Potentials of African Star Apple (*Chrysophyllum albidum*) Fruit Shell Adsorbent in Recovery of Valuable Hydrocarbons for Spent Engine Oil

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Keywords: Spent engine oil, hydrocarbon recovery, *Chrysophyllum albidum* shell adsorbent.

Abstract. Inventory of spent engine oil continuously increase and indiscriminately disposed of at auto-mechanics garages. Adsorptive separation established to be indispensable in recovery of these hydrocarbons was carried out using *Chrysophyllum albidum* (African star apple) fruit shell – a renewable resource. In this study, clay pretreated spent engine oil was recovered in a fixed bed adsorption processes and the recovered adsorbate components determined by GC-MS analysis. The results showed African star apple fruit shell adsorbent effective in recovering n-hexane solubilized spent lubricating oil. The study concluded that using the developed African star apple fruit shell adsorbent, an agricultural waste adsorbent in the recovery of waste lubricating oil will enhance greatly the nation's economy.

Introduction

Lubricant is a composited organic substance, capable of reducing friction between surfaces, usually metals in physical contact, thereby reducing the heat generated by the motion of the contacting surfaces. Functions of the lubricating oil are; cooling of surfaces when applied, transmitting forces and transporting foreign particles off the contacting surfaces [1]. Thus, lubricating oils play dual function of heat removal and that of friction reduction [1-3]. Lubricating oil from petroleum consists mainly complex mixtures of hydrocarbons. It mostly consists of isoalkanes with slightly longer branches, mono cycloalkanes and mono aromatics with several branches on the ring [2].

The main ingredient of lubricating oil is the base oil, obtained either from crude oil or synthesized. Additives are then mixed with the base oil is to enhance its ability to act as a film layer between contact surfaces. Therefore there are different grades of lubricating oil with varying quality and unique purpose, and this determines the types of additives added [1].

According to Kadjas [4], lubricating oil is made up of base oil stock between 71.5-96.2 wt% and 3.8-28.5 wt% of additives blended together based on grade and specific duty. Various types of additives in typical lubricating oil composition is shown in Table 1[4].

Waste lubricating oil is distinctly a stable, almost homogeneous spread of undergirded base oil and additives contaminated with scrapings of metals from bearing surfaces, varnish, gums and other compounds from the degradation of the fresh engine oil [5]. About 50 % of base oil globally are naphthenes containing largely cyclic compounds derived from naphthenic crude stocks. Chlorinated solvents may also be present in fairly large amount in SEO as a result of the degradation of additive packages. Sometimes, halogenated substances may results from addition of chlorine and bromine as lead scavengers in leaded gasoline. Polynuclear aromatic hydrocarbons (PAHs) contents made this spent lubricant carcinogenic [5]. Therefore, reclamation of the waste into virgin lubricating oil would be useful alternative to protect the environment. Recycling waste lubricating oil has embellished economic advantage due to high percentage of recoverable base oil than that from crude oil.

Table 1. Composition of typical lubricating oil

Ingredients	Wt %
SAE 30 or 40 base oil stock	71.5-96.2
Additives	
Metallic detergent	2.0-10.0
Ash less dispersant	1.0-9.0
Antioxidant/anti wear	0.1-2.0
Friction modifier	0.1-3.0
Pour point depressant	0.1-1.5
Antifoam [ppm]	2.0-15.0

Source: Kajdas, C, (2000) [4]

Used lubricating oil is one of the massive liquid wastes in the world that needs to be recovered for improved global economy.

Globally, several million tonnes of spent engine oil [SEO] are generated annually and disposed of discretely into the environment [6]. SEO had been handled basically three ways: (a) open disposal of the SEO on land, garbage heap and sewerage system, (b) reclamation of base-oil from SEO and (c) extracting the et al. heat content of SEO by combustion processes [1, 7].

In the course of usage, lubricating oils undergo degeneration and become contaminated by picking up contaminants from the system environment, including, residual lubricating oil, solids materials from frictional effects as well as corrosion products, soot, combustion products and dirt [8]. The contamination could include unsaturated hydrocarbons, aldehyde, phenolic compound, acidic compound, gums, additive, metals, varnish, and others [8]. Degradation involves changes in the hydrocarbons' molecular structure resulting from cracking, isomerization and polymerization reactions actuated by high temperatures in the crankcase of the running engine. Degradation results in formation of low hydrocarbon chain molecules and oxidation products such as polymerized or condensed molecules known as sludge and gum. In spite of impurities, a large amount of the base oil part in the SEO is usually preserved due to the high stability of the base oil [9]. SEO is an anthropogenic pollutant due to its toxicity, so dumping in the ground diminishes soil efficiency and affects negatively the edibility of the plants grown on it. Incineration of SEO releases PAHs to the environment while landfill disposal leads to seepage into underground water. Also, SEOs are used in all core industrial sectors such as railways, marine, manufacturing and transport for lubrication [10].

If managed properly, waste oil can be a very valuable resource. About 65-75% SEO content are base oil, which would constitute loss of valuable natural resource if burnt or dumped indiscriminately. [7]. Several methods reportedly utilized to recovery of spent lubricating oil in the literature include, but not limited to distillation [11], thermal dehydration [12], acid treating [13] solvent extraction, hydro treating [14] and combination of these methods [11 - 15]. Adsorptive removal of contaminants needs to be explored to adequately appropriate the hydrocarbons in the SEO. More so that Eleni et. al. [16] reported adsorption and membrane filtration to optimally remove contaminants from most industrial effluents. Several agricultural materials have been evaluated as adsorbent such as sawdust, sugarcane fiber, palm kernel shell, groundnut husk, maize cobs, sugar beet pulp, bamboo chips [17-22]). So, agricultural wastes materials having potentials as adsorbents could be extended to this purpose serving both environmental and economic values. The objective of this present study therefore, is to utilize waste agriculture materials as adsorbents for recovery of base oil hydrocarbons from spent engine oil. The expectation is conservation of environment, clean-up of wastes and energy generation.

Processing of fruits generates a lot of waste products including *Chrysophyllum albidum* seed shell. The activated carbon from *Chrysophyllum albidum* seed shell has been experimented for the adsorption of cadmium in wastewater among other toxic metals. It was also reported to have sequestering potentials for cadmium in waste water [23]. Extending the application of *Chrysophyllum albidum* seed shell to recovery of spent engine-oil will serve a dual purpose of economic recycling of waste petroleum product and environmental clean-up of agricultural wastes, more so that the

inventory of spent engine oil for disposal will be reduced drastically. It will equally serve as low-cost industrial adsorbent.

This paper thus presents new frame work for spent oil re-usability, adapting African star apple seed shell which have hitherto been a waste agricultural matter, as adsorbent for that purpose.

Materials and Methods

Spent Lubricating Oil used for this study was collected from service station in Oshogbo, Osun State, South western Nigeria. It lies on coordinate 7°46' North 4°34' East. The sample was obtained from a heavy duty diesel truck after being used. The sample collected was transferred to a plastic container, stored away from light at room temperature. After a period of one (1) month, it was noticed that the suspended particles had settled under gravity. The sample was then decanted and the sludge containing the solid impurities, kept for further analysis. The decanted oil was centrifuged at 1000 rpm for 20 mins to remove the other insolubles in the spent oil.

Adsorbent Preparation and Characterization. The adsorbents used for this research were prepared from Walnut shell, Egg shell, African star apple fruit shell, and Rice husk. Wall nut and African star apple fruits as well as fresh eggs were collected from local farms, deshelled and kept for processing, while rice husk was collected from rice processing mill in Oshogbo, Osun state, south western Nigeria. The samples were grounded in a ball mill, sieved into different sizes using standard mesh. Apart from the egg shell, the samples were soaked in distilled water for 12 hour to remove water soluble matter. It was thereafter washed, boiled in distilled water for 1 hour, washed again, sundried and then oven dried at 105 °C to remove other volatiles. They were cooled and kept for analysis and use.

The adsorbent samples were characterized by determining the specific gravity at 30 °C, Bulk Density (g/m³) and Porosity (%), as well as X-ray fluorescence and the Textural analysis, using standard methods [24-25],

Specific Gravity (ASTM D 854-00). About known weight of sample (W_O) was measured into a clean dry pre-determined weight pycnometer (W_P) and the weight of pycnometer and sample was determined (W_{PS}). Distilled water was added to the sample to about 70 percent filled and allowed to soak for 5 minutes. Entrapped air was removed using vacuum pump connected to the pycnometer for 5 minutes. The pycnometer was then filled to mark with distilled water, cleansed and weighed (W_B). The pycnometer was emptied, cleansed and then filled with distilled water only and weighed (W_A).

The specific gravity was calculated as

$$\text{Specific gravity, SG} = \frac{W_O}{W_O + (W_A - W_B)} \quad (1)$$

Where,

W_O = weight of dry sample, $g = W_{PS} - W_P$

W_A = weight of pycnometer filled with water

W_B = weight of pycnometer filled with water and sample

Porosity and Bulk Density. A clean dry density bottle was weighed (W_{DB}). The bottle was filled with water, corked and reweighed (W_{BA}), small quantities of samples were gradually put into the bottles with little amount of water and weighed again (W_{BB}). The bulk density and porosity were calculated using the following expressions.

$$\text{Bulk density} = \frac{\text{mass of wet sample} = W_{BB} - W_{DB}}{\text{volume of the density bottle} = V_{DB}} \quad (2)$$

$$\text{porosity, } \eta = \frac{V_V}{V_{DB}} = \frac{\text{volume of void}}{\text{volume of the density bottle}} \quad (3)$$

$$\text{The volume of void, } V_V = V_{DB} - V_S \quad (4)$$

where, V_s is the volume of sample and it is given by

$$V_s = M_s / SG \rho_w \quad (5)$$

Where M_s = mass of solid, SG = specific gravity, and ρ_w = density of water.

Textural Properties. Texture Profile Analysis of the sample was performed using TA.XT plus Texture Analyzer (Stable Micro Systems Ltd., Godalming, Surrey, UK). The sample was compressed to 30% with a 100 mm diameter compression plate (P/100) for texture profile analysis (TPA) at test speed of 5 mm/s, trigger force of 30 g-auto for a period of 5 s. The maximum force required to break the cookies was noted as hardness and gumminess and chewiness values were calculated [26].

XRF Analysis. X-Ray Fluorescence was used to analyze the elemental composition of the sample based on surface analysis. The sample was irradiated with X-rays in an energy dispersive X-ray fluorescence spectrometer (Shimadzu EDXRF-702HS) operated at 40 kV and 18 mA. The intensity of element $K\alpha$ counts per second (cps/ μ A) was obtained from the sample X-ray spectrum using the Shimadzu EDX software package.

Fourier transformed infrared spectroscopy (FTIR). The type of functional groups of the sample was determined using SHIMADZU Happ-Genzel Fourier Transform Infrared Spectrophotometer. The samples were dried in an oven at 60 °C to remove the moisture. About 0.2 mg of sample and 2 mg of potassium bromide were mixed and ground finely before the mixture was compressed to pellet. The infrared spectra of these samples were measured in the transmission of a wavelength -ln umber range between 4000 and 400 cm [27].

Clay Preparation. Clay sample used to pretreat the SEO was collected from a deposit in Oshogbo, washed with clean water and then with distilled water, sun dried then oven dried at temperature of 110 °C for five (5) hours to eliminate the volatiles and organic matters in the clay. The sample was then allowed to cool gradually. The clay sample was then crushed and ground to particle size of ≤ 0.100 mm and stored in cool dry place for use.

Pre Treatment of SEO. Approximately 100 ml of centrifuged spent lubricating oil sample was mixed with 20 g of the clay in a beaker and heated to 130 °C, stirring continuously for one (1) hour with the electric stirrer maintained at the temperature of 130 °C. The sample was then allowed to cool and then decanted. This process was carried out in fume controlled hood.

Adsorption Process. A 2.5 cm diameter graduated glass pipe was packed with the adsorbent to a height of 14 cm separately. The oil and each of the solvents were mixed in the oil:solvent ratio of 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7 and 1:10 and the mixture shaken thoroughly to homogenize. It was observed that mixing was effective for oil to solvent ratio of 1:5 and above. This preliminary evaluation revealed hexane as the suitable solvent for the mobile phase due to its high miscibility, hence ability to carry the compounds of the SEO. Therefore, oil to solvent ratio 1:5 and 1:10 were considered for this research and hexane as the solvent eluant. The mixture was then pour into the packed column and allowed to run through the bed. The eluate from the column was collected and taken for GC-MS analysis.

Gas Chromatography Mass Spectrometry Analysis. The Gas Chromatography and Mass Spectrometry (GC-MS) analysis was done using a Varian 3800 gas chromatography equipped with an Agilent MS capillary column (30 m x 0.25 mm i.d.) connected to a Varian 4000 mass spectrometer operating in the EI mode (70ev; m/z 1 – 1000; source temperature 230 °C and a quadrupole temperature 150 °C). The column temperature was initially maintained at 200 °C for 2min, increased to 300 °C at 4 °C/min, maintained for 20 min at 300 °C. The carrier gas was nitrogen at a flow rate of 1.0 ml/min. The inlet temperature was maintained at 300 °C with a split ratio of 50:1. A sample volume of 1 μ l in chloroform was set to scan in the range of m/z 1- 1000 with electron impact (EI) mode of ionization.

Results and Discussion

Preparation of Adsorbent. The African star apple fruit shell adsorbent has bulk density, specific gravity and porosity of 0.40 g/m³, 0.92 and 12.5 % respectively. The specific gravity value is close to the value of 0.89 reported by Olufunmilola and Oladapo [28] at the same temperature of 30 °C.

In studying the effect of particle size on the adsorption process, the adsorbent was sieved with standard mesh to two fractions; the first fraction with particle size of $\leq 6 \mu\text{m}$ were close to being powdery and the second fraction which have the particle size of 1.18 mm were granular in nature. The 1.18 mm fraction was used for the adsorption based on experience and literature [29]. The XRF analysis reported in Table 2 showed main chemical composition Mg, Na and K constituting 95 percent component of the ASA adsorbent with K amounting to 74.14 %. It has low concentration of heavy metals with chromium having less than 2.4 % occurrence and Pb, Cu and Cd less than 0.022 % Titanium has 0.108 percent occurrence.

Table 2. XRF analysis of ASA sample

S/N	Parameters	Symbol	Composition (mg/g)	Occurrence (wt %)
1	Phosphorus	P	2.20	0.579
2	Zinc	Zn	0.23	0.061
3	Iron	Fe	3.82	1.006
4	Calcium	Ca	0.86	0.226
5	Magnesium	Mg	39.42	10.377
6	Sodium	Na	40.00	10.529
7	Potassium	K	281.64	74.137
8	Chloride	Cl	0.57	0.150
9	Aluminum	Al	0.22	0.058
10	Lead	Pb	0.08	0.021
11	Chromium	Cr	8.94	2.353
12	Copper	Cu	1.02	0.268
13	Cadmium	Cd	0.01	0.003
14	Titanium	Ti	0.41	0.108
15	Loss of ignition	LOI	0.47	0.124
	Total		379.89	100.000

The result of textural analysis of the sample showed that the adsorbent has hardness of 87.14 N, gumminess of 75.56 N and Chewiness of 75.03 N. These parameters indicates moderate cohesiveness and compactness of the adsorbent.

FTIR analysis. The wave number range of FT-IR spectrum (Fig. 1) is from 4000 cm⁻¹ to 400 cm⁻¹. The peaks located at 1758.06 and 2710.33 cm⁻¹ are the characteristic of carbonyl group stretching from aldehydes and ketones [30] and C-H stretching of aldehyde of 2841.53 cm⁻¹ of aldehyde [31]. The ethereal C-O-C stretching is observed at 1410 cm⁻¹. The absorption at 936.25 cm⁻¹ is due to -OH group bending vibration of carboxylic acid. The peaks in the range 1242.65 – 1117.08 cm⁻¹ are significant of amines -C-N stretching. This observation reflected the report of Ajayi et al [32] that major components of African star apple seed shell comprised stigmasterole, myricetin-3-rhamnoside, beta amyryn acetate, eleagnine and gentisic acid. The spectrum is significantly similar to that observed for the Chrysophyllum albidum seed oil [33]. It can be concluded that hydroxyl, carboxyl, carbonyl and hydrocarbonyl groups are the main components of ASA adsorbent with presence of amine and halides.

Fig 1. FT-IR Spectrum of ASA Adsorbent

GC-MS Analysis Result. The experimental results of the Gas Chromatography-Mass Spectrometry (GC-MS) analysis for all the recovered samples from the adsorptive chromatographic separation of spent lubricating oil are presented for the fresh lubricating oil, used lubricating oil and that of recovered oil in Tables 3, 4 and 5, respectively. Several compounds were identified in the fresh lubricating oil including phytane ($C_{20}H_{42}$) having the highest occurrence of 12.00 weight %. The least occurring compound identified is 2, 4-bis-(t-butyl)-methoxy benzene ($C_{16}H_{26}O_2$) having 0.04 weight % occurrence. About 60 weight percent of the compounds are unsaturated which are either cyclic, benzyl or enyl derivatives. Its GC-MS chromatogram is shown in Fig 2. The longest carbon chain compound identified in the fresh lubricating oil sample is N-dotriacontane ($C_{32}H_{66}$) which is a saturated hydrocarbon and occur at 0.54 weight percent. This corroborates the report of Taiwo and Bello [11] that the lubricating oil usually contains hydrocarbons with $\leq C_{32}$ carbon length. The compounds identified in untreated SEO using GC-MS analysis (Fig. 3), showed dibenzo-thiophene ($C_{12}H_8S$) having the highest occurrence of 9.46 weight %, and perylene ($C_{20}H_{12}$) with 0.02 weight %, being the lowest occurrence compound in the sample. Comparing Tables 3 and 4, it could be observed that almost all compounds present in the fresh lubricating oil are present in spent lubricating oil. This revealed lubricating oil as a petroleum product which is not fully consumed during use, corroborating the report of [15]. However, acetic acid ($C_2H_4O_2$), acetaldehyde (C_2H_4O), 1, 2- benzene dicarboxylic acid ($C_8H_6O_4$) and dibutyl ester ($C_{12}H_{22}O_4$) are not present in the fresh oil. The presence of these compounds could have resulted from contamination of the lubricating oil due to usage in the engine.

Fig 2. GC spectrum of fresh lube oil

Similarly, some compounds, such as, oleanane ($C_{30}H_{52}$), N-dortriacontane ($C_{32}H_{66}$), tetradecane trimethyl ($C_{17}H_{32}$), hopane ($C_{30}H_{52}$) occurring in VEO were not found in the SEO implying possible conversion or breakdown of these hydrocarbons, which were in the range C17 to C30. Oleanane, gammacerane and hopanes are C30 isomers of pentacyclic triterpenoid. Thermal degradation of these terpenoids could lead to dehydrogenation producing aromatic systems, or epoxidation, or oxidative cleavage of double bond resulting to aldehyde or ketone generation, or allylic oxidation and rearrangement to form alcohols, ketones and aldehyde [34, 35]. A schematic representation of these possible conversion of terpenoids is given in Fig. 4.

Fig 3. GC spectrum of untreated spent engine oil

Acetic acid occurrence in the spent lubricating oil might have resulted from oxidation of light naphtha components which could have been obtained from catalytic cracking of Biphenyl or fluorene and even naphthalene present in the fresh lubricating oil, oxidized by oxygen or even air to give peroxides, decomposing further to produce acetic acid [36, 37].

The above oxidation requires metal-based catalyst which could have been obtained from metal scrapings resulting from rubbing surfaces due to friction. The presence of these compounds are probably responsible for the contamination of the spent lubricating oil.

Table 3. Identified Compounds from GC-MS Analysis of FEO Sample

S/N	Compound	Molecular Formula	Molecular Mass	wt %
1	Naphthalene	C ₁₀ H ₈	128.17	1.45
2	Floroethene	C ₂ H ₃ F	62.50	0.08
3	Propan-2-ol	C ₃ H ₈ O	60.10	1.02
4	Butadiene	C ₄ H ₆	54.06	0.19
5	Biphenyl	C ₁₂ H ₁₀	154.21	1.83
6	Acenaphthylene	C ₁₂ H ₈	152.20	3.80
7	Pyrene	C ₁₆ H ₁₀	202.25	9.63
8	Perylene	C ₂₀ H ₁₂	252.32	0.32
9	Anthracene	C ₁₄ H ₁₀	178.23	6.08
10	Ethylene glycol	C ₂ H ₆ O ₂	62.07	4.81
11	Tridecanol	C ₁₃ H ₂₈ O.	200.40	0.35
12	Pristane	C ₁₉ H ₄₀	268.51	0.72
13	Phytane	C ₂₀ H ₄₂	282.56	11.70
14	Steranes	C ₂₉ H ₅₂	400.74	2.69
15	Dibenzo-thiophene	C ₁₂ H ₈ S	184.26	6.44
16	Benzo-naphtho-thiophene.	C ₁₆ H ₁₀ S	234.32	3.83
17	Phenanthrene	C ₁₄ H ₂₈ O ₂	228.12	5.32
18	Oleanane	C ₃₀ H ₅₂	412.75	1.75
19	Gammacerane,	C ₃₀ H ₅₂	412.75	1.50
20	Decamethylcyclopentasiloxane	C ₁₀ H ₃₀ O ₅ Si ₅	370.77	2.90
21	N-Dotriacontane	C ₃₂ H ₆₆	450.88	0.54
22	Fluorene	C ₁₃ H ₁₀	166.32	5.06
23	Chrysene	C ₁₈ H ₁₂	228.29	3.77
24	Tetradecane 2,6,10 trimethyl	C ₁₇ H ₃₂	240.72	8.47
25	Benzo[k]fluoranthrene	C ₂₀ H ₁₂	252.32	1.11
26	2-Ethyl-1-hexanol	C ₈ H ₁₈ O	130.23	0.54
27	Decanoic acid methyl ester	C ₁₁ H ₂₂ O ₂	186.30	0.09
28	2,4-bis-(t-butyl)-methoxy benzene	C ₁₆ H ₂₆ O ₂	250.38	0.04
29	Cyclopenta (cd) pyrene	C ₁₈ H ₁₀	226.28	0.90
30	Hopanes	C ₃₀ H ₅₂	412.75	0.18
31	Indeno(1,2,3-cd)pyrene	C ₂₂ H ₁₂	276.34	4.81
32	Dibenzo(ah)anthracene	C ₂₂ H ₁₄	278.35	3.34
33	Benzo(ghi)perylene	C ₂₂ H ₁₂	276.34	1.16
34	3,5-bis(t-butyl)-Phenol	C ₁₄ H ₂₂ O	206.32	0.62
35	Benzo(a)pyrene	C ₂₀ H ₁₂	252.31	3.01

Table 4. GC-MS Analysis for Untreated Spent Lubricating Oil

S/N	Compound	Molecular Formula	Molecular Mass	wt %
1	Naphthalene	C ₁₀ H ₈	128.17	2.75
2	Acetic acid	C ₂ H ₄ O ₂	60.05	3.84
3	Propan-2-ol	C ₃ H ₈ O	60.10	0.02
5	Butadiene	C ₄ H ₆	54.06	0.16
6	2,6-bis- (t-butyl)Phenol	C ₁₄ H ₂₂ O	206.33	1.38
7	Acetaldehyde	C ₂ H ₄ O	40.06	2.96
8	Acenaphthylene	C ₁₂ H ₈	152.2	1.90
9	Pyrene	C ₁₆ H ₁₀	202.25	4.07
10	Perylene	C ₂₀ H ₁₂	252.32	0.02
11	Anthracene	C ₁₄ H ₁₀	178.23	3.45
12	Ethylene glycol	C ₂ H ₆ O ₂	62.07	2.02
13	Tridecanol	C ₁₃ H ₂₈ O.	200.40	0.12
14	Pristane	C ₁₉ H ₄₀	268.51	0.13
15	Phytane	C ₂₀ H ₄₂	282.56	5.21
16	Steranes	C ₂₉ H ₅₂	400.74	5.26
17	1,2-Benzene dicarboxylic acid	C ₈ H ₆ O ₄	400.74	3.43
18	Dibenzo-thiophene	C ₁₂ H ₈ S	184.26	9.46
19	Benzo-naphtho-thiophene.	C ₁₆ H ₁₀ S	234.32	4.29
20	Phenanthrene	C ₁₄ H ₂₈ O ₂	228.12	1.48
21	1,1-Diphenyl hydrazine	C ₁₂ H ₁₂ N ₂	184.24	1.19
22	Decamethylcyclopentasiloxane	C ₁₀ H ₃₀ O ₅ Si ₅	370.77	5.50
23	Fluorene	C ₁₃ H ₁₀	166.32	5.85
24	dibutyl ester	C ₁₂ H ₂₂ O ₄	230.30	5.64
25	Chrysene	C ₁₈ H ₁₂	228.29	3.11
26	Benzo[k]fluoranthrene	C ₂₀ H ₁₂	252.32	4.61
27	2-Ethyl-1-hexanol	C ₈ H ₁₈ O	130.23	0.38
28	Decanoic acid methyl ester	C ₁₁ H ₂₂ O ₂	186.30	0.44
29	2,4-bis-(t-butyl)-methoxy Benzene	C ₁₆ H ₂₆ O ₂	250.38	0.27
30	Cyclopenta (cd) pyrene	C ₁₈ H ₁₀	226.28	2.13
31	Indeno(1,2,3-cd)pyrene	C ₂₂ H ₁₂	276.34	6.51
32	Dibenzo(ah)anthracene	C ₂₂ H ₁₄	278.35	4.87
33	Benzo(ghi)perylene	C ₂₂ H ₁₂	276.34	3.53
34	3,5-bis(t-butyl)-Phenol	C ₁₄ H ₂₂ O	206.32	0.25
35	Benzo(a)pyrene	C ₂₀ H ₁₂	252.31	3.70

Fig. 4. Schematic representation of terpenoids conversion

The pretreated SEO using the clay sample has a clearer colour relative to the untreated sample. Its kinematic viscosity of $278.4 \text{ mm}^2\text{s}^{-1}$ was less than the untreated SEO having viscosity of $292.6 \text{ mm}^2\text{s}^{-1}$ reported by Taiwo and Bello [11] indicating removal of some impurities. This was also observed to result from removal of heavy aromatics alongside the sludge while recovering spent engine oil using calcined clay [38]. The identified hydrocarbons are reported in Table 4 and has very much less compounds than that obtained for untreated SEO. For instance, propan-2-ol, fluorene, butadiene, 2,6-bis-(t-butyl) phenol, pristane, phytane, stearates, benzo-naphtho-thiophene, 1,1-diphenyl hydrazine, decanoic acid methyl ester, 3,5-bis(t-butyl)-phenol had been eliminated by the clay by either conversion or and adsorption on the clay pore spaces. This finding presents clay as a low-cost industrial adsorbent.

The clay treated SEO was then ran through column packed with ASA adsorbent and GC spectrum is reported in Fig 5. The components presented by the MS fragmentation is given in Table 6. It has about 70 weight percent aromatics including dibenzo-thiophene with relative occurrence of 18.32 weight % as the highest occurring compound, followed by cyclopenta(cd)pyrene with 10.28 weight % with perylene having the least occurrence of 0.02 weight % respectively. Relative to the clay treated sample, components like chrysene, benzo(a)pyrene, 2-bromonaphthalene, dibenzo(ah)anthracene and flouranthene were trapped in the adsorbent. It could be observed that most of the trapped compounds have carbon atoms ≥ 20 in the molecules. In the preliminary evaluation of the eluting solvents, it has been discovered that the ASA adsorbent was unable to separate the SEO thus the utilization of clay for pretreatment of the spent oil. A combination of clay/ASA therefore formed a good adsorbent for recovering hydrocarbons which are majorly aromatics, from the SEO. This process offers an improved re-refining option to the distillation process which is energy intensive. The aromatics are useful feedstock to petrochemical industries.

The possible reactions during lubricant usage in the crankcase were thermal dehydrogenation, ring opening, epoxidation, cracking, and condensation of aromatics such as, phenyloctane, biphenyl, fluorene, 9,10-dihydrophenanthrene, naphthalene, phenanthrene, pyrene, and benzo(a)anthracene which are base oil components or additives in the lubricant formulation [39].

Table 5. GC-MS Analysis for Clay treated Spent Lubricating Oil

S/N	Compound	Molecular Formula	Molecular Mass	wt %
1	Naphthalene	C ₁₀ H ₈	128.17	2.85
2	Acetic acid	CH ₃ COOH	60.05	5.12
3	Acetaldehyde	C ₂ H ₄ O	40.06	3.96
4	Acenaphthylene	C ₁₂ H ₈	152.20	1.55
5	Pyrene	C ₁₆ H ₁₀	202.25	4.55
6	Perylene	C ₂₀ H ₁₂	252.32	0.02
7	Anthracene	C ₁₄ H ₁₀	178.23	3.17
8	Ethylene glycol	C ₂ H ₆ O ₂	62.07	1.62
9	Tridecanol	C ₁₃ H ₂₈ O	200.40	0.07
10	1,2-Benzene dicarboxylic acid	C ₈ H ₆ O ₄	400.74	4.59
11	Dibenzo-thiophene	C ₁₂ H ₈ S	184.26	11.80
12	Phenanthrene	C ₁₄ H ₁₀	228.12	0.93
13	Decamethylcyclopentasiloxane	C ₁₀ H ₃₀ O ₅ Si ₅	370.77	7.19
14	dibutyl ester	C ₁₂ H ₂₂ O ₄	230.30	7.53
15	Chrysene	C ₁₈ H ₁₂	228.29	0.99
16	benzo(k)fluoranthene	C ₂₀ H ₁₂	252.30	3.45
17	2-Ethyl-1-hexanol	C ₈ H ₁₈ O	130.23	0.70
18	2,4-bis-(t-butyl)-methoxy Benzene	C ₁₆ H ₂₆ O ₂	250.38	1.17
19	Cyclopenta (cd) pyrene	C ₁₈ H ₁₀	226.28	6.52
20	Indeno(1,2,3-cd)pyrene	C ₂₂ H ₁₂	276.34	7.61
21	Dibenzo(ah)anthracene	C ₂₂ H ₁₄	278.35	6.17
22	Benzo(ghi)perylene	C ₂₂ H ₁₂	276.34	5.23
23	Benzo(a)pyrene	C ₂₀ H ₁₂	252.31	1.07
24	2-bromonaphthalene	C ₁₀ H ₇ Br	207.07	2.41
25	benzo(a)anthracene	C ₁₈ H ₁₂	228.30	3.47
26	Fluoranthene	C ₁₆ H ₁₀	202.26	2.85
27	Fluorene	C ₁₃ H ₁₀	166.323	3.48

Fig. 5. GC-MS Spectrum of eluate from ASA Adsorbent

Table 6. GC-MS Analysis for Eluate from African Star Apple Fruit Shell Adsorbent

S/N	Compound	Molecular Formula	Molecular Mass	wt %
1	Naphthalene	C ₁₀ H ₈	128.17	4.43
2	Acetic acid	CH ₃ COOH	60.05	7.98
3	Acetaldehyde	C ₂ H ₄ O	40.06	2.46
4	Acenaphthylene	C ₁₂ H ₈	152.20	3.98
5	Pyrene	C ₁₆ H ₁₀	202.25	7.10
6	Perylene	C ₂₀ H ₁₂	252.32	0.02
7	Anthracene	C ₁₄ H ₁₀	178.23	4.93
8	Ethylene glycol	C ₂ H ₆ O ₂	62.07	2.52
9	Tridecanol	C ₁₃ H ₂₈ O.	200.40	0.08
10	1,2-Benzene dicarboxylic acid	C ₈ H ₆ O ₄	400.74	7.13
11	Dibenzo-thiophene	C ₁₂ H ₈ S	184.26	18.32
12	Phenanthrene	C ₁₄ H ₂₈ O ₂	228.12	1.44
13	Decamethylcyclopentasiloxane	C ₁₀ H ₃₀ O ₅ Si ₅	370.77	11.20
14	dibutyl ester	C ₁₂ H ₂₂ O ₄	230.30	11.72
15	2-Ethyl-1-hexanol	C ₈ H ₁₈ O	130.23	1.09
16	2,4-bis-(t-butyl)-methoxy Benzene	C ₁₆ H ₂₆ O ₂	250.38	1.93
17	Fluorene	C ₁₃ H ₁₀	166.32	4.08
18	Cyclopenta (cd) pyrene	C ₁₈ H ₁₀	226.28	10.28

Conclusion

This study showed hexane as effective solvent in solubilizing the SEO for its adsorptive separation. Pretreatment with clay is significant for efficient recovery of aromatic hydrocarbons suitable as feedstock for petrochemical industries. African star apple fruit shell, a renewable agricultural waste, can appropriately serve effectively as adsorbent in combination with clay material, for separation of the spent lubricating oil. The textural analysis revealed ASA as compact adsorbent while GC-MS spectrometer served an effect instrumentation for characterizing the product of adsorption.

Acknowledgements

The authors appreciate Department of Chemical Engineering, Afe-Babalola University, Ado-Ekiti for the assistance in conducting the instrumental analysis. Also, the technical staff of the Department of Chemical Engineering of Obafemi Awolowo University, Ile-Ife in fabrication of all the experimental rigs used.

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