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# Effective adsorption of phenols using nitrogen-containing porous activated carbon prepared from sunflower plates

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**Abstract**−Nitrogen-containing porous carbons, the 800SP-$NH_3$, were synthesized using sunflower plates as the major carbon source carbonized at 800 °C and activated with concentrated aqueous ammonia at the same temperature. The porous carbons were characterized by nitrogen physical adsorption-desorption, surface area analyzer, FT-IR, and SEM. The adsorption properties of the porous carbons towards phenols were also investigated by batch methods. The test results show that the average pore diameter of porous carbon is smaller than 2 nm, and nitrogen-containing chemical groups are formed on its surface. The adsorption capacity for phenol, 4-chlorophenol, and p-nitrophenol is 316.5 mg/g, 330.24 mg/g and 387.62 mg/g due to its developed pore structure and nitrogen-containing chemical groups. The adsorption isotherm data greatly obey the Langmuir model.

Keywords: Porous Carbon, Nitrogen-containing, Adsorption, Phenols, Sunflower Plate

## INTRODUCTION

Phenols, used widely in chemicals, pharmaceuticals, petroleum, coal gasification, papermaking, wood, rubber, dye and pesticide industries, are considered as priority organic pollutants by the US, China, and other countries due to their carcinogenic and highly toxic effects on organisms, unpleasant taste and odor even at low concentrations. In the US, according to the Environmental Protection Agency (EPA) regulations, the phenol content in the wastewater must be less than 1 mg/L [1]. In China, according to the Chinese integrated wastewater discharge standard (GB 8978-1996), the maximum permitted concentration of volatile phenols is 0.5 mg/L for standard A effluent and 2.0 mg/L for standard C effluent [2]. In Korea, the maximum permitted concentration of volatile phenols is 0.5 mg/L. Therefore, the effective removal of phenols from wastewater is very important and has attracted considerable research and practical interest.

Various methods, such as degradation [3-6], oxidation [7-9], solvent extraction [10,11], membrane separation [12-14], and adsorption [1,15-41], have been established and developed for removing phenols from wastewater. Among them, adsorption is an effective and widely used method to remove phenols from wastewater due to its higher capability and its relatively simple operability. Porous activated carbon has been deemed as one of the efficient adsorbents for removal of phenols from wastewaters because of its high surface area, well-developed internal pore structure and controllable surface functional groups. Biomass and polymers are the commonly used precursors to prepare porous carbons. Compared with traditional non-renewable precursors, many agricultural wastes and industrial byproducts have been used as renewable precursors for activated carbon such as fruit shell, straw, peels, sewage sludge, fly ash, bagasse and so on [1,21-41].

In general, porous activated carbon is prepared at higher temperature and has few surface functional groups on its surface. So, the adsorption of porous carbon is mainly physical adsorption, and the adsorption capacity was poor. Besides the physical or porous structure, the surface functional groups are considered as the main influence factor of adsorption. To improve its adsorption property, surface chemical modification of porous carbon is desired. For example, nitrogen-containing chemical groups were incorporated after $NH_3$ or $HNO_3$ treating [42-44]. After chemical modification, its adsorption properties improved markedly.

In this work, nitrogen-containing porous carbons are synthesized using sunflower plates as raw material carbonized at 800 °C and activated with concentrated aqueous ammonia at 800 °C. The pore structure was determined, and the surface chemical groups of resultant porous carbon were characterized. Its adsorption properties for phenols were also investigated.

## EXPERIMENTS

### 1. Materials and Instruments

Sunflower plates were obtained from a local farm in Shanxi Province, China. They were washed to remove mud and other impurities, dried at 105 °C for 24 h, subsequently crushed and sieved prior to the carbonization. Phenols and concentrated aqueous ammonia of analytical reagent were both purchased from Beijing chemical reagents factory, China.

Instruments used in this study were as follows: JWGB JW-BK132F surface area analyzer (Beijing, China), S-4800 field emission micro-

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scope (Hitachi, Japan), FTIR4800S infrared spectrometer (Shimadzu, Japan), THZ-92C constant temperature shaker (Boxun Medical Treatment Equipment Factory of Shanghai, China), Unic-2602 UV spectrophotometer (Unic Company, American).

**2. Synthesis of Porous Carbon**

First, a certain amount of sunflower plate powder was carbonized in charcoal furnace at 800 °C for 2 h with heating rate of 3 °C/min with $N_2$ flow of 50 ml/min, and then activated in the same charcoal furnace using concentrated aqueous ammonia replacing the $N_2$. Finally, the resultant samples were washed with distilled water until neutral and dried at 80 °C for 24 h. The unactivated porous carbon, porous carbon activated with concentrated aqueous ammonia was denoted as 800SP and 800SP-$NH_3$, respectively.

**3. Characterizations**

The $N_2$ adsorption-desorption isotherms of 800SP and 800SP-$NH_3$ were obtained at 77 K using surface area analyzer. The samples were degassed under vacuum at 300 °C for 3 h prior to the measurement. The surface areas ($S_{BET}$) were estimated by Brunauer-Emmett-Teller (BET) method. The total pore volumes ($V_{total}$) were evaluated from the liquid volume of $N_2$ at a relative pressure (P/Po) of 0.99. And the average pore diameters were from $S_{BET}$ and $V_{total}$ assuming an open-ended cylindrical pore model without pore networks. Micropore volume ($V_{micropore}$) was determined by Horvath-Kawazoe (HK) method, and mesopore volume ($V_{mesopore}$) was calculated by subtracting off $V_{micropore}$ from $V_{total}$. The pore size distribution was determined by Barret-Joymer-Hanlenda (BJH) model.

The morphology of 800SP and 800SP-$NH_3$ was examined by scanning electron microscope. The samples were dried at 105 °C for 2 h and coated with a thin gold film to give electrical conduction on the carbon external surface. Fourier transform infrared (FT-IR) spectrum of the sample was measured on FTIR4800S spectrometer using the usual KBr pellet technique (Shimadzu, Japan).

**4. Adsorption Experiments**

Batch equilibrium adsorption experiments were performed using about 0.01 g of adsorbent and 50 mL of phenols solution. After adsorption reached equilibrium, the adsorbent separated from the samples by filtering and the filtrate was analyzed with a UV spectrophotometer. The influences of contact time and initial phenols concentration were studied by batch method. The adsorption capacity ($Q_e$) was calculated according to the following equation:

$$Q_e=[(C_0-C_e)/m]\times V$$

where, $C_0$ and $C_e$ is the initial and equilibrium concentration of phenols in the solution (mg/L), V is the volume of the solution (L), and m is the dosage of adsorbent (g).

## RESULT AND DISCUSSION

**1. Characterization of Porous Carbon Structure**

The $N_2$ adsorption-desorption isotherms of the 800SP and 800SP-$NH_3$ at 77 K are shown in Fig. 1.

It is clear that the shape of $N_2$ adsorption-desorption isotherm changes after being activated with concentrated aqueous ammonia. 800SP gives type I and II with a hysteresis loop of type $H_2$. This indicates that 800SP has a great quantity of mesopores, while 800SP-$NH_3$ gives a steep type I isotherm with a small hysteresis loop of type $H_4$. The adsorption of $N_2$ increases rapidly at low relative pressure (P/Po<0.10) and then approaches a plateau with increasing the relative pressure. The adsorption and desorption curves were almost overlapped, which indicates that a large amount of micropores with a highly narrow pore size distribution were developed.

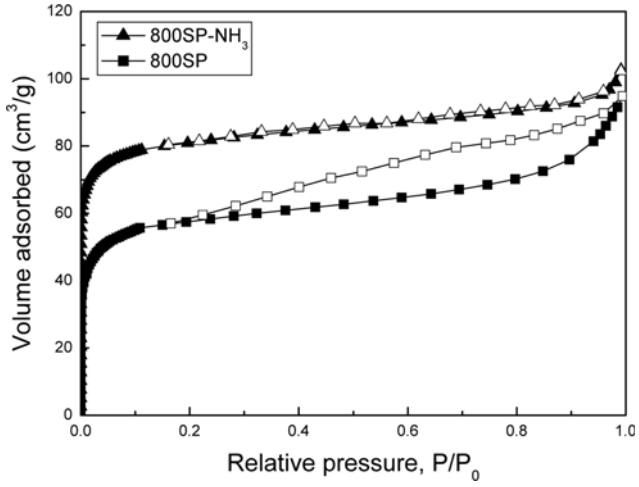


**Fig. 1. $N_2$ adsorption-desorption isotherms.**

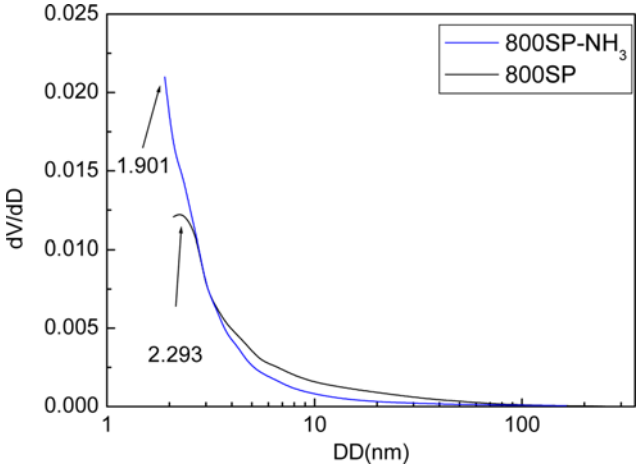


**Fig. 2. Pore size distributions of porous carbons.**

The pore size distributions and most probable pore size of samples are shown in Fig. 2. The pore properties of the 800SP and 800SP-$NH_3$ are listed in Table 1.

The pore size distribution is narrow, the average pores size of 800SP-$NH_3$ was 1.942 nm, and the $V_{micropore}$ of 800SP-$NH_3$ accounted for 75.40% of $V_{total}$. These indicate again that there is a large number of micropores in 800SP-$NH_3$. It can also be seen that the BET special surface area and pore volume is increased after activation

**Table 1. The pore structure parameters**

| Samples | $S_{BET}$ ($m^2$/g) | $V_{total}$ ($cm^3$/g) | $V_{micropore}$ ($cm^3$/g) | $V_{mesopore}$ ($cm^3$/g) | Pore size (nm) |
|---|---|---|---|---|---|
| 800SP | 221.09 | 0.147 | 0.075 | 0.072 | 2.655 |
| 800SP-$NH_3$ | 385.26 | 0.289 | 0.218 | 0.071 | 1.942 |

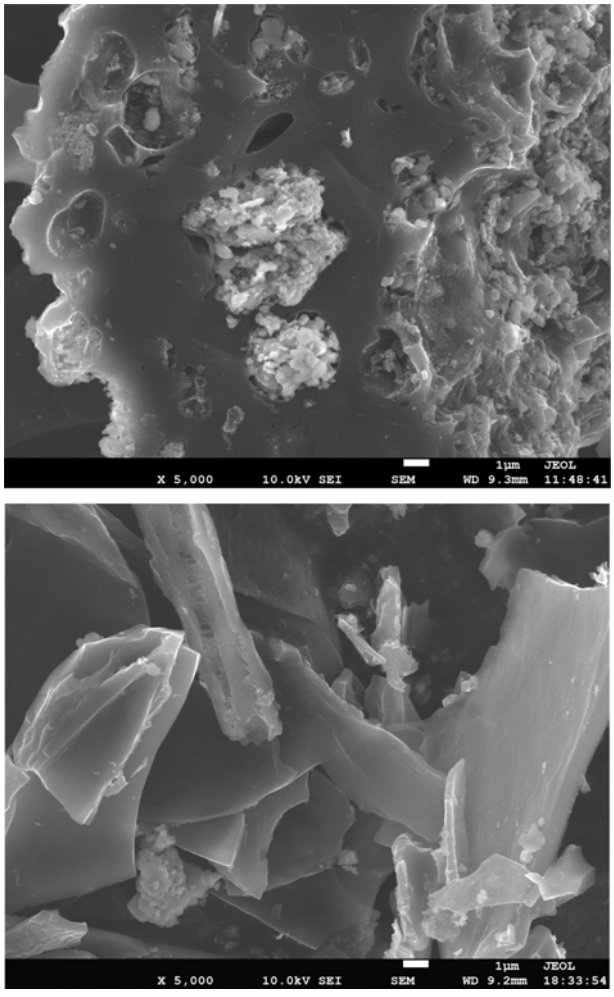


**Fig. 3. SEM images of porous carbons. (a) 800SP, (b) 800SP-$NH_3$.**

with concentrated aqueous ammonia. The increase of BET special surface area and pore volume indicated that the number of pores increased.

The SEM images of porous carbons are shown in Fig. 3.

The surface of the 800SP is relatively coarse as some carbon particles fill the big pores and are attached to the surrounding surface. When the 800SP is activated, the surface becomes smooth, because the filled and attached carbon particles are removed. So, the BET special surface area and pore volume increases. This is consistent with the former structure analysis.

The presence of the nitrogen-containing groups in the prepared porous carbons is confirmed by FT-IR spectroscopy (Fig. 4).

In the spectra of 800SP-$NH_3$, new adsorption bands appeared at 711 and 1,618 $cm^{-1}$. These are assigned to the characteristic absorption of N-H. This evidenced the introduction of amine in the surface of activated carbon.

**2. Adsorption Properties of Porous Carbon Towards Phenols**

The kinetic adsorption curve of the 800SP and 800SP-$NH_3$ towards phenols is shown in Fig. 5.

The saturated adsorption capacity of the 800SP and 800SP-$NH_3$ towards phenol is 128.9 mg/g and 316.5 mg/g, respectively. The adsorption capacity of 800SP-$NH_3$ is higher than that of 800SP. This

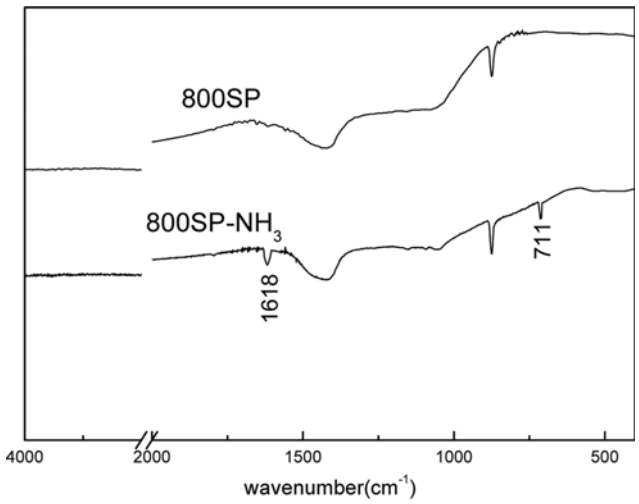


**Fig. 4. FT-IR spectra.**

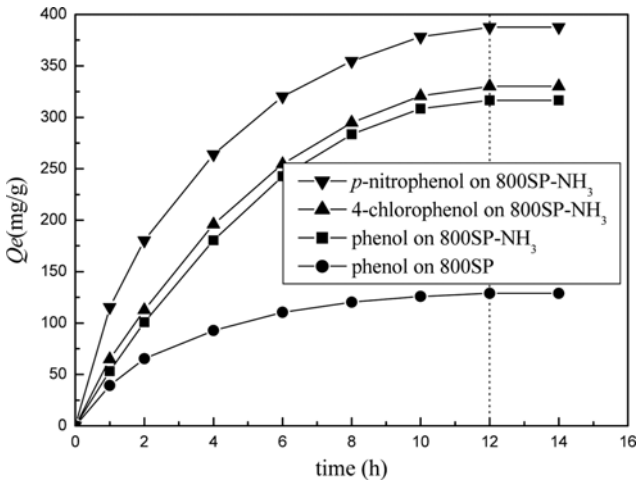


**Fig. 5. Adsorption kinetic curves of 800SP and 800SP-$NH_3$ for phenols. Temperature: 20 °C; pH 6.**

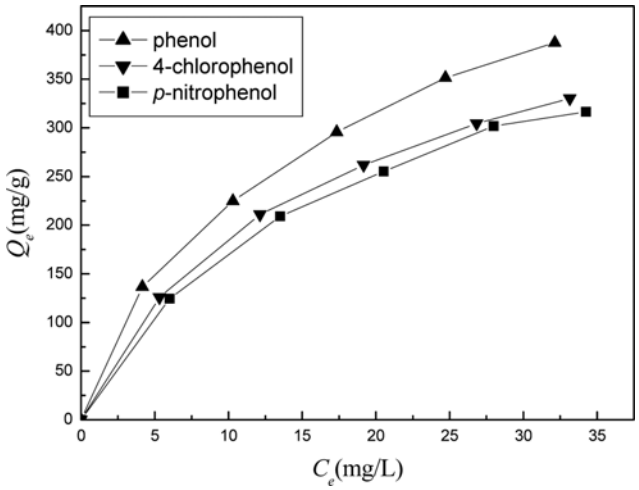


**Fig. 6. Adsorption isotherms of 800SP-$NH_3$ towards phenol. Temperature: 20 °C; Time: 12 h; pH 6.**

**Table 2. Comparisons of adsorption capacity (mg/g) towards phenols by other AC adsorbents**

| Precursors of AC adsorbents | Adsorbate | Adsorption capacity | Reference |
|---|---|---|---|
| Sunflower plates | Phenol | 316.5 | This study |
| Sunflower plates | 4-Chlorophenol | 330.24 | This study |
| Sunflower plates | *p*-Nitrophenol | 387.62 | This study |
| Cherry stone | Phenol | 85 | [1] |
| Corn grain | Phenol | 190 | [21] |
| Date-pit | Phenol | 70 | [22] |
| Avocado kernel seeds | Phenol | 85 | [23] |
| Hydrothermal char | Phenol | 75 | [24] |
| Sewage sludge | Phenol | 190 | [25] |
| Sewage sludge | 4-Chlorophenol | 320 | [25] |
| Brown seaweed | Phenol | 15 | [26] |
| Tabacco residues | Phenol | 12 | [27] |
| Oil palm empty fruit bunch | 2,4-Dichlorophenol | 250 | [28] |
| Almond shell | Phenol | 125 | [29] |
| Almond shell | *p*-Nitrophenol | 210 | [29] |
| Vine shoots | Phenol | 75 | [29] |
| Vine shoots | *p*-Nitrophenol | 220 | [29] |
| Pokeweed | Phenol | 170 | [30] |
| Vinegar lees | Phenol | 120 | [31] |
| Bagasse fly ash | Phenol | 3.22 | [32] |
| Coffee grounds | *p*-Nitrophenol | 100 | [33] |
| Melon seeds | *p*-Nitrophenol | 97 | [33] |
| Orange peels | *p*-Nitrophenol | 100 | [33] |
| Sewage sludge | Phenol | 176 | [34] |
| Sugarcane bagasse | Phenol | 25 | [35] |
| Soybean straw | Phenol | 278 | [36] |
| Albizia lebbeck seed pods | 4-Chlorophenol | 247.9 | [37] |
| Coconut shell | Phenol | 60 | [38] |
| Olive stone | Phenol | 27 | [39] |
| Switch grass | Phenol | 94 | [40] |
| Eggshells | Phenol | 180 | [41] |
| Lgnite activated carbon | Phenol | 230 | [45] |
| S.D. Fine Chemicals Boisar, India | Phenol | 140 | [46] |
| CPG-LF | Phenol | 80 | [47] |
| MN-200 | Phenol | 50 | [47] |
| XAD-2 | Phenol | 70 | [47] |

is attributed to the developed pore structure, high specific surface and the surface modification with the functional groups in the 800SP-$NH_3$ structures.

Additionally, the 800SP-$NH_3$ prepared in this study possesses higher adsorption capacity for other phenols than previously reported porous carbons including some commercialized activated carbons, and the comparisons are shown in Table 2. This illustrates that 800SP-$NH_3$ possesses very strong adsorption ability and high affinity for phenols, and they can be used to remove effectively phenols.

The adsorption isotherm of 800SP-$NH_3$ towards phenol is shown in Fig. 6.

To investigate the equilibrium adsorption behavior of phenol on porous carbon, it was important to have a satisfactory description of the quantitative relationship between the two phases in the adsorption system. The adsorption isotherm is fitted by the Langmuir model [48,49].

$$\text{Langmuir isotherm: } C_e/Q_e = C_e/Q_0 + 1/(KQ_0)$$

where $C_e$ (mg/L) was the equilibrium concentration, $Q_e$ (mg/g) was the equilibrium adsorption capacity, $Q_0$ (mg/g) was the monolayer sorption capacity, K (L/mg) was the Langmuir constant related to the adsorption energy.

The linear regression equations, parameters and the correlation coefficient are listed in Table 3.

From the values of $R^2$ in Table 3, it can be concluded that the Langmuir equations fit best to the experimental data. Thus, the applicability of monolayer coverage of phenol on the surface of the activated carbon is confirmed.

**Table 3. Adsorption linear regression equations of 800SP-$NH_3$ towards phenol**

| Adsorption model | Langmuir |
|---|---|
| Linear regression equation | $C_e/Q_e=0.002C_e+0.0378$ |
| $R^2$ | 0.9954 |
| K | 0.053 |
| $Q_0$ | 500 |

## CONCLUSION

Nitrogen-containing porous carbon with high surface area and large pore volume was synthesized successfully from sunflower plates carbonized at 800 °C and activated with concentrated aqueous ammonia at the same temperature. The BET special surface area is as high as 311.79 $m^2$/g. The microporous structure and presence of nitrogen-containing groups was confirmed. The nitrogen-containing microporous carbon displayed fast and high adsorption capacities for phenols due to its developed pore structure and nitrogen-containing chemical groups, the adsorption capacities towards phenol, 4-chlorophenol, and *p*-nitrophenol were 316.5 mg/g, 330.24 mg/g and 387.62 mg/g, respectively. The adsorption isotherm data greatly obey the Langmuir model.

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