

# WASTE FOAM POLYURETHANE TO PRODUCE NITROGEN DOPED POROUS CARBON TO ADSORB CARBON DIOXIDE

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**Abstract:** The purpose of this study is to obtain activated carbon adsorbent with good carbon dioxide adsorption performance by pyrolysis of waste polyurethane, and solve the two problems of environmental pollution and carbon dioxide emission of waste polyurethane. At 600°C, the waste polyurethane was carbonized with urea and activated with KOH at 800°C. The obtained product has large specific surface area, pore size of 0.5nm-1nm, and good adsorption capacity of UC-5-1.5, which is 6.5mmol/g at 1 bar at 0°C. In this study, foam polyurethane was used as raw material, nitrogen was doped by mixing different nitrogen sources and activated by KOH to obtain porous carbon adsorbent. The prepared adsorbent has larger specific surface area and higher carbon dioxide adsorption capacity.

**Keywords:** Activated carbon; Waste polyurethane; Carbon dioxide adsorption; Selectivity

## 1 INTRODUCTION

Since the Industrial Revolution, the continuous emission of greenhouse gases has led to a continuous rise in atmospheric temperature, of which carbon dioxide is the main factor leading to climate warming [1]. With the progress and development of industrial technology, a large number of emissions of industrial waste gas, the concentration of carbon dioxide in the atmosphere continues to increase, from 331ppm to 420ppm, and is still increasing, if not controlled will cause inestimable consequences to the environment. Carbon dioxide capture, storage and conversion (CCUS) can solve the problem of increasing the average temperature of atmospheric environment caused by excessive carbon dioxide emission [2].

Carbon dioxide capture can be divided into pre-combustion capture, oxygen-rich combustion capture and post-combustion capture. Pre-combustion capture is the reaction of fuel with oxygen, air and water vapor under certain conditions, mainly to produce CO<sub>2</sub> and H<sub>2</sub>; Oxygen-rich combustion capture is the use of pure O<sub>2</sub> (95-99%) instead of air for oxygen rich combustion, resulting in high CO<sub>2</sub> concentration of flue gas; The separation of carbon dioxide from the flue gas produced by the combustion of the fuel in the air is called postcombustion capture. Among them, post-combustion capture has a good prospect in solving the problem of environmental CO<sub>2</sub> concentration [3]. Amine washing is the most important commercial CO<sub>2</sub> adsorption method, its technology is mature and the amount of CO<sub>2</sub> adsorption is large, but it has the disadvantages of large corrosion to the equipment and high regeneration cost [4]. Therefore, the research of solid adsorbents has been further increased, including carbon-based adsorbents, metal-organic frameworks, zeolite, mesoporous silica, oxides and so on. And carbon-based adsorbent because of its cheap and easy to obtain, large specific surface area, easy to regenerate, low sensitivity to water has good industrialization potential, so choose carbon material as carbon dioxide solid adsorbent [6].

In order to solve the problem of environmental pollution, the general selection of biochar or plastic waste as raw materials, by one step or two step method to obtain, one step method is the direct roasting of the mixture of carbon source and activator KOH directly mixed stalk activation, two-step method is the carbonization, activation into two steps roasting [4-5]. The huge amount of polyurethane waste is difficult to degrade, will exist in the environment for decades or even hundreds of years, is bound to bring serious damage to the environment, direct disposal, land landfill, direct incineration and other commonly used treatment methods will cause varying degrees of damage and pollution to the surrounding landscape, water, soil and air [7-11].

In this study, foam polyurethane was used as raw material, nitrogen was doped by mixing different nitrogen sources, and activated by KOH to obtain porous carbon adsorbent. The prepared adsorbent has larger specific surface area and higher carbon dioxide adsorption capacity. It is also environmentally friendly. The CO<sub>2</sub> adsorption capacity was measured by BET and fixed bed dynamic adsorption method.

## 2 EXPERIMENTAL

### 2.1 Material

Choose waste foam polyurethane as the raw material for preparing activated carbon. The raw material is then crushed in the micro plant crusher to obtain the polyurethane powder. Potassium hydroxide (99%), (C<sub>6</sub>H<sub>11</sub>NO<sub>4</sub>) N (99%), (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>) (99%), (C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>) (99%) were purchased from China National Pharmaceutical Group Co., LTD. N<sub>2</sub> (99.99%) and carbon dioxide (10%) were supplied by Deyi Gas Co., LTD.

### 2.2 Foam Polyurethane Carbonization

The foam polyurethane is crushed to less than 40 mesh, mixed with urea, melamine, dicyandiamine grinding, screening suitable nitrogen sources, and mixed with the foam polyurethane in different proportions [12-14]. It was put into a quartz boat and carbonized in a tube furnace. Under 100ml/min nitrogen atmosphere, it was heated to the specified temperature at the heating rate of 10°C/min, and kept for 15 minutes to carbonize it. It was recorded as UC-X, where X was the weight ratio of N content in urea.

### 2.3 Carbon Activation

After carbonizing the foamed polyurethane, it is ground and mixed separately with different proportions of KOH (KOH: C=0.5, 1,1.5, 2,3). It was put into a nickel boat and activated in a tube furnace: under 100ml/min nitrogen atmosphere, it was heated to the specified temperature at the heating rate of 10°C/min, kept for 2 hours to activate it, after activation, it was washed to neutral with 1mol/L hydrochloric acid while ultrasonic, and dried in an oven at 105°C for 12h after centrifugation [15]. Recorded as UC-X-Y, Y is the ratio of KOH to C.

### 2.4 Characterization

The structural properties of AC samples were determined by  $n_2$  adsorption-desorption isotherm at 77 K using American Micromeritics ASAP 2460. Prior to the measurement, the sample was vacuumed at 150 ° C for 12 hours. Based on the  $N_2$  adsorption-desorption isotherm, the specific surface area (SBET) was calculated using the Brunauer-Taylor equation (BET), the total pore volume ( $V_t$ ) was calculated at  $P/P_0 = 0.99$ , the micropore volume ( $V_{mi}$ ) was calculated using the T-diagram method, and the mean pore width ( $D_p$ ) was calculated using  $4V_t/SBET$ . Composition and composition of surface elements The properties of the elements have been studied using X-ray photoelectron spectroscopy (XPS) (Skalb 250Xi, Thermo Fisher Science, USA).The static carbon dioxide adsorption capacity of the samples was determined by thermogravimetric analyzer. All AC samples were degassed at 100 ° C for 24 hours and then adsorption measurements were taken

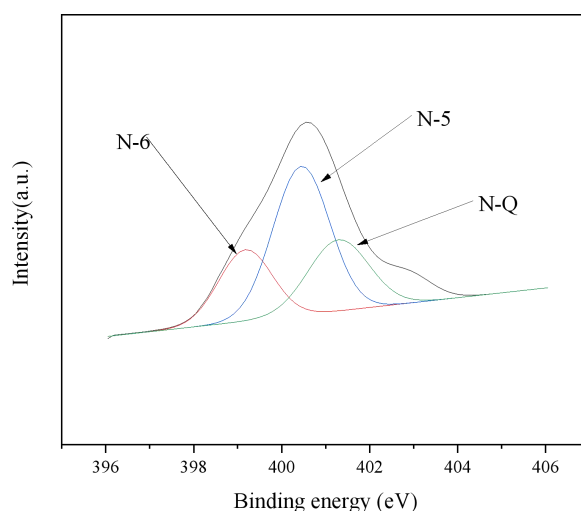
### 2.5 Adsorption Measurement

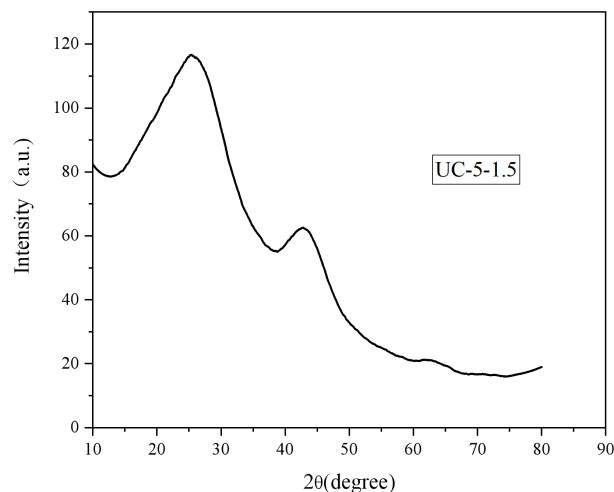
The adsorption capacity of the screened sample was preliminarily measured by DSC3+ thermogravimeter. The adsorption capacity of the screened sample was increased from 10°C /min to 100°C at 30°C and maintained for 30min to achieve the purpose of pretreatment.After cooling to 30°C, at 30°C, the adsorption experiment was carried out with 10% carbon dioxide, adsorption for 30min; Then heat up to 100°C and keep it for 30min to desorption. BET was used to test the adsorption capacity of the sample at 0°C and pure  $CO_2$ .

## 3 RESULT AND DISCUSSION

### 3.1 XPS/XRD

Sample UC-5-1.5, for example, contains 90.81wt%C, 0.74wt%N, 8.45wt%O. The properties of N groups on the surface of the adsorbent were identified by X-ray photoelectron spectroscopy (XPS). As Figure 1, the selected sample presents two beads centered on 399.2,400.4, and 401.3ev indexed as pyridine-N (N-6), pyrrole-N (N-5), and pyridine-oxide (N-Q). These nitrogen-rich carbon surface properties can enhance carbon dioxide absorption, and N-5 is more  $CO_2$ -friendly than N-6. The XRD profile of UC-5-1.5 is shown in the Figure 2. Two wide diffraction peaks were observed near 23° and 43°, corresponding to the (002) and (100) diffraction patterns of amorphous graphite carbon, indicating that the sample is amorphous.



**Figure 1** The XPS of UC-5-1.5**Figure 2** The XRD of UC-5-1.5

### 3.2 BET

From Table 1, the specific surface area and pore size of the samples were different due to different doped carbon sources and different proportions of doped urea. The specific surface area of doped urea was the largest, reaching 1,742.03m<sup>2</sup>/g, while the specific surface area of undoped and doped melamine and dicyanodiamine was significantly lower than that of doped urea. Among the doped urea with different contents, the specific surface area of doped 5% urea was the largest. The pore sizes of the two nitrogen sources doped with melamine and dicyanodiamine were smaller than those doped with urea, and even slightly lower than those of the undoped nitrogen source. The results showed that the activated carbon doped with 5% urea had the highest specific surface area of 1,742.03m<sup>2</sup>/g and the largest pore size of 2.55nm.

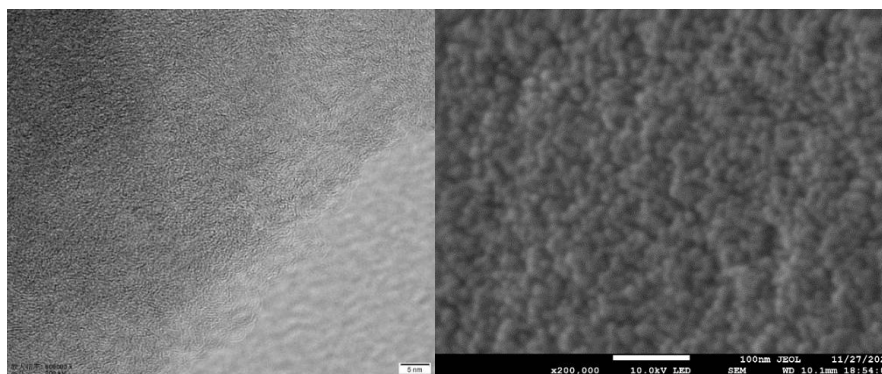
**Table 1** Textural Parameters and CO<sub>2</sub> Adsorption Capacities of the As-Prepared Adsorbents

Sample	SBET (m <sup>2</sup> /g)	Dave(nm)	Vt (cm <sup>3</sup> /g)
C-1.5	1,340.90	2.18	0.69
UC-1-1.5	1,497.28	2.18	0.67
UC-3-1.5	1,617.62	2.38	0.61
UC-5-1.5	1,742.03	2.55	0.62
UC-7-1.5	1,614.79	2.36	0.82
MC-5-1.5	1,391.39	1.95	0.77
DC-5-1.5	1,493.62	2.10	0.73

### 3.3 SEM/TEM

Scanning electron microscopy(SEM) was employed to study the morphology of the representative sample UC-5-1.5. As illustrated in Figure 3, the SEM image reveals that UC-5-1.5 possesses.

The porous structure and detail morphology of UC-5-1.5 was further studied using transmission electron microscopy(TEM). As showing in Figure 3 plentiful wormhole-like micropores can be observed. To determine the crystallite structure of UC-5-1.5.

**Figure 3** The TEM/SEM of UC-5-1.5

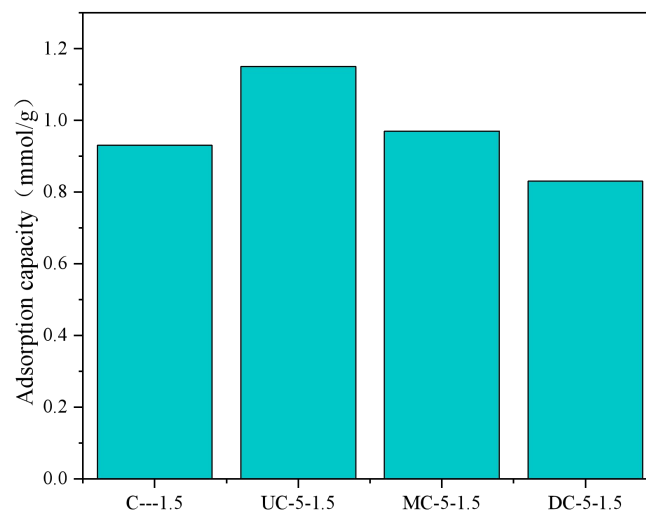
### 3.4 Adsorption Performance

In order to explore the influence of activated carbon carbonation temperature and activation temperature on CO<sub>2</sub> adsorption capacity, the following sets of experiments were done: the carbonation temperature (400-700 °C) and activation temperature (400-800 °C) were changed and the adsorption capacity was measured by thermogravimetric adsorption. From Table 2, when the carbonation temperature is 600 °C, the adsorption capacity is the best, and when the activation temperature is 800 °C, the adsorption capacity is the best.

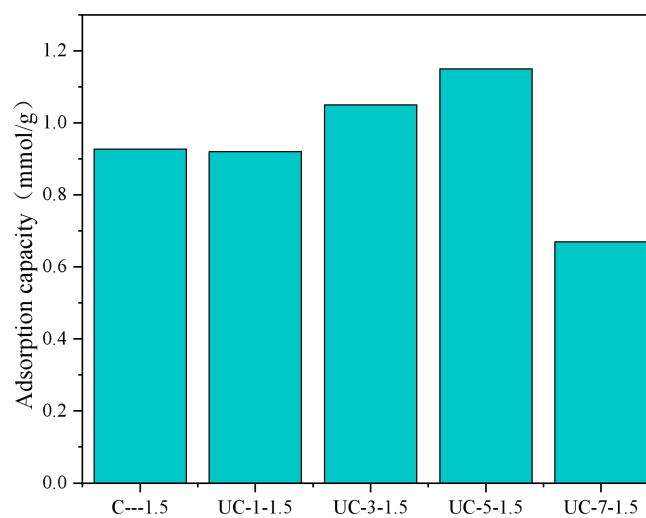
**Table 2** Effect of Carbonization Temperature and Activation Temperature on Adsorption Capacity

Sample	Adsorption (CO <sub>2</sub> , mmol/g)	Sample	Adsorption (CO <sub>2</sub> , mmol/g)
UC-5-400-1.5-800	0.95	UC-5-1.5-400	0.43
UC-5-500-1.5-800	0.61	UC-5-1.5-500	0.79
UC-5-600-1.5-800	1.15	UC-5-1.5-600	0.83
UC-5-700-1.5-800	0.8	UC-5-1.5-700	0.76
		UC-5-1.5-800	1.15

The best adsorbent was screened by the thermo-gravimetric adsorption amount and the static adsorption amount. From Figure 3 and Figure 5, by comparing the static adsorption and thermo-gravimetric adsorption amount of doping different nitrogen sources, the thermo-gravimetric adsorption amount of doped urea can reach 1.15mmol/g is much higher than the adsorption amount of doped melamine and dicyanodiamine. Similarly, the trend of static adsorption is the same. The static adsorption amount of urea doping is 3.2mmol/g much higher than that of doping other types of nitrogen sources

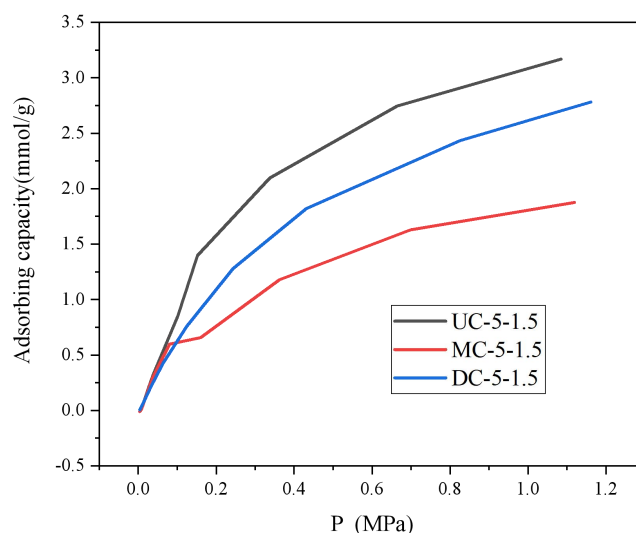


**Figure 4** Adsorption Amount of Different Nitrogen Source Doping

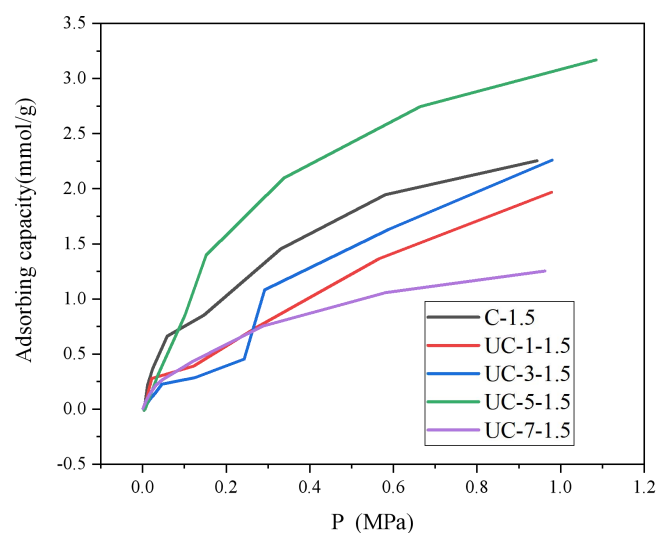


**Figure 5** Data Graph of Adsorption Capacity of Different Urea Content

Comparing the influence of different doped urea content on the adsorption capacity, from Figure 4 and Figure 6, it can be seen that whether it is static adsorption or thermogravimetric adsorption, the activated carbon with a doped N content of 5% is higher than that with other N content. Activated carbon, further indicating that the doped 5% activated carbon has the highest adsorption capacity for CO<sub>2</sub>.



**Figure 6** Static Adsorption of Different Nitrogen Sources



**Figure 7** Static Adsorption Data of Different Urea Content

#### 4 CONCLUSION

Using foam polyurethane as raw material, urea, melamine and diammonium dicyanide were mixed to doping nitrogen, and then activated by KOH to obtain porous carbon adsorbent. The prepared adsorbents have larger specific surface area and higher adsorption capacity of carbon dioxide. The adsorption capacity of porous carbon-based adsorbent obtained by urea mixed with foam polyurethane is the best 3.2mmol/g (225°C, 1bar). KOH activation can obtain a larger specific surface area, so that the adsorbent has a larger CO<sub>2</sub> diffusion and adsorption capacity. On the other hand, KOH can improve the alkalinity of the adsorbent and further improve the CO<sub>2</sub> adsorption performance.

#### COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

#### REFERENCES

- [1] Gurwinder S, Jangmee L, Ajay K, et al. Emerging trends in porous materials for CO<sub>2</sub> capture and conversion. *Chemical Society reviews*, 2020, 49(13): 4360-4404.
- [2] Wang L, Sun F, Hao F, et al. A green trace K<sub>2</sub>CO<sub>3</sub> induced catalytic activation strategy for developing coal-converted activated carbon as advanced candidate for CO<sub>2</sub> adsorption and supercapacitors. *Chemical Engineering Journal*, 2020, 383: 123205-123205.
- [3] Gurwinder S, Jangmee L, Ajay K, et al. Emerging trends in porous materials for CO<sub>2</sub> capture and conversion. *Chemical Society reviews*, 2020, 49(13): 4360-4404.

- [4] Rao L, Liu S, Wang L, et al. N-doped porous carbons from low-temperature and single-step sodium amide activation of carbonized water chestnut shell with excellent CO<sub>2</sub> capture performance. *Chemical Engineering Journal*, 2018, 359: 428-435.
- [5] Bai R, Yang M, Hu G, et al. A new nanoporous nitrogen-doped highly-efficient carbonaceous CO<sub>2</sub> sorbent synthesized with inexpensive urea and petroleum coke. *Carbon*, 2015, 81: 465-473.
- [6] Wu Y, Wang T, Wang H, et al. Active catalyst construction for CO<sub>2</sub> recycling via catalytic synthesis of N-doped carbon on supported Cu. *Nature Communications*, 2019, 10(1): 1-7.
- [7] He S, Chen G, Xiao H, et al. Facile preparation of N-doped activated carbon produced from rice husk for CO<sub>2</sub> capture. *Journal of Colloid And Interface Science*, 2021, 582(PA): 90-101.
- [8] Rao L, Ma R, Liu S, et al. Nitrogen enriched porous carbons from d -glucose with excellent CO<sub>2</sub> capture performance. *Chemical Engineering Journal*, 2019, 362: 794-801.
- [9] Leilei D, Nan Z, Yuancai L, et al. Pyrolysis technology for plastic waste recycling: A state-of-the-art review. *Progress in Energy and Combustion Science*, 2022, 93.
- [10] Li J, Michalkiewicz B, Min J, et al. Selective preparation of biomass-derived porous carbon with controllable pore sizes toward highly efficient CO<sub>2</sub> capture. *Chemical Engineering Journal*, 2019, 360: 250-259.
- [11] Singh G, Kim Y I, Lakhi S K, et al. Single step synthesis of activated bio-carbons with a high surface area and their excellent CO<sub>2</sub> adsorption capacity. *Carbon*, 2017, 116: 448-455.
- [12] Xiaoli Z, Liyao Z, Weiliang D, et al. Solving two environmental problems simultaneously: Microporous carbon derived from mixed plastic waste for CO<sub>2</sub> capture. *Chemosphere*, 2023, 345: 140546-140546.
- [13] Environmental Research. Study Results from Zhejiang Normal University Update Understanding of Environmental Research (Superior Co<sub>2</sub> Uptake On Nitrogen Doped Carbonaceous Adsorbents From Commercial Phenolic Resin). *Ecology, Environment & Conservation*, 2020.
- [14] Xiaoyang S, Hang X, Habib A, et al. Sorbents for the Direct Capture of CO<sub>2</sub> from Ambient Air. *Angewandte Chemie (International ed. in English)*, 2020, 59(18): 6984-7006.
- [15] Urooj K, Jin S P. Chemically modified carbonaceous adsorbents for enhanced CO<sub>2</sub> capture: A review. *Journal of Cleaner Production*, 2021.