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A novel solid-state fractionation of naphthenic acid fraction components from oil sands process-affected water

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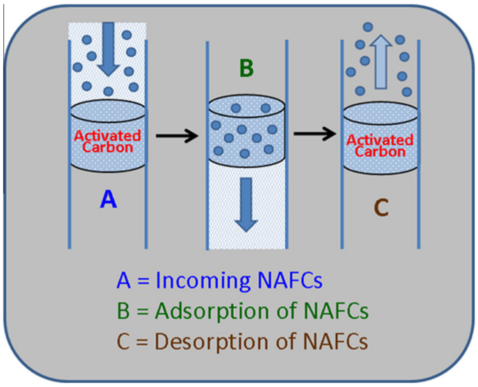
HIGHLIGHTS

- Diverse organic and inorganic sorbent materials were screened as sorbents for NAFCs.
- Carbonaceous sorbents display efficient, rapid, and cost-effective uptake.
- 95% uptake of NAFCs was observed for granular activated carbon.
- Activated carbon offers a facile and green fractionation strategy for NAFCs from OSPW.

GRAPHICAL ABSTRACT



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ABSTRACT

Various sorbent materials were evaluated for the fractionation of naphthenic acid fraction components (NAFCs) from oil sand process-affected water (OSPW). The solid phase materials include activated carbon (AC), cellulose, iron oxides (magnetite and goethite), polyaniline (PANI) and three types of biochar derived from biomass (BC-1; rice husks, BC-2; acacia low temperature and BC-3; acacia high temperature). NAFCs were semi-quantified using electrospray ionization high resolution Orbitrap mass spectrometry (ESI-MS) and the metals were assessed by inductively coupled plasma optical emission spectrometry (ICP-OES). The average removal efficacy of NAFCs by AC was 95%. The removal efficacy decreased in the following order: AC, BC-1 > BC-2, BC-3, goethite > PANI > cellulose, magnetite. The removal of metals did not follow a clear trend; however, there was notable leaching of potassium by AC and biochar samples. The bound NAFCs by AC were desorbed efficiently with methanol. Methanol regeneration and recycling of AC revealed 88% removal on the fourth cycle; a 4.4% decrease from the first cycle. This fractionation method represents a rapid, cost-effective, efficient, and green strategy for NAFCs from OSPW, as compared with conventional solvent extraction.

1. Introduction

Oil sands bitumen reserves occur globally at different sites such as the Athabasca oil sands, Canada and Orinoco Oil sands (Venezuela). Minor deposits that are not fully explored also occur in Kazakhstan, Russia and the USA (Canadian Association of Petroleum Producers, 2012). The reserves in northern Alberta, Canada are projected at 1.7 trillion barrels, with 173 billion barrels considered to be economically recoverable (Burrowes et al., 2009). A modified Clark caustic hot water technique is typically employed to extract surface mineable bitumen from the oil sands mixture

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(Schramm et al., 2000). Large volumes of water are consumed during processing, approximately 3–6 barrels per 1 barrel of oil produced (Schindler and Donahue, 2006). The oil sands industry currently operates under a zero discharge policy in accordance with the Alberta Environmental Protection and Enhancement Act (1993) and is enforced by the Government of Canada. As a result, oil sands process-affected water (OSPW) is stored on-site in tailing ponds and settling basins occupying approximately 176 km^2 (Grandia, 2013).

OSPW is saline and contains organic components which are of great concern due to their aquatic toxicity, mobility and fate in aquatic environments (Barrow et al., 2003, 2004; Headley and McMartin, 2004). The organic contaminants include polycyclic aromatic hydrocarbons (PAHs) (Colavecchia et al., 2004; Rhodes et al., 2005; Farwell et al., 2009; Kelly et al., 2009; Barrow et al., 2010) and naphthenic acid fraction components (NAFCs) (Headley and McMartin, 2004; Farwell et al., 2006; Frank et al., 2008; Headley et al., 2009a,b; Barrow et al., 2010; Grewer et al., 2010). Much research has focused on NAFCs are found ubiquitously in petroleum reservoirs and not only oil sands deposits. The principal toxic compounds in NAFCs are not well established. For example it is not known to what degree, classical naphthenic acids (i.e. saturated mono-carboxylic acids), along with oxy-acids, sulfur or nitrogen heteroatom species contribute to the overall aquatic toxicity of OSPW. Since the oil sands mining activities are accelerating in the Fort McMurray region of Alberta, Canada; there is a growing concern to evaluate potential effects on water quality and the health of aquatic biota (Dowdeswell et al., 2010; Baird et al., 2011).

Isolation of NAFCs from OSPW is important in environmental impact assessment and toxicity studies, to offset the reliance on commercially available naphthenic acids (NAs) standards. Commercial mixtures of NAs do not accurately represent the composition mixture of NAFCs in OSPW and are known to exhibit different degradation, sorption and toxicity characteristics.

Currently, there is one well-established fractionation method employed for the large volume extraction of NAFCs from OSPW using a solvent–solvent extraction approach (Rogers et al., 2002). In this contribution, we report the development of a facile solid-phase extraction (SPE) method that compares eight types of sorbent materials. The SPE method proposed herein offers significant advantages when compared with conventional solvent-based methods because it relies on adsorptive processes that are efficient, rapid, cost-effective and environmentally friendly.

2. Materials and methods

2.1. Chemicals

Aniline (99.5% pure), acetic acid, magnetite and goethite were purchased from Sigma–Aldrich. Ammonium peroxydisulfate (APS), ammonia and sulfuric acid were obtained from Alfa Aesar, BDH Chemicals and EMD, respectively. Methanol (HPLC grade), formic acid, hydrochloric acid, and salts of the following: iron (Fe), potassium (K), phosphorus (P), calcium (Ca), magnesium (Mg), sodium (Na) and zinc (Zn), were all obtained from Fisher Scientific. All chemicals were used as received without further purification unless stated otherwise.

2.2. Sorbents

Activated carbon (AC; Norit-GCA-1240), cellulose, magnetite and goethite (Sigma–Aldrich), Biochar (BC) were generated from different sources (BC-1; rice husks, BC-2; acacia using low temperature and BC-3; acacia using high temperature processing. Polyaniline (PANI) was synthesized based on procedures described in Section 2.3.

2.3. Synthesis

PANI nanoparticles were synthesized by adding of 0.978 ml aniline (0.0107 mol) in 200 mL of Millipore water and stirred for 30 min. 2.94 g APS (0.0129 mol) was added drop-wise for 30 min. The combined solutions were mixed for 24 h. The products were washed with excess Millipore water, vacuum filtered, and dried for 24 h in an oven at 60 °C. The dried PANI was then deprotonated with excess 0.1 M ammonia. Further details on the synthesis and characterization are reported elsewhere (Mohamed et al., 2015). Low temperature biochar materials (BC-1 and BC-2) were prepared under anaerobic conditions in a double-lined rotating stainless steel drum operating at temperatures near 500 °C where acacia or rice husks were used as the carbon precursors. High temperature biochar (BC-3) was prepared as described above at temperatures above 700 °C.

2.4. Sorption–desorption

Approximately 100 mg of sorbent was added to a vial containing 20 mL of OSPW (obtained from an industrial supplier in the Athabasca oils sands region). The OSPW was centrifuged (Beckman Avanti J-E equipped with JS-5.3 rotor at 5300 rpm for 3 h) to remove suspended materials prior to addition of sorbent. The capped vials were equilibrated with shaking for 24 h on a SCILOGEX SKO330-Pro orbital shaker (500 rpm) at room temperature. Thereafter, the mixture was allowed to settle and the supernatant layer was decanted, followed by centrifugation (same procedure as above) to obtain OSPW free of particulates for analysis of NAFCs and metals. The desorption of bound adsorbate from the sorbent was achieved by washing the sorbent with 20 mL methanol whilst shaking for 24 h. The methanol extract was isolated with centrifugation (same procedure as above) and then analyzed for NAFCs (*cf.* Section 2.5).

2.5. Adsorption kinetics of NAFCs

The uptake of NAFCs by AC (optimal sorbent material) was evaluated using ~100 mg in vials containing 20 mL OSPW. The mixtures were incubated at various time intervals (30, 60, 120 and 180 min), as described above, and a similar workup procedure was used to analyze NAFCs (*cf.* Section 2.5). The data was using a pseudo-first order (PFO) (Lagergren, 1898) and pseudo-second order (PSO) (Ho and McKay, 1998) models, as described by Eqs. (1) and (2), respectively. Q_t and Q_e are the amount of NAFCs adsorbed at a particular time (t) and at equilibrium, respectively. k_i is a rate constant (k_1; $i = 1$) for PFO and k_2 (where $i = 2$) for the PSO, and t is time. The sum of square of errors (SSE) was used as a criterion of the "best fit" where a lower value of SSE (*cf.* Eq. (3)) indicates an optimized goodness-of-fit. The best fit was obtained by minimization of the SSE for all data across the range of experimental conditions. Q_{ti} is the experimental value, Q_{tf} is the fitted value, and N is the number of Q_e data points.

$$Q_t = Q_e(1 - e^{-k_1 t}) \tag{1}$$

$$Q_t = \frac{Q_e^2 k_2 t}{1 + k_2 t Q_e} \tag{2}$$

$$\mathrm{SSE} = \sqrt{\frac{(Q_{ti} - Q_{tf})^2}{N}} \tag{3}$$