Effect of Activation Condition on the Performance of Activated Sludge Carbon-Based Adsorbent in Diesel Desulfurization

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Abstract. Sulfur compounds in diesel oil can be removed by the adsorption technology. Based on the urban sludge as the main raw materials, activated sludge carbon-based absorbents were prepared through the cothermalization of urban sludge and rice hull by adding ZnCl₂ as the chemical activator under the different activation conditions. The obtained absorbents were characterized by nitrogen adsorption characterization and were investigated in the dibenzothiophene adsorption capacity of n-octane model oil. The characterization and the adsorption performance results showed that the amount of the micropore volume and the ratio of the micropore volume to the total pore volume played the important effects on the dibenzothiophene adsorption capacity behavior. The adsorbent could be obtained a larger amount of micropore and a bigger specific surface area, micropore specific surface and micropore volume under the activation temperature of 600 °C and the activation time of 60 min, which resulted a better behavior on the dibenzothiophene adsorption capacity of 19.9 mg S/g. The application of urban sludge in the preparation of the desulfurization adsorbent can provide a new way for the harmless and resource recovery usage.

1. Introduction
Sulfur compounds in diesel oil are mainly mercaptan, thiophene, dibenzothiophene, benzothiophene, and so on. Among the sulfur compounds, thiophene species account for more than 80% of the total sulfur compounds in diesel. When sulfur compounds in diesel are burning, SOₓ is formed, which not only corrodes and damages the engine parts in the car, but also forms acid rain to result the problem of the environmental pollution. Adsorption desulfurization has been developed in recent years which is a new desulfurization technology [1-2]. The adsorption desulfurization technology principle is that the absorbent makes the sufficient contact with the light oil containing sulfur compounds, and then sulfur-containing compounds adsorb on the adsorbent to achieve the aim of desulfurization, finally, the adsorbent containing sulfur compounds are regenerated by the approach of desorption. In the adsorption desulfurization technology, the key points are the adsorption performance and the renewable capacity of the adsorbent [2-3].

Because of cheaper and easily obtained of the sludge, the route of the preparation of sludge carbon-based absorbent becomes a new way for the treatment and recycling of urban sludge [4-5]. In this paper, an efficient and porous activated sludge carbon-based absorbent was prepared under the different activation conditions from the cothermalization of urban sludge and rice hull by adding ZnCl₂ as the chemical activator [8-9]. And then, the prepared zinc chloride activated sludge carbon-based adsorbent was applied in the deep adsorption desulfurization technology of diesel fuel in order
to provide a new way in accordance with the reduction, recycling and harmless of the solid waste.

2. Experimental

2.1. Experimental materials
Sludge was obtained from the mud cake with the treatment of dehydration processing in Wuhan Hanxi sewage treatment plant. N-octane (CP) was from Shanghai Lingfeng Chemical Reagent Co., LTD.. Dibenzothiophene (98%) was obtained from Alfa Aesar Company. ZnCl$_2$ (AP) was adopted from Sinopharm Group Chemical Reagent Co., LTD.. Strong sulfuric acid (AP) was from Shanghai FeiDa Industry and Trade Co., LTD..

2.2. Preparation of activated sludge carbon-based adsorbent
The dehydrated sludge was dried at 120 °C for application. The washed rice hull was dried at 120 °C and then was crushed and carbonized at 400 °C for 0.5 h. Subsequently, the carbonized rice hull ash and the dry sludge were mixed evenly under the mass mixing ratio of 1:1, and the mixture was called the sludge carbon-based sample. 50 wt% concentration of ZnCl$_2$ activator and the prepared sample were mixed evenly with the ratio of sample to liquid at 1:2, and then the liquid-solid mixture was impregnated at 70 °C for 12 h. Subsequently, the impregnated mixture was put in the muffle furnace at a certain temperature (500 °C, 600 °C, 650 °C and 700 °C) for a certain time (45 min, 60 min, 75 min). After calcination, a certain amount of 10 vol% sulfuric acid was poured into the activated sample immediately. And then, the obtained activated sample containing sulfuric acid was stable in the water bath at 70 °C for 1 h. Finally, the obtained sample was washed to neutral with deionized water, filtered, dried at 120 °C and grinded in turn. The obtained sample was zinc chloride activated sludge carbon-based adsorbent.

The effects of the activation temperature on dibenzothiophene adsorption capacity were used the prepared sample under the activation time of 60 min, and the influences of the activation time were adopted the prepared sample under the activation temperature of 600 °C.

2.3. Static adsorption desulfurization experiment
The experimental device of static adsorption desulfurization was shown in Figure 1. The n-octane model oil containing 300 μg S/g sulphur content was prepared from the mixture of 0.1215 g dibenzothiophene and 100 ml n-octane. During the adsorption desulfurization experimental, 0.4 g of pre-dried activated carbon-based adsorbent sample was put into the three-necked flask filled with 100 ml model oil. Subsequently, the mixture was stirred at a constant speed for 12 h at room temperature and atmospheric pressure. And then, the mixture was filtered to obtain the liquid oil phase. Finally, the sulfur analysis of the liquid oil phase was carried out to determine the dibenzothiophene adsorption capacity.

![Figure 1. Experimental device of static adsorption desulfurization](image)

2.4. N$_2$ adsorption characterization and adsorption desulfurization performance
The microscopic properties and the pore textural structures of the activated sludge carbon-based absorbent were characterized by ASAP 2020 (Micromeritics, USA). The sulfur content was
determined by GC-920 gas chromatograph (Shanghai Haixin Chromatography Co., LTD.) equipped with the chromatographic column of HP-5MS and the flame photometric detector (FPD). The determination of adsorption capacity is shown in Equation (1).

$$q = \frac{M_0 \times (C_0 - C) \times 10^{-3}}{M_{AC}}$$

(1)

Where, q is the absorbed sulfur content per gram of adsorbent, mg S·g⁻¹; M₀ is the mass of model oil, g; C₀ is the initial sulfur content in the model oil, µg·g⁻¹; C is the residual sulfur content at the adsorption equilibrium after the adsorption experimental, µg·g⁻¹; M_{AC} is the mass of adsorbent, g.

3. Results and discussion

3.1. Effect of the activation conditions on the dibenzothiophene adsorption capacity

The relationship between the adsorption capacity and the activation time was exhibited in Figure 2. In Figure 2, the adsorption capacity increases firstly and then decreases along with the increasing of the activation time from 45 min to 75 min. As we all known, in the early stage of the activation, the activation degree of the carbon in the activated sludge carbon-based material becomes higher and higher along with the increasing of the activation time. The optimum activation time can be obtained at the activation time of the fully carbon activation. When the activation time is higher than the optimum value, some changes on the textural structure and the pore distribution can be found, which result a decreasing adsorption capacity. A better performance adsorption capacity can be obtained under the activation time of 60 min.

Figure 3 showed the dibenzothiophene adsorption capacity of the activated sludge carbon-based adsorbent along with the increasing of the activation temperature from 500 °C to 700 °C. It can be found the activation temperature plays an important effect on the adsorption capacity. Along with the increasing of the activation temperature, the adsorption capacity increases firstly and then decreases. In the higher activation temperature, the effect of the ZnCl₂ becomes weaker due to a larger loss of the ZnCl₂, at the same time, the adsorbent has a larger amount of ash component due to the loss of the carbon content in the sludge. As a result, the adsorbent prepared under the higher activation temperature exhibits a worse adsorption behavior. From the adsorption capacity results in Figure 3, the optimum activation temperature is 600 °C.

3.2. Effect of the activation conditions on the textural structures of the adsorbent

The effect of the different activation conditions on the textural structure was shown in Table 1. In Table 1, the surface area, the micropore surface, total pore volume and the micropore volume increases along with the increasing of the activation time from 45 min to 60 min, respectively. In addition, the total pore volume and the average pore diameter exhibit the irregular trend of change. When the activation time increases from 60 min to 75 min, the surface area, the micropore surface, total pore volume and the micropore volume decrease rapidly, whereas the total pore volume and the average pore diameter increase obviously. Compared with the textural structures of the adsorbent
prepared under the activation time of 60 min, the micropore surface, the micropore volume and the ratio of the micropore volume to total pore volume are smaller of the adsorbent prepared under the other activation time. Combined the results of Figure 2, it can be deduced that the micropore volume of the adsorbent and the ratio of the micropore volume to total pore volume play the important roles on the dibenzothiophene adsorption performance. A better adsorption capacity can be obtained under the activation time of 60 min.

In Table 1, the specific surface area, the micropore surface and the micropore volume increase with the increasing of the activation temperature from 500 °C to 600 °C, at the same time, the average pore diameter decrease. When the activation temperature increases from 600 °C to 700 °C, the surface area, the micropore surface, the micropore volume and the average pore diameter exhibits a decreasing tendency, respectively. It is obvious that the activation temperature has an effect on the textural structure of the adsorbent. During the process of activation, the formation of new pores and the destruction of the existing pores occur at the same time. In the initial stage of the activation, the activation rate increases along with the increasing of the activation temperature from 500 °C to 600 °C to generate more micropore in the formation process of new pores. Subsequently, along with the increasing of the activation temperature, the destruction of the existing pore dominates the main status, which leads to the increasement of the mesopore number and the average pore diameter, and a decreiment of the surface area and the micropore volume, respectively. A larger special surface area, the micropore volume and the micropore area can be obtained when the activation temperature is 600 °C, which can provide a better dibenzothiophenen adsorption capacity. Regardless of the activation temperature or the activation time, it can be concluded that as long as a larger surface area and a greater amount of the micropore can be generated, a better dibenzothiophenen adsorption capacity can be obtained.

3.3. Effect of the activation conditions on the pore distribution of the adsorbent

The effect of activation time on the pore distribution was shown in Figure 4. From Figure 4, when the activation time increases from 45 min to 60 min, the amount of the pores with the pore diameter between 1 and 10 nm increases. When the activation time increases from 60 min to 75 min, the amount of the micropore decreases and the amount of the macropore increases. There is an obvious increasing of the amount of macropore under the activation time of 75 min. In the initial stage of the activation, the reaction between ZnCl$_2$ and carbon in the chain hydrocarbon or carbon in the cyclic hydrocarbon of the sludge generates the vapor of Zn and the mixing gas composed of CO, CO$_2$, H$_2$O and H$_2$. Subsequently, the generated mixing gases insert into the carbon layer for the formation of the new pore. In this stage, the process of pore formation is the main process, which results an increased adsorption capacity. In the intermediate stage of the activation, there is an balance between the pore formation and the pore destruction, as a result, the amount of the micropore and mesopore reaches a maximum value. In the last stage of the activation, the pore destruction process occupies the main status, which generates more mesopore and macropore than micropore in the adsorbent; as a result, the surface area and the micropore volume decrease and the average pore diameter increases [6-7]. Combined with N$_2$ adsorption analysis and the adsorption experimental, the activation time is one of

| Activation condition | Surface area (m$^2$.g$^{-1}$) | Micropore surface (m$^2$.g$^{-1}$) | Total pore volume (cm$^3$.g$^{-1}$) | Micropore volume (cm$^3$.g$^{-1}$) | Average pore diameter (nm) |
|----------------------|-------------------------------|-----------------------------------|----------------------------------|-------------------------------|--------------------------|
| Activation time (min)|                               |                                   |                                  |                               |                          |
| 45                   | 698.3                         | 283.3                             | 0.4145                           | 0.1235                        | 2.264                    |
| 60                   | 712.9                         | 315.9                             | 0.3493                           | 0.1441                        | 2.615                    |
| 75                   | 507.1                         | 124.7                             | 0.4350                           | 0.0532                        | 4.708                    |
| Activation temperature (°C) |
| 500                  | 688.3                         | 237.0                             | 0.3866                           | 0.1069                        | 3.020                    |
| 600                  | 712.9                         | 315.9                             | 0.3493                           | 0.1441                        | 2.615                    |
| 650                  | 587.6                         | 216.2                             | 0.3628                           | 0.0976                        | 3.310                    |
| 700                  | 546.7                         | 212.9                             | 0.3391                           | 0.0948                        | 3.340                    |
the important factors on the pore distribution and the amount of the micropore in the adsorbent. Among the experimental range of the activation time, a better dibenzothiophene adsorption capacity could be obtained with the activation time of 60 min.

Figure 4. Effect of activation time on pore distribution

Figure 5. Effect of activation temperature on pore distribution

The relationship of the activation temperature and the pore distribution was shown in Figure 5. In Figure 5, the amount of the micropore and the mesopore becomes larger along with the increasing of the activation temperature at the range of 500 °C to 600 °C, respectively. With the increase of the activation temperature at the range of 600 °C to 700 °C, there is an obviously increasing tendency on the average pore diameter and a decreasing tendency on the surface area, the micropore volume and the micropore area. Among the activation temperatures, 600 °C is the suitable value to obtain a larger amount of the micropore and the mesopore, which can give a better dibenzothiophene adsorption capacity. The reason may be that in the process of the activation under the activation temperature of 600 °C, there is a dynamic balance between the micropore generation and the micropore destruction, which can result a maximum amount of the micropore. When the activation temperature is lower than 600 °C, ZnCl₂ easily enters into the pore to react with the carbonization material and to form more micropore structure, which is beneficial to the adsorption capacity of dibenzothiophene. When the activation temperature is higher than 600 °C, on the one hand, the loss of ZnCl₂ and the organic in the sludge increases, respectively, on the other hand, the overburn of the carbon structure occurs to result the destruction of the micropore structure. Both of the reasons lead to a decreasing trend of the micropore number, as well as an increasing trend of the mesopore and the macropore number, respectively. As a result, the dibenzothiophene adsorption capacity exhibits a decreasing tendency.

4. Conclusions

The activated sludge carbon-based adsorbent was prepared using urban sludge by adding carbonized rice hull to increase carbon content and by adding ZnCl₂ as chemical activator under different activation conditions. Under the activation time of 60 min and the activation temperature of 600 °C, a higher amount of micropore and mesopore can be obtained, at the same time, the surface area, the micropore surface area and the micropore volume reach a maximum value, respectively. In addition, the relationship between the dibenzothiophene adsorption capacity and the textual structure of the adsorbent shows that the amount of the micropore volume and the ratio of the micropore volume to the total pore volume play the important effects on the adsorption performance. A better performance of the dibenzothiophene adsorption capacity using the activated sludge carbon-based adsorbent prepared under the optimum conditions can be obtained, which is 19.9 mg S/g. In addition, the activated sludge carbon-based adsorbent is prepared using urban sludge as the raw material, which can provide a new way for harmless sludge and resource utilization.

Acknowledgments

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