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Experimental study on desulfurization at low temperature with plasma modified calcium-based adsorbent

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Abstract. Activated carbon and quicklime were used to prepare complex calcium based adsorbent for flue gas desulphurization. The desulfurization properties of adsorbent were analyzed on fixed bed. The results showed that the desulfurization effect of the composite adsorbent was best when the ratio of activated carbon to calcium was 1:2, the water heating time was 24 hours and heating temperature was 90 °C. At the same time, low temperature plasma technology is used to ionize the composite adsorbent, increase the number of surface chemical functional groups of the adsorbent, and then improve its desulfurization efficiency. The effect of modification time and power on desulfurization efficiency was studied. The results show that low temperature plasma ionization modification can obviously improve the desulfurization performance of composite adsorbent.

1. Introduction

According to the latest China Statistical Yearbook in 2018, China's energy consumption has consumed 4.49 billion tons of standard coal in 2017, 7.9 times that of 1978 [1]. China's energy reserves are extremely unevenly distributed, and coal resources are relatively abundant [2]. China's coal utilization is mainly based on power generation, and it is difficult to change the pattern of coal-fired power for a long time in the future [3]. Therefore, coal-fired flue gas treatment has great significance for environmental protection in China. At present, the removal of SO₂ and NO_x in the coal-fired industry are divided into desulfurization technology and denitration technology. Among them, the desulfurization technology [4, 5] is divided into flue gas desulfurization of pre-combustion, combustion and post-combustion. Among them, desulfurization after combustion [6] is currently the most extensive and mature technology.

The activated carbon materials have excellent adsorption performance because of great specific surface area and pore structure, which results in excellent surface physical properties [7, 8]. On the other hand, calcium-based adsorbents [9, 10] are widely used as industrial adsorbents in desulfurization processes after combustion for the low cost and abundant reserve. At present, researchers in various countries are developing in-depth and comprehensive development of high-activity calcium-based desulfurizers, and blending other reagents to improve the performance of desulfurizers [11]. Activated carbon has a large specific surface area and pore density, and has strong adsorption properties. The surface is suitable for implanting various active groups; and the calcium-based adsorbent itself has a good desulfurization effect. Combining the two is expected to produce a highly efficient composite adsorbent. At the same time, the application of low temperature plasma technology [12, 13] in the modification of adsorbents has also attracted researchers' attention. Low temperature plasma technology is capable of producing a large number of reactive groups on the



surface of the material in contact with air, and a portion of these reactive groups can be supported on the surface of the material. Therefore, low temperature plasma technology is a good surface modification technology. The results of many low-temperature plasma-modified activated carbons also show that the activated carbon after low-temperature plasma treatment can improve its adsorption performance.

Therefore, this study will use low temperature plasma technology to modify the desulfurization performance of activated carbon calcium-based adsorbents. The composite calcium-based adsorbent was prepared by impregnation method, and the surface of the adsorbent was modified by low temperature plasma, and the desulfurization performance of the composite adsorbent before and after modification was evaluated on a fixed bed.

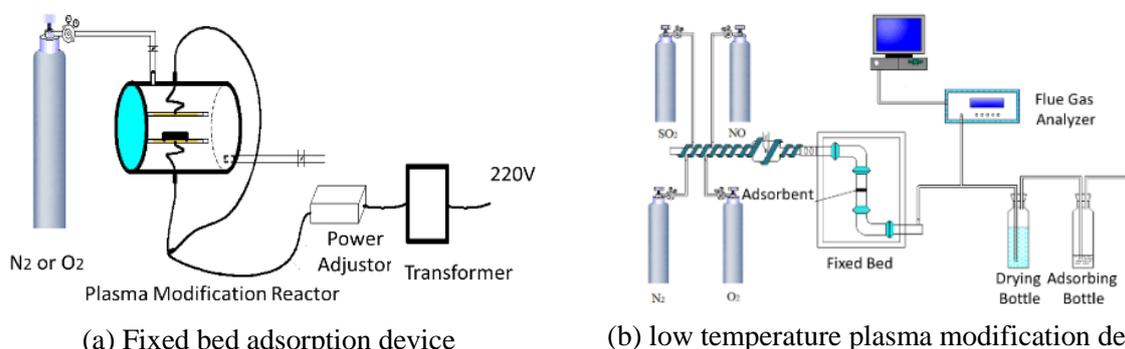
2. Materials and methods

2.1 Adsorbent preparation

The adsorbent was prepared by impregnation. 100 mesh activated carbon powder and CaO powder were mixed in proportion, and the mixing ratio was 1:0/1:1/1:2/2:1/0:1. The drug was placed in a 500 ml beaker and deionized water was added to a thermostatic magnetic stirrer. The set temperature was 90 °C and the stirring time was 24 h. Then the sample was filtered off, dried in an oven at 105 °C, and finally the sample was taken out of the oven and ground into a powder. After the preparation of the composite calcium-based adsorbent is completed, the prepared adsorbent is subjected to low-temperature plasma modification, and the modification time and plasma power are changed to obtain different modified composite adsorbents.

2.2 Removal of SO₂

The fixed bed adsorption device is shown in **Figure 1 (a)**. The system is composed of four parts: the simulated flue gas distribution device, the fixed bed adsorption device, the flue gas analysis device and the exhaust gas treatment device. The simulated flue gas is prepared proportionally by cylinder gas, and N₂ is used as the balance gas. The SO₂/NO concentration in the simulated atmosphere was calibrated and measured using a Seitron C500 flue gas analyzer and then fully reacted through a fixed bed containing the target adsorbent. After adsorbed, the simulated flue gas was analyzed by the flue gas analyzer, and the excess gas is discharged through the exhaust gas treatment device. The low temperature plasma modification is shown in **Figure 1 (b)**. The cylindrical outer casing is provided with a high-pressure wire hole of air inlet and outlet, high-voltage electrode plate and ground electrode plate. The high and low voltage electrode plates are embedded with a certain size of copper plate in the center of the quartz plate as an electrode, and a quartz forms a barrier medium. The copper plate is connected to the high voltage power source by a welding high voltage line. The high-voltage AC power supply (0-30kV, 20kHz) will provide energy between the two electrodes, and after the regulator is adjusted, a discharge channel is established. The high-voltage electrode plate and the ground electrode plate are horizontally inserted into the horizontal groove of the multi-pitch slotted quartz plate, and can be taken out to the outside when used, so that the modified sample can be conveniently placed. The ground electrode plates can be inserted into different grooves according to different required spacing. The pitch adjustment of the device for realizing the surface properties of the dielectric barrier-modified low-temperature plasma-modified material. When the device is used, the solid material to be modified is uniformly placed on the ground electrode plate, the high voltage electrode is connected with the high voltage terminal of the high voltage power supply, the ground electrode is connected with the low voltage terminal of the high voltage power supply, and then grounded, and the injection voltage is adjusted by adjusting the output voltage of the high voltage power supply. Energy, obtain a discharge plasma, and achieve plasma modification of the sample.



(a) Fixed bed adsorption device (b) low temperature plasma modification device
Figure 1 Fixed bed adsorption device and low temperature plasma modification device

3. Results and discussion

3.1 AC and CaO ratio optimization

The ratio of AC to CaO of the adsorbent was changed, and the SO₂ removal performance of the adsorbent was evaluated. The simulated flue gas components include N₂, O₂ and SO₂, the oxygen volume fraction is 6%, the SO₂ concentration is 700 ppm, and the simulated flue gas total flow is 2 L/min. The fixed bed adsorption temperature is 80 °C. The experimental results of the unit mass adsorption amount and the maximum adsorption efficiency of SO₂ are shown in **Figure 2** (0:1 of the original CaO as a control group, and the desulfurization efficiency was 29.01%). It can be seen from the figure that after adding CaO to activated carbon, the desulfurization efficiency is significantly higher than that of activated carbon. The doping of CaO on activated carbon can improve the adsorption performance of the calcium-based adsorbent. Comparing the five data sets, the 1:1 composite calcium-based adsorbent has the best desulfurization effect, reaching 29.56%. The adsorption performance of the original AC is extremely poor, only 18.51%. Therefore, the composite adsorbent of this ratio will be studied below.

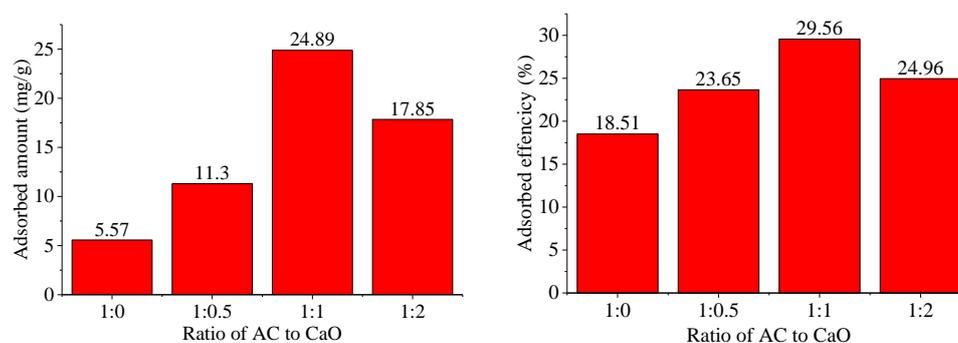


Figure 2 SO₂ unit mass adsorption capacity and maximum adsorption efficiency

3.2 Effect of NO on SO₂ removal

NO is another important pollutant in coal-fired flue gas. To study the effect of NO on SO₂ adsorption, NO is added to the simulated flue gas. The adsorption temperature was 80 °C, the SO₂ concentration was 700 ppm, and the O₂ concentration was 6%. The result is shown in **Figure 3**. It can be seen from the figure that compared with the simple adsorption of SO₂, the removal efficiency of SO₂ is obviously increased after the addition of NO, and the desulfurization result shows a strong regularity. The desulfurization efficiency is 44.16% under the condition of NO concentration of 600 mg/m³, indicating that NO has a strong promoting effect on the removal of SO₂, but the adsorption amount per unit mass of adsorbent shows a downward trend. This indicates that there is competitive adsorption between NO and SO₂.

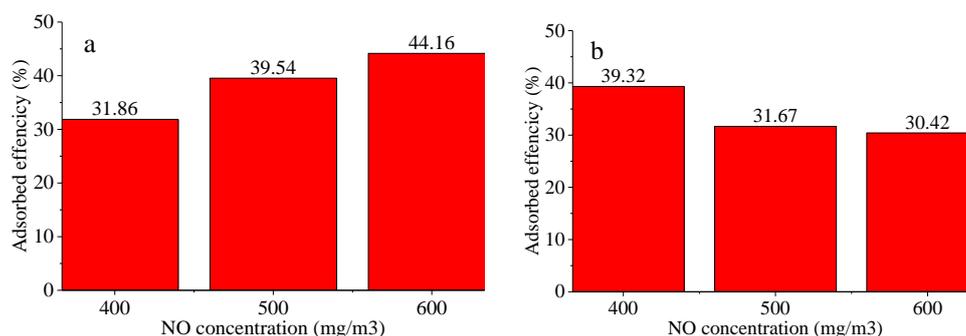


Figure 3 NO effect (a SO₂ adsorption efficiency; b NO adsorption efficiency)

3.3 Effect of plasma modification time on desulfurization

Based on the best composite calcium-based adsorbent with the ratio 1:1, plasma modification were applied to improve the performance of composite adsorbent. The effect of modification time on the desulfurization of the composite calcium-based adsorbent was investigated. The experimental results are shown in **Figure 4**. It can be seen from **Figure 4** that the desulfurization efficiency of the composite calcium-based adsorbent is not significantly improved for 1 min and 5 min. When the modification time is 10 min, the desulfurization efficiency is significantly increased to 48.98%. It is speculated that because the modification time is short, the plasma technology does not adequately modify the surface of the adsorbent, and the physicochemical properties of the adsorbent surface change less, resulting in less change in adsorption capacity. Comparing the desulfurization performance of the 10 min desulfurization data with the original composite calcium-based adsorbent, the maximum removal efficiency is increased by 23.87% and the unit mass adsorption capacity is increased by 67.18%, and the removal efficiency is significantly higher than the original composite calcium. This indicates that the chemisorption ability of the reactive functional group is very good, and the reactive functional group implanted by low-temperature plasma modification greatly increases the adsorption capacity per unit mass of the adsorbent.

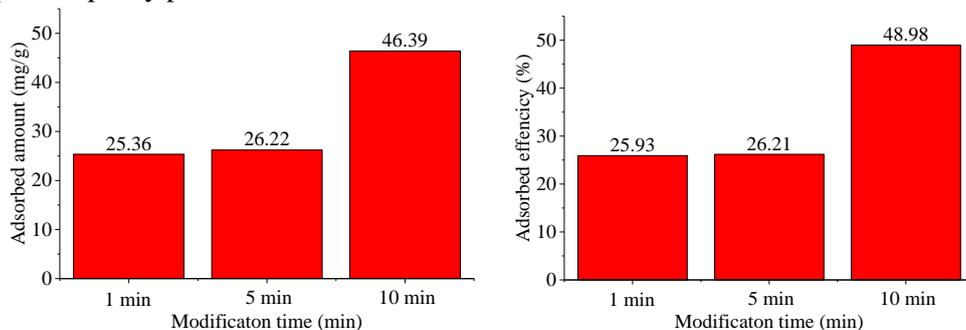


Figure 4 Effect of plasma modification time

3.4 Effect of modified power on desulfurization

The power of the plasma modification was set to study its effect on the desulfurization effect of the adsorbent. The result is shown in **Figure 5** below. It can be seen from the figure that with the increase of the modified power, the desulfurization efficiency and the adsorbent per unit mass of the adsorbent both show an increasing trend, and both of them reach the maximum at the same time under the modified condition of 66W. Compared with the original calcium-based adsorbent, the desulfurization efficiency after modification is obviously increased. When the power is 66W, the desulfurization efficiency is close to 50%, and the adsorption amount per unit mass of adsorbent is also obviously increased. When the surface is modified by low temperature plasma, the composite calcium base is combined. The desulfurization efficiency of the adsorbent is obviously increased, which is due to that the plasma modification process increases the number of oxygen-containing functional groups on the

surface of the adsorbent and promotes the adsorption and reaction of SO₂ on the surface of the adsorbent.

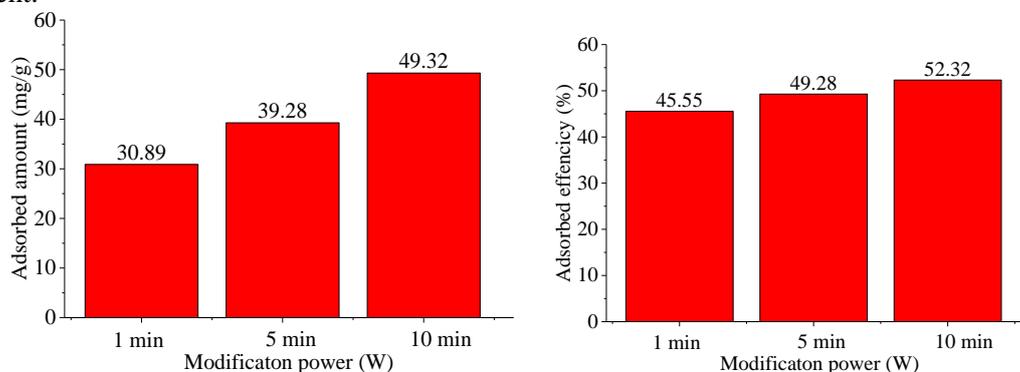


Figure 5 Plasma modification power impact

4. Conclusion

In this study, composite calcium-based adsorbents were prepared, and the desulfurization performance of the composite adsorbents was studied in a fixed-bed reactor. The optimal preparation conditions of the composite calcium-based adsorbent were optimized. The composite calcium-based adsorbent was modified by low temperature plasma. The effects of modification power and time on the adsorbent performance were studied. The results show that the composite calcium-based adsorbent prepared by AC and CaO has a good desulfurization performance with the ratio of 1:1. Low temperature plasma modification power and time are important parameters affecting the modification effect. The presence of NO promotes the desulfurization of the composite calcium-based adsorbent. Experiments show that low temperature plasma technology has great development potential in desulfurization of modified composite calcium-based adsorbents.

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