

Enhancing lead adsorption in waste lubricant oil with activated clay as bleaching earth

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Abstract. Waste lubricant oil is categorized as hazardous waste that contains several contaminants such as polycyclic aromatic hydrocarbon, chlorinated hydrocarbon, and heavy metals. Among these contaminants, lead has been known as one of the contributive contaminants in used lubricant oil in varied concentrations. To remove this contaminant, adsorption process was carried out by using clay as natural adsorbent (bleaching earth). In order to enhance the adsorption efficiency, the clay was activated by acidification with 1 M, 1.5M, 2 M H₂SO₄ or calcination in the temperature 300°C, 450°C, 600°C. The activated clay indicated the increase of montmorillonite percentage in clay up to 68% and clay's surface area up to 67 m²/g from its origin characteristics. The adsorption process showed notable improvement of clay adsorption capacity in removing lead in shorter contact time. The lead removal curve showed that the optimum adsorption condition can be obtained by the use of activated clay with 1.5 M H₂SO₄ and calcined in temperature 450°C. The optimum adsorption contact time with acid and calcination activated clay was 30 minutes and 180 minutes respectively.

1 Introduction

The purification of waste lubricant oil by the adsorption process can be carried out using various types of adsorbents such as activated carbon, zeolites, clays, and other adsorbents. However, from an economic point of view, clay adsorbent is one of the most promising because it is ubiquitous in the environment. Commonly, clay is known as bleaching earth which is used in the refining of palm oil process. This bleaching earth is generally constituted of up to three types of clay minerals. They are bentonite, attapulgite, and sepiolite.

The adsorption process itself is influenced by many factors such as temperature, acidity, particle size, porosity, and one of the most important is the surface area regarding the surface area of the adsorbent, the larger the surface area of the adsorbent, the greater the amount of adsorbate that can be absorbed. The surface area of the adsorbent can be increased by the activation process.

The activation of adsorbents can be done physically and chemically. The physical activation process for adsorbents is usually done by the heating process. For the heating at a temperature of 100-200°C, the water molecules that fill the space between the layers in the

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adsorbent will be lost (evaporated), while for heating at higher temperatures that is 500-700°C causes the process of water molecules to come out of the crystal circuit so that the adjacent OH group will release each water molecule [1]. The chemical activation is carried out by the addition of a chemical compound. One of the types of chemical activation is by the addition of weak or strong acid in the present study sulfuric acid (H_2SO_4) is used as the activating agent. The addition of sulfuric acid to the clay adsorbent can increase the surface area and porosity of the clay adsorbent so that the adsorption capacity of the clay is greater [2]. The increase of adsorption power in this clay is caused by the removal of the impurities from the pores of adsorbent by adsorbent oxidation [3]. By activating the clay adsorbent, it is expected to decrease the amount of concentration required in the adsorption process and accelerate the contact time on the adsorption process so that it can optimize the energy.

2 Materials and methods

2.1. Materials

The clay adsorbent used in this study was originating from Sukabumi, West Java, Indonesia. The used lubricant waste was taken from one of the workshops in the area of South Jakarta, Indonesia.

2.2. Clay preparation

The clay taken directly from nature was then prepared by heating at a temperature of 260-300°C to remove the water content found in the clay soil. After that, the clay was refined to the size of 200 mesh.

2.3. Clay activation

Chemically activation was done by the addition of sulfuric acid (H_2SO_4) with acid concentration variations of 1 M, 1.5 M, and 2 M. The acid mixed into the clay is 5 mL for every 1 g of clay into the beaker glass. Furthermore, the stirring of acid and clay was done at 200 rpm speed for 60 minutes. After the stirring then the H_2SO_4 acid was removed and then aquades washed the clay until the H_2SO_4 solution gone. After the washing process then the clay was filtered with filter paper to separate the water from clay. Then the clay residue after filtration is heated to a temperature of 105°C (in an oven) so that there's no moisture content. After reaching the room temperature then the sample was refined back up to 200 mesh in size.

Physical activation was done by calcining clay with temperature 300°C, 450°C, and 600°C in the furnace. The process occurred for 4 hours.

2.4 Adsorption process

The adsorption process was carried out at a heating temperature of 120°C and a stirring speed of 435 rpm. In the present study, the volume of waste lubricant used in one adsorption was 300 mL (preheated at 120°C for 5 min), and after the adsorption, precipitation was carried out for 24 hours and then the lubricating oil was decanted. The adsorption contact time was 30, 60, 180, and 300 minutes.

2.5. Sample analysis

2.5.1 Clay characterization

Clay characterization included composite mineral composition analysis and surface area of the Sukabumi clay. The analysis of clay mineral composition was used PANanalytical as XRD tool with temperature measurement at 25°C. The number of samples required in this test ranged from 1-2 g. A further analysis was carried out by analyzing the surface area with BET that was done by draining nitrogen gas at a temperature of 77.3 °K. The specification tool or instrument used was QuadroSorb Station 3. The number of samples required in this study was 1-2 g of clay.

2.5.2 Lubricant oil characterization

The characterization of lubrication oil conducted before and after the adsorption process included the measurement of final lead concentration, viscosity, pour point, flash point, specific gravity, TBN, and moisture content. The measurement of lead was carried out at each of the contact time of the adsorption process. Meanwhile, the measurements for other lubricant characteristics were performed at the beginning, before the adsorption process and after the activation and optimum contact, time was obtained. The test methods used in each analysis were summarized in Table 1 as follows.

Table 1. Testing methods.

Parameter	Testing methods
Lead concentration	X-Ray Fluorescence Spectrometry
Kinematic viscosity 40°C	ASTM D445
Flash Point	ASTM D92
Pour Point	ASTM D97
Specific Gravity	Density Meter
Total Base Number (TBN)	ASTM D2896-15
Moisture content	ASTM D95-13

3 Results and discussion

3.1. The effects of clay activation

3.1.1 The effects on the clay surface area

Fig. 1 shows the effects of clay activation using strong acid H₂SO₄ and calcination. The activation with 1 M H₂SO₄ increased the surface area significantly (about 62 m²/g). This increase is due to impurities present on the clay surface and covering the pores are dissolved with the acid thus increasing the absorption of the inert gas in the test, resulting in a larger surface area than the surface area of the clay sample before activation.

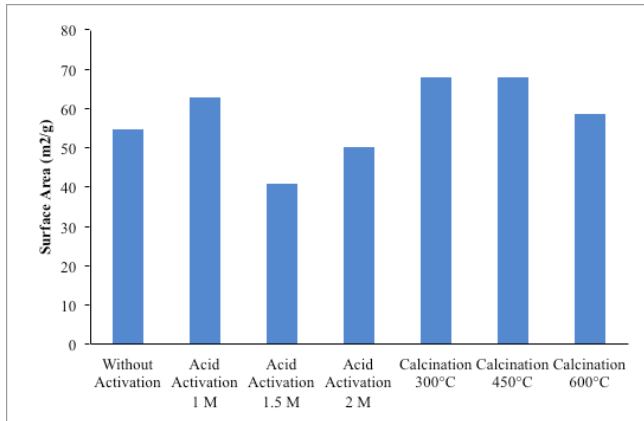


Fig. 1. Surface area of the activation result.

Inactivation with calcination, the highest surface area, was obtained at calcination of 450°C (68 m²/g). This is due to the dehydration and dehydroxylation process which forms a stable oxide. However, if the heating exceeds the optimum limit, then there will be an irreversible dehydroxylation process which causes deformation of the clay mineral composition. This causes the decrease of surface area.

3.1.2 The effects on the clay mineral composition

Fig. 2 shows the effect of clay activation process on the percentage of clay mineral composition. Sukabumi clay is known consist of montmorillonite, clinoptilolite, and quartz mineral. Both acid and calcination activation processes can increase the percentage of montmorillonite which plays an important role in binding Pb ions in used lubrication oil.

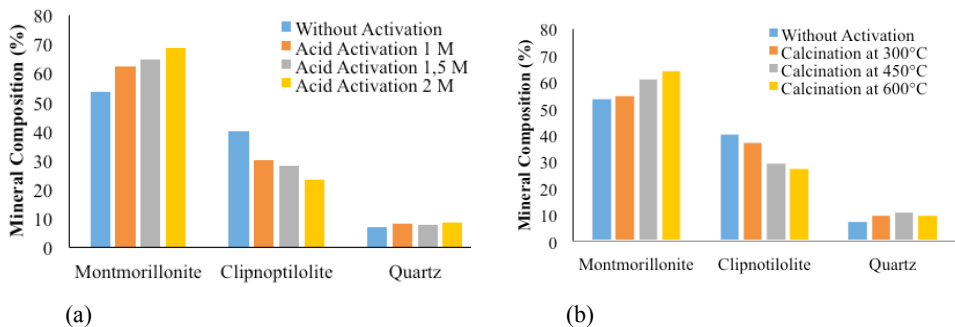


Fig. 2. Mineral composition resulted from (a) acid activation (b) calcination.

In the acid activation process, the use of 1 M, 1.5 M, and 2 M H₂SO₄ increased the percentage of montmorillonite which initially was 53.53% to 62%, 64.47%, and 68.44%. Likewise, during the calcination activation process at 300°C, 450°C, and 600°C, the percentage of montmorillonite increased to 54.33%, 60.86%, and 63.86%.

The activation process using acid provides H⁺ ions which can replace the cations present in the clay. At the time of contact with the acid, most of the SiO₄ bonds will not change (still intact) while the Al³⁺ and Mg²⁺ ions will exit from the octahedral bond [4]. The decomposition of the octahedral layer is closely related to the resistance of the compound to the influence of the acid. With the existence of the phenomenon, there will be changes in mineral composition in the clay.

Meanwhile, in the calcination process, the percentage change of this clay compound can be caused by dehydroxylation event or the release of OH group on the clay. In montmorillonite, it is known that the formation of this mineral will take place optimally until the calcination of 800°C. However, in some literature states that the montmorillonite dehydroxylation events can occur at temperatures of 500°C and 650°C thus affecting the formation of tetrahedral silica and octahedral aluminum in the clay layer [5].

3.2. Adsorption experiment result

The Fig. 3. and Fig. 4. shows the difference of Pb adsorption by clay without activation and with activation. The use of non-activated clays can exclude Pb metal in the used lubrication oil by 68% within 300 minutes. After the clay is activated with acid and calcination, there is an increase in the percentage of Pb removal in shorter contact time.

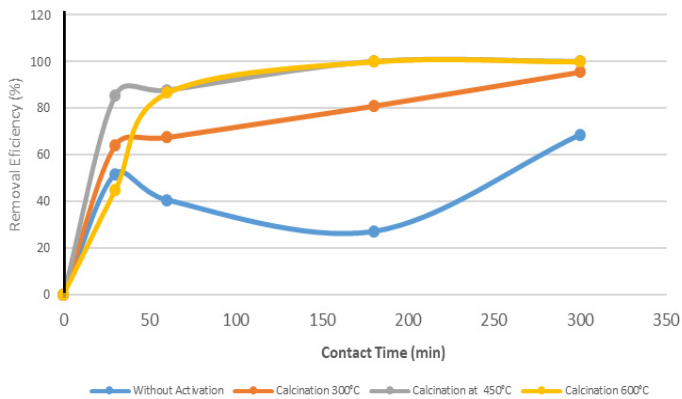


Fig.3. Removal efficiency of lead after adsorption process with clay activated by calcination.

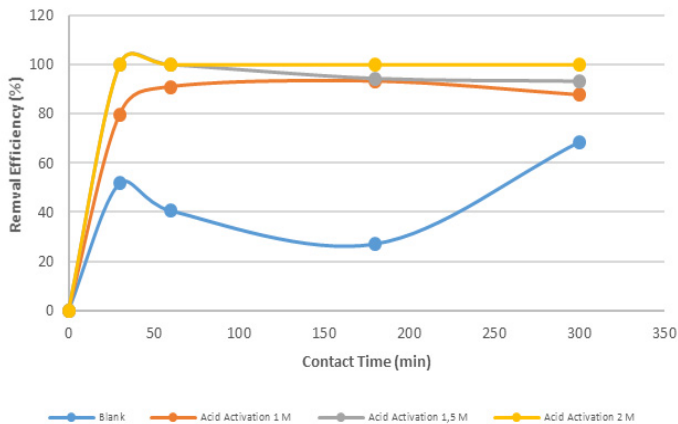


Fig.4. Removal efficiency of lead after adsorption process with clay activated by acid.

The graph of adsorption result by using acid activated clay on the graph, it can be seen that the optimum lead metal removal occurred at adsorption by using activated clay 1.5 M and 2 M. within 30 minutes of adsorption time. The 30 minutes reaction time is chosen

considering the equilibrium time of the adsorption process by using acid-activated clays. A 30-minute time is also selected for energy efficiency in the adsorption process. Considering the raw material, the concentration of acid selected at the adsorption process is 1.5 M of acid, since the lead removal at 30 minutes with the activated clay of the concentration has reached 100%.

For the adsorption using activated clays with calcination, the optimum adsorption process occurs at the activation with calcination at 450°C and at 180 min adsorption time. Under these conditions, the removal of lead has reached 100%. It also occurs in calcination activated clays at a temperature of 600°C. However, considering energy efficiency, the optimum condition of 450°C is chosen.

The optimum adsorption contact time (especially calcination) of this study was similar to the study conducted by Akpomie, Folasegun, and Dawodu [6] where lead removal reached its optimum percentage at adsorption contact time about 150-200 minutes. Furthermore, the percentage of lead removal which was able to reach 100% possibly caused by the low initial concentration of lead, which was 0.89 mg/L. The detection limit factor for the XRF device was 0.04 mg/L, hence the number of removal percentage was high.

The increase in the efficiency of this removal can be attributed to the increase of montmorillonite. Montmorillonite itself is a composition of clay composed of two layers of tetrahedral silica flanking one layer of octahedral alumina. The silica and alumina then undergo isomorphous substitution resulting in a negative charge on the clay so that the clay can bind the positive ions in the used lubricating oil. Also, in montmorillonite also formed another active side called surface interlayer where the formation of this surface will also greatly affect the adsorption process that occurs [7].

3.3. The effects of adsorption process on lubricant characteristics

Table 2. compares the characteristics of lubrication oil before and after the reaction. The result shows that the use of activated clay in adsorption process can recover some of lubricant oil characteristics such as viscosity, flash point, specific gravity and total base number.

Table 2. Result of characterization of used lubricant after adsorptions.

Characteristics	Fresh oil	Used oil	Recycled oil (acid treatment)	Recycled oil (Calcination)
Kinematic Viscosity 40°C (cst)	67.23	51.44	49.11	53.14
Flash point (°C)	238	196	212	206
Pour point (°C)	-39	< -36	< -36	< -36
Specific Gravity (g/cm ³)	0.853	0.846	0.853	0.853
Total base number (mg/KOH g)	6.43	5.82	6.9	6.53
Moisture content (%)	0	< 0.5	< 0.5	< 0.5

The viscosity of the lubrication oil was increased to 53.14 cst after using calcination activated clays but decreased to 49.11 cst when using acid-activated clays. The increased viscosity value after using the used lubrication oil can be due to the SiO₂ content in the clay that reacts with the lubrication oil when the adsorption process took place. On the other hand, the viscosity of recycled lubricant oil with acid activated clay showed the opposite

result. This is similar to previous studies which suggest that the presence of H_2SO_4 may decrease the value of viscosity [8]. Regarding the flashpoint value, there is an increase in flashpoint to $206^\circ C$ and $216^\circ C$ using the acid and calcination-activated clays. Meanwhile, the lubrication oil pour point after being processed does not change from its initial condition that is $<-36^\circ C$. This result can be due to the limitations of the tool that can only read a pour point value up to $-36^\circ C$. The next test is specific gravity. From the test result, it is known that the specific gravity of used lubricant samples used in this research is $0.846 g/cm^3$ where this value is almost close to the value of specific gravity of new lubricants.

The insignificant value of specific gravity between used lubrication oil with new lubrication oil causes when the oil is processed, the specific gravity value can be returned to its initial condition. The previous study have also shown the similar result (no significant change in specific gravity value changes), that the specific gravity value of the used lubricant sample is 0.91 and the specific gravity value for the new lubricant is 0.90 [9]. From TBN test result, the lubrication oil underwent an increase from its initial condition of 5.82 mg/KOH g to 6.9 and 6.53 mg/KOH g after using acid and calcination-activated clays. Later, the moisture content test indicated that the moisture content of the lubricant sample after treated with activated clay did not change from the initial condition of the used lubricant oil which is $<0.5\%$.

4 Conclusions

This study showed that adsorption with (acidified or calcinated) activated clays could eliminate almost of leads content in the used lubricants. The optimum clay activation condition for acidification and calculations method is 1.5 M and $450^\circ C$, respectively. The optimum adsorption time was found 30 min for acid activated clay and 180 min for calcinated activated clay. Regarding pour point, flash point, specific gravity, and moisture content, the treated lubricant shows characteristics close to a new lubricant. However, the viscosity value is still quite far from the new lubricant standards and requires additional additives. Therefore, this study showed that the utilization of bleaching earth as an adsorbent could be a promising solution to treat hazardous waste such as lubricant oil.

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