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Evaluation of CO_2 adsorption with eucalyptus wood based activated carbon modified by ammonia solution through heat treatment

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HIGHLIGHTS

- Activated carbon was prepared from eucalyptus wood with H_3PO_4 and modified by NH_3.
- AC surface chemistry and micropore structure improved by ammonia modification.
- AC modified by ammonia showed enhanced CO_2 loading relative to the untreated AC.
- Incorporation of nitrogen group in ACs increased their adsorption capacities.
- Adsorption isotherm, kinetic and thermodynamics of ammonia-treated AC were studied.

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ABSTRACT

Eucalyptus wood was used to produce activated carbon by chemical activation with H_3PO_4 as an adsorbent for adsorption of CO_2. It was subjected to thermal treatment with the ammonia solution at 400 and 800 °C in order to improve CO_2 capture. The textural and surface characteristics of the prepared activated carbons were determined from the analysis of N_2 adsorption isotherms, elemental analysis, Fourier Transform Infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM), acid–base Boehm titration and X-ray photoelectron spectroscopy (XPS). The results show that the modification of activated carbon at high temperature enhanced BET surface area and micropore volume. The results indicate that the physical parameters such as surface area, lower pore diameter, and larger micropore volume of carbon samples show influence on the adsorbed amount of CO_2. The adsorption behavior of CO_2 onto carbon samples was experimentally evaluated by volumetric method at temperatures ranging from 288 to 348 K and pressure range of 0–16 bar. The CO_2 adsorption capacity achieved by modified carbon was 3.22 mmol/g at 1 bar and 303 K which became more than the virgin carbon (2.9 mmol/g). The equilibrium CO_2 adsorption data were fitted by Langmuir and Freundlich isotherms models. The thermodynamic parameters were investigated and indicated that the adsorption process was spontaneous and exothermic in nature and physisorption was the dominant mechanism for CO_2 adsorption.

1. Introduction

Carbon dioxide is an important greenhouse gas released from power plants, gas processing industries, refineries, chemical and petrochemical industries, iron and steel industries, and cement industries [1,2]. The removal of carbon dioxide from flue gases achieves potential benefits including reduction of air pollution and global warming [1,3]. Currently, various CO_2 capture technologies such as solvent absorption, adsorption, cryogenics, membranes, microbial, and etc. are utilized to reduce it [2]. Adsorption is considered one of the most appealing technologies that can be applied in industries due to the low energy requirement, cost advantage, and simplicity of applicability over a relatively wide range of temperatures and pressures [4,5].

Among the many well-known adsorbents, activated carbons are a promising adsorbent for CO_2 adsorption due to large surface area and porosity, surface functionalization, easy to design pore structure, availability, low energy requirement for regeneration, hydrophobicity, and they are inexpensive [3,6]. It has been documented that CO_2 capture performance of activated carbon is depended on structural properties including surface area and pore

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size distribution, and the surface chemistry [6]. The modification of activated carbon surface by basic groups (amine groups) can enhance the adsorption capacity of acidic gases such as CO_2 [7]. Nitrogen can be incorporated into carbon structure by two techniques: (1) impregnation with nitrogen containing reagents (such as paraphenylenediamine, 4-aminobenzylanine,tri-ethylenetetramine, etc.) which lead to blockage of the porous structure and cause decrease in adsorption capacity of activated carbon [8,9] and (2) by preparing activated carbon from nitrogen containing polymers or by heat treatment of activated carbon with gaseous ammonia [5,7,9].

Heat treatment of activated carbon with ammonia was studied by several researchers. Pevida et al. [9] modified the surface of commercial activated carbon with ammonia at different temperatures, in the 200–800 °C range for CO_2 capture. The results showed that ammonia heat treatment at high temperature enhanced CO_2 adsorption capacity. Plaza et al. [10] investigated two different methods for production of CO_2 adsorbent from almond shells by ammonia treatment in pure ammonia (amination) and in a mixture of gases containing ammonia and oxygen (ammoxidation). They suggested that amination seem to be a suitable modification method for preparing effective CO_2 adsorbent. Shafeeyan et al. [5] investigated the effect of surface chemistry onto CO_2 adsorption capacity of activated carbon by two procedures: ammonia treatment without preliminary oxidation and amination of oxidized carbon at 400 °C and 800 °C. It was found that oxidation followed by ammonia treatment at 800 °C was a promising modification method for the preparation of activated carbon for CO_2 adsorbent which significantly improved the CO_2 uptake.

The objective of this study was to develop activated carbon adsorbent based eucalyptus wood with high CO_2 uptake capacity by heat treatment at 400 °C and 800 °C. The previous studies modified activated carbon with pure gaseous ammonia to incorporate amine groups into its structure lead to enhanced CO_2 adsorption. However, in this study, ammonia solution was applied for heat treatment which is expected to improve the amount of nitrogen incorporated into carbon and also CO_2 adsorption capacity.

2. Materials and methods

2.1. Materials

Eucalyptus camaldulensis wood residue was collected from Nour area in the north region of Iran, and was used as raw material for preparation of the activated carbon. This material was first crushed and then dried at 70 °C, ground, and sieved to obtain particle size in the range of 0.4–0.8 mm. Their properties, including ash content, volatile matter content and moisture content were determined by ASTM standard test procedures which were 4.8 wt., 80.4 wt., and 5 wt. respectively. The chemical (ultimate) analysis of eucalyptus wood was shown in Table 1. Furthermore, the chemicals for production of activated carbon such as phosphoric acid (H_3PO_4), hydrochloric acid (HCl, 37%) and ammonia solution (25%) used in this research were purchased from Merck Company (Germany).

Table 1
Chemical analysis of the raw material and the obtained activated carbon samples.

Sample	Ultimate analysis (wt.%)				
	C	H	N	S	O[a]
Raw material	48.2	6.2	<0.5	<0.1	44.1
Unmodified AC	77.78	1.68	0.52	0	20.03
AC-NH-400	70.35	1.32	3.14	0	25.19
AC-NH-800	77.46	1.65	7.76	0	13.12

[a] Calculated by difference.

2.2. Preparation of activated carbon

The activated carbon was produced from eucalyptus wood by chemical activation with H_3PO_4 by impregnation ratio of 2 g/g. The carbonization temperature was 450 °C. The detailed procedure of the preparation of activated carbon samples has been previously described [11].

2.3. Activated carbon surface modification

Eucalyptus wood based activated carbons was functionalized with ammonia, according to the method reported by Shafeeyan et al. [5] and Zhu et al. [12], while the modifying agent phase changed. They functionalized the surface of activated carbon samples with pure gaseous ammonia but in this study, heat treatment was conducted by ammonia solution as follows: first, the nitrogen gas was blown on the ammonia solution and then was introduced into the reactor.

For modification, first, 4 g of activated carbon was placed in the center of a tubular quartz reactor and then held in electrical furnace under a flow of 200 l/min nitrogen. The temperature was increased with heating rate of 10 °C/min to 400 °C. When the temperature reached 400 °C, the nitrogen gas was changed to ammonia at the same flow rate as the above-mentioned procedure. After holding 2 h at this temperature, the sample cooled down to 100 °C under the flow of ammonia and then changed back to nitrogen and was cooled to room temperature. The prepared sample was denoted as AC-NH-400. This route was conducted for modification of another activated carbon sample at 800 °C and the obtained matter named AC-NH-800.

2.4. CO_2 adsorption measurement

The CO_2 adsorption performance of activated carbon samples was evaluated using volumetric method. The schematic diagram of volumetric apparatus is shown in Fig. 1. The apparatus consisted of two high-pressure stainless steel vessels including the gas and adsorption cells, the volume of which was 144 ml and 30 cm^3, respectively. Both cells were placed into thermostatic water circulating bath (77960 Seelbach, Julabo Co, Germany) to keep the temperature constant during CO_2 adsorption. Two high precision pressure transducers measured the changes in pressure in gas and adsorption cell in each CO_2 adsorption experiment.

Prior to CO_2 adsorption experiments, activated carbon was degassed at 100 °C for about 24 h and the system was evacuated by vacuum pump. Helium gas was utilized as non-adsorbing gas to determine the dead volume. The CO_2 adsorption experiments were conducted at pressures ranging from 0 to 16 bar at different temperatures (288–348 K). Using the SRK equation of state in MATLAB program the amount of CO_2 adsorbed on activated carbon samples was calculated.

2.5. Characterization of activated carbon

The textural characterization of activated carbon samples was determined by N_2 adsorption isotherms at 77 K using ASAP (Micrometrics 2020, USA). Before starting the adsorption measurements, all the samples were degassed at 250 °C under vacuum for 2 h. The BET surface areas were calculated using BET (Brunauer, Emmet and Teller) method from adsorption data in the relative pressure range of 0.001–0.3. Total pore volume was measured from the amount of nitrogen adsorbed at P/P_0 0.99. MP method was used to determine the micropore volume while the mesopore volume was calculated by subtracting micropore volumes from total pore volume. The mesopore distribution was determined by applying the Barret–Joyner–Halenda (BJH) method. FT-IR spectra of the