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# The development of activated carbon from corncob for CO<sub>2</sub> capture

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The accumulation and incineration of crop waste pollutes the environment and releases a large amount of CO<sub>2</sub>. In this study, corncob crop waste was directly activated using solid KOH in an inert atmosphere to prepare porous activated carbon (AC) to capture CO<sub>2</sub>, and to introduce N-containing functional groups that favour CO<sub>2</sub> adsorption, urea was mixed with corncob and KOH to prepare N-doped AC. The physical and chemical properties of the AC were characterized, and the effects of the mass ratio of KOH and urea to corncob, the activation temperature and time as well as regeneration were investigated to explore the optimal preparation process. The pores in the AC are mainly micropores, with the specific surface area and pore volume reaching 926.07 m<sup>2</sup> g<sup>-1</sup> and 0.40 cm<sup>3</sup> g<sup>-1</sup> for KOH-activated corncob and 1096.70 m<sup>2</sup> g<sup>-1</sup> and 0.48 cm<sup>3</sup> g<sup>-1</sup> after N-doping; the C–O plus O–H ratio and the –NH– ratio, which favour CO<sub>2</sub> adsorption in N-doped AC were 6.04 and 1.92%, respectively. The maximum adsorption capacities for KOH-activated corncob before and after N-doping were 3.49 and 4.58 mmol g<sup>-1</sup>, respectively, at 20 °C and remained at 3.44 and 4.52 mmol g<sup>-1</sup> after ten regenerations. The prepared corncob-based AC showed good application prospects for CO<sub>2</sub> capture.

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## 1. Introduction

As a responsible country, despite the great pressure from all aspects, China is still taking positive measures to capture CO<sub>2</sub> to fulfill the double carbon target. Due to the characteristics of the energy structure and the dependence on coal, coal-fired power plants are undoubtedly one of the largest CO<sub>2</sub> emission points, where the CO<sub>2</sub> concentration is 9–15 vol%. Solid sorbents are acknowledged for their potential in capturing CO<sub>2</sub>,<sup>1–4</sup> and many researchers have made a substantial contribution in this respect.<sup>5–26</sup>

Quyang *et al.* synthesized SiO<sub>2</sub> nanowires from fibrous sepiolite and impregnated these nanowires with different amines to prepare composite solid sorbents, in which the optimal adsorption capacity of tetraethylenepentamine (TEPA)-functionalized SiO<sub>2</sub> was 3.7 mmol g<sup>-1</sup> at 75 °C for 60 vol% CO<sub>2</sub>.<sup>5</sup> Wang *et al.* impregnated branched polyethylenimine (PEI) onto commercial multiwalled carbon nanotubes and prepared composites to investigate the effect of H<sub>2</sub>O and O<sub>2</sub> on CO<sub>2</sub> capture, and the results showed that H<sub>2</sub>O had a positive effect, while O<sub>2</sub> had a negative effect on CO<sub>2</sub> adsorption.<sup>12</sup> Chang *et al.* synthesized the zeolitic imidazolate framework (ZIF-8), in which MgO and ZnO were

successfully confined; MgO-confined ZIF-8 showed fast chemisorption kinetics at room temperature, while ZnO-confined ZIF-8 showed physisorption characteristics.<sup>23</sup> The above sorbents all showed good CO<sub>2</sub> adsorption performance, but the expensive supporting materials, active components or complex preparation process caused high CO<sub>2</sub> capture costs, and the development of low-cost CO<sub>2</sub> sorbents is an effective way to reduce CO<sub>2</sub> capture costs.<sup>27–37</sup> Rehman *et al.* explored nitrogen-containing porous carbons derived from chitosan by a carbonization combining activation process. This material showed a rich microporous structure and N-containing functional groups, and the maximum adsorption capacity reached 6.36 mmol g<sup>-1</sup> at 273 K for 100 vol% CO<sub>2</sub>.<sup>26</sup> Wang *et al.*<sup>29</sup> prepared porous lignite chars from low rank Ordos coal by the activation method, and the CO<sub>2</sub> adsorption capacity was 1.35 mmol g<sup>-1</sup> at 20 °C for 15 vol% CO<sub>2</sub>.<sup>28</sup> Biomass is also used as the raw material to prepare porous carbons as sorbents.<sup>38–41</sup> Ding *et al.* prepared seaweed-based porous carbons from sargassum and enteromorpha by a one-step KOH activation method, in which the specific surface area and pore volume separately reached 291.8 m<sup>2</sup> g<sup>-1</sup> and 0.24 cm<sup>3</sup> g<sup>-1</sup>, and the maximum CO<sub>2</sub> adsorption capacity was 1.05 mmol g<sup>-1</sup> at 25 °C (12% CO<sub>2</sub>).<sup>38</sup> Pramanik *et al.* developed the cotton stalk-based porous carbon with the specific surface area of 2695 m<sup>2</sup> g<sup>-1</sup>, and the adsorption capacity of 4.24 mmol g<sup>-1</sup> at 298 K (100% CO<sub>2</sub>) was achieved.<sup>40</sup>

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China is a large agricultural country, and every year, millions of crop wastes are stacked or burned, which not only induces serious environmental pollution problems but also releases large amounts of CO<sub>2</sub> and increases the greenhouse gas effect. In this study, corncob, which is common in Shandong Province, China, was used as the raw material, KOH and urea were used as the activator and nitrogen source, respectively, to prepare the AC by a one-step activation method. The pore structure, surface functional groups and morphology of the AC were characterized. The CO<sub>2</sub> adsorption capacities at different KOH or urea to corncob mass ratios, activation temperatures and times, and adsorption temperatures were investigated, and the correlations between adsorption performance and pore properties and functional groups were analysed.

## 2. Experimental section

### 2.1 Materials

Corn cob was collected from rural Weifang city, Shandong Province, China. KOH (GR, 85%) and urea (AR, 99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd, Shanghai, China. HCl (CR, 36–38%) was purchased from Laiyang Fine Chemical Factory, Shandong Province, China. N<sub>2</sub> and CO<sub>2</sub> with a purity of 99.999% and a mixed gas of 85 vol% N<sub>2</sub>/15 vol% CO<sub>2</sub> were provided by Weiyang Gas Co., Ltd, Shandong Province, China.

### 2.2 Preparation of the corncob-based AC

Corn cob was washed with running water and deionized water, dried in an oven at 80 °C, and then crushed into powder below 100 meshes for use. KOH and urea were also pulverized to a powder for use. The AC was prepared with a simple one-step activation method.

Corn cob and KOH were separately weighed according to a certain mass ratio and uniformly mixed. The mixture was tiled in a tube furnace, and N<sub>2</sub> was passed through for 30 minutes to remove the adsorbed air. Then, the temperature of the tube furnace was elevated at a rate of 5 °C min<sup>-1</sup> to the activation temperature and remained at this temperature for a certain time, which is the activation time. Subsequently, the system was cooled to 100 °C, and N<sub>2</sub> was discontinued. The black powder collected from the tube furnace was ground, was washed repeatedly with diluted HCl and deionized water until the pH was close to 7, and was then dried in a vacuum oven at 85 °C for 24 h. The dried black powder was the AC, which were named CKa-T(b), where C represents corncob; K represents KOH; T is the activation temperature, °C; a is the KOH to corncob mass ratio; and b is the activation time, h.

The N-doped AC was also prepared with the one-step method. Corn cob, KOH and urea were separately weighed according to a certain mass ratio and uniformly mixed, and then the above process was repeated. What is different is that the temperature was first raised to 450 °C for 0.5 h and then to the activation temperature, and the N-doped AC was named

CNcKa-T(b), where N represents urea, and c is the mass ratio of urea to corncob.

### 2.3 Characterization

The N<sub>2</sub> adsorption–desorption isotherms for corncob-based AC were collected on an ASAP 2460 (Micromeritics, USA) by the physical adsorption of N<sub>2</sub> at the critical temperature of 77 K. The BET surface area ( $S_{\text{BET}}$ ) was obtained according to the Brunauer–Emmett–Teller (BET) equation, the total pore volume ( $V_t$ ) was calculated according to the adsorption capacity of N<sub>2</sub> when the relative pressure ( $P/P_0$ ) reached 0.995, the micropore volume ( $V_{\text{micro}}$ ) was confirmed from the  $t$ -plot curve, and the pore size distribution curves were obtained from the desorption branch according to the density functional theory (DFT) method.

The X-ray photoelectron spectroscopy (XPS) was applied to the corncob-based AC using an EscaLab 250Xi (Thermo Scientific, USA). The surface morphology was collected from a JSM-7500F scanning electron microscope (JEOL, Japan).

### 2.4 CO<sub>2</sub> adsorption and regeneration

The adsorption and regeneration of the prepared AC were performed on an online fixed bed adsorption device. A total of

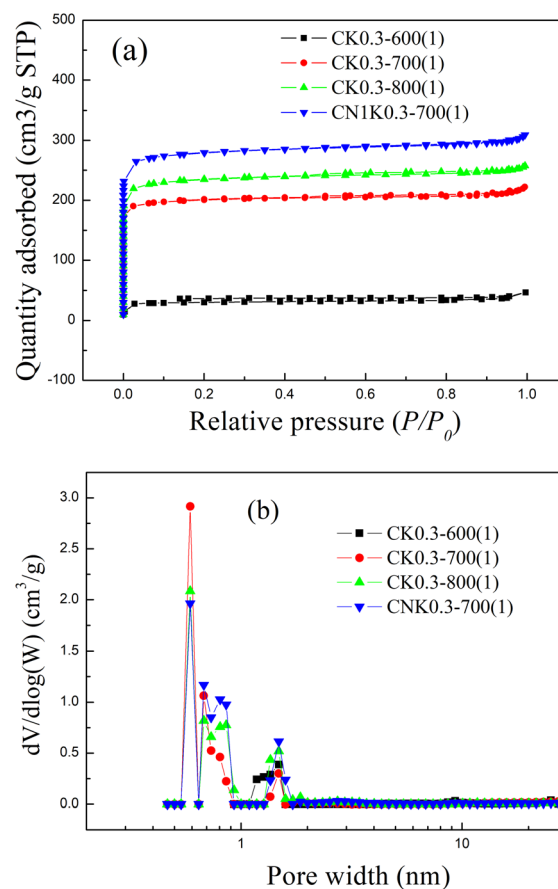


Fig. 1 The (a) N<sub>2</sub> adsorption–desorption isotherms and (b) pore size distribution curves for KOH-activated corncob before and after N-doping.



Table 1 The textural pore properties for KOH-activated corncob before and after N-doping

Sample	$S_t$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{micro}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_t$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{micro}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	Micro-porosity (%)	Average pore diameter (nm)
CK0.3-600(1)	120.72	108.34	0.07	0.04	57.14	2.38
CK0.3-700(1)	796.96	763.36	0.34	0.30	88.24	1.73
CK0.3-800(1)	926.07	872.08	0.40	0.34	85.00	1.72
CN1K0.3-700(1)	1096.70	1032.29	0.48	0.40	83.33	1.74

0.4 g of the sample was fixed in the centre of the quartz tube, in which the inner diameter was 0.8 cm and length was 50 cm, and  $\text{N}_2$  was passed through while the temperature was raised to 100 °C and held for 60 min to drive away preadsorbed air. Then, the temperature was reduced to the desired adsorption temperature, and inlet  $\text{N}_2$  was converted to the mixed gas. Here, the  $\text{CO}_2$  adsorption process began, and  $C_0$  and  $C$ , which were recorded from the online gas chromatograph, represent the  $\text{CO}_2$  concentration in the inlet and outlet of the reactor, respectively. As adsorption proceeded, the  $\text{CO}_2$  concentration in the outlet continuously increased, and when  $C$  equaled  $C_0$ , the adsorption process was completed, and the sorbent reached a saturated adsorption state; here, the  $\text{CO}_2$  adsorption

capacity was the saturated adsorption capacity. The inlet was then converted to  $\text{N}_2$ , and the temperature was raised to 100 °C to desorb the adsorbed  $\text{CO}_2$ . As desorption proceeded,  $C$  continuously decreased; when  $C$  equaled 0, the desorption process finished, and the sorbent was regenerated. Ten adsorption–desorption regenerations were performed on the chosen samples.

## 3. Results and discussion

### 3.1 Characterization

**3.1.1 BET.** The  $\text{N}_2$  adsorption–desorption isotherms, pore size distribution curves and textural pore properties for KOH-

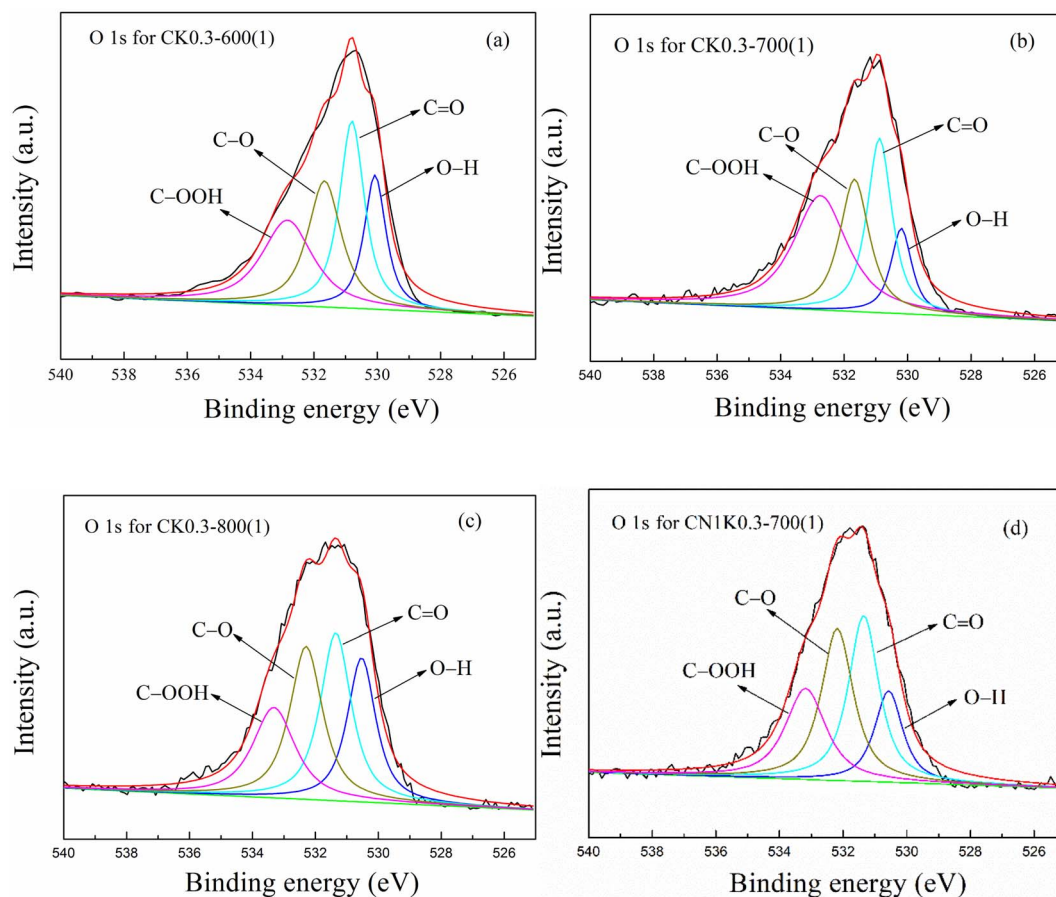


Fig. 2 The O 1S spectra for KOH-activated corncob before and after N-doping.



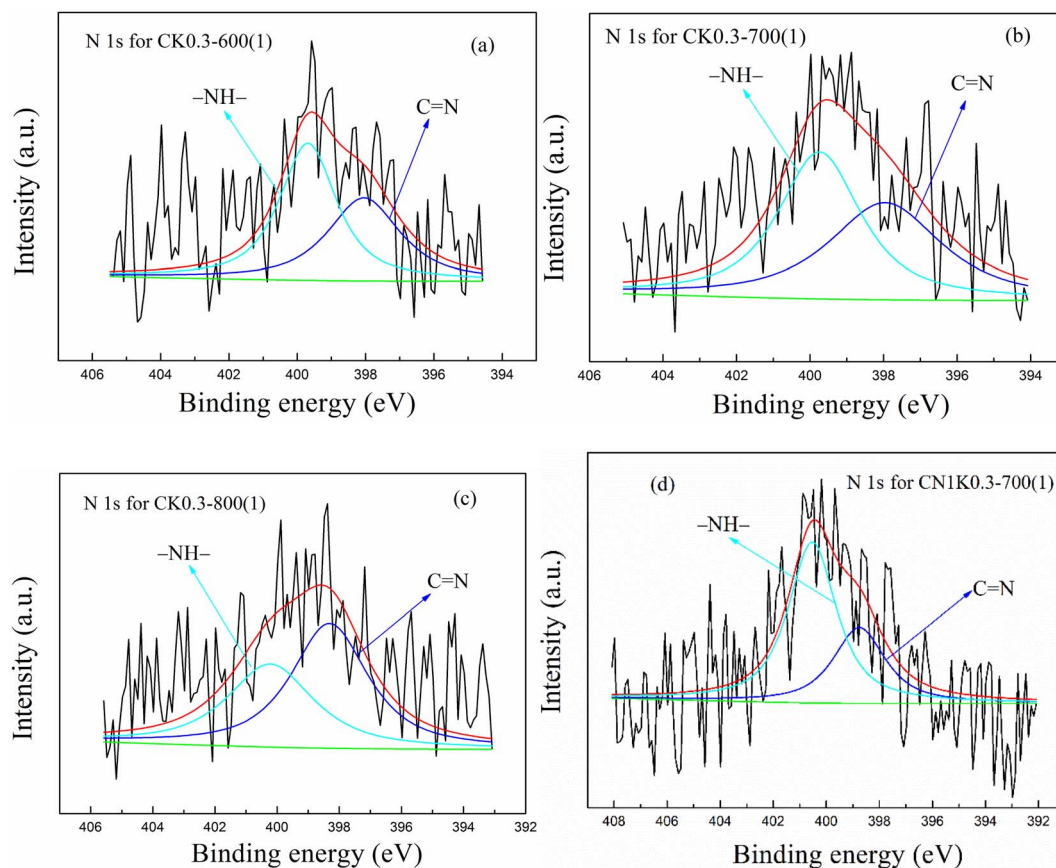


Fig. 3 The N 1S spectra for KOH-activated corncob before and after N-doping.

activated corncob before and after N-doping are shown in Fig. 1(a), (b) and Table 1, respectively. In Fig. 1(a), the  $N_2$  adsorption–desorption isotherms showed a sharp rise and type I curve at the initial adsorption stage and then a mild increase with a narrow type H4 hysteresis loop, suggesting that the pores in corncob-based AC were mainly micropores with partial mesopores,<sup>15,27</sup> which could also be proven from the pore size distribution curves in Fig. 1(b). As seen from Table 1, for KOH-activated corncob, as the activation temperature increased from 600 to 800 °C, the specific surface area and pore volume increased from 120.72 to 926.07  $m^2 g^{-1}$  and 0.07 to 0.48  $cm^3 g^{-1}$ , respectively. For CN1K0.3-700(1), the specific surface area

and pore volume were 1096.70  $m^2 g^{-1}$  and 0.48  $cm^3 g^{-1}$ , respectively, which were significantly higher than the corresponding values of 796.96  $cm^2 g^{-1}$  and 0.34  $cm^3 g^{-1}$  for CK0.3-700(1).

**3.1.2 XPS.** The O 1S and N 1S spectra for the KOH-activated corncob before and after N-doping are shown in Fig. 2(a–d) and 3(a–d), and the corresponding peak area ratio for every functional group is listed in Table 2. As shown in Fig. 2 and 3, the O 1S spectra in KOH-activated corncob before and after N-doping were all categorized into four peaks at 530.07, 530.80, 531.67 and 532.84 eV, which are attributed to hydroxyl group (–OH), carbonyl, lactone or ketone group (C=O), ether

Table 2 The peak area ratios of different O species for KOH-activated corncob before and after N-doping<sup>a</sup>

Sample	O (%)					–OH (%)	–C=O (%)	C–O (%)	–COOH (%)
	O (%)	–OH	–C=O	C–O	–COOH				
1	27.26	18.20	28.83	26.06	26.90	4.96	7.86	7.10	7.33
2	21.55	11.04	26.65	24.08	38.23	2.38	5.74	5.19	8.24
3	20.43	22.67	28.52	21.05	27.76	4.63	5.83	4.30	5.67
4	13.12	15.95	31.16	30.11	22.79	2.09	4.09	3.95	2.99

<sup>a</sup> 1, 2, 3 and 4 represents CK0.3-600(1), CK0.3-700(1), CK0.3-800(1) and CN1K0.3-700(1), respectively.





**Table 3** The peak area ratios of different N species for KOH-activated corncob before and after N-doping<sup>a</sup>

Sample	N (%)	N (%)			
		C=N	-NH-	C=N (%)	-NH- (%)
1	2.86	43.53	56.47	1.24	1.62
2	2.97	47.84	52.16	1.42	1.55
3	2.00	57.23	42.77	1.14	0.86
4	2.89	33.71	66.29	0.97	1.92

<sup>a</sup> 1, 2, 3 and 4 represents CK0.3-600(1), CK0.3-700(1), CK0.3-800(1) and CN1K0.3-700(1), respectively.

or alcohol group (C-O) and carboxyl group (-COOH), respectively.<sup>38,42,43</sup> The N 1S spectra in KOH-activated corncob before and after N-doping were all divided into two peaks at 398.31 and 400.21 eV, which are attributed to pyridinic nitrogen (C=N) and pyrrolic nitrogen (-NH), respectively.<sup>37,38,42</sup> Generally, -OH, C-O and -NH promote CO<sub>2</sub> adsorption,<sup>42</sup> which is further discussed.

As shown in Table 2, for KOH-activated corncob, as the activation temperature increased from 600 to 800 °C, the peak area ratio for -NH decreased from 1.62 to 0.86%, that for C-O

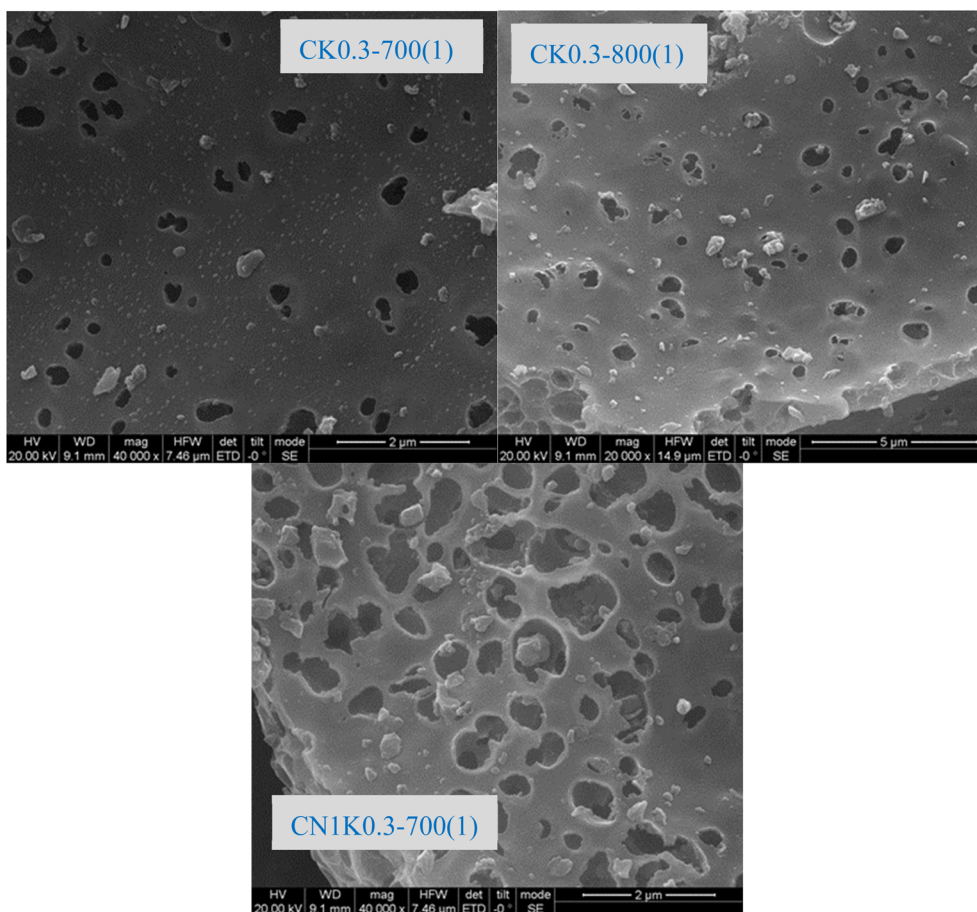
decreased from 7.10 to 4.30%, that for -OH first decreased from 4.96 to 2.38 and then increased to 4.63%, and that for -OH plus C-O first decreased from 12.07 to 7.57 and then increased to 8.93% (Table 3).

After N-doping, the ratio for -OH, C-O, -OH plus C-O, and -NH in CN1K0.3-700(1) was 2.09, 3.95, 6.04 and 1.92%, respectively, which all obviously increased compared with the corresponding value for CK0.3-700(1), suggesting that N-doping increased the functional groups that promote CO<sub>2</sub> adsorption.

**3.1.3 SEM.** Fig. 4 shows the SEM micrographs of KOH-activated corncob before and after N-doping, and the activated corncob exhibited a rough and porous surface. As the activation temperature increased from 700 to 800 °C, the porous nature of the KOH-activated corncob was more obvious, and became much more developed after N-doping. The above phenomenon is consistent with the results of BET characterization.

### 3.2 The CO<sub>2</sub> adsorption performance of KOH-activated corncob

**3.2.1 The effect of the KOH to corncob mass ratio.** The amount of activator influences the activation degree, pore development and surface functional group formation of the



**Fig. 4** SEM micrographs of KOH-activated corncob before and after N-doping.



biomass, so the effect of the KOH to corncob mass ratio on CO<sub>2</sub> adsorption was investigated. The breakthrough adsorption curves and saturated adsorption capacity for KOH-activated corncob at different KOH to corncob mass ratios are displayed in Fig. 5(a) and (b). Here, the activation temperature, activation time and adsorption temperature were fixed at 700 °C, 1 h and 20 °C, respectively.

With the mass ratio increasing from 0 to 1, the breakthrough adsorption curve first moved towards the right and then left, so the saturated adsorption capacity first increased and then decreased, and the optimal adsorption capacity of 3.49 mmol g<sup>-1</sup> appeared when the mass ratio was 0.3. More KOH promoted more corncob to be pyrolysed and to react, so more developed pores were formed, but too much KOH overreacted the corncob, etched the formed pores and collapsed the formed framework,<sup>29,38</sup> so the adsorption capacity displayed an increasing trend first and then a decreasing trend.

In view of the optimal adsorption capacity appearing at a mass ratio of 0.3, the mass ratio was fixed at 0.3 in the following investigation.

**3.2.2 The effect of activation temperature and time on CO<sub>2</sub> adsorption.** The activation temperature and time also play important roles in pore development and functional group formation during biomass activation. The mass ratio was fixed

as 0.3, and the activation time was determined to be 1 h to investigate the effect of activation temperature on CO<sub>2</sub> adsorption of KOH-activated corncob at 20 °C.

The breakthrough adsorption curves and saturated adsorption capacity for KOH-activated corncob at different activation temperatures are shown in Fig. 6(a) and (b), respectively. As the activation temperature increased from 600 to 800 °C, the breakthrough curve in Fig. 6(a) first moved right and then moved left, and the corresponding saturated adsorption capacity first increased and then decreased, as shown in Fig. 6(b), with the optimal adsorption capacity appearing at 700 °C and being 3.49 mmol g<sup>-1</sup> for CK0.3-700(1).

The mass ratio and activation temperature were fixed at 0.3 and 700 °C, respectively, to investigate the effect of activation time on CO<sub>2</sub> adsorption at 20 °C. The breakthrough adsorption curves and saturated adsorption capacity for KOH-activated corncob at different activation times are shown in Fig. 7(a) and (b), respectively. The adsorption performance also showed an increasing and then decreasing trend, and the best value appeared when the activation time was 1 h.

Generally, a higher activation temperature and a longer activation time promote a more adequate reaction between

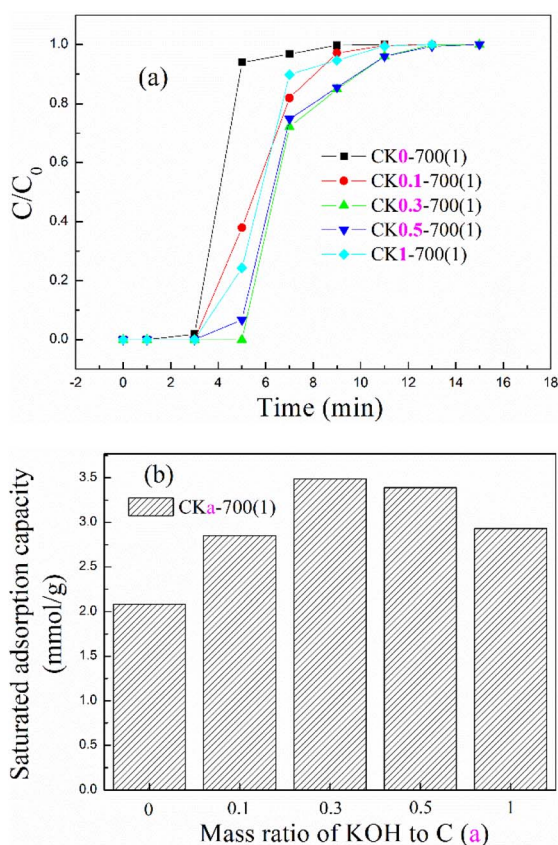


Fig. 5 The (a) breakthrough adsorption curves and (b) saturated adsorption capacity for KOH-activated corncob at different KOH to corncob mass ratios.

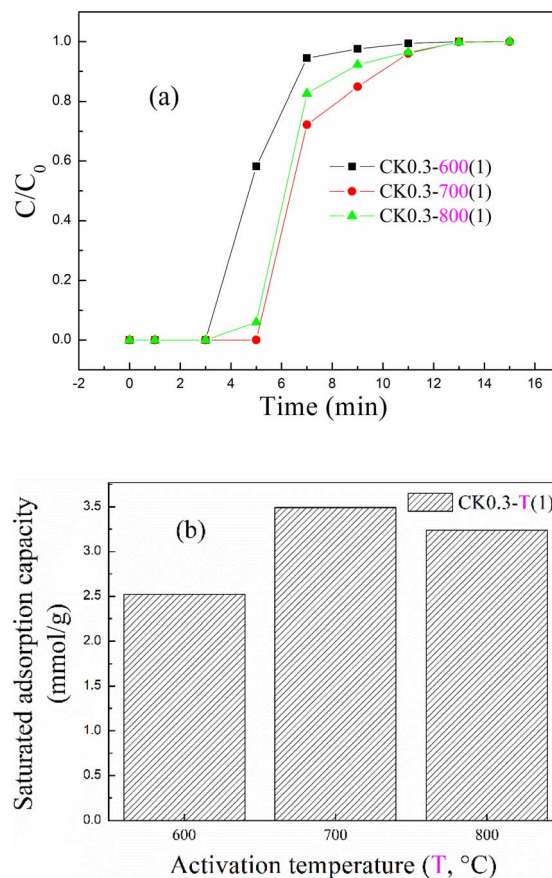


Fig. 6 The (a) breakthrough adsorption curves and (b) saturated adsorption capacity for KOH-activated corncob at different activation temperatures.



KOH and corncob, so the pore structure and surface functional groups became more developed; however, too high a temperature and too long a time also caused an overreaction between KOH and corncob, which might cause pore framework collapse or favour further decomposition of functional groups.<sup>29,38</sup> Therefore, the adsorption performance for KOH-activated corncob first showed increasing trends and then decreasing trend, and the optimal temperature and time were determined to be 700 °C and 1 h, respectively.

According to the above study, CK0.3-700(1) suggested an optimal adsorption capacity of 3.49 mmol g<sup>-1</sup> at 20 °C when the mass ratio of KOH to corncob was 0.3, and the activation temperature and time were 700 °C and 1 h, respectively.

### 3.3 The effect of N-doping on CO<sub>2</sub> adsorption of CK0.3-700(1)

Urea was mixed with KOH and corncob to introduce more N-containing functional groups to improve CO<sub>2</sub> adsorption. The breakthrough adsorption curves and saturated adsorption capacity for N-doped CK0.3-700(1) at different mass ratios of urea to corncob are shown in Fig. 8(a) and (b). After N-doping, the breakthrough adsorption curve in Fig. 8(a) moved right, suggesting that N-doping improved the adsorption performance of KOH-activated corncob, as shown in Fig. 8(b). After

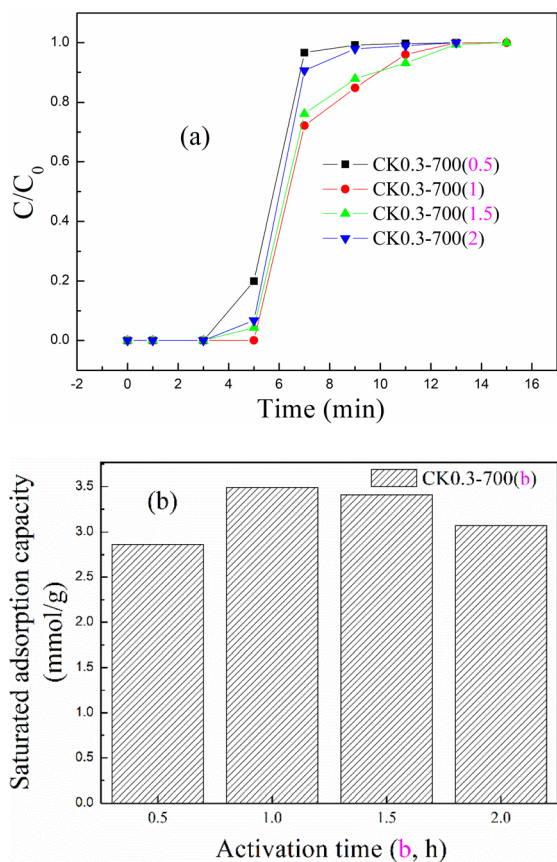


Fig. 7 The (a) breakthrough adsorption curves and (b) saturated adsorption capacity for KOH-activated corncob at different activation times.

N-doping at mass ratios of 0.5, 1 and 1.5, the saturated adsorption capacity was 4.24, 4.58 and 4.26 mmol g<sup>-1</sup>, representing increasing of 21.8, 31.4 and 22.2%, respectively, compared with CK0.3-700(1). According to the BET and XPS characterization results comparing CN1K0.3-700(1) and CK0.3-700(1), not only the specific surface area and pore volume but also the ratio of -OH, C-O, and -NH groups that favoured CO<sub>2</sub> adsorption<sup>42</sup> all increased, which improved CO<sub>2</sub> adsorption.

### 3.4 Linear correlation analysis

Linear correlation fitting was conducted on the corncob-based AC data, and the fitting results between the saturated adsorption capacity and  $S_{\text{BET}}$ ,  $V_t$ ,  $V_{\text{micro}}$ , the N-H group ratio and the O-H plus C-O group ratio are shown in Fig. 9(a-e), respectively. As suggested in Fig. 9, the saturated adsorption capacity did not fit well with any of the above factors, suggesting that the adsorption performance of the corncob-based AC did not completely rely on the pore properties or the surface functional groups but had close relations with both, which could explain why the saturated adsorption capacity did not continuously increase as the activation temperature or time increased.

In summary, the optimal preparation process for KOH-activated corncob appeared when the KOH to corncob mass

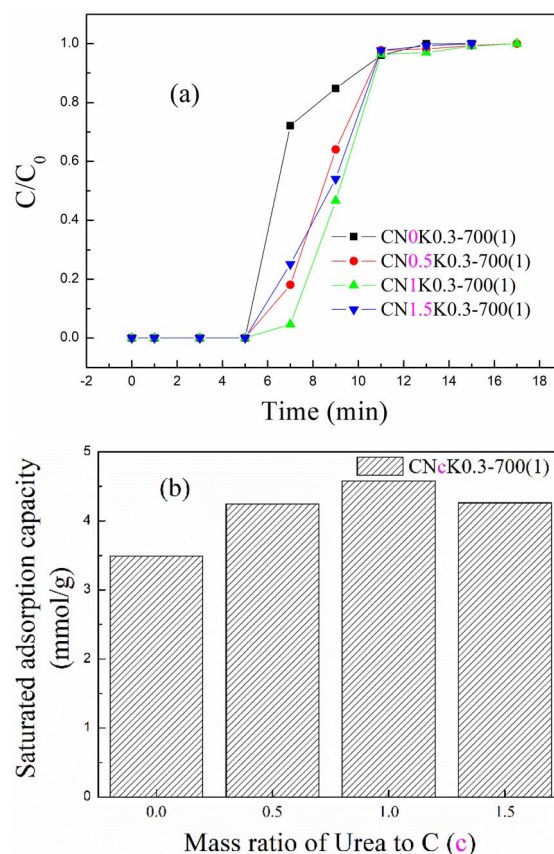


Fig. 8 The (a) breakthrough adsorption curves and (b) saturated adsorption capacity for N-doped CK0.3-700(1).





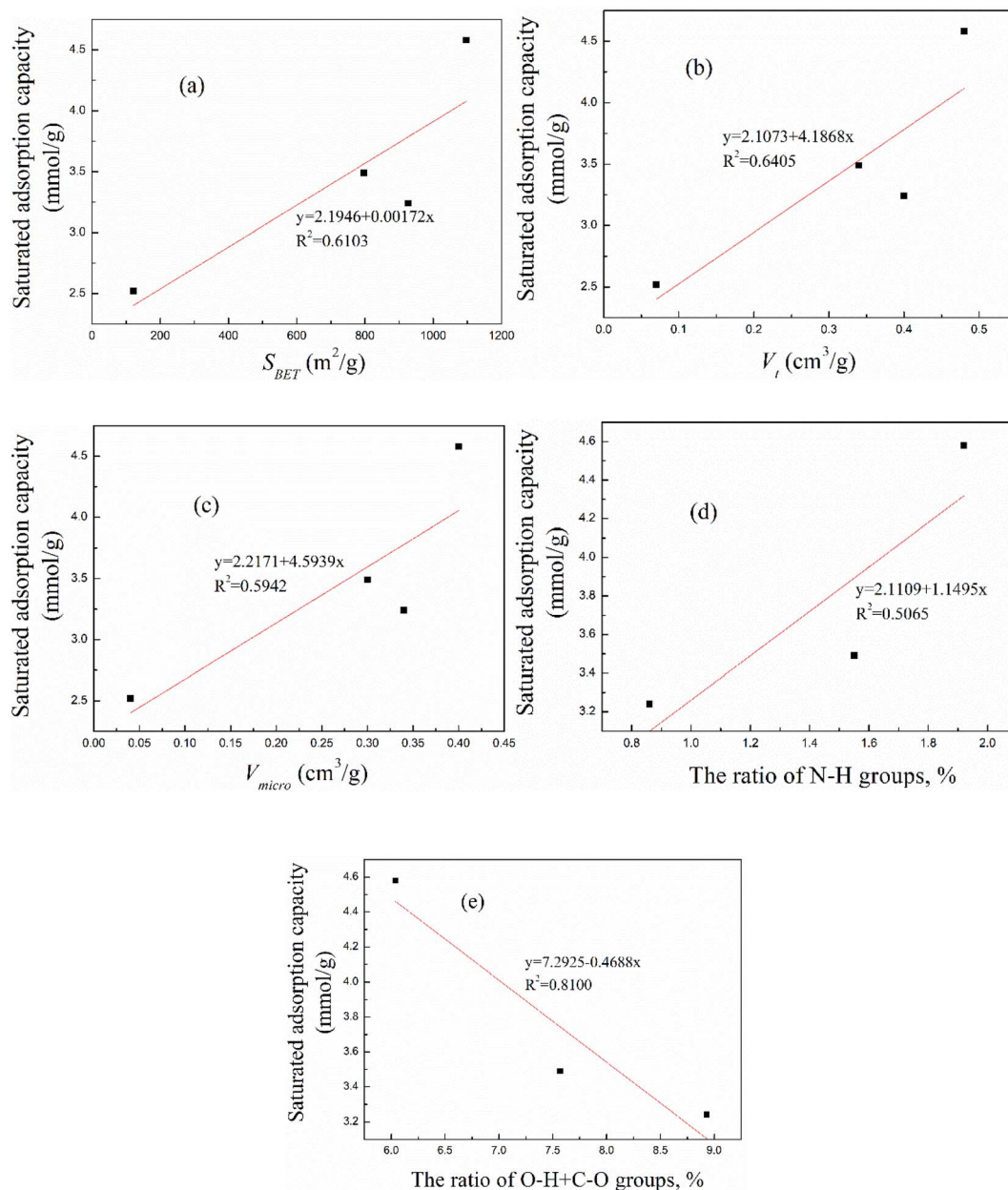


Fig. 9 The linear correlation analysis between the adsorption performance and (a)  $S_{BET}$ , (b)  $V_t$ , (c)  $V_{micro}$ , (d) the N-H group ratio and (e) the O-H plus C-O ratio.

ratio was 0.3, the activation temperature and time were 700 °C and 1 h, respectively, and the optimal urea to corncob mass ratio was 1 for N-doped KOH-activated corncob.

### 3.5 Regeneration of KOH-activated corncob before and after N-doping

In view of the good adsorption performance, CK0.3-700(1) and CN1K0.3-700(1) were selected to further investigate ten adsorption-desorption regeneration performances. The adsorption and regeneration temperatures were separately set as 20 and 100 °C.

The saturated adsorption capacity for corncob-based AC is shown in Fig. 10. For both CK0.3-700(1) and CN1K0.3-700(1), after ten regenerations, the adsorption capacity all showed an insignificant drop, and the values for both were 3.44 and 4.52  $mmol\ g^{-1}$ , which are reductions of only 1.43 and 1.31% compared with the corresponding values of the fresh sorbent, which were 3.49 and 4.58  $mmol\ g^{-1}$ , respectively. Both CK0.3-700(1) and CN1K0.3-700(1) showed good regeneration performance, and the prepared corncob-based AC has potential for  $CO_2$  capture.





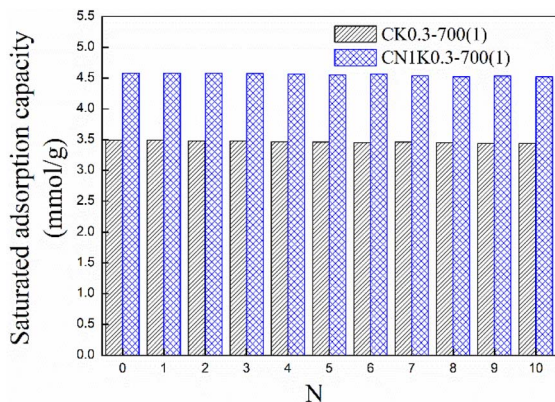


Fig. 10 The saturated adsorption capacity for CK0.3-700(1) and CN1K0.3-700(1) after regeneration.

## 4. Conclusions

A simple one-step activation method for the preparation corncob-based AC before and after N-doping suggested the development of a microporous structure and abundant O- and N-containing surface functional groups, which promote CO<sub>2</sub> adsorption. The CO<sub>2</sub> adsorption capacity for KOH-activated AC before and after N-doping reached 3.49 and 4.58 mmol g<sup>-1</sup>, respectively, and remained at 3.44 and 4.52 mmol g<sup>-1</sup> after ten regenerations. In addition, the linear correlation results showed that the adsorption was related to both the pore structure and the functional groups and was not dependent on either.

The development of corncob-based AC not only reduces the environmental pollution problem caused by the accumulation and incineration of crop waste and realizes waste resource utilization but also reduces the CO<sub>2</sub> capture costs.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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