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CO_2 Adsorption by Nitrogen-Doped Carbons Prepared from Biomass Soybean

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ABSTRACT

Nitrogen-doped activated carbon was synthesized by protein source from biomass soybean. Soybean is a significant and cheap source of protein which is nitrogen base compound. This work is intended to new carbonaceous adsorbents with nitrogen content in the carbon framework that applying CO_2 capture. The activated carbon was characterized using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and Fourier-transform infrared spectroscopy. Characterization results show nitrogen and oxygen functional group in activated carbon. This adsorbent has sufficient porosity whit high content of nitrogen (12 % wt.) makes it one of suggestion for CO_2 capture. The experimental value of adsorption modeled by Langmuir adsorption isotherm and good agreement capacity. The synthesized activated carbon demonstrates high CO_2 capture with 3.21 mmol/g at 25 ºC and 2 mmol/g at 50 ºC. The results showed that nitrogen doped of carbons can be used as potential adsorbent for CO_2 capture.

KEYWORDS

Activated carbon, Carbon dioxide, Nitrogen, Soybean, Adsorption.

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INTRODUCTION

One of the main causes of global warming is carbon dioxide which enters the atmosphere through burning fossil fuels and result of certain chemical reactions (refinery, cement manufacture, *etc*.). Carbon dioxide has become a serious problem for climate and sustainable human population on earth. This has promoted enormous research efforts in creating adsorbents for carbon capture and storage (CCS) technologies [1,2]. There are numerous challenges related to capturing and separation of CO_2. Conventional unit operations of CO_2 removal such as chemical absorption processes with amine-based solvents have some disadvantages that including high energy requirements, equipment corrosion, solvent degradation and expensive setup [3].

A column packed with activated carbon as sorbent for CO_2 capture have several advantages such as, lower energy requirements, milder operating conditions, *etc*. The adsorption technique is inexpensive set-up and operation and easy regeneration. Moreover, activated carbon has high adsorption capacity for CO_2 components rather than other nano-porous materials [1,3]. In recent years, researchers have been interested in new types of porous carbons for CO_2 capture which create from cheap and accessible materials and enhanced the adsorption selectivity and capacity. To increase selectivity and capacity of adsorption, often modified sorbent prepared by several method [4]. One of the modification method for adsorption of CO_2 in carbon porous is heteroatom doping [5,6]. Activated carbon have some intrinsic properties, these need to be controllably modified for many applications. One possible route is added atoms of a different element into the porous carbon networks as heteroatom dopants [7,8]. Carbon dioxide is a weak Lewis acid, so it has been tendency to interaction with nitrogen functionalities onto the surface of activated carbon which lead to increase performance of CO_2 capture [9].

The activated carbon can be obtained from various material like petroleum coke [5], waste rubber tires [10], polymer [11], *etc*. Among these materials, soybean and banana peel contain natural nitrogen atoms [1]. Soybean include proteins, nucleic acids and other nitrogen-containing components that are source of nature nitrogen which is cultivated worldwide [12]. In this study, soybean was obtain with nitrogen functionality onto the carbon surface. Protein in soybeans as a source of carbon and nitrogen is converted into activated carbon doped with nitrogen by pyrolysis under chemical activation. This N-doped carbon demonstrated high adsorption capacity of carbon dioxide. Absorption was carried out at two different temperatures (25 and 50 ºC).

EXPERIMENTAL

Biomass soybean was procured from Mosama Co. in Iran. First, the biomass soybean was washed by deionized water to remove dust and other impurities, and then dried at 105 ºC. It was crushed for carbonization. HCl and KOH (98 %) was purchased from Merck.

Preparation of activated carbon: In order to prepare activated carbon from soybean, the biomass soybean was firstly grounded and then put in cylindrical furnace and then, the temperature was ramped in 10 ºC/min up to 700 ºC. The pyrolysis was performed under N_2 (inert gas) flow with 100 cm^3/min. At the second step, 5 g of carbons were washed with 1 M KOH solution. Next, the mixture was stirred for 5 h at room temperature and then filtered and dried. Carbon put in horizontal cylindrical furnace under nitrogen flow at 350 ºC to get porous carbon. This activated carbon was washed with deionized- water for several times until the pH value approached 7 and dried.

Materials characterizations: The morphology of nitrogen doped activated carbons was investigated with scanning electron microscopy (SEM, Phenom ProX, Netherland) with gold coating combined with energy dispersive X-ray spectroscopy (EDX) by scanning electron microscopy (SEM, Phenom ProX, Netherland). X-ray diffraction (XRD) analysis was carried out by X'Pert Pro, Philips in 2θ range of 10-70º using $CoK_{\alpha 1}$ (α = 1.78897 Å) radiation and the working voltage and current of X-ray source are 40 kV and 40 mA, respectively. Perkin-Elmer infra-red spectrophotometer was used for the investigation of the surface functional groups.

CO_2 adsorption measurements: The CO_2 adsorption capacities determined using an experimental setup based on volumetric method. Carbon dioxide adsorption isotherms were performed at 323 and 348 K and pressures ranging from 0 to 1 bar. 100 mg of N-doped activated carbon was loaded into the adsorption cell. Constant temperature circulating bath was applied to maintain the setup at two temperatures. The adsorption capacity at different equilibrium pressure of CO_2 was determined by utilizing the difference of initial and final pressures in adsorption cell. The adsorbate gas was pure CO_2 (99.90 %) and the set-up was made as per reported method [13].

Adsorption isotherms: Adsorption isotherm describes relationship between the concentration of a compound sorbed to the solid phase and the concentration of the same compound in the bulk in contact with the solid phase that plotting at constant temperature. The Langmuir is a well-known equation assumes that a monolayer coverage of adsorbate takes place on a homogenous adsorption sites. The Langmuir isotherm equation is as follow:

$$q = q_m \frac{bP}{1+bP} \quad (1)$$

where q (mmol/g) is the amount of gas adsorbed per unit mass of adsorbent, q_m (mmol/g) is maximum adsorption capacity, P is the pressure and b is the Langmuir constant related to rate adsorption [14].

RESULTS AND DISCUSSION

Characterization of N-doped activated carbon: The morphology of nitrogen-doped activated carbon was investigated by scanning electron microscopy (SEM) analysis which is shown in Fig. 1. The carbon sample contains numerous sphere-like on the surface of larger particles, which are produced as a consequence of the hydrothermal carbonization of glucose and the saccharides present in the defatted soybean residue. Energy-dispersive X-ray spectroscopy (EDX) profile corresponding to SEM image confirmed the presence of nitrogen in porous carbon. Fig. 2 shows the EDX spectrum of nitrogen-activated carbon that clearly indicates the carbon-nitrogen peaks. Another item that is visible from the spectrum of EDX is the high purity of activated carbon. The EDX spectrum shows the nitrogen content in porous carbon is around 12%.

X-ray powder diffraction (XRD) is a rapid analytical technique primarily exerted for phase identification of a crystalline material and can provide information on unit cell dimensions. As can see in Fig. 3, two broad and weak peaks at 2θ equal to 28º and 51º were observed in the XRD pattern of activated carbon obtained biomass soybean which can be assigned to (002) and (100) diffractions of amorphous carbon [15]. As observed the asymmetric and board peaks represent the amorphous composition, but high temperature of the pyrolysis causes carbon surface partially crystalline [16]. In general, XRD peaks exhibit little crystallinity, which is a merit for absorbents.

The FTIR spectra of activated carbon sample was recorded to verify the successful existence of N-containing groups as shown in Fig. 4. The absorption band at 1620 and 3417 cm^{-1} are associated with the H-O-H bonding and hydroxyl groups, respectively [17]. Peak at 1381 cm^{-1} is associated with symmetrical stretching vibration of $-NO_2$. In addition, 1079 cm^{-1} is related to $-NH_2$ vibration bands. The band at 1088 cm^{-1} is due to C-N stretching oscillation of R_2NH structure. The band seen nearby 2924 cm^{-1} could be ascribe to ($-CH_2-$) [14]. All these materials characterizations test show the existence of surface N- and O-containing functional groups.

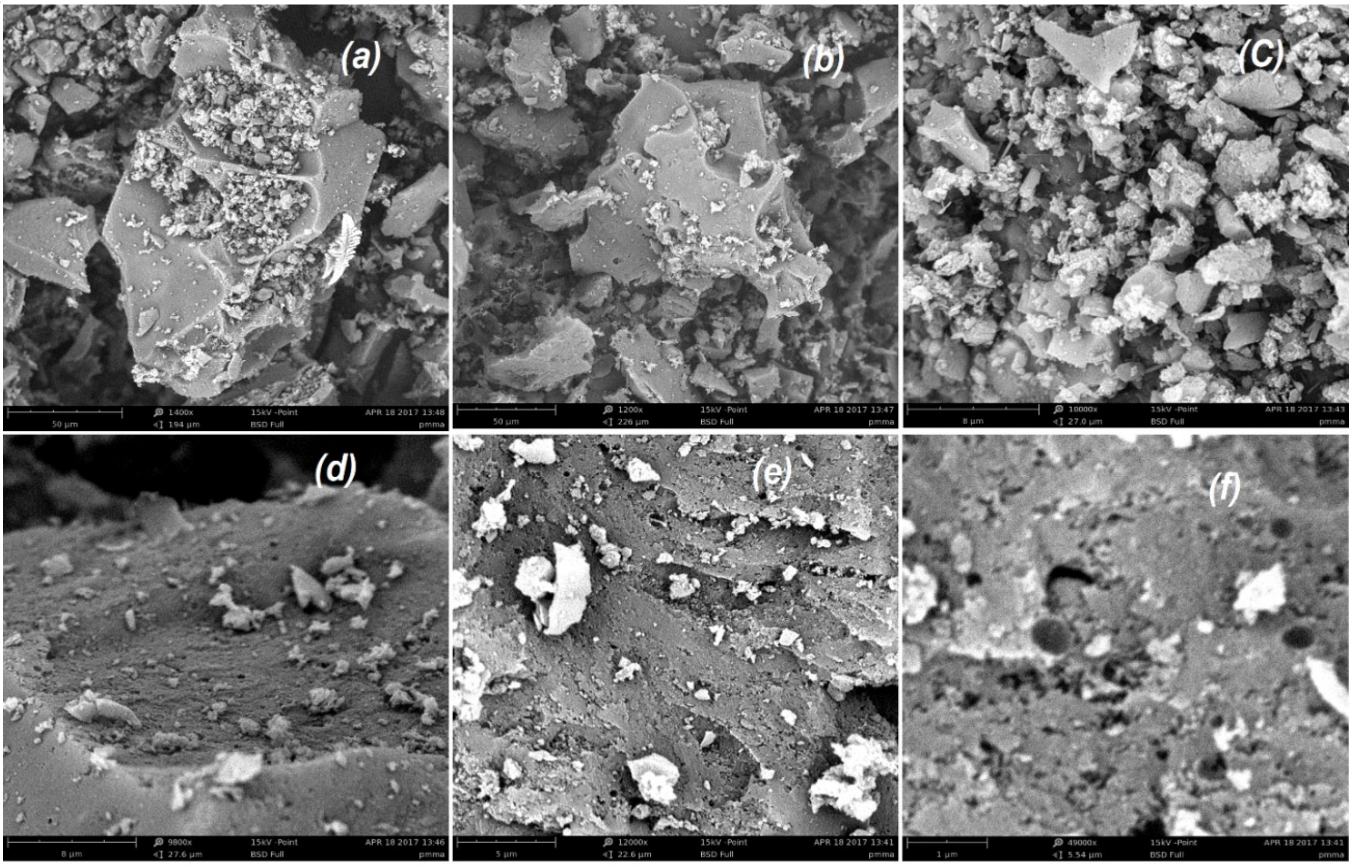

Fig. 1. SEM images of bio soybean activated carbon

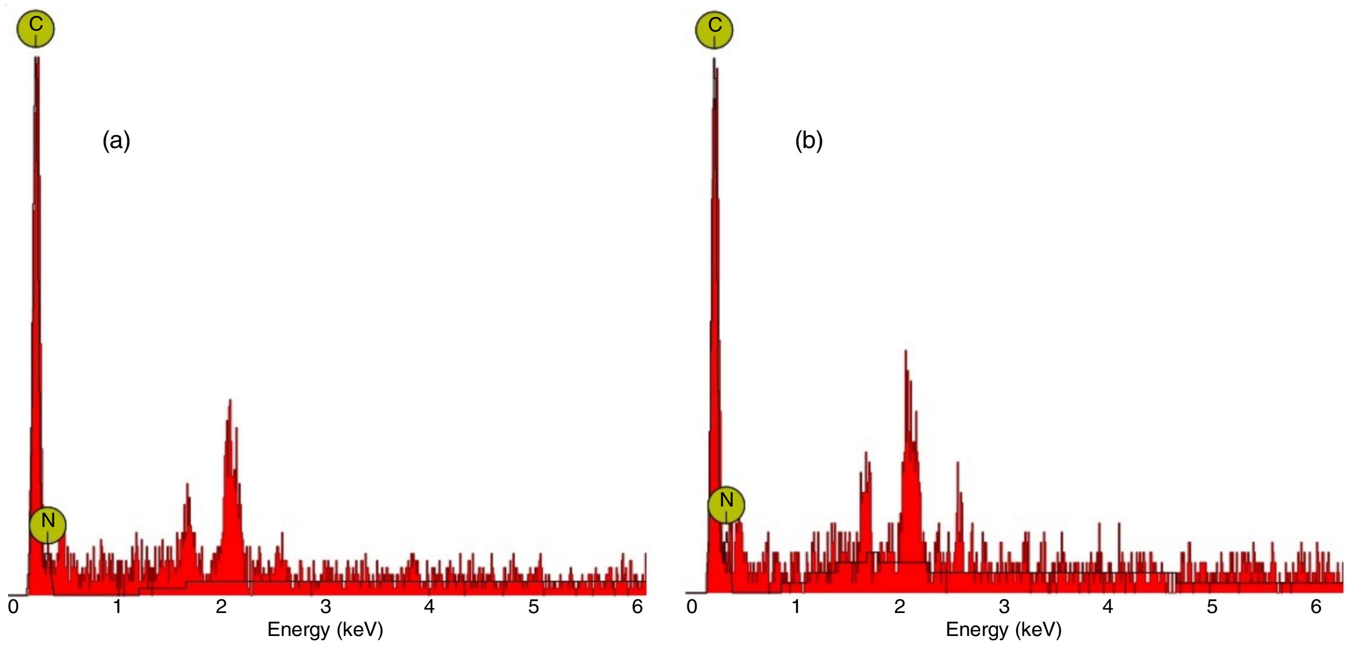

Fig. 2. EDX line analysis of N-doped carbon

Adsorption of CO_2: It is generally believed that high CO_2 adsorption capacity depends on large specific surface area and advanced pore structure [18]. The CO_2 adsorption capacity of activated carbon sorbent was investigated under 1 bar at 25 and 50 ºC (Fig. 5). The CO_2 capture by adsorbent rich in nitrogen has been less studied. As compared to commercially available activated carbons, the N-doped carbon with short diffusion distance, fast mass diffusion, high selectivity and well-defined for CO_2 adsorption [19]. It is observed that CO_2 adsorption at 323 K was 3.21 mmol/g and at 348 K was 2 mmol/g that was carried out by fitting experimental data to Langmuir isotherm. The CO_2 adsorption in nitrogen-doped carbon can be explained by acid-base interactions and hydrogen. The temperature effect on adsorption capacity is high. Correlation coefficient

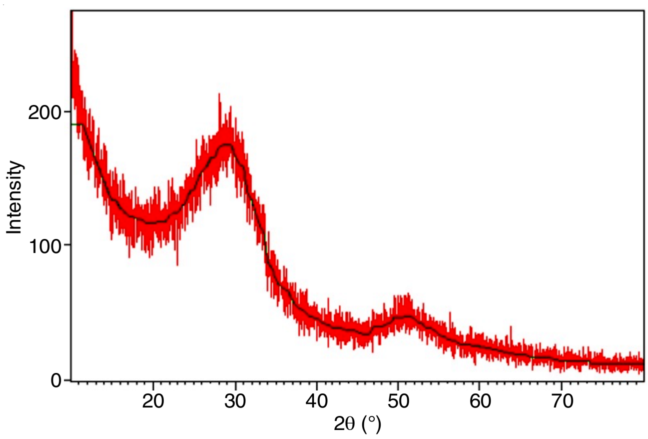

Fig. 3. XRD patterns of the activated carbon

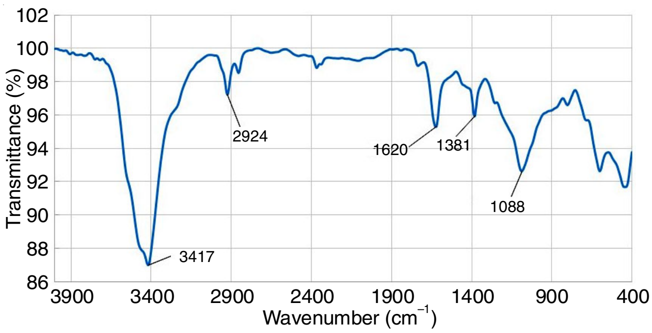

Fig. 4. FT-IR spectra of N-doped activated carbon

of Langmuir isotherm measured and had values of 0.96 and 0.98 for 323 and 348 K, respectively (Table-1). The adsorption capacity of activated carbon for carbon dioxide is not high, if it is compared with other same work. The low adsorption capacity can be assumed that pyrolysis temperature was low and some pore were closed by undesired particles.

TABLE-1
LANGMUIR ISOTHERM FOR CO_2 ADSORPTION

Temp. (K)	Sorption capacity (mmol/g)	Langmuir isotherm constant ($mbar^{-1}$)	Correlation coefficient (r^2)
323	3.21	0.0045	0.96
348	2	0.0025	0.98

Conclusion

Biomass soybean was applied as precursors to prepare of N-doped activated carbon. The sample was characterized by EDX which shows that nitrogen content in porous carbon is ~ 12 % wt. Moreover, CO_2 adsorption indicates that nitrogen functional group on carbon surface with FT-IR that lead to high adsorption capacity in carbon dioxide. This is because CO_2 is a weak Lewis acid, so it has been tendency to interaction with nitrogen functionalities onto the surface of activated carbon. The CO_2 adsorption capacity reached 3.21 mmol/g at 25 ºC and 2 mmol/g at 50 ºC and may be better with increase in pyrolysis temperature.

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