



Research article

Preparation of activated petroleum coke for removal of naphthenic acids model compounds: Box-Behnken design optimization of KOH activation process



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ABSTRACT

This study employed Box-Behnken design and response surface methodology to optimize activation parameters for the production of activated petroleum coke (APC) adsorbent from petroleum coke (PC) to achieve highest adsorption capacity for three model naphthenic acids. Activated petroleum coke (APC) adsorbent with a BET surface area of 1726 m²/g and total pore volume of 0.85 cc/g was produced at the optimum activation conditions (KOH/coke mass ratio) of 3.0, activation temperature 790 °C, and activation time 3.47 h. Effects of the activation parameters on the adsorption performances (adsorption capacity and kinetics) were investigated. With the APC obtained at the optimum activation condition, the maximum adsorption capacity of 451, 362, and 320 (mg/g) was achieved for 2-naphthoic acid, diphenylacetic acid and cyclohexanepentanoic acid (CP), respectively. Although, generally APC adsorbents with a higher specific surface area and pore volume provide better adsorption capacity, the textural properties (surface areas and pore volume) are not the only parameters determining the APC adsorbents' adsorption capacity. Other parameters such as surface functionalities play effective roles on the adsorption capacity of the produced APC adsorbents for NAs. The KOH activation process, in particular the acid washing step, distinctly reduced the sulfur and metals contents in the raw PC, decreasing the leaching potential of metals from APC adsorbents during adsorption.

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1. Introduction

Each year, several million tonnes of oil sands process-affected water (OSPW) is produced from the bitumen extraction process in Alberta, Canada (McQueen et al., 2017). More than 3 barrels of fresh water is required for the production of every barrel of bitumen (Xu et al., 2008). There are different kinds of organic compounds in OSPW such as polyaromatic hydrocarbons (PAHs), bitumen, and naphthenic acids (NAs). NAs are the main source of toxicity of OSPW (Frank, 2008; Scarlett et al., 2013) and need to be removed before process water can be discharged in the aquatic environment.

Petroleum coke (PC) is an inexpensive by-product of petroleum industry that can be used to produce highly porous activated

carbon (Pourrezaei et al., 2014; Zhang et al., 2015) for treatment of OSPW. The main problem of PC is its high sulfur content (Pourrezaei et al., 2014), presence of heavy metals, and low surface area. Different researchers have attempted to use PC with or without activation for removal of organics from wastewaters (Gamal El-Din et al., 2011; Kubota et al., 2011; Pourrezaei et al., 2014; Sarkar, 2013; Yuan et al., 2010; Zubot et al., 2012), where research efforts have been made in PC activation in order to maximize its surface area and minimize the sulfur and heavy metal contents. Activation of PC has been realized by either chemical or physical method (Azargohar and Dalai, 2008). The chemicals such as KOH (Bai et al., 2015; Hill et al., 2014; Otowa et al., 1997), H₃PO₄ or CaCl₂ (Lacerda et al., 2015), ZnCl₂ and H₂SO₄ (Wu et al., 2005), and NaOH (Kacan, 2016) are the most common agents used in activation of carbonaceous precursors. Although the detailed mechanism of chemical activation of carbonaceous material is not fully understood yet (Diaz-Terán et al., 2003; Raymundo-Piñero et al., 2005), in general, chemical activation by alkalis consists of solid–solid or solid–liquid

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reactions involving the hydroxide reduction and carbon oxidation to generate porosity. During the reactions, CO, CO₂ and H₂ evolution was observed (Raymundo-Piñero et al., 2005). Also, potassium may form –OK groups by the oxidation of cross-linking carbon atoms, and the formation of surface groups in the edge of the lamellae would cause the separation of carbon lamellae (Diaz-Terán et al., 2003). The other mechanism of KOH activation of PC could be dehydration of KOH into K₂O at elevated temperatures, and then reduced into metallic potassium by carbon. Metal potassium then intercalates into pseudo-graphitic layers to develop the porosity after washing the treated carbon with HCl and water to completely remove residual K, K₂O, K₂CO₃, and KOH (Qiao et al., 2006). Furthermore, existence of volatile compounds in PC might cause formation of pores at elevated temperatures during the activation process (Qiao et al., 2006).

The objective of this study was to determine the optimum conditions of the KOH activation process for PC in order to maximize the adsorption capacity of naphthenic acids model compounds. KOH was selected as the agent for PC activation because of its effectiveness, availability and cost (Kawano et al., 2008). Produced APC adsorbents exhibited significant adsorption capacities for the removal of model NAs (Niasar et al., 2016; Zhang et al., 2015). The APC has the potential to be used in many processes such as wastewater treatment (Pourrezaei et al., 2014; Yuan et al., 2010; Zhang et al., 2015), decolorization, gas separation, catalysts for oxidative reactions and reductive reactions, etc. (Wu et al., 2005).

The main objective of this research was to obtain the optimum parameters (i.e., temperature, KOH/coke ratio, and the activation time) for the KOH activation process for PC using surface response methodology (SRM) in order to maximize the adsorption of naphthenic acid model compounds. A Box-Behnken design was employed to find the optimum condition of the process. The obtained APC adsorbents were then tested for adsorption of three naphthenic acid model compounds (cyclohexanepentanoic acid, 2-naphthoic acid, and diphenylacetic acid) and adsorption capacity was chosen as the objective function in the optimization. There is the possibility of metal ions and organics leaching out from APC (Pourrezaei et al., 2014), therefore, another objective of this work was to track the sulfur and heavy metals such as vanadium, nickel, and cobalt in PC before and after activation, as well as possible leaching of these metals and other organics during the adsorption process. To this end, the sulfur and heavy metal contents of PC were measured before and after activation, and the water phase after the adsorption process was analyzed for composition of metal ions and the dissolved organics concentration (DOC).

2. Material and methods

2.1. Materials and chemicals

The Syncrude petroleum coke (PC), used in this study as the precursor of activated carbon adsorbents, was supplied by NEW-ALTA Corporation (Burlington, ON). The raw PC has a BET surface area of <15 m²/g and a total pore volume of <0.01 cm³/g. The chemicals such as KOH, 2-naphthoic acid, cyclohexanepentanoic acid, HPLC-grade acetonitrile were purchased from VWR Company, (Mississauga, ON, Canada) and diphenylacetic acid, sulfuric acid 98%, hydrochloric acid 37%, perchloric acid 70%, and nitric acid 70% from Sigma-Aldrich, Canada. All chemicals were ACS reagent-grade and used without further purification. The basic properties of the selected model naphthenic acids are shown in Supplementary Table S1.

2.2. Petroleum coke activation

Potassium hydroxide (KOH) was used as the chemical agent for activation of PC. KOH and PC at different mass ratios were mixed together with adequate amount of water to make a thick slurry. The mixture was heated in an electric tubular furnace at approx. 20 °C/min up to a specific temperature for a specific period of time in nitrogen flow (5 mL/min). After the specific activation time elapsed, the reactor was cooled down to room temperature in presence of nitrogen gas, followed by washing the activated petroleum coke (APC) with HCl (37%) to remove the excess potassium hydroxide as well as some ash components. Then the sample was washed with sufficient amount of distilled water until the pH of the filtrate was equal to the pH of distilled water. In the next step, the washed APC was dried in air at 110 °C, then cooled down and stored in a sealed sample container for further use.

2.3. Surface characterization

A Nova 1200E, surface area and porosity analyzer (QuantaChrome Co.) was used to measure the pore size distribution and specific surface area of the prepared samples. SEM images were taken on an LEO (Zeiss) 1540 × B FIB/SEM microscope at UWO nanofabrication facility. This system was equipped with a sample transfer airlock, allowing rapid sample changes without disrupting the high vacuum of main chamber. The samples were coated with a thin layer of Osmium metal with a Filgen OPC80T Osmium Plasma coater before imaging by SEM. The Osmium film would enhance the secondary electron yield, prevent sample charging and reduce damage to delicate materials from the electron beam during imaging.

2.4. ICP analysis

ICP was applied for metal analysis of the PC samples before and after activation. In sample preparation, about 1 g of solid sample was grounded with a mortar-pestle. Then, 800 mg of grounded sample was weighed and put in a 250 mL beaker and mixed with 10 mL (70 wt%) nitric acid under gentle heating, followed by the addition of 8 mL (70 wt%) perchloric acid until the solution became colorless. After cooling, 30 mL of water was added, followed by gentle heating for 10 min. After the solution was cooled down, the volume of the solution was adjusted to 100 mL with MilliQ water. Subsequently, the solution was filtered through a 0.45 μm filter to remove any particulate matters. Finally, 12 mL of particle-free sample was used for ICP analysis.

2.5. Leaching test

In order to investigate leaching of any organic or inorganic compounds from the APC, about 1 g of the APC material was weighed and mixed with 250 mL MilliQ water under stirring for 24 h. DOC and ICP analyses were then performed to measure the organics and metals leached from APC adsorbents. Only, the APC samples which had very high adsorption capacity were tested for leaching.

2.6. Design of experiments and statistical analysis

The Box-Behnken design (Supplementary Fig. S1) was employed to optimize the PC activation parameters such as activation temperature, KOH/coke mass ratio and activation time. For each parameter, three levels were selected: such as temperature, 650, 750, and 850 °C, KOH/coke ratio, 1, 2, and 3, and time of activation, 60, 120, and 180 min. The ranges of parameters were chosen based

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