

Characteristics of nitrogen-enriched activated carbon prepared from waste medium density fiberboard by potassium hydroxide

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Abstract Most waste of medium density fiberboard (MDF) is burnt, which could release toxic gases and pollutants to the environment. So, the re-using waste of MDF is highly desired. The nitrogen atoms of waste medium density fiberboard originate from urea–formaldehyde resin adhesive used in the manufacturing process, so nitrogen-enriched activated carbons could be prepared easily. Nitrogen-enriched activated carbons were prepared from waste MDF by potassium hydroxide. The activation temperature was ranged from 600 to 900 °C, and the chemical agent/waste MDF varied from 1 to 5. Iodine number was used to evaluate the adsorption ability of waste MDF activated carbons. The pore properties including surface area, pore volume and pore size distribution were determined by N₂ adsorption. The method of elemental analysis and XPS were used to estimate how nitrogen functional groups changed with different activation conditions. The results showed that the adsorption of iodine number of activated carbons was ranged from 661 to 1350 mg/g. The surface area of waste MDF activated carbons was different from 941 to 1876 m²/g and total pore volume was from 0.455 to 0.949 cm³/g. The pore size distribution indicated that waste MDF activated carbons included both micropores and mesopores, and the analysis of element implied that the contents of nitrogen varied from 0.41 to 2.31 %.

Keywords Activated carbon · Waste MDF · Chemical activation

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Introduction

Activated carbon (AC) is predominantly a solid with a large internal surface area and pore volume. It is one of the most important adsorbents used in industry. This adsorbent is mainly used for separation and purification of gaseous and liquid mixtures [1–3]. The nature of the precursor, activation method, and activation conditions determines the characteristics of porosity in ACs, including pore size distribution, pore shape and surface chemistry [4, 5].

There are basically two methods for preparing AC: physical and chemical activation [6]. In the chemical method, the starting material is impregnated with a chemical agent, acid or base, and the blend is heated to a temperature. Chemical activation reduces the formation of tar and other byproducts, thereby increasing carbon yield [7, 8]. The type and the amount of the chemical agents used are important to enhance the quality and quantity of the AC obtained.

Great potential exists for developing AC products from waste wood. According to statistics of city environment, 6 billion wastes are generated in China each year, and waste wood accounts for 1 %, which is about 60 million tons [9, 10]. Most of the waste wood is burnt, which releases toxic gases and pollutes the environment. So, preparing the AC from waste wood will reduce costs and environmental impacts. Also, it will develop sustainable wood industry.

Nowadays, the modification of activated carbon is widely used in the field of adsorption. It is focused mostly on the development of the material with basic oxygen or nitrogen groups. It is indeed well known that nitrogen-containing surface groups confer to AC an increased ability to absorb acid gases [11, 12] and phenolic compounds [13]. Usually, there are several methods for obtaining the AC enriched in nitrogen. One of the methods is carbonization

followed by activation of plastics containing nitrogen in their structure [14]. Another method of getting nitrogen-enriched AC is the exposure of the preliminary AC to nitrogen compounds in elevated temperatures [15, 16]. A very effective process of nitrogen introduction into carbons is ammoxidation [17, 18]. In the waste MDF, nitrogen is provided by the adhesive: urea–formaldehyde and melamine–formaldehyde resins, dispersed all through the board, and the impregnating each particle of wood. So, the preparation of nitrogen-enriched AC from waste MDF can be accessible.

In this study, ACs were produced from waste MDF by chemical activation with potassium hydroxide. The effects of activation temperature and KOH/MDF on the yield and adsorption ability were investigated. Also, the structural characteristics were characterized by pore structures and BET surface area. In addition, the content of N was discussed to explore the changes of N under different conditions in the process of activation. The nitrogen-enriched activated carbon will apply to adsorb phenolic compounds.

Materials and methods

Materials

Waste MDF was collected from wood processing factory in Beijing Forestry University. MDF was consisted of poplar and urea–formaldehyde resin (wt, 12 %). KOH with analytical grade was purchased from Beijing Lanyi chemical reagent.

Methods

In carbonization step, MDF was cut into 20 cm × 10 cm × 3 cm pieces and then these pieces were heated up to a carbonization temperature of 500 °C at a heating rate of 100 °C/h, and were held this temperature for 1 h. The samples were then ground and screened out with sieves. The fraction in the particle diameter ranged from 40 to 60 mesh. The particle samples were dried in a 105 °C oven for 4 h.

In activation step, dried samples with the mass of 3 g were soaked in a 50 % KOH solution for 16 h at the investigated impregnation (1:1, 2:1, 3:1, 4:1 and 5:1). The soaked samples were placed in a nickel boat, and then carbonized at the desired temperatures (600, 700, 800 and 900 °C) in an electric furnace under nitrogen flow. Then samples were held at desired temperature for 50 min before cooling down. Then, these ACs were washed sequentially with a 0.5 N HCl solution. Consecutively, ACs were repeatedly washed with hot distilled water until the pH of solution reaches 6–7. Finally, these ACs were dried in an oven for 6 h at 105 °C.

Characterization

The yield of AC was calculated by equation:

$$Y = \frac{M_1}{M_2} \times 100 \% \quad (1)$$

where M_1 is weight of AC and M_2 is weight of oven-dried MDF.

Iodine number was determined at 303 K based on the Standard Test Method ASTM Designation: D4607-86.

The pore structure characteristics of the samples were measured by N₂ adsorption isotherm at −196 °C using an ASAP 2010 Micromeritics. BET surface area was calculated from N₂ adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation [19]. The Dubinin–Radushkevich (DR) equation was used to calculate the micropore volume from the N₂ adsorption data. The micropore surface areas were then determined from the values obtained from the micropore volumes [20]. The pore size distribution of the ACs was determined by density functional theory (DFT) method [21].

The elemental analysis (contents in carbon, hydrogen, and nitrogen) of the ACs was made in a CHNS Analyzer (ThermoFinnigan Flash, EA, 1112 series).

In addition, the chemical composition and state of the ACs were determined by X-ray photoelectron spectroscopy (XPS) with an ESCALAB 250 (VG Scientific, UK) instrument.

Results and discussion

The effect of KOH/MDF on yield and iodine number

The ratio of impregnation agent/raw material has been found to be the most important parameter in a chemical activation process. The effect of KOH/MDF was studied when starting material was soaked in a 50 % KOH solution for 16 h. And all the samples were activated by heating at 800 °C for 50 min. The experimental results were shown below.

It can be seen from Fig. 1 that when the ratio was 1, the yield was 26.02 %. However, when the ratio increased, the yield decreased. The minimum yield was 19.45 % when the ratio was 5. The behavior in the weight loss between 1 and 5 impregnation ratios was due to the larger evolution of volatiles.

The maximum iodine number was 1035 mg/g when the ratio was 3. It could be expected, with increasing of ratio, more pores would be formed. However, when the ratio reached a certain value, the pores would be widen and burnt off. It was observed from Fig. 1, when the ratio increased from 1 to 3, the iodine number increased from

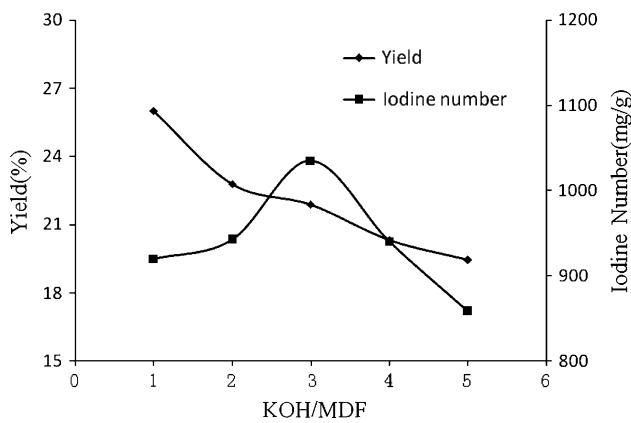


Fig. 1 Effect of KOH/MDF on yield and iodine number

920 to 1035 mg/g. Then, with the ratio increasing, the iodine number decreased. The trends could be found in several reports, such as Feirro et al. [22] and Wang et al. [23].

The effect of activation temperature on yield and iodine number

The effect of activation temperature was studied when starting material was soaked in a 50 % KOH solution for 16 h with an impregnation ratio of 3:1. The experimental results were shown below.

Figure 2 depicted the effect of activation temperature on the yield of AC. When carbonization temperature ranged from 600 to 800 °C, the rate of weight loss was high primarily due to the initial large amount of volatiles that can be easily released with increasing temperature as well as the loss of moisture to a lesser extent.

The iodine adsorption capacity of the AC increased from 661 to 1350 mg/g with an increase in the range of 600–850 °C, after then, decreased from 1350 to 1242 mg/g with an increase in the range of 850–900 °C. It was probably that when the activation temperature reached a certain value, the pores would be widened and burnt off.

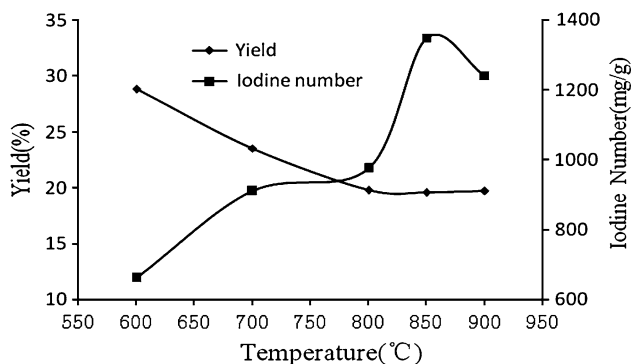


Fig. 2 Effect of temperature on yield and iodine number

Table 1 Elemental analysis of the ACs

Activated carbons prepared from MDF		Elemental analysis				
KOH/MDF	Activation temperature (°C)	C (wt, %)	H (wt, %)	N (wt, %)	O (wt, %)	Ash (wt, %)
1:1 (AC1)	800	78.97	1.20	2.31	12.01	5.51
1:2 (AC2)	800	80.29	0.95	1.98	10.86	5.92
1:3 (AC3)	800	85.48	0.86	1.38	7.53	4.75
1:4 (AC4)	800	86.84	0.83	1.42	6.04	4.87
1:5 (AC5)	800	86.81	1.10	0.58	6.46	5.05
1:3 (AC6)	700	74.15	1.15	2.13	15.99	6.58
1:3 (AC7)	800	85.48	0.86	1.38	7.53	4.75
1:3 (AC8)	850	90.44	0.57	1.33	3.24	4.42
1:3 (AC9)	900	89.45	0.69	0.41	4.98	4.47

Similar trends were also found by Sudaryanto et al. [21] when high surface area ACs were prepared from cassava peel by KOH activation. Yang and Lua [24] reported that AC was prepared from pistachio-nut shells by potassium hydroxide activation.

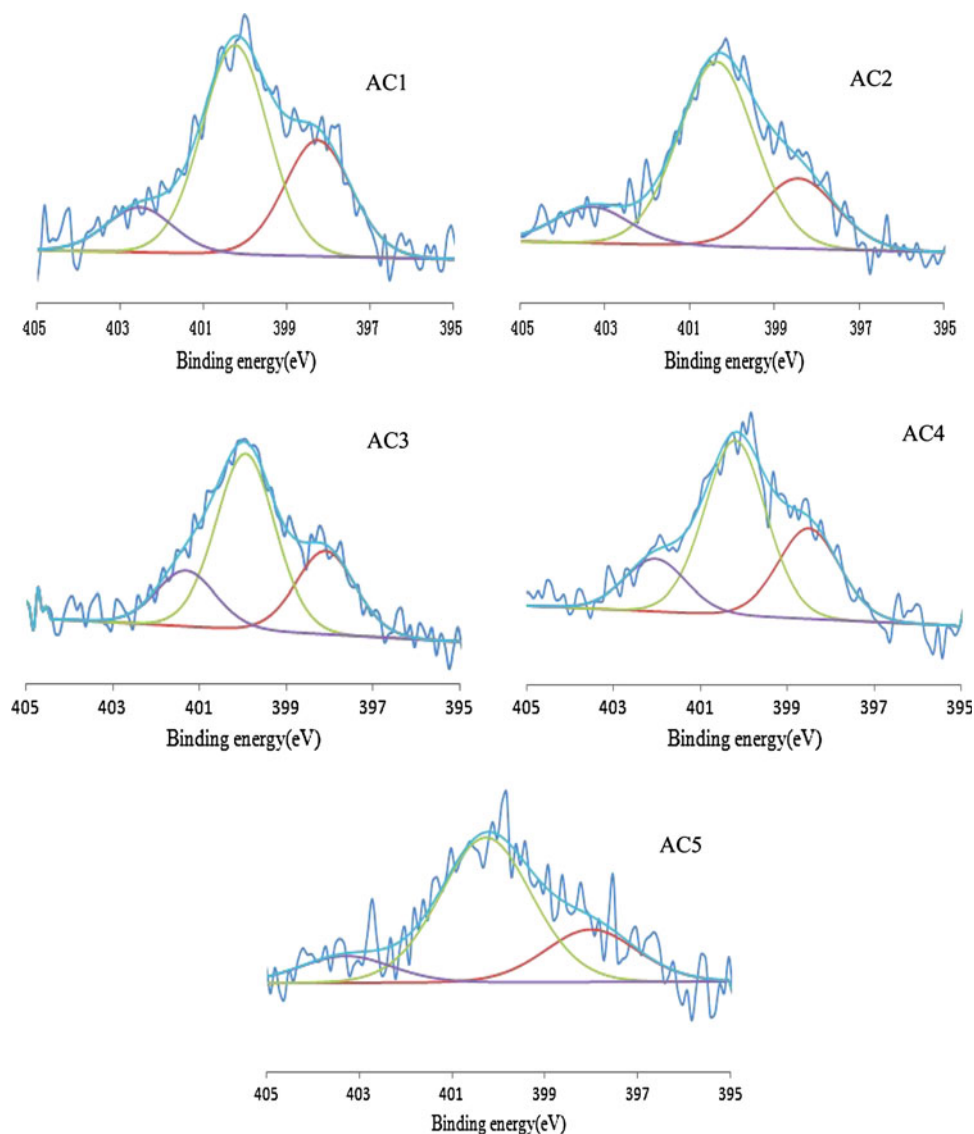
Elemental analysis

Table 1 showed the elemental analysis of the ACs prepared according to the experimental conditions. As temperature increased, the content of N decreased, which was due to the volatilization of unstable functional groups containing N. Also, the content of N decreased when the ratio of KOH/MDF increased. Nitrogen was present at levels ranging typically from 2.31 to 0.41 %. The content of N in the most of ACs samples was higher than commercial ACs (the content of nitrogen in commercial AC was normally lower than 0.5 %). As a result, the content of N in the waste MDF activated carbon decreased with the increasing of activation temperature and impregnation ratio in the process of activation.

XPS study

Figures 3 and 4 showed N1s XPS spectra of the ACs prepared from MDF. The peaks with higher binding energies can be ascribed to N-6 (pyridinic nitrogen, 398.7 ± 0.3 eV), N-5 (pyrrolic nitrogen and pyridinic nitrogen in association with oxygen functionality, 400.3 ± 0.3 eV), N-Q (quaternary nitrogen, nitrogen substituted with carbons in the aromatic grapheme structure, 401.4 ± 0.5 eV), N-X and oxidized nitrogen (402–405 eV). Except for the N-Q, all nitrogen functionalities are located at the edge of the graphene structure [25–27]. Types of nitrogen surface functional groups were presented in Table 2. It could be seen from Table 2 that the dominant nitrogen species in the most

Fig. 3 N1s XPS spectra of AC of different impregnation ratio (gram chemical agent/gram wood fiberboard waste = 1, 2, 3, 4, 5)



of AC was N-5. The types and contribution of particular nitrogen species on AC's surfaces differed although they have almost the same content of nitrogen on the surface. According to the experimental data, the chemical state of nitrogen could be sensitively changed by the activation temperature and the impregnation ratio.

Textural characterization

Table 3 listed the physical properties of the ACs at different impregnation ratio while the activation temperature was 800 °C and the activation time was 50 min. The adsorptive capacities were related to their specific area, pore volumes and pore size. As the impregnation ratio increased from AC1 to AC3, BET surface area and pore volume increased. The maximum BET surface area of 1178 m²/g and the 0.414 cm³/g of micropore volume were obtained at 1:3.

After that, increasing the ratio, the BET surface area decreased. An increase in the amount of activating agent promoted the contact area between MDF and activating agent. Therefore, the surface area of the AC increased.

Table 4 showed the structural characteristics of the ACs at different activation temperature while the KOH/MDF was 3 and the activation time was 50 min. It can be seen from Table 4 that the maximum BET surface area of 1876 m²/g and total pore volume of 0.949 cm³/g were obtained at 850 °C. From AC6 to AC7, both surface area and micropore volume increased significantly. And with AC7, AC8 had a lower microporosity and more mesopore volume. When temperature increased from 850 to 900 °C, the BET surface area decreased.

We prepared activated carbon from waste MDF which would be used to adsorb phenolic compounds in future. So, both high BET surface area and high content of N were desired. Considering all the factors, AC8 was suitable

Fig. 4 N1s XPS spectra of AC of different activation temperature (700, 800, 850, 900 °C)

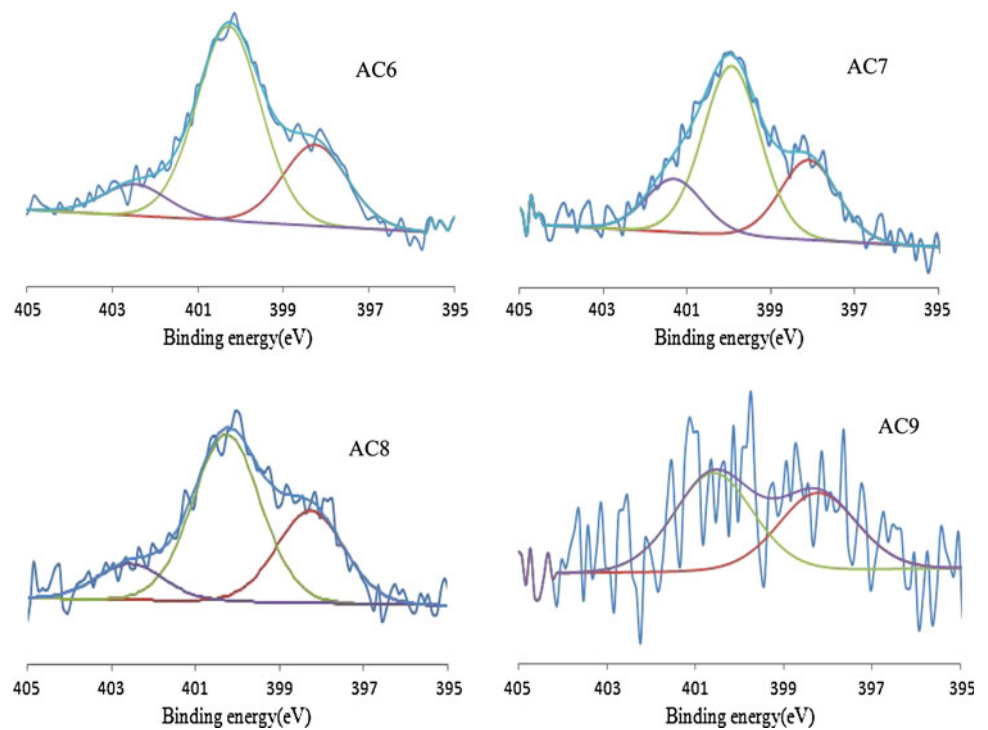


Table 2 Distribution of N species obtained from the deconvolution of the N1s peaks

Sample	N-6, pyridinic nitrogen [25–27] (398.7 ± 0.3 eV)	N-5, pyrrolic nitrogen, pyridone [25–27] (400.3 ± 0.3 eV)	N-Q, quaternary nitrogen [25–27] (401.4 ± 0.4 eV)	N-X, oxidized nitrogen [25–27] (402–405 eV)
AC1	31.34	56.58	–	12.18
AC2	23.95	63.37	–	12.68
AC3	26.28	56.04	17.68	–
AC4	28.26	55.08	–	16.66
AC5	23.55	64.44	–	12.01
AC6	26.29	63.39	–	10.32
AC7	26.28	56.04	17.68	–
AC8	31.24	56.58	–	12.18
AC9	43.99	56.01	–	–

Table 3 Structural characteristics of the activated carbons with different impregnation ratio ($T = 800\text{ °C}$)

KOH/MDF	S_{BET} (m ² /g)	S_{mi} (m ² /g)	S_{me} (m ² /g)	V_{tot} (cm ³ /g)	V_{mi} (cm ³ /g)	V_{me} (cm ³ /g)
1:1 (AC1)	993	854	139	0.476	0.396	0.080
1:2 (AC2)	1146	877	269	0.549	0.401	0.148
1:3 (AC3)	1178	899	279	0.572	0.414	0.158
1:4 (AC4)	1134	707	427	0.567	0.322	0.245
1:5 (AC5)	1123	435	688	0.600	0.192	0.408

S_{BET} , surface areas; S_{mi} , micropore area; S_{me} , mesopore area; V_{tot} , total pore volumes; V_{mi} , micropore volumes; V_{me} , mesopore volumes

nitrogen-enriched AC for phenolic compounds. The BET surface area was 1876 m²/g and the content of N was 1.33 %. Mykola et al. [28] prepared nitrogen-enriched AC

treated with melamine and urea in elevated temperatures. The content of N was 2.9 % and BET surface area was 732 m²/g.

Table 4 Structural characteristics of the activated carbons with different temperature (KOH/MDF = 3)

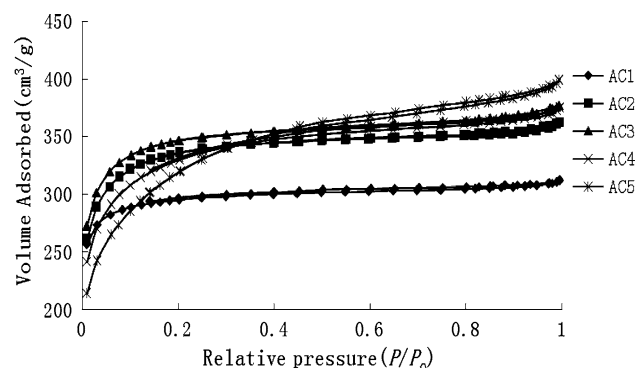
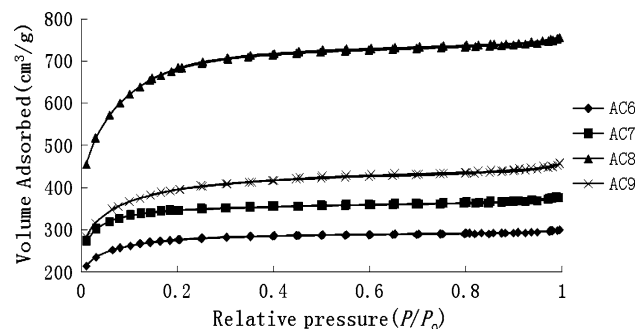
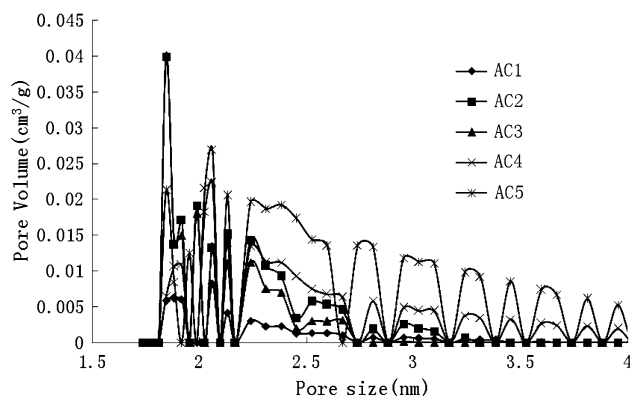
Temperature (°C)	S_{BET} (m ² /g)	S_{mi} (m ² /g)	S_{me} (m ² /g)	V_{tot} (cm ³ /g)	V_{mi} (cm ³ /g)	V_{me} (cm ³ /g)
700 (AC6)	941	646	295	0.455	0.298	0.157
800 (AC7)	1178	899	279	0.572	0.414	0.158
850 (AC8)	1876	931	945	0.949	0.406	0.543
900 (AC9)	1362	818	544	0.686	0.372	0.314

S_{BET} , surface areas; S_{mi} , micropore area; S_{me} , mesopore area; V_{tot} , total pore volumes; V_{mi} , micropore volumes; V_{me} , mesopore volumes

N₂ adsorption–desorption isotherms

Figure 5 showed the nitrogen adsorption–desorption isotherms of ACs from MDF at different impregnation ratio. AC1–AC4 showed almost flat plateau at higher relative pressures, showing type 1 isotherm. Type 1 indicated that the samples were microporous materials. But, the small hysteresis loops seen on the adsorption–desorption isotherms were due to the existence of mesopores [29]. In addition, throughout the entire pressure range, AC5 revealed a gradual increase in nitrogen uptake. So, the isotherm was more likely of type 2. As can be seen from the Fig. 5, the adsorption capacity increased with increasing impregnation ratio, which indicated the widening of microporosity.

Figure 6 depicted the nitrogen isotherms at different activation temperature. All the samples were type 1

**Fig. 5** Nitrogen adsorption–desorption isotherms for prepared activated carbons with variable impregnation ratio**Fig. 6** Nitrogen adsorption–desorption isotherms for prepared activated carbons with variable activation temperature**Fig. 7** Pore volume of prepared activated carbons with variable impregnation ratio

isotherm. They were micropore and mesopore materials. With increasing temperature from 700 to 850 °C, the adsorption increased. However, when the temperature increased from 850 to 900 °C, the adsorption decreased. It probably because that pores were burn off.

Pore size distribution

The pore size distribution was described as structural heterogeneity of the porous material and closely to both equilibrium characteristics and kinetics of these materials used in industrial purposes [30]. This study assumed that micropores are <2 nm wide, mesopores are 2–50 nm wide, and macropores are more than 50 nm wide [31].

As can be seen from the Figs. 7 and 8, the pores of the prepared AC included micropores and mesopores. From the Fig. 7, with increasing ratio of KOH/MDF, the mesopores increased. It could be found from the Fig. 8 that the AC8 had the most mesopores. Similar results were obtained by Sudaryanto et al. [21].

Conclusions

In this study, nitrogen-enriched activated carbons were prepared from waste MDF by KOH activation. The adsorption of iodine number of ACs was ranged from 661

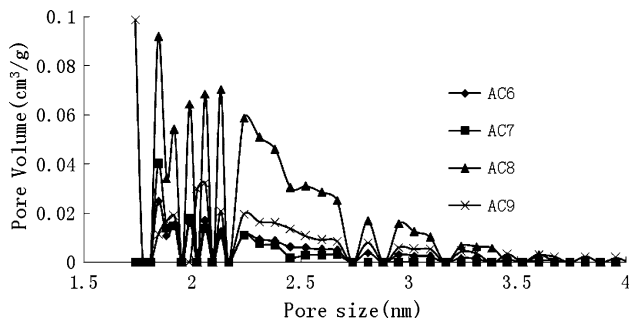


Fig. 8 Pore volume of prepared activated carbons with variable temperature

to 1350 mg/g. The final products were micropores and mesopores activated carbons with the surface area varying from 941 to 1876 m²/g and total pore volume varying from 0.455 to 0.949 cm³/g. The content of nitrogen in the AC was different from 0.41 to 2.31 %.

According to the experimental results, waste MDF is a suitable material for nitrogen-enriched activated carbon. It could easily absorb acid gases and phenolic compounds. In future, we will study phenol adsorption on nitrogen-enriched activated carbon. Also, we will investigate how the content of N and nitrogen species affect the phenol adsorption.

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