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Adsorption of Lubricant Waste by Porous Materials: A Review

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Abstract

The rapid development of technology today cannot be separated from the role of various kinds of machines to produce or increase the use value of an item. The more the engine operates, the more lubricant is used. Lubricants are included in the category of B3 waste (Toxic Hazardous Materials) so that they have a negative impact on the environment. Nearly 50% of all mineral lubricants enter the environment and cause irreparable environmental damage due to direct contact with water and soil. One of the efforts that can be done to reduce the B3 content in used lubricants is adsorption using a porous adsorbent. This study aims to see the relationship between the physical and chemical properties of the adsorbent with the physical and chemical properties of the adsorbate. This research was conducted by studying the literature of scientific articles with related topics. The results showed that some contaminants such as organic compounds, inorganic species, soot, hydrocarbons, and ash can be adsorbed with various adsorbents, namely modified sawdust, bentonite, fly ash, activated carbon, activated alumina, and zeolite Y derived from kaolin.

Keywords: *Adsorbate; B3 waste; contaminants*

Introduction

Lubricants are one of the most important fluids used in almost all vehicles and machines. Lubricants play an important role in heat transfer and friction reduction by reducing the heat generated in an internal combustion engine. In use, lubricants undergo changes such as degradation and contamination.

The high temperature inside the machine triggers isomerization, cracking and polymerization reactions. This causes a change in molecular structure resulting in degradation.

Degradation causes the formation of low molecular weight compounds and oxidation products. Oxidation products include polymerized or condensed molecules called gums and sludge. Currently, lubricant waste is one of the most abundant liquid wastes and requires further handling, however, it is discharged more into the environment and causes many problems. Used lubricants are thrown into the ground, sewers, or sent to landfills which eventually seep into the ground or float on the surface of the water (Mohammed, 2013).

Lubricants are chemical substances, which can be found in the form of liquid, solid, or gas but are generally in the form of a liquid, which are given between two moving objects in the engine to reduce friction. Lubrication is needed so that the engine is not easily damaged due to over-heating and excessive heat friction. The function of the lubricant is to reduce the occurrence of wear on the parts that rub against each other, as a coolant, carrying heat from the bearings, the lining on the cylinder wall as a seal that prevents the release of combustion gases. (Purjiyono, 2019).

Lubricant waste is included in the category of B3 waste (Toxic Hazardous Materials) which requires special handling. Along with the increase in the number of motorized vehicles and motorized machines, the volume of used lubricant waste continues to increase (Azharuddin, 2020). 50% of the total lubricant enters the environment. Lubricants that enter the environment will come into direct contact with water and soil, causing irreversible environmental damage (Adhvaryu and Erhan, 2002; Reeves *et al.*, 2017). One kilogram of acid in lubricants can contaminate millions of liters of clean water (McNutt, 2016). The B3 content contained in lubricant waste includes polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, and heavy metals (Kemala, 2019). Used lubricants also store combustion residues that are acidic, corrosive, and deposits (Candra, 2016).

Azharuddin (2020) utilizes waste lubricants into liquid fuel which is processed using the pyrolysis process. In addition to waste utilization, many studies have also focused on reducing pollution, such as that conducted by Kemala (2019) who carried out the adsorption of lead (Pb) using activated clay as an adsorbent. Various kinds of adsorbents derived from nature, both activated and unactivated, have been tested for their effectiveness in reducing various elements/compounds that degrade environmental quality. Purification of lubricant waste by the adsorption process can be carried out using various types of adsorbents such as zeolite, activated carbon, clay, and other adsorbents (Kemala, 2019). Kemala (2019) utilizes clay activated by acidification using sulfuric acid (H_2SO_4) for lead (Pb) adsorption because it is a heavy metal that has the potential to become an environmental pollutant. Clay adsorbents are one of the most promising because they are easy to find.

Candra (2016) uses activated charcoal to reduce the viscosity of used lubricants. In 2017, Hasyim used activated bentonite as an adsorbent for the adsorption of ferrous metal (Fe). Meanwhile, Mohammed (2013) used a combination of extraction and adsorption methods to remove sludge, increase flocculation, and improve the physical properties of waste lubricants. The advantages of combining the extraction and adsorption methods include: (a) requires less liquid organic solvents; reduces the effect of global warming, (b) half the process is carried out under ambient conditions, (c) uses local resources, (d) generates less waste, and (e) requires lower costs and operations (Mohammed, 2013).

Based on the many studies that have been carried out until now, the authors are encouraged to conduct a literature study on the development of research on adsorbents which is intended to reduce the negative impact on used lubricants. Various kinds of adsorbents have different characteristics from each other so that this literature study is expected to be able to classify the adsorbate (adsorbed substance) and the appropriate adsorbent based on physical and chemical properties.

Methods

The research was carried out with qualitative methods in the form of literature studies by collecting data or sources about adsorbent to reduce the negative impact of used oil on the environment based on the phrase adsorbent, porous material, and wasted lubricants adsorption. The method used for this research is a literature review to compare the results of 6 articles that is obtained from Journal Hazardous Materials, Journal of Industrial and Engineering Chemistry, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Process Safety and Environmental Protection, Environmental Science and Pollution Research, and Korean Journal of Chemical Engineering as can be seen in Table 1. A literature study (systematic qualitative review) was conducted on scientific articles related to the development of adsorbents to reduce contamination of used lubricants published in the last 5-10 years. The steps taken in this study include:

(1) selecting the topic to be reviewed,
(2) tracking and selecting relevant articles,
(3) analyzing articles, and
(4) organizing writing reviews.

Table 1. Articles Sources

No.	Journal	Title
1	Journal of Hazardous Materials, 2018, 350, 38-45	Natural adsorbent based on sawdust for removing impurities in waste lubricants
2	Journal of Industrial and Engineering Chemistry, 2015, volume, 23, 154-162	Application of Iranian nano-porous Ca-bentonite for recovery of waste lubricant oil by distillation and adsorption techniques
3	Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2018, 202, 214-221	Management of adsorbent content in waste motor oil regeneration by spectrophotometrical study and effective acidification in production of nano-porous clay
4	Environmental Science and Pollution Research, 2019, 26, 23257-23267	Efficient removal of contaminants from waste lubricant oil by nano-porous bentonite produced via microwave-assisted rapid activation: process identifications and optimization
5	Powder Technology, 2006, 166(1), 47-54	Properties and potential applications of zeolitic materials produced from fly ash using simple method of synthesis
6	Environmental Science and Pollution Research, 2020, 27, 37210-37217	Regeneration of the waste lubricating oil based upon flyash adsorption / solvent extraction
7	Korean Journal of Chemical Engineering, 2017, 34(9), 2435-2444	Re-refining of used lubricant oil by solvent extraction using central composite design method
8	American Journal of Chemical Engineering, 2020, 8(1), 11-18	Adsorption of Heavy Metals Contaminants in Used Lubricating Oil Using Palm Kernel and Coconut Shells Activated Carbons
9	Egyptian Journal of Petroleum, 2018, 27, 221-225	Recycling of used engine oil by different solvent
10	Egyptian Journal of Chemistry, 2022, 65(13), 151-160	Ultrasonic-assisted Hydrothermal Synthesis of Zeolite Y Adsorbent from Natural Kaolin for the Recycling of Waste Engine Oil

Result and Discussion

This research was conducted by processing research data from previous and reputable scientific journals both nationally and internationally related to adsorbents to reduce the negative impact of lubricant waste on the environment. A total of 15 scientific articles were compiled to obtain data related to the physical and chemical properties of adsorbents and adsorbates. The data were selected based on the type of adsorbate so that 7 (seven) articles were obtained in almost the same adsorbate group as those summarized in Table 2.

Table 2. Summaries of Analyzed Journal

Adsorbent	Active Substance	Adsorbate	Information
NaOH and triethanolamine modified sawdust (Chen, 2018)	Hydroxyl functional group	Organic compounds (aromatic) and inorganic species	• Optimal in Si, Fe, Cu, aromatic, and oxidation products adsorption • There is an increase in adsorption capacity for aromatic and oxidation products due to the presence of functional groups and fine pores but has stable adsorption capacity for impurities under different adsorption conditions • The metal is trapped in the resin and forms chemical bonds with the modified sawdust resulting in a very high increase in adsorption capacity for Fe, Cu, Al, and Si metals compared to unmodified sawdust
Ca-bentonite from clay (Salem, 2015)	Sulfuric acid and nitric acid	Soot in lubricating oil due to incomplete combustion	• Activation of bentonite with sulfuric acid produces an efficient adsorbent in removing color in waste lubricating oil compared to natural bentonite and activation of bentonite with nitric acid • Lubricating oil contaminant absorption is affected by acidification conditions where acid concentration plays an important role in the adsorption capacity. Increasing of acid concentration from 0.50 M to 1.00 M made absorbance decrease sharply. The presence of sulfuric acid give maximum removal of contaminants in lubricant oil • Factors that affect the recovery of lubricant waste include: the type of acid, the concentration of the adsorbent, and the length of time used. • Nanopore size with a diameter of 12 nm is preferred to remove contamination from lubricating engine oil
Bentonite from nano porous clay (Shabanzade, 2018)	Acetic acid, sulfuric acid and hydrochloric acid	Contaminants from waste lubricating oil	• Adsorbent consumption can be reduced by changing the bentonite structure and physico-chemical properties and looking at acidification factors such as acid proportion, adsorbent dosage, powder/acid ratio, and acidification residence time • Acid mixing for the manufacture of porous powders is an efficient factor to achieve minimum recovery ratio • Acetic acid combined with sulfuric acid plays an effective role in the development of porous structures and increased adsorption of contaminants. Activated bentonite is able to increase the extra capacity for

			waste oil regeneration, in which acid as an activator plays an important role in increasing the adsorption capacity ● Powders produced under optimal conditions contain nanopores with a diameter of about 11nm ● Thermal treatment of the clay for 30 minutes increased the adsorption efficiency by increasing the number of mesopores
Ca-bentonite (Shabanzade, 2018)	Sulfuric acid, hydrochloric acid and acetic acid	Contaminants from waste lubricating oil	● Determination of the exact acid composition, optimal microwave power, irradiation time, and powder/acid ratio is determined by carrying out waste lubricant extraction in a batch system ● The maximum purification time requires 15 minutes of acidification time and the power optimal condition identified is 600 W ● Bentonite activation using microwaves affects recovery efficiency by developing a certain surface area but still being able to maintain the layer structure. The acetic acid content in the micro-assisted acidification process must be controlled in the range of 0-50% to obtain an effective adsorbent in the purification of used lubricant waste. Microwaves can shorten the residence time to achieve maximum efficiency compared to the performance produced by conventional methods. Acid used in bentonite activation plays an important role to produce an efficient adsorbent which it should be controlled in the range of 0-50% ● The adsorption ratio increased with increasing proportion of hydrochloric and sulfuric acids and decreased with increasing proportion of acetic acid
Fly ash (Derkowski, 2006)	Na-X (FAU), NaP1 (GIS), sodalite	Heavy metal ions	● Fly ash-based adsorbents are made with the following mixtures: X = fly ash + 200 mL temperature: 75 °C; 3 M NaOH solution; P = fly ash+200 mL of 1M NaOH solution+100ml of 3M NaCl solution; boiling state (temperature: approx. 105 °C); S = 10g fly ash + 400 mL 5M NaOH solution + 200 ml 3M NaCl solution; boiling conditions (temperature: approx. 105 °C) ● The fly ash-based adsorbents have significant increase in cation exchange capacity (CEC), ranging from 5.5 to 239meq100g−1. They also exhibit a high ability to adsorb heavy metal ions (over 40mg g−1) and retain complex and organic molecules, particularly material X
Fly ash (Ouyang, 2020)	Fly ash	Impurities in the lubricating oil waste	● Characteristics of the adsorption efficiency of fly ash is higher than that of activated clay. adsorption and regeneration of waste lubricants found optimal conditions at an agitation time of 60 minutes, an

			adsorption temperature of 90 °C, a dose of 12% fly ash, and an agitation speed of 950 r/min • The isopropanol/isobutanol flyash extraction adsorption process (isopropanol:isobutanol = 1:1, mass ratio) is an optimal process for waste oil regeneration, where the waste oil index can be increased to a kinematic viscosity of 43.28 mm^2/s, acid number 0.13 mgKOH/g, 0.12% mechanical impurities, and 114 µg/g moisture
Activated bentonite (Daham, 2017)	Activated bentonite	ash in used lubricating oil	• This study used solvent extraction followed by the adsorption method to obtain base oil from used oil which found optimal conditions at a solvent/used oil ratio = 2.4 volume/volume, a temperature of 54 °C, and a mixing speed of 569 rpm for 1-butanol • The optimal conditions for adsorption with activated bentonite are bentonite/used oil ratio = 15% wt/volume, temperature of 120 °C, and contact time of 90 minutes • Different flocculation agents, including Sodium hydroxide (NaOH), Potassium hydroxide (KOH), and Monoethylamine (MEA), were utilized in conjunction with the solvent. These agents resulted in an improved separation efficiency. The most favorable outcome was achieved when employing 2 grams of MEA per kilogram of solvent, leading to an increase in sludge removal from 12.6% to 14.7%
Palm Kernel and Coconut Shells Activated Carbons (Opoku, 2020)	Activated carbon	Heavy metals	• Activated carbon adsorbents produced from palm kernel and coconut shells. For copper, iron, zinc, cadmium, lead, chromium, and magnesium adsorption, the R2 (correlation coefficients) values indicate a good fit to the Langmuir adsorption isotherm model, as they are close to 1. This suggests that the activated carbons produced from palm kernel and coconut shells can effectively adsorb heavy metals such as copper, iron, zinc, cadmium, lead, chromium, and magnesium. The DW (Durbin-Watson) values, which measure autocorrelation, are greater than 1 for the solute, confirming the basis of the modeling. The Pr > F (significance) values are less than 0.0001 for all metals, indicating the significance of the results. • Activated carbons derived from palm kernel and coconut shells can be used as high-performance adsorbents with a higher adsorption capacity for various heavy metal contaminants in used lubricating oil • The adsorption capacity can be affected by various factors, including the particle size of the activated carbon, the specific surface area, and the chemical properties of the activated carbon itself. Oil palm and coconut shells have a complex porous structure and a

			large surface area, thereby increasing their adsorption capacity for heavy metals
Activated Alumina (Osman, 2018)	Acid–base surface hydroxyl groups	Carboxylic acid	• Extraction by solvent mixture A (toluene, butanol, and methanol) was the most effective in removing sludge in used engine oil, with a maximum percentage of 52%. Solvent mixture B (toluene, butanol and ethanol) removed 36.7% of the sludge, while solvent mixture C (toluene, butanol and isopropanol) removed a lower percentage of 18.9% • The raffinate percentages for solvent mixtures A, B, and C were 48%, 63.3%, and 81.1%, respectively. The raffinate produced from solvent mixture A is yellow, indicating that it is free of mud or solid impurities. In contrast, the raffinate produced from solvent mixtures B and C is black • The experiment was continued by adsorption with activated alumina. It states that the activated alumina causes the used oil to turn yellow for solvent A, B, and C, indicating an improvement in color quality. There is no significant difference observed in the raffinate percentage (the liquid remaining after the extraction process) and the sludge percentage (the solid impurities removed) when using the three solvent mixtures. This implies that the effectiveness of the solvent mixtures in removing sludge from the used oil is similar when followed by adsorption with activated alumina
Kaolin (Ahmed, 2022)	Zeolite Y	Heavy metals	• Zeolite Y adsorbent is synthesized from natural kaolin using the ultrasonic-assisted hydrothermal technique. This research also examines the application of the synthesized Zeolite Y in the recycling of waste lubricant engine oil, which is a novel approach • Zeolite Y adsorbent efficiently removes chrome, copper, iron, lead, and zinc from the waste engine oil. • Zeolite Y adsorbent from natural kaolin's characterization revealing new structural and morphological properties, and its successful application in the recycling of waste lubricant engine oil, leading to high-quality recycled oil • At of 25 °C, the removal efficiencies for Zeolite Y were found to be 35.71% for Cr^{3+}, 66.67% for Cu^{2+}, 92.17% for Fe^{2+}, 63.02% for Pb^{2+}, and 95.24% for Zn^{2+}. At 40 °C, the removal efficiencies increased to 47.14% for Cr^{3+}, 76.19% for Cu^{2+}, 92.93% for Fe^{2+}, 70.70% for Pb^{2+}, and 96.31% for Zn^{2+}. The effectiveness of zeolite Y in removing heavy metals from waste engine oil with higher removal efficiencies was observed at a higher temperature

In the adsorption process of lubricant waste there are 2 substances that play a role in it, the solute (adsorbate) and the absorbent (adsorbent). Adsorbate is a solute that is absorbed by the surface of the solid pore in the adsorption process (Paryanto, at al. 2018). The characteristics of the adsorbate in order to be well absorbed by the pore surface of the solid are the size of the adsorbate, the type of polarity of the adsorbate, and the type of bonding of the adsorbate (Atikah, 2017). The adsorbate absorbed from lubricating oil is based on the results of a review of several journals including organic compounds, inorganic species, soot, hydrocarbons, and ash. Meanwhile, an adsorbent is a substance on the surface of a solid pore that is able to absorb fluids in the adsorption process (Widodo, *et al.* 2020). The characteristics of adsorbents to absorb well are having active pores, pure pores, adsorbent pore volume, large contact surface, and cannot react with adsorbate (Atikah, 2017). The adsorbents selected in the adsorption process of lubricating oil waste were based on the results of reviews from several journals including sawdust modified NaOH and triethanolamine, Ca-bentonite from clay, bentonite from nano-porous clay, Ca-bentonite, fly ash, and activated bentonite. The chemical interaction that occurs between the adsorbent and the adsorbate due to the formation of covalent bonds and ionic bonds in the adsorption process so as to form a single layer (monolayer) of adsorbate on the surface of the adsorbent (Suryawan, 2004).

Modified Sawdust

Research conducted by Chen, *et al.* (2018) using sawdust modified NaOH and triethanolamine, with the active substance of the hydroxyl functional group, able to adsorb organic compounds (aromatic) and inorganic species. NaOH and triethanolamine modified sawdust are good in adsorption of Si, Fe, Cu, aromatics, and oxidation products. Modification of sawdust with sodium hydroxide and triethanolamine improves surface properties and increases adsorption capacity.

The aromatic and oxidation products are adsorbed with sawdust whose adsorption capacity is greatly increased due to the presence of functional groups and fine pores. In addition to aromatic compounds and oxidation products which are well-adsorbed, some metals can also be well adsorbed such as Fe, Cu, Al, and Si. The adsorption capacity of modified sawdust for Fe, Cu, Al, and Si was greatly increased compared to unmodified sawdust due to the formation of chemical bonds between resins in which metals were trapped in the modified sawdust.

The adsorption performance varies slightly at different temperatures, which indicates that the modified sawdust exhibits high stability in the test temperature range of 60-120 C. The sawdust can reach its saturated adsorption state efficiently and quickly within the first two hours and the content of wear elements in waste lubricant changes little over time. The wear element content also changes slightly which is possible because the particle size is small enough to exclude internal diffusion. In short, the modified sawdust has a stable adsorption capacity for impurities under different adsorption conditions.

Bentonite

A research conducted by Salem, *et al.* (2014) used activated bentonite as adsorbent for waste lubricant. Bentonite is activated by sulfuric acid and nitric acid. The adsorbate is the soot in the lubricating oil due to incomplete combustion. Activated bentonite with sulfuric acid produces an efficient adsorbent in removing color in waste lubricating oil compared to natural bentonite and activated bentonite with nitric acid.

The manufacture of nanoporous adsorbents is carried out by giving acid treatment to natural clay. The pore structure of the adsorbent depends on several important factors such as concentration, type of acid, and residence time. The distance between the montmorillonite layers was observed to decrease by about 2.7 Å due to the presence of sulfuric acid which caused the replacement of hydrogen ions. The results are very promising for reducing the adsorbent content in the regeneration of lubricant waste.

Another research in bentonite as adsorbent for waste lubricant conducted Shabanzade, *et al.* (2018). They used bentonite adsorbent from nano-porous clay activated by acetic acid, sulfuric acid, and hydrochloric acid in the removal of contaminants from lubricant waste. The study aims to determine the potential of activated bentonite as an effective adsorbent in removing contaminants in lubricant waste. Hydrochloric acid activated bentonite was not efficient in adsorption and removal of contaminants from lubricant waste, while acetic acid and sulfuric acid activated bentonite were very effective in removing lubricant waste contaminants. Changes in the original bentonite structure and changes in the physico-chemical properties of the powder aim to reduce the adsorbent consumption depending on the acidification factor.

The minimum recovery ratio can be achieved by looking at the mixing of acids in the preparation of porous powders. The porous powder has nanopores with a diameter of about 11 nm produced under optimal conditions. The pore size of around 11 nm can provide a potential reduction of adsorbent consumption up to 33%. Clay which was thermally treated for 30 minutes increased the adsorption efficiency due to an increase in the number of meso pores.

Various acids are also used in clay modification. The HCl-modified clay was reported as unable to provide suitable adsorption efficiency for waste lubricant recovery but in contrast to sulfuric acid which was able to produce proper adsorption efficiency and acetic acid could act as a second agent in significantly increasing the acidity process.

Removal of used lubricant contaminants depends on powder/acid ratio and acidification residence time. The acidification residence time for 1 hour had almost no effect on contaminant removal but instead damaged the clay structure.

Shabanzade, *et al.* (2019) using adsorbent Ca-bentonite activated with sulfuric acid, hydrochloric acid, and acetic acid on contaminants from lubricant waste. Lubricant waste consists of fuel, glycol, hydrocarbons, sulfates, nitrates, oxidation products, and soot. The adsorption ratio will increase if the proportion of hydrochloric acid and sulfuric acid is increased and the adsorption ratio will decrease if the proportion of acetic acid is increased.

The optimal radiation time to achieve maximum dye absorption is 23 minutes. This encourages the formation of new pores to become less significant and the micropores or mesopores continue to widen to become larger. Microwave-activated bentonite increases the specific surface area while maintaining the layer structure thereby contributing to recovery efficiency. Microwaves can be used in the manufacture of adsorbents by controlling acetic acid in the range of 0-50% to produce an effective adsorbent in the purification of waste lubricants. Microwaves can shorten the residence time so that better efficiency is obtained compared to conventional methods.

Research conducted by Daham, *et al.* (2017) also used activated bentonite in the removal/absorption of ash contained in lubricant waste. Research method used in this research is solvent extraction followed by adsorption to obtain base lubricant from used lubricant. This study uses a central composite design (CCD) to simulate the sludge output from lubricant waste and to find the optimal conditions. The adsorption process in this study aims to separate the metals in used oil and then improve the color of the base oil extract and achieve the ash content for the base oil content according to Iraqi standards. The results obtained are:

1. Increasing the lubricant waste refining process variables using the Response Surface Methodology (RSM)
2. The re-purification method requires low energy because it does not require high temperature and low pressure
3. The extraction process is better with the use of 1-Butanol than MEK

4. The addition of MEA, KOH, and NaOH as flocculants proved the ability of butanol solvent to remove sludge in the extraction process
5. Increase in percent sludge removal from 12.6% to 14.7% with the addition of 2 g/kg MEA into the solvent
6. Bentonite/oil ratio of 15 wt/vol%, temperature of 120 oC, and contact time of 90 minutes are the best conditions for adsorption using activated bentonite

Fly Ash

Derkowski, *et al.* (2006) used zeolitic material produced from fly ash. A low-energy procedure proposed for synthesizing zeolitic materials from fly ash. This process involves the production of three different zeolite materials (X, P, and S) that are rich in specific zeolite phases, namely Na–X (FAU), NaP1 (GIS), and sodalite (SOD). The synthesis is achieved by using NaOH and NaCl solutions under atmospheric pressure at temperatures below 110 °C.

After synthesizing the zeolitic products, their composition and physicochemical properties are analyzed and compared to both the raw fly ash and commercial adsorbents. Experiments were carried out by mixing oil with a zeolytic adsorbent that had been synthesized at 20:1wt. ratio, storage 30 minutes at 50 °C for transformer oil or 70 °C for turbine oil. The purification efficiency (Eref) obtained was calculated using two methods, namely the reduction of acidity and the level of bleaching. The zeolitization process during adsorbent synthesis leads to a significant increase in cation exchange capacity (CEC), ranging from 5.5 to 239meq100g^{-1}. The zeolitic materials also exhibit a high ability to adsorb heavy metal ions (over 40mgg^{-1}) and retain complex and organic molecules, particularly material X. These properties make zeolitic products suitable for the adsorptive purification of waste and working lubricating oils, enabling their commercial applications in the petroleum industry.

The leachability of toxic elements from the zeolitic materials after standard post-reaction washing is found to be environmentally safe, ensuring compliance with environmental safety standards.

Fly ash has a higher absorption efficiency characteristic compared to activated clay. The results of research conducted by Ouyang and Zhang (2020) show that fly ash has a good effect on adsorption lubricant waste. The solvent extraction-adsorption process has a better effect on the regeneration of lubricant waste compared to the adsorption-solvent extraction process. Especially the isopropanol/isobutanol extraction process (isopropanol:isobutanol = 1:1, mass ratio) flyash-extraction is an optimal process for the regeneration of waste oil.

The experimental results show that the optimum process conditions for adsorption and regeneration of used oil with flyash are as follows: agitation time of 60 minutes, adsorption temperature of 90 °C, flyash dose of 12% and agitation rate of 950 r/min. The solvent-adsorption extraction process is superior to the solvent-adsorption-extraction process in terms of the regeneration effect of waste lubricating oil. Isopropanol/isobutanol solvent extraction (isopropanol:isobutanol = 1:1, mass ratio)-adsorption is an optimal process for waste oil regeneration, which increases the kinematic viscosity to 43.28 mm^2/s, acid number of 0.13 mgKOH/g, mechanical impurities of 0.12%, and moisture of 114 μg/g.

Activated Carbons from Palm Kernel and Coconut Shells

Opoku, *et al.* (2020) presented findings and analysis on the adsorption ability of activated carbon from palm kernel and coconut shells in removing contaminated heavy metals in used lubricating oil. Experimental results show that activated carbon produced from oil palm and coconut kernel shells has a significant adsorption capacity for heavy metals such as lead (Pb), cadmium (Cd), and mercury (Hg) in used lubricating oil. Analysis shows that this activated carbon is able to bind heavy metal ions on its surface, reducing the concentration of heavy metals in used lubricating oil.

In addition, this study also shows that activated carbon from oil palm and coconut kernel shells has a complex porous structure and a large surface area. This contributes to an increase in the adsorption capacity of activated carbon for heavy metals because the larger surface area provides more space for the interaction between activated carbon and heavy metals.

The research work conducted by Opoku, et. al. (2020) focuses on investigating the adsorption of heavy metal contaminants in used lubricating oil using chemically activated carbon adsorbents derived from palm kernel and coconut shells that was prepared by impregnation with 1 M of K2CO3 and NaHCO3 solution then left for 3 hours in the room temperature. The samples were subjected to activation for a duration of 40 minutes at a carbonization temperature of 800°C using a Carbolite Muffle Furnace. After activation, the produced activated carbons underwent a washing step with a 0.5 M glacial acetic acid solution. They were then rinsed thoroughly with distilled water until the pH of the samples reached a range of 6 to 7.

Following the washing and rinsing process, the samples were sun-dried and passed through a sieve with a mesh size of 500 μm. The portions of activated carbons retained on the sieve were further dried in an oven for 1 hour and subsequently stored in airtight containers

Samples used in this experiment are 3 months old used lubricating oil (A), 6 months old used lubricating oil (B), and virgin lubricating oil (C) as a control.

The results of the study as seen in Table 3 and Table 4 demonstrate the effectiveness of the adsorption mechanism using activated carbons from palm kernel and coconut shells in removing certain heavy metals, including zinc, cadmium, and magnesium from the used lubricating oil. For example, after the filtration process, the concentration of zinc decreases from 16.475±0.950 ppm to 10.375±0.171 ppm in sample A when treated with activated carbon adsorbent from palm kernel shell. Similarly, the concentration of zinc in sample B when treated with activated carbon adsorbent from palm kernel shell also decreases from 14.575±0.272 ppm to 5.450±0.3000 ppm.

The research also highlights that while coconut shell-activated carbon is effective in removing lead metals, palm kernel-activated carbon is not. The concentration if chromium can be reduced slightly using palm kernel shells but actually increased in sample B using coconut shell adsorbents. However, neither palm kernel nor coconut shell activated carbons are suitable for the removal of copper and iron metals, as indicated by the increase in their concentrations after the filtration process.

The equilibrium adsorption data obtained from the experiment were analyzed using the Langmuir isotherm model and high coefficient of correlation (R2) values were obtained for different heavy metals, including copper, cadmium, lead, chromium, iron, zinc, and magnesium. The high R2 values indicate a good fit of the Langmuir model to the adsorption data.

Based on the results and statistical analysis, it can be concluded that the Langmuir model provides a better fit for the adsorption data due to its high coefficient of correlation (R2 ≈ 1). Furthermore, the recovered oil from the process can potentially be reused.

Table 3. Mean, ±SD of virgin and used lubricating oil samples before and after filtration with Palm Kernel Shell

Samples	Control (C)		Sample A		Sample B	
	Before	**After**	**Before**	**After**	**Before**	**After**
Cu (ppm)	0.001±0.000	0.075±0.013	0.150 ±0.008	0.400±0.018	0.220±0.096	0.230±0.008
Fe (ppm)	1.502±0.092	1.150±0.129	4.650±0.159	8.500±0.258	3.350±0.289	3.400±0.183
Zn (ppm)	2.833±0.034	8.325±0.275	16.475±0.950	10.375±0.171	14.575±0.272	5.450±0.300
Cd (ppm)	0.020±0.008	0.000±0.000	0.020±0.008	0.018±0.009	0.030±0.008	0.000±0.000
Pb (ppm)	1.000±0.093	1.650±0.039	1.045±0.478	1.648±0.097	1.525±0.222	2.388±0.070
Cr (ppm)	0.410±0.051	0.065±0.013	0.400±0.065	0.210±0.026	0.445±0.039	0.135±0.013
Mg (ppm)	41.900±0.258	0.350±0.026	5.450±0.265	0.900±0.025	21.475±0.650	0.505±0.013

Table 4. Mean, ±SD of virgin and used lubricating oil samples before and after filtration with Coconut Shell

Samples	Control (C)		Sample A		Sample B	
	Before	**After**	**Before**	**After**	**Before**	**After**
Cu (ppm)	0.001±0.000	0.001±0.000	0.150 ±0.008	0.780±0.014	0.220±0.096	0.790±0.026
Fe (ppm)	1.502±0.092	3.650±0.625	4.650±0.159	13.500±0.942	3.350±0.289	14.125±0.618
Zn (ppm)	2.833±0.034	0.6700±0.071	16.475±0.950	5.838±0.344	14.575±0.272	5.400±0.280
Cd (ppm)	0.020±0.008	0.001±0.000	0.020±0.008	0.001±0.000	0.030±0.008	0.001±0.000
Pb (ppm)	1.000±0.093	0.563±0.172	1.045±0.478	0.410±0.037	1.525±0.222	0.438±0.222
Cr (ppm)	0.410±0.051	0.348±0.049	0.400±0.065	0.388±0.046	0.445±0.039	0.528±0.055
Mg (ppm)	41.900±0.258	1.475±0.171	5.450±0.265	3.625±0.222	21.475±0.650	0.645±0.037

Activated Alumina

Osman, *et al.* (2018) purified waste lubricating oil using a new mixture of solvent extraction and active alumina adsorbents. The solvent mixtures used were A (toluene, butanol and methanol (A), B (toluene, butanol and ethanol), and C (toluene, butanol and isopropanol) for extraction process. Extraction process using solvent A, B, and C then is followed by an adsorption process using activated alumina as an adsorbent.

The experimental results showed that extraction with solvent mixture A removed the maximum percent of sludge (52%) followed by solvent mixture B (36.7%) and solvent mixture C removed a lower percentage (18.9%). The raffinate percentage of the A solvent mixture was 48%, the B solvent mixture was 63.3%, and the C solvent mixture was 81.1%. The raffinate produced from the solvent mixture A is yellow because it is free of mud while the raffinate produced from the solvent mixture B and C is black due to the high solubility of the solvent mixture A, which is 23.2 (g/m^3)1/2 compared to the solubility of the solvent mixture B is 22.2 and the solubility of the C solvent mixture is 21.5 g/m^3. The dielectric constant of the solvent mixture A is higher than that of the solvent mixture B and C. Because the length of the chain of carbon atoms in the solvent decreases and the polarity decreases, its ability to remove sludge increases.

The solvent mixture A has higher solubility and dielectric constant, so it has maximum efficiency for sludge removal. Methanol removes more heavy components than ethanol and isopropanol because of its higher dielectric constant.

The use of activated alumina improves the color quality of the used oil for the three types of solvent mixtures, namely turning yellow. Raffinate percentage and sludge percentage in used oil are not much different for the three solvent mixtures.

The adsorption behavior of alumina ions (Al_2O_3) arises from the hydroxyl groups on the acid-base surface. This protonation and deprotonation of surface hydroxyl groups influence the surface oxide to develop electrical charges that promote adsorption. The exchange of cations and anions occurs at the hydroxyl sites of acids (–OH) and bases (–OH).

Solvent extraction refined oil and activated alumina were also analyzed according to standard methods in ASTM for density, carbon residue, ash content, pour point, water content, sulfur content, viscosity, and total acid content.

The analysis results show that the density of used oil before being treated is higher than refined oil due to the presence of sludge and a higher percentage of sulfur compounds. Used oil's pour point is lower than that of refined oil. All measured properties have been upscaled to reasonable values such as moisture content, ash content, carbon residue and sulfur content. The ash content value indicated the presence of metal impurities which had been reduced by 89.5% in raffinate oil in solvent mixture A. The acid value also decreased because organic, inorganic acids, esters, phenolic compounds, lactones, and resins had been properly separated. The viscosity of refined oil has increased due to the conversion of impurities in the used oil. The sulfur content decreased from 0.82 wt% for used oil to 0.64, 0.67, 0.666 wt% for solvent mixtures A, B and C respectively. It can be seen that the properties of the refined oil have the best performance.

Kaolin

Ahmed, *et al.* (2020) synthesized natural zeolite Y kaolin via ultrasonic-assisted hydrothermal technique. The results of the synthesis are used as adsorbents to adsorb waste lubricants. Parameters of recycled engine oil such as flash point, dynamic viscosity, kinematic viscosity, viscosity index, pour point, sulfur content, heavy metal content, sulfur content, ash content and carbon residue were analyzed and compared with pure and waste oils. The results showed that zeolite Y adsorbents efficiently removed heavy metals, especially chromium, copper, iron, lead, and zinc which were present in waste engine oil. Removal efficiency of 35.71% Cr^{3+}, 66.67% Cu^{2+}, 92.17% Fe^{2+}, 63.02% Pb^{2+} and 95.24% Zn^{2+} were obtained for Zeolite Y at 25 ^{o}C while 47.14% Cr^{3+}, 76.19% Cu2+, 92.93% Fe2+, 70.70% Pb2+ and 96.31% Zn2+ were obtained for Zeolite Y at 40 oC.

Furthermore, the viscosity index of the waste oil treated with zeolite Y was reduced to 327, compared to the viscosity index of virgin oil (326) and untreated waste oil (336). This suggests that the zeolite Y treatment improves the viscosity properties of the recycled oil.

Limitation of this study is sample sizes that are too small can not adequately support claims of having achieved valid conclusions about effectivity of adsorbent material.

Conclusion

Adsorption of used lubricants using sawdust, activated bentonite, fly ash, activated carbon, activated alumina, and kaolin are several options that are feasible to be developed in further research. The adsorption capacity of the modified sawdust increased in the adsorption of Si, Fe, Cu, as well as aromatic and oxidation products because of the presence of hydroxyl groups. Bentonite with various modifications can reduce contamination in used lubricants such as color, contaminants, hydrocarbon products, and ash. Other materials, namely fly ash, can also reduce heavy metal ions and other impurities in used lubricants, which have a higher adsorption efficiency than activated clay. This is one of the potentials that can be developed in the future. Activated carbon from palm kernel and coconut shells can be used as high-performance adsorbents with a higher adsorption capacity for various heavy metal in used lubricating oil such as Zn, Cd, Cr, and Mg. Activated alumina can be used as adsorbent for carboxylic acid of organic compound. Zaolite Y derived from kaolin is effective in heavy metals removal from waste engine oil in higher temperature.

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