



# Adsorption of acid-extractable organics from oil sands process-affected water onto biomass-based biochar: Metal content matters



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## HIGHLIGHTS

- Biochar from six local biomass sources were prepared and characterized.
- Aluminum and iron content of biochar correlated positively with adsorption capacity.
- Adding iron in biochar by impregnation method increased adsorption capacity.
- Metal sites acting as Lewis acids can form coordination bonds with the naphthenates.
- Effects of combined acidification with biochar adsorption was purely additive.

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## ABSTRACT

The impact of biochar properties on acid-extractable organics (AEO) adsorption from oil sands process-affected water (OSPW) was studied. Biochar from wheat straw with the highest ash content (14%) had the highest adsorption capacity (0.59 mg/g) followed by biochar from pulp mill sludge, switchgrass, mountain pine, hemp shives, and aspen wood. The adsorption capacity had no obvious trend with surface area, total pore volume, bulk polarity and aromaticity. The large impact of metal content was consistent with the carboxylates (i.e., naphthenate species) in the OSPW binding to the metals (mainly Al and Fe) on the carbon substrate. Although the capacity of biochar is still approximately two orders of magnitude lower than that of a commercial activated carbon, confirming the property (i.e., metal content) that most influenced AEO adsorption, may allow biochar to become competitive with activated carbon after normalizing for cost, especially if this cost includes environmental impacts.

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## 1. Introduction

In surface mining processes, three volumes of freshwater are used for each volume of bitumen produced and the used water, called oil sands process-affected water (OSPW), is stored in tailings ponds (Allen, 2008b). OSPW contains salts, suspended solids, heavy metals, and dissolved organic compounds, a fraction of which are

extractable with acid (hence the term acid-extractable organics, AEO) and these compounds create acute toxicity to aquatic organisms, mammals and birds (Allen, 2008a). To reclaim the tailings ponds into natural ecosystems, the AEO concentrations must be reduced (Kannel and Gan, 2012). Adsorption with activated carbon (AC) has been widely tested at the laboratory level for the removal of AEO from wastewater but its application is not economically feasible (Quinlan and Tam, 2015). According to a recent study (Inyang and Dickenson, 2015), the replacement of AC with charred biomass (i.e., biochar), which is less energy-intensive in terms of production, reduces the adsorbent cost from US\$1500/ton AC to US\$245/ton biochar. Additional tax credits and/or carbon taxes may further improve the situation for biochar, especially if sourced locally so that transportation is minimal (Ahmed et al., 2016).

Bandosz (2006) suggested that AC requires a surface area

*Abbreviations:* AC, activated carbon; AEO, acid-extractable organics; AITF, Alberta Innovates -Technology Future; FTIR, Fourier transform infrared spectroscopy; DRIFTS, diffuse reflectance infrared spectroscopy; NA, naphthenic acids; NLDFT, non-local density functional theory; OSPW, oil sands process-affected water; TOC, total organic carbon.

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greater than 500 m<sup>2</sup>/g and porosity greater than 0.33 mL/g, possibly with nitrogen surface functionalities, to maximize AEO uptake. Biochar has a relatively low surface area and porosity, and to minimize its cost and environmental impact, biochar should be subjected to no additional processing. Thus, knowledge of the factors that influence adsorption of the desired compound (AEO) is required to identify the appropriate biomass source. The AEO in OSPW are mainly composed of naphthenic acids (NA, (Grewer et al., 2010), which are a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids. The compounds are represented by a general chemical formula C<sub>m</sub>H<sub>2m+z</sub>O<sub>x</sub> (x = 2 to 5), where m indicates the carbon number and z is an even integer less than or equal to zero that specifies the number of hydrogen atoms lost due to the addition of rings (Clemente and Fedorak, 2005). NA have both hydrophilic (carboxyl) and hydrophobic (non-polar aliphatic) groups with or without one or more fused or bridged rings (Clemente and Fedorak, 2005). Despite the polar carboxylic group, the aliphatic tail in NA results in low solubility in water (Clemente and Fedorak, 2005).

The solubility is, however, dependent on pH and can be increased under alkaline conditions (pH 8 ± 0.7) where essentially all the NA are deprotonated, forming naphthenates (Moustafa et al., 2014). Also, solubility is higher in water with greater ionic strength, such as OSPW, and so the concentration in the tailings pond varies between 20 and 130 mg/L compared to 1–5 mg/L in ground and surface water in the Alberta oils sands region (Allen, 2008a). The sodium, calcium, and magnesium cations present in the OSPW stabilize naphthenates as dissolved metal (M) naphthenate salts, M<sup>n+</sup>(RCOO<sup>-</sup>)<sub>n</sub> (Moradi et al., 2013). Because of their anionic surfactant character, naphthenates may also form colloids in water, resulting in a negative zeta potential (Ćirin et al., 2015).

Naphthenates generally adsorb on carbonaceous materials through hydrophobic interactions, hydrogen bonding (if the carbon has oxygen and/or nitrogen surface groups) and electrostatic interactions (Moustafa et al., 2014; Inyang and Dickenson, 2015). The most prevalent naphthenic acids contain 13–15 carbon atoms with 2–3 rings (z = -4, -6) and molecular weights in the range of 140–450 g/mol. The hydrophilic moiety (carboxylic group) is much smaller (molecular weight of ~45 g/mol) than the hydrophobic tail (alkane R group and ring) (Quinlan and Tam, 2015) such that the hydrophobic interaction likely dominates for adsorption on activated carbon (Moustafa et al., 2014). On essentially non-porous biochar, however, there will be relatively few sites for this type of adsorption. Biochar does contain metal sites depending on its composition. In particular the minerals can participate in coordination bonds with naphthenates upon contact. The surface metal-naphthenate coordination bonds are stronger than the interaction experienced between Group I and II metal ions and naphthenate in solution (Bala et al., 2007).

Biochar from rice husks and acacia have been shown to adsorb AEO of OSPW but at much lower capacities than activated carbon from coal (Iranmanesh et al., 2014; Mohamed et al., 2015). These researchers did not discuss how the AEO adsorbed on the biochar. Given the above information, our hypothesis was that biochar samples with higher metal contents would have higher adsorption capacities. To test this hypothesis, several local biomass sources – wheat straw, pulp mill sludge, switchgrass, mountain pine, hemp shives, and aspen wood – were converted to biochar, characterized, and then the uptake of AEO from OSPW on these samples measured. To further confirm the hypothesis, the biochar sample with the highest uptake was acid-washed to remove its metal content while the biochar with the lowest uptake was impregnated with iron to increase the metal content.

There appears to be confusion and/or misunderstanding in the literature regarding the impact of pH on precipitation of AEO. For

example, Niasar et al. (2016) mentioned that the adsorption capacity of two adsorbents (Norit AC ROW 0.8 SUPRA and petroleum coke-derived AC) decreased with increasing pH, and Kannel and Gan (2012) stated that low pH values of OSPW facilitated increased NA adsorption on petroleum coke AC. In both examples, precipitation was not mentioned. Thus, the influence of pH on adsorption capacity was also investigated in this study to determine if a synergistic effect existed between precipitation and adsorption.

## 2. Materials and methods

### 2.1. Materials

The biomass sources for this study were wheat straw (Alberta, Canada), pulp mill sludge (Alberta, Canada), switchgrass (Ontario, Canada), beetle infested mountain pine wood (Alberta, Canada), hemp shives residue (Alberta, Canada) and aspen wood chips (Alberta-Pacific Forest Industries Inc., Alberta, Canada). For comparison, a commercial AC - Norit AC (Sigma Aldrich, Missouri, USA) – was also tested. Metal removal of a biochar sample was performed with hydrochloric acid and nitric acid (BDH VWR Analytical, Philadelphia, USA), while metal impregnation of another sample was performed using ferrous nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Strem Chemicals, Massachusetts, USA). OSPW was collected from an oil sands tailings pond in April 2014 (Pond 7, Suncor Energy Inc., Alberta, Canada) and stored at 4 °C. The composition of this water was determined before the adsorption experiments. The total organic content of the water changed by less than 10% over the course of the experiments.

### 2.2. Preparation of biochar

Wheat straw, pulp mill sludge, switchgrass, mountain pine and hemp shives biomass (6–55 kg per batch, depending on the density) were heated in a 500 L rotary drum batch pyrolyzer at 10 °C min<sup>-1</sup> with no sweep gas to 600 °C and held at this temperature for 0.5 h. The yields of biochar were 25–30%. The biochar from aspen wood was prepared differently to obtain a material with a higher surface area. The aspen wood chips were heated in a vertical down-flow packed bed reactor set-up described in detail elsewhere (Veksha et al., 2014). Briefly, 7.5 g of biomass (particle diameter 0.3–2.0 mm and particle length 0.3–5.0 mm) was heated at 4 °C min<sup>-1</sup> under nitrogen (N<sub>2</sub>) flow (space velocity 1 min<sup>-1</sup>) to 600 °C and pyrolyzed with this gas flow for 0.5 h. After pyrolysis, the reactor was cooled to 70 °C in N<sub>2</sub> and the produced biochar was collected. The yield of aspen wood biochar was ~24%.

The metal content of the biochar from aspen wood was increased by the direct hydrolysis of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with 6 g of sample using the procedure described by Hu et al. (2015); while that of the biochar from wheat straw was decreased by acid washing with aqua regia (3 M HCl: 1 M HNO<sub>3</sub>), rinsing with distilled water to return to a neutral pH, followed by drying at 105 °C for 12 h. The first sample is called Fe/Aspen wood while the latter sample is called Acid-washed wheat straw. Acidified hemp shives and switchgrass were prepared by the impregnation of 13% and 10% H<sub>2</sub>SO<sub>4</sub> on the biochar samples, respectively, followed by drying at 105 °C for 12 h.

### 2.3. Adsorption tests

Biochar and AC were evaluated for the adsorption of AEO from OSPW using a batch method. The sample (0.4 g of biochar or 0.02 g AC) was placed in a glass vial and then 20 mL of OSPW (at 25 °C) was added. The mixtures were shaken at 25 °C and 225 rpm in an

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