Short Communication

Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K_2CO_3 activation

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ABSTRACT

Rice husk (RH), an abundant by-product of rice milling, was used for the preparation of activated carbon (RHAC) via KOH and K_2CO_3 chemical activation. The activation process was performed at the microwave input power of 600 W for 7 min. RHACs were characterized by low temperature nitrogen adsorption/desorption, scanning electron microscopy and Fourier transform infrared spectroscopy. The adsorption behavior was examined using methylene blue as adsorbate.

The K_2CO_3-activated sample showed higher yield and better pore structures and adsorption capacity development than the KOH-activated sample, with a BET surface area, total pore volume and monolayer adsorption capacity of 1165 m^2/g, 0.78 cm^3/g and 441.52 mg/g, respectively. The results revealed the feasibility of microwave heating for preparation of high surface area activated carbons from rice husks via K_2CO_3 activation.

1. Introduction

Activated carbon adsorption has been recognized as an effective means for reducing organic chemicals, chlorine, heavy metals, unpleasant tastes and odours from gases or liquid waste streams (Wen et al., 2011). Despite its prolific use in adsorption processes, the biggest barrier to wider applications of activated carbons are the cost-prohibitive lengthy pyrolysis and activation processes, which involve high energy consumption, require large equipment, and are prone to generate unsuitable heating rates, resulting in detrimental effects on the quality of the activated carbons (Yang et al., 2010). Therefore, it is necessary to find a rapid and easy route for the preparation of activated carbon.

Although microwave heating is today a mature technique which finds wide applications in material science, food processing and analytical chemistry, there are relatively few studies on the preparation of activated carbon by microwave heating (Foo and Hameed, 2009a). According to the Food and Agriculture Organization (FAO), approximately 120 million tons of RH biomass waste is generated annually by the rice milling industries (UNCTAD, 2008). Some of these materials could potentially be used to make higher-value products (Foo and Hameed, 2009b). In the current study, rice husk was used as a low-cost material to prepare activated carbons using potassium hydroxide (KOH) and potassium carbonate (K_2CO_3) as activating agents under microwave irradiation.

Structural, functional and pore size characterizations of the prepared adsorbents were performed, and their adsorption equilibriums for methylene blue and their nitrogen isotherms were elucidated.

2. Methods

2.1. Adsorbate

Methylene blue (MB), a cationic dye purchased from Merck Limited Company, Malaysia was chosen as the model adsorbate. Working solutions were prepared from an aqueous stock solution (1000 mg/L) by dilution with distilled water.

2.2. Preparation and characterization of adsorbent

Rice husk (RH) was obtained from a local rice milling factory and processed as described by Foo and Hameed (2011). Briefly, the dried sample was carbonized at 700 °C under purified nitrogen (99.995%) flow. The char produced was soaked in potassium hydroxide (KOH) or potassium carbonate (K_2CO_3) solution with an KOH/char (or K_2CO_3/char) impregnation ratio of 1:0.75 (wt.%). The activation step was conducted in a tubular glass reactor with a microwave input power of 600 W and irradiation time of 7 min. The activated products were washed with deionized water and 0.1 N hydrochloric acid until the pH of the washing solution reached 6–7. Activated carbons obtained from KOH and K_2CO_3

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activation were denoted as KAC and KCAC, respectively. The yield (Y) of the carbon samples was estimated by:

$$Y(\%) = \frac{m}{m_0} \times 100\% \tag{1}$$

where m is the weight of activated carbon and m_0 is weight of the air-dried biomass.

Scanning electron microscope (SEM) analysis was performed to study the textural structure of adsorbent before and after the activation process. Surface physical properties of char, KAC and KCAC were characterized with a Micromeritics ASAP 2020 instrument, using N_2 as the adsorbate at 77 K, while surface functional groups of char, KAC and KCAC were detected by Fourier transform infrared (FTIR) spectroscopy (FTIR-2000, PerkinElmer) by scanning in the range of 4000–400 cm^{-1}. The ash content was determined according to ASTM D 2974 (ASTM D 2974-87, 1987) by igniting the oven-dried sample in a muffle furnace at 750 °C until the heating sample was completely ashed. The ash content was expressed as the percentage of mass of the oven-dried sample.

2.3. Equilibrium sorption studies

Equilibrium sorption studies were conducted in a set of 250-mL Erlenmeyer flasks containing 0.10 g adsorbent and 200 mL dye solutions with various initial concentrations (50, 100, 200, 300, 400, and 500 mg/L). The flasks were agitated in an isothermal water-bath shaker at 120 rpm and 30 °C until the equilibrium was reached. MB uptake at equilibrium, q_e (mg/g), was calculated by Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V(L) is the volume of the solution, and W(g) is the mass of adsorbent used. The effect of pH on MB removal was tested by varying the pH from 2 to 12, with initial MB concentration of 300 mg/L, RHAC dosage of 0.10 g/200 mL and adsorption temperature of 30 °C.

2.4. Equilibrium modeling

Equilibrium data were simulated using Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) isotherm models:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e \tag{3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where Q_0 (mg/g) and K_L (dm^3/g) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively; and K_F (mg/g) (L/mg) and $1/n$ are the Freundlich adsorption constant, and a measure of the adsorption intensity.

3. Results and discussion

3.1. Characterization of RHAC

The examination into the textural structures of RH derived char and activated carbons were evaluated from scanning electron micrographs (Supplemental Fig. 1). The images showed that the pores formed during the carbonization stage were narrow, constricted and dispersed by deposited tarry substances. The microwave irradiated samples (KAC and KCAC) demonstrated highly porous structures, implying pores development during the microwave irradiation.
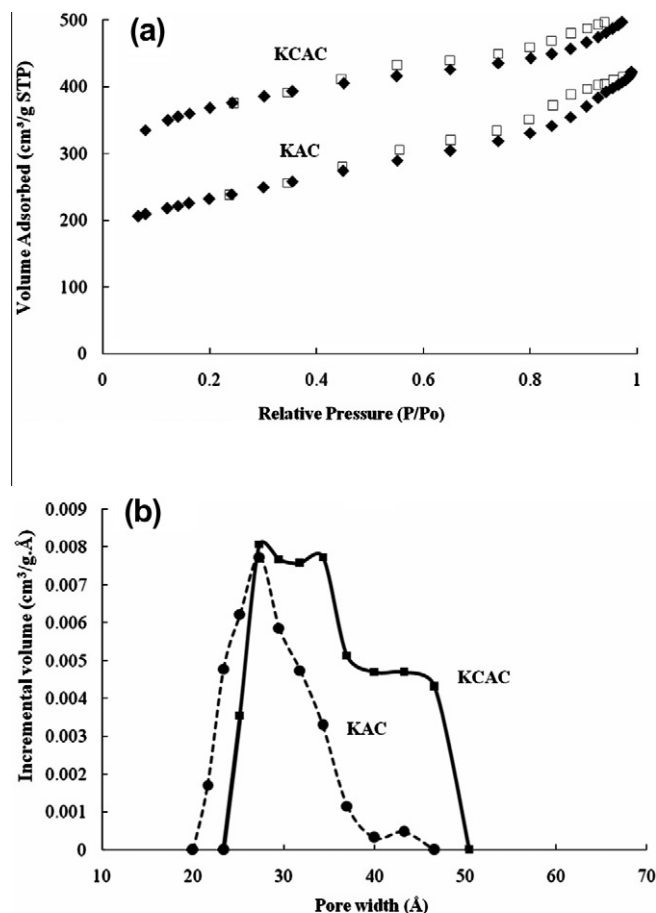

Fig. 1. Nitrogen isotherms (a) and pore size distributions (b) of KAC and KCAC.

The FTIR spectrum of char (Supplemental Fig. 2) reveals peaks at 3233, 2375, 1421, 1076, 802, and 460 cm^{-1}, indicative of the presence of N–H, C≡C (alkynes), in-plane O–H blend, C–O–C (esters, ether or phenol), out-of-plane C–H bending vibrations, and C–H (benzene derivatives) functional groups. Whereas, intensive peaks for KAC and KCAC were observed 3436, 3247, 2362, 1421, 1261, 1054, 913, and 802 cm^{-1} that could be assigned to N–H, –CH_2 (alkyl), C≡C (alkynes), in-plane O–H blend, –OH (hydroxyl), C–O stretch, –R–COO and out-of-plane C–H derivatives.

The corresponding nitrogen isotherms of KAC and KCAC present a I–II hybrid shape of the referred International Union of Pure and Applied Chemistry (IUPAC) classification, associated with a combination of microporous and mesoporous structures (Fig. 1a). Detailed characteristics of the porosity of char, KAC and KCAC are summarized in Table 1. The pore properties of KAC and KCAC were significantly improved compared to char, since additional pores developed during the microwave irradiation stage. According to Marsh and Rodriguez-Reinoso (2006), porosity development by KOH activation is associated with gasification:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \tag{5}$$
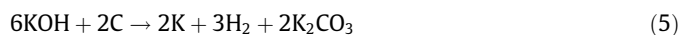
Concurrently, K_2CO_3 activation involved the reduction of K_2CO_3 under inert condition to form K, K_2O, CO and CO_2. The potassium compound formed during the activation step diffuses into the internal structure of char matrix, widens the existing pores and creates new porosities, in according with the following reactions (McKee, 1983):