ADSORPTION OF CIPROFLOXACIN FROM WATER BY
ADSORBENTS DEVELOPED FROM OAT HULLS

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Saskatoon

By

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ABSTRACT

Water contamination with antibiotics is a serious threat for human health as the presence of antibiotics in water can cause antibiotics resistance in pathogens. Ciprofloxacin (CIP) is one of the most frequently detected antibiotics in water. Adsorption has shown to be one of the promising methods for removal of antibiotics from water. Although a number of adsorbents were investigated previously for removal of CIP from water, precursors in use were expensive, and scarce in some parts of the world. As such, development of adsorbents made of abundantly available and inexpensive raw materials, which can simultaneously offer high CIP adsorption capacity, is needed.

In this work, for removal of ciprofloxacin (CIP) from water, adsorbents were developed from raw oat hulls. Raw oat hulls were pretreated by using phosphoric acid impregnation and microwave heating, respectively. Surface morphology and surface area of raw and pretreated oat hulls were investigated by Scanning Electron Microscopy (SEM) and surface area analysis, respectively. Results indicated substantial enhancement in adsorbents’ porosity and remarkable increase in surface area after the pretreatment procedure.

Effects of influential parameters such as solution pH, adsorbents dose and temperature on CIP adsorption capacity were studied. Results revealed that the optimum adsorbents dose was 0.3 mg/L and the optimum pH value was 7. CIP adsorption equilibrium and kinetic were investigated at three temperatures of 288, 298 and 318 K. The results were modeled using adsorption isotherms, and kinetic models. The maximum adsorption capacity obtained was 83 mg/g at the pH of 7 and a temperature of 318 K. The Freundlich model was the best to simulate the experimental data at all the three temperatures among the tested models. This suggested that adsorption of CIP took place
on heterogeneous sites on the surface of the adsorbents. The pseudo second order model was the best fit to the kinetic data. This indicated that adsorption step may be the rate controlling mechanism of the process. Desorption experiments showed low desorption efficiency, hence implying strong interactions existing between CIP molecules and the adsorbent surface. Thermodynamic analysis revealed that CIP adsorption on pretreated oat hulls was spontaneous, endothermic along with an increase in entropy.
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DEDICATION

This thesis is dedicated to my parents, sisters, brother and my beloved friend Homa Hamidi for their never quenching love and emotional support.
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### ABBREVIATIONS

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<tr>
<td>AOP</td>
<td>Advanced Oxidation Process</td>
</tr>
<tr>
<td>BET</td>
<td>Brunner-Emmet-Teller</td>
</tr>
<tr>
<td>CIP</td>
<td>Ciprofloxacin</td>
</tr>
<tr>
<td>EDA</td>
<td>Electron Donor Acceptor</td>
</tr>
<tr>
<td>FQ</td>
<td>Fluoroquinolone</td>
</tr>
<tr>
<td>PZNC</td>
<td>Point of Zero Net Charge</td>
</tr>
<tr>
<td>RSS</td>
<td>Residuals Sum of Squares</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>WWTP</td>
<td>Waste Water Treatment Plants</td>
</tr>
<tr>
<td>Term</td>
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<td>$C_i$</td>
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<td>Activation energy (kJ/mol)</td>
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**Greek letters**

<table>
<thead>
<tr>
<th>Term</th>
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<td>$\alpha$</td>
<td>Initial adsorption rate (mg/g.hr)</td>
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CHAPTER 1. INTRODUCTION

Antibiotics are one of the most important groups of pharmaceutical compounds that are extensively used either for prevention or treatment of diseases (Chen et al., 2011). As antibiotics are not well metabolized in humans and animals bodies, they continuously emerge in aquatic environment. In addition, as these compounds can only be partially removed in waste water treatment plants (WWTP), therefore even the treated outlet effluents of these systems contains amounts of antibiotics (Wan et al., 2012). Existence of antibiotics, even at low concentrations, in aquatic environment can lead to development of antibiotic resistance within bacteria. This causes the normally effective antibiotics to not work well or to fail completely in curing illnesses (Kümmerer, 2003; Homem and Santos, 2011). Prolonged interactions even with one type of antibiotic, can cause antibiotic resistance against an entire group of antibiotics (De Witte et al., 2009). There is a global scientific and social concern in this regard that has gained researchers’ attention to find efficient and applicable methods for removal of antibiotic from water resources in the previous years.

Antibiotics are classified to various groups, based on their chemical and physical features. Amongst various groups fluoroquinolones (FQs) are one of the most widely prescribed antibiotics for treatment of bacterial and respiratory infections (Tesar et al. 2004, Ferreira et al. 2016). Ciprofloxacin (CIP) is a widely prescribed antibiotic in the FQ category (Nakata et al., 2005). CIP was reported to have a high concentration in aquatic environment compared to many other antibiotics (Guerra et al., 2014, Ashfaq et al., 2017). As such, research has been performed to investigate removal of CIP from water using various methods.

De Bel et al. (De Bel et al., 2009) investigated removal of CIP from water using oxidation method (CIP initial concentration of 15 mg/L and pH=7). Although their results showed removal
of 57% of initial CIP content, the oxidation final products showed to be more toxic than CIP. Baginska et al. (2015) studied CIP molecules biodegradability potential (CIP initial concentration =24 mg/L) (Baginska et al., 2015). Their observations showed 0% degradation for CIP molecules. Their conclusion was consistent with other studies indicating CIP molecules to be non-biodegradable (Al-Ahmad et al. 1999; Kümmerer et al. 2000). Vasconcelos et al. (2009) used photo-oxidation (initial CIP concentration of 100 µg/L, 150 W and pH=9) for removal of CIP from water. They discovered that the products of CIP using this process are non-biodegradable and their exposure to environment can be associated with further detrimental effects (Vasconcelos et al., 2009). Each of the employed methods had their own corresponding limitations. However, among various utilized methods, adsorption could be a promising and popular technology for this aim due to its relative ease in operation and efficiency in removal of antibiotics compared to other methods. Nevertheless, research on removal of antibiotics, in particular CIP, using adsorption method is still at its early stage.

Using adsorbents made of biomaterials may enhance cost-effective and eco-friendly aspects of adsorption technology. Adsorbents developed from raw materials containing lignin and cellulose were effective in removal of organic compounds (Suhas et al., 2016). Investigation of Gergova et al. (1994) on pyrolysis of various agricultural raw materials showed that the higher lignin content in the raw materials led to achieving higher pore volume (Gergova et al., 1994). Kennedy et al. (2004) reported that lignin played the major role in achieving adsorbents with high porosity and high surface area from raw agricultural by-products (Kennedy et al., 2004). On the other hand, da Silva Lacerda et al. (2015) discovered as the cellulose content in the raw material increased, higher BET surface area was achieved (da Silva Lacerda et al., 2015). However, the degree that these compounds, lignin and cellulose, individually contribute in development of
adsorbents with high porosity and high surface area is not yet determined and needs more investigations (Suhas et al., 2016).

Oat hulls, as inexpensive and abundantly available agricultural by-products, can be the virtuous option for development of bio-adsorbents. Canada is the second largest oat producer in the world in 2013 (Alvares et al., 2013). In addition, oat hulls contain mainly cellulose (48% wt.% (dry)), hemicellulose (16% wt.% (dry)) and lignin (32% wt.% (dry))(Perruzza, 2010) which were showed to be the potential structural compounds in removal of organic contaminants (Yan and Niu, 2017). However, hitherto no research has been designed to investigate the capability of adsorbents made of oat hulls for removal of organic pollutants from waste water. As such, this research was designed to investigate removal of CIP, as a typical representative of antibiotics, using adsorbents made of oat hulls, a model of lignocellulosic materials.

The primary structure of this thesis is organized as follows:

In Chapter 2, a literature review of the research topic was performed with the focus on importance of this research subject, previous investigations and challenges in this area. Then, in Chapter 3, knowledge gaps, research objective and hypothesis are identified. In Chapter 4, materials and methods used in this research were indicated in detail. Subsequently, in Chapter 5, the results are reported and discussed. Finally, in Chapter 6, the conclusions achieved were illustrated and further recommendations were given for future work.
CHAPTER 2. LITERATURE REVIEW

2.1 Emergence of antibiotics in water resources

Antibiotics are extensively used by human and animals for either prevention or treatment of diseases (Chen et al., 2011). Antibiotics were detected in the surface water, ground water, seawater, drinking water, WWTPs and hospital effluents (Homem and Santos, 2011). Their presence, has been reported in Canada (Nakata et al., 2005; Guerra et al., 2014), United States (Nakata et al., 2005; He et al., 2015), Germany (Gartiser et al., 2007), Italy, France, Greece, Sweden (Andreozzi et al., 2003), Switzerland (Andreozzi et al., 2003), China (Jia et al., 2012; Dong et al., 2016) and Japan (Ghosh, 2016). It was revealed that two-third of the total amounts of antibiotics consumed were released to the sewage system in Germany (Gartiser et al., 2007). Sources of antibiotics in aquatic environment include humans and animals. Extensive usage of antibiotics by these two main groups contributes to emergence of antibiotics in environment (Barrett, 2015). Human and veterinary antibiotics can be excreted to the environment through urine and feces. Also, inappropriate and direct disposal of unused and expired antibiotics discharged as waste is another source of contamination (Kemper, 2008; Homem and Santos, 2011). Moreover, as the current waste water treatment plants (WWTPs) can only partially remove antibiotics from water, the treated effluents of WWTPs still contain some amounts of antibiotics (Barrett, 2015).

2.1.1 Ciprofloxacin emergence in water

Fluoroquinolones (FQs) represent an important and widely prescribed group of antibiotics (Ferreira et al., 2016). Ciprofloxacin (CIP) is the mostly prescribed antibiotic in fluoroquinolone category. In addition, CIP is known to be the most typical representative of the fluoroquinolone category (Nakata et al., 2005; Peng et al., 2016). In oral dose of CIP about 40-50% is discharged
unchanged in urine, 20-30% is excreted through feces after 5 days and only 15% is metabolized (Plant et al., 2011; Plant et al., 2012). Previous investigations revealed that CIP was presented in water with relatively higher concentrations compared to many other pharmaceuticals (Guerra et al., 2014; Dong et al., 2016; Ghosh, 2016). The study performed by Guerra et al. (Guerra et al., 2014) on six different wastewater treatment plants (WWTPs) in Canada revealed that CIP had the highest concentration (median of 600 ng/L) among all antibiotics in effluent samples. Furthermore, another study conducted by Ashfaq et al. (Ashfaq et al., 2017) on five waste water treatment plants in Pakistan showed that CIP had the highest concentration among all presented antibiotics in waste water. In general, the concentration of CIP in waste water effluents was reported to be lower than 1 µg/L (Wang et al., 2017). However, this value reached up to 31 mg/L for waste streams discharged from hospitals (Larsson et al., 2007).

2.1.2 Threats associated with existence of antibiotics in water

Occurrence of antibiotics in aquatic environment is a serious threat for ecosystem since continuous presence of antibiotics, even at low concentrations, in water can cause resistance of bacterial species towards antibiotics. This reduces the therapeutic effects of antibiotics against human and animal pathogens (Kümmerer, 2003; Homem and Santos, 2011). As an example, a study conducted in Canada over 19 hospitals revealed that about 20% of overall sampled bacteria showed resistance towards cephalosporins, fluoroquinolones, and gentamicin antibiotics (Zhanel et al., 2008). Also, another survey performed in Canada illustrated that the proportion of bacteria with resistance to methicillin (type of antibiotic) increased from 1% to 6.1% from in 1995 to 1999 (Simor et al., 2001) and from 4.2% to over 50.0% from 2001 to 2006 (Zhanel et al., 2008).

Another serious issue with antibiotic presence in water resources is that irrigation of plants with water containing antibiotics leads to uptake of antibiotics by plants. This results in exposure
of antibiotics to the food chain. Also, existence of antibiotics in plants decreases the biodegradation potential of plant materials such as stem, leaves, root which are the main food source for aquatic life in rivers (Barrett, 2015). Even it was indicated that photosynthesis mechanism of plants such as algae can be suppressed in the presence of antibiotics in water (Aksu and Tunç, 2005).

2.2 Methods for antibiotic removal

Previous studies have investigated removal of antibiotics from waste water using various methods such as oxidation, biodegradation, photodegradation and adsorption. The methods used for removal of antibiotics mainly were dependent on the chemical characteristics of antibiotics, concentration of antibiotics in effluent and cost of the process (Homem and Santos, 2011). Current WWTPs using conventional methods including biological processes, filtration, coagulation, flocculation and sedimentation are not capable of effective removal of antibiotics from waste water (Homem and Santos, 2011; Liang et al., 2014). This can be due to antibiotics chemical stability, antibiotics toxicity to microorganisms used in conventional processes and antibiotics low biodegradability (Homem and Santos, 2011; Barrett, 2015). Further explanation on the current treatment methods used for this purpose are described in detail in the following sections.

2.2.1 Oxidation

Oxidation is a waste water treatment process for removal of organic and sometimes inorganic pollutants. In this process, in the presence of a strong oxidant pollutants are oxidized to intermediates that are supposed to be less stable and hazardous. These intermediates may also have potential for biodegradation (Barrett, 2015).

Various oxidants can be used in this process including chlorine gas, hypochlorite and hydroxyl radical. In advanced oxidation processes (AOP) oxidants are subjected to an energy
source or catalyst and intermediate radicals with significantly high reactivity and oxidation potential are produced (Plant et al., 2011). Examples of AOPs are ozonation, Fenton, photo-Fenton and photolysis. (Le-Minh et al., 2010; Homem and Santos, 2011). In AOP there is the probability that the final products of the process are more toxic than the initial pollutants. Such a case has been reported for ozonation of CIP (De Bel et al., 2009). Also, AOP requires energy source and the cost of reagents can be high (Andreozzi, 1999).

2.2.2 Biodegradation

Biodegradation is a waste water treatment method widely used for removal of toxic organic pollutants in waste water treatment plants (WWTP) (Kümmerer et al., 2000). In this method, metabolism of pollutants takes place by microorganisms (Young and Häggblom, 1991), either in an aerobic or anaerobic situation (Mass et al., 2014). Degradation of pollutants in a controlled bio-process leads to obtaining environment-friendly final products (Mass et al., 2014). This process may not be a good treatment option for pollutants with high toxicity as they can be toxic for microorganisms (Homem and Santos, 2011).

Previous studies revealed that fluoroquinolone antibiotics were poorly biodegraded in biological treatment systems (Jia et al., 2012; Gong et al., 2016), in particular it was reported that CIP is resistant to biodegradation in the aqueous system (Kümmerer et al., 2000; Girardi et al., 2011; Gong et al., 2016).

2.2.3 Photodegradation

Photodegradation can be an important elimination pathway for removal of organic pollutants depending on the light-sensitivity characteristics of the compounds (Kümmerer, 2009). Photodegradation can take place directly or indirectly. In the direct method pollutants absorb
photon which leads to degradation of pollutants to new stable products (Halmann, 1996). In an indirect method absorption of photon by photosensitizers including hydrogen peroxide leads to production of reactive compounds that cause degradation of pollutants (Remucal, 2014). Light source, pH, characteristics of presented impurities can play significant roles in obtaining less or more stable and toxic final products (Plant et al., 2012). Fluoroquinolone antibiotics are susceptible to photodegradation (Sturini et al., 2012). However, the reduction percentage of CIP through photodegradation was shown to be low, unless a catalyst such as TiO$_2$ and a light source such as UV were used (Palmisano et al., 2015). Furthermore, it was revealed that rate of CIP degradation was low at high CIP concentration. (Torniainen et al., 1996). In addition, final products of photodegradation may be more of a concern from environmental aspect (Barrett, 2015).

2.2.4 Adsorption

Adsorption is a surface-based phenomenon in which the molecules in the fluid phase have the affinity to adhere on the solid surface (Homem and Santos, 2011; Barrett, 2015). Adsorption is a widely used treatment method in waste water industry that has been used for removal of various pollutants including antibiotics, heavy metals and dyes. (Gupta et al., 2009). Adsorption can take place by various mechanisms such as cation exchange, surface complexation, cation bridging and hydrogen bonding. (Barrett, 2015; Liang et al., 2014). Adsorption processes can be classified mainly into two groups: chemical adsorption and physical adsorption. In physical adsorption, the forces between adsorbate and solid surface are relatively weak (mostly van der Waals interactions), while the forces in chemical adsorption are strong. In chemical adsorption, formation of chemical bonds takes place between adsorbate and solid surface. In physical adsorption, the nature of the process is reversible. However, in chemical adsorption detachment of adsorbed compounds from
solid surface can be difficult (Gupta et al., 2009; Barrett, 2015). Table 2.1 shows a comparison between these two types of adsorption (Liang et al., 2014).

Table 2.1. Characteristics of physical and chemical adsorption (Liang et al., 2014)

<table>
<thead>
<tr>
<th>Physical adsorption</th>
<th>Chemical adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low heat of adsorption</td>
<td>High heat of adsorption</td>
</tr>
<tr>
<td>Monolayer or multilayer</td>
<td>Monolayer only</td>
</tr>
<tr>
<td>Only significant at relatively low temperatures</td>
<td>Possible over a wide range of temperatures</td>
</tr>
<tr>
<td>Rapid and reversible</td>
<td>May be slow and irreversible</td>
</tr>
<tr>
<td>No electron transfer, although polarization of sorbate may occur</td>
<td>Electron transfer leading to bond formation between sorbate and solid surface</td>
</tr>
</tbody>
</table>

Among the aforementioned treatment methods, adsorption has shown to be a promising technology for removal of antibiotics, in particular CIP, due to the reasonable efficiency offered, relatively low-cost, profitability and relatively ease in operation (Barka et al., 2010). However, further investigations on development of adsorbents needs to takes place in order to achieve an economic and eco-friendly process along with relatively high adsorption uptake values. Adsorption efficiency is mainly dependent on two criteria: characteristics of adsorbents in use and operating conditions.

2.3 Adsorbents

In the adsorption process using adsorbents with high porosity, high surface area, suitable pore size and functional groups can significantly contribute to achieving high efficiency of the process (Gupta et al., 2009). In the previous research on removal of antibiotics from waste water,
Various adsorbents were used. These adsorbents include activated carbon (Huang et al., 2013), zeolite (Genç and Dogan, 2015), montmorillonite (Wang et al., 2010), kaolinite (Li et al., 2011), goethite (Zhang and Huang, 2007), magnetite (Rakshit et al., 2013), birnessite (Jiang et al., 2013) and pumice (Genç and Dogan, 2015). Activated carbon is widely used for this purpose and has shown successful performance due to having a highly porous structure (Ali and Gupta, 2006; Huang et al., 2013). However, in general the precursors in use for activated carbon preparation were costly, and hence the application of activated carbon is hindered (Huang et al., 2013). Therefore, finding alternative raw materials to be used as the source for activated carbon preparation requires more investigations.

Using adsorbents made of raw bio-materials for removal of metal ions has been studied since 1970 (Subramaniam, 1970). In the past years, investigations on their applications for removal of antibiotics from water have gained interests among researchers. The biomass can be used directly or after being subjected to series of chemical and thermal treatments. In order to obtain cost-effective and efficient adsorbents made of biomaterials with the potential of practical utilization at industrial scale, there are some basic factors that need to be considered. Biomaterials in use should have the elemental compounds and functional groups that favor adsorption process. In addition, they should be inexpensive and abundantly available in environment (Volesky, 2007).

2.3.1 Algal biomass

Algae is abundantly available in oceans at various parts of the world. Adsorbents made of algae showed to have relatively high potential for removal of metals (Vilar et al., 2007). Adsorption potential of algae may be contributed to the fiber-like structure of cell walls and presence of
polysaccharides matrix (Sheng et al., 2004). Previous research showed that the maximum removal efficiency obtained for removal of CIP using algal biomass was 36% (Ferdowsi et al., 2015).

2.3.2 Chitinous biomass

It has been claimed that chitin is the second abundant polysaccharide produced in the world. Chitin and chitosan can be obtained from waste of seafood shells through chemical processes. Also, chitosan is gained through alkaline deacetylation of chitin. Adsorbents made of biomaterials containing chitin or chitosan had relatively high potential for removal of metals (Gerente et al., 2007; He et al., 2016).

2.3.3 Plant materials and agricultural by-products

A number of investigations have been conducted using plant materials and agricultural by-products for removal of various pollutants from waste water. Maximum adsorption capacity using number of adsorbents made of raw material for removal of CIP from water is given in Table 2.2.

**Table 2.2.** Adsorbents made of plant materials and agricultural by-products for CIP removal

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arundo donax based activated carbon</td>
<td>418</td>
<td>(Sun et al., 2012a)</td>
</tr>
<tr>
<td>Bamboo based activated carbon</td>
<td>210</td>
<td>(Peng et al., 2015)</td>
</tr>
<tr>
<td>Flax based activated carbon</td>
<td>200</td>
<td>(Hu and Wang, 2016)</td>
</tr>
<tr>
<td>Date palm leaflets based activated carbon</td>
<td>120</td>
<td>(El-Shafey et al., 2012)</td>
</tr>
<tr>
<td>Moringa Oleifera</td>
<td>80</td>
<td>(Paul et al., 2016)</td>
</tr>
<tr>
<td>Hazelnut based activated Carbon</td>
<td>65</td>
<td>(Balarak et al., 2016)</td>
</tr>
</tbody>
</table>
Oat is one of the most important cereal crops and is abundantly available worldwide. (Alvarez et al., 2013). Oat hulls are the by-products of oat milling in food processing industries (Galdeano and Grossmann, 2006). Previous investigations suggested that biomass materials, primarily containing cellulose, hemicellulose and lignin, can convert into adsorbents with enhanced porous structure and high surface area, through phosphoric acid and microwave assisted pretreatment procedure. For instance, Hosseinzade et al. (Hesas et al., 2013) subjected apples waste, representative of lignocellulose material, in phosphoric acid followed by microwave radiation. In their investigations, high removal efficiency of contaminants was obtained owing to porous structure and high surface of area of developed adsorbents. For other investigations, using lignocellulosic bio materials such as peanut hulls (Zhong et al., 2012), cotton stalk (Deng et al., 2010), Ficus carica fiber (Gupta et al., 2013)and barley straw (Yan and Niu, 2017) the results similarly indicated that using phosphoric acid impregnation followed by microwave heating led to obtaining adsorbents with high porosity.

The composition of oat hulls on average are as follows: cellulose (48% wt.% (dry)), hemicellulose (16% wt.% (dry)) and lignin (32% wt.% (dry)) (Perruzza, 2010). This suggests that adsorbents made of raw oat hulls can have potential for removal of CIP and even other similar organic compounds from waste water. However, oat hulls have only been used for removal of arsenic and dye from waste water, hitherto (Chuang et al., 2005; Banerjee et al., 2016).

2.4 Ciprofloxacin

Ciprofloxacin (CIP), as a fluoroquinolone antibiotic, is one of the most widely prescribed antibiotics in humans and animals. CIP was proven to be effective in treatment of various bacterial
infections such as bone respiratory and urinary infections. CIP molecular formula is C\textsubscript{17}H\textsubscript{18}FN\textsubscript{3}O\textsubscript{3} and the molecular weight is 331.346 g/mol (Louie, 1994).

![Chemical structure of CIP](image)

**Figure 2.1.** Chemical structure of CIP

As shown in Figure 2.2, CIP molecules exist in various forms at different pH values. The first and second acid dissociation constants of groups, pKa\textsubscript{1} and pKa\textsubscript{2}, are corresponding to the carboxylic and N-moiety groups, respectively. At pH values lower than the pKa\textsubscript{1}, the amine group are protonated and hence the CIP\textsuperscript{+} (cationic form) is the dominantly presented in the media. However, at pH values higher than pKa\textsubscript{2} carboxyl and N-moiety groups are deprotonated, resulting in CIP\textsuperscript{-} (anionic form) mostly present in the system (Avisar et al., 2010).

The Chemical Structure and physicochemical features of ciprofloxacin are given in Table 2.3.
Table 2.3. Characteristics of ciprofloxacin (Ahmed, M. B et al., 2015; Peng et al., 2015)

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Purity</th>
<th>Molecular weight</th>
<th>CAS</th>
<th>pKa₁</th>
<th>pKa₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ciprofloxacin</td>
<td>C₁₇H₁₈FN₃O₃</td>
<td>≥ 98%</td>
<td>331 g/mol</td>
<td>85721-33-1</td>
<td>5.46 ± 0.13</td>
</tr>
</tbody>
</table>

2.5 Adsorption equilibrium

2.5.1 Factors affecting adsorption in a batch system

Batch adsorbers are widely used in waste water treatment industry. They are known to be suitable for adsorbents of small particle size. Batch adsorbers are advantageous where the adsorption step is not continuously demanded, scale of operation is small and a long contact time is required (Crini and Badot, 2008; Worch, 2012). Adsorption in the batch system is affected by a number of parameters including adsorbent dose, contact time, solution pH, agitation, existence of other ions or components, initial adsorbate concentration and adsorbents particle size. In what follows, the effect of a number of these parameters on adsorption are discussed. It should be noted that in the following context, when effect of one specific parameter on adsorption is discussed, it is assumed that the rest of parameters are kept constant within the system.

2.5.1.1 Effect of adsorbent dose

In general, the trend of adsorption capacity with an increase in adsorbent dose was shown to be as follows: initially increasing, reaching a maximum value and finally decreasing. The initial increase in adsorption capacity can be due to the fact that increasing in adsorbent dose resulted in availability of more active sites (Chen et al., 2015). Some researchers postulated that the descending trend of adsorption capacity at a higher range of adsorbent dose can be attributed to
active sites overlapping and adsorbents partial aggregation. This can be due to relatively high adsorbents mass and lack of their proper dispersion in the system (Ahmaruzzaman, 2008). Esposito et al. (Esposito et al., 2001) also observed that the decrease in adsorption capacity of cadmium on biomass was lower at higher adsorbent concentrations. They hypothesised that due to their relatively larger size, cadmium ions only adhered to readily accessible external active sites, but not those in the bulk of solid mass. They concluded that the effective adsorbent surface area, known as the area contributing to adsorption in fact, determined the adsorption capacity instead of the total surface area present in the solution. However, further investigation is required in order to provide an in-depth explanation.

2.5.1.2 Effect of pH

In general, effect of pH on adsorption depends on the characteristics of the adsorbents used and speciation of antibiotics at different pH values in water (Wu et al., 2010; Li et al., 2011; Sun et al., 2012a). Point of zero net charge (PZNC) of the adsorbent indicates the condition at which the net charge density on the surface of adsorbents is zero. At pH values above the PZNC of adsorbents, the surface charge of adsorbents is negative while the surface charge is positive at lower pH values (Sun et al., 2012a). On the other hand, adsorbate molecules may have different surface charge at different pH values (Figure 2.3). For instance, at pH lower than 4, almost 99% of CIP molecules exist as CIP\(^+\) (cationic). While at pH higher than 10, over 95% of CIP molecules are presented in CIP\(^-\) form (anionic). At the pH solution coinciding 7, the CIP\(^0\) (zwitterion) is dominant within the system (Wu et al., 2010). Therefore, whether pH can favor adsorption or not may depend upon the impact of pH on both adsorbents and adsorbate molecules (Wu et al., 2010; Li et al., 2011; Qin et al., 2014). In the previous investigations on removal of CIP from water using montmorillonite (Wu et al., 2010), arundo donax linn (Sun et al., 2012a), pomelo peel (Sun et al.,
2016) and carbon nanotubes (Li et al., 2015) it was observed that CIP adsorption was favored, wherever the dissimilarity of adsorbents and CIP molecules charges occurred. This is mainly due to the fact that when adsorbate molecules and adsorbent surface have dissimilar charges, electrostatic attraction forces tend to exist which can benefit adsorption process. However, occurrence of same sign charges of adsorbent surface and adsorbate molecules leads to electrostatic repulsion suppressing adsorption.

![Figure 2.3](image.png)

**Figure 2.3.** Speciation of CIP at different pH values (Avisar et al. 2010)

2.5.1.3 Effect of contact time

At initial stages of contact time, adsorption takes place rapidly due to higher adsorbate concentrations leading to existence of stronger mass transfer driving forces. In addition, more uncovered active sites are available. As time passes, adsorption rate decreases gradually. Finally the rate of adsorption reaches a steady state condition which is due the fact that system has approached a dynamic equilibrium (Wu et al. 2015). For an initial CIP concentration of 100 ppm, it was reported that in the first 80 minutes there was a sharp increase in the adsorption rate. A mild increase was observed from 80 to 100 minutes and after that a steady trend was achieved (Zhang
et al., 2011). The shorter time needed to reach equilibrium leads to faster removal of pollutants, and hence is considered as an advantage for a given adsorbent (Gupta et al., 2009).

2.5.1.4 Effect of temperature

Temperature affects equilibrium, rate, spontaneity and randomness of the adsorption processes. An increase in temperature can affect the adsorption process favourably or adversely, mostly based on the endothermic or exothermic nature of adsorption. Previous studies on removal of CIP using adsorbents such as modified coal fly ash (Zhang et al., 2011) and carbon made of date palm leaflets (El-Shafey et al., 2012) showed that adsorption tends to be endothermic and increase in temperature led to a higher adsorption capacity and adsorption rate. In the case of using modified coal fly ash, an increase of 20 K in temperature led to an approximate 40% increase in the adsorption capacity (Zhang et al., 2011). However, when carbon prepared from lignin was used as the adsorbent for removal of CIP from water, the adsorption phenomena showed to be exothermic and favored at lower temperatures (Huang et al., 2013).

2.5.2 Adsorption equilibrium models

2.5.2.1 Langmuir model

The Langmuir isotherm is the most commonly applied isotherm for fitting equilibrium data. The basic assumptions of this model are: (1) monolayer adsorption occurs on the adsorbent surface which has finite number of similar active sites, (2) no interactions take place between adjacent adsorbed molecules, (3) active sites have equal affinities toward the adsorbate molecules, (4) adsorption process is reversible (Tran et al., 2016; Huang et al., 2013). Although, in many real cases, these assumptions may not be satisfied, as the Langmuir model can successfully fit the data, it is widely used (Gao et al., 2012). It is defined by the following equation:
\[ q_e = q_{\text{max}} \frac{K_L C_f}{1 + K_L C_f} \] 

(2.1)

- \( q_{\text{max}} \): maximum adsorption capacity at complete monolayer coverage (mg/g);
- \( q_e \): equilibrium adsorbate uptake (mg/g);
- \( K_L \): affinity parameter (L/mg);
- \( C_f \): equilibrium (final) concentrations of the sorbate (mg/L);

\( K_L \) is defined as the affinity parameter related to the bonding energy of the sorbate species to the surface (Voilesky, 2007). The essential feature of the Langmuir model can be evaluated using a dimensionless constant known as separation factor, \( R_L \). The formula of this constant is as follows:

\[ R_L = \frac{1}{1 + K_L C_0} \] 

(2.2)

- \( C_0 \): initial adsorbate concentration (mg/L);
- \( K_L \): affinity parameter (L/mg);

The \( R_L \) values between zero and unity indicate favorable adsorption occurring. When the \( R_L \) value approaches one, it can be an indication of very low values of \( K_L \), and as such is denoted as unfavorable adsorption.

**2.5.2.2 Freundlich model**

The Freundlich model is the earliest empirical sorption model (1932) widely in use to express the non-ideal sorption equilibrium data on heterogeneous surface. This model can be applied to systems in which multilayer adsorption is presented (Dada et al., 2012). This model assumes that stronger binding sites with higher affinity towards to adsorbate molecules are the first
to be occupied. In addition, binding strength tends to reduce at higher surface coverage (Tan et al., 2009). The Freundlich model is expressed by the following equation:

\[ q_e = k_f c_f^{1/n} \]  

(2.3)

\( q_e \): equilibrium value of sorbate uptake (mg/g);

\( k_f \): Freundlich isotherm constant (mg\(^{1/(1/n)}\) L\(^{1/n}\) g\(^{-1}\));

\( c_f \): equilibrium (final) concentrations of the adsorbate (mg/L);

\( n \): adsorption intensity;

\( n \), known as the Freundlich intensity parameter, is an indication of existing adsorption driving forces and heterogeneity degree of the surface (Aljeboree et al., 2014). The parameter \( n \) is a dimensionless falling in the rage of 0 to 10 (0 < \( n < 10 \)). If the value of \( n \) is higher than 10 an irreversible isotherm is then obtained (Trans et al., 2016). Values of \( n \) greater than unity indicates of a preferential adsorption, and less than unity indicates a poor adsorption (Huang et al., 2013). \( k_f \) is an indication of the adsorption capacity of the adsorbents in use (Subramaniam, 1970).

2.5.2.3 Temkin Isotherm

Temkin isotherm describes adsorption processes taking place on heterogeneous surfaces, considering the assumption that heat of adsorption decreases linearly with coverage owing to adsorbate-adsorbent interactions (Subramaniam, 1970; Tan et al., 2009). In principle, Temkin isotherm assumes chemical adsorption taking place through strong electrostatic interactions between adsorbate molecules and adsorbent surface (Gao et al., 2012). Temkin isotherm can be presented by the following expression:

\[ q_e = B \ln A + B \ln c_f \]  

(2.4)
\( q_e \): equilibrium value of sorbate uptake (mg/g);

\( C_f \): equilibrium (final) concentrations of the adsorbate (mg/L);

B (mg/g) and A (L/mg) known as Temkin model’s constants are related to the heat of adsorption and maximum binding energy, respectively.

**2.5.3 Adsorption kinetic models**

Kinetic studies provide crucially important information on the time needed for reaching equilibrium, rate of adsorption process and adsorption potential rate limiting steps. If an adsorbent is targeted to be used in waste water treatment facilities, at industrial scales, in addition to its high adsorption capacity and removal efficiency, high adsorption rate is also an essential required characteristic (Aljeboree et al., 2014). In this study, four kinetic models of pseudo-first order, pseudo-second order, Elovich and intra particle diffusion models are selected to evaluate the experimental data.

**2.5.3.1 Pseudo-first-order kinetic model**

The pseudo-first-order kinetic model indicates rate of adsorption is directly correlated to the difference of uptake at equilibrium and time \( t \), shown as \((q_e - q_t)\) in the equation (Miyah et al., 2015). The equation is expressed as follows (Ho and McKay, 1999; Demirbas et al., 2004):

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]  

(2.5)

\( q_e \): adsorption capacity at equilibrium (mg/g);

\( q_t \): adsorbate uptake at time \( t \) (mg/g);

\( k_1 \): rate constant of pseudo first-order adsorption model (1/hr);
Equation (2.6) is obtained when equation (2.5) is integrated with boundary conditions of $q_t=0$ and $q_t = q_e$ at time $t=0$ and $t=t$, respectively:

$$\ln (q_e - q_t) = \ln (q_e) - k_t t$$ (2.6)

### 2.5.3.2 Pseudo-second-order model

The pseudo-second-order kinetic model is known to be successfully applied in systems where the rate controlling step is chemisorption (Ho and McKay, 1999). This model is expressed by equation (2.7). $k_2$ (g/mg.hr) is the rate constant of the pseudo second-order adsorption model. $q_e$ and $q_t$ are the amount of antibiotics adsorbed (mg/g) at equilibrium and time $t$, respectively.

$$\frac{dq_t}{dt} = k_2 (q_e-q_t)^2$$ (2.7)

Equation (2.8) is obtained by integration of equation (2.7) with the boundary conditions of $q_t=0$ and $q_t=q_e$ at time $t=0$ and $t=t$, respectively:

$$\frac{1}{q_e-q_t} = \frac{1}{q_e} + k_2 t$$ (2.8)

Equation 2.8 can be rearranged in a linear form, as shown below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$ (2.9)

Based on equation (2.9) by plotting the value of $\left(\frac{t}{q_t}\right)$ versus $(t)$ equilibrium concentration $(q_e)$ can be determined. However, in the pseudo-first-order kinetic model the equilibrium concentration should be known prior to fitting the experimental data to the model. Whether the experimental data are reasonably fitted by the predicted model or not is generally evaluated based on the correlation coefficient ($r^2$). The higher the correlation coefficient, the more acceptable the predicted model is (Yeddou and Bensmaili, 2005).
In addition, based on the rate constants of pseudo second order kinetic model activation energy can be determined using the following equation:

$$\ln k_2 = \frac{-E_a}{R} \left(\frac{1}{T}\right) + \ln D$$  \hspace{1cm} (2.10)

$k_2$: pseudo second order model rate constant;

$E_a$: activation energy (kJ/mol);

$R$: universal gas constant (kJ/mol K);

$D$: Arrhenius constant (kJ/mol);

In general, the activation energy for a physical adsorption process is lower than 4.2 kJ/mol, while for a chemical adsorption process is higher than 4.2 kJ/mol (Debowale et al., 2007).

### 2.5.3.3 Elovich model

In general, the Elovich equation can be applied in systems where the nature of adsorption is chemisorption and the adsorbent surface is heterogeneous (Demirbas et al., 2004). The equation corresponding to this model is as follows:

$$q_t = \frac{1}{\beta} \ln (\alpha\beta) + \frac{1}{\beta} \ln(t)$$  \hspace{1cm} (2.11)

$q_t$: adsorbate uptake at time $t$ (mg/g)

$\alpha$: initial adsorption rate (mg/ g. hr)

$\beta$: Elovich constant (g/mg)
2.5.3.4 Intra particular diffusion model

In general, for adsorption process to take place adsorbate molecules need to transfer from bulk phase to the solid surface and then penetrate in the adsorbents pores. Typically diffusing through pores is a slow step. Whether diffusion within the pores is the rate-limiting step or not, it can be determined based on intra particular diffusion model (Equation 2.12):

\[ q_t = k_{in} t^{1/2} + C \]  \hspace{1cm} (2.12)

\( q_t \) is the adsorbate uptake at time \( t \) (mg/g). The diffusion rate parameter (\( k_{in} \)) can be determined from the slope of the line modeling \( q_t \) versus \( t^{1/2} \). Also, the value of \( C \) (mg/g), as the constant indicative of boundary layer thickness, can be determined through the intercept of the line (Aljebooree et al., 2014). If the fitted line expressing the data with this model passes through origin, it can be concluded that the intra particle diffusion is the rate limiting mechanism. Otherwise, other mechanisms along with intra particle diffusion can be responsible for the kinetics of process. In this case, the boundary layer thickness can be a determinant factor in adsorption rate (Gupta et al., 2013).

The intra particle diffusion model can be presented by various lines having different slopes in a particular adsorption process. Typically, at the beginning of the process, the fitted model shows a sharp trend line. This can be attributed to diffusion of adsorbate molecules within macropore or penetration from bulk to the surface leading to occurrence of external surface adsorption. However, as time further passes, the fitted line of the model shows a relatively smooth trend, indicating a gradual increase in adsorbate uptake. This implies that at this stage, the intra particle diffusion mechanism is the controlling step of the process (Tan et al., 2009).
2.6 Desorption of adsorbents

Desorption and reuse of adsorbents in adsorption-desorption cycles makes the process more attractive from economic and environmental aspects, particularly when adsorbents are expensive (Wang and Chen, 2009). Regeneration of adsorbents can take place through various methods such as thermal, electrochemical, ultrasonic and chemical (Kulkarni and Kaware, 2014). Chemical regeneration offers a number of advantages in comparison with other methods. For instance in chemical regeneration, loss of adsorbents due to burn-off that occurs in thermal regeneration is prevented. Also, further recovery of adsorbate is feasible by applying additional separation methods such as distillation. (Martin and Ng, 1984; David, 1999). In the chemical desorption process, adsorbents are set in desorption agents at specific operating conditions such as pH value and temperature for a predetermined time. The desorption agents should be non-destructive for adsorbents, environmental-friendly, efficient, and inexpensive (Wang and Chen, 2009). Selection of the appropriate eluents for the process is highly dependent on the nature of adsorbents in use and the mechanism of adsorption. For instance, alkaline solution was used when negatively charged adsorbate molecules were adhered to the positively charged surface of adsorbents through electrostatic attractions. Using alkaline solution causes the surface of adsorbent to become negative, and hence repulsion of adsorbate molecules and solid surface to occur (Vijayaraghavan and Yun, 2008).

2.7 Adsorption Thermodynamics

To determine thermodynamic feasibility, adsorption mechanism and process spontaneity, evaluation of thermodynamic parameters is an essential step. The thermodynamic parameters
including change of standard Gibbs free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) were obtained through thermodynamic functions expressed as follows:

\[
ΔG° = -RT \ln Kc
\]

(2.13)

\[
ΔG° = ΔH° - TΔS°
\]

(2.14)

The equilibrium constant of \( Kc \) can significantly impact the values obtained for the thermodynamic parameters of \( ΔG°, ΔS°, \) and \( ΔH° \). \( Kc \) can be determined through various methods using different adsorption coefficients such as the Langmuir isotherm constant (\( K_L \)) and Freundlich isotherm constant (\( K_F \)). In this research, \( Kc \) has been assumed to be same as the Langmuir constant (\( K_L \)). However, as \( Kc \) needs to be dimensionless, the value of \( K_L \) is multiplied by a factor of \( 10^6 \) which is the density of pure water in mg/L (Tran et al., 2016).
CHAPTER 3. KNOWLEDGE GAPS & HYPOTHESIS & RESEARCH OBJECTIVES

3.1 Knowledge gaps

Based on the literature review, there is an incentive to develop cost-effective and high-performance adsorbents based on oat hulls for removal of CIP from waste water. Knowledge gaps for this purpose were identified as follows:

1. Adsorbents made of oat hulls have not been developed and characterized for removal of CIP from waste water.

2. Effects of operating parameters including operating temperature, solution pH, initial adsorbate concentration and contact time on adsorption of CIP from water using pretreated oat hulls have not been investigated before.

3. Equilibrium isotherms and kinetic models for adsorption of CIP from water on adsorbents made of oat hulls need to be investigated.

4. Thermodynamic analysis of CIP adsorption on pretreated oat hulls has not been conducted hitherto.

5. Desorption and reuse of adsorbents made of oat hulls loaded with CIP has not been investigated.

3.2 HYPOTHESIS

Based on the previous investigations, adsorbents developed from lignin and cellulose materials, through chemical and thermal treatments, were shown to have the potential in removal of organic compounds with similar structure as CIP (Sun et al., 2012; Yan and Niu, 2017). Composition of oat hulls is mostly cellulose (48% wt. % (dry)) and lignin (32% wt. % (dry)). As such, it is hypothesized that adsorbents made of oat hulls through chemical and thermal treatments can successfully remove CIP from water.
3.3 RESEARCH OBJECTIVES

The overall objective of this research is to investigate the capability of oat hulls for removal of CIP from waste water. Based on the knowledge gaps, the determined objectives are proposed as follows:

1. Development of low-cost adsorbents from oat hulls through chemical and/or thermal treatments.
2. Investigation of the effects of operating parameters including operating temperature, solution pH, adsorbents dose and contact time on adsorption performance.
3. Determination of adsorption kinetics, equilibrium isotherms and corresponding theoretical models that successfully express the experimental data of CIP adsorption on pretreated oat hulls.
CHAPTER 4. MATERIALS AND METHODS

4.1 Raw oat hulls preparation

Raw oat hulls used in this study were supplied from Richardson Milling Martensville, Saskatoon, Saskatchewan. Oat hulls were air dried, and sieved to obtain the particle size range of 0.425 to 1.18 mm. The W.S Tyler stainless steel sieves were used for this purpose.

4.2 Pretreatment method

Investigation of Yan and Niu (2017) showed that for raw materials (barley straw) containing mostly lignin and cellulose, their pretreatment method leads to obtaining high quality porous structure (Yan and Niu, 2017). Hence, as oat hulls are almost identical to barley straw in regards to their composition, the same procedure was used in this work. The pretreatment method proposed by Yan and Niu (Yan and Niu, 2017) is as follows:

20 g of dry Oat hulls were soaked in 400 ml of 5% phosphoric acid and stirred by means of a magnet (100 rpm) for 24 hours. Then, wet samples were heated by aid of a 700 W industrial microwave for 9 minutes. The temperature of the samples in the microwave was measured using the temperature program software linked to the microwave based on which a maximum temperature of 800 °C was observed. After radiation, samples were allowed to be cooled in air. Afterwards, samples were heated in water at 75 °C for removal of residual H₃PO₄ for 30 minutes and washed with deionized water subsequently. Then, samples were filtered and extensively washed with deionized water to reach a constant pH (pH=4). Finally, the wet samples were dried in oven at 105 °C for 24 hours. Heating the samples in water and washing them extensively leads to removal of chemical agent (H₃PO₄) from the pore structure and allows the pore structure to be available for sorption process (Azargohar, 2009).
Microwave has been used for heating of the samples due to providing a number of advantages compared to conventional methods such as oven. Microwave heating has the capability of creating porous structure in the precursors, requires less activation time and heats the sample uniformly preventing hot spots to occur (Sun et al., 2012a). Activation of raw materials using phosphoric acid has shown promising results. In comparison to using other agents for pretreatment, phosphoric acid offers a number of advantages such as lower activation temperature (around 400°C), less corrosive towards equipment, development of mesoporous structure which favors adsorption of larger size molecules (Sun et al., 2016).

4.3 CIP solution preparation

In the present work, CIP stock solution was prepared using ultrasound technique. Dissolving some fluoroquinolone antibiotics, in particular for ciprofloxacin in water, may be time consuming and even take up to days. However, by using ultrasound assisted technologies the required time for preparing the solution can be decreased considerably. To obtain the desired concentration of stock solution (60 mg/L), predetermined amounts of CIP powders were mixed with millipore water and placed in the sonicator. Temperature of the sonicator was adjusted at 37°C and the sonication time was set as 30 minutes. At the end, a transparent CIP solution was achieved. CIP stock solution was diluted to obtain further desired CIP concentrations of 4.8 ppm, 12 ppm, 24 ppm, 36 ppm, 48 ppm and 60 ppm. Although the actual CIP concentration in waste water is in general lower than this tested range, due to limitations of the HPLC apparatus used in this work to detect very low CIP concentrations, the aforementioned initial CIP concentrations were investigated.

In order to confirm no degradation of CIP molecules through sonication, a CIP sample solution (Ci=60 mg/L) was also prepared by stirring the dispersed mixture of CIP powder and
water for three days at 27 °C. Comparison of the two prepared solutions concentrations revealed less than 5 % difference.

### 4.4 Adsorption experiments

The adsorption experiments were conducted in the batch mode. 5 mg of pretreated oat hulls were added to 100 mL vials containing 50 ml simulated CIP contaminated waste water solution. Solutions pH were adjusted using 0.01 M H$_2$SO$_4$ or 0.01 M NaOH. The vials were shaken at 180 rpm until equilibrium was reached. Adsorption experiments were run in triplicate and the average values with corresponding standard deviations were reported. Adsorption capacity of adsorbates were determined according to equation (6.1). In deriving this equation it is assumed that the volume of solution is constant through the entire process and adsorbents are initially free of adsorbates (Mohammed-ridha, 2014).

$$ q_e = \left( \frac{C_f - C_i}{m} \right) \times V $$  \hspace{1cm} (4.1)

$C_i$ and $C_f$ are the antibiotic initial and equilibrium concentration (mg/L), respectively. The parameter $m$ is the dry mass of fresh adsorbent (g) and the parameter $V$ is the solution volume (L).

### 4.5 Desorption experiments

Desorption of CIP loaded adsorbents was performed at extreme acidic and alkaline conditions, pH=1 and pH=11. Desorption experiments were performed immediately after adsorption, at the same temperature. The CIP loaded adsorbents were transferred to bottles with 50 ml milipore water. The pH of water was adjusted to the predetermined pH values using 37 % HCl and 0.1 M NaOH. Desorption efficiency was determined as the value of CIP released in water through desorption over the content of CIP loaded on adsorbents initially.
4.6 Analyses

Filtration of supernatant of adsorption samples was done by 0.20 µm Acrodisc Syringe Filter (Pall Corporation). Then, concentration of CIP in the filtrate was analyzed by high performance liquid chromatography (HPLC, Agilent Technologies 1260). Acetonitrile and 0.1 formic acid were used in HPLC as the mobile phase. According to the calibration curve derived for CIP the concentration of samples was determined.

4.7 Adsorbents characterization

Particle size distribution of pretreated and raw oat hulls were obtained using Mastersizer 2000 (Malvern Instruments). Surface morphology of raw and pretreated oat hulls were studied using Scanning Electron Microscopy (SEM, JSM 6010LV, JEOL). Textural properties, surface area and porosity of pretreated and raw oat hulls were obtained by a pore size analyzer (Micromeritics, ASAP 2020) using nitrogen adsorption-desorption isotherms at 77 K. BET surface area was determined using Brunauer, Emmet and Teller (BET) method. Before the adsorption, samples were preliminary degassed by being imposed to a vacuum condition for 24 hours at temperature of 443 K. The point of zero net charge (PZNC) was determined based on a salt titration method. In the present work, 20 mg of pretreated adsorbents were in contact for 6 hours with 0.2 M sodium sulfate and water, separately. Then, certain amounts of 0.1 M H₂SO₄ and 0.1 M NaOH were added to the samples and pH of solutions were measured. Changes in pH versus the added values of acid and base was plotted for both solutions. Based on the intersection of the plots, PZNC was determined. FTIR measurements were performed on an Illuminat IR spectrometer (Smith’s Detection) attached to a Renishaw Invia Reflex microscope (Renishaw Incorporation). Samples were secured onto a borosilicate slide and the IR beam was focussed onto the sample.
FTIR spectra were an average of 512 spectra collected at room temperature in the 4000-650 cm$^{-1}$ range using 4 cm$^{-1}$ resolution.
CHAPTER 5. RESULTS AND DISCUSSION

5.1 Adsorbents characterization

The surface area, total pore volume, adsorbents porosity and surface functional groups can play important roles in adsorption process. As such, these parameters were investigated using various characterization techniques.

![Figure 5.1. Raw oat hulls (a), pretreated oat hulls (b)](image)

5.1.1 Determination of point of zero net charge (PZNC)

Adsorbents particles in liquid medium can result in either dissociation or association of protons. This is mainly dependent on the characteristic of adsorbents and solution pH. In the acidic condition, interaction of adsorbents surface and solution protons is facilitated leading to positive surface charge of the adsorbents. While at alkaline condition, loss of protons from adsorbents surface is more favorable resulting in negative surface of adsorbents (Čerović et al., 2007). The pH at which the net surface charge of adsorbents equals to zero is known as the point of zero net
charge. The point of zero net charge (PZNC) was determined based on a salt titration method (Yan and Niu, 2017). In this method changes of pH versus added amounts of acid and base is depicted for adsorbents soaked within two background solutions that have different ionic strengths. The intersection of the obtained graphs coincides with PZNC of adsorbents. As it is shown in Figure 5.2 and Figure 5.3, the PZNC for pretreated and raw oat hulls were determined as pH of 4.3 and 7.1, respectively.

![Graph](image)

**Figure 5.2.** Determination of Point of Zero Net Charge of pretreated oat hulls. 20.0 ± 0.2 mL water or 0.2 M Na₂SO₄ solution, 20 ± 2 mg pretreated oat hulls, 298.15 ± 0.50 K. Error bars are standard deviation
Figure 5.3. Determination of Point of Zero Net Charge of raw oat hulls. 20.0 ± 0.2 mL water or 0.2 M Na$_2$SO$_4$ solution, 20 ± 2 mg pretreated oat hulls, 298.15 ± 0.50 K. Error bars are standard deviation

5.1.2 Particle size distribution

Results of particle size distribution analysis are given in Figure 5.4. According to this figure, pretreated oat hulls had the volume mean diameter of 625 µm with the median of 586 µm. While for the raw oat hulls, the volume mean and median diameters were 1236 µm and 890 µm, respectively. In addition, for pretreated oat hulls, it was discovered that 10% and 90% of the particles have a particle size lower than 219 µm and 1143 µm, respectively. Whereas for raw oat hulls 10% and 90% of the particles showed to have a particle size value of lower than 535 µm and 2236 µm, respectively. As the results demonstrates, the particle size distribution curve shifted to smaller particle size region through pretreatment process. A substantial precursor weight loss was
also observed after the pretreatment process. The decrease in particle size and weight of samples can be attributed to the gasification of carbonaceous compounds, water dehydration bonds and decomposition of some existed organic compounds within the precursor (Sun et al., 2016, Timur et al., 2006).

![Particle size distribution graph]

**Figure 5.4.** Raw and pretreated oat hulls particle size diameter distributions

### 5.1.3 Scanning electron microscopy (SEM)

Results of SEM analysis for raw and pretreated oat hulls are shown in Figure 5.5. Many pores were created through the pretreatment process. The porosity developed through pretreatment mainly depends on two factors: activation conditions and nature of precursor (Timur et al., 2006). Phosphoric acid impregnation leads to cleavage of some of bond within precursor structure. This
is followed by formation of new phosphate and polyphosphate bridges, which can link and result in formation of bio-phosphate polymers. For instance, the carbon of pretreated oat hulls and phosphoric acid can interact together leading to formation of C–O–PO$_3$ and C–PO$_3$ bonds. The non-reversible expansion state of matrix taking place due to insertion of these phosphoric groups could be a well accessible porous structure after removal of acid molecules. At temperature higher than 400 °C, there is a potential for phosphate and polyphosphate bridges to break leading to contraction of porous structure and decrease in surface area (Castro et al., 2000; Yeddou and Bensmaili, 2005; Rosas et al., 2008; Ye et al., 2017).

![Figure 5.5. SEM images (a) raw oat hulls (b) pretreated oat hulls](image)

**Figure 5.5.** SEM images (a) raw oat hulls (b) pretreated oat hulls

### 5.1.4 Surface area analysis

Surface area of raw and pretreated oat hulls was determined using Brunauer, Emmet and Teller (BET) method (Table 5.1). The results demonstrated that surface area of oat hulls was increased remarkably through pretreatment process. This can be attributed to expansion of pores due to insertion of phosphoric acid molecules within them. In addition, dehydration occurred through heating at high temperature can be another influential parameter (Zhou et al., 2017). As
water molecules leave the precursor structure, a higher surface area will be available (Zhou et al., 2017).

**Table 5.1.** Surface area of raw and pretreated oat hulls

<table>
<thead>
<tr>
<th></th>
<th>Raw oat hulls</th>
<th>Pretreated oat hulls</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m²/g)</td>
<td>&lt;1</td>
<td>460</td>
</tr>
</tbody>
</table>

The nitrogen adsorption isotherm was obtained for pretreated oat hulls (Figure 5.6). According to Figure 5.6, the isotherm is type IV, with hysteresis loop, based on IUPAC (International Union of Pure and Applied Chemistry) adsorption isotherms classification (Sing, 1994). This implies co-existence of both micro (pore size <2) and meso pores (2 nm < pore size < 50 nm) with narrow slit-like structure. The hysteresis can be attributed to the intra particle porosity resulting from arrangement of neighboring fibers (Chen, 2007; Rouquerol & Maurin, 2014; Thommes et al., 2015).

The total pore volume for pretreated oat hulls was determined according to the volume of nitrogen adsorbed, as liquid, at the relative pressure of 0.98. The surface area determination was based on the assumption that the area for nitrogen molecules is 0.162 nm². From the sum of microporous surface area (S_{micro}) and t-plot external surface area (S_{ext}) values, BET surface area was determined. The subtraction of the total pore (V_{0.98}) and microporous (V_{micro}) volumes gives the mesoporous volumes (V_{mes}). The average particle size diameter was determined to be 2.13 nm.

**Table 5.2.** Characteristic of pretreated oat hulls

<table>
<thead>
<tr>
<th>V_{0.98} (cm³/g)</th>
<th>V_{micro} (cm³/g)</th>
<th>Microporosity (%)</th>
<th>V_{mes} (cm³/g)</th>
<th>S_{BET} (m²/g)</th>
<th>S_{ext} (m²/g)</th>
<th>S_{micro} (m²/g)</th>
<th>dp=4V_{0.98}/S_{BET} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.16</td>
<td>65</td>
<td>0.09</td>
<td>461</td>
<td>158</td>
<td>303</td>
<td>2.13</td>
</tr>
</tbody>
</table>
The pore size distribution of the pretreated oat hulls was determined based on the Barrrett–Joyner–Halenda (BJH) method using desorption branch (Figure 5.7). According to the BJH results, the maximum concentration of pores occurred at the diameter range of 1-10 nm with an average pore diameter of 3.73 nm.

Figure 5.6. Pretreated oat hulls BET isotherm obtained from N$_2$ adsorption at 77 K
Chuang et al. (2005) developed adsorbents from raw oat hulls through pyrolysis method for removal of arsenic (Chuang et al., 2005). Although the documented BET surface area (522 ± 21.4 m² g⁻¹) for their adsorbents was slightly higher than this work, the activation time used in their pre-treatment method was 10 times higher.

### 5.1.5 Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) analysis was performed to investigate surface functional groups existing on raw oat hulls, pretreated oat hulls, CIP powder and CIP-loaded oat hulls. Results are shown in Figure 5.8.
On the spectrum of raw oat hulls, the peak shown at 1200 cm\(^{-1}\) implies C-H bonds. The disappearance of this peak in pretreated oat hulls suggested breakage of some C-H bonds through chemical and thermal pretreatment. In addition, emergence of peak at 2500 cm\(^{-1}\) in pretreated oat hulls spectrum refers to O-H groups, indicating creation of hydroxyl groups through pretreatment process. The band appeared at 1600 cm\(^{-1}\) in the pretreated oat hulls spectrum can indicate existence of C=C bonds in aromatic rings (Sun et al., 2012b).

At CIP spectrum the peak appeared at 900 cm\(^{-1}\) can correspond to existence of C-H bonds in CIP molecules aromatic rings. This peak is also observed at the CIP loaded adsorbents spectrum which supports adsorption of CIP molecules taking place. The peak observed at 1500 cm\(^{-1}\), in CIP spectrum, is indicative of C=O bonds corresponding to carboxylate groups in the molecule structure. While, the peaks at the range of 1200 to 1400 cm\(^{-1}\) can be attributed to amino groups in
the piperazine moiety (Wang et al., 2010). The peak at 1600 in CIP and also at CIP loaded adsorbents spectrums denotes for C=O (keton) groups (Jiang et al., 2013).

5.2 Adsorption equilibrium

5.2.1 Effect of influential parameters on adsorption equilibrium

Effects of various parameters on adsorption of CIP on pretreated oat hulls was investigated. In addition, effect of pretreatment procedure on enhancing the adsorption capacity was evaluated. The experiments were all performed using the same CIP initial concentration (36 mg/L). All operating conditions were kept unchanged except the one being targeted to optimize. Mass balance was performed to determine the CIP adsorption capacity of adsorbents. Modeling of experimental data was performed using OriginPro modeling software.

5.2.1.1 Effect of adsorbents dose

The effect of adsorbents dose on adsorption capacity and removal efficiency was evaluated here in order to determine the minimum dosage of pretreated oat hulls needed to reach maximum CIP adsorption capacity. Results indicated that the highest CIP adsorption capacity was achieved at the adsorbents dose of 0.3 mg/L. Hence, this dosage was employed in the rest of experiments. As it is shown in Figure 5.9, adsorption capacity increased initially with increase in adsorbents dose. However, further increase in adsorbents mass also lead to obtaining lower CIP adsorption capacity (lower adsorption capacity). Similar phenomenon was observed in previous investigations, and was explained that the observed trend can be due to adsorbents sites overlapping (Garg et al., 2003; Nuhoglu and Malkoc, 2009; Ahmaruzzaman, 2008). Despite of all the presented justifications by researchers, further investigation is required in order to provide in depth explanation of the observed trend.
Figure 5.9. Effect of adsorbent dose on CIP adsorption capacity. 15 mg ± 0.3 mg pretreated oat hulls, 50.0 ± 0.5 mL CIP solution, pH=7, initial CIP concentration (Ci= 36 mg/L), 72 hrs, and 298.15 ± 0.50 K. Error bars are standard deviation

5.2.1.2 Effect of pH

CIP molecules have different charges at different pH values. For instance, at pH values less than the CIP first acid dissociation constant (pK_{a1}=5.9) CIP^+ (cationic CIP) is the dominant form in the media as the amine group is protonated. In the pH range of 5.9 to 8.89, between CIP first and second acid dissociation constants (pK_{a1} and pK_{a2}), respectively, CIP^0 (zwitterionic CIP) is the dominant form since the deprotonation of carboxylic group occurs simultaneously with the protonation of amine group. After the pH of 8.89 (pK_{a2}), CIP^- (anionic CIP) tends to be dominant due to deprotonation of carboxylic and amine functional groups taking place (Wu et al., 2010).
The effect of pH on CIP adsorption was studied in the pH range of 3 to 10 at 1-pH-unit increments, using 0.01 M H$_2$SO$_4$ or 0.01 M NaOH. The results are shown in Figure 5.10. Although, mechanisms involved in CIP adsorption on the pretreated oat hulls can be complicated, based on the experimental results a number of possible mechanisms can be hypothesised.

![Figure 5.10. Effect of pH on CIP adsorption capacity. 15 mg ± 0.3 mg pretreated oat hulls, 50.0 ± 0.5 mL CIP solution, initial CIP concentration (Ci= 36 mg/L) and 298.15 ± 0.50 K. Error bars are standard deviation](image)

The relatively lower adsorption capacity obtained at pH 3, can be due to the fact that as pH is lower than the adsorbents PZNC (pH=4.3), the adsorbents surface is positively charged. Also, the CIP$^+$ is the dominant in the media. As such, electrostatic repulsion can occur. Competitive adsorption may also take place between H$^+$ and CIP$^+$ towards the negative sites of adsorbents. In addition, at low pH range the other possible scenario is that low valence cations of adsorbents...
surface may exchange with CIP$^+$ molecules leading to adsorption of adsorbate through a cationic exchange mechanism.

As pH increases, adsorbents surface net charge tends to become less positive, reaching a neutral state at pH of 4.3 (PZNC) and at higher pH values than PZNC the adsorbents surface is negatively charged. The increase in adsorption capacity occurring at pH 5 corroborates occurrence of electrostatic attraction between negatively charged surface of adsorbents and CIP$^+$. At the pH of 7, the zwitterion form of CIP reaches its maximum percentage. This facilitates existence of electrostatic attraction between negatively charged atoms of carboxyl groups within CIP$^0$ and positively charged sites of the adsorbents surface (Li et al., 2014). In addition, at the pH solution of 7, hydrophobicity of CIP molecules is at its extreme level, as such the lowest solubility of CIP molecules tends to occur at this point. This fact leads to more interactions of CIP molecules and pretreated oat hulls, favoring adsorption process. Contribution of hydrophobic interactions in CIP adsorption occurring at pH of 7 was also observed in previous papers (Li et al., 2014).

The adsorption capacity was relatively constant in the pH range of 8 to 10. This may be due to the fact that at this pH range hydrophobic interactions have suppressed electrostatic forces (Li et al., 2014). The decrease in CIP adsorption capacity at a pH over 7 can be attributed to the repulsion CIP$^-$ and negative surface charge of the adsorbents. In spite of the negative charge of adsorbents surface and CIP$^-$ molecules, adsorption still took place at pH values over 7. This indicated that other mechanisms such as complexations, hydrogen bonding or EDA (Electron Donor Acceptor) interactions may be responsible for adsorption taking place at this pH range. At pH over 9, protonated amino groups of CIP molecules may interact with negative surface of adsorbent through electrostatic interactions (Gao et al., 2012). The $\pi$-$\pi$ and n-$\pi$ electron donor acceptor interactions (EDA) can be one of the involved mechanisms in adsorption when the
adsorbate is an organic compound with an aromatic ring. EDA interactions occur between electron-rich and electron-poor entities (Zhu and Pignatello, 2005). The benzene ring in CIP can act as the electron acceptor, particularly due to the high electronegativity of available fluorine group. FTIR analysis revealed that C=C bonds in aromatic rings and hydroxyl are the present functional groups on the surface of pretreated oat hulls. These two groups can serve as the electron donors. This provides the possibility of EDA interactions to occur. However, as carboxylic groups present on the surface of adsorbents, EDA interactions between CIP molecules and pretreated oat hulls surface can be suppressed since these functional groups act as electron acceptors (Li et al., 2014).

Another possible mechanism taking place can be hydrogen bonding. On the surface of pretreated oat hulls there are functional groups such as hydroxyl and carboxyl that due the containing oxygen can provide the potential for the hydrogen bonding taking place between these groups and carbonyl group or/and hydroxyl groups of CIP. Even at acidic conditions the free H+ in the media can contribute to hydrogen bonding taking place between adsorbents surface oxygen functional groups and CIP molecules (Peng et al., 2015).

Optimum pH was determined to be 7, as maximum CIP adsorption capacity occurred at this pH value. As such, further experiments in this research were conducted at this pH value.

5.2.1.3 Effect of temperature

Temperature affects both equilibrium, rate of adsorption, spontaneity and randomness of the adsorption processes. Adsorption of CIP on pre-treated oat hulls was investigated at three temperatures of 288 K, 298 K and 318 K (Figure 5.11). The temperature of 298 K was chosen to study as it is the room temperature at normal conditions. Also, temperatures of 20 K higher than
room temperature (318 K) and 10 K lower than room temperature (288 K) were chosen to study. In industrial scale, changes in temperature of waste water streams require using cooling and heating equipment and utilizing energy. This can be done along with more capital and operational costs. Hence, in this research, effect of relatively close temperatures to room temperature was investigated on CIP adsorption on pretreated oat hulls.

As results demonstrated, CIP uptake tends to increase at higher temperature conditions. For instance, CIP uptake increased approximately 80% (from 40 to 72 mg/g) with 30 K increase in operating temperature, giving the idea that adsorption is favored at high temperatures and has an endothermic nature.

**Figure 5.11.** Effect of temperature on CIP uptake. 15 mg ± 0.3 mg pretreated oat hulls, 50.0 ± 0.5 mL CIP solution, initial CIP concentration (Ci= 36 mg/L) and pH=7. Error bars are standard deviation
5.2.1.4 Effect of pretreatment

Comparison of raw and pretreated oat hulls performance in removal of CIP from water is shown in Figure 5.12. As it is evident, the adsorption capacity using pretreated oat hulls was up to 600% higher. This can be due to great improvement of precursor porosity and creation of acid groups on adsorbents surface. These consequences, that correspond to increase in adsorption capacity, were also observed by other researchers who pretreated lignocellulose raw materials with phosphoric acid and subsequently with heat (Yan & Niu, 2017, Sych et al., 2012).

![Figure 5.12. Effect of pretreatment on CIP equilibrium isotherm of CIP. 15 mg ± 0.3 mg pretreated oat hulls, 50.0 ± 0.5 mL CIP solution, pH=7 and 298.15 ± 0.50 K. Error bars are standard deviation](image)

5.2.2 Isotherm modeling

Batch adsorption experiments were conducted at three different temperature of 288 K, 298 K and 318 K at the optimum pH (pH=7) and subsequently, equilibrium isotherms were obtained.
Afterwards, the Langmuir, Freundlich and Temkin isotherms were used to model the experimental data (Figure 5.13).

Figure 5.13. Experimental and fitted data of CIP equilibrium adsorption. 15 mg ± 0.3 mg pretreated oat hulls 50.0 ± 0.5 mL CIP solution and pH=7. Error bars are standard deviation.

The determined isotherms constants and their corresponding correlation coefficients are documented in Tables 5.3.
**Table 5.3. Adsorption isotherm modeling results**

<table>
<thead>
<tr>
<th>Langmuir model</th>
<th>T (K)</th>
<th>k (mg/L)</th>
<th>$q_{max}$ (mg/g)</th>
<th>$r^2$</th>
<th>RSS* ((mg/g)$^2$)</th>
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<td>151</td>
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<tr>
<td></td>
<td>318</td>
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<td>87</td>
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<th>Freundlich model</th>
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<th>$K_F$ (mg$^{1-(1/n)}$ L$^{1/n}$ g$^{-1}$)</th>
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<th>$r^2$</th>
<th>RSS ((mg/g)$^2$)</th>
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</tr>
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</table>

<table>
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<th>Temkin model</th>
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<th>B (mg/g)</th>
<th>$r^2$</th>
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<td>9</td>
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<td>100</td>
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<tr>
<td></td>
<td>298</td>
<td>9</td>
<td>11</td>
<td>0.9421</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>16</td>
<td>12</td>
<td>0.9753</td>
<td>170</td>
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</tbody>
</table>

*RSS: residual sum of squares, calculated as $\Sigma (q-e_{cal})^2$

The correlation coefficient $(r^2)$, close to unity for all the models, demonstrates marginal deviation of predicted and experimental data. However, based on higher values of $r^2$ and lower values of RSS (residuals sum of squares) the Freundlich model is suggested to be the best fit to express experimental data. This implies adsorption of CIP to take place on heterogeneous sites on the surface of pretreated oat hulls. The values of $K_F$ which is an indication of adsorption capacity has increased at higher temperature conditions, implying increase in temperature is beneficial for
the process. Likewise, values of $K_L$ have increased at higher temperatures indicating a stronger adsorption taking place (Wang et al., 2017). Increase in temperature can increase diffusion rate of molecules and decrease in liquid viscosity which facilitates easier movement of adsorbate molecules towards and through adsorbents pores. Maximum adsorption capacity at 288 K was enhanced by 27 % and 53 % through 10 °C and 20 °C increase in solution temperature, respectively.

As the adsorption isotherms have not reached a strict plateau, it can be assumed that progressive saturation of adsorbents surface occurs due to the gradual occupancy of adsorbents surface sites by adsorbate molecules (Giles et al., 1974).

Whether the adsorption is favorable at the examined conditions can be evaluated based on the two aforementioned criteria: adoption intensity parameter ($n$) and separation factor ($R_L$), derived from the Freundlich and Langmuir models, respectively. Values of $n$ greater than unity indicates a favorable adsorption taking place, and $R_L$ values lower than one implies favorable adsorption occurring. The change of $R_L$ values versus changes in operating conditions (temperature and CIP initial concentration) is shown in Figure. 5.14. According to this figure, as all the reported $R_L$ values were lower than unity it can be concluded that CIP adsorption on pretreated oat hulls was favorable at all studied conditions. $R_L$ values decreased with an increase in temperature and CIP initial concentration. This indicates adsorption to be more favorable at higher temperatures and higher CIP initial concentration.
Figure 5.14. Changes of $R_L$ with temperature and initial concentration

5.3 Adsorption Kinetics

5.3.1 Effect of influential parameters on adsorption kinetics

Adsorption rate differs at various temperatures and initial adsorbate considerations. As such, in this research, the effect of these two important parameters on adsorption kinetics was scrutinized.

5.3.1.1 Effect of temperature

Temperature affects equilibrium, rate of adsorption, and spontaneity and randomness of the adsorption processes. Kinetic data were obtained at 288 K, 298 K and 318 K for maximum studied initial CIP concentrations, 60 mg. As it is shown in Figure 5.15, the required time to reach equilibrium decreased considerably with increase in temperature, implying a higher adsorption rate taking place at higher temperatures. The required time to reach equilibrium is approximately 60 hours at $T=318$ K. However, the equilibrium time needed at $T=288$ K is 100 hours. This
indicates that 30 K increase in temperature can lead to almost 40% reduction in required time to reach equilibrium. Increase in CIP uptake and also adsorption rate at elevated temperatures can be results of higher mobility of CIP molecules, lower viscosity of media, and creation of new active sites (Peng et al., 2015).

Figure 5.15. Effect of temperature on CIP adsorption kinetic data. 15 mg ± 0.3 mg pretreated oat hulls, 50.0 ± 0.5 mL CIP solution, initial CIP concentration (Ci=60 mg/L) and pH=7. Error bars are standard deviation

5.3.1.2 Effect of initial adsorbate concentration

In this study, in order to further understand the effect of initial adsorbate concentration on adsorption kinetics for six different CIP concentrations (4.8, 12, 24, 36, 48 and 60 ppm) kinetic data were obtained at temperatures of 288 K, 298 K and 318. Results are shown in Figures 5.16, 5.17 and 5.18.
As it is shown, at higher adsorbate initial concentrations more time is required to reach equilibrium. This is due to the fact that at higher concentrations more adsorbate molecules need to transfer from bulk and adhere to the surface of adsorbent. In addition, repulsive forces may exist between adsorbate molecules which this factor can be enforced at higher initial concentrations (Reza et al., 2014). For instance, at T=318 K, the required time for reaching equilibrium increased from 5 hrs to 32 hrs with an increase in initial concentration from 4.8 mg/L to 60 mg/L. Moreover, adsorption rate has shown to enhance considerably with increase in initial concentration. This may be due to higher mass transfer driving force existing at higher initial concentrations of adsorbate molecules, favoring a faster adsorption.

![CIP adsorption kinetic data](image)

**Figure 5.16.** CIP adsorption kinetic data. 15 mg ± 0.3 mg pretreated oat hulls, 50.0 ± 0.5 mL CIP solution, pH=7 and T=318 ± 0.5 K. Error bars are standard deviation
Figure 5.17. CIP adsorption kinetic data. 15 mg ± 0.3 mg pretreated oat hulls, 50.0 ± 0.5 mL CIP solution, pH=7 and T=298 ± 0.5 K. Error bars are standard deviation.

Figure 5.18. CIP adsorption kinetic data. 15 mg ± 0.3 mg pretreated oat hulls, 50.0 ± 0.5 mL CIP solution, pH=7 and T=288 ± 0.5 K. Error bars are standard deviation.
CIP removal efficiencies at various temperatures and initial concentrations are shown in Figure 5.19. As it can be seen, at a constant initial concentration, removal efficiency tends to increase at higher temperature conditions. Also, at a constant temperature, removal efficiency exhibited to be higher at lower CIP initial concentrations. This can be mainly due to the fact that at lower CIP initial concentrations, the ratio of vacant available active sites to the adsorbtae molecules was at a sufficient level for most of CIP molecules to be adsorbed (Tan et al., 2009).

Figure 5.19. CIP removal efficiency at different temperatures and initial concentrations. 15.0 ± 0.1 mg pretreated oat hulls, 50.0 ± 0.5 mL CIP solution and solution pH=7
5.3.2 Kinetic modeling

Kinetic data were obtained at maximum studied CIP initial concentration ($C_i=60$ppm) at three temperatures 288, 298, 318 K. The determined parameters and correlation coefficients corresponding to the kinetic models applied for expressing experimental data are tabulated in Table 5.4. In addition, graphical representation of fitted models are shown in Figure 5.20. Both the pseudo first and second order rate constants increased at higher temperature conditions, reflecting stronger interactions of surface-adsorbate and faster adsorption rate occurring with increase in temperature. The initial rate of adsorption (tabulated in the values of $kqe^2$) also increased from 8 to 24 mg/(g.h), when temperature was raised from 288 K to 318 K.

According to Table 5.4, CIP uptake in experimental ($q_{exp}$) and calculated ($q_{cal}$) mode are more consistent in pseudo-second order model compared to those calculated using pseudo-first order model. In addition, the correlation coefficient values are closer to unity and RSS (residual sum of squares) values are lower for the fitted curves using pseudo-second order model. Therefore, although other fitted models have of $r^2$ values relatively close to unity, it was concluded that pseudo-second order model is the best fit among the tested models. This implies that adsorption to be the dominant rate-limiting step and the adsorption is controlled by electron exchange or sharing between adsorbate and adsorbent (Putra et al., 2009). In the fitted line of intra particle diffusion model, the initial sharp increase can be corresponded to the adsorption of CIP molecules to the exterior surface of pretreated oat hulls and diffusion within mesoporous. As such, a higher adsorption rate was observed. As the saturation relatively occurred at the exterior surface of adsorbents, the intra particle diffusion mechanism tend to be dominant within the system, which the gradual final increase in CIP uptake can be attributed to this step (Reza et al., 2014).
Table 5.4. Adsorption kinetic modeling results

### Pseudo-first order model

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$q_{e, \text{exp}}$ (mg/g)</th>
<th>$k_1$ (hr$^{-1}$)</th>
<th>$q_{e, \text{cal}}$ (mg/g)</th>
<th>$r^2$</th>
<th>RSS ((mg/g)$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>60</td>
<td>0.041</td>
<td>43</td>
<td>0.9914</td>
<td>4262</td>
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<tr>
<td>298</td>
<td>70</td>
<td>0.073</td>
<td>54</td>
<td>0.9645</td>
<td>4627</td>
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<tr>
<td>318</td>
<td>86</td>
<td>0.088</td>
<td>69</td>
<td>0.9742</td>
<td>4447</td>
</tr>
</tbody>
</table>

### Pseudo- second order model

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$q_{e, \text{exp}}$ (mg/g)</th>
<th>$K_2$ (g/mg.hr)</th>
<th>$q_{e, \text{cal}}$ (mg/g)</th>
<th>$r^2$</th>
<th>RSS ((mg/g)$^2$)</th>
<th>$Kq_e^2$ (mg/g.hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>60</td>
<td>$2.13 \times 10^{-3}$</td>
<td>62</td>
<td>0.9953</td>
<td>460</td>
<td>7.67</td>
</tr>
<tr>
<td>298</td>
<td>70</td>
<td>$2.9 \times 10^{-3}$</td>
<td>72</td>
<td>0.9983</td>
<td>454</td>
<td>14.21</td>
</tr>
<tr>
<td>318</td>
<td>86</td>
<td>$3.03 \times 10^{-3}$</td>
<td>90</td>
<td>0.9988</td>
<td>421</td>
<td>24.41</td>
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</table>

### Elovich model

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\alpha$ (mg/hr)</th>
<th>$1/\beta$ (mg/g)</th>
<th>$r^2$</th>
<th>RSS ((mg/g)$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>40</td>
<td>9</td>
<td>0.9608</td>
<td>282</td>
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<tr>
<td>298</td>
<td>74</td>
<td>11</td>
<td>0.9571</td>
<td>315</td>
</tr>
<tr>
<td>318</td>
<td>105</td>
<td>13</td>
<td>0.9386</td>
<td>459</td>
</tr>
</tbody>
</table>

### Intra particle diffusion model

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k_{in}$ (hr$^{-1/2}$)</th>
<th>$C$ (mg/g)</th>
<th>$r^2$</th>
<th>RSS ((mg/g)$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>5</td>
<td>14</td>
<td>0.9647</td>
<td>237</td>
</tr>
<tr>
<td>298</td>
<td>7</td>
<td>19</td>
<td>0.9612</td>
<td>213</td>
</tr>
<tr>
<td>318</td>
<td>9</td>
<td>23</td>
<td>0.9563</td>
<td>346</td>
</tr>
</tbody>
</table>
Figure 5.20. Fitted models of CIP Kinetic data on pretreated oat hulls at three different temperatures. Blue color line (T= 388K), orang (T= 298 K) and grey (T= 288 K), initial CIP concentration (Ci= 60 mg/L)

As the line representing intra particle diffusion has not passed through the origin, it can be concluded that intra particle diffusion is not the only rate controlling step in the process. Deviation from origin is proportional to the boundary layer mass transfer resistance (Sun et al., 2012a). CIP molecules tend to have a planar orientation with dimensions of 13.5 Å, 3 Å and 7.4 Å (Carabineiro et al, 2011). Whereas, the average pore diameter of the adsorbents is 21.3 Å. As the dimensions of adsorbate molecule is less than the pore diameter, there is a tendency for the molecules to diffuse within the solid pores (Tan et al., 2009, Cheung et al., 2007).
According to the pseudo second order rate constants obtained at the above three temperatures, the activation energy was determined as 8.07 kJ/mol (regression line $r^2=0.71$) by Equation 2.10. The energy falls within the range of physical adsorption ($< 4.2$ kJ/mol)(Yan and Niu, 2017).

5.4 Desorption

Desorption experiments were conducted at extreme pH conditions, pH=1 and pH =11 (Figure 5.21). The two pH values were chosen because at the extreme low and high pH values, the surfaces of adsorbent and CIP molecules both have charges of same sign, desorption of adhered adsorbate molecules may occur as a result of the electrostatic repulsion.

In addition, pronounced existence of protons at low pH value can lead to exchange of protons with positive CIP molecules adsorbed on adsorbent surface, leading to release of adsorbed CIP molecules. This assumption could further be supported by observing minor increase in pH value. However, the desorption efficiency obtained was relatively low (19% at pH=1, and 14 % at pH=11). The results indicated strong bonding between CIP molecules and pretreated oat hulls. Therefore, future investigation on enhancing desorption efficiency is recommended.
**Figure 5.21.** Effect of pH on CIP desorption by pretreated oat hulls. 15.0 ± 0.1 mg pretreated oat hulls, 50.0 ± 0.5 mL millipore water, CIP initial concentration Ci= 60 ppm, T=298 ± 0.5 K

### 5.5 Thermodynamic parameters calculation

To determine thermodynamic feasibility, understanding the nature of the mechanism corresponding to adsorption and spontaneity of process, evaluation of thermodynamic parameters is an essential step. Thermodynamic parameters including change in Gibbs free energy ($\Delta G^\circ$), entropy ($\Delta S^\circ$) and enthalpy ($\Delta H^\circ$) were obtained through thermodynamic functions as expressed in equations 2.12 and 2.13. The equilibrium constant of $K_c$ can significantly impact the values of other thermodynamic parameters such as $\Delta G^\circ$, $\Delta S^\circ$ and $\Delta H^\circ$. $K_c$ can be determined through various methods using different adsorption coefficients such as the Langmuir isotherm constant ($K_L$), Freundlich isotherm constant ($K_F$) and distribution coefficient ($K_d$). In this research, $K_c$ was determined from the Langmuir constant. However, as $K_c$ needs to be dimensionless the value of
$K_L$ is multiplied by a factor of $10^6$ which is the density value of pure water in mg/L (Tran et al., 2016).

**Table 5.5.** Thermodynamic parameters

<table>
<thead>
<tr>
<th>T(k)</th>
<th>Kc (L/mg)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>0.19</td>
<td>-29</td>
<td>+17</td>
<td>+163</td>
</tr>
<tr>
<td>298</td>
<td>0.29</td>
<td>-30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>0.39</td>
<td>-34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results of thermodynamic analysis are listed in Table 5.5. The positive value of $\Delta H^\circ$ indicates endothermic nature of adsorption phenomenon which is in agreement with the results revealing that increase in temperature and leads to higher CIP uptakes. In addition, based on the values of $\Delta H^\circ$ the binding mechanisms contributing to the adsorption can be determined. $\Delta H^\circ$ lower than 40 kJ/mol is indicative of physisorption while values higher than 40 kJ/mol imply to chemisorption processes (Yan and Niu, 2017). According to obtained $\Delta H^\circ$, the nature of CIP adsorption on pretreated oat hulls appeared to be physisorption. Thermodynamic study showed that CIP adsorption on pretreated oat hulls is a spontaneous and thermodynamically favorable phenomenon. The positive value of $\Delta S^\circ$ is an indicative of increase in randomness occurring during CIP adsorption at the solid- solution interface. This implies that CIP adsorption leads to disruption of hydration shell surrounding the surface of adsorbents and re-orientation of water molecules around the adsorbents surface will be less ordered. Obtaining more negative values of $\Delta G^\circ$ with increase in temperature, indicates increase in spontaneity of CIP adsorption at higher temperature conditions.
5.6 Comparison of pretreated oat hulls with previously studied adsorbents

In order to assess the CIP adsorption capacity of the pretreated oat hulls, a comparison between the maximum adsorption capacities (q_{max}) obtained in this work with that reported in literature was made. According to Table 5.6, the pretreated oat hulls have higher adsorption capacity compared to the adsorbents indicated. In addition, pretreated oat hulls can be less costly and more eco-friendly than a number of previously used adsorbents for removal of CIP from water.
### Table 5.6. CIP adsorption capacity for a number of previously studied adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Maximum capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrous oxides of Al</td>
<td>0.01</td>
<td>(Gu and Karthikeyan, 2005)</td>
</tr>
<tr>
<td>Hydrous oxides of Fe</td>
<td>0.02</td>
<td>(Gu and Karthikeyan, 2005)</td>
</tr>
<tr>
<td>Modified coal fly ash</td>
<td>2</td>
<td>(Zhang et al., 2011)</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>7</td>
<td>(Mackay et al. 2008)</td>
</tr>
<tr>
<td>Aluminum hydroxide</td>
<td>13</td>
<td>(Gu and Karthikeyan, 2005)</td>
</tr>
<tr>
<td>Red mud</td>
<td>17</td>
<td>(Balarak et al., 2016)</td>
</tr>
<tr>
<td>Goethite</td>
<td>19</td>
<td>(Zhang et al. 2007)</td>
</tr>
<tr>
<td>Illite</td>
<td>33</td>
<td>(Wang et al., 2011)</td>
</tr>
<tr>
<td>Biocomposite fibers</td>
<td>40</td>
<td>(wu et al., 2013)</td>
</tr>
<tr>
<td>Birnessite</td>
<td>57</td>
<td>(Jiang et al., 2013)</td>
</tr>
<tr>
<td>Hazelnut based activated Carbon</td>
<td>65</td>
<td>(Balarak et al., 2016)</td>
</tr>
<tr>
<td>Magnetic carbon composite</td>
<td>75</td>
<td>(Shi et al., 2013)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>77</td>
<td>(Genc and Dogan, 2015)</td>
</tr>
<tr>
<td>Pretreated oat hulls</td>
<td>83 ± 3</td>
<td>This work</td>
</tr>
</tbody>
</table>
CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Pretreated oat hulls were capable of CIP removal from the simulated contaminated water. Porosity and surface area of raw oat hulls were substantially enhanced through the pretreatment procedure. The BET surface areas were found to be less than 1 m$^2$/g for raw oat hulls. However, this value increased up to 460 m$^2$/g for pretreated oat hulls. According to obtained N$_2$ adsorption/desorption isotherms and their classification as type IV of IUPAC isotherms, it was concluded that both micro and meso pores coexisted in the pretreated oat hulls structure. Micropores constitute 65% of total volume of pretreated oat hulls. The PZNC was determined to be 7.1 and 4.3 for raw and pretreated oat hulls, respectively.

Investigation of the effects of operating parameters including adsorbent dose, solution pH and temperature optimization of adsorption performance was performed. The optimum adsorbent dose was found to be 0.3 mg/L and the optimum solution pH determined to be 7. Adsorption was observed to decrease considerably at pH values lower than 5. This was mainly attributed to the fact that surface of adsorbent and CIP molecules have similar charges at this pH range, and hence electrostatic repulsion was occurring. In addition, strong competition between CIP$^+$ and protons to adsorb to the functional groups of adsorbent was another contributing factor. At pH of 7, maximum adsorption capacity was achieved as electrostatic attraction forces were present due to dissimilarity in the sign of adsorbent surface and CIP molecules charges. Moreover, at this pH the hydrophobicity of CIP molecules was at its extreme high level which was favoring CIP adsorption as well.
It was also discovered that adsorption is favored at higher temperature conditions, as maximum adsorption capacity increased from 51 mg/g to 83 mg/g by increasing temperature from 288 K to 318 K. Moreover, it was revealed that adsorption rate tends to be higher at elevated temperature conditions. The experimental equilibrium isotherm data most closely followed Freundlich model, indicating adsorption on heterogeneous sites taking place in the process. The experimental kinetic data were best fitted by pseudo second order model, implying adsorption of CIP molecules on the surface to be the rate limiting step in the process. Upon thermodynamic analysis it was discovered that adsorption process nature is spontaneous, endothermic and along with increase in randomness. Comparison of the developed pretreated oat hulls and previously investigated adsorbents used for removal of CIP showed that higher value of adsorption capacity was obtained in this work. In conclusion, pretreated oat hulls showed to have the potential for removal of CIP molecules.

In this work, removal of CIP from simulated waste water using adsorbents made of oat hulls was investigated. As a basic assumption of this research, CIP tend to be the only contaminant existed in water. However, coexistence of other compounds such as metals, ions, other antibiotics may also occur in water resources. As interactions between CIP and these compounds can alter adsorption behavior, further future research in this regard is demanded. In addition, low values of desorption efficiency does not offer the possibility of economic reusing of regenerated adsorbents within the cycle. As such, more studies taking place on discovering new methods for effective regeneration of used adsorbents are required. In addition, based on this research and previous investigations it was discovered that raw materials containing cellulose, hemi cellulose and lignin, can be converted to adsorbents that have high surface area and porosity through phosphoric acid and microwave induced pretreatment. However, it is not yet clear that which of these constitutional
compounds in raw oat hulls plays the major role in achieving adsorbents with high surface area and porosity. This requires further investigation.
REFERENCES


10.15376/biores.8.2.2950-2966.


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