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Petroleum coke adsorption as a water management option for oil sands process-affected water

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ABSTRACT

Water is integral to both operational and environmental aspects of the oil sands industry. A water treatment option based on the use of petroleum coke (PC), a by-product of bitumen upgrading, was examined as an opportunity to reduce site oil sands process-affected water (OSPW) inventories and net raw water demand. Changes in OSPW quality when treated with PC included increments in pH levels and concentrations of vanadium, molybdenum, and sulphate. Constituents that decreased in concentration after PC adsorption included total acid-extractable organics (TAO), bicarbonate, calcium, barium, magnesium, and strontium. Changes in naphthenic acids (NAs) speciation were observed after PC adsorption. A battery of bioassays was used to measure the OSPW toxicity. The results indicated that untreated OSPW was toxic towards *Vibrio fischeri* and rainbow trout. However, OSPW treated with PC at appropriate dosages was not acutely toxic towards these test organisms. Removal of TAO was found to be an adsorption process, fitting the Langmuir and Langmuir–Freundlich isotherm models. For TAO concentrations of 60 mg/L, adsorption capacities ranged between 0.1 and 0.46 mg/g. This study demonstrates that freshly produced PC from fluid cokers provides an effective treatment of OSPW in terms of key constituents' removal and toxicity reduction.

1. Introduction

Oil sands consist of sand, silt, clay, water, and bitumen. Typically, the material processed contains by weight about 10% bitumen, 85% mineral solids, and 5% water (Liu et al., 2005). Syncrude Canada Ltd. (SCL) operates an integrated oil sands surface mining and upgrading facility in the Athabasca deposit of Alberta's oil sands, north of Fort McMurray in close vicinity to the Athabasca River, Alberta, Canada. SCL's operation consists of a surface mine that provides more than 500 kilotonnes of oil sand per day to an extraction plant. Water digestion and then flotation produce a bitumen-rich froth that is upgraded to a light sweet crude oil suitable for refining. In 2010, Alberta's synthetic crude oil production (SCO) exceeded 125×10^3 m^3/d, of which about 40% was produced by SCL (ERCB, 2011).

There are two major sources of water used at the SCL operation: raw water imported from the Athabasca River and oil sands process-affected water (OSPW). Raw water is used primarily for boiler feed water to produce steam and for cooling tower make-up with smaller volumes to satisfy potable water requirements. While this imported water accounts for about 15–20% of the water needs, the largest source is recycled OSPW. OSPW refers to the water that has been in contact with oil sands or released (dewatered) from tailings deposits and retained in settling basins. OSPW is recycled for plant needs, primarily for bitumen extraction based on a warm water ore digestion process. Currently, OSPW is retained on site and there is no active return to the regional watershed. Other environmental inflows that enter the OSPW inventory requiring engineered containment include precipitation/runoff water, groundwater (aquifer depressurization), and oil sands formation water. The only waters returned to the Athabasca River are treated sanitary effluent.

To produce SCO, SCL operates three fluid cokers that reject carbon from the bitumen feedstock in the form of petroleum coke (PC). Approximately 15% of the extracted bitumen is converted to coke and stored on site (Jang and Etsell, 2005). SCL produces about 20 kg of PC per barrel of SCO produced. In 2010, about 2.2 million tonnes of PC was produced based on a SCO production of 108 million barrels. Consequently, significant volumes of PC are available for potential uses such as water treatment and reclamation.

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Adsorption onto activated carbon is an effective technique to remove recalcitrant organic compounds from aqueous solutions (Drikas et al., 2009; Petrova et al., 2010; Zoschke et al., 2011). The use of activated carbon in water treatment applications has resulted in research to find low-cost carbon alternatives such as peat, fuller's earth, activated slag, wool carbonizing waste, rice husk, and PC, among other materials (Singh et al., 2003; Ahmaruzzaman and Sharma, 2005; Crittenden et al., 2005). Intrinsic adsorptive capacity has been associated with PC. It has been used to remove metals and phenol (Zamora et al., 2000) as well as free phase bitumen from wastewater (Majid and Parks, 1999). Activated PC produced by physical or chemical activation (DiPanfilo and Egiebor, 1996) has been found to be effective for removing color and chlorinated organic compounds from pulp mill effluent (Shawwa et al., 2001) as well as polycyclic aromatic hydrocarbons from water (Yuan et al., 2010). Recently, Small et al. (2012) investigated the use of activated PC as an available adsorbent for naphthenic acids (NAs) removal.

PC is a potentially viable adsorbent that can be used to treat OSPW to a sufficient quality for its return to the environment and/or for certain plant reuse applications. In this study, PC was used as an adsorbent to treat OSPW, in particular for the removal of total acid-extractable organics (TAO) and NAs. A battery of bioassays including Microtox™, rainbow trout, *Ceriodaphnia dubia*, and *Daphnia magna* was used to assess the adsorption effectiveness to remove acute toxicity. Equilibrium studies modeled using different adsorption isotherms as well as adsorption kinetics were also conducted.

2. Materials and methods

2.1. OSPW and petroleum coke samples

Different sources of OSPW were collected from SCL at various times between 2006 and 2008. These waters were used to assess the efficiency of PC for removal of OSPW constituents. PC samples were collected from the burner of SCL's fluid cokers 8-1 and 8-2. The PC samples were cooled, and then sieved using a No. 16 (1.18 mm) mesh screen to separate particles approximately larger than 1 mm. A total of 29 PC samples were submitted to ACME Laboratories Ltd. in Vancouver, British Columbia, Canada, for elemental analyses.

2.2. Short- and long-term adsorption experiments

Short-term adsorption experiments were conducted to assess the efficiency of PC to remove TAO from various sources of OSPW. Adsorption isotherm experiments were completed using OSPW from three sources: (1) outflow of Syncrude's active west in-pit (WIP) tailings facility; (2) outflow of the recycle water (RCW) pond; and (3) dike drainage from the sand dike comprising the Mildred Lake Settling Basin (MLSB). OSPW samples were collected from the respective water source into 20-L plastic pails. Fourteen isotherm experiments were completed at room temperature (~20 °C) by adding OSPW to varying weights of PC in 500-mL glass containers to produce solution concentrations of up to 40 weight percent (wt.%).

Longer-term adsorption experiments were completed to assess changes in OSPW quality following exposure to PC for extended periods. PC saturated with OSPW was placed in three columns, from which OSPW was withdrawn over time. A large clear acrylic column, denoted as the 2.75-m column, was 0.15 m in diameter and 2.75 m high. Two small Pyrex glass columns, denoted as Columns A and B, were 0.15 m in diameter by 1 m high. Fig. S1 in the Supplementary material shows a schematic diagram of the PC columns used to assess the OSPW quality. The 2.75-m column was filled to the 2-m level with OSPW saturated PC collected from SCL's 8-2 coke slurry discharge line on August 14, 2007. Columns A and B were filled to the 80-cm level with OSPW saturated PC collected on July 21, 2008 from SCL's 8-2 coke slurry discharge line. Water samples representing residence times (contact time with PC) between 0 and 435 days were collected from the test columns. The collected water samples were filtered using a 0.45 μm syringe filter prior to chemical analyses.

2.3. Adsorption kinetics experiments

Adsorption kinetics experiments were conducted in a mixed batch reactor. The reactor consisted of a sealed 4-L steel container immersed in a constant temperature water bath, and fitted with a mechanical mixer to provide constant agitation. The experiments were conducted using OSPW collected from SCL's WIP and PC collected from coker 8-1. To simulate the engineering design basis for slurry concentrations in SCL's coke transport pipeline, OSPW was added to the PC to form mixtures approximately 23 wt.% PC. At predetermined times, 120 mL aliquots of solution were removed from the container and immediately filtered with a 0.45 μm syringe filter.

2.4. Analytical determination

Major cations and trace metals present in OSPW were measured using a Varian Vista-RL inductively coupled plasma atomic emission spectrometer (ICP-AES) equipped with radial mounted torch, Sturman-Masters V-groove nebulizer and Sturman-Masters spray chamber. Anions were determined using a Dionex-DX 600 series ion chromatograph fitted with an Ion-Pac AS4A-SC analytical column (4 × 250 mm). A 3 mM sodium bicarbonate/2.4 mM sodium carbonate eluent was used at a flow rate of 2 mL/min to separate the anions at a constant temperature of 30 °C. Alkalinity was measured using a titration method (Metrohm Model 751 titrator with LL micro-glass electrodes) titrated with 0.1 M hydrochloric acid.

Concentrations of TAO were measured in OSPW before and after PC treatments using a Fourier transform infrared spectroscopy (FT-IR) method described by Jivraj et al. (1996). Briefly, the TAO were quantified by acidifying the sample to pH ~ 2 and double extracting the precipitate with dichloromethane. The extracts were combined, evaporated to dryness, and reconstituted into a fixed volume of dichloromethane. The infrared light adsorption at wavelengths 1705 and 1745 cm^{-1} was obtained using a Nicolet model 8700 FT-IR spectrometer manufactured by Thermo Electron Corporation.

In order to assess which of the TAO constituents corresponded to NAs, an ultra pressure liquid chromatography/mass spectrometric (UPLC/MS) method for identification of specific NAs groups was applied. Selected water samples were submitted to the University of Alberta Division of Analytical and Environmental Toxicology for quantitative and qualitative characterization of NAs using a Waters Acquity UPLC system. The detection was performed in-line with a high resolution QStar Pulsar i mass spectrometer equipped with a Turbo Ion Spray source (Applied Biosystems/MDS Sciex, Concord, Ontario, Canada) operated in negative ion mode and run using Analyst QS 1.1 software. Chromatographic separations were run on a Waters UPLC phenyls BEH column (150 × 1 mm, 1.7 μm) using a gradient mobile phase of (A) 10 mM ammonium acetate solution prepared in Optima-grade water and (B) 10 mM ammonium acetate in 40% acetone and 60% methanol. Gradient elution was: 1% B for 2 min, and ramped to 60% B by the third minute. At times of seven and 13 min, the mobile phase was 70% B and 95% B, respectively. At 14 min, the phase was returned to 1% B over a 5.8 minute interval. The flow was 0.110 mL/min and column temperature was 50 °C. The separation of NAs was based on the carbon number (n), degree of cyclization (z), and extent of alkyl branching. The concentration of total NAs was estimated by the sum response of all the UPLC-HRMS peak areas with exact masses corresponding to NAs ($C_nH_{2n+Z}O_2$). Details of the technique are provided in Pérez-Estrada et al. (2011).

Elemental analyses of PC samples were conducted using an ICP mass spectrometry (Perkin-Elmer Elan 9000) after drying and fusing