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USED LUBRICATING OIL TREATMENT USING ACID ACTIVATION CLAY AS ADSORBENT FOR OIL RECOVERY

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ABSTRACT. *The aim of this study was to assess the effectiveness of activated clay as an adsorbent in the recycling of used lubricating oil (ULO). To accomplish this, the research primarily concentrated on identifying the optimal parameters for the application of organic acids—specifically acetic acid and citric acid—in the acid activation of clay during the adsorption process. Montmorillonite K-10 clay served as the adsorbent and was activated to facilitate ULO recovery. According to the experimental findings, citric acid at a concentration of 1.0 mol/L for a reaction time of 45 minutes proved to be the most effective for ULO recovery. The optimal activated clay exhibited a viscosity of 95.10 cP and a density of 0.663 g/mL, achieving a water removal rate of 0.036% and sludge removal of up to 9.20%. Moreover, clay treated with citric acid produced a current of 1.3293 A, in comparison to 1.5721 A for acetic acid under identical conditions, as measured by Ultraviolet-visible (UV-Vis) spectrophotometry. The conditions involving citric acid at 1.0 mol/L for 45 minutes were further investigated using a scanning electron microscope (SEM) to analyze the clay before and after activation. Results indicated that the surface of the unmodified clay was smoother with fewer visible pores, whereas the activated clay displayed a more porous structure, with noticeable pores and cracks. The activated clay's average pore diameter was found to be larger, reflecting a 32.19% increase in pore size compared to the unmodified clay. Additionally, a considerable enhancement in pore area was observed, with the average pore size increasing from 1.614 µm to 2.077 µm, suggesting improved adsorption performance following activation. Fourier transform infrared spectroscopy (FTIR) was utilized to characterize and compare the recovered oil, revealing that activated clay treated with citric acid at 1.0 mol/L for 45 minutes was superior in eliminating most remaining contaminants, such as soot, water, fuel residues, carbonyl groups, discoloration, and other impurities compared to its pre-activated state.*

KEYWORDS. Used lubricating oil, adsorbent, viscosity, activated clay, Montmorillonite K-10 clay

INTRODUCTION

Lubricating oils, a diverse group of lubricants, are employed to reduce wear, heat, and friction among mechanical components in contact with one another. To enhance their properties, such as antioxidant effects, corrosion resistance, and anti-foaming capabilities, commercial base oils are often blended with various additive formulations (Moura et al., 2010). Over time, the lubricating oil undergoes changes due to oxidation, contamination, and degradation, rendering it unsuitable for further use and necessitating its replacement (Josiah & Ikiensikimama, 2010). Used lubricating oil (ULO) poses significant environmental hazards as it contains toxicants, carcinogens, and chronic aquatic toxicants. The gases emitted from waste oil can cause tissue irritation, particularly from compounds such as ketones, aldehydes, and aromatic chemicals. Additionally, elevated levels of heavy metals may adversely affect human health, particularly the prostate and respiratory systems (Vural, 2020). If ULO is not handled, treated, or disposed of properly, it can have harmful environmental consequences (Diphare *et al*., 2013). Typically, ULO contains high levels of contaminants, including carbon residues, asphaltenic materials, heavy metals, and water (Abdel-Jabbar et al., 2010). Such pollutants can significantly contribute to environmental contamination, with each volume of ULO capable of polluting at least 250,000 volumes of water (Udonne *et al*., 2016). Therefore, effective management of this hazardous waste is crucial to transform it into a valuable resource while ensuring environmental safety.

Lubricating oil degrades over time due to usage under various operating conditions. Several factors contribute to this degradation, with moisture absorption from the surrounding air being a primary cause that leads to a cloudy appearance or strong odor in the oil. The mechanisms underlying the degradation of used lubricating oil (ULO) include oxidation, thermal breakdown, micro dieseling, additive depletion, electrostatic spark discharge, and contamination. Oxidation alters the oil's viscosity, resulting in the formation of varnish, sludge, and sediment, as well as causing additive depletion, base oil breakdown, filter clogging, loss of foam properties, and increases in acid numbers, rust, and corrosion. Additionally, additive depletion can impede its ability to detect degradation levels and provide insights into specific degradation mechanisms. The contaminants found in ULO arise from both degradation processes and the operating environment. Waste components from engine oils and other lubricants—such as ash, soot, and solid metal particles resulting from wear—are examples of environment-derived contaminants (Rahman *et al*., 2008). According to Rațiu *et al*. (2020), there are four contamination mechanisms: built-in contamination, external ingression, internal generation, and mechanism-induced contamination.

According to Oladimeji *et al*. (2018), conventional treatment methods for used lubricating oil (ULO) include acid-clay treatment, solvent extraction, vacuum distillation, and hydrogenation. Solvent extraction and adsorption techniques are gaining attention due to their ability to produce high-quality products with lower costs, reduced energy consumption, minimized waste, and greater convenience (Mohammed *et al*., 2013). Despite various advanced technologies proposed for ULO recycling, such as supercritical separation, microwave pyrolysis, and catalytic processes, they are often deemed inefficient as they entail high energy demands, incomplete contaminant removal, elevated costs, and challenges for

scaled industrial application. Previous studies indicate that conventional acid-clay methods are low-cost but raise environmental concerns due to the use of inorganic acids, which can lead to corrosion of equipment and other environmental issues (Zhansheng *et al*., 2006; Opoku-Mensah *et al*., 2023). Therefore, utilizing weak acids to activate clay is preferable, as it mitigates environmental hazards by avoiding the release of harmful gases like sulfur dioxide and lessening the detrimental effects on equipment compared to stronger acids like hydrochloric and sulfuric acids (Hegazi *et al*., 2017). Key factors considered during processing include surface area and pore volume, properties influenced by the type of acid used and pore size. According to Khan *et al*. (2015), larger pore sizes facilitate more efficient removal processes. Additionally, solvent extraction combined with adsorption presents a promising approach for oil regeneration. Recent research has explored using solvent extraction followed by adsorbent activation to regenerate oil (Ani *et al*., 2023; Rosa *et al*., 2020; Velasco-Calderón *et al*., 2020). This combined method is considered more environmentally friendly, economically viable, practical, and less energy-intensive than other recycling methods. Variations in parameters during the acid activation process can enhance the physical and chemical properties of the recovered oil. Important parameters include the type and molar concentration of acids, temperature, contact time, the acid-to-clay ratio, and mixing speed, all of which influence the final adsorption properties of the clay. Table 1 presents different types of acids employed in various studies, along with comments on their usage.

Table 1. Factors influence on chosen acid for acid activation clay

Type of Acid	Findings	References
• Acetic acid • Formic acid	• Acetic acid is the best in treating used oil compare to formic acid • Have no reaction with base oil compare to sulfuric acid. • Did not emit poisonous gases to the atmosphere like sulphur dioxide. • Unlike sulfuric acid, have no adverse effects on the processing machinery. • Due to the base oil's low reactivity; fewer additives may be needed to recycle the base oil.	Hegazi *et al.*, 2017
• Oxalic acid • Acetic acid • Phosphoric acid • Citric acid	• Oil's colour, smell, and taste can be improved by rubbing it on a surface active substance that adsorbs undesirable particles from the oil. • Oxalic acid gives the best results among the other acids.	Khan *et al.*, 2015

• Acetic acid	• This process involve the addition of acetic acid and the result showed improvements on kaolin adsorbent on adsorption capacity due to separation of water content and butanol breaking contained in the ULO. • However, using glacial acetic acid show unsatisfied result as it not helping as acetic acid function.	Riyanto *et al.*, 2018

This study primarily investigates the use of acid-activated clay as an adsorbent in conjunction with the solvent extraction process for the recovery of used lubricating oil (ULO). Montmorillonite K-10 clay was selected as the adsorbent and activated for this purpose. Montmorillonite K-10 was specifically chosen due to its status as an eco-friendly solid catalyst and its unique properties, such as ion exchange capacity and swelling characteristics, which enhance its ability to adsorb other ions in its interlayers (Kumar *et al*., 2014). Its high surface area contributes to significant adsorption capabilities (Uddin, 2018). Furthermore, Montmorillonite is favored for its cost-effectiveness compared to other clays, including smectite, kaolinite, and vermiculite (Alekseeva et al., 2019). Among various solvents tested, including methyl ethyl ketone (MEK), 1-hexanol, and 2-butanol, 1-butanol demonstrated the highest efficiency in removing sludge contaminants from the oil (Kamal *et al*., 2009). Additionally, potassium hydroxide (KOH) was incorporated as it serves as a coagulant for contaminants and can be effectively absorbed by the adsorbent or eliminated during the sludge extraction process (Riyanto *et al*., 2018).

MATERIALS AND METHODS

Materials

This study utilized several key chemicals, including acetic acid, citric acid, Montmorillonite K-10 clay, 1-butanol, potassium hydroxide (KOH), used lubricating oil (ULO), virgin lubricating oil (VLO), and distilled water. The Montmorillonite K-10 was obtained from Acros Organics in Belgium, while 1-butanol and KOH were sourced from Sigma-Aldrich. The Montmorillonite K-10 clay was in granular form, and the lubricant examined was PETRONAS Syntium 3000 5W-40, which has a viscosity range of 5 at low temperatures to 40 at high temperatures. The ULO sample was gathered from a local workshop located in Menggatal, Kota Kinabalu, Malaysia.

Pretreatment of ULO

Prior to the solvent extraction, the used oil was initially subjected to a dehydration process to eliminate excess water and light hydrocarbons. This dehydration was performed at a temperature ranging from 120 to 210°C for one hour using a water bath setup on a hot plate within a fume hood. Following this, the used lubricating oil underwent the solvent extraction process.

Solvent Extraction Procedure

In this solvent extraction method, 1-butanol served as the solvent and was combined with the oil that had previously undergone a dehydration process. The solvent-to-oil ratio was set at 3:1, and the mixture was stirred for 15 minutes at a speed of 350-400 rpm, with the addition of 2 g of KOH, to ensure thorough mixing while minimizing oil loss due to sludge formation. Subsequently, the mixture was allowed to settle for 24 hours at room temperature before being filtered using oil filter paper and a vacuum pump (Riyanto et al., 2018; Mohammed *et al*., 2013). The final step of the solvent extraction involved evaporating the excess 1-butanol from the oil using a vacuum distillation column. The used lubricating oil then underwent an adsorption process utilizing clay as the adsorbent.

Adsorption Experiment

The modification of clay through an activation procedure was carried out following the method described by Salem *et al*. (2015), with some adjustments. A total of 40 g of dry Montmorillonite K-10 clay was mixed with 250 mL of various concentrations of acetic acid and citric acid, specifically 0.2, 0.3, 0.4, 0.5, and 1.0 mol/L. The mixture was then heated to a temperature range of 80 to 100°C. At this temperature, reactions were conducted for different durations of 10 and 45 minutes before the mixture was filtered and washed with distilled water to remove any excess acid and ions. In the final step, the clay filtrate underwent a drying process in an oven at 60°C for 24 hours to ensure maximum moisture removal (Khan *et al*., 2015). The activated clay was subsequently ground to achieve a fine texture. For the oil treatment, 15 g of the activated clay was added to 60 mL of oil and allowed to contact for 30 minutes at a moderate speed to optimize physical properties, after which it was left to settle for one hour at room temperature (Abdel-Jabbar et al., 2010). This was followed by a centrifugation process at 3000 rpm for 30 minutes, leading to the filtration of the final recovered oil. Table 2 provides the names of each activated clay sample.

Table 2. Naming of each samples of activated clay

Sample	Type of clay	Sample naming
1	Montmorillonite K-10, XC	Inactivated Montmorillonite K-10
2	Activated Acetic Acid, AA-1	AA 0.2 mol-1 (10 min)
3	Activated Acetic Acid, AA-2	AA 0.2 mol-1 (45 min)
4	Activated Acetic Acid, AA-3	AA 0.3 mol-1 (10 min)
5	Activated Acetic Acid, AA-4	AA 0.3 mol-1 (45 min)
6	Activated Acetic Acid, AA-5	AA 0.4 mol-1 (10 min)
7	Activated Acetic Acid, AA-6	AA 0.4 mol-1 (45 min)
8	Activated Acetic Acid, AA-7	AA 0.5 mol-1 (10 min)
9	Activated Acetic Acid, AA-8	AA 0.5 mol-1 (45 min)
10	Activated Acetic Acid, AA-9	AA 1.0 mol-1 (10 min)

11	Activated Acetic Acid, AA-10	AA 1.0 mol-1 (45 min)
12	Activated Citric Acid, CA-1	CA 0.2 mol-1 (10 min)
13	Activated Citric Acid, CA-2	CA 0.2 mol-1 (45 min)
14	Activated Citric Acid, CA-3	CA 0.3 mol-1 (10 min)
15	Activated Citric Acid, CA-4	CA 0.3 mol-1 (45 min)
16	Activated Citric Acid, CA-5	CA 0.4 mol-1 (10 min)
17	Activated Citric Acid, CA-6	CA 0.4 mol-1 (45 min)
18	Activated Citric Acid, CA-7	CA 0.5 mol-1 (10 min)
19	Activated Citric Acid, CA-8	CA 0.5 mol-1 (45 min)
20	Activated Citric Acid, CA-9	CA 1.0 mol-1 (10 min)
21	Activated Citric Acid, CA-10	CA 1.0 mol-1 (45 min)

Water content removal

The detection of water content in used lubricating oil (ULO) was conducted through a series of steps. First, the ULO was pre-treated by filtration to remove contaminants, such as small debris, using a sieve. Next, an empty 250 mL beaker was weighed on an electronic balance. Then, 100 mL of the ULO was measured using a measuring cylinder and transferred to the beaker, with the final measurement of the 100 mL of treated ULO recorded. The sample was subsequently heated in an oven at 250°C to evaporate any water residue, as described by Hamawand *et al*. (2013). After heating for an hour, the samples were allowed to cool to room temperature and then weighed again. The final weight was documented, and the weight of the dehydrated ULO was calculated. The percentage of water removal was determined using Equation (1), where the initial mass refers to the mass of the oil prior to drying, and the final mass refers to the mass of the oil after drying, measured in grams. (Zheng *et al*., 2014).

$$Water\ removal, \% = \frac{initial\ mass\ (g) - final\ mass\ (g)}{initial\ mass\ (g)} \times 100 \quad (1)$$

Sludge removal

The removal of sludge occurred during the adsorption process of the lubricant oil. In this process, 15 g of adsorbent was added to 60 mL of used lubricating oil (ULO) at a temperature of 90°C to facilitate the settling of sludge, which is a type of contamination in the oil. After 30 minutes, the mixture of adsorbent and oil was centrifuged to separate the oil from the sludge. Prior to transferring the oil, the mass of the centrifuge tube was recorded. Then, 20 mL of oil was measured with a measuring cylinder and transferred into the centrifuge tube, after which the total mass was measured again. The oil and sludge mixture were then centrifuged at 4000 rpm for one hour to achieve separation. This resulted in the formation of two layers in the centrifuge tube, with sludge at the bottom and sludge-free oil on top. The sludge-free oil was carefully transferred to a beaker with the aid of a dropper. Following this, the centrifuge bottle containing the sludge was dried in an oven to solidify it. Subsequently, the mass of the centrifuge bottle with the sludge was weighed using an electronic balance. Finally, the quantity of sludge generated per

20 mL of oil was determined by subtracting the combined mass of the tube and sludge from the mass of the tube and the 20 mL of oil. The mass of sludge produced per 20 mL of oil was calculated using Equation (2), where *W*dry refers to the mass of the sludge in grams (Daham et al., 2017).

$$Sludge\ \ removal, \% = \frac{Wdry}{Woil} \times 100 \quad (2)$$

Density

To determine the densities of the oil samples at room temperature, the density formula (density = mass/volume) was used (Abu-Elella et al., 2015). Each oil sample was carefully poured into a density bottle with a known mass and volume. The masses of both the oil and the bottle were recorded, and the mass of the oil was then calculated using the known volume of the bottle. By utilizing the recorded mass and volume, the density was subsequently calculated using Equation (3):

$$Density = \frac{Mass\ of\ the\ sample\ oil,\ \ g}{Volume\ of\ the\ sample\ oil,\ \ mL} \quad (3)$$

Viscosity

The DV-E Viscometer, a digital device, was used to measure the viscosity of the regenerated oil. The established method required choosing a suitable spindle and pouring an appropriate amount of the regenerated oil into a beaker. The beaker was placed under the spindle, and the spindle was submerged to the specified line. Consistent factors, such as temperature, spindle size, and spindle speeds, were kept uniform for all samples. Once the motor was activated, the instrument displayed the measured viscosity in centipoise (cP), and the highest value was noted for further analysis.

Recovered ULO Characterization

The lubricating oil sample obtained from the regeneration process was analyzed to determine its suitability for reuse. This sample was then compared with the characteristics of a fresh oil sample to facilitate the evaluation of the effectiveness of the treatment in restoring the properties of new oil. Additionally, the recovered oil underwent analysis using Fourier-transform infrared spectroscopy (FTIR), Ultraviolet-Visible (UV-Vis) Spectroscopy, and scanning electron microscopy (SEM) for morphological assessment.

Functional group and chemical structure analysis using FTIR

FTIR was utilized to analyze the functional groups and chemical structure of the oil. The FTIR instrument employed in this study operates within a wave number range of 400 to 4000 cm^{-1} (Salem et al., 2015). Our primary focus is on examining the structure of the treated oil and identifying the functional groups associated with fuel residue, ash, carbonyl groups, water, and other contaminants. If the clay treatment

results in an increase in unsaturated hydrocarbons and a reduction in straight-chain hydrocarbons, it suggests an enhanced adsorption capacity performance (Khan et al., 2015). Therefore, FTIR was applied to the recovered oil to assess the effectiveness of contaminant removal in the oil's chemical structures.

Recovered oil concentration analysis using UV-Vis Spectroscopy

The recovered oil was analyzed using UV-Vis spectroscopy to assess the concentrations and the UV wavelengths absorbed. The treated lubricating oil's color was evaluated at a peak wavelength of 510.02 nm for all samples to facilitate easier comparisons, as referenced in the study by Salem *et al*. (2015). Prior to this analysis, modified oil samples (1 mL) were diluted with kerosene (10 mL) because kerosene is more compatible with mass spectrometric analysis (Shigidi *et al*., 2020).

Surface analysis using SEM

The surface characteristics, including pore shape, distribution, and size, of both modified and unmodified CAC were analyzed using a Hitachi Scanning Electron Microscope (SEM). SEM enabled direct observation of microstructural changes on the surface of the modified Montmorillonite K-10 clay, allowing for a comparison with the unmodified version. Magnifications between 100x and 3000x were utilized to capture high-resolution images. The surface morphology, including pore size and porosity, of both the unactivated and activated Montmorillonite K-10 clay was evaluated using *ImageJ*, a Java-based image processing software developed by researchers at the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation at the University of Wisconsin. *ImageJ* is freely available for download on Microsoft Windows and features a user-friendly interface tailored for calculating distances and areas as well as generating statistical graphs based on the results (Chilev, 2017).

RESULTS AND DISCUSSION

FTIR Analysis of ULO and VLO

Figure 1 displays the components present in both types of oil based on the peaks and transmittance observed in the FTIR analysis. VLO serves as a reference for further detailed studies. The analysis revealed that virgin lubricants primarily consist of hydrocarbons, specifically -CH and -CH_2 groups, with peaks at 1374.05 and 1374.59 cm^{-1} corresponding to -CH and peaks at 2854.26 and 2854.48 cm^{-1} associated with -CH_2, which are evident in both VLO and ULO. Additionally, a band at 968.17 cm^{-1} indicates the presence of additive compounds, particularly anti-wear additives, which were present in the existing lubricating oil but undetected in ULO (Patty and Lokollo, 2016). This may be attributed to the consumption of additives that enhance lubricating performance during use. Long-chain hydrocarbons were also confirmed, indicated by a peak at 2919 cm^{-1} (Timur, 2017). Components such as carbonyl-containing degradation products (C=O), resulting from oxidation, were not detected. In contrast, ULO contains various contaminants, including soot, carbonyl oxidation products, sulfur oxidation products,

and water. It was noted that used lubricating oils predominantly consist of paraffinic, naphthenic, and aromatic molecular structures. Paraffinic compounds are characterized by straight chains of normal alkanes, while naphthenic compounds consist of cycloalkanes, which contain at least one six-carbon ring with single or double bonds, and aromatic structures include ringed compounds (Zeng *et al*., 2016).

The FTIR analysis also identified components such as OH (3600 – 2500 cm^{-1}), C=O (1900 - 1600 cm^{-1}), and C-O (1500 – 900 cm^{-1}), indicating the presence of alcohols, ketones, aldehydes, carboxylic acids, and esters. A prominent band at 3338.79 cm^{-1} suggests the presence of hydroxyl groups from water molecules in ULO. Soot contamination was also detected, with peaks around 2000 cm^{-1} at 2074.59 cm^{-1} and 1962 cm^{-1}. The peak at 1750 cm^{-1} corresponds to carbonyl oxidation products with a C=O functional group, which may include lactones, esters, aldehydes, ketones, carboxylic acids, and salts. Moreover, sulfur oxidation products were found in both oils at 1159.75 cm^{-1}. According to Zhu *et al*. (2019), oxidation occurs over time, even if the oil is not used or stored under optimal conditions. The presence of unexpected compounds may result from exposure to high temperatures or air during storage or handling, leading to chemical modifications in the lubricant formulation. Furthermore, Adamczewska *et al*. (2005) noted that oxidation is a significant concern for lubricating oils, which is why they have a limited shelf life. Overall, ULO was confirmed to contain various contaminants, including fuel, glycol pollution, oxidation, nitration, sulfation products, soot, and water contamination, in contrast to VLO (Abu-Elella *et al*., 2015).

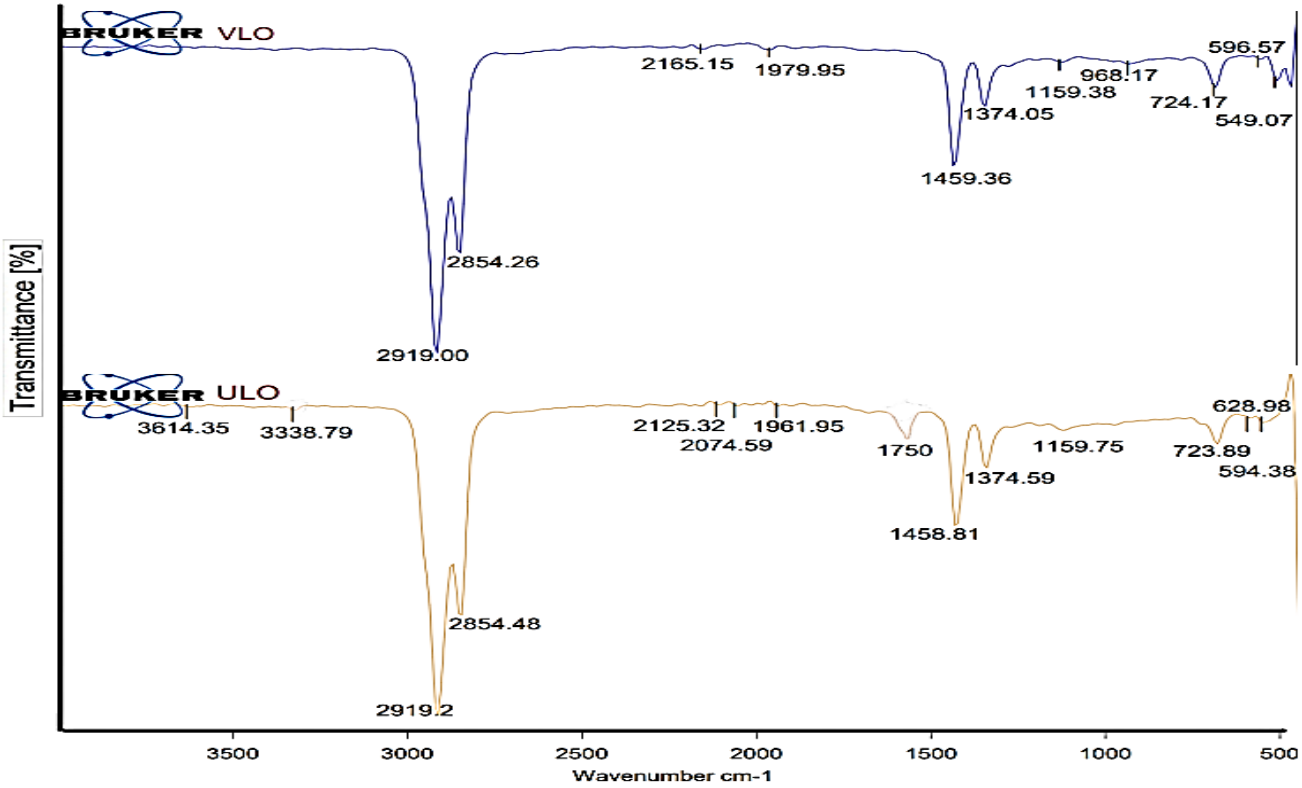

Figure 1: The comparison of wavelength signals detected in the FTIR analysis between used lubricating oil (ULO) and virgin lubricating oil (VLO).

Table 3 also presents a comparative analysis of various properties, including the effectiveness of water removal, the amount of sludge removed following the acid activation of clay, as well as the density and viscosity of the treated lubricating oil. The results highlight the differences in performance metrics, providing valuable insights into how the treatment process impacts the overall quality and characteristics of the lubricating oil.

Table 3. Water content and sludge removal in used lubricating oil (ULO) after acid activation of clay; and density and viscosity of the treated lubricating oil.

Samples	Water content removal, %	Sludge removal, %	Density, g/mL	Viscosity at room temperature, cP
AA-1	0.036	4.27	0.713	117.32
AA-2	0.024	3.82	0.879	116.54
AA-3	0.011	6.33	0.795	118.23
AA-4	0.012	5.48	0.753	115.76
AA-5	0.012	3.51	0.980	115.32
AA-6	0.012	4.95	0.708	113.50
AA-7	0.024	5.04	0.864	116.21
AA-8	0.036	8.31	0.793	113.29
AA-9	0.036	3.97	0.671	110.67
AA-10	0.036	1.90	0.711	113.25
CA-1	0.036	6.55	0.733	114.45
CA-2	0.024	6.32	0.740	115.20
CA-3	0.024	3.13	0.820	114.20
CA-4	0.036	4.96	0.812	114.80
CA-5	0.024	6.34	0.760	115.27
CA-6	0.036	4.19	0.700	116.80
CA-7	0.024	7.47	0.640	112.43
CA-8	0.024	7.77	0.703	99.95
CA-9	0.036	8.33	0.732	99.79
CA-10	0.036	9.20	0.663	95.10

Water content removal

The water content found in lubricating oil was categorized as chemical contamination. According to Hamawand *et al.* (2013), water enters the oil through moisture absorption, condensation from humid air, combustion byproducts, and neutralization as engine oil is hygroscopic in nature. Udonne (2011) states that the presence of water in engine oil was inevitable due to factors like air cooler and engine cooling system leaks causing atmospheric condensation. Table 3 presents the results of the water content levels. t was evident that all twenty samples of used lubricating oil (ULO) analyzed in this study contained water, which confirmed its presence in each sample. This finding is consistent with the data from the

FTIR analysis, indicating that complete removal of water occurred after treatment with 1.0 mol/L of citric acid for 45 minutes. According to Assunção Filho *et al*. (2010), among the methods involving (ethanol+activated carbon), (2-propanol+activated carbon), and (1-butanol+activated carbon) for determining the base oil, the combination of ethanol solvent and activated carbon achieved the highest reduction in water content, with a decrease of 58.33%.

Sludge removal

As stated by Hamawand et al. (2013), the poly-condensation and polymerization reactions that occur in used engine oil with high molecular weight result in the formation of insoluble products known as sludge. This phenomenon is linked to the secondary oxidation phase, which occurs at elevated temperatures. During this phase, the viscosity of the oil increases due to the poly-condensation of oxygenated products produced in the primary oxidation phase, such as carboxylic acids. Moreover, it has been noted that sludge formation is exacerbated as the adsorbent properties of clay improve (Devi *et al*., 2016). In this study (Table 3), clay activated with 1.0 mol/L citric acid for 45 minutes showed the highest sludge removal rate at 9.20%. This enhancement is likely attributed to the adsorbent characteristics of the clay, including its pore structure, surface area, acidity, and the effects of different concentrations, reaction times, and types of acids used in treatment. Chen *et al*. (2018) noted that effective adsorbent properties can significantly capture products resulting from oxidation, nitrification, and sulfide formation in lubricating oil. Increasing the acid concentration can enhance the surface area of the clay and decrease its hygroscopic properties (Suhdi & Wang, 2021). Additionally, the presence of ash plays a crucial role in sludge removal, as it can hinder adsorption performance by weakening the mechanical strength of the carbon (Zulkania *et al*., 2018). Furthermore, the level of purity of the carbon, indicated by the ash content, affects adsorption performance by leading to inactive sites and clogging of pores (Martínez-Mendoza *et al*., 2020; Yusufu *et al*., 2012).

Density

In this study, the densities of virgin lubricating oil (VLO) and used lubricating oil (ULO) were measured, with values recorded at 0.533 g/mL and 0.824 g/mL, respectively. The results show that ULO exhibits a higher density than VLO as well as all treated lubricating oil samples. The increased density of ULO can be attributed to the solid particles present within it. Additionally, the density of ULO rises due to contaminants such as metals and oxidation products that accumulate while the oil is in use (Hamawand et al., 2013). Consequently, the aim of recovering ULO was to restore its density properties. The CA-10 clay samples exhibited a density of 0.663 g/mL, the closest to that of VLO (Table 3). This indicates that the properties of the clay were particularly effective in removing contaminants, resulting in a lower density compared to the untreated oil. It is important to note that density is influenced by temperature, with variations occurring as temperature changes. The density of lubricating oil is significantly affected

by its composition; oils rich in aromatic compounds tend to have a higher specific density compared to those consisting predominantly of saturated compounds, which results in a lower specific gravity (Udonne, 2011).

Viscosity

The viscosity of the regenerated oil was measured using a DV-E Viscometer at 600 rpm, with the same spindle size applied across all samples for consistency in comparison. Initially, the virgin lubricating oil (VLO) and used lubricating oil (ULO) were evaluated, yielding recorded viscosities of 87.9 cP and 123.7 cP, respectively. The viscosities of VLO and ULO were thus found to be 87.9 cP and 123.7 cP, respectively (Table 3). Among the treatments, the optimal viscosity that was closest to VLO was achieved with citric acid at a concentration of 1.0 mol/L over a 45-minute activation period, resulting in a viscosity of 95.10 cP. However, this finding contrasts with results reported by Hegazi *et al*. (2017), which indicated that ULO had a lower viscosity compared to VLO when various regeneration methods were compared. The lower viscosity might be attributed to the combustion of oil, leading to a fuel mixture that dilutes the lubricants (Młynarczak & Sikora, 2014). This underscores the influence of specific contaminants on viscosity. It is crucial to understand how different contaminants affect the viscosity of lubricants since particulate matter can infiltrate the lubricants and alter their chemical properties, leading to increased viscosity. Other contributing factors include elevated temperatures during operation that can result in oxidation by-products, polymerization, and carbon deposits, all of which can further increase viscosity (Raţiu *et al*., 2021).

UV-Vis Spectrophotometry Analysis

Based on the FTIR analysis presented in Table 3, treatment with citric acid at a concentration of 1.0 mol/L for 45 minutes proved to be optimal, resulting in a density of 0.663 g/mL, a sludge removal rate of 9.20%, and a viscosity of 95.10 cP, making it nearly as refined as the recorded virgin lubricating oil (VLO). To further clarify the physical properties discussed, chemical analyses, including UV-Vis spectrophotometry, were performed to identify which clay treatment resulted in the lowest absorbance of contaminants in the treated lubricating oils. UV-Vis spectrophotometry also characterized the color changes of all refined oils based on their UV absorbance. This analysis was conducted at a peak wavelength of 510.02 nm across all samples to facilitate easier comparison, following the methodology established by Salem et al. (2015). Several factors influence the adsorption properties of clay, ultimately impacting the quality of the oil. Various investigations were carried out, exploring different molar concentrations of various types of acids at varying activation times.

Figure 2 illustrates the effect of molar concentration on the absorbance value after a 10-minute activation period. Additionally, surface morphology, pore diameter, and pore size were characterized

using SEM to examine the differences before and after the activation of Montmorillonite K-10 based on the optimal conditions. The UV-Vis spectrophotometry analysis revealed that as the molar concentration of both acids increases, their absorbance decreases. This reduction in absorbance signifies that less light is transmitted, indicating a lower concentration of oil as the colors appear lighter. The most favorable result was observed with citric acid at a concentration of 1 mol/L, yielding an absorbance of 1.5721 A. This effect may be attributed to the presence of H+ ions in the clay, which can replace cations (Kemala *et al*., 2019), thereby enhancing the adsorption properties of the clay. Additionally, Khan *et al*. (2015) reported that 1N of organic acids is optimal for the activation process. Similarly, Salem *et al*. (2015) found that a concentration of 1.0 mol/L exhibited the most significant reduction in absorbance compared to other molar concentrations.

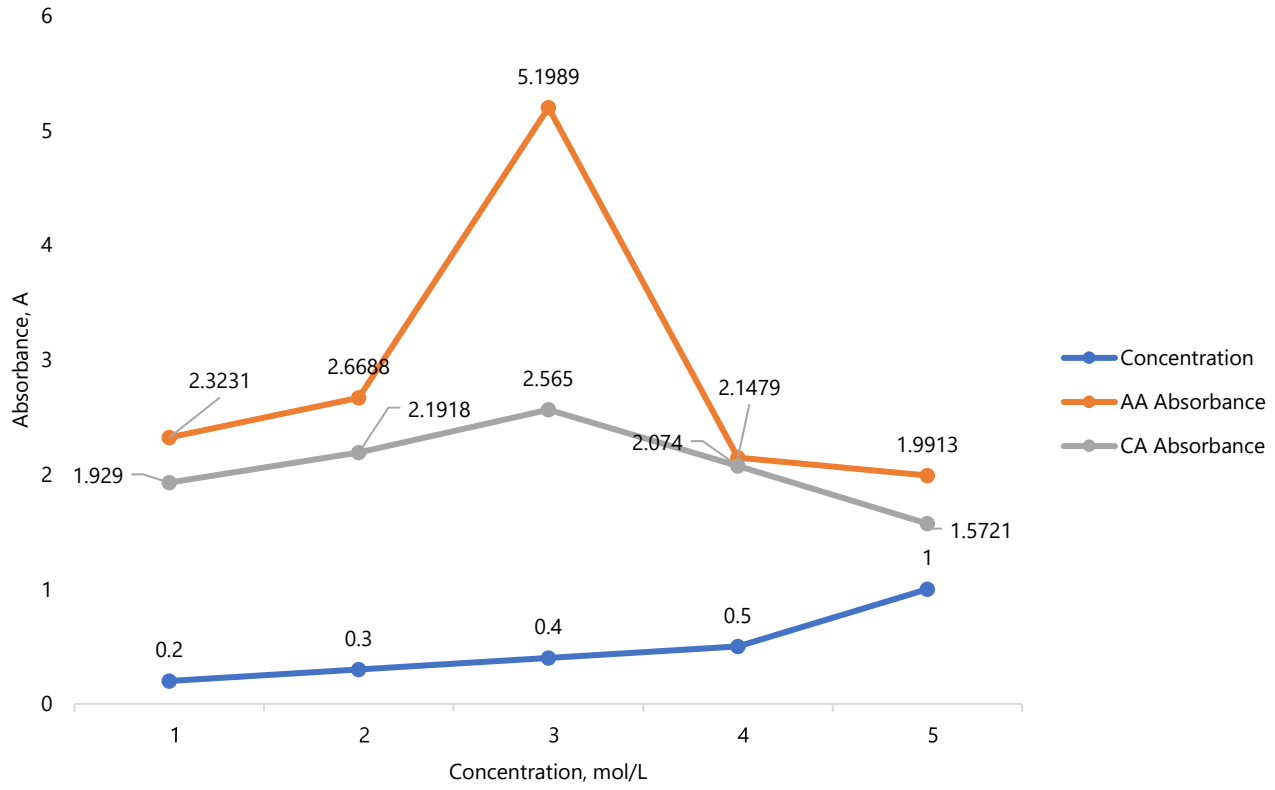

Figure 2. The effect of acid molar concentration on absorbance after a 10-minute activation period.

The second investigation aimed to compare both types of acid at varying molar concentrations, maintaining a reaction time of 45 minutes. A similar trend was observed during this reaction, where an increase in molar concentration led to an overall decrease in the absorbance of the refined oil. Figure 3 shows that citric acid provided the best absorbance, measuring 1.3293 A at a concentration of 1 mol/L. Across both investigations, citric acid demonstrated superior performance compared to acetic acid in terms of oil quality. This could be attributed to citric acid exhibiting sharp peaks in the FTIR analysis,

which indicates a strong presence of unsaturated esters and saturated aliphatic hydrocarbons (Khan *et al*., 2015). Their findings suggest that a higher concentration of these compounds enhances the adsorption capacity of the activated clay.

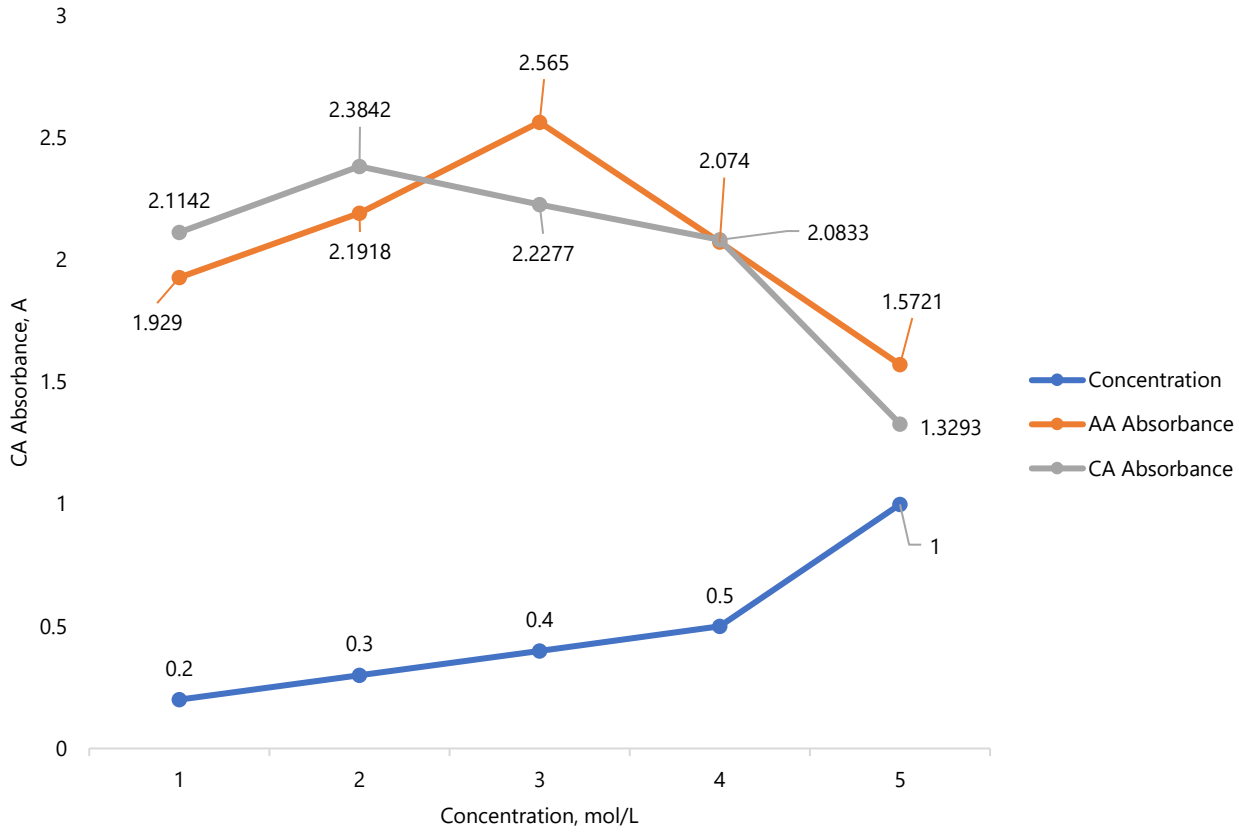

Figure 3. The effect of acid molar concentration on absorbance after a 45-minute activation period.

In comparing the activation times, it was observed that as the duration increased from 10 to 45 minutes, the absorbance of both citric acid and acetic acid at a concentration of 1 mol/L decreased (Figure 4). This indicates that a lower concentration of contaminants was being adsorbed from the oil over time, suggesting that the clay effectively removed these contaminants. Thus, the reaction time during acid activation of the clay is a critical factor in determining the quality of the refined oil. According to Kemala *et al*. (2019), the adsorption capacity of the clay improves with longer reaction times. When evaluating which acid was more effective after 45 minutes, citric acid exhibited the lowest absorbance at 1.3293 A, compared to 1.5721 A for acetic acid. This further confirms that acid activation with citric acid resulted in better refinement of the oil. In conclusion, all treated samples demonstrated lower absorbance compared to the used lubricating oil (ULO). The adsorption process effectively improved the color of the ULO, indicating that citric acid at a concentration of 1.0 mol/L for 45 minutes serves as the optimal parameter for achieving well-refined oil.

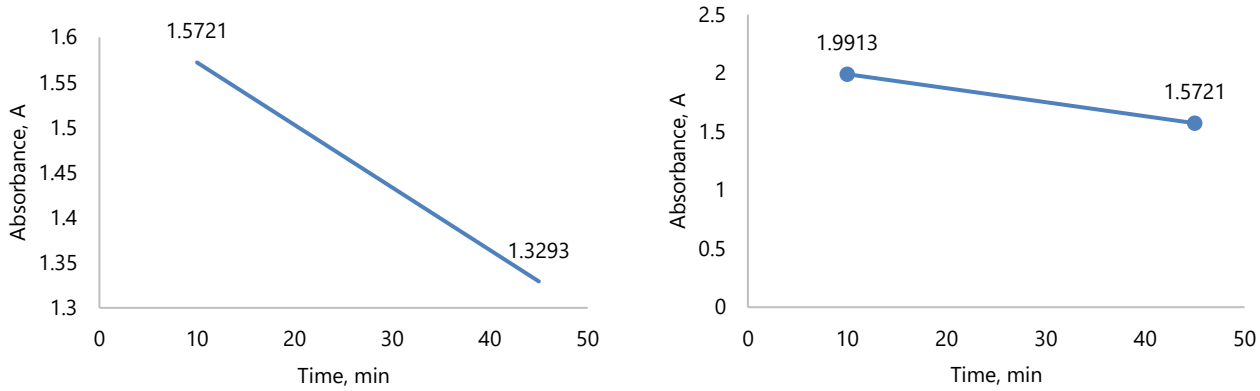

Figure 4. The obsorbance performance of various acids at different activation times

SEM Analysis on Activated Clay

Morphological Structure

To investigate the morphological structure, SEM analysis was performed based on the optimal parameters established from earlier characterizations of both activated and inactivated Montmorillonite K-10 clay. SEM images were taken at a magnification of 1500x, with an accelerating voltage of 15 kV and a pressure of 70 Pa for all samples. As shown in Figure 5, the surface of unmodified Montmorillonite K-10 appeared smoother, with less visible pores compared to the activated clay. Although the surface of the unmodified clay exhibited some scattered pores, it did not show any visible cracks (Figure 5(a)). In contrast, the surface-modified Montmorillonite K-10, depicted in Figure 5(b), displayed more distinct pore development with various shapes, sizes, and agglomerations.

Adsorption takes place because the surface particles of the adsorbent behave differently than those in the bulk. Chemical adsorption is distinguished by the stronger interactions between the adsorbate and adsorbent, resulting from covalent bonds and electrostatic forces, unlike physical adsorption (Ameri et al., 2020). Various factors have a significant impact on the effectiveness of the adsorption process. Ajemba & Onukwuli (2013) state that the efficiency of adsorption using activated clay improves with time. Additionally, temperature affects adsorption efficacy, and increasing the dosage of the adsorbent in a solution enhances the adsorption process. Zhang et al. (2017) observed that before treatment, the kaolin structure had distinct edges and a relatively smooth surface, which altered after activation. Amari et al. (2018) found that acid activation led to the formation of fine-grained aggregates of clay platelets, irregular arrangements of curved flakes, and coalesced flakes following activation.

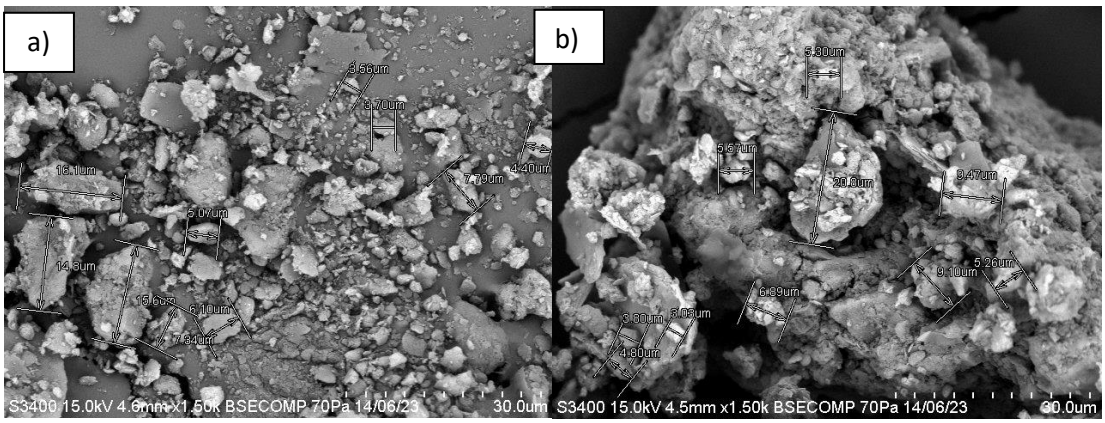

Figure 5. SEM images showing a) the clay before activation and b) the clay after activation (CA 1.0 mol/L, 45 minutes)

Surface Morphology Analysis of Modified Montmorillonite K-10 Clay

Analyzing surface morphology, including the average Feret diameter, average pore size, surface area, and porosity, is crucial for identifying enhancements on the surface that may improve the adsorption of adsorbate molecules. SEM images of both unmodified and modified Montmorillonite K-10 clay at a magnification of 1500x were examined using *ImageJ* software. The average Feret diameter and average pore size data were utilized to create a histogram reflecting the distribution of average measurements, while porosity data was obtained directly from the software.

Average Feret diameter

The Feret diameter, commonly referred to as "caliper length," represents the diameter of the circumscribed circle or the maximum distance between any two points along the perimeter of an object. The average Feret diameter was utilized to compute the pore diameter of the samples, as the pores do not have fixed shapes or sizes due to the activation process. Figure 6 indicates that the average pore diameters for unmodified and modified Montmorillonite K-10 were 5.701 µm and 7.536 µm, respectively. This demonstrates a notable increase in pore diameter in comparison to the raw material, with a 32.19% increment in pore diameter for modified Montmorillonite K-10 clay. According to the International Union of Pure and Applied Chemistry (IUPAC), all Montmorillonite samples exhibit micropores (< 2 nm) that facilitate the movement of adsorbates into mesopores (> 2 nm) (Dutta *et al.*, 2018). The enhanced pore diameter of modified Montmorillonite K-10 clay indicates that citric acid effectively expanded the pores in its carbonaceous structure. Research by Temuujin et al. (2004) showed that using acid activation, particularly leaching, on montmorillonite-rich clay from Tuulant (Mongolia) led to the production of a silica material with improved porosity. This porosity consisted of micropores ranging from 3-5 nm and mesopores ranging from 6-10 nm. Temuujin *et al*. also suggested that the formation of mesopores resulted from the delamination of the card-house structure rather than from the condensation of micropores.

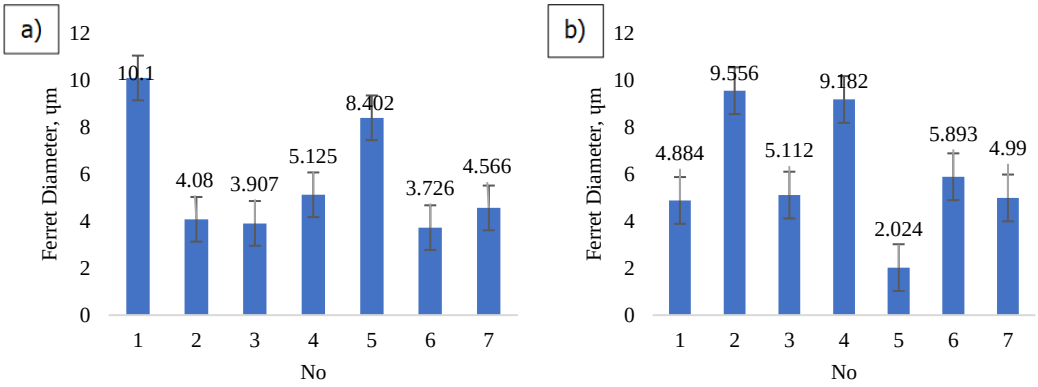

Figure 6. Ferret diameter distribution for a) before activation and b) after activation (CA 1.0 mol/L, 45 minutes)

Average pore size, surface area and porosity

Pore size is a crucial factor in the adsorption of contaminants. A larger pore size is vital as it reveals whether a pore is blocked, partially blocked, or completely open due to impurities. Increased pore size on the surface indicates that impurities were removed during the activation process, resulting in a greater number of active sites, which enhances the adsorption performance of Montmorillonite K-10 clay. Figure 7 shows the pore size distribution of both unmodified and modified Montmorillonite K-10 clay. The average pore sizes were measured at 1.614 µm for the unmodified clay and 2.077 µm for the activated version. Notably, the modified clay exhibited a considerable enhancement in pore area compared to the unmodified counterpart (Ravichandran & Sivasankar, 1997). The application of an acid, such as citric acid at a concentration of 1 mol/L, can significantly create well-defined pores that are advantageous for the adsorption process, as it makes the surface more acidic (Wahyuningsih *et al*., 2020). This indicates that acid-modified Montmorillonite K-10 clay has pronounced and uniform pore structures on its surface, suggesting that the modified clay has an increased porosity. Thus, modified Montmorillonite K-10 clay is an effective adsorbent for adsorption purposes.

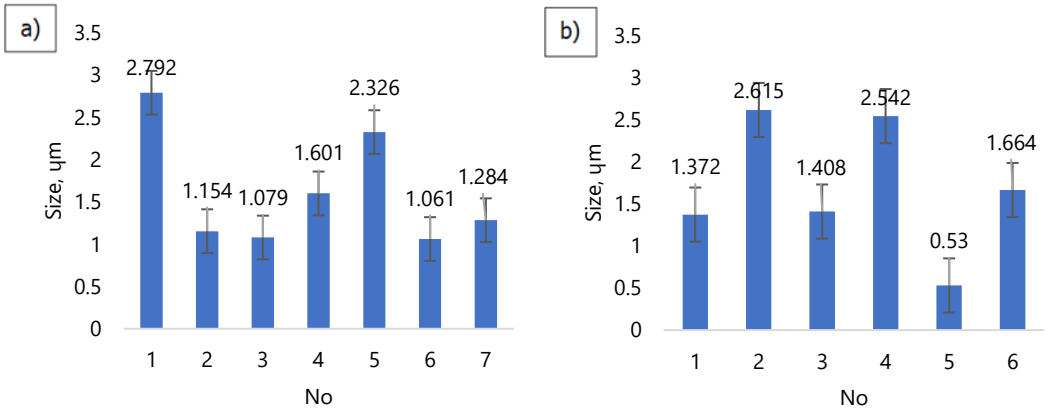

Figure 7. Pore size distribution for a) unmodified Montmorillonite K-10, b) modified Montmorillonite K-10 (CA 1.0 mol/L, 45 minutes)

Table 4 presents the pore characteristics determined using *ImageJ* software. Modified Montmorillonite K-10 clay exhibits a greater surface area than its unmodified counterpart. This increase in porosity may be attributed to the findings from previous studies, which noted that the surface area of acid-activated clay rose threefold to 93.9 m^2/g (Temuujin *et al*., 2003). Similarly, Zhang *et al*. (2017) reported that the specific surface area of kaolin increased from 8.18 m^2/g to 31.21 m^2/g following treatment with citric acid during the activation process. Furthermore, acid treatment of clays causes the replacement of exchangeable cations with H+ ions. Additionally, this activation process dissolves both organic and inorganic impurities, substituting diatomic and triatomic cations with H^+ ions. This behavior underscores the clay's role as a Bronsted-Lowry acidic active site, facilitating the adsorption of organic impurities, such as anionic dyes, through electrostatic attraction while potentially forming covalent bonds with cationic dyes (Bijang *et al*., 2019). The acid activation process also generates microporous spaces in the treated sample because of clay exfoliation. The extent of ion removal during acid activation is influenced by various factors, including the type of acid employed, the concentration of acid, the temperature during the activation reaction, the duration of contact between solid and liquid phases, the stirring rate of the mixture, the particle size of the solid, and the mass ratio of liquid to solid (Amari *et al*., 2018). These factors collectively enhance the effectiveness of the acid activation process on the clay. According to the data, all properties of ULO significantly improved after being treated with citric acid-activated clay, indicating that the activation process effectively removed contaminants through its adsorption capacity. Moreover, SEM results confirmed that the activation of clay successfully increased the surface area, which corroborates the theory that organic matter leached out from the clay upon the introduction of acid (Amari *et al*., 2018).

Table 4. Pore characteristics of unmodified and modified Mntmorillonite K-10

Type of clay	Average pore size, (μm)	Surface area, (m^2/g)	Porosity, %
Inactivated	1.614	162.25	41.36
1.0 mol/L CA, 45 minutes activation	2.077	245.76	47.18

FTIR Analysis of Treated Lubricating Oil

Figure 8 shows the components found in used lubricant oil (ULO) after treatment with clay, as indicated by the peaks and transmittance in the FTIR analysis. In this context, ULO serves as a reference for comparison. The results demonstrate that the treatment improved the removal of unwanted substances in the lubricant oil. For example, the presence of soot was highest before clay treatment, but after treatment, it was reduced from a value of 2075 cm^{-1} to an undetectable level in the activated Montmorillonite K-10 clay. This indicates that the activated clay effectively and eliminated soot from the lubricants. Additionally, the water hydroxyl group (OH) in the range of 3600 cm^{-1} – 2500 cm^{-1} was also successfully

removed during the adsorption process (Zeng et al., 2016). The results from the FTIR peaks further confirmed that activated clay achieved satisfactory removal of water.

Conversely, sulfur oxidation products showed only a minor reduction in peak absorbance, decreasing from 1160 cm^{-1} to 1157 cm^{-1}. Thus, the acid-activated clay used in this experiment was ineffective in removing sulfur oxidation products from the processed ULO. According to Abu-Elella *et al*. (2015), while sulfur oxidation products remained, nitration products were still detected at a peak of 1599.43 cm^{-1} for C=O, with the peak at 1750 cm^{-1} being effectively eliminated by citric acid-activated clay. A similar outcome was reported by Dabai *et al*. (2019), where sulfuric and oxalic acid treatments also resulted in no carbonyl compounds in used Oando Oleum Super lubricant oil. Therefore, the activation of clay using weak acids demonstrated satisfying results, like other methods. However, citric acid-activated clay did reveal the presence of fuel residue in the recovered lubricating oil. Although fuel was still present in terms of absorbance, its intensity was lower than that of the ULO (Aguilar *et al*., 2020). Thus, it can be concluded that activated Montmorillonite K-10 clay was effective in removing water, carbonyl compounds, and soot during the regeneration of ULO.

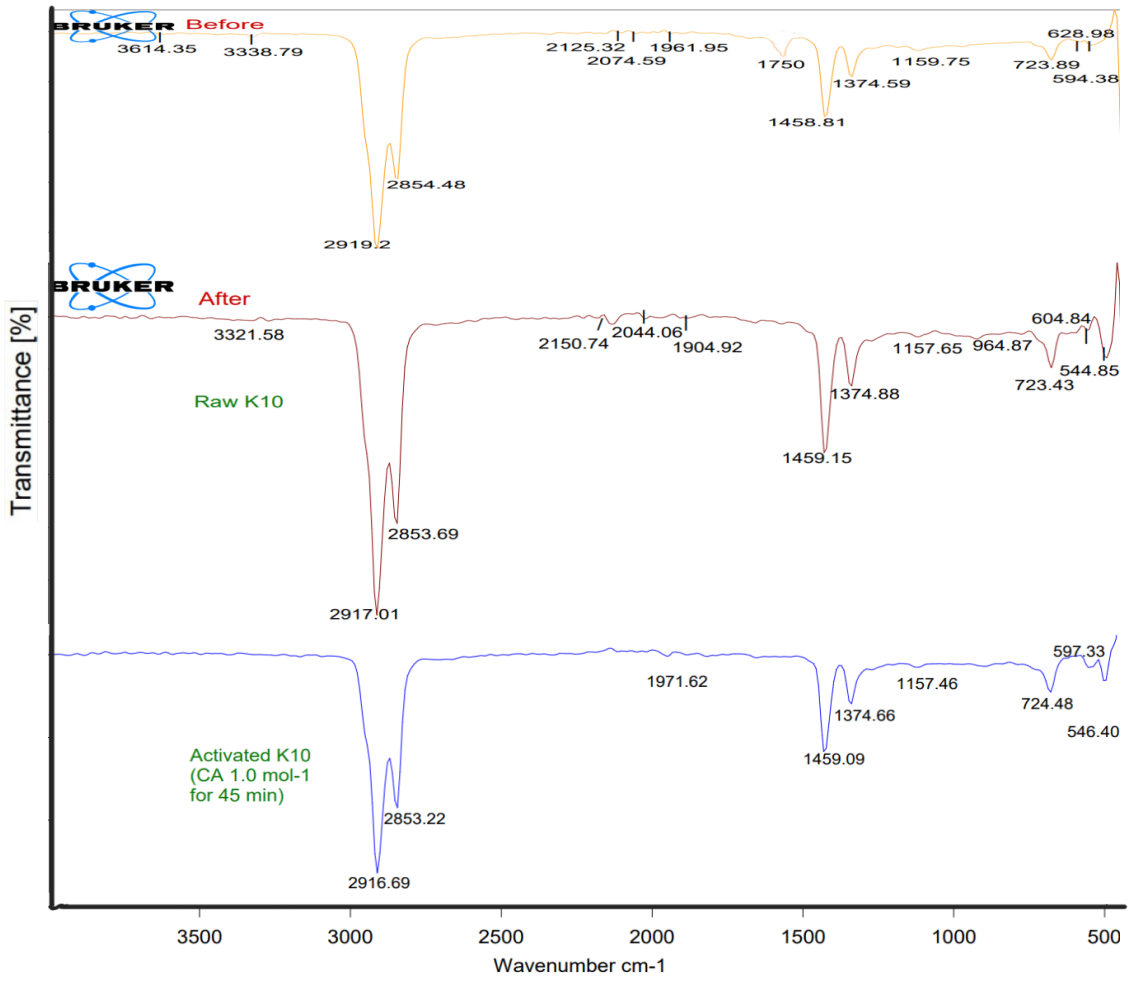

Figure 8. FTIR analysis conducted before and after treatment with clays.

CONCLUSIONS

In conclusion, the acid activation process has been shown to enhance the properties of clay, with activated Montmorillonite K-10 clay exhibiting greater adsorption capacities than its unactivated form. Following the acid activation, the recycled used lubricant oil (ULO) demonstrated both physical and chemical property improvements compared to untreated lubricating oil. The treatment with citric acid at a concentration of 1.0 mol/L for 45 minutes emerged as the optimal parameter, yielding satisfactory results, including a color change, a water content reduction of 0.036%, a sludge removal percentage of 9.20%, a density of 0.824 g/mL, and a viscosity of 95.10 cP.

The adsorption process resulted in noticeable color changes, confirmed by UV-Vis spectroscopy, which indicated a reduction in absorbance compared to ULO. The lowest absorbance value of 1.3292 A for the recycled ULO was achieved under specific operating parameters: acid type, acid concentration, and reaction time. Physical property assessments revealed that activated Montmorillonite K-10 clay effectively removed water, sludge, and viscosity. The results indicate that the activation process significantly increased the pore size, pore diameter, and overall surface area, all of which are crucial for effective adsorption.

FTIR analysis confirmed that the activated clay successfully removed carbonyl compounds and carboxylic acid components that were present in untreated oil. The unmodified clay had a smoother surface with fewer visible pores, whereas the activated clay exhibited a more porous structure with noticeable pores and cracks. The average pore diameter of the activated clay was larger, reflecting a 32.19% increase in pore size compared to the unmodified clay. Furthermore, the activated clay displayed a substantial enhancement in pore area relative to the unmodified version, with the average pore size increasing from 1.614 μm to 2.077 μm. In summary, acid activation treatment is the most effective method for recycling ULO, significantly improving its quality to a level nearly comparable to that of virgin lubricating oil (VLO).

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