ENGINEERED BIOCHARS FOR THE REMOVAL OF METALLIC, ORGANIC AND EMERGING CONTAMINANTS FROM AQUEOUS SOLUTIONS

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2013
To God, and my family, as none of this would have been possible without their love and support
ACKNOWLEDGMENTS

I would like to extend my deepest gratitude toward those individuals who have made an immense contribution to the successful completion of this research and also made my PhD journey a worthwhile one.

Firstly, I am grateful to God for being my anchor and guide, and my family, in particular my parents, Mr. and Mrs. Ime Sampson Inyang for all their encouragement and continuous support toward my academic endeavors. Mum and Dad, your encouragement and advice helped me persevere during the challenging times in my doctoral research.

Secondly, my sincere appreciation goes to my advisor, Dr. Bin Gao and all my committee members, Dr. Andrew Zimmerman, Dr. Pratap Pullammanappallil, Dr. Jean Claude Bonzongo, and Dr. Ben Koopman for their input in improving the quality of my research. I am especially grateful to Dr. Bin Gao for his patience and continuous guidance in ensuring the timely completion of this research. Your critique and counsel were valuable in improving the quality of this research. For constantly challenging me to think scientifically and develop strong research Hypotheses, I am grateful to you Dr. Zimmerman. Thank you for serving as Co-chair on my committee. I am also thankful to Dr. Pratap Pullammanappallil for introducing me to a career of research in academia and for serving on my committee. To Dr. Koopman and Dr. Bonzongo, I am grateful for your critique and insightful suggestions that were valuable in the interpretation of my experimental data.

Thirdly, special thanks go to my friends: Samriddhi Buxy, Zhouli Tian, Gayathri Ramohan, Samuel Aso and Congrong Yu as well as my Environmental Nanotechnology group members: Ying Yao, Lei Wu, Yuan Tian, Lin Liu, Yining Sun, Zhou Yanmei, June
Fang, Chen Hao, Ming Zhang, Dr. Yu Wang and Dr. Xue Yingwen. Your friendship, co-operation and support made my research experience a pleasurable one. I also appreciate the technical input and assistance rendered to me by the technical staff of the Particle Engineering and Research Center, and Agricultural and Biological Engineering Department in the design of my experiments.

Finally, I save my last and special thanks for my church family: the Falades, Maryann, and Melissa King; my mentor, Abhay Koppar; my U.S. moms: Susie Studstill and Donna Rowland. I am so grateful for all the love, support and encouragement you have shown me over the years. Thank you for making my stay in Gainesville, a memorable one.
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<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
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<td>AC-Fe</td>
<td>Iron modified activated carbon</td>
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<td>AgNP</td>
<td>Silver nanoparticles</td>
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<tr>
<td>BC</td>
<td>Bagasse biochar</td>
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<td>BC-CNT</td>
<td>Carbon nanotube-coated bagasse biochar</td>
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<td>BC-SDBS-CNT</td>
<td>Sodium dodecylbenzenesulfonate-dispersed carbon nanotubes bagasse biochar nanocomposites</td>
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<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
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<td>CNT</td>
<td>Functionalized or non-functionalized multi-walled carbon nanotubes</td>
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<tr>
<td>DAWC</td>
<td>Digested animal waste biochar</td>
</tr>
<tr>
<td>DLVO</td>
<td>Derjaguin-Landau-Verwey-Overbeek</td>
</tr>
<tr>
<td>DWSBC</td>
<td>Digested whole sugar beet biochar</td>
</tr>
<tr>
<td>EDL</td>
<td>Electrostatic double layer interactions</td>
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<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
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<tr>
<td>ENPs</td>
<td>Engineered nanoparticles</td>
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<tr>
<td>F</td>
<td>Freundlich</td>
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<tr>
<td>FTIR</td>
<td>Fourier transforms infra-red spectroscopy</td>
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<tr>
<td>HC</td>
<td>Hickory biochar</td>
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<tr>
<td>HC-CNT</td>
<td>Carbon nanotube-coated hickory biochar</td>
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<tr>
<td>HC-Fe</td>
<td>Iron modified hickory biochar</td>
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<td>Sodium dodecylbenzenesulfonate-dispersed carbon nanotubes hickory biochar nanocomposites</td>
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<tr>
<td>L</td>
<td>Langmuir</td>
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<tr>
<td>LL</td>
<td>Langmuir-Langmuir</td>
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<td>LW</td>
<td>Lifshitz-Vander waals attraction energy</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
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</tr>
<tr>
<td>MB</td>
<td>Methylene blue</td>
</tr>
<tr>
<td>NTiO2</td>
<td>Nano-titanium dioxide</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium dodecylbenzenesulfonate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SPY</td>
<td>Sulfapyridine</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
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<tr>
<td>UV-VIS</td>
<td>Ultra-violet visible spectroscopy</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

ENGINEERED BIOCHARS FOR THE REMOVAL OF METALLIC, ORGANIC AND EMERGING CONTAMINANTS FROM AQUEOUS SOLUTIONS

By
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August 2013

Chair: Bin Gao
Cochair: Andrew Zimmerman
Major: Agricultural and Biological Engineering

Engineered biochars combining high tech materials with low-cost biomass-derived materials hold great promise for the removal of traditional contaminants like heavy metals and organic compounds as well as emerging contaminants (e.g., pharmaceutical residues and nanoparticles) from wastewater. In this work, biochars were synthesized and activated using various techniques, and the resulting modified biochars were evaluated for their abilities to sorb various heavy metals, dyes, engineered nanoparticles (ENPs), or antibiotics. First, anaerobically digested whole sugar beet and digested animal waste residues were pyrolyzed into biochar. The sorption capacity (200 mmol kg\(^{-1}\)) of these two biochars for Pb was comparable to that of commercial activated carbons and the removal of Pb was mainly controlled by precipitation. Next, elemental iron (Fe) was impregnated onto raw hickory biochar (HC) and activated carbons (AC). These carbon-based sorbents could sorb and retain ENPs from aqueous solutions and the iron modification of these sorbents improved their sorption ability by reducing electrostatic repulsions between the negatively charged ENPs and carbons. Third, carbon nanotubes (CNTs) biochar nanocomposites were
synthesized by pyrolyzing dried mixtures of CNT suspensions sorbed to raw biomass of different types. The addition of CNTs significantly enhanced the physiochemical and sorptive properties of the biochars with CNT hickory and sugarcane biochars made using 1% CNT suspensions, exhibiting the greatest thermal stabilities, surface areas and MB sorption capacities. MB sorption onto the raw and modified biochars was predominantly influenced by electrostatic attraction of positively charged MB to negatively charged biochars. Lastly, surfactant-dispersed CNT biochar nanocomposites were produced by dip-coating hickory or bagasse biomass in 1% sodium dodecylbenzenesulfonate (SDBS)-dispersed CNT solutions and then pyrolyzing the coated biomass. The SDBS-CNT chars had the highest removal of Pb and SPY than the unmodified or CNT-biochars in both single and binary solute systems via multiple sorption mechanisms. In summary, the modification techniques presented here are time and cost-efficient and have shown beneficial results for the treatment of a wide array of contaminants.
CHAPTER 1
ENGINEERED BIOCHARS FOR THE REMOVAL OF METALLIC, ORGANIC AND EMERGING CONTAMINANTS FROM AQUEOUS SOLUTIONS

Introduction

Wastewater contamination by toxic organic chemicals, heavy metals and other emerging pollutants has become a world-wide environmental concern (Wang et al., 2010b). The undesirable effects of these contaminants to human health and aquatic ecosystems have further necessitated stringent regulations on their discharge levels to environmental waters. Today, municipal wastewater treatment plants play a major role in limiting the pollution of these contaminants in aquatic environments (Li et al., 2013). But, recent research studies (Gardner et al., 2013; Katsou et al., 2012; Lou & Lin, 2008) have shown that conventional wastewater treatment technologies no longer suffice in completely eliminating these contaminants from treated waters. Moreover, the fate of some contaminants (e.g., emerging pharmaceutical and nanoparticle products) in wastewater systems is not yet fully understood. Thus, environmental remediation studies developing new water treatment technologies for these contaminants are increasing.

The presence of elevated concentrations of heavy metals from point and non-point sources in aqueous streams continues to pose challenges in environmental remediation due to their non-biodegradable nature. Therefore, maximum contaminant levels of many heavy metals are set by the United States Environmental Protection Agency (USEPA), close to 0 ppm. In addition to aqueous streams, heavy metals such as cadmium, copper, lead and nickel occur in contaminated soils which makes their mobility of great concern (Uchimiya et al., 2010). For instance, lead can complex with
organic compounds in soil organic matter to form organo-metallic complexes, and further increase its environmental persistence.

Unlike heavy metals, most organic contaminants are biodegradable and often found in trace concentrations in aquatic systems. Remediation studies on organic contaminants (Es'haghi et al., 2011; Lin & Xing, 2008; Mishra et al., 2010; Zhang et al., 2012c) however, indicate that even at trace concentrations, certain organic compounds such as phenol, dyes, and dioxins could be bio-persistent, and pose severe health problems to living organisms (Fu et al., 2003). Specifically, dyes are a class of colored chemicals used in various industries including textile, leather, paper, and plastic industries. But, some water-soluble aromatic dyes (e.g., azo dye, methylene blue and congo red) are suspected carcinogens that also induce chronic effects on exposed microorganisms (Yu & Fugetsu, 2010). Wastewater containing dyes are difficult to treat due to their stability to light and resistance to aerobic digestion. Because, the presence of dyes also produce aesthetic problems, their removal from wastewater systems is pertinent to improving the quality of treated water.

Emerging contaminants typify a class of potentially toxic pollutants including natural or synthetic chemicals, whose effects or presence is largely unknown because they have been recently introduced in the environment (Smial, 2008). Pharmaceutical residues, personal care products, nanomaterials and perfluoro-chemicals are examples of emerging contaminants. Among these named pollutants, pharmaceutical residues from widely used human and veterinary drugs are considered one of the most frequently detected contaminants in wastewaters (Jesus Garcia-Galan et al., 2011; Radke et al., 2009). Like pharmaceutical residues, there have also been increased concentrations of
engineered nanoparticles in wastewater systems due to their widespread applications in many household and industrial products (Nowack & Bucheli, 2007). Also, while engineered nanoparticles have high mobility in soil and water and are easily eluted from water treatment systems due to their small size (Christian et al., 2008); pharmaceutical residues are bio-persistent and not wholly degraded by anaerobic microbes in many treatment plants (Radjenovic et al., 2009; Radke et al., 2009). But, the uptake of these emerging materials from wastewater is advantageous because their sorbed products can be further used as purification and disinfection agents in water.

Biochar is a porous, environmental, and ubiquitous carbon sorbent derived from the thermal treatment of carbonaceous materials in a closed system, under anaerobic conditions (Uchimiya et al., 2010). Today, research on eco-friendly biochar is increasing due to its many applications in carbon sequestration, soil fertility enhancements, energy generation, and environmental remediation (Crombie et al., 2013; Inyang et al., 2011b; Liu et al., 2013; Namgay et al., 2010; Spokas et al., 2012; Yao et al., 2011b). In particular, the application of biochar to environmental remediation is attractive due to the abundance and low-cost of waste biomass that can be used for biochar production.

Several research studies (Inyang et al., 2011b; Ippolito et al., 2012a; Ko et al., 2004; Liao et al., 2012; Yao et al., 2013a; Yao et al., 2012b; Zhang et al., 2012a) have investigated the removal of various contaminants, particularly, dyes, pharmaceutical residues, and heavy metals by biochars produced from a variety of materials. In many cases, the effective removal of these contaminants by biochars was attributed to the modification of their physiochemical properties. But, since no known study exists for the
sorption of nano-particles on biochar, engineered biochars may also be considered for immobilizing nanoparticles on biochar surface.

**Biochar Engineering: Existing Research and Limitations**

Biochar engineering or modification can be defined as the application of processing techniques to improve the sorptive properties of biochar. Engineering methods for improving biochar's properties may be physical, chemical or biological, and these methods are discussed in greater detail in the following section:

**Physical Engineering**

Physical engineering of biochar is performed to increase its surface area and pore volume, and may include mechanical processes such as milling of the raw biomass (prior to pyrolysis), or finished biochar material (Peterson et al., 2012). For instance, the pulverization of peanut, soybean and canola straws prior to pyrolysis resulted in higher sorption of copper for the respective pulverized straw biochars than the non-pulverized chars.

Biochars can also be physically modified by manipulating pyrolytic conditions to improve the porosity or oxygen functionalities of biochar surface. Specifically, physical modification of chars by the passage of oxidizing gases such as steam and CO₂, or a combination of both in pyrolytic reactors are known to burn off loose, dangling carbon atoms and widen existing pores on the chars making them more accessible to the molecules of adsorbed contaminants (Lu et al., 2008). Moreover, depending on the nature of the feedstock, steam application could reduce highly acidic functional groups (e.g. carboxylic and lactonic groups), and enlarge weakly acidic groups (e.g. phenolic groups) (Borchard et al., 2012). Heavy metals and cationic dyes in aqueous solutions
have been shown to easily sorb onto these negatively charged sites on biochar surfaces
(Carrier et al., 2012; Cheng et al., 2008).

One drawback to this method of physical modification however, is the additional
energy input required for the generation of steam during the modification process. The
cost of the additional energy employed could increase the cost of the engineered
biochar, making it a less cost-effective treatment option.

**Chemical Engineering**

Chemical engineering of biochar involves the incorporation of alkaline (e.g.,
KOH, NaOH), acidic (e.g., ZnCl$_2$, H$_3$PO$_4$, H$_2$O$_2$), or organic materials (e.g., hydrogel and
aerogel), and recently, metallic oxides and nanoparticles in biochar to produce active
carbons with enhanced surface chemistries and functionalities (Ippolito et al., 2012b)
(Karakoyun et al., 2011; Li et al., 2012; Xue et al., 2012; Zhang et al.).

Generally, the use of KOH or ZnCl$_2$, and steam activation has been industrially
employed in producing commercial activated carbons (Azargohar & Dalai, 2008). This is
because the presence of Zn or K constituents intercalated within the C-structure of
biochar during modification, forces apart the crystallite units forming biochar’s structure,
and the subsequent washing of the modified char, to remove some of these
constituents, frees up the interlayer spaces containing these elements, yielding more
porous chars (Marsh, 1987). But, the removal of Cu by KOH-steam modified pecan
shell biochar was found to occur by the interaction of Cu with oxygen functional groups
on the surface sites of the char (Ippolito et al., 2012b). This suggests that modification
by KOH also increases oxygen functionalities (O-H groups) on the surface of modified
biochars, in addition to increasing the porosity of the chars. In contrast, p(acrylamide)
chicken biochar activated with HCl and hydrogel was suggested to improve the sorption of phenol by increased hydrophobic interactions.

Two limitations to these methods of modification however, are the laborious techniques employed and increased processing cost from the use of many cross-linkers and binders to improve the bonding of chemical reagents to biochar.

**Biological Engineering**

Biological engineering has been recently proposed as another modification method for improving the sorptive properties of biochar (Inyang et al., 2010). The degradation of biomass substrates by microbes during aerobic or anaerobic treatment processes could yield more porous carbon structures, when the resulting sludge residuals are pyrolyzed. For instance, the sorption of fluoroquinolone antibiotics on wastewater sludge biochar was attributed to the enhanced porosity of the sludge residual material (Yao et al., 2013a).

Typically, the process of anaerobic digestion involves the microbial uptake and assimilation of organic carbon (e.g., hemicellulose and cellulose portions), which would (depending on the feedstock) result in higher concentration of inorganic, cationic (P, K, Ca, Mg, N, and S) and anionic species (CO$_3^{2-}$, PO$_4^{3-}$, MgO) on the digested residuals. The removal of Pb on digested bagasse biochar which was 20 times better than undigested bagasse biochar (Inyang et al., 2011a), was attributed to the precipitation of cerasite (PbCO$_3$) mineral from slowly released carbonate species interacting with Pb. These results confirm the possibility of biologically engineered biochars to be used in the uptake of contaminants. Despite these results however, the practical application of digested biochars is limited by a paucity of studies utilizing digested biochars in sorption studies.
**Research Objectives**

In order to overcome the limitations associated with existing biochar activation techniques, the overarching objective of this study was to develop biochars using cost-effective modification techniques requiring less labor; yet achieving high removal efficiencies of metallic, emerging and organic contaminants. The central Hypothesis of this study was that the modification techniques employed could enhance the physiochemical properties or functionalities of biochar, and increase their sorption capacities for selected contaminants: (a) nanoparticles, (b) heavy metals, (c) cationic dyes, and (d) pharmaceutical residues. The three methods employed for the engineering of the biochars were: (1) anaerobic digestion, (2) chemical modification of biochars by iron-impregnation and immobilization of filtered nanoparticles, and (3) pyrolysis of nano-particle coated biomass composites. Postulated Hypotheses and specific research objectives are discussed further in the following section:

**Hypothesis 1**

The process of anaerobic digestion does not convert all of the biomass feedstock to methane, but could concentrate inorganic components (e.g., phosphates, carbonates, and oxides) in the residues that when converted to biochar can be slowly released to bind with dissolved heavy metals.

**Objective 1**

Determine whether biochars converted from anaerobically digested biomass other than sugarcane bagasse (from previous work) can be used as effective sorbents to remove heavy metals from water. The specific objectives of this study were to:

- Evaluate the removal efficiency of lead, copper, nickel and cadmium from aqueous solution by two digested biochars.
Determine the removal characteristics of lead from solution on the digested biochars.

Investigate the mechanisms of lead removal on the digested biochars.

**Hypothesis 2**

Chemically impregnated iron on negatively charged biochar surfaces can reduce electrostatic repulsions, and favor the attachment of negatively charged engineered nanoparticles (ENPs) during filtration.

**Objective 2**

Evaluate and compare the effectiveness of several carbon-based materials including biochar, in retaining three types of ENPs: nano titanium dioxide (NTiO\(_2\)), silver nanoparticle (AgNP), and multi-walled carbon nanotubes (CNT). The specific objectives of this study were to:

- Evaluate and compare the ability of the carbon materials to sorb and filter the ENPs.
- Compare the mobility of the three ENPs in the carbon filters.
- Determine whether biochar can be used as an effective filter media for the ENPs.

**Hypothesis 3**

The carboxyl group incorporated in biochars by pyrolyzing carboxyl functionalized CNT-coated biomass could provide extra high affinity sorption sites to bind cationic dyes like methylene blue on biochars.

**Objective 3**

Identify a simple, synthesis method for producing hybrid CNT-biochar composite materials and test the sorption potential of the produced hybrid biochar materials for methylene blue removal. The specific objectives of this study were to:
• Characterize the hybrid-CNT biochar materials to investigate the effect of CNT on the physiochemical properties of the chars.

• Examine the influence of pH, contact time, and ionic strength conditions on the sorption capacity of the hybrid sorbents.

• Elucidate and understand the interaction mechanisms governing the sorption of MB onto hybrid CNT-biochar sorbents.

Hypothesis 4

The dispersion of CNT by the surfactant will increase individual CNT threads in suspensions that can be anchored to the biomass prior to pyrolysis and increase high affinity sorption sites on the produced surfactant-modified biochar nanocomposites that can bind sulfapyridine and lead.

Objective 4

Modify hickory and bagasse biochars using sodium dodecylbenzenesulfonate (SDBS) surfactant-dispersed CNT and examine their removal ability for sulfapyridine (SPY) and lead (Pb). The specific objectives of this study were to:

• Examine the effect of SDBS-dispersed CNT on the properties of SDBS-CNT-coated hickory and bagasse biochar nanocomposites.

• Determine the sorption capacity of Pb and SPY on SDBS-dispersed CNT hickory and bagasse biochars in a single solute system

• Investigate co-sorption interaction mechanisms between SPY and Pb in a binary solute system for both SDBS-CNT biochars.

• Elucidate and differentiate sorption mechanisms controlling the sorption of Pb and SPY on hickory and bagasse-SDBS-CNT coated biochars respectively.
Organization of Dissertation

To achieve the stated objectives of this research as outlined in Chapter 1, this dissertation was organized into six Chapters. Chapter 2 examined the use of anaerobic digestion as a “biological” activation method for biochar and also tested the efficiency of digested biochars to sorb heavy metals. Based on findings presented in Chapter 2, it was established that digested biochars had the potential to sorb heavy metals via precipitation mechanism. Thus, Chapter 3 focused on the modification of biochar surface by iron impregnation/precipitation as well as examining how effective iron modified carbons were in filtering nanoparticles. But, overall results presented in Chapter 3 pointed to a low retention of CNTs even with these iron-modified carbons compared to other nanoparticles. Accordingly, Chapter 4 examined the possibility of incorporating CNTs in the biochars by a dip-coating procedure and evaluating the potential of these CNT-modified biochar nanocomposites to remove MB from aqueous solutions. Results from Chapter 4, confirmed that incorporating CNT in biochars improved their sorption capacity for MB. Next, Chapter 5 further examined the effect of increasing the CNT contents of biochars by using SDBS in dispersing CNT. SDBS-dispersed CNT biochar composites were then used to sorb Pb and SPY in single and binary solute systems. This dissertation culminated in Chapter 6, where relevant conclusions were drawn from Chapters 1 to 5, and plausible recommendations for future work were presented.
CHAPTER 2
REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTIONS BY BIOCHARS DERIVED FROM ANAEROBICALLY DIGESTED BIOMASS

Introduction

Heavy metals pose a risk to public health because of their toxic, non-biodegradable nature, and widespread occurrence in natural and human-altered environments. They are mainly introduced into the environment from point sources such as discharges from mining, metal plating, battery, and paper industries. Lead, copper, cadmium, and nickel are among the most toxic and carcinogenic heavy metals that could cause serious environmental and health problems. The United States Environmental Protection Agency (USEPA), therefore, has established very strict maximum contaminant level goals for these heavy metals in natural waters (Table 2-1).

Many methods have been developed to address these stringent environmental regulations which necessitate removal of heavy metal compounds from waste water. Traditional water treatment technologies, such as precipitation, ion exchange, electrocoagulation, membrane filtration, and packed-bed filtration have been found to be effective in reducing heavy metal concentrations (Akbal & Camci, 2011; Boudrahem et al., 2011; Malamis et al., 2011). Most of these technologies however, may be associated with high operation cost and/or sludge disposal problems (Sud et al., 2008). These disadvantages have increased the need of developing alternative and low-cost water treatment technologies for heavy metal contaminants. Biosorbents therefore have been suggested to be a potential candidate to satisfy this need to remove toxic metals

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from wastewater (Demirbas, 2009). For example, Demirbas (2008) indicated that agricultural by-products and in some cases appropriately modified could be used to develop cost-effective technologies to treat heavy metals in both industrial and municipal wastewater.

Biochar is a pyrogenic carbon-rich material, derived from thermal decomposition of biomass in a closed system with little or no oxygen (Das et al., 2008; Lehmann et al., 2006; Van Zwieten et al., 2010). When cheap biomass, particularly agricultural by-products, is used for biochar produce, the cost of biochar production is mainly associated with the machinery and heating, which is only about $4 per gigajoule (Lehmann, 2007). The use of biochar as a low-cost sorbent to remove metallic contaminants from aqueous solutions is an emerging and promising wastewater treatment technology, which has already been demonstrated in previous studies (Beesley & Marmiroli, 2011; Liu & Zhang, 2009; Uchimiya et al., 2010).

Biochars converted from agricultural residues, animal waste, and woody materials have been tested for their ability to sorb various heavy metals, including lead, copper, nickel, and cadmium (Cao et al., 2009a; Uchimiya et al., 2011; Uchimiya et al., 2010). In addition, anaerobically digested biomass has been found to be a good feedstock to produce biochars with suitable physicochemical properties to serve as a low-cost sorbent (Inyang et al., 2010; Yao et al., 2011a). A recent study indicated that biochar converted from anaerobically digested sugarcane bagasse is a far more effective sorbent of lead than biochar from undigested bagasse and even more effective than commercial activated carbon (Inyang et al., 2011b). It is suggested that anaerobic digestion could be used as a new activation method (i.e. 'biological activation') to create
high-efficiency carbon-based sorbents for heavy metals (Inyang et al., 2011b). In addition, this method may also provide other benefits, such as producing renewable bioenergy through anaerobic digestion and pyrolysis and reducing waste management cost. However, there is still a paucity of data showing the universal applicability of 'biologically activated' biochars to water purifications. Particularly, it is unclear whether biochars converted from other digested biomass types also have superior ability to remove heavy metals from water (Inyang et al., 2011b).

Sugar beets and dairy manure are two of the most common biomass types used in anaerobic digesters to produce bioenergy. Sugar beets are traditionally used for sugar production; however, they require rapid processing to maximize sugar extraction and minimize spoilage. Traditionally, dairy waste could be applied directly to agricultural lands as amendment for soils, but there are increasing concerns over the potential risk of surface and ground water contamination (Hooda et al., 2000). Recent studies suggest that anaerobic digestion could be an effective waste management strategy to reduce the volume of sugar beets and dairy waste as well as to generate bioenergy (Brooks et al., 2008; Fang et al., 2011; Wang et al., 2010a). Because most bacterial digestion processes cannot utilize all the feedstock materials, it is therefore important to develop methods to handle the residuals. To our knowledge, however, little research has been conducted to develop methods to process anaerobic digestion residuals, particularly with respect to using the digested biomass to make biochar-based sorbents.

The overarching objective of this work was to determine whether biochars converted from anaerobically digested biomass other than sugarcane bagasse can be used as effective sorbents to remove heavy metals from water. Two biochars were
produced from anaerobically digested dairy waste and whole sugar beets in the laboratory through slow pyrolysis. Batch sorption experiments were used to examine the sorption behaviors of heavy metals on the biochars and the physicochemical properties of the pre- and post-sorption biochars were determined. Mathematical models were used to help data analysis and interpretation of sorption mechanism. The specific objectives of this work were to: (1) evaluate the removal efficiency of lead, copper, nickel and cadmium from aqueous solution by the two biochars; (2) determine the sorption characteristics of lead on the biochars; and (3) understand the sorption mechanisms of lead on the biochars.

**Materials and Methods**

**Materials**

Digested dairy waste residue was produced by a single-stage, thermophilic, anaerobic digester at the Dairy Research Unit of the Animal Science Department, University of Florida (UF) in Gainesville, FL. Digested whole sugar beet residue was obtained from a two-stage, thermophilic, high-solids sequencing, anaerobic digester in the Sequential Batch Anaerobic Composting (SBAC) pilot plant at UF. The residues were pressed, de-watered, then stored in air-tight plastic bags, and refrigerated prior to use.

To make the biochars, the residue materials were first dried at 80 °C. About 500 g of the dried feedstocks were converted into biochar through slow pyrolysis at 600 °C for 2 h in a N₂ environment in a furnace (Olympic 1823HE) following the procedures of (Yao et al., 2011a). The resulting biochars are referred to as DAWC (digested animal waste char) and DWSBC (digested whole sugar beet char). The biochar samples were ground and sieved to 0.5 - 1 mm sized particles. After several rinses with deionized (DI)
water to remove impurities such as ash, both DAWC and DWSBC samples were dried at 80 °C for further testing.

All chemical reagents used were of high purity grades from Fisher Scientific (Suwanee, Georgia). Stock solutions of 1000 ppm lead (II) nitrate, cadmium (II) nitrate tetrahydrate, nickel (II) nitrate hexahydrate, and copper (II) nitrate trihydrate were prepared by dissolving appropriate amount of chemicals in DI water.

Biochar Properties

Carbon, hydrogen, and nitrogen contents of the biochars were determined using a CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion followed by infrared detection of resulting CO₂, H₂ and NO₂ gases. Major inorganic elemental constituents of the biochars were determined using the EPA 200.7 method of acid digestion followed by analysis by inductively coupled plasma with atomic emission spectroscopy (ICP-AES).

The pH of the biochar samples was measured by combining biochar with DI water in a mass ratio of 1:20. The solution was then hand stirred and allowed to stand for 5 min before measurement with a pH meter (Fisher Scientific Accumet Basic AB15).

Biochar surface potential was determined by measuring the zeta potential (ζ) of colloidal biochar suspensions obtained through sonication according to the procedure of (Johnson et al., 1996). Charge mobility of each biochar suspension was determined using a Brookhaven Zeta Plus (Brookhaven Instruments, Holtsville, NY) and Smoluchowski’s formula was used to convert the electric mobility into zeta potential.

Specific surface areas of the biochars were determined on a Quantachrome Autosorb1 surface area analyzer. N₂ adsorption isotherms measured at 77 K and interpreted using Brunauer, Emmet, and Teller (BET) theory yielded mesoporous
surface area (pores > 1.5 nm) and CO\textsubscript{2} adsorption isotherms at 273K were interpreted using Monte Carlo simulations of the non-local density functional theory and yielded microporous surface area (pores < 1.5 nm).

**Sorption of Heavy Metals**

An initial evaluation of the sorption ability of DAWC and DWSBC was performed using a mixed heavy metal solution containing Pb\textsuperscript{2+}, Cu\textsuperscript{2+}, Cd\textsuperscript{2+}, and Ni\textsuperscript{2+}. The concentration of each metal in the solution was adjusted to be 0.1 mmol L\textsuperscript{-1}. About 0.1 g of the test biochar was added into 68 mL digestion vessels (Environmental Express) and mixed with 50 mL of the heavy metal solution at room temperature (22 ± 0.5 °C). After shaking in a reciprocating shaker for 24 h, the vessels were withdrawn and filtered immediately through 0.1 µm pore size nylon membranes (GE cellulose nylon membranes). The Ni, Cu, Cd and Pb concentrations in the filtrates were determined using ICP-AES (Perkin Elmer Plasma 3200RL). The sorbed heavy metal concentrations were calculated based on the difference between the initial and final metal concentrations in the supernatant. Vessels without the sorbent (biochar) or the sorbates (metals) were included as experimental controls.

**Sorption of Lead**

Sorption kinetics of lead on DAWC and DWSBC were determined by mixing 50 mL of 200 ppm Pb\textsuperscript{2+} solution with 0.1 g of each sorbent in the digestion vessels at room temperature, and shaking over the course of a 24 h period. Sample solutions with their corresponding blank controls were withdrawn at specific time intervals to examine sorption kinetics. The mixtures were immediately filtered and the filtrates were stored for further analysis.
Sorption isotherms were obtained by adding 0.1g of each biochar to 50 mL of 
Pb\textsuperscript{2+} solutions with varying concentrations (5 to 600 ppm) in each vessel and shaken for 
24 h. The solutions were then filtered and pH values of the filtrates were recorded. Both 
the filtrates and lead-laden biochars were collected for further analysis. The lead-laden 
biochars were washed with DI water several times and oven dried before analysis.

For all lead sorption experiments, blank experiments without the sorbent or 
sorbate were included as experimental controls, which indicated that there was no 
addition or loss of lead in the experiments. Lead concentrations in the filtrates were 
determined with the ICP-AES. Lead concentrations on the biochars were calculated 
based on the differences between initial and final aqueous solutions. All the sorption 
experiments (mixed heavy metals and lead) were performed in duplicate and the 
average values are reported here. Additional analyses were conducted whenever two 
measurements showed a difference larger than 5%.

**Post-sorption Characterizations**

Scanning electron microscopy (SEM) coupled with energy dispersive 
spectroscopy (EDS) was used to examine surface morphology and elemental 
composition of both pre-sorption and post-sorption (lead-laden) DAWC and DWSBC. 
The tested samples were mounted on carbon stubs using carbon conductive paint. The 
samples were placed under a JEOL JSM-6330F field-emission SEM equipped with an 
Oxford EDS. During operation, the accelerating voltage of the instrument was 
maintained at 10 kV and varying magnifications were used.

X-ray diffraction (XRD) analysis was conducted on both pre- and post-sorption 
biochar samples to identify possible crystalline structures. A computer-controlled X-ray 
diffractometer (Philips Electronic Instruments) equipped with a stepping motor and
graphite crystal monochromator was used. Fourier transform infra-red (FTIR) analysis was used to characterize functional groups present on the biochar surfaces. The biochar samples were directly mounted on the diamond base of a Nicolet 6700 FTIR (Thermo Scientific) and a transparent polyethylene film was used to cover the samples for the FTIR analysis.

**Results and Discussion**

**Biochar Properties**

CHN analysis revealed that DAWC contained much more carbon than DWSBC (Table 2-2), probably because the feedstocks were from different types of anaerobic digesters. DAWC also had higher nitrogen content but slightly lower hydrogen content than DWSBC (Table 2-2). Elemental analysis showed that the two biochars had various amounts of inorganic elements and slightly higher amounts of Ca (5.5%) and K (2.3%) were present in DWSBC and DAWC, respectively (Table 2-2). These inorganic elements originated from nutrients rich in plant and animal residues, but the most predominant component in both biochars was carbon.

Previous studies have shown that physiochemical properties of biochars, such as pH, surface potential, and surface area, are important factors controlling their environmental applications (Inyang et al., 2010). Both DAWC and DWSBC were alkaline with a relatively high pH (Table 2-3), which is similar to the biochars obtained from anaerobically-digested sugarcane bagasse (Inyang et al., 2010). This suggests that the two biochars could be good conditioners for acid soils. The surface potential measurements indicated that DAWC had more negative surface charge than DWSBC which may be related to its higher surface area and pore volume (Table 2-3). All of
these data seem to suggest a greater potential for DAWC to sorb abundant positively charged heavy metals.

**Sorption of Mixed Heavy Metals**

Both DWSBC and DAWC showed good ability to remove the mixture of four heavy metals from aqueous phase (Figure 2-1). The removal efficiency of the four metals by DWSBC was higher than 97%, indicating this biochar has a strong affinity for all the tested heavy metals. DAWC also showed high removal efficiency for Pb²⁺ (99%) and Cu²⁺ (98%), but relatively low removal efficiency for Cd²⁺ (57%) and Ni²⁺ (26%).

Previous studies indicated that the effectiveness of biochar in the immobilization of heavy metals strongly depends on the metal contaminant type (Uchimiya et al., 2010). The two biochars, however, showed different trends in removal rates (ability) for the four metals in the mixed solution, indicating both metal and biochar type played important roles. Although the differences were very small, the removal ability of DWSBC for the metals followed the order of Cd>Ni>Pb>Cu. In contrast, DAWC followed the order of Pb>Cu>Cd>Ni, which is consistent with the removal efficiency trend of biochars converted from poultry litter (Uchimiya et al., 2010).

According to Shi et al. (2009), high sorption of Pb²⁺ from solution on sorbents through surface electrostatic attraction could be attributed to its high electronegativity constant (2.33), which results in a high tendency for specific adsorption. However, the electronegativity constants of Ni²⁺, Cu²⁺, and Cd²⁺ are 1.93, 1.90, and 0.69, respectively, is not consistent with the heavy metal removal trends for either DAWC or DWSBC. Surface electrostatic interaction, therefore, might not be a dominant heavy metal removal mechanism for these biochars. Other mechanisms, such as precipitation and surface complexation, should also be considered (Cao et al., 2009a; Inyang et al.,
2011b; Uchimiya et al., 2011). In the following sections, sorption of lead on DAWC and DWSBC was examined in greater detail to improve current mechanistic understanding of heavy metal removal by biochars from anaerobically digested biomass.

**Lead Sorption Kinetics**

DAWC and DWSBC sorbents showed similar lead sorption kinetics and reached apparent sorption equilibrium after about 24 h (Figure 2-2). There was an initial rapid increase in lead removal followed by a slow down as sorption approached equilibrium. Pseudo-first-order, pseudo-second-order, and Elovich models were used to simulate the sorption kinetics data collected. The governing equations can be written as (Gerente et al., 2007; Yao et al., 2011b).

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

First order \hspace{1cm} (2-1)

\[ q_t = \frac{k_2q_e^2t}{1+k_2q_e^2t} \]  

Second order \hspace{1cm} (2-2)

\[ q_t = \frac{1}{\beta} \ln(\alpha t + 1) \]  

Elovich \hspace{1cm} (2-3)

Where \( q_t \) (mmol kg\(^{-1}\)) and \( q_e \) (mmol kg\(^{-1}\)) are the amounts of lead sorbed at time \( t \) and at equilibrium respectively; \( k_1 \) (h\(^{-1}\)) and \( k_2 \) (kg mmol\(^{-1}\) h\(^{-1}\)) are the first-order and second order apparent sorption rate constants, respectively; and \( \alpha \) (mmol kg\(^{-1}\) h\(^{-1}\)) and \( \beta \) (kg mmol\(^{-1}\)) are the initial Elovich sorption and desorption rate constant at time \( t \), respectively. The first order, second order and Elovich models reproduced the sorption data closely for both biochars with coefficients of correlation all above 0.94 (Figure 2-2). While the Elovich model had the best fit for DWSBC with an \( R^2 \) of 0.97, the second-order model was a better fit for DAWC with an \( R^2 \) of 0.95 (Table 2-4). Fittings of the three models to DWSBC Pb sorption were slightly better than that of DAWC (Table 2-4),
suggesting that sorption of lead on DAWC was more energetically heterogeneous. Although those models assume different mechanisms (Gerente et al., 2007), comparisons of the fittings did not help reveal the governing mechanisms of lead sorption on the two biochars because there were only slight differences among the simulated results (Figure 2-2).

A plot of the pre-equilibrium sorbed Pb amounts against the square root of contact times for both biochar sorbents showed a strong linear dependency with an \( R^2 \) of 0.90 and 0.98 for DAWC and DWSBC, respectively (Figure 2-3). This strong linear relationship, along with the slow sorption rate prior to reaching equilibrium for both sorbents, suggests diffusion-controlled removal of Pb\(^{2+}\) by the two biochars. This diffusion rate could be controlled by each biochar’s intrapore dimensions, either for a surface adsorption or precipitation removal mechanism. The more rapid approach to Pb sorption equilibrium by DAWC and its larger pore volume is consistent with this interpretation.

**Lead Sorption Isotherms**

The lead sorption isotherms on the two biochars showed a very rapid increase in solid-phase concentrations, removing close to all the lead at low equilibrium solution concentrations (Figure 2-4). Above lead equilibrium solution concentrations of 0.5 mmol L\(^{-1}\), there was very little additional lead removal. Similar phenomena was observed for lead removal by biochars made from anaerobically digested bagasse, in which precipitation was shown to be the dominant sorption mechanism (Inyang et al., 2011b). Previous studies have demonstrated that slow release of negatively charged ions, such as carbonate and phosphate, from biochars can precipitate heavy metal ions,
particularly lead (Cao et al., 2009a; Inyang et al., 2011b). Because Pb$^{2+}$ has strong chemical affinity with those ions, biochar sorbents may completely remove lead from aqueous solutions when its initial concentration is low. When the initial lead concentration is high, however, Pb$^{2+}$ can consume all the available anions in solution and thus the isotherms will reach a plateau.

Comparisons between solution pH before (i.e., before adding biochar) and after sorption for different initial lead concentrations in the isotherm experiment (Figure 2-5) support the surface precipitation mechanism of lead removal by the two biochars. When the initial lead concentrations were low, solution pH increased from about 5 to about 10 after the lead was removed, which is consistent with the alkali nature of the biochars (Table 2-3). This was because initial lead concentration of lead was not high enough to consume all the carbonate and/or phosphate ions released by the biochars. Because both carbonate and phosphate have strong buffer capacities, their release from biochars could increase solution pH even if lead precipitation on biochar surfaces might release some H$^+$ under certain conditions. When the amount of lead in the solution was greater, the solution pH stayed unchanged or became lower because of the full consumption of these alkali ions (Figure 2-5). The fact that final pH reached the minimum at the same solvent concentration at which isotherm curve reached plateau further confirmed the importance of the surface precipitation mechanism (Figures 2-4 and 2-5).

The Langmuir (L), Freundlich (F) and Langmuir-Langmuir (LL) models were used to simulate the sorption isotherms of lead on the two biochars. These governing
equations (Equations 2-4 – 2.6) can be written as (Cao et al., 2009a; Gerente et al., 2007):

\[ q_e = \frac{KS_{\text{max}}C_e}{1 + KC_e} \]  

(2-4) Langmuir

\[ q_e = K_f C_e^n \]  

(2-5) Freundlich

\[ q_e = \frac{K_1S_{\text{max}}C_e}{1 + K_1C_e} + \frac{K_2S_{\text{max}}C_e}{1 + K_2C_e} \]  

(2-6) Langmuir-Langmuir

Where \( S_{\text{max}} \) (mmol kg\(^{-1}\)) is the maximum amount of Pb sorbed; \( K \) (L mmol\(^{-1}\)) and \( K_f \) (mmol\(^{(1-n)}\) L\(^n\) kg\(^{-1}\)) are the Langmuir adsorption constant related to the interaction bonding energies and the Freundlich equilibrium constant, respectively; \( C \) (mmol L\(^{-1}\)) is the equilibrium solution concentration of the sorbate; and \( n \) is the Freundlich linearity constant.

The models fit the experimental sorption data of DWSBC well, but failed to describe that of DAWC (Figure 2-3). The best-fit model for DAWC isotherm was the Freundlich model, but the \( r^2 \) was only 0.416 (Table 2-4). The failure of these models was probably due to the higher heterogeneity of DAWC, which was converted from digested dairy waste, a highly heterogeneous feedstock, a mixture of components with different compositions.

For lead sorption on DWSBC, the two Langmuir-based models (i.e., L and LL models) simulated the data better \((r^2 > 0.930)\) than the Freundlich model \((r^2 = 0.808)\) (Table 2-4). Although Langmuir-based models are developed for weak physical sorption, L or LL model can be used to describe the sorption of metals on biochars through precipitation (Cao et al., 2009a; Inyang et al., 2011b). Inyang et al. (2011b), indicated that precipitation of lead on biochar derived from anaerobically digested
bagasse could be modeled with the L model with a large bonding constant (K = 189 L mmol$^{-1}$). The Langmuir sorption constant for the DWSBC tested in this study was also very high (K = 266 L mmol$^{-1}$), confirming a strong affinity of lead. The Langmuir sorption capacity of lead sorption on the DWSBC was around 197 mmol kg$^{-1}$, which is comparable to that of commercial activated carbons (101 - 395 mmol kg$^{-1}$) and other biochar sorbents (11 - 680 mmol kg$^{-1}$) (Beesley & Marmiroli, 2011; Cao et al., 2009a; Inyang et al., 2011b; Liu & Zhang, 2009; Mohan et al., 2007; Uchimiya et al., 2010).

Although the Langmuir model could not be used, a rough estimation of the lead sorption capacity of DAWC directly from the plateau of the isotherm indicated that it should be even higher (> 200 L mmol$^{-1}$) than that of DWSBC (Figure 2-4). This confirms that biochars converted from anaerobically digested biomass can be used as effective sorbents to remove lead from aqueous solutions.

**Post-Sorption Characteristics and Sorption Mechanisms**

SEM image analysis of the post-sorption (Pb-laden) DAWC and DWSBC revealed the presence of many hexagonal and prismatic crystalline structures on their surfaces (Figure 2-6). The corresponding EDS spectra of the SEM image focusing area showed very high peaks of lead element, which demonstrated the presence of lead on surfaces of the post-sorption biochars. This strongly suggests the precipitation of lead mineral(s) from aqueous solution onto the biochar surfaces, because both the elemental analysis (Table 2-2) and the SEM-EDS analysis of pre-sorption biochars (Figure 2-7) showed no lead or crystals of this type in the original biochars.

Compared to pre-sorption biochars, XRD spectra of post-sorption biochars showed several new peaks at specific d-values associated with lead minerals, further supporting the precipitation mechanism of lead removal by the two biochars (Figure 2-
As discussed above, carbonate and/or phosphate released from the biochars can react with lead in aqueous solution to form stable minerals on biochar surfaces through following reactions in Equations 2.7 - 2.9:

\[ \text{Pb}^{2+} + \text{CO}_3^{2-} \rightarrow \text{PbCO}_3 \text{ cerrusite} \quad (2-7) \]

\[ 2\text{HCO}_3^- + 3\text{Pb}^{2+} + 4\text{OH}^- \rightarrow \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 + 2\text{H}_2\text{O} \text{ hydrocerrusite} \quad (2-8) \]

\[ 5\text{Pb}^{2+} + 3\text{H}_2\text{PO}_4^- + X^- \rightarrow \text{Pb}_5(\text{PO}_4)_3X_{(s)} + 6\text{H}^+ \text{ pyromorphite} \quad (2-9) \]

Where X can be either F\(^-\), Cl\(^-\), Br\(^-\), or OH\(^-\). Three types of lead minerals, cerrusite (PbCO\(_3\)), hydrocerrusite (Pb\(_3\)(CO\(_3\))\(_2\)(OH)\(_2\)), and pyromorphite (Pb\(_5\)(PO\(_4\))\(_3\)Cl), were identified in the post-sorption DAWC, indicating lead removal by DAWC could be controlled by all the three precipitation mechanisms (Equations 2.7 - 2.9). This was probably because DAWC was converted from a complicated feedstock (digested dairy waste) and thus could release both carbonate and phosphate to react with heavy metals in solution. Because of this heterogeneity, the ability of biochar from digested manure to sorb aqueous heavy metals might tend to fluctuate among samples, which may explain why the three sorption models failed to describe the isotherms of lead sorption on DAWC. In spite of the fluctuation, biochar converted from anaerobically digested dairy waste still has an unexceptionable ability to remove heavy metals from water (Figures 2-4).

Only one lead precipitate (hydrocerrusite), however, was found on the post-sorption DWSBC. Similarly, hydrocerrusite was also found in a recent study of lead sorption through precipitation on biochar converted from anaerobically digested sugarcane bagasse (Inyang et al., 2011b). XRD spectra of the pre-sorption biochars indicated the existence of calcite (CaCO\(_3\)) in both DAWC and DWSBC, which could be
the source of carbonates released into the solution. Carbonate minerals such as calcite have also been found in other biochars converted from other anaerobically digested biomass (Yao et al., 2011a). Anaerobic digestion may concentrate exchangeable cations, such as Ca$^{2+}$, K$^+$, Na$^+$, into residue materials (Gu & Wong, 2004; Hanay et al., 2008). Those cations could react with the dissolved CO$_2$ during anaerobic digestion to form carbonate minerals during slow pyrolysis (Inyang et al., 2010).

Surface organic functional groups of the two biochars converted from anaerobically digested biomass were characterized using FTIR spectroscopy (Figure 2-9). Functional group distributions of DAWC and DWSBC were similar to biochars made from other types of digested biomass (Inyang et al., 2010; Yao et al., 2011a). Although the two biochars had relatively high surface areas (Table 2-3), comparisons of pre- and post-sorption FTIR spectra for both DAWC and DWSBC showed high similarity, which provides no evidence of lead adsorption on biochar through interacting with the surface functional groups.

**Conclusion**

This study indicated that biochars produced from anaerobically digested biomass (dairy waste and sugar beets) can effectively remove heavy metals from aqueous solutions. The lead sorption capacity of the two biochars used in this study is comparable to that of commercial activated carbons. Thus, biochar converted from anaerobically digested biomass can be used as an alternative sorbent for activated carbon or other water purifiers to treat heavy metals in wastewater. High metal removal efficiency of biochars from digested feedstock suggests that anaerobic digestion could be used as a means of ‘biological activation’ to make high quality biochar-based sorbents.
Table 2-1. Summary of sources, health effects, and maximum contaminant levels of selected heavy metals in water (USEPA).

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Source</th>
<th>Potential health effect</th>
<th>Maximum contaminant level (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>Corrosion of household plumbing, erosion of natural deposits</td>
<td>Delays in physical or mental development in children, kidney problems and high blood pressure in adults</td>
<td>0.0</td>
</tr>
<tr>
<td>Copper</td>
<td>Corrosion of household plumbing, erosion of natural deposits</td>
<td>Gastrointestinal distress over short term, liver and kidney damage over long term</td>
<td>1.3</td>
</tr>
<tr>
<td>Nickel</td>
<td>Corrosion of steel pipes and metal fittings, erosion of rocks with nickel ore deposits, discharge from electroplating and battery industries.</td>
<td>Decreased body and organ weight.</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Corrosion of galvanized pipes, erosion of natural deposits, discharge from metal refineries, runoff from waste batteries</td>
<td>Itai-itai disease, renal and kidney damage, emphysema, hypertension and testicular atrophy</td>
<td>0.005</td>
</tr>
</tbody>
</table>
Table 2-2. Elemental composition (% mass based) of biochars used in this study.

<table>
<thead>
<tr>
<th>Biochar</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Zn</th>
<th>Mn</th>
<th>Cu</th>
<th>Fe</th>
<th>Al</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAWC</td>
<td>65.42</td>
<td>0.68</td>
<td>3.63</td>
<td>24.35</td>
<td>0.36</td>
<td>2.33</td>
<td>1.89</td>
<td>0.55</td>
<td>0.02</td>
<td>0.02</td>
<td>-a</td>
<td>0.09</td>
<td>0.16</td>
<td>-a</td>
</tr>
<tr>
<td>DWSBC</td>
<td>66.67</td>
<td>1.07</td>
<td>0.43</td>
<td>20.15</td>
<td>0.54</td>
<td>1.51</td>
<td>0.64</td>
<td>5.5</td>
<td>1.08</td>
<td>0.04</td>
<td>0.01</td>
<td>1.54</td>
<td>1.3</td>
<td>-a</td>
</tr>
</tbody>
</table>

a:<0.01

Table 2-3. Relevant physiochemical properties of biochars used in this study

<table>
<thead>
<tr>
<th>Biochar</th>
<th>pH</th>
<th>CO₂ Surface Area (m²/g)</th>
<th>N₂ Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Zeta Potential (mv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAWC</td>
<td>10.0</td>
<td>555.2</td>
<td>161.2</td>
<td>0.147</td>
<td>-29.18</td>
</tr>
<tr>
<td>DWSBC</td>
<td>9.0</td>
<td>128.5</td>
<td>48.6</td>
<td>0.034</td>
<td>-15.85</td>
</tr>
</tbody>
</table>
Table 2-4. Best-fit model parameters of lead removal from aqueous solutions on DAWC and DWSBC

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Model</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>Parameter 3</th>
<th>Parameter 4</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAWC</td>
<td>First-order</td>
<td>$k_1 = 0.280$</td>
<td>$q_e = 266$</td>
<td>–</td>
<td>–</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>Second-order</td>
<td>$k_2 = 0.00100$</td>
<td>$q_e = 311$</td>
<td>–</td>
<td>–</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>$\alpha = 174$</td>
<td>$\beta = 0.014$</td>
<td>–</td>
<td>–</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>$K = 928$</td>
<td>$S_{max} = 248$</td>
<td>–</td>
<td>–</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>$K_f = 248$</td>
<td>$n = 0.0619$</td>
<td>–</td>
<td>–</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>Double Langmuir</td>
<td>$K_1 = 1120$</td>
<td>$S_{max1} = 234$</td>
<td>$K_2 = 0.0023$</td>
<td>$S_{max2} = 1.90$</td>
<td>0.12</td>
</tr>
<tr>
<td>DWSBC</td>
<td>First-order</td>
<td>$k_1 = 0.181$</td>
<td>$q_e = 203$</td>
<td>–</td>
<td>–</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>Second-order</td>
<td>$k_2 = 0.000760$</td>
<td>$q_e = 250$</td>
<td>–</td>
<td>–</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>$\alpha = 67.7$</td>
<td>$\beta = 0.0150$</td>
<td>–</td>
<td>–</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>$K = 266$</td>
<td>$S_{max} = 197$</td>
<td>–</td>
<td>–</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>$K_f = 189$</td>
<td>$n = 0.140$</td>
<td>–</td>
<td>–</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>Double Langmuir</td>
<td>$K_1 = 351$</td>
<td>$S_{max1} = 172$</td>
<td>$K_2 = 2.87$</td>
<td>$S_{max2} = 43.90$</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Figure 2-1. Removal of heavy metals from aqueous solution by the two biochars converted from anaerobically digested biomass.
Figure 2-2. Kinetics of lead removal from solution by the two biochars converted from anaerobically digested biomass. A) DAWC and B) DWSBC
Figure 2-3. Relation between the amounts of Pb removed by the two biochars converted from anaerobically digested biomass. A) DAWC and B) DWSBC and square root of time before equilibrium.
Figure 2-4. Isotherms of lead removal from solution by the two biochars converted from anaerobically digested biomass. A) DAWC and B) DWSBC.
Figure 2-5. Changes in solution pH during lead removal from solution by the two biochars converted from anaerobically digested biomass. A) DAWC and B) DWSBC.
Figure 2-6. SEM image (left) and corresponding EDS spectra (right) of post-sorption lead loaded digested biochars. A) DAWC and B) DWSBC at 10,000 X. The EDS spectra were recorded at the location shown in the SEM image.
Figure 2-7. SEM image (left) and corresponding EDS spectra (right) of pre-sorption digested biochars. A) DAWC and B) DWSBC at 5000X. The EDS spectra were recorded at the same location shown in the SEM image.
Figure 2-8. XRD spectra of pre- and post-sorption digested biochars. A) DAWC and B) DWSBC.
Figure 2-9. FTIR spectra of pre- and post-sorption digested biochars. A) DAWC and B) DWSBC.
CHAPTER 3
FILTRATION OF ENGINEERED NANOPARTICLES IN CARBON-BASED FIXED BED COLUMNS

Introduction

Engineered nanoparticles (ENPs) have become the foundation of a novel brand of technology, impacting consumer products, manufacturing techniques, and material usages (Albrecht et al., 2006). This can be attributed to their intrinsic properties, such as high surface area to volume ratio, small size (1-100nm), and unsaturated surface atoms that readily bind to other atoms (Christian et al., 2008; Ghaedi et al., 2012b). In addition, most ENPs exhibit various quantum effects such as resonance, optical properties, mechanical strength, thermal and electrical conductivity that can be exploited in the development of various household and industrial applications (Nowack & Bucheli, 2007). The projected global demand for nano-material products is expected to reach $1 trillion dollars in 2015 (Eckelman et al., 2008; Nowack & Bucheli, 2007), which will increase loadings of ENPs to the environment and further pose a risk to soil and groundwater systems.

ENPs may be released into the environment from both point sources (e.g., production facilities, landfills, and wastewater treatment plants) and non-point sources (e.g., accidental spills and wear from ENP products) (Nowack & Bucheli, 2007). As a result, the occurrences of ENPs in aquatic systems, particularly from municipal discharges and wastewater treatment plants, have been reported in several recent studies (Baun et al., 2008; Isaacson et al., 2009; Upadhyayula et al., 2012). Because of

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the potential toxic effect of ENPs to aquatic ecosystems (Petersen et al., 2010; Tervonen et al., 2009; Wiesner et al., 2009), it is crucial to develop cost-effective treatment technologies to remove them from water systems. To our knowledge, however, only little research has been conducted to study the removal of aqueous ENPs, particularly with respect to evaluating the removal ability of carbon-based filters to ENPs in aqueous solutions.

Biochar is pyrogenic black carbon derived from the thermal degradation of carbon-rich biomass in an oxygen-limited environment. Recent studies have demonstrated that biochars can be used as low-cost adsorbents to remove various contaminants from water (Inyang et al., 2011b; Inyang et al., 2012; Xue et al., 2012; Yao et al., 2011a; Yao et al., 2011b). It is estimated that the production cost of biochar from a typical biomass is around 0.076 U.S. dollar per kilogram (Yoder et al., 2011), much lower than other commercial carbon-based adsorbents including activated carbon (1.44 – 2.93 U.S. dollar per kilogram) (Lima et al., 2008). This promising new carbon material (particularly after further modifications) could be used as potential filter media to remove ENPs from water, although further testing is still needed. Most biochars are predominantly negatively charged (Inyang et al., 2010; Yao et al., 2012c), and may readily bind positively charged ENPs through electrostatic attractions. Plant and animal derived biochars produced at relatively high temperatures (> 400 °C) may also contain disordered aromatic hydrocarbon sheets that can donate or accept π-electrons for electrostatic attractions and bonding of ENPs on oxidized graphene sheets in biochars (Keiluweit & Kleber, 2009). The possibility of retaining ENPs on biochars is further enhanced by the presence of functional groups of different surface charges that co-exist
within the outer surface and pores of biochars. These functional groups could coordinate, or complex with ENPs to sequester them on biochar surfaces.

Today, several modification/engineering methods have been recently developed to improve the retention of biochar based sorbents to aqueous contaminants (Xue et al., 2012; Yao et al., 2011a), which could also be applied for the removal of ENPs. Nevertheless, most current studies have focused on the use of activated carbons and other high tech sorbents to remove ENPs from water (Ghaedi, 2012; Ghaedi et al., 2012a; Ghaedi et al., 2012b; Marahel et al., 2012; Yao et al., 2012a) and, there is no research effort devoted to the development of a biochar-based technology for the removal of aqueous ENPs.

Filtration and transport of ENPs in porous media, particularly in artificial soil columns packed with quartz sand, have been recently investigated (Lecoanet & Wiesner, 2004; Tian et al., 2010; Tian et al., 2012c; Tian et al., 2011; Wang et al., 2012a). Findings from those studies have demonstrated that the retention and transport of ENPs in porous media are controlled by several factors, such as surface charge, particle shape and size, and solution chemistry (Lecoanet & Wiesner, 2004; Tian et al., 2012d; Tian et al., 2011). The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has been applied to quantify the attractive and repulsive interaction forces between ENPs and porous medium grains (Tian et al., 2010). In addition, it has been reported that theories and models developed for simulating the filtration and transport behaviors of colloidal particles in porous media can be modified or applied directly to that of ENPs (Tian et al., 2010). Thus, it is anticipated that those theories and models could also be used to describe the filtration of ENPs in carbon-based filters (porous media).
The overarching objective of this study was to evaluate and compare the effectiveness of several carbon-based materials, including biochar, in retaining three types of ENPs: nano titanium dioxide (NTiO$_2$), silver nanoparticle (AgNP), and multi-walled carbon nanotubes (CNT). These nanoparticles are among the most popular ENPs employed in industrial and household applications (El-Sheikh et al., 2007; Ghaedi, 2012; Leonard & Setiono, 1999; Li et al., 2011a; Lu et al., 2009; Sumesh et al., 2011). A biochar produced from hickory wood (HC), an activated carbon (AC), and Fe-modified HC and AC were used as carbon sorbents in both batch and fixed-bed settings to test their sorption of the three ENPs. Simulations of mathematical models (i.e., DLVO theory and colloid transport model) were used to help data analysis and aid in the interpretation of experimental results. The specific objectives of this study were to: (a) evaluate and compare the ability of the carbon materials to sorb and filter the ENPs, (b) compare the mobility of the three ENPs in the carbon filters, and (c) determine whether biochar can be used as an effective filter media for the ENPs.

Materials and Methods

Materials

NTiO$_2$, AgNP, and CNT nanoparticle powders were obtained from Sinonano Company (China), Particle Engineering and Research Center (University of Florida), and Shenzhen Nanotech Port Co. (China), respectively. Their solutions were prepared by adding 20 mg each to 200 mL of de-ionized (DI) water and sonicated in an ultrasound homogenizer (Model 300 V/T, Biologics, Inc.) for 1 h at pulse intervals of 12 mins. The resulting suspensions were used as stock solutions for subsequent batch-sorption and filtration studies. Zeta potential and the effective diameters (i.e., hydrodynamic diameters) of the nanoparticles were measured with a 10 ppm
suspension diluted from the stock (same solution chemistry) using a Brookhaven Zeta Plus (Brookhaven Instruments, Holtsville, NY), and followed the procedures of previous studies (Tian et al., 2010; Wang et al., 2012a).

Hickory chips were obtained from the UF North Florida Research and Education Center as feedstock for biochar production. About 500 g of the dried hickory chips were converted into HC through slow pyrolysis at 600 °C for 2 h in a nitrogen environment in a furnace (Olympic 1823HE), following the procedures of (Inyang et al., 2012). Granular AC (coconut shell, steam activated) was purchased from Fisher Scientific (Suwanee, Georgia). All other chemical reagents employed in this study were of high purity grade, from Fisher Scientific, Suwanee, Georgia. The HC and AC samples were ground and sieved to 0.5 – 1 mm sized particles. After several rinses with deionized distilled water, both HC and AC were dried at 80 °C for further testing and Fe-modification. The iron modified carbons (i.e., HC-Fe and AC-Fe) were produced using previously reported method (Chen et al., 2007; Thirunavukkarasu et al., 2003). Briefly, 2g each of HC and AC were added to 8 mL of 2 M Fe(NO$_3$)$_3$ solution, about 3ml of 10 M NaOH was then added to create an iron-precipitate on the carbon surfaces. The mixtures were dried at 105 °C and then rinsed with DI water before use. Quartz sand (1.3mm-sized) was obtained from Standard Sand and Silica Co. as reference filter media. The sand was washed sequentially with tap water, 10% nitric acid and deionized water, and baked at 550 °C to remove metal oxides and organic impurities before use (Tian et al., 2010).

**Batch Sorption**

An initial evaluation of the sorption ability of HC, HC-Fe, AC, AC-Fe and sand to the nanoparticles was performed in batch experiments. About 0.1 g of each sorbent was added into 68ml digestion vessels (Environmental Express), and mixed with 50ml of 10
ppm ENP solutions at room temperature of \((22 \pm 0.5 \, ^\circ C)\). The sample solutions with their corresponding blanks and experimental controls (without sorbent or sorbate) were agitated for 3 h on a reciprocating shaker, and withdrawn at the end of 3 h to examine their sorption capacities on a UV-VIS spectrophotometer. Measurements of NTiO2, AgNP, and CNT concentrations on the UV-VIS spectrophotometer were conducted at wavelengths of 655 nm, 645 nm, and 255 nm, respectively (Tian et al., 2010; Wang et al., 2012a). ENP concentrations on the sorbents were calculated based on the differences between initial and final aqueous solutions. The experiments were performed in duplicate and average values were used in the analysis.

**Column filtration**

The carbon sorbents were wet-packed with sand in laboratory columns measuring 1.56 cm in diameter and 5.6 cm in height following the procedures of Xue et al. (Xue et al., 2012). About 5.5 g of sand was used at each end of the column to help distribute the flow, and the carbon sorbent was sandwiched between the sand inside the column. The heights of the lower sand, carbon, and upper sand layers in the column were 2.34 cm, 1.28 cm, and 2.50 cm respectively. Columns packed with sand only were also used in the experiment. For each experiment, the column was first flushed with DI water for 2 h to equilibrate it. A peristaltic pump (Masterflex L/S, Cole Parmer Instrument, Vernon Hills, IL) was then connected to the influent (bottom) of the column to maintain an upward flow rate of 1 ml min\(^{-1}\). The filtration experiment was initiated by switching the influent to a 10 ppm ENP solution for 3 h followed by 2 h of DI water flushing. Effluent samples from the columns were collected with a fraction collector (IS-95 Interval Sampler, Spectrum Chromatography, Houston, TX) during the experiment to determine the ENP concentrations with the UV-VIS spectrophotometer.
Characterizations

Carbon, hydrogen, and nitrogen contents of the carbon sorbents were determined using a CHN elemental analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion followed by infrared detection of the resulting CO₂, H₂ and NO₂ gases. Major inorganic elemental constituents, pH, zeta potential, and surface area of all the sorbents were determined using previously reported methods (Inyang et al., 2012; Yao et al., 2011a). Bulk density of the carbon sorbents and sand materials were determined using the tap and fill method reported previously (Abdullah & Wu, 2009). X-ray diffraction (XRD) analysis was conducted on these HC, HC-Fe, AC, AC-Fe samples to identify possible crystalline structures. A computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator was used to obtain diffraction patterns.

Mathematical Models

The filtration and transport of the ENPs in fixed-bed columns was described by the advection-dispersion equation (ADE) based on the colloid filtration theory (Yao et al., 1971):

\[
\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} 
\]

\[
\frac{\rho_b}{\theta} \frac{\partial S}{\partial t} = k_d C
\]

(3-1)

(3-2)

Where \( C \) is the sorbate concentration in pore water (mg L\(^{-1}\)), \( t \) is the time (min), \( \rho_b \) is the medium bulk density (g L\(^{-1}\)), \( \theta \) is the dimensionless volumetric moisture content (porosity), \( S \) is the adsorbed particle concentration (mg g\(^{-1}\)), \( z \) is the distance travelled in the direction of the flow (cm), \( D \) is the dispersion coefficient (cm\(^2\) min\(^{-1}\)), \( v \) is the average
linear pore-water velocity (cm min\(^{-1}\)), and \(k_d\) is the removal or deposition rate constant (min\(^{-1}\)). Equation (3-1) was solved numerically with a zero initial concentration, pulse-input and a zero concentration-gradient boundary conditions for the carbon layer. The Levenberg-Marquardt algorithm was used to estimate the value of the model parameters by minimizing the sum-of-the squared differences between model-calculated and measured effluent ENPs concentrations over multiple calculation interactions.

The classic DLVO theory was used to determine the interaction energies between the ENP and filter media (Shen et al., 2007). The Lifshitz-van der Waals attraction energy (\(\Delta G^{LW}\)) (Equation 3-3) and the electric double layer repulsion energy (\(\Delta G^{EDL}\)) for a sphere-plate system (Equation 3-4) were used to determine the total DLVO energy between the ENPs and sorbents (Tian et al., 2010; Vanoss et al., 1990):

\[
\Delta G^{LW} = -\frac{A}{6} \left[ \frac{r}{h} + \frac{r}{h+2r} + \ln\left( \frac{h}{h+2r} \right) \right]
\]

(3-3)

\[
\Delta G^{EDL} = 64\pi\varepsilon\varepsilon_0 \left[ \frac{kT}{ze} \right]^2 \tanh\left[ \frac{ze\psi_1}{4kT} \right] \tanh\left[ \frac{ze\psi_2}{4kT} \right] \exp(-kh)
\]

(3-4)

\[
\psi = \zeta \left( 1 + \frac{d}{r} \right) \exp(\kappa z)
\]

(3-5)

Where \(A\) is the Hamaker constant, \(h\) is the separation distance, \(r\) is the radius of the sorbent, \(\varepsilon\) is the dielectric constant of the medium (78.4 for water, \(\varepsilon_0\) is the vacuum permittivity (8.854*10\(^{-12}\) C\(^2\)N\(^{-1}\)m\(^{-2}\)), \(k\) is the Boltzmann’s constant (1.381*10\(^{-23}\) C\(^2\)J K\(^{-1}\)), \(T\) is the temperature, \(z\) is the valence electrolyte, \(e\) is the electron charge (1.602*10\(^{-19}\) C), \(\psi_1\) and \(\psi_2\) are the surface potentials of the ENPs and the filter medium (carbon and
sand surface) for respective zeta potential, $\zeta$, and $k$ is the reciprocal of the Debye length.

**Results and Discussion**

**Properties of ENPs and Carbons**

Elemental analysis of the carbon sorbents (Table 3-1) showed that AC, HC, AC-Fe, and HC-Fe had varied amounts of inorganic constituents with more predominant amounts of carbon observed. In particular, elemental iron content in the raw carbon materials (AC and HC) was observed to significantly increase by a 100 fold after impregnation with iron in AC-Fe and HC-Fe. Slightly higher amounts of iron were noted in AC-Fe (2.33 %) than in HC-Fe (1.03 %), probably because AC (pH 7.1) is less basic than the HC (pH 8.5). Recently, Nieto-Delgado and Rangel-Mendez (Nieto-Delgado & Rene Rangel-Mendez, 2012; Ofir et al., 2007) suggested that irons may be more effectively anchored on acidic carbons than on basic ones.

Typically, the precipitation of Fe (III) on carbon surfaces is known to enhance their interaction with negatively charged contaminant species, such as phosphate, arsenic, and colloids (including ENPs) (Chen et al., 2007; Nieto-Delgado & Rene Rangel-Mendez, 2012; Ofir et al., 2007; Wang et al., 2012b). Moreover, the precipitation may promote the electron transfer of $O_2$ from the aqueo-iron complex to the metal cation (i.e., Fe), weakening the O-H bond of the complex, to release protons into the reaction media (Nieto-Delgado & Rene Rangel-Mendez, 2012; Ofir et al., 2007). As a result, the pH of AC-Fe (4.7) and HC-Fe (4.9) was observed to be lower than that of their original carbons. The zeta potential values of AC-Fe and HC-Fe were also less negative than the AC and HC (Table 3-2), confirming the presence of iron particles on carbon surfaces. All ENPs used in this study were predominantly negatively charged at
their original pH (Table 3-2). Surface areas and pore volumes of the ENPs were much smaller than those of the carbon materials, suggesting that the ENPs could also be physically sorbed on the surface sites within the carbon matrix.

**Batch Sorption**

Batch experiments demonstrated that the carbons were better sorbents than the pure sand (Figure 3-1). In addition, iron-impregnation improved the sorption of the ENPs on the carbon sorbents. This improvement was more significant in the removal of CNT (Figure 3-1 a) and NTiO₂ (Figure 3-1 b) than in the removal of AgNPs by the iron-modified carbons (Figure 3-1 c). The raw carbons showed lower removal of the ENPs and the lowest removal was observed for CNT, possibly because of the surface similarities between the carbon sorbents and the CNT (both surfaces are highly negatively charged). The removal of the three ENPs by the Fe-modified biochar (HC-Fe) (with lower loadings of Fe) was the highest and was even higher than that of Fe-modified activated carbon (AC-Fe). This indicated that the biochar-based sorbent could be a better (more cost-effective) option to be used in the filter for ENPs. Although the removal efficiency trends of ENPs by carbon materials can be evaluated from batch sorption studies, batch experiments usually are conducted under optimized conditions, which may not reflect ‘real’ sorption efficiency of the sorbents under dynamic conditions. For example, although the solution chemistry of the batch and column experiments was identical, the contact time between ENPs and adsorbents of the adsorption experiments (i.e., 3 h) was much longer than that of the filtration tests (less than 3 mins).

**ENP Filtration and Transport in Fixed-Bed Columns**

The transport of the ENPs in the fixed-bed columns (Figure 3-2 a - c) showed rapid breakthrough responses and the effluent concentrations reached a plateau about
30 mins after the ENP injections. The breakthrough curves returned to the baseline level after the columns were flushed with DI water, reflecting the completion of the breakthrough process. Peak concentrations of ENPs in the columns packed with unmodified carbons (i.e. HC or AC) were similar to or even higher than that in the reference sand columns, indicating the HC or AC could not improve the ENP filtration in the fixed-bed columns. This result is different from findings in the batch sorption experiments, probably due to difference in sorption dynamics of the two systems as discussed above. Except the AC-Fe filters for AgNP, performances of the iron-modified carbon (i.e., AC-Fe or HC-Fe) filters were better and the peak breakthrough concentrations of the ENPs were lower than that of other sorbents. This further confirmed that iron modification can improve the removal of ENPs by the filters.

Previous studies have reported that the interaction between impregnated metal oxyhydroxides, including Fe(OH)_3, and colloidal/nanosized particles can increase intra-particle bridging and reduce the electron double layer repulsions to facilitate particle deposition in filter media (Ofir et al., 2007; Yao et al., 1971). Among all the filters, HC-Fe showed the best filtration performance for all the ENPs, which is consistent with the batch sorption experimental data. The iron modified biochar is a better ENP filter material than AC-Fe and can be used to remove ENPs from water. Among the three ENPs, CNT showed the highest peak breakthrough concentrations for all the tested experimental conditions, which corresponded to the findings of the batch study. The poor interactions between CNT and pyrolyzed carbons (AC and HC) may have resulted from high amorphicity and relatively few graphitic sites on the carbons that could have limited π-π interactions between the CNT and the carbon (Keiluweit & Kleber, 2009).
addition, previous studies have also indicated that tubular CNTs may have higher mobility in porous media than spherical ENPs because they can orient parallel to the streamlines in the flow to reduce their retention (Tian et al., 2012a; Tian et al., 2011).

Under the tested experimental conditions, surfaces of the three ENPs and carbon materials were all negatively charged (Table 3-2). The solution chemistry therefore was unfavorable for the attachment of the nanoparticles to the carbon surfaces (Tian et al., 2012d; Wang et al., 2012a), which explains why the HC and AC enabled columns showed no difference to the reference sand column. Although, the presence of iron hydroxides on the carbon surfaces did not alter the overall surface charge to positive (Table 3-2), it greatly reduced the surface potential, to promote the deposition of nanoparticles on carbon surfaces (enhance attachment efficiency) (Morales et al., 2011; Wu et al., 2012b). Because, iron hydroxides are positively charged under most practical circumstances, they may also introduce charge heterogeneity to the carbon surfaces, which could serve as the sorption sites dominating the filtration and transport of nanoparticles in the fixed-bed columns (Tian et al., 2010; Tian et al., 2012c).

**Modeling of ENPs Filtration and Transport**

The ADE model reproduced the experimental data closely with good coefficients of correlation ($R^2 > 0.90$) (Table 3-3). The model estimated removal rate constants ($k_d$) for the ENPs in various filter media as ranging between 0.04 - 0.07 min$^{-1}$ for NTiO$_2$, and 0.05 - 0.07 min$^{-1}$ for AgNP, with least retention rates for CNT ranging from 0.005 - 0.02 min$^{-1}$, further supporting the discussion above. As shown in Table 3-3, the $k_d$ values of the iron modified carbons were generally much higher than that of the other sorbents, except for the $k_d$ of AgNP removal by the AC-Fe. The $k_d$ values of HC-Fe were the
highest for each nanoparticle, further confirming that the iron-modified biochar can be used as an alternative, low-cost adsorbent for the treatment of ENPs in wastewater.

The optimized filter length \( L_0 = -\frac{v}{k_d} \ln \frac{C}{C_0} \), where \( v \) (cm min\(^{-1}\)) is the fluid pore velocity and \( C/C_0 \) is 0.001, at which 99.9% of the ENPs are filtered from the solution (Wang et al., 2008), was calculated using the model-estimated \( k_d \). Compared to other ENPs, the estimated \( L_0 \) values were highest (422 – 1450 cm) for CNT (Table 3-3), indicating it requires more filter material for its complete removal, especially for the unmodified carbons. The \( L_0 \) values for NTiO\(_2\) and AgNP ranged between 141 – 217 cm and 118 -170 cm, respectively, indicating these two ENPs require less amount of filter media to remove them from solution. Although the HC-Fe was the most effective, it still requires the filter to be designed at 116, 118, and 422 cm to remove NTiO\(_2\), AgNP, and CNT, respectively.

DLVO interaction energy profiles were calculated to evaluate the relative contributions of van der Waals and electrostatic interactions to the interactions between the ENPs and carbon or sand surfaces. The Hamaker constants of the van der Waals interactions between the ENPs and the filter media in water were determined from previously reported individual Hamaker value of pyrolyzed carbon (6x10\(^{-20}\) J) (Maurer et al., 2001), sand (8.8x10\(^{-20}\) J) (Tian et al., 2010), CNT (8.2x10\(^{-20}\) J) (Tian et al., 2010), NTiO\(_2\) (6x10\(^{-20}\) J) (Butt et al., 2005), and for AgNP (38.5x10\(^{-20}\) J) (Butt et al., 2005). Electrolyte concentrations of the filtrate solutions were assumed as 0.001 M for raw carbons and quartz sand, while 0.01 M was assumed for the iron impregnated carbons.

For all the ENPs, the interaction energy profiles were characterized by the absence of an attractive primary minimum and the presence of high energy barriers in
both sand and carbon media (Figure 3-3). In particular, the highest energy barriers were observed for CNT transport in both sand and carbon media ranging between 135 – 235 KT (Figure 3-3 a), with no obvious secondary minimums observed for the unmodified carbons. The presence of such high energy barrier would limit the deposition of the CNT on the unmodified carbon surface, which is consistent with the batch and column experimental data. A deep secondary minimum well for CNT was observed for the iron-modified carbons (HC-Fe and AC-Fe) at separation distance of 7 nm (Figure 3-3 a), suggesting that the CNT can attached to the iron-modified carbon surfaces through secondary-minimum deposition (Tufenkji & Elimelech, 2005). Because effective diameter (hydrodynamic diameter) was used in the calculations to determine the DLVO interaction between tubular CNTs and the filter media, the results may not reflect the actual interactions and may overestimate the repulsive forces (Tian et al., 2012d; Wang et al., 2008). Previous studies of CNT transport in porous media, however, suggested that this approach might be used as exploratory estimations (Tian et al., 2010; Tian et al., 2012c; Tian et al., 2011; Wang et al., 2008). A new or modified DLVO theory is thus necessary to better describe the filtration of CNTs in carbonaceous filters.

Much lower energy barriers were observed for both NTiO2 (15 – 40 KT, Figure 3-3 b) and AgNP (15 - 60 KT, Figure 3-3 c) to the sorbents, which correlates with earlier findings of higher filtration of NTiO2 and AgNP in the columns. Similarly, the DLVO energy profiles for AgNP and NTiO2 (Figure 3-3 b and c) did not show any obvious secondary minimums for the deposition of AgNP and NTiO2 on the raw carbons (HC and AC), but showed shallow secondary minimum wells at separation distance of ~20 nm for the iron-modified carbons. This also suggested that AgNP and NTiO2 can attach
to the iron-modified carbon surfaces through secondary-minimum deposition (Tufenkji & Elimelech, 2005).

In addition to electrostatic interactions, the existence of other possible mechanisms was further probed using XRD analysis (Figures 3-4). XRD patterns, however, did not show any crystalline structures on the post-filtration samples (Figures 3-10 and 3-11). This result could rule out the possibility of any precipitation mechanisms for the attachment of the ENPs on the carbon surfaces.

**Conclusion**

The removal efficiencies of unmodified and iron-impregnated carbons to three ENPs were evaluated with both experimental and modeling investigations. The results indicated that iron-impregnation improved the removal ability of the carbons for the ENPs. Among all the carbon sorbents, the iron-modified biochar was the best filter material, suggesting that biochar-based sorbents can be used in low-cost filters for ENP removal. Because CNT showed high mobility in all the carbon-enabled filters, additional investigations are still needed to further modify the biochar to enhance its ability to remove CNTs from water.
### Table 3-1. Elemental composition of carbon materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P%</th>
<th>K%</th>
<th>Ca%</th>
<th>Mg%</th>
<th>Zn%</th>
<th>Mn%</th>
<th>Cu%</th>
<th>Fe%</th>
<th>Al%</th>
<th>Ni%</th>
<th>Pb%</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>O%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>0.02</td>
<td>0.24</td>
<td>0.82</td>
<td>0.13</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>0.01</td>
<td>0.06</td>
<td>a</td>
<td>a</td>
<td>81.81</td>
<td>2.17</td>
<td>0.73</td>
<td>14.02</td>
</tr>
<tr>
<td>HC-Fe</td>
<td>0.02</td>
<td>0.03</td>
<td>0.43</td>
<td>0.16</td>
<td>a</td>
<td>0.02</td>
<td>a</td>
<td>1.03</td>
<td>0.03</td>
<td>a</td>
<td>a</td>
<td>80.54</td>
<td>1.65</td>
<td>1.34</td>
<td>16.48</td>
</tr>
<tr>
<td>AC</td>
<td>0.01</td>
<td>0.09</td>
<td>0.17</td>
<td>0.08</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>0.02</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>86.07</td>
<td>0.12</td>
<td>1.17</td>
<td>17.05</td>
</tr>
<tr>
<td>AC-Fe</td>
<td>a</td>
<td>0.02</td>
<td>0.14</td>
<td>0.04</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>2.33</td>
<td>0.03</td>
<td>a</td>
<td>a</td>
<td>75.06</td>
<td>0.61</td>
<td>0.57</td>
<td>23.77</td>
</tr>
</tbody>
</table>

a < 0.01%

### Table 3-2. Physiochemical properties of filter materials and engineered nanoparticles (ENPs).

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>BET N2 Surface area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Zeta Potential (mv)</th>
<th>Effective diameter (nm)</th>
<th>Bulk density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>8.5</td>
<td>431.0</td>
<td>0.20</td>
<td>-43.7</td>
<td>n.d</td>
<td>0.4</td>
</tr>
<tr>
<td>HC-Fe</td>
<td>4.9</td>
<td>12.5</td>
<td>0.00</td>
<td>-18.8</td>
<td>n.d</td>
<td>0.4</td>
</tr>
<tr>
<td>AC</td>
<td>7.1</td>
<td>956.2</td>
<td>0.30</td>
<td>-28.9</td>
<td>n.d</td>
<td>0.6</td>
</tr>
<tr>
<td>AC-Fe</td>
<td>4.7</td>
<td>1090.0</td>
<td>0.03</td>
<td>-19.8</td>
<td>n.d</td>
<td>0.5</td>
</tr>
<tr>
<td>Sand</td>
<td>6.5</td>
<td>nd</td>
<td>nd</td>
<td>-40.4</td>
<td>n.d</td>
<td>1.4</td>
</tr>
<tr>
<td>CNT</td>
<td>6.6</td>
<td>142.0</td>
<td>0.10</td>
<td>-46.3</td>
<td>140.0</td>
<td>n.d</td>
</tr>
<tr>
<td>TiO2</td>
<td>6.8</td>
<td>58.8</td>
<td>0.00</td>
<td>-11.0</td>
<td>90.0</td>
<td>n.d</td>
</tr>
<tr>
<td>AgNP</td>
<td>7.9</td>
<td>30.7</td>
<td>0.00</td>
<td>-35.1</td>
<td>52.4</td>
<td>n.d</td>
</tr>
</tbody>
</table>

nd- not determined
Table 3-3. Best-fit model parameters for ENP transport in various filter media.

<table>
<thead>
<tr>
<th>Filter Media</th>
<th>Nanoparticles</th>
<th>$K_d$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>Maximum column length $L_{\text{max}}$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>NTiO$_2$</td>
<td>0.045</td>
<td>0.992</td>
<td>173</td>
</tr>
<tr>
<td>HC</td>
<td>NTiO$_2$</td>
<td>0.038</td>
<td>0.961</td>
<td>206</td>
</tr>
<tr>
<td>HC-Fe</td>
<td>NTiO$_2$</td>
<td>0.067</td>
<td>0.995</td>
<td>116</td>
</tr>
<tr>
<td>AC</td>
<td>NTiO$_2$</td>
<td>0.036</td>
<td>0.996</td>
<td>217</td>
</tr>
<tr>
<td>AC-Fe</td>
<td>NTiO$_2$</td>
<td>0.055</td>
<td>0.991</td>
<td>141</td>
</tr>
<tr>
<td>Sand</td>
<td>CNT</td>
<td>0.006</td>
<td>0.965</td>
<td>1430</td>
</tr>
<tr>
<td>HC</td>
<td>CNT</td>
<td>0.008</td>
<td>0.908</td>
<td>1045</td>
</tr>
<tr>
<td>HC-Fe</td>
<td>CNT</td>
<td>0.019</td>
<td>0.933</td>
<td>422</td>
</tr>
<tr>
<td>AC</td>
<td>CNT</td>
<td>0.005</td>
<td>0.997</td>
<td>1450</td>
</tr>
<tr>
<td>AC-Fe</td>
<td>CNT</td>
<td>0.014</td>
<td>0.994</td>
<td>567</td>
</tr>
<tr>
<td>Sand</td>
<td>AgNP</td>
<td>0.046</td>
<td>0.930</td>
<td>170</td>
</tr>
<tr>
<td>HC</td>
<td>AgNP</td>
<td>0.062</td>
<td>0.989</td>
<td>129</td>
</tr>
<tr>
<td>HC-Fe</td>
<td>AgNP</td>
<td>0.066</td>
<td>0.985</td>
<td>118</td>
</tr>
<tr>
<td>AC</td>
<td>AgNP</td>
<td>0.053</td>
<td>0.993</td>
<td>147</td>
</tr>
<tr>
<td>AC-Fe</td>
<td>AgNP</td>
<td>0.048</td>
<td>0.993</td>
<td>166</td>
</tr>
</tbody>
</table>
Figure 3-1. Removal efficiency of ENPs in batch sorption study. A) CNT, B) NTiO2, and C) AgNP.
Figure 3-2. Filtration and transport of ENPs in fixed-bed columns. A) CNT, B) NTiO$_2$, and C) AgNP.
Figure 3-3. Derjaguin-Landau-Verwey-Overbeek (DLVO) energy interactions between filter media and ENPs. A) CNT, B) NTiO₂, and C) AgNP.
Figure 3-4. XRD patterns for A) raw and post filtration carbons loaded with AgNP and B) raw and post filtration carbons loaded with NTiO₂. Minerals detected were peak labeled as C for calcite (CaCO₃), A for anatase (TiO₂), Q for quartz (SiO₂), and Ag for metallic silver (Ag).
CHAPTER 4
SYNTHESIS, CHARACTERIZATION AND DYE SORPTION ABILITY OF CARBON NANOTUBES-COATED BIOCHAR COMPOSITES

Introduction

The use and release of organic dyes in many industrial products are a threat to water systems (Iriarte-Velasco et al., 2011). The complex aromatic structure of dyes makes them of low biodegradability and stable toward light and chemical treatments (Ai & Jiang, 2012). Methylene blue (3,7-bis(Dimethylamino)-phenothiain-5-iium chloride) is a cationic dye found in many industrial effluents that may induce aesthetic, and more importantly health problems such as cancers, reproductive and neurological disorders in humans and aquatic organisms (Yan et al., 2011). A number of treatment techniques including ionic exchange, adsorption, coagulation, membrane filtration and photocatalysis have been extensively tested for the removal of dyes from wastewater (Cheng et al., 2012; Kannan & Sundaram, 2001; Lee et al., 1999; Malakootian & Fatehizadeh, 2010; Ramkumar et al., 2010). Among these methods, adsorption is known to be a more economical and simple treatment approach (Ai & Jiang, 2012). Thus, research on low-cost, high-capacity adsorbents for organic dyes is increasing (Ma et al., 2012).

Biochar is a low-cost, porous, carbon-rich product derived from the thermal degradation of organic matter in an oxygen-limited environment (Lehmann, 2007). The benefits of employing eco-friendly biochar in wastewater treatment technologies have already been established (Inyang et al., 2012; Inyang et al., 2011c; Kasozi et al., 2010; Xue et al., 2012; Yao et al., 2011c; Zhang & Gao, 2013). In addition, a recent study showed that ENPs may bind to biochar surfaces (particularly after modification) to a greater extent than to commercial activated carbons (Inyang et al., 2013). Thus, marrying existing biochar technology with emerging nanotechnology to create hybrid
biochar nanocomposites, has great potential to create a new class of environmentally-friendly and cost-effective sorbents to treat a wide array of contaminants (Yao et al., 2011a; Yao et al., 2013b; Zhang et al., 2013a; Zhang et al., 2013b; Zhang et al., 2012a; Zhang et al., 2012b).

Carbon nanotubes (CNTs) are cylindrical tubes of graphene material that exhibit exceptional properties such as ultra-low weight, high mechanical strength, and thermal and chemical stability (Zhang et al., 2009). The potential use of CNTs as adsorbents has generated much interest (Ai & Jiang, 2012; Li et al., 2011b; Tian et al., 2013a; Tian et al., 2013b; Tian et al., 2012b) because the hollow, layered structure of CNTs endows them with characteristically high specific surface areas and correspondingly high sorption capacities for various contaminants (Ma et al., 2011; Tian et al., 2012b). Moreover, chemically functionalized CNT surfaces, grafted with specific functional groups (carboxyl, hydroxyl, amine, fluorine) provide high-affinity sorption sites for increased binding of target pollutants such as dyes via electrostatic attractions or π-π electron bonding (Ma et al., 2012; Theodore et al., 2011; Wang, 2009). Despite these sorptive properties, practical application of CNTs remains limited by its poor solubility, and rapid aggregation in its native state (Lee et al., 2008). Several research efforts have been made to overcome these limitations, by loading CNTs on sorptive supports using sol gel (Es’haghi et al., 2011), crosslinking agents (Salipira et al., 2008), and carbon vapor deposition (CVD) growth techniques (Huang et al., 2012; Zhang et al., 2009). However, the high cost and formation of by-products with many of these methods has made it necessary to consider other supports. Thus, biochar is examined here as such a potential, low-cost support for CNTs.
The overarching objective of this study was to develop a simple method to synthesize hybrid CNT-biochar nanocomposite materials and test their potential applications. Our specific objectives were to: (1) characterize the CNT-biochar nanocomposite, (2) determine the effects of CNT hybridization on the physiochemical properties of the biochars, (3) examine the influence of pH and ionic strength conditions on the sorption of MB on the CNT-biochar nanocomposite, and (4) elucidate and understand the interaction mechanisms governing the sorption of MB on the CNT-biochar nanocomposite.

**Materials and Methods**

**Materials**

Carboxylic acid-functionalized multi-walled CNTs with diameters ranging 10-20 nm were purchased from the Sinonano Company (P. R. China). Hickory chips and sugarcane bagasse biomass were obtained from the North Florida Research and Education Center of the University of Florida. The biomass feedstocks were dried and milled to 500 µm size fraction. Methylene blue (C₁₆H₁₈ClN₃S, molecular weight, 319.86 g) and other chemicals employed in this study were of analytical grade and obtained from Fisher Scientific, Georgia.

**Preparation of CNT-biochar Nanocomposite**

CNT suspensions were prepared by adding either 20 mg (0.01% by weight) or 2 g (1% by weight) of CNT powder to 200 ml of deionized (DI) water. The CNT suspensions were sonicated in an ultrasound homogenizer (Model 300 V/T, Biologics, Inc.) for 1 h at pulse intervals of 12 min. The resulting suspensions were designated as CNT-0.01% and CNT-1%, respectively, and used for the preparation of CNT-biochar nanocomposite.
Milled hickory chips and sugarcane bagasse biomass (feedstocks) were converted to CNT-biochar nanocomposite following a dip-coating procedure (Schoen et al., 2010a; Zhang et al., 2012a). Specifically, 10 g of each feedstock were placed in 100 ml of the CNT suspensions and stirred for 1 h using a magnetic stirrer at 500 rpm, after which, the dip-coated CNT treated feedstocks were removed and oven-dried at 105 °C. Next, the dried CNT-treated feedstock were each placed in a quartz tube, inside a tubular furnace (MTI, Richmond, CA) and pyrolyzed at 600 °C for 1 h in a flowing N₂ environment. In addition, untreated feedstocks were also converted into biochars using the same pyrolysis conditions. The resulting biochars produced were designated as hickory chips (HC), CNT-modified hickory chips (HC-CNT-0.01% and HC-CNT-1%), sugarcane bagasse (BC), and CNT-modified sugarcane bagasse (BC-CNT-0.01% and BC-CNT-1%). All biochars were rinsed with distilled, de-ionized water several times; oven dried, and sealed in glass containers for subsequent testing.

**Characterization**

Elemental carbon, hydrogen, nitrogen and oxygen content (C, H, N, and O); zeta potential, pH, and surface areas of the sorbents were determined using previously reported methods (Inyang et al., 2012; Yao et al., 2011a). Thermogravimetric analysis (TGA) was performed in a stream of air at a heating rate of 10 °C min⁻¹ with a Mettler TGA/DSC1 analyzer (Columbus, OH) to test the thermal stability of the samples. The morphology of modified CNT-biochar composites was examined by transmission electron microscopy (JEOL 2010F TEM). Physiochemical features of the samples were investigated by Raman spectroscopy (Renishaw Bio Raman).
Sorption of Methylene Blue

An initial evaluation of the sorption ability of the chars was conducted using MB solution in batch sorption experiments. About 25 mg of each test biochar was mixed in 50 ml digestion vessels (Environmental Express) with 12.5 ml of 20 mg L\(^{-1}\) MB solution at room temperature (22 ± 0.5 °C). The sample solutions and their corresponding blanks and experimental controls (without either sorbent or sorbate) were agitated for 24 h on a reciprocating shaker, then filtered through 0.22 µm pore size nylon membrane (GE cellulose nylon membranes). Measurements of MB concentrations in the filtrates were determined using a Thermo Scientific EVO 60 UV-VIS spectrophotometer at a wavelength of 665nm. Sorbed amounts of MB on test biochars were calculated as the difference between the initial and final aqueous MB solution concentrations. Sorption experiments were conducted in duplicate and the average values are reported here.

Following the initial evaluation experiments, sorption kinetics and isotherm studies of MB sorption on unmodified biochar (HC and BC) and CNT-biochar nanocomposites (HC-CNT-1% and BC-CNT-1%) were conducted. To examine sorption kinetics, 25 mg of each sorbent was mixed with 12.5 ml of 20 mg L\(^{-1}\) MB solution in 50 ml digestion vessels at room temperature. The sample solutions and their corresponding controls were withdrawn from the agitator at time intervals of about 1 h up to 24 h and filtered through 0.22 µm pore size nylon membranes for measurements. The pH of the filtered sample solutions were noted prior to and after sorption experiments. Sorption isotherms were obtained by adding 25 mg of each biochar to 12.5 ml, MB solutions of varying concentrations (5 – 80 mg L\(^{-1}\)). Sorption kinetics and isotherm experiments were performed in triplicate and the average results are presented with standard deviations.
Effect of pH and Ionic Strength

The effect of pH on MB sorption by the CNT-modified and unmodified biochar sorbents was evaluated by adding 25 mg of each biochar to 12.5 ml of 20 mg L\(^{-1}\) MB solutions in 50ml digestion vessels with pH condition ranging 2 – 10, adjusted by adding aqueous solutions of either 0.1 M NaOH or 0.1mM HCl. To study the effect of ionic strength, pre-determined amounts of NaCl were added to obtain 0.01 M, 0.05 M, 0.1 M, and 0.5 M ionic strength solutions. The sample mixtures and their corresponding blanks were agitated for 24 h, and then filtered and treated as described above. Sorption experiments at different pH or ionic strength were conducted in triplicate.

Results and Discussion

Biochar Properties

The properties of both hickory (HC) and bagasse biochars (BC) were generally improved by the addition of 1% CNTs (Table 4-1). In particular, the surface areas of HC-CNT-1% and BC-CNT-1% were about 1.2 and 40 times greater than their unmodified control biochars (HC and BC) surface areas, respectively, suggesting more CNTs were anchored to BC than to HC. In addition, the pore volume of the sorbents also increased with the addition of the CNTs (Table 4-1), indicating the CNT pretreatment could potentially increase the porosity of the biochars. Results of the zeta potential measurements showed that the surfaces of the hybrid biochar sorbents also became increasingly negatively charged with increasing amounts of CNTs added, probably because the CNTs used in this work are negatively charged (zeta potential -46.3 mv).

TGA profiles of HC and BC samples exhibited a slightly higher thermal stability with increasing introduction of CNTs (Figure 4-1 a and b), though, the difference in stability was more obvious for BC-CNT nanocomposites. The thermal degradation of
pyrolyzed carbon materials, typically show loss of moisture (50 – 100 °C), followed by the disappearance of transformation carbon (e.g., aliphatic C-C groups) from 100 – 350 °C, and finally, the formation of graphitic chars beyond 350 °C (Chen et al., 2008; Zhang et al., 2012a). Weight losses in both modified and unmodified biochars were insignificant until 350 °C, thereafter, comparatively greater weight losses (~80 %) were observed in the unmodified chars from about 350 - 500 °C than modified chars (~70 %). The thermal decomposition behavior of the CNT-1% biochars, particularly, BC-CNT-1% closely resembled the CNT thermal curve, degrading at about 400 °C.

Features of the Raman spectra (Figure 4-2 a and b) include the disorder mode D-band (~1350 cm⁻¹) induced by sp³ hybridization and the tangential mode G-band, representing crystalline graphitic/sp² carbon stretching vibrations (1500-1600 cm⁻¹) (Rong et al., 2013; Theodore et al., 2011). Generally, the D-band originates from defects and functionalities (e.g., -OH, -C=O, -COOH, and -F) within CNT walls (Osswald et al., 2005), and increased I_D/I_G indicates higher defect concentration (increased functional groups) on the sorbents surface (Theodore et al., 2011). Unmodified HC and BC biochars had lower I_D/I_G ratios (1.12 and 1.11 respectively), than CNT (1.78) (Table 4-1). But, after incorporating CNTs onto the biochars, I_D/I_G ratios of the hybrid HC-CNT and BC-CNT samples increased, indicating increased functionalities on the hybrid sorbents. TEM images of HC-CNT-1% and BC-CNT-1% (Figure 4-3) showed the presence of tubular CNT bundles (diameter, 15 – 25 nm) on the char surfaces which further demonstrated the incorporation of CNT in the biochar nanocomposites.

**Methylene Blue Removal Efficiency of Biochars**

Though MB was sorbed by both modified and unmodified biochars, MB removal efficiencies increased with increasing CNT additions (Figure 4-4). The highest removal
of MB by the sorbents was observed for HC-CNT-1% (47% removal) and BC-CNT-1% (64% removal). These findings are consistent with characterization results which showed the most improvements in specific surface area/pore volume and surface chemistry properties (e.g., zeta potential and Raman functionality) of biochars with additions of 1% CNT. Several mechanisms have been proposed for the interaction of organic contaminants with pristine and functionalized CNT including hydrophobic interaction, hydrogen bonding, electrostatic attractions and π - π interactions between graphitic surfaces of CNT and organic molecules containing C=C bonds (Ai & Jiang, 2012; Ma et al., 2011; Mishra et al., 2010). To elucidate the sorption interaction between the hybrid-CNT-sorbents and MB, further testing under varied conditions was conducted using the HC-CNT-1% and BC-CNT-1%.

Sorption Kinetics

Sorption versus time profiles for the sorbents showed different sorption behaviors for the biochars (Figure 4-5 a - d). For instance, pseudo-equilibrium times for MB sorption were reached in the order of BC-CNT-1% < HC < BC < HC-CNT-1%. The sorption kinetic data were simulated with the pseudo-first order, pseudo-second order, and Elovich models. The CNT-biochar nanocomposites exhibited much better correlation of the experimental data with first and second order models ($R^2 > 0.75$) than HC and BC ($R^2 < 0.59$, Table 2). The first ($k_1$) and second order ($k_2$) sorption rate constants were higher for HC (1.08 and 1.90 $h^{-1}$) and BC (18.94 and 19.44 $h^{-1}$) than for their respective modified chars (HC-CNT-1% (0.97 and 0.67 $h^{-1}$) and BC-CNT-1% (13.08 and 5.16 $h^{-1}$)), suggesting faster initial uptake of MB on the unmodified biochars. This could be attributed to the fact that the CNT-biochar nanocomposites have larger porosities (pore volume), which could increase the diffusive interaction time to delay the
initial MB sorption. Intraparticle diffusion kinetic plots were linear and well-correlated with MB sorption ($R^2 > 0.75$) for all sorbents (Figure 4-6), confirming the importance of the diffusive interaction between the MB and the sorbents.

The pseudo-second order model, which predominantly describes chemisorption processes and interaction of functional groups on sorbents with contaminants (Gerente et al., 2007), was the best fit for BC-CNT-1% sorption kinetics data ($R^2 = 0.96$). This suggests stronger affiliations of MB to the $-\text{COOH}$ functionality on BC-CNT-1% than present for the unmodified biochars. The Elovich model, which also evaluates chemisorption mechanisms (Chien & Clayton, 1980), did very well modeling MB sorption by HC-CNT-1% ($R^2 = 0.98$) and may also due to the involvement of carboxyl groups in MB sorption.

**Sorption Isotherms**

Equilibrium isotherms of HC, BC, HC-CNT-1%, and BC-CNT-1% (Figure 4-7 a - d) showed increasing uptake of MB with increasing concentrations of aqueous MB until apparent maximum sorption capacity was reached. Sorption capacities of HC-CNT-1% and BC-CNT-1%, indicated via Langmuir modeling (2.4 and 5.5 mg g$^{-1}$, respectively), were almost twice those of their respective unmodified biochar, (1.3 and 2.2 mg g$^{-1}$, respectively). Similar sorption capacities were reported for some carbonaceous waste materials but the observed values are much lower than those of some other hybrid CNT materials (Table 4-3), suggesting further investigations are still needed to optimize the synthesis of the CNT-biochar nanocomposites to improve their sorption capacities to MB.

While both Langmuir and Freundlich models reproduced the sorption isotherm data reasonably well, the Langmuir-Freundlich (L-F) model fit both unmodified and
modified biochars ($R^2 > 0.90$) best (Table 4-2 and Figure 4-7), indicating the sorption of MB on the biochar base sorbents could be controlled by multiple mechanisms. In literature, the L-F model is often used to describe the sorption of chemicals by heterogeneous materials, including biochars, through multiple processes (Jeppu & Clement, 2012; Kasozi et al., 2010). In this work, the sorption of MB on the CNT-biochar nanocomposites could be controlled by two processes: 1) MB sorbed onto high affinity binding sites within CNT and 2) MB sorbs to biochar itself as the CNT sites become filled.

**Effect of pH**

Solution pH can influence both the surface charge of a sorbent as well as the degree of ionization and conformation of a sorbate (such as MB) (Dias et al., 2002; Ma et al., 2012; Pavan et al., 2008). With increasing pH, there was an increase in MB sorption by all the biochars, until pH of 7, above which, no significant pH dependence was observed (Figure 4-8 a). Similar trends have been reported in the literature for MB sorption on other sorbents (Iriarte-Velasco et al., 2011; Pavan et al., 2008). All the biochars used in this study were predominantly negatively charged in DI water (Table 1), which would promote the sorption of positively charged MB (pKa 3.8) by electrostatic attraction (Dias et al., 2002). In particular, the electrostatic attraction of positively charged MB to the CNT-biochar nanocomposites should increase with increasing pH (below 7) because of the increasing deprotonation of the functional (e.g., carboxyl and hydroxyl) groups of the CNTs within the biochar matrix. On the other hand, because MB consists of benzene rings, which can participate in π-π electron-donor-acceptor reactions with graphene in CNTs, π-π coupling may be another important mechanism promoting the sorption of MB on the CNT-biochar nanocomposites. In this case, a low
pH should favor the sorption of strong π-donor compounds (Iriarte-Velasco et al., 2011; Ji et al., 2009; Zhu et al., 2004).

**Effect of Ionic Strength**

The presence of cations such as Na⁺ have been shown previously to reduce the sorption of MB onto fungus (Maurya et al., 2006). In theory, when electrostatic forces between sorbent surfaces and sorbate ions are attractive, an increase in ionic strength will decrease the sorption capacity of the sorbate due to competition of Na⁺ ions with positively charged MB for sorption sites (Ma et al., 2012). Here, MB sorption onto all the biochar based sorbents decreased somewhat as concentrations of NaCl increased from 0.01 to 0.1 M (Figure 4-8 b and c), confirming involvement of electrostatic interaction in MB sorption. With 0.5 M of NaCl, however, there was no significant decrease, and even a slight increase in MB sorption by some of the sorbents. This effect has been reported previously and may arise from dimerization or aggregation of dye molecules at very high salt concentrations (Ma et al., 2012; Mukerjee & Ghosh, 1970) and is independent of MB interactions with the sorbent.

**Conclusion**

Characterization of the sorbents indicated that the physiochemical properties (e.g., surface area, porosity, and thermal stability) of the biochars were enhanced by additions of CNTs. The BC-CNT-1% char had the highest sorption capacity to MB among all the sorbents, likely because it may have anchored more CNTs judging from its better thermal stability, higher surface area, and larger pore volume. The data collected suggests that electrostatic attraction was the dominant mechanism for sorption of MB onto the chars, but chemisorption such as pi-pi bonding should not be ruled out.
as a contributing sorption mechanism. Intrapore diffusion was also likely to control the rate at which MB was removed from solution onto the biochar based sorbents.

Though the overall sorption capacity of the CNT-hybridized chars studied were lower than those of some other hybrid sorbents reported in literature, the synthesis procedure employed here is simple, inexpensive, and can be further optimized. The results presented have established the potential of biochar-CNT hybrid sorbents to be used for environmental remediation of dyes and possibly other organic pollutants. In addition to their low cost, they may provide additional environmental benefits, such as carbon sequestration and soil amelioration.
Table 4-1. Structural and physiochemical properties of the biochar based sorbents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Zeta potential (mV)</th>
<th>BET N2 surface area (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
<th>O %</th>
<th>Raman intensity (disorder/order ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>7.3</td>
<td>-28.8</td>
<td>289</td>
<td>0.001</td>
<td>81.8</td>
<td>2.2</td>
<td>0.7</td>
<td>15.3</td>
<td>1.11</td>
</tr>
<tr>
<td>HC-CNT-0.01%</td>
<td>7.4</td>
<td>-33.2</td>
<td>257</td>
<td>0.003</td>
<td>84.1</td>
<td>2.5</td>
<td>0.4</td>
<td>13</td>
<td>1.14</td>
</tr>
<tr>
<td>HC-CNT-1%</td>
<td>7.5</td>
<td>-41.4</td>
<td>352</td>
<td>0.138</td>
<td>80.3</td>
<td>2.1</td>
<td>0.2</td>
<td>17.4</td>
<td>1.30</td>
</tr>
<tr>
<td>BC</td>
<td>6.9</td>
<td>-32.7</td>
<td>9</td>
<td>0.000</td>
<td>76.4</td>
<td>2.9</td>
<td>0.8</td>
<td>19.9</td>
<td>1.12</td>
</tr>
<tr>
<td>BC-CNT-0.01%</td>
<td>7.0</td>
<td>-34.1</td>
<td>120</td>
<td>0.008</td>
<td>79.3</td>
<td>2.2</td>
<td>0.8</td>
<td>17.7</td>
<td>1.15</td>
</tr>
<tr>
<td>BC-CNT-1%</td>
<td>7.3</td>
<td>-44.6</td>
<td>390</td>
<td>0.220</td>
<td>85.7</td>
<td>1.7</td>
<td>0.7</td>
<td>11.9</td>
<td>1.28</td>
</tr>
</tbody>
</table>
Table 4-2. Summary of models and best-fit parameters of the sorption kinetics and isotherms.

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Model*</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>Parameter 3</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>First order ( q_t = q_e (1-e^{-kt}) )</td>
<td>( k_1 = 1.08 )</td>
<td>( q_{e1} = 0.80 )</td>
<td>-</td>
<td>0.464</td>
</tr>
<tr>
<td></td>
<td>Second order ( q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} )</td>
<td>( k_2 = 1.90 )</td>
<td>( q_{e2} = 0.89 )</td>
<td>-</td>
<td>0.588</td>
</tr>
<tr>
<td></td>
<td>Elovich ( q_i = \frac{1}{\beta} \ln(\alpha t + 1) )</td>
<td>( \alpha = 10.86 )</td>
<td>( \beta = 8.19 )</td>
<td>-</td>
<td>0.761</td>
</tr>
<tr>
<td></td>
<td>Langmuir ( q_e = \frac{K S_{max} C_e}{1+KC_e} )</td>
<td>( K = 1.10 )</td>
<td>( S_{max} = 1.28 )</td>
<td>-</td>
<td>0.930</td>
</tr>
<tr>
<td></td>
<td>Freundlich ( q_i = K F C_e^n )</td>
<td>( K_F = 0.62 )</td>
<td>( n = 0.19 )</td>
<td>-</td>
<td>0.748</td>
</tr>
<tr>
<td></td>
<td>L-F ( q_e = \frac{S_{max}(KC_e)^n}{1+(KC_e)^n} )</td>
<td>( K = 1.16 )</td>
<td>( S_{max} = 1.24 )</td>
<td>( n = 9.23 )</td>
<td>0.940</td>
</tr>
<tr>
<td>HC-CNT-1%</td>
<td>First order</td>
<td>( k_1 = 0.97 )</td>
<td>( q_{e1} = 2.10 )</td>
<td>-</td>
<td>0.759</td>
</tr>
<tr>
<td></td>
<td>Second order</td>
<td>( k_2 = 0.67 )</td>
<td>( q_{e2} = 2.28 )</td>
<td>-</td>
<td>0.869</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>( \alpha = 22.2 )</td>
<td>( \beta = 3.11 )</td>
<td>-</td>
<td>0.978</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>( K = 17.92 )</td>
<td>( S_{max} = 2.40 )</td>
<td>-</td>
<td>0.851</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>( K_F = 1.44 )</td>
<td>( n = 0.14 )</td>
<td>-</td>
<td>0.764</td>
</tr>
<tr>
<td></td>
<td>L-F</td>
<td>( K = 40.47 )</td>
<td>( S_{max} = 2.40 )</td>
<td>( n = 27.86 )</td>
<td>0.987</td>
</tr>
<tr>
<td>BC</td>
<td>First order</td>
<td>( k_1 = 18.94 )</td>
<td>( q_{e1} = 1.90 )</td>
<td>-</td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>Second order</td>
<td>( k_2 = 19.44 )</td>
<td>( q_{e2} = 1.92 )</td>
<td>-</td>
<td>0.336</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>( \alpha = 27107.52 )</td>
<td>( \beta = 7.32 )</td>
<td>-</td>
<td>0.764</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>( K = 2.09 )</td>
<td>( S_{max} = 2.20 )</td>
<td>-</td>
<td>0.917</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>( K_F = 1.07 )</td>
<td>( n = 0.20 )</td>
<td>-</td>
<td>0.797</td>
</tr>
<tr>
<td></td>
<td>L-F</td>
<td>( K = 2.24 )</td>
<td>( S_{max} = 2.20 )</td>
<td>( n = 1.81 )</td>
<td>0.920</td>
</tr>
</tbody>
</table>
Table 4-3. Summary of models and best-fit parameters of the sorption kinetics and isotherms continued

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Model*</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>Parameter 3</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-CNT-1%</td>
<td>First order</td>
<td>$k_1 = 13.08$</td>
<td>$q_{e1} = 4.30$</td>
<td>-</td>
<td>0.935</td>
</tr>
<tr>
<td></td>
<td>Second order</td>
<td>$k_2 = 5.16$</td>
<td>$q_{e2} = 4.37$</td>
<td>-</td>
<td>0.956</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>$\alpha = 699779.76$</td>
<td>$\beta = 3.91$</td>
<td>-</td>
<td>0.799</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>$K = 4.84$</td>
<td>$S_{max} = 5.50$</td>
<td>-</td>
<td>0.961</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>$K_F = 3.02$</td>
<td>$n = 0.18$</td>
<td>-</td>
<td>0.757</td>
</tr>
<tr>
<td></td>
<td>L-F</td>
<td>$K = 5.12$</td>
<td>$S_{max} = 5.50$</td>
<td>$n = 1.08$</td>
<td>0.961</td>
</tr>
</tbody>
</table>

*: $q_t$ and $q_e$ are the amount of sorbate removed at time $t$ and at equilibrium, respectively (mg g⁻¹), and $k_1$ and $k_2$ are the first-order and second-order sorption rate constants (h⁻¹), respectively. $\alpha$ is the initial sorption rate (mg g⁻¹) and $\beta$ is the desorption constant (g mg⁻¹). $K$ and $K_F$ are the Langmuir bonding term related to interaction energies (L mg⁻¹) and the Freundlich affinity coefficient (mg⁻¹ Lⁿ g⁻¹), respectively. $S_{max}$ is the Langmuir maximum capacity (mg g⁻¹). $C_e$ is the equilibrium solution concentration (mg L⁻¹) of the sorbate, and $n$ is the Freundlich linearity constant.
<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Methylene blue adsorption capacity (mg g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-CNT-1%</td>
<td>2.6</td>
<td>This work</td>
</tr>
<tr>
<td>BC-CNT-1%</td>
<td>6.2</td>
<td>This work</td>
</tr>
<tr>
<td>Microwaved modified bamboo biochar</td>
<td>35.3</td>
<td>(Liao et al., 2012)</td>
</tr>
<tr>
<td>Fly ash-stabilized hydrogen titanate nanosheets</td>
<td>0.6</td>
<td>(Hareesh et al., 2012)</td>
</tr>
<tr>
<td>Blast furnace sludge</td>
<td>6.4</td>
<td>(Wang et al., 2005)</td>
</tr>
<tr>
<td>Activate coir pith carbon</td>
<td>5.9</td>
<td>(Kavitha &amp; Namasivayam, 2007)</td>
</tr>
<tr>
<td>Graphene-carbon nanotube hybrid</td>
<td>82.0</td>
<td>(Ai &amp; Jiang, 2012)</td>
</tr>
<tr>
<td>Magnetite loaded multi-walled carbon nanotube</td>
<td>48.1</td>
<td>(Ai et al., 2011)</td>
</tr>
<tr>
<td>Powdered activated carbon</td>
<td>91.0</td>
<td>(Yener et al., 2008)</td>
</tr>
<tr>
<td>Alkali-activated carbon nanotubes</td>
<td>400.0</td>
<td>(Ma et al., 2012)</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>46.2</td>
<td>(Yao et al., 2010)</td>
</tr>
</tbody>
</table>
Figure 4-1. Thermogravimetric analysis profiles of biochar based sorbents. A) HC and HC-CNT composites and B) BC and BC-CNT composites.
Figure 4-2. Raman spectra of biochar based sorbents. A) HC and HC-CNT composites and B) BC and BC-CNT composites.
Figure 4-3 Transmission electron micrographs for A) HC-CNT-1% and B) BC-CNT-1% samples at 50000X magnification.
Figure 4-4. Methylene blue removal efficiencies of biochar based sorbents.
Figure 4-5. Sorption kinetics plots of biochar based sorbents. A) HC, B) HC-CNT-1%, C) BC and D) BC-CNT-1%.
Figure 4-6. Intraparticle diffusion kinetics plots for A) HC and B) BC sorbents.
Figure 4-7. Sorption isotherms of biochar based sorbents. A) HC, B) HC-CNT-1%, C) BC, and D) BC-CNT-1%.
Figure 4-8. Effects of solution chemistry on methylene sorption on biochar based sorbents. A) pH effects, B) ionic strength effects on HC and HC-CNT-1%, and C) ionic strength effects on BC and BC-CNT-1%.
CHAPTER 5
SIMULTANEOUS SORPTION OF SULFAPYRIDINE AND LEAD BY BIOCHAR MODIFIED WITH SURFACTANT-DISPERSED CARBON NANOTUBES

Introduction

Human and veterinary pharmaceutical-antibiotics in water systems have been and remain a public concern due to chronic toxic effects and potential development of antibiotic resistance in microbial populations (Challis et al., 2013; Ji et al., 2009; Schwarz et al., 2012). Sulfonamide antibiotics (SA) are a popular class of broad-spectrum antibiotics whose metabolites are not wholly digested in animal systems, but can be leached into water bodies when sulfonamide-contaminated animal manure are applied to soils (Kurwadkar et al., 2007). Research studies (Diaz-Cruz et al., 2008; Gobel et al., 2004; Radke et al., 2009) have reported high concentrations of SA and their metabolites in waterways, and their total elimination in conventional water treatment plants has yet to be demonstrated (Jesus Garcia-Galan et al., 2012). Sulfapyridine (SPY) is a fairly water-soluble SA often detected at high concentrations in wastewaters (70 – 227 ng L\(^{-1}\)) (Gobel et al., 2004; Jesus Garcia-Galan et al., 2011; Thiele-Bruhn et al., 2004). Typically, wastewater treatment plants are operated at short hydraulic residence times (~ 40 h), whereas residues of SPY and their metabolites require longer residence times (32 – 62 days) to be completely degraded (Gros et al., 2010; Radjenovic et al., 2009). Thus, the potential contamination of environmental waters by SPY in treated wastewater effluents is likely (Gros et al., 2010).

Lead (Pb) is a long-standing toxic heavy metal pollutant found in wastewater and industrial effluents (Muhammad et al., 2006). The effects of heavy metals, like Pb in the environment can be severe because it is non-biodegradable and environmentally persistent, even at low concentrations. Specifically, bioaccumulation of Pb in human
and animal tissues has been linked to hypertension, mental retardation, renal impairment, and reproductive disorders (Pokras & Kneeland, 2008). Among several treatment options aimed at minimizing Pb concentrations in wastewater, sorption has been generally recognized as an effective and relatively economical treatment approach (Huang et al., 2012). Moreover, previous research on the application of low-cost biosorbents (after modification) have reported higher uptake of Pb compared to some commercial activated carbons (Inyang et al., 2012; Yao et al., 2011c).

Biochar is a porous, carbon-rich material derived from the thermal treatment of biomass in a closed system under anaerobic conditions. The properties and constituents of biochar are heterogeneous and vary extensively with thermal treatment conditions (Chen et al., 2012). Also, recent studies (Chen et al., 2008; Chun et al., 2004; Kasozi et al., 2010) have described biochar as a “combustion continuum” product comprising of highly carbonized and less-carbonized organic matter. While, the carbonized matter with condensed aromatic compounds, can act as an adsorbent; the less-carbonized, amorphous fraction acts as a partition/absorption phase (Amymarie & Gschwend, 2002; Chen et al., 2008; Keiluweit et al., 2010). These two phases may well sorb Pb and SPY.

Like biochar, carbon nanotubes (CNTs) are a promising, new class of sorbents composed of covalently bonded carbon sheets with high specific surface areas that can effectively sorb heavy metals and organic compounds (Huang et al., 2012; Ji et al., 2009; Lin & Xing, 2008; Tian et al., 2012b). Yet, practical application of CNTs is limited by its poor solubility and propensity to aggregate into bundles (Matarredona et al., 2003). Functionalization of CNTs and the use of surfactants in CNTs dispersion are two
suggested means of overcoming these limitations (Clark et al., 2011; Lin & Xing, 2008). Also, our previous study (Inyang et al., 2013) had demonstrated that biochar could serve as a low-cost support for CNTs, and the incorporation of CNTs into biochar significantly improved its sorption ability for methylene blue. The combination of surfactant-dispersed CNTs with biochar can be suggested as a means of optimizing the process of producing CNT-biochars because the surfactant-dispersion of CNT would increase the amount of individual CNT threads to be anchored onto biochar for the sorption of Pb and SPY.

Thus, the overarching objective of this study was to synthesize sodium dodecyl benzene sulfonate (SDBS)-dispersed CNT biochar nanocomposites from hickory chips and sugarcane bagasse biomass (HC-SDBS-CNT and BC-SDBS-CNT, respectively), and determine their sorption potential for SPY and Pb in aqueous solutions. Our specific objectives were to: (1) examine the effects of SDBS dispersed-CNT on the properties of SDBS-CNT-biochar nanocomposites, (2) determine the sorption capacity of Pb and SPY on SDBS-CNT biochar nanocomposites in a single solute system, (3) examine interactions between SPY and Pb in a binary solute system on SDBS-CNT biochar nanocomposites, and (4) elucidate and differentiate sorption mechanisms controlling the sorption of Pb and SPY on SDBS-CNT biochar nanocomposites.

**Materials and Methods**

**Materials**

Hickory chips and sugarcane bagasse biomass were obtained from UF North Florida Research and Education Center, and dried and milled to < 500 µm size fractions. Carboxylic acid functionalized multi-walled carbon nanotubes (CNTs) with diameter, 10-20 nm and purity > 95 % was purchased from Sinonano Company (P.R.
China). All reagents used in this study were of high purity grade. Sulfapyridine (99% Sigma, mol. wt. 249.29 g mol\(^{-1}\)), lead nitrate and sodium dodecylbenzenesulfonate (SDBS, mol. wt. 348.48 g mol\(^{-1}\)) surfactant were obtained from Sigma-Aldrich Co. (St. Louis, MO), and Fisher Scientific, Georgia, respectively. The chemical properties of SPY used in this study are presented in Table 5-1. SPY solutions (5 – 60 mg L\(^{-1}\)) were prepared by sonicating pre-determined amounts of SPY in known volumes of deionized, distilled water for 1 h, and the solutions left to stand for 1 – 3 days until complete dissolution.

**Preparation of Surfactant-dispersed CNT Biochar Nanocomposites**

Surfactant-based CNT suspensions were prepared by adding 2 g each of CNTs and SDBS powder (1% by weight) to 200ml of deionized, distilled water. Surfactant-CNT-suspensions and CNT-suspensions containing 2 g of CNTs powder without SDBS were each sonicated in an ultrasound homogenizer (Model 300 V/T, Biologics, Inc.) for 1 h at pulse intervals of 12 min. The resulting suspensions, designated as CNT (without surfactant), and SDBS-CNT (with surfactant) were used for the preparation of CNT-biochar nanocomposites.

SDBS-dispersed CNT biochars and CNT-biochars (without SDBS) were produced by dip-coating milled sugarcane bagasse and hickory chips biomass (feedstocks) each in SDBS-CNT and CNT suspensions respectively, before converting the coated biomass to SDBS-CNT biochars and CNT-biochars following previously reported procedure (Schoen et al., 2010b; Zhang et al., 2012a). Specifically, 10 g of milled sugarcane bagasse and hickory chips biomass were each dip-coated in 100 ml of SDBS-CNT or CNT suspensions, and stirred for 1 h on a magnetic stirrer at 500 rpm, after which, the dip-coated CNTs treated feedstock were removed and oven dried at
105 °C. Next, dried SDBS-CNT and CNT feedstocks along with untreated feedstocks were each placed in a quartz tube and slowly pyrolyzed at 600 °C for 1 h inside a tubular furnace (MTI, Richmond, CA) under a flowing N2 environment. The resulting biochars were tagged as SDBS-dispersed CNT modified hickory and bagasse biochars (HC-SDBS-CNT and BC-SDBS-CNT), CNT-modified hickory and bagasse biochars without SDBS (HC-CNT and BC-CNT), and pristine hickory and bagasse biochars (HC and BC). All samples were stored in plastic vials for further testing.

**Characterization**

Thermogravimetric analysis (TGA) of the biochars was performed in a stream of air at a heating rate of 10 °C min⁻¹ with a Mettler TGA/DSC1 analyzer (Columbus, OH) to test the thermal stability of the chars. Elemental carbon, hydrogen, nitrogen and oxygen content (C, H, N, and O); zeta potential, pH, and surface areas of the sorbents were determined using previously reported methods (Inyang et al., 2012; Yao et al., 2011a). Fourier transform infra-red analysis of pre- and post-sorption SDBS-CNT biochars loaded with SPY was conducted to elucidate the interaction mechanisms during sorption.

**Sorption of Lead and Sulfapyridine in Single-Solute System**

The modified and pristine biochars were preliminary assessed for their sorption ability of lead and SPY by mixing 25 mg of each biochar with 12.5 ml of 40 mg L⁻¹ Pb(NO₃)₂ or 20 mg L⁻¹ SPY in 50 ml digestion vessels (Environmental Express) at room temperature. The sample solutions and their corresponding blank controls were agitated for 24 h on a reciprocating shaker and withdrawn at specific time intervals and filtered through 0.22 µm pore size nylon membranes (GE cellulose nylon membranes). Concentrations of SPY and Pb concentrations in filtrates were determined using a
Thermo Scientific EVO 60 UV-VIS spectrophotometer at a wavelength of 260 nm, and an inductively coupled plasma spectrometer (ICP-AES), respectively. The sorbed amounts of Pb and SPY on test biochars were each calculated as the difference between their initial and final aqueous solution concentrations. All sorption experiments were conducted in triplicate and the average values are presented with standard deviations.

Following preliminary sorption assessments, Pb and SPY sorption kinetics and isotherm studies were conducted on surfactant-CNT modified biochars (HC-SDBS-CNT and BC-SDBS-CNT) in a single solute system using similar procedures. Sorption kinetics were examined by mixing 25 mg of each biochar with 12.5 ml of 40 mg L⁻¹ Pb(NO₃)₂ or 20 mg L⁻¹ SPY respectively, in 50 ml digestion vessels at specific intervals from 1 to 24 h and filtered to 0.22 µm. The pH of sample solutions was monitored prior to and after sorption experiments. Pb and SPY sorption isotherms were also determined by mixing 25 mg of each biochar with 12.5 ml of varying concentrations (5 – 100 mg L⁻¹) of Pb(NO₃)₂ or (10 – 60 mg L⁻¹) of SPY in 50 ml digestion vessels.

Co-sorption of Lead and Sulfapyridine in Binary-Solute System

Co-sorption of Pb and SPY by SDBS-CNT biochars in a binary solute system was examined. The effect of Pb on SPY sorption was determined by mixing 25 mg of each biochar with 12.5 ml of 20 mg L⁻¹ SPY and different concentrations of Pb (0.05 – 0.5 mM). Likewise, the effect of SPY on Pb sorption was tested by mixing 25 mg of each biochar with 12.5 ml of 40 mg L⁻¹ Pb and different concentrations of SPY (0.02 – 0.2 mM). Binary solute-sample mixtures of Pb and SPY and their corresponding blank controls were agitated on a reciprocating shaker for 24 h, withdrawn and treated as
described above for the single solute system. Co-sorption experiments were also conducted in triplicate.

**Results and Discussion**

**Biochar Properties**

The physiochemical properties of pristine hickory (HC) and bagasse (BC) biochars were generally improved by the addition of CNT, but no obvious changes in physiochemical properties were observed after the addition of SDBS-CNT to the biochars (Table 5-1). Although, there was a slight increase in the surface area (from 351 to 359 m$^2$ g$^{-1}$) and pore volume (from 0.14 to 0.27 cc g$^{-1}$) of HC-SDBS-CNT, there was no corresponding improvement in BC-SDBS-CNT. Typically, the sonication of surfactant-CNT suspensions would debundle CNT aggregates either by steric or electrostatic repulsions (Bandyopadhyaya et al., 2002; Clark et al., 2011; Ham et al., 2005; Matarredona et al., 2003; Vaisman et al., 2006), which should increase the amount of CNT threads in solution that can be anchored to the coated-biomass and produced biochar (Vaisman et al., 2006) but the corresponding improvements in the physiochemical properties of the biochars were not obvious.

TGA profiles of the SDBS-CNT biochar nanocomposites (Figure 5-1) showed higher stability than pristine biochars, and in some cases, greater thermal stability than CNT-biochars. All the carbons showed insignificant weight losses during thermal treatment until 350 °C, after which CNT, or biochars began to degrade. However, unlike BC-SDBS-CNT, slightly higher stability was observed in HC-SDBS-CNT profile than HC-CNT, which is consistent with the small improvements in its physiochemical properties. This could also indicate that more CNT may have anchored to the surface of HC-SDBS-CNT biochar than BC-SDBS-CNT. But, the higher thermal stability of HC-
SDBS-CNT could also be attributed to the presence of more aromatic, lignin components in hickory compared to the bagasse biomass.

**Preliminary Biochar Assessments**

Lead and SPY were both sorbed onto pristine and CNT-biochars (Figure 5-2), but SDBS-CNT biochars removed the most SPY and Pb. Specifically, the amounts of SPY sorbed increased in the order of pristine biochar < CNT-biochar < SDBS-CNT-biochar, with highest removal efficiencies of 86 % and 56 % SPY for HC-SDBS-CNT and BC-SDBS-CNT, respectively. Distribution coefficients, Kd for SPY on the modified SDBS-CNT chars were 3111 and 655 L kg\(^{-1}\) for HC-SDBS-CNT and BC-SDBS-CNT, respectively which are much higher than previously reported Kd values for sulfamethaxole (2 – 104 L kg\(^{-1}\)) sorption on biochar (Yao et al., 2012b), and SPY (1.1 – 5.6 L kg\(^{-1}\)) sorption on soil organic matter (Haham et al., 2012). Likewise, HC-SDBS-CNT and BC-SDBS-CNT biochars had the most Pb removal efficiency (71 % and 53 %, respectively), than CNT-biochars, or pristine biochars. Given the heterogeneity of the synthesized SDBS-CNT biochars, the possibility of multiple mechanisms participating in Pb or SPY sorption onto SDBS-CNT chars cannot be ruled out. Further sorption and characterization studies were conducted on SDBS-CNT biochar to investigate these possibilities.

**Sorption Kinetics**

Sorption kinetics of SPY or Pb in a single solute system is shown in sorption versus time profiles (Figures 5-3 a and b). Both Pb and SPY sorption onto SDBS-CNT-biochars occurred at an initially fast rate with 30 – 50 % of SPY or Pb sorbed during the first 1 h, thereafter, the rate of Pb and SPY gradually slowed down until equilibrium states were reached. Rate-limited pseudo first order, pseudo second order, and Elovich
models (Table 5-2) were used to simulate the sorption kinetic data but, only best fitted models plots are graphed (Figures 5-3 a and b). The Elovich model best-fit the kinetic sorption data for SPY on both biochars ($R^2 > 0.90$), but the simulated Elovich rate constant for HC-SDBS-CNT was 50 times greater than for BC-SDBS-CNT. The Elovich model evaluates chemisorption mechanisms, such as chemical bondings between contaminants and heterogeneous surfaces such as SDBS-CNT biochars. But, pH of SPY sample solutions remained at pH 6 – 7 below its pKa$_2$ value of 8.4, before and after sorption, so that most of the SPY was protonated and neutral which could encourage hydrophobic interactions between neutral SPY species and hydrophobic CNT/biochar sites. Moreover, the protonation of SPY would increase the electron accepting ability of its amine group, and encourage π-π electron donor acceptor interactions between graphene in CNTs or biochar and SPY (Ji et al., 2009).

In the case of Pb, the pseudo-second order modeled sorption onto both SDBS-CNT chars well, but the Elovich model had a much stronger fit for HC-SDBS-CNT ($R^2 = 0.98$) than BC-SDBS-CNT ($R^2 = 0.66$) which had a better fit with the second order model ($R^2 = 0.82$). The interactions of Pb to oxygen containing functional groups in CNT/biochars via complexation or electrostatic attraction are possible sorption mechanisms for Pb sorption on SDBS-CNT biochars. Intra-particle diffusion plots for pre-equilibrium sorption of SPY and Pb (Figure 5-4 a and b) fit both SDBS-CNT biochars which implies that diffusion also influenced the rate of Pb and SPY sorption into the pores of modified biochars.

**Sorption Isotherms**

Isotherms for the sorption of Pb and SPY onto SDBS-CNT chars are presented in Figure 5-5 a and b. Experimental equilibrium data for SPY and Pb were simulated
with Langmuir (L), Freundlich (F) and Langmuir-Freundlich (L-F) models, and the best fit model parameters were presented (Table 5-2). The L-F-model best reproduced SPY sorption ($R^2 > 0.89$) on both biochars, which suggests that multiple controlling sorption mechanisms may occur. The L-F model has been applied to the sorption of chemicals on heterogeneous materials, including biochars (Jeppu & Clement, 2012; Kasozi et al., 2010).

Pb sorption data was also well fit with the L-F model ($R^2 > 0.87$). The L-bonding term, $K$ (L mg$^{-1}$) was 40 times higher for BC-SDBS-CNT (1.66) than HC-SDBS-CNT (0.04) which suggests that the affiliation of Pb on BC-SDBS-CNT was more influenced by surface sorption. Previous sorption isotherm study (Inyang et al., 2011) for Pb sorption on pristine, unmodified BC had also shown that Pb bonding on BC was similar to activated carbon (with similar Langmuir bonding term) and mainly surface controlled.

**Co-sorption of Lead and Sulfapyridine in Binary-Solute Systems**

Sorption capacities for SPY for HC-SDBS-CNT (7.7 - 8.7 mg g$^{-1}$) and BC-SDBS-CNT (4.4 – 4.5 mg g$^{-1}$) in the binary-solute system were similar to the single-solute system for HC-SDBS-CNT (8.64 mg g$^{-1}$) and BC-SDBS-CNT (4.8 mg g$^{-1}$), which showed that there was limited interaction between SPY and Pb (Figure 5-6 a). Likewise, sorption capacities for Pb for HC-SDBS-CNT (13.1 -13.3 mg g$^{-1}$) and BC-SDBS-CNT (10.0 – 10.4 mg g$^{-1}$) in the binary-solute system were similar to the single-solute system for HC-SDBS-CNT (14.4 mg g$^{-1}$) and BC-SDBS-CNT (13.2 mg g$^{-1}$) (Figure 5-6 b). Student t-test analysis also showed that there was no significant dependence of the amounts of SPY or Pb sorbed on either biochars with increasing Pb or SPY concentrations. A previous study reported that the presence of exchangeable cations in solution increased the sorption of SPY on soil organic matter via their complexation with
the amine and -SO₂ groups in SPY (Haham et al., 2012; Schwarz et al., 2012). But, there have also been previous studies that found no interaction between the heavy metal and organic contaminant during co-sorption (Cao et al., 2009b; Wu et al., 2012a).

Co-sorption studies for Pb and SPY indicate that the sorption of Pb or SPY on the SDBS-CNT-biochars was site specific, and there was likely no significant competition between SPY and Pb for functional groups on the SDBS-CNT biochar matrix. Additionally, complexation of Pb with the amine or SO₂ groups in SPY may not have occurred. Further evidence of insignificant competition for functional groups between Pb and SPY was observed in the FTIR spectra of the SPY loaded SDBS-CNT biochars which showed no change in the functional chemistry of SDBS-CNT chars after SPY sorption (Figure 5-7). The SPY sorption process in single and binary solute systems for either SDBS-CNT biochars (Figure 5-8) could have occurred via the following: (1) π-π electron donor acceptor reactions between graphite in CNT or carbonized biochar matter and the amine group in SPY; (2) hydrophobic interactions between SPY and hydrophobic sites on CNT/biochar sites; and (3) physical sorption of SPY on SDBS-CNT biochar surfaces. While, Pb sorption on SDBS-CNT biochars may have also occurred by: (1) Pb complexing with oxygen containing functional groups in biochar and CNT, (2) physical sorption of Pb on the surface of the modified biochars, and (3) electrostatic interaction between the dissociated carboxyl group in CNT and Pb.

**Conclusions**

The incorporation of SDBS-CNT into biochar improved their sorption capacities for Pb and SPY even though, no obvious improvements in the physiochemical properties (e.g., surface area, pore volume, and zeta potential) of the modified SDBS-CNT biochars were observed. Despite limited improvements in their properties, both
SDBS-CNT biochar nanocomposites effectively removed Pb or SPY from single-solute and binary solute aqueous solutions. Binary solute systems however showed no significant change in the sorption capacities of the biochar nanocomposites from their sorption in a single solute system, suggesting site-specific sorption interactions and no significant competition for functional groups between SPY and Pb. The synthesized SDBS-CNT biochar nanocomposites show that they have the potential to be employed as alternative treatment technologies for the remediation of metallic and organic contaminants. Furthermore, because of the anti-microbial properties of SPY, the SPY laden SDBS-CNT biochars can be further exploited for disinfection purposes.
Table 5-1. Physiochemical properties of carbons used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Zeta potential (mV)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
<th>O %</th>
<th>H/C</th>
<th>(O+N)/C</th>
<th>Pka₁/Pka₂</th>
<th>Log Kow</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>8.50</td>
<td>-46.34</td>
<td>142</td>
<td>0.115</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>HC</td>
<td>7.25</td>
<td>-28.84</td>
<td>289.2</td>
<td>0.001</td>
<td>81.81</td>
<td>2.17</td>
<td>0.73</td>
<td>14.02</td>
<td>0.027</td>
<td>0.17</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>HC-CNT</td>
<td>7.49</td>
<td>-41.42</td>
<td>351.5</td>
<td>0.138</td>
<td>80.30</td>
<td>2.08</td>
<td>0.22</td>
<td>17.40</td>
<td>0.026</td>
<td>0.22</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>HC-SDBS-CNT</td>
<td>6.74</td>
<td>-42.65</td>
<td>359</td>
<td>0.27</td>
<td>77.69</td>
<td>2.07</td>
<td>0.19</td>
<td>20.05</td>
<td>0.027</td>
<td>0.26</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BC</td>
<td>6.94</td>
<td>-32.72</td>
<td>9.3</td>
<td>0</td>
<td>76.44</td>
<td>2.93</td>
<td>0.79</td>
<td>19.84</td>
<td>0.038</td>
<td>0.26</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BC-CNT</td>
<td>7.31</td>
<td>-44.58</td>
<td>390</td>
<td>0.22</td>
<td>85.73</td>
<td>1.74</td>
<td>0.66</td>
<td>11.88</td>
<td>0.020</td>
<td>0.14</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BC-SDBS-CNT</td>
<td>6.72</td>
<td>-32.21</td>
<td>336</td>
<td>0.167</td>
<td>84.30</td>
<td>1.98</td>
<td>0.63</td>
<td>13.09</td>
<td>0.023</td>
<td>0.15</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SPY</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2.9/8.4</td>
<td>0.35</td>
</tr>
</tbody>
</table>

ND – Not determined
Table 5-2. Best fit model parameters for sorption kinetics and isotherms.

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Model*</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>Parameter 3</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-SDBS-CNT</td>
<td>First order ( q_t = q_e(1 - e^{-kt}) )</td>
<td>( k_1 = 12.94 )</td>
<td>( q_{e1} = 7.36 )</td>
<td></td>
<td>0.524</td>
</tr>
<tr>
<td></td>
<td>Second order ( q_t = k_2q_2^2t/1+k_3q_2^2t )</td>
<td>( k_2 = 2.41 )</td>
<td>( q_{e2} = 7.52 )</td>
<td></td>
<td>0.638</td>
</tr>
<tr>
<td></td>
<td>Elovich ( q_t = \frac{1}{\beta} \ln(\alpha t + 1) )</td>
<td>( \alpha = 11567.56 )</td>
<td>( \beta = 1.58 )</td>
<td></td>
<td>0.923</td>
</tr>
<tr>
<td></td>
<td>Langmuir ( q_t = \frac{K_Smax C_e}{1 + KC_e} )</td>
<td>( K = 0.13 )</td>
<td>( S_{max} = 27.90 )</td>
<td></td>
<td>0.894</td>
</tr>
<tr>
<td></td>
<td>Freundlich ( q_t = K_f C_e^n )</td>
<td>( K_F = 3.98 )</td>
<td>( n = 0.61 )</td>
<td></td>
<td>0.891</td>
</tr>
<tr>
<td></td>
<td>L-F ( q_t = \frac{s_{max}(KC_e)^n}{1+(KC_e)^n} )</td>
<td>( K = 0.10 )</td>
<td>( S_{max} = 31.05 )</td>
<td>( n = 0.93 )</td>
<td>0.895</td>
</tr>
<tr>
<td>BC-SDBS-CNT</td>
<td>First order ( q_t = q_e(1 - e^{-kt}) )</td>
<td>( k_1 = 1.24 )</td>
<td>( q_{e1} = 3.87 )</td>
<td></td>
<td>0.664</td>
</tr>
<tr>
<td></td>
<td>Second order ( q_t = k_2q_2^2t/1+k_3q_2^2t )</td>
<td>( k_2 = 1.34 )</td>
<td>( q_{e2} = 3.86 )</td>
<td></td>
<td>0.811</td>
</tr>
<tr>
<td></td>
<td>Elovich ( q_t = \frac{1}{\beta} \ln(\alpha t + 1) )</td>
<td>( \alpha = 205.14 )</td>
<td>( \beta = 2.21 )</td>
<td></td>
<td>0.910</td>
</tr>
<tr>
<td></td>
<td>Langmuir ( q_t = \frac{K_Smax C_e}{1 + KC_e} )</td>
<td>( K = 0.02 )</td>
<td>( S_{max} = 19.36 )</td>
<td></td>
<td>0.889</td>
</tr>
<tr>
<td></td>
<td>Freundlich ( q_t = K_f C_e^n )</td>
<td>( K_F = 0.87 )</td>
<td>( n = 0.65 )</td>
<td></td>
<td>0.908</td>
</tr>
<tr>
<td></td>
<td>L-F ( q_t = \frac{s_{max}(KC_e)^n}{1+(KC_e)^n} )</td>
<td>( K = 0.00 )</td>
<td>( S_{max} = 122.63 )</td>
<td>( n = 0.69 )</td>
<td>0.907</td>
</tr>
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Table 5-2. Best fit model parameters for sorption kinetics and isotherms continued.

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Model*</th>
<th>Parameter 1</th>
<th>Parameter 2</th>
<th>Parameter 3</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HC-SDBS-CNT</strong></td>
<td>First order</td>
<td>$k_1 = 1.00$</td>
<td>$q_{e1} = 11.52$</td>
<td></td>
<td>0.847</td>
</tr>
<tr>
<td></td>
<td>Second order</td>
<td>$k_2 = 0.13$</td>
<td>$q_{e2} = 12.30$</td>
<td></td>
<td>0.932</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>$\alpha = 106.90$</td>
<td>$\beta = 0.56$</td>
<td></td>
<td>0.979</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>$K = 0.81$</td>
<td></td>
<td>$S_{\text{max}} = 15.2$</td>
<td>0.819</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>$K_F = 6.82$</td>
<td></td>
<td>$n = 0.21$</td>
<td>0.873</td>
</tr>
<tr>
<td></td>
<td>L-F</td>
<td>$K = 0.04$</td>
<td>$S_{\text{max}} = 28.03$</td>
<td>$n = 0.33$</td>
<td>0.877</td>
</tr>
<tr>
<td><strong>BC-SDBS-CNT</strong></td>
<td>First order</td>
<td>$k_1 = 10.82$</td>
<td>$q_{e1} = 9.81$</td>
<td></td>
<td>0.786</td>
</tr>
<tr>
<td></td>
<td>Second order</td>
<td>$k_2 = 1.65$</td>
<td>$q_{e2} = 9.98$</td>
<td></td>
<td>0.816</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>$\alpha = 124066.96$</td>
<td>$\beta = 1.44$</td>
<td></td>
<td>0.657</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>$K = 2.16$</td>
<td></td>
<td>$S_{\text{max}} = 13.7$</td>
<td>0.935</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>$K_F = 7.24$</td>
<td>$n = 0.17$</td>
<td></td>
<td>0.898</td>
</tr>
<tr>
<td></td>
<td>L-F</td>
<td>$K = 1.66$</td>
<td>$S_{\text{max}} = 14.7$</td>
<td>$n = 0.62$</td>
<td>0.954</td>
</tr>
</tbody>
</table>

$q_t$ and $q_e$ are the amount of sorbate removed at time $t$ and at equilibrium, respectively (mg g$^{-1}$), and $k_1$ and $k_2$ are the first-order and second-order sorption rate constants (h$^{-1}$), respectively. $\alpha$ is the initial sorption rate (mg g$^{-1}$) and $\beta$ is the desorption constant (g mg$^{-1}$), $K$ and $K_F$ are the Langmuir bonding term related to interaction energies (L mg$^{-1}$) and the Freundlich affinity coefficient (mg$^{(1-n)}$ L$^n$ g$^{-1}$), respectively, $S_{\text{max}}$ is the Langmuir maximum capacity (mg g$^{-1}$), $C_e$ is the equilibrium solution concentration (mg L$^{-1}$) of the sorbate, and $n$ is the Freundlich linearity constant.
Figure 5-1. Thermogravimetric analysis of pristine and modified. A) HC and B) BC sorbents.

Figure 5-2. Preliminary assessments for sorption of SPY and Pb onto biochars
Figure 5-3. Kinetic plots for sorption of A) SPY and B) Pb onto surfactant-CNT-modified biochars.

Figure 5-4. Intra-particle diffusion plots for sorption of A) SPY and B) Pb onto surfactant-CNT-modified biochars
Figure 5-5. Isotherms for sorption of A) Pb and B) SPY onto surfactant-CNT-modified biochars.

Figure 5-6. Co-sorption of Pb and SPY in binary solute system (a – b).
Figure 5-7. Fourier transform infra-red analysis of SDBS-CNT biochars and SPY laden SDBS-CNT biochars.

Figure 5-8. Possible sorption mechanisms for SPY and Pb sorption on SDBS-CNT modified biochars.
CHAPTER 6
ENGINEERED BIOCHARS FOR THE REMOVAL OF METALLIC, ORGANIC, AND EMERGING CONTAMINANTS FROM AQUEOUS SOLUTIONS

Conclusions

The overarching objective of this study to develop useful biochars using cost-effective activation techniques requiring less cost and labor; yet achieving high removal efficiencies for traditional (e.g., heavy metals and dyes) and emerging contaminants such as nanoparticles and pharmaceutical residues, was achieved in most cases. The important findings critical to this research work are summarized as follows:

First, biochar produced from anaerobically digested dairy waste (DAWC), and sugar beets (DWSBC) residuals could effectively remove lead, cadmium, nickel and copper from aqueous solutions. In particular, their sorption capacity for lead was comparable to that of commercial activated carbons and precipitation was considered the primary mechanism controlling the sorption of lead. Lead was precipitated on digested anaerobically digested biochars because of its reaction with slowly released carbonate or phosphate ions within DAWC or DWSBC. Moreover, the presence of these carbonate and phosphate deposits within the digested biochar matrix makes them good soil conditioners, particularly in acidic soils. Based on the performance and potential applications of anaerobically digested biochars, digested biochars can be competitive water purification products in the market of adsorbents.

Second, chemically activated carbons from iron impregnation/precipitation on carbon surfaces generally improved their retention for CNT, and NTiO₂, but were not effective for improving AgNP retention. In addition, among all the ENPs, CNT had the highest mobility and the most environmental risk of being released from filter media because over 90% of the CNT was released from the columns. But, iron-modified
biochars showed better retention of CNT than raw biochars and commercial activated carbons, and may be considered as more cost-effective options than activated carbons for mobilizing CNT. Still, the retention of ENPs on the carbon-based filter media, was only slightly improved by iron-impregnation of the carbons and an optimization of process conditions may be required (e.g., reducing flow rate and increasing column length) to enhance the retention of ENPs on the carbons.

Third, incorporating CNT with biochar to make hybrid CNT-biochar nanocomposites was beneficial in improving the physiochemical properties and sorptive properties of hickory (HC) and bagasse (BC) biochars. Specifically, the addition of 1% CNT by weight in BC dramatically increased its surface area by 40 times and also doubled its sorption capacity for MB via electrostatic attractions mechanisms. Additionally, the effect of solution chemistry on the sorption of MB on biochars was evident for both modified and unmodified biochars. Thus, in order to maximize the sorption of MB on raw and CNT-modified biochars, low ionic strength conditions and an optimum pH of 7 should be maintained to reduce the competition effect between MB and other cations.

Lastly, depositing SDBS-dispersed CNT onto biochar matrix (SDBS-CNT biochar nanocomposites) generally improved their sorption capacities for Pb and SPY compared to CNT-biochars (without surfactants) or pristine hickory (HC) and bagasse (BC) biochars. But, slight improvements in the physiochemical properties (e.g., thermal stability, surface area, pore volume, and zeta potential) of the SDBS-CNT biochar nanocomposites were only observed in HC-SDBS-CNT biochars, which might be due to higher CNT contents. In addition, higher thermal stability of HC-SDBS-CNT may be due
to more aromatic lignin components of HC-SDBS-CNT compared to BC-SDBS-CNT. Sorption of Pb and SPY onto SDBS-CNT biochars was likely influenced by multiple mechanisms such as surface adsorption, electrostatic attraction, complexation and π-π bondings. The use of high temperature biochars (> 700 °C) with significant graphite contents can also be suggested to improve retention of SPY when combined with graphite-rich CNT because of enhanced π-π couplings.

In conclusion, this study has shown that biochars from low cost materials can be modified to produce “activated biochars”, for sorbing a wider array of contaminants. In some cases, the sorption capacities of these modified biochars were comparable and even surpassed commercial activated carbons for some contaminants. In addition to high sorption capacities, these modified biochars have resulted in the improvement of physiochemical properties including, higher thermal stabilities comparably better than emerging sorbents such as carbon nanotubes in some instances. Moreover, the modification techniques employed here in this study are simple, and non-laborious. These modified biochars could be potential cost-effective technologies for water purification, soil fertility enhancements and carbon sequestration.

**Recommendations**

The research studies presented here opens exciting avenues to improve the process of biochar production and activation, as well as expand the application of biochar for remediation purposes. Possible avenues to improve the potential of this research for practical applications which can be considered for further studies are outlined in the following:

Firstly, the process of filtering ENPs on the biochars did not achieve high retention of ENPs on the carbon-based filter media. Therefore, modifying solution
chemistries and process conditions, (e.g., increasing the column length, and reducing flow rates, and increasing the ionic strength of the filter media) may be considered to maximize the retention of ENPs in the carbon filter media.

Secondly, SDBS-CNT biochars showed great potential for removing SPY and Pb from aqueous solutions, but the improvements in the properties of BC-SDBS-CNT may have been limited by SDBS-dispersion of CNT. The physiochemical properties of BC-SDBS-CNT may be improved by examining the optimum SDBS to CNT ratios that can be employed to maximize the sorptive properties of BC-SDBS-CNT.

Finally, recycling SPY laden SDBS-CNT biochar nanocomposites for disinfection purposes can be considered to exploit the anti-microbial properties of SPY. Further study examining the potential of these materials to be used in reducing bacterial or algal populations in environmental systems would be advantageous.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Mandu Ime Inyang was born in Lagos, Nigeria. She received her Bachelor of Technology degree in chemical engineering from Ladoke Akintola University of Technology, Oyo state, Nigeria in 2005. Prior to her graduation, she served as an Intern in the National Engineering and Technical Company (NETCO), Lagos, Nigeria, where she gained experience in process design. After graduation, she worked as a chemistry instructor, teaching chemistry to National Diploma students in the Basic and Applied Science Department, Niger state polytechnic, Zungeru, Nigeria before proceeding to the United States for graduate studies. Mandu began her graduate research as a research scholar/exchange student in the Bioprocess laboratory, Agricultural and Biological Engineering Department where she was involved in the pilot scale production of biodiesel from waste vegetable oil for six (6) months and gained experience in the characterization of biodiesel according to ASTM fuel quality standards. At the end of her exchange program, she enrolled in a master’s program in Agricultural and Biological Engineering Department and continued her research in renewable energy. During her master’s, Mandu served as a research assistant working in the Bioprocess, and Environmental Nanotechnology Laboratories. She gained experience in generating biogas from anaerobic digestion of biomass materials, and converting the digestion residuals to carbon adsorbents. She immediately proceeded to continue doctoral studies in agricultural and biological engineering, at the end of her master’s in the field of environmental nanotechnology. Her doctoral research has focused on the engineering of hybrid carbon adsorbents using anaerobic digestion, chemicals and nano-materials to improve their sorption capacity for a wider range of contaminants. Mandu attributes her success to a firm trust, and unwavering confidence in God.