

Study on Regeneration Technology of Waste Engine Oil

Chenglei Wang¹, Shiqi Xu¹, Shixin Zhang¹, Tianxiang Niu¹, Yuyan Yang², and Yingrui Zhu¹

¹ School of ShanDong JiaoTong University, Weihai 264200, China

² School of LinYi University, Linyi 276000, China

Abstract

With the development of transportation industry, engine oil plays an increasingly important role in modern society, which is followed by the disposal of a large number of waste engine oil. Waste oil can be reused through waste oil regeneration technology, which can not only save resources, but also contribute to the protection of ecological environment. In this paper, inorganic ceramic membrane filtration process and biochar-activated clay adsorption process are combined to regenerate waste engine oil.

Keywords

Used Oil; Regenerate; Adsorption Process.

1. Introduction

With the population growth, industrial progress and the development of automobile transportation, lubricating oil plays an increasingly important role in modern society. Working in a high temperature environment, engine oil will become waste engine oil due to its contact with metals, air, etc. and impurities generated under the action of various physical and chemical oxidation [1], which will make the engine oil age and deteriorate, and reduce its physical and chemical properties. After the lubricating oil is used, the base oil still occupies the main position, and the proportion of deteriorated components is only between 1% and 2.5% [2]. Therefore, it is only necessary to choose a suitable regeneration technology to remove impurities in waste oil, so that it can be recycled, which can not only save resources, but also protect the environment and conform to the trend of green and sustainable development [3].

According to the research status of waste oil recycling technology at home and abroad, including the problems related to waste oil recycling technology at present, this paper improves and optimizes the technology currently used. The improved process greatly improves the regeneration quality and recovery rate of waste engine oil, and also reduces the input of activated clay and production cost, which provides a reference for the treatment of waste oil produced in the process of petroleum and petroleum products manufacturing.

2. Detection, Analysis and Experimental Design of Waste Engine Oil

In order to study the main components of pollutants in waste engine oil and choose the corresponding treatment methods, it is necessary to test its main performance indicators. In this paper, the engine oil of a 4S shop of an automobile is selected, and the comparison of new and used oil is shown in Fig. .

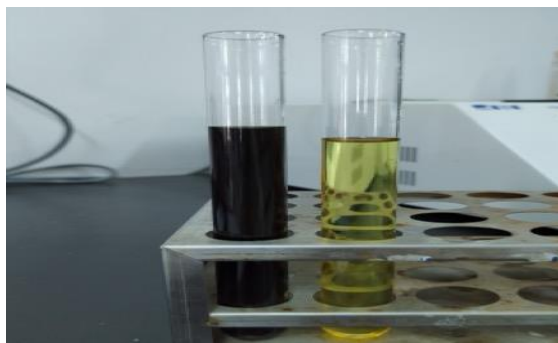


Fig. 1 Waste oil (left) and new oil (right) of engine oil in an automobile 4S store

2.1 Test Results and Analysis of Physical and Chemical Properties

The test results of physical and chemical properties of new waste oil are shown in Table.

Table 1. Test results of physical and chemical properties of different oil samples

Performance index	waste oil	new oil	Engine oil use index	test method
chrominance	>9	3.5	\	GB/T6540-84
Light transmittance (%)	\	87.4	\	TB/T2214-1991
Density (g/mL)	0.90	0.87	\	GB/T1337-92
Kinematic viscosity (40°C) (mm ² /s)	81.67	59.24	\	GB/T265-88
Kinematic viscosity (100°C) (mm ² /s)	12.3	10.01	9.3-12.5	GB/T265-88
Open flash point (°C)	174	225	≥200	GB/T3536-2008
Pour point (°C)	-15	-36	<-35	GB/T3535-2006
Moisture (%)		>trace	≤trace	GB/T260-2016
Total acid value (mg KOH/g)	0.24	0.02	report	GB/T264-1983
Mechanical impurities (%)	0.97	0.01	≤0.01	GB/T511-88

According to Table, the physical and chemical properties of different oil samples are analyzed as follows:

- (1) Visually, we can see that the color of waste oil has changed from bright yellow to black, which may be due to mechanical impurities mixed in the engine oil during use, oxidative deterioration of its components due to the increase of engine oil temperature, carbon particles and sulfides mixed in the engine oil due to incomplete combustion of gasoline [4];
- (2) The light transmittance of waste oil decreases, and the density, kinematic viscosity and pour point increase, which may be due to the decomposition and sedimentation of additives in engine oil, and the oxidation of engine oil to produce a large number of impurities such as colloid and asphaltene [5];
- (3) The decrease of flash point may be due to the increase of light components in engine oil;
- (4) The occurrence of moisture may be due to cooling water leakage, etc.
- (5) The increase of total acid value may be due to the increase of oil temperature, which leads to the production of organic acids [6];
- (6) The increase of mechanical impurities may be due to the fact that sediment, dust, metal chips, etc. enter the oil during the use of the engine oil, resulting in precipitate insoluble in the engine oil [7].

To sum up, the physical and chemical properties of waste oil samples have changed seriously.

2.2 Elemental Analysis of Waste Engine Oil

The element content in engine oil can reflect its quality and usage. In this paper, the SPEC Q100 spectrometer of Speiche Technology Company as shown in Fig. is used to determine the elements of waste engine oil.

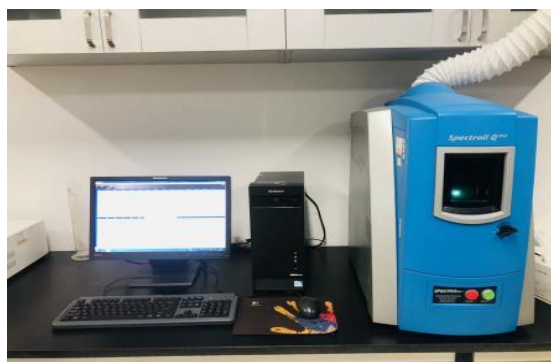


Fig. 2 Automatic comprehensive oil analysis detector (spectrometer)

Table 2. Comparison of element contents of waste oil and new oil

Project	Pollution element				Additive element				Wear element			
Element name	B	Si	Na	Ca	P	Zn	Mg	Mo	Fe	Pb	Cu	Al
Waste engine oil (µg/g)	0.55	13.6	2.7	1469	648	778	10.2	64.9	12.8	2.0	3.7	2.8
New engine oil (µg/g)	0.2	3.1	0.9	1824	727	957	11.3	85	1	1.1	0	1

Engine oil contains pollution elements, additive elements and wear metal elements [8]. It can be seen from Table that the detected waste engine oil samples contain pollution elements such as B, Si and Na, additive elements such as Ca, P, Zn, Mg and Mo, and wear metal elements such as Fe, Pb, Cu and Al. By comparing the elemental contents of new waste oil, it was found that the contents of B, Si and Na in waste oil increased, the components of Fe, Pb, Cu and Al also increased, and the contents of Ca, P, Zn, Mg and Mo decreased [9]. The content of wear metal elements reflects the wear degree of engine oil, and the increase of the content indicates that the wear of mechanical parts is serious, and metal debris enters the engine oil [10]; The increase of pollution element B content may be due to the leakage of cleaning agent into oil, the increase of Si may be due to the leakage of dust from pipeline into oil, and the increase of Na may be due to the leakage of coolant into oil [11]; The decrease of additive element content indicates that the engine oil consumes additives during use [12].

2.3 Experimental Design

Membrane filtration experiment and biochar-activated clay adsorption experiment were used to treat waste engine oil. Technical route of waste engine oil treatment Fig.3 shows the proposed experimental flow chart.

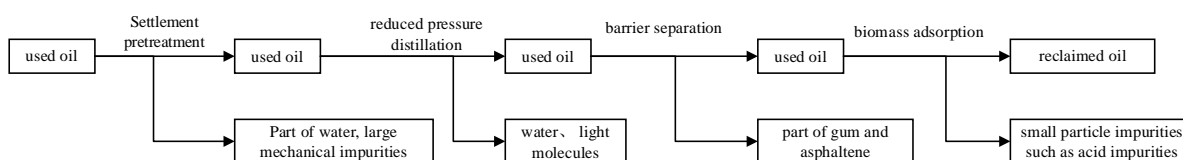


Fig. 3 Technical route of waste engine oil treatment

3. Experimental Study on Oil Filtration of Inorganic Ceramic Membrane

Inorganic ceramic membrane has a special selective separation function, which can separate macromolecular impurities such as asphaltene through oil [13]. In this experiment, it is used as the

filter material, the supporting layer is TiO₂ and Al₂O₃, the membrane layer is TiO₂ and ZrO₂, and the pore size is 0.1 μm and 0.2 μm.

3.1 Membrane Filtration Experimental Device

As shown in Fig.4, the membrane filtration separation device assembled in the laboratory is mainly composed of a constant temperature funnel, an inorganic ceramic membrane, a suction filter bottle, a buffer bottle, a vacuum pump and a plastic tube. The filtration efficiency is improved by heating the temperature of oil products through a constant temperature funnel, and the pressure difference inside and outside the membrane is increased by a pump to speed up filtration.

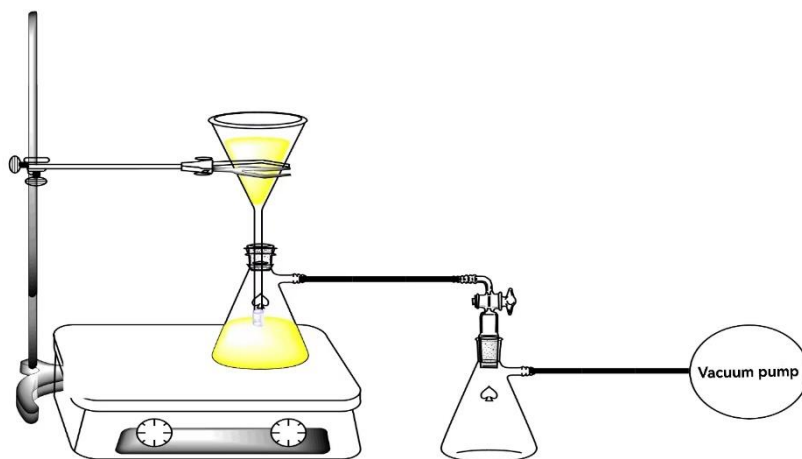


Fig. 4 Inorganic ceramic membrane filtration device

3.2 Research and Selection of Membrane Pore Size

In order to facilitate the experiment, the oil filtered by membrane with a pore size of 0.1 μm is counted as 001#, the oil filtered by membrane with a pore size of 0.2 μm is counted as 002#, the waste oil sample is counted as 003#, and the new oil sample is counted as 004#.

3.2.1 Effect of Membrane Pore Size on Mechanical Impurity Content of Oil Products

The comparison results of mechanical impurity content and waste oil of oil filtered by two kinds of membrane pores are shown in Fig.5.

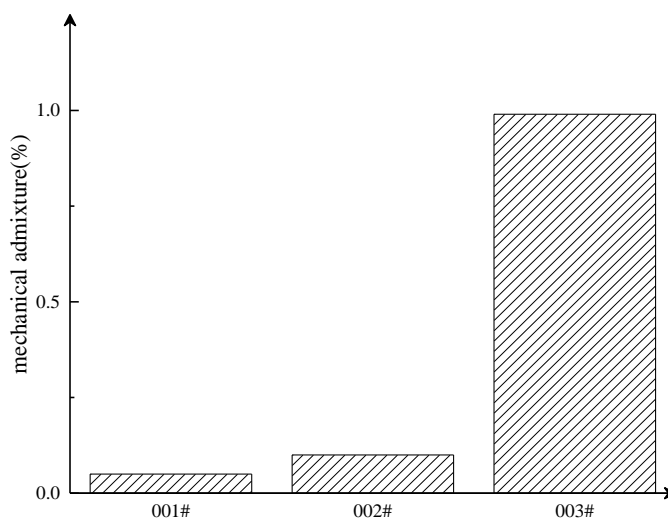


Fig. 5 Comparison histogram of mechanical impurity content of each oil sample

As can be seen from the above figure, the impurity content after filtration with 0.1 μm inorganic ceramic membrane is the least, indicating that the smaller the pore size, the more impurities can be separated and the better the purification effect is.

3.2.2 Effect of Membrane Pore Size on Oil Light Transmittance

As shown in Fig.6, the light transmittance of oil products filtered by two kinds of membranes is compared with that of new oil. It can be seen that there is little difference in light transmittance of oil products filtered by two kinds of membranes. Although there is still a gap compared with new oil, it still has obvious effect in comparing the light opacity of original waste oil, so the membrane with 0.2 μm aperture will be selected.

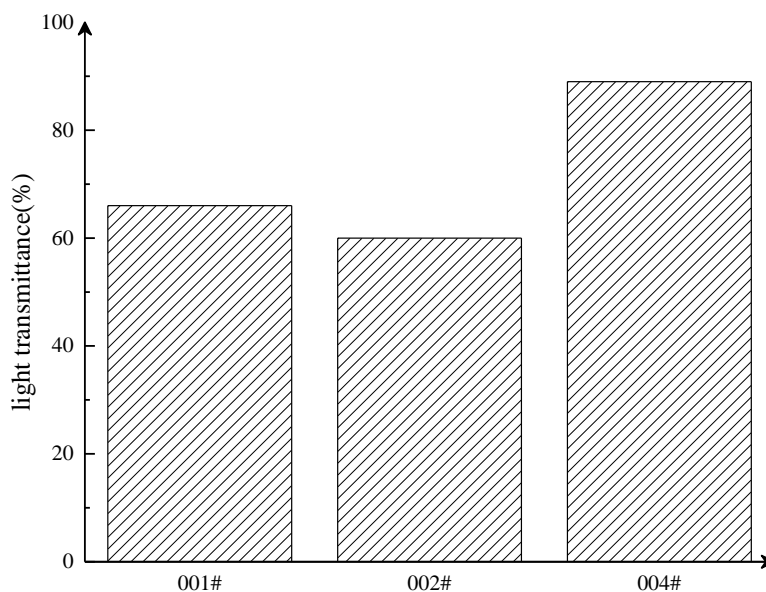


Fig. 6 Histogram of light transmittance comparison of oil samples

3.2.3 Effect of Membrane Pore Size on Acid Value of Oil Products

The comparison between the acid value of the oil filtered by two kinds of membrane pores and the new waste oil is shown in Fig. 7.

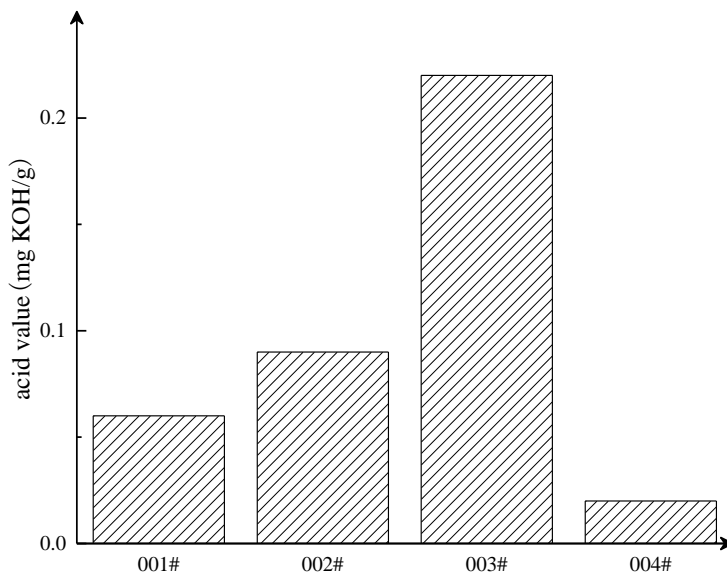


Fig. 7 Comparison histogram of acid value of each oil sample

As can be seen from the above figure, the acid value of the oil products after two kinds of membrane filtration is obviously less than that of the original waste oil, and the effect of the two kinds of membranes is not much different, so the acid removal effect of the membrane with a pore size of 0.2 μm has met the requirements.

3.2.4 Effect of Membrane Pore Size on Kinematic Viscosity of Oil Products

As shown in Fig.8, the kinematic viscosity of oil at 40°C filtered by two kinds of membrane pore sizes is compared with that of new waste oil. It can be seen that the viscosity of waste oil is higher than that of new oil, indicating that the content of impurities such as colloid is higher; After two kinds of membrane filtration, its viscosity decreased and impurities decreased, but there is still a gap compared with new oil, so it should be refined later.

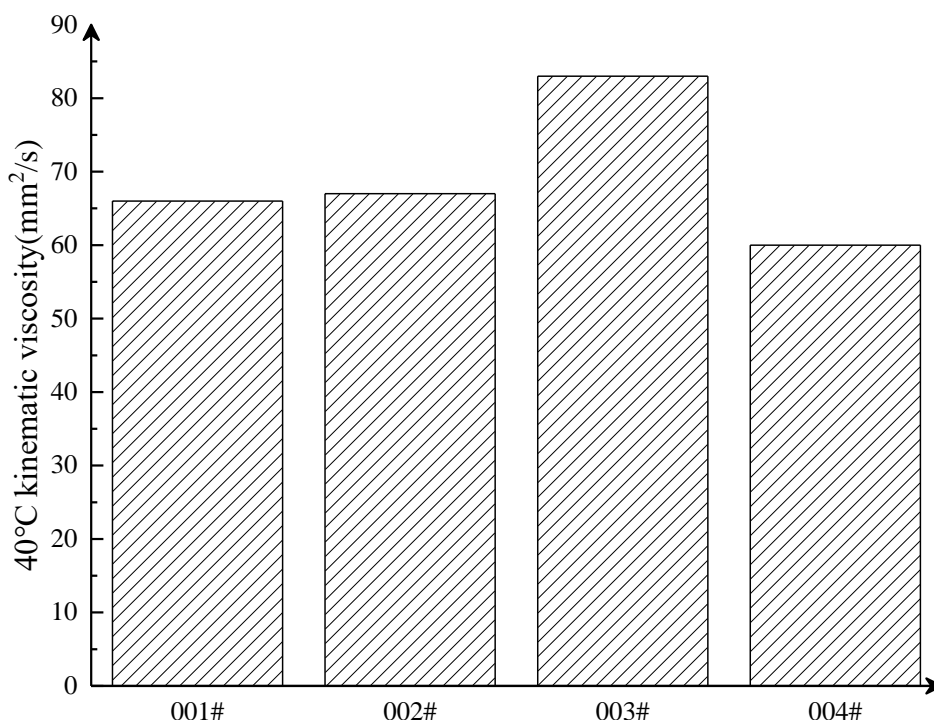


Fig. 8 Viscosity comparison diagram of each oil sample at 40°C

3.3 Optimum Technological Conditions

Through the above research, it is concluded that the inorganic ceramic membrane with a pore size of 0.2 μm is used to filter the oil sample at 80°C. The final oil sample has a mechanical impurity content of 0.08%, a light transmittance of 60.84%, an acidity of 0.08 mg KOH/g, a kinematic viscosity of 63.21 mm²/s at 40°C, and a membrane filtration flux of 196.1 L/(m² h).

4. Study on Optimization of Biochar-activated Clay Adsorption Material

There are still a few impurities in the oil that has been filtered by membrane, so the final refining is carried out by activated clay refining [14]. In this paper, low-cost and environmentally-friendly biomass raw materials and activated clay adsorption process are adopted for refining.

4.1 Sorbing Material

4.1.1 Biochar

Corn stalk stands out among many biomass adsorbents with the characteristics of environmental protection and low cost, and it can be used as adsorbent only by activation treatment [15], as shown in Fig.9, which is light yellow in color and powdery.



Fig. 9 Biomass appearance

4.1.2 Carclazyte

Activated clay from leping city Hongyu bleaching technology co., ltd was used in the experiment, as shown in Fig.10.



Fig. 10 Appearance of activated clay

The main components of activated clay are SiO₂, Al₂O₃, Fe₂O₃, etc. Its indexes are shown in Table 3.

Table 3. Indicators of activated clay

Project	Index
Exterior	Grayish white powder
Granularity	96.1%
Activity degree	148.1 mol/kg
Decolorization rate	93.7%
Moisture	6.4%
Free acid	0.14%
Heavy metal content (Pb)	≤10 mg/kg
Arsenic content	≤3 mg/kg

4.1.3 Activation Condition

In this paper, corn stalk was selected and NaOH was used as activator to prepare biochar adsorbent. The optimum conditions were as follows: activation temperature was 800°C, activation time was 1 h, and the mass ratio of NaOH to corn stalk was 3:1.

4.1.4 Adsorption Material Analysis

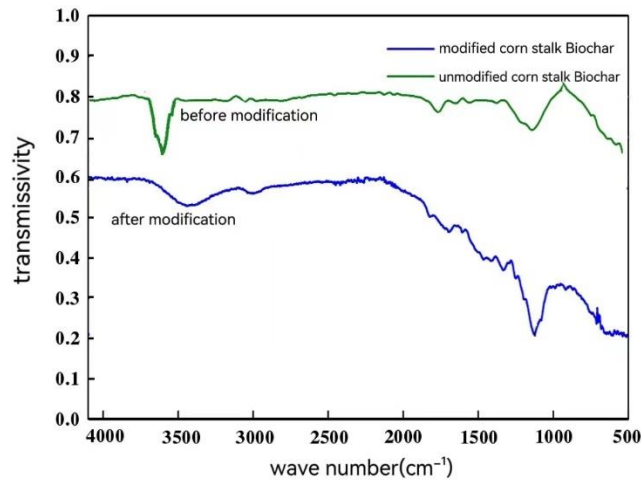


Fig. 11 Infrared spectrum of corn straw biochar adsorbent before and after activation

Fig.11 shows the FTIR of corn stalk biochar adsorption material before and after activation. As can be seen from the figure, the surface functional groups of biochar materials have changed obviously after activation. Among them, the peaks at 1370~1701 cm^{-1} show C=O, aromatic C=C and -COO- characteristic peaks, indicating that the internal chemical bonds of the activated material are destroyed; The peak value of the modified corn stalk biochar adsorption material is higher at 3600 cm^{-1} , which means that the hydroxyl content in the modified corn stalk biochar adsorption material has increased, which can make the material show stronger oleophobicity, and the adsorption material can more easily combine with molecules other than oil removal, thus improving the adsorption capacity of impurities [16].

4.2 Study on Adsorption Process of Biochar-activated Clay

Adsorption by biochar-activated clay is a key process of waste oil regeneration, and its treatment will affect its quality.

4.2.1 Study on Adsorption Process of Biochar

(1) Adsorption temperature

The effects of 110°C, 120°C and 130°C on the light transmittance of 100 g oil sample were investigated under the conditions of 6% adsorbent and adsorption for 40 min. The experimental results are shown in Fig.12.

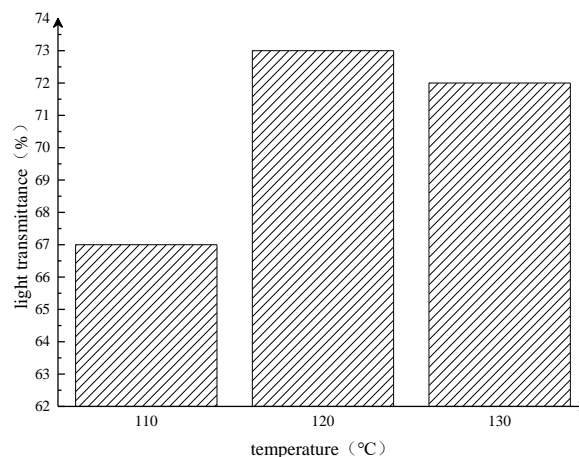


Fig. 12 Effect of adsorption temperature on light transmittance of regenerated oil

As can be seen from Fig.12, the light transmittance at 120°C is the largest, and that at 130°C is lower than the former. This is mainly because the viscosity of oil decreases at a certain temperature, which makes it easy for adsorbents to absorb impurities in oil. However, if the temperature is too high, it will cause oil to be oxidized and form colloid, which will reduce the efficiency of adsorbents, the recovery rate of regenerated oil and the light transmittance [17]. Therefore, 120°C is the best adsorption temperature for biochar adsorption.

(2) Adsorption time

The effects of 40 min, 50 min and 60 min on the light transmittance of 100 g oil sample were investigated under the conditions of 6% adsorbent and 120°C. The experimental results are shown in Fig.13.

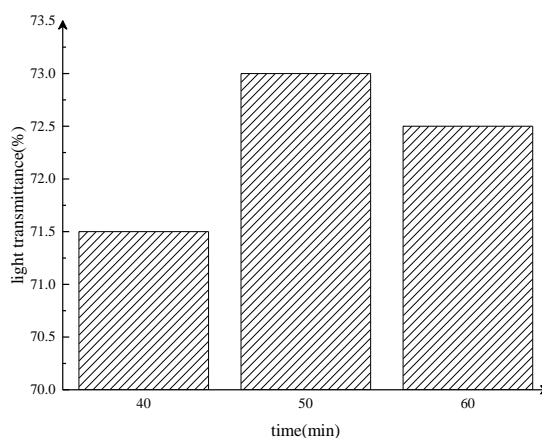


Fig. 13Effect of adsorption time on light transmittance of regenerated oil sample

As can be seen from Fig.13, the light transmittance reaches the maximum at 50 min and decreases at 60 min. This is because the adsorption time is increased, which makes the contact with impurities more thorough, thus improving the adsorption rate. After 50 min, the adsorption capacity of biochar reached saturation. Therefore, 50 min will be chosen as the best adsorption time.

(3) The amount of biochar

The light transmittance of 100 g oil sample with different amounts of biochar (4%, 6% and 8%) was investigated under the adsorption conditions of 120°C and 50 min. The experimental results are shown in Fig.14.

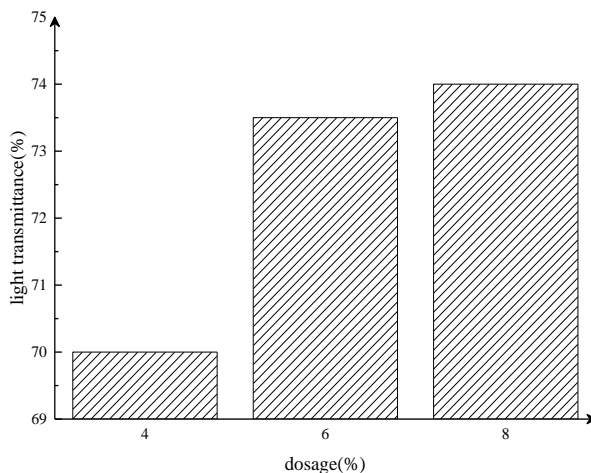


Fig. 14Effect of biochar dosage on light transmittance of regenerated oil

As can be seen from Fig.14, the light transmittance in the reclaimed oil increases with the increase of the added amount. With the increase of the addition amount, the adsorption decoloration effect also increases, thus improving the quality of recycled oil. However, after excessive use, it has little effect on purification, and it will increase the loss of raw materials and decrease the yield. Therefore, in biochar, 6% is the best adsorption dose.

To sum up, in the adsorption process of biochar, the adsorption effect is the best when the dosage of biochar is 6%, the adsorption temperature is 120°C and the adsorption time is 50 min.

4.2.2 Study on Adsorption Process of Activated Clay

(1) Adsorption temperature

Activated clay can't absorb naphthenic acid in waste oil at low temperature, so it should be heated. Using 50 g of oil sample that has been adsorbed by biochar, adding 4% activated clay, after 30 min, the effects of 75°C, 85°C and 95°C on the light transmittance of reclaimed oil were investigated. The experimental results are shown in Fig.15.

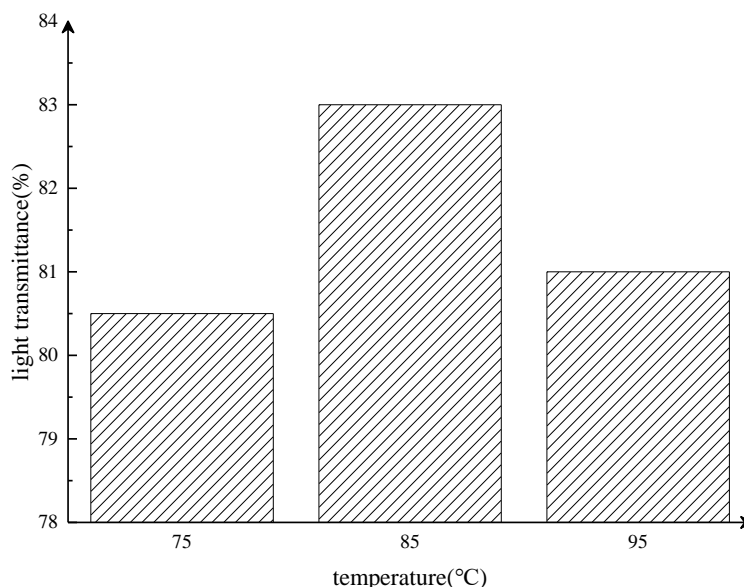


Fig. 15Effect of adsorption temperature on light transmittance of regenerated oil sample

As can be seen from Fig.15, the light transmittance reaches the maximum at 85°C, and decreases at 95 C.. This is because at low temperature, the viscosity of oil is high and the adsorption of activated clay is weak. With the increase of temperature, the viscosity of lubricating oil decreases, the contact between oil and activated clay increases, and the adsorption force of activated clay increases, thus realizing decoloration. However, high temperature will deepen the color of the oil oxidized, and at the same time, some originally absorbed colored substances will return to the oil, which will reduce its light transmittance. Therefore, the optimum process temperature is 85 C.

(2) Adsorption time

Using 50 g of oil sample that has been adsorbed by biochar and adding 4% activated clay at 85°C, the effects of 20 min, 30 min and 40 min on the light transmittance of regenerated oil were investigated. The experimental results are shown in Fig.16.

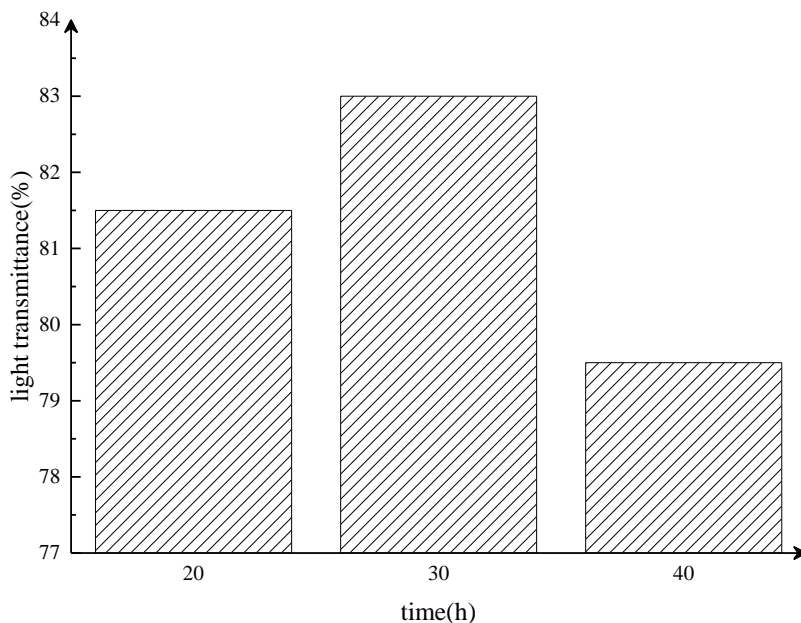


Fig. 16 Effect of adsorption time on light transmittance of regenerated oil sample

As can be seen from Fig.16, the light transmittance of oil is the highest at 30 min. With the extension of reaction time, the contact between activated clay and oil sample is more, and the adsorption of activated clay is better, and its light transmittance is also better. However, the adsorption of activated clay may have reached saturation at 40 min, so the best process time is 30 min.

(3) dosage of activated clay

Using 50 g of oil sample that has been adsorbed by biochar, after 30 min at 85°C, the effects of different amounts of activated clay (1%, 2%, 3%, 4%, 5%, 6%) on the light transmittance of reclaimed oil were investigated. The experimental results are shown in Fig.17.

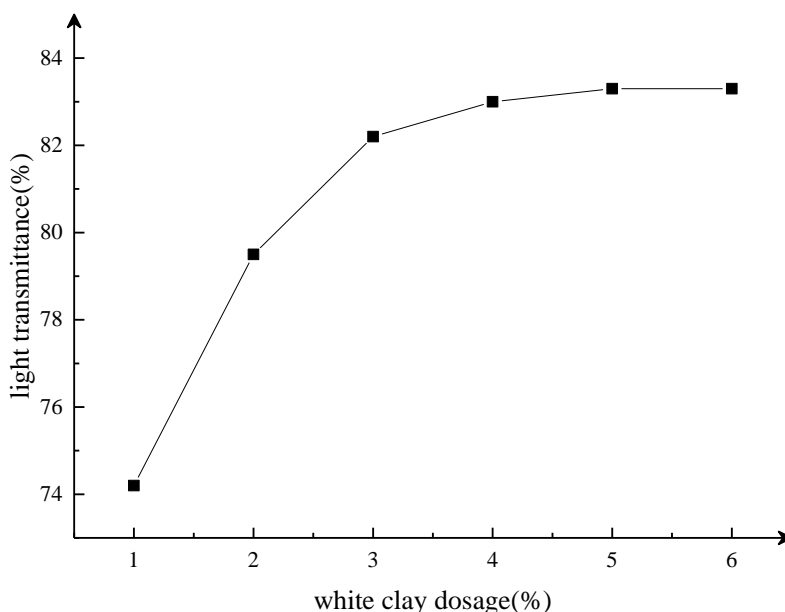


Fig. 17 Effect of the amount of activated clay on the light transmittance of regenerated oil sample

As can be seen from Fig.17, the greater the amount of activated clay, the greater the light transmittance of oil, indicating that the greater the amount of activated clay, the better the effect.

However, with the increase of activated clay, its absorption tends to saturation, so its light transmittance increases slowly. In order to improve the decolorization efficiency and reduce the production cost, 4% activated clay can obtain satisfactory decolorization results.

To sum up, in the activated clay adsorption process, the adsorption effect is the best when the amount of activated clay is 4%, the adsorption temperature is 85°C and the adsorption time is 30 min. The light transmittance of the oil treated by this process can reach 83.22%, which is close to that of new oil.

4.2.3 Optimum Process of Biochar-activated Clay Adsorption and Clay Adsorption

To sum up, the optimum conditions for the adsorption experiment of biochar-activated clay are respectively 6% of biochar addition, 120°C of adsorption temperature, 50 min of adsorption time and 4% of activated clay addition, 85°C of adsorption temperature and 30 min of adsorption time. After this process, the recovery rate of reclaimed oil is about 77% and the light transmittance is 83.22%, which meets the standard requirements of new oil.

4.3 Comparative Analysis of Biochar-activated Clay Adsorption and Clay Adsorption

In order to prove that biochar-activated clay adsorption is superior to the traditional single activated clay adsorption process, 100 g of waste oil filtered by membrane was poured into a 250 ml beaker, heated to 85°C, added with 10% activated clay, mixed and placed in a drying oven, and precipitated at 105°C for 12 h. The precipitated sample was filtered by 0.1 µm filter membrane and compared with the oil adsorbed by biochar-activated clay. The results are shown in Fig.18.



Fig. 18 Comparison of adsorption effects between single activated clay adsorbent and biochar activated clay

(From left to right: Adsorption and purification of oil by biochar activated clay, clay refined oil and membrane separation oil).

As can be seen from the above figure, the chromaticity of the oil after adsorption by biochar-activated clay is obviously lower than that by adsorption by clay alone, which shows that the adsorption process by biochar-activated clay can achieve better decoloration effect and meet the needs of actual production. Therefore, the biochar-activated clay adsorption process is selected in this paper to refine the oil separated by membrane, and the treatment effect is remarkable.

5. Conclusion

In this paper, waste engine oil is taken as the research object, and a new method of recycling waste engine oil is put forward. The main research results are as follows:

The main results are as follows:

- (1) The activation process of biochar adsorbent was explored, and the optimal reaction process was obtained: activation temperature was 800°C, activation time was 1 h, and the mass ratio of NaOH to corn stalk was 3:1.

(2) The process of biochar-activated clay was explored, and the optimum conditions of its adsorption experiment were 6% biochar addition, 120°C adsorption temperature, 50 min adsorption time and 4% activated clay addition, 85°C adsorption temperature and 30 min adsorption time respectively. After this process, the recovery rate of reclaimed oil is about 77% and the light transmittance is 83.22%, which meets the standard requirements of new oil.

Acknowledgments

Natural Science Foundation.

References

- [1] B. Zhong, B.Y. Chen, S.J. Yang: Discussion on Recycling Technology of Waste Engine Oil, Guangxi Journal of Light Industry, Vol. 36 (2020), No. 7, p.105-106.
- [2] M.F. Wen, Y.F. Zhou, S.B. Ouyang, et al: Study on regeneration process of waste lubricating oil by flocculation-vacuum distillation, Journal of Jiangxi University of Science and Technology, Vol. 42 (2021), No. 4, p.42-49.
- [3] M. Asmita, S. Hammad, K. Usha, et al: Pyrolysis of waste lubricating oil/waste motor oil to generate high-grade fuel oil: A comprehensive review, Renewable and Sustainable Energy Reviews, Vol. 150 (2021), No. 1, p.11-14.
- [4] J.X. An: Analysis on the present situation and development trend of lubricating oil market at home and abroad, Synthetic lubricating material, Vol. 48 (2021), No. 1, p.42-47.
- [5] Z.X. Li, X.M. Zhang, L.G. Chen, et al: Research progress on regeneration technology of waste lubricating oil, Journal of chongqing technology and business university (Natural Science Edition), Vol. 38 (2021), No. 5, p.10-16.
- [6] W. Fan, W. Yu, J. Cong: Application Overview of Membrane Separation Technology in Coal Mine Water Resources Treatment in Western China, Mine Water and the Environment, Vol. 1 (2021), No. 2, p.1-10.
- [7] G.L. Wei, W.J. Li: Determination of Trace Elements in Lubricating Hydraulic Oil by Atomic Emission Spectrometry, Baotou steel technology, Vol. 40 (2014), No. 4, p.46-49.
- [8] D.Y. Wan, Z.X. Wang: Analysis of metal elements in engine oil sample and its application in diesel engine, Petroleum drilling and production machinery, Vol. 5 (1984), p.61-69.
- [9] R.J. Zhang: Study on adsorption refining process of phase change paraffin and lubricating oil, (MS., South China University of Technology, China 2011), p.29.
- [10] X.M. Zhang, D. Yu, W. Yun, et al: Research and application progress of decoloration technology for waste lubricating oil, Applied chemical industry, Vol. 43 (2014), No. 6, p.1128-1132.
- [11] M. Fan, D.J. Wu, X.X. Xiong, et al: Study on regeneration technology of treating waste industrial lubricants with activated carbon, Comprehensive utilization of resources in China, Vol. 38 (2020), No. 6, p.1-3.
- [12] H.Y. Zhu, J.N. Wu, X. Zhai, et al: Adsorption treatment of waste turbine oil, science and technology of west china, Vol. 10 (2011), No. 1, p.6-7.
- [13] Y. Wu, X.M. Deng, X.M. Zhang: Study on treatment of waste lubricating oil with soil-loaded fulvic acid composite adsorbent, Applied chemical industry, Vol. 44 (2015), No. 12, p.2260-2263.
- [14] G.Q. Liu, H.L. Wang, Y.F. Li, et al: Silica gel contact refining waste lubricating oil, Acta petrolei sinica (Petroleum Processing), Vol. 31 (2015), No. 6, p. 1425-1429.
- [15] Z.S. Zhang, Y.J. Kang, Y.L. Liu: Research progress on decoloration technology of vegetable oil, Journal of Henan University of Technology (Natural Science Edition), Vol. 39 (2018), No. 1, p. 121-126.
- [16] W. Yun, Y. Dong, X. Zhang, et al: Effects of operating parameters on chroma of cuts from waste oil in molecular distillation, Chemical Industry and Engineering Progress, Vol. 33 (2013), No. 5, p. 1312-1316.
- [17] Z.J. Jiao, X.M. Zhang: Experimental study on compound regeneration of waste lubricating oil by pickling-alkali washing-clay, Journal of chongqing technology and business university (Natural Science Edition), Vol. 1 (2008), No. 5, p. 505-508.