorption site energy distribution shifted to the higher end when temperature increased. It is related to the binding force of adsorbate and adsorbent. As mentioned earlier, the CBZ adsorption could be related to EDA interactions which were one of the key mechanisms of antibiotics adsorption by thermally treated biochars (Foster & Fyfe, 1966). Specifically, the above mentioned interactions could be formed between the π -acceptors of CBZ and the π -donors of the aromatic π -system of the activated hydrochars in the present system. These interactions can be enhanced at higher temperatures. As a result, the site energy distribution moved to the higher end.


Figure 6. 3 Site energy distribution of CBZ sorption on steam activated hydrochars developed from flax shives (SAHC-H₃PO₄-6 h). 50.0 ± 0.5 mL CBZ solution, 5.0 ± 0.1 mg hydrochars.



Figure 6. 4 Site energy distribution of CBZ sorption on steam activated hydrochars developed from oat hulls (SAHC-H₃PO₄-12 h). 50.0 ± 0.5 mL CBZ solution, 5.0 ± 0.1 mg hydrochars (0.425-1.18 mm).

It was considered that weighted mean represents the strength of interactions (affinity) between adsorbate molecules and activated hydrochars (Carter et al., 1995). In order to determine the weighted mean $\mu(E^*)$ of site energy distribution of CBZ adsorption on the activated hydrochars in this work, Eq. (6.9) was used. The higher value of the weighted mean of site energy shows stronger adsorption affinity (Carter et al., 1995). The CBZ adsorption on the steam activated hydrochars developed from flax shives at 40°C had a slightly higher weighted mean (13.3 kJ/mol) compared with that at 30°C (11.2 kJ/mol) and 20°C (7.7 kJ/mol), indicating slightly stronger interaction between the adsorbent and CBZ at a higher temperature. Similar phenomena were observed in the case of oat hulls, the respective values are 15, 12.9, and 8.0 kJ/mol.

Adsorption affinity is associated with interaction between adsorbate and adsorbent. As discussed before, π - π EDA interactions are considered to be one of the main mechanisms of antibiotic adsorption on the thermal treated biochars. They are the attraction formed between electron-deficient (acceptors) and electron-rich (donors), which are polar interactions (Foster & Fyfe, 1966). In this work, the interaction between the π -acceptors of CBZ and the π -donor of the steam activated hydrochars was enhanced at higher temperature. Therefore, the affinity of the adsorption increases. This may explain the weighted mean of site energy which slightly increases with increasing temperature. However, further investigation on adsorption mechanism needs to be done.

In addition, the slightly higher values of weighted mean in the case of oat hulls in comparison with flax shives are consistent with the results of *Ks* that interaction between CBZ and the oat hulls steam activated hydrochars are slightly stronger. Again, more study on CBZ adsorption mechanism is necessary.

6.2. Thermodynamics

Thermodynamic parameters provide important information to elucidate adsorption mechanism, thermodynamic feasibility and spontaneity of an adsorption process. Thus, in this work, thermodynamic parameters were determined for adsorption of CBZ on the steam activated hydrochars with the highest capacity developed from each of the two feedstocks, flax shives and oat hulls. Specifically, standard Gibbs free energy change of adsorption, ΔG° (kJ/mol), was determined by Eq. (2.2), and the standard entropy change, ΔS° (J/mol·K), and standard enthalpy change, ΔH° (kJ/mol), by Eq. (2.4). According to these equations the equilibrium constant of K_c is an important parameter associated with the thermodynamic parameters. There are various methods to determine this constant. For examples, the constant has been obtained from different isotherms, such as Langmuir isotherm constant (K_L) , Freundlich isotherm constant (K_F) , Sips isotherm constant (K_s) , distribution coefficient (K_d) , etc. (Tran et. al 2016). The Sips constant K_s (l/mg) was used in this research. It is to note that there are issues existing in conversion of the units of the adsorption equilibrium constants for determining the above mentioned thermodynamic parameters in current literature. A recent article provided critical review on this issue (Lima et al., 2019). The authors of this research concurred with the approach proposed by the review article to convert the unit of adsorption equilibrium constant Ks to dimensionless because of suitability of the proposed conversion and nature of the present adsorption system. Specifically, according to Eq. (27) recommended in the review article, the adsorption equilibrium constant Ks (L/mg) in the present work was first multiplied by 1000 to convert the unit in L/g, then multiplied by the molecular weight of adsorbate CBZ, 236.3 g/mol to transform Ks in L/mol, and the value was further multiplied by molar concentration of water 55.51 mol/L to become dimensionless for determining the above mentioned thermodynamic parameters. Then the thermodynamic parameters were determined by Eqs. (2.3) and (2.4) through the values of converted Kc at three temperatures (20, 30, 30)40°C), and are presented in Table 6.1. The sign of ΔG° values is negative indicating the adsorption involving CBZ and the steam activated hydrochars was spontaneous. In addition, increase of the absolute value of Gibbs free energy (ΔG°) at higher temperatures indicated increased adsorption interaction and affinity between the adsorbent and CBZ. Furthermore, the positive sign of enthalpy change (ΔH°) shows the adsorption was endothermic. Generally, a value of $|\Delta H|$ less than 20 (kJ/mol) indicated physical adsorption, while chemical adsorption usually has values in the range of 80 -400 (kJ/mol) (Chen et al., 2017; Liu and Zhang 2009). The values of ΔH° (73-84 kJ/mol) obtained in this work are close to the lower end of energy range of chemisorption. It was discussed before, π - π EDA interaction could be a key mechanism of CBZ adsorption.

However, the flax shives and oat hulls steam activated hydrochars contain multiple functional groups, thus diversified mechanism may be involved. The detailed discussion on adsorption mechanisms are in Chapter 7.

Values of ΔS° provide information on the randomness at the solid-solution system (Bekçi et al., 2007). The positive values of ΔS° obtained in this work indicate the randomness increased in the CBZ adsorption process. This could be resulted from that disruption of hydration shell around the surface of adsorbents, and less order reallocation of water molecules around the adsorbent's surface in CBZ adsorption. The results also indicated that the CBZ adsorption on the steam activated hydrochars was favorable.

Flax shives (SAHC-H ₃ PO ₄ -6h)												
	K _s (L/mg)	K _s (-)	$\Delta G^{\circ} (kJ/mol)$	Δ H° (kJ/mol)	Δ S° (J/mol)							
20 °C	0.11	1.47E+6	-34	0.2	+400							
30 °C	0.50	6.56E+6	-39	+83								
40 °C	0.98	1.29E+7	-42									
Oat hulls (SAHC-H ₃ PO ₄ -12h)												
	K _s (L/mg)	K _s (-)	$\Delta G^{\circ} (kJ/mol)$	Δ H° (kJ/mol)	Δ S° (J/mol)							
20 °C	0.2	2.62E+6	-36		+350							
30 °C	1.28	1.69E+7	-42	+66								
40 °C	1.57	2.06E+7	-44									

Table 6. 1 Thermodynamic parameters for adsorption of CBZ on steam activated hydrochars.

6.3. Chapter Summary

In this chapter, the approximate site energy, distribution and weighted mean of CBZ adsorption on the steam activated hydrochars was determined based on the Sips

isotherm modeling results. When the CBZ concentration is low, the CBZ molecules were first adsorbed on the adsorption sites with higher energy. Afterwards, they occupied adsorption sites with lower energy when CBZ concentration was increased. Besides, the site energy distribution curves shifted to the higher end when temperature increased, showing CBZ adsorption favored at higher temperatures. The higher weighted mean of site energy distribution obtained at 40°C, indicated slightly stronger adsorption affinity and interactions between the adsorbents and CBZ at a higher temperature. The thermodynamic analysis revealed that the adsorption of CBZ onto the steam activated hydrochars was spontaneous and endothermic. The site energy and thermodynamical parameters of the distribution. steam activated hydrochars developed from either flax shives or oat hulls were similar because they have similar composition.

CHAPTER 7 CBZ ADSORPTION MECHANISMS

In this chapter, mechanisms of CBZ adsorption were analyzed in aid of experimental adsorption results, and analyses of Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and Near-edge X-ray absorption fine structure spectroscopy. The results and discussion of this chapter are important to understand the fundamental science and engineering of CBZ adsorption on hydrochars and steam activated hydrochars.

7.1. Mechanisms of Carbamazepine Adsorption

In general, mechanisms of interactions between pharmaceuticals and activated carbons during adsorption may include all or some of the following aspects: 1) π - π electron-donor-acceptor (EDA) interactions between the basal plane of the activated carbons and the aromatic ring of the adsorbate; 2) electrostatic attraction-repulsion between the functional groups of adsorbate and adsorbent with opposite charges; 3) hydrogen bonding which is a dipole-dipole attraction formed between adsorbent surface functional groups and pharmaceutical molecules; and 4) hydrophobic interactions between hydrophobic groups on adsorbate and adsorbent (Franz et al., 2000; Lladó Valero, 2016). However, contributions of the above mentioned mechanisms could vary in different pharmaceuticals adsorption.

To investigate the specific contributions of the aforementioned mechanisms in CBZ adsorption on hydrochars and steam activated hydrochars, the following analyses were made.

7.1.1. Hydrophobic Interactions

mentioned above, hydrophobic As interaction could be one type of the interactions between pharmaceuticals and activated carbons. In order to predict hydrophobic interaction between adsorbent adsorbate, the and octanol-water distribution coefficient (Kow) of adsorbate is often used. Specifically, higher value of indicates higher hydrophobic interaction, thus higher possibility of adsorbate Kow being adsorbed by hydrophobic interaction (Chen, et al., 2017).

CBZ has a value of Kow (2.45) which is at the intermediate level of the values of the pharmaceuticals shown in Table 2.2. Accordingly, this indicates CBZ has the intermediate level of hydrophobicity among the pharmaceuticals. In the molecule of CBZ, there are aromatic rings which are hydrophobic. Besides, there are -C=O and -NH₂ groups linked to the aromatic rings which can form hydrogen bonds with water molecules, thus make CBZ also have a certain degree of hydrophilicity though not high. As such, hydrophobic interaction could exist in CBZ adsorption but not the sole mechanism. This was confirmed by the results of CBZ desorption shown in Chapter 9 of this thesis that CBZ adsorbed on the adsorbents was more effectively desorbed in ethanol compared with methanol and water though not all of CBZ were desorbed. Similar analysis was reported in the removal of CBZ with activated carbon produced by pomelo peel (Chen et al., 2017), porous carbon materials developed from metal-organic frameworks (MOFs) (Chen et al., 2020), pine-wood nanobiochar (Naghdi et al., 2016), and nanofiltration (NF) membranes (Nghiem et al., 2005). Overall, hydrophobic interaction contributed to CBZ adsorption on hydrochars or steam-activated hydrochars, however, it is not the sole mechanism.

7.1.2. Electrostatic Attraction between CBZ and Adsorbents with Opposite Charges

The surface charge of hydrochars and steam activated hydrochars of both flax shives and oat hulls in this work are around zero at pH 3-4, the details of which are presented in Chapter 5 of this thesis. These adsorbents had positive charges at pH < 3, and negative charge at pH > 4.

In addition, the p*Ka* values of CBZ were 2.3 (carbonyl group) and 13.9 (amine group). Thus, at pH 2 - 10 investigated in this work, CBZ molecules were positively charged with protons. Thus, the electrostatic attraction between CBZ molecules and the adsorbents with opposite charges existed at the tested pH range. However, it was insignificant because the adsorption capacity of CBZ did not change significantly as pH was varied from 2 to 10, as shown in the results of pH effect in Chapter 5. This was also observed in CBZ adsorption by activated carbons, biochars, and additional carbon materials (Chen et al., 2020; Chen et al., 2017; Nghiem et al., 2005). Therefore, electrostatic attraction between CBZ and adsorbents with opposite charges contributed to CBZ adsorption, however, the role is not significant.

7.1.3. Hydrogen Bonding

It is known that hydrogen bonding forms between an electronegative atom and a hydrogen atom which is covalently bonded with another electronegative atom. N, O and F often serve as the electronegative atoms.

To investigate the groups containing electronegative atoms in the CBZ adsorption systems, FTIR analysis was done on CBZ, raw flax shives and oat hulls, and their hydrochars and steam activated hydrochars. Figures 7.1 and 7.2 shows the results of hydrochars and steam activated hydrochars, respectively.

The spectrum of CBZ (Figure 7.1 A) showed peaks at ~1384 cm⁻¹ (–NH deformation), 3462 cm^{-1} (–NH valence vibration), 1675 cm^{-1} (–CO–R vibration), and 1598 cm^{-1} (aromatic –C=O and –C=C– vibration), which were identified according to the information provided in literature (Suresh et al., 2006). CBZ has -NH₂, –C=O and aromatic rings. The N and O containing groups could form hydrogen bonding with the electronegative atoms contained in the functional groups of the adsorbents.

On the spectra of raw flax shives (Figure 7.1A) and raw oat hulls (Figure 7.1 B), peaks of -O-H stretching ($3200-3600 \text{ cm}^{-1}$) and bending ($\sim 1205 \text{ cm}^{-1}$) were observed, which were related to phenolic, carboxylic and alcoholic groups, respectively (Huff et al., 2014; Cao & Harris, 2010). Besides, peaks of -C-O stretching (1023 cm^{-1}) and carboxyl groups -COOH (1029 cm^{-1}) were found (Uchiyama et al., 2011).

Raw flax shives and oat hulls samples in this work mainly contained cellulose, hemicellulose and lignin with a small amount of protein, which had -OH, -C-O and -COOH. Furthermore, peaks at the range of 1450-1650 cm⁻¹ are attributed to aromatic structure (-C=C) of lignin (Liu et al., 2010a). The peak at approximately ~2922 cm⁻¹ indicates -C-H stretching groups (Jian et al., 2018).

After hydrothermal treatment, the above mentioned $-OH (3334 \text{ cm}^{-1})$, $-C-O (1023 \text{ cm}^{-1})$, $-COOH (1029 \text{ cm}^{-1})$, $-C=C (1450-1650 \text{ cm}^{-1})$, and $-C-H (2922 \text{ cm}^{-1})$ and aromatic structures still existed, as shown on the spectra of hydrochars thermally treated for 6 and 12 h in both cases of flax shives (Figure 7.1 A) and oat hulls (Figure 7.1 B). It is also to note that the peaks at about 1700 cm⁻¹ in hydrochars are attributed to carbonyl groups C=O, and those at ~1230 cm⁻¹ can be ether bonds -C-O-C. They present in carboxyls, aldehydes, esters, and quinones (Fuertes et al., 2010; Koch et al., 1998; Pradhan & Sandle, 1999).

The above mentioned oxygen containing groups -C-O-C, C=O, -C-O, COOH, and -OH on the hydrochars could form hydrogen bonding with $-NH_2$ and -C=O of CBZ, contributing to CBZ adsorption. It was also reported that hydrogen bonding formed between NH_2 of CBZ molecules and another electronegative atom oxygen in the functional groups such as carboxyls and hdyroxyls of aromatic structures in carbon-based adsorbents (Chen et al., 2020; Chen, et al., 2017).

In addition, the intensity of -C-O and -C-H vibration reduced on the spectra of hydrochars in comparison with those of the raw materials, indicating significant amount of -C-O and -C-Hcontaining structure was decomposed during hydrothermal treatment.

As for the effect of CBZ adsorption on the FTIR spectra of the hydrochars, it was observed that the peaks of the oxygen containing groups –C–O–C, C=O, –C–O, COOH, and –OH on the spectra of the CBZ loaded hydrochars did not change significantly compared with the blank adsorbents. This could be because hydrogen bonding is relatively weak which could not be detected by the FTIR analysis in this work.



Figure 7. 1 FTIR analyses of A) CBZ, raw flax shive, flax shive hydrochar samples and flax shive hydrochar samples loaded with CBZ. B) Raw oat hulls, oat hull hydrochar samples and oat hull hydrochar samples loaded with CBZ.



Figure 7. 2 FTIR analyses of flax shives and oat hull steam activated hydrochars with and without CBZ loaded.

As for the steam activation hydrochars of flax shives and oat hulls, the spectra were flat compared to those of the hydrochar samples, as shown in Figure 7.2. The results indicated that steam activation decomposed significant numbers of the surface groups containing oxygen. For examples, the peaks of -C-O-C, C=O, -C-O, COOH, and -OH observed on the spectra of the raw materials and hydrochars are invisible on the spectra of blank steam activated hydrochars, which is consistent with the findings of Haberhauer et al. (1998). It was reported that steam activated hydrochars had more aromatic structures, and less oxygen-containing and alkyl groups (Jian et al., 2018b; Huff et al., 2014; Xiaoyan Cao et al., 2011). Thus, hydrogen bonding in CBZ adsorption by steam activated hydrochars is likely not important. In addition, the spectra of steam activated hydrochars with and without CBZ are similar.

Furthermore, it is known that solution pH can affect not only electrostatic attraction between groups with opposite charges but also hydrogen bonding. As discussed before, the effect of pH on CBZ adsorption capacity of hydrochars and steam activated hydrochars was insignificant at the tested pH range of 2-10, thus it again supported that hydrogen bonding existed but was not the predominant mechanism of CBZ adsorption in this work. Similar conclusion was made in CBZ adsorption by activated carbons, biochars and additional carbon materials (Chen et al., 2020; Chen et al., 2017; Ncibi and Sillanpää, 2017; Naghdi et al., 2016; Nghiem et al., 2005).

7.1.4. π - π Electron-Donor-Acceptor (EDA) Interactions

 π - π EDA interactions are noncovalent and specific, which occurred extensively between electron-poor and electron-rich compounds (Hunter & Sanders, 1990). This interaction appears between two aromatic rings where one aromatic ring has electron-donating ability and serves as π electron donor, and the other has electron-withdrawing ability and serves as π electron acceptor. Besides, π - π EDA interaction also forms between an aromatic ring and a functional group. In this case, the lone electron pair of the functional group is π electron donor and the aromatic ring is π electron acceptor (Yuki et al., 2007).

In the adsorption of aromatic compounds on carbon-based adsorbents containing aromatic structures, π - π EDA interactions have been considered. Usually, with an increase in the π -electron-donating ability or polarizability of π -system of the substitutes in the aromatic structure of the adsorbents, strength of donor increases, and somehow strength of the acceptor is related to the number and electron-withdrawing ability of substitutes in the aromatic compounds (Chen et al., 2007).

It was considered that activated carbons, biochars, and similar carbon materials usually were strong π -donors because they contained π -electron donor groups, for instance, electron-rich OH and aromatic benzene rings (Chen et al., 2017). On the other hand, because of aromatic rings and the amide groups having electron-withdrawing capability, CBZ is counted as a π -electron acceptor (Cai & Larese-Casanova, 2014b). Hence, π - π EDA interactions have been suggested as an important mechanism in the CBZ adsorption by activated carbons and similar carbon materials. In order to investigate the mechanisms of CBZ by hydrochars and steam activated hydrochars developed from flax shives and oat hulls in this work, XPS analysis was done.

The analysis was based on that the surface chemical environment of hydrochars and steam activated hydrochars changed after adsorption of CBZ. Then analysis of XPS spectra of the raw flax shives and raw oat hulls, selected hydrochars (flax shive based HC-H₃PO₄-6h and oat hull based HC-H₃PO₄-12h) and steam activated hydrochars (flax shive based SAHC-H₃PO₄-6h and oat

hull based SAHC-H₃PO₄-12h) with higher CBZ loadings were conducted in comparison with their respective blank materials, and pure CBZ. The results are presented as follows.

7.1.4.1. X-Ray Photoelectron Spectra (XPS)

The XPS scan survey spectra of hydrochars and steam activated hydrochars in comparison with raw flax shives and oat hulls and CBZ are presented in Figures 7.1 and 7.2, respectively. The results show that carbon was the primary element followed by oxygen then nitrogen. The order is consistent with that observed by elemental composition determined by sample combustion, as presented in Chapter 4. The small amount of nitrogen on hydrochars and steam activated hydrochars (0.04 -0.59%) could be from the small amount of protein in raw flax shives and oat hull samples. After CBZ adsorption, the nitrogen contents of the hydrochars and steam activated hydrochars increased 1.4 to 4.6 times because CBZ contains nitrogen atoms. The results confirmed that CBZ was adsorbed on the surface of the adsorbents, and steam activated hydrochars had higher CBZ uptake. However, considering the low absolute contents of nitrogen, the scan results of C1s and O1s instead of N1s are further presented with discussion as follows. The N1s scan spectra are provided in Appendix B.



Figure 7. 3 XPS spectra of hydrochars (flax shives, oat hulls), along with the adsorbed CBZ.



Figure 7. 4 XPS spectra of CBZ and steam activated hydrochars based on flax shives (A) and oat

hulls (B).

The C 1s XPS spectra of CBZ, hydrochar and steam activated hydrochars of flax shives before and after adsorption of CBZ are presented in Figures 7.5 and 7.6, and those of oat hulls are in Figure 7.7, respectively. The functional groups and binding energy are summarized in Table 7.1.

	CBZ	Flax shives		Oat hulls		Flax shives		Oat hulls	
Bond assignment (eV)		HC-H ₃ PO ₄ -6h		HC-H ₃ PO ₄ -12h		SAHC-H ₃ PO ₄ -6h		SAHC-H ₃ PO ₄ -12h	
		blank	+ CBZ	blank	+ CBZ	blank	+ CBZ	blank	+ CBZ
					C 1s				
C–C (graphitic carbon)	284.50	284.50	284.50	284.50	284.50	284.50	284.50	284.50	284.50
C-O; C-N	285.88	285.64	285.59	285.64	285.62	285.94	285.87	286.05	285.88
С-ОН, С-О-С	-	286.76	286.90	286.91	286.99	-	-	-	-
C=O (carbonyl)	288.50	288.20	288.53	287.72	288.76	288.35	288.45	287.8	288.29
O–C=O (carboxyl or ester)	-	289.46	289.80	289.45	289.6	-	-	289.01	289.39
					O 1s				
C=0	531.15	531.65	531.50	531.78	531.7	531.66	531.56	531.75	531.56
(O=C*)- 0	532.81	532.92	532.85	532.93	532.8	532.93	532.79	532.80	532.79
С-О-С	-	533.87	534.00	533.95	534	533.62	533.82	533.44	533.81
Oxygen in Water molecules	-	535.23	535.50	535.52	535.5	-	-	-	-

Table 7. 1 Summary of the peaks of the important functional groups on the C1s and O1_s XPS spectra of flax shive and oat hull adsorbents.

The C1s spectra of CBZ were fitted with three peaks at the binding energy of 284.5, 285.83, and 288.38 eV, corresponding to C–C, C–N, and C=O of CBZ molecule, as seen in Table 7.1. As discussed previously, CBZ is counted as a π -electron acceptor because the amide group in the molecule has the electron-withdrawing capability.

In the case of hydrochar based on flax shives (HC-H₃PO₄-6h), the C1s spectrum was deconvoluted into five peaks at 284.5, 285.64, 288.20, 286.76, and 289.46 eV. They were attributed to C–C, C–O/C–N, C=O, C-OC/C-OH, and O-C=O, respectively (Nariyan et al., 2020; Chen et al., 2020; Tam et al., 2020; Peiris et al., 2019; Nielsen et al., 2014; Zhu et al., 2014). On the spectrum of the steam activated hydrochar flax shive (SAHC-H₃PO₄-6h), the number of peaks reduced to three at 284.5, 285.94, and 288.35 eV. They were assigned to C–C, C–O/C–N, and C=O, respectively. The results show that after steam activation, O-C=O and C-OC/C-OH on the surface of hydrochars were decomposed, thus were not detected on the surface of steam activated carbon.

Similarly, for the oat hull hydrochars (HC-H₃PO₄-12h) (Table 7.1), the C1s spectrum was deconvoluted into five peaks at 284.5, 285.64, 286.91, 287.72, and 289.45 eV, which were assigned to C–C, C–O/C–N, C=O, C-OC/C-OH, and O-C=O respectively (Nariyan et al., 2020; Chen et al., 2020; Tam et al., 2020; Peiris et al., 2019; Nielsen et al., 2014; Zhu et al., 2014). However, for the steam activated hydrochar developed from oat hulls (SAHC-H₃PO₄-12h), the C1s spectrum was deconvoluted into four peaks at 284.5, 286.05, 287.80, and 289.01 eV, attributed to C–C, C–O/C–N, C=O, and O-C=O, respectively. The group C-OC/C-OH was not detected on the spectrum of steam activated hydrochars, similar to that in the case of flax shives because they were decomposed. In addition, the oat hull sample contained small amounts of starch and protein. The carboxyl groups could be from the protein and oxidized starch residues.

Though aromatic structures of hydrochars and steam activated hydrochars were identified in the FTIR analysis, they were not detected by the current method of XPS. Future research in this respect is necessary.

Importantly, it is to note that the binding energies of C1s in C=O, C-O-C/C-OH, and O-C=O of all the hydrochars and steam activated hydrochars of flax shives and oat hulls slightly increased after CBZ adsorption, as shown in Table 7.1. Similar results were obtained by Chen and colleagues in CBZ adsorption on porous carbon materials made from metal–organic frameworks (MOFs) (Chen et al., 2020; Chen et al., 2017a). They considered that the increase in the binding energy was because electron density of the atoms reduced on the surface of the hydrochars and steam activated hydrohars after CBZ adsorption through the π - π EDA interaction.

Besides, the above mentioned O-containing groups on the surface of the hydrochars and steam activated hydrochars have lone electron pairs and are electron-rich, which, together with the aromatic rings on the surface, are π -electron donors. They interacted with the π -electron acceptor CBZ, contributing to CBZ adsorption. As a result, the binding energy of these O-containing groups on the surface increased.

In addition, it was observed a slight decrease in the binding energy of carbon in C-N/C-O groups of the steam-activated hydrochars and hydrochars. Similar results were obtained in CBZ adsorption by the carbon materials derived from MOFs (Chen et al., 2020; Chen et al., 2017a). They considered it was because the C-N structure of CBZ molecule adsorbed on the adsorbents interfered. More analysis in the respect is necessary.



C 1s

Figure 7. 5 C1s spectra of CBZ.



Figure 7. 6 C1s spectra of flax shive steam activated hydrochar (A and B), hydrochar (C and D) before and after CBZ adsorption.



Figure 7. 7 C1s spectra of CBZ, oat hull activated hydrochar (A and B), hydrochar (C and D) before and after CBZ adsorption.

Figures 7.8, 7.9 and 7.10 show the O1s XPS spectra of CBZ as well as hydrochars and steam activated hydrochars based on flax shives and oat hulls. The respective data are also summarized in Table 7.1.

Two peaks of 531.15 and 532.72 eV in the spectrum of CBZ were attributed to O=C and $(O=C^*)$ –O respectively. For hydrochars of flax shivesS and oat hulls, four peaks were identified (Table 7.1 and Figure 7.8) which were attributed to O=C–O in carboxyl, C=O in carbonyl or ketone, C–O–C in ether or epoxy, and oxygen in H₂O (Nariyan et al., 2020; Chen et al., 2020; Tam et al., 2020; Peiris et al., 2019; Nielsen et al., 2014; Zhu et al., 2014). In addition, for the steam activated hydrochar, the three groups C–O–C, O=C–O, and C=O remained but oxygen in H₂O was not detected. This was expected because steam activation was done at 850°C, H₂O molecules in the hydrochars were evaporated.

After the adsorption of CBZ on the hydrochars and steam activated hydrochars, the binding energies of O=C–O and C=O had a slight reduction. Similar results were obtained in CBZ adsorption by the MOFs based carbon materials (Chen et al., 2020; Chen et al., 2017). They considered this reduction was because hydrogen bonding formed between CBZ and these groups. However, because the content of O was much lower than that of C of the hydrochars and steam activated hydrochars in this work, the contribution of hydrogen bonding may not be predominant.

In addition, there was a slight increase in the binding energy of C–O–C of the hydrochars and steam activated hydrochars. Similar observation and analysis was obtained by Chen et al. (2020) and Chen et al. (2017a) in their study on carbon polyhedrons and pomelo peel for CBZ adsorption. They related it to the reduction of electron density after CBZ adsorption through the π – π EDA interaction. Moreover, the slight changes in the binding energies after CBZ adsorption followed a similar trend in both the flax shive and oat hull based hydrochars and steam activated hydrochars.

Overall, it can be considered that π - π EDA interaction had an important role in adsorption of CBZ on hydrochars and steam-activated hydrochars. Such an EDA interaction was considered to be important in CBZ adsorption by similar carbon materials (Chen et al., 2020; Chen et al., 2017a).

Because of the challenges of elucidating the mechanism of CBZ adsorption, additional spectral analysis was done in the next section.



0 1s

Figure 7. 8 O1s spectra of CBZ.



Figure 7. 9 O1s spectra of flax shive steam activated hydrochar (A and B), hydrochar (C and D) before and after adsorption.



Figure 7. 10 O1s spectra of oat hull steam activated hydrochar (A and B), hydrochar (C and D) before and after adsorption.

7.1.4.2. Near-Edge X-Ray Absorption Fine Structure (NEXAFS) Spectroscopy

In order to provide additional information about the contribution of π - π EDA interactions through the aromatic structures of CBZ and the flax shive and oat hull based hydrochars and steam activated hydrochars, NEXAFS analysis was done.

The C K-edge NEXAFS spectra of raw flax shives, raw oat hulls, their derivatives (hydrochars and steam activated hydrochars) before and after CBZ adsorption, and CBZ were obtained. The detailed method can be found in Chapter 3 of this thesis.

Figure 7.11 presents the results of the flax shive based adsorbents in comparison with CBZ. The C K-edge fine structures revealed the different carbon bonding environments in the flax shives via hydrothermal carbonization and steam activation. The spectrum of raw flax shives in Figure 7.11 shows a resonance peak at an energy level of 285.55 eV, which was attributed to the $C1s \rightarrow \pi^*_{C=C}$ transitions of the carbon bonded to the aromatic carbon, alkylated and protonated carbonyl substituted aryl-C, ascribed to the inherent lignin content in the raw flax shives (Latham et al., 2018; Keiluweit et al., 2010). Upon hydrothermal carbonization for 6h (HC-H₃PO₄-6h), the peak was shifted down to 285.32 eV and the peak intensity increased. With further treatment with steam activation (SAHC-H₃PO₄-6h), the peak intensity continually increased. This could be due to more aromatic structures of carbon generated during the hydrothermal and steam activation treatments (Latham et al., 2018; Keiluweit et al., 2010). The results were consistent with the results of FTIR analysis in this work that aromatic structures were identified in hydrochars and steam activated hydrochars. The aromatic structures had π -electrons and could be served as π -electron donors.

In addition, the spectrum of CBZ shows a peak at 285.5 eV, which was attributed to the aromatic carbon ring bonded to nitrogen (C = C*- N). Similar results for CBZ were obtained from FTIR (Figure 7.1 A) in this work. It was discussed before that CBZ had an amide group, which had the electron withdrawing capability. As a result, CBZ can be counted to be the π -electron acceptor. Thus, π - π EDA interactions between the aromatic structures of CBZ and of the hydrochars and steam activated hydrochars are considered to be significant in adsorption of CBZ. In addition, due to the increased amounts of aromatic structures, the steam activated hydrochars

(SAHC-H₃PO₄-6h) had the highest CBZ adsorption capacity followed by the hydrochar (HC-H₃PO₄-6h), then by the raw flax shives, the detailed data of which were reported in Chapter 6. Furthermore, solution pH did not affect the capacity of adsorption significantly in a wide range of pH 2-10. Thus, based on all the results obtained by adsorption experiments and spectra analyses, π - π EDA interactions are considered to be a primary mechanism in the CBZ adsorption. The relatively strong binding of CBZ on the steam activated hydrochar through π - π EDA interactions may lead to that the peak of the aromatic structure was not detected on the CBZ loaded steam activated hydrochar, as shown in Figure 7.1. Further investigation is needed in future research.

Moreover, a peak at 288 eV was visualized on all the spectra except for that of CBZ loaded steam activated hydrochars (SAHC-H₃PO₄-6h+CBZ) in Figure 7.11, which corresponded to $C1s \rightarrow \pi^*_{C=0, C-OH, C-OOH}$ transitions representing phenolic, carbonyl, and ester C, respectively. These groups were also found in hydrothermal carbons developed from sucrose treated at high temperatures (400, 600, and 800 °C) (Latham et al., 2018). Beside, at a higher energy, i.e., 289.5 eV, $C1s \rightarrow \pi^*_{C=0, R-COOH}$ transitions were observed, which were observed in thermal treated wood and grass samples as well (Keiluweit et al., 2010; Heymann et al., 2011).

The carboxylic groups (-COOH) observed in the present work could be from the small amount protein in the raw flax shives, and/or generated by thermal treatments (hydrothermal and stema activation). Moreover, it was also observed that the peak intensities of the above mentioned oxygen containing groups decreased after thermal treatment, indicated some of them were decomposed during the hydrothermal and steam activation treatment. The results are consistent to those obtained by FTIR (Figures 7.1 A and 7.3) and XPS (Figures 7.6 B and 7.6 D) analyses in this work. The groups such as carboxyls and hydroxyls are polarizable. Surface sites near the polarized edge sites were π -donors with rich electrons in adsorption of aromatic compounds on black carbon substances (McDermott & McCreery, 1994). Thus, they could form π - π EDA interaction with CBZ. In addition, it was discussed above, hydrogen bonding can be formed between these groups of the adsorbents and the amide and carbonyl groups of CBZ. However, such a mechanism was not predominant.

Overall, thermal treatments (hydrothermal carbonization at 220°C, and steam activation at 850°C) of flax shives resulted in the increment in the aromaticity and loss of the groups which were associated with aliphatic and oxygen-containing groups.

Outcomes of the C K-edge NEXAFS spectroscopy supported that the π - π EDA interaction between π^* carbon atom in the benzene ring linked to N of CBZ molecules as π -electron-acceptor (C = C* - N), and the aromatic π^* C=C of hydrochar and steam activated hydrochar of flax shives as π -electron-donor is significant in CBZ adsorption. In addition, the aforementioned oxygencontaining groups having lone electron pairs could also serve as π -electron donor to form π - π EDA interaction with CBZ. However, it is expected to be insignificant particularly in the case of steam activated hydrochars because of loss of the oxygen-containing groups at the high temperature steam treatment.



Figure 7. 11 Stacked C 1s NEXAFS spectra for flax shives, hydrochar, steam activated hydrochar and CBZ loaded steam activated hydrochar. (A) 6 h for hydrothermal treatment in the present of H₃PO₄ (B) 12 h for hydrothermal treatment in the present of H₃PO₄.

Wang et al. (2007) and Zhu et al. (2005) also reported that the π - π EDA interaction was dominant in the organic compounds adsorption on activated chars/carbons.

Therefore, the π - π EDA interactions between the hydrochars and steam activated hydrochars and CBZ are a significant mechanism in CBZ adsorption.

Figure 7.11 B further shows that the results of flax shives hydrothermally treated for 12 h and their derivatives after steam activation. It can be seen that the results are generally similar to those of flax shives hydrothermally treated for 6 h and their derivatives, however, the peak intensities of aromatic structure are relatively lower. This could be due to that more aromatic structures were decomposed during the longer hydrothermal treatment time, 12 h. As a result, the adsorbents had a lower CBZ adsorption capacity than the adsorbents hydrothermally treated for 6 h.

Analysis of the C K-edge NEXAFS spectra of oat hulls and their derivatives (hydrochar and steam activated hydrochar) was also carried out in an approach similar to that in the analysis of flax shive based adsorbents. The results are presented in Figure 7.12. Analysis of the NEXAFS spectra demonstrated that the hydrochars and steam activated hydrochars derived from oat hulls also followed the similar mechanisms as analyzed for the case of flax shives. This is because both materials contain similar components.



Figure 7. 12 Stacked C 1s NEXAFS spectra for oat hulls, hydrochar, steam activated hydrochar and CBZ loaded steam activated hydrochar. (A) 6 h for hydrothermal treatment in the present of H₃PO₄.(B) 12 h for hydrothermal treatment in the present of H₃PO₄.

As discussed in Chapter 2 (Literature Review), it was considered that heat of physical adsorption is usually lower than 80 kJ/mol, while that of chemical adsorption is higher than 80 kJ/mol (El-Araby et al., 2017). In this work, the adsorption heat of CBZ adsorption was about 80-83 kJ/mol, as shown in Chapter 6 of the thesis. It is at the margin of differentiating physical and chemical adsorption. Considering all the analyses in this chapter, CBZ adsorption by the hydrochars and steam activated hydrocars are predominantly physical adsorption, which include π - π EDA interactions, hydrophobic interaction, electrostatic attraction, and hydrogen bonding, among which the former two mechanisms are more significant.

7.2. Chapter Summary

The mechanisms of CBZ adsorption by hydrochars and steam activated hydrochars were elucidated in aid of CBZ adsorption experiments and analyses of FTIR, XPS and NEXAFS in this chapter. CBZ adsorption by the hydrochars and steam activated hydrocars are predominantly physical adsorption. The π - π EDA interactions between CBZ and the hydrochars and steam activated hydrochars are a significant mechanism in CBZ adsorption. Hydrophobic interaction also contributed to CBZ adsorption. Electrostatic attraction between the CBZ molecules, and the hydrochars and steam activation hydrochars with opposite charges contributed to the total CBZ adsorption, however, was not significant. Hydrogen bonding formed between -NH₂, and -C=O of CBZ and oxygen containing groups - C=O, C-OH, C-OOH, and R-COOH of hydrochars and steam hydrochars, but again was not predominant.

In addition, thermal treatments enhanced the aromatic structures of the adsorbents contributing to the π - π EDA interactions, thus enhanced CBZ adsorption. In this respect, the impact of steam activation was more significant than hydrothermal treatment.

In general, CBZ adsorption of flax shives and oat hulls based hydrochars and steam activated hydrochars followed similar mechanisms because of their similar composition.

CHAPTER 8 CARBAMAZEPINE ADSORPTION KINETICS AND MODELING

Contribution of this chapter to overall Ph.D. work

In this chapter, the characteristics of adsorption rate by the treated flax shives and oat hulls in the forms of hydrochars and steam activated hydrochars were studied. CBZ was used as a model pharmaceutical pollutant in artificially contaminated water. The kinetics of CBZ adsorption was investigated at various rational speed, temperature and time. Four different kinetic models of pseudo-first-order kinetic, pseudo-second-order kinetic, Elovich, and the intraparticle diffusion models were used to analyze the experimental CBZ adsorption kinetic data.

8.1. Adsorption Kinetic Models

8.1.1. Pseudo-First-Order Kinetic Model

This model is known as the Lagergren rate equation. It assumes in this model that adsorption process rate is proportional to the difference between uptake of adsorbate at time t and at equilibrium (Miyah et al., 2015).

The equation is given as follows (Demirbas et al., 2004):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{8.1}$$

where q_t and q_e (mg/g) represent the uptake at time *t* and equilibrium. k_1 (1/h) is the rate constant of the pseudo-first-order adsorption.

8.1.2. Pseudo-Second-Order Kinetic Model

The pseudo-second-order kinetic model assumes that the overall adsorption rate is limited by chemisorption, which is proportional to the squared of the available active sites of the adsorbent surface. It is effectively used in adsorption processes where chemisorption is the controlling step. Besides, the model has been popularly used to describe pharmaceutical adsorption (Ho, 2006; Ho and McKay, 1999).

The model is presented by Eq. (8.2).

$$\frac{t}{q_t} = \frac{1}{k_2 \ q_e^2} + \frac{1}{q_e} t \tag{8.2}$$

where k_2 (g/mg·h) is the adsorption rate constant, and q_t and q_e (mg/g) also represent the uptake of antibiotics at time *t* and equilibrium, respectively. In addition, based on the rate constants obtained from the pseudo-second-order kinetic model, activation energy can be determined using the Arrhenius equation as follows:

$$\ln k_2 = \frac{-E_a}{RT} + \ln D \tag{8.3}$$

where E_a (kJ/mol) represents activation energy, D (g/mg·h) is the pre-exponential factor, a constant and T (K) is temperature. R (kJ/K·mol) denotes universal gas constant. In general, the activation energy of physiosorption is lower than 40 kJ/mol while that of chemiosorption is higher than 40 kJ/mol (Anirudhan & Radhakrishnan, 2008).

8.1.3. Elovich Model

This model is applied for systems with heterogeneous surface and chemical adsorption (Demirbas et al., 2004).

The equation for this model is defined as:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$$
(8.4)

where α (mg/g·h) represents initial adsorption rate, β (g/mg) denotes the Elovich constant, and q_t (mg/g) is adsorbate uptake at time *t*.

8.1.4. Intra Particle Diffusion Model

When adsorbent is porous, adsorbate transfers from the bulk phase to the adsorbent surface, and further diffuses inside the adsorbent pores. The intraparticle diffusion model describes the diffusion rate within the pores (Aljeboree et al., 2014).

$$q_t = k_{in} t^{1/2} + C \tag{8.5}$$

where q_t is the adsorbate uptake at time t (mg/g). The diffusion rate parameter (k_{in}) is determined by the slope of the line modeling q_t versus $t^{\frac{1}{2}}$. Also, the value of C (mg/g), as the constant indicative of boundary layer thickness, can be obtained through the intercept of the line. If the model fitted line crosses the origin (0,0), that means the adsorption rate is controlled by intraparticle diffusion. Otherwise, intraparticle diffusion in addition to external diffusion may control the overall adsorption rate of the process. At this condition the thickness of boundary layer is determinant in the adsorption rate (Vinod Kumar Gupta et al., 2013).

8.2. Rotational Speed

Rotational speed affects external mass transfer. To determine the impact, CBZ adsorption on the hydrochars was operated for 48 h and that on steam activated hydrochars for 2 h at various rotational speeds (80-220 rpm). The results are presented in Figure 8.1. The above mentioned adsorption time was chosen because they are the time at which the respective adsorption equilibrium was reached at the rotational speed of 220 rpm. As shown in this figure, the CBZ adsorption uptake of both the hydrochars and steam activated hydrochars made from either flax shives or oat hulls increased as the rotational speed increased till about 170 rpm, afterwards, it remained stable. By increasing the agitation rate, the values of external mass transfer coefficient rises (Walker et al., 2003; Zarraa, 1995). According to the principles of external mass transfer, a thin layer of fluid is close to the adsorbent surface where a resistance between the viscos force and the fluid movement is critical to affect mass transfer.



(I)

Figure 8. 1 Effect of rotational speed on adsorption uptake of CBZ on (I) flax shives and (II) oat hulls ((A) hydrochars (CBZ concentration 50 mg/L, adsorbent dosage 5mg, pH 6.0±0.2, 40°C, 48 h for flax shives and 72 h for oat hulls) and (B) steam activated hydrochars (CBZ concentration 50 mg/L, adsorbent dosage 5mg, pH 5.8-6, 20°C, 2 h)).

Adsorbate molecules have to transport through this layer in order to reach the adsorbent surface. Thickness of the layer is inversely proportional to the squared speed of solution passing along the solid particle which is affected by rotational speed (Srivastava et al., 2011). In general, a thinner boundary layer leads to a lower resistance and a higher external mass transfer rate (Walker et al., 2003).

Thus, increase of rotational speed can lead to increase of external mass transfer rate by decreasing the resistance of the surface film (Saruchi et al., 2016). Based on the results, the following experiments were done at a rotational speed of 220 rpm to reduce the impact of external mass transfer resistance. In addition, it is noticeable that throughout the adsorption process, CBZ uptake of the hydrochars treated for 6 h is higher that of adsorbents treated for 12 h. It indicated that treating for 12 h may lead to loss of functional groups or structure for CBZ adsorption.

8.3. Effects of Operation Parameters on Adsorption Kinetics

8.3.1. Impact of Temperature and Time

8.3.1.1. Hydrochars

To investigate the effects of temperature $(20-40^{\circ}C)$ and time on the CBZ adsorption on hydrochars based on flax shives and oat hulls, adsorption experiments were done at a pH of 6.0 ± 0.2 and an initial CBZ concentration of 50 mg/L. Figures 8.2 and 8.3 show the CBZ uptake (qt) versus time at 20, 30, and 40 °C in the cases of flax shive and oat hull based hydrochars, respectively.

It is noticeable in the above mentioned two figures that at the tested conditions, there was generally a rapid adsorption of CBZ within the first 24 hour which then slowed down till reached equilibrium at 48 h or 72 h. The reason for the initial rapid adsorption was mostly because of fast diffusion to the adsorption sites more easily accessible on the surface, followed by slower intraparticle diffusion. This phenomenon is similar to levofloxacin adsorption with pretreated barley straw (Yan & Niu, 2017).

In addition, the CBZ uptake of the hydrochars thermally treated for 6 h (HC-H₃PO₄-6h) had relatively higher or similar uptake than that of those treated for 12 h (HC-H₃PO₄-12h). The
longer hydrothermal treatment time may decompose a portion of active sites for CBZ adsorption. Thus 6 h was adequate.

In addition, the trend in Figure 8.2 A and Figure 8.3 (A-B) with the hydrochars treated with NaOH are a bit different from the other hydrochars, that being said, at the beginning the CBZ adsorption had a sharp increase followed by a decrease in the uptake then gradually became stable. This was probably because of desorption taking place (Jamil et al., 2014). At the beginning there were more vacant active binding sites available and more CBZ molecules were able to attach rapidly and easily on the adsorbents, however the available sites reduced as time passed and the remaining sites were difficult to adsorb more CBZ because the adsorbed CBZ molecules were repulsive to CBZ molecules in liquid phase (Mustapha et al., 2014; Mor et al., 2019). In the meanwhile, desorption of CBZ took place (Jamil et al., 2014) followed by a decrease in the CBZ uptake. When the adsorption rate and desorption rate equaled to each other, the adsorption reached equilibrium. NaOH is a strong base which may create structures of hydrochars different from those treated by H₃PO₄. This may form a future area of research.



Figure 8. 2 Adsorption dynamics of carbamazepine onto flax shive hydrochars (A) HC-NaOH-6h. (B) HC-NaOH-12h. (C) HC-H₃PO₄-6h. (D) HC-H₃PO₄-12h (CBZ concentration 50 mg/L, 5.0 ± 0.1 mg adsorbent , pH 6.0±0.2 and 96 h, rotational speed 220 rpm).



Figure 8. 3 Adsorption dynamics of carbamazepine onto oat hull hydrochars (A) HC-NaOH-6h. (B) HC-NaOH-12h. (C) HC-H₃PO₄-6h. (D) HC-H₃PO₄-12h (CBZ concentration 50 mg/L, 5.0 ± 0.1 mg adsorbent , pH 6.0±0.2, 96 h and rotational speed 220 rpm).

In addition, according to Figures 8.2 and 8.3, an increase of temperature from 293.15 K to 313.15 K led to increase of the initial slope of the kinetic data, indicating the adsorption rate increased. By increasing the temperature, the interaction between the adsorbent and the adsorbate increased the molecular motion which made the uptake of molecules into the pores more easily, causing adsorption rate to increase.

Overall, the performance of flax shives and oat hulls hydrochars in adsorption was similar at the experimental conditions. These materials had similar components such as cellulose, hemicellulose, and lignin, which led to the comparable performance for CBZ adsorption.

8.3.1.2. Steam Activated Hydrochars

Because of their higher surface areas and yields, hydrochars treated with H₃PO₄ were selected for steam activation and used for the kinetic study. The influence of exposure time on CBZ adsorption by steam activated hydrochars is demonstrated in Figure 8.4. It can be seen that the uptake of CBZ with the steam activated flax shive and oat hull had a sharp increase within 2 h followed by a slower, incremental uptake step. About 93% of the CBZ adsorption capacity was achieved at 2 h while the equilibrium was observed at around 4 h for SAHC-H₃PO₄-6h and around 8 h for SAHC-H₃PO₄-12h. The CBZ adsorption rates of the steam activated hydrochars are much faster than those of the hydrochars (48 or 72 h presented in the above section). The rapid adsorption was because of the high surface areas of the steam activated hydrochars of flax shives and oat hulls, being 793 and 527 m²/g for SAHC-H₃PO₄-6h and 618 and 495 m²/g for SAHC-H₃PO₄-12h, respectively. They are much higher than those of the hydrochars (12 and 28 m²/g for flax shive and oat hull based ones hydrothermally treated for 6h, HC-H₃PO₄-6h) and 16 and 29 m²/g hydrothermally treated for 12 h, HC-H₃PO₄-12h). The detailed results and discussion of the surface areas are presented in Chapter 4 of the thesis.

The above mentioned phenomenon is similar to CBZ adsorption by multi-walled carbon nanotubes (Ncibi & Sillanpää, 2017; Cai & Larese-Casanova, 2014a), and granular activated carbon (Cai & Larese-Casanova, 2014a).

It was stated that available surface area and π - π EDA interactions between adsorbate and adsorbent are two main significant factors increasing the adsorption rate (Cai et al., 2014a).

It was determined in Chapter 8 of the thesis that π - π EDA interactions together with hydrophobic, hydrogen bonding, and electrostatic attraction were the mechanisms of CBZ adsorption in this work.

In addition, since the initial rate of CBZ adsorption by the steam activated hydrochars was fast, varying temperature at the tested range of temperature (20-40°C) did not have a significant effect on it at the experimental conditions. Furthermore, the steam activated hydrochars SAHC-H₃PO₄-6h had either similar or slightly higher CBZ uptake than SAHC-H₃PO₄-12h. Thus the former was selected for the kinetic modeling work in the next section.



Figure 8. 4 Adsorption dynamics of carbamazepine onto steam activated hydrochars (I) Flax shives (A) SAHC-H₃PO₄-6h (B) SAHC-H₃PO₄-12h (II) Oat hulls (A) SAHC-H₃PO₄-6h.(B) SAHC-H₃PO₄-12h. (CBZ concentration 50 mg/L, adsorbent dosage 5mg, initial pH 6.0±0.2, 8 and 24 h, rotational speed 220 rpm, 20°C).

8.4. Kinetic Modeling

To further analyze the kinetics of CBZ adsorption, the experimental kinetic data (described in Section 8.1) were simulated by the pseudo-first-order kinetic model (Eq. 8.1) (Demirbas et al., 2004), pseudo-second-order kinetic model (Eq. 8.2) (Ho and McKay, 1999), Elovich model (Eq. 8.4) (Demirbas et al., 2004), and the intraparticle diffusion model (Eq. 8.5) (Aljeboree et al., 2014). These models having different physical-chemical assumptions are commonly used to simulate dynamic adsorption. The hydrochars with higher CBZ uptake were selected in the modeling work (i.e. hydrochars impregnated in H₃PO₄ and hydrothermally treated for 6 h). Specifically, the hydrochars (HC-H₃PO₄-6h) and their steam activated hydrochars (SAHC-H₃PO₄-6h) developed from flax shives and oat hulls were selected for analysis in aid of the kinetics modelling. Table 8.1 summarizes the modeling results and the estimated parameters. Figures 8.5 and 8.6 show the simulated lines together with the experimental data. The results demonstrated that among the tested models, for both flax shive and oat hull based hydrochars, the pseudo-second-order kinetic model had the highest values of R² (0.98-0.99) and lower simulation errors (residual sum of squares (RSS). Besides, the values of adsorption capacity of hydrochars determined by this model are consistent to those obtained by the experiments.

The pseudo-second-order kinetic model assumes the rate-limiting step to be chemisorption by valence forces via connection among electrons of adsorbate and adsorbent, or covalent bonding formed by electron exchange (Ho & McKay, 1999 a). In this work, it was considered that π - π EDA interactions together with hydrophobic, hydrogen bonding, and electrostatic attraction were the mechanisms of CBZ adsorption, which were physical in nature. However, the π - π EDA interactions are specific though noncovalent, which occurs widely among electron-donor and electron-acceptor compounds (Hunter & Sanders, 1990). Such interactions could be important in the CBZ adsorption rate. It was also reported that the π - π EDA interactions were dominant in pharmaceutical adsorption by biochars or activated carbons (Nan Cai, 2015).

In addition, kq_e^2 in Table 8.1 was used to calculate the initial CBZ adsorption rate for both flax shives and oat hulls. The rate constantly increased with increasing temperature from 293.15 to 313.15 K. This was because the equilibrium adsorption capacity q_e increased, leading to an increase of the adsorption driving force (q_e-q_t) ; and the adsorption rate constant increased as well at the elevated temperature. It is noteworthy that the rate constant, k_2 , obtained for the CBZ adsorption of oat hull and flax shive hydrochars are similar. The results once again confirmed that the two materials containing similar components have similar kinetics.

Though the pseudo-first-order kinetic model generated acceptable values of R^2 , its RSS values are numerous times higher than those of the other models. Besides, the values of adsorption capacity of hydrochars determined by the pseudo-first-order kinetic model are constantly lower than those determined by the experiments and thus this model did not provide with satisfactory results.

The Elovich model generated lower R^2 values. In addition, the simulated lines did not cross the original point (0,0) that is inconsistent to the experimental data. As for the intraparticle diffusion model, the relatively lower values of R^2 indicated this model was not suitable.

	Flax shive (HC-H ₃ PO ₄ -6h)						Oa						
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$													
Temperature	q _{e,exp} (mg/g)	k1(h-1)	qe,,cal		R ²	RSS ((mg/g) ²)	q _{e,exp} (mg/g)	k1	qe,,cal	R ²	RSS	((mg/g) ²)	
(K)			(mg/g)					(h ⁻¹)	(mg/g)				
293	35	0.04	29		0.94	980	28	0.06	24	0.98	1	42	
303	34	0.041	21		0.93	3437	41	0.06	20	0.87	74	405	
313	47	0.070	33		0.94	4751		0.08	19	0.94	14351		
					Pseudo- se	cond-order kineti	c model						
Temperature	$q_{e, exp}(mg/g)$	$K_2(h^{-1})$	$q_{e,cal}$	\mathbb{R}^2	Kqe ² (mg/g.h)	$RSS((mg/g)^2)$	$q_{e, ex}(mg/g)$	$K_2(h^{-1})$	$q_{e,cal}$	\mathbb{R}^2	Kq _e ²	RSS	
(K)			(mg/g)						(mg/g)		(mg/g.h)	$((mg/g)^2)$	
293	35	2.81 ×10 ⁻⁶	38	0.98	3.43	124	28	2.71 ×10 ⁻⁶	32	0.99	2.12	75	
303	34	5.65 ×10 ⁻⁶	36	0.99	6.53	153	41	7.95 ×10 ⁻⁶	42	0.99	13.35	114	
313	47	6.44 ×10 ⁻⁶	49	0.99	14.23	86	48	1.27 ×10 ⁻⁵	49	0.99	29.37	77	
						Elovich model							
Temperature	$\alpha(mg/g.hr)$	$1/\beta(mg/g)$		\mathbb{R}^2	RS	$S((mg/g)^2)$	α (mg/g.hr)	$1/\beta(mg/g)$	\mathbb{R}^2		RSS ($(mg/g)^2$)		
(K)													
293	14	6.58		0.90		197		6.22	0.93		108		
303	36	5.43		0.93		87		6.99	0.90		212		
313	60	7.82		0.95		114	237	6.60	0.91		177		
					Intrapa	rticle diffusion mo	odel						
Temperature	kin(hr-1/2)	C (mg/g)		\mathbb{R}^2		RSS $((mg/g)^2)$	Kin (hr ^{-1/2})	C (mg/g)	R ²		RSS $((mg/g)^2)$		
(K)													
293	4	4.74		0.91		171	3.52	1.56	0.9	0	8	42	
303	3	10.78		0.88		143	3.67	15.62	0.73		1245		
313	4	18.0		0.80		524	3.22	26.03	0.6	0.68		610	

Table 8. 1 Adsorption kinetic modeling results for flax shive hydrochars (HC-H₃PO₄-6h) and oat hull hydrochars (HC-H₃PO₄-6h).



Figure 8. 5 Fitted models of CBZ kinetic data on pretreated flax shive hycdrochars (H₃PO₄-6h)
(Ci=50 mg/L and T=313 K, 303 K, and 298 K). (A) Pseudo-first-order kinetic model; (B)
Pseudo-second-kinetic model; (C) Elovich model; (D) Intra particle diffusion.



Figure 8. 6 Fitted models of CBZ kinetic data on pretreated oat hull hydrochars (H₃PO₄-6h)
(Ci=50 mg/L and T=313 K, 303 K, and 298 K). (A) Pseudo-first-order kinetic model; (B)
Pseudo-second-kinetic model; (C) Elovich model; (D) Intra particle diffusion.

	Pseudo-first-order kinetic model												
Temperature	q _{e,exp}	$k_1(h^{-1})$	q _{e,,cal} (n	ig/g)	R ² R	SS $((mg/g)^2)$	q _{e,exp}	$k_1(h^{-1})$	q _e ,	,cal	R ²	RSS	
(K)	(mg/g)						(mg/g)		(mg	g/g)		$((mg/g)^2)$	
293	100	0.75	46		0.91	30530	100	0.70 49.89		.89	0.93	44294	
303	100	0.73	39		0.84	35271	100	0.60	35.51		0.85	41012	
313	100	0.92 29		0.68	44032	100	1.22	36.59		0.86	35573		
					I	Pseudo- secon	d-order kinetio	c model					
Temperature	qe, exp	K ₂ (h ⁻¹)	q e, cal	\mathbb{R}^2	Kqe ²	RSS	qe, exp	$K_2(h^{-1})$	qe, cal	\mathbb{R}^2	Kqe ²	RSS	
(K)	(mg/g)		(mg/g)		(mg/g.hr)	$((mg/g)^2)$	(mg/g)		(mg/g)		(mg/g.hr)	$((mg/g)^2)$	
293	100	5.88×10 ⁻⁵	103	1	588	583	100	7.39×10 ⁻⁵	102	100	738	951	
303	100	6.13×10 ⁻⁵	101	1	612	588	100	6.53 ×10 ⁻⁵	101	100	653	317	
313	100	9.09×10 ⁻⁵	100	1	910	786	100	12.50 ×10-5	100	100	1250	848	
						Elovich	n model						
Temperature	α (mg/g.hr) $1/\beta$ (mg		g/g) R ²		RSS $((mg/g)^2)$		α (mg/g.hr)	1/β (mg/g)	R ²		I	RSS $((mg/g)^2)$	
(K)													
293	328×10 ⁶	6.3	0	.61	1455		437×10 ⁴	6.09	0.63			1319	
303	996×10 ⁵	5.7	0.61		1218		374×10 ⁵	5.26	0.65			884	
313	992×10 ⁵ 5.0		0.57		11	17	758×10 ²	4.5	0.54		1031		
						Intraparticle	diffusion mod	el					
Temperature	in (hr ^{-1/2}) C (n		mg/g) R ²		RSS $((mg/g)^2)$		kin (hr-1/2)	C (1	C (mg/g)		R ²	RSS ((mg/g) ²)	
(K)													
293	2.80	85.	85.0 0.34		2514		2.7	4 84	84.54		0.35	2309	
303	2.58	84.1	0.35		2080		2.4	1 84	84.90		0.37	1594	
313	2.20	85.8	32	0.31	1	805	1.9	5 87	87.32		0.28	1622	

Table 8. 2 Adsorption kinetic modeling results for flax shive steam activated hydrochars (HC-H₃PO₄-6h) and oat hull steam activated hydrochars (HC-H₃PO₄-6h).

In addition, the results show that the steam activated hydrochars had much higher adsorption rate constants ((5.88-12.50) X10⁻⁵ h⁻¹) than the respective hydrochars ((2.82-12.50)X10⁻⁶ h⁻¹)). As a result, the initial rate of CBZ adsorption on the steam activated hydrochars calculated from Kq_e^2 was higher. This is again because the surface areas of the steam activated hydrochars are above those of the hydrochars, demonstrating the effectiveness of steam activation in creating porous structure of adsorbent. The result is similar to the high adsorption rate of the sewage sludge hydrochar compared to the raw material because of the increased surface area (Ferrentino et al., 2020).



Figure 8. 7 Fitted models of CBZ kinetic data on pretreated (A) flax shive steam activated hydrochar (H₃PO₄-6h) (B) oat hull steam activated hydrochar (H₃PO₄-6h) (Ci=50 mg/L and T=313 K, 303 K, and 298 K). Pseudo-second-order kinetic model.

Based on the rate constants regressed by the pseudo-second-order kinetic model (Table 8.1), the activation energy of CBZ adsorption by the flax shive and oat hull based hydrochars (HC- H_3PO_4 -6h) was determined to be 31.8 and 59.1 kJ/mol, respectively, through the linearized Arrhenius equation (Eq. 8.3).

In addition, activation energy obtained for the steam activated hydrochars (SAHC-H₃PO₄-6h) made from flax shives and oat hulls, were 16.45 and 19.7 kJ/mol respectively. They are much smaller compared to those of the hydrochars, indicating that the adsorption by steam activated hydrochars requires less energy, is readily reversible and attains equilibrium rapidly.

8.5. Chapter Summary

Based on the investigation of the CBZ adsorption kinetics of the hydrochars and steam activated hydrochars developed from flax shives and oat hulls, the following results are summarized.

By increasing the rotational speed from 80-170 rpm in the CBZ adsorption system, external mass transfer was enhanced. Further increasing rotational speed from 170 to 220 rpm did not make a significant impact.

Flax shives and oat hulls are both cellulosic materials and have a similar composition. Thus, either hydrochars or steam activated hydrochars made from the aforementioned materials have similar kinetics for CBZ adsorption. In addition, steam activated hydrochars demonstrated much faster adsorption than hydrochars because they have a much higher surface area.

The experimental kinetic data of both hydrochars and steam activated hydrochars were successfully simulated by the pseudo-second-order kinetic model. Compared with those of the hydrochars, the adsorption rate constants of the steam activated hydrochars were much higher. The activation energy determined based on the rate constants demonstrated the CBZ adsorption by the steam activated hydrochars had smaller activation energy than that by the hydrochars. Thus, it required less energy, was readily reversible and attained equilibrium rapidly.

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CHAPTER 9 DESORPTION OF ADSORBED CARBAMAZEPINE AND REUSE OF ADSORBENTS

Contribution of this chapter to overall Ph.D. work

In this chapter, desorption of CBZ from hydrochars and steam activated hydrochars was investigated with various organic solvents and water at different pH values. In addition, reuse of the selected hydrochars and steam activated hydrochars were studied. Overall, the results demonstrated that the highest desorbed efficiency was obtained with organic solvent ethanol. The regenerated adsorbents were re-usable.

9.1. Effects of Organic Solvents on CBZ Desorption

To understand the fate of adsorbed pollutants, and regenerate and reuse adsorbents is important. According to the stability of the complex form of pharmaceutical-hydrochar/steam activated hydrochar, desorption of CBZ was investigated. Various solvents such as ethanol, methanol and water were used in the desorption experiments. The desorption efficiencies of CBZ from flax shives and oat hulls hydrochars and steam activated hydrochars using ethanol, methanol, or water (without pH adjustment), or combination of the solvents are presented in Figures 9.1, 9.2, 9.3, and 9.4, respectively.

According to the results, desorption of CBZ molecules from the steam activated hydrochars were faster compared to that from the hydrochars. Besides, the highest desorption efficiency was obtained by using ethanol for both hydrochars and steam activated hydrochars. The performance was similar in the cases of flax shives and oat hull adsorbents. Specifically, the time required to reach desorption equilibrium with the hydrochars and steam activated hydrochars was 96 and 8 h, respectively. The faster desorption speed could be because steam activated hydrochars have much higher surface area (527 and 793 m²/g for oat hull and flax shive steam activated hydrochars, respectively) than hydrochars (28 and 12 m²/g), which was reported in Chapter 4 of this thesis. In addition, the initial loading of CBZ on the steam activated hydrochars (102-103 mg/g) was higher than that of hydrochars (42-47 mg/g).

The driving force and the equilibrium CBZ desorption efficiency in the case of steam activated hydrochars is also higher, resulting in a faster desorption speed. For example, in the case of flax shives, the desorption efficiency of 58 and 54 % were achieved from the steam activated hydrochars (SAHC-H₃PO₄-6h and SAHC-H₃PO₄-12h) and 32 and 31% from the hydrochar (HC-H₃PO₄-6h and SAHC-H₃PO₄-12h).

The achieved results also demonstrated that ethanol was more effective in CBZ desorption compared with other solvents used in this work such as methanol and water. For example, in the case of flax shives, the desorption efficiency of CBZ with the steam activated hydrochars (SAHC-H₃PO₄-6h and SAHC-H₃PO₄-12h) using ethanol as the sole solvent was in the range of 54 -58 % while the value was 43-55% when methanol and 9-12% when water was used. Similar results were obtained in other study of CBZ adsorption by granular activated carbon (Cai, 2015). In that work, ethanol was also used in desorption to analyze the possibility of chemisorption versus physisorption based on that it was expected to easily desorb physisorbed CBZ because of high solubility of CBZ in ethanol (20.8 g/L while 0.125 g/L in water at room temperature) and favored hydrophobic attraction (Cai, 2015; Cai and Larese-Casanova, 2014).

The results proved that elution of CBZ loaded hydrochars and steam activated hydrochars with ethanol or other similar organic solvents is feasible. It was also considered that using such organic solvents for desorption are cost-saving for application of this kind of materials in the water treatment (Cai, 2015; Cai and Larese-Casanova, 2014).



Figure 9. 1 Desorption of CBZ from flax shive hydrochars A) HC-H₃PO₄-6h and B) HC-H₃PO₄-12h. 10 mL solvent, 2 mg dry adsorbent with an initial CBZ uptake of 47 mg/g and 42 mg/g for HC-H₃PO₄-6h and HC-H₃PO₄-12h hydrochars respectively obtained by adsorption at 40°C and 20°C for desorption.



Figure 9. 2 Desorption of CBZ from flax shive steam activated hydrochars (A) SAHC-H₃PO₄-6h and (B) SAHC-H₃PO₄-12h. 10 mL solvent, 2 mg dry adsorbent with an initial CBZ uptake of 103 mg/g and 102 mg/g for SAHC-H₃PO₄-6h and SAHC-H₃PO₄-12h steam respectively obtained by adsorption and desorption at 20°C.

Furthermore, it is noticeable that though the desorption performance in the cases of oat hulls and flax shives adsorbents are similar, the desorption efficiencies in the case of oat hull based steam activated hydrochars (49-53%) and hydrochars (26-27%) were slightly lower than those in the case of flax shives steam activated hydrochars (54-58%) and hydrochars (31-32%) when desorbing with ethanol. This supports that CBZ molecules had weaker interactions with the flax shives adsorbents than the adsorbents developed from oat hulls. It is also consistent to the results presented in Chapter 6 (Section 6.1) that the slightly higher values of weighted mean of site energy distribution of CBZ adsorption by the oat hulls adsorbents in comparison with the flax shives adsorbents indicated the interaction between CBZ and the oat hulls adsorbents are slightly stronger. Again, more study on CBZ desorption mechanism is necessary.



Figure 9. 3 Desorption of CBZ from oat hull hydrochars (A) HC-H₃PO₄-6h and (B) HC-H₃PO₄-12h. 10 mL solvent, 2 mg dry adsorbent with an initial CBZ uptake of 49 mg/g and 41 mg/g hydrochars respectively obtained by adsorption at 40°C and 20°C for desorption.



Figure 9. 4 Desorption of CBZ from oat hull steam activated hydrochars (A) SAHC-H₃PO₄-6h and (B) SAHC-H₃PO₄-12h. 10 mL solvent, 2 mg dry adsorbent with an initial CBZ uptake of 102 mg/g steam activated hydrochars respectively obtained by adsorption and desorption at 20°C.

9.2. Effect of pH on CBZ Desorption

As discussed before, pH may affect charge of adsorbate and adsorbent, thus may influence adsorption as well as desorption of adsorbed adsorbate with charges. In the present experiments, three different pH levels (2, 6 and 10) were investigated in desorption of CBZ loaded on the hydrochars and steam activated hydrochars. The results presented in Figure 9.5 shows that desorption efficiency was very low in the tested wide range of pH 2-10. Specifically, the values in all the cases of hydrochars were lower than 7% and those in the cases of steam activated hydrochars were lower than 13%, while above 20% and 50% respectively when desorbing using ethanol. In addition, the desorption efficiency did not change significantly at the wide pH range (2 -10). As mentioned above, solution pH may affect charge state of adsorbate and adsorbent, thus possibly impacting their electrostatic attraction.

However, the low desorption efficiency at various pH again confirmed that the contribution of electrostatic attraction to overall CBZ adsorption existed, but was insignificant. It was reported that electrostatic attraction was the predominant mechanism in Ni²⁺ adsorption by raw barley straw (Thevannan et al., 2010) and Au(CN)²⁻ adsorption by crab shells (Niu, 2002), in which systems the adsorbates existed as ions or anions with significant amount of charges. CBZ is an organic compound, which has aromatic structures and weak base groups such as amino and carbonyl. As discussed in Chapter 7 of the thesis that the hydrochars and steam activated hydrochars also had aromatic structures and functional groups such as hydroxyls, carboxyls, and so on. The desorption results indicated that the CBZ adsorption on steam activated hydrochars may involve multiple mechanisms such as π - π EDA interaction, hydrophobic, hydrogen bonding, and electrostatic attraction, but of different levels of importance. It was reported that π - π EDA interaction is stronger than electrostatic attraction and hydrogen bond, and similar to inner-, and outer-sphere complex formation (Keiluweit & Kleber, 2009).



Figure 9. 5 Effect of pH on desorption of CBZ from (I-A) flax shive hydrochars and (I-B) steam activated hydrochars. 10 mL solvent, 2 mg dry adsorbent with an initial CBZ uptake of 46.32 mg/g (HC-H₃PO₄-6h), 39.2 mg/g (HC-H₃PO₄-12h), 95.70 mg/g (SAHC-H₃PO₄-6h), and 81.53 mg/g (SAHC-H₃PO₄-12h) obtained by adsorption at 40°C for hydrochars and 20°C for steam activated hydrochars. (II-A) oat hull hydrochars and (II-B) steam activated hydrochars. 10 mL solvent, 2 mg dry adsorbent with an initial CBZ uptake of 47.15 mg/g (HC-H₃PO₄-6h), 40.64 mg/g (HC-H₃PO₄-12h), 87.71 mg/g (SAHC-H₃PO₄-6h), 87.16 mg/g (SAHC-H₃PO₄-12h) obtained by adsorption at 20°C for steam activated hydrochars. All the desorption experiments were done at 20°C.

9.3. Reuse of Adsorbents

Regeneration and reuse of adsorbents are crucial in terms of sustainability and economic aspects of adsorbents. After regeneration using ethanol, the hydrochars and steam activated hydrochars were used for six CBZ adsorption-desorption cycles. As shown in Figure 9.6, steam activated hydrochars had higher adsorption capacities throughout the six adsorption-desorption cycles though the CBZ adsorption capacities gradually decreased with repeated cycles in all the investigated cases. The decrease could be a result of reduction in both number of functional groups of the hydrochars and steam activated hydrochars available for CBZ adsorption because CBZ molecules loaded on the adsorbents were not completely desorbed in the previous steps of desorption and they occupied the adsorption sites. For example, the adsorption capacity of flax shives based steam activated hydrochars (Figure 9.6 A) decreased from 61 to 50 mg/g (decreased 18.3 %) in the first three cycles, and down to about 40 mg/g (decreased 34.4 %) in the sixth cycle. In the case of oat hulls adsorbents, these values decreased from 52 to 42 mg/g (decreased 19%) in the first three cycles, and to 38 mg/g (decreased 26.9 %) in the sixth cycle. Fortunately, the capacities after six adsorption - desorption cycles are still higher than those of CBZ adsorption by sewage sludge/fish waste (37.2 mg/g) (Nielsen et al., 2015), peanut shell-biochars (3.39 mg/g) (Chu et al., 2017), carbon polyhedrons (21.3 mg/g) (Chen et al., 2020), Fe₃O₄ nanoparticles (2.2 mg/g)(Ghosh et al., 2013), mesoporous silica SBA-15 (0.16 mg/g) (Bui & Choi, 2009) and so on.

These results showed that the steam activated hydrochars have higher capability to treat wastewater containing CBZ. On the other hand, desorption efficiency could be further enhanced.



Figure 9. 6 Adsorption capacity of CBZ during six adsorption-desoprtion cycles. (I) flax shive steam activated hydrochars (A) and hydrochars (B) and (II) oat hull steam activated hydrochars

(A) and hydrochars (B). (For adsorption: CBZ concentration 50 mg/L, 10ml solvent adsorbent dosage 5 mg, pH 5.8-6, adsorption time was 48 and 72 h for flax shive and oat hull hydrochars respectively at40°C, 2h for flax shive and oat hull steam activated hydrochars at 20°C. Desorption was done in 10 mL ethanol, 2 mg dry adsorbent with an initial CBZ uptake of 24.9 mg/g (flax shive-HC-H₃PO₄-6h), 61.6 mg/g (flax shive-SAHC-H₃PO₄-6h), 20.7 mg/g (oat hull-HC-H₃PO₄-6h), 51.8 mg/g (oat hull-SAHC-H₃PO₄-6h). Desorption time was 8h for steam activated hydrochars and 96 h for hydrochars.

9.4. Chapter Summary

The results obtained from this chapter demonstrated that desorption of CBZ from the steam activated hydrochars developed from flax shives and oat hulls was faster than that from the respective hydrochars. Among the selected solvents, ethanol was the most efficient in desorption compared with methanol, water, and combination of the aforementioned solvents. Desorption efficiency of CBZ from the hydrochars and steam activated hydrochars derived from oat hulls was slightly lower compared to those from the flax shive adsorbents because of the slightly weaker interactions between CBZ and the flax shive adsorbents. Varying solution pH slightly changed the desorption efficiency, however, the impact was insignificant. The results again indicated minimal contribution of electrostatic attraction to overall CBZ adsorption. The regenerated steam activated hydrochars (flax shives and oat hulls) after 6 adsorption-desorption cycles still had higher CBZ adsorption capacities than a number of adsorbents reported by other researchers.

CHAPTER 10 CONCLUSIONS, SIGNIFICANT CONTRIBUTIONS,

AND RECOMMENDATIONS

10.1. Conclusions and Significant Contributions

In this work, a novel adsorption technology was developed by successfully producing adsorbents of hydrochars and steam activated hydrochars from flax shives and oat hulls for effectively adsorbing CBZ, a model pharmaceutical pollutant from the artificial contaminated water. The adsorbents were characterized on surface chemical and physical properties. CBZ adsorption equilibrium, mechanisms, kinetics, and desorption were investigated to contribute to the knowledge of fundamental science and engineering of adsorption, and apply the technology in water/wastewater treatment. Specific conclusions and contributions are drawn as follows.

- 1. Hydrothermal carbonization enhanced the pore structure and surface area of raw flax shives and raw oat hulls. Steam activation was more effective in creating pore structure and generating high internal surface area of the adsorbents. In addition, hydrothermal treatment at a relatively low temperature such as 220°C slightly increased the carbon content, and decreased the oxygen content and ratio of H/C of the flax shive and oat hull adsorbents while the impact of steam activation in the respects are much more significant. These thermal treatments generated aromatic structure and functional groups such as carbonyls or carboxyls which were important for CBZ adsorption.
- 2. The developed hydrochars and steam activated hydrochars adsorbents have noticeably increased CBZ adsorption capacities in comparison with raw flax shives and oat hulls though they had different elemental composition and surface areas. The capacities are also higher than numerous adsorbents reported in literature. Again, the impact of steam activation on adsorption capacity is more significant.

Although CBZ adsorption was slightly higher at about pH 6, the effect of pH (2-10) was not significant. This technology has a potential for application in treatment of contaminated water at a wide pH range. The results also indicate that the adsorption mechanism is not mainly through electrostatic attraction or hydrogen bonding. Besides, the CBZ adsorption capacity of steam activated hydrochars increased with an increase of temperature from 20°C to 40°C, indicating the endothermic adsorption.

- 3. The CBZ adsorption isotherms were successfully simulated by the Sips isotherm which considered Langmuir type adsorption on heterogeneous surface. Based on the modeling results, the site energy distribution and the weighted mean were determined. The higher weighted mean of site energy obtained at a higher temperature, 40°C, indicated stronger adsorption affinity. Thermodynamic analysis of the adsorption of CBZ on the activated hydrochars indicated the process was endothermic and spontaneous.
- 4. The mechanisms of CBZ adsorption by hydrochars and steam activated hydrochars were elucidated in aid of CBZ adsorption experiments and analyses of FTIR, XPS and NEXAFS. CBZ adsorption by the hydrochars and steam activated hydrocars are predominantly physical adsorption. The π-π EDA interactions between CBZ and the hydrochars and steam activated hydrochars are a significant mechanism in CBZ adsorption. They involved in the π-π EDA interaction between the aromatic π* C=C of hydrochar and steam activated hydrochar of the adsorbents as π-electron-donor and π* carbon atom in the benzene ring attached to N of CBZ molecules as π-electron-acceptor (C = C* N). In addition, the oxygen-containing groups -C=O, COH, and R-COOH having lone electron pairs could also serve as π-electron donor to form π-π EDA interaction with CBZ. Besides, hydrophobic interaction also contributed to CBZ adsorption. Electrostatic attraction between the CBZ molecules, and the hydrochars and steam activation hydrochars with opposite charges contributed to the total CBZ adsorption, however, was not significant. Hydrogen bonding formed between -NH₂, and -C=O of CBZ and oxygen containing groups -C=O, C-OH, C-OOH, and R-COOH of hydrochars and steam hydrochars, but again was not predominant.

In addition, thermal treatments enhanced the aromatic structures of the adsorbents contributing to the π - π electron-donor-acceptor interactions, thus enhanced the CBZ adsorption. In this respect, the impact of steam activation was more significant than hydrothermal treatment. In general, CBZ adsorption of flax shives and oat hulls based hydrochars and steam activated hydrochars followed similar mechanisms because of their similar composition.

5. Flax shives and oat hulls are both cellulosic materials and have a similar composition. Thus, either hydrochars or steam activated hydrochars made from the aforementioned materials have similar kinetics for CBZ adsorption. In addition, steam activated hydrochars demonstrated much faster adsorption than hydrochars because they have a much higher surface area.

The experimental kinetic data of both hydrochars and steam activated hydrochars were successfully simulated by the pseudo-second-order kinetic model. The higher adsorption rate constants of the steam activated hydrochars compared with that of the hydrochars again confirmed faster adsorption speed. The activation energy determined based on the rate constants demonstrated the CBZ adsorption by the steam activated hydrochars had smaller activation energy than that by the hydrochars. Thus, it required less energy, was readily reversible and attained equilibrium rapidly.

6. Desorption of CBZ loaded on the hydrochars and steam activated hydrochars was enhanced using ethanol in comparison with methanol and water. Varying solution pH did not effectively desorb CBZ. Regenerated adsorbents were reusable. However, this area of research could be further investigated.

This work demonstrated that flax shives and oat hulls are promising feedstocks to make hydrochars and steam activated hydrochars for effective adsorption of CBZ and other pharmaceutical pollutants with similar structure.

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10.2. Recommendations for Future Work

Based on the results obtained from the work, the following recommendations were made to further improve the research.

- It is recommended to carry on the hydrothermal experiments in a higher pressure in order to produce bio-oil in addition to hydrochar adsorbents. This may add additional values to the process. Investigation can be done on the feedstocks such as oat hulls and flax shives and their produced bio-oils in terms of ultimate production conditions, compositions, and application.
- 2. Introduction of heteroatom in the carbon network during the hydrothermal process could be another area of future research. Addition of oxygen, nitrogen, phosphorus, sulphur and boron can improve electrical conductivity, material stability and catalytic performance because of increased number of active sites, acidity/basicity, and hydrophobicity/hydrophilicity.
- 3. Desorption of CBZ loaded on the hydrochars and steam activated hydrochars to generate the adsorbents needed to be further enhanced. Better understanding of the desorption mechanism is necessary. In addition, proper treatment of desorbed CBZ is essential to avoid pollution.
- 4. The percentage ash contents in the steam activated adsorbents increased at 850°C, which resulted in higher adsorption. In general, this behavior is related to the increased release of volatile matter and the increased consumption of fixed carbon. Better understanding of the relation between the amount of ash content and higher adsorption uptake is necessary.
- 5. π - π EDA interactions and hydrophopbic interaction were proposed as the important mechanisms in the adsorption of CBZ on flax shive and oat hull steam activated hydrochar/hydrochars. However, when applying the adsorption technology in a real aquatic system, mechanisms such as π - π EDA interactions, hydrophobic, electrostatic attraction, and hydrogen bonding may simultaneously take place in the adsorption of pharmaceuticals on flax shive and oat hull steam activated hydrochar/hydrochars. In addition, they may affect one another. Therefore, further investigations on the binding strengths of EDA interactions, electrostatic attraction, and other interactions are neccesary.
- 6. The range of micro-pollutant concentration should be adjusted to real conditions. Due to the detection limit of the HPLC available to this work, the range of concentration of pharmaceutical CBZ used in this study was in the order of mg/L, while most of the reported

CBZ concentrations in water bodies and water streams were at ppb level (μ g/L) and even at ppt level (ng/L). Adsorption need be done at such low concentrations.

- 7. The presence of Ni²⁺ suppressed the adsorption of CBZ on steam activated hydrochars/hydrochars at the tested pH values (2.0, 4.0, 6.0, 8.0 and 10.0) in this work. The mechanisms such as the interaction of SAHC-H₃PO₄-CBZ-nickel (metal) and HC-H₃PO₄-CBZ-nickel should be further investigated.
- 8. Based on the current work, pilot studies should be considered for future research through packed column adsorption systems using real industrial wastewater containing the pharmaceutical pollutants in the presence of metals such as nickel ions and other metals to investigate the effect of competitive adsorption.
- 9. It is recommended to investigate the adsorption kinetics at various particle sizes of the adsorbents.
- 10. It is recommended to study the performance of the same feedstock from different country or regions.
- 11. It is necessary to analyze the ash composition and investigate its roles in CBZ adsorption.

PUBLICATIONS, CONFERENCE PRESENTATIONS, AND AWARDS

Journal Publications:

- Aylin Aghababaei, Ramin Azargohar, Ajay K. Dalai, Jafar Soltan, and Catherine Hui Niu. 2021. "Effective adsorption of carbamazepine from water by adsorbents developed from flax shives and oat hulls: key factors and characterization". Industrial Crops and Products, 170, 113721. https://doi.org/10.1016/j.indcrop.2021.113721.
- Aylin Aghababaei, Ramin Azargohar, Ajay K. Dalai, Jafar Soltan and Catherine Hui Niu. 2021. "Adsorption of carbamazepine from water by hydrothermally and steam activated agricultural by-products: equilibrium, site energy, and thermodynamic studies" Submitted to Chemical Engineering Communication. https://doi.org/10.1080/00986445.2021.1922893.
- Aylin Aghababaei, Venu Borugadda, Ajay Dalai and Catherine Hui Niu. "Investigation on kinetics of carbamazepine contaminant adsorption with novel agricultural by-products based adsorbents", in preparation.
- Aylin Aghababaei and Catherine Hui Niu. "Porous carbons derived from agricultural byproducts for adsorption of carbamazepine – desorption, mechanism and effect of nickel, in preparation.

Conference Presentation:

- 5) Aylin Aghababaei and Catherine Hui Niu. "Kinetic studies and site energy distribution analysis of carbamazepine sorption by agriculture biosorbents". 69th Canadian Chemical Engineering Conference, CSCHE 2019. Halifax, NS, Canada, Oct 20-23, 2019.
- 6) Aylin Aghababaei, Catherine Hui Niu. "Adsorption of Carbamazepine from water by hydrothermal carbonisation of flax-shives: Equilibrium and thermodynamic studies". 68th Canadian Chemical Engineering Conference, CSCHE 2018. Toronto, ON, Canada, Oct 28-31, 2018.
- Aylin Aghababaei and Catherine Hui Niu. "Drying air using oat hull based adsorbent"
 67th Canadian Chemical Engineering Conference, CSCHE 2017. Edmonton, AB, Canada, Oct 22-25, 2017.

Awards:

- 1) Recipient of Devolved Scholarship of the Department of Chemical and Biological Engineering at the University of Saskatchewan in 2016, 2017, 2018, and 2019.
- 2) Winner of the Best Poster Competition, College of Engineering at the University of Saskatchewan in 2019.
- 3) Recipient of travel award at the University of Saskatchewan in 2016, 2017, 2018 and 2019.

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APPENDICES

A. Life Cycle Assessment

A1. Impact Category Descriptions

The following impact categories, as used by CML2.7 (2007) method, are described below (simapro manual PRe Consultants, 2008)

Acidification potential: Refers to the compounds that are precursors to acid rain. These include sulfur dioxide (SO₂), nitrogen oxides (NOx), nitrogen monoxide (NO), nitrogen dioxide (N₂O), and other various substances.

Climate change: Climate change is related to emissions of greenhouse gases to air. The characterization model as developed by the Intergovernmental Panel on Climate Change (IPCC) was selected for development of characterization factors. Factors are expressed as Global Warming Potential for time horizon 100 years (GWP100), in kg carbon dioxide/kg emission. The geographic scope of this indicator is at global scale.

Depletion of abiotic resources: Abiotic depletion refers to the depletion of nonliving (abiotic) resources such as fossil fuels, minerals, clay, and peat.

Eutrophication: This category indicates the enrichment of the aquatic ecosystem with nutritional elements, due to the emission of nitrogen or phosphor containing compounds.

Freshwater aquatic Eco-toxicity: This category indicator refers to the impact on fresh water ecosystems, as a result of emissions of toxic substances to air, water and soil. Ecotoxicity Potential (FAETP) are calculated with USES-LCA, describing fate, exposure and effects of toxic substances. The time horizon is infinite. Characterization factors are expressed as 1,4-dichlorobenzene equivalents/kg emission. The indicator applies at global/continental/ regional and local scale.

Human toxicity: This category concerns effects of toxic substances on the human environment. Health risks of exposure in the working environment are not included. Characterization factors, Human Toxicity Potentials (HTP), are calculated with USES-LCA, describing fate, exposure and effects of toxic substances for an infinite time horizon. For each toxic substance HTP's are expressed as 1.4-dichlorobenzene equivalents/ kg emission. The geographic scope of this indicator determines on the fate of a substance and can vary between local and global scale.

Marine aquatic ecotoxicity: Refers to impacts of toxic substances on marine ecosystems (see description freshwater toxicity).

Ozone layer depletion: It is an indicator of emissions to air that cause the destruction of the stratospheric ozone layer.

Photochemical oxidation: It is secondary air pollution, also known as summer smog. It is formed in the troposphere caused mainly by the reaction of sunlight with emissions from fossil fuel combustion creating other chemicals.

Terrestrial ecotoxicity: Terrestrial toxicity is defined as the study of the effects of a chemical substance to terrestrial organisms and terrestrial plants.

A2. Life Cycle Analysis System Boundary, Inventory and Impact Assessment

To evaluate environmental impacts during production of steam activated hydrochars, life cycle analysis was carried out using flax shives and oat hulls as model materials according to ISO 14044 standard (International Organization for Standardization (ISO), 2006). The use of chemical reagents, energy, and water was evaluated at each stage of the steam activated hydrochar production and the detailed procedure is shown in Figure A.1 (flax shives) and A.2 (oat hulls). The energy provided to the production process was in the form of electricity for drying, stirring, heating, steam generation, and activation. At each stage, the energy demand was calculated during life cycle inventory (LCI). The functional unit of this analysis was to produce 1 kg of steam activated hydrochar from flax shives or oat hulls via acid treatment and steam activation methods. The wastewater and solvents produced at each stage were disposed of according to the chemical waste management system developed by the University of Saskatchewan and the environmental impacts related to the disposal of liquid wastes were considered in the LCI. The database used in the study was obtained from the laboratory experiments and information on the environmental burdens.

The use of primary resources in the materials and electricity production were obtained from Ecoinvent database (*ecoinvent - the world's most consistent & transparent life cycle inventory database*, 2007). The CML baseline method (2015) was used to make life cycle impact assessment (LCIA) according to ISO standard 14044 (2006). To identify the most impacting categories, normalization was used. In the impact analysis, the following impact categories were taken into account: acidification potential, climate change, depletion of abiotic resources, eutrophication, freshwater aquatic ecotoxicity, human toxicity, marine aquatic ecotoxicity, ozone layer depletion, photochemical oxidation, and terrestrial ecotoxicity.



Figure A. 1 Life cycle analysis system boundaries to produce 1 kg (functional unit) of steam activated hydrochars from flax shives.



Figure A. 2 Life cycle analysis system boundaries to produce 1 kg (functional unit) of steam activated hydrochars from oat hulls.

During the production of steam activated hydrochar from flax shives and oat hulls, positive and negative contributors were calculated at all the manufacturing stages. At each stage, all the contributors have been identified and quantified in terms of global/localized impact categories. The single score results are reported in Table A.1 since this process has not been compared with any other process and normalized values were not mentioned. From the table, global warming potential seems to be the major contributor towards the global impacts; depletion of abiotic resources and marine aquatic toxicity are considered as localized impact categories. The entire manufacturing process is dominated by the stages of water, acid, and solvent washings followed by drying, steam generation, which is mandatory for activation of hydrochar. During all the stages, electricity was used as a major source of energy (7 KW), which was the main reason for the contribution of global warming potential (77.76 kg CO₂ eq.) and other impact categories such as depletion of abiotic resources (951.73 MJ) because coal was used to produce electricity. This explains the strong impact of climate change and depletion of abiotic resources; which is related to the environmental burdens with respect to electrical energy production. Treatment of the flax shives and oat hulls with phosphoric acid and ethanol leads to the damage of natural resources and causes environmental burdens to produce these chemicals industrially. Further, human toxicity potential (14.66 kg 1,4-dichlorobenzene eq.) and marine aquatic ecotoxicity (10282.64 kg 1,4dichlorobenzene eq.) were found to be significant impact categories for aquatic species due to the wastewater disposal at each stage during water washings, phosphoric acid treatment, and ethanol washing. Other impact categories such as depletion of abiotic resources, acidification potential, and freshwater aquatic ecotoxicity have very little impact on the entire process as it shows lower results.
Impact category	Reference unit	Result
Acidification potential (AP)	kg SO ₂ eq.	0.47
Climate change (GWP 100 years)	kg CO ₂ eq.	77.76
Depletion of abiotic resources (elements, ultimate		
reserves)	kg antimony eq.	2.8E-04
Depletion of abiotic resources (fossil fuels)	MJ	951.73
Eutrophication Potential (EP)	kg PO ₄ eq.	3.64
Freshwater Aquatic Ecotoxicity (FAETP inf.)	kg 1,4-dichlorobenzene eq.	0.11
Human Toxicity Potential (HTP inf.)	kg 1,4-dichlorobenzene eq.	14.66
Marine Aquatic Ecotoxicity (MAETP inf.)	kg 1,4-dichlorobenzene eq.	10282.64
Ozone Layer Depletion (ODP steady state)	kg CFC-11 eq.	4.97E-06
Photochemical Oxidation (high Nox)	kg ethylene eq.	0.34
Terrestrial ecotoxicity (TETP inf.)	kg 1,4-dichlorobenzene eq.	0.22

Table A. 1 Single score impact results of life cycle assessment of steam activated carbon production from hydrochar using CML baseline method.

A3. Summary

According to the results achieved in this chapter, it was summarized that global warming potential seems to be the major contributor towards the global impacts; depletion of abiotic resources and marine aquatic toxicity are considered as localized impact categories. Electricity and depletion of abiotic resources were the main reason for the contribution of global warming potential. The treatment of the flax shives and oat hulls with phosphoric acid and ethanol leads to the damage of natural resources and causes environmental burdens to produce these chemicals industrially. Further, human toxicity potential and marine aquatic ecotoxicity were found to be significant impact categories for aquatic species due to the wastewater disposal at each stage during water washings, phosphoric acid treatment, and ethanol washing. Other impact categories such as acidification potential, depletion of abiotic resources, and freshwater aquatic ecotoxicity have very little impact on the entire process as they show lower values.

B. N 1s Spectra

According to the results (Figure 7.4 and Table B.1), the atomic percentage of N on the surface of Flax shive-SAHC-H₃PO₄-6h and Oat hull-SAHC-H₃PO₄-12h increases to 0.23 and 0.07%, respectively after adsorption of CBZ. Figure B1 shows the high-resolution N1s spectra. There are two peaks at 399.65 and 400.9 eV observed on the N 1s spectrum of CBZ, attributed to C–N and N–H (Chen et al., 2020; Chen et al., 2017b). After adsorption, the N 1s spectra of Flax shive-SAHC-H₃PO₄-6h and Oat hull-SAHC-H₃PO₄-12h indicate overlay of the adsorbents and pure CBZ; The N-H peaks in the form of NH₄ indicates the interaction of the pharmaceutical and the bioadsorbent. According to Figure B1, the peaks of C-N and N-H slightly shifted to higher values because of the π - π EDA interaction between the steam activated hydrochars and CBZ. The π -electron donor groups of steam activated hydrochars had the ability to increase the electron cloud density of N atoms in CBZ molecule, leading to an increase of the binding energy of C–N and N–H in CBZ. This is similar to the removal of CBZ with activated carbon produced by pomelo peel (Chen etal., 2017) and the removal of CBZ with the carbon materials made from MOFs (Chen et al., 2020).

Sample	Carbon (%)	Oxygen (%)	Nitrogen (%)	
CBZ	85.62	5.35	9.04	
Flax shive adsorbents				
Raw flax shives	79.38	18.86	1.75	
SAHC-H ₃ PO ₄ -6h	82.60	17.35	0.05	
SAHC-H ₃ PO ₄ -6h+CBZ	84.44	15.33	0.23	
HC-H ₃ PO ₄ -6h	85.69	14.07	0.27	
HC-H ₃ PO ₄ -6h+CBZ	80.64	19.11	0.89	
Oat hull adsorbents				
Raw oat hulls	90.32	8.62	1.06	
SAHC-H ₃ PO ₄ -12h	87.57	12.39	0.04	
SAHC-H ₃ PO ₄ -12h+CBZ	83.07	16.85	0.07	
HC-H ₃ PO ₄ -6h	82.65	16.76	0.59	
HC-H ₃ PO ₄ -6h+CBZ	84.31	14.85	0.84	

Table B. 1 Content of major elements (atomic%) on the surface of adsorbents before and after adsorbed CBZ.



Figure B. 1 N 1s. spectra of A) CBZ; B) Flax shive-SAHC-H₃PO₄-6h; and C) Oat hull-SAHC-H₃PO₄-12h.

In addition, the analysis was also carried out for hydrochars. The N 1s spectra results of Flax shive-HC-H₃PO₄-6h and Oat hull-HC-H₃PO₄-12h are shown in Figures 7.5 and B2. The hydrochars derived from oat hulls and flax shives also follow the same trend as that for the steam activated hydrochars. After adsorption, the two main peaks of C-N and N-H (in the form NH₄) shifted to higher values, which also indicated the $\pi - \pi$ EDA interaction. Similar observation was obtained by Chen et al. (2020) and Chen et al. (2017a) in their study on carbon polyhedrons and pomelo peel to adsorb CBZ from aqueous solution.



Figure B. 2 N 1s. spectra of A) Flax shive-HC-H₃PO₄-6h B) Oat hull-HC-H₃PO₄-12h.

C. Effect of Ultrasonic Assistance

To further enhance adsorption speed, ultrasound was applied in CBZ adsorption. For this experiment, the steam activated hydrochars (SAHC-H₃PO₄-6h and SAHC-H₃PO₄-12h) made from flax shives and oat hulls were used for CBZ adsorption at 20°C for 20-120 minute. The results are presented in Figure C1. The first observation when applying ultrasonication was homogenous dispersion of the adsorbents in the solution and fractionation of the adsorbents prepared from flax

shives and oat hulls into smaller particles. Ultrasonication increased the adsorption from the beginning till 100 minutes. At 120 minutes (2 h), the uptakes achieved with and without ultrasonication are approximately the same, indicating adsorption approached equilibrium. At 100 min, the adsorption uptake achieved with ultrasonication is close to the equilibrium which was reached at 120 min without ultrasonication. The reason for the increase in the total adsorption rate was because nanobubbles were created through ultrasonication. The nanobubbles helped to disperse the activated hydrochars aggregates into smaller fractions, thus increasing the surface area and exposure of the active sites leading to an increase of the adsorption rate (Oleszczuk & Xing, 2011). By the increase in the exposure time of the ultrasonication the adsorption became stable and reached equilibrium.



Figure C. 1 Influence of ultrasonication on the removal of Carbamazepine with steam activated hydrochars (I) Flax shives. (II) Oat hulls (initial concentration 50 mg/L, adsorbent dosage 5mg, temperature 20 ± 2 °C and pH 5.8-6, 35Khz, WU stands for With Ultrasonication and WOU stands for With Out Ultrasonication).

D. Adsorption of Carbamazepine on Flax Shive based Hydrochar and Steam Activated Hydrochar in the Presence of Nickel Ions

The simultaneous presence of pharmaceuticals and heavy metals in water or wastewater can alter the fate of pharmaceuticals in the environment (Turk Sekulic et al., 2019). Nickel is used in most of the industries, such as porcelain enameling, manufacturing of sulfate, production of paints and batteries, electroplating, and mineral processing (Yan, 2017). When it is released into the environment, nickel is related with illnesses such as lung cancer, chronic bronchitis, nausea dermatitis, and gastrointestinal distress, therefore threatening human health (Flores-Garnica et al., 2013; Sharma & Singh, 2013). In addition, it may affect the fate of pharmaceutical pollutants. Currently, nickel is one of the metals commonly existing in wastewater, thus one of the concerns in the water sources. As such, being a representative of heavy metals, nickel ion was selected as a model in this work to estimate its effect on adsorption of CBZ.

The experiments were conducted using the hydrochars and steam activated hydrochars made from flax shives in the presence of Ni²⁺ in a batch mode by mixing 5.0 ± 0.1 mg dry hydrochar/steam activated hydrochar with a 10.0 mL CBZ-nickel solution (50 mg/L of each adsorbate) at 20 and 40 °C for 2 and 72 h in the cases steam activated hydrochar and hydrochar respectively at a wide range of pH 2-10.

According to Figure D.1, by adding Ni^{2+} to the solution the adsorption capacity of CBZ on hydrochars and steam activated hydrochars were slightly suppressed at the measured pH values of 2-10 except for the case of steam activated carbons at pH 6 and 8. The slight suppression can be because of the competition of cation Ni^{2+} with CBZ for the negatively charged adsorption sites of the hydrochars and steam activated hydrochars. The result was similar to the adsorption of norfloxacin on montmorillonite in the presence of Cu^{2+} at pH 4.5 (Pei et al., 2011), adsorption of levofloxacin by pretreated barley straw in the presence of Ni^{2+} (Bei Yan, 2017), and adsorption of ciprofloxacin and Ni^{2+} on activated carbon (Sun et al., 2014). Ni^{2+} is usually adsorbed by electric attraction because it is a cation. The slight decrease of CBZ adsorption capacity in the presence of nickel ions in this work again confirmed the contribution of electric attraction in CBZ adsorption existed but was not the major mechanism. At the pH values of 6 and 8, CBZ adsorption capacity slightly increased in the presence of Ni²⁺. Similar phenomenon was observed in co-adsorption of ciprofloxacin and Ni²⁺ on activated carbon based on Arundo donax Linn (Sun et al., 2014) and co-adsorption of tetracycline and copper²⁺ on montmorillonite (Wang et al., 2008). The reason may be that a portion of Ni²⁺ ions interacted with CBZ to form Ni²⁺-CBZ complexes, leading to slight increase of positive charge of CBZ thus enhancing CBZ adsorption. In addition, steam activated hydrochars has higher surface area and more functional groups than hydrochars which could donate more electrons. Thus more Ni²⁺-CBZ complexes were adsorbed on the steam activated hydrochar surface, as a result, the total CBZ uptake increased. However, the increase was insignificant. When pH was above 8, significant amounts of OH⁻ were present in the solution, which may interact with Ni²⁺. Thus, formation of Ni²⁺-CBZ complexes was suppressed.



(I)



Figure D. 1 Effect of nickel on CBZ adsorption by flaxshive (I) hydrochars: (A) HC-H₃PO₄-6h. (B) HC-H₃PO₄-12h (II) steam activated hydrochars: (A) SAHC-H₃PO₄-6h. (B) SAHC-H₃PO₄-12h.

Besides, the effect of CBZ on nickel ion adsorption was investigated. According to Figure D2, the presence of CBZ decreased the Ni²⁺ adsorption on hydrochars and steam activated hydrochars compared with that in the absence of CBZ at the same pH values. A number of possible impacts of an organic chemical on metal adsorption were proposed (Jia et al., 2008; Zhou et al., 2004). Specifically, they are as follows: (1) Forming ternary surface complexes increased metal adsorption capacity; (2) The dissolved organic ligands competed with the surface ligands for dissolved metal, which suppressed metal adsorption; (3) The organic chemical competed with metal ions for active sites of adsorbent, thus decreased metal adsorption; and (4) Changes of solution pH because of the presence of the organic chemical, which influenced metal adsorption. In this work, the decreased metal sorption could be mainly because of the competition among the dissolved organic ligands (-NH₃⁺) and dissolved metal nickel (Ni⁺²) for the surface sites. This result concurred with the past research that some water-solvent natural matters regularly reduced metal adsorption (Sun et al., 2014; Ashworth & Alloway 2007). Besides, nickel ion (Ni²⁺⁾ is smaller than CBZ molecule, it can diffuse into the pores and access the sites of the adsorbents more easily. Moreover, as discussed previously, the mechanisms of adsorption of the two adsorbates are different. Specifically, electrostatic attraction was the main mechanism in adsorption of nickel ion (Ni²⁺) while adsorption of CBZ was mainly through π - π EDA interactions together with hydrophobic interaction, electrostatic attraction and hydrogen bonding.

In addition, according to the literatures nickel precipitates as nickel hydroxide (Ni(OH)₂) starting at pH 3, being more evident at pH 9. Nickel precipitates completely at pH 11 (Escudero et al., 2017). How nickel precipitation affected the adsorption process needs to be further investigated.



(II)



Figure D. 2 Effect of CBZ on nickel adsorption by flaxshive (I) hydrochars: (A) HC-H₃PO₄-6h. (B) HC-H₃PO₄-12h (II) steam activated hydrochars: SAHC-H₃PO₄-6h. (B) SAHC-H₃PO₄-12h.

(I)