

January 2008

# Sorption Of Pahs And Copper (ii) By Aspen Wood Fibers

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**SORPTION OF PAHS AND COPPER (II) BY ASPEN WOOD FIBERS**

A Thesis Presented

by

LIYUAN HUANG

Submitted to the Graduate School of the  
University of Massachusetts Amherst in partial fulfillment  
of the requirements for the degree of

MASTER OF SCIENCE

SEPTEMBER 2008

Department of Plant, Soil, and Insect Sciences

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## **DEDICATION**

*To my parents Xianlin Huang and Ruiyin Huang*

## ACKNOWLEDGMENTS

I am most thankful to my thesis advisor, Professor Xing, for his guidance, support and patience throughout these years. I would also like to thank my committee members, Dr. David Reckhow, Dr. Stephen Simkins, and Dr. Stephen J. Herbert, for their valuable time, insightful questions and suggestions.

I would like to thank the following people for their help with laboratory work involved in my research: Hamid Mashayekhi, Kun Yang, Pan Bo, Baoliang Chen, Daohui Lin, Wei Jiang, Lei Song, Elizabeth Johnson, Xilong Wang, Seunghun Kang, Saikat Ghosh, Karen Heymann, and Nica. I would also like to thank Dr. Peter Veneman, Mickey Spokas and Emily Stockman for their kind help and letting me share their laboratory.

Finally, I would like to thank my friends and family here and in China for their encouragement, love and support throughout these years.

## ABSTRACT

### SORPTION OF PAHS AND COPPER (II) BY ASPEN WOOD FIBERS

SEPTEMBER 2008

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The sorption and desorption of phenanthrene and pyrene on treated and untreated aspen wood fibers were studied to evaluate the sorption mechanisms of polycyclic aromatic hydrocarbons (PAHs). Those samples were characterized using elemental analysis, porosity analysis, Solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and batch sorption experiments with phenanthrene and pyrene. Results from NMR and FTIR spectra indicated that bleaching removed aromatic moieties, yielding the highest polarity and increased porosity, whereas hydrolysis removed parts of hemicelluloses and cellulose, producing a matrix with more aromatic moieties. All PAH isotherms on treated and untreated aspen wood fibers fitted well to the Freundlich equation and bleached (BL) had the highest  $N$  value, followed by untreated (UTR), low temperature hydrolyzed (LHY) and high temperature hydrolyzed (HHY). The results suggest aromatic moieties and polarity of wood fibers mainly contribute to PAH sorption and desorption.

Copper (Cu) sorption by aspen wood fibers, cellulose and lignin was also examined to understand Cu sorption mechanism. Our results showed that solution pH greatly influenced Cu sorption. Cu sorption steadily increased from pH 1.5 to 4.5, and a

maximum sorption was observed at ~ pH 5.5 for all the samples. Sorption isotherms fitted well to Langmuir equation. BL had a highest sorption capacity, followed by UTR, cellulose (CEL), and HHY, while lignin(LIG) had little Cu sorption. The results suggested carboxyl and hydroxyl mainly contributes to Cu sorption, and ion-exchange plays a major role in Cu sorption. Additionally, Cu sorption capacity on all sorbents decreased with the increase of initial concentrations of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  or  $\text{Al}^{3+}$ . At low initial concentrations of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  or  $\text{Al}^{3+}$ , Cu sorption decreased with increasing concentrations of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  or  $\text{Al}^{3+}$ , which confirms that ion-exchange plays a main role on Cu sorption on aspen wood fibers.

This study demonstrated that aspen wood fibers are a potential sorbent for PAHs and Cu, and chemical modifications of the wood matrix can effectively increase PAH and Cu sorption efficiency. These results may have implications for the treatment of stormwater runoff and other PAH and heavy metal contaminated liquids.



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# CHAPTER 1

## INTRODUCTION

### 1.1. Literature Review

#### 1.1.1 Wood

Wood is a remarkable material with great value and importance in the world economy. It is used extensively as a structural material, fuel, or industrial raw material in many parts of the world. As a renewable natural resource, it is available in large quantities at relatively low costs. Wood is also a heterogeneous material and consists of three major components, cellulose, hemicellulose, and lignin. The chemical composition of wood cannot be defined precisely as it varies with tree part (root, stem, or branch), wood species, geographic location, climate and soil (Pettersen, 1984). In general, cellulose (Figure 1-1A) makes up 40-45% of the dry weight of wood (Pettersen, 1984; Schniewind, 1989); it is a collection of linear polysaccharides of 2,000- 265,000 molecules (Liu et al., 2006). Layers of cellulosic polymers are stacked by van der Waals' forces to form a strong crystalline structure (Stamm, 1964). Hemicellulose (Figure 1-2B) also makes up the wood matrix; it is formed by five- and six-carbon ring sugars, and has a lower molecular weight than cellulose (Siau, 1983). Lignin (Figure 1-3C) is a natural polymer, which is biologically produced through random polymerization processes with a great structural heterogeneity. It consists of complex three-dimensional building blocks involving six-carbon rings and functional groups such as methoxyls, phenolic hydroxyls, phenolic ethers, aliphatic hydroxyls, and carbonyls (Siau, 1983). Most of the lignin resides in the secondary cell walls of the

wood fibers and ray cells. The remainder of the wood is made up by inorganic minerals, extractives (e.g. waxes, proteins, resins), and aliphatic biopolymers (e.g., cutin and cutan). The extractives contribute to the wood properties, such as color, odor, or decay resistance (Pettersen, 1984). Aspen wood is composed of 51% cellulose, 26% hemicellulose, 21% lignin, and 1% others (Fengel and Wegner, 1989). The chemical differences among these three components result in significant variability in the wood's ability to interact with cations, anion and organic contaminants. For instance, cellulose and hemicelluloses provide for strong hydrogen bonding due to their polyhydroxyl and polycarboxylic structures. Conversely, Lignin is a hydrophobic polymer, its phenylpropane units may constitute relatively hydrophobic regions, therefore attracting hydrophobic compounds. Wood fibers are renewable and available abundantly at no or low cost. Many studies have indicated wood fibers have sorption potential for contaminants (Garbarini and Lion, 1986; Mackay and Gschwend, 2000; Boving and Zhang, 2004). Boving and Zhang (2004) reported that aspen wood fibers have a potential sorption ability for organic chemicals such as pyrene and phenanthrene.

### **1.1.2 Polycyclic Aromatic Hydrocarbons**

PAHs are found at elevated concentrations in stormwater runoff and waste water streams. They originate from anthropogenic sources. The release of PAH pollutants from urban and industrial areas, including those resulting from widespread application of fertilizers, pesticides, herbicides, and burning of gasoline, impinges on the quality of surface and ground water (Barbash and Resek, 1996; Bemknopf et al., 1997). Runoff may also contain elevated levels of organic compounds (Boving and Zhang, 2004). With precipitation, these contaminants wash off surfaces or erode from agricultural land,

collect in drainage structures, and eventually discharge into surface- or groundwater bodies, potentially allowing the contaminants to enter drinking water resources.

It is well known that PAHs are carcinogenic, mutagenic, and teratogenic. Due to their toxicity, much attention has been paid to how to remove them from water bodies. Previous studies reported that aliphatic biopolymers can also significantly sorb organic contaminants from water (Chefetz et al., 2000; Gunasekara et al., 2003). In addition, sorption isotherms can be very nonlinear. These recent data indicate that aliphatic biopolymers can be as important as aromatic polymers such as lignin for sorbing organic compounds (Gunasekara et al., 2003). Furthermore, sorption mechanisms by various wood components and their individual contributions are not clearly understood. Thus, it is difficult to design and implement a wood-based filtration plan for cleanup of contaminated water. Therefore, research on how different wood materials react with contaminants in water is important and needed.

### **1.1.3 Heavy Metals and Copper**

Heavy metal pollution in water is also a major problem, because metals are not subject to bacterial degradation or other breakdown, and also cannot be chemically transformed or destroyed, thus, they are persistent in our environment (ElNady and Atta, 1996), and a threat to human life and the environment (Igwe and Abia, 2006). Similar to PAH contaminants, elevated concentrations of heavy metals, such as zinc and copper have been detected in urban stormwater runoff (Hares and Ward, 1999). The sources of heavy metals in stormwater runoff and waste water streams are numerous. The major contributors of metals in non-industrial areas are washings of road surfaces, parking lots, automobiles, building materials and lawn fertilizers (Davis et al., 2001; Ray et al., 2006)



as shown in Figure1-2, and the sources of heavy metal pollution in industrial areas include manufacturing processes, smelting and refining, electricity generation, agricultural fertilizers, refuse and wastewater treatment (Nriagu and Pacyna, 1988). Heavy metals enter the human body through food, water, and air. They become toxic when they are not metabolized by the body and accumulate in the soft tissues. In general, heavy metals are systemic toxins with specific neurotoxic, nephrotoxic, fetotoxic and teratogenic effects. Heavy metals can directly influence human behavior by impairing mental and neurological functions, influencing neurotransmitter production and utilization, and altering numerous metabolic processes. In addition, toxic metals can increase allergic reactions, cause genetic mutation, compete with “good” trace metals for biochemical bond sites, and act as antibiotics, killing beneficial bacteria. Copper is one of the most widespread and toxic heavy metal contaminants in the environment (O'Connell et al., 2006). In urban runoff, vehicle brake emissions are one of main sources for copper release (Davis et al., 2001).

Great attention has been paid to the methods for metal removal from wastewaters and urban stormwater runoff because heavy metals cause serious environmental problems. A number of methods are used to remove toxic metals from water such as ion exchange, reverse osmosis, chemical precipitation, membrane technologies, and electrochemical treatment. However, those methods do not always provide a satisfactory removal rate to meet pollution control limits and/or the adsorbents/chemical agents are too expensive (Chan and Fu, 1998; Bailey, Olin et al., 1999; Rengaraj et al. 2001; Benito and Ruiz, 2002; Saha et al., 2003; Demirbas et al., 2008; El-Ashtoukhy et al., 2008). The interest in innovative methods to clean up

contaminated water has been increasing (Mackay et al., 1985). Many natural materials have been studied in previous research such as peat, sawdust, peanut and hazelnut shells, and other organic materials (Table1-1) for treating metal-contaminated wastewater (Bryant et al., 1992; Brown et al., 2000; Schneegurt et al., 2001). The results of these studies showed that sorption by using natural materials is an effective, efficient, and economic in comparison to traditional methods for water decontamination application (Schneegurt et al., 2001; O'Connell et al., 2006), because biomass materials are abundant and easily available at a very low cost.

Sorption mechanism of heavy metals on biosorbents can be generally explained by considering different kinds of chemical and physical interactions between the heavy metals in solution and the functional groups present in the biosorbent (Pagnanelli et al., 2000). They demonstrated that cell walls which consist mainly of polysaccharides, proteins, and lipids, offer many functional groups which can bind ions such as carboxylate, hydroxyl, amide, and amino groups. Overall, several mechanisms are used to explain copper sorption on biosorbents (Wang and Chen, 2006): physical sorption, ion exchange, complexation, and precipitation. Kuyucak and Volesky (1988) and Aksu et al. (1992) reported that the sorption of copper and other metal cations by dead biomass took place through van der Waals' forces (Crowell, 1996) between cations and cells walls. Surface complexation is regarded as a predominant mechanism operating in metal sorption (Merdy et al., 2002). Cabral (1992) found that complexation was the only mechanism responsible for the removal of Cu and other heavy metals from aqueous solution when they studied the accumulation of metal cations on *Pseudomonas syringae*.

On the other hand, cell walls of natural biomass contain quite a high percentage of polysaccharides as basic building blocks, thus ion-exchange between bivalent metal ions and counter ions of the polysaccharides (Tsezos and Volesky, 1981) is considered a main sorption mechanism and has been studied in detail (Muraleedharan and Venkobachar, 1990; Venkobachar, 1990). Thus, there are discrepancies within the literature about which mechanism plays the more important role, complexation or ion exchange, and information for heavy metal sorption mechanisms by wood fiber are lacking.

Solution pH significantly impacts the sorption of heavy metals, because it controls the surface charge of the adsorbent, the degree of ionization and the speciation of the sorbates (Darnall et al., 1986; Ho et al., 1995; Schiewer and Volesky, 1996; Kalavathy et al., 2005; El-Ashtoukhy et al., 2008). The pH effect on sorption of heavy metals was clearly shown in Figure 1-3 and Figure 1-4. It is not clear in the reviewed literature about the influence of ion strength and cations in Cu sorption. For example, Wolf et al. (1977) reported Cu sorption decreased in the presence of Calcium (Ca) (Figure 1-5). However, Lu and Allen (2001) observed that Cu sorption on suspended particulate matter was not significantly affected by Ca.

#### **1.1.4 $^{13}\text{C}$ NMR and DRIFT Analysis**

Solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy has become an important tool for examining the chemical structure of natural organic materials and the chemical changes associated with modification. This non-destructive method can help researchers obtain an overview of the structures of organic samples (Baldock et al., 1997; Kogel-Knabner, 1997). The changes in shape and magnitude of peaks on a NMR

spectrum compared to the initial NMR spectrum can tell us the structural differences before and after certain chemical treatment. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) is also a non-destructive analytical technique which is primarily used to detect the functional groups of organic material samples. In our study, these two methods were used to examine the structure and functional groups of untreated and treated wood fibers.

## **1.2 Hypothesis**

Many studies suggested that biomass materials showed a high sorption affinity for both organic and metal contaminants. Aspen wood fibers are heterogeneous biomass materials, therefore, we can hypothesize that those fibers also exhibit a high sorption capacity for polycyclic aromatic hydrocarbons and copper.

## **1.3 Study Objectives**

As described in the introduction, studies in the literature provided useful data, however, sorption mechanisms by wood fibers and methods to improve its sorption capacity of PAHs and copper (II) are still not clear. Further, structural characteristics for wood fibers and their relationship with PAHs and copper (II) sorption capacity and nonlinearity have yet to be studied in detail. Advances in these areas of research could provide new directions for the more effective application of wood-based waste water filters. The objectives of this study were to

- 1) Characterize in detail untreated and chemically modified aspen wood fibers by using elemental and porosity analysis, solid-state  $^{13}\text{C}$  NMR and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

- 2) Examine the sorption/desorption behaviors of two common PAHs (phenanthrene, pyrene) with aspen wood fibers
- 3) Determine the relationship of PAH sorption/desorption with the porosity, polarity and structural components (e.g., aromatic moieties) and to evaluate sorption capacity of copper (II) on treated and untreated aspen wood fibers
- 4) Examine the sorption behaviors of copper (II) with aspen wood fibers, cellulose and lignin
- 5) Examine the effect of pH and ionic strength on copper sorption

#### **1.4 Justification**

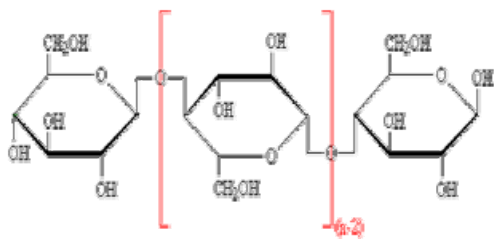
The release from urban and industrial areas (including those resulting from widespread application of agrochemicals) of PAHs and heavy metals clearly impinge on the quality of surface and ground water (Barbash and Resek, 1996; Bemknopf et al., 1997; Faure et al., 2000). Additionally, the excessiveness and thickness of forest can cause severe wildfires which can damage soils, water quality and quantity, fisheries, plant communities, wildlife habitat, and endanger species. Forest thinning or prescribed burns are necessary because it can reduce the accumulation of hazardous fuels and restore forest health. Forest Service and Interior Department have treated more than 2 million acres with thinning and prescribed burns (HFI, 2002). Thinning activities produce large quantities of low-quality, low-value wood, such as small diameter logs. In addition to forest thinning, wood wastes are generated from discarded construction and demolition landfills. Several studies showed that wood fibers can remove organic chemicals effectively and efficiently from aqueous phase as addressed in the literature.

On the background of these forest management activities and the above described water pollution problems, we propose a novel and value-added utilization of this underutilized resource: converting wood into filters for water purification rather than using more expensive and complex water purification methods (such as membrane filters). This work will help us better understand the mechanisms of organic and heavy metal sorption on wood fibers, and provide a new direction for the application of wood fibers as renewable and low-cost sorbents. Additionally, these results may have implications for the treatment of stormwater runoff and other PAH contaminated liquids

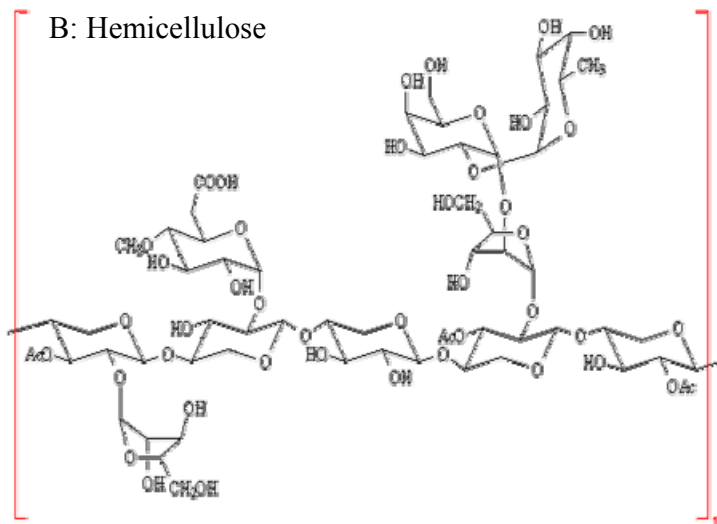
Table 1-1. Comparison of adsorbent capacity of various adsorbents, taken from Igwe and Abia (2006).  $Q_0$ : maximum Cu sorption capacity.

S/N	Adsorbent	$Q_0$ (mg/g)
1	Hydroous Fe oxide with polyacrylamide	43.0
2	Chemvion F.400 GAC	20.22
3	$\text{Cu}^{2+}$ impregnated chemvion F-400 GAC	17.23
4	Activated alumina	17.61
5	Y(III) impregnated alumina	14.45
6	Alumina	13.64
7	La(III) impregnated alumina	12.88
8	Waste Fe(III)/Cr(III) hydroxide	11.02
9	Activated alumina	5.02
10	Activated Bauxite	3.89
11	Activated Carbon	1.05
12	Activated Carbon Darco	3.75
13	$\text{Al}_2\text{O}_3/\text{Fe}(\text{OH})_3$	0.09

A: Cellulose



B: Hemicellulose



C: Lignin

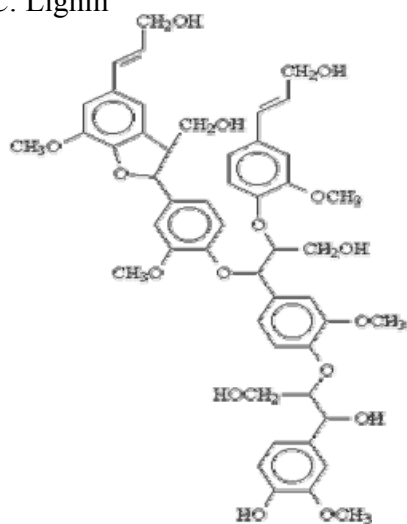


Figure1-1. The structures of cellulose(A), hemicellulose (B) and lignin (C).



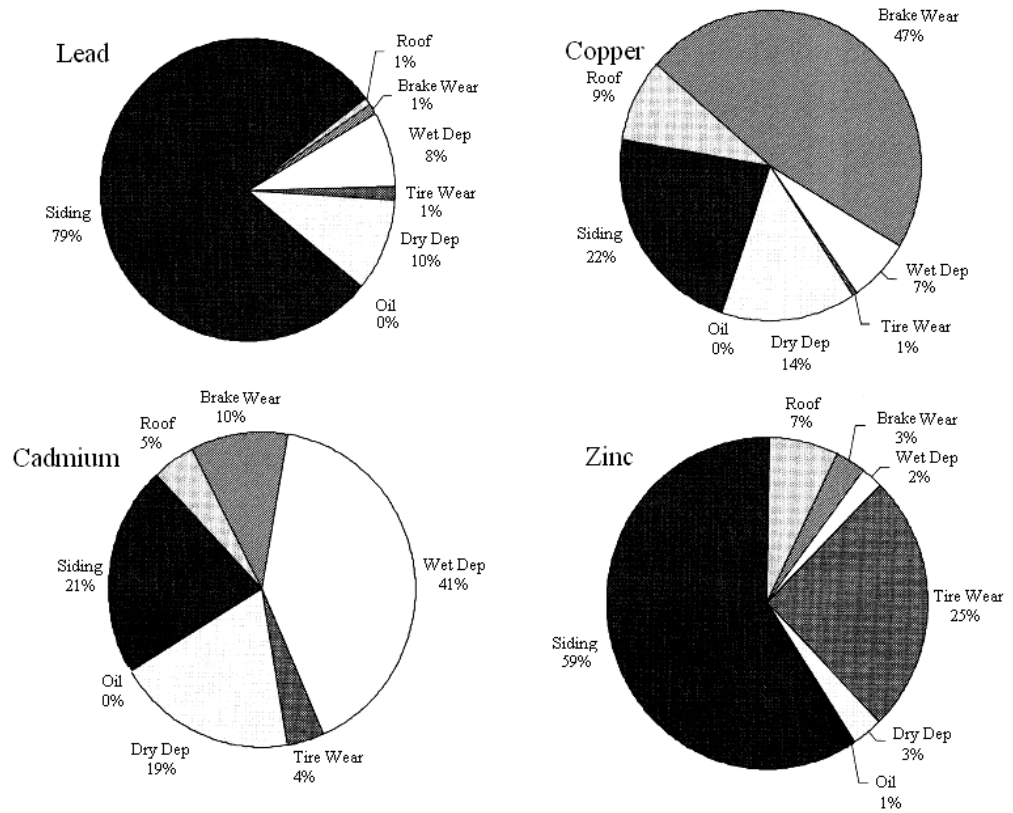


Figure 1-2. Estimated contributions of various sources of metals in urban residential stormwater runoff, taken from Davis et al. (2001).

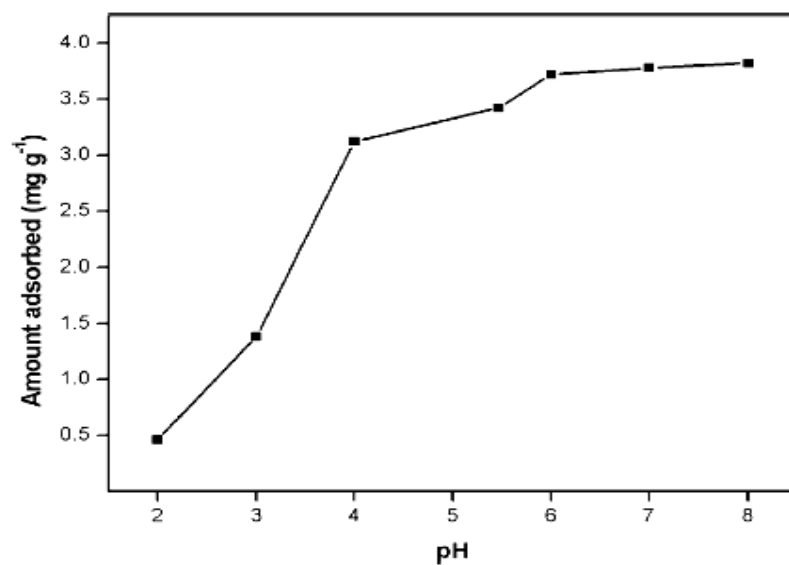


Figure 1-3. Effect of pH on Cu (II) removal by rubber wood sawdust (RSAC). Conditions: adsorbent dosage 0.5 g/100 ml, concentration 20 mg L<sup>-1</sup>, temperature 30 °C, taken from Kalavathy et al. (2005).

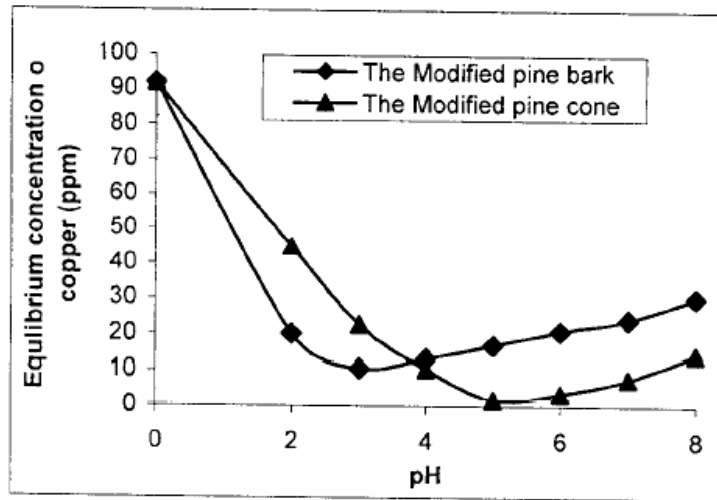


Figure 1-4. Effect of pH on copper removal, taken from Argun et al. (2005)

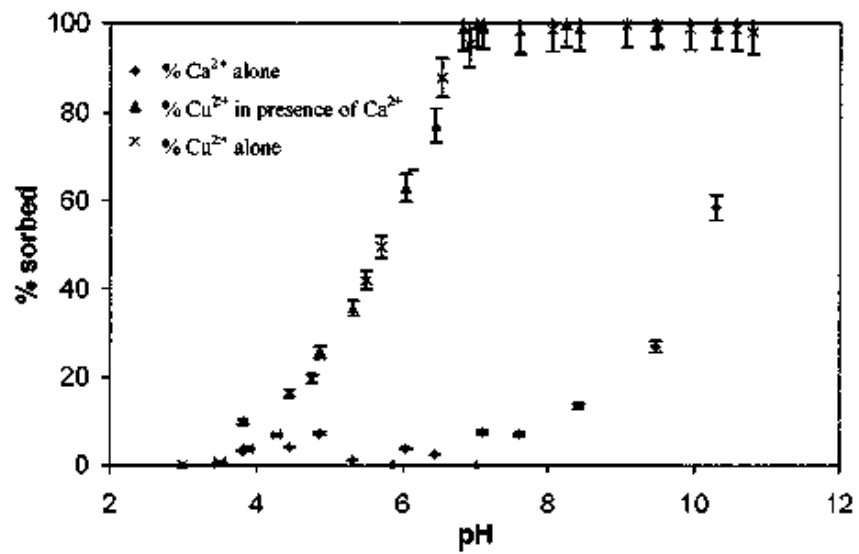


Figure1- 5. Cu<sup>2+</sup>/Ca<sup>2+</sup> competitive binding as a function of pH on lignin straw, taken from Merdy et al. (2002).

## CHAPTER 2

### SORPTION OF PAHS BY ASPEN WOOD FIBERS

#### 2.1 Abstract

Sorption and desorption experiments for phenanthrene and pyrene using untreated and treated (bleaching and hydrolysis) aspen wood fibers were examined to understand their sorption mechanisms. The wood was characterized by elemental and porosity analysis, solid-state  $^{13}\text{C}$  NMR and DRIFTS. Bleaching removed aromatic components, yielding the highest polarity and increased porosity, whereas hydrolysis removed a large percentage of hemicelluloses and parts of amorphous cellulose, producing a matrix with more aromatic moieties, lower polarity and higher porosity than the untreated wood fibers. All isotherms fitted well to the Freundlich equation and the  $N$  values had a decreasing trend from bleached (BL), untreated (UTR), low temperature hydrolyzed (LHY) to high temperature hydrolyzed (HHY) wood fibers. BL fibers had the lowest sorption capacity ( $K_{OC}$ ) for both phenanthrene and pyrene. HHY had the highest  $K_{OC}$  because of its highest aromatic carbon content and lowest polarity. The results suggest aromatic moieties and polarity of wood fibers play significant roles in PAHs sorption and desorption. Thus, both aromatic components and polarity should be considered when predicting the PAH sorption/desorption by aspen wood fibers of PAHs. This study demonstrated that aspen wood fibers are a potential sorbent for PAHs and that chemical modifications of the wood matrix can effectively increase its sorption efficiency. These results may have implications for the treatment of stormwater runoff and other PAH contaminated liquids.

#### 2.2 Introduction

Persistent organic pollutants (POPs), such as PAHs are commonly detected at elevated concentrations in stormwater runoff and waste water streams. PAHs originate from predominantly anthropogenic sources, such as incomplete combustion of fuels and discharges from industrial and waste water treatment plants. Once in the environment, PAHs are recalcitrant due to their low solubility and resistance to biodegradation. Some PAHs are carcinogenic and exhibit toxicity even at very low concentration (Monson et al., 1995; Arfsten et al., 1996). A number of conventional and innovative treatment methods for PAH contaminated water have been developed. Although activated carbon is probably one of the most effective conventional methods for the removal of PAHs from water, its comparatively high cost typically prohibits the treatment of large amounts of wastewater and stormwater streams. Thus, innovative filter materials have been proposed that rely on low cost and readily available natural materials (Low et al., 2004). A few studies (Severtson and Banerjee, 1996; Mackay and Gschwend, 2000; Boving and Zhang, 2004) examined the sorption of organic chemicals to wood and wood products. All these studies observed linear isotherms for nonpolar compounds with water-saturated woods. However, Gunasekara et al. (2003) observed nonlinear isotherms for naphthalene by lignin, a major component of wood. Wood is a heterogeneous material and consists of three major components, cellulose, hemicellulose, and lignin. The chemical differences among these three components result in significant variability in the wood's ability to interact with water and organic contaminants. For instance, cellulose and hemicelluloses provide for strong hydrogen bonding due to their polyhydroxyl and polycarboxylic structures. Conversely, the lignin phenylpropane units may provide relatively hydrophobic regions, therefore attracting

hydrophobic compounds. Mackay and Gschwend (2000) observed that wood-water partition coefficients for monoaromatic hydrocarbons exhibited a positive relationship with the wood's fractional lignin content, probably because cellulose and hemicelluloses contributed very little to the uptake of those chemicals (Xing et al., 1994). A similar result was reported by (Garbarini and Lion, 1986) when they studied the sorption of toluene and trichloroethylene to wood polymers. In studying sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol by pulped wood fibers, Severtson and Banerjee (1996) demonstrated that sorption is governed by the interaction of the acid form of these compounds with lignin, and, quite interestingly, their results also showed that sorption was unaffected by fiber surface area. Although these past studies were very elegant in their execution and provided useful data, exact sorption mechanisms by the wood and methods to improve its sorption capacity remain largely unknown. Further, structural characteristics of wood samples and their relationship with its sorption capacity and nonlinearity have yet to be studied in detail. Advances in these areas of research could provide new directions for the application of wood-based waste water filters. The objectives of this study were to characterize in detail untreated and chemically modified aspen wood (*Populus tremula*) fibers by using elemental and porosity analysis, solid-state  $^{13}\text{C}$  NMR and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Batch experiments were employed to examine the sorption/desorption behaviors of two common PAHs (pyrene, phenanthrene) with aspen wood fibers, and determine the relationship of PAH sorption/desorption of PAHs with the porosity, polarity and structural components (e.g., aromatic moieties) of the wood fibers. Aspen wood was selected as the study material because it is readily available in

fiber form and has already been proven to effectively remove PAHs under laboratory conditions (Boving and Zhang, 2004).

## **2.3 Materials and Methods**

### **2.3.1 Sorbent**

Untreated aspen wood (UTR) fibers (length: up to 30 cm with a diameter of approximately 1 mm) were obtained from the American Excelsior Company, Arlington TX. Two different chemical treatments were used to remove predetermined structural components from the aspen wood. First, bleaching removed aromatic components (Gunasekara et al., 2003) by treating 10 g dry aspen wood with 100 g of sodium chlorite, 100 mL of acetic acid, and 1000 mL of deionized distilled water for three times, ~7 h for each time. Bleached samples are referred to as BL. The second treatment (hydrolysis) involved treating aspen wood fibers with 300 mL of 6 M HCl /g dry wood. Low temperature hydrolysis (LHY) was performed at 70 °C for 2 h, followed by hydrolysis at room temperature for another 18 h. High temperature hydrolysis (HHY) was conducted under refluxing condition (~ 100 °C) for 2.5 h. Following the chemical treatments, the solid residue was separated from the solution and rinsed with deionized distilled water. All wood samples were freeze-dried, cut into 2-10 mm long segments, and stored in capped containers.

### **2.3.2 Characterization of Sorbents**

Dry weight-based C, H, and N contents of all samples were determined using a Vario ELIII elemental analyzer (Elementar, Germany) with the oxygen concentration calculated by mass difference. The ash content was measured by heating the wood samples at 740 °C for 4 h. Effective polarity (PI) was calculated by:  $PI = 0.702 -$



0.00353AR for organic mixture of natural sorbents, where AR is the percent of aromatic C as measured using solid-state CPMAS  $^{13}\text{C}$  NMR (Xing et al., 1994). The mass atomic ratio,  $[(\text{N}+\text{O})/\text{C}]$  of sorbents, was calculated from their elemental compositions and the atomic weights of O, N, and C. Porosity of all samples was determined using a Nova 2000 BET-  $\text{N}_2$  Analyzer (Boynton Beach, FL). Samples were degassed at  $90^\circ\text{C}$  for 10 h prior to the adsorption measurements. The micropore volume was calculated using the Dubinin-Raduskhevich (DR) equation at  $P/P_0=0.05$  (Ismail and Rodgers, 1992). The total pore volume (including micropores and mesopores) was determined at  $P/P_0=0.95$ . Because macropore volume was negligibly small, mesopore volume was computed as the difference between total and micropore volumes (Sanchez et al., 2001). Surface area was calculated using the multi-point Brunauer-Emmett-Teller (BET) method (Yang et al., 2006). Solid-state CPMAS-TOSS  $^{13}\text{C}$  NMR spectra were obtained with a Bruker DSX-300 spectrometer (Karlsruhe, Germany) operated at the  $^{13}\text{C}$  frequency of 75 MHz. Except for the number of scans (3000-6000), the instrument was run under the same conditions as the one used by Chen et al. (2005). Within the 0-220 ppm chemical shift range, structural carbon assignments were: aliphatic carbons (0-50 ppm), methoxyl carbons (50-61 ppm), carbohydrate carbons (61-96 ppm), anomeric carbons (96-109 ppm), aromatic carbons (109-165 ppm), carboxyl and carbonyl carbons (163-190 ppm), and ketone carbons (190-220 ppm). All samples were analyzed by DRIFTS using a Perkin-Elmer (Spectrum One) infrared spectrophotometer (Wellesley, MA), following the procedure of Chen et al. (2005).

### 2.3.3 Sorption Experiment

<sup>14</sup>C-Labeled and unlabeled phenanthrene (>98% purity) and pyrene (>99% purity) were purchased from Sigma-Aldrich Chemical company and were used without further purification. For the batch sorption isotherm experiments 8, 15 or 35 mL-vials were used. The background solution (pH 7) consisted of 0.01 M CaCl<sub>2</sub> in deionized distilled water with 200 mg/L NaN<sub>3</sub> as a biocide. Due to their low water solubility (Table 2-1), stock solutions of labeled and unlabeled phenanthrene and pyrene were prepared in methanol before adding to the aqueous background solution, and the aqueous solution was mixed for approximately 2 h. Initial concentrations of solutes were controlled to have the final equilibrium concentration ranges about spanning 2.5 orders of magnitude (Yang et al., 2006). The total amount of methanol in the solution did not exceed 0.1 vol. %. The solute-containing solution was added to the vials with the wood fibers. The solid-solution ratios were adjusted to obtain 30-85% sorption of solutes at apparent equilibrium. Each isotherm had 9-12 concentration points; each point, including blanks (i.e., without wood fibers), was run in duplicate. The vials were sealed with aluminum foil-lined Teflon screw caps and were kept shaking 3 d for phenanthrene and 4 d for pyrene at 23 ± 1°C. Preliminary experiments indicated that apparent equilibrium was reached before 3 d for phenanthrene and before 4 d for pyrene (Figure 2-1). After equilibration, the vials were centrifuged at 2800 rpm for 20 min, and approximately 0.8 mL of the supernatant was added to ScintiVerse cocktail (7 mL) for scintillation counting (Bechman [Fullerton, CA] LS6500). The solute loss was less than 4% of the initial concentrations, which is within the experimental uncertainty range of the analyses by scintillation counting; therefore sorbed chemical concentrations were

determined by mass balance calculations. All sorption data were fitted to the Freundlich equation:

$$S = K_F C^N$$

where  $S$  is the sorbed concentration ( $\mu\text{g/g}$ ),  $C$  is the liquid-phase equilibrium solution concentration ( $\mu\text{g/mL}$ ),  $K_F$  is the sorption capacity coefficient [ $(\mu\text{g/g})/(\mu\text{g/mL})^N$ ], and  $N$  (dimensionless) is the Freundlich exponent which describes isotherm nonlinearity.

#### **2.3.4 Desorption Experiment**

Immediately after completion of the sorption experiments, desorption experiments were performed by sequential decant-refill steps (Weber et al., 2002). Five concentrations were used for each desorption experiment. Solids were separated from the aqueous solutions by centrifugation at 2800 rpm for 20 min. About half of the supernatant (including  $\sim 0.8$  mL for liquid scintillation counting) was exchanged with the same amount of background solution. The sealed vials were shaken 3 d for phenanthrene and 4 d for pyrene at  $23 \pm 1^\circ\text{C}$ . The suspensions were centrifuged and around 0.8 mL of supernatant was analyzed. The above desorption experiment was repeated two more times. After each desorption step, the concentration of labeled phenanthrene or pyrene was determined by liquid scintillation counting. The amount of sorbate remaining on the wood at each desorption step was calculated as the difference between the initially sorbed and the desorbed amount. The total desorption percentage was calculated by the sum of three consecutive desorbed amounts ( $\mu\text{g/g}$ ) divided by the initial sorbed concentration ( $\mu\text{g/g}$ ).

## **2.4 Results and Discussion**

### **2.4.1 Elemental composition**

Elemental compositions of the four wood samples are shown in Table 2-2. The ash content of each sample was less than 0.3% of the total weight. BL had the lowest C content and highest O content, thus, the highest polarity. In contrast, HHY had the highest C content, but lowest O content, thus, the lowest polarity. LHY had a similar [(N+O)/C] but its effective polarity was lower than UTR. This shows that the chemical treatments successfully changed the chemical composition of wood matrix.

### **2.4.2 Porosity analysis**

Except for the slight decrease of BL's micropore volume, both bleaching and hydrolysis greatly enhanced the total porosity (Table 2-2). For instance, the micropore volume was three and eight times greater for LHY and HHY, respectively, compared to UTR. The mesopore volume was about three (BL), five (LHY) and 39 (HHY) times higher and the pore surface area was about three (BL), eight (LHY), and 15 (HHY) times larger compared to UTR.

### **2.4.3 Solid-State <sup>13</sup>C NMR**

<sup>13</sup>C NMR results for the four samples are presented in Figure 2-2 and Table 2-3. The peaks around 21 ppm and 172 ppm were assigned to methyl C and carbonyl C in acetyl groups of hemicelluloses (Martinez et al., 1991), respectively. The 55.8 ppm peak was from methoxy groups (OCH<sub>3</sub>) which is probably the most characteristic functional group for lignin. The signals located at 83 ppm and 88 ppm were from C-4 in amorphous and crystalline celluloses, respectively. The peaks between 71 ppm and 74 ppm were assigned to C-2, C-3, and C-5 in cellulose, whereas the strong peak at 104

ppm was associated with anomeric carbon (C-1). The peaks in the region of 131-137 ppm were assigned to the ring carbons in which the ring was not substituted by strong electron donors such as oxygen and nitrogen (Schnitzer and Preston, 1983). The multiple peaks in the range from 145-163 ppm were from the carbons of phenolic components, mainly the syringyl and guaiacyl units in lignin (Hawkes et al., 1993). The peak around 153 ppm was due to C-3 and C-5 of syringyl units involved in ether linkages at C-4 and C-3 and C-4 in guaiacyl units (Haw et al., 1984). The peak at 146 ppm was from C-4 in guaiacyl units with free phenolic OH at C-4 (Hawkes et al., 1993).

The  $^{13}\text{C}$  NMR spectra illustrate that bleaching and hydrolysis caused structural modifications of aspen wood matrix. Most notably, bleaching reduced the fraction of the aromatic carbon (109-163 ppm) from 14.2 % to 7.5 %. The removal of aromatic components increased the effective polarity from 0.670 to 0.693 (Table2-2). Hydrolysis effectively removed hemicelluloses in both hydrolyzed samples, which is supported by the almost disappearance of the peaks around 21 ppm and 172 ppm in LHY and HHY. Consequently, the aromatic C increased to 17.9 % for LHY and 32.7 % for HHY. Further, the increase of the peak at 88 ppm in LHY and HHY indicates that hydrolysis enhanced the crystallinity of cellulose. Hence, hydrolysis led to a more hydrophobic material because O-containing moiety content was reduced and sorption of water by crystalline cellulose is less than amorphous cellulose (Pizzi, 1993).

Concurrent with the increasing signals of aromatic C in the region of 109-163 ppm in HHY, the intensity of the 55.8 ppm peak increased significantly. Also, the increasing intensities at 146 ppm indicate the cleavage of aryl ether in wood lignin leading to the formation of phenolic hydroxyl group (Lai and Guo, 1992). Moreover, the intensities

around 131-137 ppm in HHY were much stronger than that of other samples. The shift of maximum peaks reveals alteration of hydrolyzed aspen wood that concurred with changes of the porosity and polarity of the wood matrix. Similar evidence was presented by Pisarnitsky et al. (2004), who found that heating of oak wood under acidic conditions changed the traditional aroma characteristic of the oak by increasing its relative content of guaiacol, syringyl, acetovanillon, propiovanillon.

#### **2.4.4 DRIFT**

The DRIFT spectra between 4000 and 450  $\text{cm}^{-1}$  for the four wood samples are presented in Figure 2-3. A broad and strong band in the region from 3324 to 3346  $\text{cm}^{-1}$  was assigned to the stretching vibration of hydroxyl group, indicative of hydrogen bonding. The absence of absorption around 3600  $\text{cm}^{-1}$  suggests that there were no appreciable free hydroxyl groups present in these four samples (Chen et al., 2005). A strong methylene/methyl vibration was observed at 2895  $\text{cm}^{-1}$  in UTR, BL and LHY (2939  $\text{cm}^{-1}$  for HHY).

The absorption bands at 1740  $\text{cm}^{-1}$  mainly arose from the carbonyl (C=O) linkage in acetyl ester groups from hemicelluloses (Ajuong and Redington, 2004). Because carbonyl groups occur abundantly within the polymer components of wood, they tend to dominate in the branched-chain hemicellulose polymer (Kimura et al., 1992). It is evident that ester carbonyl groups of hemicelluloses dominated in UTR and BL. However, this DRIFT band became obscure in the two hydrolyzed samples because hemicelluloses were readily decomposed under acidic conditions (Yang et al., 2004). Conversely, the absorption bands around 1718 (LHY) and 1704  $\text{cm}^{-1}$  (HHY) were attributed to carbonyl stretching of unconjugated ketone and conjugated carboxylic

groups in lignin (Matuana et al., 2001). This indicates that the C=O group is only weakly H-bonded (Cao et al., 1993). The intensity of the carbonyl group was remarkably lower in LHY than in the other samples. Conversely, it was high in HHY, showing that some ether linkages in lignin or lignocellulose complexes like  $\beta$ -O-4 linkages were cleaved under high temperature (Barker and Owen, 1999).

The absorption bands at 1595 and 1505  $\text{cm}^{-1}$  were assigned to aromatic ring carbon skeletal stretching (Ajuong and Redington, 2004; Yang et al., 2004). The 1595  $\text{cm}^{-1}$  band was also attributive to the stretching of conjugated C=O group (Pandey, 1999). These two bands were similar in UTR and LHY, but almost completely disappeared in BL. In contrast, and consistent with the NMR data, these bands became very strong in the HHY. This indicates for one that bleaching caused the cleavage of aromatic ring and, second, hydrolysis under high temperature led to the increase of aromatic moieties.

Absorption bands around 1462 and 897  $\text{cm}^{-1}$  were ascribed to CH and  $\text{CH}_2$  units. The band at 1462  $\text{cm}^{-1}$  was assigned to C-H deformation in methyl and methylene in syringyl unit from lignin (Herring et al., 2004). It became sharper and stronger after hydrolysis at high temperature, but weaker after bleaching. The band at 897  $\text{cm}^{-1}$  was assigned to  $\text{CH}_2$  wagging from carbohydrates (Pandey, 1999; Herring et al., 2004). Its relative intensity was strong in UTR, BL, and LHY, but almost disappeared in HHY.

Absorption bands at 1273, 990 and 617  $\text{cm}^{-1}$  were from C-O single bonded in carbohydrates (Kimura et al., 1992). Generally, the intensities of these bands were decreasing in order: BL, UTR, LHY and HHY. This underlined that hemicelluloses and parts of cellulose were easy to hydrolyze in an acidic environment, especially at high temperature. However, the absorption band at 1250  $\text{cm}^{-1}$  was attributable to C-O single

bonds in lignin (Pandey, 1999). A pronounced intensity increase of this peak was observed in HHY. These data again suggest the relative lignin content was higher after hydrolysis, but lower after bleaching. This finding is in good agreement with the NMR results.

#### **2.4.5 Sorption of Phenanthrene and Pyrene**

Sorption isotherms were fitted well by the Freundlich model (Figures 2-4 and 2-5). The Freundlich exponent,  $N$  (Table 2-4) ranged from 0.869 to 0.985 for phenanthrene and from 0.900 to 0.948 for pyrene. Except for that of BL, all isotherms were nonlinear. Nonlinearity was also reported by Mackay (1998) and likely resulted from aromatic moieties which are responsible for condensed domains (Gunasekara et al., 2003). Xing (2001) observed that there was a positive relationship between aromatic carbons and isotherm nonlinearity for several soil humic acids. For both phenanthrene and pyrene, removal of large percentages of aromatic moieties by bleaching apparently resulted in a more linear, partition-type sorption while the increase in aromaticity after hydrolysis led to more nonlinear, adsorption-type behavior; however, some isotherm  $N$  values were not significantly different (Table 2-4). Nonlinear isotherms in this work differed from the results of some previous studies (Severtson and Banerjee, 1996; Mackay and Gschwend, 2000; Boving and Zhang, 2004) in which linear isotherms were observed for wood materials. Mackay and Gschwend (2000) explained that nonlinear isotherms of benzene to pine sawdust (Mackay, 1998) may be due to the incomplete water saturation of the wood. However, three days were sufficient to achieve water saturation of thin aspen wood fibers in our experiments. It appears that linear sorption in



aforementioned studies may be due to relatively high solute concentrations and/or narrow concentration ranges.

A precise comparison between  $K_F$  values is not possible due to their different units as a result of nonlinearity (Chen et al., 1999). Hence, concentration-dependent organic carbon-normalized sorption capacity ( $K_{OC}$ ) was calculated by the content of organic carbon of wood sample and  $K_d$  values at three equilibrium concentrations (Table 2-4). Bleaching and hydrolysis resulted in great differences in  $K_{OC}$ . For instance, BL's  $K_{OC}$  values were only about 40 % for phenanthrene and 60 % for pyrene relative to those of UTR. However,  $K_{OC}$  values of LHY were about two (pyrene) and three (phenanthrene) times greater than those of UTR. Even greater  $K_{OC}$  values were determined for HHY (i.e., eleven times larger for phenanthrene and fourteen times higher for pyrene relative to UTR). A positive relationship between  $K_{OC}$  values and aromatic C content was observed (Figure 2-6A). This may be attributed to hydrophobic effect,  $\pi$ - $\pi$  electron donor – acceptor ( $\pi$ - $\pi$  EDA) interactions, and polarizability effect (Zhu et al., 2004; Nguyen et al., 2005; Zhu and Pignatello, 2005). Aromatic rings in lignin-type structures may favor polarizable interactions with organic solutes, especially those with high polarizability such as pyrene and phenanthrene. Zhu et al. (2004) and Zhu and Pignatello (2005) reported the importance of  $\pi$ - $\pi$  EDA interactions between  $\pi$ -donors such as PAHs and  $\pi$ -acceptor groups in natural organic matter including polycarboxylated aromatic rings. In studying the effect of the quality of soil organic matter on sorption of naphthalene, Xing (1997) reported that the  $K_{oc}$  values increased with increasing aromaticity. Similar results were reported by Young and Weber (1995). Furthermore, several studies (Garbarini and Lion, 1986; Xing et al., 1994) indicated that

cellulose and hemicelluloses, which mainly consist of polar aliphatic moieties, exhibit little measurable uptake of monoaromatic hydrocarbons, while lignin, containing primarily aromatic moieties, showed great affinity for hydrocarbons. This is confirmed by the results from Kleinert (1940), who found that isolated lignin took up 3.53 mMoles phenol/g, whereas only 0.025 mMoles phenol/g were sorbed to isolated amorphous cellulose.

In addition to aromatic moieties, the polarity of the sorbent can significantly affect the sorption capacity of organic contaminants (Rutherford et al., 1992; Chen et al., 2005). In this study, the polarity, (N+O)/C, of the four samples were in an order: BL > UTR ~ LHY > HHY. Figure 2-6B shows an apparently negative relationship between the  $K_{OC}$  values and (N+O)/C of the sorbents. HHY with the lowest polarity had the greatest  $K_{OC}$  values, followed by LHY, UTR, and BL. In studying cross-correlation of polarity curves to predict sorption coefficients of nonionic organic contaminants (Xing et al., 1994) used the effective polarity (PI) to more accurately predict the  $K_{OC}$  for soil organic matter. This is because polarity expressed by [(O+N)/C] does not consider the effect of configuration and structure on sorption. As shown in Figure 2-6C, when effective polarity (PI) is used (Xing et al., 1994), a clear relationship is obtained over that between  $K_{OC}$  and [(O+N)/C], indicating the location of O and N in the chemical structure of the wood can be important for sorption. For UTR, lignin-rich moieties may be dispersed among carbohydrates rich in polyhydroxyl and carboxylic groups (Mackay, 1998). These functional groups can produce strong hydrogen bonds within the wood and also with water. This may prevent PAH molecules from accessing the aromatic cores due to the surrounding polar components (Chen et al., 2005). For LHY, however,

hydrolysis destroyed some of those hydrogen bonds and modified structure and configuration of the wood, leading to the decrease of effective polarity from 0.670 to 0.657. Thus, PAH molecules might more easily get access to the aromatic cores of the hydrolyzed wood, which increased the  $K_{OC}$  in comparison with UTR.

In this study, HHY had the greatest  $K_{OC}$  values and the highest porosity, followed by LHY, BL and UTR. HHY showed much higher porosity than other samples, which may partly contribute its high sorption capacity. However, the BL matrix had a higher porosity than UTR, its  $K_{OC}$  values were lower. Thus, the porosity might not be the primary factor regulating sorption capacity.

#### **2.4.6 PAHs Desorption**

Desorption data are presented in Figure 2-7 and 2-8. Differences in the degree of hysteresis were observed between chemically treated samples. For instance, in BL, no desorption hysteresis took place at any phenanthrene or pyrene concentration. Conversely, for HHY pronounced hysteresis occurred at all concentrations of phenanthrene and pyrene, reflecting that desorption of these compounds from this wood matrix was comparatively difficult. The possible reasons for the difference in hysteresis between these wood samples may be as follows. First, bleaching successfully removed a large part of aromatic moieties and produced a more expanded matrix (consisting of mainly holocellulose) in which a reversible sorption mechanism dominated. In contrast, hydrolysis, especially under high temperature, removed most hemicelluloses and part of the cellulose, yielding a more aromatic matrix in which irreversible adsorption might dominate. In studying the sorption of phenol, Kleinert (1940) found that adsorption by cellulose followed Henry's reversible solution equilibrium law, while sorption by

isolated lignin was described well by the Freundlich equation. These results reveal that aromatic moieties also play an important role in hysteresis, i.e., higher aromaticity, more leads to more apparent hysteresis. Second, desorption behavior was also affected by polarity. For BL, high polarity may have weakened the interactions between this sorbent and PAH molecules (Chefetz et al., 2000), which contributed to the easy release of PAHs molecules from the wood matrix. In contrast, PAH molecules were only slightly desorbed from the low polarity samples, LHY and HHY, because of strong hydrophobic interactions and  $\pi$ - $\pi$  EDA interactions (Zhu and Pignatello, 2005).

## **2.5 Conclusion**

In conclusion, our results demonstrate that both aromatic moieties and polarity are important for PAH sorption and desorption in aspen wood fibers. The  $K_{OC}$  values increased with increasing aromatic moieties, and with decreasing polarity of the sorbent. This study also indicates that effective polarity can predict sorption capacity of aspen wood fibers more accurately than mass atomic ratio, [(N+O)/C], because effective polarity considers sorbent configuration and structure. Furthermore, structural modifications could substantially enhance the  $K_{OC}$  and retention time of PAHs, which is critical for developing novel and low-cost technologies for the remediation of wastewater using wood materials.

## **2.6 Acknowledgements**

This work was supported by McIntire-Stennis program (MAS 00090) and the Federal hatch program (MAS 8532).

Table 2-1. Chemical Properties of Phenanthrene and Pyrene

PAH	MW <sup>a</sup>	LogK <sub>ow</sub> <sup>b</sup>	C <sub>s</sub> <sup>c</sup> (25°C)
Phenanthrene	178.2	4.57	1.29
Pyrene	202.3	5.18	0.135

<sup>a</sup>MW: molecular weight (g/mol); <sup>b</sup>K<sub>ow</sub>: octanol-water partition coefficient; <sup>c</sup>C<sub>s</sub>: water solubility (mg/L) (Walters and Luthy, 1984).

Table 2-2. Elemental Composition, Polarity and Porosity of Four Aspen Wood Samples

Sample <sup>a</sup>	C (%)	O <sup>b</sup> (%)	H (%)	N (%)	(N+O)/C	AR <sup>c</sup>	PI <sup>d</sup>	V <sub>micro</sub> <sup>e</sup> cm <sup>3</sup> /g	V <sub>meso</sub> <sup>f</sup> cm <sup>3</sup> /g	V <sub>T</sub> <sup>g</sup> cm <sup>3</sup> /g	SA <sup>h</sup> m <sup>2</sup> /g
UTR	46.7	46.6	6.38	0.340	0.754	14.2	0.670	0.0006	0.0006	0.0012	0.62
BL	43.4	50.2	6.26	0.126	0.870	7.50	0.693	0.0005	0.0017	0.0022	2.11
LHY	46.7	46.6	6.52	0.164	0.752	17.9	0.657	0.0016	0.0032	0.0049	4.74
HHY	57.6	36.9	5.49	0.055	0.481	32.7	0.605	0.0049	0.0233	0.0282	9.39

<sup>a</sup> UTR: untreated aspen wood; BL: bleached aspen wood; LHY and HHY: hydrolyzed aspen wood under low temperature and high temperature (~100 °C), respectively. <sup>b</sup> Oxygen content was calculated by the mass difference. <sup>c</sup> AR = percent aromatic C as measured by CPMAS <sup>13</sup>C NMR. <sup>d</sup> PI (effective polarity) = 0.702-0.00353AR. <sup>e</sup> V<sub>micro</sub>: micropore volume calculated from the equation of Dubinin-Raduskhevich (DR). <sup>f</sup> V<sub>meso</sub>: mesopore volume calculated by the difference between total pore volume and micropore volume. <sup>g</sup> V<sub>T</sub>: total pore volume measured as the amount of nitrogen adsorbed at P/P0=0.95 (Sanchez et al., 2001). <sup>h</sup> SA: surface area calculated from the multi-point BET method (Yang et al., 2006).

Table 2-3. Structural Carbon Distributions (%) as Obtained from  $^{13}\text{C}$  NMR Integration Results of Aspen Wood Samples

Sample	Distribution of C (%) chemical shift, ppm <sup>a</sup>								Aliphatic <sup>b</sup> C (%)	Aromatic <sup>c</sup> C (%)
	0-50	50-61	61-96	96-109	109-145	145-163	163-190	190-220		
UTR	9.20	8.00	50.6	12.4	8.30	5.90	4.20	1.40	80.2	14.2
BL	5.30	2.60	61.7	15.0	5.00	2.60	5.90	2.10	84.5	7.5
LHY	4.70	6.60	53.2	14.0	11.9	6.00	1.80	1.80	78.5	17.9
HHY	15.9	10.9	25.1	10.0	25.0	7.70	2.60	2.80	62.0	32.7

<sup>a</sup> Within the 0-220 ppm chemical shift range, structural carbon assignments were: aliphatic carbons (0-50 ppm), methoxyl carbons (50-61 ppm), carbohydrate carbons (61-96 ppm), anomeric carbons (96-109 ppm), aromatic carbons (109-165 ppm), carboxyl and carbonyl carbons (163-190 ppm), and ketone carbons (190-220 ppm). <sup>b</sup> total aliphatic carbon region (0-109ppm); <sup>c</sup> total aromatic carbon region (109-163 ppm)

Table 2-4. Sorption Coefficients and Freundlich Model Parameters of Phenanthrene and Pyrene by Aspen Wood Samples

PAH	Sample	Log $K_F^c$	$N$	$R^2$	$K_{oc}$ ( $\mu\text{g/g OC}$ )		
					Equilibrium Concentration ( $\mu\text{g/mL}$ )		
					C = 0.01	0.05	0.1
PHEN <sup>a</sup>	UTR	3.19±0.028	0.928±0.019	0.997	4660	4150	3940
	BL	2.83±0.019	0.985±0.013	0.996	1800	1750	1740
	LHY	3.59±0.023	0.887±0.013	0.996	14000	11700	10800
	HHY	4.26±0.014	0.869±0.007	0.999	57500	46600	42600
PY <sup>b</sup>	UTR	3.67±0.028	0.922±0.013	0.995	14400	12700	12000
	BL	3.45±0.047	0.948±0.022	0.994	8200	7600	7300
	LHY	3.99±0.044	0.912±0.019	0.994	31075	27000	25400
	HHY	4.89±0.044	0.900±0.019	0.994	213500	182000	170000

<sup>a</sup> PHEN: phenanthrene. <sup>b</sup> PY: pyrene. <sup>c</sup>  $K_F$  unit = ( $\mu\text{g/g}$ )( $\mu\text{g/mL}$ )<sup>-N</sup>



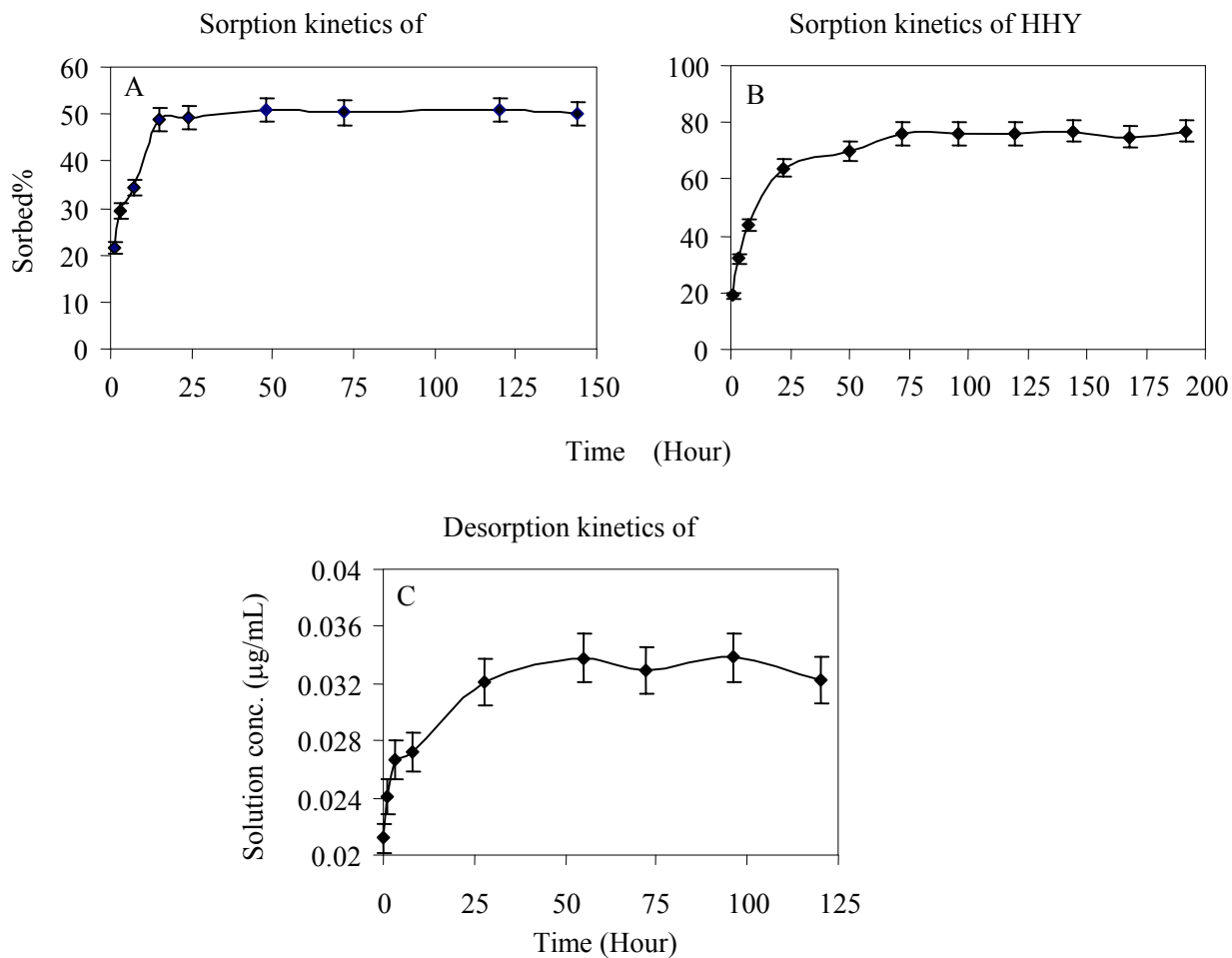


Figure 2-1 Phenanthrene sorption/desorption kinetics. Sorption kinetics of UTR (A) and HHY (B) at an initial concentration at 0.8 ppm, desorption kinetics of HHY (C) at an initial concentration at 0.18 ppm.

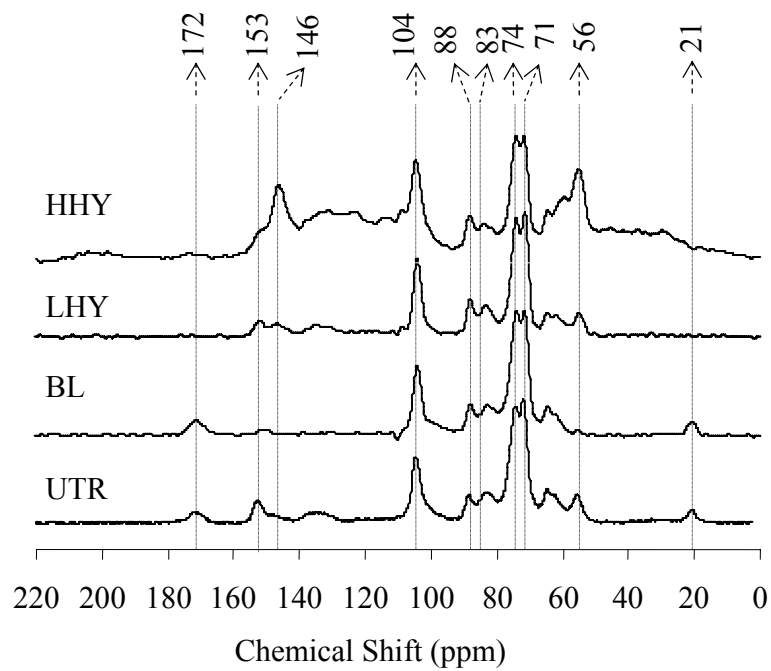


Figure 2-2. Solid-state  $^{13}\text{C}$  NMR Spectra of UTR, BL, LHY and HHY. Aliphatic C (0-109 ppm), Aromatic C (109-163 ppm) and COOH/C=O (163-220 ppm).

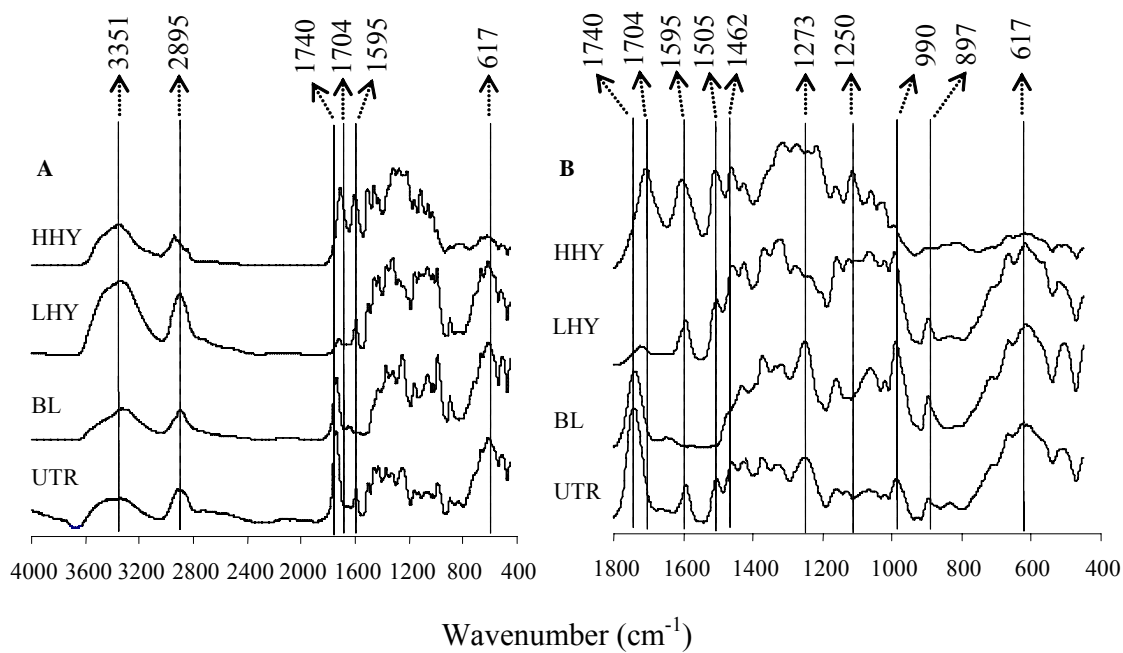


Figure 2-3. DRIFT spectra of UTR, BL, LHY and HHY. A: 450-4000  $\text{cm}^{-1}$ ; B: 450-1800  $\text{cm}^{-1}$ .

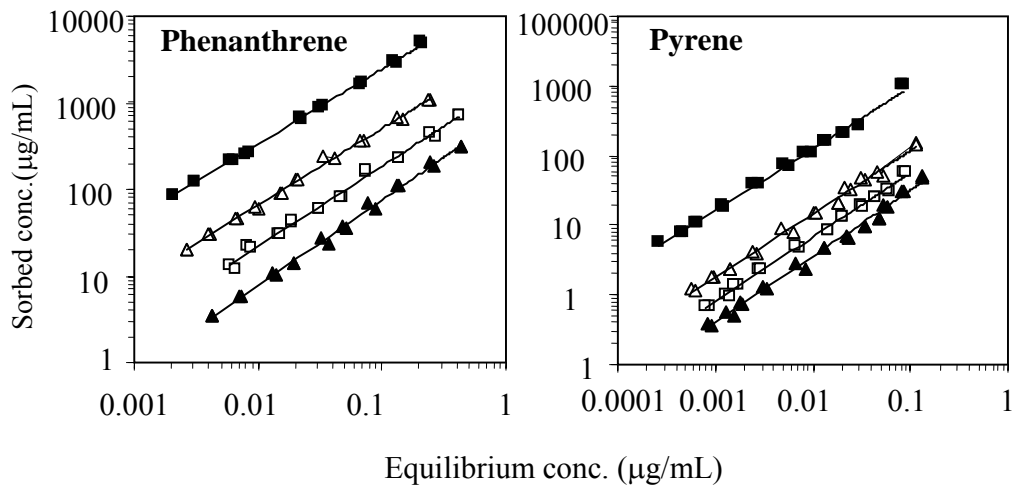


Figure 2-4. Sorption isotherms of phenanthrene and pyrene by UTR (○), BL (▲), LHY (△) and HHY (■). The y-axis scale is different for phenanthrene and pyrene.

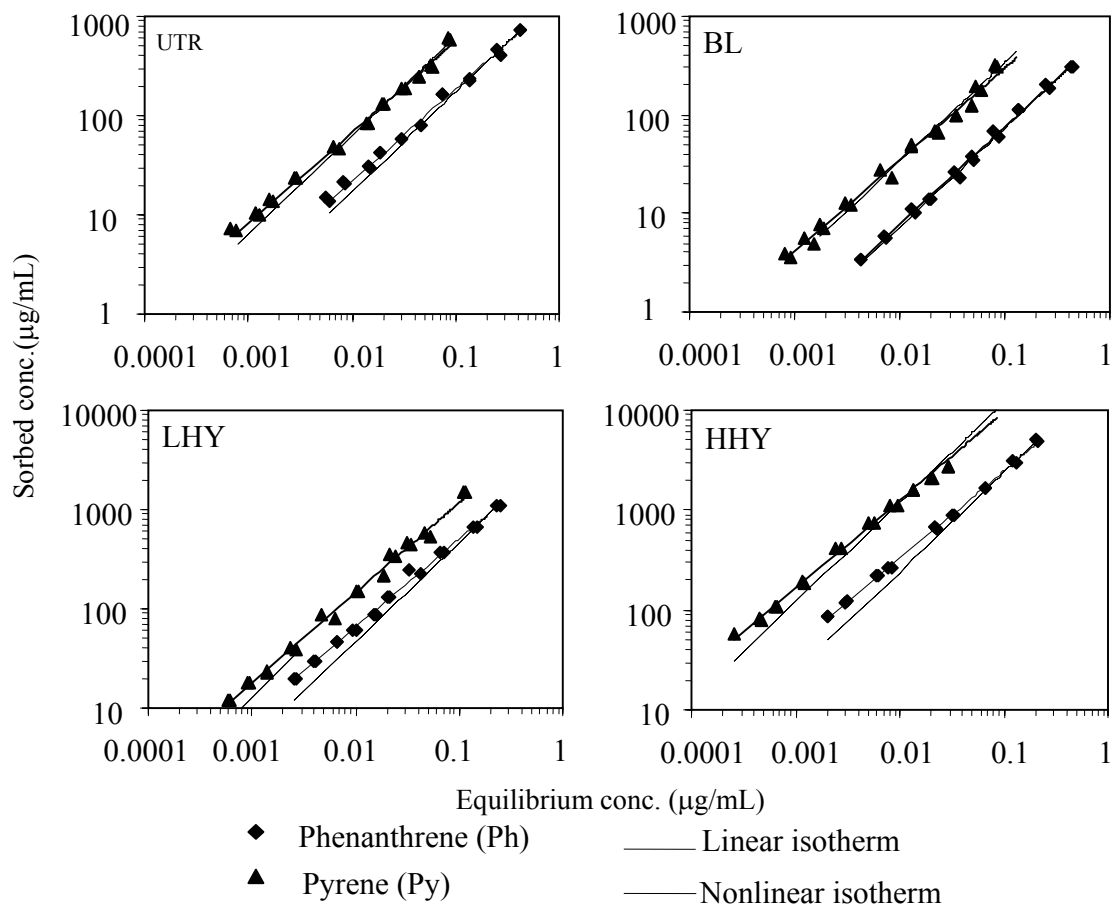


Figure 2-5. Comparisons of linear and nonlinear isotherms of phenanthrene and pyrene for UTR, BL, LHY and HHY. The y-axis scale for LHY and HHY is different from the other two graphs. Linear isotherm model failed to fit the low concentration data. It is noted that the yield was ~70% for bleaching and ~60% for low temperature hydrolysis and ~40% for high temperature hydrolysis based the on original fiber mass used.

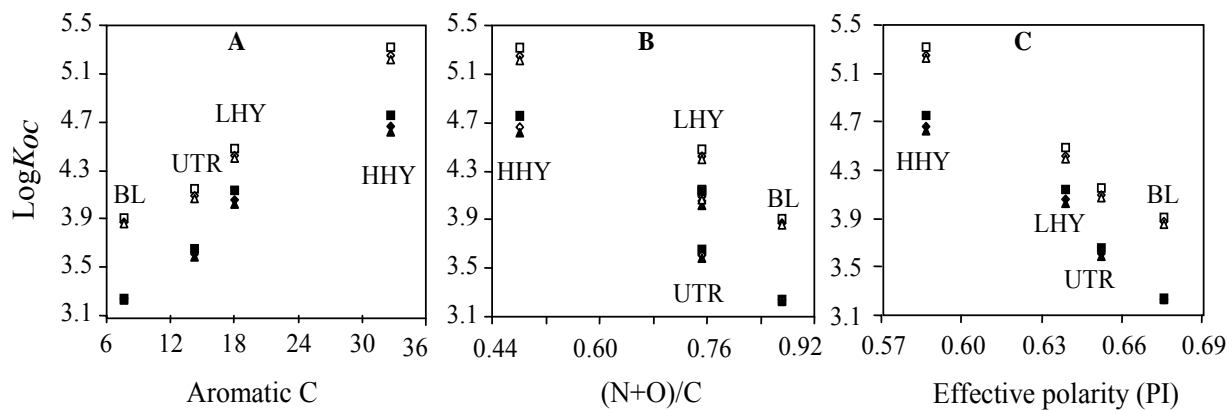


Figure 2-6. Relationship between  $\log K_{OC}$  and aromatic carbon content (A), mass ratio [(N+O)/C] (B), or effective polarity (C) at three equilibrium concentrations: Phenanthrene: 0.01 ( $\blacksquare$ ), 0.05 ( $\blacklozenge$ ) and 0.1  $\mu\text{g/mL}$  ( $\blacktriangle$ ); pyrene: 0.01 ( $\square$ ), 0.05 ( $\diamond$ ) and 0.1  $\mu\text{g/mL}$  ( $\triangle$ ).

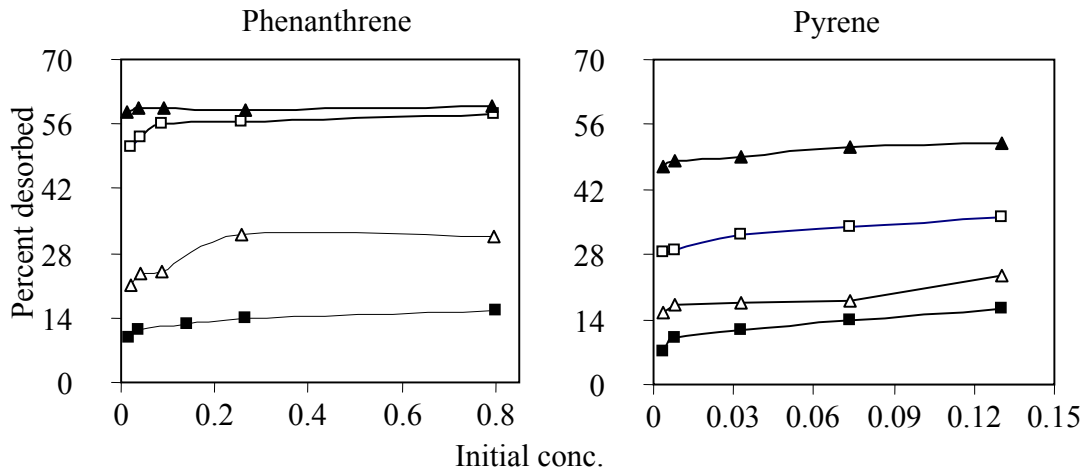


Figure 2-7. Desorbed percentages of phenanthrene and pyrene from UTR (□), BL (▲), LHY (△) and HHY (■). These percentages were based on the initially sorbed mass and the the sum of three sequential desorption steps. Each point represents the average of duplicates. The desorption percentage order: BL > UTR > LHY > HHY.

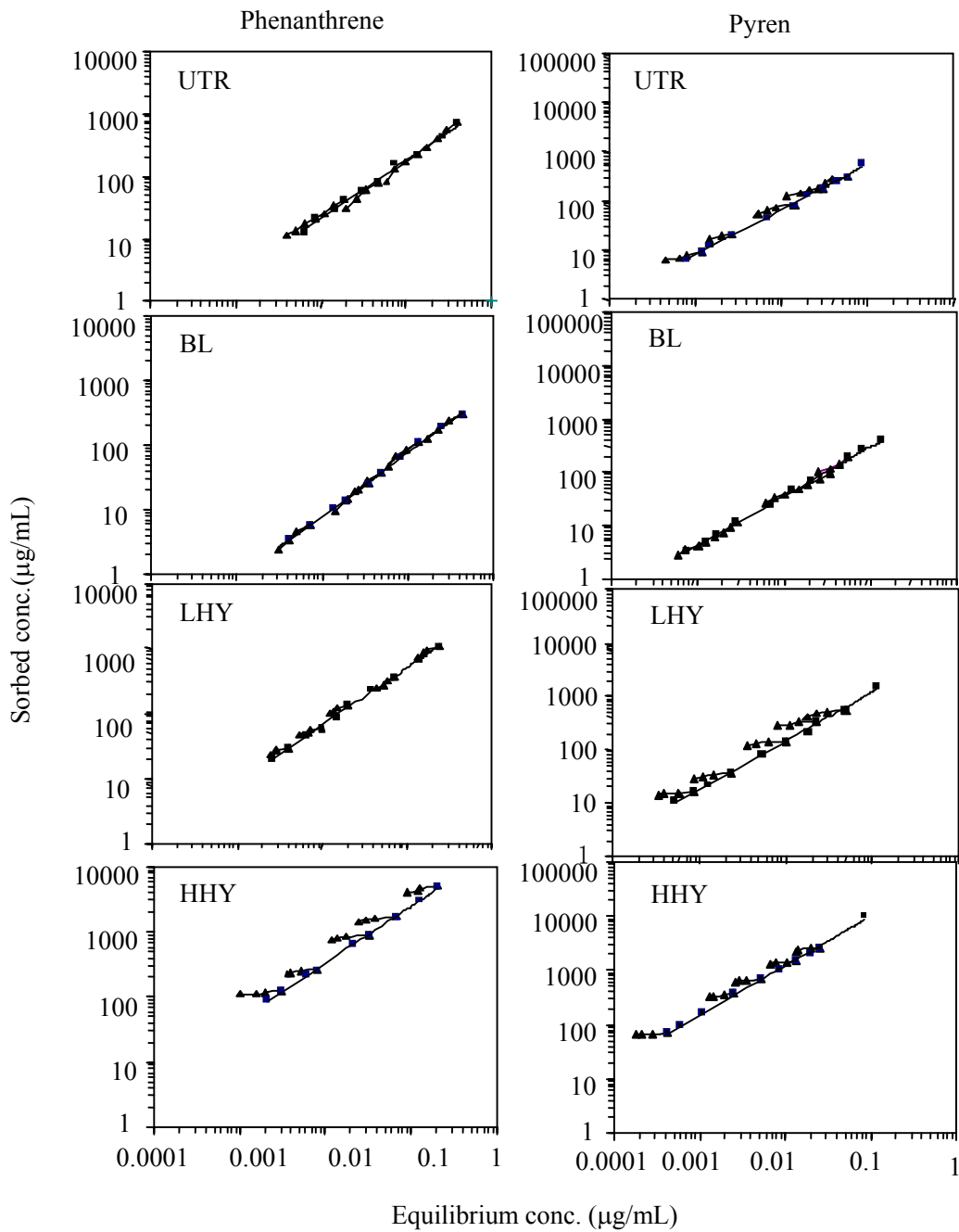


FIGURE 2-8 Sorption and desorption isotherms of phenanthrene and pyrene: sorption(■); desorption (▲). The y-axis scale is different for phenanthrene and Pyrene.



## CHAPTER 3

### SORPTION OF Cu (II) BY ASPEN WOOD FIBERS

#### 3.1 Abstract

Sorption of Cu by untreated and treated (bleaching and hydrolysis) aspen wood fibers, cellulose and lignin was examined to understand their Cu sorption behaviors. Aspen wood fibers were characterized by solid-state  $^{13}\text{C}$  NMR and DRIFT. Bleaching broke aromatic components, and increased hydrophilicity of the fibers, whereas hydrolysis reduced carbohydrate content, producing a more hydrophobic structure. Our results showed that solution pH greatly affected  $\text{Cu}^{2+}$  sorption. The sorption percentage of Cu steadily increased from pH 1.5 to 4.5, and a maximum sorption amount was found at around pH 5.5 for all the samples. All isotherms fitted well to the Langmuir equation and bleached sample (BL) had a highest sorption capacity, followed by untreated (UTR), cellulose (CEL), and hydrolyzed (HHY), while lignin (LIG) had little Cu sorption under studied condition. The results suggested carboxyl ( $-\text{COOH}$ ) and hydroxyl ( $-\text{CHOH}$ ) in carbohydrates mainly contribute to Cu sorption for our sorbents, and ion-exchange may be the main sorption mechanism on the studied sorbents. Additionally, the sorption capacity of Cu on all sorbents decreased with the increase of the initial concentrations of  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  or  $\text{Al}^{3+}$ . Cu sorption decreased fast at low initial concentrations of  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  or  $\text{Al}^{3+}$ , and slowed down with further increasing concentration of  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  or  $\text{Al}^{3+}$ , which further confirms that the main sorption process of Cu on aspen wood fibers is ion-exchange

### **3.2 Introduction**

Copper (Cu) is one of the most widespread heavy metal contaminants in the environment (O'Connell et al., 2006) and one of the most toxic heavy metals to living organisms. Copper usually deposits in brain, skin, liver and myocardium and can cause anemia, liver and kidney damage, and stomach and intestinal irritation (Davis et al., 2000). High Cu levels in drinking water can cause vomiting, abdominal pain, nausea and diarrhea. Drinking water copper concentrations of more than 1.3 mg/L are considered detrimental. Elevated Cu concentrations have been detected in urban stormwater runoff (Hares and Ward, 1999). Major sources of Cu in non-industrial areas include runoff from road surfaces and parking lots, automobile corrosion, building materials, and lawn fertilizers (Davis et al., 2001; Ray et al., 2006). For example, it has been estimated that in urban runoff about 1.5 mg/km-vehicle Cu is released from automobile brake abrasion (Malmqvist, 1983; Davis et al., 2001). Industrial sources of copper pollution include manufacturing processes, smelting and refining, electricity generation, refuse and wastewater treatment (Nriagu and Pacyna, 1988).

Cu removal from wastewater and urban stormwater runoff has received great attention, and a number of physical and chemical methods are now used to remove Cu from water, including ion exchange, reverse osmosis, chemical precipitation, membrane technologies, and electrochemical treatment. Of these methods, precipitation with chemical and electrochemical methods are the most widely used treatments to remove Cu from wastewater (Wang and Chen, 2006). However, the disposal of the precipitates and the ineffectiveness of precipitation at low Cu concentration is problematic (Wang and Chen, 2006). Additionally, precipitation can only reduce the dissolved metal

concentration to the solubility product level, which is often much higher than the discharge permit standards (Brown et al., 2000). Ion exchange treatment is the second most widely used method for Cu removal (Wang and Chen, 2006). However, this method is rarely economical, although it can reduce Cu to a very low level (Tiravanti et al., 1997). Similarly, activated carbon efficiently removes heavy metals from drinking water (Miretzky et al., 2006), but it is too costly to treat wastewater (Sun and Shi, 1998) or to clean runoff/stormwater. Overall, most copper treatment methods fail to meet the pollution control limits and/or the adsorbents/chemical agents are too expensive (Chan and Fu, 1998; Bailey et al., 1999; Rengaraj et al., 2001; Benito and Ruiz, 2002; Saha et al., 2003). This is especially the case when treating urban runoff water, because 1) the Cu concentrations in runoff are usually not as high as those in wastewater from plants, and 2) the runoff volume is huge. For these reasons, interest in innovative methods to clean up contaminated water has been increasing (Mackay et al., 1985). Many natural materials such as peat, sawdust, peanut and hazelnut shells have been studied for treating metal-contaminated wastewater (Bryant et al., 1992; Brown et al., 2000; Schneegurt et al., 2001). The results of these studies showed that Cu sorption using natural materials is effective, efficient, and economical in comparison to traditional methods for water decontamination (Schneegurt et al., 2001; O'Connell et al., 2006), because biomass materials are abundant and easily available at a very low cost.

Cu sorption to biomass depends on the initial pH of the reaction mixture because pH dramatically influences surface activities of sorbents (Acemioglu and Alma, 2004; Horsfall and Spiff, 2004). According to Pagnanelli et al. (2000) cell walls of *Arthrobacter sp.* have many functional groups, such as carboxylate, hydroxyl, amide,

and amino groups that are attractive binding sites for  $\text{Cu}^{2+}$ . Wang and Chen (2006) showed that both ion exchange and complexation are processes facilitating Cu sorption on biosorbents. Surface complexation in particular is considered a predominant mechanism in metal binding especially because of the complexing ability of carboxylic moieties. Merdy et al. (2002) reported that that carboxylic and alcoholic coordination sites, in addition to phenolic groups, could be involved in the complexation with metal cations as shown by X-ray photoelectron spectroscopy (XPS) measurements. Cabral (1992) reported that complexation was the only mechanism responsible for Cu and other heavy metals removal from aqueous solution when they studied the accumulation of metal cations by *Pseudomonas syringae*. Relative to surface complexation, ion exchange becomes important when cell walls of natural biomass contain a high percentage of polysaccharides as basic building blocks. Under these circumstances, ion-exchange between bivalent metal ions and counter ions of the polysaccharides (Tsezos and Volesky, 1981) is considered as a main mechanism (Muraleedharan and Venkobachar, 1990; Venkobachar, 1990). Ho et al. (1995) reported that the equilibrium pH decreased as the initial nickel concentration increased, consistent with the principles of ion-exchange because as more nickel ions are adsorbed onto the peat, more hydrogen ions are released, thereby decreasing the pH. Ion exchange was also found to be responsible for Cu biosorption by the fungi *Lucidum* and *Aspergillus niger* (Muraleedharan and Venkobachar, 1990).

Ion exchange, however, can be hindered by the presence of other ions. For instance, Wolf et al. (1977) observed that increasing aqueous  $\text{Ca}^{2+}$  concentration resulted in decreasing Cu sorption on humic substances of heavy metals, including  $\text{Pb}^{2+}$ ,

$\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . However, Cu sorption on suspended particulate matter was not significantly affected by  $\text{Ca}^{2+}$  concentration ranging from  $2.5 \times 10^{-4}$  to 0.1M over a pH range from 3 to 9 (Lu and Allen, 2001). They also found that ionic strength (I) did not have any noticeable influence on Cu sorption if  $I > 0.01\text{M}$  and  $\text{NaNO}_3$  was used instead of  $\text{Ca}(\text{NO}_3)_2$ . However, a small but noticeable decrease in Cu sorption with increasing I at low ionic strength ( $I < 0.01\text{ M}$ ) was detected. Dissanayke (1981) observed that the presence of  $\text{Na}_2\text{SO}_4$  with 0.01 M concentration reduced the sorption of metals and concluded that the reduction of adsorption when monovalent ions were present indicates a buffering action of sorption sites. In another study, Merdy et al. (2002) observed that  $\text{Ca}^{2+}$  did not compete with Cu for adsorption sites on straw lignin, indicating that  $\text{Ca}^{2+}$  occupies nonspecific sites and Cu ions are specifically adsorbed on lignin straw. Therefore, opposing views exist on the influence of ion strength and presence of competing cations on Cu sorption.

In addition to ion exchange effects, pH is found to be one of the main factors in determining Cu removal efficiency. For instance, Lu and Allen (2001) reported that  $\text{Cu}^{2+}$  starts to precipitate as Cu hydroxide when the pH was greater than 6. Also, the sorption distribution coefficient ( $K_D$ ) of Cu to suspended particulate matter increased in a pH range from 6 to 7, and a maximum  $K_D$  value was found between pH 7-8. At higher pH value the  $K_D$  value decreased and Cu precipitated. In this study we examined aspen wood fibers as a natural filter material for Cu and studied the influence of pH and ionic strength on Cu sorption. The hypothesis was that Cu sorption onto aspen wood is through ion-exchange and the presence of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Al}^{3+}$  will decrease Cu sorption. The particular objectives of this study were 1) to examine the sorption behaviors of Cu

(II) on treated and untreated aspen wood fibers, and 2) to examine the effects of pH and ionic strength on Cu sorption. The following summarizes the methods used to test the hypothesis and to examine the results from the copper treatment test performed with aspen wood.

### **3.3 Materials and Methods**

#### **3.3.1 Sorbent.**

Untreated aspen wood (UTR) fibers were obtained from the American Excelsior Company, Arlington, TX. Bleaching (BL) and hydrolysis (HHY) removed different structural components from aspen wood fibers. UTR, BL, HHY, cellulose (CEL) and lignin (LIG) were chosen as sorbents. The latter two sorbents were purchased from Sigma Aldrich Chemical Co.

#### **3.3.2 Sorbate.**

Cu nitrate [ $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ , >99% purity], sodium nitrate [ $\text{NaNO}_3$ ], calcium nitrate [ $\text{Ca}(\text{NO}_3)_2$ ], and aluminum nitrate [ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ] were purchased from Sigma-Aldrich Chemical Co. and were used as received. A Standard solution of 1000  $\mu\text{g}/\text{mL}$  of  $\text{Cu}^{2+}$  purchased from Fisher Company was used for preparation of standard curves.

#### **3.3.3 Characterization of Sorbents.**

Dry weight-based C, H, and N contents of all samples were determined using a Vario ELIII elemental analyzer (Elementar, Germany) with the oxygen concentration calculated by mass difference. Solid-state CPMAS-TOSS  $^{13}\text{C}$  NMR spectra were obtained with a Bruker DSX-300 spectrometer (Karlsruhe, Germany) operated at the  $^{13}\text{C}$  frequency of 75 MHz. Except for the number of scans (3000-6000), the instrument

was run under the same conditions as the one used by Chen et al. (2005). Within the 0-220 ppm chemical shift range, the structural carbon assignments were: aliphatic carbons (0-50 ppm), methoxyl carbons (50-61 ppm), carbohydrate carbons (61-96 ppm), anomeric carbons (96-109 ppm), aromatic carbons (109-165 ppm), carboxyl and carbonyl carbons (163-190 ppm), and ketone carbons (190-220 ppm). All samples were analyzed by DRIFT using a Perkin-Elmer (Spectrum One) infrared spectrophotometer (Wellesley, MA), following the procedure of Chen et al. (2005).

### **3.3.4 pH Effect on Sorption**

The pH experiments were conducted using 8 mL-vials for UTR, BL, HHY, CEL and LIG at an initial concentration of  $\sim 3.5 \mu\text{g/mL Cu}^{2+}$ . The pH values of the solutions ranged from 1.50 to  $\sim 6.00$  and were adjusted with 0.01~1 M  $\text{HNO}_3$  or 0.01~1 M  $\text{NaOH}$ . The vials were sealed with Teflon screw caps and kept shaking for three days at  $23 \pm 1^\circ\text{C}$ .

### **3.3.5 Sorption Experiments**

Cu sorption was investigated by batch experiments in nominal 8 mL-vials with  $\sim 8.4$  mL of solution. A pH value of 5.5 was used for sorption isotherms to avoid formation of  $\text{Cu}_2(\text{OH})_2^{2+}$ ,  $\text{Cu}(\text{OH})_2^0$  and  $\text{Cu}(\text{OH})^{1+}$  (Apak et al., 1998; Acemioglu and Alma, 2004). The pH values of the solutions were adjusted with 0.01~1 M  $\text{HNO}_3$  or 0.01~1 M  $\text{NaOH}$ . Each isotherm had 9 to 10 concentration points; each point, including blanks (i.e., solution without wood fibers) was run in duplicate. The range of initial Cu concentrations ranged from 0.01 to  $8 \mu\text{g/mL}$  in deionized water. The vials were sealed with Teflon screw caps and kept shaking for three days at  $23 \pm 1^\circ\text{C}$ . After equilibration, the solutions were filtered with glass filters (45nm pore size cut-off) and approximately

3 mL of the filtered solution was taken for analysis by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES). Sorbed chemical concentrations were determined by mass balance calculations. The sorption data were fitted by the Langmuir equation,

$$q = q_{\max} b C_e / (1 + b C_e)$$

where  $q$  is the amount of solute adsorbed per unit weight of sorbent, ( $\mu\text{g/g}$ ),  $C_e$  is solute equilibrium concentration,  $\mu\text{g/mL}$ ,  $q_{\max}$  is the maximum adsorption capacity of the sorbent,  $\mu\text{g/g}$ , and  $b$  is the adsorption affinity constant,  $\text{mL}/\mu\text{g}$ .

### 3.3.6 Effect of Ion Strength and Cations ( $\text{Na}^+$ , $\text{Ca}^{2+}$ and $\text{Al}^{3+}$ ) on $\text{Cu}^{2+}$ Sorption

Experiments were conducted with five samples (UTR, BL, HHY, CEL and LIG) at an initial concentration of  $\sim 3.5 \mu\text{g/mL}$   $\text{Cu}^{2+}$  (as background solution). The stock solutions of  $\text{NaNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{Al}(\text{NO}_3)_3$  were prepared in background solution (i.e.  $3.5 \mu\text{g/mL}$   $\text{Cu}^{2+}$ ). From these stock solutions, the test solutions of  $\text{NaNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{Al}(\text{NO}_3)_3$  at the concentrations listed in Table 3-1 were in background solution. The vials containing the various wood samples submerged in the test solutions were kept shaking for three days at  $23 \pm 1^\circ\text{C}$  at  $\sim \text{pH } 5.5$  for  $\text{Ca}^{2+}$  and  $\text{Na}^+$  with  $\text{Cu}^{2+}$  and  $\text{pH}=3.75$  for  $\text{Al}^{3+}$  with  $\text{Cu}^{2+}$ .

## 3. 4 Results and Discussion

### 3.4.1 Solid-State $^{13}\text{C}$ NMR

$^{13}\text{C}$  NMR results of the five wood samples are presented in Figure 3-1. and Table 3-2. The  $^{13}\text{C}$  NMR spectra illustrate that bleaching and hydrolysis caused structural modifications of aspen wood matrix. In particular, the peaks around 21 ppm and 172 ppm were attributed to methyl C and carbonyl C in hemicelluloses, respectively



(Martinez et al., 1991). The 56 ppm peak was from the lignin's methoxy groups ( $\text{OCH}_3$ ) (Seiichi et al., 1998). The signals located at 83 ppm and 88 ppm were from C-4 in amorphous and crystalline celluloses, respectively. The peaks between 71 ppm and 74 ppm were assigned to C-2, C-3, and C-5 in cellulose, whereas the strong peak at 104 ppm was associated with anomeric carbon (C-1). The peaks in the region of 131-137 ppm were assigned to the ring carbons in which the ring was not substituted by strong electron donors such as oxygen and nitrogen (Schnitzer and Preston, 1983). The multiple peaks in the range from 145-163 ppm were from the carbons of phenolic components, mainly the syringyl and guaiacyl units in lignin (Hawkes et al., 1993). The peak at 146 ppm was from C-4 in guaiacyl unit with free phenolic OH at C-4 (Hawkes et al., 1993) whose signal is strong in both HHY and LIG. There is almost no signal of  $-\text{COOH}$ ,  $-\text{COO}-$  and aromatic carbons for CEL or of carbohydrate carbons for LIG consistent with their structures. Overall, the NMR results demonstrate that bleaching and hydrolysis of the wood effectively increased its hydrophilic and hydrophobic properties, respectively.

### **3.4.2 DRIFT.**

The DRIFT spectra between 4000 and 450  $\text{cm}^{-1}$  for the five samples are shown in Figure 3-2. A broad and strong band in the region from 3324 to 3346  $\text{cm}^{-1}$  was assigned to the stretching vibration of hydroxyl group, indicative of hydrogen bonding. A strong methylene/methyl vibration was observed at 2895  $\text{cm}^{-1}$  in UTR, BL and CEL, and 2939  $\text{cm}^{-1}$  for HHY and LIG.

The absorption bands at 1740  $\text{cm}^{-1}$  mainly arose from the carbonyl ( $\text{C}=\text{O}$ ) linkage in acetyl ester groups from hemicelluloses (Ajuong and Redington, 2004). Because

carbonyl groups occur abundantly within the polymer components of wood, they tend to dominate in the branched-chain hemicellulose polymer (Kimura et al., 1992). It is evident that ester carbonyl groups of hemicelluloses dominated in both UTR and BL. However, this DRIFT band became obscure in HHY because hemicelluloses were readily decomposed under acidic conditions (Yang et al., 2004). Conversely, the absorption bands around  $1704\text{ cm}^{-1}$  in HHY and LIG were attributed to carbonyl stretching of unconjugated ketone and conjugated carboxylic groups in lignin (Matuana et al., 2001).

The absorption bands at  $1595$  and  $1505\text{ cm}^{-1}$  were assigned to aromatic ring carbon skeletal stretching (Ajuong and Redington, 2004; Yang et al., 2004). The  $1595\text{ cm}^{-1}$  band was also attributive to the stretching of conjugated C=O group (Pandey, 1999). These two bands were similar in UTR and HHY, but almost completely disappeared in BL. In contrast, these bands became very strong in the HHY, indicating that bleaching caused the cleavage of aromatic ring.

Absorption bands around  $1462$  and  $897\text{ cm}^{-1}$  were ascribed to CH and CH<sub>2</sub> units. The band at  $1462\text{ cm}^{-1}$  was assigned to CH deformation in methyl and methylene in syringyl unit from lignin (Herring et al., 2004). It became sharper and stronger after hydrolysis, but weaker after bleaching. The band at  $897\text{ cm}^{-1}$  was assigned to CH<sub>2</sub> wagging from carbohydrates (Pandey, 1999; Herring et al., 2004). Its relative intensity was strong in UTR and BL, but almost disappeared in HHY and no signal in LIG.

Absorption bands at  $1273$ ,  $990$  and  $617\text{ cm}^{-1}$  were from C-O single bond in carbohydrates (Kimura et al., 1992). Generally, the intensities of these bands were decreasing in order: BL, UTR, CEL, HHY and LIG. This underlined that

hemicelluloses and parts of cellulose were easy to hydrolyze in an acidic environment. However, the absorption band at  $1250\text{ cm}^{-1}$  was attributable to C-O single bonds in lignin (Pandey, 1999). High intensity of this peak was observed in HHY and LIG. These data again suggest that the relative lignin content was higher after hydrolysis, but lower after bleaching. This finding is in good agreement with the NMR results.

### **3.4.3 Effect of pH on $\text{Cu}^{2+}$ Sorption**

Cu sorption onto biomass is changed by the initial pH of the reaction mixture, because pH dramatically influences surface activities of sorbents (Acemioglu and Alma, 2004; Horsfall and Spiff, 2004). Our results showed (Figure 3-3) that pH greatly affected Cu sorption onto UTR, BL, CEL and HHY. The amount of Cu sorption percent by all sorbents steadily increased from an initial pH value of 1.5 to 4.5, and a maximum sorption amount was observed at around a pH of 5.5 for all the samples. This result is consistent with the results reported by Davis et al. (2003) that Cu displayed a maximal or near maximal sequestration at a pH value near to the dissociation constant of carboxylic acids ( $\text{pK}_a \approx 5$ ) in brown algal biomass. This may be explained by noting that an excess of hydrogen ions can compete effectively with Cu for sorption sites at low pH value, and less  $\text{H}^+$  ions compete with  $\text{Cu}^{2+}$  at high pH value. Other researchers (Darnall et al., 1986; Ho et al., 1995; Schiewer and Volesky, 1996; Kalavathy et al., 2005) suggested a similar explanation for the way that heavy metal cations displace  $\text{H}^+$  from hydroxyl groups of cellulose, hemicelluloses and lignin.

BL had a sharp increase in Cu sorption from pH 2-4 compared to other samples. The possible reason is that BL has more -COOH group as known from the results of FTIR and MNR. In a range of pH from 1.5 to 5, -COOH groups play a major role in Cu

sorption onto sorbents. With an increase in pH above 5, phenol groups become more active in Cu sorption. However, the increase of sorption in our experiment was not significant, indicating phenol groups contributed little Cu sorption capacity by those sorbents, consistent with the sorption results of HHY and LIG (not shown) which had low COOH groups but high phenolic groups. Pagnanelli et al. (2005) reported that metal ions mainly interacted with -COOH groups of natural biomass in acidic environments, and phenolic sites are mainly active over pH 5-6. Similar results were observed by other researchers (Benedetti et al., 1995; Plette et al., 1996). For sample CEL, Cu may be sorbed onto the outer surface of the microfibrils by complex formation with hydroxyl groups (Belford et al., 1959; Michie, 1961) and ion-exchange with  $H^+$ . And ion-exchange may play the main role in Cu sorption according to the decreased Cu sorption with the increase of Na concentrations, as described below.

#### **3.4.4 Sorption Isotherms**

The results of the Cu sorption experiments are shown in Figure 3-4. All data were fitted with the Langmuir equation (Table 3-3) and it was found that except for sample LIG, the fit with the Langmuir equation was quite good.

All samples, except LIG, sorbed Cu from the aqueous phase. Sample BL had a highest sorption capacity and it seems sorption process did not reach that maximum capacity within our experimental concentrations in contrast to UTR, CEL and HHY in which maximum sorbed levels were reached. Bleaching enhanced the Cu sorption, while hydrolysis decreased Cu sorption. The possible reason is that bleaching introduces oxygen-containing groups (Table 3-4) due to breakage of benzene carbon ring and introduction of -COOH groups, making the surface of the wood more

hydrophilic and amenable to enhanced Cu sorption (Saha et al., 2003). Conversely, hydrolysis removed carbohydrate moieties from the wood, which led to the increase of hydrophobic structure and reduced Cu sorption. With regard to sample CEL, Cu may exchange with  $H^+$  in hydroxyl groups, or Cu may be adsorbed as a monolayer on the outer surface of the microfibrils by complex formation with hydroxyl groups of the cellulose molecules (Belford et al., 1959; Michie, 1961). The results further indicate that lignin has negligible sorption. This result differs from previous studies (Srivastava et al., 1994; Lebow and Morrell, 1995; Lalvani et al., 1997). For instance, Lebow and Morrell (1995) and Lalvani et al. (1997) both reported Cu uptake by lignin and concluded that phenolic hydroxyl groups were the primary reaction sites.

#### **3.4.5 Effect of Ionic Strength**

The sorption capacity of Cu on all sorbents decreased with increasing  $Ca^{2+}$ ,  $Na^+$  or  $Al^{3+}$  concentrations (Figure 3-5 and 3-6). Cu sorption decreased at low  $Ca^{2+}$ ,  $Na^+$  or  $Al^{3+}$  concentrations with increasing concentrations of  $Ca^{2+}$ ,  $Na^+$  or  $Al^{3+}$ . This result indicates that competitive sorption between  $Ca^{2+}$  or  $Na^+$  and  $Cu^{2+}$  is occurring. That is, at low concentrations of the co-sorbates, there are more sorption sites occupied by Cu ions, while at high concentrations of  $Ca^{2+}$ ,  $Na^+$  or  $Al^{3+}$ , the  $Cu^{2+}$  ion is losing the competition for sorption sites. This trend in decreasing Cu sorption at high co-sorbent concentration is indicative of ion-exchange. Also, comparing the effects of co-sorbent ions at same ionic strength, Cu sorption dropped more extensively in the presence of  $Ca^{2+}$  compared to  $Na^+$ . This is because  $Ca^{2+}$  has stronger exchange ability with Cu than  $Na^+$  does, which further confirms that ion-exchange is the main sorption mechanism. This is consistent with the result reported by Wolf et al. (1977), while it is different from the

results observed by Lu and Allen (2001) and Merdy et al. (2002). In the case of Lu and Allen (2001), it was found that ionic strength ( $2.2 \times 10^{-3}$  to 0.1M NaNO<sub>3</sub>) did not significantly influence Cu sorption.

### **3.5 Conclusion**

Our results demonstrate that a solution's pH greatly affected Cu<sup>2+</sup> sorption onto aspen wood, and that maximum sorption occurred at around pH 5.5 independent on which kind of treatment the wood samples had undergone. The results also suggested that carboxyl (-COOH) and hydroxyl (-CHOH) in carbohydrates are the main contributors to Cu sorption to aspen wood fibers and CEL. Also, ion-exchange was identified as the main sorption mechanism in this study. Additionally, the Cu sorption capacity of all sorbents was influenced by the presence of Ca<sup>2+</sup>, Na<sup>+</sup> or Al<sup>3+</sup> with significant differences between Na and Ca ions. Further bleaching of the wood enhanced Cu sorption. Altogether, the results described herein are critical for developing novel and low-cost wood-based treatment technologies for polluted runoff and wastewater.

### **3.6 Acknowledgements**

This work was supported by McIntire-Stennis program (MAS 00090) and the Federal hatch program (MAS 8532).

Table 3-1. Concentrations of three chemicals that will be used

#	NaNO <sub>3</sub> (M)	Ca(NO <sub>3</sub> ) <sub>2</sub> (M)	Al(NO <sub>3</sub> ) <sub>3</sub> (M)
1	DI	DI	DI
2	0.0001	0.0001	0.0001
3	0.0005	0.0005	0.0005
4	0.0025	0.0025	0.0025
5	0.005	0.005	0.005
6	0.025	0.025	0.025
7	0.05	0.05	0.05
8	0.1	0.1	0.1
9	0.2	0.2	

Table 3-2 Structural Carbon Distributions (%) as Obtained from <sup>13</sup>C NMR Integration Results of Five Samples

Sample	Distribution of C (%) chemical shift, ppm <sup>a</sup>								Aliphatic <sup>b</sup> C (%)	Aromatic <sup>c</sup> C (%)
	0- 50	50- 61	61- 96	96- 109	109- 145	145- 163	163- 190	190- 220		
UTR	9.20	8.00	50.6	12.4	8.30	5.90	4.20	1.40	80.2	14.2
BL	5.30	2.60	61.7	15.0	5.00	2.60	5.90	2.10	84.5	7.50
HHY	15.9	10.9	25.1	10.0	25.0	7.70	2.60	2.80	62.0	32.7
CEL	0	1.60	75.3	17.6	0	0	2.80	2.70	94.5	0
LIG	13.5	14.0	9.10	6.60	34.0	15.3	3.30	4.30	43.2	34.0

<sup>a</sup> Within the 0-220 ppm chemical shift range, structural carbon assignments were: aliphatic carbons (0-50 ppm), methoxyl carbons (50-61 ppm), carbohydrate carbons (61-96 ppm), anomeric carbons (96-109 ppm), aromatic carbons (109-165 ppm), carboxyl and carbonyl carbons (163-190 ppm), and ketone carbons (190-220 ppm). <sup>b</sup> total aliphatic carbon region (0-109ppm); <sup>c</sup> total aromatic carbon region (109-163 ppm)



Table 3-3. Parameters of Langmuir Equation of Four Samples

Samples	$q_{max}$ ( $\mu\text{g/g}$ )	b	R
UTR	2240 $\pm$ 60	3.4 $\pm$ 0.49	0.993
BL	6900 $\pm$ 820	0.47 $\pm$ 0.11	0.990
HHY	1200 $\pm$ 30	1.85 $\pm$ 0.22	0.995
CEL	1620 $\pm$ 40	11.1 $\pm$ 1.61	0.991

Table 3-4. Elemental Composition and Polarity of Five Samples  
(Huang et al., 2006; Wang et al., 2007)

Sample	C (%)	O <sup>a</sup> (%)	H (%)	N (%)	(N+O)/C
UTR	46.7	46.6	6.38	0.340	0.754
BL	43.4	50.2	6.26	0.126	0.870
HHY	57.6	36.9	5.49	0.055	0.481
CEL	41.1	52.2	6.62	0	0.942
LIG	65.7	28.6	5.58	0.17	0.328

<sup>a</sup>Oxygen content was calculated by the mass difference.

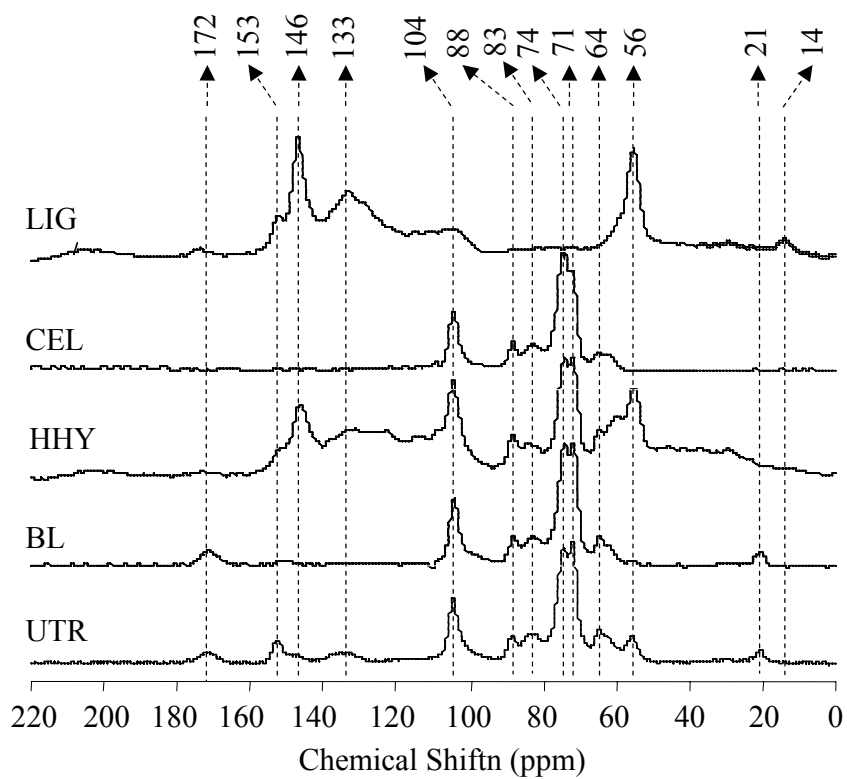


Figure 3-1. Solid-state  $^{13}\text{C}$  NMR Spectra of UTR, BL, HHY, CEL and LIG. Aliphatic C (0-109 ppm), Aromatic C (109-163 ppm) and COOH/C=O (163-220 ppm).

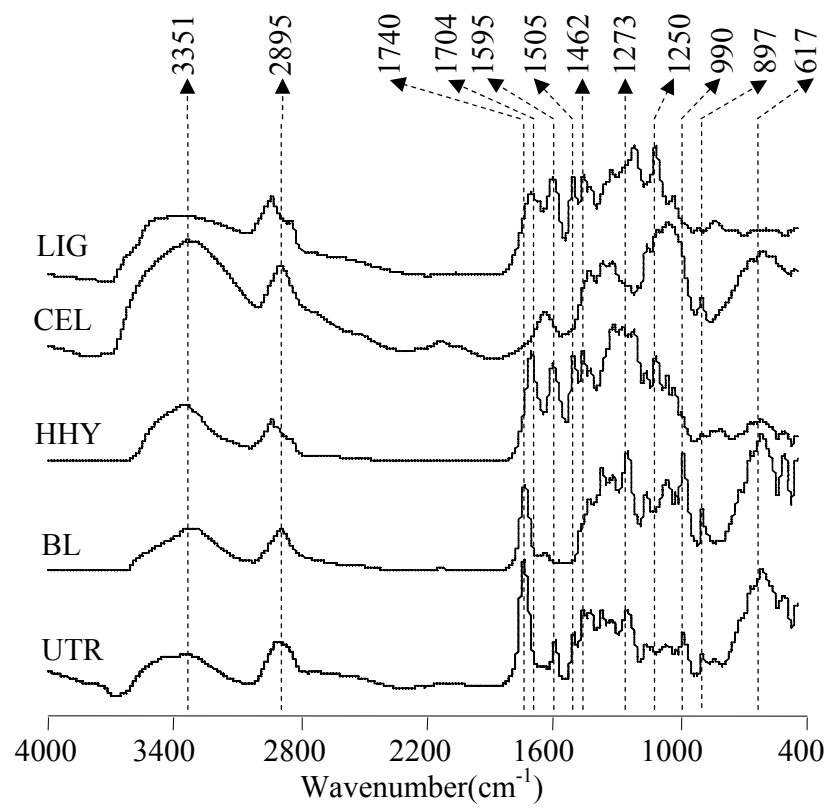


Figure 3-2. DRIFT spectra of UTR, BL, HHY, CEL and LIG. 450-4000  $\text{cm}^{-1}$

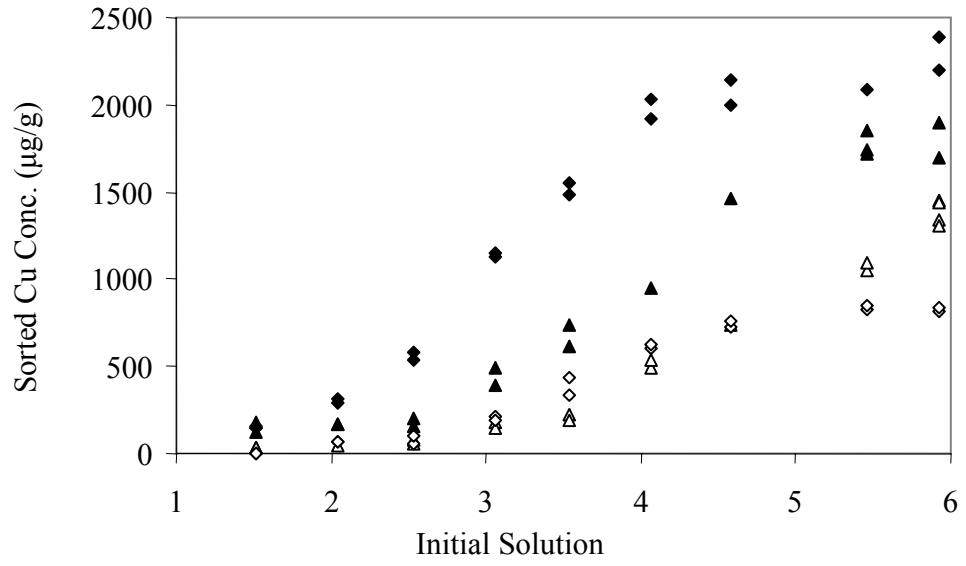


Figure 3-3. Effect of pH on  $\text{Cu}^{2+}$  sorption on UTR (▲), BL (◆), HHY (◇) and CEL(Δ)

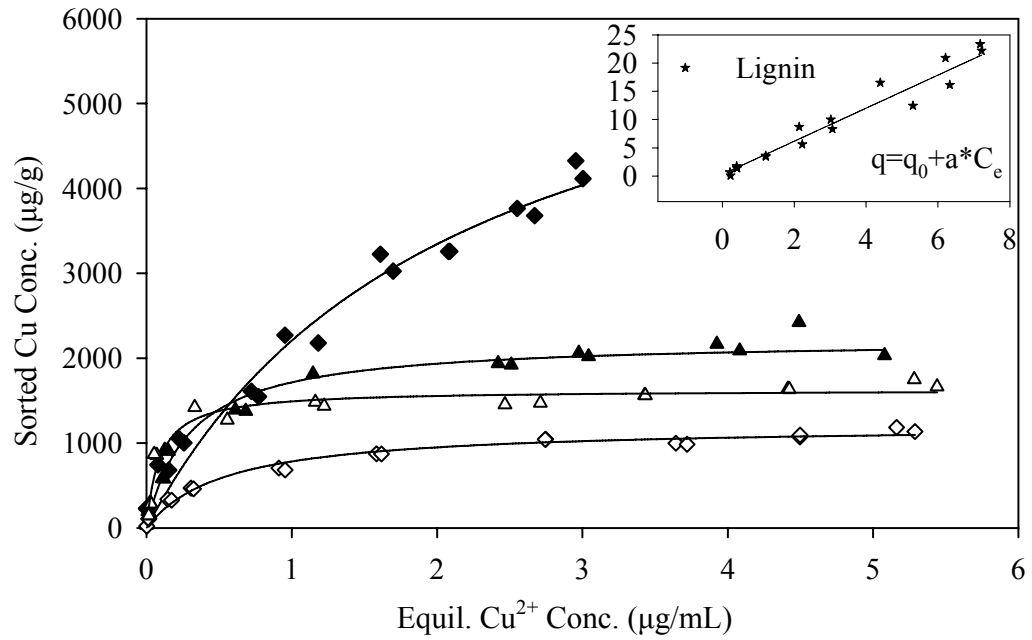


Figure 3-4. Cu<sup>2+</sup> sorption isotherms by UTR (▲), BL (◆), HHY (◇) and CEL(Δ)

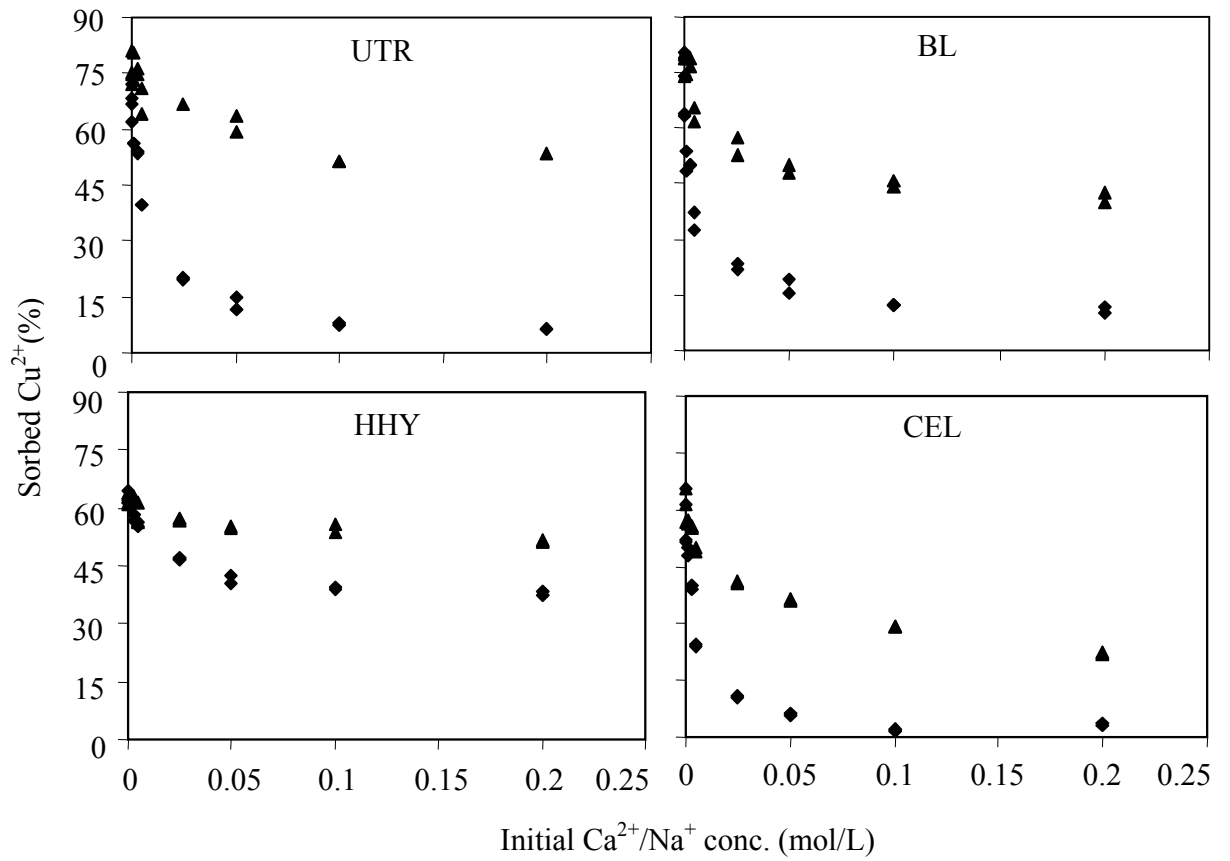


Figure 3-5. Effect of Ca<sup>2+</sup>/Na<sup>+</sup> on Cu sorption by UTR, BL, HHY and CEL. Na<sup>+</sup> (▲) and Ca<sup>2+</sup> (◆)

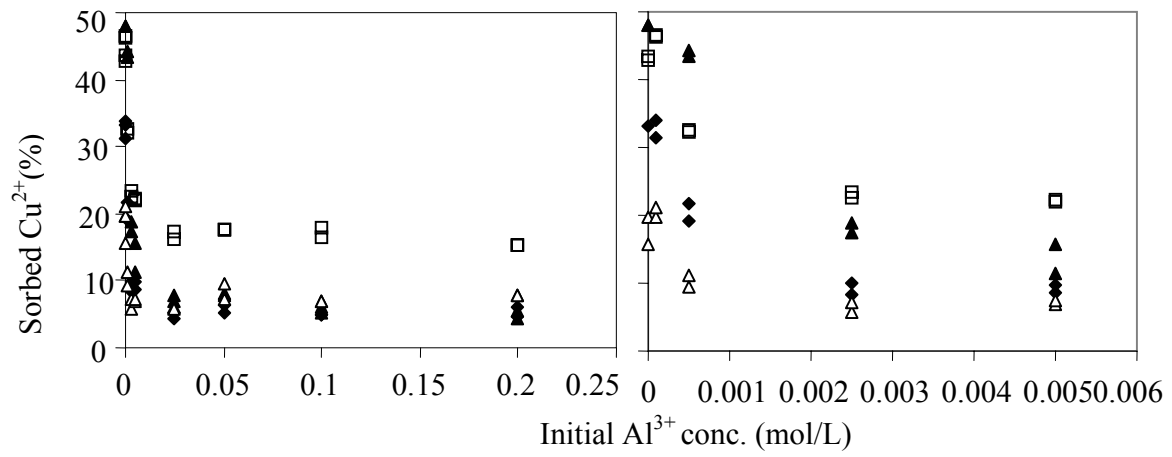


Figure 3-6. Effect of Al<sup>3+</sup> on Cu sorption by UTR (▲), BL (◆), HHY (◇) and CEL(Δ)



## CHAPTER 4

### CONCLUSIONS AND FUTURE WORKS

#### 4.1 Conclusions

In this thesis, our results demonstrate that both aromatic moieties and polarity are important for PAH sorption and desorption in aspen wood fibers. This study also indicates that effective polarity can predict sorption capacity of aspen wood fibers more accurately than mass atomic ratio,  $[(N+O)/C]$ , because effective polarity considers sorbent configuration and structure. Furthermore, structural modifications could substantially enhance the  $K_{OC}$  and retention time of PAHs

Our results also demonstrate that solution pH greatly affected  $Cu^{2+}$  sorption, and a maximum sorption amount was found at around pH 5.5 for aspen wood fibers and cellulose. The results suggested carboxyl ( $-COOH$ ) and hydroxyl ( $-CHOH$ ) in carbohydrates mainly contributes to Cu sorption on aspen wood fibers and cellulose, and ion-exchange may be the main sorption mechanism on the studied sorbents. Additionally, Cu sorption capacity of all sorbents was influenced by the presence of  $Ca^{2+}$ ,  $Na^+$  or  $Al^{3+}$ . Furthermore, bleaching could enhance Cu sorption. Our results will be useful for developing novel and low-cost technologies for the remediation of wastewater using wood materials.

#### 4.2 Future works

Many interesting works can be envisioned from the standpoints of sorption/desorption experiments on wood fibers systems:

(1) To determine the competitive sorption behaviors on treated and untreated aspen would fibers between PAHs.

(2) To determine the competitive sorption behaviors on treated and untreated aspen would fibers between heavy metals.

(3) To characterize various wood products and to determine what fundamental chemical and physical properties of wood promote the attenuation of pollutants from contaminated water.

(4) To evaluate and determine the maximum sorption capacity and effective lifetime of different woods when treating a given mixture of contaminants in water.

(5) To conduct column and pilot scale studies.

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