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Production, characterization, and evaluation of activated carbons from de-oiled canola meal for environmental applications

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ABSTRACT

The objective of this study was the utilization of waste canola meal to produce activated carbons for environmental applications. Activated carbons were produced from de-oiled canola meal (DOCM) by slow-pyrolysis followed by physical (steam and CO_2) and chemical (NH_3 and KOH) activations. Physico-chemical characteristics of the precursor and activated carbons were investigated using BET, FTIR, SEM, TGA, Boehm, CHNSO, and particle size analysis. The effect of activation methods on porous structure and surface chemistry of activated carbons was investigated. Activated carbons produced from canola meal were evaluated for their efficiency as adsorbents for ammonium ion adsorption from aqueous solutions. The effect of pH, surface area, and surface functional groups of activated carbons was examined on adsorption of ammonium ion at 260.0 mg/L. The role of both porous structure and surface functionality of activated carbons was studied as a function of adsorption of ammonium ion. The results showed that the maximum adsorption (q_e) of ammonium ion was 55.4 mg/g for steam activated carbon, 17.9 mg/g for CO_2 activated carbon, 56.7 mg/g for ammonia-treated activated carbon, and 148 mg/g for KOH activated carbon.

1. Introduction

Canada is the largest producer and exporter of canola (rapeseed) worldwide. In 2013, Canada processed 9.0 million tons of canola seed that yields approximately 3.0 million tons (MT) of canola oil and 4.0 million tons of canola meal as a by-product (Canola Council of Canada, 2013). The Canola Council of Canada (CCC) targets a 45% increase in canola oil production by 2015, which will also result in the generation of a large amount of canola meal.

Canola meal is used in the production of industrial enzymes, antibiotics, bio-pesticides, vitamins, and other bio-chemicals (Ramachandran et al., 2007). It is used in cattle, swine, fish, and poultry farms (Canola Council of Canada, 2011) due to its high nutritional value, but the presence of anti-nutritional agents such as phytic acid, sinapine, phenolic compounds, and glucosinolate (Table 1) limit its utilization as animal feed (Bell, 1993). Glucosinolate (an organic compound that contains sulfur and nitrogen) breaks down into toxic metabolites such as aglucones, isothiocyanates, thiocyanates, and nitriles in the digestive tract of animals that cause sickness, hypothyroidism, and liver damage (Canola Meal Guide, 2009). For this reason, agricultural industries use a considerable amount of canola meal as fertilizer (Bonnardeaux, 2007) and as a medium component in the fermentation process for the production of enzymes (Jensen et al., 1990). Recently, partially carbonized de-oiled canola meal was used as a support for the preparation of solid-acid catalysts for bio-diesel production (Rao et al., 2011).

There is a growing demand for activated carbons produced from agricultural and forest by-products and residual wastes. Activated carbon is produced from various carbonaceous materials like coconut shell (Gratuito et al., 2008), rubber wood (Srinivasakannan and Zailani Abu Bakar, 2004), synthetic crude coke (DiPanfilo and Egiebor, 1996), broiler litter (Lima et al., 2008), oil palm shell (Alam et al., 2007), paper mill sludge (Khalili et al., 2000), waste walnut shell (Kim et al., 2001), bagasse and rice husk (Kalderis et al., 2008), natural cellulose (jute and coconut) (Phan et al., 2006), almond shell, hazelnut shell, and apricot stone (Aygün et al., 2003), lignite (Skodras et al., 2002), acorns and olive seeds (Walid, 2001).

Abbreviations: ACs, activated carbons; AOCS, American Oil Chemists' Society; BOC, biochar (Pyrolized canola meal); CAC, CO_2 activated carbon; CCC, Canola Council of Canada; CM, canola meal; DOCM, de-oiled canola meal; SAC, steam activated carbon; NAC, NH_3 activated carbon; VMD, volume mean diameter.

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Table 1
Composition of canola meal and de-oiled canola meal.

Composition	Canola meal[+]	De-oiled canola meal from this work
Oil (%)	3.5	3.4
Protein (%)	36.0	38.8
Fiber (%)	11.8	12.0
Moisture (%)	7.0	6.0
Ash (%)	7.2	7.0
Carbohydrate (%)	34.7	35.9
Antinutritional factors		
Phytic acid (%)	3.3	–
Glucosinolates (μmol/g)	7.2	–
Phenolics		
Sinapine	1.0	–
Tannins	1.5	–

[+] http://www.canolacouncil.org/oil-and-meal/canola-meal/nutrient-composition-of-canola-meal/.

Activated carbon is used in fields for water and air treatments (Brasquet and Le Cloirec, 1997), as adsorbents in gas filters (Shiue et al., 2010), in hydrogen production (Ginosar et al., 2011; Wang et al., 2011a; Abbas and Daud, 2009; Zhang et al., 2007), adsorption for Cu^{2+} ion (Kim et al., 2001), H_2S oxidation (Rambabu et al., 2013; Bagreev and Bandosz, 2001), and CO_2 capture (García et al., 2011; Plaza et al., 2010).

Ammonium ion is a major pollutant in surface and ground water, due to industrial, municipal, and agricultural waste water streams. In high concentrations, it is toxic to human health, flora, and fauna, and contributes to oxygen depletion in the environment and eutrophication of surface water. The National Academy of Sciences and many European countries have recommended a limit of the concentration of ammonia at 0.5 mg/L in drinking water (Chapman, 1992). Canadian drinking water guidelines limit free ammonia concentration in distribution system below 0.1 mg/L, and preferably below 0.05 mg/L, measured as nitrogen (Health Canada, 2013). Presently, the average concentration of ammonia reported in hazardous waste sites is 1 to 1000 ppm in soil samples and up to 16 ppm in water samples (ToxProfile of Ammonia, ASTDR); therefore, there is an urgent need to produce cost-effective adsorbents to remove ammonium ion (NH_4^+) from water for industrial and domestic use. Scientists are putting enormous efforts to develop newer processes to reduce the levels of ammonium ion in water and air, but the technologies are not commercially amenable due to high cost and longer processing time.

The main objectives of the present study are: (1) utilization of de-oiled canola meal (DOCM) for the production of high surface area activated carbons using steam, CO_2, ammonia, and KOH activation; (2) characterization of activated carbons; (3) to evaluate and compare the efficiency of activated carbons produced by different activation methods for ammonium ion adsorption from aqueous solutions.

2. Materials and methods

2.1. Materials

Canola meal obtained from Bungi Oil Industries (Saskatoon, SK, Canada) was sieved to particle size ranging from 250 to 1000 μm. Analytical grade chemicals KOH and NH_4OH were obtained from VWR chemicals. Ammonia, nitrogen, and air were procured from Praxair Canada.

2.2. Reactor set-up and production of activated carbons

A schematic of the experimental set-up for physical and chemical activation processes and the experimental procedure were described in our previous study (Rambabu et al., 2013). Canola meal (100 g) was de-oiled by Soxhlet extraction (AOCS, 2001) using haxanes and a schematic of the preparation of de-oiled canola meal (DOCM) is presented in Fig. 1. Canola meal was obtained from Bungi oil industries which was produced from canola seeds by solvent extraction process that involves dehulling, screw pressing, and the removal of monounsaturated omega-9 fatty acid. DOCM produced after Soxhlet extraction was used for preparing activated carbons. The samples were named according to their activation methods: Bio-char as BOC (prepared at 500 °C by pyrolysis of DOCM); steam-activated carbon as SAC; CO_2 activated carbon as CAC; NH_3 treated activated carbon as NAC, and KOH activated carbons as KAC.

2.2.1. Steam activation

A tubular-fixed bed reactor was used for the activation process. BOC (10.0 g) was placed in the reactor, and the nitrogen flow was adjusted to 50 mL/min. The temperature was increased to reach the activation temperature (700–900 °C) at a heating rate of 3 °C/min. Experimental parameters such as the effects of activation temperature, water flow rate (7–9 g/h), and activation time (60–120 min) were studied to determine optimum operational conditions. Once the activation temperature was reached, steam was injected into the system and the activation was carried out for the required activation time. After activation, the sample was cooled to ambient temperature under N_2 at a flow rate of 50 mL/min.

2.2.2. CO_2 activation

BOC (7.0 g) was loaded into the reactor and then heated to 800 °C at a rate of 3 °C/min with N_2 gas at a flow rate of 50 mL/min. Then CO_2 gas was introduced into the reactor at a flow rate of 24 mL/min for 120 min. After activation, the solid sample was cooled to room temperature under N_2 flow (Zhang et al., 2004).

2.2.3. KOH activation

KOH activation was accomplished in two steps. In the first step, 3 wt% of KOH and 1 wt% BOC were mixed in 100 mL of water. This mixture was shaken at 150 rpm for 2 h at room temperature and then kept at 105 °C in a hot air oven for overnight. In the second step, 10.0 g of KOH impregnated BOC was placed in a fixed-bed reactor under nitrogen flow (50 mL/min), then heated to 300 °C at 3 °C/min and continued at this temperature for 1 h to prevent carbon loss (Otowa et al., 1997). Further the temperature was increased at the same heating rate to reach the activation temperature of 800 °C, and the chemical activation was carried out for 120 min at this temperature. The KOH activated biochar was washed with water, followed by 0.1 M HCl, and then washed with distilled water to remove potassium compounds. When the pH of the washed water was in the range of 7 ± 0.2, the samples were dried at 105 °C for 6 h (Aik Chong Lua and Ting Yang, 2004).

2.2.4. NH_3 treatment

The reactor was loaded with 10 g of BOC, and the reactor temperature was increased to 700 °C at a rate of 3 °C/min under N_2 flow at a rate of 50 mL/min. After the activation temperature was reached, the gas was switched to ammonia and activation was performed for 120 min at an NH_3 flow rate of 50 mL/min. The reactor was cooled down to room temperature at the end of the run under N_2 atmosphere (Przepiórski, 2006).

2.3. Ammonium ion adsorption

The experiments for ammonium ion adsorption were conducted at an initial concentration of 260.0 mg/L of ammonium hydroxide at room temperature (20 °C). Activated carbon (1.25 g) was added to 125 mL of ammonium hydroxide solution in a sample bottle. The sample bottles were shaken at 200 rpm using an orbital

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