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Surface amination of activated carbon and petroleum coke for the removal of naphthenic acids and treatment of oil sands process-affected water (OSPW)

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HIGHLIGHTS

- KOH activation of petroleum coke produced highly mesoporous activated carbon (PAC).
- PAC showed superior adsorption performance in removal of model naphthenic acids.
- Treatment of AC/PAC by ammonia gas is effective for increasing adsorption capacity.
- The adsorption capacity of all adsorbents decreased with increasing pH.
- Both PAC and AC could remove almost 99% of the TOC of OSPW at pH 3.5.

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ABSTRACT

To enhance the removal of model naphthenic acids (NA) from synthetic wastewater and removal of organics in oil sands process-affected water (OSPW) by adsorption, surfaces of commercial charcoal-derived activated carbon (AC) and proprietary petroleum coke-derived activated carbon (PAC) were modified. Two different amination processes including a single stage treatment with ammonia gas at an elevated temperature and a two-step treatment of nitration followed by reduction were adopted. All adsorbents showed excellent capacity for the model NAs and OSPW at low pH ($\leqslant$4.0). Ammonia treatment was more effective on improvement of adsorption capacity than the nitration followed by reduction method. The effect was more significant for commercial activated carbon compared to PAC, especially for multi-component adsorption at pH 8.0. The kinetics of adsorption improved significantly by the surface modification methods indicating great potential for these adsorbents in continuous column operation.

1. Introduction

Each day large volumes of oil sands process-affected water (OSPW) are being produced during the extraction of bitumen in oil sands industry in northern Alberta [1,2]. OSPW contains different polyaromatic hydrocarbons (PAHs), bitumen, as well as naphthenic acids (NAs) [3,4], which not only are the major source of toxicity in OSPW [5–8], but also create operational problems such as corrosion of the equipment during bitumen recovery process [9]. A recent report indicates that about 720 billion liters of OSPW that were produced during the extraction of bitumen from Canadian oil sands industry have been stored in tailing ponds covering approximately 170 km^2 [10]. Water treatment and management strategies are urgently needed for OSPW recycling in order to reduce the withdrawal of fresh water from the Athabasca River and to permit the safe release of treated OSPW to the receiving environment by removing these compounds [11].

Until now, different methods such as advanced oxidation [12], membrane processes [13], biological treatment [14], and adsorption [3,15] have been tested for the removal of organics including naphthenic acids from OSPW. Although efficient, membrane processes are highly susceptible for fouling in treating OSPW [16]. In

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addition, filtration methods are not cost effective due to large pressure heads needed to treat large volumes of contaminated water. Biological treatments although cost-effective, are often slow, and toxic compounds present in OSPW affect the efficiency and survival of the microorganisms. NAs are poorly biodegraded in the holding ponds in the field [17]. Among all the different treatment methods, adsorption has gained significant attention due to its efficiency and fast removal rates [3]. Recent studies on petroleum coke (PC), a relatively inexpensive and abundant feedstock, used as an adsorbent after activation, have brought renewed attention to the use of adsorption processes for OSPW treatment [15,18,19]. Gamal El-Din et al. [3] demonstrated that adsorption using PC followed by ozonation is an efficient process of removing NAs from OSPW.

PC based adsorption processes have been used for treatment of a wide variety of wastewaters [20–22]. However, raw PC has low surface area and consequently low adsorption capacity. Various surface activation methods have been adopted for increasing the specific surface area and porosity, and customization of PC surface characteristics depending on the properties of the compounds to be adsorbed. Most of the earlier research used chemical activation methods using KOH or some other alkali metal hydroxides [23,24]. Although, microporous surface area and micropore volume are important factors for adsorption, surface functionality and solution pH play significant roles in determining the equilibrium adsorption capacity of polar compounds such as naphthenic acids. The existence of nitrogen-containing functional groups on the surface of adsorbent generally provides basic properties, which improves removal of polar compounds such as organic acids, due to dipole–dipole interactions, H-bonding and covalent bonding [25,26].

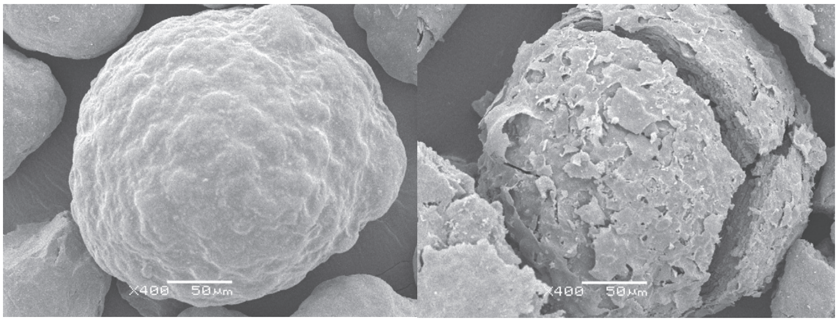
There are several ways of introducing nitrogenous groups on the carbonaceous adsorbents including chemical activation using urea–formaldehyde, melamine–formaldehyde, tetraethylenepentamine (TEPA), direct treatment of surface with nitrogen containing reagents such as ammonia and amines, and the surface impregnation with amine-containing compounds with varying success depending on the nature of adsorbates [20,23].

The objective of this research is to enhance removal of naphthenic acids from synthetic solution using surface modified activated carbon adsorbents. Two types of activated carbon adsorbents were used, a commercial activated carbon (AC), and a proprietary petroleum coke activated carbon (PAC). Two different methods were used to introduce nitrogen-containing functionality on the surface of both AC and PAC: (1) a one-step process where direct ammonia gas was used to introduce –NH_3 group on the surface, and (2) a two-step process including an electrophilic substitution to introduce nitrate group, followed by reduction of the nitrate to NH_2. The adsorption performances of the surface modified AC and PAC by these two methods were compared in removal of 3 model naphthenic acids from pure water, and removal of total organic carbon (TOC) from real oil sand process-affected water (OSPW).

2. Material and methods

2.1. Materials

The commercial activated carbon (AC) used in this study was an extruded activated charcoal (Norit ROW 0.8 SUPRA) (CAS Number: 7440-44-0), purchased from Sigma–Aldrich Canada Co. The petroleum coke (PC) and the oil sands process-affected water (OSPW) were supplied by NEWALTA Corporation (Burlington, ON). The chemicals such as KOH, 2-naphthoic acid, 1,4-cyclohexanedicarboxylic acid, HPLC grade acetonitrile were purchased from VWR company. Diphenylacetic acid was purchased from Sigma–Aldrich Canada Co. The properties of the selected



(a) (b)

Fig. 1. SEM images of PC before (a) and after (b) activation.

Table 1
Comparison of surface properties of AC and PAC with and without surface modification.

Sample name	Micropore area (m^2/g)	Mesopore area (m^2/g)	Total area (m^2/g)	Micropore volume (cm^3/g)	Total pore volume (cm^3/g)	Pore size (nm)
AC	766	634	1399 ± 27	0.3	0.7	2.0
AC–NH_2	520	435	955 ± 7	0.3	0.5	2.0
AC–NH_3	778	488	1266 ± 23	0.4	0.6	2.0
PC	12	0	12 ± 0.2	0	~0	1.2
PAC	439	1004	1443 ± 13	0.2	0.8	2.1
PAC–NH_2	277	689	967 ± 8	0.1	0.5	2.1
PAC–NH_3	254	770	1024 ± 7	0.1	0.5	2.1