Experimental Study on Modified Fruit Shell Carbon for Methane Adsorption and Decarbonization

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Modification of activated carbon has the potential to improve its adsorption and separation capacity. Different concentrations of ammonia (6%, 9%, 12%, 15%) and treatment times (4 h, 6 h, 8 h, 10 h) were used to modify jujube shell carbon and coconut shell carbon in ultrasonic washing equipment. Biogas adsorption experiments were carried out with modified activated carbon to study the effect of adsorption and decarbonization on activated carbon surface functional groups. After modification, the surface alkaline functional groups of activated carbon increased, the acidic functional groups decreased, and the adsorption performance of CO_2 was enhanced. In addition, the specific surface area and total pore volume of activated carbon decreased, the average pore size increased, and the degree of graphitization increased. In the experimental research range, under ultrasonic conditions, jujube shell carbon impregnated with 12% ammonia water for 4 h and coconut shell carbon impregnated with 9% ammonia water for 10 h had the best modification effect. The adsorption capacity for CO_2 was 1.83 and 1.745 mmol/g, respectively, which increased by 0.8 mmol/g and 0.599 mmol/g, respectively, compared with the unmodified sample.

INTRODUCTION

It is necessary to transition from carbon-based fossil fuels to renewable and clean energy in order to maintain sustainable development and economic growth. Biogas is a high-quality renewable energy source with advantages such as renewability, low pollution, and wide distribution. However, biogas has not yet achieved high-quality utilization in China, mainly due to its high content of carbon dioxide. Biogas decarbonization and quality improvement has potential to alleviate the energy crisis.

Among the existing methods for capturing CO_2, adsorption is the most promising technology for industrial applications due to its high efficiency, low cost, and ease of operation over a relatively wide temperature range. The adsorption effect mainly depends on the choice of adsorbent, and the commonly used carbon dioxide adsorption materials are carbon molecular sieves, activated carbon, zeolite, calcium oxide, and metal organic frameworks (MOFs). Activated carbon has the advantages of low price, large specific

surface area, high porosity, stable chemical structure, and controllable surface functionalization, *etc*. It is widely used in industrial adsorption fields. Activated carbon is a non-polar adsorbent, so it is often used to adsorb non-polar substances, and its adsorption capacity for polar substances is weak. The adsorption capacity of activated carbon mainly depends on its pore structure and surface chemical properties. Research has shown that the adsorption of CO_2 gas is greatly influenced by the structure of the adsorbent, mainly by the volume of micropores. The larger the proportion of micropores, the better the adsorption effect (Sanchez *et al*. 2014). Liu *et al*. studied the influence of surface functional groups of activated carbon on the adsorption process (Liu and Wilcox 2012). When the hydroxyl and carboxyl groups of surface oxygen-containing functional groups exist, the adsorption of activated carbon on CO_2 will be enhanced. These oxygen-containing functional groups have high electronegativity, which enables them to serve as basic adsorption sites. Therefore, the modification of activated carbon will introduce new chemical functional groups, which can significantly improve the adsorption capacity of activated carbon and enhance its selective adsorption. Currently, common modification methods include acid modification, alkali modification, loaded metal modification, and ultrasonic modification (Zheng *et al*. 2019). By modification, the chemical properties of the surface of activated carbon can be changed, making it a more targeted adsorbent. Research has shown that the introduction of Lewis bases can increase the affinity of materials for carbon dioxide, as carbon dioxide can act as a Lewis acid. Therefore, introducing nitrogen containing functional groups on the surface of activated carbon through modification can significantly enhance its adsorption capacity for CO_2 (Petrobic *et al*. 2021).

Waralee Dilokekunakul used bamboo waste as raw material to prepare activated carbon through heat treatment. The activated carbon was then modified to nitrogen rich and oxygen rich carbon through urea, air oxidation, and KOH activation. The results showed that nitrogen rich carbon exhibits the strongest CO_2 affinity and maximum CO_2 adsorption capacity. Under certain conditions of pore width and functional groups, the higher the temperature, the lower the CO_2 affinity (Dilokekunakul *et al*. 2020). Ipeaiyeda *et al*. (2020) studied the effects of ammonia and ammonium acetate on the physical and chemical properties, morphology, and porous structure of activated carbon produced from coconut shells and palm fruit shells. The results showed that the surface area of activated carbon ranged from 934 to 1646 m^2/g. After modification, the pores of activated carbon were slightly widened, the BET surface area slightly increased, and the pore size increased. Zhang *et al*. (2010) modified high specific surface area activated carbon (AC) using ammonia solution immersion and microwave radiation under N_2 or H_2, respectively. The results showed that after surface modification, the content of C and N elements in the sample increased compared to the original AC, while the content of O elements decreased. Compared with the original activated carbon, the more alkaline groups on the surface of activated carbon, the higher its adsorption capacity for CO_2. The adsorption capacity of CO_2 by microwave irradiation modified AC in N_2 atmosphere was 3.75 mmol/g at 1 atm and 293 K, which increased by 28% compared to the original AC (Zhang *et al*. 2010). Zhang studied the effects of non-cavitating and cavitating states on pore volume, surface area, surface functional groups and microscopic morphology. The results showed that ultrasonic enlarges the surface area and pore size of activated carbon, which mainly affected the pore volume. Ultrasonic cavitation also promoted the increase of activated carbon porosity, mainly affecting the increase of specific surface area and micropore volume, but excessive cavitation would lead to the decrease of activated carbon porosity (Zhang *et al*. 2019). In summary, both alkali modification and ultrasonic modification can

change the pore structure of activated carbon, which is conducive to adsorption. However, few scholars have combined the two modification methods to study the adsorption separation of CO_2/CH_4.

In this study, coconut shell activated carbon and date shell activated carbons were used as raw materials. The materials were soaked with ammonia and modified by ultrasonic oscillation. The purpose of this study was to introduce nitrogenous functional groups on the surface of activated carbon through ammonia modification to enhance the adsorption capacity of CO_2 and expand the pore channels of activated carbon and increase its porosity through ultrasonic cavitation. Through a self-made adsorption device, the physical and chemical properties of the modified activated carbon and its adsorption and separation effect on CO_2/CH_4 are studied, providing reference for the preparation of high CO_2/CH_4 separability modified activated carbon.

EXPERIMENTAL

Materials and Instruments

The adsorption material had been prepared using a pyrolysis temperature of 1200 °C, to make steam-activated coconut shell activated carbon (1-2 mm) and date shell activated carbon (1 to 2 mm). The activated carbon was purchased from Gongyi City Sanle water purification materials factory. The aqueous ammonia, used as modifier, was purchased from Yantai Shuangshuang Chemical Co., Ltd. The mixture used as an artificial biogas with a volume ratio of 60% CO_2 and 40% CH_4, was purchased from Henan Yuanzheng Special Gas Co., Ltd. The instruments used are shown in Table 1.

Table 1. Experimental Instruments

Instrument Name	Specification and model	Manufacturer
Fourier transform infrared spectrometer (FTIR)	IR-960	Tianjin Ruian Technology Co., LTD
Fully automatic specific surface area and pore analyzer	BELSORP-mini II	Michick Bayer Co., Ltd., Japan
Laser confocal micro Raman spectrometer	HR-Evolution	HORIBA, France
Ultrasonic cleaner	KS-5200E	Kunshan Jielimei Ultrasonic Instrument Co., Ltd
Gas chromatograph	G1180A	Agilent Technologies Co., Ltd
DHG Series Heating and Drying Oven	DHG-9070A	Shanghai Jinghong Experimental Equipment Co., Ltd
Multipurpose vacuum pump for circulating water	SHZ-D(III)	Zhengzhou Dufu Instrument Factory

Methods

The mass concentration of the ammonia modifiers was set to 4 levels (6%, 9%, 12%, 15%), the modification time was set to 4 durations (4 h, 6 h, 8 h, 10 h), and the modification temperature was set to 30 °C. Each group took 8 g carbon, put it in a 100 mL conical bottle, and 100 mL of ammonia solution of different concentrations was poured in and sealed. After modification, the sample was placed in the oven and dried at 105 °C for 12 h. After that, the BET specific surface area analyzer, Fourier transform infrared

spectrometer and Raman spectrometer were used to characterize the sample. The adsorption experiment was conducted by self-made adsorption device (Fig. 1) to determine the adsorption and separation effect of the sample on CO_2/CH_4.

The adsorption and desorption curves of AC on N_2 before and after modification were measured by BELSORP-mini II automatic specific surface area and micropore analyzer at 77K, and the total pore volume was calculated by the MP method. The functional groups of AC surface were measured by IR-960 Fourier transform infrared spectrometer with wavenumber ranging from 4000 to 400 cm^{-1}. The degree of AC carbonization was determined by HR-Evolution laser confocal micro-Raman spectrometer. The wavelength of excitation source was 532 mm, and the wavenumber range was 2000 to 500 cm^{-1}.
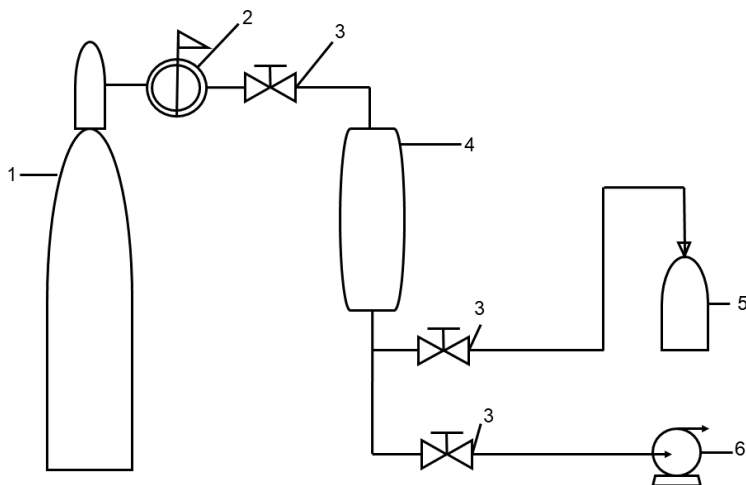

Fig. 1. Diagram of adsorption device. 1 - Biogas bottle; 2 - Pressure reducing valve; 3 – Valve; 4 - Adsorption column; 5 - Gas collecting bag; and 6 - Vacuum pump

Sample Screening Markers

Based on the results of sample adsorption and separation of methane and carbon dioxide, certain unmodified samples and samples with better adsorption effect were selected after modification, and they were labeled separately. Unmodified coconut shell carbon was labeled as AC0, coconut shell carbon soaked in 12% ammonia for 4 h was labeled as AC1, coconut shell carbon soaked in 9% ammonia for 6 h was labeled as AC2, coconut shell carbon soaked in 9% ammonia for 8 h was labeled as AC3, and coconut shell carbon soaked in 9% ammonia for 10 h was labeled as AC4. Unmodified jujube shell charcoal was labeled as AC5, jujube shell charcoal soaked in 12% ammonia for 4 h was labeled as AC6, jujube shell charcoal soaked in 12% ammonia for 6 h was labeled as AC7, jujube shell charcoal soaked in 9% ammonia for 8 h was labeled as AC8, and jujube shell charcoal soaked in 9% ammonia for 10 h was labeled as AC9.

RESULTS AND DISCUSSION

Adsorption Results of Modified Activated Carbon on Carbon Dioxide in Biogas

The device shown in Fig. 1 was used for the adsorption experiment, and the content of CH_4 and CO_2 in the gas after passing the adsorption column was detected by gas chromatograph. The results are shown in Figs. 2 to 5.

The adsorption and decarbonization effect of modified activated carbon samples on simulated biogas was better than that of unmodified activated carbon. When the modification time was the same, the decarbonization effect of activated carbon on biogas was first enhanced and then weakened with the increase of ammonia concentration in the range of 6 to 15% mass fraction. Taking jujube shell charcoal soaked in ammonia water for 4 h under ultrasonic oscillation conditions as an example, the modified sample showed the best decarbonization effect on biogas when the ammonia water concentration was 12%, and the CH_4 content in biogas increased from 60% to 89.2%. After the unmodified sample adsorbs and decarbonizes biogas, the CH_4 content in biogas was only 73.6%.

When the concentration of the modifier was the same, as the modification time increased, the effect of activated carbon on biogas decarbonization also first increased and then it deteriorated. Taking coconut shell charcoal soaked in 9% ammonia water under ultrasonic oscillation conditions as an example, after 10 h of modification, the sample showed the highest decarbonization effect on biogas. The CH_4 content in biogas increased from 60% to 87.3%, while the unmodified sample adsorbed and decarbonized biogas, resulting in a CH_4 content of 75.5%.

The experimental data also showed that when the ammonia concentration was 15% and the modification time was 10 h, the decarbonization effect of coconut shell charcoal and jujube shell charcoal on simulated biogas was not as good as that of unmodified activated carbon. This is due to the fact that high modifier concentration and long modification time can cause damage to the pore structure of activated carbon, which is irreversible. The pore collapses, the pore is blocked, and the pore volume and specific surface area of the micropores decrease, resulting in poor adsorption and decarbonization effect (Ma *et al*. 2022).
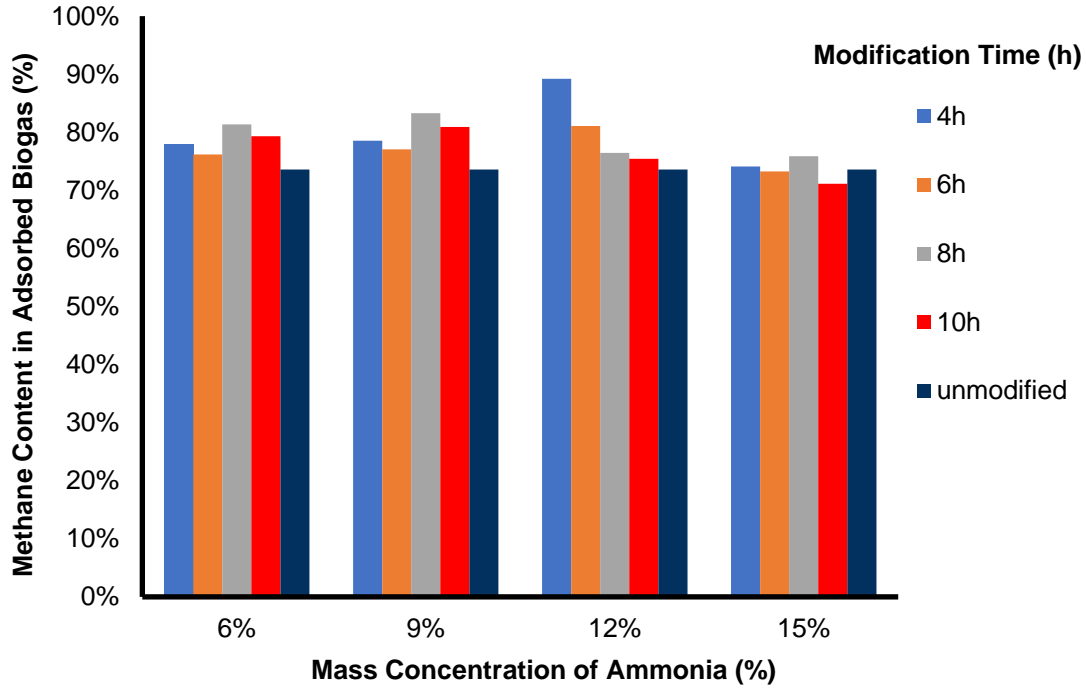
Fig. 2. Adsorption and separation of CO_2 by biogas from jujube shell carbon treated with ammonia impregnation and ultrasonic oscillation
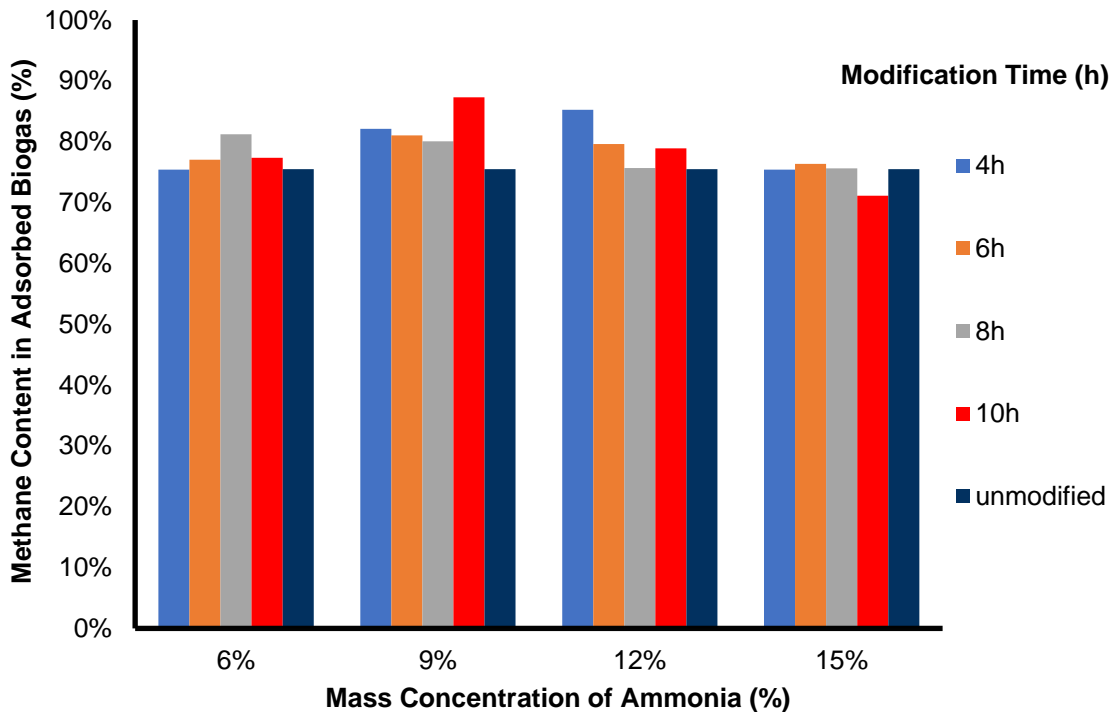

Fig. 3. Adsorption and separation of CO_2 by biogas from coconut shell carbon treated with ammonia impregnation and ultrasonic oscillation
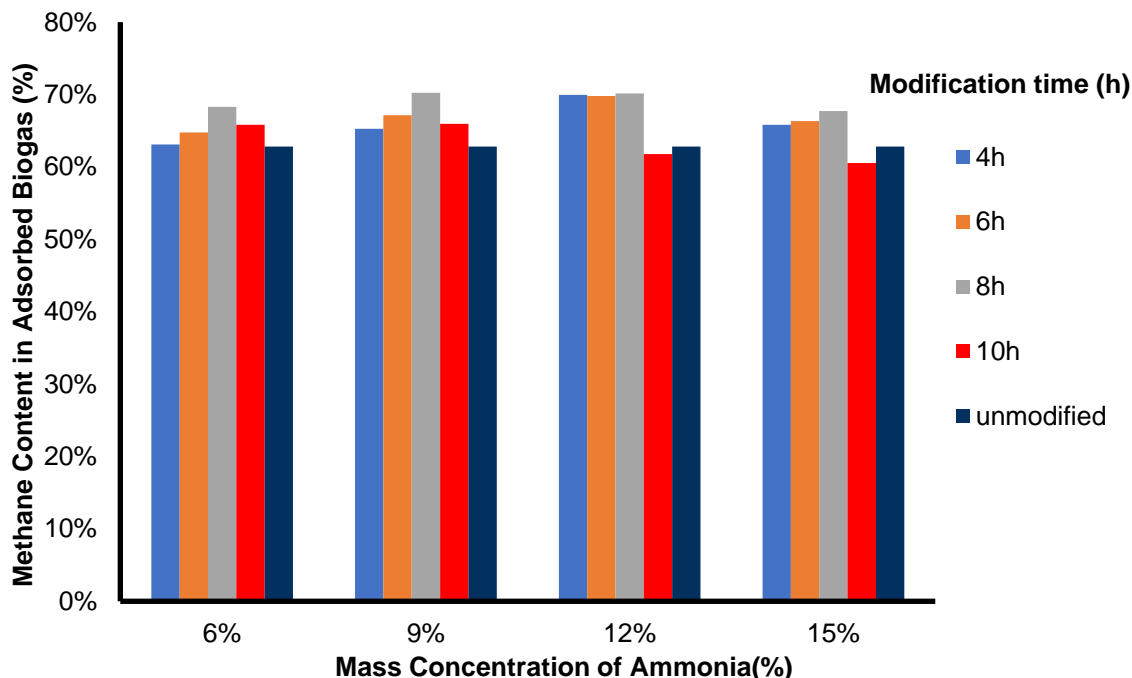
Fig. 4. Adsorption and separation of CO_2 from biogas by ammonia modified jujube shell carbon
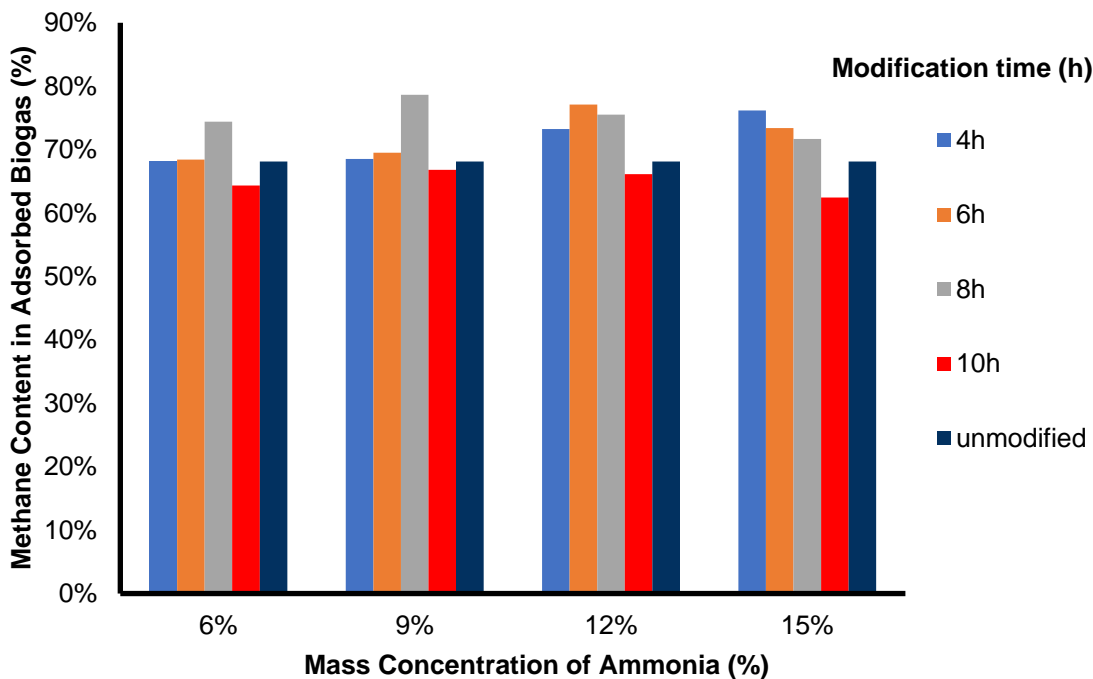

Fig. 5. Adsorption and separation of CO_2 from biogas by ammonia modified coconut shell carbon

When the ammonia concentration was 6% and the modification time was 4 h, the decarbonization effect of coconut shell charcoal and jujube shell charcoal on biogas was not ideal. This may be due to the short modification time, which leads to incomplete physical adsorption, or it may be due to the low ammonia concentration, which introduces fewer alkaline functional groups on the surface of activated carbon during the modification process and weak chemical adsorption. By comparing and analyzing the Fourier transform

infrared spectra, it was found that the functional group absorption peak of jujube shell activated carbon was significantly stronger than other conditions at an ammonia concentration of 12% and an ultrasonic immersion time of 4 h, and the stretching vibration of carbonyl and O-H bonds was stronger; Coconut shell activated carbon exhibited strong absorption peaks of functional groups, especially the stretching vibration of O-H groups in hydroxyl groups, when the ammonia concentration is 9% and the ultrasonic immersion time was 10 h. The higher specific surface area can be expected to enhance the adsorption capacity of the mixture, but it is not conducive to gas separation. That is, the adsorption capacity of activated carbon for methane was also enhanced, reducing the adsorption selectivity of modified activated carbon.

Sample Functional Group Analysis

Activated carbon adsorption can be divided into physical adsorption and chemical adsorption. The surface of activated carbon can be rich in functional groups, including oxygen containing functional groups and nitrogen containing functional groups, such as carboxyl, hydroxyl, carbonyl, lactone, aldehyde, ether, lactam, pyridinamide, *etc*. (Li 2018). These functional groups play an important role in the adsorption of activated carbon. Generally speaking, the acid groups in oxygen containing functional groups have strong affinity for polar substances, Alkaline groups have a strong affinity for non-polar substances (Lei 2013).

The modified jujube shell carbon and coconut shell carbon were detected by FTIR spectrum. Several groups of samples with better CO_2/CH_4 separation effect after modification were selected. The infrared spectra are shown in Figs. 6 and 7.

The absorbance peaks of functional groups of unmodified activated carbon were small and weak, while the modified activated carbon exhibited a strong absorbance peak between 3480 and 3270 cm^{-1}, which is due to the hydrogen bond generated by O-H groups in the alcohol hydroxyl group and phenolic hydroxyl group, and the O-H group is stretched and vibrated to form a peak with a wide spectral band. At the same time, the stretching vibration of N-H enhances this peak, because the wave number range of both is roughly the same (Shafeeyan *et al*. 2011). The absorbance peak at 1100 to 1000 cm^{-1} is the stretching vibration of the C-O bond, the absorbance peak at 1125 to 1110 cm^{-1} is the C-O-C antisymmetric stretching vibration of the ether, the absorbance peak at 1180 to 1160 cm^{-1} is the stretching vibration of C-N, and the peak at 1280 to 1150 cm^{-1} may be caused by the stretching vibration of C-OH in phenols. The absorbance peak at 850 to 780 cm^{-1} is related to the C-H group at the edge of the Simple aromatic ring. The absorbance peak at 1730 to 1630 cm^{-1} is the stretching vibration of quinone carbonyl and ester carbonyl C=O, and there may also be the presence of lactone groups. The stretching vibration of carbonyl C=O in carboxylic acids may occur in the range 1760 to 1660 cm^{-1} (Dizbay-Onat *et al*. 2018).

The absorbance peak of ammonia modified activated carbon in the range of this wave number in the figure is significantly weakened. The reason is that ammonia reacts with the acidic functional groups on the surface of activated carbon, resulting in a decrease in the number of acidic functional groups, such as carbonyl C=O in carboxylic acid, which indicates that ammonia modification can change the number of functional groups on the surface of activated carbon.
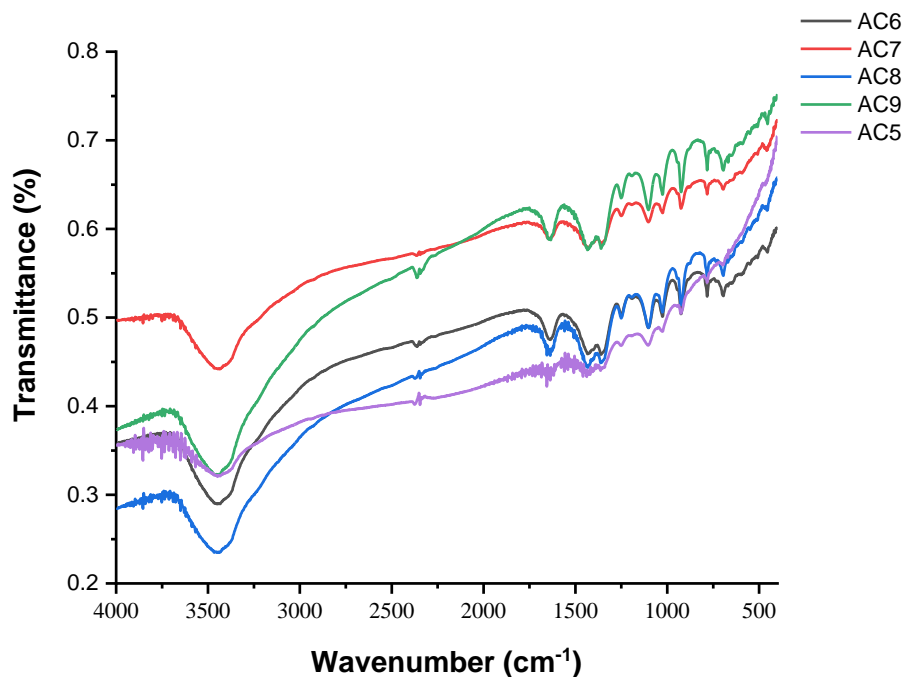
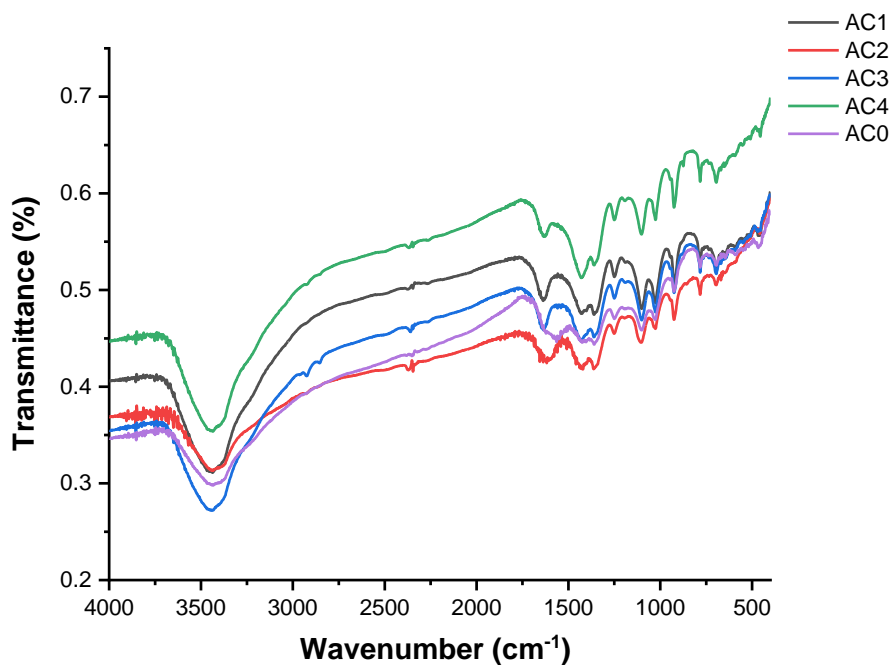**Fig. 6.** Functional group analysis of jujube shell activated carbon

Fig. 7. Functional group analysis of coconut shell activated carbon

After modification with ammonia solution, the surface of activated carbon has more alkaline functional groups, which can enhance the adsorption and separation effect of CH_4 and CO_2. From Figure 6, it can be seen that as the modification time increases, the absorbance peak of functional groups gradually weakens, which is particularly evident at 3480 to 3270 cm^{-1}, which may be due to the excessive reaction time leading to the collapse

of activated carbon pores, the destruction of pore structure, and a decrease in the number of surface functional groups.

Analysis of Structural Properties of Samples

Raman spectroscopy is now considered to be a very important technical means to characterize the relationship between the structure and properties of carbon materials. For carbon materials, the most studied are peak D and peak G, which are located at 1300 and 1560 cm^{-1}, respectively, where peak D represents SP^3 (disordered carbon) and peak G represents SP^2 (graphitic carbon). There are many different types of defects in carbon materials, such as holes and cracks, *etc*. Peak D reflects the degree of irregularity of the crystal, peak G represents the degree of regularity of the crystal, and their ratio I_D/I_G reflects the degree of disorder of the crystal structure. The greater the ratio, the lower the degree of graphitization. Conversely, the smaller the ratio, the more regular crystal structure, the higher the degree of graphitization (Schuepfer *et al*. 2020). In this experiment, the wavelength of excitation light source was selected to be 532 mm, and the wave number range was 2000 to 500 cm^{-1}. The spectra of date shell activated carbon and coconut shell activated carbon detected by Raman spectroscopy are shown in Figs. 8 and 9.
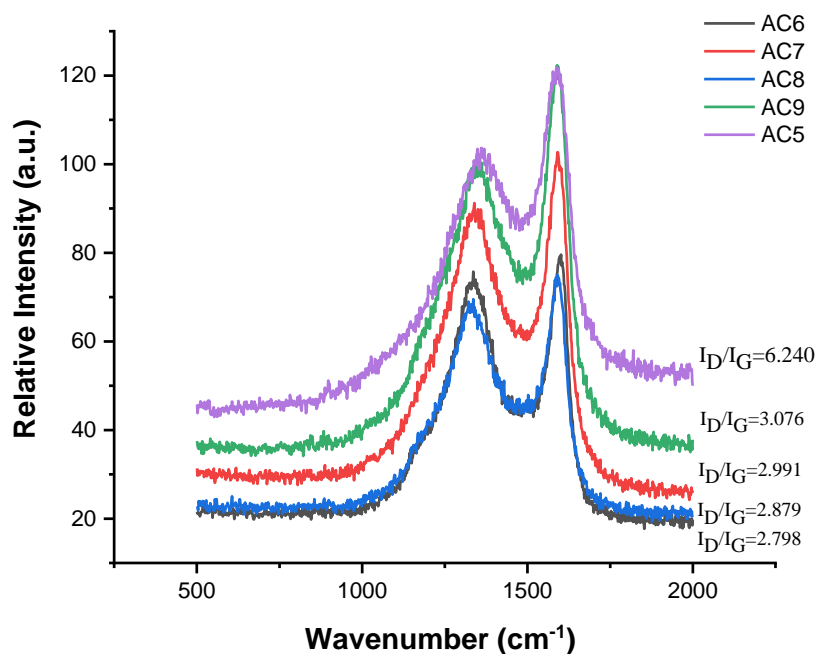

Fig. 8. Raman spectrum analysis of jujube shell activated carbon

The I_D/I_G of unmodified date shell carbon was 6.240, and the I_D/I_G of unmodified coconut shell carbon was 3.152. The I_D/I_G value of the unmodified sample was greater than that of similar modified samples for both date shell carbon and coconut shell carbon, indicating that the modification process increases the regular crystal structure of activated carbon and enhances the degree of graphitization of activated carbon. Compared with the two activated carbons, the I_D/I_G value of coconut shell activated carbon is small on the whole, and the graphitization degree is higher. Among them, the sample AC4 has the highest graphitization degree, and the I_D/I_G is 2.036. It also has the best adsorption effect on CO_2 in biogas, and the CH_4 content after adsorption was 87.3%.
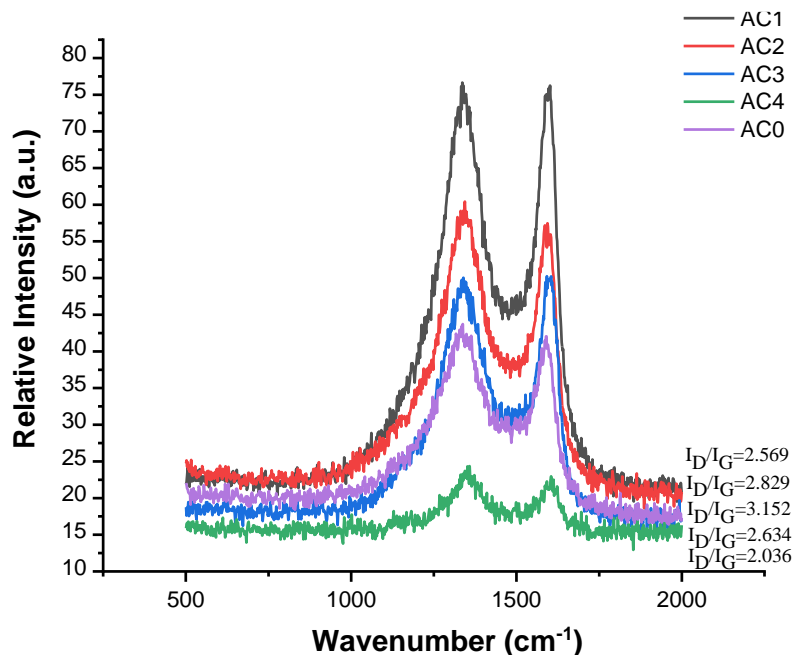
Fig. 9. Raman spectrum analysis of coconut shell activated carbon

Analysis of Specific Surface Area and Pore Size

The pore structure parameters of activated carbon before and after modification are shown in Table 2. The pore size distribution of the optimized sample of modified activated carbon is shown in Figs. 10 and 11.

Table 2. Pore Structure Parameters of Activated Carbon Before and After Modification

Samples	$S_{BET}/(m^2/g)$	$d_p/(nm)$	$V_{total}/(cm^3/g)$	$V_{micro}/(cm^3/g)$
AC0	444.43	1.5168	0.2082	0.2013
AC1	419.54	1.5628	0.1864	0.1857
AC2	442.73	1.5252	0.1964	0.1940
AC3	431.83	1.6306	0.2070	0.1955
AC4	394.64	1.5709	0.1778	0.1749
AC5	113.75	2.3843	0.0530	0.0440
AC6	75.16	8.5027	0.0372	0.0355
AC7	84.14	7.0463	0.0392	0.0368
AC8	91.02	5.7597	0.0496	0.0423
AC9	109.94	2.8483	0.0546	0.0514

The adsorption performance of activated carbon materials depends on their pore structure, especially micropores and mesopores. From Table 2, it can be seen that the average pore size of coconut shell carbon was less than 2 nm. Combined with the pore size distribution map of coconut shell carbon, the proportion of micropores was the highest at about 0.7 nm, indicating that coconut shell carbon contained a very rich amount of micropores. The pore size of jujube shell charcoal was slightly larger than that of coconut shell charcoal, with the largest proportion of micropores at about 1 nm, and jujube shell charcoal with relatively small specific surface area had a larger pore size.
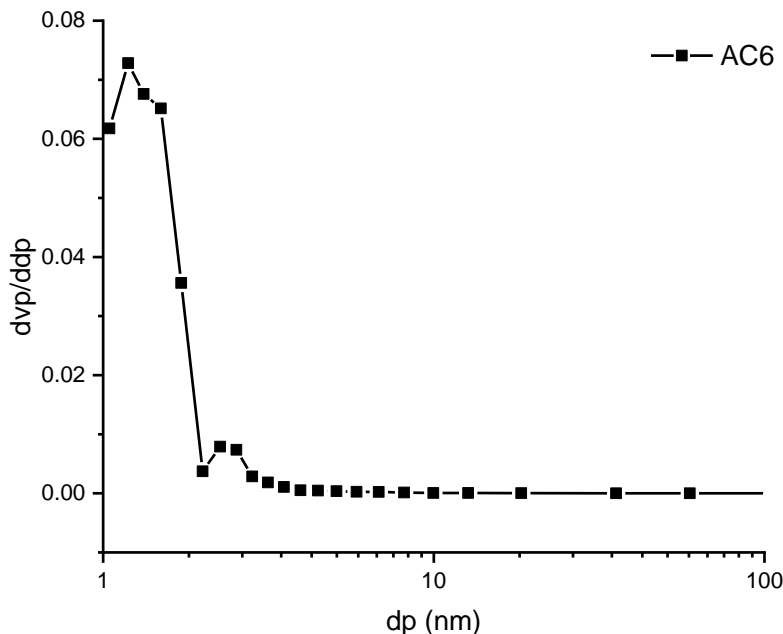
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Fig. 10. Pore size distribution of jujube shell activated carbon optimal sample
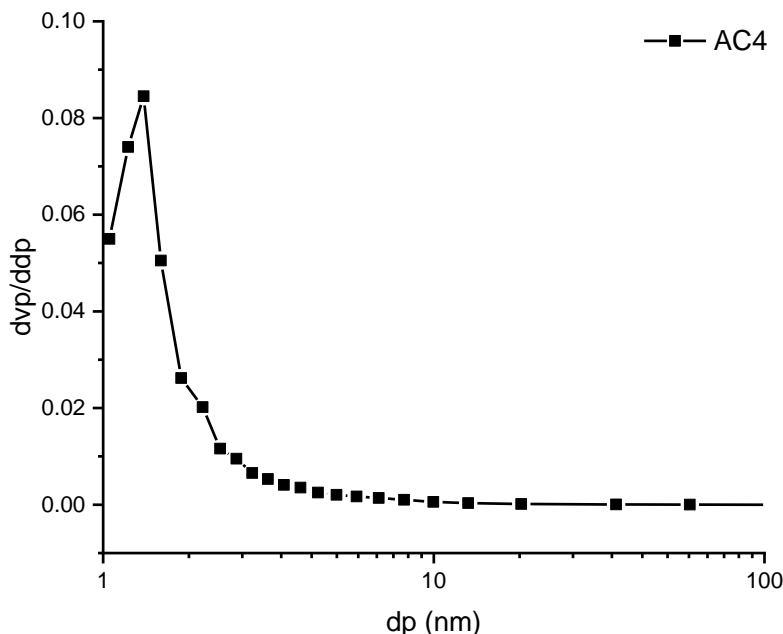

Fig. 11. Pore size distribution of coconut shell activated carbon optimal sample

The two samples with the best adsorption and separation performance for CO_2/CH_4: coconut shell carbon sample AC4 had a specific surface area of 39$\underline{5}$ m^2/g, an average pore size of 1.57 nm, a total pore volume of 0.178 cm^3/g, and a microporous volume of 0.175 cm^3/g; The specific surface area of jujube shell charcoal sample AC6 was 75.2 m^2/g, with an average pore size of 8.50 nm, a total pore volume of 0.0372 cm^3/g, and a microporous volume of 0.0355 cm^3/g. Overall, after modification with ammonia water, the specific surface area and total pore volume of activated carbon decrease, the average pore size increases, and the number of mesopores increases. CO_2 is a subcritical gas, and molecular

condensation occurs in larger pores, resulting in an increase in CO_2 adsorption capacity (Li 2013). The decrease in the total pore volume of the specific surface area may be due to the excessive generation of oxygen-containing and nitrogen-containing groups, which block some narrow micropores. AC4 and AC6 are the samples with the smallest specific surface area in coconut shell charcoal and jujube shell charcoal, respectively, possibly due to the highest amount of alkaline functional groups generated after modification.

CONCLUSIONS

1. After being modified by ammonia immersion and ultrasonic oscillation, activated carbon exhibited the presence of N-containing functional groups, resulting in an increase in surface alkaline functional groups and a decrease in acidic functional groups. The modification enhanced the adsorption of non-polar substances and enhanced the adsorption and separation effect of CO_2 and CH_4.

2. The ultrasonic oscillation modification treatment with ammonia immersion resulted in an increase in the regular crystal structure and enhanced graphitization degree in the fruit shell activated carbon. The maximum I_D/I_G value of the experimental sample was 2.04.

3. After being modified with 6% to 15% ammonia water for 4 to 10 h, the specific surface area and total pore volume of activated carbon in the experiment decreased, while the average pore size increased. Among them, the coconut shell carbon sample AC4 with the best adsorption and separation effect for CO_2 and CH_4 in biogas had a specific surface area of 395 m^2/g, an average pore size of 1.57 nm, a total pore volume of 0.178 cm^3/g, and a microporous volume of 0.175 cm^3/g. The specific surface area of jujube shell charcoal sample AC6 was 75.2 m^2/g, with an average pore size of 8.50 nm, a total pore volume of 0.0372 cm^3/g, and a microporous volume of 0.0355 cm^3/g.

4. In the experiment of activated carbon samples adsorbing and decarbonizing biogas, the sample modified with 12% ammonia solution for 4 h in an ultrasonic oscillation environment showed the best adsorption and decarbonization effect, increasing the CH_4 content in simulated biogas from 60% to 89.2%. Compared with unmodified fruit shell carbon, it increased by 15.6%, with a unit adsorption capacity of 1.83 mmol/g and an increase of 0.8 mmol/g compared to unmodified samples; Coconut shell carbon showed the best adsorption and decarbonization effect in an ultrasonic oscillation environment after being modified with a concentration of 9% ammonia solution for 10 h, resulting in an increase in CH_4 content in simulated biogas from 60% to 87.29%. Compared with unmodified coconut shell carbon, it increased by 11.8%, with a unit adsorption capacity of 1.74 mmol/g and an increase of 0.599 mmol/g compared to unmodified samples.

ACKNOWLEDGMENTS

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