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Surface modification of bone char for removal of formaldehyde from air

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ABSTRACT

The aim of this study was to evaluate the adsorption performance of bone char (BC) modified with acetic acid for formaldehyde removal from polluted air. The porous structure, surface characteristics and functional groups involved in formaldehyde adsorption were determined using the Brunauer–Emmett–Teller (BET) method, scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) and Fourier transform infrared spectroscopy (FTIR), respectively. It was found that the modified BC has a higher specific surface area than the original BC. The maximum surface area of the modified BC was 118.58 m^2/g. The FTIR spectrum of modified BC indicated that the hydroxyl and carboxyl groups on the BC surface played a significant role in the adsorption of formaldehyde by modified BC. The breakthrough, equilibrium time and adsorption capacity of modified BC were greater than the original BC. Moreover, the results showed that at initial concentrations of 20, 50, 100 and 200 mg/L, the equilibrium times for BC and modified BC were 85, 75, 65 and 45 min and 95, 85, 70 and 50 min, respectively. It seems that the formaldehyde adsorption capacity of modified BC depends on both physical and chemical properties. These results showed that modified BC can be used as an efficient adsorbent for formaldehyde removal.

1. Introduction

Formaldehyde is a common industrial chemical used for the production of various compounds. Formaldehyde has been extensively used for the production of building materials such as pressed wood, wallpaper, and paint. The formaldehyde produced from industrial activities could be emitted for a long time after its production [1,2]. People are mostly exposed to formaldehyde by inhalation, which causes headaches, difficulty breathing and aggravated asthma symptoms [3]. Moreover, formaldehyde has been categorized as a human carcinogen by the International Agency for Research on Cancer (IARC) and as a probable human carcinogen by other health-related organizations [4]. Formaldehyde, an indoor volatile organic compound (VOC), exists in modern building and household products [5]. Therefore, it seems the purification of ambient air containing formaldehyde is essential for improving indoor air quality and human health. Various engineering processes are used to remove VOCs such as formaldehyde from ambient air [6]. These techniques are categorized into two broad groups: oxidation and recovery. Oxidation methods could convert volatile organic compounds into non-toxic materials such as carbon dioxide and water. These methods have several disadvantages, such as the difficulty of VOC recovery from air, high cost and high energy usage [7]. By comparison, the recovery of organic solvents is a more practical process, based on energy savings and environmental effects. Recovery methods include adsorption by solid sorbents, absorption by liquid sorbent, ion-exchange, condensation and membrane technology [8]. Among the presented methods, the adsorption method is considered to be the most promising method for recovery of volatile organic compounds. With regard to effectiveness and simplicity, the adsorption method can be used for formaldehyde removal, because it is selectively possible to adsorb a pollutant via the pore structure of the adsorbent [9]. In the adsorption process, the characteristics of the adsorbate and adsorbent determine adsorption efficiency. Therefore, the selection of a suitable adsorbent is critical. There are different materials that can be proposed as an adsorbent for the removal of organic pollutants [10]. Carbonaceous adsorbents such as activated carbon were extensively utilized to remove organic pollutants from air [11]. However, it has been shown that activated carbon produced from conventional sources could not efficiently remove formaldehyde vapor from air. Among the materials used for adsorbent synthesis, BC has been widely used for the removal of different pollutants from drinking water [12]. It has been proposed that poorly crystallized apatite, such as BC, can be used as an effective adsorbent because of its low cost and availability [13,14]. Many animals have a large number of bones that can be used as feedstock or fuel for energy

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generation after slaughterhouse processing. On the other hand, functional groups on the surface of BC show an ideal adsorption capacity for polar or polarizable molecules after suitable modification. Increasing attention has been paid to modified adsorbents for the removal and recovery of different pollutants such as metal ions [15], organic dyes [16], and immobilization of enzymes or proteins [17]. These applications could be related to the functional groups on the surface of adsorbents, which can be modified appropriately. In the present work, we perform a study of the modification of BC by acetic acid as a weak organic acid. Treating adsorbent with an acid leads to an efficient elimination of surface impurities and formation of additional functional group [18]. To the best of our knowledge and based on the literature, there is no previous report on the adsorption of formaldehyde using modified BC. Hence, the objective of the present study was to investigate the removal of formaldehyde as a model of VOCs using modified BC. To reveal the relationship between structure and adsorption properties of the modified BC, the surface characterization of the adsorbent was determined using BET, SEM and FTIR. Also, the breakthrough time and adsorption capacity of BC for formaldehyde removal were investigated to evaluate the process.

2. Materials and methods

2.1. Preparation of modified BC

Bones from cattle and sheep were crushed into pieces of 10–15 cm in length, then rinsed three times in deionized water for 4 h to remove fat and residual protein pieces. The resulting bone fragments were dried at 110 °C overnight and cooled in a desiccator. Pyrolysis of the bones was performed in a rectangular furnace at 450 °C for 4.5 h to produce BC. The BC was pulverized using ASTM standard sieves (20–40 mesh). Modification of the BC was carried out by impregnating BC with acetic acid (1 N) solution. Briefly, 3 g of BC was added to 50 mL acetic acid (1 N) at room temperature and allowed to stand for 12 h. The BC was dried in an oven at 110–120 °C for 5 h.

2.2. BC characteristics

Specific surface areas of the prepared BC were determined by the nitrogen adsorption–desorption isotherms measured by a Gas Sorption Analyzer (Quantachrome Corp., NOVA-1200). The specific surface areas were calculated using the BET method. Pore diameter and pore size distribution were determined by the Barrett–Joyner Halenda (BJH) method. The BC structure was analyzed using SEM (XL, 30 Philips). FTIR spectroscopy was used to identify the functional groups involved in formaldehyde adsorption before and after the adsorption process. The samples were ground to an average diameter of 0.5 μm. The transmission spectra of the samples were recorded using a KBr pellet containing 0.1% sample. The 12.7 mm diameter, 1 mm thick pellets were prepared in a manual hydraulic press and dried overnight at 100 °C before the spectra were recorded. The spectra were measured from 4000 to 400 cm^{-1} and recorded on a 1760X spectrometer (Perkin-Elmer, Germany).

2.3. Reactor setup

A schematic diagram of the reactor for formaldehyde adsorption in a continuous flow mode is shown in Fig. 1. The adsorption column was made from a Pyrex glass tube (5 mm diameter and 100 mm in length) loaded with an average weight of 100 mg adsorbent. The system consists of three sections: feed system, adsorption column and gas detection equipment. The feed system includes an air pump, a dehumidifier, a rotameter, the formaldehyde solution and a mixer equipped with an electric fan, which can adjust and control the influent formaldehyde concentration.

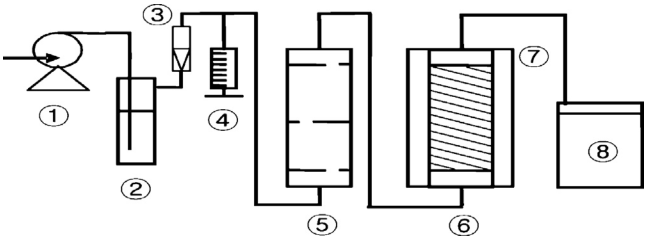

Fig. 1. Schematic flow diagram of experimental reactor [(1) air pump, (2) drying bottle, (3) flow meter, (4) formaldehyde solution, (5) mixing chamber, (6) adsorption bed, (7) jacket, (8) detector].

2.4. Experimental procedure

Formaldehyde solution and acetic acid were purchased from Merck Co. Formaldehyde vapor was generated by flowing air through the formaldehyde solution to the adsorption column. The concentrations of gaseous formaldehyde generated in the experiments were 20, 50, 100 and 200 mg/L. The temperature of the adsorption column was maintained at 25 °C throughout the experiment. The breakthrough measurements were made with a constant contact time for all experiments. Formaldehyde was injected until adsorption reached equilibrium. When the effluent concentration of the formaldehyde reached its specified influent concentration (i.e., 100% breakthrough), measurement of the effluent gas concentration was stopped. The concentrations of formaldehyde at the outlet were measured by a direct reading instrument (PhoCheck 5000) with a photo ionization detector (PID).The equilibrium adsorption capacity of BC for formaldehyde adsorption was calculated by the following equation:

$$q = (C_i - C)/w \times V \tag{1}$$

where q is the equilibrium adsorption capacity (mg/g), C_i and C are the initial and final concentration of formaldehyde (mg/m^3), respectively, and V is the volume of air (m^3).

3. Results and discussion

3.1. Adsorbent characteristics

Various properties of the adsorbents are presented in Table 1. The results showed that BC modified by impregnation with acetic acid solution yields a higher specific surface area. SEM micrographs with 5000× magnification are shown in Fig. 2. The SEM micrographs show that modified BC has fewer cavities and pores than unmodified BC. The composition of BC and modified BC was analyzed by energy dispersive X-ray (EDX) measurement, as shown in Fig. 3. The EDX analysis shows that the phosphorus and calcium contents in modified BC were less than in BC. The maximum surface area of the modified BC was 118.58 m^2/g. This property may be attributed to the removal of $CaCO_3$ from BC, due to the reaction of $CaCO_3$ with acetic acid. Hence, the modification process could change the surface characteristics of BC. Kumagai et al. showed that adsorption of formaldehyde and acetaldehyde vapor using rice

Table 1
Characteristics of the BC structure.

Adsorbent	Pore volume (cm^3/g)	BET (m^2/g)	Density (g/cm^3)	Pore diameter (nm)
BC	0.367	105.24	0.645	13.95
Modified BC	0.374	118.58	0.594	12.62