Effect of Zinc Chloride on the Sludge Carbon-Based Adsorbent in Diesel Desulfurization

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Abstract. Sulfur compounds in diesel oil can be removed by adsorption technology. Based on urban sludge as the main raw materials, activated sludge carbon-based absorbent was prepared through the cothermalization of urban sludge and rice hull by adding ZnCl$_2$ as the chemical activator. The obtained absorbent was characterized by nitrogen adsorption, elemental analysis, FT-IR characterization. The textural structure and pore distribution results showed that the amount of the micropore and the surface area played the important roles on the adsorption capacity. The elemental analysis results revealed that the percentage of C element was the key factor in the adsorption experimental. FT-IR characterization results illustrated that the oxygen-containing groups on the absorbent surface increased significantly with the addition of ZnCl$_2$ activator, especially the amount of alcohol hydroxyl groups and quinone hydroxyl groups. ZnCl$_2$ activated sludge carbon-based absorbent was applied in the adsorption capacity of dibenzothiophene with model oil. As a result, the adsorption capacity was up to 19.9 mg S /g at ZnCl$_2$ concentration of 50 wt %, which can provided a new way for harmless and resource recovery of urban sludge.

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. SO$_x$ is formed when sulfur compounds in diesel are burning at high temperature, which not only corrodes and damages the engine parts in the car, but also forms acid rain to result the environmental pollution problem. 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 make the sufficient contact with the light oil containing sulfur compounds, and sulfur-containing compounds in light oil adsorbed on the adsorbent to achieve the aim of the desulfurization. In the adsorption desulfurization technology, the key points are the better 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 from the sludge of municipal sewage plant by adding zinc chloride as an activator. And then, the prepared zinc chloride activated sludge carbon-based absorbent was applied in the deep adsorption desulfurization 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
Urban 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. ZnCl₂ (AP) was adopted from Sinopharm Group Chemical Reagent Co., LTD.. Strong sulfuric acid (AP) was from Shanghai FeiDa Industry and Trade Co. LTD.. 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.

2.2. Preparation of zinc chloride 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, the dried rice hull was crushed and carbonized at 400 °C for 0.5 h. Subsequently, the carbonized rice hull ash and dry sludge were mixed evenly under the mass mixing ratio of 1:1, which was called the sludge carbon-based sample.

A certain concentration (30 wt%, 40 wt%, 50 wt%, 60 wt%) of zinc chloride solution and the sludge carbon-based sample were mixed evenly with the ratio of material to liquid at 1:2, then the liquid-solid mixture was impregnated at 70 °C for 12 h. Subsequently, the impregnated mixture was put in the muffle furnace at 600 °C for 1 h for activation. After calcination, a certain amount of 10 vol% sulfuric acid were poured into the activated sample immediately, and then the mixed sample containing sulfuric acid was stable in the water bath at 70 °C for 1 h. Finally, the mixture sample was washed to neutral with deionized water, filtered, dried and grinded to acquire the zinc chloride activated sludge carbon-based adsorbent.

2.3. Characterization of activated sludge carbon-based adsorbent
The microscopic properties and pore structure of the samples were characterized by ASAP 2020 (Micromeritics, USA), the Vario EL III elemental analyzer (Elementar Analysen systeme GmbH, Germany) was carried out on the element analysis of the samples, and FT-IR was analyzed by the infrared spectrometer Magna-IR 550 (Nicolet, USA).

2.4. Static adsorption desulfurization experiment
The experimental device of static adsorption desulfurization was shown in Figure 1. In the experimental, 0.4 g of pre-dried zinc chloride activated carbon-based adsorbent 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 adsorption capacity of dibenzothiophene.

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

2.5 Adsorption desulfurization performance of the adsorbent
The sulfur contents of the model oil and the liquid oil phase were 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).

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

Where, \(q\) is the absorbed sulfur content per gram of adsorbent, mg S·g\(^{-1}\); \(M_0\) is the mass of model oil, g; \(C_0\) and \(C\) is the initial sulfur content in the model oil and the residual sulfur content in the model oil at the adsorption equilibrium, respectively, µg·g\(^{-1}\); \(M_{AC}\) is the mass of adsorbent, g.

3. Results and discussion

3.1 Effect of ZnCl\(_2\) concentration on textural structure and pore distribution

The textural structures and the pore distribution of the activated sludge carbon-based adsorbents are shown in Table 1 and Figure 2.

| ZnCl\(_2\) concentration | 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) |
|--------------------------|-----------------------------|-------------------------------|---------------------------------|---------------------------------|--------------------------|
| 30%                      | 429.7                       | 113.0                         | 0.2722                          | 0.0503                          | 3.428                    |
| 40%                      | 487.9                       | 149.0                         | 0.2871                          | 0.0668                          | 3.172                    |
| 50%                      | 712.9                       | 315.9                         | 0.3493                          | 0.1441                          | 2.615                    |
| 60%                      | 658.7                       | 256.8                         | 0.3339                          | 0.1165                          | 2.719                    |

In Table 1, the specific surface area, the micropore surface, the total pore volume and the micropore volume increases when the concentration of ZnCl\(_2\) increases from 30 wt% to 50 wt%, respectively. At the same time, the average pore diameter decreases firstly and then increases a little. The main reason is that, within a certain concentration of ZnCl\(_2\) from 30 wt% to 50 wt%, the increasing of ZnCl\(_2\) concentration is conducive to the full activation of sludge-rice hull based mixed material, which leads to the pore-making movement of the adsorbent dramatically[6-7]. As a result, the specific surface area and the micropore volume increase, as well as the average pore diameter decreases. When the concentration of ZnCl\(_2\) increases from 50 wt% to 60 wt%, the specific surface area, the micropore surface, the total pore volume and the micropore volume drop a little.

In Figure 2, when the concentration of ZnCl\(_2\) is in a lower level, the pore size of the sludge carbon-based adsorbent were mainly micropore and mesopore. When the concentration of ZnCl\(_2\) solution increases up to 50 wt%, the amounts of the micropore and the mesopore reach the maximum value. Keep increasing the concentration of ZnCl\(_2\) up to 60 wt%, the amounts of the micropore and the mesopore decrease whereas the amount of the macropore increases. The influence of ZnCl\(_2\) activator on the specific surface area and the pore diameter distribution of the sludge carbon-based adsorbent is mainly due to the reaction between ZnCl\(_2\) and carbon atoms of the adsorbent in the addition process[8]. Along with the increasing dosage of ZnCl\(_2\), the activation reaction speed accelerates, which means ZnCl\(_2\) activator continues the activation reaction in the micropore. Therefore, the values of micropore volume and the specific surface area of the adsorbent increase in Table 1. However, when the concentration of ZnCl\(_2\) solution is greater than 50 wt%, because the carbon atoms on the active site may have been basically consumed, excessive ZnCl\(_2\) would react with the skeleton carbon atoms around the micropore, which cause the collapsion of the micropore structure[6-7]. As a consequence, the amount of the micropore decreases, the amount of the macropore increases, and the specific surface area decreases in a higher ZnCl\(_2\) concentration.
3.2 Effect of ZnCl₂ concentration on elements distribution

Elements distribution of the activated sludge carbon-based adsorbent was shown in Figure 3. In Figure 3, element percentage composition curves show that both of the content of N and H decrease along with the increasing of ZnCl₂ concentration. The reason may be that the reaction of amination occurs between ZnCl₂ and peptide or amino acid in the sludge to form ammonia. The content of C element increases firstly and then decreases with the increasing of ZnCl₂ concentration. When the concentration of ZnCl₂ is 50 wt%, the element concentration of C in the adsorbent reaches the highest value of 64.8%.

3.3 Effect of ZnCl₂ concentration on FT-IR characterization

FT-IR analysis was carried out to investigate the relevant information of functional groups on the surface of the non-activated and activated adsorbents, as shown in Figure 4. Combining with the IR spectral bands on the surface of carbon oxygen groups[8], it can be found that there is an obvious enhancement strength at the peak of 3420 cm⁻¹ on the surface of the activated adsorbent, which suggests that there is an increase of alcohol functional groups. There is a certain strengthening of the bimodal peaks near 2921 cm⁻¹ and 2850 cm⁻¹, which indicates the enhancement of C-H bond. The enhancement and deviation of the peak near 1600 cm⁻¹ indicates that the increase of the content of quinone and C=C aromatic functional groups. However, there is almost no reflection peak in the range of 1100 to 1500 cm⁻¹, which indicates that carbon-based materials contains little contents of carbonate impurities, carboxyl-carbonate and lactone groups. The strength and the width of the peak near 1062 cm⁻¹ is still stronger and narrower, respectively, which reveals that the content of C-OH functional groups on the surface of the sludge carbon-based adsorbent have been changed by adding ZnCl₂. Therefore, from FT-IR characterization results, it can be found that there is a lot of oxygen-containing groups on the surface of the activated sludge carbon-based adsorbent, such as alcohol hydroxyl, phenolic hydroxyl, carboxyl and quinone species, especially the concentration of ZnCl₂ activator of 50 wt%. 
3.4 Effect of ZnCl$_2$ concentration on the dibenzothiophene adsorption capacity

The concentration of ZnCl$_2$ as activator on the dibenzothiophene adsorption capacity for the model oil was illustrated in Figure 5. It is obviously that the addition of ZnCl$_2$ has an important role on the adsorption capacity of dibenzothiophene. In Figure 5, the adsorption capacity curve shows an increasing tendency when the concentration of ZnCl$_2$ increases from 30 wt% to 50 wt%; however, the adsorption capacity decreases when the concentration of ZnCl$_2$ increases from 50 wt% to 60 wt%. The maximum adsorption capacity can be reached 19.9 mg S/g when ZnCl$_2$ concentration is 50 wt%. It can be deduced that too low or too high of ZnCl$_2$ concentration would inhibits the adsorption of dibenzothiophene in the model oil.

Under the action of ZnCl$_2$ activator, the pores in the adsorbent form by dehydration, condensation and wetting inflation. During the formation of pores, non-volatile poly-condensation carbon can be formed by the condensation of carbon-containing compounds to generate the developed porous structure. Therefore, when the concentration of ZnCl$_2$ activator is in a relatively higher level near 50 wt%, the dehydration condensation is contributed to the formation of pores which results the well developed porous structure of the activated adsorbent. However, if the concentration of ZnCl$_2$ activator is in a higher level more than 50 wt%, ZnCl$_2$ may be removed unclean during the process of washing the pyrolysis products and the residual ZnCl$_2$ remains on the microporous surface of the activated sample, which results a decreasing adsorption capacity. Therefore, it is very important to adopt a suitable amount of the addition of ZnCl$_2$ for the preparation of the adsorbent.

4. Conclusions

The activated sludge carbon-based adsorbent was prepared using urban sludge as the raw materials by adding carbonized rice hull to increase carbon content and by adding ZnCl$_2$ as the chemical activator. Due to the addition of ZnCl$_2$, it is beneficial to the full activation of sludge carbon-based adsorbent and to the enhancement of the pore-forming movement. As a result, there is an increasement of the specific surface area and the micropore volume, as well as a decrement of the average pore diameter, respectively. The textural structure and pore distribution results show that the amounts of the micropore and the mesopore increase along with the increasing of addition of ZnCl$_2$ activator, as a result, a larger surface area of 712.9 m$^2$·g$^{-1}$ and the micropore volume of 0.1441 cm$^3$·g$^{-1}$ can be obtained with ZnCl$_2$ concentration of 50 wt%. Due to the formation of ammonia from the reaction between ZnCl$_2$ activator and peptides or amino acids in the sludge, the element distribution results mean that both N and H element contents decrease along with the increasing of the concentration of ZnCl$_2$, while C concentration reaches the maximum value of 64.8% at 50 wt% ZnCl$_2$ concentration. The FT-IR characterization results show that there is an increasement of oxygen-containing groups on the surface of the activated adsorbent compared with the non-activated sample, especially the contents of alcohol hydroxyl groups and quinone hydroxyl groups. A better performance of the dibenzothiophene adsorption capacity can be achieved using the sludge carbon-based adsorbent by
adding 50 wt% ZnCl₂ activator. The method of using sludge as the adsorbent can provide a new way for harmless sludge and resource utilization of the urban sludge.

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References

[1] Ahmad, W., Ahmad, I., Ishaq, M., Ihsan, K. (2017) Adsorptive desulfurization of kerosene and diesel oil by Zn impregnated montmorillonite clay. Arab. J. Chem., 10(2): 3263–3269.
[2] Al-Zubaidy, I.A.H., Tarsh, F.B., Darwish, N.N., Abdul Majeed, B.S.S., Al Sharafi, A., Chacra, L.A. (2013) Adsorption process of sulfur removal from diesel oil using sorbent materials. J. Clean. Energy. Technol., 1(1):66–68.
[3] Seredych, M., Bandosz, T.J. (2010) Adsorption of dibenzothiophenes on nanoporous carbons: identification of specific adsorption sites governing capacity and selectivity. Energy Fuels, 24: 3352–3360.
[4] Liu, B., Wei, J.Z., Lei, J.M., Meng, H.S., Zhou, X.B.(2019) Straw Sludge Adsorbent Preparation and Characteristics of Research. J. Harbin Univer. Sci. Technol.(China), 24(2):109-114.
[5] Zhang, C., Sun, L.N.(2018)Current Situation and Recycling Development Prospects of Sludge Treatment and Disposal. Heilongjiang Agricultural Sciences(China), 9: 158-161.
[6] Gao, Y.D., Wang, S.H., Yu, X.Y., Bao, Z.X.(2019)Preparation of activated carbon from cotton fiber by zinc chloride.Applied Chemical Industry(China), 48(4): 853-856.
[7] Liu, S.J., Gao, S., Tang, Z.S., Cui, C.L.(2017) Study on preparation of activated carbon from Jujube-stone with zinc chloride. Applied Chemical Industry(China), 46(2):299-231.
[8] Yu, M.X., Li, Z., Xia, Q.B., Wang, S.W. (2007) Effect of thermal oxidation of activated carbon surface on its adsorption of dibenzothiophene. J. Chem. Ind. Eng. (China), 58(4):938-943.