Treatment of Waste Lubricating Oil by Chemical and Adsorption Process Using Butanol and Kaolin

Riyanto$^{1,4}$, B Ramadhan$^{2}$, D Wiyanti$^{3}$

$^{1,2,3}$Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Islam Indonesia, Jl. Kaliurang KM 14.5 Sleman Yogyakarta

$^4$email: riyanto@uii.ac.id

Abstract. Treatment of waste lubricating oil by chemical and adsorption process using butanol and kaolin has been done. Quality of lubricating oil after treatment was analysis using Atomic Absorption Spectrophotometer (AAS) and Gas Chromatography-Mass Spectrometry (GC-MS). The effects of the treatment of butanol, KOH, and kaolin to metals contain in waste lubricating oil treatment have been evaluated. Treatment of waste lubricating oil has been done using various kaolin weight, butanol, and KOH solution. The result of this research show metal content of Ca, Mg, Pb, Fe and Cr in waste lubricating oil before treatment are 1020.49, 367.02, 16.40, 36.76 and 1.80 ppm, respectively. The metal content of Ca, Mg, Pb, Fe and Cr in the waste lubricating oil after treatment are 0.17, 9.85, 34.07, 78.22 and 1.20 ppm, respectively. The optimum condition for treatment of waste lubricating oil using butanol, KOH, and kaolin is 30 mL, 3.0 g and 1.5 g, respectively. Chemical and adsorption method using butanol and kaolin can be used for decrease of metals contain in waste lubricating oil.

1. Introduction

It is estimated that more than 30.3 billion liters of used oil are produced every year. The waste of lubricant oil is generated mostly from vehicles and engines. This lubricant waste has a very high hazardous content from ash, carbon residue, asphaltenes, materials, metals, water, and other dirty materials produced during lubricants inside the machine. Used oils as hazardous wastes if disposed directly into the environment, especially rivers, seas and lakes create problems, such as the problem of disposing of used oil into water bodies not only contaminate water but also harmful to freshwater and marine life [1,2].

The waste of lubricant oil can be produced from various human activities such as industry, mining, and workshop. Lubricating oil wastes is including B3 waste is flammable so that if not handled the management and disposal will endanger human health and the environment. Currently, this liquid waste has been dumped into the environment and created many problems. Lubricating oil wastes are dumped on the ground, under a ditch, or sent to a landfill, which is eventually absorbed into the ground or floats on the water surface [3]. The management of this lubricating oil wastes to make used oil not pollute the environment and the nature of used oil becomes more harmless or even can be used again as new oil. Lubricating oil wastes management also aims to create a healthy environment for people's lives. Moreover, the handling of used oil well done, it will be able to provide benefits for industries that reuse used oil as a lubricant of various equipment, because used oil can still be used for lubricant again by way of different use before.
Components in lubricating oil wastes are hydrocarbons, polymer additives, carbon particles, water and metals [3]. The content of metals in lubricating oil wastes is not derived from lubricant base material but derives from additives added, metal, contaminants from petrol fuel containing lead, dust, dirt from the air, refrigerant and cooling water used to cool the machine. The process of lubricating oil wastes aims to make waste oil used to be a new oil that does not contain metal because the metal content in used oil is not useful.

Lubricating oil wastes processing is widely used, among others, by using a combination of solvent extraction and adsorption methods [3] using the addition of sulfuric acid, phosphoric acid, acetic acid and acids [4], using treatment of solvent/clay extraction [5]. Some of the processing that has been done, among others, used oil processing using various absorbent [6], and used oil recycling processes with new washing agents such as acetic acid belonging to Hamawand et al. [7]. According to Udonne, et al. [1] on the comparison of four recycled lubricant methods used: clay-processing, clay-distillation, acid treatment and charcoal processing methods or active clay. Recycling of engine oil waste is done using acetic acid. The recycling process takes place at room temperature. The advantage of using acetic acid is that it does not react or only reacts slightly with base oil [7]. Research from Abro et al. [8] on the ratio of engine lubricants enhanced by the extraction of composite solvents, solvents, and acid treatment methods.

A mineral may be referred to as kaolin clay if the kaolin mineral composition is more than 50% of the mineral composition [9]. Kaolin minerals can be found in nature in the form of pure kaolin and other kaolin minerals such as halloysite, nakrit and dicrit and other clay minerals such as smectite, illit and mica as main components and feldspar and quartz as impurities [10].

Kaolin is a clay mineral with a 1:1 layer structure with a base unit composed of a tetrahedral sheet of SiO$_4^{4-}$ and an octahedral sheet with Al$^{3+}$ as an octahedral cation. In addition, kaolin widely used in the field of drugs, cosmetics, wine purifiers, and carrier materials for insecticides, pesticides, fungicides, crayon fillers, pencils, oil adsorbents, fertilizers, and also catalyst [10-12].

In this paper present of the treatment of waste lubricating oil by chemical and adsorption process using butanol and kaolin. Treatment of waste lubricating oil is using various kaolin weight, butanol, and KOH solution. After treatment of waste lubricating oil has been evaluated is the metal content of Ca, Mg, Pb, Fe and Cr. Analysis of the metal contains in waste lubricating oil before and after treatment has been done using Atomic Absorption Spectrophotometer (AAS).

2. Experimental Section

2.1 Materials and Instrumentation
The material has been used in this research is the waste of lubricant oil, butanol (Merck), sodium hydroxide (Merck), Kaolin (JP-100), nitric acid (Merck), hydrochloride acid (Merck), n-hexane (Merck) and acetonitrile (Merck). All chemicals used are analytical grade (pro analysis) and use distilled water. Instrumentation has been used in this research is furnace (Vulcan A-550), rotary evaporator (Buchi) and Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer PinAcle 900T).

2.2 Treatment of Waste Lubricating Oil
Lubricating oil waste of 15 mL was put into a 250 mL beaker glass. Thereafter, 45 mL of n-butanol solution was added to dissolve the used oil and 2 g of KOH. After that, take 45 mL of n-butanol solution and mix it with oil and stir it evenly. KOH is incorporated into a mixture of used oil with n-butanol slowly gradually so as not to form the salt. After all mixed then stirred evenly using a magnetic stirrer for 1 hour with a temperature of 60 °C and filtered. Then the kaolin is put in the used oil. After stirring with a magnetic stirrer for 1 hour then stirring for 24 hours then filtered with Buchner funnel and using the vacuum pump. This filtering process is done for many times until the kaolin is completely lost. After that, an evaporation process is done to take n-butanol in the mixture. Block diagram of treatment of lubricating oil waste to new lubricating oil can be seen in Figure 1.
2.3 Preparation of lubricating oil waste for metals analysis
The waste of lubricant oil sample weighed 5 g and put into porcelain cup and heated with oven with temperature 105 °C for 3 hours. After the oven and then put into the furnace with a temperature of 600 °C to ash. Samples added 5 mL of concentrated HNO₃ to dissolve the ash and add 5 mL of concentrated HCl solution. Then heat until the smoke in the solution was lost. The solution is put in a 100 mL volumetric flask and added distilled water until the mark and the sample is ready to be tested with AAS.

3. Result and Discussion

3.1 Effect of kaolin on metals in waste lubricating oil after process
The metals that are the main focus of this research are Ca, Mg, Pb, Fe, and Cr. The metals were studied using the ratio of butanol to used oil which is 3:1 where butanol is 45 mL and 15 mL of used oil waste sample. Initially, used waste lubricating oil was first tested before the research to find of metal content in waste oil samples used. In the sample of waste oil was first obtained Ca, Mg, Pb, Fe, and Cr is 1020.49; 367.02; 167.40; 36.76 and 1.80 mg/kg, respectively. The purpose of adding butanol solution is to break up the water content with the metal in waste oils so that the water content and metal content are separated and can be absorbed by kaolin, while the addition of KOH aims as the coagulant or it can also precipitate metals so it can be absorbed easily by kaolin.

Table 1. Effect of treatment using kaolin to waste lubricating oil

| No | Metals | Before treatment in mg/kg | After treatment with kaolin (g) in mg/kg | Standard |
|----|--------|--------------------------|----------------------------------------|----------|
|    |        |                          | 0.5         | 1.0        | 1.5       |          |
| 1.  | Ca     | 1020.49                  | 0.72        | 0.17       | 2.38      | 1103.00  |
| 2.  | Mg     | 367.02                   | 58.90       | 9.85       | 8.34      | 870.80   |
| 3.  | Pb     | 167.40                   | 58.94       | 34.07      | 47.06     | 16.00    |
| 4.  | Fe     | 36.76                    | 90.21       | 78.22      | 4.15      | 2.76     |
| 5.  | Cr     | 1.80                     | 1.23        | 1.20       | 1.23      | 0.12     |

Figure 1 shown is the effect of treatment using kaolin to waste lubricating oil. In the first variation of using kaolin of 0.5 g obtained metal content on Ca metal of 0.72 mg/kg. While on metal Mg and Pb is 58.90 and 58.94 mg/kg, respectively. For the content of Fe and Cr are 90.21 and 1.23 mg/kg,
respectively. In this first variation when compared with the metal content of the waste oil sample there was a decrease in Ca, Mg, Pb, and Cr metals. As for Fe metal, it experienced a significant increase from 36.76 mg/kg to 90.21 mg/kg. This may happen considering that in this process of using kaolin absorbent containing Fe metal also. It could be when the filtration process is less than the maximum so that the Fe metal in the sample of oil waste mixed with the absorbent kaolin. To minimize this it is advisable to use the softest filter paper with repetition of approximately three times, so it is expected that the kaolin absorbent can be filtered to the maximum.

3.2 Effect of treatment with acetic acid

This study used acetic acid solution to help break down or separate the water content with the compounds and metals contained in the waste oil. Table 2 shown of the effect of treatment using acetic acid to waste lubricating oil.

| No | Metals | Treatment with acetic acid (mg/kg) | Standard |
|----|--------|----------------------------------|----------|
| 1. | Fe     | 70.84                            | 2.76     |
| 2. | Ca     | 12.71                            | 1103.00  |
| 3. | Mg     | 3.00                             | 870.80   |
| 4. | Pb     | 5.56                             | 16.00    |
| 5. | Cr     | 28.00                            | 0.12     |

In Table 2 above, the effect of the addition of acetic acid, butanol, and KOH using kaolin absorbent on metal concentration in waste oil. This treatment can decrease the metal content obtained in the waste sample of waste oil maximally because it is expected with the addition of the acetic acid can help butanol in breaking or separating the water content contained in waste oil sample so that it can be absorbed maximally by kaolin absorbent. However, the results obtained are even less good compared with the results of the third variation where the results of the third variation can approach the standard metal content in the new oil. Thus it can be concluded that the addition of weak acids such as glacial acetic acid does not help to break down or separate the organic compound and the metal content contained in the waste oil sample.

Adsorption metal in kaolin is mechanism chemical and physical adsorption. Kaolin contains SiO$_2$ 46.54%, Al$_2$O$_3$ 39.50%, and H$_2$O 13.96% at the time of metal adsorption accompanied by H$^+$ release, then H$^+$ ion is substituted by the metal ion (cation) [13]. Figure 2 shown the mechanism of chemical adsorption of the Ca metal in kaolin

Figure 2. Mechanism of chemical adsorption of the Ca metal in kaolin

Kaolin has a skeletal structure, containing empty space occupied by cations and free water molecules allowing the exchange of ions and the absorption of chemical compounds. The evaporation of water content then the space occupied by the free water molecule becomes empty so that when adsorption is
very possible the absorption of ions. Figure 3 shown is the mechanism of physical adsorption Ca metal in kaolin.

![Mechanism of physical adsorption](image)

**Figure 3.** Mechanism of physical adsorption Ca metal in kaolin

### 3.3 Effect of butanol concentration

Metals content of used lubricating oil is not derived from lubricant base material but derives from additives added, metal, contaminants from petrol fuel containing lead, dust, dirt from the air, refrigerant and cooling water used to cool the machine. Table 3 shown the effect of treatment using butanol to metal content in waste lubricating oil.

| Metals | Lubricating oil waste (mg/kg) | Lubricating oil waste after treatment using butanol (mg/kg) | Standard (mg/Kg) |
|--------|-------------------------------|----------------------------------------------------------|-----------------|
| Fe     | 365.13                        | 16.89, 11.08, 35.99                                       | 2.76            |
| Ca     | 1019.00                       | 6.76, 2.51, nd*                                          | 1103.00         |
| Mg     | 325.88                        | 12.77, 5.58, 24.71                                       | 870.80          |
| Pb     | 181.00                        | 98.26, 7.16, 9.16                                        | 16.00           |
| Cr     | 10.72                         | 2.88, nd*, nd*                                           | 0.12            |

*nd is not detection

Variation of butanol with oil of butanol ratio: used oil (2:1) for Fe, Ca, Mg, Pb, Cr produced metal is 16.89; 6.76; 12.77; 98.26; 2.88 mg/kg, respectively. In the case of waste oil treatment using butanol solvent can significantly decrease Fe, Ca, Mg, Pb, and Cr content of metal in used oil and mean that butanol succeeds in reducing the metal in used oil which is characterized by the deposition of a layer of mud under a beaker. Maximum standards according to ASTM D5185 metal is Fe, Ca, Mg, Pb, Cr is 2.76, 1103.00, 870.80, 16.00 and 0.12 mg/kg, respectively. The Ca, Mg, and Cr metals do not exceed the standard but high concentrations of Fe and Pb metals are still high.

### 3.4 Effect of KOH concentration

Variations of butanol can be obtained that the best variation of butanol is 3:1 after that done KOH variation as much as 1, 2 and 3 g. The addition of KOH increases the ability of alcohol to remove sludge from waste oil. Table 4 shown is the effect of treatment using KOH concentration to waste lubricating oil.

| Metals | Lubricating oil waste (mg/kg) | Lubricating oil waste after treatment using KOH (mg/kg) | Standard (mg/Kg) |
|--------|-------------------------------|--------------------------------------------------------|-----------------|
| Fe     | 34.32                         | 1.20, 8.83, 62.00                                       | 0.11            |
| Ca     | 74.32                         | 1.20, 8.83, 62.00                                       | 0.11            |
| Mg     | 1.20                          | 8.83, 62.00                                             | 0.11            |
| Pb     | 8.83                          | 62.00, 0.11                                            | 0.11            |
| Cr     | 62.00                         | 0.11                                                   | 0.11            |

Variation of KOH of 3 g for Fe, Ca, Mg, Pb and Cr is 74.32, 1.20, 8.83, 62.00, and 0.11 mg/kg, respectively. KOH variation of 3 g also decreased the concentration of each metal when compared with used oil, but when compared with variation KOH 1 and 2 g there is an increase in Fe and Pb high metal. The Pb metal does not exceed the ASTM D5185 standard, while the Fe metal exceeds the ASTM D5185 standard. The increase in the metal is probably due to KOH not reacting perfectly in the process so it is less effective at helping butanol increase sludge. The likelihood of the increase in metal concentration
is also due to less optimal adsorption process so that metals that passes from kaolin adsorbent only slightly.

### Table 4. Effect of treatment using KOH concentration to waste lubricating oil

| Metals | Lubricating oil (mg/kg) | Lubricating oil waste after treatment using KOH concentration (mg/kg) | Standard (mg/kg) |
|--------|------------------------|---------------------------------------------------------------------|-----------------|
|        |                        | 1 g | 2 g | 3 g |                        |                  |
| Fe     | 365.13                 | 39.30 | 11.08 | 74.32 | 2.76 |
| Ca     | 1019.00                | 0.80 | 2.51 | 1.20 | 1103.00 |
| Mg     | 325.88                 | 5.43 | 5.57 | 8.83 | 870.80 |
| Pb     | 181.00                 | 28.51 | 7.16 | 62.00 | 16.00 |
| Cr     | 10.72                  | nd | nd | 0.11 | 0.12 |

**nd** is not detection

Based on Table 4 it can be concluded that KOH variations of 1, 2, and 3 g decrease for each metal, although there is a rising metal. The more KOH added in the waste oil treatment the better it is to lower the metal content of the used oil, but the most optimal addition of KOH is 2 g. The best KOH variation is 2 g. This is in accordance with the study Mohammed et al. which states that the addition of 2 g of KOH to butanol in the solvent has been shown to significantly increase the removal of sludge from waste oil [3].

### Conclusions

The effect of butanol on the waste oil treatment is for the deposition of the mud layer under the beaker and acts as a solvent for the extraction-flocculation in reducing Fe, Ca, Mg, Pb, and Cr, while the KOH effect is as coagulant to increase the flocculation of the dirt, oil with the solvent, helping the butanol solvent in forming sludge. The best butanol variation used to reduce the Fe, Ca, Mg, Pb, and Cr on the used oil is 3:1, and for the best KOH variation is 2 g. The more butanol and KOH used, the better it is in reducing the metal content.

### References

[1] Udonne J D 2011 *Journal of Petroleum and Gas Engineering*. 2 12
[2] Udonne J D and Bakare O A 2013 *International Archive of Applied Sciences and Technology*. 4 28
[3] Mohammed R R, Ibrahim A R, Taha H A and McKay G 2013 *Chem. Eng. J.* 220 343
[4] Abu-Elella R, Ossman M E, Farouq R and Abd-Elfatah M 2015 *International Journal of Chemical and Biochemical Sciences*. 7 57
[5] Emam A E and Shoaib M A 2012 *Refining of Used Lube Oil by Solvent/Clay and Acid/Clay Percolation Processes* (Egypt: Department of Refining Engineering and Petrochemicals, Suez Canal University)
[6] Shakirullah M, Ahmad I and Saeed M 2006 *Journal of the Chinese Chemical Society*. 5 32 335
[7] Hamawand I, Yusaf T and Rafat S 2013 *Energies*. 6 1023
[8] Abro R, Chen X, Harijan K, Dhakan Z A and Ammar M 2013 *Chem. Eng.* 2013 1
[9] Dombrowski T 2000 *The Origin of Kaolinite* (Westerville: American Ceramic Society)
[10] Ekosse G E 2000 *Applied Clay Science* 16 5-6 301
[11] Belver C, Muoz M A B and Vicente M A 2002 *Chem.Mater.* 14 2033
[12] Murray H H 2000 *Appl. Clay Sci.* 34 39
[13] Bhattacharyaa G K and Gupta S S 2008 *Advances in Colloid and Interface Science*. 140 114