

Removal of organic acids from water using biochar and petroleum coke

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Abstract

Alberta produces large volumes of oil sands process-affected water (OSPW) as a result of bitumen extraction and upgrading processes. Naphthenic acids (NAs) and other organic acids (OAs) comprise the main constituents of OSPW that can be acutely toxic to aquatic life. The recycling, safe return or storage of OSPW into the environment is a major challenge for the oil sands industry. Therefore, proper treatment technologies that are effective but inexpensive are needed. In this study, we tested the ability of a biochar (BC) produced from wheat straw and petroleum coke (PC) to remove two model organic acids (OAs) from aqueous solution: lauric acid (LA) and 1-methylcyclohexenecarboxylic acid (MCA). The results showed that BC was generally a more effective sorbent than PC, likely because BC has higher surface area and higher functional group densities than PC. More LA than MCA sorbed to both BC and PC due to the saturated 12-carbon chain of LA which renders it more hydrophobic than MCA. An admixture of BC and PC removed more LA from solution than was expected from its component parts, which may indicate a synergy between BC and PC in removing certain OAs from solution. This study shows that BC and PC might be useful materials for on-site treatment of organic acids. However, the use of PC may also be problematic due to release of significant heavy metals and sulfur to aqueous solution.

1. Introduction

The Alberta oil sands are composed of a mixture of water, sand and bitumen, with the latter being recovered by surface mining and by in-situ steam injection (Kelly et al., 2009). Bitumen extraction from surface-mined oil sands in Alberta, Canada is commonly achieved using the Clark hot water process (79-93°C) that uses caustic soda to separate bitumen from other constituents such as clay, sand, dissolved metals and organic compounds including naphthenic acids (NAs), polycyclic aromatic hydrocarbons (PAHs), and other organic acids (OAs) (Giesy et al., 2010; Kelly et al., 2009, 2010). As a consequence, oil sands process-affected water (OSPW), generated on site during upgrading processes, produces tailings materials that contain high concentrations of OAs and PAHs (Ahad et al., 2013). Due to a zero-discharge policy by the province of Alberta, OSPW is stored in on-site tailing ponds, which cover an area of more than 130 km² (Giesy et al., 2010; Kelly et al., 2009). The Clark hot water process is water-intensive; one cubic meter of oil sands processing creates four cubic meters of OSPW and two to four barrels of water are required to extract one barrel of oil (Giesy et al., 2010). It is estimated that over a billion cubic meters of tailings water will be held in containment systems in the Athabasca region by 2025 as a result of the zero discharge policy.

NAs and other organics in OSPW are also persistent pollutants, and have been found in groundwater and surface waters taken near to oil sands tailings ponds (Frank et al., 2014; Kelly et al., 2010; Kelly et al., 2009). Importantly, NAs and OAs in OSPW can accumulate in fish and other aquatic life forms, and pose risks to aquatic ecosystems and shallow freshwater aquifers (Ahad et al., 2013; Frank et al., 2008; Leung et al., 2001, 2003; Peters et al., 2007; Quagraine et al., 2005; Rogers et al., 2002). The proper handling of these large volumes of OSPW is a major challenge for the oil sands industry. To remove OAs from OSPW, several methods have been

studied, including biodegradation, catalytic decarboxylation (using Ag_2O), membrane separation, and ozonation (Azad et al., 2013; Gamal El-Din et al., 2011; Iranmanesh et al., 2014; Quinlan and Tam, 2015; Scarlett et al., 2012, Zhang et al., 2006). These methods are effective in removal of OAs from wastewater, but are considered to be expensive, so their use is generally limited (Iranmanesh et al., 2014; Scott et al., 2008). Adsorption by activated carbon (AC) and nickel based alumina also showed promising results in removal of OAs from water, but are still expensive to implement (Azad et al., 2013; Gamal El-Din et al., 2011; Iranmanesh et al., 2014; Zubot et al., 2012). Two additional treatments materials that have received considerable recent attention are biochar (BC) and petroleum coke (PC). These materials are or can be produced near oil sand operations at low cost (Franknel et al., 2016; Gamal El-Din et al., 2011; Mohan et al., 2014; Ok et al., 2015; Pourrezaei et al., 2014). BCs are composed of a heterogeneous mix of carbonaceous materials with a range of surface functional groups that are activated by the thermal alteration of organic materials. BC surface functional groups are documented to be effective in the removal of organics (*e.g.*, trichloroethylene and sulfamethazine) and heavy metals contaminants from water (Ahmad et al., 2013, 2014; Rajapaksha et al., 2014; Uchimiya et al., 2012). The biochar pyrolysis temperature plays an important role in the stability, distribution and concentrations of surface functional groups, and thus the ability of the biochar to uptake pollutants from aqueous solution (Uchimiya et al., 2012; Vithanage et al., 2015). PC is a byproduct of the processing of oil sands, is abundantly available at mining sites, and may prove a good sorbent for OAs depending on its activation and the solution conditions (*e.g.*, pH, water chemistry) (Gamal El-Din et al., 2011; Zubot et al., 2012). Due to its high sulfur content, PC is not generally considered useful for energy for heat generation, but may be used as an abundant and free-of-charge sorbent to treat OSPW (Zubot et al., 2012). A few previous studies have used

PC as a pretreatment material before ozonation and have shown that PC can substantially remove acid extractable organics with carbon number (n) from 12 to 16, and in some cases for compounds with $n > 18$ and relatively high molecular weight (i.e., 200 amu or more). However there remains a gap in understanding the sorptive behavior of PC to lower molecular weight organics ($n < 12$) and molecular weight < 200 amu. (Gamal El-Din et al., 2011; Mohammed et al., 2015). The smaller molecular weight OAs in OSPW generally exhibit greater toxicity to aquatic species than that larger molecular weight OAs, and have been overlooked in previous studies (Bauer, 2013).

In this study, we used the low molecular weight and low carbon number OAs methylcyclohexenecarboxylic acid (MCA) (142.1 amu; $n = 8$) lauric acid (LA) (200 amu; $n = 12$), and determined the effectiveness of BC, PC, and a combination of BC and PC to remove these aromatic (MCA) and aliphatic (LA) organic acids from aqueous solution. Overall, the objectives of this study were: (1) to assess the effectiveness and determine the feasibility of using BC and PC to remove OAs from water and (2) evaluate the use of admixtures of BC and PC for the removal of smaller molecular weight OAs.

2. MATERIALS AND METHODS

2.1 Chemicals and Reagents

Distilled, deionized water (DDW) with $18.2 \text{ M}\Omega \cdot \text{cm}$ resistivity at 25°C was used for preparing stock solutions and for all experiments. Hydrochloric acid (HCl), sodium bicarbonate (NaHCO_3), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), calcium chloride (CaCl_2), barium chloride (BaCl_2) and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) were all of analytical grade and purchased from Fisher Scientific. Two organic acids: lauric (or dodecanoic)

acid and 1-methylcyclohexenecarboxylic acid were purchased from Sigma Aldrich (Milwaukee, USA).

2.2 Biochar and Petroleum Coke Production

BC produced from wheat straw was obtained from the Alberta Biochar Initiative (ABI). To produce the biochar, raw feedstocks were placed in a batch carbonizer and heated from 20°C to 500°C in 60 min under limited oxygen conditions. Following, the temperature was held between 500°C to 550°C for 30 min. The biochar yield was 30 to 33% on the basis of dry mass. Biomass characterization data for BC (e.g. volatiles content, fixed carbon, aeration porosity, water holding capacity, total porosity, bulk porosity and EC) were obtained from ABI and are presented in Supplementary Information Table 1.

The PC was collected from an oil sand processing plant in the Athabasca Oil sands. The processing plant produces fluid coke as a by-product which is composed of fine particles, and a temperature of approximately 350°C used during the upgrading process. Both the BC and PC were ground using mortar and pestle, and then sieved using a No. 16 (1.18 mm) mesh screen. The fractions that passed through the sieve were used for OA sorption experiments.

2.3 Characterization of Biochar and Petroleum Coke

2.3.1 pH and point of zero charge

To measure the pH of BC and PC, 0.5 g of BC or PC were added to 50 ml of deionized water (1% w/v) and shaken for 24 h at 200 rpm prior to the pH measurement (Novak et al., 2009). The point of zero charge (pzc) of BC and PC was measured using a series of 15 ml solutions of 0.01 M NaNO₃ which were adjusted to pH values from 2 to 11 in polypropylene tubes using small aliquots of concentrated NaOH and HCl. Solutions were boiled to remove dissolved CO₂ before

the addition of HCl and NaOH. BC and PC were mixed into these solutions at a 1:50 solid:solution ratio, such that the tubes were filled to remove any head space. Test tubes were placed on a rotary shaker and allowed to equilibrate for 24 h at 100 rpm. Following, the final pH was measured and plotted against initial pH, and point of zero charge (pzc) determined as the pH at which the initial and final pH curves intersected (Dastgheib et al., 2004; Yang et al., 2004). Measurements for each material were run in duplicate.

2.3.2 Proximate analysis

The moisture contents of BC and PC were estimated using a drying oven (ThermoScientific HERATHERM) held at 105°C for 24 h. Moisture content was calculated considering the weight loss after heating the BC and PC to a constant weight (Ahmad et al., 2012; Ahmad et al., 2013). Mobile (volatile) matter, which is considered to be the uncarbonized portion of BC and PC after heating at 450°C for 30 min, was determined using a Thermolyne 62700 furnace. Ash content of BC and PC was estimated as the weight loss of BC and PC after heating at 700°C for 30 min in the same furnace. The residual matter was calculated as the remnant portion of the biomass after deducting the total weight loss of moisture, ash and mobile matter. All of the measurements were run in duplicate.

2.3.3 Surface area and elemental composition

The specific surface area, pore volume and pore size distribution of BC and PC were measured in duplicate using an Autosorb Quantachrome 1MP, according to the Brunauer - Emmett - Teller (BET) and the Barret - Joyner - Halender (BJH) methods (Leofanti et al., 1998). Samples were degassed at 423 K for 8 h. The specific areas were determined from N₂ adsorption isotherms, and pore size distribution was determined from the N₂ desorption isotherms (see Alessi et al., 2014).

The elemental compositions of BC and PC, including C, N, H, S, and O, were determined using a Carlo Erba EA1108 Elemental Analyzer by combusting the solid materials at 1000°C.

2.3.4 Morphological and spectral analyses

The surface physical morphologies of BC and PC were characterized using a Zeiss EVO MA 15 LaB₆ filament scanning electron microscope (SEM), at magnifications ranging from 61× to 875× with a resolution of approximately 5 nm, to obtain high resolution images of BC and PC. To identify their physical morphology, samples were carbon coated with a Leica EMSCDE005. Backscattered images were collected using a Si diode detector. Secondary electron images were obtained using an Everhart-Thornley detector. Energy dispersive X-ray spectroscopy (EDS) data were acquired to obtain semi-quantitative elemental compositions at selected locations. EDS data were collected using a Peltier-cooled 10 mm² Bruker Quantax 200 Silicon drift detector with 123 eV resolution.

Fourier transform infrared spectroscopy (FT-IR) measurements were carried out to measure changes in the infrared vibrational bands of BC and PC before and after LA and MCA were sorbed to each material using Thermo Nicolet 8700 FTIR. To conduct the sorption experiments, solutions containing either LA or MCA at 12.5 g L⁻¹, and either BC or PC at 10 g L⁻¹, were prepared at pH 8.65 and allowed to equilibrate. For FTIR analyses, solids from the sorption experiments were diluted with KBr at a 3% sample to 97% KBr ratio. Spectra were collected at a resolution of 4 cm⁻¹ with 32 successive scans, and were collected in a wavenumber range of 400-4000 cm⁻¹. Baseline corrections and normalization were done using a modified script to that described by Felten et al. (2015). Spectra were area normalized between 1650 –

1525 cm^{-1} since that peak changes the least during pyrolysis, making the biochars more comparable (Shu-Lai Mok et al., 1992).

2.3.5 Metal leaching from BC and PC

To investigate the metal leaching potentials of BC and PC, these materials were placed in polypropylene tubes containing 15 mL solutions of 0.01 M NaNO_3 at 0.1, 1, 10 and 20 g solids L^{-1} . Solution pH was set to 8.65, a value that is within the range of OSPW pH (Gamal El-Din et al., 2011) and the test tubes were sealed and shaken at 200 rpm for 24 h. The resulting supernatants were filtered through 0.45 μm membranes (Millex HP) and analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) (iCap 6000; Fisher Scientific).

2.4 Boehm Titrations

To determine the concentrations of acidic functional groups in BC and PC, the modified Boehm titration method was used (Fidel et al., 2013). Boehm titrations determine the acidic functional group concentrations of sorbents between three pK_a ranges: 5 to 6.4, 6.4 to 10.3, and 10.3 to 13. Briefly, BC and PC were mixed with 0.05 M HCl at a 50:1 solution volume to biochar mass ratio, and were shaken at 200 rpm for 24 h. BC and PC were then washed twice with 1 M CaCl_2 , and finally washed four times with deionized water at 50:1 solution volume to BC or PC mass ratio. The samples were then dried for 60 h at 50°C. 0.5 g of pre-treated material were added to 25 ml of the three bases used in the Boehm method (0.05 M solutions of NaHCO_3 , Na_2CO_3 and NaOH) and shaken at 200 rpm for 24 h. Aliquots were then passed through 0.45 μm nitrocellulose membranes using a Büchner funnel apparatus (Fidel et al., 2013; Goertzen et al., 2010). To remove DOC and carbonate ions, the separated aliquots were mixed thoroughly with

an equivalent volume of 1 M BaCl₂ solution. Finally, 0.05 M and 0.01 M NaOH were added to the extracts of NaHCO₃ and Na₂CO₃, respectively, to make the NaOH:BaCl₂:extract ratio 1:1:1. These mixtures were immediately shaken at 200 rpm for 1 h, then centrifuged at 8,000 g for 30 min, and the resulting supernatants were filtered through 0.02 µm nylon Anotop membranes (Sigma Aldrich, Milwaukee, WI). The resulting aliquots were acidified to pH < 2 using 12.1 M HCl and then titrated with standardized 0.01M NaOH using a Titroline 6000 titrator (SI Analytics, Mainz, Germany). All treatments above were also performed on solutions of 0.01 M NaNO₃ as a blank, and the resulting blank values were subtracted from experimental values (Fidel et al., 2013; Goertzen et al., 2010). Experiments were run in triplicate.

2.5 Adsorption Experiments

Adsorption experiments were carried out to determine the adsorptive capacity of BC and PC for two OAs as a function of OA and sorbent concentrations at a fixed pH (8.65) representative of oil sand tailings ponds. Lauric acid (LA) and 1-methylcyclohexenecarboxylic acid (MCA) adsorption experiments were conducted in 10 mL borosilicate test tubes at LA or MCA concentrations ranging between 0 and 12.5 mg l⁻¹, and with solids concentrations of 0.1 g l⁻¹, 1 g l⁻¹, 10 g l⁻¹ and 20 g l⁻¹. Systems with BC, PC, and 1:1 mixtures by mass of BC and PC were studied. The pH of the experiments was held constant by adding 0.1 M HEPES buffer set to the target pH. Experimental test tubes were placed on a rotary shaker at 60 rpm for 24 h, and afterward centrifuged for 30 min at 8,000 g to remove the solids from solution. The resulting supernatants were filtered through 0.45 µm membranes (Millex HP) prior to analysis.

OAs analyses were performed using a 3200 QTRAP tandem mass spectrometer in negative mode with multiple reactions monitoring (MRM). An Agilent 1260 auto-sampler injected 20 µL of sample and an Agilent 1200 binary pump delivered 700 µL min⁻¹ of mobile

phase (50% water and 50% methanol) to the mass spectrometer. Samples were introduced directly to the mass spectrometer via electrospray ionization (ESI); no separation was performed. Typical mass spectrometer conditions were as follows: source temperature 500°C, curtain gas 15 psi, nebulizer gas (GS1) 40 psi, auxiliary gas (GS2) 40 psi, interface heater (ihe) ON, collision-activated dissociation (CAD) gas high, ion spray voltage (IS) -4500 V, declustering potential (DP) -50 V, entrance potential (EP) -10 V, collision energy (CE) -10 V, collision cell exit potential (CXP) -3 V. The system was controlled by Analyst 1.5.1 software (ABSciex) (Wang et al. 2013).

Standard curves were prepared using a range of OA concentrations, from 0.025 mg l⁻¹ to 25 mg l⁻¹. The entire range of standards could not be fitted adequately with a linear or quadratic function, so the calibration curve was separated into three portions (<1.25 ppm, 1-10 ppm and 10-25 ppm) with three concentration points in each. Samples were quantitated against the appropriate curve as determined by their peak areas. Samples were injected in duplicate; standard injections were made in triplicate.

2.6 Adsorption Model

A mass-normalized distribution coefficient (K_d) isotherm approach was used to model the extent of adsorption of OAs onto BC and PC. The equilibrium sorption capacity was estimated according to the method of Ahmad et al. (2013), using the following equation:

$$Q_e = [C_0 - C_e]VM^{-1} \quad (1)$$

where,

Q_e = amount of OAs adsorbed on adsorbent (i.e., BC and PC) at equilibrium (mg/g),

C_0 = initial concentration of OAs in solution (mg/L),

C_e = concentration of OAs in solution at equilibrium (mg/L),

V = volume of solution (L) used, and

M = mass of adsorbent (i.e., BC and PC) used (g).

In this way, the linear isotherm model is expressed as:

$$Q_e = K_d C_e \quad (2)$$

where K_d is the linear partitioning coefficient.

3. Results and Discussion

3.1 Characteristics of BC and PC

The pH, pzc, moisture content, mobile matter, ash content and fixed matter of BC and PC are presented in Table 1. The moisture contents of BC and PC are 2.7% and 0.06%, respectively, while the mobile matter of BC and PC are 33.0% and 17.4%, respectively. These properties can be explained in that the removal of volatile matter and the emission H_2O , CO_2 and CH_4 is higher in BC than that of PC (Ahmad et al., 2013; Rajapaksha et al., 2014). However, the ash content of BC (17.0%) is higher than in PC (5.3%), which is explained by the accumulation of alkaline minerals and organic matter in BC (Ahmad et al., 2013; Rajapaksha et al., 2014). The fixed matter represents the fully carbonized organic matter, which is higher in PC (77.2%) than in BC (47.3%).

Major elements (C, H, N, S, O) and molar ratios of H/C, O/C, (O+N)/C and (O+N+S)/C are given in Table 2. The elemental composition data are consistent with the SEM-EDS measurements (Supplementary Information Tables 1 and 2). As noted previously, elemental compositions determined using EDS are semi-quantitative. The elemental composition data

showed that both BC and PC are primarily composed of C; BC contains nearly 70% C, whereas PC contains nearly 80% C. The elemental H and O content in BC (2.6% and 8.65%, respectively) was higher than that of PC (1.83% and 3.08%, respectively), which is attributed to the higher water vapor content of PC (Ahmad et al., 2012; Ahmad et al., 2013; Rajapaksha et al., 2014). PC has a higher content of N and S; 1.74% and 7.1%, respectively, whereas, BC contains only a trace amount of S (0.07%). The high content of sulfur in PC matches with the previous analyses of Alberta oil sand PC (Puttaswamy and Liber, 2011; Puttaswamy and Liber, 2012). Leaching of the sulfur content from PC into water during its use as a sorbent is of concern.

The molar ratios of H/C and O/C are measures of aromaticity and maturation, respectively. BC has relatively low H/C and O/C molar ratios (Table 2) compared to the BCs used in several recent studies (*e.g.*, Ahmad et al., 2012, 2013; Rajapaksha et al., 2014), which may be attributed to different parent biomass and production pyrolysis conditions. PC also shows relatively low H/C and O/C molar ratios. Generally, biomass with lower H/C and O/C ratios is considered to be more stable, aromatic, and have decreased polarity (Spokas, 2010). Specifically, higher aromaticity corresponds to the removal of polar surface functional groups, and a higher degree of carbonization (Ahmad et al., 2012, 2013; Krull et al., 2009). Lower H/C and O/C ratios increase the hydrophobicity of the biomass, a phenomenon which is also observed in our BC and PC samples. Figure 3 shows that the absorbance bands for aromatic ring stretching (1627 and 1598 cm^{-1}) are more pronounced for BC than for PC. Additionally, there is less contribution in BC, of OH stretching in the 1627 cm^{-1} region than in PC. Latta et al. (2014) suggested that the properties of the sorbing dissolved organic acids in solution may be more important than those of the biochar itself, although there is some evidence that micro- and nano-porosity of biochar and

other natural organic matter may also play a substantial role in the uptake of dissolved organics (Han et al., 2014).

The sorption of dissolved organic molecules to BC and PC may correlate directly with O/C or H/C ratios, or other factors such as surface area, porosity, size of the sorbing organic molecule, and the temperature of pyrolysis. BC has approximately five times the BET surface area of PC. However, the BJH pore size distribution and pore volume show that BC has a smaller average pore size distribution and pore volume than PC. BC and PC have pore volumes of 18 to 22, and 38 to 42 cc/g (Table 2), respectively. This supports the hypothesis that, besides physical and chemical sorption, nano-porosity of the BC and PC may contribute significantly to the uptake of OAs from solution. SEM images of the surface layers of the BC particles show that they are eroded following washing, leaving behind flaky material and a roughened surface (Figures 1A and 1B). Furthermore, Si nodules were observed on many BC particles, consistent with its parent biomass, wheat straw, which has relatively high silica and nutrient content compared to average biomass (Atik and Ates, 2012; Wei et al., 2015). EDS showed that the nodules are comprised of more than 70% Si and O, and that the ratio of Si:O is close to 1:2, consistent with SiO₂(s) (Figure 1C and Supplementary Information Tables 2 and 3). These Si nodules contain proton-active silanol functional groups (>Si-O-H) that may play some role in the adsorption of metals or polar organics. Biochars also contain a high fixed carbon content and host high concentrations of carbon-based surface functional groups, which are likely to play a key role in metal and organic sequestration from solution (Uchimiya et al., 2012). Elemental concentrations determined by EDS show that BC is comprised primarily of C, O, and Si, with smaller but considerable concentrations (> 0.1%) of K, Ca, Mg, P, S, and Al (Supplementary Information Table 2).

SEM images of PC indicate that the material is comprised primarily of semi-spherical, smooth beads that range from approximately 100 to 200 μm in diameter, although larger agglomerates of these beads on the millimeter-scale are present (Figures 2A and 2B). Like BC, PC is mainly composed of C, Si, and O (Figure 2C) and EDS analyses indicate significant concentrations ($> 0.1\%$) of Si, Al, Fe, Ti, Ca, K, and Na are also present (Supplementary Information Table 3), in agreement with elemental analysis data. No significant differences in elemental composition were observed between EDS data collected on individual beads and cemented agglomerates of beads. While PC has high sulfur and relatively low Si concentrations in the solid, the composition of BC shows the opposite trend.

The FT-IR spectra of BC and PC before and after LA and MCA interaction are shown in Figure 3. Table 3 identifies the main types of IR bands present in BC and PC. The type and number of IR bands in both BC and PC are quite similar, however the PC has more aliphatic and silica content than BC ($1300\text{-}900\text{ cm}^{-1}$), and more conjugated C=O and/or OH bonds (1627 cm^{-1}). Both the LA and MCA interaction with BC cause a decrease in the aliphatic esters and alcohol groups in the 1186 cm^{-1} and 1116 cm^{-1} regions, likely due to partial dissolution of the biochar (Figure 3). Since there is no change in the peak at 1056 cm^{-1} it is assumed that the OA adsorption does not affect the silica content of the biochar. In PC, the LA and MCA interact with the aliphatic ethers and silanol groups at the surface by increasing the absorbance at those bands in the 1116 and $1060/1056\text{ cm}^{-1}$ region. LA also significantly increases the bands at 1627 cm^{-1} , which relates to the aromatic C=C ring and conjugated C=O group on the material. Unlike LA, MCA does not interact with PC in the 1598 and 1627 cm^{-1} region, and instead shows an increase in absorbance in peaks at 1176 , 1116 , and 1060 cm^{-1} , indicating that MCA interacts with phenols, aliphatic carboxyl groups, and silanol groups at the petroleum coke surface.

The Boehm titrations show that the total reactive sites per gram of materials is higher in BC (1.5 mmol/g) than PC (0.98 mmol/g) for three cumulative pKa ranges (i.e., pKa 5 to 6.4; pKa 6.4 to 1.3 and pKa 10.3 to 13). This indicates that BC has more carboxylic, phenolic and lactonic groups than PC, which is in line with the results of FT-IR analyses that show higher BC band intensities than PC. This result is perhaps not surprising, considering the higher surface area and molar O/C and H/C ratios of BC.

3.2 OAs sorption

The adsorption of two model OAs to BC, PC and a 1:1 mixture by mass of BC and PC were studied. LA is a fatty acid that has a 12-carbon saturated chain with a carboxylic acid head group (Figure 4A). MCA has similar -COOH functionality, but is connected to a toluene molecule (Figure 4B) (Wang and Kasperski, 2010). These two low molecular weight organic acids have differing functionalities, and are highly soluble compared to most OAs found in OSPW (Wang and Kasperski, 2010; Wang et al., 2013). We studied these two compounds to investigate differences in the adsorption of small straight-chain versus cyclic organics and low molecular OAs in OSPW. Adsorption data were modelled successfully using the linear distribution coefficient (K_D) approach, suggesting that the sorption capacity for both sorbents was not achieved. Because of the lower solubility of LA (*ca.* 55 mg L⁻¹ at 25°C), and the need to compare LA and MCA sorption at equivalent aqueous concentrations, it was not possible to conduct batch experiments at higher acid concentrations where the sorbents may reach the sorption maximum for each OA, and where nonlinear modeling approaches, such as the Freundlich and Langmuir isotherms, would be employed. The removal of the model OAs from solution by 0.1 g l⁻¹ and 1 g l⁻¹ solid concentrations (PC, BC, and PC + BC) was very low (within the error of detection by HPLC-MS), and so those data are not presented here.

Figures 5 and 6 show the results of LA and MCA sorption experiments (between 0 to 12.5 mg l⁻¹ LA or MCA), at 10 g l⁻¹ and 20 g l⁻¹ sorbent concentrations, respectively. The slope of the linear equation in each panel is equivalent to the value of K_D as calculated in Equations 1 and 2. Generally the adsorption of both LA and MCA is higher to both sorbents at 20 g l⁻¹ than at 10 g l⁻¹ sorbent, and BC is a better sorbent than PC for both OAs at both sorbent concentrations (Figures 5, 6). At 20 g l⁻¹ BC, nearly all LA was removed from solution (Figure 5A). High extents of LA removal from solution for the 20 g l⁻¹ and 10 g l⁻¹ experiments were also observed when a 1:1 admixture (by mass) of BC and PC was used (Figure 5E and 5F). This suggests that combining these two materials may be a promising solution to removing organic acids from solution. In terms of percentage of LA removal, at 20 g l⁻¹, the BC, PC, and BC+PC experiments removed approximately 98%, 65% and 96%, respectively, and at 10 g l⁻¹, 44%, 9%, and 68% of the LA in solution, respectively.

Our results show that BC and PC also removed MCA from the solution but to a lesser extent than LA. At equivalent 10 g l⁻¹ concentrations of sorbent, BC, PC, and BC+PC experiments removed only 18%, 2.5%, and 7% of MCA from solution, respectively (Figure 6A to 6F). Unlike LA, the mixture of BC+PC does not display increased MCA removal from solution (Figure 6E and 6F), but instead acts as a simple admixture. However, the sorption of MCA is much greater to BC (Figure 6A and 6B) than to PC (Figure 6C and 6D). Our model fits show that the K_D for LA sorption increases from 0.004 ml mg⁻¹ for PC to 0.217 ml mg⁻¹ for BC, and for MCA sorption, K_D increases from 0.001 ml mg⁻¹ for PC to 0.080 ml mg⁻¹ for BC. Generally lower OA solubility results in higher K_D values (Janfada et al., 2006), and the K_D values for LA versus MCA sorption are consistent with the higher solubility of LA. Furthermore, the sorption of aromatic compounds, such as MCA, may be limited by the size of the aromatic

molecule (single benzene ring here) compared to aliphatic hydrocarbons (Murzin et al., 1997). That the sorption of OAs is higher onto BC than PC may also be due to the higher surface area of BC. Since PC has higher aromaticity than BC, it is expected that the removal of OAs from solution should be lower for PC, yet the higher micropore volume of PC may play a role in the sorption of the model OAs by PC (Ahmad et al., 2012, 2013; Han et al., 2014; Rajapaksha et al., 2014). As pH was held constant for all experiments, it should not have impacted the sorptive behavior of BC and PC in the isotherm experiments.

The leaching data show that the use of PC may be restricted due to its release of metals including, Cr, V, Pb, and the non-metal, S. Although PC released significant concentrations of Cr, V and Pb (Table 4), these concentrations are well below the maximum concentration limits (MCL) in Canadian guidelines for drinking water quality (Health Canada, 1996). However leachates from PC have also been found to be acutely toxic to *Ceriodaphnia dubia*, a species of the small freshwater crustacean family *Daphniidae*, which are commonly-used model organisms for toxicity assessments. Daphnids comprise an important food source to fish and other aquatic life, and are among the first organisms to show a toxic response (Puttaswamy et al., 2010; Santore et al., 2001). The release of Ni and V from PC generally brings into question the suitability of PC as a sorbent to remove OAs and metals from OSPW. By contrast, BC does not leach heavy metals at concentrations of concern (Table 4), and thus, may be a more suitable sorbent.

4. Conclusions

In this study, we used BC and PC to remove OAs from aqueous solution. BC and PC were characterized to determine their morphologies, composition and functional group concentrations. We performed batch studies to assess the uptake of LA and MCA by BC, PC, and BC+PC. BC,

produced in Alberta near the Athabasca oil sand mine region, showed more promise as a sorbent for both model organic acids, although PC removes significant OAs from solution and is available on-site. The OAs tested here provide a basis to study the removal of a broader range of model organic acids pertinent to OSPW, to further characterize the impacts of OA molecule size and functionality.

Mixtures of BC and PC seem to be promising to remove organic acids from solution. The use of PC as a sorbent for organic acids in OSPW is of concern because it may release heavy metals of environmental concern into the processed waste stream. The mixture of PC and BC to remove OAs may be most effective because not only are OAs removed, but BC may adsorb metals released from PC (Ahmad et al., 2014). Combining the two sorbents as a new treatment method may have the potential to remove OAs from OSPW at a relatively low cost, a process that can reduce the impact of OSPW on surface and ground water, and ultimately aquatic ecosystems.

Although supported by our results, this conjecture would require more extensive experimental testing to validate across a wide range of operational conditions (*e.g.*, pH, water chemistry, BCs, and PC compositions). Generally, BC, or perhaps admixtures of BC and PC, would be most effective at removing the model organic compounds tested here from aqueous solution.

Acknowledgements

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Figure 1. Scanning electron microscopy (SEM) images of (A, B) BC, and (C) EDS spectra of image B.

Figure 2. Scanning electron microscopy (SEM) images of PC at (A) 500x magnification, and (B) 1540x magnification. (C) EDS spectrum of image B.

Figure 3. FT-IR spectra of BC and PC before (black dotted lines and black solid lines, respectively) and after interaction with LA (blue lines) and MCA (red lines).

Figure 4. Skeletal formula of (A) dodecanoic (or lauric) acid, and (B) 1-methylcyclohexanecarboxylic acid.

Figure 5. Adsorption data for lauric acid onto (A) BC at 20 g l⁻¹ (B) BC at 10 g l⁻¹; (C) PC at 20 g l⁻¹, (D) PC at 10 g l⁻¹ and (E, F) a 1:1 mixture by mass of BC and PC at 20 g l⁻¹ and 10 g l⁻¹, respectively.

Figure 6. Adsorption data for MCA onto (A) BC at 20 g l⁻¹; (B) BC at 10 g l⁻¹; (C) PC at 20 g l⁻¹, (D) PC at 10 g l⁻¹ and (E, F) a 1:1 mixture by mass of BC and PC at 20 g l⁻¹ and 10 g l⁻¹, respectively.

Table 1. pH, pzc and percentage moisture contents, mobile matter, ash content and fixed matter of BC and PC.

Table 2. Elemental composition, molar ratio, BET surface area, and pore volume and pore size distribution of BC and PC.

Table 3. Assignments of principal infrared vibrational bands (Ibarra et al., 1996; Srivastava et al., 2006).

Table 4. Metal leaching from BC and PC.

Figure 1

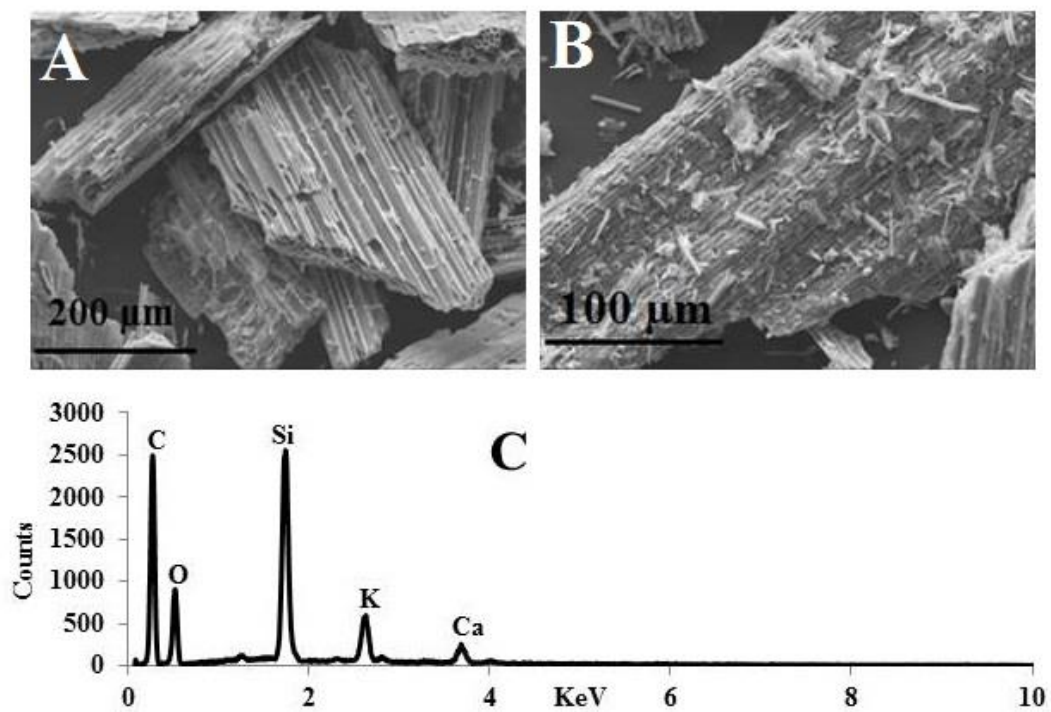


Figure 2

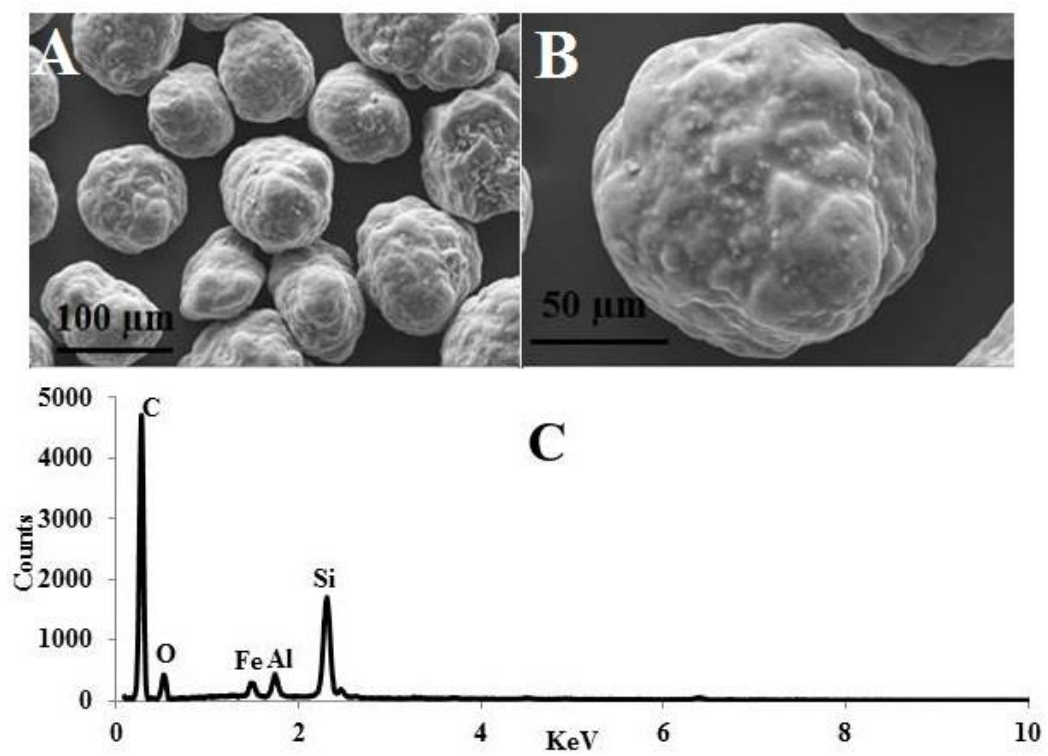


Figure 3

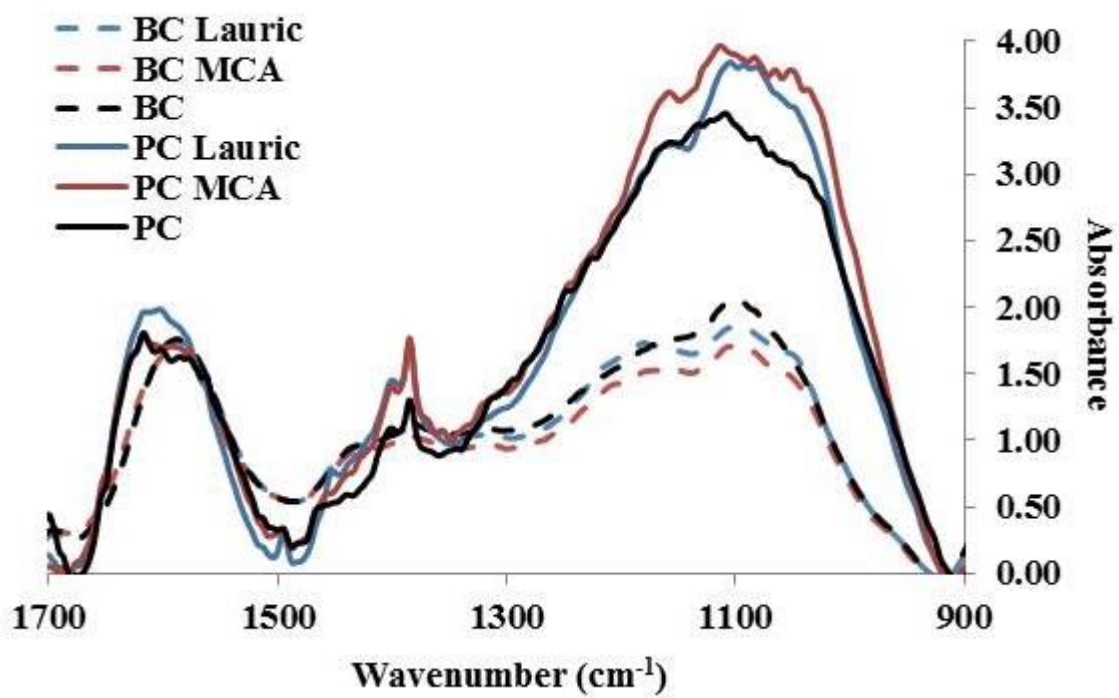


Figure 4

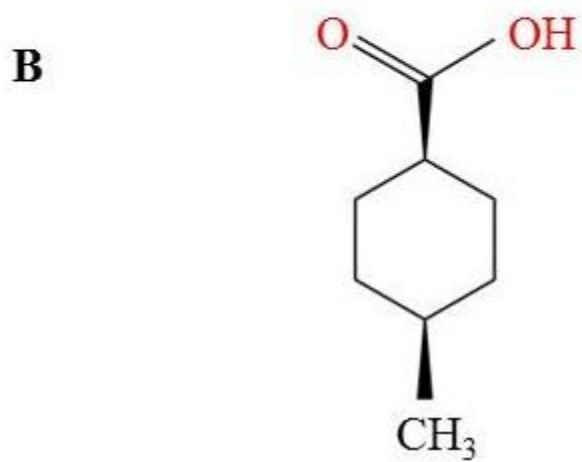
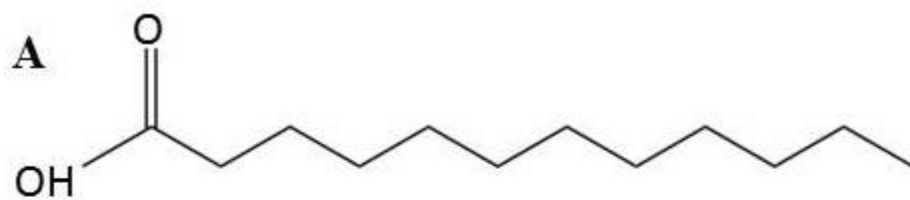


Figure 5

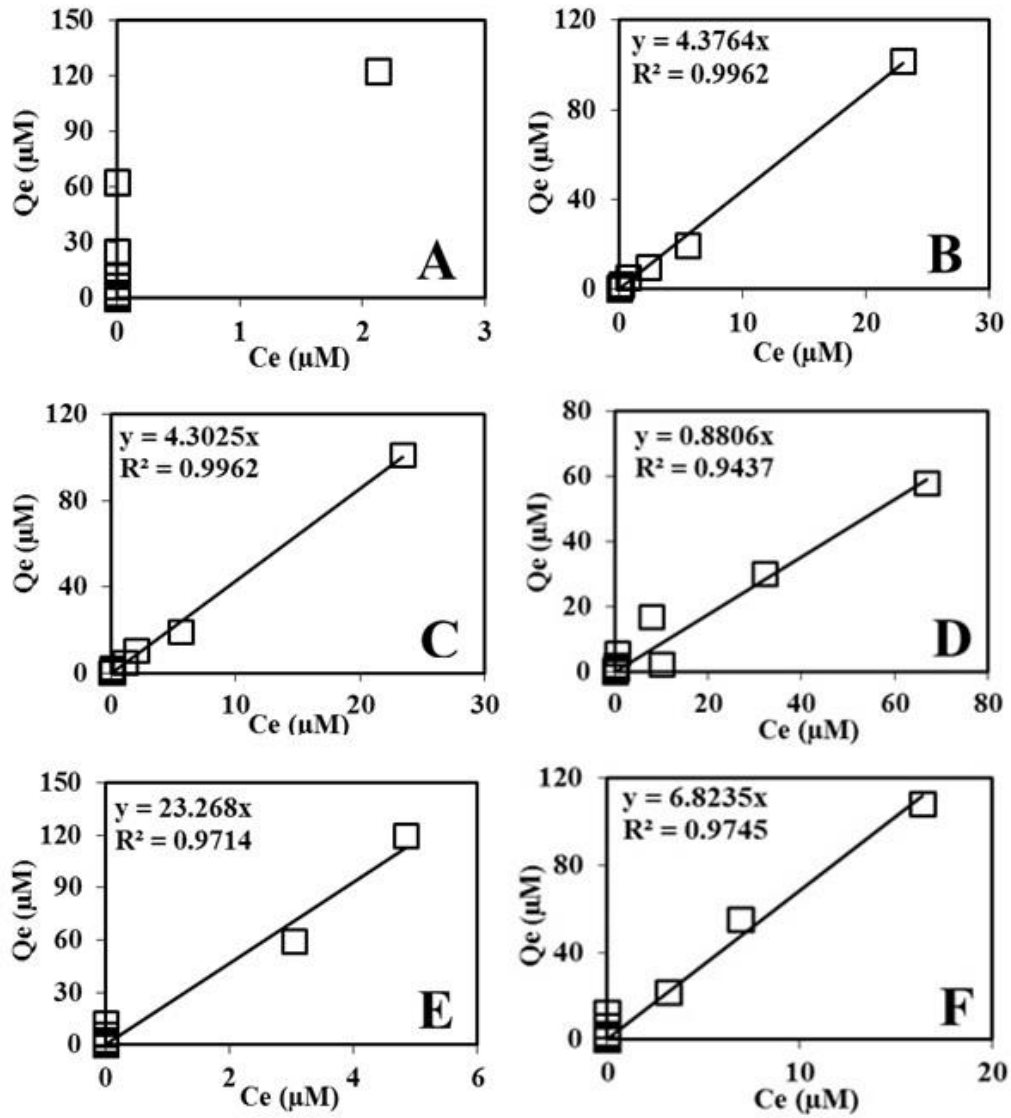


Figure 6

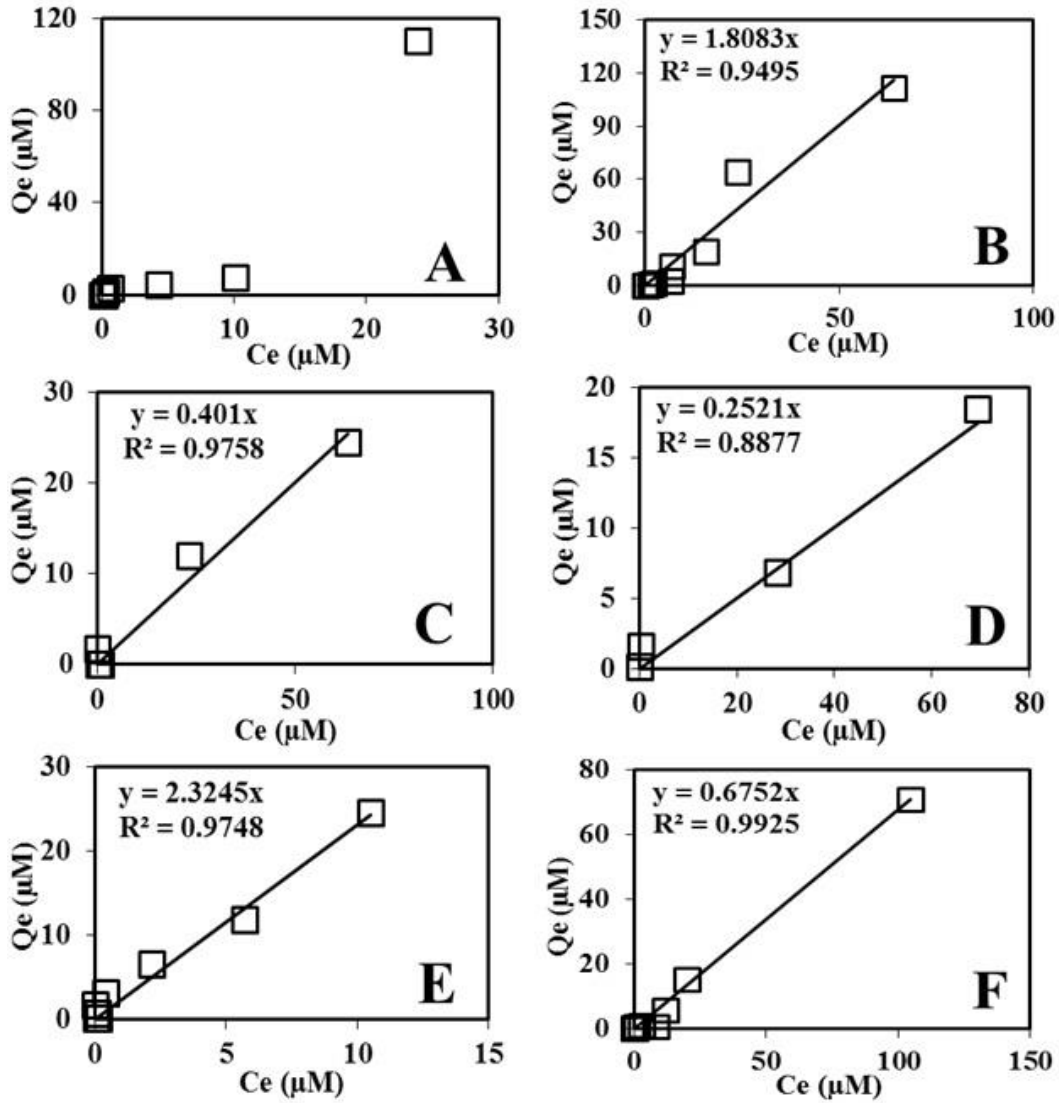


Table 1

Sample	pH	pzc	Moisture contents (%)	Mobile matter (%)	Ash content (%)	Fixed matter (%)
BC	6.77	6.4	2.7	33.02	17	47.3
PC	5.83	2.5	0.06	17.4	5.33	77.2

Table 2

Sample	C	H	N Wt (%)	S	O	H/C	O/C	(O+N)/C	(O+N+S)/C	Surface area (m ² /g)	Pore volume (cc/g)	Distribution of pore size (Å)
BC	69.68±0.52	2.58±0.03	0.81±0.01	0.07±0.01	8.65±.99	0.04	0.12	0.10	0.01	26.64	18 to 22	5.0E-03
PC	78.68±0.12	1.83±0.01	1.74±0.02	7.10±0.13	3.08±0.01	0.28	0.04	0.048	0.05	5.68	38 to 42	6.2E-04

Table 3

PC Wavenumber (cm ⁻¹)	BC Wavenumber (cm ⁻¹)	Assignment
1627		Aromatic C=C , conjugated C=O, and -OH stretching
1598	1598	Aromatic C=C ring stretching
1459	1442	Aliphatic CH deformations
1405	1398	Aromatic CH-(CH ₃) and OH deformation
1386		Aliphatic CH ₃ deformation
1176	1186	C-O phenols and ethers
1116	1116	Aliphatic C-O-H stretching and -OH deformation
1060	1056	Aliphatic ether C-O-C, and alcohol C-O, and Si-O

Table 4

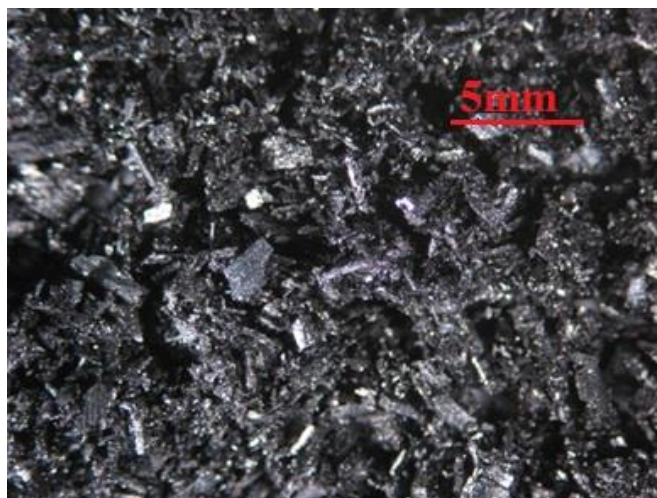
Sample ID	Cr (mg l ⁻¹)	Fe (mg l ⁻¹)	Mn (mg l ⁻¹)	Mo (mg l ⁻¹)	Pb (mg l ⁻¹)	Si (mg l ⁻¹)	V (mg l ⁻¹)
0.1 g l ⁻¹ PC	nd	0.0024	0.0019	nd	nd	0.2379	nd
0.1 g l ⁻¹ BC	nd	0.0029	0.0008	nd	nd	0.3879	nd
1 g l ⁻¹ PC	0.0007	0.0014	0.0004	nd	nd	0.3970	0.0065
1 g l ⁻¹ BC	nd	nd	nd	nd	0.0008	1.6370	nd
10 g l ⁻¹ PC	0.0024	0.0052	0.0003	0.0043	nd	0.0742	0.0682
10 g l ⁻¹ BC	nd	nd	0.0022	0.0003	0.0024	9.6530	nd
20 g l ⁻¹ PC	0.0039	0.0056	0.0003	0.0072	0.0006	0.1578	0.1004
20 g l ⁻¹ BC	nd	nd	0.0034	0.0005	0.0037	nd	0.0069

*nd = not detected

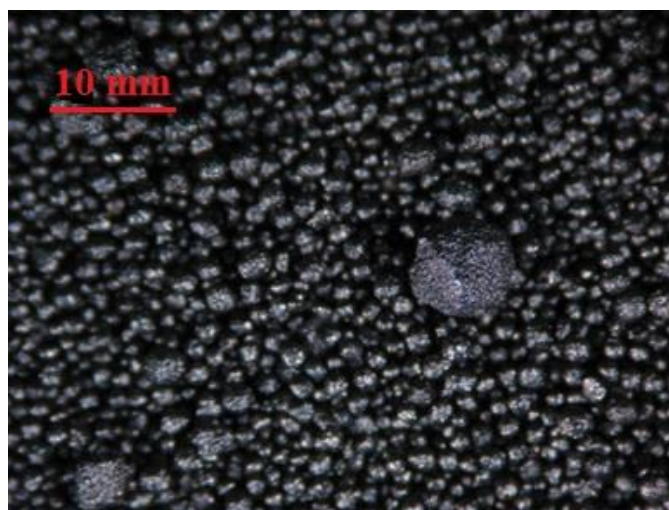
Supplementary Information Figure 1. Light Microscopy Images.

Light microscopy images of (A) BC produced by the Alberta Biochar Initiative, and (B) of PC.

A



B



Supplementary Information Table 1. Typical characterization results of BC

Test	Average (d.b.)	Unit of measure
Volatiles	5.0	%
Fixed carbon	76.5	%
Aeration porosity	26.0	%
Water holding capacity	59.0	%
Total porosity	85.0	%
Bulk density	78.0	Kg/m ³
EC	1.2	mS/cm

Supplementary Information Table 2. Elemental composition of BC estimated from SEM-EDS analysis

1

Element	Atomic number	Series	Unnormalized C (wt. %)	Normalized C (wt.%)	Atom. C (at. %)	Error (1 sigma) (wt. %)
C	6	K-series	48.00	56.33	67.56	6.19
O	8	K-series	23.62	27.72	24.96	3.34
Si	14	K-series	8.30	9.74	5.00	0.38
Cl	17	K-series	2.86	3.35	1.36	0.13
Ca	20	K-series	1.86	2.18	0.78	0.09
Mg	12	K-series	0.26	0.31	0.18	0.04
K	19	K-series	0.14	0.16	0.06	0.03
S	16	K-series	0.10	0.12	0.05	0.03
Al	13	K-series	0.06	0.08	0.04	0.03
P	15	K-series	0.00	0.00	0.00	0.00
	Total		85.21	100.00	100.00	

2

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14 Supplementary Information Table 3. Elemental composition of PC estimated from SEM-EDS
 15 analysis

Element	Atomic number	Series	Unnormalized C (wt. %)	Normalized C (wt. %)	Atm. C (at. %)	Error (1 ⁶ sigma) ₁₇ (wt. %)
C	6	K-series	75.34	75.34	83.73	9.24 18
O	8	K-series	14.64	14.41	12.02	2.33 19
S	16	K-series	6.88	6.77	2.82	0.28 20
Si	14	K-series	1.10	1.08	0.51	0.08
Al	13	K-series	0.90	0.89	0.44	0.07
Fe	26	K-series	0.72	0.71	0.17	0.06
Ti	22	K-series	0.26	0.27	0.08	0.04
Ca	20	K-series	0.12	0.12	0.04	0.03
K	19	K-series	0.12	0.12	0.04	0.03
Na	11	K-series	0.11	0.11	0.06	0.04
Cl	17	K-series	0.11	0.10	0.04	0.03
Mg	12	K-series	0.08	0.07	0.04	0.03
		Total	101.55	100.00	100.00	