Effects of Activation Conditions on the Properties of Sludge-Based Activated Coke

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ABSTRACT: Sewage sludge and waste biomass are unavoidable byproducts of municipal and industrial processes. Both materials have significant carbon contents. Activated coke with a developed pore structure can be obtained after its physical activation. In this study, sewage sludge and waste poplar bark were used as precursor materials to prepare activated coke by steam, carbon dioxide gas, and their mixtures. The effects of different concentrations of activation gas on the activated coke product were investigated. Through nitrogen adsorption analysis, it was found that activated coke has a higher specific surface area and better pore structure when activated in gas containing 20% steam. The activated coke prepared by carbon dioxide gas activation has higher microporosity than that prepared by steam activation. Infrared spectrum analysis shows that steam activation is beneficial to the formation of free hydroxyl functional groups. Through scanning electron microscopy analysis, the pores of activated coke prepared by steam activation appeared to extend deeper in the structure of the coke, while the pores of activated coke prepared by carbon dioxide activation appeared to have fine circular structures. The activated coke prepared by the activation of mixed gas appeared to have ablated particles on the surface due to the ablation of the pore structure. In order to prepare activated coke with excellent adsorption performance, the physical and chemical properties of activated coke under different activation conditions were studied in detail.

1. INTRODUCTION

Sludge is an inevitable byproduct of sewage treatment. Due to the acceleration of the urbanization process and the improvement of sewage discharge standards, sludge production has been increasing.1 Traditional sludge treatment approaches include marine discharge, incineration, composting, and land utilization,2 all of which may cause environmental problems. Therefore, it is urgent to find an effective method for sludge treatment and utilization. Landfill treatment of sludge is the most widely used method with the advantages of simplicity and low cost. However, due to pollution and lack of material recycling, it is not considered as a sustainable technology.3 With the continuous tightening of sludge treatment standards, the cost of sludge treatment is increasing. Considering the balance between ecology and economy, the sludge recovery products should have a high economic value to compensate for the treatment cost.4 Sludge is essentially a carbon-containing organic matter, which can be used as a raw material for the production of activated coke adsorbents. Activated sludge can be used to adsorb various organic pollutants, heavy metals, and acid gases.5 Compared with commercial activated coke, the performance of sludge-based activated coke is generally poor due to its low carbon content and high ash content, which limits its application. Biomass is generally considered to be a carbon-neutral material, which can store carbon during growth through photosynthesis.6,7 In recent years, sugarcane bagasse, corn straw, and coconut shell were added into the sludge to prepare composite-activated coke,8 which showed good adsorption performance in practical applications. Bhunia et al.2 successfully prepared a safe and effective activated carbon adsorbent by adding straw into sludge. Chen et al.5 used ZnCl2 activated sludge to prepare activated coke. By analyzing its physical and chemical properties, they found that the sludge-derived activated coke showed a special affinity for nonpolar adsorbent. The activated coke preparation technology of sludge has become more and more mature for the past few years. The composite activated coke is prepared by mixing sludge as a raw material and biomass. The raw materials are easily available, and their cost is low. It belongs to the reuse of solid waste and has obvious economic, social, and environmental benefits.

With the rapid development of economy, energy consumption increases significantly. As a result, a large number of...
polluting gases are released, leading to deterioration of air quality and endangering people’s health.\(^9\) Therefore, it is particularly important to find an efficient adsorbent for polluting gases. Activated coke is a material with a developed pore structure, strong selective adsorption capacity, large specific surface area, and easy regeneration performance.\(^{10−12}\) Under certain conditions, activated coke can adsorb, remove, purify, refine, or recover certain substances in liquids or gases. It has been proven that activated coke is an effective adsorbent for removing various inorganic and organic pollutants dissolved in gaseous or aqueous environments.\(^{13−16}\) Activated coke can be prepared from most carbon-containing materials after carbonization and activation, such as coal,\(^{17}\) stone tar,\(^{18}\) waste biomass\(^{19}\) (plant straw, coconut shell, apricot kernel, date kernel, walnut shell, etc.), wood\(^{20}\) and lignin,\(^{21}\) and other high-carbon materials.\(^{22,23}\) Through the activation process, the activated coke with a well-developed pore structure was obtained by removing the material-blocking pores. At present, the main activation methods are chemical activation and physical activation.\(^{24−26}\) Chemical activation involves impregnation of the raw material with a variety of chemical reagents, such as phosphoric acid,\(^{27}\) potassium hydroxide,\(^{28}\) and zinc chloride.\(^{29}\) The raw material can be directly activated after mixing with an activator.\(^{30}\) Impregnants are mostly used as dehydrating agents and oxidants, affecting pyrolysis and inhibiting the formation of tar, thus increasing carbon production.\(^{31}\) Physical activation consists of two steps. First, the carbonaceous precursor is carbonized under an inert atmosphere, and then the carbonized product is activated with an activator (usually a gas) at a higher temperature.\(^{32}\) The activation process leads to the enlargement of pore size, resulting in the creation of new pores.\(^{33}\) The adsorption capacity of activated coke is closely related to its developed internal pore structure, surface area, and extensive surface functional groups.\(^{34}\) It is generally believed that the size of the pores of activated coke determines the selectivity to the adsorbent, the surface area determines the adsorption capacity, and the functional groups induce different chemical characteristics on the surface of activated coke. Studies have shown that changing the chemical properties of activated coke can improve its adsorption performance.\(^{35,36}\)

In general, the physical and chemical properties of activated coke largely depend on the activation process and the properties of raw materials.\(^{37}\) In the process of physical and chemical activation of activated coke, different activation methods have different effects on the physical and chemical characters and adsorption performance of activated coke. Therefore, it is crucial to find efficient activation conditions for the development of carbon structures. The surface area, pore volume, and porosity of activated coke are related to the types of raw materials used and the activation methods.\(^{38}\) Molina-Sabio et al.\(^{39,40}\) conducted activation experiments on coke using steam and CO\(_2\) gas as activator gases. The results showed that the activation with CO\(_2\) plays a major role in the generation of micropores. At the initial stage of activation, steam has the effect of pore expansion, which reduces the microporosity of the product. The pore structures of activated coke products obtained by the two activated gases are different. It is mainly caused by the difference of oxygen functional groups on the surface of the activated cokes. The effects of different activation atmospheres on the activated coke products are different. The oxidation properties of typical gaseous physical activators are relatively mild. In the activation process, a single substance can participate in the reaction or several substances can be combined, such as CO\(_2\)-H\(_2\)O.\(^{41}\) Li et al.\(^{42}\) generated activated cokes from mixtures of coal and biomass. They reported that steam (H\(_2\)O) enhanced the pore broadening of the product and promoted the formation of mesoporous structures, while CO\(_2\) promoted additional development of microporous structures. Other studies have shown that different activation temperatures have different effects on activated coke. Saka\(^{43}\) prepared activated coke by the zinc chloride activation method. With the activation temperature increasing from 300 to 600 °C, the specific surface area of activated coke obtained also increased accordingly.

Saygılı et al.\(^{44}\) prepared activated coke by using residues of industrial grape processing as raw materials and the zinc chloride activation method. The optimum activation temperature for preparing activated coke by the zinc chloride activation method was reported to be 600 °C. Higher activation temperatures led to the collapse of the formed pores, and the volatilization amount of zinc chloride increased, resulting in the waste of activator and the increase in production cost. The effects of different activation times on the properties of activated coke were examined by Ahmed and Theydan\(^{45}\), who prepared activated coke by activating the jujube nucleus with zinc chloride. When the activation time increased from 0.5 to 3.5 h, the activated coke yield decreased. They found that the volume of mesopores increased during the first 1.25 h. With the increase in activation time, mesopores began to collapse into larger pores.

When using biomass as a raw material to prepare activated coke, activated coke has more active parts and a richer pore structure compared with those prepared from sewage sludge. It is due to the high carbon content of biomass. The residual solid carbons after carbonization have large specific surface areas, so it can be used as adsorbents after physical activation. The usual choices of physically activator gases are steam, carbon dioxide, air, or mixtures thereof.\(^{46}\)

In this work, waste sludge and poplar bark from the furniture industry were used as raw materials. Previous pertinent research studies were conducted in this laboratory under carbonization conditions\(^{47}\) and found that a semi-coke sample most suitable for further activation could be prepared at a ratio of sludge to biomass of 1:2, carbonization temperature of 300 °C, and process time of 30 min.\(^{37}\) In this investigation, the resulting semi-coke was activated with different concentrations of CO\(_2\) gas and steam, respectively, in order to prepare powdered activated coke. The material is a good adsorbent for gas pollutants, but it is affected by many factors in the preparation process.\(^{48}\) The experiments herein examined the influence of the activation atmosphere during the activation of the semi-coke. The production rate, specific surface area, and pore structure distribution of the activated coke product were investigated. The effects of different activators on the surface area, pore structure, and functional chemical groups were monitored. The physicochemical properties of activated coke prepared by gas-phase activation with different activators were analyzed. It is helpful for the industrial production of sludge-based activated coke with large specific surface areas, rich pore structures, and rich functional group structures. It points out the direction for the industrial-directed production of activated coke with excellent adsorption performance.
2. EXPERIMENTAL SECTION

2.1. Preparation of Activated Coke. The raw materials for preparing sludge-based activated coke were sewage sludge from Jinan Everbright Third Plant and discarded poplar bark from the furniture manufacturing industry. The proximate analysis of the raw materials was performed based on the GB/T 212-2008 Chinese standards in an electric oven (SE-DHG) and muffle furnace (SE-MF6000). Ultimate analyses for carbon, hydrogen, and nitrogen were carried out in an elemental analyzer (CHN-2200) according to GB/T 30733-2014 standards. The results are shown in Table 1. The raw materials have significant carbon content, which indicates that they are suitable precursors for preparing activated coke.

The raw materials were crushed and ground in a Small Size Pulverizer 800Y manufactured by Yongkang Boou Hardware Products Co., Ltd. Samples with particle sizes of 100–200 μm were selected for these experiments. After 12 h of drying in an electric drying oven at 105 °C, the products were stored in an enclosed container for further use. In these experiments, the sample ratio of sludge to biomass was 1:2. The materials were first carbonized at 300 °C for 30 min with a nitrogen flow rate of 500 mL/min.47,49,50 Subsequently, activation experiments were carried out under different activation atmospheres as shown in Table 2, with nitrogen used as the balance gas. After activation, the carbon was cooled to room temperature under a N2 atmosphere. The value obtained in the experiments is the average of two or three experimental measurements. After characterizing and analyzing the prepared activated coke products, the optimal activation conditions were determined. The activation temperature was set at 800 °C with an activation time of 1 h, based on recommendations in the literature.42,45,51,52

2.2. Experimental System. Figure 1 shows the experimental system for preparing activated coke. The experimental system includes a gas distribution device, a reaction device, and an exhaust gas detection and absorption device. The gas supply system for carbonization and activation includes a N2 tank, a CO2 tank, a steam generator, and connecting pipes. The CO2 gas supplied by the CO2 gas tank and the steam supplied by the steam generator were used as the activated gas for physical activation. The steam-generating device was composed of a microinjection pump, a heating cable, and a temperature control device. The temperature of the heating cable was adjusted to maintain a constant temperature of 120 °C using the temperature control device. The procedures included checking the steam meter, converting the required steam flow into liquid water flow, and adjusting the steam flow through the microsyringe pump. The experiment used a horizontal high-temperature tube heating furnace, which included a temperature control device (thermocouple in the furnace), a heating device, and a high temperature resistant quartz tube. A filter was used to remove dust particles from the exhaust gas. The gas scrubber was used to absorb the exhaust gas generated by the reaction.

2.3. Sample Characterization. The activated coke yield is the ratio of the final weight to the initial raw material weight53

$$\text{yield} = \frac{M_{\text{char}}}{M_0} \times 100\%$$

(1)

$M_{\text{char}}$ is the quality of activated coke generated after activation, and $M_0$ is the quality of the raw material.

In order to determine the Brunauer–Emmett–Teller (BET) surface area, total volume porosity, and microporosity of each activated coke in the physical activation process, a BSD-PM high-performance specific surface area analyzer produced by Beijing BSD Company was used to measure the N2 adsorption isotherm at 77.3 K. The adsorption data is obtained in the range of relative pressure $P/P_0$ of $10^{-3} - 0.99$. The samples were degassed in vacuum at 105 °C for 4 h. The BET surface area is calculated according to the BET equation.54 The microporous surface ($S_{\text{micro}}$), outer surface ($S_{\text{ext}}$), and micropore volume ($V_{\text{mic}}$) are evaluated using the t-plot method, based on the adsorption isotherm data ($P/P_0$) in a relative pressure range of 0.1–0.3.

A Sigma 300 field emission scanning electron microscope (SEM) produced by Zeiss is designed with a mature Gemini optical system, with a resolution of more than 0.8 nm. SEM is done to observe the surface microstructure of the samples. This method can visually display the specific voids and surface structure of the sample surface and verify the pore structure analysis. The functional groups on the surface of the samples were analyzed by using a Nicolet IS 5 FT-IR Fourier transform spectrometer.

Table 1. Proximate and Ultimate Analysis of Tested Samplea

| samples         | proximate analysis (wt %) (ad) | ultimate analysis (wt %) (ad) |
|-----------------|-------------------------------|-------------------------------|
|                 | M    | V    | A    | FC   | C    | H    | S    | N    | O    |
| sludge          | 5.83 | 52.67| 40.07| 1.43 | 29.32| 4.38 | 1.11 | 5.02 | 60.17|
| poplar bark     | 7.76 | 72.85| 13.95| 1.04 | 44.96| 5.63 | 0.13 | 0.73 | 48.55|

Note: M, moisture; V, volatile; A, ash; FC, fixed carbon; ad, air dry.

Table 2. Experimental Conditions for Physical Activation of Biomass and Sewage Sludge Charsa

| serial number | activation atmosphere | activation temperature | activation time |
|---------------|-----------------------|------------------------|----------------|
| 1             | 20% CO$_2$            | 800 °C                 | 1 h            |
| 2             | 40% CO$_2$            | 800 °C                 | 1 h            |
| 3             | 60% CO$_2$            | 800 °C                 | 1 h            |
| 4             | 80% CO$_2$            | 800 °C                 | 1 h            |
| 5             | 100% CO$_2$           | 800 °C                 | 1 h            |
| 6             | 10% H$_2$O            | 800 °C                 | 1 h            |
| 7             | 20% H$_2$O            | 800 °C                 | 1 h            |
| 8             | 30% H$_2$O            | 800 °C                 | 1 h            |
| 9             | 40% H$_2$O            | 800 °C                 | 1 h            |
| 10            | 20% CO$_2$, 10% H$_2$O| 800 °C                 | 1 h            |
| 11            | 40% CO$_2$, 10% H$_2$O| 800 °C                 | 1 h            |
| 12            | 60% CO$_2$, 10% H$_2$O| 800 °C                 | 1 h            |
| 13            | 80% CO$_2$, 10% H$_2$O| 800 °C                 | 1 h            |
| 14            | 20% CO$_2$, 20% H$_2$O| 800 °C                 | 1 h            |
| 15            | 40% CO$_2$, 20% H$_2$O| 800 °C                 | 1 h            |
| 16            | 60% CO$_2$, 20% H$_2$O| 800 °C                 | 1 h            |
| 17            | 80% CO$_2$, 20% H$_2$O| 800 °C                 | 1 h            |

aN$_2$ was used as the balance gas.
3. RESULTS AND DISCUSSION

3.1. Steam Activation Experiments. The steam activation process is simple and has low environmental pollution. It mainly uses steam to react with carbon. Steam activation is beneficial to the preparation of activated coke with a high specific surface area and rich pore structure. The main reaction is

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]  

(2)

The reaction is endothermic. Steam is attached to the surface of the carbon, which breaks down to release hydrogen, and oxygen is then separated from the surface of the carbon as carbon monoxide.

3.1.1. Effect of Steam Mole Fraction (the Ratio of Steam Flow to Total Gas Flow) on Activated Coke Yield. Figure 2 shows that when the steam mole fraction increases from 10 to 40%, the yield of activated coke decreases. On the whole, the yield of activated coke decreases with the increase in the steam mole fraction. As the mole fraction of steam increases, the steam reacts faster with unstable carbon atoms. The gas products are continuously separated from the surface of biomass-activated coke, resulting in a continuous decrease in the yield of activated coke.  

3.1.2. Effect of Steam Mole Fraction on the Specific Surface Area of Activated Coke. Under the condition that pollutants can enter the pores, the larger specific surface area is more conducive to the adsorption of pollutants. Figure 3 shows the trend of the specific surface area of the activated coke as the steam mole fraction increases from 0 to 40%. With the increase in the steam mole fraction, the specific surface area of the activated coke first increases and then decreases. The specific surface area of the activated coke reaches its maximum value at 20% steam mole fraction.

3.1.3. Effect of Steam Mole Fraction on the Structure of Activated Coke. The porosity and pore structure of activated coke are important properties for its adsorption effective-
ness. The microporous structure is very favorable for the adsorption of small molecules in the gas and liquid phase, while the mesoporous and macroporous structures mainly adsorb large-molecular-weight organic substances. Table 3 shows the change trend of the pore structure of activated coke with different steam mole fractions. When the steam mole fraction is 10%, the proportion of micropores reaches the maximum of 74.3%. The average pore size increases with the increase in the steam mole fraction. When the steam mole fraction is 20%, the activated coke has the highest total specific surface area and micropore specific surface area. With the increase in the steam mole fraction, the proportion of micropores decreases. With the increase in the number of carbon atoms, gasification (see eq 2) destroys the existing microporous structure and produces more medium and large pores. It results in a decrease in the specific surface area and, as a result, a decrease in the proportion of micropores.

Figure 4 shows the pore size distribution of the activated coke product prepared by activation under different steam mole fractions.

| activation conditions | total specific surface area (m²/g) | micropore specific surface area (m²/g) | total pore volume (mL/g) | micropore volume (mL/g) | average pore size (nm) | micropore ratio (%) |
|-----------------------|-----------------------------------|----------------------------------------|-------------------------|------------------------|------------------------|---------------------|
| 10% H₂O               | 341.2                             | 253.5                                  | 0.2852                  | 0.1164                 | 3.344                  | 74.30               |
| 20% H₂O               | 453.2                             | 305.0                                  | 0.3836                  | 0.1454                 | 3.386                  | 67.30               |
| 30% H₂O               | 274.7                             | 177.9                                  | 0.2667                  | 0.0842                 | 3.884                  | 64.75               |
| 40% H₂O               | 199.0                             | 117.2                                  | 0.2232                  | 0.0562                 | 4.487                  | 58.90               |
| 20% CO₂               | 166.9                             | 135.5                                  | 0.1201                  | 0.0592                 | 2.878                  | 81.18               |
| 40% CO₂               | 134.9                             | 109.3                                  | 0.0979                  | 0.0472                 | 2.902                  | 81.02               |
| 60% CO₂               | 178.0                             | 161.4                                  | 0.1063                  | 0.0690                 | 2.388                  | 90.66               |
| 80% CO₂               | 196.8                             | 183.0                                  | 0.1078                  | 0.0774                 | 2.191                  | 92.99               |
| 100% CO₂              | 170.6                             | 153.9                                  | 0.1044                  | 0.0647                 | 2.448                  | 90.19               |
| 10% H₂O, 20% CO₂      | 207.0                             | 159.1                                  | 0.1750                  | 0.0719                 | 3.381                  | 76.83               |
| 10% H₂O, 40% CO₂      | 199.3                             | 158.7                                  | 0.1571                  | 0.0695                 | 3.153                  | 79.62               |
| 10% H₂O, 60% CO₂      | 221.5                             | 183.5                                  | 0.1535                  | 0.0788                 | 2.772                  | 82.83               |
| 10% H₂O, 80% CO₂      | 183.8                             | 151.4                                  | 0.1333                  | 0.0663                 | 2.900                  | 82.35               |
| 20% H₂O, 20% CO₂      | 212.5                             | 177.4                                  | 0.1439                  | 0.0774                 | 2.709                  | 83.50               |
| 20% H₂O, 40% CO₂      | 147.6                             | 132.2                                  | 0.0977                  | 0.0559                 | 2.649                  | 89.60               |
| 20% H₂O, 60% CO₂      | 211.6                             | 167.1                                  | 0.1524                  | 0.0738                 | 2.881                  | 78.94               |
| 20% H₂O, 80% CO₂      | 197.8                             | 156.9                                  | 0.1521                  | 0.0689                 | 3.076                  | 79.30               |

Figure 4. Pore size distribution of activated coke prepared by activation by different steam mole fractions.

3.2. Carbon Dioxide Activation Experiments. The physical activation method of carbon by dioxide gas is similar to the steam activation method, both of which remove the unstable carbon atoms in the carbon material to produce developed porous structures. There is no opening process in the early stage of steam activation, and the microporous structure of the carbon material is directly enlarged. However, CO₂ activation needs to go through opening, expanding, and forming stages. The basic reaction of the CO₂ activation method is as follows:

\[
\text{CO}_2 + \text{C} \rightarrow 2\text{CO}
\]

3.2.1. Effect of CO₂ Mole Fraction (the Ratio of the Flow of CO₂ Gas to the Total Gas Flow) on Activated Coke Yield. When the CO₂ mole fraction increases from 0 to 100%, the change of activated coke yield is shown in Figure 2. With the increase in the CO₂ mole fraction, activated coke yield first decreases and then remains stable. The decrease in activated coke yield with the CO₂ mole fraction is related to the reaction of eq 3. The increase in the CO₂ mole fraction increases the reaction rate. The consumption of unstable carbon atoms is accelerated, and the amount of gas released increases, resulting in a decrease in the yield. When the unstable carbon atoms are exhausted, the yield remains approximately constant.
3.2.2. Effect of CO₂ Mole Fraction on the Specific Surface Area of Activated Coke. Figure 3 shows the specific surface area of the activated coke product changed with the CO₂ mole fraction after activation under different CO₂ mole fractions. With the increase in the CO₂ mole fraction, the specific surface area of the activated coke decreases first, then increases, and finally decreases. This has a similar conclusion to the change of the specific surface area of activated coke prepared by CO₂ activation studied by Li et al.⁴⁸ CO₂ activation mainly plays a pore-forming role on activated coke. In the early stage of reaction, the original pores were widened and new pores were formed, and the specific surface area increased. With the increase in the CO₂ mole fraction, a large amount of activated carbon on the surface of the activated coke is replaced, the pore structure on the surface collapses, and the specific surface area of the activated coke decreases. When CO₂ gas enters the activated coke matrix through its network of pores, the pore-forming rate is greater than the surface collapse rate, and the specific surface area of the activated coke increases. As the CO₂ mole fraction continues to increase, the internal activation of activated coke is excessive, resulting in the collapse of the pore structure and the decrease in the specific surface area.

3.2.3. Effect of CO₂ Mole Fraction on the Structure of the Activated Coke Hole. Table 3 shows the effect of different CO₂ mole fractions on the pore size distribution of activated coke. Compared with the average pore size of activated coke produced by steam activation, shown in Table 3, the average pore size of activated coke produced by CO₂ activation is smaller. The activated coke generated by CO₂ activation has a large proportion of micropores, which indicates that CO₂ as an activator can promote the enrichment and development of micropore structures. The specific surface areas and micropore ratios of the activated coke obtained by different CO₂ mole fractions have little difference. At a mole fraction of 80% CO₂, the highest specific surface area and micropore ratio of the activated coke were obtained.

The pore size distribution of activated coke prepared by CO₂ activation is shown in Figure 5. The activated coke shows a strong peak in a range of 0.6−2 nm. It shows that the distribution of micropores near the aperture is rich. Nabais et al.⁵⁹ prepared activated coke by activating coke endocarp and found that the activated coke generated by CO₂ activation had a higher specific surface area and pore volume compared with the samples generated by steam activation. However, according to the data in Table 3, compared with the samples generated by steam activation, the specific surface area and pore volume of the activated coke generated by CO₂ activation are relatively small. The carbon content in the sludge is not high, which in turn leads to a low porosity.

3.3. Experimental Investigation of Mixed Activation of Steam and CO₂. The gasification potential of the gas physical activator is mild, and it can react with many kinds of substances in addition to single substances in the activation process.⁴¹ In the study of a single activator, it was found that activated coke with relatively low proportion of micropores was obtained by steam activation, while the CO₂ activator mainly promoted the further development of micropores. However, macropores, mesopores, and micropores all play a key role in the adsorption performance of activated coke. Therefore, mixed activator gases, with different concentrations of steam and carbon dioxide, were explored.

3.3.1. Effect of Mixed Activation on Activated Coke Yield. Figure 6 shows the changes in the yield of activated coke prepared after activation at different CO₂ mole fractions when the steam mole fractions were 10 and 20%, respectively. With the increase in the CO₂ mole fraction, the yield of activated coke increased first and then decreased slightly when the water vapor mole fraction was 10%. The yield of activated coke prepared at 20% steam mole fraction decreased monotonically with increasing CO₂. These results indicate that the increase in any activator concentration aggravates the carbon ablation and decreases the yield. The activated coke yield obtained from activation with 20% steam mole fraction decreased significantly, indicating that the activated coke yield was greatly affected by mixing with CO₂ gas at a higher steam mole fraction.

3.3.2. Effect of Mixed Activation on the Specific Surface Area of Activated Coke. Figure 7 shows the change of specific surface area of activated coke after activation with different CO₂ mole fractions when the steam mole fractions are 0, 10, and 20%. With the increase in the CO₂ mole fraction, the specific surface area of activated coke goes through a process of decreasing, increasing, and almost remaining unchanged. When the CO₂ mole fraction increases from 0 to 10%, the edges of the carbon surface react with CO₂ and the specific surface area decreases. When the CO₂ mole fraction increases from 20 to 40%, the surface contact between CO₂ and carbon increases.

![Figure 5](https://example.com)  
**Figure 5.** Pore size distribution of activated coke prepared by activation by different CO₂ mole fractions.

![Figure 6](https://example.com)  
**Figure 6.** Effect of mixed activation on activated coke yield.
Additionally, a large amount of surface carbon is replaced by CO, which leads to a decrease in the specific surface area of activated coke. The CO₂ mole fraction increased from 40 to 60%, and the specific surface area of the activated coke increased. After CO₂ contacts the surface carbon, the remaining CO₂ enters the carbon and starts to form new pores. The formation of new pores is faster than the collapse rate of the original pores. When the CO₂ mole fraction increases from 60 to 80%, the specific surface area of the activated coke decreases. The pores are formed because the two activators act on different active sites. Activation removes carbon atoms from the interior of the particle. The result is that the closed pores open and the open pores expand. When the concentration is higher, the density of the pores becomes larger, resulting in the walls between adjacent holes being ablated.

3.3.3. Effect of Mixed Activation on the Structure of the Activated Coke Hole. As shown in Table 3, compared with the pure steam mole fraction, under the same steam mole fraction, the total surface area and the specific surface area of the micropores of the mixed activator gases are smaller. Compared with pure CO₂ activation, the total surface area and micropore specific surface area of mixed activation were larger at the same CO₂ mole fraction. CO₂ activation is mainly pore forming, while steam activation is mainly pore expanding. Combined with the results of elemental analysis, displayed in Table 1, the carbon content in the sludge is lower, resulting in a low porosity during activation. The micropore ratio of activated coke prepared by mixed activation is between that of single activation, and the pore size is deemed satisfactory.

As shown in Figure 8, the activated coke obtained by mixed activation has an obvious peak in a range of 0.7−1.2 nm. It indicates that the pore structures within this pore aperture range are rich. The peak value of the pore volume of activated coke at 10% steam mole fraction is higher and narrower than that at 20% steam mole fraction, indicating that the activated coke with 10% steam mole fraction is more abundant in the micropore structure.

3.4. Comparative Analysis of Surface Morphology. 3.4.1. Surface Morphology of Raw Materials. The SEM images of sludge sample (a) and poplar bark sample (b) without carbonization and activation process can be seen in Figure 9. Different from poplar bark samples, the surface of sludge samples was rough and uneven. The raw materials of the initial sludge and poplar bark have no obvious pore structure, which need to be further modified to achieve pore enrichment.

3.4.2. Surface Morphology of Activated Coke. The surface topography of the activated coke obtained by steam and carbon dioxide activation is shown in Figure 10a,b, respectively. In both cases, an obvious pore structure can be observed, but the pore morphology is completely different. The pore structure of activated coke prepared by activation in a steam atmosphere is deeper, and the pore size distribution is more uniform. Compared with activated coke activated by steam and carbon dioxide, activated coke activated by carbon dioxide has larger pores.

Figure 10c−f shows the surface topography of activated coke prepared by mixing different mole fractions of steam and CO₂ activators. Compared with the activated coke obtained by a single activator, the surface of the activated coke is rougher. In Figure 10c,d, obvious white particles on the surface of activated coke can be observed. This is mainly due to the high concentration of steam and the violent reaction, resulting in a large amount of surface burning loss and ash exposure. These small white particles can be associated with coalesced ash and sintered particles.62
3.5. Evolution Mechanism Analysis of Functional Groups on the Surface of Activated Coke. 3.5.1. FTIR Map of Raw Materials. Figure 11 shows the Fourier infrared absorption spectra of sludge and poplar bark. It can be seen from the figure that the two have more absorption peaks in a range of 4000—400 cm$^{-1}$, which indicates that they have abundant surface functional groups. The sludge has an obvious wide peak in a range of 3500—3200 cm$^{-1}$, which is formed by...
Figure 10. Surface morphology of activated coke: (a) 80% CO₂ mole fraction; (b) 20% steam mole fraction; (c) 40% CO₂ mole fraction, 10% steam mole fraction; (d) 60% CO₂ mole fraction, 10% steam mole fraction; (e) 40% CO₂ mole fraction, 20% steam mole fraction; (f) 60% CO₂ mole fraction, 20% steam mole fraction.
the stretching vibration of the hydroxyl groups in alcohol, phenol, and carboxylic acid. The peak value of sludge in a range of 2800−3000 cm$^{-1}$ is formed by the saturated C−H stretching vibration. Both sludge and poplar bark have absorption peaks of C=O and aromatic C=C around 1800−1500 cm$^{-1}$, and the peak value of sludge is more obvious, which indicates that both of them have aromatic rings. The stretching vibration region of C−O is between 1300 and 1000 cm$^{-1}$, which indicates that both raw materials contain this functional group.

A wave number range of 900−700 cm$^{-1}$ is the absorption section of aromatic C−H. At about 650 cm$^{-1}$ wave number, the out-of-plane bending vibration peak of hydroxy −OH is located when hydrogen bond association occurs.

3.5.2. FTIR Spectrum Analysis of Activated Coke. Figure 12 displays the FTIR spectra of coke obtained upon activation under different conditions in a wave number range of 3700−3500 cm$^{-1}$. The activated coke produced by steam activation has a strong peak in this range. However, there is no obvious peak for CO$_2$ activation and mixed activator activation. During steam activation, there is a peak in a wave number of 3700 cm$^{-1}$, which is mainly the free hydroxyl group, and the peak disappears in the mixed activation and carbon dioxide activation. This shows that steam activation can contribute to the formation of free hydroxyl functional groups in activated coke.

Compared with the infrared spectra of the raw materials shown in Figure 11, the peak of the activated coke in a range of 1800−1500 cm$^{-1}$ is obviously weakened. This is related to the high-temperature oxidation reaction in the activation process. When the volatiles are released, it brings about the rupture of bridge bonds, the cleavage of oxygen-containing functional groups, and the condensation of aromatic rings, forming a graphite-like microcrystalline structure. All the activated coke products have peaks in a wave number range of 1500−1300 cm$^{-1}$, which proves the existence of aromatic compounds.

4. CONCLUSIONS

The experimental results of preparing activated coke show that the maximum specific surface area of activated coke was 453.2 m$^2$/g when activated with 20% steam mole fraction alone at 800 °C for 1 h. Compared with CO$_2$ activation and mixed gas activation, the specific surface area of steam-activated coke was larger. Steam activation contributed to the formation of free hydroxyl functional groups in activated coke. The pores of activated coke prepared by steam activation appeared to have a deeper structure extending inward. The pores of activated coke prepared by CO$_2$ activation consisted of fine round pore structures. Compared with a single activator, gas activation of a mixed activator is more likely to cause “burning loss” of activated coke. The activated coke prepared by CO$_2$ activation has higher microporosity. Through experimental exploration, it points out the direction for the directional production of activated coke with a high specific surface area, high microporosity, and high adsorption performance in the future.

(1) When steam was used alone for activation, the yield of activated coke decreased with the increase in the steam mole fraction, whereas the specific surface area increased first and then decreased. The pore structure of activated coke prepared by steam activation was mainly microporous, with a limited mesoporous structure. The pore structure was extensive, and the pore size distribution was relatively uniform. Steam activation contributed to the formation of free hydroxyl functional groups in activated coke.

(2) When neat CO$_2$ was used for activation, with the increase in the CO$_2$ mole fraction, the activated coke yield decreased first and then remained approximately
unchanged, whereas the specific surface area decreased first, then increased, and finally decreased. The proportion of activated coke micropores was large, which indicates that CO2 as an activator can promote the enrichment and development of the micropore structure. (3) Compared with the activated coke obtained by a single activator gas, it can be found that the surface of the activated coke prepared by mixed activation was rougher. This shows that mixed gas activation is more likely to cause the burning loss of activated coke.

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Notes
The authors declare no competing financial interest.

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