Research Article

Regeneration of Spent Lubricant Refining Clays by Solvent Extraction

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Step-by-step solvent extraction was used to regenerate spent clay by recovering the adsorbed oil in lubricating oil refining clay. Several polar and nonpolar solvents were tested, and petroleum ether (90–120°C) and ethanol (95 v%) were selected as the nonpolar and polar solvents, respectively. The spent clay was first extracted using petroleum ether (90–120°C) to obtain ideal oil and then extracted with a mixed solvent of petroleum ether (90–120°C) and ethanol (95 v%) two or three times to obtain nonideal oil before being extracted with ethanol and water. Finally, the clay was dried at 130°C to obtain regenerated clay. The total oil recovery can be more than 99 wt% of the adsorbed oil. The recovered ideal oil can be used as lubricating base oil. Shorter storage times for spent clay produce better regeneration results. The regenerated clay can be reused to refine the lubricating base oils.

1. Introduction

In the process of petroleum refining, clay has been used to adsorb coloring and unstable impurities from lubricating base oils. The clay used in this process had a particle size of approximately 100–300 mesh. Usually, clay is added to the base oils and mixed together at a dosage of approximately 1–6 wt%. Clay then adsorbs impurities and is finally separated by filtration, thus producing spent clay. It is customary in oil refineries to discard spent or used clay by dumping it in areas adjacent to the refinery. The discarded clay may contain as much as 30–50% of oil by weight, about two-thirds of which is lubricating base oil. Unused and unrecovered spent clay pollutes the environment and gradually diminishes a valuable natural resource. It is therefore imperative to research new ways of recovering and recycling spent clay from petroleum refining processes.

However, only a limited number of studies exist in the literature regarding recovery of spent clay used in lubricating base oil refining. Most studies focus on the recovery of spent clay of animal and vegetable oil refinement. In one process,

the used clay is burnt in a furnace to free it from adsorbed oil and impurities. Calcined clay was further treated by mineral acids to increase its bleaching power [1]. Difficulties in controlling the burning process and overheating in the furnace often result in destruction of the clay's structure, and the burning oil during clay regeneration may contribute to atmospheric pollution.

Solvent extraction processes for recovery of oil from spent bleaching clay have been suggested. Solvent extraction provides a higher yield and a better quality of oil than other methods. Some researchers have adopted a mixed approach to regenerate used clay: solvent extraction plus acid washing and/or heat treatment are used in conjunction. Ng et al. used MEK, hexane, methanol, and CO_2 as solvents to extract the spent clay in a mixed approach and successfully recovered the surface area of spent clay [2]. In a similar mixed approach, Santos used organic solvents to regenerate spent clay, which was used as fresh clay in lubricating oil refining [3]. Kucharz et al. also disclosed a process that utilized solvent extraction, oxidation, and acid wash to regenerate the spent bleaching clays and acid-activated smectite catalyst granules [4]. Feuge

and Janssen described the regeneration of spent earth by solvent extraction using acids, ethers, and ketones. A low molecular weight ketone was found to be the most effective solvent [5].

Simpson et al. [6] and Paull [7] disclosed a regeneration procedure by first extracting the clay and then carbonizing it, and the residual matter was burned into a coating of activated carbon, which is more active than the original clay. Shuman and Springs adopted hydrogenation of spent clay at a temperature of 750–1000°F and a pressure of 500–2000 psig and washed the treated clay with a solvent to recover the oils [8]. This method is difficult to realize in industry because of the high pressure and temperature requirements and the difficulty of feeding solid clay into the continuous reactor.

Waldmann and Eggers used CO_2 under supercritical conditions to extract and regenerate spent bleaching clay [9]. Although an acceptable amount of oil was removed, carotenoid removal was not achieved by this extraction. Al-Zahrani designed extraction experiments on spent bleaching clay to recover oil using methyl ethyl ketone (MEK), acetone, petroleum ether, and hexane solvents at optimum conditions. Reactivation of the deoiled clays by calcination was investigated. The bleaching efficiency of the reactivated clays varied between 86 and 94% [10, 11]. Nebergall et al. detailed a method to regenerate spent vegetable processing clay by three steps: first, extract the clay with a solvent; second, oxidize the clay to remove the residual oil using peroxides such as hydrogen peroxide; and third, wash the extracted and oxidized clay with aqueous acid. The process is economically infeasible due to the high quantity of peroxides used (approximately five to ten times of the clay) and their high cost [12].

A different approach by Boey subjected spent bleaching clay to ultrasound-aided *in situ* transesterification with a cosolvent to convert the oil into methyl esters (biodiesel). The remaining bleaching clay was calcined at 500°C and reutilized for bleaching. *In situ* transesterification and heat regeneration helped to restore pores without adversely affecting the clay structure. The use of ethyl methyl ketone (EMK) as the cosolvent in the *in situ* transesterification process produced clay with better bleaching qualities [13, 14]. Lee et al. studied various alcohols and hydrocarbons as solvents to extract the residual oil in spent bleaching clay from palm oil refining. All of the extracted oils, irrespective of the solvent used, have poorer quality than crude palm oil, and the solvents could reach a maximum oil recovery of only 44% [15].

Though many efforts have been devoted to developing procedures for regenerating spent clay and recovering the absorbed oil, there is no clear economically feasible approach to effectively remove all oils from spent clay and completely regenerate its adsorption capacity. While most methods use acid and heat treatment to recover clay activity, this method may cause the clay to lose structure. The above mentioned solvent extraction did not use mixed solvent, and the extraction was performed just once. Indeed, if the oils adsorbed in the spent clay are effectively removed, the adsorbing capacity can be restored to its original state. This paper studied the new method of step-by-step solvent extraction using a combination of nonpolar and polar solvents to remove almost all of
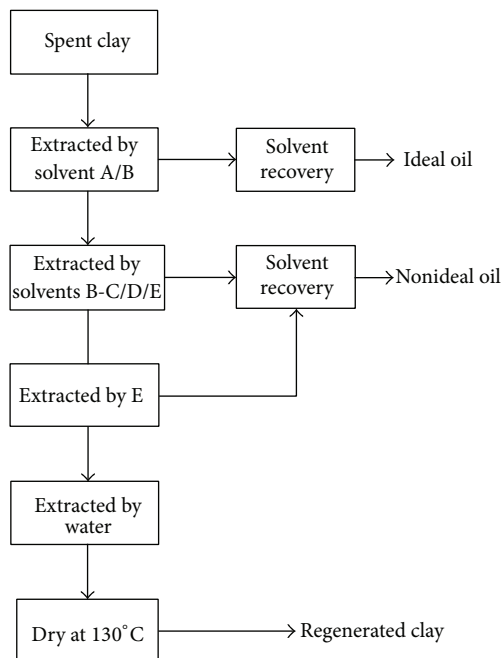
Scheme 1: Regeneration step.

the oils adsorbed and thus recover the adsorption capacity of clay. Additionally, the oils were separated into the ideal components and the nonideal components as lubricating base oils. The regeneration process was industrialized.

2. Experimental

2.1. Feed Stock. Spent clay and fresh clay were sampled from Yantai Liude lubricant Corp. of China, and the properties of spent clay are shown in Table 1. Petroleum ether with boiling range of 60–90°C, solvent A, and petroleum ether with boiling range of 90–120°C, solvent B, were produced by China Shanghai Reagent Corp. Methanol (solvent C), ethanol (solvent D), 95 v% ethanol (solvent E), and isopropyl alcohol (solvent F) were analytically pure reagents produced by Laiyang Shuangshuang Chemicals Corp. of China. Lubricating base oil was sampled from an oil refinery of China.

2.2. Extract Device and Process. A three-neck flask with an electric stirrer was charged with 100 g of spent clay and 70–120 mL of solvent A or solvent B (Scheme 1). Then, the flask was heated to 50–90°C and stirred for 5–60 min. The solvent and the clay were then separated by filtration. The filtrate was vaporized to recover the solvent and oil. The oil extracted using either solvent A or solvent B was called ideal oil because of its low color and good characteristics as a lubricant. The residual clay after filtration was again charged into the flask and was extracted according to the above conditions one to three times by solvents B-C/D/E/F, respectively, where solvents B-C/D/E/F refers to the mixtures of solvents B and C, solvents B and D, solvents B and E, and solvents B and F. Then, the clay was finally extracted by solvent E and water. The filtrates extracted by solvents B-C/D/E/F were collected

TABLE 1: Properties of spent clay.

Appearance	Oil content, wt%
Black	33.56

and vaporized to recover the solvents and oil which is labeled as nonideal oil because of its poor quality as lubricants. The regenerated clay and recovered oils were finally dried in a vacuum drier at 130°C and −0.08 MPa for 2 h:

The ideal oil recovery

$$= \frac{\text{recovered ideal oil weight}}{\text{oil weight in spent clay}} \times 100\%,$$

The nonideal oil recovery

$$= \frac{\text{recovered nonideal oil weight}}{\text{oil weight in spent clay}} \times 100\%.$$

(1)

2.3. Determination of Oil Content in Spent Clay.
The oil content was determined by first calcining the spent clay in a muffler roaster at 750°C until its weight did not change (approximately 2 h). The fresh clay was also treated according to the above method. The weight loss of spent clay minus the weight loss of equivalent calcined fresh clay was considered as the oil content.

2.4. Clay Characterization.
The BET surface area of the clay was determined by N_2 physical adsorption at 77 K using ASAP2010 surface area and porosity analyzer.

The activity of the clay was determined by mixing clay and 300 mL of untreated lubricating base oil into a 500 mL three-neck flask with a nitrogen inlet. Under constant stirring using an electric stirrer, the mixture was heated to 180°C for 40 min. Then, the temperature was lowered to 140°C, and the mixture was filtered to separate the oil and the clay. The color number of the refined oil was measured according to GB/T6540.

3. Results and Discussion

3.1. Nonpolar Solvent Extraction.
Nonpolar solvents (solvents A and B) can extract the low-polar components such as saturation hydrocarbons and single- or two-ring aromatic hydrocarbons while polycyclic aromatic hydrocarbons and resins remain adsorbed in the clay. To study the effect of solvents A and B, 100 g spent clay and 100 mL of solvent A or solvent B were mixed at 50°C to extract the ideal oil. 100 mL of mixed solvent composed of 80 mL of nonpolar solvent and 20 mL of solvent E was used to extract the above treated clay twice to recover the nonideal oil. The effects of solvents A and B on the recovery of ideal and nonideal oil are shown in Table 2.

It can be seen from Table 2 that the petroleum ethers with different boiling ranges have different effect on recovering oil from spent clay. The petroleum ether with boiling range of 90 to 120°C can extract more oil from spent clay. Thus, solvent B was selected as the ideal nonpolar solvent.

TABLE 2: Effect of petroleum ethers with different boiling range.

Solvent	Ideal oil recovery, %	Nonideal oil recovery, %	Total oil recovery, %
A: petroleum ether (60–90°C)	50.36 ± 2	37.25 ± 0.5	87.61 ± 0.5
B: petroleum ether (90–120°C)	55.12 ± 2	42.61 ± 0.5	97.73 ± 0.5

TABLE 3: Effect of polar solvents.

Solvent	Ideal oil recovery, %	Nonideal oil recovery, %	Total oil recovery, %
C	54.23	33.97	88.20
D	54.23	38.14	92.37
E	54.23	43.50	97.73
F	54.23	36.35	90.58

3.2. Effect of Polar Solvents.
The polar solvents tend to displace other polar components in petroleum such as resin and polycyclic aromatic hydrocarbons. To study the effect of solvent polarity, solvent B was used as the nonpolar solvent, and solvents C/D/E and F were used as the polar solvents. First, the spent clay was extracted using solvent B at a ratio of 100 mL solvent B to 100 g spent clay, and then the clay was separated by filtration. The extraction procedure was repeated two more times with a mixed solvent (solvent B plus a polar solvent). The polar solvent possessed a ratio of 20% (v) in the mixed solvents. The filtrates were vaporized and dried to recover the oils and solvents. Table 3 shows the effect of solvent choice on oil recovery.

It can be seen from Table 3 that the polar solvents are much more effective in recovering the nonideal oil adsorbed in clay. The strong polarity of the solvents is helpful for the polar solvent molecules to displace the resins. Due to its low boiling point, it is easier to recover solvent E (95% ethanol) by vaporization, which also accounts for a higher yield in recovery of oils. Based on its high effectiveness in oil recovery and low environmental toxicity, solvent E was selected as the polar solvent.

3.3. Effect of the Concentration of Ethanol.
Solvent E (95% ethanol) was selected as the polar solvent. Solvent D (pure ethanol) also showed comparable effectiveness at oil recovery. It is therefore important to understand whether a difference in ethanol concentration could be a factor in solvent effectiveness. First, the spent clay was extracted using solvent B at a ratio of 100 mL solvent B to 100 g spent clay, and the filtered clay residue was again extracted twice using the mixed solvent at various ethanol concentrations. The polar solvent possessed a ratio of 20% (v) in the mixed solvents. The extraction was performed for 30 min at 50°C. The filtrates were vaporized and dried to recover the oils and solvents. The effect of different ethanol concentration is shown in Figure 1.

Oil was successfully recovered at concentrations of ethanol between 80 and 100%; however, the highest oil
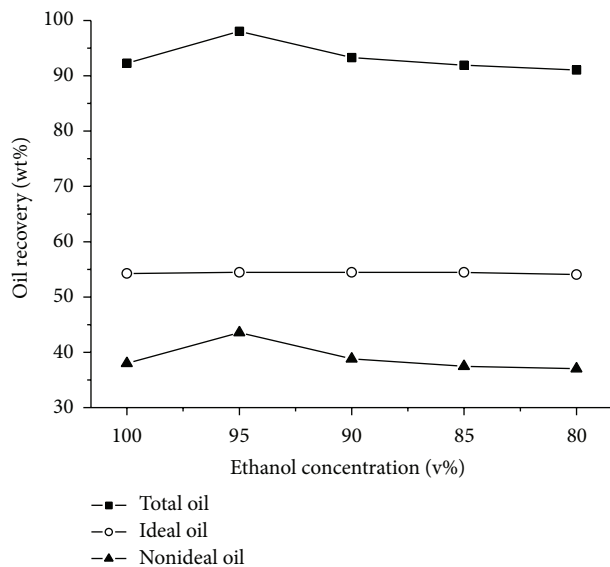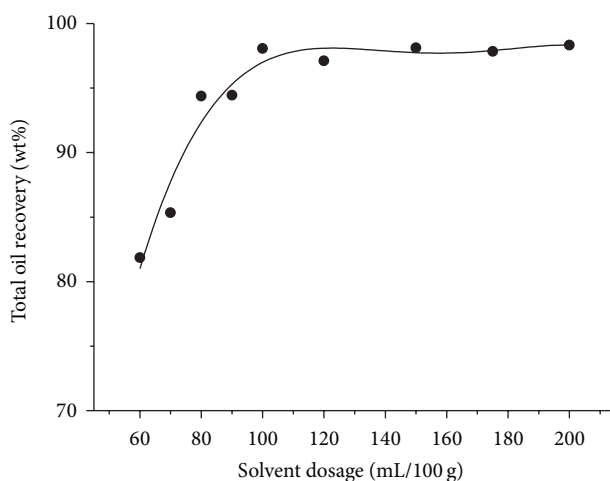
Figure 1: Effect of ethanol concentration.

Figure 2: Effect of solvent dosage.

recovered coincided at 95% (v) ethanol. This is beneficial for the recovery of solvent E because the coboiling point component is 95% (v) for ethanol aqueous solution, which was produced in the regeneration process.

3.4. Effect of the Dosage of Solvents. The effect of the solvent dosage is shown in Figure 2. The spent clay was first extracted by solvent B at a ratio of 60–200 mL solvent B to 100 g spent clay, and then the filtered clay was extracted twice by the solvent mixed with B and E (possessing a ratio of 20% (v) in the mixed solvents). The extraction temperature and time were 50°C and 30 min, respectively. The filtrates were vaporized and dried to recover the oils and solvents.

Figure 2 shows the effect of the solvent dosage on oil recovery: total oil recovery increased with solvent dosage but remained relatively constant after the dosage reached 100 mL solvent per 100 g spent clay. Solvent dosage of 100 mL/100 g is
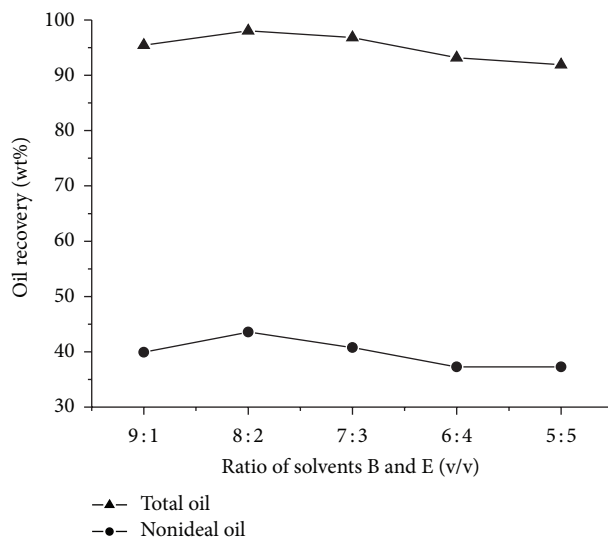

Figure 3: The effect of the ratio of solvents B and E.

selected as optimal dosage for oil recovery with conservative energy consumption during separation.

3.5. Effect of the Ratio of Solvents B and E. The spent clay was first extracted by solvent B with a ratio of 100 mL of solvent B and 100 g of spent clay. The filtered clay was further extracted twice using a solvent mixed with B and E for 30 min at 50°C. The filtrates were vaporized and dried to recover the oils and solvents. The effect of the ratio of solvents B and E is shown in Figure 3.

It can be seen from Figure 3 that the nonideal oil and total oil recovery are the highest when the ratio of solvents B and E is 8 : 2 (v/v).

3.6. The Effect of Extraction Temperature. The spent clay was first extracted by solvent B with a solvent to clay ratio of 100 mL/100 g, and then the first extracted clay was extracted twice more using the solvent mixed with B and E and an 8 : 2 ratio of B and E. The extraction time was kept constant at 30 min. The filtrates were vaporized and dried to recover the oils and solvents.

It can be seen from Figure 4 that the total oil recovery increases with the extraction temperature and reaches a summit between 50 and 70°C. The viscosity of oil absorbed in the clay decreases with an increase of extraction temperature. High temperature is not beneficial to adsorption; therefore, when the temperature is high, the oil recovery is also high. As the temperature reaches above the boiling point of solvent E (78°C), oil recovery decreases due to a change in concentration of the mixed solvent. At optimal conditions, more than 99% of the oil was recovered in these experiments.

3.7. Effect of Extraction Time. The spent clay was first extracted by solvent B with a solvent to clay ratio of 100 mL/100 g, and then the first extracted clay was extracted twice more using the solvent mixed with B and E and an 8 : 2 ratio of B and E. The extraction temperature was kept constant
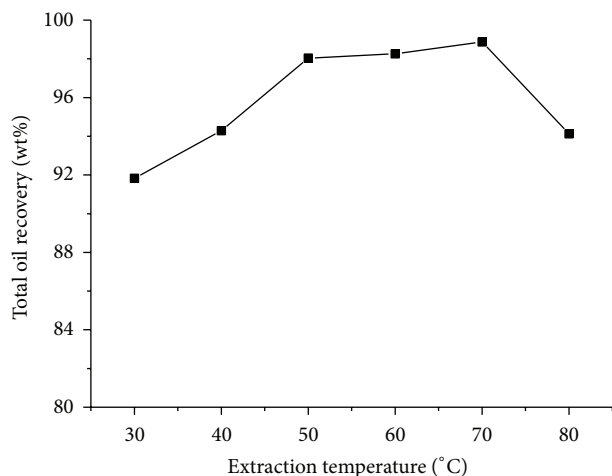
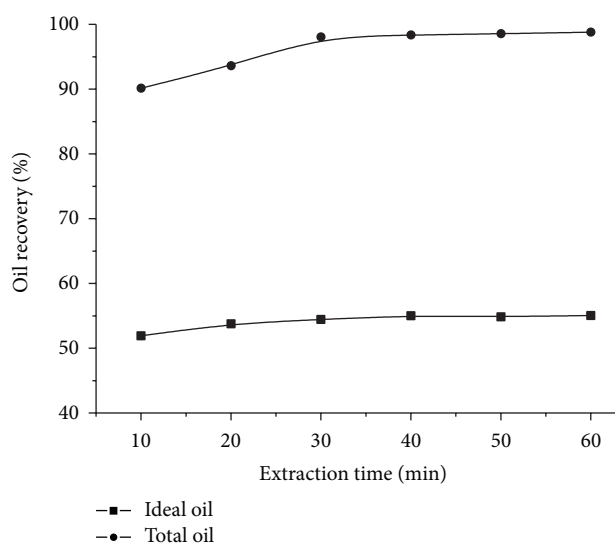FIGURE 4: The effect of extraction temperature.

FIGURE 5: Effect of the extraction time.

at 60°C, and the effect of extraction time was studied. The filtrates were vaporized to recover the oils and solvents.

It can be seen from Figure 5 that oil recovery increases with time for the first 30 min, but the rate of recovery slows considerably afterwards as most of the oil has been recovered by that time. Considering the extraction efficiency, a suitable extraction time is 30–40 min.

3.8. Effect of Multiple Extractions. Extraction times are also important to the extraction effects. Usually, ideal oil can be easily extracted from spent clay, but the resin and polycyclic aromatic hydrocarbons provide difficulty during the extraction process due to their high adsorption strength. Thus, multiple extractions may offer a superior mode of recovery for resin and polycyclic aromatic hydrocarbons. Table 4 shows the extraction procedures used during the experiment. The extractions were finished under the best extraction conditions.

TABLE 4: Extraction procedure of different times.

Extraction times	Extraction times		
	Extraction with solvent B	Extraction with solvents B and E	Extraction with solvent E
2	1	1	0
3	1	2	0
4	1	2	1
5	2	2	1
6	2	2	2

TABLE 5: The influence of storage time on the oil recovery.

Storage time, h	Ideal oil, g/100 g (spent clay)	Nonideal oil, g/100 g (spent clay)	Total oil, g/100 g (spent clay)
0	18.2	14.6	32.8
24	18.1	14.5	32.6
48	18.1	14.4	32.5
72	18.0	14.4	32.4
168	17.9	14.3	32.2

It can be seen from Figure 6 that the oil recovery increases with increasing number of extractions. After three extractions, only a marginal improvement in oil recovery is observed. The surface area (Figure 7) also shows the same trend as the total oil recovery with the multiple extractions. It is therefore suitable to limit the number of extractions between 3 and 4 considering the high cost of operation.

3.9. Effect of Spent Clay Storage Time. When the spent clay was produced, it was first stored in the storeroom and then was delivered to the processing unit. The storage time may influence the regeneration effect. To research the effect of the storage time, we refined the lubricating base oil with the freshly activated clay (surface area of $219.6 \, \text{m}^2/\text{g}$) to obtain spent clay. The spent clay was stored at room temperature for 0 to 168 h. Then, the spent clay was extracted four times, as shown in Table 4.

It can be seen from Figure 8 that the surface area of regenerated clay decreases evidently with increased storage time. The ideal oil and nonideal oil recovery all decreased with the storage time (see Table 5). Oil may deteriorate with increased storage time because of oxidation (ideal oil decreased) and the adsorption strength also becomes strong with the storage time. So the oil recovery decreased. Therefore, it is advisable to store spent clay for a shorter period of time prior to regeneration.

3.10. Characterization of Regenerated Clay and Oils. The regenerated clay and newly activated clay were used to refine the lubricating base oil.

Table 6 shows that regenerated clay has a similar ability to lower the oil color number as fresh clay. Surface area also indicates that regenerated clay recovered most of its
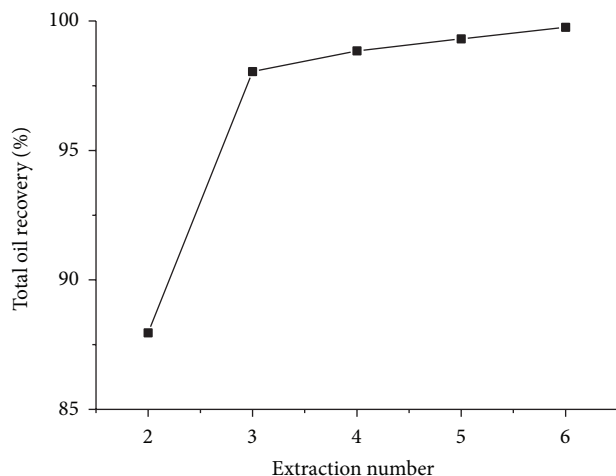
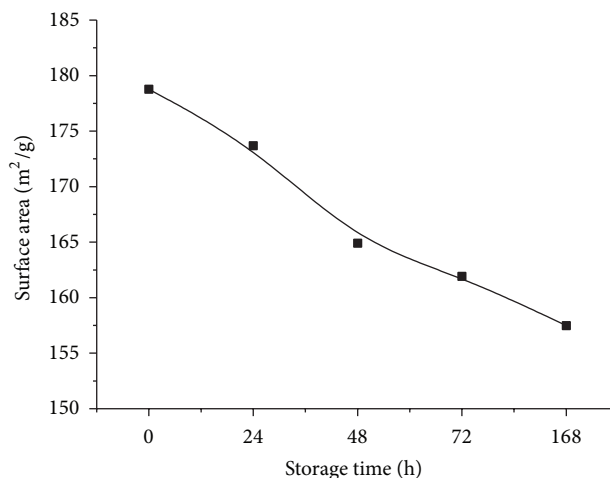Figure 6: Effect on oil recovery of extraction number.
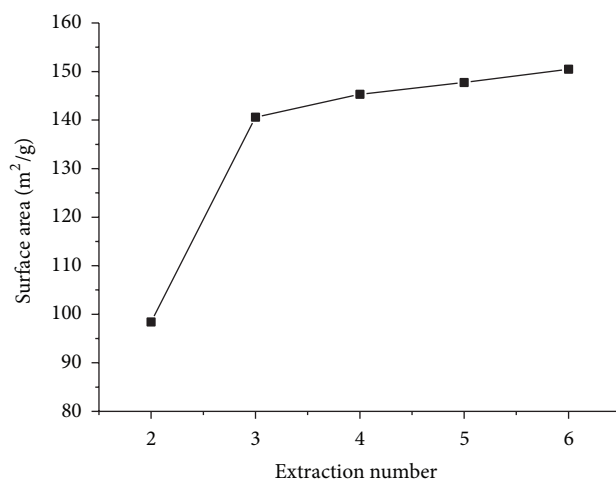

Figure 8: Effect of storage time of spent clay.

Figure 7: Effect on the surface area of extraction number.

Table 7: Characters and components of ideal oil.

Items	Data
Color number	2.0
Viscosity (40°C/100°C), mm^2/s	31.5/5.4
Viscosity index	107
Total acid number, mg KOH/g	0.03
Components, wt%	
Saturated fraction	88.51
Light aromatic fraction	8.16
Middle aromatic fraction	1.05
Heavy aromatic and resin fraction	2.28

Table 8: Characters and components of nonideal oil.

Items	Data
Color number	>5
Viscosity (100°C), mm^2/s	66.4
Total acid number, mg KOH/g	0.27
Components, wt%	
Saturated fraction	2.5
Aromatic fraction	15.7
Resin fraction	81.8

Table 6: Characterization of regenerated clay.

Items	Fresh clay	Regenerated clay
Surface area, m^2/g	219.6	150.5
Color number of unrefined oil	3.0	3.0
Clay dosage used, wt%	5.0	5.0
Color number of refined oil	2.0	2.0

adsorption capacity, and it can again be used to refine the lubricating base oils.

Table 7 shows the characteristics and components of recovered ideal oil. The ideal oil extracted from spent clay possesses good characteristics as lubricating base oils; thus, this extraction method is useful for regenerating spent clay and separating the ideal and nonideal oils.

Table 8 shows the characteristics and components of recovered nonideal oil. The nonideal oil extracted from spent clay possesses dark color, high viscosity, high acid number, and high resin content. So, most polar components are recovered in the nonideal oil.

4. Conclusions

The combination of petroleum ether (90–120°C) and ethanol (95%) can remove almost all of the adsorbed oils in the spent clay from lubricating oil refining. The spent clay should first be extracted by petroleum ether (90–120°C) and then by the mixed solvent of petroleum ether (90–120°C) and ethanol (95%) two or three times. Finally, the clay is to be extracted by ethanol and water. The recovered ideal oil can be used as lubricating base oil. Storage of spent clay for shorter times before regeneration provides the best results. The regenerated clay can be reused to refine the lubricating base oils.

Conflict of Interests

The authors declare no competing financial interests.

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