Study on new decolorization technology of waste lubricating oil

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Abstract. The decolorization and regeneration of waste lubricating oil is an important measure to prevent pollution and protect the environment. In view of the serious pollution of the traditional decolorization process of waste lubricating oil, according to the reasons for the color of waste lubricating oil, the decolorization effect of waste lubricating oil under different experimental conditions was investigated by the combination of chemical method and adsorption method, taking the total decolorization rate and total oil yield rate as evaluation indexes. The experimental results showed that: in 150 g waste lubricating oil, the mass fraction of 22% ammonium chloride solution was added, the upper layer was taken after centrifugation, and the decolorization rate was up to 11.74%. 30 ml of 15% sodium hydroxide solution was added into the obtained upper layer solution, and the upper layer was centrifuged and the total decolorization rate was 19.19%. Then attapulgite clay was used to adsorb and depressurize the obtained upper solution, through single factor experiment, the better conditions of adsorption decompression filtration were obtained as follows: attapulgite clay content was 15% of the mass fraction of waste lubricating oil, decolorization temperature was 50℃, pressure of 65.6-66.7 kPa was reduced for 5 minutes. After the above decolorization steps, the total decolorization rate and total oil yield of waste lubricating oil are 84.31% and 79.32%, respectively.

1. Introduction
According to the latest report of American Fredonia Group, global lubricant demand will grow at an average annual rate of 2.6% in the next few years[1]. Waste lubricating oil contains a lot of harmful substances to human body, such as carcinogenic polycyclic aromatic hydrocarbons, polychlorinated biphenyls and various kinds of heavy metal ultrafine particles, which will be discarded into the environment, causing serious environmental pollution, and recycling will bring great economic benefits[2]. The traditional decolorization process of waste lubricating oil is mainly based on sulfuric acid-clay refining technology. First, the waste oil is dehydrated, followed by acid pickling with concentrated sulfuric acid of 5% of the quality of waste lubricating oil, and then refining with clay of 18% of the quality of waste lubricating oil under atmospheric pressure. The cost of acid residue treatment is very high, it is more and more urgent to develop clean waste lubricant treatment technology[3]. During the use of lubricating oil, due to mechanical friction or operation, incomplete combustion of impurities such as metal wear powder and ash powder, organic acid colloid and asphalt like substances are generated, which make the lubricating oil discolor [4]. The main decolorization methods are chemical method and adsorption method. For waste lubricating oil, the chemical method currently used has poor decolorization ability and serious discoloration, so the sulfur pollution in the oil can not be removed after use. If only adsorption method is used, the quality of adsorbent used is as
high as 30% of the quality of waste lubricating oil. Because of the adsorption of excessive adsorbent, the loss of oil is greatly increased, and the decolorization rate is relatively low[5]. The mechanism of decolorization by chemical method is different from that by adsorption method. Through a large number of experiments, this study combines chemical method and adsorption method to discuss the decolorization of waste lubricating oil, and provides theoretical basis for determining the appropriate decolorization method and process for waste lubricating oil recovery.

2. Materials and methods

2.1. Test material
Waste lubricating oil (dark brown, Fujian Century Toyota Automobile Service Co., Ltd.); silica (Hubei Yichang Silicon Material Co., Ltd.); attapulgite clay (Jiangsu Xuyi Zhongyuan Attapulgite Clay Co., Ltd.); activated carbon (Fujian Quanzhou Carbon Chemical Co., Ltd.); reagents such as sodium hydroxide, ammonium chloride, petroleum ether, etc. All of them are analytical pure.

2.2. Decoloring principle
Waste lubricants generally contain metal salt-type cleanliness additives. The presence of these heavy metals not only causes heavy metal pollution, but also forms dark complexes with other substances in the use process[5-6]. Therefore, the removal of heavy metals should be considered first. Alkali washing can not only reduce the acid value of waste lubricating oil, but also produce soap feet containing surface active substances, which can absorb some pigments in waste lubricating oil and make the color of waste lubricating oil lighter[6]. Under certain conditions, some adsorbents adsorb pigments and impurities in waste lubricating oil by van der Waals force to decolorize the waste lubricating oil[7]. Therefore, only by combining chemical method with adsorption method can impurities and pigments in waste lubricating oil be removed.

2.3. Analysis method
(1) Lubricating oil chroma determination: according to GB/T6540-1986 standard determination.
(2) Lubricating oil chroma calculation:

\[ Y = \frac{B_0 - B_1}{B_0} \times 100\% \]

Formula: \( Y \) - decolorization rate of waste lubricating oil; \( B_0 \) - original color of waste lubricating oil; \( B_1 \) - color of waste lubricating oil after decolorization. The total decolorization rate is the sum of decolorization rates of each process.

(3) Oil yield calculation:

\[ Z = \frac{M_0 - M_1}{M_0} \times 100\% \]

Formula: \( Z \) - oil yield of waste lubricant; \( M_0 \) - weight of waste lubricant before decolorization, g; \( M_1 \) - weight of waste lubricant after decolorization, g. The total oil yield is the sum of the oil yield of each process.

2.4. Experimental method
The 150 g waste lubricating oil was heated and stirred for 40 minutes in a 500 mL beaker with different mass fractions of heavy metal removal agent at 30°C of intelligent constant temperature digital display electric heating plate. Then it was transferred to a high speed centrifuge for separation. The phase chroma was taken and the decolorization rate was calculated. The measured upper phase was moved into a 500 mL beaker, and sodium hydroxide solution with 15% mass fraction was added to it[8]. After 20 minutes of stirring reaction at 30°C, it was transferred to a high-speed centrifuge for centrifugal separation. The upper phase was taken to measure the chroma and calculate the decolorization rate. Then the measured upper phase is poured into a Brinell funnel with adsorbent and
filter cloth, and the decolorized waste lubricating oil is obtained by vacuum filtration at room temperature. After determining its chroma, the final decolorization rate and oil yield are calculated.

3. Results and analysis

3.1. Dosage of heavy metal remover

The aqueous solution of ammonium chloride is weak acidic and corrosive to ferrous metals and other metals, it has double decomposition occurs with heavy metal salt in waste lubricating oil, the resulting heavy metal salts are either dissolved in water or precipitated, ammonium chloride aqueous solution can be used as heavy metal remover\[9\]. The 150 g waste lubricating oil was accurately weighed in a 500 mL beaker and 20 mL of ammonium chloride aqueous solution with different mass fractions of 14%, 16%, 18%, 20%, 22% and 24% was added. After 40 minutes of stirring reaction, it was transferred to a high-speed centrifuge for centrifugal separation. The phase chromaticity was taken and the decolorization rate was calculated. The results are shown in Figure 1.

![Figure 1](image1.png)

**Figure 1.** Effect of amount of remover on decolorization rate.

From the experimental results of Figure 1, it can be seen that the decolorization rate of waste lubricating oil is different under the action of different concentration of ammonium chloride aqueous solution. With the increase of the concentration of ammonium chloride aqueous solution, the decolorization rate of waste lubricating oil increases gradually. When the concentration of ammonium chloride aqueous solution reaches 22%, the decolorization rate of waste lubricating oil is the highest. This is due to the double decomposition reaction between ammonium chloride and heavy metals in waste lubricating oil, and the formation of heavy metal salts is transferred to the water phase, which makes the color of waste lubricating oil lighter\[9\]. When the concentration of ammonium chloride aqueous solution exceeds 22%, the decolorization rate of ammonium chloride aqueous solution increases little. This is because when the concentration of ammonium chloride aqueous solution exceeds a certain value, there is no substance in the waste lubricating oil to react with it again, so the decolorization rate does not increase.

3.2. Alkali washing decolorization

After removing heavy metals, the waste lubricating oil is moved into a 500 mL beaker. 15, 20, 25, 30, 35 and 40 mL sodium hydroxide solution with 15% mass fraction is added to the oil. After 20 minutes of stirring reaction at 30°C, the oil is transferred to a high-speed centrifuge for centrifugal separation. The phase colorimetry is taken and the total decolorization rate is calculated. The results are shown in Figure 2.
From the experimental results in Figure 2, it can be seen that using lye to treat waste lubricating oil, the total decolorization rate at the beginning is directly proportional to the amount of alkali liquor, Reach the highest value when the amount of alkali solution is 35ml, after that, the amount of alkali liquor increased, but the decolorization rate decreased. The reason is that with the increase of the amount of alkali solution, more soap feet are produced, the adsorption of pigments is strengthened, and the decolorization rate is higher. When the amount of alkali is too much, the formation of soap foot is accelerated and the contact time with waste lubricating oil is shortened, which affects the effective adsorption of pigments[8], so the decolorization rate decreases.

3.3. Selection of adsorbents
At room temperature, three adsorbents (white carbon black, attapulgite clay and activated carbon) with 13% of waste lubricating oil mass fraction are added into the Buchner funnel prepared for filter cloth. After spreading, the waste lubricating oil with the decolorization rate measured after alkali washing is poured into the funnel for decolorization by vacuum filtration. The pressure of 65.6-66.7 kPa is reduced for 5 min. The total decolorization rate and total oil yield are shown in Table 1.

| Name of adsorbent   | Total decolorization/% | Total oil yield /% |
|---------------------|------------------------|--------------------|
| White carbon black  | 70.01                  | 77.56              |
| Attapulgite Clay    | 75.16                  | 80.69              |
| Activated carbon    | 72.34                  | 74.27              |

It can be seen from the experimental results in Table 1 that under the same decolorization conditions, the total decolorization rate and total oil yield of waste lubricating oil by different adsorbents with the same dosage, and the total decolorization rate and total oil yield of attapulgite clay are more prominent. Therefore, the ideal adsorbent is attapulgite clay.

3.4. Decolorization of attapulgite clay

3.4.1. Effect of decolorization temperature on decolorization. Attapulgite clay with 13% mass fraction of waste lubricating oil was added to the funnel prepared for the filter cloth. After being laid flat, the waste lubricating oil heated to 30, 40, 50 and 60℃ after alkali washing was poured into the funnel for decolorization by vacuum drainage. The decolorization rate and total oil yield were as shown in Table 2 after vacuum drainage for 5 minutes at 65.6-66.7 kPa pressure.
Table 2. Effect of decolorization temperature on total decolorization.

| Decolorization temperature /℃ | Total decolorization /% | Total oil yield /% |
|-------------------------------|-------------------------|-------------------|
| 30                            | 75.47                   | 80.82             |
| 40                            | 77.63                   | 83.25             |
| 50                            | 80.59                   | 85.70             |
| 60                            | 72.11                   | 86.34             |

The experimental results in Table 2 show that temperature has a great influence on total decolorization rate and total oil yield. The total decolorization rate increases with the increase of temperature when the temperature is lower than 50℃, and decreases when the temperature is higher than 50℃. This is because with the increase of temperature of waste lubricating oil, the viscosity of waste lubricating oil decreases, the speed of movement between molecules increases, the speed of mass transfer accelerates, the pigment molecules in waste lubricating oil are easier to diffuse to the surface of adsorbent, and the probability of adsorbent adsorption increases, so the total decolorization rate increases. When the temperature is higher than 50℃, the chromoplasts in waste lubricating oil are oxidized into new pigments, which results in the deepening of oil color. The higher the temperature, the more difficult to remove pigments are generated[10], and the total decolorization rate decreases. The obtained oil increases with the increase of temperature, because attapulgite clay adsorbs pigments physically. It is a reversible process. At the same time, it also adsorbs pigments. With the increase of temperature, the rate of desorption increases, resulting in more pigments being desorbed from adsorbents and flowed into the drainage fluid, thus making oil. The total decolorization rate increases, but also decreases at 60℃. Considering comprehensively, decolorization temperature of 50℃ should be adopted.

3.4.2. Effect of adsorbent dosage on decolorization. Add 12%, 13%, 14%, 15%, 16% attapulgite clay of waste lubricating oil into the Buchner funnel prepared with filter cloth, after tiling up, pour in the waste lubricating oil heated to 50℃ after alkali washing and decolorization by vacuum filtration, at the pressure of 65.6 -- 66.7kpa, vacuum extraction and filtration were conducted for 5 min, the total decolorization rate and total oil yield are shown in Table 3.

Table 3. Effect of adsorbent dosage on decolorization.

| Adsorbent dosage /% | Total decolorization /% | Total oil yield /% |
|---------------------|-------------------------|-------------------|
| 12                  | 78.13                   | 87.26             |
| 13                  | 80.52                   | 85.61             |
| 14                  | 82.79                   | 82.43             |
| 15                  | 84.27                   | 79.35             |
| 16                  | 84.65                   | 76.84             |

The experimental results in Table 3 show that the total decolorization rate increases and the total oil yield decreases with the increase of adsorbent dosage. This is because when the dosage of adsorbent is small, it is not enough to adsorb the pigments in the waste lubricating oil, and it can not achieve the desired decolorization effect. When the amount of adsorbent exceeds 15% of the mass fraction of waste lubricating oil, the amount of adsorbent continues to increase. Because the macromolecule pigments in waste lubricating oil have been basically adsorbed by adsorbent, the decolorization effect of waste lubricating oil is not obvious. At the same time, the loss of waste lubricating oil is increased because the amount of adsorbent is increased, the adsorbent surface area is increased, and more lubricating oil is adsorbed at the same time, the excessive amount of adsorbent not only contributes little to the decolorization effect, but also causes the waste of adsorbent and the loss of lubricating oil.
Considering comprehensively, the suitable amount of adsorbent is 15% of the mass fraction of waste lubricating oil.

3.4.3. Effect of vacuum drainage time on decolorization. Attapulgite clay with 15% mass fraction of waste lubricating oil was added to the funnel prepared for the filter cloth. After being laid flat, waste lubricating oil heated to 50°C after alkali washing was poured into the funnel for decolorization by vacuum filtration. Under pressure of 65.6-66.7 kPa, decolorization rate and total oil yield were 3, 4, 5, 6 and 7 minutes, as shown in Table 3.

Table 4. Effect of vacuum filtration time on total decolorization.

| Vacuum drainage time /min | Total decolorization /% | Total oil yield /% |
|---------------------------|--------------------------|-------------------|
| 3                         | 85.14                    | 73.28             |
| 4                         | 84.63                    | 77.56             |
| 5                         | 84.31                    | 79.32             |
| 6                         | 84.30                    | 79.40             |
| 7                         | 84.28                    | 79.41             |

The experimental results in Table 4 show that, in the process of vacuum filtration, on the one hand, the pigments in waste lubricating oil are adsorbed and removed; on the other hand, the total decolorization rate decreases with the prolongation of vacuum filtration time, especially after more than 5 minutes. This is because in high temperature environment, some pigments in waste lubricating oil are oxidized to produce refractory pigments[8]. Pigments previously adsorbed on adsorbents will also be sucked down. The total oil yield increased with the prolongation of vacuum filtration time, but after the vacuum filtration time exceeded 5 minutes, the total oil yield did not increase significantly, indicating that the waste lubricating oil had been basically pumped out. Considering comprehensively, 5 minutes is the best time for vacuum filtration.

3.5. Single factor experimental results and verification of decolorization of attapulgite clay
Using the single factor experimental results mentioned above, the decolorization of waste lubricating oil was carried out three times under the conditions of 15% of the mass fraction of waste lubricating oil with attapulgite clay, decolorization temperature 50°C and vacuum drainage time 5 min. The total decolorization rates were 84.25%, 84.29%, 84.32%, and the total oil yield was 79.36%, 79.34%, 79.37, respectively. The results of single factor experiment are similar to those of single factor experiment, which indicates that single factor experiment results are reliable and the error may come from the limitation of operation accuracy and experimental conditions.

3.6. Comparison of results between new decolorization process and traditional decolorization process
Table 5 shows the total decolorization rate and total oil yield of waste lubricating oil after decolorization by new decolorization process and traditional decolorization process. It can be seen that the total decolorization rate and total oil yield obtained by the new decolorization process are much higher than that of the traditional decolorization process, so the new decolorization process is the best one.

Table 5. The results of new decoloration process and traditional decoloration process are compared.

| Decolorization                  | Total decolorization /% | Total oil yield /% |
|---------------------------------|--------------------------|-------------------|
| New decolorization process      | 84.30                    | 79.35             |
| Traditional decolorization tech | 67.82                    | 50.19             |
4. Concluding remarks

(1) The results show that the decolorization process is simple and easy to operate. As a heavy metal removal agent, ammonium chloride plays a certain role in the decolorization of waste lubricating oil. When the mass fraction of ammonium chloride aqueous solution reaches 22%, the decolorization rate of waste lubricating oil is the highest. Alkali washing can reduce the color of waste lubricating oil. When sodium hydroxide solution with 15% mass fraction is added at 30 mL, the total decolorization rate reaches the highest. Among the three adsorbents of silica, attapulgite clay and activated carbon, attapulgite clay has the best decolorization effect on waste lubricating oil.

(2) The results of single factor experiments on decolorization of attapulgite clay show that the optimum technological conditions are as follows: the dosage of attapulgite clay was 15% of the mass fraction of waste lubricating oil, the decolorization temperature was 50 ℃, and the vacuum extraction and filtration under pressure of 65.6--66.7kpa for 5min, under this condition, the total decolorization rate and total oil rate of waste lubricating oil are 84.31% and 79.32% respectively. Waste lubricants change from dark brown to light yellow.

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