Adsorption of Phosphate and Copper by Pine Sawdust Biochars and Economic Analysis

by

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Abstract

Applying engineered biochar for environmental management is a novel approach to realize biochar's potential as a low cost remediation material and for carbon sequestration. Systematic studies investigating effects of pyrolysis condition on biochars' properties and their subsequent adsorption ability for anions and cations in solution are lacking. In this thesis, pine sawdust biochars produced at 300 and 550 °C with and without steam activation were assessed for its sorption capacity for phosphate and copper (Cu (II)) in aqueous solutions using batch sorption experiments, including isotherm and kinetic studies.

For phosphate adsorption, the four biochars removed about 2 to 4% of phosphate from an aqueous solution and the maximum adsorption capacity of the four biochars were around 1.0 to 1.4 mg g^{-1}, which were not affected by adjustment of the solution pH and biochar application rate. The repulsion forces between biochar surfaces and phosphate ions were suspected to be the main cause of the low affinity of phosphate to the biochars. Cu (II) adsorption by biochar was studied in a synthetic oil sands process-affected water because Cu (II) is the most abundant metal in the water and it exceeds the relevant guidelines. For adsorption of Cu (II), Langmuir and the pseudo-second order models were the best-fit for isotherm and kinetic studies, respectively. The maximum adsorption capacities of the biochars made at 550 °C were 2.5 mg g^{-1}, which was thirty-fold higher than those made at 300 °C. However, steam activation did not affect biochars' sorption capacity. The kinetic study suggested that chemisorption involving valence forces was the limiting factor of the sorption, and ion exchange and precipitation were likely the primary mechanisms rather than complexation with functional groups. This study implied that pine sawdust biochars produced at 550 °C have a large potential to remove Cu (II) from aqueous solutions.

To verify the cost effectiveness of applying biochar material for remediation of contaminated water, a hypothetical case study of producing and applying the pine sawdust biochar to the Mildred Lake Settling Basin was conducted. The cost of the whole project was around US$543,000, and the benefits that could be materialized mainly came from carbon sequestration. The net present value was between US$-182 to US$-111 per ton of biochar, varying with the carbon price in the market. Transportation was a significant portion of the total cost and the largest contributor to greenhouse gas emission. More comprehensive economic studies and life cycle assessment are needed to evaluate the economics of a biochar production-application system to advance implementation of biochar technologies in the future.

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List of Abbreviations and Symbols

BC	biochar
BC300	biochar produced at 330 °C without steam activation
BC550	biochar produced at 550 °C without steam activation
BC300-S	biochar produced at 330 °C with steam activation
BC550-S	biochar produced at 550 °C with steam activation
BET	Brunauer-Emmett-Teller
BMPs	best management practices
C	carbon
CBA	cost benefit analysis
Ca	calcium
Ca/P	calcium to phosphorus ratio
$CaCl_2$	calcium chloride
CH_4	methane
CO_2	carbon dioxide
CO_2eq	equivalent carbon dioxide
H	hydrogen
H_2O	water
H/C	hydrogen to carbon
Cu	copper
CCME	Canadian Council of Ministers of the Environment
FTIR	Fourier-transform infrared
GHG	greenhouse gas emission
GREET	greenhouse gas, regulated emissions, and energy use in transportation
IBI	International Biochar Initiative

ICP-MS	inductively coupled plasma mass spectrometry
Mg	magnesium
MLSB	Mildred Lake Settling Basin
N	nitrogen
N_2O	nitrous oxide
NaCl	sodium chloride
NPV	net present value
O	oxygen
O/C	oxygen to carbon
(O+N)/C	oxygen and nitrogen to carbon
OSPW	oil sands process affected-water
pH_{pzc}	pH at the point of zero charge
P	phosphorus
SEM	scanning electron microscopy
T	temperature
b	constant related to sorption affinity
C	intercept
C_e	equilibrium concentration of solution, mg L^{-1}
h	initial sorption rate, mg g^{-1} min
k_1	pseudo-first order rate constant, L min^{-1}
k_2	rate constant of the pseudo-second order adsorption, g mg^{-1} min
K_f	indicator of adsorption capacity
k_i	intraparticle diffusion rate, mg g^{-1} $min^{0.5}$
n	indicator of adsorption intensity

q_e	amount of the metal adsorbed per unit weight of biochar, mg g^{-1}
Q_{max}	maximum adsorption capacity, mg g^{-1}
q_t	adsorbed amount of sorbate at time t (min), mg g^{-1}
q_e	adsorbed amount of metal ion at equilibrium, mg g^{-1}
t	time

Chapter 1. Biochar, the black carbon on the earth

1. Introduction

1.1 Definition and background

Biochar, a type of charcoal, is a carbonaceous solid material produced from thermal treatment of carbon-rich biomass in an oxygen-limited environment (IBI, 2012; Lehman and Joseph, 2009). Biochar is a recalcitrant material, which could be applied as soil amendments and as well as to mitigate climate change by sequestrating carbon in a long term. The use of biochar dates back to thousands of years ago in Amazon Basins (Lehman and Joseph, 2009). While charcoal and activated carbon are familiar carbon materials to the public, biochar is a relatively new material that has been brought into the public's sight in the last decade (Lehman, 2007). When climate change becomes a hot button, biochar research is taking a leap because of biochar's reluctant nature to degradation, stabilizing carbon in environment. Clarifying the definitions of biochar, charcoal and activated carbon can help understand their history, production, functions and inter-relationships.

Charcoal, activated carbon and biochar are all black carbon material, carbon residues from incomplete combustion processes (Goldberg, 1985). Nomenclature of the three materials reflects either the unique formation process or techniques employed for their characterization. Char or black carbon, is defined as any carbonaceous material residue from pyrolysis such as charcoal, soot, smoke, fly ash (Lehnman and Joseph, 2009). Charcoal is the source of charred organic matter for producing fuel and energy, and it is also commonly referred to pyrogenic carbonaceous material that is produced from pyrolysis or fires in the scientific community. Activated carbon, a type of charcoal, has to be treated with physical or chemical methods to modify surface properties such as porosity and surface area. Activated carbon is mostly applied in industry as filters (Lehmann and Joseph, 2009). Activation techniques can be also applied into production of biochar to make activated biochar (Ahmad et al., 2014).

1.2 Biochar production and properties

Biochar can be made from a variety of feedstocks with high carbon content. Biomass used as feedstock for biochar production can be unprocessed, such as plant residues from agricultural and forestry industries, or processed, such as waste sludge and animal manure. A number of thermal chemical conversation techniques including slow pyrolysis, fast pyrolysis, gasification, hydrothermal carbonization, and flash carbonization (Meyer et al., 2011) can be employed to produce biochar. Different production techniques are developed based on the demand of end products, and such techniques and resulting end products are summarized in Table 1. Among these, slow pyrolysis is known to produce the highest yield of biochar while fast pyrolysis and gasification are usually used to produce biofuel/bio-oil and syngas. Thus, for carbon storage slow pyrolysis is the most ideal method for producing biochar. This thesis mainly focuses on biochar from slow pyrolysis.

It is worth noting that biochar is not a single product but a broad naming of biochar produced from various feedstocks and pyrolysis conditions. The idea of engineering specific biochar to solve problems at hands is prevalent, leading to innovation of biochar technologies. Producing biochar from such a large variety of potential feedstocks results in biochar products with diverse characteristics, which determines their feasibilities for different applications such as soil amendment, carbon sequestration and pollution control.

Biochar properties are commonly identified through proximate and ultimate analysis including surface area, pore structure, pH, elemental composition, functional groups, and so on. The pyrolysis condition includes peak temperature, pressure, residue time, and flow rate. Among these, pyrolysis temperature has the most pronounced impact on properties of biochar followed by pyrolysis heating rates (Lua et al., 2004). Feedstock such as plant biomass is typically composed of hemicellulose, cellulose and lignin (Rutherford et al., 2012). The thermochemical transformation and charring process of plant biomass in slow pyrolysis follow the order by hemicellulose, cellulose and lignin (Kumar et al., 2011; Rutherford et al., 2012). At low heating rates, cellulose starts to decompose as low as 250 °C (William and Besler, 1996), and cellulose is mostly converted to organic vapors and aerosols when 400 °C is reached (Brown et al., 2015). The biochar yield slowly reduces with increasing temperature.

Element composition such as C, H, N and O and molar H/C and O/C ratios are key indictors often being investigated in biochar surface chemistry. Carbon concentration usually increases while H, O, N concentrations decrease as pyrolysis temperature increases (Ahmad et al., 2014). These changes are also proved by Fourier transformed infrared (FTIR) spectra indicating higher aromaticity and loss of polar functional groups with increasing temperatures (Ahmad et al., 2012; Uchimiya et al., 2013). Another important characteristic of biochar structure is the specific surface area, and it usually increases as pyrolysis temperature increases by means of forming internal pores, channel structure, and release of volatile matters (Ahmad et al., 2012). Certain types of biochar are also known to bring liming effect to soil and water, as well as to enhance cation exchange capacity (Ahmad et al., 2012; Ahmad et al., 2014; Kim et al., 2013). Other benefits such as increasing crop yield, improving microbial activities and stabilizing metals are reported, but uncertainties of the benefits are acknowledged. Benefits rely on biochar type and application environment, and only can be realized when feedstocks, production methods, and application conditions are well understood and carefully selected.

2. Biochar in environmental management

Biochar is usually used as a soil amendment, for carbon storage, as a remediation material, and for energy. The motivations considering environmental management behind these functions are improving soil quality, mitigating climate change, controlling pollution and producing bioenergy. Environmental management is defined as the process of dealing with environmental problems based on available resources to enhance environmental qualities and human welfare. It is a multidisciplinary practice involving decision making built on scientific knowledge, socioeconomic evaluation and resources. Biochar in environmental management is not just a product, but a system considering input and output. Benefits of biochar cannot be well understood and often overestimated unless it is being perceived as a system that considering input and output (Lehmann and Joseph, 2015). In a biochar system, the input includes biomass, installation of pyrolysis facility, transportation and human resources involved, and the output is usually the products, carbon storage, and other benefits.

In terms of biochar's benefits, a question frequently being provoked is how does biochar show its competitiveness compared with other alternatives? For example, biochar is known as a soil amendment and can potentially improve crop yield through retaining nutrients and water, however, fertilizers can also improve the crop yield faster and cheaper. Comparison between biochar and fertilizer therefore is necessary before suggesting biochar application.

Best management practices (BMPs) is a concept adopted by Canada and United States in water and agricultural management (Fisheries and Oceans Canada and Government of British

Columbia, 2015; Mckay, 2010). BMPs have to create benefits and are at least as profitable as exiting practices (Feather and Amacher, 1994). If the purpose is to improve crop yield but the biochar is not as feasible as fertilizers, biochar application is not realistic and viable. The BMPs in biochar application should be based on clear motivations and assess benefits in a biochar system setting in order to make sensible comparison with the other alternatives.

Many studies marked biochar as low cost material and renewable energy without meaningful comparison with other alternatives. For examples, some researchers promoted the use of biochar as soil amendments with a liming effect to substitute other amendments, but this conclusion is solely based on the benefits of biochar without comparing with other amendments (Zwieten et al., 2010). Likewise, some researchers applied biochar to remediate metal and organic contamination, however, they did not provide evidences of advantages of biochar application over other treatments, and the only benefit was based on carbon sequestration (Zhang et al., 2013). Due to the lack of field-scale data and also constrained by many factors before applying biochar, in fact, risks of negative impacts and uncertainties of using biochar were identified (Mukherjee and Lal, 2014). Unless regulatory frameworks articulate carbon credits and provide incentives, large-scale applications of biochar would likely not occur.

3. Biochar application in aquatic environments

There has been considerable interest in applying biochar to remove excess elements and contaminants from aquatic environments. Biochar can act as effective sorbents or filter to improve water quality. The adsorption efficiency of biochar in sorption batch experiments varies with biochar properties, pyrolysis temperature, solution chemistry, application rate, and competing ions.

Adsorption isotherm is vital to interpret adsorption phenomenon in environmental studies. The most common isotherm models include Langmuir, Freundlich, Langmuir-Freundlich and Temkin equations. According to Tan et al. (2015), the majority of research evidence showed that adsorption of metals on biochar material fits Langmuir or Freundlich model better than other models. Each model has its unique assumptions that explain sorption equilibrium. The Langmuir isotherm assumes the adsorption surface is homogenous, and single layered with limited adsorption sites (Gu et al., 1994). Freundlich model assumes heterogeneous and multiple layer adsorption (Weber and Huang, 1996). The sorption is dependent on the properties of sorbent, sorbate and solution environment. In other words, biochar properties, metal species and water chemistry greatly affect the sorption process. For example, for copper adsorption, researchers found the Langmuir fits better than other models (Chen et al., 2011b; Tong et al., 2011). Lead adsorption in the study of Lu et al. (2012) fitted better with the Freundlich equation. Biochar is also effective in removing organic contaminants including pesticide, antibiotics, herbicide and dyes (Tan et al., 2015). Adsorption of organic contaminants also shows good fitting with the Langmuir or Freundlich model.

Biochar has also been evaluated for removing ammonium, nitrate, and phosphate to mitigate nutrient pollution in aquatic environments. After adsorption, biochar loaded with ammonium, nitrate, and phosphate are proposed as a slow-release fertilizer to enhance soil fertility, as such biochar may contain abundance of valuable nutrients and help plant growth. For instance, Yao et al. (2013) recovered phosphate using Mg-modified biochar and applied the biochar in soil and their results showed that the biochar had fertilizer effect. Similarly, the Langmuir and Freundlich equations also showed ideal fit (Tan et al., 2015).

Adsorption kinetics reveals strong relationship between surface chemistry and sorption equilibrium, and sorption mechanisms that involve mass transport and chemical reaction (Boutsika et al., 2014; Tan et al., 2015). The most popular models employed to study biochar's sorption capacity include the pseudo-first order, the pseudo-second order and intraparticle diffusion model. Adsorption of metals by biochar usually follows the pseudo-second order model (Tan et al., 2015). According to Ho and McKay (1999), the pseudo-second order model is based on the assumption that the sorption is chemical sorption which may involve valence forces. Similarly, adsorption of organic contaminants such as methylene blue dye (Sun et al., 2013) also follows the pseudo-second order model.

4. Biochar industry

Biochar industry emerged in the 1970s when biomass was incinerated to generate bio-oil, syngas and biochar for bioenergy (Lehman and Joseph, 2009). But until recently, biochar's value as a soil amendment and for carbon storage is being recognized and relevant literature is surging. As indicated by a survey conducted by IBI (Jirka and Tomlison, 2014), the biochar industry is still in a developing phase where new investments are being made every day, and an increasing trend in revenues from biochar sales of existing businesses has been seen. The most common use of biochar in current commercial market activity is focused on using it as a soil amendment to improve soil quality (Jirka and Tomlison, 2014). It is more targeted to small-scale, high-end gardening and horticultural uses than large-scale industrial or agricultural uses due to relatively high production and capital costs. Its uncertainties in demonstrated value for large applications further adding difficulties to its large commercialization.

IBI (Jirka and Tomlison, 2014) identifies biochar related enterprises into three categories: those that produce and/or sells biochar products, those that manufacture biochar production equipment, and those that engage in biochar-related businesses such as consulting and product development. As of 2013, more companies are engaged in manufacturing production equipment than in biochar production and sales or consulting. Most of the biochar-related companies are based in North America and Europe. However, many studies indicate that there is potential for biochar production and subsequent industrial development in different countries.

For instance, in Malaysia, tonnes of agricultural wastes are produced, with oil palm production being the major contributor. These agricultural wastes can be utilized as feedstocks to produce biochar to reduce the volume of waste and to improve soil fertility. Biochar production may be carried out directly on farm sites to reduce transportation and labour costs (Rebitanim et al., 2013). In Indonesia, charcoal products from wood wastes, mangroves and coconut shells are produced, which are used as soil amendments in forest rehabilitation and exported to countries in Southeast and East Asia (Okimori et al., 2003). Japan imports approximately half of its charcoal needs from Southeast Asia for use in agriculture, tree rehabilitation, water purification, sewage treatment etc (Ogawa and Yasuyuki, 2010). The average retail price of biochar reported by IBI (2014) is US$2249.82 t^{-1}. The economic viability of biochar production is influenced by feedstock cost, biochar price and energy prices (Kung et al., 2013).

With more feedstock and production research, equipment development, and education of consumers about the benefits of biochar application in improving environmental qualities, the number of biochar-related businesses and biochar product sales are expected to increase in the future.

5. Thesis structure and study objectives

This thesis is organized into five chapters. The first chapter is introduction and the last chapter is conclusions and future studies. The main subject being studied in this thesis is pine sawdust biochar, and investigation of its adsorption performance in aquatic environment is being presented in Chapter 2 and 3. In Chapter 2, the pine sawdust biochar was evaluated for its capacity in recovering phosphate from an aqueous solution, and the biochar was characterized on a microscopic scale to study the effect of pyrolysis condition (temperature and activation) on its adsorption capacity. In Chapter 3, the biochar was applied in synthetic oil sands process-affected water to adsorb copper. Various models of adsorption isotherm and kinetics were applied to interpret the adsorption mechanism. Phosphate and copper represent an anion and a cation, respectively, and the study results could infer to the biochar's adsorption for other similar ions to some extent.

Chapter 4 provided a case study that hypothetically applying the pine sawdust biochar into tailings ponds water in Athabasca oil sands region, and conducted a cost-benefit study in the perspective of biochar's life cycle to give socioeconomic implications in real-world applications.

This thesis aims to improve our understanding of the pine sawdust biochar's adsorption abilities for essential nutrient phosphorus and common metal copper in aquatic environments. As well as to enhance our knowledge on how pyrolysis condition affects the pine sawdust biochar's properties and subsequent adsorption phenomenon for the two elements. In addition, possibilities about implementing this research was investigated by a cost benefit analysis. Though this reality check is hypothetical, it aims to provide valuable information when such kind of study is relatively scarce at the current stage, and it is also a study future research could potentially base on.

Table 1-1. Biomass thermochemical conversion technologies and product distribution.

Thermochemical	Temp (°C)	Gas	Liquid	Solid	Major intended project
Carbonization	300-1200	60-70	3-5	10-35	Charcoal; solid fuel and industrial input
Fast pyrolysis	400-600	20-40	40-70	10-25	Bio-oil, chemical products and fuels
Slow pyrolysis	300-700	40-75	0-15	20-50	Biochar, soil amendment, carbon sequestration and bioremediation
Gasification	500-1500	85-95	0-5	5-15	Syngas; gaseous fuel for heat and power; and gas to liquid
Hydrothermal processing	200-400	0-90	0-80	0-60	Various chemical products
Combustion	1000-1500	95	0	5	Energy converted to heat and power

Adapted from Boateng et al. (2015).

Chapter 2. Do high pyrolysis temperature and steam activation favor phosphate adsorption on pine sawdust biochars?

1. Introduction

Phosphorus (P) is a limiting nutrient for the growth of algae in many aquatic environments and increased P concentrations in water bodies such as lakes, ponds and rivers cause eutrophication (Hutchinson, 1973; Schindler et al., 2008). Human activities such as changing forest land to agricultural or urban use, P fertilization on agricultural land, and livestock production have greatly increased P abundance in the environment in recent years (Anderson et al., 2002; Smith et al., 1999). In a recent study of Lake Winnipeg (Schindler, 2012), the severe eutrophication problem was also related to the increased intensity and frequency of spring floods, which had enhanced the flow of nutrient from the landscape to the lake, as well as draining of wetlands that could function as buffer zones for runoffs (Schindler, 2012).

The need to reduce P input and remove P from the waterbodies to minimize eutrophication problems has been widely recognized (Bennett et al., 2001; Schindler, 2012). There are numerous technologies to remove P from waterbodies to mitigate eutrophication. Conventional technologies to remove P include electro-dialysis, reverse osmosis, and ion exchange (Morse et al., 1998; Yeoman et al., 1988). However, these technologies are usually applied on a small scale and require sophisticated equipment. Chemical treatments are to add divalent or trivalent metal salts to precipitate P, and settle the insoluble metal phosphate down in the polluted water. One of the disadvantages of such chemical treatments is that the effective removal of P relies on precise application rates, solution pH, reaction temperature, and other co-existing chemicals in the environment. In addition, the creation and handling of a large amount of sludge can be a problem

(Morse et al., 1998; Özacar, 2003). Biological P removal using activated sludge to uptake P can avoid the use of chemicals and excessive production of sludge (Morse et al., 1998). However, more complex operation and plant configurations related to high economic input are required. Other techniques such as crystallization and magnetic attraction are either energy intensive or require specialized equipment (Morse et al., 1998). Cost effective materials that are easy to use should be explored to deal with eutrophication problems.

Adsorption using waste materials containing lime, alum, and iron salts (Morese et al., 1997) has been demonstrated cost-effective in removing P from solution, and does not generate extra sludge as well. For instance, iron oxide tailings (Zeng et al., 2003) and red mud (López et al., 1997) were effective for P removal from aquatic environments. Karaheorgiou et al. (2007) reported the effective removal of P by calcite under basic pH and high Ca to P ratios, and the removal effectiveness was time dependent. Ugurlu and Salman (1998) used fly ash that contains calcite to adsorb P, which was effective under proper temperatures.

Biochar, as a recalcitrant carbon material, has been widely studied in terms of its role in carbon sequestration and as soil amendments. Biochar is usually produced from carbon-rich biomass through thermal decomposition in oxygen limited environments (Lehmann and Joseph, 2009; IBI, 2015; Sohi, 2012). Biochar can act as an effective adsorbent for both organic and inorganic matters in the soil and water (Ahmad et al., 2014; Mohan et al., 2014). Biochar's capacity in removing P crosses a wide range. For instance, Chen et al. (2011a) found that biochar made from iron treated orange peel powders had a removal capacity of 1.2 mg g^{-1}. Yao et al. (2011) reported that biochar derived from anaerobically digested sugar beet tailings had superior P adsorption capacity (133.1 mg g^{-1}) under a range of pH and competing ion conditions. In another study, Yao et al. (2013) used magnesium-modified biochar with an adsorption capacity over 100 mg g^{-1} to recover phosphate from aqueous solutions. The adsorption capacity of biochar is largely dependent on its surface characteristics (e.g., surface area, the type and density of surface charge, elemental composition, and functional groups on the surface), which are shaped by feedstock type and production condition (Ahmad et al., 2014; Cao and Harris, 2010). However, there's no study has been conducted to understand the effect of pyrolysis condition on biochar's removal capability for P.

During pyrolysis of biomass, thermal degradation and carbonization of lignin, semi cellulose and cellulose are the mainly involved processes. High temperature leads to high degrees of carbonization, resulting in growth of aromatic and graphitic structure (Uchimiya et al., 2011a), and reduction of amorphous content (Chen et al., 2008). In order to achieve better adsorption, enlarging surface area by steam activation is a common practice applied during biochar production. In addition, steam activation can lead to easy access to functional groups by releasing blocked volatile matters in biochar's pores (Ahmad et al., 2014; Lima et al., 2010).

Sawdust is a by-product from sawmills, and is often disposed as waste materials. Making biochar out of sawdust and using the biochar as an adsorbent for removing P from polluted water has the dual function of waste utilization and pollution reduction. There have been few studies on sawdust biochar's adsorption capacity for P. Currently, no study has been conducted to understand the effect of pyrolysis temperature and steam activation on sawdust biochar's removal capability for P. The objectives of this study were: 1) to test the feasibility of using sawdust biochar to remove P from aqueous solutions; and 2) to evaluate the effect of temperature and steam activation on the effectiveness of biochar for P adsorption. We hypothesized that pine sawdust biochar was feasible for phosphate removal, and those produced at the higher temperature with steam activation would have better adsorption capacity for phosphate. Batch sorption experiments including isotherm and kinetic studies were conducted to evaluate the adsorption effectiveness, and also to investigate the mechanisms for P sorption. Effects of biochar application rate and pH of solution on P adsorption were also studied.

2. Materials and methods

2.1. Biochar production

Sawdust from pine trees was obtained from a sawmill company in Seoul, South Korea. The sawdust was washed with deionized water, air dried, and grounded to less than 1.0 mm in size for biochar production. Biochars were produced at two temperatures (300 and 550 °C) with a heating rate of 7 °C min^{-1} for two hours under limited oxygen. Steam activation was applied to half of the samples produced at each temperature in a modified N11/H Nabertherm (Germany) furnace (Rajapaksha et al., 2014). For steam activation, samples were treated with 5 mL min^{-1} of steam for an additional 45 minutes under the peak temperature after pyrolysis. Four biochars (BC300, BC300-S, BC550 and BC550-S) were produced. The letters “BC”, “S” represented biochar and steam activation, respectively. Values “300” and “550” represented the peak temperatures used in pyrolysis.

2.2. Biochar characterization

The pH of biochar was determined in 1% (w/v) biochar/deionized water suspension using a pH meter (Thermo Orion, 710A, Beverly, MA, USA). Elemental composition (C, H, O, N) of each biochar was determined through a dry combustion method using an elemental analyzer (Carlo Erba, EA1108, Milan, Italy). Moisture, mobile matter, ash, and residence matter contents were determined following Ahmad et al. (2013) and Rajapaksha et al. (2014). Surface functional groups of biochars were characterized by Fourier-transform infrared spectroscopy (FTIR, Thermo Nicolet, 8700, Madison, WI, USA). All peak assignments in the FTIR spectra were based on previous studies (Cao and Harris, 2010; Rajapaksha et al., 2014). Surface morphologies were examined using a scanning electron microscopy (SEM, Zeiss EVO MA 15, Jena, Germany).

The point of zero charge (pH_{pzc}) was determined by pH drift method originally developed for activated carbon (Yang et al., 2004). This method has been widely used to determine pH_{pzc} for biochars (Dastgheib et al., 2004; Uchimiya et al., 2011b; Yang et al., 2004). Briefly, all biochars were washed with 0.1 M HCl (27 g biochar L^{-1}) by constant stirring for 1 hour to remove soluble salts, rinsed with deionized water, and dried overnight at 80 °C. $CaCl_2$ solution (5 mM) was then boiled to remove CO_2 and cooled to room temperature. A biochar sample (0.06 g) was added to 20 mL of $CaCl_2$ solution pre-adjusted to pH 3, 4, 6, 8, 10 using 0.5 M HCl or NaOH followed by equilibration for 24 hours in a shaker prior to pH_{pzc} measurement. The pH_{pzc} was determined after the final pH was measured and plotted against the initial pH. The pH_{pzc} is the point where the curve pH_{final} vs. $pH_{initial}$ crosses the line $pH_{initial} = pH_{final.}$ The Brunauer-Emmett-Teller (BET) specific area of the four biochars was determined in duplicates by nitrogen isotherms at 77 K using a gas adsorption analyzer (Quantachrome Autosorb 1 MP, Quantachrome, Boynton Beach, FL, USA).

2.3. Sorption experiment

Biochars were washed by deionized water and oven dried at 80 °C before the sorption experiment. The washing operation removed soluble salts on the biochar surface. Phosphorus solutions with a range of concentrations were prepared by dissolving KH_2PO_4 (certified A.C.S., Fisher Scientific) in deionized water. The isotherm experiment was conducted with a concentration range from 0 to 40 mg P L^{-1} solution without controlling pH or at pH 7.0 ± 0.1 adjusted by 0.1 M of HCl or NaOH. Biochar application rates of 2, 4, 12, 20 g L^{-1} were used to study the effect of solid/solution ratio on phosphate adsorption. Centrifuge tubes (corning) were used for sorption, and samples were shaken for 48 hours for equilibrium. After equilibrium, suspended mixtures were filtered through 0.45 μm nylon membrane filters. The phosphate concentrations in the extracts were determined by the ascorbic acid method (USEPA, 1992). All treatments were performed in triplicates. The kinetic study was conducted at an initial concentration of 20 mg P L^{-1} with a biochar application rate of 2 g L^{-1} at pH 7.0 ± 0.1. The total experiment time used for the kinetic study was 50 hours. Samples were collected every 10 hours to determine the phosphate concentrations. All experiments were conducted in triplicates at room temperature (295 K), and the average values are reported.

3. Results and discussion

3.1. Effects of pyrolysis temperature and steam activation on biochar properties

Pyrolysis temperature affected the properties of pine sawdust biochars. Biochars produced at the lower temperature (BC300 and BC300-S) had pH values around 5 while those produced at the higher temperature (BC550 and BC550-S) had basic pH (Table 2-1). The pH_{pzc} of each biochar was around 4, therefore, the four biochars had negatively charged surfaces under the pH conditions of each biochar. Increasing the pyrolysis temperature increased the porosity of biochar as mobile matter was removed, resulting in higher surface areas in BC550 and BC550-S (Table 2-1). Further, the surface area of BC550-S was substantially increased by steam activation. Steam activation liberates syngas, enables coalescence of small pores and enlarges internal cavities, resulting in increased microporosity (Ahmad et al., 2014; Demirbas, 2004;

Rajapaksha et al., 2014). The SEM images showed that BC550 and BC550-S were more porous than BC300 and BC300-S, and BC500-S with more open ends has the most porous structure (Fig. 2-2). The molar H/C, O/C, and (O+N)/C ratios are indicators of surface aromaticity, polarity and oxygen functionality, respectively (Rajapaksha et al., 2014). The reduction of these values with increasing temperature indicates that carbonization and development of aromatic and graphitic structures (Uchimiya et al., 2010a). The lower ratio of O/C and higher fixed carbon concentrations showed that biochars made at 550 °C were more aromatic, and less polar. Steam activation did not cause any compositional change or aromaticity, according to the elemental analysis (Table 2-1).

The O-H stretching from 3200 to 3500 cm^{-1} and the aliphatic C-H stretching from 2820 to 2080 cm^{-1} of BC300 and BC300-S were higher than that of BC550 and BC550-S, indicating that the abundance of hydrogen-bonded hydroxyl groups and aliphatic compounds in BC300 and BC300-S were higher than that in BC500 and BC500-S. The peaks of carboxyl C=O stretching (1700-1740 cm^{-1}), aromatic C=C stretching as well as C=O (1600 cm^{-1}), aromatic C-H, and symmetric C-O stretching (1030-1110 cm^{-1}) decreased in BC550 and BC550-S as compared with BC300 and BC300-S, indicating a decrease in the polar functional groups with increasing pyrolysis temperature. This is consistent with the elemental analysis where BC500 and BC550-S were more aromatic. The reduction of these polar functional groups resulted from dehydration and depolymerization reactions, which also led to the growth of aromatic and graphitic structures (Bourke et al., 2007; Uchimiya et al., 2011b).

3.2. Effects of pyrolysis temperature and steam activation on P adsorption

For the four biochars, about 0.4 mg g^{-1} of phosphate was being released in deionized water without adding P in the isotherm study (Fig. 2-3). The four biochars incurred litter adsorption when the equilibrium concentrations were below 20 mg L^{-1}. Except for BC550-S, slowly increasing trends were observed when the equilibrium concentrations were greater than 20 mg L^{-1}. Maximum adsorbed amounts of P for four biochars were between 1.0 to 1.4 mg g^{-1} at pH 7 (Fig. 2-3). However, the adsorption patterns of four biochar were not suitable for Langmuir, Freundlich or any other isotherm modeling. At initial concentration of 20 mg L^{-1} and application rate of 2 g L^{-1}, about 2 to 4% P was removed by the biochars (Fig. 2-4). Each biochar's adsorption capacity did not change when the pH was uncontrolled (Fig. 2-4).

Taking the negative charged surfaces of biochars into consideration, it may not be surprising that the four biochars showed little capacity to adsorb P from the solution. The net charge on biochar's surface was negative because the value of their positive charges was much smaller than their negative charges (Beesley et al., 2011; Lehmann et al., 2011). Mujherjee et al. (2011) reported that biochars always have negatively charged surface unless under low pH conditions. The pH affects biochar's surface charge and thus biochar's adsorption capacity (Kumar et al., 2010). Under ambient conditions, biochars produced at 300 °C remained acidic, but the pH was above the pH_{zpc}, and as a result little P adsorption was observed for BC300 and BC300-S. In the isotherm study, it is also worth to note that 20 mg L^{-1} was similar to a transitional point from where adsorption started increasing with P loading. In the kinetic study with an initial concentration of 20 mg L^{-1}, the adsorption did not show a particular pattern as well and made it difficult for modeling (Fig. 2-5), and was close to zero after 40 hours. It might be hard for adsorption to occur at the concentration of 20 mg L^{-1}. There might be some interactions between releasing and adsorbing of P on biochars associated with the P concentrations in the solution.

In the work of Yao et al. (2011) pH at around 4 resulted in the highest sorption capacity of biochars made from anaerobically digested sugar beet. But they did not explore details on electrostatic interaction between adsorbent and adsorbate under different pH. Kuma et al. (2010) observed that the highest sorption capacity was below pH_{pzc}, and the sorption capacity decreased sharply when pH was greater than pH_{pzc}, because adsorption of anions is mostly favored at solution pH lower than pH_{pzc} of the adsorbent. Similar to biochar, the adsorption capacity of activated carbon is also affected by solution pH. Jayson et al. (1981) used activated carbon to orthophosphate, and observed a sharp drop of adsorption when solution pH was greater than pH_{pzc} of the activated carbon. For adsorption of negatively charged dyes, activated carbon's adsorption capacity also decreased when negative charges developed with increase of the solution pH (Iqbal and Ashaq, 2007). In contrast, when $pH > pH_{pzc}$, the uptake of cationic dyes was greatly favored due to increased electrostatic force of attraction (Kushwaha et al., 2014). Therefore, in determining the most favorable pH condition for adsorption, the surface charge potential and pH_{pzc} of biochar should be determined prior to sorption experiments.

For each biochar, increasing the application rate from 2 to 4, 12, 20 g L^{-1} did not increase the adsorption (Fig. 2-6). Determining optimum adsorbent addition rate is critical when considering the cost of application and operation. Kuma et al. (2010) demonstrated that the P removal increased with the increasing adsorbent application rate until it plateaued out and then remained constant afterwards. The application rate to achieve the highest removal was found to be 4 g L^{-1}. Theoretically, adsorbent application rate should not affect the shape of isotherm (Limousin et al., 2006), which means that the adsorption capacity is not related to the amount of adsorbent added. The adsorption amount is expected to have a linear relationship with solid/solution ratio or the adsorbent application rate, but a too high solid/solution ratio may affect the sorption capacity due to the aggregation of materials (Limousin et al., 2006). In this study, the adsorption amount should have increased with the application rate if adsorption existed. The lack of relationship between biochar addition rate and the amount of P adsorbed further confirms that there was little adsorption of P by the four biochars we studied.

3.3. Possible mechanisms for biochar adsorption of P

Physical and chemical interactions including dispersive force, electrostatic interaction, complexation, and precipitation are possible mechanisms (Ahmad et al., 2014) that govern the interplay between biochar surface and P ions in the solution. These factors are controlled by the characteristics of biochar surface and solution chemistry. High surface area is usually favorable for adsorption, especially for organic matter (Lehmann and Joseph, 2009). In this study, higher surface area or higher oxygen functionality did not help improve adsorption. Functional groups are important biochar surface properties that are better preserved at low pyrolysis temperatures that encourage the development of biochar surface amphoteric features and surface charge (Lehmann and Joseph, 2009). For the four biochars, the surface charge originated from functional groups is mostly from oxygen-related functional groups. Solution chemistry plays an important role in changing surface charges through altering functional groups. When solution pH is greater than the pH_{pzc} of biochars, functional groups act as a Lewis base and display negative charges.

Another contributor to surface charge is the graphitic structure (Radovic et al., 2001). For activated carbon, graphene layers where most surface area resides account for most of the surface charges. In $pH > pH_{pzc}$, the negative charge developed on graphene layers is believed to be more strong and detrimental to adsorption of the same charged chemicals (Radovic et al., 2001). Compared to activated carbon, biochar pyrolyzed at low temperatures (less than 700 °C) undergoes structural changes from amorphous to turbostratic with disordered graphitic stacks (Keiluweit et al., 2010; Uchimiya et al., 2011b). Biochars produced at 550 °C would gain some initial graphitic structure. The developed aromatic structures in BC550 and BC550-S also tend to be π electron donors (Uchimiya et al., 2011b). Therefore, among the four biochars, BC550 and BC550-S exhibited more negative surface charges than BC300 and BC300-S.

Most adsorption materials used for P removal contain divalent and trivalent metal ions such as magnesium, Ca, aluminum and iron that can precipitate and complex with P, thereby removing P from aqueous solutions (Westholm, 2006). The release of P may also occur due to the low Ca content in biochar (Yao et al., 2012; Jung et al., 2015). For biochars that do not contain abundant metal ions, it will be difficult for adsorption to occur when repulsive electrostatic forces exist. For example, Yao and coworkers (2012) tested thirteen biochars for P adsorption and found that most of them had little or no ability to adsorb P in a sandy soil. Recently, Jung et al. (2015) found that among the five different biochars they tested only the biochar derived from peanut shell had good adsorptive capacity because of a proper Ca/P ratio. Apparently, biochar's adsorption capacity largely depends on feedstocks with different mineral compositions.

5. Conclusions

Four pine sawdust biochars showed little affinity for adsorption of P from aqueous solution. The adsorption violated the common belief that a high surface area and oxygen functionality could enhance adsorption performance. This was attributed to the electrostatic repulsion between biochar surfaces and P species in the solution. One should be selective when using biochar to adsorb P. Future studies should select biochars with appropriate mineral content or incorporate trivalent and divalent metals which could precipitate with P to achieve effective adsorption.

Table 2-1. Proximate and ultimate analysis and surface area of biochars produced at 300 and 550 °C with and without steam activation. “S” represents steam activation of biochar.

Sample	Proximate analysis					
	pH[a]	pH_{pzc}	Moisture content (%)	Mobile matter (%)	Resident matter (%)	Ash (%)
BC300	4.92 ± 0.01	3.93	2.11 ± 0.05	55.90 ± 2.41	39.31 ± 1.90	2.70 ± 0.05
BC300-S	4.82 ± 0.03	3.89	3.26 ± 0.03	54.43 ± 1.90	38.38 ± 2.88	3.92 ± 0.03
BC550	8.16 ± 0.06	3.56	3.31 ± 0.08	27.71± 3.23	62.61 ± 0.45	6.39 ± 0.16
BC550-S	7.46 ± 0.05	3.43	3.29 ± 0.06	19.70 ± 2.89	71.64 ± 1.10	5.37 ± 0. 23

	Ultimate analysis							
	C[b] (%)	H[b] (%)	O[b] (%)	N[b] (%)	Molar H/C	Molar O/C	Molar (O+N)/C	BET surface area ($m^2 g^{-1}$)
BC300	62.7	4.1	27.1	0.34	0.78	0.32	0.07	< 1
BC300-S	64.0	3.8	24.0	0.42	0.71	0.28	0.05	< 1
BC550	78.0	2.3	10.2	0.57	0.35	0.10	0.01	189.2
BC550-S	69.6	2.1	9.3	0.37	0.36	0.10	0.02	397.1

[a] Mean ± standard deviation (SD) in triplicate determinations.

[b] Ash and moisture free.

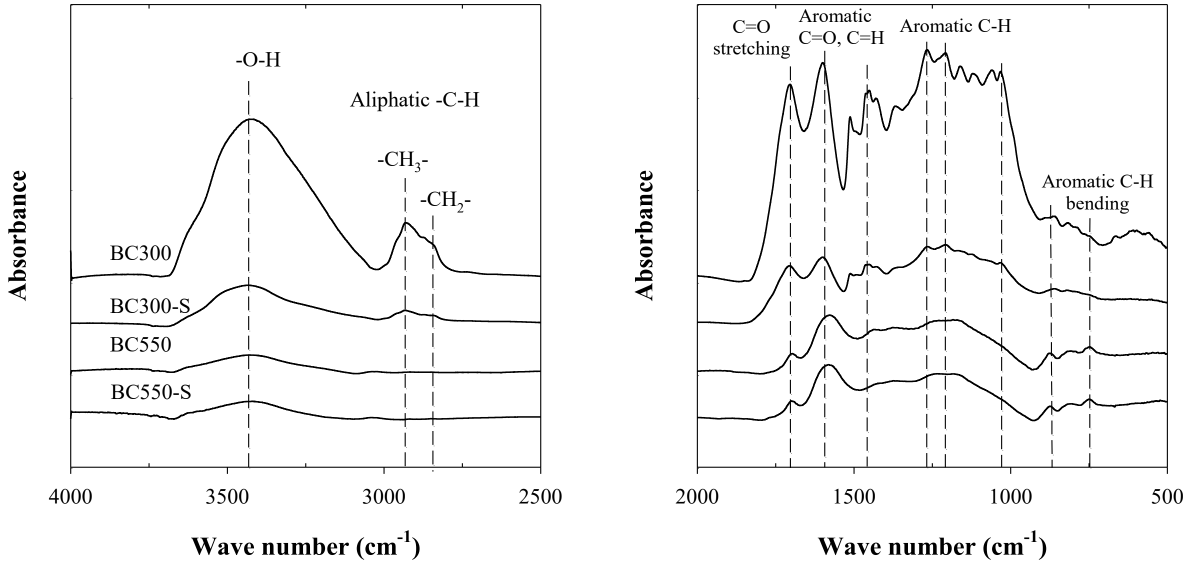

Fig. 2-1. FTIR spectra of the four biochars (BC300, BC300-S, BC550, and BC550-S).

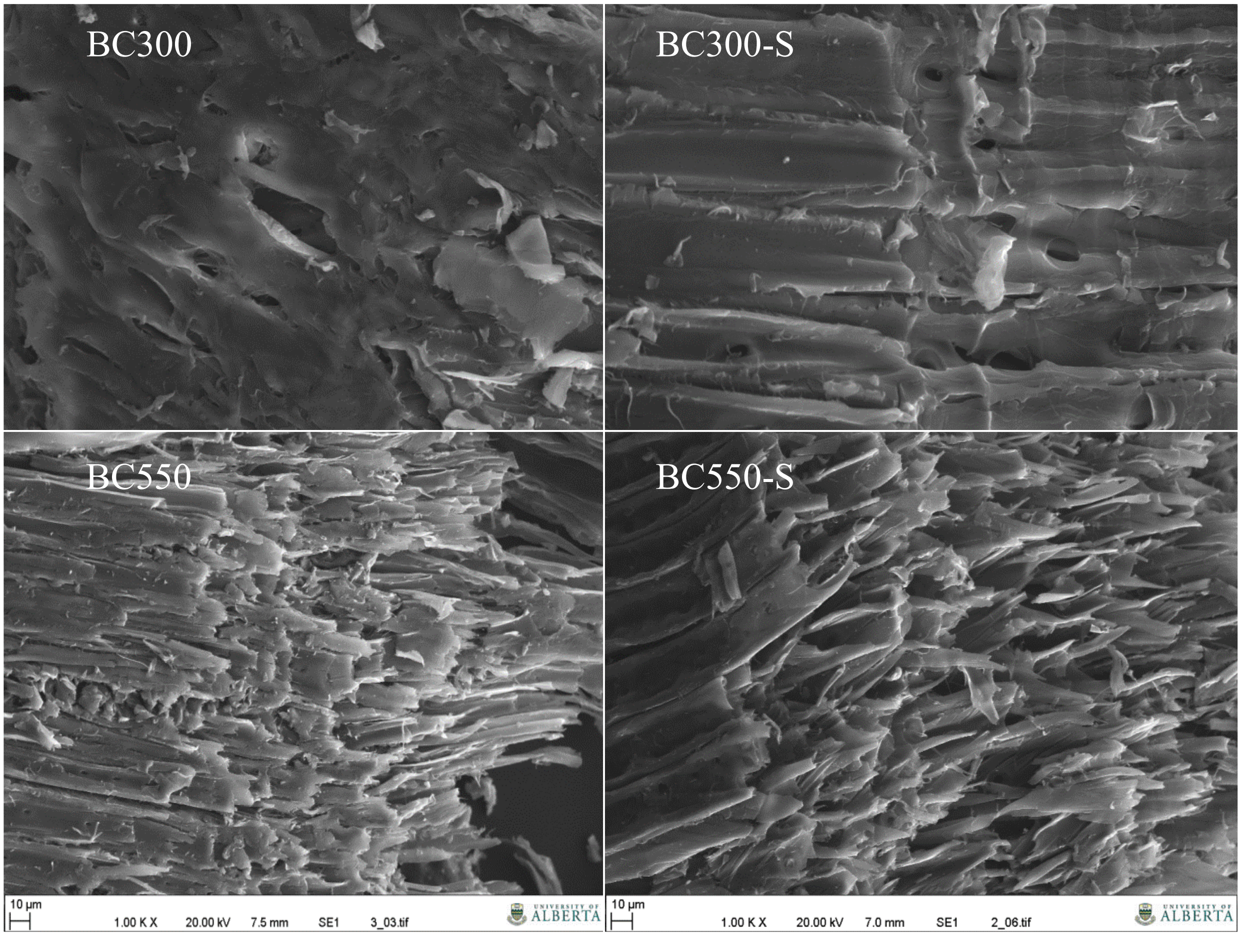

Fig. 2-2. SEM images of the four biochars (BC300, BC300-S, BC550, and BC550-S).

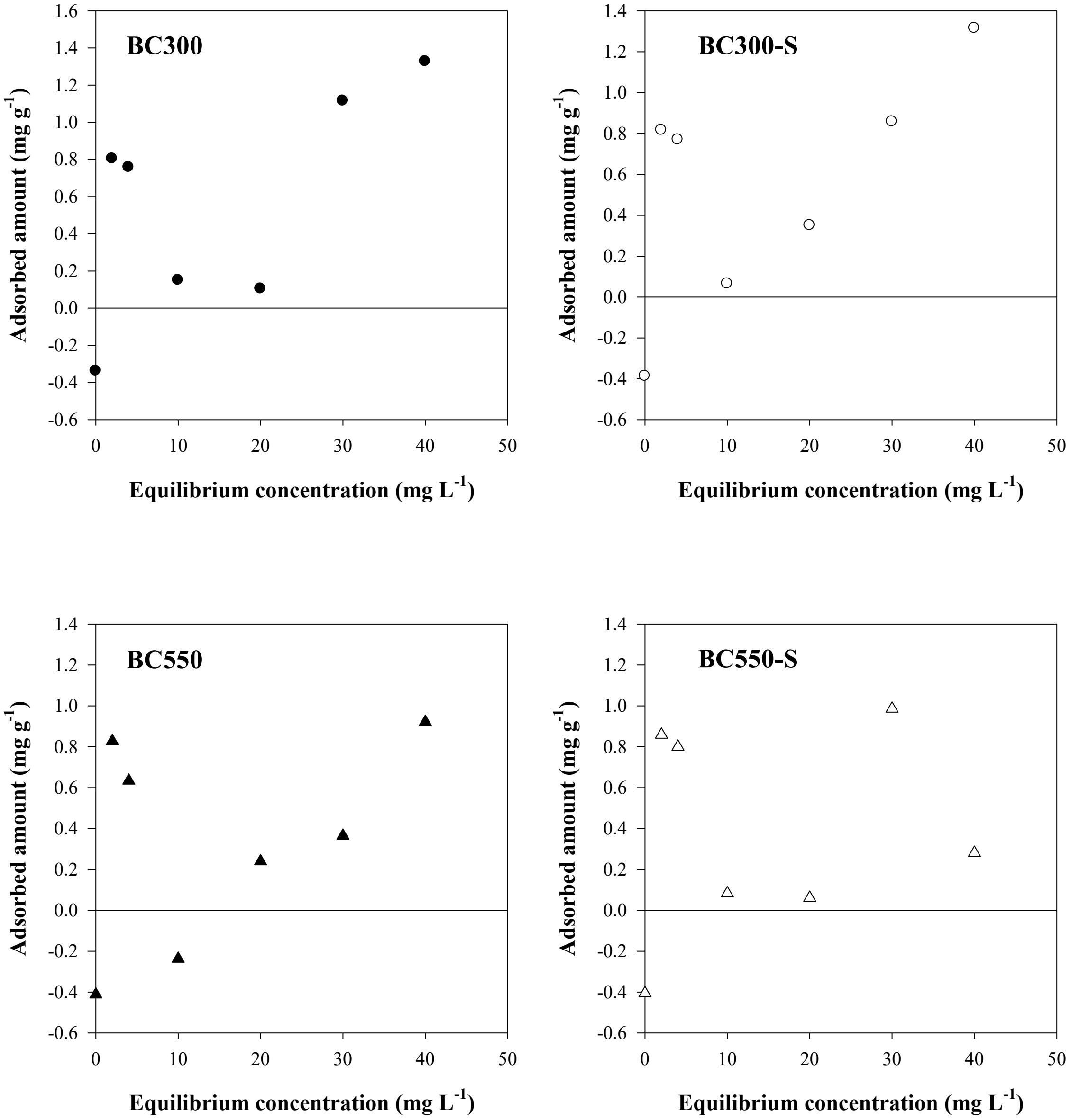

Fig. 2-3. Relationships between equilibrium phosphate concentrations and adsorbed amounts of phosphate in isotherm studies for the four biochars (BC300, BC300-S, BC550 and BC550-S). Biochar application rate = 2 g L^{-1}, pH = 7, T = 295 K, t = 48 h.

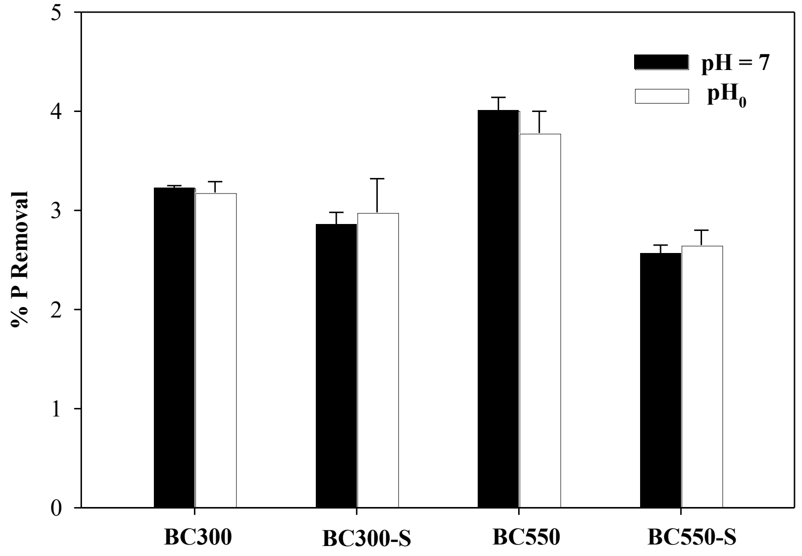

Fig. 2-4. P removal percentage under constant pH (pH = 7) and uncontrolled pH (pH_0) condition using four biochars (BC300, BC300-S, BC550 and BC550-S). Biochar application rate = 2 g L^{-1}, T = 295 K, t = 48 h.

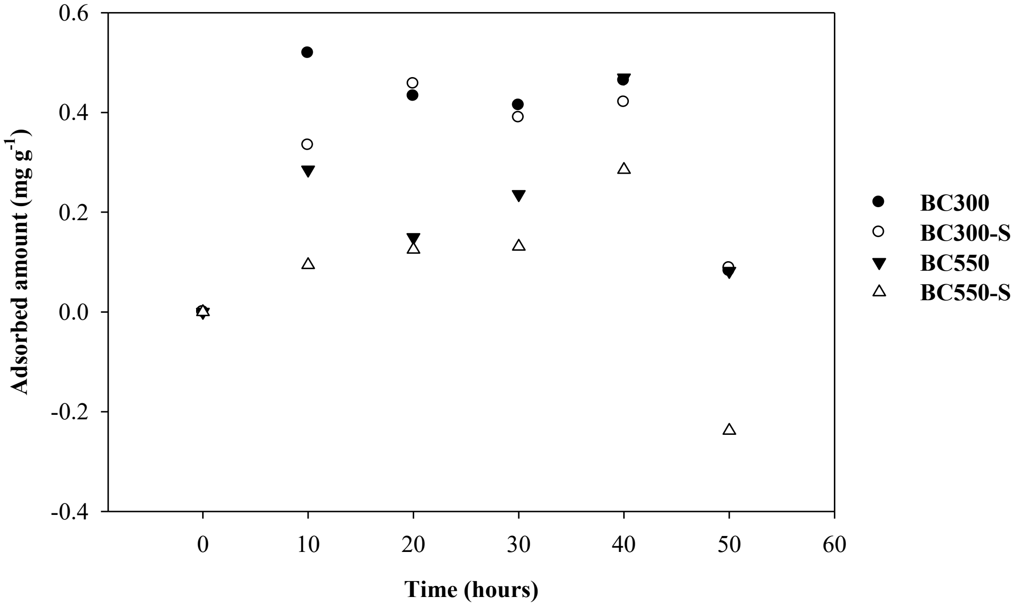

Fig. 2-5. Effect of application rate on the adsorption of P using four biochars (BC300, BC300-S, BC550 and BC550-S). T = 295 K, t = 48 h, pH = 7.

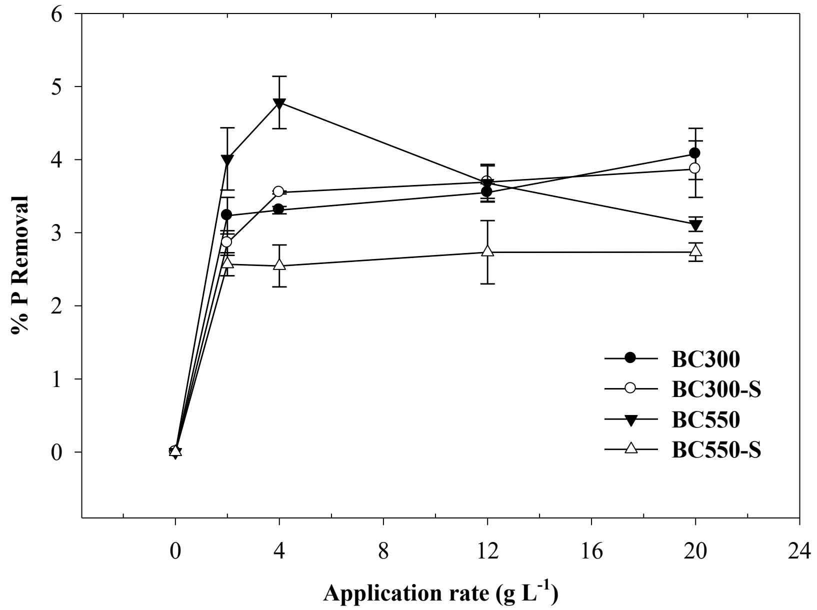

Fig. 2-6. Phosphate concentrations in solution with initial concentration of 20 mg L^{-1} for the four biochars (BC300, BC300-S, BC550 and BC550-S) within 50 hours. Biochar application rate = 2 g L^{-1}, T = 308 K, pH = 7.

Chapter 3. Sorption of copper by pine sawdust biochars as affected by pyrolysis temperature and steam activation in synthetic oil sands process-affected water

1. Introduction

Ongoing oil sands mining activities in northern Alberta cause various environmental issues. Along with the surface disturbance caused by mining, enormous amounts of tailings including oil sands process affected-water (OSPW) consisting of water, fine particles, organic contaminants and heavy metals are produced (Mikula et al., 1996). Due to the "zero discharge" policy into surface waters, over 1 billion m^3 OSPW that cannot be recycled are stored onsite (Del Rio et al., 2006). Copper (Cu (II)) is the most abundant metal in the OSPW (Allen, 2008; Pourrezaei et al., 2014), and its concentration exceeds the environmental quality guidelines for Alberta surface waters (Government of Alberta, 2014), water quality guideline of the Canadian Council of Ministers of the Environment (CCME, 2014). In some of the tailings ponds, Cu (II) concentration can be five hundred-fold greater than the CCME guideline (Allen, 2008; Pourrezaei et al., 2014). The elevated concentration of Cu (II) is very toxic to aquatic lives, and can cause server capillary damage and nerve system irritation to human (Aksu and Isoglu, 2005).

Cost effective adsorbents for Cu (II) removal are in demand for large-scale applications such as OSPW. Biochar, a carbonaceous material, has been proven as a very effective adsorbent for metals (Ahmad et al., 2014; Beesley et al., 2010; Manyà, 2012; Mohan et al., 2014). Numerous studies have reported that biochars' adsorption capabilities for Cu (II) removal (Chen et al., 2011b; Pellera et al., 2012; Tong et al., 2011; Uchimiya et al., 2010a; Xu et al., 2013). Biochar is usually produced from wastes and agricultural residues, and its adsorption capacity for Cu (II) varies with feedstocks and pyrolysis condition. Pyrolysis condition including pyrolysis temperature and activation techniques greatly shape biochar's surface characteristics. There is a rising interest in investigating how pyrolysis condition affects adsorption capacity by developing different surface characteristics, and therefore tailoring biochars to meet specific needs. Steam activation is one of the activation techniques used to increase surface area, enhance porous structure and modify other properties (Lima et al., 2010). Uchimiya et al. (2010b) studied biochar derived from poultry broiler litter manure pyrolyzed at 350 and 700 °C with and without steam activation to adsorb deisopropylatrazine, and they found that biochar produced at 700 °C with steam activation had the greatest adsorption resulting from the surface area and aromaticity. However, whether increasing surface area and aromaticity could improve sorption for Cu (II) is unknown. In addition, surface functional groups that closely interact with metal ions are associated with pyrolysis condition. An increasing of pyrolysis temperature that withdraws oxygenated functional groups could be unfavorable for metal sorption (Uchimiya et al., 2011b). Steam activation may offset temperature's effect by increasing oxygen containing functional groups (Manyà, 2012). Therefore, there is a controversy needed to be resolved to understand comprehensive roles of surface area and functional groups caused by different pyrolysis condition.

Application of biochar into OSPW has never been explored, by conducting batch sorption experiments including isotherm and kinetic studies using synthetic OSPW, this study aimed to achieve the following objectives 1) to test the effectiveness of biochar in removing Cu (II) in synthetic OSPW; 2) to understand the effects from pyrolysis temperature and steam activation on biochar's sorption performance for Cu (II); 3) to evaluate the relative contribution of each surface characteristic on biochar's adsorption performance for Cu (II).

2. Materials and methods

2.1. Biochar production and sorption experiment

Pine sawdust biochars were produced at 300 and 550 °C, with or without steam activation using the same method described in Lou et al. (2015). The four biochars produced are BC300, BC300-S, BC550, and BC550-S. The letters “BC”, “S” represented biochar and steam activation, respectively. Values “300” and “550” represented the peak temperatures used in pyrolysis. The biochars were characterized by proximate and ultimate analyses, and also analyzed for surface area, surface morphology and functional groups (Lou et al., 2015). According to published research among numerous tailings ponds, synthetic OSPW was prepared by $CaCl_2$ and NaCl with ionic strength of 0.05 (Allen, 2008; Pourrezaei et al., 2014).

$CuCl_2$ (Fisher scientific, reagent) was dissolved into the synthetic OSPW to make the aqueous solution. Corning centrifuge tubes (50 mL) were applied for the batch sorption experiment. Adsorption isotherm was examined by adding 0.025 g biochar into 25 mL of Cu (II) solutions of different concentrations ranging from 10 to 1000 $\mu g\ L^{-1}$. The mixture was agitated in reciprocating and shaken for 24 hours. After equilibrium, solid and liquid phases were separated by centrifugation at 3,000 rcf for 15 min. Ten mL of the liquid was filtrated through 0.45 μm pore size membranes afterwards. The filtrate was immediately acidified to $pH<2$ with HNO_3 and concentrations of metals were determined using inductively coupled plasma mass spectrometry (ICP-MS, Thermo scientific, ICAP-Q, Bremen, Germany). The metal concentrations were detected using ICP-MS. All experiments were conducted in triplicate and the average values were reported.

2.2. Sorption models

The isotherm data were analysed with Langmuir and Freundlich equations. Langmuir model is expressed as:

$$q_e = \frac{Q_{max} b C_e}{1+bCe}$$

where q_e (mg g^{-1}) is the amount of the metal adsorbed per unit weight of biochar, C_e (mg L^{-1}) is the equilibrium concentration of solution, and Q_{max} (mg g^{-1}) is the maximum adsorption capacity and b the constant related to the affinity.

The Freundlich model is given by:

$$q_e = K_f {C_e}^{1/n}$$

where K_f and n are indicators of adsorption capacity and intensity, respectively. The values of K_f and n were evaluated based on the experimental data.

Adsorption kinetics of Cu (II) on the biochars was determined similarly by adding the same amount of biochar into 25 mL solution with an initial concentration of 20 mg L^{-1} in corning tubes. At appropriate time intervals, the tubes were withdrawn, and solution was extracted and filtered in the same way as the isotherm study.

Three kinetic models including pseudo-first order, pseudo-second order and intraparticle diffusion equations were used to interpret the kinetic data (Rajapaksha et al., 2011).

The pseudo first order equation assuming non-dissociating adsorption is expressed as below (Lagergren, 1898; Ho and Mckay, 1998)

$$\log\ (q_e - q_t) = \log\ (q_e) - \frac{k_1 t}{2.303}$$

where q_t (mg g^{-1}) is the adsorption amount of metal ion at time t (min), q_e (mg g^{-1}) is the adsorbed amount of metal ion at equilibrium, and k_1 (L min^{-1}) is the pseudo-first order rate constant. The kinetic parameters can be obtained by plot log $(q_e - q_t)$ vs. t.

The pseudo-second order equation which assumes chemisorption is expressed as (Ho and McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} - \frac{t}{q_e}$$

The initial sorption rate, h (mg g^{-1} min), as $t \rightarrow 0$ can be defined as:

$$h = k_2 {q_e}^2$$

where k_2 (g mg^{-1} min) is the rate constant of the pseudo-second order adsorption.

Intraparticle diffusion, the rate of which is dependent on the rate at which components diffuse towards one another and the model is expressed as:

$q_t = k_i t^{1/2}$ +C

where k_i constant (mg g^{-1} $min^{0.5}$) is the intraparticle diffusion rate, and C is the intercept.

3. Results and discussion

3.1. Pyrolysis condition and biochar properties

Proximate and ultimate characterization of the biochars is presented in our previous study (Lou et al., 2015). Surface areas of the biochars substantially increased with increasing pyrolysis temperature. Steam activation did not increase the surface area of biochar produced at 300 °C, but doubled the surface area of biochar produced at 550°C. The mobile matter greatly decreased with the increasing peak temperature. Mobile matter in BC300, BC300-S, BC550, BC550-S are 56%, 54%, 28% and 18% respectively. The high temperature helped releasing more volatile matters and emission of CO_2, H_2O and CH_4 (Ahmad et al., 2013). On the contrary, ash content and fixed carbon content increased significantly as increasing peak temperature, indicating higher mineral content and higher carbon storage at pyrolysis temperature of 550°C. The H%, O%, molar H/C and O/C values are key indicators of biochar properties. The lower values of these indicators suggest higher aromaticity and lower oxygen functionality, because increasing peak temperature improves depolymerisation of cellulose, increases the degree of carbonization, and develops graphitic structure (Ahmad et al., 2013; Uchimiya et al., 2011b). Evidently, BC550 and BC500-S have significantly lower values of molar H/C and O/C compared to BC300 and BC300-S. FTIR by investigating surface functional groups further confirmed the fact that higher pyrolysis temperature lead to less hydrogen-bonded hydroxyl groups (Lou et al., 2015).

Steam activation treatment for biochars produced at each temperature did not modify the elemental composition, aromaticity or functional groups as reported by (Azargohar and Dalai, 2008). The same result was also reported by Rajapaksha et al. (2014). The steam activation only doubled the surface area (189.2 to 397.1 $m^2\ g^{-1}$) for biochar produced at 550 °C. The increasing surface area resulted from temperature and steam activation by combustion and emission of volatile matters and gases. The unsuccessful attempt of increasing surface area for BC300 may be related to insufficient combustion and appropriate steam supply speed and time.

3.2. Adsorption isotherm and kinetics

The Cu (II) adsorption isotherms were fitted into the non-linear regression and shown in Fig. 3-1. The adsorption constants and correlation coefficients for Cu (II) onto pine sawdust biochars obtained from the Langmuir and Freundlich isotherms are given in Table 3-1. Correlation coefficients suggested that the Langmuir model fits the BC550 and BC550-S data better than the Freundlich model with R^2 0.98 for both. For BC300 and BC300-S, the Langmuir model can also be adopted (R^2 0.96 and 0.94, respectively). The Langmuir model is usually served to estimate the maximum uptake values where they could not be reached in the experiments, and it assumes monolayer adsorption on a homogeneous surface. According to the Langmuir parameters, the maximum adsorption capacities of BC550 and BC550-S for Cu (II) are above 2.5 mg g^{-1}, much higher than those made at 300 °C, both of which are below 0.1 mg g^{-1}. The parameter b is associated with the affinity of the binding sites that allows comparisons of the affinity of biochars towards the metal ions. BC300 and BC300-S had a higher affinity for Cu (II) (0.25 and 0.20 L mg^{-1}, respectively) than BC550 and BC550-S (0.09 and 0.10 L mg^{-1}, respectively). Higher surface area usually contributes to better adsorption for organic matters but did not enhance the adsorption of Cu (II). High surface area enlarged by abundant micropores may be favourable for organic matters to partition into the pores, but it does not necessary increase binding sites for Cu (II) due to different sorption mechanisms.

Based on previous studies that investigated biochar derived from plant biomass and produced from slow pyrolysis, the pine sawdust biochars' adsorption capacities for Cu (II) are considered as moderate. Tong et al. (2011) reported that biochars derived from straws of peanut, canola and soybean removed 0.03-0.09 mg Cu (II) g^{-1}. Zheng et al. (2010) found pinewood biochars had a similar adsorption capacity of 2.75 mg g^{-1}.

Kinetics study indicated that for BC550 and BC550-S, the most sorption of Cu (II) occurred within the first five hours. The sorption increased rapidly at the beginning and reached equilibrium slowly at around 12 hours (Fig. 3-2). Specifically, within first one hour contact time about 90 % of the Cu (II) was removed in the solution with BC550 and 80 % for BC550-S. The general two-phase adsorption, consisting predominantly of a rapid phase and a relatively slow phase is a common phenomenon (Pellera et al., 2012). This can be explained by the abundant availability of active sites on biochar surface which becomes progressively saturated with time. For BC300 and BC300-S, the equilibrium was reached at the first two hours, and this is likely due to the limited adsorption sites on the surface. The parameters of the three models are listed in Table 3-2. The pseudo-second order with R^2 value of BC550 and BC550-S reached 0.99, and BC300 and BC300-S are 0.85 and 0.91, respectively, fitting the data better than other models (Fig. 3-3). The higher values of sorption parameters k_2 and h showed that the sorption of BC500 and BC550-S were faster than BC300 and BC300-S. This result suggested that chemisorption or chemisorption involved valence forces was the limiting factor of the adsorption (Ho and Mckay, 1999). This is consistent with many studies illustrated in recent review articles (Ahamd et al., 2014; Mohan et al, 2014; Tan et al., 2015).

3.3. Adsorption mechanisms

Ahmad et al. (2014) summarized the mechanisms related to metal removal by biochars including physical sorption (electrostatic attraction), chemical sorption (ion exchange and surface complexation), and precipitation. Electrostatic attraction includes the interaction between metal cations and negatively charged carbon surface, and sorption involving delocalized π electrons. Specifically, the likely sorption occurred in this study could be: 1) Electrostatic interaction between negatively charged biochar surface and Cu (II), which also including cation-π interaction between delocalized π electrons and Cu (II); 2) ionic exchange between protons or cations at the surface of acidic carbon and Cu (II); and 3) complexation with oxygenated (acid) functional groups (Uchimiya et al., 2011b) and 4) precipitation between mineral salts (e.g. phosphate and carbonate salts) and Cu (II).

Delocalized π electrons from aromatic rings can form weak electrostatic bonding with cations. Increasing in pyrolysis temperature increased the aromaticity along with more delocalized π electrons can induce more Cu(II) sorbed to biochar produced at °C due to cation- π interaction. On the other hand, the increasing in pyrolysis temperature from 300 to 550 °C reduced oxygen functional groups, and consequently reduction of complexation for the BC550 and BC550-S could be expected. Uchimiya and coauthors reported that cottonseed hull biochars produced at low temperatures with a high O/C ratio had a better capacity to retain Cu (II), and also emphasized the importance of oxygen functional groups in adsorbing heavy metals (Uchimiya et al., 2011b). However in this study, by plotting adsorption capacity against biochar properties (Fig. 3-4), adsorption capacities of the biochars are negatively correlated to H%, O%, and molar H/C and O/C. This indicates that adsorption through complexation with functional groups such as phenolic –OH did not contribute much to the adsorption. Stronger Cation- π interaction in BC550 and BC500-S contributed to better adsorption performance, but it did not domain the process likely, as the kinetic results disclosed chemisorption (valence involved) controlled paradigm. Xu et al. (2013) attributed 98% of the adsorption of Cu (II) on manure biochar to the precipitation with carbonates and very little was through complexation by phonetic –OH and delocalized π electrons. As evidence, in our previous study we observed small amount of phosphate was released by the pine sawdust biochars in deionized water (Lou et al., 2015), and thereby precipitating with of Cu (II).

In addition, it can be speculated that exchange between ionizable protons and Cu (II), and replacing alkaline earth metal cations present in biochars such as Na, Ca and Mg (Chen et al., 2007) are the other two possible chemical sorption involved in the process. The high ash content that is mineral component in BC550 and BC550-S might explain that cation exchange were more active than BC300 and BC300-S, resulting in better adsorption. Quantifying protons and cations before and after sorption can better elucidate the mechanisms.

4. Conclusions

Converting pine sawdust into biochar and utilize it as Cu (II) adsorbent in treating OSPW is a cost effective option. Producing biochar at the low temperature by preserving biomass features with more oxygenated functional groups did not contribute much to the sorption as opposed to conventional notions. On the other hand, the high temperature improved Cu (II) sorption mainly through enhanced chemical process including precipitation and ion exchange, and minor contribution by cation- π interaction. Steam activation as an extra effort designed to enhance sorption properties did not achieve the desired results received from biochar's sorption for organic matters. Surface area was not a significant factor for better Cu (II) sorption and needlessly to be incorporated in future biochar production. A critical attitude towards biochar's sorption capacity towards metals such as Cu (II) is necessary when evaluating the various pyrolysis conditions especially for those promoted as positive solutions for sorption, especially in large-scale application such as OSPW where production cost is significant.

Table 3-1. Parameters of Cu (II) sorption by four biochars from Langmuir and Freundlich models.

Langmuir isotherm			
	b (L μg^{-1})	Q_{max} (mg g^{-1})	R^2
BC300	0.25	0.078	0.98
BC300-S	0.20	0.093	0.94
BC550	0.09	2.961	0.99
BC550-S	0.10	2.742	0.98
Freundlich isotherm			
	K_f	n	R^2
BC300	16.68	0.40	0.98
BCs300	19.09	0.48	0.93
BC550	373.61	0.48	0.99
BCs550	422.34	0.43	0.97

Table 3-2. Kinetic parameters of Cu (II) sorption by four biochars from pseudo-first order, pseudo-second order and intraparticle models.

		Pseudo-first order			
Biochar	q_e	q_{cal}	k_1	R^2	
BC300	0.10380	-1.820	-0.334	0.84	
BC300-S	0.11092	-0.879	-0.713	0.91	
BC550	0.9098	-2.344	-0.301	0.93	
BC550-S	0.9004	-1.773	-0.319	0.99	
		Pseudo-second order			
	q_e	q_{cal}	k_2	h	R^2
BC300	0.1038	0.09953	-0.1622	-0.0016	0.89
BC300-S	0.1109	0.09535	-0.1812	-0.0016	0.92
BC550	0.9098	0.91625	0.13175	0.1106	0.99
BC550-S	0.9004	0.91383	0.07268	0.0611	0.99
		Intraparticle diffusion model			
	q_e	k_s	C	R^2	
BC300	0.1038	-0.0067	0.258	0.566	
BC300-S	0.1109	-0.0089	0.294	0.670	
BC550	0.9098	0.0043	0.810	0.920	
BC550-S	0.9004	0.01	0.692	0.889	

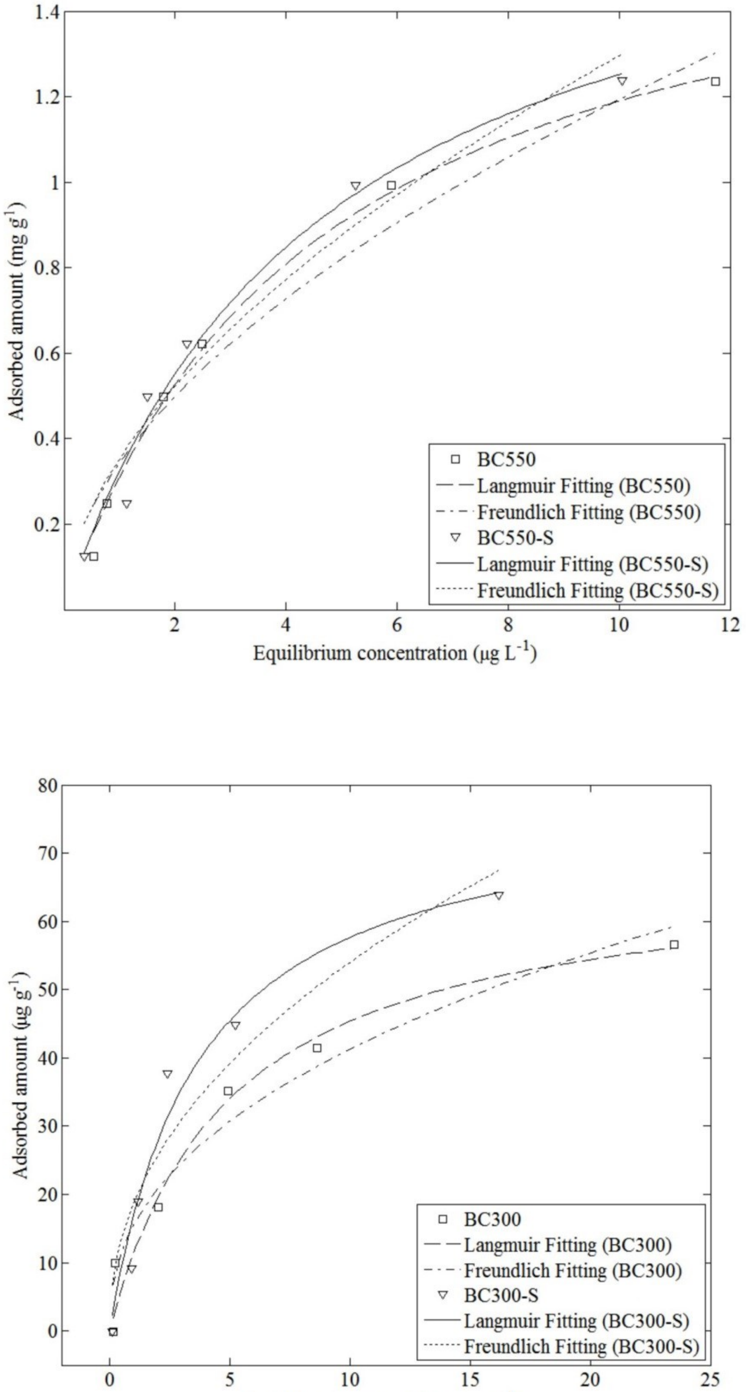

Fig. 3-1. Isotherm and Freundlich modeling for Cu (II) adsorption on four biochars (BC300, BC300-S, BC550 and BC550-S).

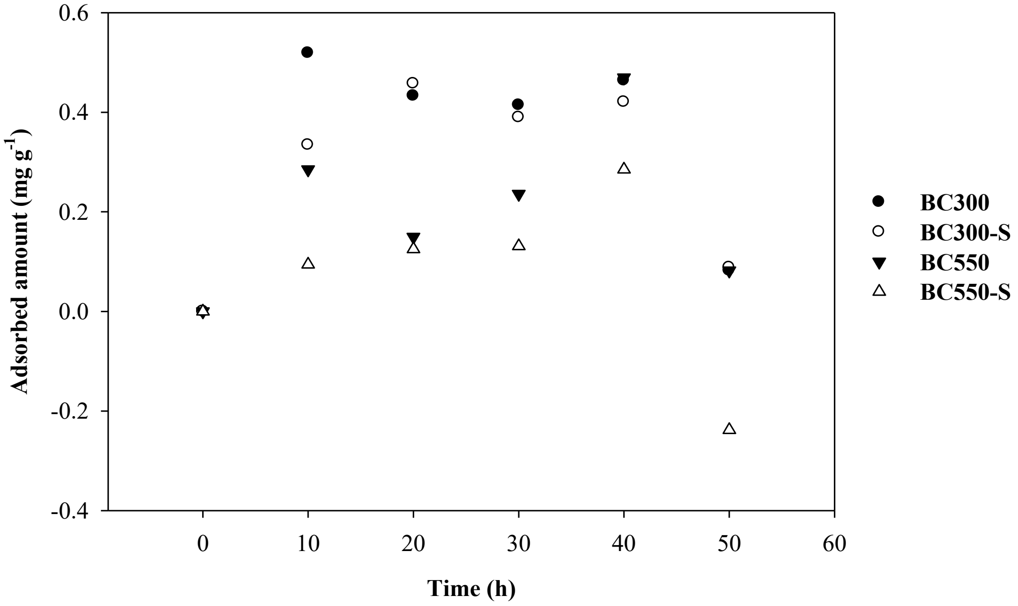

Fig. 3-2. Adsorption kinetics for four biochars (BC300, BC300-S, BC550, and BC550-S).

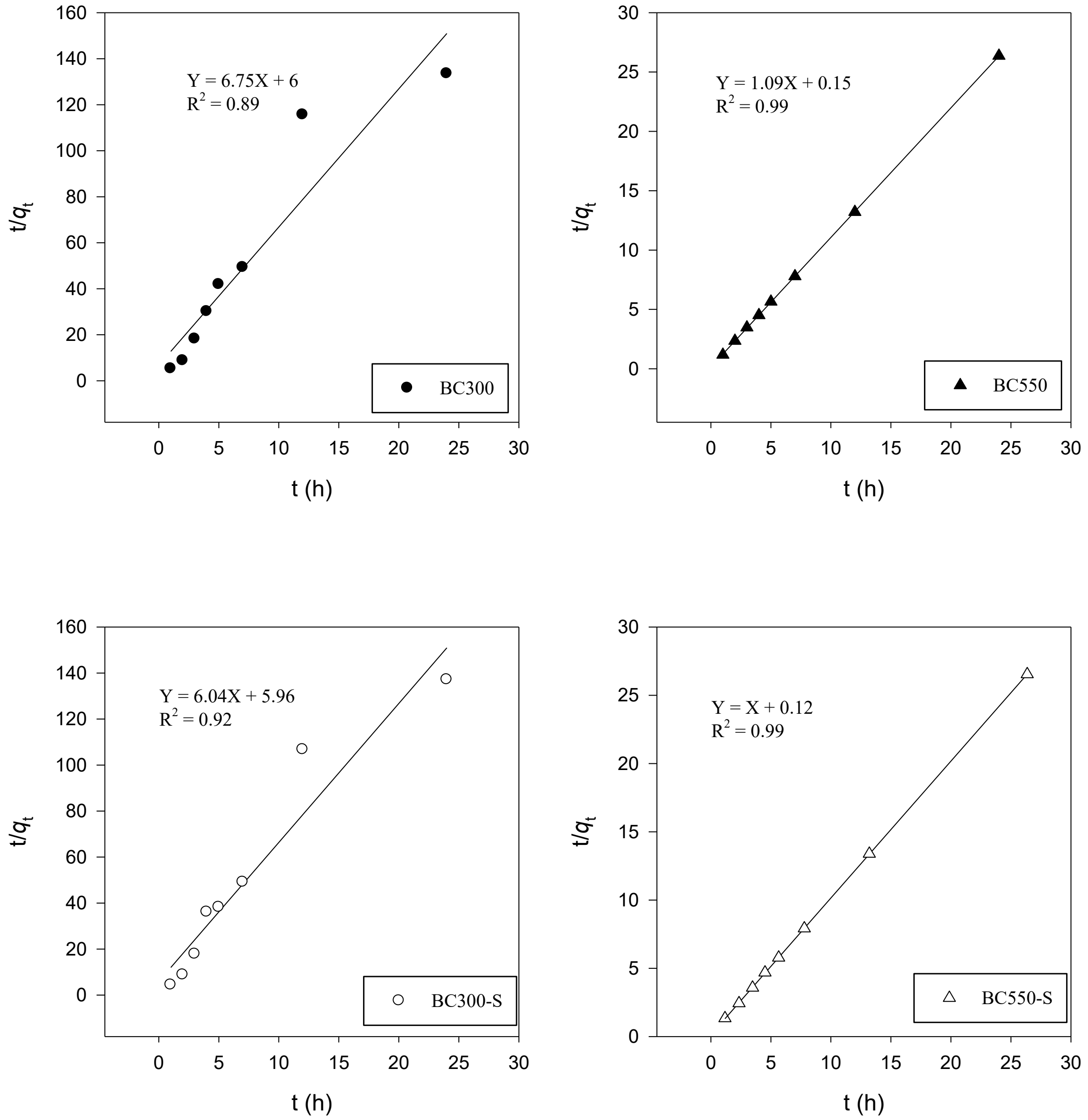

Fig. 3-3. The pseudo-second order model fitting for BC300, BC300-S, BC550, and BC550-S.

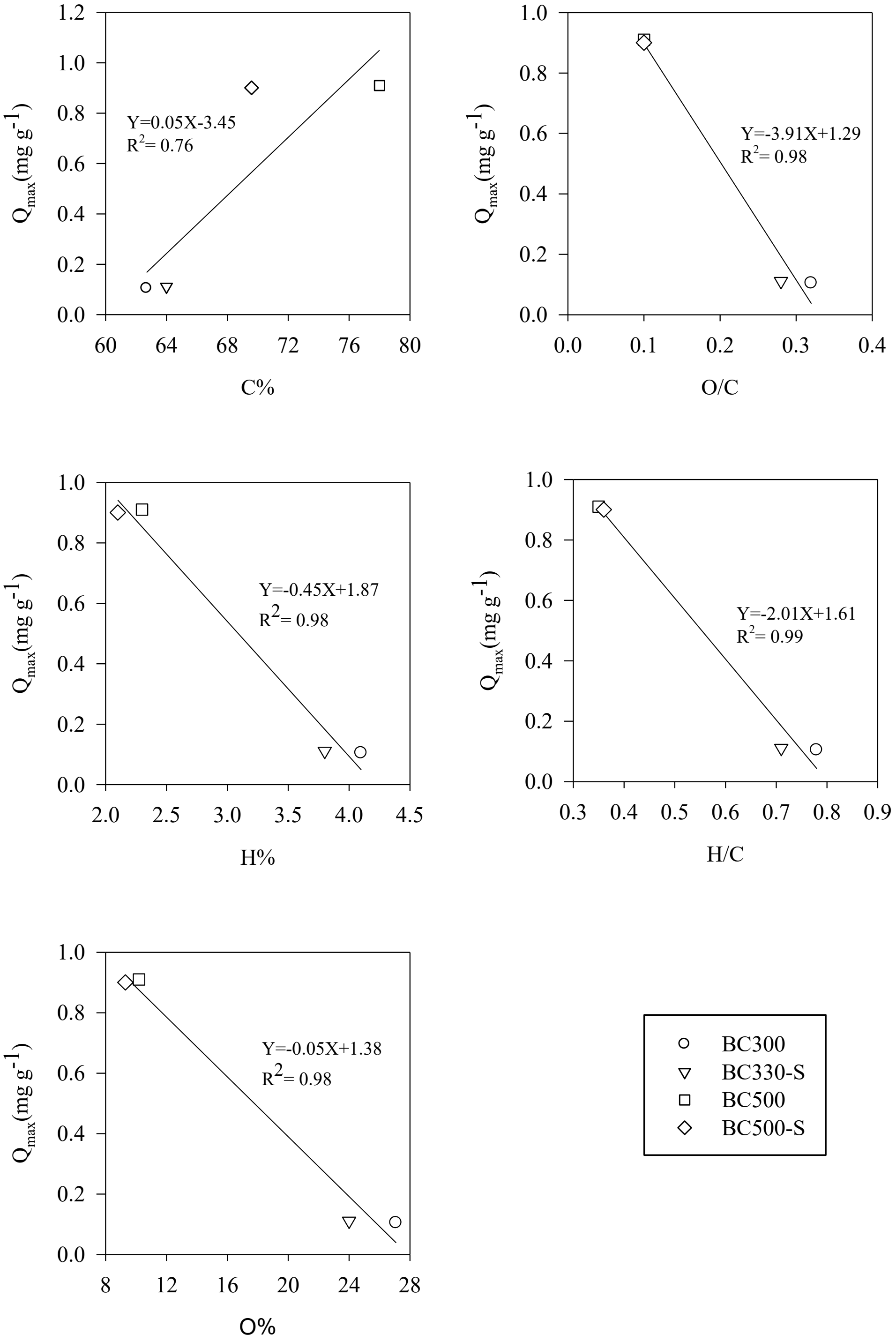

Fig. 3-4. Sorption capacities of Cu(II) as a function of biochar properties including C%, H%, O%, molar H/C, and O/C.

Chapter 4. How much does it cost to apply biochar for environmental management? ---- A cost-benefit analysis of applying a pine sawdust biochar to Mildred Lake Settling Basin in Alberta, Canada

1. Introduction

An energy system based on carbon-rich fossil fuels in human society has resulted in the emission of large quantities of greenhouse gases (GHG), causing unprecedented pressure on future climate. Biochar technologies are innovated and developed as an efficient way to sequester carbon along with many other agronomic benefits. The International Biochar Initiative (IBI) reported that there was a dramatic increase in the number of publications in the peer-reviewed scientific literature associated with biochar in recent years. The number increased from approximate 50 in 2008 to 400 in 2013 (Jirka and Tomlison, 2014). Despite the rapid increase in the number of scientific publications, there are knowledge gaps that need to be addressed between research and implementation to give a clear vision on status quo and future direction for researchers and decision makers (Shackley et al., 2015). To implement a new technology, decision makers and project managers are very keen in knowing the cost and benefit entailed in the system. However, there is not much information available on the economic evaluation of the biochar production-application system. Even though it is a rapidly developing field, the biochar technology is still in its early phase of development and there are many inconsistencies regarding technical operations within the industry (Shackley et al., 2015).

This study is supplementary to technical research in previous chapters in this thesis. In Chapter 3, a pine sawdust biochar was proved very effective as a remediation material in aquatic environments. After obtaining such a positive result, it is natural to provoke the question, how realistic it is to implement the research to solve emerging problems. Effective communication with practitioners or policy makers is not limited to the research results, but a systematic view on facts about possibilities, cost and benefits.

In our previous study (Chapter 3), we found that the pine saw dust biochar produced at 550 °C could remove up to 99% of the copper contained in synthetic oil sands process-affected water (OSPW), and therefore it would be a very promising remediation material to be used in tailing ponds to treat copper contamination. Being very similar to activated carbon, biochar with its unique porous structure and high surface area is also an ideal material for removing organic contaminants such as polycyclic aromatic hydrocarbons, naphthalene, pyrene etc. (Ahmad et al., 2014; Chen et al., 2008). But does producing the pine sawdust biochar and applying it into the tailings ponds make any economic sense, and help to achieve compliance with legal requirements? This chapter aims to do a reality check about applying the positive results from Chapter 3.

2. Economic evaluation of biochar system

Economists have not reached any consensus on the methods of evaluating the economics of biochar system. Simple economic analyses such as cost-benefit analysis (CBA) are appreciated by investors and project managers constantly seeking to maximize the benefits and profitability of the system. There have been a number of studies focusing on production technologies and biochar functions with significant environmental benefits revealed in these studies greatly support the application of biochars (Ahmad et al., 2014; Novak et al., 2008; Mohan et al., 2014; Shackley et al., 2015). However, to commercialize biochar production and application to realize its benefits needs concrete evidence of cost effectiveness. Compared to research on biochar technologies, there has been little research conducted in the area of economic assessment of biochar systems. Peer-reviewed articles that include CBA that have been published are summarized in Table (4-1).

The CBA is the most commonly used tool for evaluating profitability, and indicating the likelihood of commercialization to some extent (Boardman et al., 1996). By calculating the net present value (NPV), the difference between the present value of cash inflows and the present value of cash outflows, to reflect the current value of a project that will continue to operate for years into the future. The greater the NPV is, the more economically viable the proposed project will be (Shackley et al., 2015). These studies (Table 4-1) directly or indirectly calculated NPV, by doing a sensitive analysis, they all implied that the potential net benefits of biochar production system is dependent on the feedstock used, the conversion technology employed, or the inclusion of carbon credits that reflect the social value of GHG emission. To conduct a proper CBA, an analyst's perspective or a global perspective is appropriate. In this perspective, revenue should not be counted as benefits (Broadman, 1996), which was inappropriately taken by many studies. The scope of benefits in existing studies is also limited to carbon storage and agricultural gains in the soil. Biochar is also a well-recognized remediation material comparable to activated carbon, and its economical assessment in removing contaminants in aquatic environments should be explored to advocate this application in the future.

The typical costs and benefits included in published CBAs typically fall under the following headings (McCarl et al., 2009).

Costs are caused by:

- feedstock collection
- feedstock transportation
- feedstock storage and pre-processing
- biochar hauling and application

- pyrolysis unit construction and operation

And benefits are from:

- energy sale (biochar/charcoal, bio-oil, and syngas)
- biochar-induced agronomic and environmental gains
- carbon offset credits (where applicable)

Net present value can be calculated by:

$$NPV\,(i,N) = -R_0 + \sum_{t=0}^{N} \frac{R_t}{(1+i)^t}$$

Where:

NPV = net present value
R_0 = initial investment
R_t = cash flow at time (t)
i = discount rate
t = time of the cash flow

3. Case study

3.1. Case description

Oil sands tailings ponds were used to store OSPW due to the “zero discharge” policy of the Government of Alberta (Government of Alberta, 2010). There is currently about 77 square kilometres of OSPW in Alberta (Government of Alberta, 2015). The Mildred Lake Settling Basin (MLSB; Appendix) (57.42° N, 111.38° W) owned by Syncrude Canada Ltd. is located on the north side of the Mildred Lake lease area, 40 km north of Fort McMurray (Alberta Energy Regulator, 2013). The total OSPW volume in MLSB is 2.5 million m^3 (Alberta Energy Regulator, 2013). The properties of OSPW in MLSB were summarized in Allen (2008).

This case study investigated the cost and benefits entailed in the whole biochar production-application system. The transportation cost is typically a significant portion of the total cost (Roberts et al., 2010; Shackley et al., 2015). Ideally, the biochar production and application sites should be in a close distance to minimize the cost. When searching for biochar suppliers, we found that there were no convenient sources for users to find biochar information sorted by geological locations, and biochar advertisements are usually dispersed in many different websites. Therefore, we developed an online search engine associated with biochar (Chen and Lou, 2015) to provide users with locations and concise information about producers based in North America. According to the search results, the nearest pyrolysis unit that has the potential to supply enough biochar required in this study is located in Prince George, BC (53.85° N, 122.73° W). Close to the pyrolysis plant, a lumber mill which produces 980,000 tons of pine sawdust annually is about 3 km away. The pine sawdust is typically piled as a waste by-product of sawmills. We assumed that this mill is willing to donate and also voluntarily transport the pine sawdust material to the plant for biochar production. The biochar will be produced in the pyrolysis plant by slow pyrolysis, transported to the destination, and applied in MSLB.

The baseline scenario in this study is that the pine sawdust is not utilized and piled in the mill, and the OSPW remains untreated, therefore there is no benefit and cost occurred in the baseline scenario. The system boundaries are centered on the production, transportation and application of biochar and its by-products (Fig. 4-1). The inflow to the system is biomass and energy input where outflow are biochar products and applications. Electricity was put in a dotted dash box because the current system only support self-sustaining electricity, and the plant has not constructed substations to allow the electricity to flow into the market.

3.2. Biochar production and transportation

Sawdust in many countries is still discarded as a troublesome by-product of sawmilling operation, and often disposed of in landfills, causing many environmental problems. In Alberta, part of sawdust and shaving material is being used as animal bedding material or directly incinerated for heat generation on site, but the market price for sawdust material is not consistent. Considering it is a waste material, the opportunity cost was assumed to be zero in this study. Feedstock collection fee mainly includes the excavation and handling of the material involving machinery rentals and labour costs. The lumber mill company is assumed to donate the material and ship the material to avoid gate fee if sent to a landfill.

Pine sawdust is stored at the pyrolysis facility where it is pre-processed and pyrolyzed. For pre-processing, the biomass is usually cut into proper size and dried to a final moisture content of less than 5%. The feedstock is dried in a large rotary drier. The moisture content in the pine sawdust is 24.5% (Zhang and He, 2006), and the sawdust material does not require resizing in this study. The re-sizing and drying equipment is incorporated in the pyrolysis plant during construction.

The pine sawdust biochar was produced at 550 °C with a heating rate of 7 $°C\ min^{-1}$ by slow pyrolysis. Slow pyrolysis typically involves the low temperature (300-550 °C) conversion of biomass with long residence time, resulting in high yields of biochar (Brown et al., 2011; Field et al., 2013; Gaunt and Lehmann, 2008). According to Shackley et al. (2011), pyrolysis units are typically classified into small-scale, medium-scale and large-scale depending on feedstock amount that unit can process. The pyrolysis unit used in this study is assumed to be a large-scale unit, which could process 184,800 t of oven dried feedstock per year with 36% of biochar yield (Shackley et al., 2011). There is a lack of data on the realistic cost of slow pyrolysis, and we assumed that pyrolysis was done using a large pyrolysis unit in the UK. In a study from the UK Biochar Research Center, the capital cost includes all design, equipment, construction, civils and commission cost estimated for a large-scale facility is about US$4.12 million, which equals to US$22.8 when averaged to per ton biomass processed for a twenty-year lifespan project with a discount rate of 8% (Shackley et al., 2011). Hinode-Cho Tokyo, the largest slow pyrolysis facility in the world has a very close capital cost of US$22.2 per ton of biomass (Masek et al., 2010). The operational and labour cost of producing biochar from sawmill residues calculated by the UK Biochar Research Center (Shackley et al., 2011) is about US$5.0 t^{-1}. The cost information in the study of Shackley et al. (2011) was reported to be based on real operational data.

Slow pyrolysis requires the use of diesel fuel for heat generation at the beginning. After the process is initiated, no further diesel fuel is required. All the syngas produced during pyrolysis is assumed to be used to generate heat for drying the feedstock and supporting the system to continue operation. Currently, this pyrolysis unit can only support the electricity needed within the plant and does not contribute to the national grid. Based on the heating value of the products, we calculated that it has a potential to generate 93.39 MWh per ton of biomass pyrolysed (Calculation 4, Appendix), and would create a significant profit for the system if the electricity could be sold to the commercial market. The maximum capacity and efficiency of the generator is limited, and it cannot utilize all the heat and covert it to usable electricity to be transmitted to various substations (Kung et al., 2013).

Diesel fuel consumption and associated emissions were modeled for the transport of 1214 km from the pyrolysis plant to the MLSB site in Fort McMurray. The cost was estimated by modeling transport in heavy trucks using default payload capacity and fuel economy values from a trucking cost model (Norris, 2009), and the GHG emissions was modeled with GREET software that evaluates GHG, regulated emissions, and energy use in transportation (Field et al., 2013; Roberts et al., 2010; Wang, 2008). It analyses the transportation fuel cycle by compiling the upstream energy and air emissions for electricity generation, fossil fuel production and combustion, transportation, and agricultural inputs. We assumed that semi-trucks with a payload of 23 t (80% loading) are used for the shipping.

3.3. GHG accounting

The average residence time of biochar is about 1000 years or longer at 10 °C mean annual temperature (Lehmann, 2007). For this assessment, we assumed that slow pyrolysis has been optimized for high yields of stable carbon, and a conservative estimation of 80% of the carbon in the biochar is stable (Baldock and Smernik, 2002). The remaining 20% of carbon is labile and released into the atmosphere as biogenic CO_2 within the first few years of application. The fixed carbon content in the pine sawdust biochar characterized in our previous studies is about 62.2% (Chapter 2).

Carbon sequestrated by biochar is 0.174 t for ton of biomass, and total carbon of 1378.3 t for all biomass (Calculation 3, Appendix). The GHG emitted by a semi-truck that consumes conventional diesel including main GHG CO_2, N_2O, black carbon, which is equivalent to 26 kg CO_2-equivalent emission (CO_2eq) /100 km of calculated by USEPA Greenhouse Gas Equivalencies Calculator (Calculation 6, Appendix; USEPA, 2015b). The total transportation sector will release 0.9 Mg of CO_2eq. The majority GHG emission comes from transportation. GHG emission generated from pyrolysis operation and biochar application accounted for about 5% of the total GHG emission.

3.4. Cost and benefit

The total cost including feedstock harvesting and pre-processing, transportation, pyrolysis and application is US$542,955.18 for all biomass involved, averaged to US$206.37 per ton biochar, which is close to US$169.8, the cost of producing sawdust biochar in a larger-scale pyrolysis plant in the UK (Shackley et al., 2011). Among the total cost, the feedstock harvesting and preprocessing, transportation, pyrolysis and application each accounted for 1.3, 53.5, 40.5 and 4.65%, respectively (Fig. 2).

Roberts et al. (2010) examined the full life-cycle energy, GHG emission balance, and economic feasibility of biochar using life cycle assessment method. They found that the economic viability of the pyrolysis system for biochar production is largely dependent on the cost of feedstock production, pyrolysis, and the value of carbon offsets, and feedstock that needs waste management, such as yard waste for it has the highest potential for economic profitability. Consistently, the transportation distance also created a significant hurdle to the economic profitability. McCarl et al. (2009) undertook a full CBA for biochar in the context of the US mid-west. This is for a 70,000 t (feedstock) y^{-1} plant, costing US$24 million, assuming a 20-year lifetime and a discount rate of 12%. McCarl et al. (2009) concluded that slow and fast pyrolysis of maize residue for biochar production and energy by products is not profitable. The NPV for fast pyrolysis is -US$45 t^{-1} feedstock and -$70 t^{-1}feedstock for slow pyrolysis. The data from their study was also inferred, not derived from an operating plant.

In economic analysis, many impacts central to sustainability and environmental qualities are considered as externalities because the current market does not have a direct mechanism for pricing the goods (USEPA, 2015a). For instance, Field et al. (2013) simplified biochar's environmental benefits (e.g. carbon sequestration, N_2O suppression and crop yield improvement) as liming effects to soil. Benefits considered in other studies typically are enhanced crop yield and avoided fertilizer use. In the aquatic environment, the associated benefits would be related to the mortality of aquatic life and reduced risk of toxic effects. However, these non-market values are still need to be developed for OSPW research. Therefore, benefits evaluation in this study is only limited to carbon storage and reduced GHG emission. Revenues will also be considered as zero in many circumstances because biochar markets are very uncertain and thus not financeable at the current stage (Shackley et al., 2015).

The economic assessment has its uncertainty because of the ambiguous carbon price, and technical constraints in the production chain also leads to a large variability in the net profitability. Low (US\$20 t^{-1}) and high (US\$80 t^{-1}) scenarios for pricing CO_2 have been used to calculate the benefits in IPCC reports (IPCC, 2007). The NPV is US\$-480,551.8 (US\$-182.6 t^{-1} biochar) for the low price scenario and US\$-293,341.6 (US\$-111.5 t^{-1} biochar) for the high price scenario (Calculation 7, Appendix).

4. Summary

This cost-benefit analysis conducted in this thesis chapter was aimed to complement the technical part of the thesis to provide a systematic view of biochar application for environmental management and implementation. This study estimated the cost of producing, transporting and applying biochar in the form of its life cycle. The whole study is hypothetical, and the pyrolysis model was based on a large pyrolysis unit in the UK. The cost was estimated based on available tools and previous studies. The benefit being considered was the carbon credit in the current market by producing biochar. Other benefits including enhancement of environmental qualities and social benefits were not studied. The NPV is between US$-186.37 to US$-126.37, depending on the carbon price.

Notably, to help with this study, an online database of all the biochar business in North America was developed. This would provide valuable information for future studies or individuals interested in studying or using biochar. The main barrier in the economic estimation of biochar is the lack of precise data, which makes the estimation very challenging and subject to many uncertainties. The cost also varies greatly depending on the country due to different production techniques used and labour and set-up costs. It is hard to generalize the cost model at current stage. Complete studies at local scales including biochar experimentation in the field, followed by a life cycle assessment and economic evaluation will be needed to innovate upcoming developments.

Table 4-1. Overview of cost-benefit analysis.

	Brown et al. (2010)	Field et al. (2013)	Galinto et al. (2011)	Granastein et al. (2009)	Kung et al. (2013)	McCarl et al. (2009)	Roberts et al. (2010)	Shackley et al. (2011)	Harsono et al. (2013)
Country	US	US	US	US	Taiwan, China	US	US	UK	Malaysia
Feedstock	Corn stover	Pine waste, spent grain	Herbaceous woody feedstock	Forest thinnings	Poplar trees	Corn stover	Switchgrass, Corn stover, Yard waste	Various virgin & non virgin sources	Palm oil empty fruit bunches
Biochar Source	Fast, slow	Fast, slow	Purchased ($87-$350 t^{-1})	Fast pyrolysis	Fast & slow pyrolysis	Fast & slow pyrolysis	Slow pyrolysis	Slow pyrolysis	Slow pyrolysis
Crop biochar applied to	Not specified	Winter wheat	Winter wheat	Not specified	Rice	Corn	Corn	n/a	Palm oil
Agronomic benefits monetized	n/a	Fertilization reduction, liming, yield	Fertilization reduction, liming, yield	Biochar sold for $114.5-$191 t^{-1}	Fertilization reduction, water reduction, seed reduction, yield	Fertilization reduction, liming, seeds, yield	Fertilization reduction	n/a	n/a
GHG considered	C storage	N_2O suppression, C storage	C storage	C storage	N_2O suppression, C storage	N_2O suppression, C storage	N_2O suppression, C storage	C storage	C storage

Adapted from Shackley et al. (2011).

Table 4-2. Cost of producing the pine sawdust from a large-scale pyrolysis unit in a 20-year's project with a discount rate of 8%.

	Unit price (US\$ y^{-1})[1]	Amount	Cost (US\$)
Feedstock harvesting, preprocessing			
Feedstock source and storage	0 t^{-1}	7914 t	0
Caterpillar excavator (including operator)	98 h^{-1}	40 h	3960
Feedstock storage	0.4 t^{-1}week^{-1}	7914 t	3165.2
Transportation (including loading and unloading)			
Biochar storage including proper containment[3]	22.8 t^{-1}	2631.58 t	62631.6
Transportation (including labor)[4]	1593.89 per trip	143 trips	227926.3
Pyrolysis facility[3]			
Capital cost	22.8 t^{-1}	7914 t	180439.2
operational cost	5 t^{-1}	7914 t	39570
Application			
Biochar storage[3]	0.4 t^{-1} week^{-1}	2631.58 t, 4 weeks	4210.88
Application including (tractor, spreader, labor, blower)[3]	8 t^{-1}	2631.58	21052
Total cost			542,955.18
Average cost (per ton of biochar)			206.37

[1] 1CAD = 0.82 USD

[2] Wages and salaries according to Government of Alberta (2015)

[3] Shackley et al. (2011)

[4] Calculation 5; Trucking cost model, Appendix

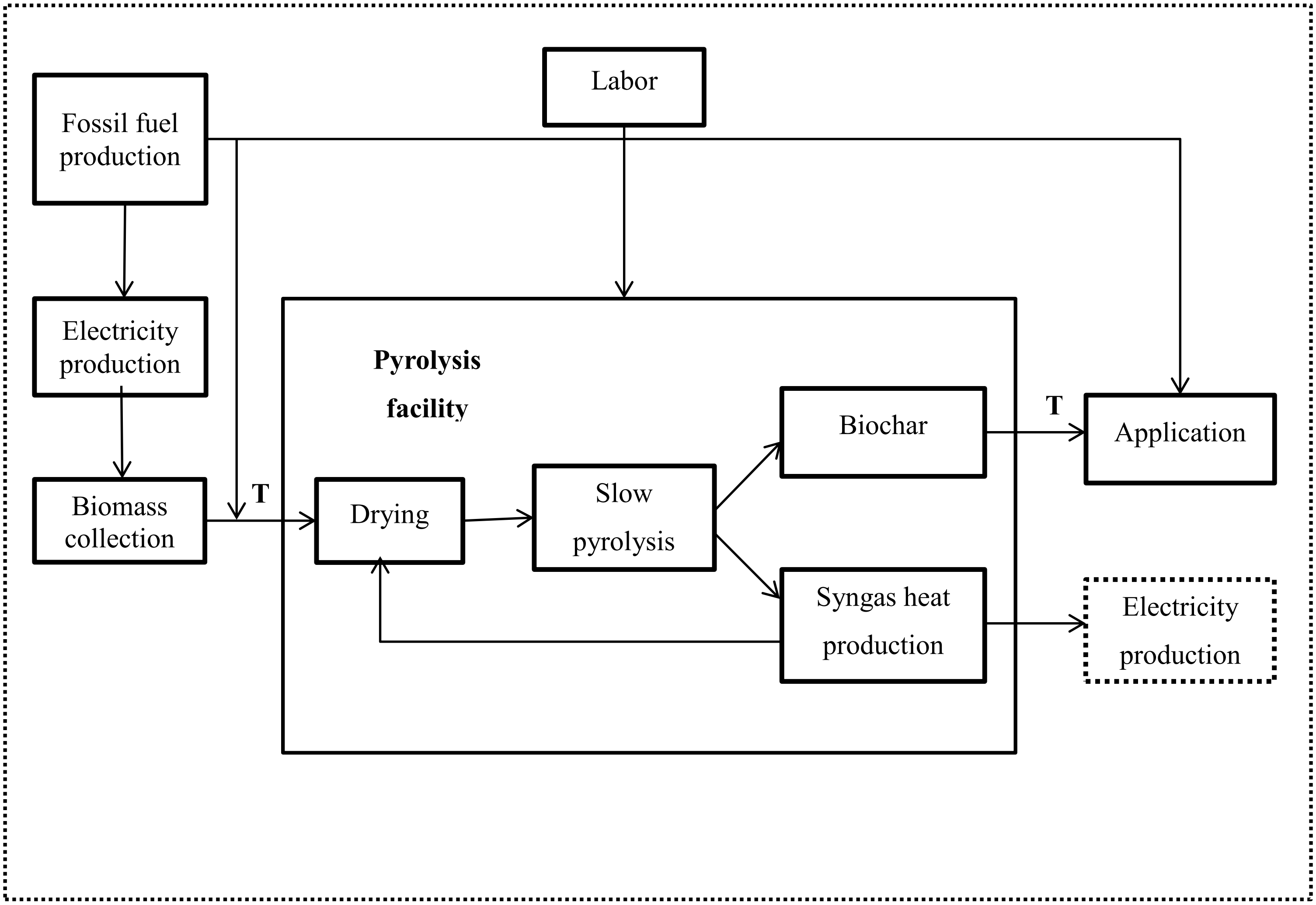

Fig. 4-1. System boundaries for the CBA in this study. Adapted from Roberts et al. (2010).

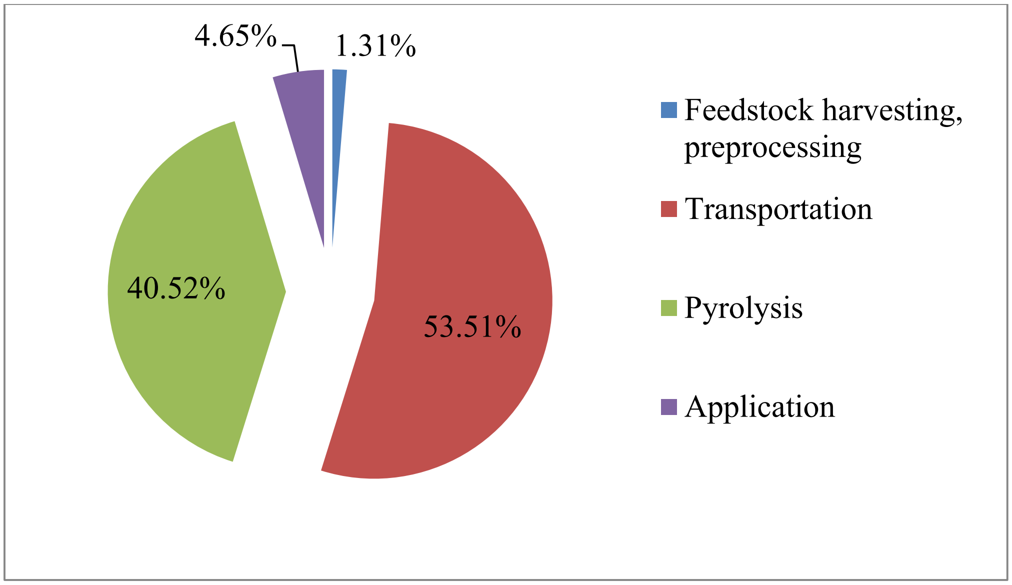

Fig.4-2. Cost composition of the biochar system.

Chapter 5. Summary, Conclusions and Future Studies

1. Summary

The goal of this thesis research was to explore biochar's potential in managing eutrophication and metal contamination in aquatic environments. This thesis examined biochar's capability in removing phosphate from an aqueous solution, as well as removing metal copper from the oil sands process-affected water (OSPW). Biochar could be engineered through pyrolysis choices to attain particular surface characteristics that are favorable for adsorption (Novak et al., 2008). Under this concept, the effects from pyrolysis condition including temperature and steam activation were studied in order to select appropriate pyrolysis condition for the adsorption of phosphorus and copper on biochar.

The specific objectives were to:

1. Study the effects of temperature and steam activation on the pine sawdust biochar's properties;
2. Study the pine sawdust biochar's adsorption capacity and mechanism for phosphorus in aqueous solution as a function of pyrolysis condition;
3. Study the pine sawdust biochar's adsorption capacity and mechanism for removing copper from synthetic OSPW.

In addition, a chapter complementary to the above research was constructed to demonstrate the economics of a biochar production-application system. This was done by a hypothetical case study where we calculated costs and benefits of producing biochar at the closest pyrolysis plant and applying biochar into OSPW.

The first chapter introduced the basic concept and functions of biochar, its production technologies, and providing a general picture of its status both in biochar research and industry. After addressing the knowledge gaps, the study objectives and thesis structure were introduced. Chapter 2 and 3 are the data chapters of this thesis. These two chapters examined the adsorption effectiveness and scientific reasons behind the adsorption. The approach used for studying the sorption phenomenon was by batch sorption experiments including isotherm and kinetic studies. Explicit characterization work has also been done to study the pyrolysis effects (temperature and steam activation) on the surface characteristics of biochar. Techniques on microscopic scale including scanning electron microscope (SEM) image, Fourier transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) nitrogen adsorption technique were employed to analyze surface morphologies, functional groups and specific surface area, respectively.

The results obtained from Chapter 2 showed that the pine sawdust biochar studied had little affinity for phosphate regardless of the pyrolysis temperature used and whether steam activation was applied. This was caused by the negatively charged surface on the biochar that repulses anions. In contrast in Chapter 3, we found that the biochar had a strong capacity for adsorbing cations and was able to remove 99% of copper in the synthetic OSPW. Specifically, the biochar produced at the higher temperature had a greater adsorption (thirty-fold greater) capacity for copper, and steam activation did not affect copper adsorption by the biochar. The adsorption of copper is mostly chemical reaction involved based on the sorption kinetics. Contrary to the conventional theory which says that the sorption of metals on biochar was mainly caused by complexation with functional groups, our results showed that the biochar with lesser functional groups but higher aromaticity and mineral content contributed most to the sorption. It further proved that biochar's sorption ability and mechanism differ among feedstocks, pyrolysis condition and application media, and this has to be well understood before application in any case. Biochar's functions are not universally applicable in all environments.

Following the data chapters, to solve the debate surrounding biochar economics and carbon emission, Chapter 5 conducted a cost-benefit analysis for producing biochar and applying it in the remediation of OSPW contaminated with cupper. The cost was reasonable and close to some of the existing operations, and it is not "sky high" as it is often suspected. The greatest cost and largest portion of greenhouse gas emission was all from the transportation sector. The benefit mostly originated from the carbon sequestrated and was subject to the uncertainties of the carbon market. The net present value was between US$-182 to US$-111 per ton of biochar, varying with the payment for carbon sequestration. We also developed a website (www.biocharoundyou.com) that allows people to search for biochar business in a set of radiuses to help with the study, as well as to provide valuable information to future studies.

2. Research limitations

There were several major limitations and technical constraints throughout the whole study. The experiments were lab based and did not include any field test. For the materials being used in this study, 1) the pine sawdust material was not sourced locally, and species were unknown. The results achieved by the pine sawdust biochar in this study may not support biochar produced from local pine species. 2) The lack of real OSPW samples because oil sands companies were unwilling to provide samples. The OSPW is a very complex system composed of many contaminants and its properties also vary among tailings ponds. It is very hard to simulate the OSPW, and there are very limited publications available at present. Whether the research results are applicable in real OSPW samples needs to be tested. However, the focus of the study was to investigate the physical and chemical processes involved in the biochar-solution interface, and to understand the fundamental sorption mechanisms. The existence of these limitations does not affect the research conclusions under this scope. In Chapter 4, cost data for the economic analysis of the biochar system was based on existing literature instead of from real operation.

3. Conclusions

Biochar surface properties that control sorption with contaminants in aqueous solutions are greatly affected by its pyrolysis temperature. Steam activation can increase biochar surface area significantly but does not affect chemical properties of biochar, and therefore no effects on the sorption of phosphate or copper were seen. We concluded that in biochar manufacturing, steam activation is not a necessarily step to be incorporated when considering to use biochar for sorption purposes. In aqueous solutions, biochar may not be an ideal sorbent for anions such as phosphate due to its negatively charged surface while it is a promising material for adsorbing cations such as copper. The cost of biochar production and environmental management mostly depends on pyrolysis operation and transportation cost. The uncertainties of the carbon price make the benefits highly uncertain as well. At the current stage of biochar development, it is difficult to claim that biochar is a low-cost material in North America, and implement biochar technologies without any incentives such as payment for carbon sequestration is not realistic as well.

4. Suggestions for future research

Future research could expand to field scales by practicing in OSPW and trophic water. Desorption experiments could also be conducted to study the stability of the biochar in environments and further understand the sorption mechanisms. In general, biochar are being studied at lab scales by a large number of scientists across a wide range of disciplines, fundamentals of pyrolysis techniques and biochar properties are much better understood than it was ever before, however, experimentations at large scales are in need to give valuable implications in environmental management (Lehmann and Joseph, 2015). Overall, some major gaps need to be addressed in biochar research are listed below:

- Biochar experimentation at lager scales;
- Biochar application methods in aquatic environments;
- Engineered biochar for solving complex contamination issues;
- Develop databases that predict/report biochar properties and possible functions based on selections of feedstock and production methods;
- Optimize production methods for both carbon sequestration and bio-energy source for win-win situation in environment and economy;
- Life cycle assessment and comprehensive economic studies of biochar system based on real plant experiences (Mohan et al., 2014; Shackley et al., 2015).

Biochar is a promising technology in many aspects, however, we also have to recognize that the benefits of biochar in soil and water are not equivalent in environments, and there is an absence of empirical evidence to support the benefits. Because of a lack of a dominant technological design in biochar production and application (Shackley et al., 2011), it is difficult to evaluating the costs as well. To form biochar's industrialization chain that leads to zero waste and a low carbon system, future study should be grounded on local development and practical experiences to achieve waste material utilization, carbon sequestration and bioenergy production.

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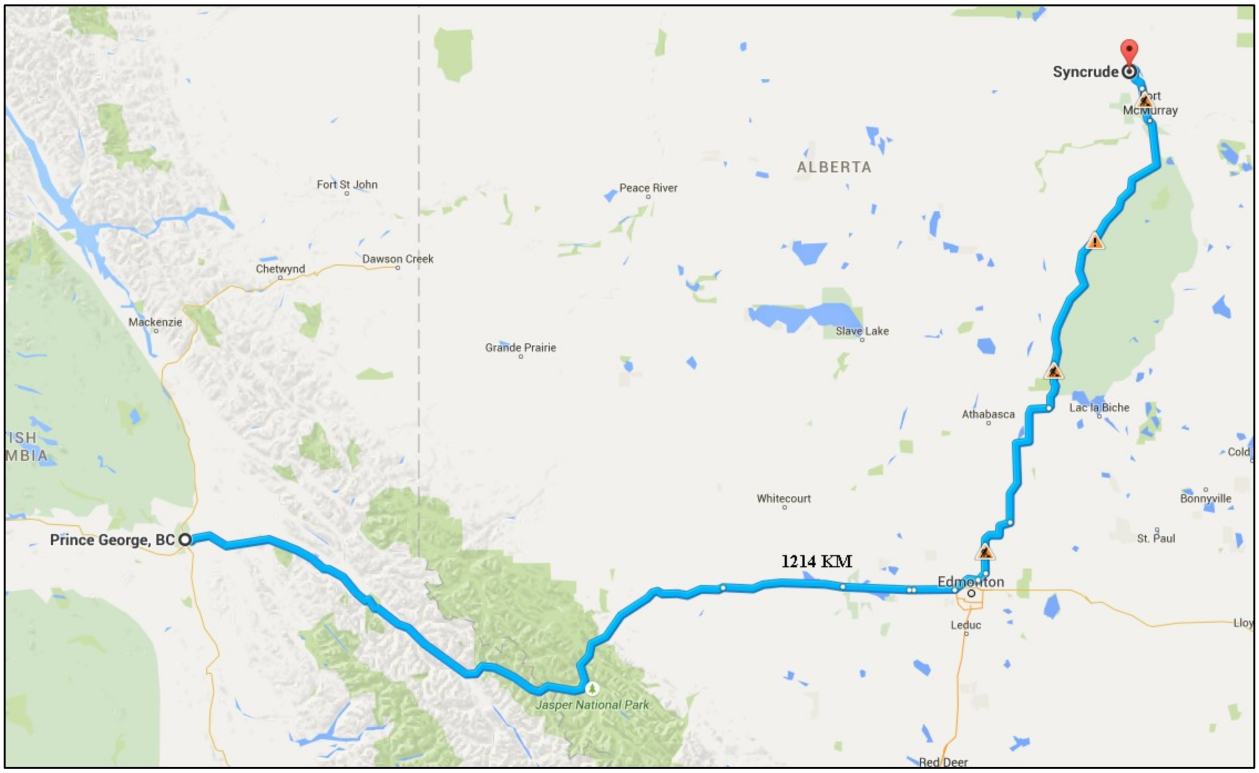
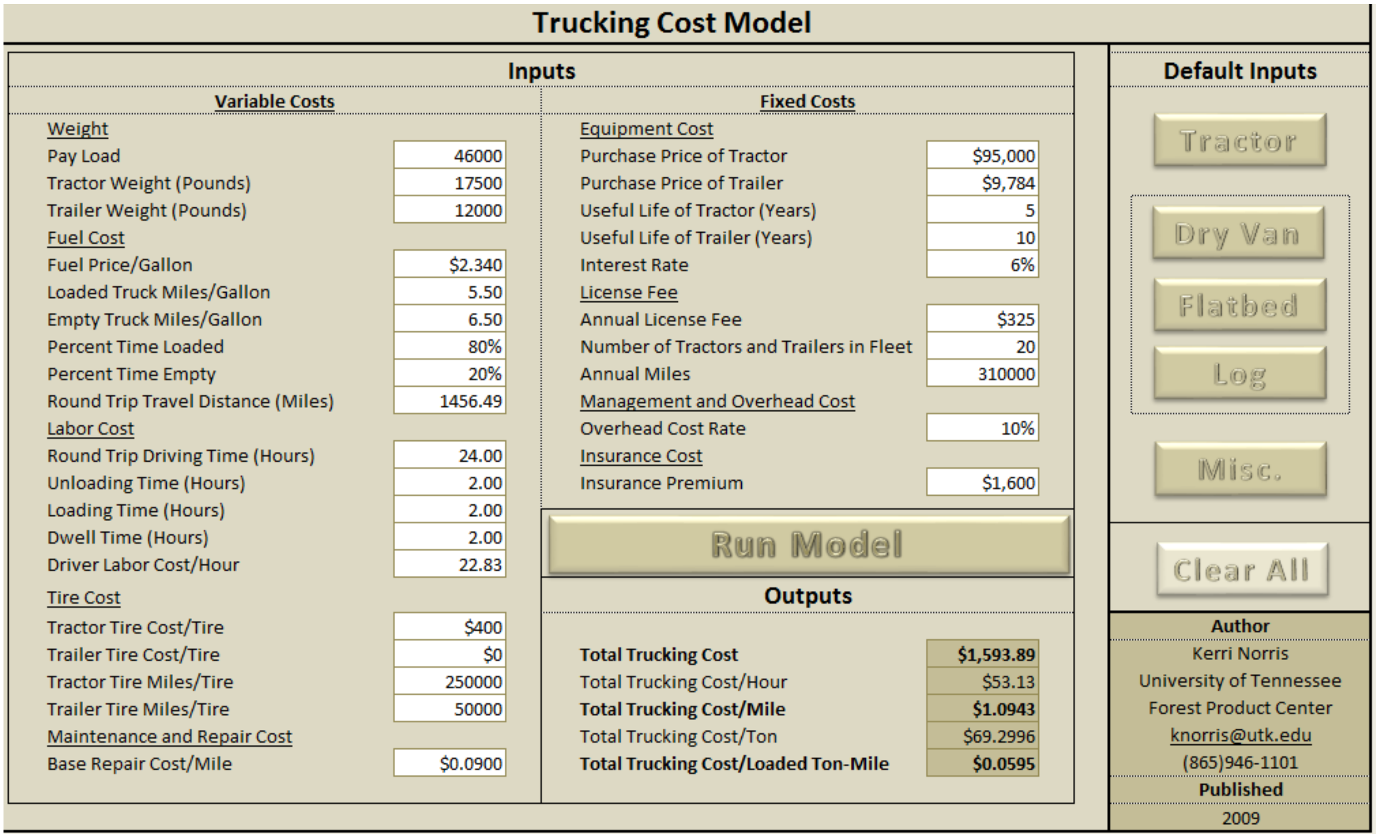
Appendix

Site map



MLSB site map

Trucking cost model



Trucking Cost Model

Inputs

Variable Costs

Weight	
Pay Load	46000
Tractor Weight (Pounds)	17500
Trailer Weight (Pounds)	12000
Fuel Cost	
Fuel Price/Gallon	$2.340
Loaded Truck Miles/Gallon	5.50
Empty Truck Miles/Gallon	6.50
Percent Time Loaded	80%
Percent Time Empty	20%
Round Trip Travel Distance (Miles)	1456.49
Labor Cost	
Round Trip Driving Time (Hours)	24.00
Unloading Time (Hours)	2.00
Loading Time (Hours)	2.00
Dwell Time (Hours)	2.00
Driver Labor Cost/Hour	22.83
Tire Cost	
Tractor Tire Cost/Tire	$400
Trailer Tire Cost/Tire	$0
Tractor Tire Miles/Tire	250000
Trailer Tire Miles/Tire	50000
Maintenance and Repair Cost	
Base Repair Cost/Mile	$0.0900

Fixed Costs

Equipment Cost	
Purchase Price of Tractor	$95,000
Purchase Price of Trailer	$9,784
Useful Life of Tractor (Years)	5
Useful Life of Trailer (Years)	10
Interest Rate	6%
License Fee	
Annual License Fee	$325
Number of Tractors and Trailers in Fleet	20
Annual Miles	310000
Management and Overhead Cost	
Overhead Cost Rate	10%
Insurance Cost	
Insurance Premium	$1,600

Outputs

Total Trucking Cost	**$1,593.89**
Total Trucking Cost/Hour	$53.13
Total Trucking Cost/Mile	**$1.0943**
Total Trucking Cost/Ton	$69.2996
Total Trucking Cost/Loaded Ton-Mile	**$0.0595**

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Model from Norris (2009); wages and salaries based on Government of Alberta (2015).

Calculation

Calculation 1. Biochar and biomass amount required for application

Mildred Lake Settling Basin	
OSPW	$2.5 * 10^6$ m^3
Biochar application rate	1 g L^{-1}
Biochar production yield	35%

Total biochar required with 5% loss during transportation and application:

$2.5 * 10^6 * 1$ kg m^{-3}/ 1000 t/(1-5%) = 2631.58 t

Total biomass required to produce biochar with 5% loss:

2631.58 t/35% /(1-5%) = 7914 t

Calculation 2. Energy required for biomass drying

Initial water content	24.5%
Final water content	5%
Energy required for evaporation (MJ kg^{-1})	3.48

For 1 ton biomass to dry, energy required is:

1*1000 kg *(24.5% - 5%)* 3.48 MJ kg^{-1} = 678.6 MJ,

With 10% heat loss:

678.9 MJ/90% = 754.33 MJ

Calculation 3. Stabilized carbon content in total

Biochar yield	35%
Fixed carbon content in the biochar	62.2%
Stable carbon content	80%

For 1 ton biomass to be pyrolysed as biochar, the amount of carbon stabilized is:

1 t * 35%* 62.2% * 80% = 0.17416 t

For 7914 t biomass,

0.17416 * 7914 t = 1378.3 t

Calculation 4. Energy produced and potential of electricity generation

	yield	Heating value (MJ kg-1)
Biochar	35%	11.4
Syngas	63.85%	15
Bio-oil	<1 %	17.3

For 1 ton biomass processed, the energy generated from syngas is:

1 * 1000 kg * 63.58% * 15 = 953,700 MJ

Energy produced from syngas (MJ)	953,700
Energy used for drying (MJ)	754.33
Efficiency of conversion	35%
Average electricity price in Canada per kWh	US$0.1

Electricity generated from syngas produced from 1 ton biomass:

1 MJ = 0.00028 MWh,

(953700 – 754.33)MJ * 35% * 0.00028 = 93.39 MWh

If all the heat can be converted to electricity and supplied to substations, revenue generated from electricity from per ton biomass pyrolysed would be:

93.39 * 1000 kWh * US$0.1 = US$9339

Calculation 5. Trips for transportation

Truck payload	23 t
Loading amount	80%
Total biomass	7914 t
Total biochar amount	2631.58 t

Trips for biomass

7914 t/ 23 t* 80% = 381.2 round trips, cost covered by the mill.

Trips for biochar

2631.58/23 t* 80% = 143 round trips

Calculation 6. GHG emission

Functional unit	100 km
Consuming energy	Conventional Diesel
[1]Emission	
CO	37.005 g
CO2	22.918 kg
CH4	35.192 g
N2O	785.094 mg
NOx	18.707 g
Black carbon	72.961 mg
GHG emission	24.313 kg
[2]CO2eq	26 kg

[1] Emission data from GREET model

[2] USEPA, Greenhouse Gas Equivalencies Calculator

GHG emission for

biomass transportation

3 km transporting distance from sawmill to pyrolysis plant, all travelling distance:

381 trips* 2* 3 km = 2286 km

CO_2eq emission: 26*2286/100= 594.36 kg

biochar transportation

Distance between pyrolysis plant and MLSB: 1214 km

1214 km * 143*2 = 347204 km

CO_2eq emission: 26* 347204/100=90273.04 kg

Total CO_2eq emission during transportation: 594.36 + 90273.04=90867.4 kg = 90.86 t

Total CO_2eq emission (5%): 5 t

Calculation 7. CO_2 stored and NVP

CO_2 Sequestrated

CO_2 sequestrated in biochar (Calculation 3): 1378.3 t carbon = 3216.03 t CO_2, subtracting the emission from other sectors, resulting in 3120.17 t of CO_2 being sequestrated.

The NPV:

The net present cost	[1]US$ 542955.18
The net present benefit	carbon price at the present market times the amount of CO_2 sequestrated

[1]The cost is the net present value calculated based on a 20-year project with the discount rate of 8%

When CO_2 is \$20 t^{-1}, the NPV= -542955.18+ 3120.17*20 = US$480551.8, which equals to US$-182.61 t^{-1} biochar.

When CO_2 is \$80 t^{-1}, the NPV= -542955.18+ 3120.17*80 = US$293341.6, which equals to US$-111.5 t^{-1} biochar.