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Research Article

Purification of waste engine oil using raw clay, acid treated clay and clay/activated charcoal

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ABSTRACT

The purification of waste engine oil was conducted utilizing locally available clay in three different forms: raw, acid-treated, and a mixture of clay with activated charcoal. A 72.6% and 70.12% purification efficiency has been achieved when employing raw and acid-treated clay, respectively. However, the purification yield decreased to 64.35% when utilizing a combination of acid-treated clay and activated charcoal. FTIR analysis confirmed the presence of alkanes and alkenes in the purified oil. The NMR and GC-MS analysis identified the presence of linear and branched alkanes and alkenes, as well as substituted-benzene compounds in the purified oil. The density of waste engine oil and the corresponding purified oil was determined to be 0.929 g/mL and 0.825 g/mL, respectively. After purification, the kinematic viscosity decreased from 192 mm^2/sec to 70 mm^2/sec at 40 °C. The AAS analysis revealed the presence of 13.28 mg/L of lead (Pb) and 91.56 mg/L of chromium (Cr) in the waste engine oil, which significantly decreased to 0.02 mg/L and 0.037 mg/L, respectively, after purification with clay mixed with activated charcoal.

Introduction

Lubricating oil, whether mineral or synthetic, plays crucial roles in minimizing friction, preventing wear and rust, dissipating heat, and purging contaminants from the engine (Kupareva et al., 2013b; Pinheiro et al., 2021; Sarkar et al., 2023). It is commonly referred to as motor or engine oil in vehicle engine applications. Typically, lubricating oil consists of 80–90% base oil and 10-20% additives (Islam et al., 2021). Base oil can be derived from either mineral oil (mineral base oil) or synthesized (synthetic base oil). Due to the lower cost of mineral oil, approximately 85% of the world's lubricant oil supply is obtained from mineral base oil, which is primarily composed of paraffinic hydrocarbons, including saturated linear (n-paraffin) and branched (iso-paraffin) alkanes (Pinheiro et al., 2021).

Lubricating oil typically comprises 86% base oil, 5% viscosity index improver (polyisobutylene, polymethacrylate), 1% oxidation inhibitor (zinc dialkyl, dithiophosphate), 4% detergent (barium and calcium sulphonates or phenates), and 4% multi-functional additives (dispersant and pour point depressant) (Kupareva et al., 2013b). The base oil, primarily composed of mineral hydrocarbons ranging from C_{18} to C_{40} (Prince, 2010; Pinheiro et al., 2021), includes n-paraffin (saturated linear alkanes), iso-paraffin (branched alkanes), naphthenes (cycloalkanes), and aromatics with boiling points ranging from 300 to 565 °C (Mang and Lingg, 2017; Pinheiro et al., 2021). Synthetic alternatives, such as polyalphaolefins (PAO), synthetic esters, and

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polyalkylene glycols (PAG), have also been developed (Pinheiro et al., 2021).

Globally, lubricating oil production reached 35.7 million tons in 2017 (Pinheiro et al., 2021). In Europe alone, consumption is approximately 5.7 million tons annually (Kupareva et al., 2013b). However, this consumption generates 2.7 million tons of waste lube oil per year in Europe, with only 0.7 million tons undergoing proper waste oil treatment (Kupareva et al., 2013b). In Bangladesh, a developing country, annual consumption stands at 0.16 million MT tons (Islam et al., 2021), yet only a limited quantity of engine oil is recycled. Unfortunately, a significant portion of used engine oil in Bangladesh is disposed of indiscriminately in drains and soil. This unregulated disposal substantially threatens the local flora and fauna and undermines ecosystem health.

Lubricants used in internal combustion engines degrade over time due to the breakdown of additives and the buildup of sludge and water. However, Mineral-based oil remains stable and resistant to oxidation (Kajdas, 2014). Waste lubricants also contain heavy metals such as lead (Pb), chromium (Cr), iron (Fe), zinc (Zn), calcium (Ca), and organic compounds like polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB), among others. The environmental impact of waste engine oils is significant as they are non-biodegradable and can hinder plant growth if disposed of in soil, potentially introducing toxic heavy metals such as lead and chromium into the food chain (Morkunas et al., 2018; Pinheiro et al., 2021). Additionally, dumping waste engine oil into water creates an organic film that impedes the oxygenation of aquatic organisms, exacerbating the adverse effects on the environment (Pinheiroet al., 2021).

As base oil remains unchanged in the waste lubricating oil, several methods have been developed to recover base oil from waste lubricant (Kajdas, 2014). A typical refining process comprises four stages: dewatering and defueling (to remove water and light hydrocarbons), de-asphalting (to remove asphalt using sulfuric acid or solvent extraction process), finishing (to improve the oil color and oxidation stability by clay treatment or hydro finishing), and fractionation to obtain base oil (Kupareva et al., 2013b).

The acid/clay process, first introduced in the US during the 1960s (Dang, 1997; Kupareva et al., 2013b; Pinheiro et al., 2021), involves pre-treating waste engine oil through processes like pre-flash or vacuum distillation to separate water and light hydrocarbons. Then, concentrated H_2SO_4 (10-15 wt %) is added to dehydrate waste oil, causing additives and sulfides to precipitate as sludge (deasphalting). Clay treatment is followed by removing organic acids and waxy substances, and the oil undergoes filtration and distillation to yield base oil (Kupareva et al., 2013b). While this process achieves 62-63% purification, the resulting oil is dark in color and has a noticeable odor (Kupareva et al., 2013b). However, challenges associated with the disposal of acid sludge and spent clay (Pinheiro et al., 2021) make this process an unpopular treatment choice. Jafariand Hassanpour(2015) mentioned that acidic sludge, a by-product of the acid/clay process, can be used as a raw material for bitumen production.

To overcome the limitations of the acid/clay process for the purification of the waste lubricant, several alternative technologies have been developed, such as Mineralöl-Raffinerie Dollbergen GmbH (MRD) solvent extraction process, Vaxon process, CEP process, Ecohuile process, Cyclon process (KTI process), Revivoil process, Snamprogetti process/IFP technology, Hylube process, Interline process (Dang, 1997; Audibert, 2006; Kupareva et al., 2013b; Kajdas, 2014; Pinheiro et al., 2021).

The Mineralöl-Raffinerie Dollbergen GmbH (MRD) solvent extraction process employs the liquid-liquid extraction principle. In the Mineralöl-Raffinerie Dollbergen GmbH (MRD) solvent extraction process, water is removed from the waste lubricating oil by dewatering it, and then light hydrocarbon is removed by vacuum distillation. In the following step, the steam-absorption process removes dissolved oxygen (O_2) from the distillate.

The distillate then enters a solvent extraction column, where the distillate combines with N-methyl-2-pyrrolidone (NMP) solvent. The aprotic NMP solvent exhibits a selective affinity for unsaturated hydrocarbons, aromatic hydrocarbons, polycyclic aromatic hydrocarbons (PAH), and sulfur compounds. The solvent containing the raffinate phase is collected at the top of the extraction column. Base oil is recovered after solvent removal in the stripping column. This process achieves an average base oil yield of 84-92% and produces high-quality base oil (Kupareva et al., 2013b; Pinheiro et al., 2021). Re-refining the used lubricating oil by vacuumdistillation/thin wiped film evaporation technique has also been developed (Saleemand Karim, 2020).

In this work, we have replaced the clay/acid process with clay/activated charcoal to avoid the formation of acid sludge. Clay/activated charcoal is effective at adsorbing heavy metals such as lead and chromium and removing degraded additives from waste engine oil.

Materials and methods

Clay was collected fromBijoypur village of Durgapurupazila of Netrokona district, Bangladesh. Activated charcoal was purchased from Loba Chemie PVT. Ltd: India and sulphuric acid from Sigma Aldrich.

2.1 Preparation of acidified clay

A mixture of 40.0 g clay and 400.0 mL sulfuric acid (1 M) was refluxed at 140 °C for 4 hours. The solution was then cooled to room temperature, and the resulting suspended materials were filtered and washed with distilled water to eliminate excess acid and soluble metal salts. Then, the washed suspension was dried at 100 °C for 14 h and calcined at 550 °C for 14.5 h in a muffle furnace. The resultant catalyst weighed 26.9 g of clay.

2.2 Characterization Techniques
Characterization of local clay

The prepared catalyst underwent comprehensive characterization employing various techniques, including X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), x-ray fluorescence (XRF), and Fourier transform infrared (FTIR) spectroscopy. XRD analysis of clay was performed using the GNR Explorer powder X-Ray diffractometer with Cu-Kα1 source at 35 KV and 25 mA and step size of 0.1^{o} with data integration time 3s per step over an angular range of 5–80° (2θ).The irradiation source was Rh x-ray at 140 mA and 30 kV. SEM images of clay and activated charcoal were obtained using the JEOL-SEM 7600F, sputtered with gold before analysis. Elemental analysis was conducted using the Shimadzu XRF-1800 (Lab Center) instrument, with a 1.0 g sample mixed and ground with 0.25 g of boric acid, followed by palletization. FTIR analysis of engine oil was conducted on the Shimadzu 8400S, Japan, with KBr pellets heated at 100 °C for 1 day before analysis, covering the 400-4000 cm^{-1} range.

Characterization of engine oil

The purified engine oil was comprehensively analyzed through GC-MS, FTIR, and ^{1}H NMR spectroscopy. GC-MS/MS analysis was performed using the Shimadzu GCMS-TQ8040, with a 0.5 μL sample injected in splitless mode on a capillary column Rxi-5ms (30 m × 0.25 mm id). The injection temperature was 250 °C, and the oven temperature program ranged from 50 °C to 300 °C. The column's flow rate and total run time were 1 mL/min and 30 min, respectively, utilizing electron impact ionization for MS detection (full scan mode 50-550 m/z). A quadrupole mass analyzer was used in GC-MS analysis. Hydrocarbon identification was performed using computer-assisted mass spectral search by NIST-MS library 2009.

Additionally, ^{1}H NMR analysis of the engine oil was conducted using the Bruker AVANCE III HD (400 MHz) instrument. A VARIAN AA240FS, atomic absorption spectrometer, was used to determine the amount of lead and chromium. The analysis mode was flame AAS mode. For the analysis of lead (Pb), a single lamp with a maximum current was 12 mA and a slit of 1.0 nm with a wavelength of 217 nm was used. For the analysis of chromium (Cr), a multi-lamp with a slit of 0.2 nm and wavelength was 357.9 nm was used. For the analysis of both metals (Pb and

Cr), the calibration curve was developed in the range of 0.1 to 2.5 ppm, and a new rational regression equation was used for the best fit of the curve. The BET-specific surface area and pore volume were determined by measuring nitrogen adsorption-desorption isotherms atliquid N_2 temperature (-196 °C) with a PMI's BET-Sorptometer (BET-201A, USA) apparatus. Before BET analysis, the samples were degassed at 120 °C under vacuum for 1.5 hours. Data obtained from the BET-Sorptometer were analyzed using BETwin software.

2.3 Purification of waste engine oil

2.3.1 Purification of waste engine oil using raw clay

500 mL waste engine oil and 100 g raw clay were mixed in a 1 L round bottle flask. The mixture was heated on a heating mantle and distilled. The distillate started transferring in the receiving flask at 80 °C and continued transferring until reaching 300 °C. The volume of the purified oil obtained was 440 mL, corresponding to a yield of 72.6%.

2.3.2 Purification of waste engine oil using 1 M H_2SO_4 treated clay

100 mL waste engine oil and 20 g acid-treated clay were mixed in a 1 L round bottle flask. The mixture was heated on a heating mantle and distilled. The distillate started transferring in the receiving flask at 100 °C until reaching 255 °C. The volume of the purified oil obtained was 85 mL, corresponding to a yield of 70.12%.

2.3.3 Purification of waste engine oil using activated charcoal and 1 M H_2SO_4 treated clay

Like the method above, 100 mL waste engine oil, 20 gacid-treated clay, and 20 g activated charcoal were mixed in a 1 L round bottle flask. The mixture was heated on heating mantle and distilled.

The distillate was heated on the heating mantle and distilled. It started to be transferred in the receiving flask at 89 °C and continued transferring until reaching 270 °C. The volume of the purified oil obtained was 78 mL, corresponding to a yield of 64.35%.

2.4 Sample preparation for metal analysis by atomic absorption spectroscopy (AAS)

A 5 g oil sample was heated in a porcelain cup at 105 °C for 3 hours. The oil was further heated in a muffle furnace at 600 °C to convert into ash. The ash was dissolved with 5 mL of concentrated HNO_3 acid and 5 mL of concentrated HCl. The resulting solution was heated until no visible smoke was observed. The solution was transferred to a 100 mL flask, and distilled water was added to achieve a final volume of 100 mL.

Results and Discussion

Characterization of local clay

The chemical compositions of raw clay (Bijoypur) and sulfuric acid-treated clay were determined by XRF (Table 1). The raw clay contains 56.60 % SiO_2 and 38.70 % Al_2O_3. The Si/Al ratio of raw clay is 2.57.

The sulfuric acid treatment increased SiO_2 content to 61%, followed by a decrease in Al_2O_3 content to 34.6%. This shift is attributed to the leaching of Al^{3+} ions from the raw clay, resulting from hydrolysis under acidic conditions. The reaction between clay and sulfuric acid is as follows:
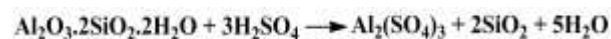
$$Al_2O_3.2SiO_2.2H_2O + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 2SiO_2 + 5H_2O$$

Table 1. Compositions (%) of raw clay and 1M H_2SO_4 treated clay by XRF.

Clay (Bijoypur Durgapur)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	MgO	SO_3	Si/Al
Raw clay	56.60	38.70	1.61	1.36	0.81	0.35	0.25	0.14	2.57
1 M H_2SO_4 treated clay	61.00	34.60	0.78	1.26	0.75	0.25	0.24	0.97	3.11

After acid treatment, the Si/Al ratio increased from 2.57 to 3.11. This increase indicates a decrease in the clay's acidity.

The SEM analysis (Fig. 1) provides insights into the morphology of clay and activated charcoal. Particle aggregation is evident in the SEM image of raw clay (1a). Following the 1 M H_2SO_4 treatment of clay (1b), surface roughness increased due to etching, generating smaller particles and an increased inter-particle distance. Notably, the SEM image of activated charcoal (1c) exhibits the presence of numerous voids, indicating the potential for metal adsorption.

The XRD analysis of raw clay (Fig. 2a) reveals that the clay is predominantly composed of silica (quartz) and a small amount of muscovite characterized as potassium aluminum silicate hydroxide, $(KAl_2(AlSi_3O_{10})(OH)_2)$. The major 2θ peaks are 19.83°, 20.93°, 26.72°, 36.61°, 39.54°, 42.51°, 50.20°, 60.02°, 68.19°, and 68.38°. Due to acid treatment of raw clay (Fig. 2b), de-alumination occurred without altering crystallinity. The major 2θ peaks of acid treated clay were observed at 19.75°, 20.91°, 26.71°, 36.61°, 39.52°, 50.19°, 60.02°, and 68.19°.
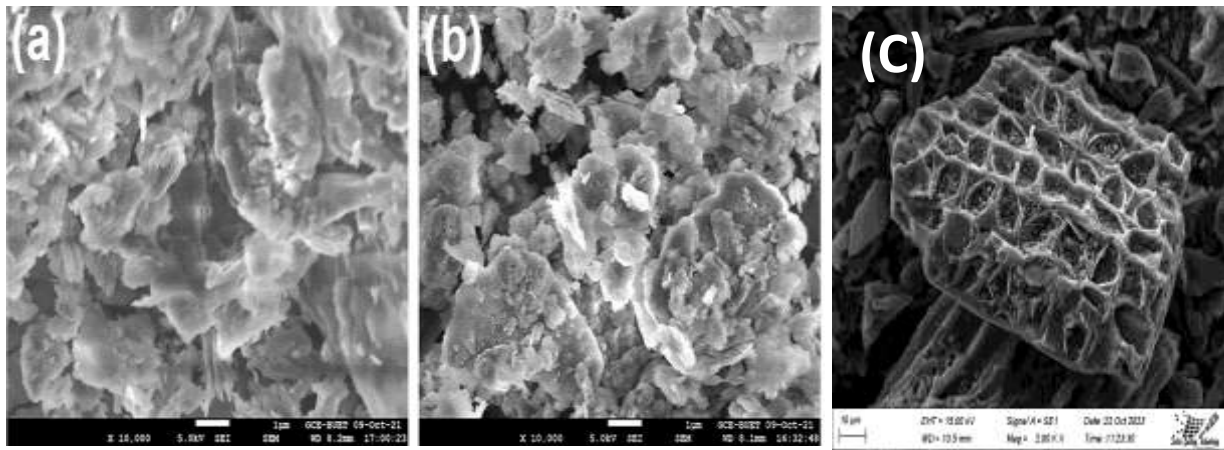

Fig. 1. Scanning electron microscope (SEM) image of (a) raw clay, (b) 1 M H_2SO_4 treated clay, and (c) activated charcoal.
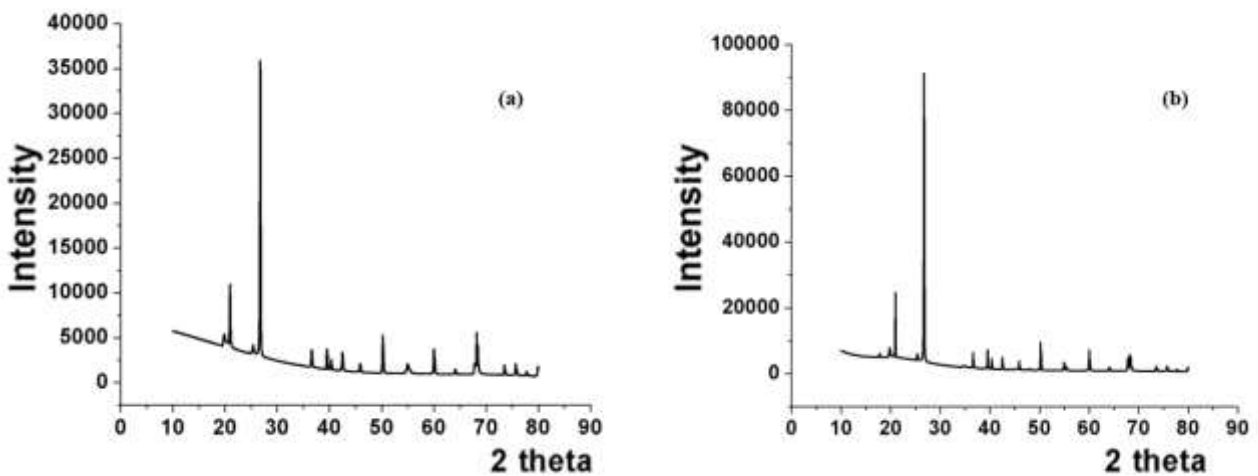

Fig. 2. XRD of raw clay (a) and 1 M acid-treated clay (b).

The BET analysis shows that the specific surface area has increased from 28.38 m^2/g to 576.80 m^2/g due to the mixing of acid-treated clay with the activated charcoal (Table 2). Similarly, the total pore volume of acid-treated clay has risen from 0.0758 cc/g to 0.4074 cc/g after mixing with the activated charcoal. The N_2 adsorption/desorption isotherms of acid-treated clay and a mixture of acid-treated clay and activated charcoal are shown in Fig. 3, displaying a type IV isotherm characteristic of mesoporous materials.
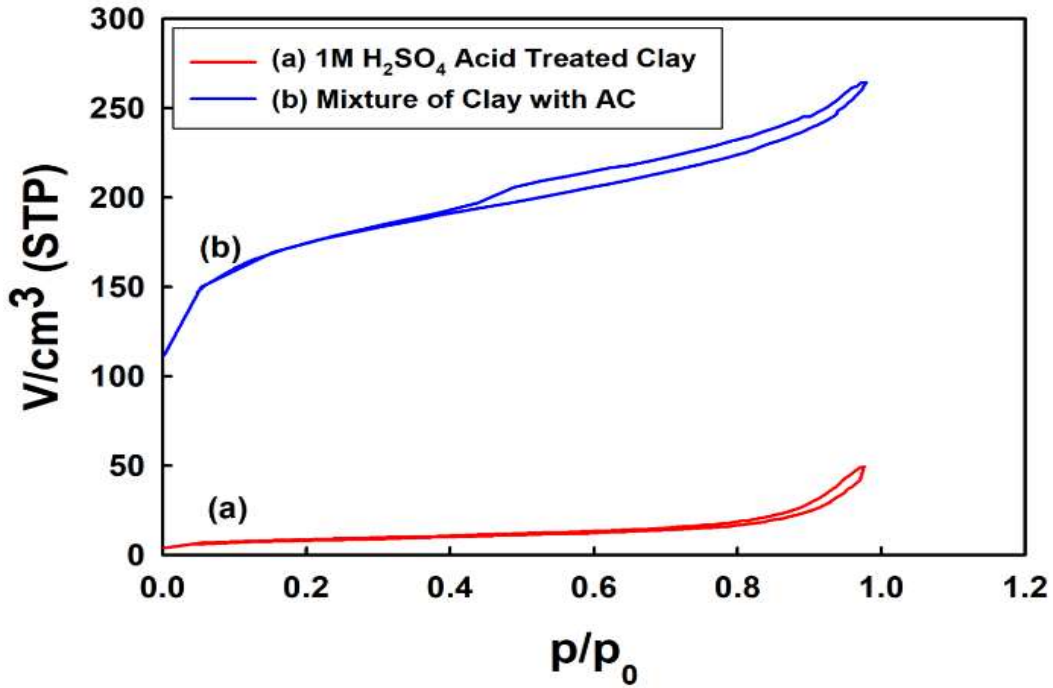

Fig. 3. N_2 adsorption/desorption isotherms of (a) 1 M acid-treated clay and (b) a Mixture of acid-treated clay with activated charcoal (AC).

Table 2. BET results of acid-treated clay and a mixture of acid-treated clay and activated charcoal

Parameter	BET specific surface area (m^2/g)	Total pore volume (scc/g)
Acid treated clay	28.38	0.0758
A mixture of acid-treated clay and activated charcoal	576.80	0.4074

Analysis of purified waste engine oil

Fig. 4 illustrates the color of engine oil before and after the purification process. Note, that the visual analysis indicates an improvement in opacity in the waste engine oil purified by clay/activated charcoal (A) in comparison to the engine oil purified exclusively by acid-treated clay (C). Table 3 outlines the purification outcomes for waste engine oil using raw clay, yielding 72.6% purified oil. Subsequently, applying 1 M sulfuric acid-treated clay resulted in an oil purification of 70.12%. However, the clay/activated charcoal process reduced oil yield, resulting in a 64.35% purified oil.

Fig. 5 represents the FTIR analysis of oil purified by clay/activated charcoal, indicating the presence of alkanes and alkenes in the oil. The C-H stretching of methyl and methylene groups within the alkane structure is discernible at 2959 cm^{-1}, 2931 cm^{-1}, and 2857 cm^{-1}. Additionally, the spectral peak at 1649 cm^{-1} and 1455 cm^{-1} correspond to C=C stretching and C-H scissoring, respectively. Furthermore, the C-H bending is evident at 735cm^{-1}. A similar FTIR spectrum was observed for oil purified by clay only.
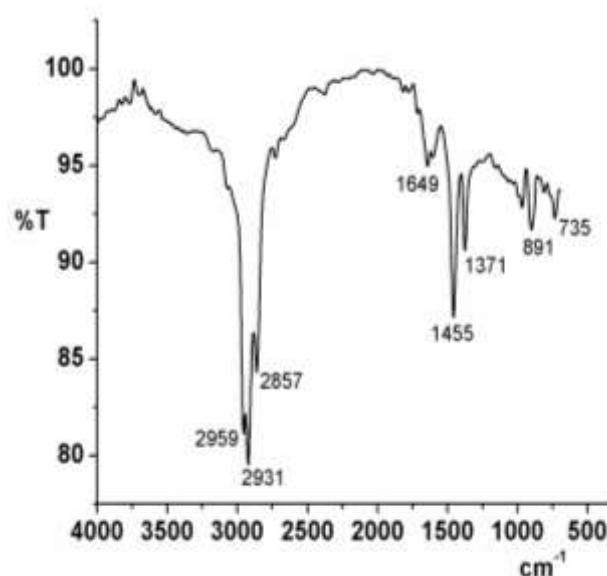

Fig. 4. Picture of engine oil purified by clay/ activated charcoal(A), waste engine oil(B), and engine oil purified by acid-treated clay (C).

Fig. 5. FTIR of purified engine oil by clay/ activated charcoal.

Table 3. Purified engine oil obtained from raw clay, acid-treated clay, and clay/activated charcoal. The density of purified engine oil is 0.825 g/ml.

Clay	Volume of waste engine oil (mL)	Mass of Clay (g)	Mass of activated charcoal (g)	Purified oil obtained (mL)	Mass of purified oil (g)	%Yield
Untreated clay	500	100	-	440	363	72.6
1M H$_2$SO$_4$ treated clay	100	20	-	85	70.12	70.12
1M H$_2$SO$_4$ treated clay	100	20	20	78	64.35	64.35

Kupareva et al., 2013a analyzed fresh and used automotive lubricating oil by FTIR spectroscopy. They reported that fresh and used motor oil contained mostly saturated compounds consisting of linear and branched-chain paraffin. Notably, the FTIR spectrum of the fresh and used oil possessed bands at 2954 - 2856 cm⁻¹, an intense band at 1463 cm⁻¹, and a less intense band at 1376 cm⁻¹, attributable to C-H vibrations. Fresh lube oil contains oxygen-containing functional groups used as friction modifiers or lubricity additives. These friction modifiers are generally polar molecules consisting of a polar functional group (ketone, ester, carboxylic acid) and a nonpolar hydrocarbon tail (Kupareva et al., 2013a). Kupareva et al. (2013a) found bands at 1747 and 1701 cm⁻¹ in the fresh oil, which arose from carbonyl groups of esters, ketones, or acids. They further inferred that the band at 1747 cm⁻¹ originated from five and seven-membered cyclic ketones while that at 1701 cm⁻¹ arose from polymethacrylate presented in fresh oil. Polymethacrylate is a viscosity modifier and a pour-

point depressant additive in fresh oil. Al-Ghoutiand Al-Atoum (2009) found thatpolymethacrylate typically arose at 1701 cm⁻¹ and 1154cm⁻¹ in the fresh oil. However, no bands at 1747, 1701 cm⁻¹, and 1154 cm⁻¹ were observed in our engine oil purified by clay/activated charcoal. In another study, Dominguez-Rosado andPichtel (2003) investigated used motor oil by FTIR and detected bands at 1704.29 cm⁻¹ and 1603.13 cm⁻¹ indicating the presence of carbonyl groups of esters, ketones, or acids. They also observed peaks at 869 cm⁻¹, 813cm⁻¹, and 1603 cm⁻¹ originating from aromatic hydrocarbons, including polycyclic aromatic hydrocarbons.

Fig. 6 represents the NMR spectrum of the engine oil purified by clay/activated charcoal. The NMR indicates the presence of aromatic protons, as evidenced by the multiplets, at around 7.5 ppm. Multiplets in the 1-2.5 ppm range are attributed to various alkane substituents. A comparable spectrum was observed in the NMR analysis of oil purified using only clay.
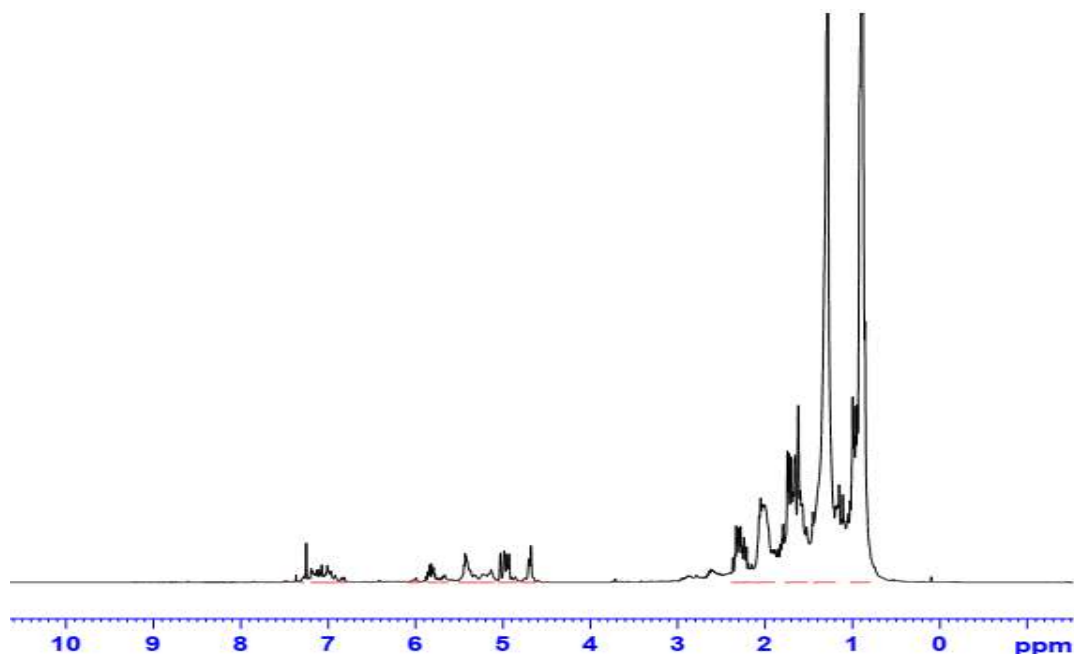

Fig. 6. NMR of purified engine oil by clay/activated charcoal.

Kupareva et al. (2013a) investigated fresh and used automotive lubricating oil by ^{1}H NMR spectroscopy. The authors reported that fresh and used oil showed aromatic protons at δ 6.95-7.05 ppm and 6.75-7.2 ppm, respectively. The olefinic protons arose at 5.65-5.5 ppm in fresh oil and 5.1-5.3 ppm in used oil. The CH_3-C proton was found at 0.9-0.8 ppm in fresh and used oil (Kupareva et al., 2013a). The researchers also reported that the fresh oil contained two high-intensity singlets at δ 5 ppm and 4 ppm and a less intense doublet at δ 4.8 ppm, indicating the presence of esters. However, no high-intensity singlet peak at 5 ppm was observed in the used lube oil. The NMRspectrum of the used lube oil showed a low-intensity singlet at 4ppm, which arosefrom esters. As reported by the study, a higher amount of esters (carbonyl groups) were present in fresh oil than in used oil. The used oil showed a broad peak at δ 2.6 ppm, which originated from organic acids formed via the chemical oxidation process in the used lube oil. In this study, we did not observe any intense singlet peak at δ 5 ppm and 4 ppm in our purified oil by clay/activated charcoal. This indicates the absence of the ester compounds in the purified oil. Aromatic protons and various alkane substituents (CH_3-C protons and –C-CH_2-C protons) were observed in the oil purified by clay/activated charcoal.

The GC-MS analysis of engine oil purified by clay/activated charcoal has been presented in Table 4. The GC-MS results confirm the presence of linear and branched alkane and alkene and substituted benzene compounds. The most notable compounds include octane, 1-octene, 2-methyl octane, 3,3-dimethyl butyl benzene, 1-nonene, 1-decene, 1,2,3-trimethyl benzene, 2-methyl-1-propenyl benzene, octadecane, 1-heptadecene, and 4-propyl heptadecane.

Kupareva et al. (2013a) conducted a comprehensive GC-MS analysis of fresh motor oil and used lube oil without purification. They reported that used lube oil contained gasoline components, short hydrocarbons, cyclic paraffins and aromatics with chain lengths ranging from C_{16} to C_{32}. However, fresh motor oil contains mostly hydrocarbons of longer chains. Both fresh motor oil and used motor oil contained alkylated diphenylamines (such as butyl-diphenylamine and octyl-diphenylamine) which was used as antioxidant additives. However, phenolic antioxidant (such as 4,4′-methylenebis(2,6-di-*tert*-butylphenol)) found in fresh oil was not observed in used motor oil. Naphthalene was found in used oil which is absent in fresh motor oil. In another study, Dominguez-Rosado et al. (2003) analysed fresh and used motor oil by GC/MS. They reported that used motor oil contained some new aliphatic and aromatic hydrocarbon compounds which were not present in the fresh motor oil. The identified new compounds in used motor oil were 1,3,5-trimethyl benzene, p-xylene and methyl ester undecanoic acid. The researchers also reported that substituted-benzene compounds and naphthalene-related compounds are more predominant in the used motor oil. In this study, various substituted-benzene compounds were observed in the purified engine oil. However, methyl ester undecanoic acid was not observed in our purified engine oil. During clay and activated charcoal treatment, some new compounds were observed other than methyl ester undecanoic acid.

To investigate the presence of heavy metals, specifically lead (Pb) and chromium (Cr), in both waste engine oil and purified engine oil, atomic absorption spectroscopy (AAS) was employed. According to the findings from the atomic absorption spectroscopy (AAS) (Table 5), the waste engine oil contained 13.28 mg/L of lead (Pb) and 91.56 mg/L of chromium (Cr). These concentrations were reduced to 4.36 mg/L for lead (Pb) and 0.35 mg/L for chromium (Cr) in the purified engine oil after purification by the acid-treated clay. However, a more significant reduction in lead (Pb) and chromium (Cr) concentrations was observed upon purification with the clay and activated charcoal mixture.The resulting lead (Pb) and chromium (Cr) content in the oil purified by clay mixed with activated charcoal was 0.02 mg/L and 0.037 mg/L, respectively

Table 4. GC-MS of purified engine oil by clay/activated charcoal.

Compound	Retention time	Area (%)
1-Octene	3.251	0.48
Octane	3.375	0.89
1,4-Pentadiene, 2,3,3-trimethyl-	3.502	0.31
Cyclopentane, 1-methyl-2-(2-propenyl)-, trans-	3.957	0.28
1-Heptene, 2,6-dimethyl-	4.195	0.30
Octane, 2-methyl-	4.499	0.28
Benzene, (3,3-dimethylbutyl)-	4.626	1.18
Tridecane, 7-methylene-	4.932	0.47
1-Nonene	5.054	0.39
O-Xylene	5.09	0.47
Hexane, 2,4-dimethyl-	5.244	1.06
Octane, 2,6-dimethyl-	6.034	0.26
1-Decene	7.548	0.54
Benzene, 1,2,3-trimethyl-	7.611	0.51
Decane	7.789	0.92
Cyclopentane, pentyl-	8.785	0.28
4-Decene, 5-methyl-, (E)-	10.202	0.53
1-Undecene	10.406	0.62
Dodecane, 2,6,11-trimethyl-	10.659	1.28
Benzene, (2-methyl-1-propenyl)-	12.032	0.67
Heptane, 4-(1-methylethyl)-	12.238	0.54
Undecane, 4-methyl-	12.408	0.54
Octadecane	12.561	0.45
Cyclohexane, 2-propyl-1,1,3-trimethyl-	13.198	0.47
Cyclopropane, nonyl-	13.377	0.61
Dodecane, 2,6,10-trimethyl-	13.629	1.32
Undecane, 3,6-dimethyl-	13.998	0.44
Tridecane, 2-methyl-	15.666	0.40
3-Tetradecene, (E)-	16.29	0.86
Nonane, 5-butyl-	16.52	1.42

Compound	Retention time	Area (%)
Dodecane	17.908	0.39
2,3-Dimethyldodecane	18.128	0.31
1-Tridecene	19.066	0.56
Octadecane, 5-methyl-	19.284	1.56
Tetradecane, 2-methyl-	20.961	0.36
2-Methyl-1-tetradecene	21.527	0.26
1-Pentadecene	21.702	0.40
Nonadecane	21.905	1.57
Hexadecane, 7,9-dimethyl-	23.058	0.26
Pentadecane, 4-methyl-	23.336	0.42
Pentadecane, 3-methyl-	23.665	0.28
1-Eicosene	25.27	0.37
Pentadecane, 2,6,10-trimethyl-	25.504	1.14
Tetradecane, 5-methyl-	25.6	0.34
Pentadecane, 8-hexyl-	26.75	1.34
1-Heptadecene	28.839	0.42
Nonadecane, 9-methyl-	31.946	0.33
Pentacosane	33.725	0.47
Triacontane	34.064	0.42
Eicosane	34.313	1.31
Heptadecane, 4-propyl-	34.37	0.45
Nonadecane, 4-methyl-	34.47	0.48
Tetratetracontane	34.513	0.72
Eicosane, 2-cyclohexyl-	34.65	0.72
Tetracontane	34.834	0.82
Dodecane, 1-cyclopentyl-4-(3-cyclopentylpropyl)-	34.885	0.76
Undecane, 4-cyclohexyl-	34.92	0.40
Hexadecane, 2,6,10,14-tetramethyl-	34.99	1.01
hexacosane	35.03	2.27
Hexadecane, 4-methyl-	35.155	0.93
Hexacontane	36.144	4.33
Hexadecane	36.73	1.70
Tetracosane	37.042	2.23
Dodecane, 6-cyclohexyl-	38.01	0.25

Activated charcoal effectively adsorbs lead (Pb) and chromium (Cr), reducing their quantity in the purified oil. BET analysis revealed an increase in specific surface area and total pore volume in the clay and activated charcoal mixture, facilitating the effective adsorption of Pb and Cr.

Table 6 presents the fuel parameter values for both waste engine oil and purified engine oil. The density of waste engine oil and the corresponding purified oil was determined to be 0.929 g/mL and 0.825 g/mL, respectively. The initial calorific value of the waste engine oil was 8530.81 KCal/Kg.

The purified engine oil exhibited an increased calorific value of 10633 KCal/Kg, as determined by a bomb calorimeter. The kinematic viscosity values at 40 °C decreased from 192 mm²/sec for waste engine oil to 70 mm²/sec for the purified oil. The flash point of the waste engine oil and the purified oil were 109 °C and 158 °C, respectively. The lower value of flash points observed in used oil was attributed to light fuels (Abro et al., 2013; Abdulkareem et al., 2014). Table 7 presents the accepted values of quality assurance of re-refined base oil (Kupareva et al., 2013b; Abdulkareem et al., 2014).

Table 5. Amount of metal contents in waste and purified engine oil (*Data obtained by Absorption spectroscopy* (*AAS*).

Metal	Waste engine oil (mg/L)	Purified engine oil	
		Acid treated Clay (mg/L)	Acid treated clay and activated charcoal (mg/L)
Lead (Pb)	13.28 ± 1.13	4.36 ± 0.37	0.02 ± 0.002
Chromium(Cr)	91.56 ± 8.95	0.35 ± 0.03	0.037 ± 0.004

Table 6. Different parametric values of waste engine oil and purified engine oil

Parameter	Method	Waste engine oil	Purified engine oil with clay/charcoal
Density at 15 °C, g/cc	ASTM D 1298	0.929	0.825
kinematic viscosity, mm²/sec	ASTM D 445	192 (at 40 °C) 29 (at 100 °C)	70 (at 40 °C) 10 (at 100 °C)
Calorific value, KCal/Kg	Bomb calorimeter	8530.81	10633
Flashpoint,°C	ASTM D 93	109	158
Pour point,°C	ASTM D 97	-13	-20
Ash (%)	ASTM D 482	0.895	0.006

Table 7. Guidelines for quality acceptance of re-refined base oil are as follows (Kupareva et al., 2013b; Abdulkareem et al., 2014).

Parameter	Value
Density at 15 °C, g/cc	0.864 to 0.895
kinematic viscosity, mm^2/sec (CST)	40-45 (at 40 °C) 6-7.5 (at 100 °C)
Viscosity index, cP	90 – 110
Flashpoint, °C	190 to 230
Pour point, °C	0 -9
Ash (%)	0.01

Conclusion

In this study, waste engine oil waspurified by locally available clay mixed with activated charcoal. Different properties were compared before and after the treatment process. A 72.6% and 70.12% purification efficiency could be achieved by employing raw and acid-treated clay, respectively. The introduction of activated charcoal in the acid-treated clay process reduced the oil yield to 64%. Notably, lead and chromium levels decreased significantly in engine oil purified by clay mixed with activated charcoal. The waste engine oil contains 13.28 mg/L of lead and 91.56 mg/L of chromium, whereas the purified oil showed a reduced level of 0.02 mg/L of lead and 0.037 mg/L of chromium when purified by clay mixed with activated charcoal. The FTIR analysis of the purified oil confirmed the presence of alkanes and alkenes. Further, the NMR and GC-MS analyses revealed the presence of linear and branched alkanes and alkenes, along with substituted-benzene compounds in the purified oil. Following the recovery of base oil from waste engine oil, the residual clay mixed with activated charcoal can be used for bitumen production.

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