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Augustine O. Ayeni*, Sarah Tagwai, Deima T. Dick, Oluranti Agboola, Ayodeji A. Ayoola, Damilola E. Babatunde, Babalola A. Oni
Department of Chemical Engineering, College of Engineering, Covenant University, Ota, Nigeria
*Corresponding Author: augustine.ayeni@covenantuniversity.edu.ng,
Tel: 08055745627

Abstract. This study aims to apply a two-stage solvent extraction and adsorption principles for base oil recovery from used lubricating oils (UBO). Methyl-ethyl ketone was utilized as the solvent for extraction and activated carbon (AC) from unripe plantain peels as the adsorbent. The activities of the solvent to oil proportions from 1:1 to 5:1 on lube oil recovery were analyzed in terms viscosity of the oil, total base number (TBN) of lubricating oil, and percent weight of metallic contents removal from used oil. The results confirm that solvent to oil ratio of 3:1 gave excellent efficiencies relating the UBO to a treated base oil (TBO) with the highest removal of contaminants, increased viscosity, high TBN after the two-stage treatments. The results after solvent extraction at varying temperatures of 30, 45, 60 ^{o}C showed the TBN increased to 32% (10.21 mgKOH/g from an initial UBO value of 6.90 mgKOH/g) at 60 ^{o}C extraction temperature. After the adsorption stage, the removal of metallic contaminants at the 60 ^{o}C extractive temperature and AC 15 wt% loading was 91% for calcium and over 91% for zinc. The optimum solvent to oil ratio of 3:1 at 60 °C yielded a base oil with a kinematic viscosity of 90.23 centiStokes, a flashpoint of 203 °C, the density of 0.909 g/ml and sulphur content of 0.64 wt%. This refined base oil obtained had close similarities with fresh Ram SN500 base oil.

1. Introduction

Lubricating oils are products obtained from the fractional distillation of petroleum between temperatures of 300 °C to 400 °C under atmospheric pressure. These are composed of saturated hydrocarbons such as alkanes that have longer chains of linear and branched paraffin, cyclic alkanes, and aromatic hydrocarbons. The saturated hydrocarbons present in lubricating oils may vary from low viscosity and molecular weight to high viscous oils with large molecular weight [1]. Among other uses of lubricating oils are: corrosion inhibition, friction reduction, and they also act as media for heat transfer [2].

A significant component of lubricating oils is base oil which accounts for 70– 90% of its composition. At the same time, the remaining fraction is made up of additives such as viscosity index improvers, corrosion inhibitors, anti-oxidants, anti-wear elements and antifoaming agents. As the service time of lubricating oil in the automobile engine progresses, the additives lose their properties, and the lubricating oil may gather some metal chips, combustion particles, water and dirt. The oil that has been degraded in this manner is referred to as used, waste or spent oil, and this will have to be removed and replaced [3]. Despite the hazardous effects of used oil on the environment, it can be considered as a valuable source of energy, and this has been explored extensively. Used oil can be re-refined into base lube oil by removing the contaminants present and processed to fuel oil, burnt to produce energy or used as feedstock for the production of various petroleum-based products. Recycling used lubricating oil is a concept that is not a new process but has been constantly improved, and hence several methods have been developed, and these include; vacuum distillation, solvent extraction, solvent extraction followed by adsorption, de-slugging and adsorption process [4].

The use of solvent extraction has been studied as an alternative method that involves the use of lower energy levels in comparison to other methods by a number of researchers [5, 6]. Solvent extraction is a treatment method of refining used lubricating oils, and this is based on the ability of a solvent to extract the base oil components from waste lubricating oil preferentially. Impurities and

additives that may be present in used oil will be rejected by the solvent and will settle based on gravity. The solvent can be regenerated by distillation for reuse. The ability of an oil to be extracted depends on the characteristics of the solvent and oil, the extraction temperature, contact time between the solvent and the feed [5]. Despite the effectiveness of the solvent extraction process, there exists a remaining section of the oxidization product present in the lube oil that can be treated by adsorption. Adsorption has been utilized in the removal of polycyclic aromatic hydrocarbons which are found present in the lube oil even after solvent extraction has been carried out [1].

This study investigates the treatment of used lubricating oil through solvent extraction and adsorption processes to recover the base oil. It entails involving various parametric determinations such as solvent to oil ratio, adsorbent to oil ratio, mixing time on oil recovery, and oil loss. The results aim to provide a basis for developing an environmentally and economically competitive method for used lubricant oil treatment.

2. Materials and methods

2.1. Materials sourcing

Used lubricating oil samples were carefully collected from an automobile workshop in the Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria. The solvent used for extraction was Methyl-ethyl ketone (99.5%) purchased from Sigma Aldrich Chemicals. Other chemical reagents used such as Propan-2-ol (99.5%) and Hexane (98 %) were purchased from Sigma Aldrich Chemicals. The adsorbent used was activated carbon prepared locally from unripe plantain peels of particle size less than 300 μm.

2.1.1 Solvent extraction. The solvent was mixed with the oil in the ratio (solvent: oil) 1:1, 2:1, 3:1, 4:1, and 5:1. The homogeneous mixtures were formed using a magnetic stirrer for 1 hour at extraction temperatures of 30, 45 and 60 °C. The mixtures were then transferred to a separating funnel and allowed to stand for 24 hours to ensure maximum separation. After 24 hours, the sludge settled at the bottom which was collected in a separate beaker, leaving the mixture of the oil and solvent at the top. The weight of the separated sludge was determined, and this wet sludge was washed with 7 cm^3 of hexane and 28 cm^3 of propan-2-ol. This removed sludge was placed in a dryer for 15 minutes at 100 °C to evaporate the excess solvents. The oily layer containing solvents and oil was distilled at atmospheric pressure and at a temperature of 80 °C (boiling point of methyl ethyl ketone) to recover the solvent and base oil. The separated base oil was then mixed with activated carbon at 30, 45 and 60 °C and the treated oil was analyzed.

2.1.2 Preparation of activated carbon. The activated carbon was prepared from unripe plantain peels obtained from a local market in Lagos, Nigeria. The unripe plantain peels were sundried for seven days and then ground to a smooth powder which was then sieved to particle sizes of less than 300 μm. The plantain peel powder was carbonized at 600 °C for 1 hour to get charcoal, and this was further activated by mixing 100 g of plantain peel powder with 100 ml of 10% phosphoric acid. The embodied carbon and activating agent was left for 24 hours to allow for maximum contact. The resulting carbon paste was dried at 100 °C for 1 hour using convention oven. The resulting carbon was cooled to room temperature. The carbon was washed with de-ionized hot water until a neutral pH was achieved.

2.1.3 Adsorption process. The solvent oil was treated with 15 wt% of the adsorbent. The mixture was stirred continuously at room temperature for 1 hour and left to allow the adsorbent to settle to the base of the oils. The treated oil is separated from the adsorbent with the aid of a filter paper. The effect of solvent-to-oil ratio and temperature on adsorption was evaluated by treating the oil sample with a constant adsorbent dosage of 15 wt% at a temperature of 30, 45 and 60 °C. The base oil obtained after adsorption was characterized to determine its properties.

2.1.4 Characterization of untreated and treated lubricating oil. The used lubricating oil (UBO) samples were obtained from the maintenance automobile workshop in the Department of Mechanical Engineering of Covenant University, Ota, Nigeria. The UBO were thoroughly mixed manual with a stirrer to obtain uniformity. The density of oils was obtained using the density bottle, and the measurements were related to the density of water. Viscosity measurements were obtained at both 40 ^{o}C and 100 ^{o}C using the vibro-iscometer cup. The flashpoint for the samples was determined using the Cleveland open cup apparatus method. The metallic content analysis was performed with atomic absorption spectrometer.

3. Results and discussion

3.1. Properties of used, treated, and Ram SN500 lubricating oil

The properties of the used, treated, and Ram SN500 oils are as given in Table 1

Table 1: Properties of used, treated, and Ram SN500 oils

Control test	Unit	Method	Values		
			UBO[a]	Treated at 3:1 ratio and 60 ^{o}C extraction-adsorption stage	Ram SN500
Density	g/ml	ASTM D 1298	0.9166	0.909	0.888
Viscosity at 40 ^{0}C	cSt	ASTM D 445	148.63	90.23	92
Viscosity at 100 ^{0}C	cSt	ASTM D 445	16.48	9.94	10.5
Viscosity index	none	ASTM D 2270	115	116	96
Flash point	^{0}C	ASTM D 92	200	203	240
TBN	mgKOH/g	ASTM D 2896	6.9	10.21	NA
Calcium	wt%	ASTM D 6481	0.2	0.083	NA
Zinc	wt%	ASTM D 6481	0.11	0.001	NA
Sulpur	wt%	ASTM D 6481	0.7	0.60	0.4

[a]Untreated base oil

3.2. Effect of extraction temperature and solvent to oil ratio on percentage oil losses

As shown in Fig. 1, the lowest oil losses are obtained at the highest solvent to oil ratio at each temperature. This can be attributed to the fact that when the solvent to oil ratio increases, the tendency for the solvent to become saturated by base oil molecules reduces, and hence the amount of base oil that can be selectively dissolved in the solvent increases. Also, as the temperature increased, the oil losses also decreased. It may be expected that oil losses should increase with increasing temperature. However, this is not the case under the prevailing conditions. The reduced oil losses at increasing temperature may be attributed to the attainment of high viscosity of the oil at increasing temperature. For example, at 60 ^{o}C, viscosity of 5:1 solvent to oil ration is 87.45 cSt unlike 68.20 cSt (Table 2) at

30 ^{o}C for the same ratio. In order words, the viscosity of the oil tended to reduce the loss of oil. The optimum result was at a temperature of 60 ˚C and solvent to oil ratio of 5:1.

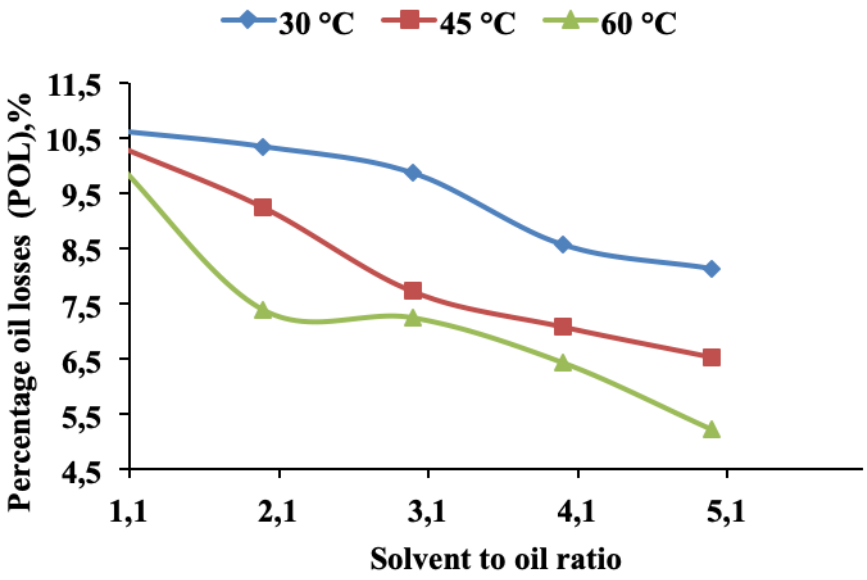

Fig. 1. Oil losses variation with solvent/oil ratio at varying temperatures

3.2.1 Effect of extraction temperature and solvent to oil ratio on oil quality. Oxidation and contamination can cause an increase in the viscosity of used oil whereas dilution with light fuels could reduce the viscosity. The viscosity at 40 ˚C of the used oil was recorded as 148.63 cSt (Table 1) which shows the presence of high molecular weight contaminants and residual aromatic compounds. This value was reduced after extraction as shown in Fig. 2. As the solvent to oil ratio was increased, these contaminants were removed, hence, the decrease in viscosity. Lowest viscosity was recorded at 45 ˚C and solvent to oil ratio of 5:1, however when compared to fresh oil whose viscosity is 92.0 cSt, the optimum process can be seen to be 3:1 ratio at 60 ˚C. The flash point of the used oil was recorded as 200 °C which increased further considering the lower temperatures (extraction at 30 ^{o}C and 45 ^{o}C) but got reduced at higher temperature of 60 ^{o}C (Fig. 3). The presence of light ends in the used oil may account for the low flash point value. However at temperatures above 45˚C, the flash point showed a decreasing trend. Since two parameters (cohesion and molecular interchange) affect fuel viscosity, there is the possibility that fuel viscosity increases with temperature. When considering cohesion, fuel viscosity decreases with temperature. When considering molecular interchange, fuel viscosity increases with temperature. This is also related to the flash point of the fuel. The total base number (which is the measurement of alaline concentration that it present in a lubricant) of treated oil increased generally with increasing temperature and viscosity (Table 2). The higher the TBN number, the more effective the lubricant will be able to destroy acid build-up thereby improving the lubricating ability of the oil.

Table 2. Properties of solvent extraction treatments of treated lubricating oil at varying temperatures and solvent to oil ratios

Solvent to oil ratio	Temp. (°C)	Viscosity at 40 °C	Viscosity at 100 °C	Density (g/ml)	Total base number (TBN)
1:1	30	84.84	9.96	0.887	9.40
	45	82.59	9.90	0.899	8.00
	60	96.89	10.23	0.907	11.00
2:1	30	75.39	9.95	0.892	8.20
	45	74.34	9.80	0.903	6.70
	60	94.63	10.05	0.908	10.89
3:1	30	74.69	9.92	0.894	6.90
	45	70.45	9.69	0.905	5.40
	60	90.23	9.94	0.909	10.21
4:1	30	71.52	9.64	0.895	6.20
	45	68.99	9.59	0.909	4.90
	60	89.13	9.72	0.910	9.89
5:1	30	68.20	9.59	0.899	6.00
	45	65.00	9.42	0.909	4.50
	60	87.45	9.65	0.914	9.56

Also, the density of the used oil was shown to be of higher value than that for the refined oils. This is attributed to the presence of sludge and sulphur compounds.

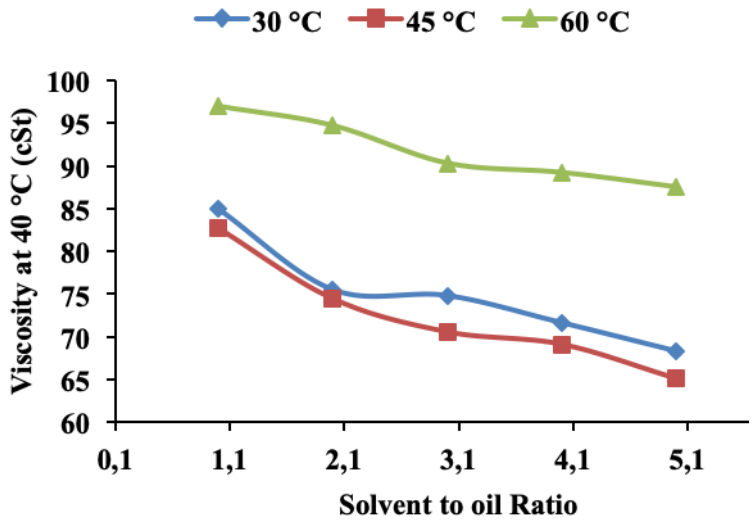

Fig. 2. Viscosity variations with solvent-to-oil ratio

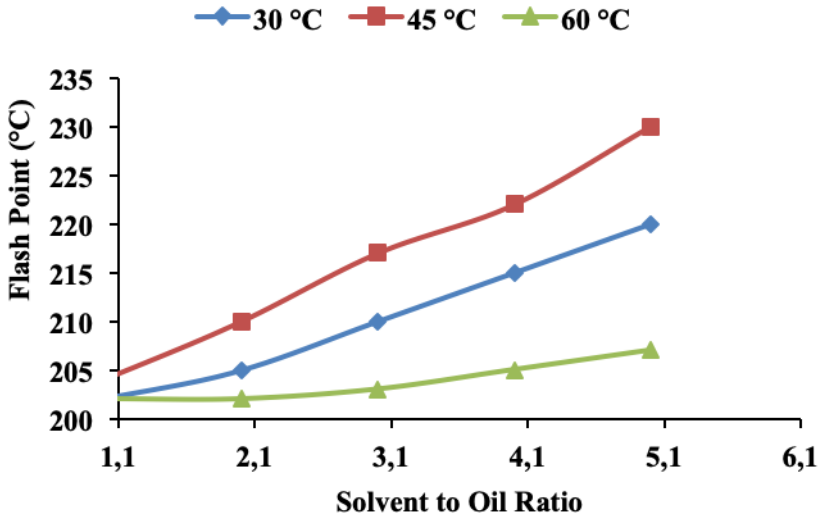

Fig. 3. Flash point variations with solvent-to-oil ratio

3.2.2 Metal and non-metal content. The rate of corrosion of metal parts can be increased when they come in contact with the metal and non-metal contents of the used oil. The additives added to the oil during production brings about the metal and non-metal content. Additives such as detergent contains the calcium element, anti-oxidant or corrosion inhibitor additives contains the zinc element while sulphur is introduced by extreme pressure additives. Metals especially the heavy metals are associated with potential toxicity or eco-toxicity [7]. Figs. 4, 5 and 6 gives the effect of solvent:oil ratio on these contents at 30, 45 and 60 ^{o}C respectively. It can be noted that increase in the temperature and solvent-to-oil ratio has the most effect on the metals and non-metals removal.

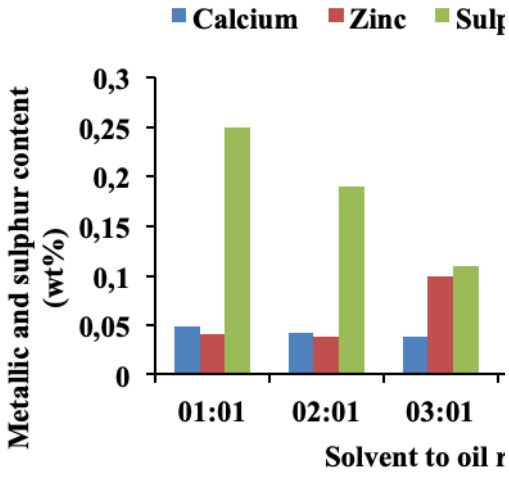

Fig. 4. Metallic and sulphur variations with solvent/oil ratio at 30 ˚C

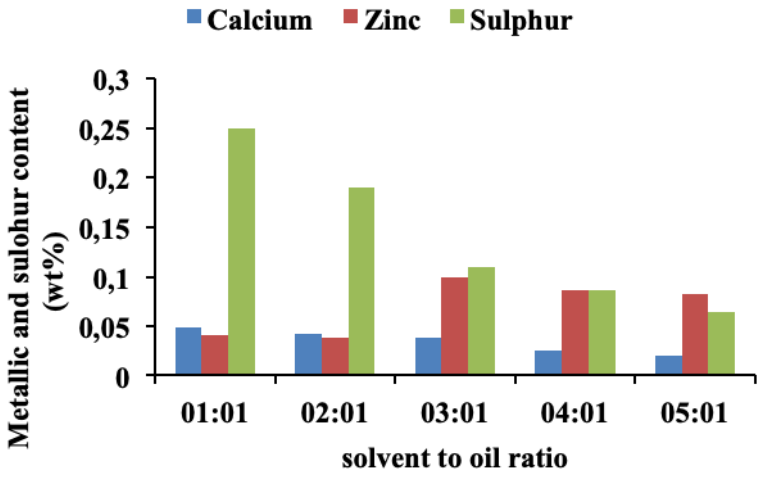

Fig. 5. Metallic and sulphur variations with solvent/oil ratio at 45 ˚C

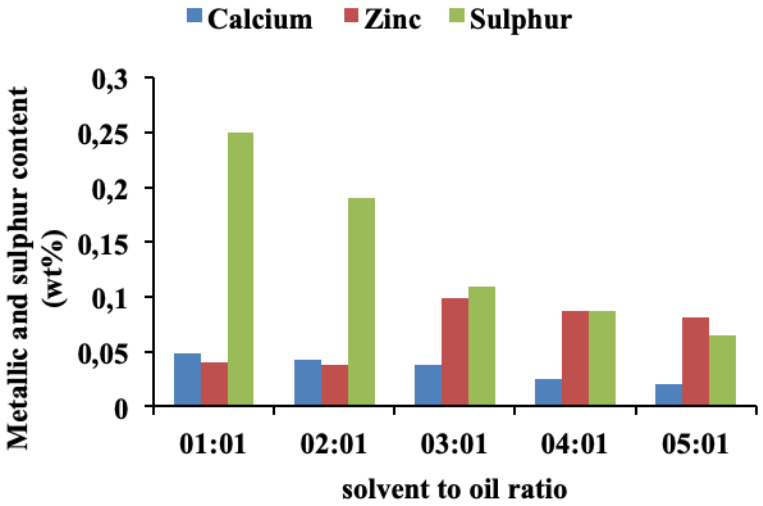

Fig. 6. Metallic and sulphur variations with solvent/oil ratio at 60 ˚C

3.3. Effect of contaminants removal by adsorbent

Adsorption aids in the removal of colour, odours, impurities and metals that may be present in the used lubricating oils. The adsorption treatment of oil is based on the ability of an adsorbent to selectively extract resinous and sulphur containing compounds, unsaturated and polycyclic material and also organic residues of sulphuric acid and solvents from oils. Adsorption was carried out with 15 wt% of activated carbon on the solvent refined oil at 30, 45 and 60 ˚C and contact time of 120 minutes. The effect of adsorbent (activated carbon) on the different solvent-to-oil ratio and properties such as density, viscosity, flash point and sulphur content were analysed. These properties were compared with fresh (Ram SN500) and used oil as shown in Table 1. The effect of adsorption temperature on viscosity is presented in Figure 7. From the results, temperature of 45 ˚C and solvent to oil ratio of 5:1 gave the lowest value of viscosity, however when compared to fresh oil, the optimum

process is seen to be at 60 °C and 3:1 solvent to oil ratio. This can be attributed to further absorption of impurities in the oil. As previously stated, the reduction in density value after extraction is attributed to the removal of sludge from the oil. After adsorption, no significant change in the density was recorded but when compared with the fresh Ram SN500 oil, the solvent to oil ratio of 1:1 gave the closet value of density. Also, the flash point of the adsorbed oil recorded no significant change after adsorption.

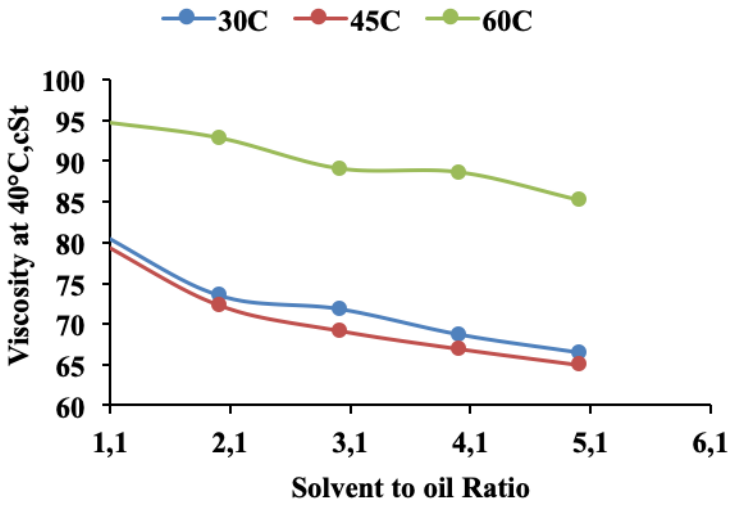

Fig. 7. Viscosity variations with solvent-to-oil ratio

3.3.1 Metal and non-metal contents. Adsorbent refining of oil is a physical method which depends on the affinity between the adsorbent and the adsorbate in the waste oil. Figs. 8, 9 and 10 show the effect of adsorption on the solvent extracted oil with respect to the metal and non-metal content in the oil at 30, 45 and 60 ˚C. When these values are compared with that obtained from solvent extraction as in Figs. 4 to 6, it is seen that as temperature increased the adsorption of metals improved in the presence activated carbon which shows a strong affinity between the metals and the activation element in the adsorbent. Comparing these values with the fresh oil in Table 1 also shows an improvement in the sulphur content with the 5:1 solvent/oil ratio at 60˚C giving the minimum value of 0.065 wt%.

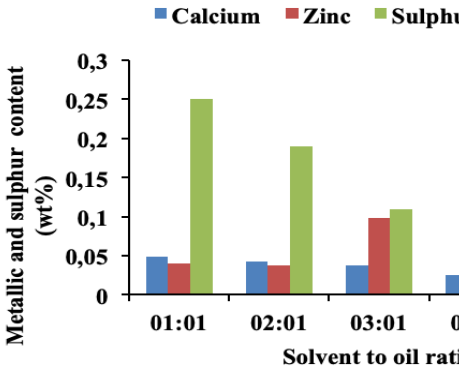

Fig. 8. Metallic and sulphur contents variation with solvent/oil ratio at 30 ˚C

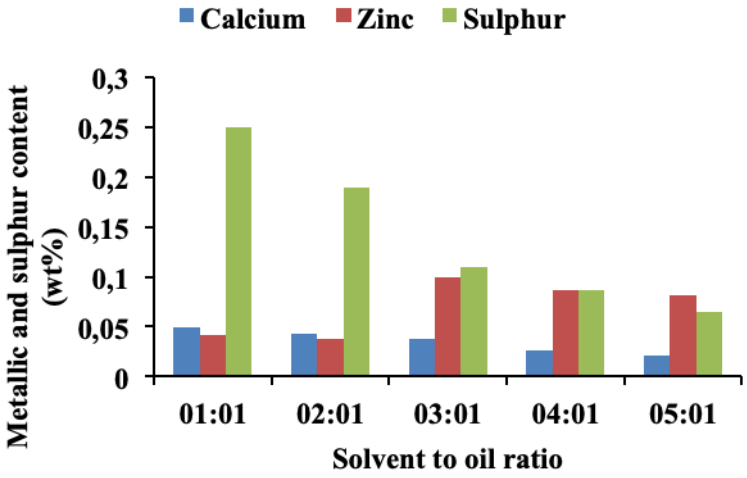

Fig. 9. Metallic and sulphur contents variation with solvent/oil ratio at 45 ˚C

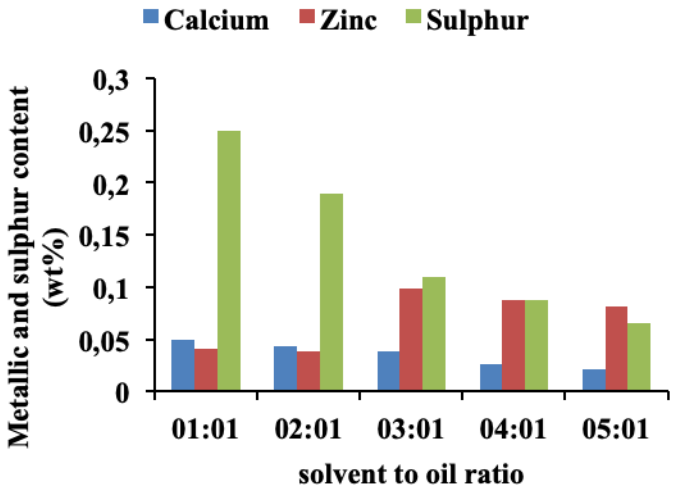

Fig. 10. Metallic and sulphur contents variation with solvent/oil ratio at 60 ˚C

4. Conclusion

Solvent extraction followed by adsorption has been found to be one of the competitive processes for the recycling of waste lubricating oil. In this paper, a two-stage performance of various solvents to oil ratio with the use of Methyl-ethyl ketone as solvent at 30, 45 and 60 ˚C, and adsorption of contaminants using activating carbon has been studied. The first stage of solvent extraction of used lubricating oil gave rise to the second stage of adsorption where activated carbon from unripe plantain peel as adsorbent was used to re-establish the main properties of the base oil. The solvent extraction had the ability to remove contaminants such as sludge. Also, properties such as the total base number, density, viscosity, flash point, as well as metallic and sulphur contents removal were enhanced. The results after solvent extraction at varying temperatures of 30, 45, 60 ^{o}C showed the total base number increased to 10.21 mgKOH/g from an initial untreated base oil value of 6.90 mgKOH/g at 60 ^{o}C

extraction temperature. After the adsorption stage, the removal of metallic contaminants at the 60 ^{o}C extractive temperature and activated carbon 15 wt% loading was 91% for calcium and over 91% for zinc. A kinematic viscosity of 90.23 centi Stokes, a flashpoint of 203 °C, the density of 0.909 g/ml and sulphur content of 0.64 wt% were recorded as optimum for 3:1 at 60 °C

Acknowledgement
The authors are grateful to the Management of Covenant University, Ota, Nigeria, for sponsoring AOA to attend ICSSD 2020 and the publication of this article.

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