N-containing activated carbons for CO2 capture
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A series of SK-activated carbons were prepared by carbonising soya beans in the presence of KOH as activation agent. Different activation temperatures were applied to study the influence of preparation conditions on the surface properties of the carbons and their CO2 adsorption capacity. It was found that the CO2 adsorption capacity is directly related to the nature of surface basic N-containing groups and that the highest CO2 adsorption capacity value was 4.24 mmol/g under 25°C and 1 atm.

Keywords: CO2 capture; adsorption; activated carbon; biomass; nitrogen doping

1. Introduction
Huge demand for energy has led to excessive emission of CO2, which has caused a serious greenhouse effect. In order to solve the global warming problem, CO2 capture technologies have attracted much attention in recent years. Among current technologies for CO2 capture, adsorption using solid porous adsorbents is regarded as the most promising method [1]. Compared with commonly used solvent absorbents in industry [2], solid adsorbents have many advantages, such as low cost, low energy consumption and low corrosion to equipment.

At present, there are several types of solid adsorbents being investigated as potential CO2 capture materials, e.g. molecular sieves, porous silica [3,4], metal–organic frameworks [5–7], membranes [8–10] and porous carbon [11,12], etc. Among these kinds of adsorbents, porous carbon is an ideal solid adsorbent owing to its large surface area, high porosity and good chemical and physical stability. Previous studies have shown that the CO2 uptake on pure porous carbons is not satisfactory. Therefore, in recent years, some basic functional groups have been introduced intentionally to porous carbons to further increase their CO2 adsorption capacity and selectivity.

Maroto-Valer et al. [13] used polyethyleneimine to modify carbons, which enhanced the CO2 uptake of the carbons. This proved that the CO2 capacity of an adsorbent is directly related to the amount of surface basic groups present. Pevida et al. [14] prepared a series of nitrogen-enriched carbons. The CO2 adsorption capacity of this series of carbons reached 2.25 mmol/g and this research proved that the surface chemistry can influence the CO2 adsorption performance. Grondein et al. [15] also used diamines to modify carbon black by impregnation. The resulting carbons exhibit a lower maximum CO2 adsorption capacity compared with the unmodified carbon, but the presence of amine groups provides a better selectivity toward CO2 adsorption. The drawback of such surface modification is that...
the impregnation process may partly block the pore structure of the carbons and decrease the CO₂ adsorption capacity [16]. Alternatively, some researchers have used N-containing precursors to prepare N-doped porous carbons directly. Li et al. [17] prepared N-enriched mesoporous carbon spheres using ethylenediamine and carbon tetrachloride as precursors via a nanocasting strategy. The CO₂ adsorption capacity of this N-enriched carbon reached 2.90 mmol/g at 25°C and 0.97 mmol/g at 75°C. Hao et al. [18] synthesised a porous carbon monolith using L-lysine as both catalyst and nitrogen source. The maximum CO₂ adsorption capacity of the resulting carbon reached 3.13 mmol/g.

Nitrogen-enriched activated carbons could also be prepared from protein-containing biomass waste, which is inexpensive and readily available [1,19,20]. After carbonisation or activation at high temperature, the nitrogen atoms in the proteins are transferred to the resulting carbons. Bean dregs, a by-product of the soya-bean milk industry, are usually used as animal feed, burned off or just dumped as waste. In this paper, the preparation is reported for the first time of a series of N-enriched activated carbons from bean dregs by KOH chemical activation. The CO₂ uptake on these carbons can reach as high as 4.24 mmol/g, which is higher than the values recently reported in the literature [21]. Based on X-ray photoelectron spectroscopy (XPS) observations, the excellent CO₂ performance of the carbons can be attributed to surface nitrogen-containing functional groups.

2. Experimental
2.1. Preparation
Bean dregs derived from the soya-bean milk industry were dried at 120°C for 5 h. Afterwards, the dregs were placed into a tubular resistance furnace and heated to 400°C under N₂ flow (about 40 cm³/min) for 1 h at a heating rate of 5°C/min to pre-carbonise the bean dregs [22,23]. The pre-carbonised product was ground with a specific amount of KOH pellet (the mass ratio between pre-carbonised product and KOH was 2) in an agate mortar. The resulting mixture was transferred into the tubular resistance furnace and then heated to a fixed activation temperature under N₂ flow (about 40 cm³/min) for 1 h at a heating rate of 5°C/min. The activated carbon obtained was washed and dried at 100°C for 6 h. The products obtained were named SK-X, where X refers to the activation temperature.

2.2. Material characterisation
The pore-structure parameters and CO₂ adsorption capacity of the activated carbons were analysed with a surface area and porosity analyser (ASAP 2010M, Micromeritics Corp.). Before analysis, the samples were degassed under vacuum at 350°C to remove moisture and other gases. Nitrogen adsorption isotherms were measured at −196°C and CO₂ adsorption isotherms were measured at both 25 and 75°C. The micropore distribution of the carbons was determined by argon adsorption at 77 K and calculated via the HK method. Before measurements, the activation carbons were degassed under vacuum at 300°C for 5 h. The microscopic morphology of the carbons was observed by scanning electron microscopy (SEM, Sirion 200 FEI, Netherlands) and transmission electron microscopy (TEM, Hitachi H800, Japan). The XPS measurements were performed with a ESCALAB220i-XL instrument (VG Scientific, UK) using a monochromated Al Kα excitation source. The survey and high-resolution spectra were collected with 100 eV and 20 eV pass energies, respectively. C 1s (284.6 eV) was used as an internal standard to correct for surface electric charge. The relative atomic concentrations on the surface were calculated using the approximate formula [24]:
\[
\frac{n_i}{n_j} = \frac{I_i}{I_j} \times \frac{\sigma_i}{\sigma_j} \times \frac{E_{ki}}{E_{kj}}
\]

where \( n \) is the number of surface atoms, \( I \) the intensity of its XPS peak, calculated from the peak area, \( \sigma \) the appropriate level of ionization cross-sections of relative elements [25], i.e. C 1s = 1.00, O 1s = 2.93, N 1s = 1.80 and Si 2p = 0.817, and \( E_k \) the kinetic energy of a photoelectron \( (E_k = h - BE, h = 1486.6 \text{ eV}) \).

The quantitative analysis was performed with CASAXPS software after Shirley background subtraction. The best peak fits were obtained using mixed 30\% Gaussian–Lorentzian line shapes at the same FWHM for all fitted peaks.

3. Results and discussion

The surface area and porosity of the activated carbons were analysed using N\(_2\) adsorption at 77 K and the isotherms are presented in Figure 1. As is shown in this figure, all carbons show a combination of type I and type IV isotherms, which exhibit both an adsorption platform at low relative pressure, indicating the presence of abundant micropores, and an obvious hysteresis loop within high relative pressure range (0.5–1.0), indicating the presence of substantial mesopores. The detailed surface area and pore-structure parameters of the carbons are listed in Table 1. It is shown that the specific surface area of the carbons increases from 710 \text{ m}^2/\text{g} to 1193 \text{ m}^2/\text{g} and the total pore volume increases from 0.44 \text{ cm}^3/\text{g} to 0.71 \text{ cm}^3/\text{g} with the rise of activation temperature, indicating that KOH as activation agent is more efficient at higher temperature.

SEM and TEM were used to observe the microscopic morphology of heat-treated bean dregs and the activated carbon SK-700 and the images are shown in Figure 2. As can be seen in Figure 2a, there are a great number of round-shaped mesopores in the heat-treated bean dregs. These mesopores may be derived from the pyrolysis of soya protein. During pyrolysis, large quantities of pyrolysis gas evolved and the carbon skeleton contracted at the same time, forming these large mesopores. As shown in Figures 2b and c, these mesopores are well preserved after KOH activation. In addition, there are a great large number of micropores, which were generated during activation according to N\(_2\) adsorption isotherms.

![Figure 1. N\(_2\) adsorption isotherms for all the carbons investigated.](image-url)
Table 1. Surface area and pore-structure parameters of the activated carbons.

| Sample | $S_{\text{BET}}$ $^a$ (m$^2$/g) | $S_{\text{Micro}}$ $^b$ (m$^2$/g) | $V_{\text{total}}$ $^c$ (cm$^3$/g) | Pore size$^d$ (nm) |
|--------|-------------------------------|---------------------------------|----------------------------------|------------------|
| SK-600 | 710                           | 608                             | 0.44                             | 2.52             |
| SK-700 | 1060                          | 907                             | 0.52                             | 2.49             |
| SK-800 | 1134                          | 962                             | 0.68                             | 2.40             |
| SK-900 | 1193                          | 992                             | 0.71                             | 2.38             |

$^a$BET specific surface area. $^b$Micropore surface area calculated by the t-plot method. $^c$Single point total pore volume measured at $p/p_0^0 \sim 0.995$. $^d$Pore size = $4V_{\text{total}}/S_{\text{BET}}$.

Figure 2. Micrographs of activated carbons: (a) SEM image of bean dregs heat-treated at 400°C; (b) SEM image of SK-700; (c) TEM image of SK-0.5-700.

The combination of meso-micropores structure would possibly benefit fast dynamic CO$_2$ adsorption/desorption operations.

According to previous investigations [18], CO$_2$ adsorption on porous carbons is closely linked to surface N-containing functional groups via acid–base interaction: if the acidic CO$_2$ molecules will react with basic nitrogen-containing groups then chemisorption will occur. Accordingly, the surface chemical properties of the activated carbons prepared in this work were analysed using XPS. The peaks at 398, 399, 400, 401 and 405 eV are attributed to pyridine, PhNH$_2$ (or −C≡NH), pyrrole, quaternary N and oxynitride, respectively. The results are presented in Table 2. The total nitrogen content is obviously inversely related to the activation temperature. When the activating temperature rises from 600°C to 900°C, the nitrogen content reduces from 3.12% to 1.27%. This indicates that high temperature will lead to the loss of nitrogen atoms during activation. It is worth noting that nitrogen atoms in pyridine and PhNH$_2$ (or −C≡NH) contain lone pair electrons which give these groups the electron-donating ability, so these kinds of groups are typical Lewis bases. In addition, although the nitrogen atom in quaternary N does not contain lone pair electrons, it is still a type of basic group [26]. It is obvious that the total basic group content is also decreased with an increase of activation temperature (Table 2). Elemental analysis results (Table 3) revealed the same trend. When the activation temperature is raised from 700°C to 900°C, the nitrogen content decreased from 3.18 wt % to 0.99 wt %.

It is generally believed that high CO$_2$ adsorption capacity depends on large specific surface area and advanced pore structure, but our study reveals a different conclusion. The relationship between BET specific surface area, $S_{\text{BET}}$, and CO$_2$ adsorption capacity of each SK carbon is shown in Figure 3a. It is obvious that the CO$_2$ adsorption capacity is not closely associated with the specific surface area. Table 1 shows that SK-900 contains the largest specific surface area and the most developed pore structure, but its CO$_2$ adsorption capacity is the lowest. The specific surface area of sample SK-700 is only 1060 m$^2$/g but its CO$_2$ adsorption capacity is the highest. In order to investigate the influence of the nitrogen
Table 2. Surface composition determined by XPS.

| Sample | Total N | Pyridine | PhNH₂/–C≡NH | Pyrrole | Quaternary N | Oxynitride | Basic groups |
|--------|---------|----------|-------------|---------|--------------|------------|--------------|
| SK-600 | 3.21    | 0.48     | 0.73        | 1.14    | 0.7          | 0.1        | 1.91         |
| SK-700 | 2.5     | 0.42     | 0.7         | 0.9     | 0.43         | 0.06       | 1.55         |
| SK-800 | 1.48    | 0.09     | 0.4         | 0.47    | 0.3          | 0.22       | 0.79         |
| SK-900 | 1.27    | 0.28     | 0.26        | 0.2     | 0.13         | 0.4        | 0.67         |

Table 3. Element content by CHNS analysis.

| Sample   | C (wt %) | N (wt %) | H (wt %) |
|----------|----------|----------|----------|
| SK-0.5-700 | 84.57    | 3.18     | 1.58     |
| SK-0.5-900 | 88.42    | 0.99     | 1.15     |

Figure 3. (a) The relationship between BET specific surface area of SK carbons and CO₂ adsorption capacity; (b) the relationship between nitrogen content of SK carbons and the CO₂ adsorption capacity on the weight basis and specific surface area basis.

content on the CO₂ adsorption capacity, the relationship between total nitrogen content and CO₂ adsorption capacity is shown in Figure 3b. It is found that the CO₂ adsorption capacity on a specific surface area basis is associated with the surface chemistry. As the content of basic nitrogen groups rises from 0.67% to 1.91%, the CO₂ adsorption capacity per unit surface area increases from $3.1 \times 10^{-3}$ mmol/m² to $5.2 \times 10^{-3}$ mmol/m². This demonstrates that the dominant factor for CO₂ adsorption may be not physisorption but chemisorption. But the specific surface area of SK-600, which contains the highest nitrogen content is extremely low, which leads to the highest CO₂ adsorption capacity on area basis but low CO₂ adsorption on weight basis. Although high activation temperature can enhance the surface area and porosity of activated carbon, it decreases the concentration of N-containing functional groups on the surface and leads to a low CO₂ adsorption capacity. We calculated the number of basic nitrogen containing groups and the results are tabulated in Table 2. The results show that the number of basic sites on carbon is proportional to CO₂ adsorption capacity of the carbon, indicating the important role of surface basic sites in CO₂ adsorption. However, the detailed interaction mechanism between N-containing groups and CO₂ molecules is not yet elucidated.
Figure 4 shows the CO$_2$ adsorption isotherms at 25°C and 75°C for the samples SK-600 to SK-900. It is observed that SK-700 shows the best CO$_2$ adsorption capacity at each temperature and the adsorption capacity is greatly affected by adsorption temperature. The CO$_2$ adsorption capacity of SK-700 decreased 58% when the adsorption temperature was raised from 25°C to 75°C. This means 58% CO$_2$ adsorbed on SK-700 was desorbed when the temperature rises from 25°C to 75°C, indicating that CO$_2$ adsorbed on the surface of activated carbon can be easily desorbed via heat treatment.

4. Conclusion
We used soya bean dregs as precursors to prepare a series of N-containing activated carbons. The CO$_2$ adsorption capacity of SK-700 reached 4.24 mmol/g at 25°C under 1 atm, which is higher than most recently reported values measured under the same conditions. It is shown that the nitrogen content on the carbon surface is a dominant factor for CO$_2$ adsorption capacity of the carbons prepared in this work.

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