

Effects of Microwave Modification on the Desulfurization and Denitrification of Activated Coke

Junhong Zhang, Zhi-jun He*, Qing Guo*, De-chao Xiao, and Wen-long Zhan

Microwave modification of activated coke is reported as a green and simple route to improve its synergistic desulfurization and denitrification. The results showed that microwave irradiation improved the specific surface area and pore volume, decreased the pore size, and activated the surface functional groups of the activated coke. Under the conditions of a microwave power of 500 W and a modification time of 30 min, the specific surface area was increased from 185.9 m²/g to 351.7 m²/g, the pore volume increased from 0.042 m³/g to 0.111 m³/g, and the characteristic peak strengths of C=C and -OH drastically increased. When the reaction temperature was 140 °C and the O₂ concentration was 10% (by volume), the desulfurization and denitrification efficiency were maintained at levels greater than 90% and 80% for 30 min and 15 min, respectively. The C-O content increased, and the C=C and -OH content decreased after undergoing desulfurization and denitrification. The desulfurization and denitrification products were primarily sulfate and nitrate. This provides theoretical support for the application of microwave modified active coke in low temperature desulfurization and denitrification.

Keywords: Activated coke; Microwave modification; Catalytic oxidation; Desulfurization and denitrification

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INTRODUCTION

The SO₂ and NO_x (which is composed of more than 90% NO) released from the combustion of fossil fuels are the primary causes of photochemical smog and haze, which are harmful to human health and the development of ecological environments (Zhao *et al.* 2015; Li *et al.* 2017). At present, the wet flue gas desulfurization (WFGD) and the selective catalytic reduction (SCR) are relatively mature (Ma *et al.* 2016; Sun *et al.* 2016). However, only the WFGD technology is used in the desulfurization process due to the poor water solubility of NO. The NO catalytic temperature is 300 °C to 400 °C for SCR technology, and it has limited usage, due to the disadvantages of high operating costs, a complex system, and a large floor area. In addition, the ammonia injection process can easily cause ammonia poisoning of the catalyst, cracking, and blocking of analytical tower, *etc.*; therefore, the denitration process cannot be reasonably utilized (Wang *et al.* 2014; Wang *et al.* 2020). The main catalysts used in the wet collaborative desulfurization and denitrification are KMnO₄, K₂FeO₄, NaClO₂ and NaClO (Fang *et al.* 2013; Hao *et al.* 2018). However, the stability of the catalysts is not good in terms of industrial application, the temperature of the oxidation-reduction denitrification process is high, and the wastewater will yield secondary pollution (Mondal and Chelluboyana 2013; Liu *et al.* 2016). The typical process of dry desulfurization and denitrification uses active coke that contains dense graphite structure to delay gas penetration time, and the use of straw biochar

as an adsorbent is emerging. (Chen *et al.* 2020; Tian *et al.* 2020a). However, the pore structure of untreated activated coke is not fully developed, and the surface functional group activity is poor, resulting in an unsatisfactory desulfurization and denitration effect (Tian *et al.* 2020b). The modification methods of acid-base immersion, heat treatment, and discharge are used to activate the surface functional groups to achieve a certain effect, but the primary goal of this research is the effect of the different physical and chemical methods on the removal rate of SO₂ and NO (Jin *et al.* 2014). The previous research has been lacking in the exploration of the function, oxidation mechanism, and pathway of the functional groups on the surface of active coke.

Microwaves can be characterized by rapid heating from the inside out, low energy consumption, no secondary pollution, and strong penetration (Kazmierczak-Razna *et al.* 2020; Liu *et al.* 2020; Zhang *et al.* 2020a). Cha (1994) and Kappe *et al.* (2002) pointed out that the reduction reaction of NO-C can be carried out under conventional conditions of 500 to 650 °C. However, the temperature of the reduction reaction is reduced to 200 °C with the usage of microwaves, but it has not been clarified that the reason why the temperature of the reaction is reduced *via* the usage of microwaves. Scholars carrying out related work (Wei *et al.* 2011; Kazmierczak-Razna *et al.* 2020) have pointed out that microwave as a catalyst can activate the physical structure of active coke and improve the surface chemical properties, therefore reducing the activation energy and temperature of the reaction, but they did not indicate the changes in the specific functional groups. If microwaves are used to activate the under-developed activated coke and improve its physical and chemical properties, then it can be used for desulfurization and denitrification, so that the purpose of high efficiency and simultaneous desulfurization and denitrification can be achieved at a lower temperature. However, there has been a lack of studies on pore structure activation and the mechanism of activated coke for desulfurization and denitrification *via* microwaves. Therefore, the pore structure and surface functional group changes of microwave-modified activated coke needed to be further analyzed, and the reaction mechanism of simultaneous desulfurization and denitrification also needs to be further investigated.

In this study, active coke was selected as the raw material, and the surface functional groups and physical and chemical properties of the active coke were optimized under a microwave field. The changes in the specific surface area, pore size distribution, and surface functional groups of the active coke *via* microwave modification were studied. Microwave-modified activated coke was used as an adsorbent to explore the effects of different temperatures and O₂ concentrations on the desulfurization and denitrification of activated coke and to compare the desulfurization and denitrification rates with unmodified activated coke to illustrate the applicability of desulfurization and denitrification by microwave-modified active coke. An X-ray diffractometer (XRD), scanning electron microscope (SEM), energy spectroscopy (EDS), infrared spectrum analyzer (FTIR), and X-ray photoelectron spectroscopy (XPS) were used to detect the phase structure, surface morphology, element distribution, surface functional groups, and the oxygenation state of S and N in the activated coke after desulfurization and denitrification, respectively. Then, the prospect of using microwave modified active coke to enhance the simultaneous desulfurization and denitrification process was explored.

EXPERIMENTAL

Experimental Scheme

The sample of activated coke was obtained from the activated coke production base located in Ningxia province of China. The industrial analysis and elemental analysis of the active coke used in this experiment are shown in Table 1.

The experimental device is shown in Fig. 1. First, approximately 30 ± 0.1 g of dried activated coke was placed in a microwave tube furnace and modified under microwave power at 500 W for 15 min. Then, the microwave device was set to a pure heating state for the desulfurization and denitrification experiments. The effects of various temperatures (120 °C, 130 °C, and 140 °C) and O₂ concentrations (0%, 5%, 10%, and 15% by volume) on the desulfurization and denitrification of microwave modified activated coke were investigated. The compressed gases SO₂, NO, and O₂ provided by steel cylinder were used to simulate the main components of coal/wood/biomass-fired flue gas by mixing in the gas-distribution system with a certain proportion, and the flow rate of compressed gas was adjusted independently by the flowmeters inside the flue gas-distribution system (Huasi, Hunan, China, HS FRQ FG3), in which the concentrations of SO₂ and NO were approximately 500 mg/m³ and 300 mg/m³, respectively, a flow rate of 30 mL/min, and a N₂ flow rate of 300 mL/min. The concentration of SO₂ and NO in the inlet and outlet was detected on line *via* a multi-functional flue gas analyzer (Guangdong, China, FGA 10 Gas Analyzer), and the measuring ranges of SO₂ and NO were 2000 and 500 mg/m³, respectively. Finally, the exhaust gas was passed into a 3 mol/L Ca(OH)₂ solution to avoid harm to the human body and environmental pollution.

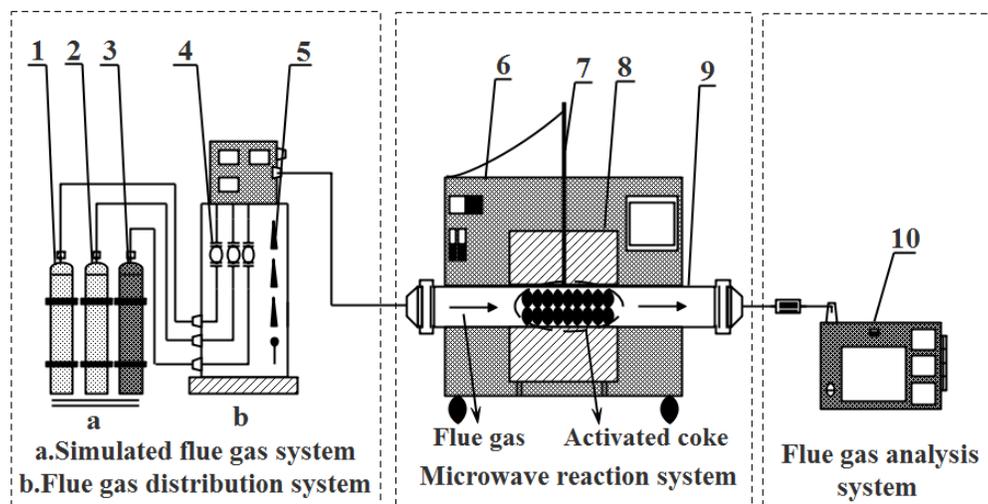


Fig. 1. The schematic diagram of the experimental device: 1. SO₂/NO; 2. O₂; 3. N₂; 4. Mass flowmeter; 5. Switch valve; 6. Microwave tube oven; 7. Thermocouple; 8. Microwave cavity; 9. Reactor; and 10. Flue gas analyzer

Sample Characterization

The C, H, O, N, and S contents of the sample were determined *via* an organic element analyzer (EURO EA3000, Beijing Liman Medical Technology Co. Ltd., Beijing, China). The industrial analysis was carried out in a muffle furnace according to national standards GB/T476 (2008), GB/T19227 (2008), GB/T2001 (2013), and GB/T2286 (2017). The adsorption/desorption isotherm and pore size distribution were measured with a N₂

adsorption instrument (Autosorb iQ2, Quantachrome, Boynton Beach, FL), and the specific surface area and pore volume of the samples were analyzed *via* the BET (Brunauer-Emmet-Teller) and BJH (Barrett-Joyner-Halenda) methods. The phase composition of the samples was detected *via* XRD (D8 ADVANCE, Bruker, Billerica, MA) analysis with Cu K α -radiation ($\lambda = 0.15406$ nm) in a range of 10° to 90° and a step/time scan mode of 10 °/min. The morphology was performed *via* a SEM (Σ IGMA HD, Carle Zeiss AG, Oberkochen, Germany), and the samples were coated with a thin layer of Au to ameliorate the quality of the images. An EDS (Σ IGMA HD, Carle Zeiss AG, Oberkochen, Germany) was used to determine the elements in the aged active coke. The functional groups in the samples were detected *via* FTIR (Cary 630, Agilent Technologies, Santa Clara, CA) with a wavenumber ranging from 4000 cm⁻¹ to 400 cm⁻¹, and the samples were mixed with KBr powder at a ratio of 1 to 200. The XPS of the aged active coke was carried out with an ESCALAB250Xi spectrometer with an Al K α source (1486.6 eV); binding energies of N 1s, S 2p, C 1s, and Ca 2p were detected at 10 kV voltage with a base pressure of 2×10^{-9} mbar.

Table 1. Industrial Analysis and Element Analysis of Activated Coke

Industrial Analysis (%)				Element Analysis (%)				
FC _{ad}	M _{ad}	A _{ad}	V _{adf}	C _{ad}	H _{ad}	O _{ad}	N _{ad}	S _{t,d}
76.78	5.86	14.05	3.31	77.50	2.00	0.09	0.63	0.73

Notes: FC_{ad} = Fixed carbon; M_{ad} = moisture; A_{ad} = Ash; V_{adf} = Volatiles

RESULTS AND DISCUSSION

Changes in the Physicochemical Properties and Surface Functional Groups of Microwave Modified Activated Coke

Changes in the physicochemical properties

As shown in Fig. 2, the adsorption/desorption isotherms of activated coke before and after microwave modification were similar. According to the division of the adsorption isotherms by IUPAC, it was a type I adsorption isotherm, which indicated that the activated coke was a composite structure of micropores and mesopores (Huang *et al.* 2008).

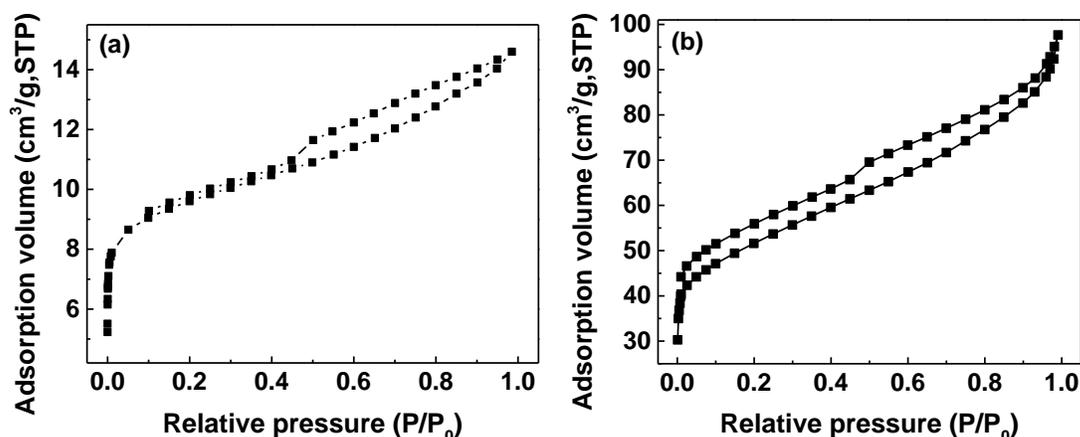


Fig. 2. Effect of microwave modification on the adsorption/desorption isotherms of activated coke: (a) the original sample of activated coke and (b) the microwave modified activated coke

The adsorption isotherm rose straight up at a low pressure, which was because the potential energy of the adjacent walls in the micropores are superimposed on each other. This drastically enhanced the adsorption of liquid nitrogen by the micropores, causing the adsorption amount to sharply increase (Huang *et al.* 2008).

A hysteresis loop appeared in the original sample of activated coke at $P/P_0 = 0.1$, which indicated that capillary condensation occurred in the mesopores of the activated coke, and the turning point means that the micropores of the activated coke were completely filled by the adsorbed molecules (Li *et al.* 2020; Tian *et al.* 2020b). At this relative pressure, the adsorption capacities of the activated coke before and after microwave modification were $9.05 \text{ cm}^3/\text{g}$ and $47.1 \text{ cm}^3/\text{g}$, respectively, which indicated that microwave-modification could promote the increase of the number of activated coke micropores, which is beneficial in terms of the adsorption of SO_2 and NO . In addition, the adsorption capacity of microwave-modified activated coke increased from $14.6 \text{ cm}^3/\text{g}$ to $97.7 \text{ cm}^3/\text{g}$, which indicated that the pore structure could be activated *via* rapid heating of microwave active factors from inside to outside. This resulted in the blocked pores opening and extending inward, which resulted in an increase of the number of micropores and mesopores. The reason for this was that the defects in the grain boundary layer of carbon atoms will bind a large number of electrons to produce a dipole relaxation phenomenon, which makes the medium have a strong microwave absorption capacity, resulting in a sharp increase in temperature, which activates the internal structure (Liu *et al.* 2020).

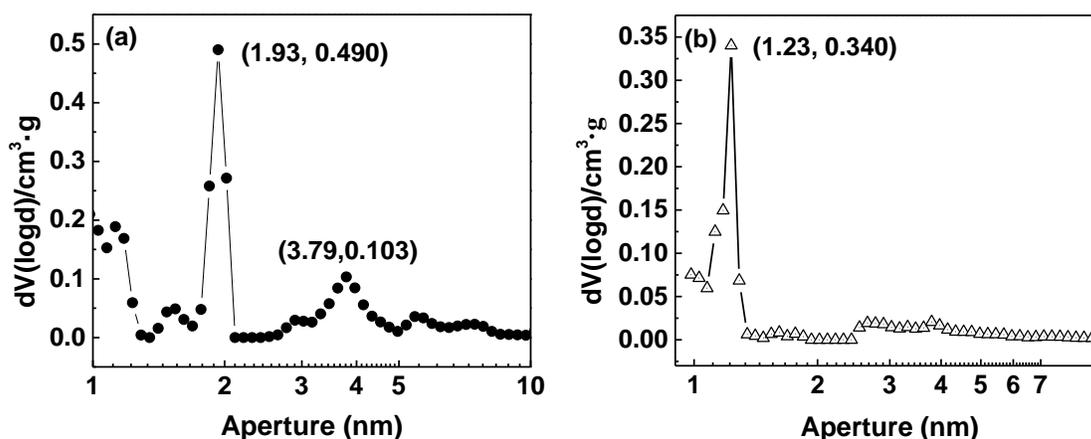


Fig. 3. Effect of microwave modification on the pore size distribution of active coke: (a) the original sample of activated coke and (b) the microwave modified activated coke

As shown in Fig. 3(a), the aperture of the original active coke was primarily concentrated at approximately 1.93 nm, but a small peak appeared at 3.79 nm. This showed that the internal structure of the active coke was primarily microporous, but there were some mesopores. After microwave modification, the characteristic peak of the pore size distribution shifted to the left, and a characteristic peak appeared at 1.23 nm (as shown in Fig. 3b), which indicated that the activation effect of the microwaves on the internal structure of active coke was partially reflected in the reduction of its pore size, which was consistent with the increase in the number of micropores in microwave modified active coke, as demonstrated by the adsorption/desorption isotherms. Related studies by Liu *et al.* (2012) have shown that the smaller the pore size, the higher the adsorption potential, and that the micropores 1.1 nm to 1.5 nm in size are the main adsorption sites of activated coke.

The average pore size of the activated coke modified by microwave was approximately 1.23 nm, which is beneficial to the removal of SO₂ and NO (Wu *et al.* 2020).

According to the BET and BJH methods, the calculated structural parameters of the original active coke and the microwave-modified active coke are shown in Table 2. It can be seen from Table 2 that the specific surface area, micropore area, total pore volume, and micropore volume of the microwave-modified activated coke increased from 185.9 m²/g, 98.8 m²/g, 0.151 cm³/g, and 0.042 cm³/g to 351.7 m²/g, 268.2 m²/g, 0.221 cm³/g, and 0.111 cm³/g, respectively. In addition, the improvement ratio of each parameter was 89.2%, 171.5%, 46.4%, and 164.3%, respectively, in comparison to the original active coke. The improvements of the structure parameters of the microwave-modified activated coke were consistent with the increase in adsorption capacity and the reduction in pore size. This demonstrated that the active factor in the microwaves promoted improvement of the pore structure during the heating process. In addition, the increase of micropore area and micropore volume of microwave modified activated coke confirmed the activation effect of microwaves on micropores. Due to the smaller molecular diameter of SO₂ and NO, the pore shrinkage will be conducive to the improvement of SO₂ and NO removal efficiency.

Table 2. Structure Parameters of Active Coke Before and After Microwave Modification

Samples	Specific Surface Area (m ² /g)	Micropore Area (m ² /g)	Total Pore Volume (cm ³ /g)	Micropore Volume (cm ³ /g)
Original active coke	185.9	98.8	0.151	0.042
Microwave-modified active coke	351.7	268.2	0.221	0.111
Variation	165.9	169.4	0.070	0.069

Infrared spectrum analysis

As shown in Fig. 4a, the characteristic peaks of the infrared spectrum of the original active coke were located at 3458 cm⁻¹ (phenol, alcohol, -OH), 2924 cm⁻¹ (aliphatic, -CH₃), 2854 cm⁻¹ (-CH₂), 1629 cm⁻¹ (C=C), 1073 cm⁻¹ (C-O), and 665 cm⁻¹ (-S-S-). Related literature pointed out that the C=C bonds have a strong reducibility of NO; in addition the strong absorption effect of phenols and alcohols (-OH) on the adsorbed SO₂ had a major effect on the desulfurization and denitrification (Lei *et al.* 2014; Chen *et al.* 2020). The infrared spectrum of the microwave-modified activated coke is shown in Fig. 4b. The absorbances related to the -CH₃, -CH₂, and -S-S- groups disappeared when compared with the original active coke. This was attributed to the complex composition and uneven distribution of the impurities in the active coke, so that different substances had different microwave absorbing capabilities. The strong absorbability of metal oxide media (Na, Mg, Al, and Mg) can form local hot spots, resulting in the -CH₃ and -CH₂ groups being converted into C=C bonds *via* heat recombination in the active coke. However, the bond energy of -S-S- is weak and decomposes when heated. The characteristic peak intensities and the enclosed area were all increased at wavenumbers of 3435 cm⁻¹ (-OH), 1633 cm⁻¹ (C=C), and 1041 cm⁻¹ (C-O). It was further verified that the internal group structure of activated coke is transformed *via* molecular recombination when subjected to microwaves. In addition, the characteristic peak position of -OH shifted from 3458 cm⁻¹ to 3435 cm⁻¹. The primary reason for this was that a strong hydrogen bond is formed between the molecules containing -OH, which caused the absorption peak position to move to a low wavenumber segment and the characteristic peak intensity and width increased. The results

of the infrared spectroscopy analysis showed that the microwave active factor could promote the reorganization and conversion of the functional groups on the surface of the active coke. This made the C=C, C-O, and -OH functional groups more abundant, and helped to improve the absorbability of the active coke for SO₂ and NO (Wu *et al.* 2020).

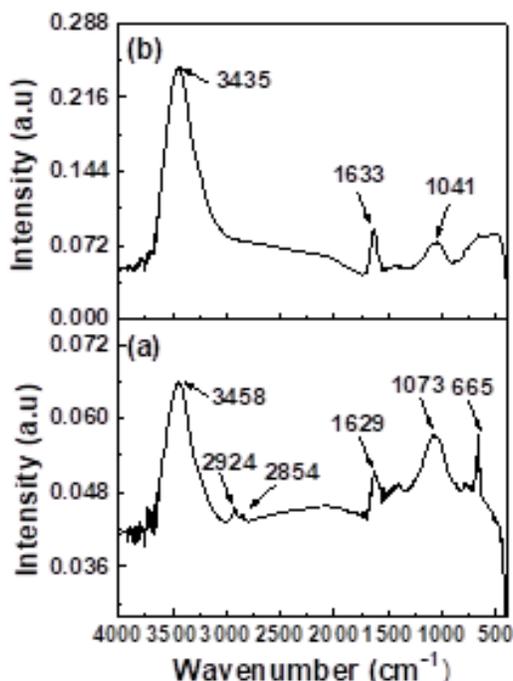


Fig. 4. Effect of microwave modification on the FTIR of active coke: (a) the original sample of activated coke and (b) the microwave modified activated coke

Effects of Different Conditions on the Desulfurization and Denitrification of Microwave Modified Active Coke

Effect of different temperatures on the removal of SO₂ and NO

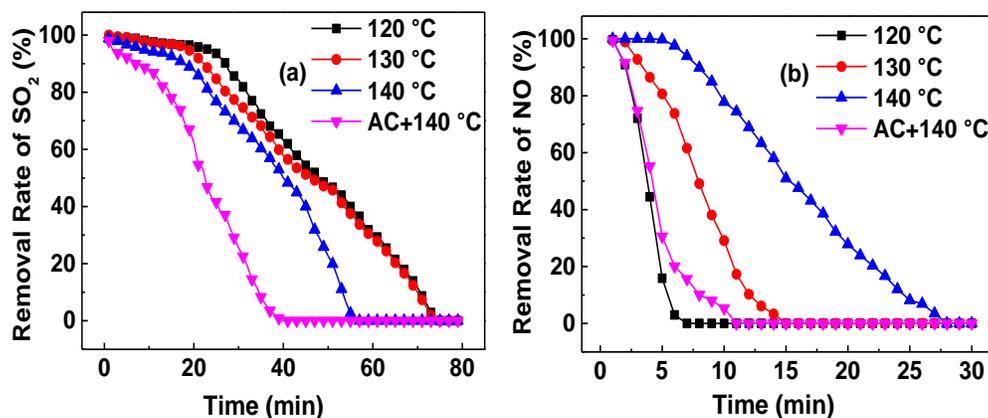


Fig. 5. Effect of the temperature on the removal of SO₂ and NO: (a) the removal rate of SO₂ and (b) the removal rate of NO, “AC” means the activated coke without microwave activation

As shown in Fig. 5a, the SO₂ breakthrough curve time was 74 min, 73 min, and 55 min at temperatures of 120 °C, 130 °C, and 140 °C, respectively. The desulfurization efficiency for all three temperature conditions was greater than 90% in the initial stage before 20 min. In addition, the difference in desulfurization efficiency was small after the first 40 min, and the desulfurization efficiency at 120 °C and 130 °C was almost the same at 40 min to 80 min. However, there was a clear difference at a temperature of 140 °C. This showed that the active coke desulfurization was primarily divided into two stages. It was primarily physical adsorption during the first 40 min, and the pore structure was the main factor restricting desulfurization. The adsorption sites in a certain quality of the activated coke are the same, so the desulfurization efficiency of the first stage was essentially the same. As the desulfurization process progressed, the reduction of the number of exposed active sites made chemical adsorption dominant, and the influence of temperature on the adsorption process was drastically enhanced, so the SO₂ outlet concentration rapidly rose at a coke desulfurization temperature of 140 °C. This indicated that the temperature increased an intensified the thermal movement of the SO₂ molecules, resulting in the short residence time of SO₂ in the active coke, which had a negative impact on desulfurization (Weng *et al.* 2020).

As shown in Fig. 5b, the temperature had a strong influence on the removal of NO. During the temperature increase from 120 °C to 140 °C, the residence time of NO on the activated coke was 7 min, 15 min, and 27 min, respectively, which indicated that an increasing temperature promoted the removal of NO. The NO concentration at the beginning of the denitrification process sharply increased at temperatures of 120 °C and 130 °C. However, the NO removal rate was 100% in the first 5 min and then it reached saturation at 28 min at a temperature of 140 °C. This showed that the denitrification process primarily depended on the chemical adsorption of the activated coke, but the optimum temperature for chemical adsorption was not reached at temperatures of 120 °C to 130 °C. In this case, the denitrification process depended only on weak physical adsorption. Therefore, the removal of NO was not effective. In addition, a competitive adsorption effect took place with the coexistence of SO₂ and NO, and the SO₂ was preferentially adsorbed on the surface of activated coke, which was also one of the reasons for the poor NO removal rate. The physical adsorption and chemical adsorption were carried out simultaneously at a temperature of 140 °C, so the removal of NO was optimized. This showed that the chemical adsorption of NO by the activated coke was promoted at a temperature of 140 °C, and also it had a certain inhibitory effect on the competitive adsorption of SO₂ (as shown in Fig. 5a). Based on the consideration of the denitrification effect, the appropriate temperature for the simultaneous desulfurization and denitrification in the experiment was 140 °C. In addition, the desulfurization and denitrification extents of the activated coke sample without microwave activation were lower than that of the modified active coke at a temperature of 140 °C, indicating that the pore structure of the microwave-activated active coke was more conducive to the adsorption of SO₂ and NO.

Effect of the O₂ concentration on the removal of SO₂ and NO

The effects of the O₂ concentration on the desulfurization and denitrification of microwave modified activated coke was investigated at a temperature of 140 °C, and the results are shown in Fig. 6. The O₂ concentration had a strong influence on the simultaneous desulfurization and denitrification process, and its effect was drastically improved at an O₂ concentration of 10% (by volume). When the O₂ concentration was 5% (by volume), the breakthrough curve of SO₂ had almost no change, but it had a strong

influence on the removal of NO. This indicated that the oxidation rate of NO was accelerated with an increase in O₂ concentration. The oxidation of NO to NO₂, which has a stronger water-soluble activity, enhanced the NO removal effect in the presence of O₂. This was consistent with the oxidation reaction between the adsorption of NO, and the free O₂ is the primary method of converting NO to NO₂ (Yang *et al.* 2013; Yao *et al.* 2019). There was an inhibitory effect on desulfurization at an O₂ concentration of 15% (by volume). The reason was that excess O₂ occupied a large number of active sites, so that the SO₂ entering the reactor could not be catalytically oxidized at the active sites; therefore, the final desulfurization efficiency was reduced. Furthermore, excess amounts of unadsorbed SO₂ exacerbated the competitive adsorption effect between SO₂ and NO, which reduced the binding capacity of NO and the adsorption sites, so the denitrification efficiency decreased compared to an O₂ concentration of 10% (by volume) (Sun *et al.* 2018).

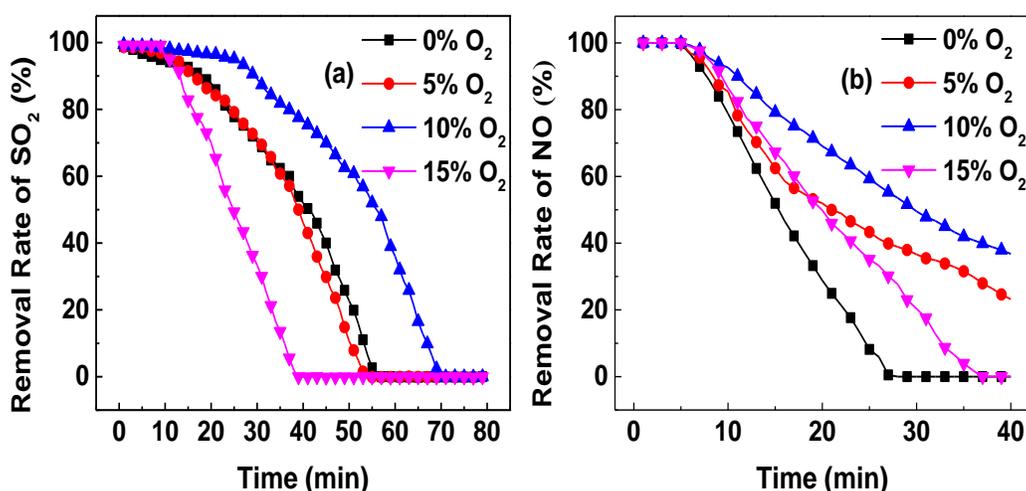


Fig. 6. Effect of the O₂ concentration on the removal of SO₂ and NO: (a) the removal rate of SO₂ and (b) the removal rate of NO

Changes in the Activated Coke Before and After Desulfurization and Denitrification

The desulfurization and denitrification products (obtained under the following conditions: 500 mg/m³ of SO₂, 300 mg/m³ of NO, a SO₂/NO flow rate of 30 mL/min, a N₂ flow rate of 300 mL/min, a temperature of 140 °C, and an O₂ concentration of 10% (by volume)) were analyzed *via* XRD, SEM/EDS, FTIR, and XPS to explore the influence of the physical and chemical properties of microwave-modified activated coke on the desulfurization and denitrification process.

Changes in phase structure and morphology

As shown in Fig. 7a, the primary phase composition of the microwave-modified activated coke was comprised of C, CaO, and Fe₂O₃. The presence of C and CaO had an important influence on the oxidation and absorption of SO₂ and NO. Compared with the activated coke before desulfurization and denitrification, the new phase structures of CaSO₄, CaCO₃, Fe(NO₃)₃, and CaS appeared in the aged activated coke (as shown in Fig. 7b). This illustrated that the desulfurization products of the microwave modified activated coke were CaSO₄ and CaS, and the denitrification product was Fe(NO₃)₃. The appearance of CaCO₃ indicated that the intermediate product CO₂ may be generated during the reaction. Figure 8 shows the scanning electron microscope (SEM) and energy spectrum analysis (EDS) of the activated coke at the different stages. It can be seen in Figs. 8a and 8b that the size of the activated coke particles decreased and changed from bulk aggregation to smaller particle size after the microwave modification treatment, which is consistent with the increase of specific surface area of the microwave-modified activated coke mentioned above, effectively increasing the active site of bare leakage on the surface of the activated coke. In addition, it can be seen from the EDS energy spectrum that the composition and content of activated coke elements were not changed significantly before and after the microwave modification, indicating that the microwave activation factor only activates the internal structure of the substance, and cannot transform the chemical composition of the substance. However, as shown in Fig. 8c, the white crystalline substances appeared in the active coke after the desulfurization and denitrification, and the surface of the surrounding active coke was flat without any traces of being burned or etched.

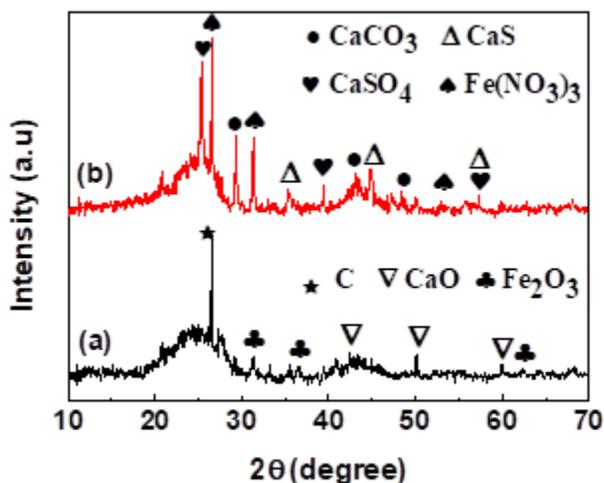


Fig. 7. XRD pattern of the activated coke before and after desulfurization and denitrification: (a) the microwave-modified active coke before desulfurization and denitrification and (b) the microwave-modified active coke after desulfurization and denitrification

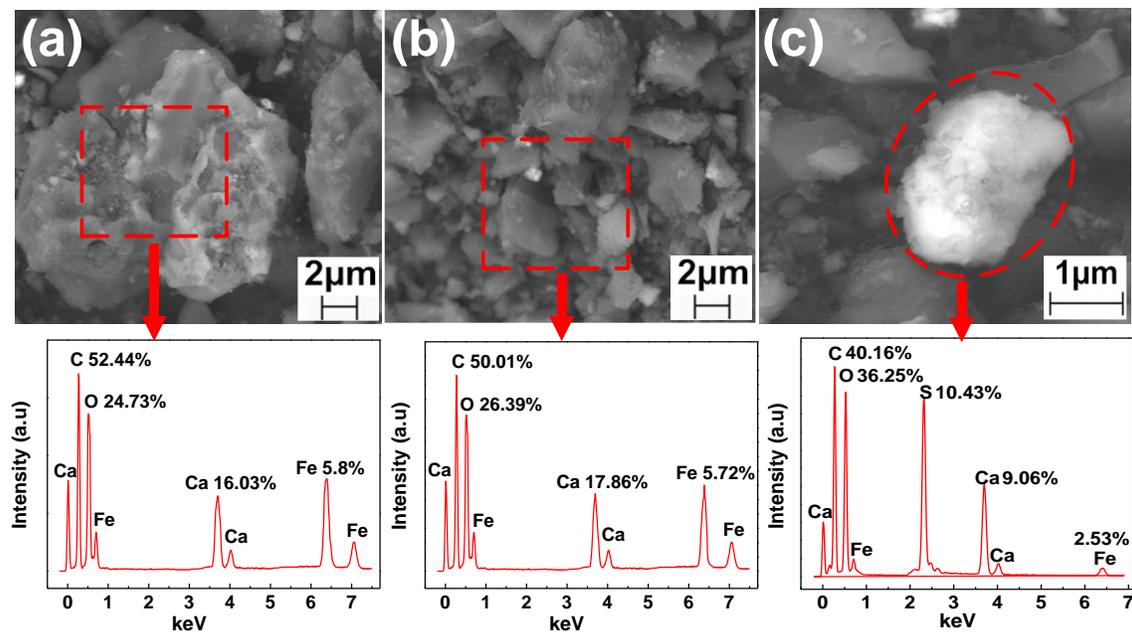


Fig. 8. SEM and EDS analysis of activated coke at different stages: (a) activated coke, (b) the microwave-modified activated coke and (c) the microwave-modified activated coke after desulfurization and denitrification

The EDS module was used to analyze the composition of the selected area, and the characteristic peak of S was detected in the energy spectrum, but the characteristic peak of N was not found. This indicated that the white crystalline material here was primarily desulfurized products (CaSO_4 and CaS). The characteristic peak of N was also not detected in other parts. The possible reason for this was that the atomic ratio of N was low, and the peak intensity was too weak; therefore, it was covered by a strong peak. However, this could also be due to the fact that NO was reduced by C to form N_2 overflow.

Surface functional group analysis

As shown in Fig. 9, the characteristic peaks of the infrared spectrum drastically changed for the activated coke after microwave modification and desulfurization and denitrification. Compared to the microwave-modified activated coke, the infrared spectrum of the activated coke showed new characteristic peaks at 600 cm^{-1} and 1400 cm^{-1} , and the characteristic peak intensity was drastically enhanced at 1116 cm^{-1} . However, the intensity of the characteristic peak at 1600 cm^{-1} and 3500 cm^{-1} was drastically reduced after desulfurization and denitrification. The corresponding functional groups were C-O, C=C, and -OH at the wavenumbers 900 cm^{-1} to 1300 cm^{-1} , at 1500 cm^{-1} to 1700 cm^{-1} and at 3000 cm^{-1} to 3700 cm^{-1} , respectively. However, the infrared spectrum shown in Fig. 9 could only reflect the changing trend of the functional groups in the desulfurization and denitrification process; it could not indicate the change in its quantity. Thus, the Peakfit software (v4.12 version) was used to fit the characteristic peaks for semi-quantitative analysis of the changes in the functional groups (as shown in Figs. 10a, 10b, 10c, 10d, 10e, and 10f).

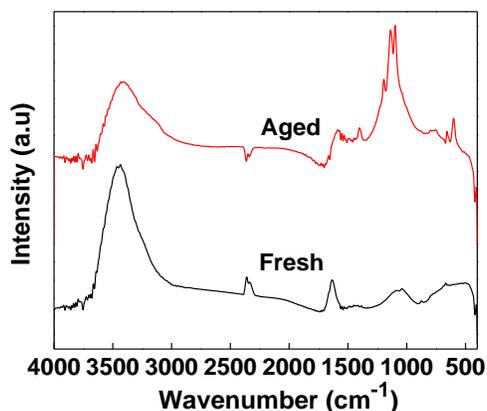


Fig. 9. FTIR spectrum of the activated coke before and after desulfurization and denitrification

The characteristic peaks at 1116.6 cm^{-1} , 1135.6 cm^{-1} , and 1211.4 cm^{-1} represented changes of the C-O groups at 900 cm^{-1} to 1300 cm^{-1} ; besides, wavelengths 1013.0 cm^{-1} and 1036.6 cm^{-1} corresponded to the characteristic peaks of silicate minerals (Zhang *et al.* 2020b). The relative content of the functional group was expressed by the closed area surrounded by the characteristic peak and the coordinate axis in the split peak fitting process. After the desulfurization and denitrification process, the area of the characteristic peak corresponding to silicate decreased, but the area of the characteristic peak corresponding to C-O increased from 4.0 to 21.5. This indicated that a large amount of new C-O functional groups were formed by the microwave-modified active coke during the removal of the SO_2 and NO (Song *et al.* 2020). Relevant literature by Xu *et al.* (2006) showed that the C-O functional groups played an important role in the adsorption of SO_2 and the oxidation of adsorbed NO, which is beneficial to the recycling of activated coke. In addition, the characteristic peak area corresponding to C=C was reduced from 2.6 to 0.9 at wavelengths of 1500 cm^{-1} to 1700 cm^{-1} , and the characteristic peak area corresponding to -OH was reduced from 54.2 to 34.3 at wavelengths of 3000 cm^{-1} to 3700 cm^{-1} . The reduced functional groups were involved in the chemical reactions of the desulfurization and denitrification process.

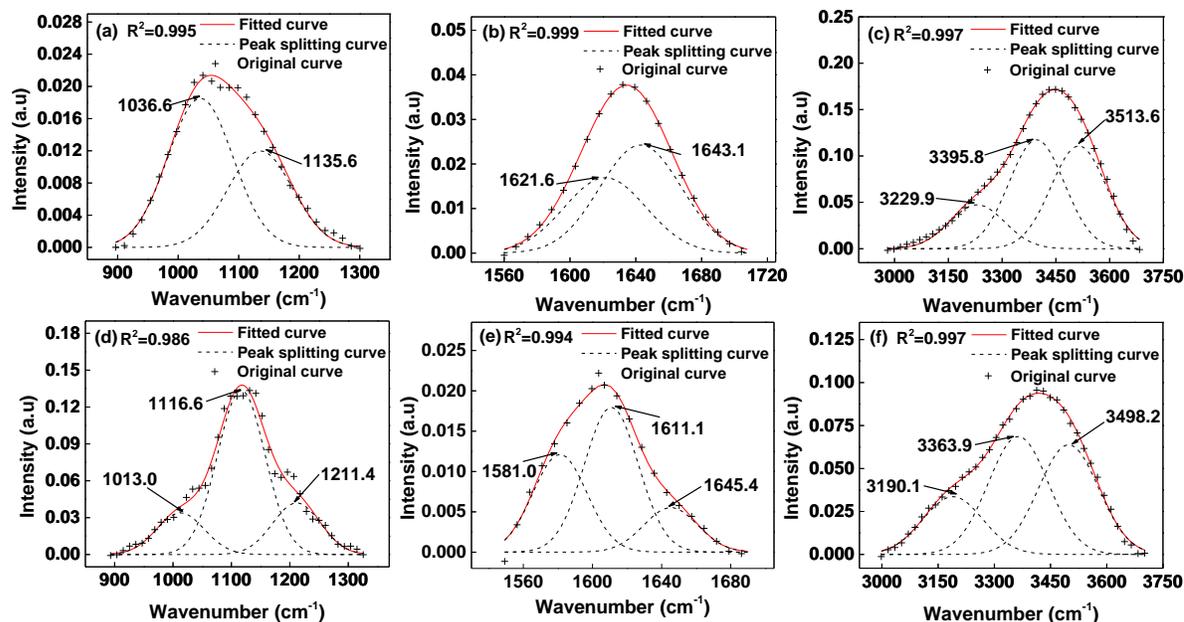


Fig. 10. (a, b, and c) FTIR spectrum of the microwave-modified activated coke before desulfurization and denitrification; and (d, e, and f) FTIR spectrum of the microwave-modified activated coke after desulfurization and denitrification

XPS characterization of the product

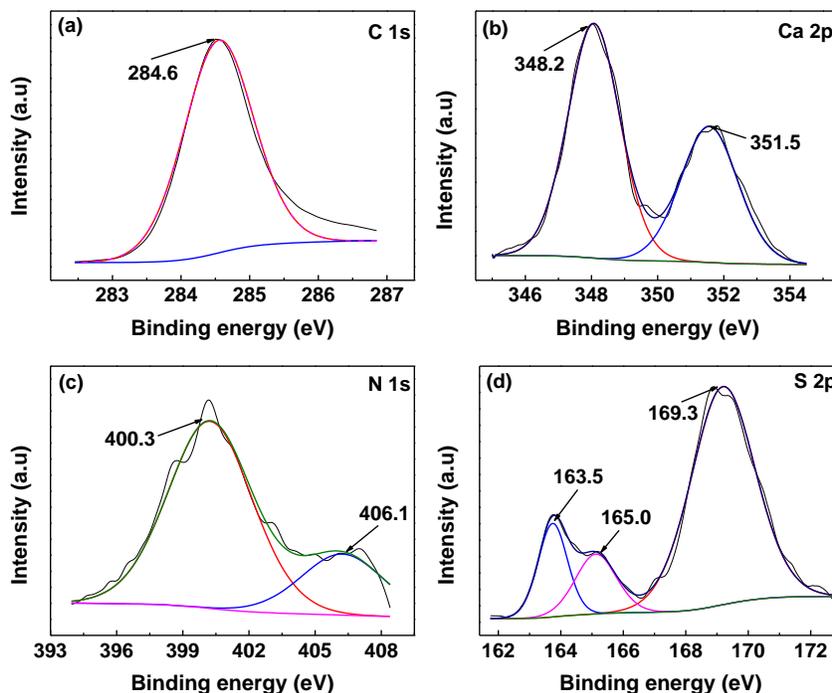


Fig. 11. XPS spectrum of the activated coke after desulfurization and denitrification

In order to further verify the presence of SO_2 and NO adsorbed by the activated coke, the valence states of C, Ca, N, and S in the activated coke after desulfurization and denitrification were analyzed *via* XPS (Ge *et al.* 2019; Xie *et al.* 2019; Zeng *et al.* 2019). The peak fitting results using CasaXPS software (v2.3 version) are shown in Fig. 11. As

shown in Fig. 11a, the photoelectron peak of C1s appeared at the binding energy of 284.6 eV, and the corresponding oxidation state of C is CO_3^{2-} , which indicated that the participating C existed in the form of carbonate in the product. The two photoelectron peaks appearing in Ca2p (as shown in Fig. 11b) were 348.2 eV and 351.5 eV in the binding energy range from 346 eV to 354 eV, respectively, and they all corresponded to the characteristic peaks of Ca^{2+} . Figure 11c shows the characteristic peak spectrum of N1s. There were two characteristic peaks at the binding energy of 400.3 eV and 406.1 eV, which correspond to the different oxidation states of nitrogen oxide. The characteristic peak with a binding energy of 400.3 eV corresponds to NO_3^{2-} , but the study on the characteristic peak at a binding energy of 406.1 eV was not clear, and it might be a nitrogen-containing impurity. It can be seen from Fig. 11d that the characteristic peaks of S2p appeared at the binding energies of 163.5 eV, 165.0 eV, and 169.3 eV. The characteristic peaks with a binding energy of 163.5 eV and 169.3 eV corresponded to SO_4^{2-} , and the characteristic peak at a binding energy of 165.0 eV was S^{2-} . No sulfite nor nitrite was detected. The detection results of the XPS were consistent with the XRD and EDS analysis, and combined with the changes of the surface functional groups gained from the FTIR characterization, it was speculated that the reaction behavior and reaction process of SO_2 and NO in activated coke were as follows, according to Eqs. 1 through 7,



The microwave energy changed the -OH and C=C functional groups of the active coke from the ground state to the excited state, which made the desulfurization and denitrification process occur, which cannot be carried out under the conventional heating conditions at a temperature of 140 °C. The reaction temperature of the desulfurization and denitrification process was reduced; therefore, the secondary heating of the flue gas was unnecessary. The simultaneous desulfurization and denitrification were obtainable at a low temperature, providing new ideas in terms of energy saving and emission reductions for the SO_2 and NO removal process.

CONCLUSIONS

1. Microwave processing can effectively improve the specific surface area and reduce the pore diameter of the active coke. When subjected to microwaves, the specific surface area of active coke was increased from 185.9 m^2/g to 351.7 m^2/g , and the pore size decreased from 1.93 nm to 1.23 nm. Microwave energy can cause the decomposition and reorganization of various functional groups in active coke. The characteristic peak intensities of the C=C and -OH functional groups were enhanced, which was beneficial to improve the desulfurization and denitrification rates of activated coke.

2. The optimum temperature and O₂ concentration of microwave-modified activated coke for desulfurization and denitrification were 140 °C and 10% (by volume), respectively. The desulfurization breakthrough curve time was 70 min, and denitrification efficiency was still maintained at 37% at 40 min. The desulfurization and denitrification rates are higher than those of the unmodified activated coke.
3. The main products of microwave-modified activated coke for desulfurization and denitrification were CaSO₄, CaS, and Fe(NO₃)₃, and the by-product was CaCO₃. After the desulfurization and denitrification processing, the characteristic peak intensity of C=C and -OH and the enclosed area weakened, but the C-O functional group content increased. The activated coke being subjected to the microwave field made the desulfurization and denitrification process occur, which cannot be carried out under the conventional heating conditions at a temperature of 140 °C.

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