BIOCHAR FROM ANAEROBICALLY DIGESTED SUGARCANE BAGASSE: ENERGY AND ENVIRONMENTAL APPLICATIONS.

By

INYANG MANDU IME

A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2010

To God, and my family, none of this would have been possible without your love and support

ACKNOWLEDGMENTS

I would like to extend my deepest appreciation towards those individuals who have contributed to make this research a success. Firstly, I am grateful to God for being my anchor, and my family, especially my parents, Mr. and Mrs. Ime S. Inyang for their continuous support and encouragement towards my academic endeavors.

Secondly, I express my sincere gratitude to my kind and patient advisor, Dr. Bin Gao, for believing in me and supporting me throughout this research study. His critique and advice were valuable to the timely completion of this work. For introducing me to a career of research in academia, I am grateful to Dr. Pratap Pullammanappallil. Thank you for serving as co-chair on my committee and your guidance throughout this research. I am grateful to Dr. Andrew Zimmerman for his criticism and time in editing the draft of this manuscript. I say thank you to Dr. Ben Koopman for serving on my committee and for providing suggestions to improve the quality of my work. I also remember Dr. Spyros S. and thank him for his advice and recommendations in initiating my Masters study. My special thanks go to Dr. Ding Wenchuan for his tireless efforts in acquiring accurate experimental data for this research work and to Orlando Lanni, and Steven Feagle for their technical input in the design and fabrication of the tubular reactor used in this study.

Finally, I would like to thank the following individuals for making my research experience a pleasurable one: My mentor, Abhay Koppar; my U.S. mothers, Susie Studstill and Donna Rowland; my room mate, Dr. Zhihong Fu; my friends: Zhouli Tian, Samriddhi Buxy, and all the group members of the Bioprocess, and Environmental Nanotechnology Laboratory. I save the last thanks for my sister, Uduak Inyang and my guardian, Dr Ademola Raji, thank you for all the assistance you have rendered to me.

TABLE OF CONTENTS

page

LIST OF TABLES

LIST OF FIGURES

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Science

BIOCHAR FROM ANAEROBICALLY DIGESTED SUGARCANE BAGASSE: ENERGY AND ENVIRONMENTAL APPLICATIONS.

By

Inyang Mandu Ime

August 2010

Chair: Bin Gao
Co-chair: Pratap Pullammanappallil
Major: Agricultural and Biological Engineering

Innovative technologies for converting carbon-rich biomass into value-added products such as biochar and biofuel may provide new solutions to meet the rising energy demands as well as to mitigate greenhouse gas emissions. This study was designed to investigate the potential of using anaerobically digested sugarcane bagasse residuals for improved biochar and biofuel production, as well as to explore the application of the biochars produced for sequestering lead from water. Raw sugarcane bagasse was anaerobically digested under thermophilic conditions (55-60 ^{o}C) to produce methane. The residue obtained from the digestion process along with fresh bagasse was pyrolyzed into biochar at 600 ^{o}C in a nitrogen gas environment for 2 hours. The digested bagasse biochar (DB600), undigested bagasse biochar (B600) and activated carbon (AC) were physiochemically characterized and then used in batch lead sorption experiments to determine their sorption abilities to lead. The Gompertz model was used to model the methane yield data, and kinetic and Langmuir models were used to simulate the sorption characteristics of lead onto the sorbents. While, the methane yield from bagasse was 84.75 L/kgVS, the biofuel yields from the pyrolyzed digested

bagasse residue and undigested bagasse were 82% and 77% of their dry weights respectively. Although, biochars (DB600 and B600) were produced from the digested residue and the raw bagasse at similar efficiencies (18% and 23% respectively), there were many physiochemical differences between the two biochar samples. Compared to B600, DB600 had higher pH, surface area, cation exchange capacity (CEC) and anion exchange capacity (AEC), as well as a more negative surface charge. AC had a much higher surface area (1100 m^2/g) than DB600 and B600 (below 20 m^2/g). Adsorption isotherm data showed that despite its low surface area, DB600 had the highest lead sorption ability, with a maximum lead sorption capacity (653.9 mmol/kg) double that of AC (395.3 mmol/kg), and about 20 times higher sorption ability than B600 (31.3 mmol/kg). Post-sorption experiment characterizations using X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicated that the enhanced sorption of lead by DB600 was partly governed by a precipitation mechanism. In addition, desorption studies showed that Pb-laden biochar samples can be regenerated by acid washing, with lead recovery rates of about 75%. The physiochemical properties reported in this study are generally desirable for soil amelioration and contaminant remediation or wastewater treatment and, thus, suggest that, the pyrolysis of anaerobically digested residues to produce biochar and biofuel may be an economically and environmentally beneficial use of agricultural wastes to meet rising energy demands as well as generate biologically activated biochar for heavy metal uptake.

CHAPTER 1
INTRODUCTION

Sugarcane *(Saccharum Officinarum L.*) is a tropical crop that accounts for two-thirds of global sugar production (D'Hont et al. 2008). In addition to the production of sugar, there has been an increased interest in value added products that can be derived from the plant (Altpeter and Oraby 2010). One important byproduct obtained from sugarcane is *bagasse*, a fibrous, residual material derived after the extraction of cane juice. In the United States, Florida alone accounts for over 850000 tons of bagasse (Burnham 2010), most of which are either burnt as a fuel in sugar mills directly or used in the production of biofuels and other value added products shown in Figure 1-1.

Recently, there has been significant interest in the conversion of bagasse to high energy products via extensive thermal degradation (combustion, pyrolysis and liquefaction) (Katyal et al. 2003). Energy products derived from the combustion of bagasse in the absence of air include: bio-oil, non-condensable gases, and the solid product, biochar. Biochar, also known as bio-charcoal is black carbon derived from the pyrolysis of any carbon-rich biomass in an oxygen-starved environment. Several studies have shown that biochar, in addition, to being used as a fuel source, can be used as an adsorbent for binding metal and organic contaminants in wastewater, and also as a soil conditioner for carbon sequestration and soil fertility amelioration (Cao et al. 2009; Chan et al. 2008; Chen et al. 2008; Gathorne-Hardy et al. 2008; Lal 2008; Liu and Zhang 2009; Mohan et al. 2007a). For example, Soltan et al., (2007) reported over 90% removal of several metal ions including lead (Pb) and iron (Fe) by sugarcane bagasse char (Figure 1-2). Thus, biochar produced from sugarcane bagasse may be a viable

and economically attractive bio-product for handling contaminant remediation in most industries such as the sugar industry.

Anaerobic digestion is one of many biomass-conversion technologies for the production of biogas. The process of anaerobic digestion is a biochemical one, involving the mineralization of organic compounds such as carbohydrates, fats, and proteins to biogas through the syntrophic action of several groups of micro-organisms in the absence of the electron acceptor, oxygen (Lai et al. 2009; Nopharatana et al. 2003). The engineered process of anaerobic digestion finds a wide variety of applications in waste treatment processes such as wastewater treatment (Appels et al. 2008; Radjenovic et al. 2009; Tomei et al. 2009), animal waste disposal (Ahn et al. 2010; Baert et al.; Costa 2009; Li et al.; Li et al. 2009; Myint and Nirmalakhandan 2009), industrial and agricultural waste treatment (Kacprzak et al. 2010; Kryvoruchko et al. 2009; Llaneza Coalla et al. 2009; Mallick et al. 2010; Mohring et al. 2009; Swapnavahini et al. 2010). In addition to these applications, anaerobic digestion has been notably used in the generation of biogas (CH_4 and CO_2) (Appels et al. 2008).

According to Yu and Schanbacher (2010), the production of biogas via anaerobic digestion involves a series of complex microbiological processes (Figure 1-3) including: (1) the hydrolysis of polymeric substances (polysaccharides, lipids and proteins) into simple sugars easily degraded by the cellulolytic bacteria; (2) the fermentation of the simple sugars into volatile fatty acids such as formic acetic acid, propionic acid, butyric acid and valeric acid, accompanied by the production of CO_2 and H_2; and (3) the conversion of these acid products into the biogas mixture of methane and carbon dioxide.

Sugarcane bagasse is an agricultural residue consisting of cellulose, hemicellulose and lignin. While the cellulose and hemicellulose portions of bagasse are more readily degraded by most microbial cultures, the lignin portion of bagasse is more recalcitrant, thus reducing the biogas potential of sugarcane bagasse. Several studies have confirmed the low biogas potential of bagasse (Figure 1-4) as a result of its recalcitrant lignin portion (Kivaisi and Eliapenda 1995; Osman et al. 2006). It is also known that the amount of biogas produced from most digested feedstock is in direct proportion to the level of degradation of the feedstock by the cellulolytic bacteria. Hence, the low biogas potential of sugarcane bagasse from anaerobic digestion suggests a high generation of residuals at the completion of the digestion process. As such, the production of the carbonaceous sorbent, biochar, from the pyrolysis of the digested bagasse residue, in addition to the generation of bio-energy from the anaerobic digestion process has been proposed in this research study as an economically attractive possibility.

The goal of this study was to investigate the generation of biogas from sugarcane bagasse and explore the feasibility of converting the solid residuals of digestion into a carbon sorbent, biochar which may be useful in the adsorption of metal contaminants. In this research thesis, chapter 2 presents an investigation of the benefits of using anaerobic digestion as a biological activation method for enhancing the adsorptive physiochemical properties of biochar produced from the digested residuals as well as the bio-energy production efficiency of biochar's production process. Chapter 3 further explores the use of biochar in sequestering the metal ion, lead, and compares

its adsorption ability to the more widely used commercial activated carbon. Chapter 4 summarizes this research work and recommends possible areas for future work.

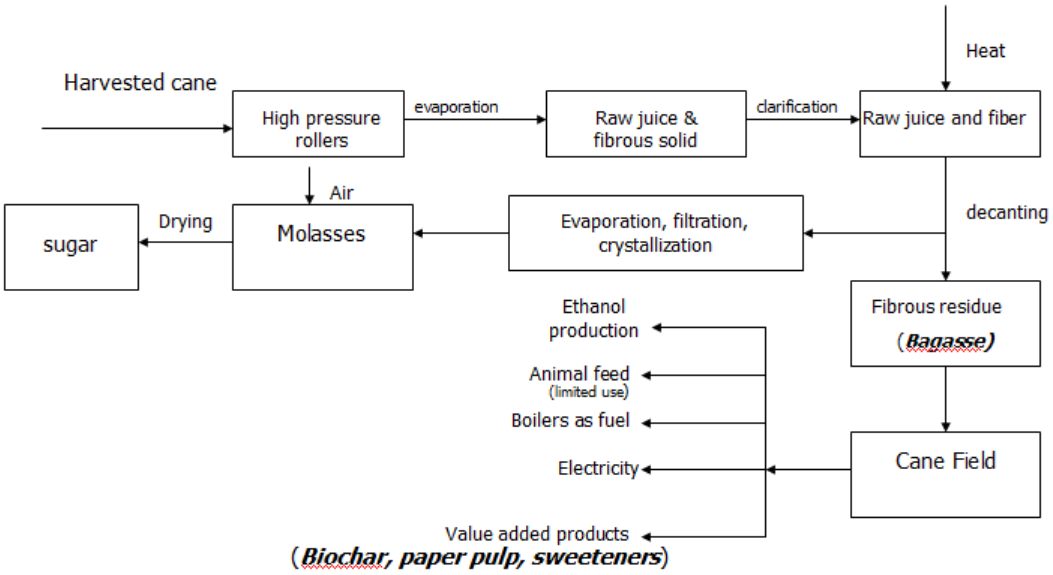


Figure 1-1. Production of sugar from sugarcane (adapted from the Natural Mill Process, Florida Crystals, Okeelanta).

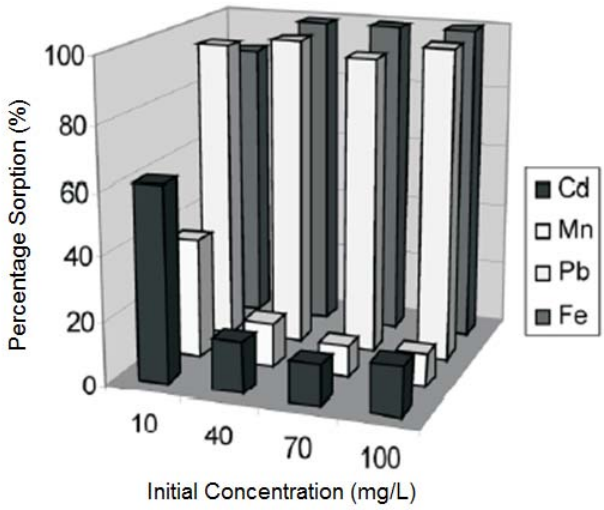


Figure 1-2. Adsorption of heavy metals by bagasse coal (adapted from Soltan et al., (2007), Aswan, Egypt)

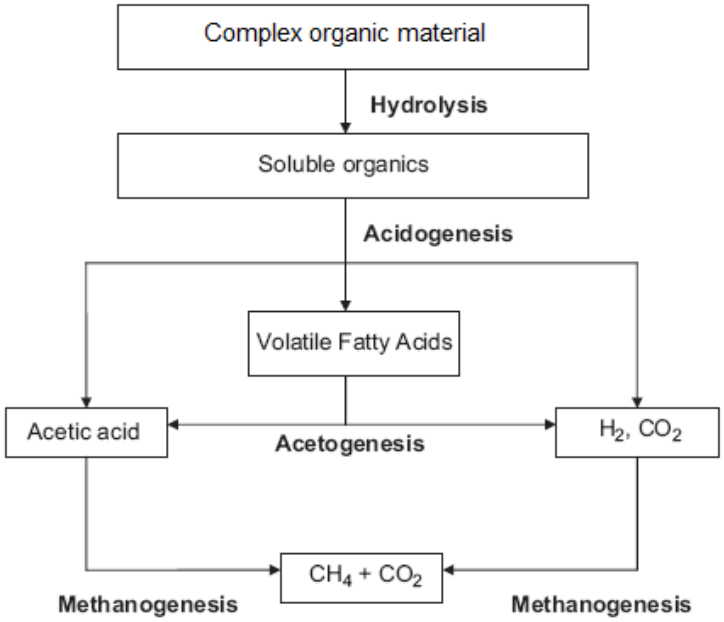


Figure 1-3. Schematic of biogasification process for methane production (adapted from Appel et al., (2008))

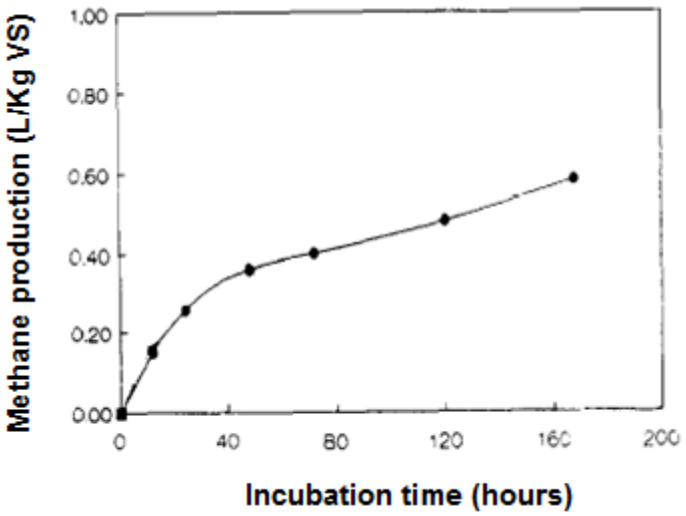


Figure 1-4. Methane yield from bagasse adapted from Kivaisi and Eliapenda (1995)

CHAPTER 2
EFFECT OF ANAEROBIC DIGESTION ON BIOCHAR PRODUCED FROM SUGARCANE BAGASSE

Introduction

The conversion of biomass into value-added products such as biofuel and biochar has attracted broad research interest. This can be attributed to the rising energy demands and concerns over greenhouse gas emissions (Burnham 2010). As one of the most popular bioenergy conversion technologies, thermal pyrolysis of carbon-rich biomass is unique because it produces biochar (charcoal) in addition to biofuel. Recent studies have highlighted the benefits of pyrolysis and biochar technologies, particularly with respect to carbon sequestration via land application of biochar (Osman et al. 2006). As a result, the conversion of biomass into biochar and biofuel has received greater attention from government regulation agencies and the general public. For example, the 2008 Farm Bill established the first federal-level policy in support of biochar production and utilization programs nationally, and biochar has been mentioned in the United Nations Framework Convention on Climate Change (UNFCC 2009).

Sugarcane bagasse is the residual material derived from sugarcane after extracting cane juice. Like most agricultural residues, bagasse is a carbon-rich biomass, highly abundant and suitable for biofuel and biochar production. Several studies have been conducted to explore the potential of biofuel production from bagasse through pyrolysis (Pandey et al. 2000), but limited attention has been paid to biofuel production from anaerobic digestion of bagasse. For instance, over 850000 tons of bagasse generated by Florida in the United States are either burnt directly as fuel in sugar mills or disposed of in landfills (Kivaisi and Eliapenda 1995). Anaerobic digestion of bagasse

could be an additional source of biofuels (Kivaisi and Eliapenda 1995; Rodriguezvazquez and Diazcervantes 1994).

Bagasse is a complex lignocellulosic material which consists primarily of 50% cellulose, 25% hemicellulose, and 25% lignin, in addition to other components such as pentosans, α-cellulose, and ash (Amjed et al. 1992). Anaerobic digestion of most lignocellulosic materials like bagasse proceeds at low loading rates, long solid retention times and low conversion efficiencies (Rodriguezvazquez and Diazcervantes 1994). A few studies showing the feasibility of biogasifying sugar cane bagasse for biofuel (mainly methane) production, have indicated the hydrolysis of cellulose as the rate limiting step and the crystallinity of cellulose as a major obstacle in the digestion process (Tyagi et al. 1988). In overcoming these challenges, researchers have suggested the use of steam explosion, acid, and alkaline pre-treatment methods to enhance the digestion of bagasse to methane (Sialve et al. 2009).

Using a variety of these anaerobic digestion pre-treatment methods, a maximum bagasse digestibility of 75% by weight has been reached (Rodriguezvazquez and Diazcervantes 1994). Consequently, at least 25% of bagasse will remain as residue after the digestion process. Residues (sludge) obtained from anaerobic digestion are often applied as compost to soils directly. Increasing concerns on the potential contamination of the food chain by toxic trace elements, however, have necessitated alternative methods of sludge recycling (Tyagi et al. 1988). Pyrolysis of anaerobically digested bagasse residue to produce biochar has been proposed as a beneficial product that could be obtained from digestion residuals (Sialve et al. 2009).

This study examined the conversion of sugarcane bagasse into biochar and biofuel using anaerobic digestion and thermal pyrolysis. Anaerobic digestion of bagasse was carried out to generate methane and possibly improve the stock material properties for biochar production. Two feedstock materials were employed in this study: raw bagasse and the residue obtained from anaerobically digested bagasse. These materials were converted into biochar and biofuel at 600^{o}C. The conversion rates of biochar and biofuel were determined. In addition, physicochemical properties (pH, surface area, and zeta potential, SEM, FTIR, CEC and AEC) of the biochars produced were characterized in laboratory.

The objectives of this study was to: 1) determine the methane potential of sugarcane bagasse via anaerobic digestion, 2) examine the feasibility of using the digested sugarcane bagasse residue as a feed stock for biochar and biofuel production, and 3) compare the physicochemical properties of biochar obtained from digested bagasse residue to those of biochar obtained from pyrolysis of sugarcane bagasse directly.

Materials and Methods.

Raw Materials

The feed stock**, s**ugarcane bagasse (sized 0.5 – 1mm), was obtained from Florida Crystals, Okeelanta, Florida and stored in air-tight trash bags and refrigerated until ready for use. Prior to the digestion of the samples, 150g aliquots of the refrigerated bagasse were dried in an oven (Fisher Scientific Isotemp 350G) at 105 ^{o}C for 24 hours. Volatile solid (VS) content of bagasse was determined by ashing 100g of the dried samples in a muffle furnace (Fisher Scientific Isotemp) at 550^{0}C for 2 hours.

The total solids (TS) and volatile solids (VS) content of the feedstock were determined gravimetrically before and after the digestion process.

Anaerobic Digestion of Sugarcane Bagasse

A thermophillic anaerobic digester was used to extract methane from raw bagasse (Figure 2-1). The design and procedures of the anaerobic digestion experiment were similar to those of Koppar and Pullammanappallil (2008). In brief, 400g of fresh bagasse (wet weight) was added to the digester and mixed with porous volcanic rocks (average grain size 25mm, from a landscaping supplier) to prevent compaction of the solids. To initiate the anaerobic digestion process, 2 L of inoculum, obtained from an existing thermophilic reactor was added to the digester containing the feedstock. The digester was then sealed and incubated at a constant temperature of 55^{o}C until the end of the experiment. The pH of the mixture was monitored daily. Methane produced from the anaerobic digester under batch conditions was monitored with a positive displacement gas meter consisting of a clear PVC U-tube filled with anti-freeze solution, solid state time delay relay (Dayton Off Delay 6X153E), a float switch (Grainger Inc.), a counter (Redington Inc.) and a solenoid valve (Fabco Air Inc.). The U-tube gas meter was calibrated in-line to determine the volume of biogas. A gas syringe was used to draw samples from the digester port daily and concentrations of methane and carbon dioxide produced was determined with a Gas Chromatograph (Fisher Gas Partitioner 1200). Anaerobic digestion was considered complete when no further gas production was recorded by the gas meters. The sealed digester was opened and emptied and the solid residue was separated from the inoculum and dried at 105 ^{0}C in the oven. A fraction of the dried residue was analyzed for TS and VS content and the remaining

mass was used for biochar production. The methane yield from the anaerobic digestion of bagasse was reported in terms of the values of VS obtained.

Biochar and Biofuel Production

Both raw bagasse and digested bagasse residue were converted into biochar using a bench scale pyrolyzer (Figure 2-2). For each experiment, 15g of dried samples were fed into a mini tubular reactor (6cm diameter cylinder, 28cm long) designed to fit a bench-top furnace (Barnstead 1500M). The tubular reactor was first purged with nitrogen gas (10 psi) and an oxygen sensor attached to the reactor ensured that the oxygen content in the reactor was less than 0.5% before it was inserted into the furnace. The reactor was purged again with N_2 along with the furnace and sealed for pyrolysis. The controller of the bench-top furnace was programmed to drive the furnace temperature to 600 ^{o}C at a rate of 10 ^{o}C/min and held at the peak temperature for 1.5 h before cooling to room temperature. Biochar produced from the pyrolysis was crushed and sieved into two size fractions to separate the ash: <0.5 mm and 0.5-1mm. Only the latter was used in the characterizations to reduce the ash content in the biochar.

Physicochemical Properties of Biochar

A range of physicochemical properties (e.g., pH, surface properties, elemental compositions, etc.) of the digested bagasse biochar (DB600) and the undigested bagasse biochar (B600) were determined using the outlined methods below:

pH

The pH of the biochar was measured by adding biochar to deionized water in a mass ratio of 1:20. The solution was then hand shaken and allowed to stand for 5 mins before measuring the pH with a pH meter (Fisher Scientific Accumet Basic AB15).

Surface area

The surface area of the biochar was determined through a surface area analyzer (NOVA 1200) using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method at 77K. Prior to the measurement of the surface areas, the samples were weighed and placed in the cell of the Gas Pycnometer (Quantachrome Ultrapyc 1000), where the true density and volume of the samples were analyzed for input in the NOVA 1200. All the samples were dried at 100 ^{o}C under vacuum before analysis.

Zeta potential

The surface potential of the samples was determined by measuring the zeta potential (ζ) of colloidal biochar according to the procedure of Johnson et al. (1996). 1g of each sample was added to 100ml of de-ionized water and the solution was shaken at 250rpm for 30mins using a mechanical shaker (Erberbach, Ann Arbor, Michigan). The shaken solution was placed in a sonic bath (Branson 3510) to break the particles into colloids and the solution filtered using a filter paper. The ζ of each supernatant solution obtained was analyzed using the Brookhaven Zeta Plus (Brookhaven Instruments, Holtsville, NY). The Smoluchowski's formula was used in converting the electric mobility into zeta potential.

Elemental carbon, hydrogen, nitrogen

Elemental carbon, hydrogen, and nitrogen of the raw bagasse, DB600, and B600 was determined using a CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion followed by infrared detection of resulting CO_2, H_2 and NO_2 gases. The oxygen content was determined by difference. It was assumed that the total dry weight of the samples was made up of C, H, N and O.

Cation and anion exchange capacity.

Cation exchange capacity (CEC) and anion exchange capacity (AEC) of the samples were determined simultaneously using the point of zero net charge method (Zelazny et al. 1996). The samples were mixed with KCl solutions to saturate the biochar's exchangeable cation and anion sites. $NaNO_3$ solutions were used to displace the bound K^+ and Cl^-. Concentrations of the displaced K^+ and Cl^- were determined using a flame atomic absorption spectrometry (FAAS; Varian 220 FS with SIPS, Walnut Creek, CA) and an ion chromatograph (Dionex ICS90), respectively. CEC and AEC of the samples were calculated based on the measured cation and anion concentrations and the sample weight.

Scanning electron microscope imaging

Scanning electron microscope (SEM) imaging of the raw materials and biochar samples was carried out using the Hitachi S-4000 FE-SEM with maximum resolution of 1.5nm. To improve the conductivity of the samples, dried DB600 and B600 were mounted on carbon stubs and sputter coated with gold prior to imaging. Varying magnifications were used to compare the structure of bagasse and biochar samples before and after the anaerobic digestion. The accelerating voltage of the instrument was maintained at 10kv.

Fourier transform infrared analysis

Fourier Transform Infrared (FTIR) analysis of B600 and DB600 was carried out to characterize the surface functional groups present on these samples. To obtain the observable adsorption spectra, B600 and DB600 were ground and mixed with KBr to 0.1 wt% and then pressed into pellets. The spectra of the samples were measured using a Bruker Vector 22 IR (OPUS 2.0 software).

Results and Discussion

In the following, the cumulative methane yield from sugarcane bagasse has been presented. The Gompertz model was used to validate the methane yield data based on the correlation between the yield of methane and the growth of the methanogenic archae. The hypothesis that anaerobic digestion could result in the enhancement of the physiochemical properties of biochar has been proven by the characterization results of biochar. A comparison of the biofuel production efficiency from the pyrolysis of the digested and undigested bagasse biochar has also been presented to show the effect of the digestion process on the amount of biofuel generated.

Methane Yield from Anaerobic Digestion of Sugarcane Bagasse

The total methane yield from the anaerobic digestion of sugarcane bagasse was about 84.75 L/kgVS at the end of 40 days (Figure 2-3). About 58% of the total dry weight of bagasse was lost at the end of the digestion process, based on mass balance calculations, which was higher than the reported value of 16% degradation in bagasse without any pre-treatments by Kivaisi and Eliapenda (1995). Similar low yields of methane from the digestion of untreated bagasse have been reported by Osman et al. (2006) with a total biogas production of 0.02 L/kgVS.

The yield in methane was still lower from anaerobic digestion of bagasse than from that of other feedstock materials such as beet pulps (336 L/kgVS) and sugar beet tailings (295 L/kgVS) (Koppar and Pullammanappallil 2008; Liu et al. 2008). This low yield can be attributed to the crystalline cellulosic structure of sugarcane bagasse. Nevertheless, the cellulose in bagasse was sufficiently degraded by the inoculum to alter the appearance of the digested residue and create a more porous structure in comparison to the raw bagasse (Figure 2-4a and 2-4b). The low yield of methane from

bagasse in this study compared to other feedstock materials could also be attributed to pH inhibition of the digestion process. During the anaerobic digestion of the bagasse, pH in the digester increased from 7.6 to 9.4 (Figure 2-5), which was above the optimum value of 7.0 - 7.5. High pH conditions have been found to suppress methanogens growth, requiring methanogenic archae to expend more energy for homeostasis than anabolism, thus resulting in slow degradation of the substrate (Gutierrez et al. 2009).

Advancement in research efforts for improving the digestion of bagasse, including hemicellulose hydrolysis and conversion of crystalline cellulose to more fermentable sugars could make sugarcane bagasse digestion a more economically attractive process for biofuel production.

Modeling Methane Yield from Sugarcane Bagasse.

Methane production in an anaerobic digester is a microbial associated growth product, often described using sigmoidal curve bacterial growth models such as the Gompertz equation (Koppar and Pullammanappallil 2008). In this study, the modified Gompertz equation derived by Zwietering et al. (1990) was used to simulate methane evolution from sugarcane bagasse, such that:

$$y = A\exp\left\{-\exp\left[\frac{\mu_m \cdot e}{A}(\lambda - t) + 1\right]\right\} \quad (2\text{-}1)$$

where y is the cumulative methane production (L/kgVS), A is the maximum methane yield potential (L/kgVS), μ_m is the maximum methane production rate (L/kgVS/day), λ is the duration of the lag phase (day), e is the Euler's number (2.72), and t is time (day). The model successfully reproduced the experimental data with R^2, exceeding 0.98 (Figure 2-3). The model-estimated A, μ_m, and λ were 81.29 L/kgVS, 5.08L/kgVS/day, and 1.96 days, respectively. These values suggest that the anaerobic

digestion efficiency of sugarcane bagasse is relatively low in comparison to other feedstock materials (Koppar and Pullammanappallil 2008; Liu et al. 2008). The digested sugarcane bagasse residue, therefore, has a better potential to be used as a feedstock material for biofuel and biochar production through pyrolysis.

Biochar and Biofuel Production from Digested and Undigested Bagasse

The biochar produced from the pyrolysis of digested bagasse residue and undigested bagasse had similar production efficiencies of 18% and 23% of the initial dry weight, respectively (Figure 2-6). The slightly lower rate of biochar production from pyrolyzed digested bagasse is probably because of the slight reduction in the carbon content of the bagasse after degradation as indicated by elemental analysis (Table 2-1). Generally, decreased formation of char during volatilization of the biomass is accompanied by increased yield in bio-oil products (Demirbas et al. 2006). The biofuel (i.e., bio-oil and non-condensable gas) production rates from the pyrolysis of digested bagasse residue and undigested bagasse were 82% and 77%, respectively, suggesting that substantial amount of biofuel can still be extracted from the digested bagasse residue through pyrolysis. These figures suggest that it is feasible to use digested bagasse residue as a feedstock for both biochar and further biofuel production.

Effect of Anaerobic Digestion on Biochar Properties

Due to its refractory nature, biochar can be used as a soil amendment to sequester carbon for long periods and as a low-cost adsorbent to remove contaminants from wastewater (Cao et al. 2009; Chan et al. 2008; Liu and Zhang 2009; Novak et al. 2009). The effectiveness of biochar in these potential applications is determined by its physicochemical properties, such as pH, surface charge, BET surface area, CEC, and

AEC. Laboratory characterizations of the DB600 and B600 revealed that anaerobic digestion had a substantial effect on those physicochemical properties (Table 2-2).

Measurements of biochar pH values showed DB600 had a higher pH (10.93) than B600 (7.66) (Table 2-2). The high pH of DB600 can be attributed to the fact that anaerobic digestion may concentrate recalcitrant cationic species (Pb, Cd, Zn, Cr, Cu, Ni) as well as exchangeable cations (Ca, Mg, Na) in the digested residue (Gu and Wong 2004; Hanay et al. 2008). The DB600 also had a higher zeta potential (-61.67 mV) in comparison to B600 (-28.1 mV), indicating that the surface charge of the DB600 was more negative than that of B600. Corresponding to the SEM images (Figure 2-4c and 2-4 d), the BET surface area of DB600 ($18 m^2/g$) was higher than that of B600 ($14 m^2/g$) and may reflect microbial utilization of more labile pore in-filling organic matter, leaving the refractory pore framework intact (Zimmerman 2010). Because pH, surface charge, and surface area are among the most important factors governing a material's interaction with chemical compounds, particularly with respect to cationic metal species, the digested bagasse biochar may therefore better sequester the metal species than non-digested bagasse biochar.

The measured CEC and AEC of DB600 were 14.30 cmolc/kg and 11.19 cmolc/kg, respectively, which were higher than those of B600 (6.64 cmolc/kg and AEC 4.194cmolc/kg). When used as a soil amendment, DB600 would likely be better able than B600 to improve the nutrient holding capacities of the soils. However both biochars would significantly improve the exchange properties of both soils and act similarly to enrichments in natural organic matter. It is further notable that the AEC found for both

chars has not been previously measured in any biochar (Cheng et al. 2008; Cheng et al. 2006; Liang et al. 2006)

The effect of anaerobic digestion on the properties of biochar produced can be further discriminated through its surface functional groups as determined by FTIR spectroscopy (Figure 2-7). It has been reported that surface functional groups present in biochar are mainly a function of the pyrolysis temperature and pyrolysis conditions under which it was produced (Chun et al. 2004). Here however, it was found that biomass pretreatment may also play a role in the resulting functional group distribution. The infra red spectroscopy of DB600 were characterized by four significant bands at wave number 3452 (O-H functional group), 2349 (O=C=O bond group), 1626 (alkene, C=C bond group), and 646 (C-H aromatic group) cm^{-1} (figure 7). The spectrum of B600 was characterized by four significant bands at wave number 3130 (O-H functional group), 1600 (alkene, C=C bond group), 1090 (phenolic, C–O stretch absorption band), and 826 (C-H aromatic group) cm^{-1}. So the major differences include the appearance of the dominant phenolic component in the undigested bagasse biochar only and the presence of inorganic carbonyl group (CO_2) in the digested bagasse biochar only.

All these functional groups have been reported by other authors as common chemical groups, characterizing many carbon sorbents (Cao et al. 2009; El-Hendawy 2003; Nguyen et al. 2009; Ozcimen and Karaosmanoglu 2004; Purevsuren et al. 2003; Suhas et al. 2007; Tsai et al. 2001). The presence of an additional phenolic, C-O stretch band with high absorption intensity in B600 at wave number 1090 cm^{-1} suggests that the alkalinity of B600 was lower than that of DB600 because the phenolic functional group promotes acidity in the biochar (Lopez-Ramon et al. 1999). This result is

corresponding to the pH measurements. Furthermore, the presence of oxygen functional groups in B600 could produce a relatively more hydrophilic characteristic than DB600 which has a greater degree of alkalinity as indicated by the FTIR. As such, the digested bagasse biochar may better sequester contaminants via precipitation at a high pH when used for contaminant remediation.

Based on the characterization of the physicochemical properties of digested and undigested bagasse biochar, it is evident that anaerobic digestion of bagasse enhances the adsorption and ion exchange abilities of biochar produced from digested relative to undigested bagasse residues. Therefore, the method of combining anaerobic digestion and pyrolysis can be used to produce additional biofuel, while generating high quality biochars to be used as low-cost adsorbents or as soil amendments.

Conclusions

In this study, anaerobic digestion of bagasse was carried out to investigate the effect of digestion on the production of biochar and biofuel. Production of biochar from the digested residue (DB600) and undigested bagasse (B600) and subsequent characterization of these biochar samples revealed an enhancement of surface and chemical properties as a major effect of anaerobic digestion. Since the characterization results obtained here, have not been reported previously, this study has established the potential of the digested bagasse biochar as a soil amendment or a low cost adsorbent based on its high ion exchange capacity and highly negatively charged surface.

Another important finding from this study was the high production efficiency of biofuels (non-condensable gases and bio-oil) from the pyrolysis of the digested bagasse residue. With the rising energy demands and security issues from the use of fossil fuels,

combining anaerobic digestion of carbon-rich biomass and subsequent pyrolysis of the residual material may be a feasible solution to the energy crisis.

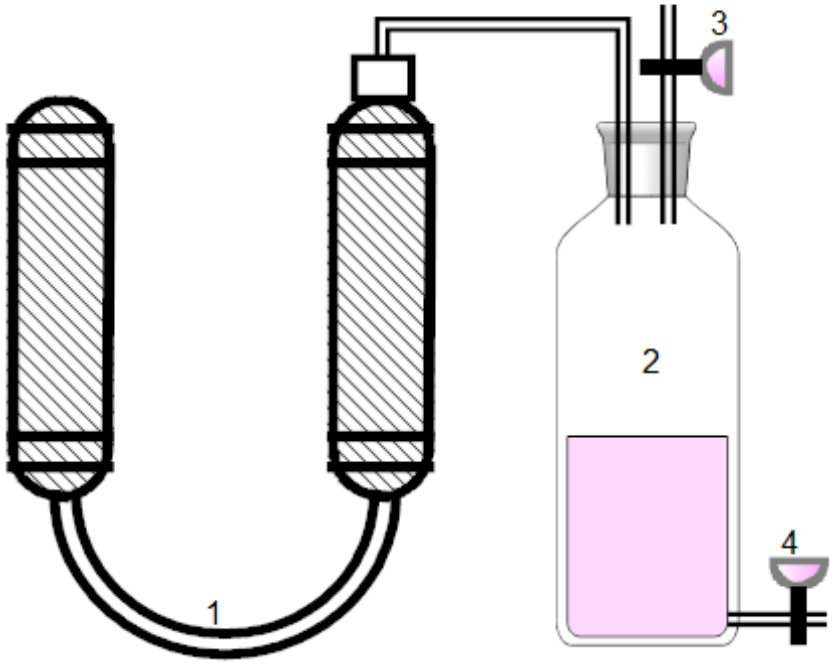
Finally, more research is required to develop methods for improving the digestibility of sugarcane bagasse and increasing cumulative methane yields, since only 84.75 L CH4/kgVS was obtained in this study. With the development of methods for improving the degradation of sugarcane bagasse, the use of anaerobic digestion as a precursor to biochar and biofuel will be an attractive economic venture.

Table 2-1. Elemental analysis of raw bagasse and biochar samples.

Sample	% C	% H	% N	% O
Raw Bagasse	46.08	6.88	0.74	46.3
DB600	73.555	2.405	-	24.04
B600	76.445	2.93	0.79	19.835

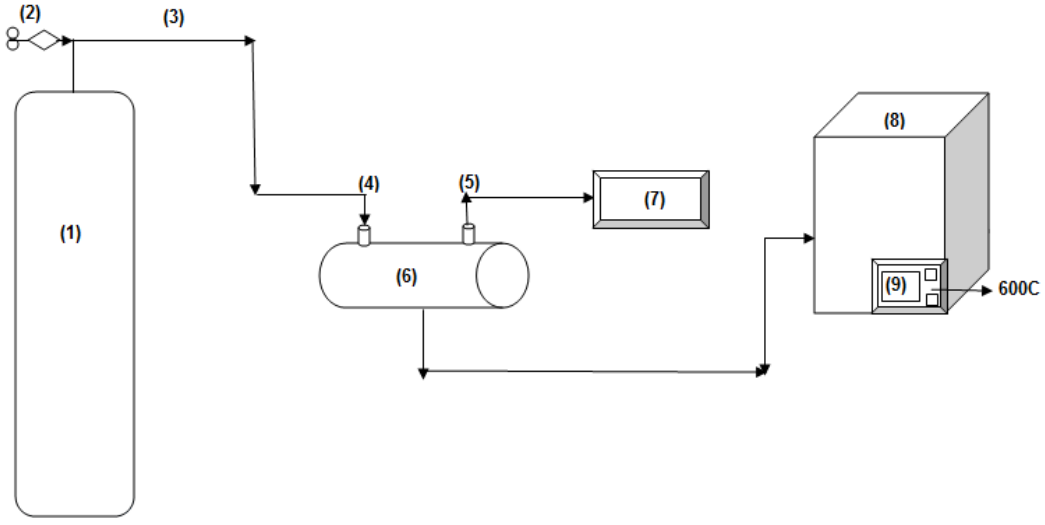
Table 2-2. Summary of the physicochemical properties of biochar samples

Sample	pH	Zeta potential (mv)	BET surface area (m^2/g)	CEC (cmolc/kg)	AEC (cmolc/kg)
DB600	10.93	-61.67	17.66	14.30	11.19
B600	7.66	-28.05	14.07	4.194	6.64



(1) U- tube Gas meter (2) Anaerobic digester (3) Drain valve (4) Gas sampler port

Figure 2-1. Schematic of experimental set-up for anaerobic digestion



(1) N2 gas cylinder (2) Valve (3) N2 gas for purging (4) inlet of the reactor (5) outlet of the reactor (5) outlet of the reactor (6) tubular pyrolytic reactor (7) O2 sensor (8) Furnace (9) Furnace controller

Figure 2-2. Schematic of the experimental set-up for pyrolysis.

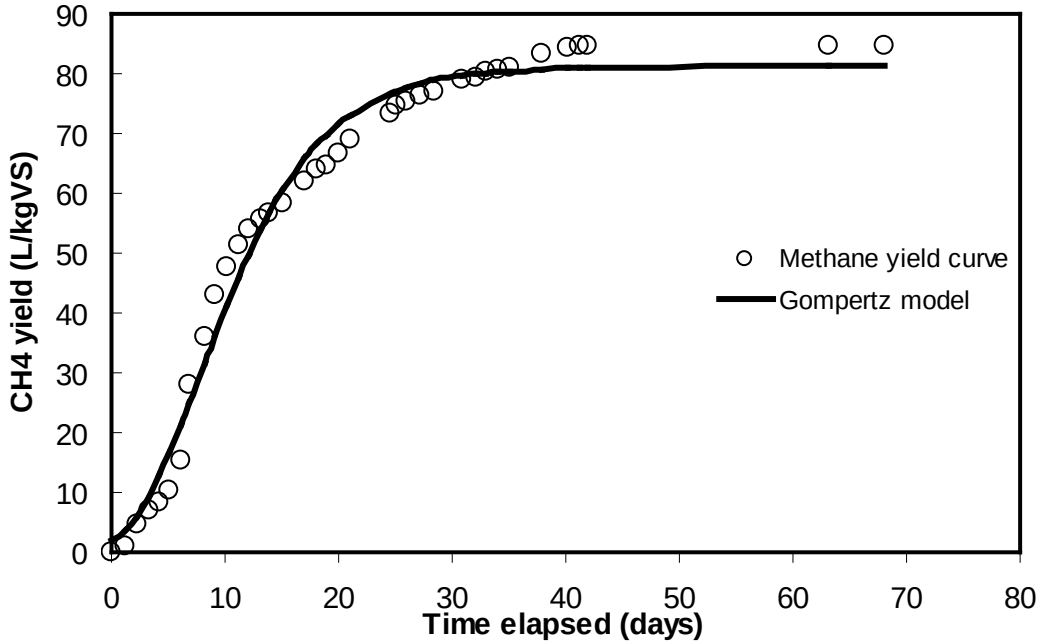
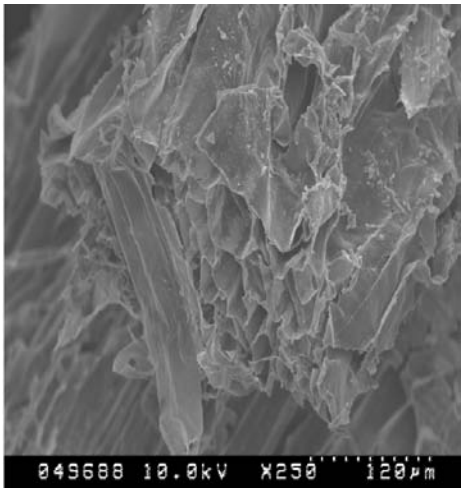
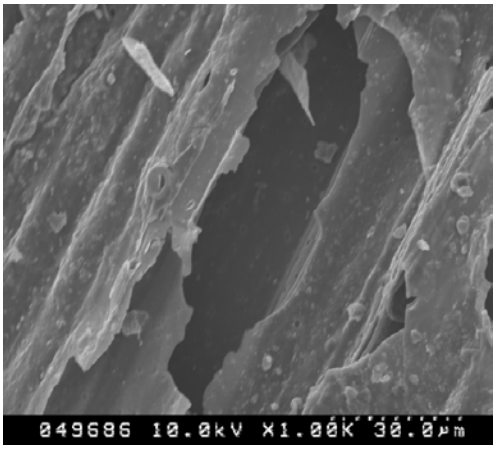


Figure 2-3. Time course of methane yield during anaerobic digestion of sugarcane bagasse.

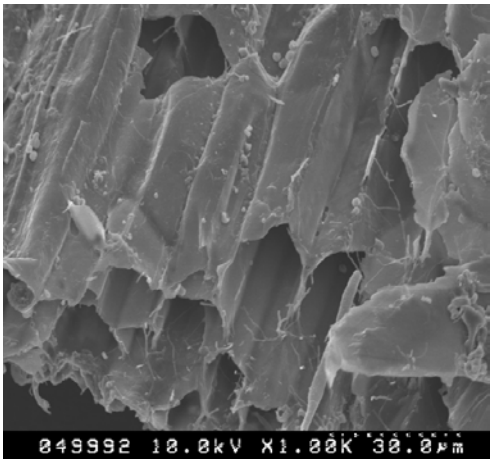
(A) Raw Bagasse



(B) Digested Bagasse Residue



(C) B600



(D) DB600

Figure 2-4. SEM images of raw bagasse A) digested bagasse residue B) raw bagasse biochar C) undigested bagasse biochar and D) digested bagasse biochar.

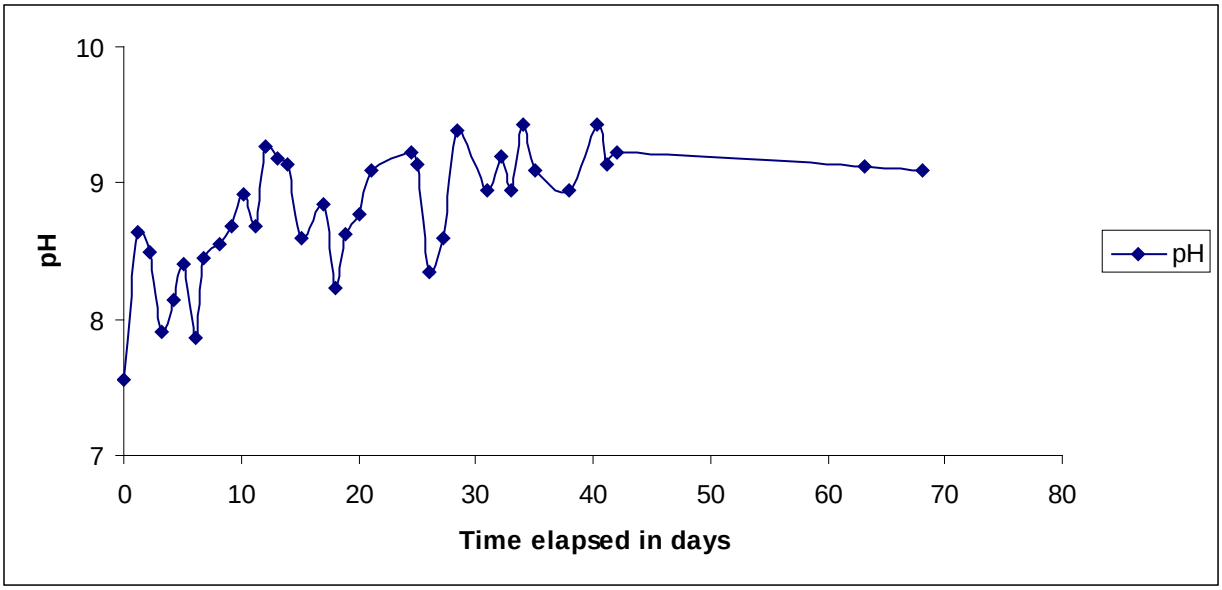


Figure 2-5. Time course of pH during sugarcane bagasse digestion.

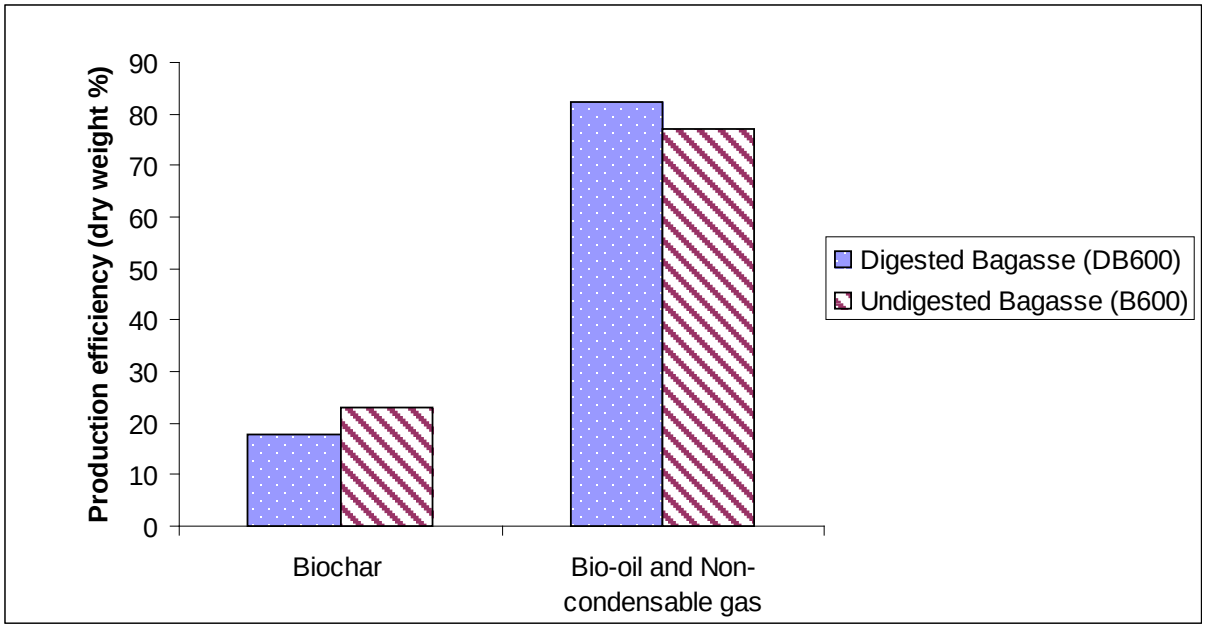


Figure 2-6. Biochar and biofuel production efficiencies from digested and undigested bagasse via pyrolysis.

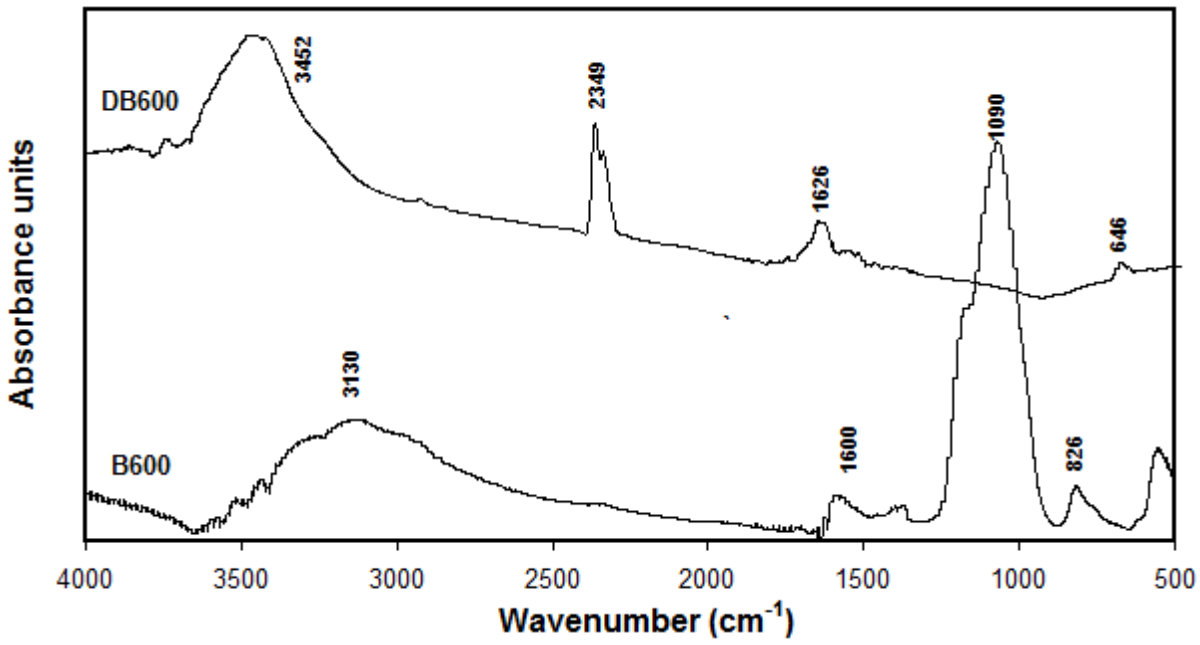


Figure 2-7. FTIR spectra of digested and undigested bagasse biochar

CHAPTER 3
ENHANCED LEAD SORPTION BY BIOLOGICALLY ACTIVATED BIOCHAR FROM SUGARCANE BAGASSE

Introduction

Heavy metal pollution in wastewater has become a pressing environmental concern due to its highly refractory nature which presents a great challenge to remediation efforts. Lead is a highly toxic heavy metal introduced to water bodies from various sources ranging from battery to ammunition industries, and it poses a risk to public health when consumed in drinking water, even at low concentrations due to bioaccumulation (Anderson et al. 1997; Claudio et al. 1997; Namihira et al. 1993; Palaniappan et al. 2009; Saleh et al. 1996) .

Various methods have been employed to remove lead from wastewater including ion exchange, chemical precipitation, membrane filtration, electrodialysis, and granular filtration (Djedidi et al. 2009; Fatin-Rouge et al. 2006; Minceva et al. 2008; Ribeiro et al. 2008; Sadrzadeh et al. 2008; Sari et al. 2007). Most of these methods, however, have high operational costs and are associated with secondary waste treatment and sludge disposal problems (Kumar 2006; Minceva et al. 2008; Navasivayam 1998). It is therefore desirable to develop alternative and less costly lead removal technologies that might minimize the problems associated with conventional wastewater treatment techniques.

Biochar is a black carbon derived from the combustions of carbon-rich biomass (e.g., agricultural residues and organic waste) in an inert atmosphere (pyrolysis). The use of biochar to remove contaminants such as metals or organic contaminants from aqueous solutions is a relatively novel and promising wastewater treatment technology. Several studies have recently reported the effective removal of lead by biochar sorbents

(Cao et al. 2009; Liu and Zhang 2009; Qiu et al. 2008; Sekhar 2008). For example, Cao et al. (2009) reported that biochar made from animal manure was six times more effective than activated carbon in adsorbing lead and had a sorption capacity of up to 680 mmol/kg, and Sekhar et al. (2008) showed biochar made from coconut shell had similar lead sorption capacity with commercial activated carbon of about 145 mmol/kg. These authors have attributed the effective lead removal by biochar sorbents to either precipitation of lead onto the biochar surface or electrostatic interactions between lead species and negatively charged functional groups on biochar's surface. Like many other traditional sorbents, the high affinity for lead and other metal ion species bound by biochar may be controlled by other mechanisms as well, including complexation, chelation, and ion exchange (Mohan et al. 2007b; Sud et al. 2008).

Studies have attempted to improve the metal sorption abilities of biochar from pyrolyzed agricultural residues such as bagasse , pine wood and rice husk . The presence of cellulose, hemicellulose, proteins, sugars, and lipids in these materials provide a variety of functional groups that can be physically activated through pyrolysis and further steam or CO_2 treatment to enhance their uptake of compounds such as lead. There has also been notable work on the chemical activation of agricultural residue derived biochar for lead sorption. To our knowledge, however, no research has explored the use of anaerobic digestion as a means of biological activation to enhance the sorption ability of agricultural residue-derived biochar.

This study investigated the enhanced removal of lead by an anaerobically digested sugarcane bagasse biochar. Raw and digested sugarcane bagasses were pyrolyzed into biochar at 600 ^{o}C in the laboratory. Bench-scale batch sorption and

desorption experiments were conducted to compare the lead sorption ability of the digested bagasse biochar to that of the undigested bagasse biochar and a commercial activated carbon. Mathematical models and material characterization techniques were used to aid the experimental data interpretation. The goal of this study was to understand the effect of anaerobic digestion on the ability of bagasse biochar to remove lead from water, and thus, develop a biological activation technology. The objectives were to: a) compare the sorption kinetics of lead onto digested and undigested bagasse biochar with lead sorption kinetics by activated carbon, b) compare the equilibrium sorption of lead onto these sorbents, c) identify the mechanisms governing lead sorption onto the biochar samples, and d) examine whether lead-laden biochar could be regenerated with acid washing.

Materials and Methods

Materials

Biochar samples were obtained by pyrolyzing the feedstock materials (digested bagasse residue and undigested bagasse) for 1.5 hours at 600 ^{o}C in a N_2 environment. The digested bagasse biochar (DB600) and raw bagasse biochar (B600) were crushed and sieved to a size fraction of 0.5-1 mm. Physicochemical properties of the biochar samples have been previously reported in chapter 2.

Lead solution was prepared from lead nitrate (certified A.C.S) from Fisher Scientific. Granulated activated carbon (AC, from coconut shell) was also obtained from Fisher Scientific and was crushed and sieved to the same size as the biochar samples. A range of physicochemical properties, including pH, surface potential, surface area, cation exchange capacity (CEC), and anion exchange capacity (AEC), of the AC were determined using methods detailed in chapter 2.

Sorption Experiments

Sorption kinetics of lead onto the sorbents (i.e., DB600, B600, and AC) was determined by mixing 50 mL $Pb(NO_3)_2$ (20 ppm) solutions with 0.1 g of each sorbent in 60 mL plastic vials at room temperature (22±0.5 ˚C). The vials were then shaken at 200 rpm in a mechanical shaker. Over the course of 24 h, the vials were withdrawn at time intervals (5, 10, 20, 40, 60, 90, 120, 180, 300 mins, and 24 h) and the mixtures were immediately filtered through 0.1 µm pore size nylon membranes (GE cellulose nylon membrane). The filtrates were then acidified by adding 1.0 M HNO_3 to maintain pH < 3 prior to measurement of Pb concentrations.

Equilibrium sorption isotherm experiments were conducted similarly using $Pb(NO_3)_2$ solutions with initial Pb concentrations ranging from 5 to 200 ppm and apparent sorption equilibrium times of 24 h. Following the experiments, the solids were collected, washed with deionized water, and dried at 100 ^{o}C in an oven before post-sorption characterizations as described in section 3.2.3.

The Pb concentrations of the liquid phase samples were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Plasma 3200). The solid phase Pb (i.e., sorbed Pb) concentration was calculated based on the difference between Pb in the initial and final aqueous solutions. Blank controls containing sorbents and solutions with no Pb were tested in parallel with each kinetic and isotherm experiment and Pb release was found to be negligible. All the experimental treatments were performed in duplicates and the average values are reported. Additional analyses were conducted whenever two measurements showed a difference larger than 10%.

Kinetic and equilibrium sorption models were used to understand the interaction mechanisms between lead and the sorbents. The model parameters were calibrated to fit the experimental data using inverse analysis techniques.

Post-Sorption Characterizations

X-ray diffraction (XRD) analysis was carried out on DB600, B600, and AC before and after Pb sorption to investigate the possible formation of Pb mineral phases using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator. Scanning electron microscope (SEM) imaging of DB600 and B600 after Pb sorption was carried out using a field emission scanning electron microscope (FE-SEM, Hitachi S-4000) with maximum resolution of 1.5 nm. The accelerating voltage of the instrument was maintained at 10 kv.

Fourier transform infrared (FTIR) spectrographic analysis of B600 and DB600 before and after sorption was carried out to characterize the samples surface functional groups and to investigate any possible interaction with the Pb ion. Samples were ground and mixed with KBr to approximately 0.1 wt. % and pressed into a pellet manually using a mechanical vice. Spectra were collected on a Bruker Vector 22 FTIR with OPUS 2.0 software.

Regeneration

Regeneration of the lead-laden sorbents was investigated by conducting Pb stripping experiments using an acid solution. Duplicates of 0.1 g sorbents were reacted for 24 h with 50 mL of 80 ppm Pb solution as described in section 3.2.2. After filtration of the duplicate lead sample solutions, aqueous Pb concentrations in the filtrates were used to determine sorbed Pb concentrations using the method described in section

3.2.2. The solids on the filters were rinsed three times with 50 mL of distilled water to remove any residual Pb. The rinsed samples were then transferred into plastic vials and mixed with 30 mL of 0.1 M HCl. These mixtures were agitated for 0.5 h using a mechanical shaker, filtered, and aqueous Pb concentration was measured in the filtrate. The regeneration rate of each sorbent was calculated based on the ratio of the amount of Pb released to the initial amount of Pb adsorbed. Sorbent samples without sorbed Pb were also treated with the acid solution following the same procedures to test for pre-existing Pb in the sorbents.

Results and Discussion

In the following, the adsorption kinetics and adsorption isotherm data have been presented for all the adsorption experiments conducted. The Langmuir model was used to validate all the adsorption data based on the L-shape plots, characterizing Langmuir model fitting. The possibility of using anaerobic digestion as a method of biologically activating sugarcane bagasse for enhanced lead removal has been proven based on the superior adsorption results obtained from DB600 in comparison with B600. The possible mechanisms responsible for the uptake of lead by the biochar samples and the activated carbon have been discussed and the post characterization results have been used to justify all the inferences drawn. The results from the regeneration of the samples are also presented here to compare the efficiency of acid washing in stripping the bound Pb species from the surface of the biochars and activated carbon.

Physiochemical Properties

The physicochemical properties that may influence the sorption abilities of the two biochar samples (DB600 and B600) have been previously reported (chapter 2) and are compared with those of AC in Table 3-1. The N_2-BET surface areas of both DB600 and

B600 were below 20 m^2 g^{-1}, much less than that of activated carbon (1100 m^2/g). These data suggest that, if surface adsorption dominates Pb sorption onto these materials, DB600 and B600 should have much lower sorption capacity than AC. Low specific surface areas are commonly reported for biochars derived from agricultural residues (Azargohar and Dalai 2006; Hammes et al. 2006; Maiti et al. 2008; Novak et al. 2010).

The CEC and AEC of all the sorbents were comparable to those of natural soils (Table 3-1). DB600 and AC had a much higher CEC than B600, while DB600 had the highest AEC compared to B600 and AC. These data suggest the possibility of using some biochars as ion exchangers that may sequester both positively and negatively charged ions from water. The zeta potential of all the samples were negative (Table 3-1), with that of DB600 being the lowest value (-61.7 mV), indicating strongly negatively charged surfaces that might facilitate the deposition of cations such as Pb onto these sorbents.

Sorption Kinetics.

The sorbents showed different lead sorption kinetic behaviors (Figure 3-1). Both DB600 and AC reached sorption equilibrium within several minutes. Lead sorption onto B600, however, was much slower and reached equilibrium after about 5 hours. A rate-limited, first-order (pseudo-first-order) kinetic model was used to simulate the experimental data:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad (3\text{-}1)$$

where q_t and q_e are the amount of lead sorbed at time t and at equilibrium (mmol kg^{-1}), respectively, and k_1 is the first-order apparent sorption rate constant (h^{-1}). This model reproduced the kinetic data closely (Figure 3-1), with correlation coefficients (R^2)

exceeding 0.98 for the three sorbents tested. Because there was no obvious difference in results for DB600 and AC, the same model simulations are shown for both in Figure 3-1. The model-estimated sorption first-order rate constants (k_1) for DB600, B600, and AC were 320.25, 0.55, and 320.25 hr^{-1}, respectively, suggesting the anaerobic digestion can transform (or 'activate') bagasse such that its biochar has sorption characteristics similar to commercial activated carbons.

Previous studies on the kinetic behaviors of metal sorption onto microporous sorbents showed that intraparticle surface diffusion may be important to the sorption process (Axe and Trivedi 2002; Weerasooriya et al. 2007). In this study, the sorption of lead onto DB600 and AC reached equilibrium quickly with no sign of diffusion limitation. This might indicate that the pores in the two sorbents were relatively large compared to some other microporous sorbents. The lead sorption kinetics of B600, however, was slower and the pre-equilibrium (i.e. before 5 h) lead sorption showed a strong linear dependency (R^2=0.98) on the square root of time (Figure 3-2). This result suggests that intraparticle surface diffusion may play an important role in controlling the sorption of lead onto the undigested bagasse biochar samples.

Sorption Isotherms.

The maximum observed Pb sorption onto DB600 was much greater than that of AC or B600 (Figure 3-3) despite its lower surface area suggesting mechanisms other than surface adsorption may be involved in the sorption process. Because all the isotherms are "L" type, the classic Langmuir model was used to simulate the sorption isotherms:

$$q_e = \frac{KQC_e}{1 + KC_e} \quad (3\text{-}2)$$

where *K* represents the Langmuir bonding term related to interaction energies (L mmol^{-1}), *Q* denotes the Langmuir maximum capacity (mmol kg^{-1}), and C_e is the equilibrium solution concentration (mmol L^{-1}) of the sorbate. Simulations using the Langmuir model fit all the isotherm data well (Figure 3-3), with R^2 exceeding 0.84. The best-fit values of the bonding term (*K*) for DB600, B600, and AC were 189.45, 13.54, and 13.52 L mmol^{-1}, respectively. These results suggest that the digested bagasse biochar has much stronger bonding ability for lead than the undigested bagasse biochar and AC. The DB600 also had the highest sorption capacity (653.9 mmol kg^{-1}), about double that of AC (395.3 mmol kg^{-1}) and about twenty times higher than that of B600 (31.3 mmol kg^{-1}). Thus, anaerobic digestion of sugarcane bagasse prior to pyrolysis activated biochar in such a way, as to increase both its sorption strength and sorption capacity for lead. Although B600 had a much lower lead sorption capacity than AC, the *K* values of the two sorbents were almost identical suggesting their sorption of lead could be controlled by similar mechanisms.

Sorption Mechanisms.

The enhanced sorption of lead by the digested sugarcane bagasse biochar (i.e., DB600) may be related to a precipitation mechanism such as that proposed by Cao et al. (2009) for Pb sorption to biochar made from animal manure. The XRD analysis identified lead minerals on the DB600 surface as hydrocerrusite – [$Pb_3(CO_3)_2(OH)_2$] and cerrusite – [$PbCO_3$] (Figure 3-4). This was further confirmed by SEM images which clearly showed mineral crystals on DB600 surface at a magnification of 10000 X after the sorption experiments (Figure 3-5). The mineral crystals were neither found on the

original biochars nor on the other biochars following Pb sorption. The precipitation of hydrocerrusite and cerrusite on the surface of DB600 might be attributed to a collective contribution from its high pH (Table 3-1) and specific surface functional groups. Comparisons of the FTIR spectra between fresh DB600 and Pb-laden DB600 reveals an almost complete disappearance of the O=C=O band at wave number 2349 cm^{-1} after Pb sorption (Figure 3-6a). This suggests that the O=C=O functional groups on the digested bagasse biochar surface played an important role in the Pb precipitations onto this biochar. This confirms the results obtained from the XRD plot based on the crystalline formation of the cerrusite on the surface of the digested bagasse biochar after adsorption of the Pb ion. The presence of the inorganic carbonyl group, CO_2 on the digested material could have resulted from the transfer of carbon dioxide in the biogas from the gaseous to the liquid phase during the digestion process. This dissolved carbon dioxide may have played a role in the formation of the carbonate group which interacted with Pb. Dissolved CO_2 in the digested residue could have served as a catalyst during the process of pyrolysis to enhance the quality of biochar produced from the process. Another possible explanation for the presence of the carbonate functional group could be from the biomass debris (dead remains of the bacterial culture). However, it would require additional experimental analysis to explore this possibility.

Previous studies have concluded that the sorption of lead onto activated carbon is mainly through a surface adsorption mechanism (Cao et al. 2009; Swiatkowski et al. 2004). In this study, both B600 and AC showed no change in XRD patterns before and after Pb sorption, providing no evidence of mineral precipitation. In addition, Langmuir model simulations indicated that the bonding energy (i.e., *K*) of lead onto B600 and AC

were almost the same. These results suggest that the sorption of lead onto B600 was probably also governed by a surface adsorption mechanism instead of precipitation. The FTIR analysis of B600 indicated a disappearance of the OH band at wave number 1080 cm^{-1} after Pb sorption (Figure 3-6b), suggesting that the deposition of lead onto the bagasse biochar surfaces was probably through coordination of a Pb d-election to a hydroxyl group, producing a -O-Pb bond (Cao et al. 2009). The FTIR spectrum of the fresh B600 also showed the strongest signal at wave number 1080 cm^{-1}, indicating that OH functional groups were abundant (Figure 3-6b). Despite this abundance, the total number of the OH functional groups on the biochar surface, however, may have been limited by its lower surface area (Table 3-1). As a result, the undigested bagasse biochar showed lower lead removal ability, on a mass basis, compared to the AC.

Regeneration

Most of the adsorbed Pb could be retrieved from the DB600 (77.4%), B600 (73.0%), and AC (77.0%) samples using the 0.1M HCl (Figure 3-7). This result suggests that acid solution can be used to regenerate the two biochar sorbents as well as the activated carbon after they are saturated with Pb ions. Acid washing has also been commonly used in regenerating other sorbents to recover metal ions (Lam et al. 2007). The release of lead from B600 and AC samples by acid washing might be controlled by similar surface desorption mechanisms. However, for DB600, Pb release likely involves the dissolution of the precipitated Pb minerals (i.e., hydrocerrusite and cerrusite) on the biochar surface.

Based on the results presented, the adsorption ability of the digested bagasse biochar clearly compares and exceeds the adsorption ability of the activated carbon despite its low surface area. A comparison of the data for the adsorption isotherm and

kinetics for DB600 and B600 clearly reflects that anaerobic digestion is a biological method of activating sugarcane bagasse, since it concentrates the presence of exchangeable ions on the surface of the biochar samples and consequently, promotes the precipitation mechanism in the adsorption of metal species. Fourier transform infrared analysis however show the potential of B600 to adsorb Pb ions but more research may be required to explore the improvement of the undigested bagasse biochar adsorption ability.

Conclusion

Both digested and undigested sugarcane bagasse biochars effectively removed lead from water, but the digested bagasse biochar showed a much better sorption ability than even a commercially activated carbon. Because bagasse is an abundant agricultural waste material, the cost to make bagasse-biochar is low. In addition, Pb-laden biochars can also be regenerated with acid solution with Pb recovery rates higher than 70%. Biochars should therefore be considered a promising alternative water treatment or environmental remediation technology for lead removal.

Biochar converted from the anaerobically digested sugarcane bagasse showed superior sorption characteristics to undigested biochar made from bagasse, suggesting the possibility of using anaerobic digestion as a means of biological activation to produce high quality, low cost, carbon-base sorbents. Biological activation of carbon through anaerobic digestion is much lower in cost and may be more effective compared to the traditional physical or chemical activation methods. Although further testing of its universal applicability (using other biomass types and adsorbing other metals) is required, biological activation of biochar can provide new opportunities for the activated carbon industry to develop innovative products to solve environmental problems.

Potential additional environmental benefits from this approach include fuel or energy produced during both the anaerobic digestion and pyrolysis due to biochar's refractory nature.

Table 3-1. Summary of physicochemical properties of the adsorbents studied.

Sample	pH	Zeta potential (mV)	BET surface area (m^2/g)	CEC (cmol/kg)	AEC (cmol/kg)
DB600	10.9	-61.7	17.7	14.3	11.2
B600	7.7	-28.1	14.1	4.2	6.6
AC	9.5	-33.9	1100.0	19.3	6.4

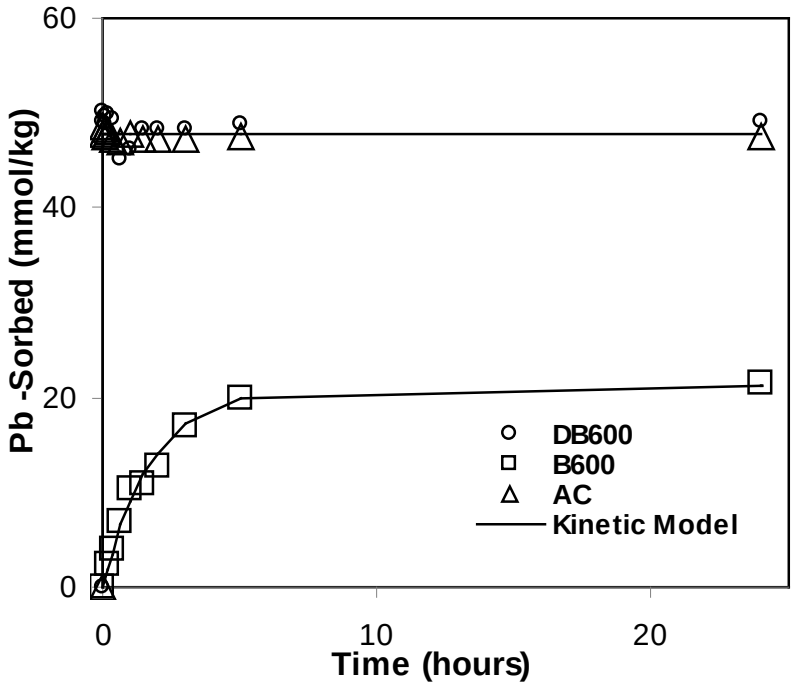


Figure 3-1. Lead sorption kinetics.

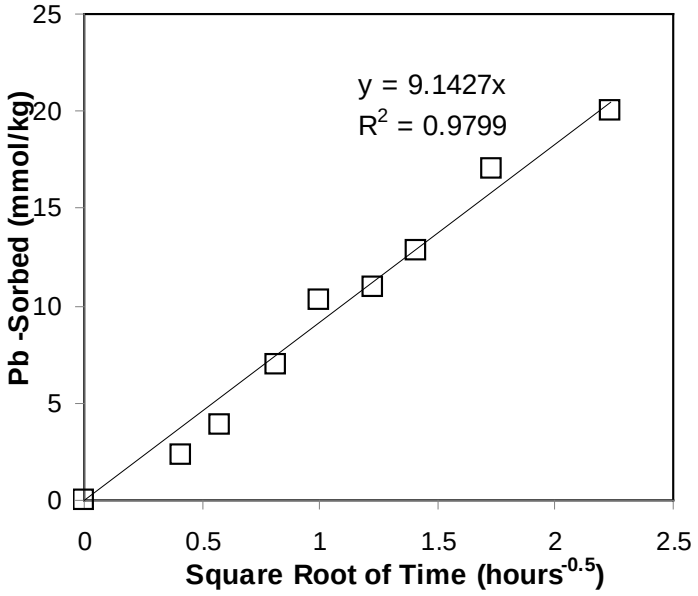


Figure 3-2. Relation between Pb sorbed onto B600 and square root of time before equilibrium.

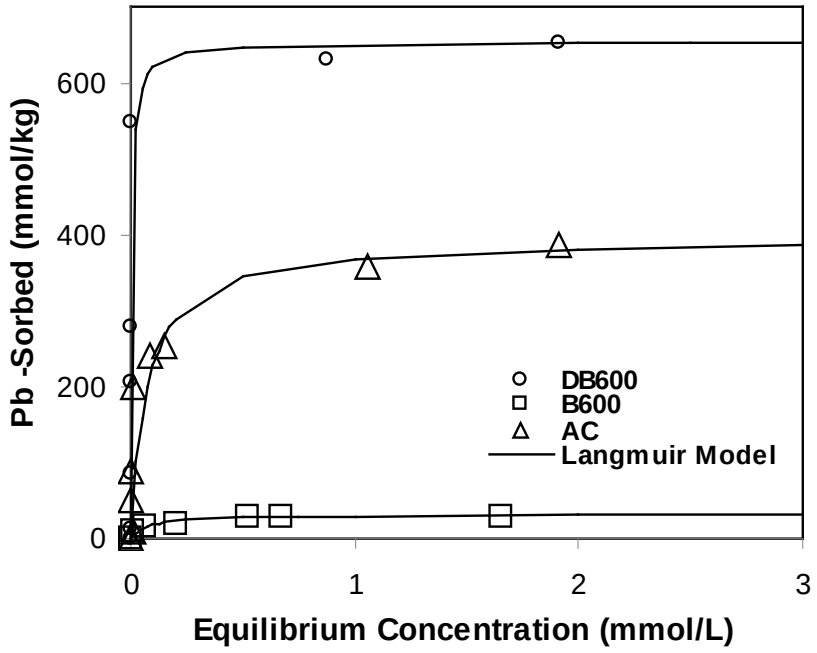


Figure 3-3. Lead sorption isotherms.

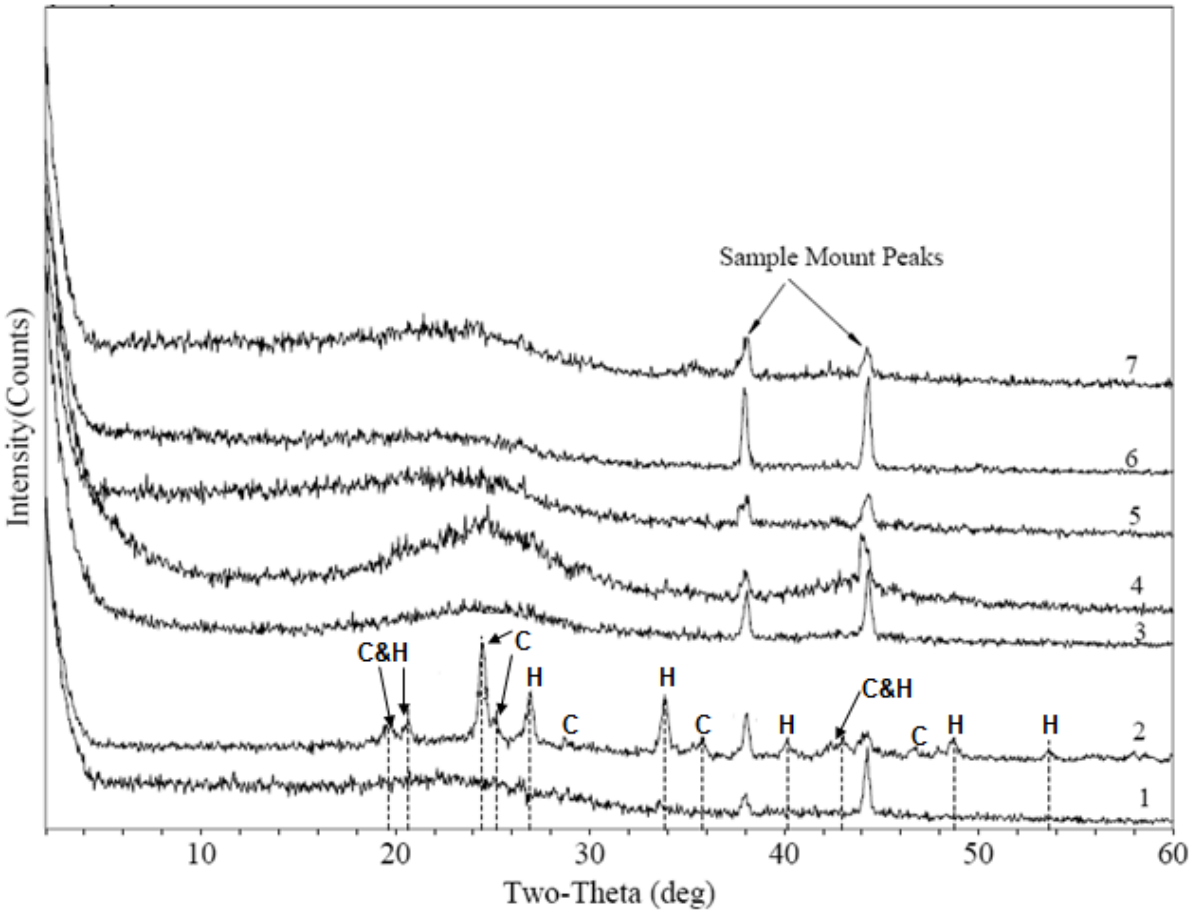


Figure 3-4. XRD patterns of (1) fresh DB600, (2) post-adsorption DB600, (3) fresh AC, (4) post-adsorption AC, (5) fresh B600, (6) post-adsorption B600, and (7) background signal. Minerals were only detected in the post-adsorption DB600 with peak labeled as H for hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$) and C for cerrusite ($PbCO_3$).

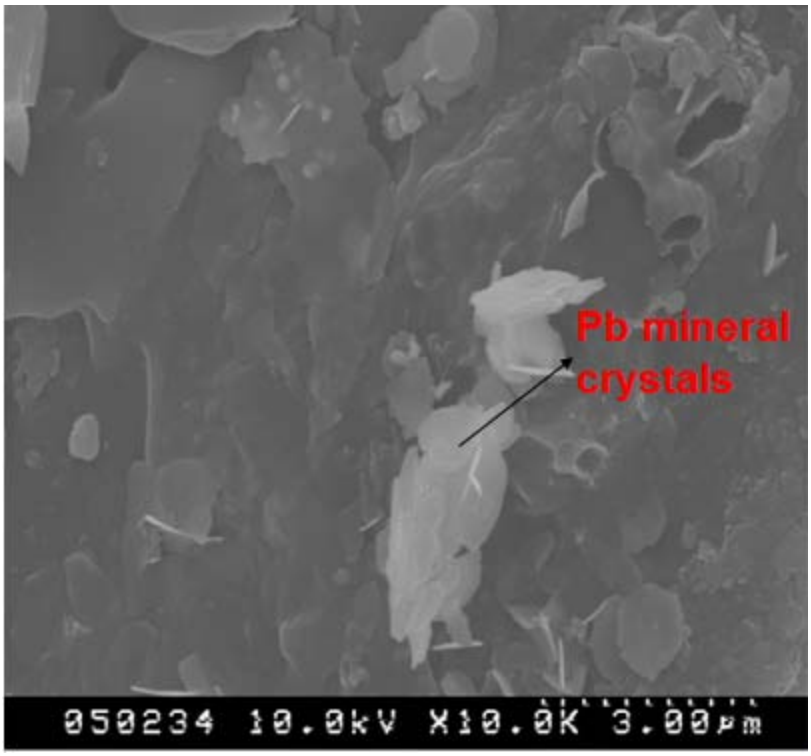


Figure 3-5. SEM image of the post-adsorption B600.

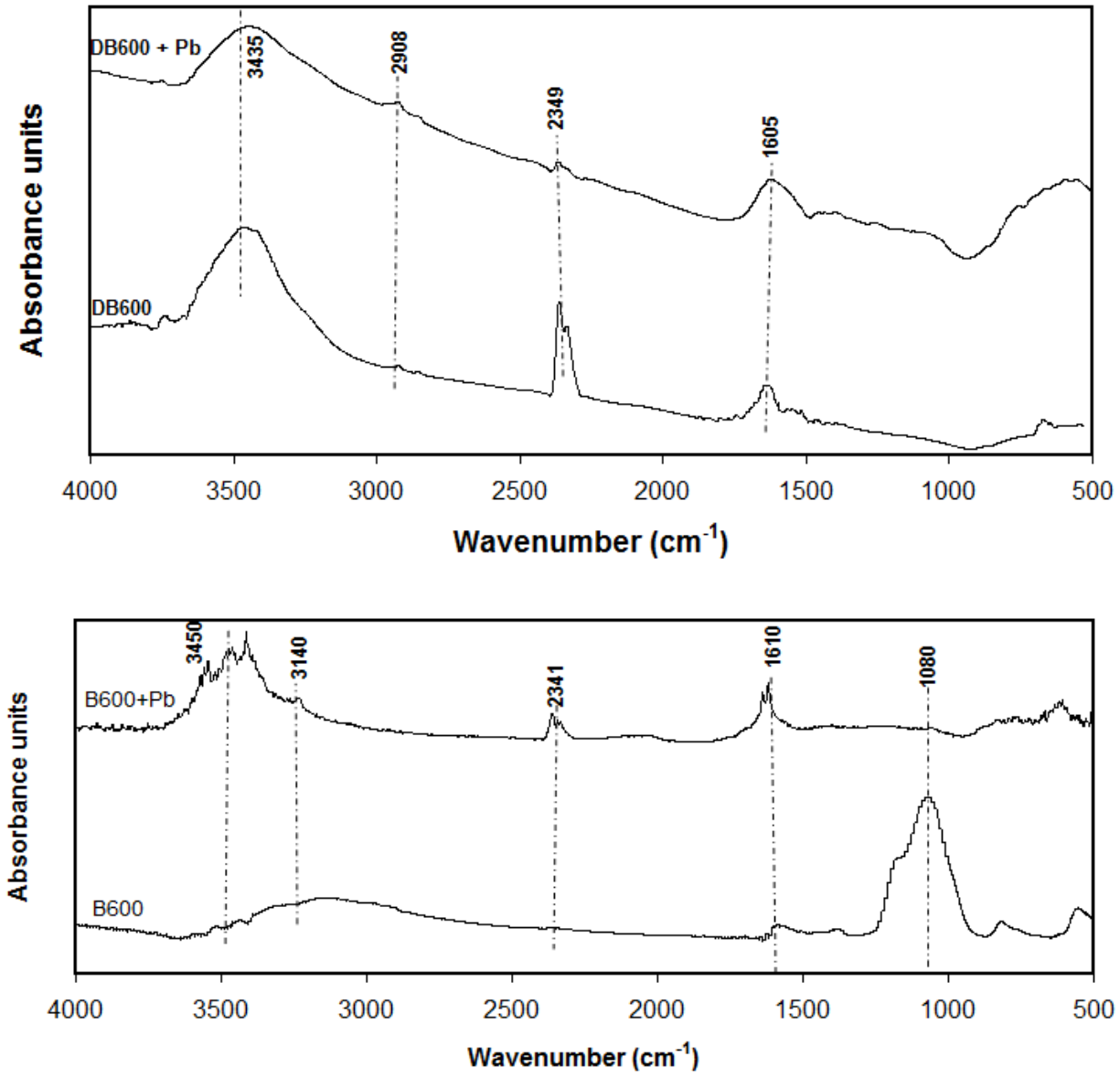


Figure 3-6. FTIR spectra of (a) fresh and post-adsorption DB600 and (b) fresh and post-adsorption DB600.

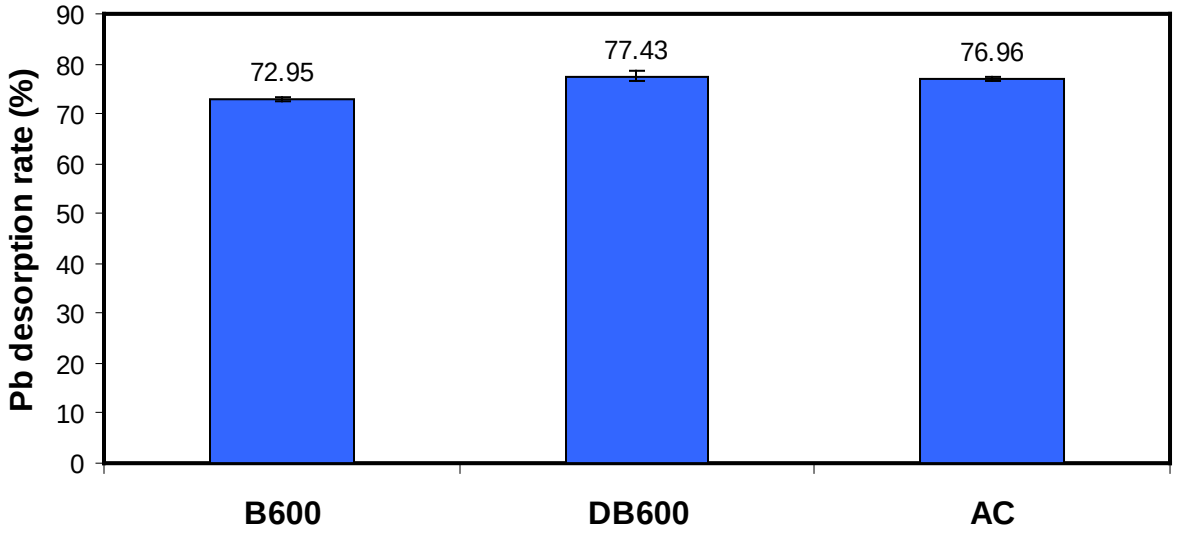


Figure 3-7. Percentage of Lead desorbed from biochars and activated carbon.

CHAPTER 4
CONCLUSION AND FUTURE WORK

Conclusion

The conclusions drawn for this research work were based on the findings from experimental studies conducted on:

- Effect of Anaerobic Digestion on Biochar Produced from Sugarcane Bagasse.
- Enhanced Lead Sorption by Biologically Activated Biochar from Sugarcane Bagasse.

These experimental studies have showed the potential of digested sugarcane bagasse residuals to be used for biofuel and biochar production. The results presented here have also shown that biochar produced from digested bagasse residuals have physiochemical properties which play a role in promoting the sequestration of the metal specie, Pb, onto biochar's surface. Thus, the overall goal of this study has been achieved as well as the specific objectives stated for both experimental studies in Chapters 1 and 2. The important findings critical to this research work were:

- Anaerobic digestion transforms the surface and chemical properties of biochar produced from digested bagasse residuals in comparison to its undigested counterpart.
- Due to its superior physiochemical properties, i.e., highly negatively charged surface and ion exchange ability, the digested bagasse biochar may have better potential than the undigested bagasse biochar to be used as either a soil amendment or as a carbon sorbent for contaminant remediation.
- A combination of anaerobic digestion of bagasse to generate methane and the pyrolysis of its digestion residual to generate non-condensable gases, bio-oils and biochar may be a feasible solution to meeting rising energy demands as well as mitigating the effect of green house gas emissions.
- In addition to its bio-energy production potential, the pyrolysis of the digested bagasse residue generates biochar with 20 time's higher sorption capacity for lead ions than the undigested bagasse biochar and also doubles the sorption capacity of activated carbon.

- Precipitation has been identified as the likely dominant mechanism favoring the high sorption ability of the digested bagasse biochar for lead, despite its low surface area. Complexation of Pb with the inorganic carbonyl group, CO_2 also played a role in the adsorption of the metal ion, Pb.

- The highest desorption rate of 77% was obtained from the digested Pb-laden biochar by acid washing of the sample compared to activated carbon and the undigested bagasse biochar.

These conclusions suggest that the production of biochar from digestion residuals serves as a low-cost alternative to meeting today's environmental and energy needs.

Future Work

The research studies presented here opens exciting avenues to explore the possibility of improving the process of biochar and biofuel production using anaerobic digestion of sugarcane bagasse as well as expanding the application of biochar for remediation purposes. Possible avenues for future work are:

- Developing effective pre-treatment methods which would reduce the long solid residence times in bagasse digestion and degrade the crystalline cellulosic structure in bagasse to promote the higher methane yield from the anaerobic digestion process.

- Investigating the potential of the digested and undigested bagasse biochar to sequester other toxic heavy metal species like copper, mercury, zinc and cadmium and organic contaminants and explore possible methods for improving the percentage regeneration or recovery of the metal laden sorbents.

- Exploring the potential of anaerobic digestion residuals derived from other agricultural waste biomass such as sugar beet tailings, wood waste, beet pulp and even animal manure for enhanced heavy metal sorption and biofuel production efficiency (bio-oil and non-condensable gases).

- Develop a better understanding of the role of anaerobic digestion in the adsorption mechanism of digested bagasse biochar using improved chemical analytical techniques such as X-ray photoelectron spectroscopy (XPS) to characterize the chemical states and functionalities on the surface of the biochar samples before and after adsorption.

LIST OF REFERENCES

Ahn HK, Smith MC, Kondrad SL, White JW. 2010. Evaluation of biogas production potential by dry anaerobic digestion of switchgrass-animal manure mixtures. Applied Biochemistry and Biotechnology 160(4):965-975.

Altpeter F, Oraby H. 2010. Sugarcane. Genetic Modification of Plants. p 453-472.

Amjed M, Jung HG, Donker JD. 1992. Effect of Alkaline Hydrogen-Peroxide Treatment on Cell-Wall Composition and Digestion Kinetics of Sugarcane Residues and Wheat Straw. Journal of Animal Science 70(9):2877-2884.

Anderson MB, Preslan JE, Jolibois L, Bollinger JE, George WJ. 1997. Bioaccumulation of lead nitrate in red swamp crayfish (Procambarus clarkii). Journal of Hazardous Materials 54(1-2):15-29.

Appels L, Baeyens J, Degreve J, Dewil R. 2008. Principles and potential of the anaerobic digestion of waste-activated sludge. Progress in Energy and Combustion Science 34(6):755-781.

Axe L, Trivedi P. 2002. Intraparticle surface diffusion of metal contaminants and their attenuation in microporous amorphous Al, Fe, and Mn oxides. Journal of Colloid and Interface Science 247(2):259-265.

Azargohar R, Dalai A. 2006. Biochar as a precursor of activated carbon. Applied Biochemistry and Biotechnology 131(1):762-773.

Baert L, De Gusseme B, Boon N, Verstraete W, Debevere J, Uyttendaele M. Inactivation of Murine Norovirus 1 and Bacteroides fragilis Phage B40-8 by Mesophilic and Thermophilic Anaerobic Digestion of Pig Slurry. Applied and Environmental Microbiology 76(6):2013-2017.

Burnham M. 2010. Energy by the Acre: Big sugar envisions its future empowered by ethanol; Energy and Environment E-News, E&E Publishing LLC.

Cao X, Ma L, Gao B, Harris W. 2009. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environmental Science & Technology 43(9):3285-3291.

Chan KY, Van Zwieten L, Meszaros I, Downie A, Joseph S. 2008. Using poultry litter biochars as soil amendments. Australian Journal of Soil Research 46(5):437-444.

Chen BL, Zhou DD, Zhu LZ. 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. Environmental Science & Technology 42(14):5137-5143.

Cheng C-H, Lehmann J, Engelhard MH. 2008. Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. Geochimica et Cosmochimica Acta 72(6):1598-1610.

Cheng CH, Lehmann J, Thies JE, Burton SD, Engelhard MH. 2006. Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry 37(11):1477-1488.

Chun Y, Sheng GY, Chiou CT, Xing BS. 2004. Compositions and sorptive properties of crop residue-derived chars. Environmental Science & Technology 38(17):4649-4655.

Claudio L, Lee T, Wolff MS, Wetmur JG. 1997. A murine model of genetic susceptibility to lead bioaccumulation. Fundamental and Applied Toxicology 35(1):84-90.

Costa LVCd. 2009. Utilization of residues of the swines and poultry keeping: potentials for production of biogas and biofertlizer. Pubvet 3(10):unpaginated.

Demirbas A, Pehlivan E, Altun T. 2006. Potential evolution of Turkish agricultural residues as bio-gas, bio-char and bio-oil sources. International Journal of Hydrogen Energy 31(5):613-620.

D'Hont A, Souza GM, Menossi M, Vincentz M, Sluys MAv, Glaszmann JC, Ulian E. 2008. Sugarcane: a major source of sweetness, alcohol, and bio-energy. Genomics of tropical crop plants:483-513.

Djedidi Z, Bouda M, Souissi MA, Ben Cheikh R, Mercier G, Tyagi RD, Blais J-F. 2009. Metals removal from soil, fly ash and sewage sludge leachates by precipitation and dewatering properties of the generated sludge. Journal of Hazardous Materials 172(2-3):1372-1382.

El-Hendawy ANA. 2003. Influence of HNO3 oxidation on the structure and adsorptive properties of corncob-based activated carbon. Carbon 41(4):713-722.

Fatin-Rouge N, Dupont A, Vidonne A, Dejeu J, Fievet P, Foissy A. 2006. Removal of some divalent cations from water by membrane-filtration assisted with alginate. Water Research 40(6):1303-1309.

Gathorne-Hardy A, Knight J, Woods J. 2008. The use of bio-char to reduce summer water stress in cereal crops. Aspects of Applied Biology(88):57.

Gu XY, Wong JWC. 2004. Identification of inhibitory substances affecting bioleaching of heavy metals from anaerobically digested sewage sludge. Environmental Science & Technology 38(10):2934-2939.

Gutierrez O, Park D, Sharma KR, Yuan Z. 2009. Effects of long-term pH elevation on the sulfate-reducing and methanogenic activities of anaerobic sewer biofilms. Water Research 43(9):2549-2557.

Hammes K, Smernik RJ, Skjemstad JO, Herzog A, Vogt UF, Schmidt MWI. 2006. Synthesis and characterisation of laboratory-charred grass straw (Oryza sativa) and chestnut wood (Castanea sativa) as reference materials for black carbon quantification. Organic Geochemistry 37(11):1629-1633.

Hanay O, Hasar H, Kocer NN, Aslan S. 2008. Evaluation for agricultural usage with speciation of heavy metals in a municipal sewage sludge. Bulletin of Environmental Contamination and Toxicology 81(1):42-46.

Johnson PR, Sun N, Elimelech M. 1996. Colloid Transport in Geochemically Heterogeneous Porous Media: Modeling and Measurements. Environmental Science & Technology 30(11):3284-3293.

Kacprzak A, Krzystek L, Ledakowicz S. 2010. Co-digestion of agricultural and industrial wastes. Chemical Papers 64(2):127-131.

Katyal S, Thambimuthu K, Valix M. 2003. Carbonisation of bagasse in a fixed bed reactor: influence of process variables on char yield and characteristics. Renewable Energy 28(5):713-725.

Kivaisi AK, Eliapenda S. 1995. Application of Rumen Microorganisms for Enhanced Anaerobic Degradation of Bagasse and Maize Bran. Biomass & Bioenergy 8(1):45-50.

Koppar A, Pullammanappallil P. 2008. Single-stage, batch, leach-bed, thermophilic anaerobic digestion of spent sugar beet pulp. Bioresource Technology 99(8):2831-2839.

Kryvoruchko V, Machmuller A, Bodiroza V, Amon B, Amon T. 2009. Anaerobic digestion of by-products of sugar beet and starch potato processing. Biomass & Bioenergy 33(4):620-627.

Kumar U. 2006. Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review. Scientific Research and Essays 1(2):33-37.

Lai TE, Koppar AK, Pullammanappallil PC, Clarke WP. 2009. Mathematical Modeling of Batch, Single Stage, Leach Bed Anaerobic Digestion of Organic Fraction of Municipal Solid Waste. Optimization in the Energy Industry. p 233-275.

Lal R. 2008. Carbon sequestration in soil. CAB Reviews: Perspectives in Agriculture, Veterinary Science, Nutrition and Natural Resources 3(030):20.

Lam KF, Fong CM, Yeung KL. 2007. Separation of Precious Metals using Selective Mesoporous Adsorbents. Gold Bulletin 40:192-198.

Li R, Chen S, Li X. Biogas production from anaerobic co-digestion of food waste with dairy manure in a two-phase digestion system. Applied Biochemistry and Biotechnology 160(2):643-654.

Li Y, Zhang C, Yang G, Bu D, Chu L, Ren G, Feng Y. 2009. Effect of temperature on the characteristics of anaerobic digestion of mixture of dung and crop straw. Journal of Northwest A & F University - Natural Science Edition 37(1):66-72.

Liang B, Lehmann J, Solomon D, Kinyangi J, Grossman J, O'Neill B, Skjemstad JO, Thies J, Luizao FJ, Petersen J and others. 2006. Black Carbon increases cation exchange capacity in soils. Soil Science Society of America Journal 70(5):1719-1730.

Liu W, Pullammanappallil PC, Chynoweth DP, Teixeira AA. 2008. Thermophilic anaerobic digestion of sugar beet tailings. Transactions of the Asabe 51(2):615-621.

Liu Z, Zhang F-S. 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. Journal of Hazardous Materials 167(1-3):933-939.

Llaneza Coalla H, Blanco Fernandez JM, Moris Moran MA, Lopez Bobo MR. 2009. Biogas generation apple pulp. Bioresource Technology 100(17):3843-3847.

Lopez-Ramon MV, Stoeckli F, Moreno-Castilla C, Carrasco-Marin F. 1999. On the characterization of acidic and basic surface sites on carbons by various techniques. Carbon 37(8):1215-1221.

Maiti S, Purakayastha S, Ghosh B. 2008. Production of low-cost carbon adsorbents from agricultural wastes and their impact on dye adsorption. Chemical Engineering Communications 195(4):386-403.

Mallick P, Akunna JC, Walker GM. 2010. Anaerobic digestion of distillery spent wash: Influence of enzymatic pre-treatment of intact yeast cells. Bioresource Technology 101(6):1681-1685.

Minceva M, Fajgar R, Markovska L, Meshko V. 2008. Comparative study of Zn2+, Cd2+, and Pb2+ removal from water solution using natural clinoptilolitic zeolite and commercial granulated activated carbon. Equilibrium of adsorption. Separation Science and Technology 43(8):2117-2143.

Mohan D, Pittman CU, Bricka M, Smith F, Yancey B, Mohammad J, Steele PH, Alexandre-Franco MF, Gomez-Serrano V, Gong H. 2007a. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. Journal of Colloid and Interface Science 310(1):57-73.

Mohan D, Pittman Jr. CU, Bricka M, Smith F, Yancey B, Mohammad J, Steele PH, Alexandre-Franco MF, Gómez-Serrano V, Gong H. 2007b. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. Journal of Colloid and Interface Science 310(1):57-73.

Mohring SAI, Strzysch I, Fernandes MR, Kiffmeyer TK, Tuerk J, Hamscher G. 2009. Degradation and Elimination of Various Sulfonamides during Anaerobic Fermentation: A Promising Step on the Way to Sustainable Pharmacy? Environmental Science & Technology 43(7):2569-2574.

Myint MT, Nirmalakhandan N. 2009. Enhancing anaerobic hydrolysis of cattle manure in leachbed reactors. Bioresource Technology 100(4):1695-1699.

Namihira D, Saldivar L, Pustilnik N, Carreon GJ, Salinas ME. 1993. Lead in Human Blood and Milk from Nursing Women Living near a Smelter in Mexico-City. Journal of Toxicology and Environmental Health 38(3):225-232.

Navasivayam C. 1998. Biosorbents for Metal Ions. Bioresource Technology 64(2):161.

Nguyen B, Lehmann J, Kinyangi J, Smernik R, Riha S, Engelhard M. 2009. Long-term black carbon dynamics in cultivated soil. Biogeochemistry 92(1):163-176.

Nopharatana A, Pullammanappallil PC, Clarke WP. 2003. A dynamic mathematical model for sequential leach bed anaerobic digestion of organic fraction of municipal solid waste. Biochemical Engineering Journal 13(1):21-33.

Novak JM, Busscher WJ, Laird DL, Ahmedna M, Watts DW, Niandou MAS. 2009. Impact of Biochar Amendment on Fertility of a Southeastern Coastal Plain Soil. Soil Science 174(2):105-112.

Novak JM, Lima I, Xing B, Gaskin JW, Steiner C, Das kC, Ahmedna M, Rehrah D, Watts DW, Busscher WJ and others. 2010. Volume 3, 2009.

Osman GA, El-Tinay AH, Mohamed EF. 2006. Biogas production from agricultural wastes. Journal of Food Technology 4(1):37-39.

Ozcimen D, Karaosmanoglu F. 2004. Production and characterization of bio-oil and biochar from rapeseed cake. Renewable Energy 29(5):779-787.

Palaniappan P, Krishnakumar N, Vadivelu M. 2009. Bioaccumulation of lead and the influence of chelating agents in Catla catla fingerlings. Environmental Chemistry Letters 7(1):51-54.

Pandey A, Soccol CR, Nigam P, Soccol VT. 2000. Biotechnological potential of agro-industrial residues. I: sugarcane bagasse. Bioresource Technology 74(1):69-80.

Purevsuren B, Avid B, Tesche B, Davaajav Y. 2003. A biochar from casein and its properties. Journal of Materials Science 38(11):2347-2351.

Qiu Y, Cheng H, Xu C, Sheng GD. 2008. Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption. Water Research (Oxford) 42(3).

Radjenovic J, Petrovic M, Barcelo D. 2009. Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Research 43(3):831-841.

Ribeiro MJ, Albuquerque CM, Labrincha JA. 2008. Removal of Pb2+ and Ni-2 ions from aqueous media by filtration through clay-based beds. Clay Minerals 43(4):647-656.

Rodriguezvazquez R, Diazcervantes D. 1994. Effect of Chemical Solutions Sprayed on Sugarcane Bagasse Pith to Produce Single-Cell Protein - Physical and Chemical-Analyses of Pith. Bioresource Technology 47(2):159-164.

Sadrzadeh M, Mohammadi T, Ivakpour J, Kasiri N. 2008. Separation of lead ions from wastewater using electrodialysis: Comparing mathematical and neural network modeling. Chemical Engineering Journal 144(3):431-441.

Saleh MA, Ragab AA, Kamel A, Jones J, ElSebae AK. 1996. Regional distribution of lead in human milk from Egypt. Chemosphere 32(9):1859-1867.

Sari A, Tuzen M, Citak D, Soylak M. 2007. Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite clay. Journal of Hazardous Materials 149(2):283-291.

Sekhar MC. 2008. Removal of lead from aqueous effluents by adsorption on coconut shell carbon. Journal of Environmental Science & Engineering 50(2):137-140.

Sialve B, Bernet N, Bernard O. 2009. Anaerobic digestion of microalgae as a necessary step to make microalgal biodiesel sustainable. Biotechnology Advances 27(4):409-416.

Soltan ME, Sirry SM, Fawzy EM. 2007. Evaluation of the sorptive capacity of sugarcane bagasse and its coal for heavy metals in solution. Journal of the Chinese Chemical Society 54(6).

Sud D, Mahajan G, Kaur MP. 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions - A review. Bioresource Technology 99(14):6017-6027.

Suhas, Carrott PJM, Carrott MMLR. 2007. Lignin - from natural adsorbent to activated carbon: a review. Bioresource Technology 98(12):2301-2312.

Swapnavahini K, Srinivas T, Kumar PL, Kumari MS, Lakshmi T. 2010. Feasibility study of anaerobic digestion of Ocimum sanctum leaf waste generated from Sanctum sanctorum. BioResources 5(1):389-396.

Swiatkowski A, Pakula M, Biniak S, Walczyk M. 2004. Influence of the surface chemistry of modified activated carbon on its electrochemical behaviour in the presence of lead(II) ions. Carbon 42(15):3057-3069.

Tomei MC, Braguglia CM, Cento G, Mininni G. 2009. Modeling of Anaerobic Digestion of Sludge. Critical Reviews in Environmental Science and Technology 39(12):1003-1051.

Tsai WT, Chang CY, Lin MC, Chien SF, Sun HF, Hsieh MF. 2001. Characterization of activated carbons prepared from sugarcane bagasse by ZnCl2 activation. Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes 36(3):365-378.

Tyagi RD, Couillard D, Tran F. 1988. Heavy-Metals Removal from Anaerobically Digested-Sludge by Chemical and Microbiological Methods. Environmental Pollution 50(4):295-316.

UNFCC. 2009. United Nations Framework Convention for Climate Change.106-114.

Weerasooriya R, Tobschall HJ, Seneviratne W, Bandara A. 2007. Transition state kinetics of Hg(II) adsorption at gibbsite-water interface. Journal of Hazardous Materials 147(3):971-978.

Yu Z, Schanbacher FL. 2010. Production of Methane Biogas as Fuel Through Anaerobic Digestion. Sustainable Biotechnology: Sources of Renewable Energy: SPRINGER. p 105-127.

Zelazny LW, He L, Vanwormhoudt A. 1996. Charge analysis of soils and anion exchange. Methods of soil analysis. Part 3 - chemical methods.:1231-1253.

Zimmerman AR. 2010. Abiotic and Microbial Oxidation of Laboratory-Produced Black Carbon (Biochar). Environmental Science & Technology 44(4):1295-1301.

Zwietering MH, Jongenburger I, Rombouts FM, Van'triet K. 1990. Modeling of the Bacterial Growth Curve -- Zwietering et al. 56 (6): 1875 -- Applied and Environmental Microbiology.

BIOGRAPHICAL SKETCH

Mandu Ime Inyang was born in Lagos, Nigeria. She received her bachelor's degree in Chemical Engineering from Ladoke Akintola University of Technology, Oyo state, Nigeria in 2005. Before her graduation, she served as an intern in the National Engineering and Technical Company, Lagos, Nigeria where she gained experience in process design. After graduation, she worked for a year as a lecturer in the Basic and Applied Sciences Department, teaching chemistry to National Diploma students in Niger State Polytechnic, Zungeru, Nigeria before she proceeded to the United States to receive her Master of Science Degree in Agricultural and Biological Engineering Department, University of Florida. At the end of her Master's program, she intends to continue research in environmental nanotechnology by pursuing her doctorate degree in agricultural and biological engineering, UF. Mandu enjoys reading, writing and watching good movies as her hobbies and has always attributed her achievements in life to a firm dependence on God.