Kinetic Modelling of the Adsorption Treatment of Waste Lubricating Oil using Activated Ukpor Clay (Bentonite)

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Abstract— *The re-refining of waste lubricating oil using activated Ukpor clay as an adsorbent was investigated. Clay activation was performed using sulphuric acid (H_2SO_4) with equivalent concentrations varying between 0.5 – 2 mol/L at a constant temperature of 90^oC for 3.5 hours. The adsorption process was studied over a fixed amount of adsorbent at ambient conditions. Adsorbent performance was determined by its effectiveness in enhancing the properties of the waste oil and in removing trace metal ions contained in them. Furthermore, the effect of contact time and the adsorption performance of the adsorbent in the recycling treatment of the lubricating oil were evaluated. The kinetic data were modelled using the Pseudo-first order, the Pseudo-second order, the intra particle diffusion and the Elovich kinetic models. Analysis carried out on the lubricating oil showed the presence of many heavy metal ions and trace elements. Ca, Pb and Zn had the highest concentrations of 804, 398 and 222 mg/L respectively, while Ba had the least concentration of 0.1 mg/L. However, with treatment using this adsorbent, the concentrations of Ca, Pb and Zn were found to considerably reduce to 3.6, 5.6 and 0.01 mg/L respectively. The concentration of Ba was equally found to reduce to 0.01 mg/L, wherein the clay sample treated with 2 mol/L H_2SO_4 gave the best result in terms of improvement in the properties of the lubricating oil as well as on the percentage removal of these heavy metals and trace elements. For best describing the process within the adsorbent and with a high correlation coefficient (R^2 value > 0.999), kinetic data were best fitted by the Pseudo-second order kinetic model and this result indicates that this adsorbent provides a good medium for the re-refining of waste lubricating oil.*

Keywords**— *Clay; recycling; adsorption; lubricating oil; kinetic models.***

I. INTRODUCTION

One of the greatest challenges of environmental management is improper management of wastes such as waste lubricating oil. These forms of wastes are usually classified as hazardous because of the high content of heavy metals inherent in them. According to [1], lubricating oil, being a petroleum based product, originally contains little or no heavy metals. However, as a result of their activities through the engines, they pick up various heavy metals and trace elements such as Manganese, Cadmium, Arsenic, Copper, Lead, etc. High value content of ash, water, asphaltenic materials, and other dirty materials have also been reported to build up during the course of lubrication inside the engine [2].

The non-biodegradable nature of waste lubricating oil as well as its carcinogenic nature [3] makes its disposal a significant challenge. In developing countries such as Nigeria, it has been reported that over 20 million gallons of waste lubricating oil, which are generated annually, are not properly disposed [4]. Improper disposal of these waste lubricating oils therefore enriches the soil with some unwanted heavy metals, which could subsequently drain into groundwater and surface water ways. Heavy metal ions like Lead (Pb) and Cadmium (Cd) are pollutants associated with human health effects such as high blood levels in Children, anthralgia, osteomalacia, colic, constipation etc [5, 6] while Chromium (Cr), Iron (Fe) and Phosphorous (P) could have a significant negative correlation on freshwater plants such as microcrustacean species eg. *Diaptomus leptopus* and *Daphnia Schodlert* [7, 8]. Waste lubricating oil contamination of soil leads to a gradual build up of trace metals which when absorbed by plants could be potentially harmful, hence constituting health risk if consumed as food by man and any other animal [9]. Because of the threats they pose, maximum allowable contamination levels exist for these heavy metals/ trace elements by several regulating agencies such as World Health Organization (WHO), United States Environmental Protection Agency (USEPA) among others [10]. Indiscriminate disposal of waste lubricating oil would not only violate these standards, but equally give rise to attendant consequences both to man and the environment. Waste oil could have more debilitating effects on the environment than they do to automotive engines, in that they could poison plants and animals, destroy soil nutrients and equally reduce aeration of the soil.

It therefore makes finding an alternative use to waste lubricating oil inevitable. One alternative use to this waste lubricating oil is its recycling using adsorbents. One of these adsorbents is activated clay (Bentonite) usually found in abundance in Sub-Saharan Africa. Activated clay has found lots of uses in recent times as a catalyst for a lot of industrial applications [11 – 14]. Application of activated clay for bleaching purposes has been extensively reported in the literature [15 – 17]. Activated clay has also been applied in the recycling of waste lubricating oil [2 - 4, 18]. Study of the rheological behaviour of clay in solution has been made using chemical [19] and thermal analysis [20].

Clay activation implies an increase in its adsorption surface area. This could be achieved with thermal treatment or by the use of reagents. Both operations can interfere with the crystal lattice structure of the clay, thus increasing the surface area for adsorption. This equally generates a system of fine pores for optimum results because of the removal of aluminium, alkaline earth metals, alkali, iron and silica from clay minerals. Being one of the most important processes that have been performed to achieve structural modification, acid activation of clays has found a wide application. Many research works show that better performance of activated clays over the un-activated ones have been obtained. Studies have shown that during the acid-activation of clay, the interlayer cations are replaced with H^+ ions and this is usually followed by partial destruction of aluminium octahedral sheets followed by subsequent dissolution of structural cations. It has been reported [21 – 22] that these required changes in the physicochemical properties of clay as a result of activation/modification depend considerably on the acid-activation condition employed, such as the reagent concentration, duration of treatment and temperature of the activation process. Finding the optimum treatment condition is therefore relative to the adsorbent material and the adsorption medium.

In this study, a simple but effective way of treatment of waste lubricating oil with the easily sourced Ukpor clay has been investigated with a view to determining its re-refining ability and the optimum condition for this process. Effect of contact time and the adsorption performance of this adsorbent in the removal of the impurities in waste lubricating oil have also been evaluated. The kinetic data were modelled using the Pseudo-first order, the Pseudo-second order, intra particle diffusion and the Elovich kinetic models.

II. METHODOLOGY

2.1 Materials and Method

The clay (Bentonite) used in this work was obtained from a clay deposit at Ukpor (5^o $57^'$ $0^{''}$ N, 6^o $55^'$ $0^{''}$E) in Nnewi-South LGA, Anambra state, Nigeria. The waste lubricating oil used was obtained from an automobile service station in Choba, Port Harcourt (4^o $47^'$ $21^{''}$N, 6^o $59^'$ $55^{''}$E) Nigeria. All the chemicals used were of analytical grade.

2.2 Adsorbent Preparation

Clay samples were sun-dried for 24 hours and ground to smaller particles using mortar and pestle. The ground samples were sieved to remove impurities and then oven dried at a temperature of 85 °C for about 1 hour.

At different experiments, 30 g portion of these clay samples was treated with 300 ml of H_2SO_4 (analytical grade) with various concentrations: 0.5, 1, 1.5 and 2 mol/L, in a glass reaction vessel placed in a regulated water bath operating at 90 ^oC for 3.5 hours [16]. The setup was heated amidst vigorous agitation using a magnetic stirrer, at the end of which slurry had been formed. The slurry was removed from the water bath and allowed to cool, after which it was filtered and the clay residue was washed several times with distilled water to a neutral pH. This was again followed by filtration. The wet residue was then dried in an oven operating at 65 ^oC for a 12 hour period to allow for steady uniform and even drying. The activated clay samples were crushed to smaller sizes, sieved to pass through a 0.245 mm sieve, weighed, and stored in air tight containers which were labelled as UK_1, UK_2, UK_3, and UK_4, where the numerical value indicates the concentration of the acid solution used for the treatment. The untreated (un-activated) clay samples were designated as UK_0.

2.3 Waste Engine Oil Regeneration Pre-treatment

Eight (8) liters of spent (waste) lubricating oil, which had been used for over a 3 month period, was first subjected to some regeneration pre-treatment processes in order to enhance their properties.

a. Pre-treatment: The waste lubricating oil was first decanted, filtered and dehydrated in order to eliminate impurities, water, gasoline, glycol solvents and light hydrocarbons.

b. Elimination of metals: 30 mL of xylene was added into a 3 L of waste lubricating oil in order to aid the precipitation of suspended solid.

c. The oil was thereafter subjected to centrifugation, filtered and stored in a clean container.

The schematic diagram of the entire process is shown in Figure 1.

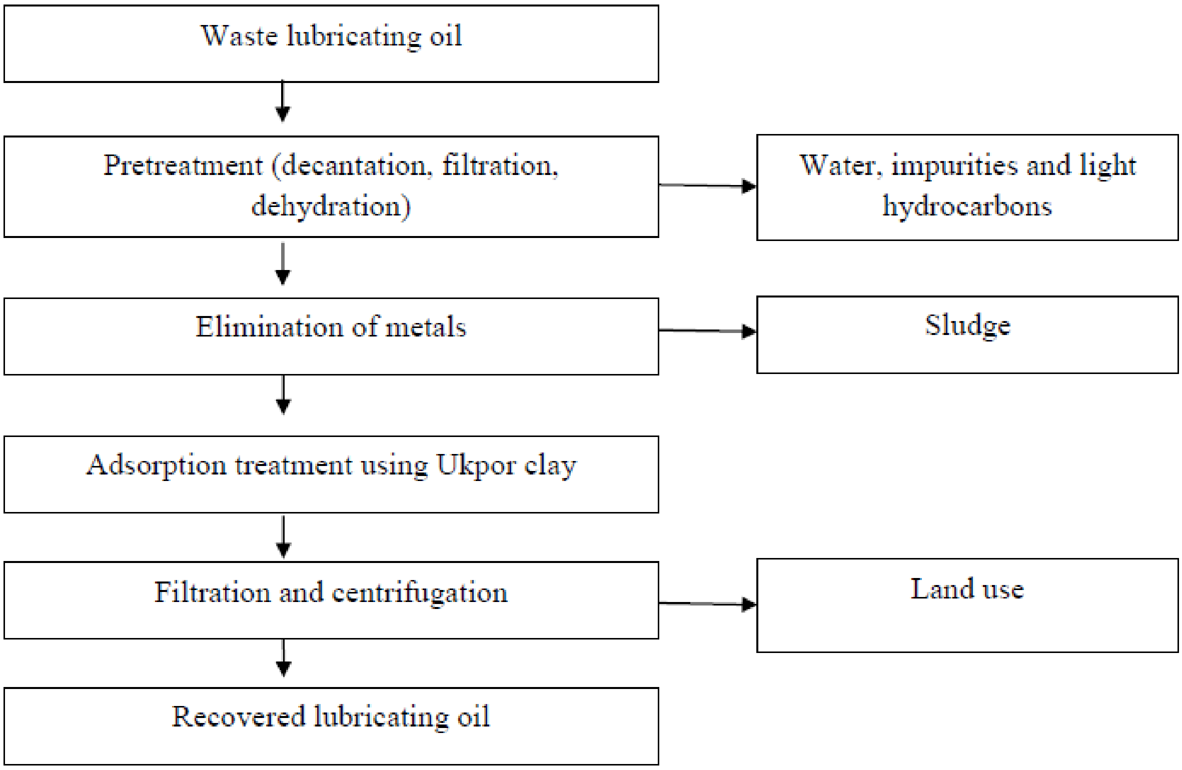

FIGURE 1: SCHEMATIC DIAGRAM OF WASTE LUBRICATING OIL RE-REFINING PROCESS USING ACTIVATED UKPOR CLAY.

2.4 Adsorption treatment process

At different experiments, 2 g portions of the activated and un-activated clay were measured into 200 mL samples of the regenerated lubricating oil sample contained in a 500 mL capacity beaker and stirred continuously using a magnetic stirrer. The mixture was shaken thoroughly for 3 hours using an electric shaker for homogeneity. The mixture was subsequently heated at 28 ^{o}C using a constant heating water bath for a 12 hour period. The resultant slurry formed was then centrifuged using a centrifuge (Model: D800) operating at 4000 rpm for 20 mins, decanted and filtered. The filtrate was stored in airtight containers and labelled accordingly.

2.4.1 Characterization of lubricating oil

The lubricating oil samples (waste and recovered) were ashed at 600 ^{o}C temperature for 6 hours and digested using 10 mL 0.02 M nitric acid and analyzed for the following heavy metals concentration using Flame Absorption Atomic Spectrophotometer Phoenix-986: Iron (Fe), Chromium (Cr), Lead (Pb), Copper (Cu), Tin (Sn), Aluminium (Al), Nickel (Ni), Silver (Ag), Silicon (Si), Boron (B), Sodium (Na), Magnesium (Mg), Calcium (Ca), Barium (Ba), Phosphorous (P), and Zinc (Zn).

The physico-chemical properties (including the density at 20 ^{0}C, viscosities at 40 ^{0}C and 100 ^{0}C, flow and flash points, water and sulphur contents, total base number (TBN) and the total acid number (TAN)) of the recovered lubricating oil were obtained using standard laboratory procedures [3, 16], while the analysis on color was performed with the aid of a Lovibond 2 cell Tintometer (ASTM D1500). The percentage color reduction of the lubricating oil was estimated with the correlation of Equation 1

$$\%\, color\ reduction = \frac{crude\ sample\ color - recovered\ sample\ color}{crude\ sample\ color} \times 100 \qquad (1)$$

The waste and the recycled oil were evaluated comparatively, and the effectiveness of the adsorbent in the re-refining process was assessed by its capability towards reducing the heavy metals content as well as in enhancing the physicochemical properties of the oil.

2.4.2 Characterization of clay sample

The physico-chemical properties of activated and un-activated Ukpor clay, which were used as the adsorbent material, were characterized with respect to their bulk density, moisture content and porosity using standard methods [23]; as well as pH, Cation Exchange Capacity (CEC) and surface area by employing conventional methods [24].

2.5 Adsorption Kinetics

The effect of contact time on the performance of activated Ukpor clay and its adsorption kinetics in the re-refining of waste lubricating oil have been studied. To achieve this, varying contact time (10 – 60 mins) were considered for the adsorption treatment process of the waste lubricating oil using the UK_4 sample (having had the best adsorption performance). Note that only the centrifugation time (as described in Section 2.4) was considered at this stage after homogeneous slurry of the lubricating oil with the adsorbent had been formed.

The kinetic modelling not only allows the estimation of sorption rates but also leads to suitable rate expression characteristics of possible reaction mechanisms [25]. The kinetic models employed in this study were Pseudo-first order, Pseudo-second order (three linear forms), intra particle diffusion and the Elovich model. The linear forms of these models were employed as shown in Table 1. Evaluation of the model parameters was done using Statistical Package for Social Scientist (SPSS 22.0 version) software.

TABLE 1
ADSORPTION KINETIC MODELS IN LINEAR FORM

Model	Type	Model equation	Plot	Eq. No
Pseudo-first order	Linear	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ Vs t	2
Pseudo-second order	Linear 1	$\frac{1}{q_e} = \frac{1}{q_t} + \left(\frac{1}{k_2 {q_e}^2}\right)\frac{1}{t}$	$\frac{1}{q_e}$ Vs $\frac{1}{t}$	3
	Linear 2	$\frac{t}{q_e} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$	$\frac{t}{q_e}$ Vs t	4
	Linear 3	$q_e = q_t - \left(\frac{1}{k_2 q_t}\right)\frac{q_e}{t}$	q_e Vs $\frac{q_e}{t}$	5
Intra particle diffusion model	Linear	$q_t = k_3 t^{1/2} + c$	q_t Vs $t^{1/2}$	6
Elovich model	Linear	$q_t = \beta \ln(\alpha\beta) + \beta \ln t$	q_t Vs $\ln t$	7

Where:

k_1 is the pseudo-first order rate constant (L/min).
k_2 is the pseudo-second order rate constant of adsorption (g/(mg×min))
k_3 is the rate constant of the intra particle transport (g/(mg×min))
α is the initial impurity sorption rate (mg/(g×min))
β is the desorption constant (g/mg) during any one experiment
c is the intraparticle diffusion constant. i.e. intercept on the q_t axis, (mg/g)
t is the contact time (min)
q_t is the amount of impurities removed at time t (mg/g)
q_e is the adsorption capacity at equilibrium (mg/g) and is given by Equation 8

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{8}$$

C_o and C_e are concentrations of impurities in the waste lubricating oil at initial and equilibrium concentrations respectively. V is the volume of the solution (L) and m is the mass of clay used (g).

The associated kinetic parameters of the experimental data were evaluated from the data obtained from the linear plots of the kinetic equations (Figures 3 – 8). Analysis of the data was based on the linear regression coefficient (R^2), hence the model with the highest R^2 value, and considering as much available adsorption sites within the adsorbent structure as possible, was chosen as the model which best describes the process. It is worth noting that the viability of this process in the recycling of specific properties of the waste lubricating oil were evaluated based on physical steps performed and results obtained at various stages of the experiment. It must however be noted that all the stages of this study were carried out under ambient conditions of temperature and pressure and posterior work must consider the possible effects of these variables in the process.

III. RESULTS AND DISCUSSION

It is clearly evident from Table 2 that the physico-chemical parameters of the clay samples are quite dependent on the extent of activation. This modification in adsorbent property could be attributed to a further transformation within the clay structure as a result of the use of higher acid concentrations. [21] reported transformation within the clay structure to result from a replacement of the interlayer cations with H^+ ions, subsequent dissolution of structural cations and generation of micro-porosity during the activation process. The results of the physico-chemical parameters indicate an improvement in the properties of the adsorbent material on activation. Increased surface area and large pore volume of the activated clay [13] could have resulted in this improved property performance.

TABLE 2
PHYSICO-CHEMICAL PROPERTIES OF UNACTIVATED AND ACTIVATED UKPOR CLAY

Property	Clay type				
	UK_0	UK_1	UK_2	UK_3	UK_4
pH	6.06	5.91	5.72	5.71	5.23
Bulk density (gcm^{-3})	1.46	1.38	1.33	1.27	1.24
Porosity	0.54	0.46	0.38	0.42	0.49
Surface area (m^2/g)	98.2	120.3	125.7	132.6	129.4
Moisture content (%)	22.30	19.60	17.70	18.20	16.55
CEC (meg/100kg)	24.20	25.27	25.42	25.25	25.21

Note: all values are a mean of 3 determinations

Generally, there is an improvement in the characteristics of the re-refined (recycled) lubricating oil as a result of its treatment with the activated Ukpor clay sample as shown in Table 3.

TABLE 3
PHYSICO-CHEMICAL CHARACTERISTICS OF LUBRICATING OIL

Properties	Lubricating oil					
	Waste	Recycled				
		UK_0	UK_1	UK_2	UK_3	UK_4
Density at 20°C (gcm^{-3})	0.8890	0.8892	0.8888	0.8880	0.8870	0.8871
Viscosity at 40°C (cSt)	104.5	120.5	107.7	110.5	105.3	118.77
Viscosity at 100°C (cSt)	11.55	11.50	11.45	11.53	11.08	11.02
Flow point (°C)	-16	-15	-15	-10	-12	-9
Flash point (°C)	104	114	120	151	151	152
Water content (% vol)	4.2	4.4	4.0	3.6	1.2	0.9
Sulphur content (ppm)	0.32	0.25	0.18	0.19	0.10	0.07
TBN (mgKOH/g)	4.7	4.3	4.1	4.2	4.3	4.1
TAN (mgKOH/g)	3.9	3.7	3.8	3.8	3.5	3.3
Colour (%)	-	45	43	55	70	80

Evident from Table 3 is a reduction in density from an initial value of 0.8890 g/cm^3 to 0.8870 g/cm^3 on treatment with the adsorbent, which is an indication that the re-refined lubricating oil became less dense as a result of the removal of the wastes contained in the oil. The viscosity of the oil was determined at temperatures of 40 ^{o}C and 100 ^{o}C. Being temperature dependent, the oil at 40 ^{o}C was found to be more viscous than that whose measurement was taken at a temperature of 100 ^{o}C. This is because this liquid characteristic relates a shearing stress to the viscosity gradient it produces in the liquid. The lowest viscosity at 100 ^{o}C was obtained with the UK$_4$ sample clay which was inferred to be indicative of the improved viscosity of the lubricating oil when treated under this condition. Best values of flash point, flow point, sulphur content, TAN and TBN were obtained at this same recycling condition. An appreciable reduction in the moisture content of the waste oil from 4.2 to 0.9 % was also recorded with the use of UK$_4$ adsorbent; it also led to a considerable reduction in the amount of impurities in the waste lubricating oil as evidenced by the color analysis on the oil. It is important to note that the color analysis further buttressed the fact that the oil obtained through recycling gave the desired end product coloration.

From the foregoing, it is evident that these properties of the waste lubricating oil were enhanced by its treatment with the adsorbent. Properties of the oil treated with the UK$_4$ clay sample were the most enhanced and this could be attributed to the high adsorptive capacity of this sample. This high adsorptive capacity of the UK$_4$ clay implies the availability of more adsorptive sites on the clay surface due to the removal of more dissolved salts in these sites, as a result of the condition of its pre-treatment.

TABLE 4
METAL ION CONTENT OF LUBRICATING OIL

Metal ion (mg/l)	Lubricating oil					
	Waste	Recycled				
		UK$_0$	UK$_1$	UK$_2$	UK$_3$	UK$_4$
Fe	56.3	27.2	3.8	2.4	1.9	1.5
Cr	2.7	0.03	0.01	0.01	0.0	0.01
Pb	398	11.6	5.6	5.8	6.5	5.6
Cu	7.2	0.9	0.0	0.01	0.0	0.003
Sn	8.3	2.4	1.6	0.4	0.4	0.2
Al	10.4	13.4	5.7	0.4	0.5	0.1
Ni	0.2	0.1	0.01	0.1	0.1	0.1
Ag	0.04	0.01	0.0	0.0	0.0	0.0
Si	19.8	2.6	1.5	1.8	1.9	1.7
B	2.5	0.9	0.04	0.02	0.02	0.02
Na	25.3	4.8	3.7	3.9	3.9	2.4
Mg	37.1	2.1	1.7	1.9	1.9	1.8
Ca	804	26.8	5.4	5.6	4.9	3.6
Ba	0.1	0.04	0.01	0.01	0.01	0.01
P	172	8.5	7.2	6.3	5.4	5.3
Zn	222	6.3	6.4	2.9	0.04	0.01

Table 4 shows the heavy metal ions contained in the waste lubricating oil. The highest values of these metals were found as follows Ca (804 mg/L), Pb (398 mg/L) Zn (222 mg/L). These were considerably reduced to 3.6, 5.6 and 0.01 mg/L respectively. These low values were obtained on treatment of the oil with adsorbent sample UK$_4$. The large pore volumes offered by the vacant adsorptive sites created by the removal of the dissolved salts in these sites due to the pre-treatment condition of this adsorbent, offered a higher surface area for the attachment of these metal ions on the clay surface, and hence their removal from the oil. On the other hand, the least heavy metal ion found in this waste oil was Ba (0.1 mg/L), which on treatment reduced to 0.01 mg/l. Generally, the concentrations of these heavy metals were found to be significantly reduced on treatment with activated clay while there remained no detectable Ag found at the end of the recycling process. [26] has also shown that removal of trace metal impurity such as Bromate from aqueous solution is feasible through adsorption.

Generally, an improved adsorption performance of Ukpor clay was observed on activation as compared to the un-activated samples in terms of the obtained characteristics of the re-refined oil. This indicates that waste lubricating oil can be recycled using clay as the adsorbent material.

From Figure 2, it was found that after 30 minutes of agitation of the mixture, the impurity removal efficiency did not significantly increase. Therefore the optimum contact time for the adsorption treatment of waste lubricating oil using this adsorbent was found to be 30 minutes, bound by experimental set-up, conditions and samples used in this study. This agrees well with the typical time observed for the attainment of adsorption equilibrium for similar types of adsorbents [27 – 28].

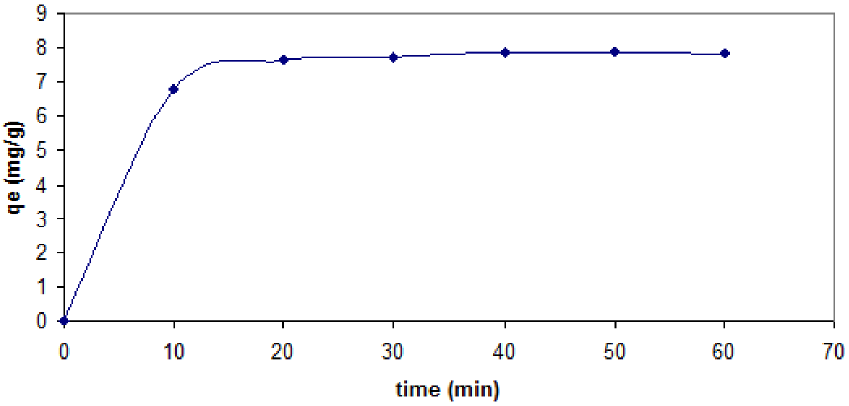

FIGURE 2: EFFECT OF CONTACT TIME ON THE ADSORPTION TREATMENT OF WASTE LUBRICATING OIL USING ACTIVATED UKPOR CLAY

The change in rate of impurity removal from the waste lubricating oil might be due to the fact that at the initial period, all adsorbent sites were vacant and the solute concentration gradient high. Subsequently, the impurity uptake rate by the adsorbent (activated clay) surfaces decreased significantly due to the decrease in adsorption sites. On the basis of this result, optimum contact time of 30 minutes has been selected for all further studies involving the use of this adsorbent in the treatment of waste lubricating oil.

From this study, it was found that at each point in time, the amount of impurities removed (q_t) did not exceed the adsorption equilibrium of the clay. It therefore shows that the Pseudo-first order kinetic model [25, 29] satisfactorily describes the relationship between the amount of impurities removed from the waste lubricating oil and the adsorption capacity of Ukpor clay at equilibrium as shown in Figure 3.

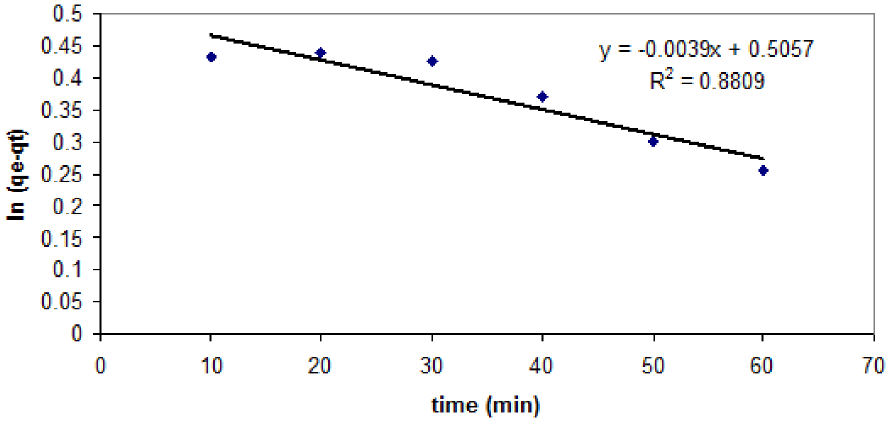

FIGURE 3: PSEUDO-FIRST ORDER KINETIC MODEL FOR RE-REFINING OF WASTE LUBRICATING OIL USING ACTIVATED UKPOR CLAY

In the Pseudo-second-order model [25], the rate-limiting step is the surface adsorption that involves chemisorption, where the removal from a solution is due to physicochemical interaction between the two phases. The plots of three linear forms of this model (Equations 3, 4 & 5) as employed in this study are presented in Figures 4, 5 & 6.

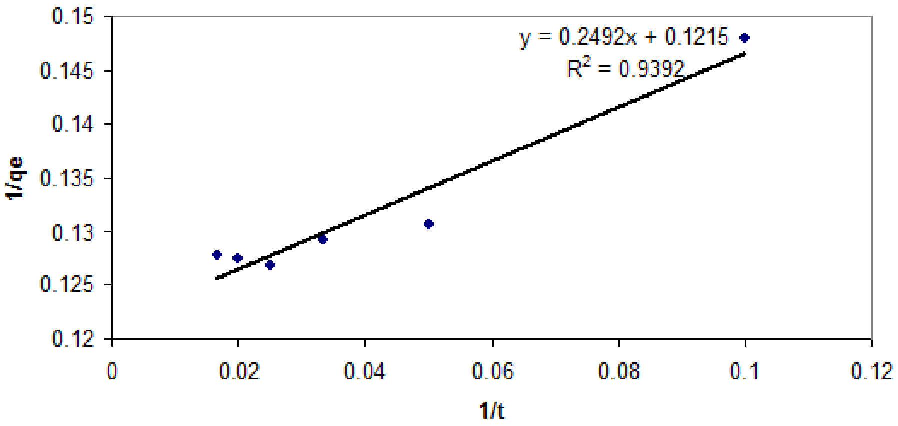

FIGURE 4: PSEUDO-SECOND ORDER KINETIC MODEL FOR RE-REFINING OF WASTE LUBRICATING OIL USING ACTIVATED UKPOR CLAY (FOR EQUATION 3)

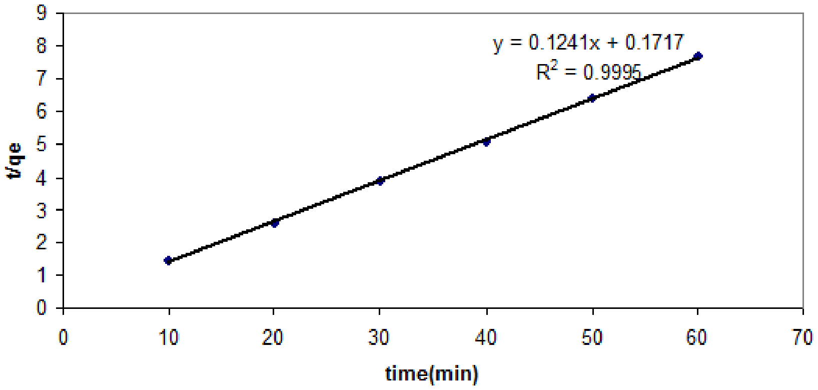

FIGURE 5: PSEUDO-SECOND ORDER KINETIC MODEL FOR RE-REFINING OF WASTE LUBRICATING OIL USING ACTIVATED UKPOR CLAY (EQUATION 4)

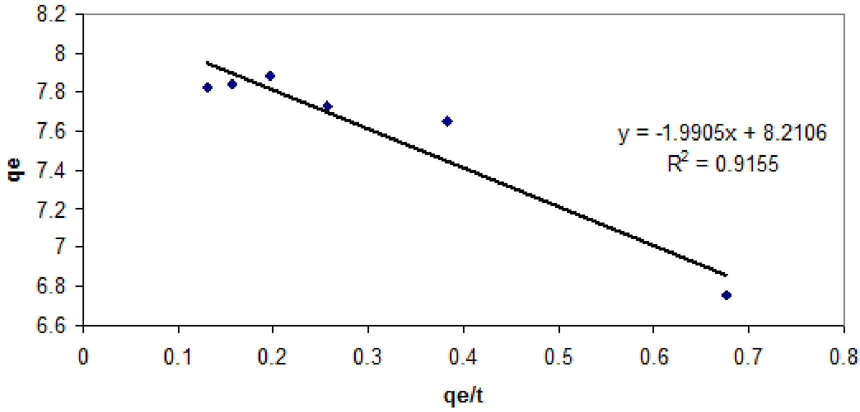

FIGURE 6: PSEUDO-SECOND ORDER KINETIC MODEL FOR RE-RECYCLING OF WASTE LUBRICATING OIL USING ACTIVATED UKPOR CLAY (EQUATION 5)

The intra particle diffusion model [30] describes adsorption processes, where the rate of adsorption describes the speed at which adsorbate diffuses towards adsorbent (i.e. the process is diffusion controlled). The intra particle diffusion model as fitted with the experimental data is presented in the plot of Figure 7.

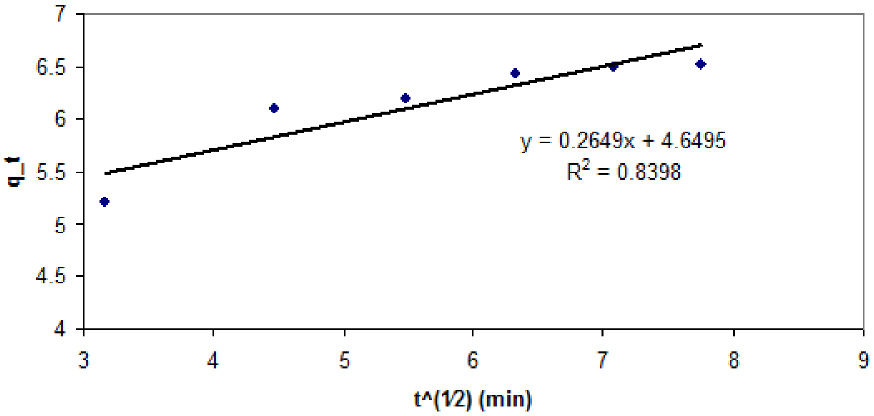

FIGURE 7: INTRA PARTICLE DIFFUSION KINETIC MODEL FOR RE-REFINING OF WASTE LUBRICATING OIL USING ACTIVATED UKPOR CLAY

Although the Elovich model [29] does not provide mechanistic evidence, it is a model suitable for highly heterogeneous systems and provides a linear relationship between the amount of impurities sorbed and the time at which the sorption takes place as shown in Figure 8.

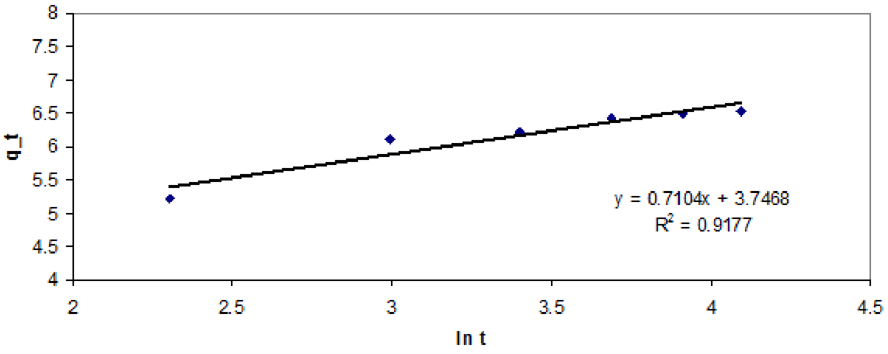

FIGURE 8: ELOVICH KINETIC MODEL FOR RE-REFINING OF WASTE LUBRICATING OIL USING ACTIVATED UKPOR CLAY

The fitted kinetic parameter estimations involving the use of the kinetic models obtained from the plots of Figures 3 - 8 are presented in Table 5.

TABLE 5
FITTED ADSORPTION MODELS KINETIC PARAMETERS FOR THE RE-REFINING OF WASTE LUBRICATING OIL USING ACTIVATED UKPOR CLAY

Model	Model constant	R^2	Equation No.
Pseudo-first order	$K_1 = 0.0039$	0.8809	2
Pseudo-second order	$K_2 = 0.0698$	0.9392	3
	$K_2 = 0.0897$	0.9995	4
	$K_2 = 0.0612$	0.9155	5
Intra particle diffusion	$K_3 = 0.2649$	0.8398	6
Elovich	$\alpha = 274$ $\beta = 0.7104$	0.9177	7

As earlier stated, the high adsorptive capacity of the UK_4 clay sample, evidenced from its effectiveness in enhancing the properties of the oil, is due to the availability of more adsorption sites on this adsorbent. This is as a result of the pre-treatment condition of the adsorbent material which resulted in the removal of excess dissolved salts in these sites, thereby creating high surface area and larger pore volumes for adsorption on this material. Consideration of these sites is therefore imperative in choosing the model which best explains the process.

From the above, it is necessary to emphasize that while the pseudo-first order model could better describe the relationship between the amount of impurities removed from lubricating oil and the adsorption capacity of the adsorbent, the intraparticle diffusion model was also limited in its approach, being able to only describe the dependence of adsorption rate on the speed at which the lubricating oil diffuses towards the bentonite. The deficiency of the Elovich model in describing similar adsorption process involving the removal of impurities in solutions [29] has been attributed to its inability to provide mechanistic evidence of the phenomenon..

However, besides consideration for the rate-limiting step, the Pseudo-second order model considers as much adsorption sites as possible within the clay particle and the equilibrium adsorption capacity at each of these sites per unit time and therefore offers a better description of the process than other models. Furthermore, with an R^2 value > 0.999, the linear 2 form of this model (Equation 4) gave the best linear fit of the experimental data and therefore best describes the re-refining process of waste lubricating oil using Ukpor clay.

IV. CONCLUSION

The recycling of waste lubricating oil using activated Ukpor clay has been successfully executed. This study employed four different concentrations of H_2SO_4 ranging between 0.5 mol/L and 2mol/L. The effectiveness of this clay type as an adsorbent was determined by their ability to effectively remove the impurities in the waste oil, as well as to enhance properties such as: density, viscosity, flow point, flash point, and reduce moisture content, sulphur content, TAN and TBN; while equally remove the trace metal ions. The results from this study indicate that activation of the clay samples improved their physico-chemical properties as adsorbent materials.

A general improvement in the properties of the recycled oil was observed on treatment with the activated clay. The best adsorption performance on the lubricating oil was obtained with the use of UK_4 sample adsorbent, in that its use greatly enhanced the properties of the oil and also reduce the trace metal content in them. All the heavy metal ions found in the waste lubricating oil were significantly reduced, with Ca (804 mg/L), Pb (398 mg/L) Zn (222 mg/L) being the highest values of these metal ions obtained in the waste oil, reduced to 3.6 mg/L, 5.6 mg/L and 0.01 mg/L respectively. Pre-treatment condition that ensured the availability of larger surface area and more adsorptive sites is the possible reason for the high adsorptive capacity of the UK_4 clay sample. The adsorption of impurities from the waste lubricating oil increased with increasing contact time with the adsorbent. Also, the decline in the adsorption performance of the UK_4 sample after 30-minutes implies that this is the optimum contact time for all further studies involving the use of this adsorbent in the recycling of waste lubricating oil, bound by experimental set-up, conditions and samples used in this study. Kinetics for the adsorption treatment of waste lubricating oil using activated Ukpor clay were obtained and fitted to different kinetic models namely: Pseudo-first order, Pseudo-second order, intra particle diffusion and the Elovich kinetic models. Of all these models, kinetic data were best fitted by the Pseudo-second order model, being able to predict the adsorption equilibrium per time in as many adsorptive sites as possible. This also gave the best linear fit having an R^2 value > 0.999. This result indicates that Ukpor clay (bentonite) is a good and effective adsorbent for the recycling (re-refining) of waste lubricating oil.

REFERENCES

[1] R.J. Irwin (1997). Environmental contaminants encyclopedia oil used motor oil entry. National park service water resources division, water operation branch, 1201, Oakridge drive, suite 250 Port Colorado. 80525 pp 65 – 84.

[2] N.M. Abdel-Jabbar, E.A.H. Al Zubaidy, M. Mehrvar (2010). Waste lubricating oil treatment by adsorption process using different adsorbents, *World academy of science, Engineering and Technology,* 4(2): 9 – 12

[3] F. Danane, A. Ahmia, A. Bakiri, N. Lalaoui (2014). Experimental regeneration process of used motor oils, *Reveu des Energies Renouvelables*, 17(2): 345 – 352.

[4] F.S. Atsar, D.T. Kukwa, R.L. Tyohemba, A. Ekpo, R.A. Wuana (2013). Cleaning of heavy metals from spent lubrication oil (SLO) by adsorption process using acid modified clay, *International Journal of Chemical science and Technology,* 3(4): 71 – 75

[5] X. Zhang, L. Yang, Y. Li, H. Li, W. Wang, B. Ye (2012). Impacts of lead/ zinc and smelting on the environment and human health in China, *Environmental monitoring assessment*, 184(4): 2261 – 2273.

[6] S. Kanran, A. Shafaqat, H. Samra, A. Sana, F. Samar, B.S. Muhammad, A.B. Saima, M.T. Hafiz (2013). Heavy metals contamination and what are the impacts on living organisms, *Greener Journal of Environmental management and public safety,* 2(4): 172 – 179.

[7] R.A. Parker, D.H. Hazelwood (1960). Some possible effects of trace elements on fresh water microcrustacean populations, multiple filter corp., Bedford mass, 344 – 347.

[8] R.I. Van Hook (1979). Potential health and environmental effects of trace elements and radionuclides from increased coal utilization, *Environmental health perspectives*, 33: 227 – 234.

[9] O.M. Agbogidi (2013). Trace metals components of *Gambaya albida* (*Linn.*) grown in soils contaminated with spent lubricating oil, *Standard scientific research and essays*, 1(5): 116 – 123.

[10] J.O. Duruibe, M.O.C. Ogwuegbu, J.N. Egwurugwu (2007). Heavy metal pollution and human biotoxic effects, *International Journal of physical sciences*, 2(5): 112 – 118.

[11] R. Mokaya, W. Jones, M. Davies, M. Whittle (1993). Chlorophyll adsorption by alumina pillared activated-clay, *J. American oil Chem Soc.*, 70: 241 – 244.

[12] C. Breen, F.D. Zahoor, J. Madejova, P. Konadel (1997). Characterization and catalytic activity of acid treated, size-fractionated smectites, *J. Phys. Chem B,* 27(1):5324 – 5331

[13] M.I. Didi, M. Suarez Barrios, S. Prates, J.M. Martin Pozas (2003). Characterization and acid activation of bentonite: a comparative study, *J. Appl. Clay Sci.*, 42(1): 336 – 344

[14] E.L. Foletto, C. Volzone, L.M. Porto (2003). Performance of an Argentinean acid-activated bentonite in the bleaching of soybean oil, *J. Chem Eng.,* 20: 139 – 145.

[15] C.A. Okwara, E.C. Osoka (2006). Caustic activation of local clays for Palm oil bleaching, *Journal of Engineering and Applied Sciences,* 1(4): 526 – 529.

[16] E.L. Foletto, G.C. Colazzo, C. Volzone, L.M. Porto (2011). Sunflower oil bleaching by adsorption onto acid-activated bentonite, *Brazilian J. Chem Eng.*, 28(1): 169 – 174.

[17] R.O. Ajemba, O.D. Onukwuli (2012). Adsorptive removal of colour pigment from palm oil using acid activated Nteje clay: Kinetics, Equilibrium and Thermodynamics, *Physicochem probl Miner Process*, 49(1):369 – 381

[18] N. Umesi (1995). Recycling used lubricating oil of an internal combustion Engine, Technical report.

[19] F. Andreola, E. Castellini, G. Lusvardi, L. Menabue, M. Romagnoli (2007). Release of ions from kaolinite dispersed in deflocculant solutions, *J. Applied Clay Science*, 36(4): 271 – 278.

[20] L. Ma, J. Zhu, H. He, Y. Xi, R. Zhu, Q. Tao, D. Liu (2015). Thermal analysis evidence for the location of zwitterionic surfactant on clay minerals, *J. Applied Clay Science*, 112: 62 – 67.

[21] M.M. Motlagh, Z.A. Rigi, A.A. Yuzbashi (2008). To evaluate an acid activated bentonite from Khorasan (Iran) for use as bleaching clay, *IUST Int J. Eng. Sci*., 19 (5-2): 83 – 87.

[22] E. Bischoff, T. Daitx, A.D. Simon, H.S. Schrekker, S.A. Liberman, R.S. Mauler (2015). Organosilane-functionalized halloysites for high performance halloysite/heterophasic ethylene-propylene copolymer nanocomposites, *J. Applied Clay Science,* 112: 68 – 74.

[23] P.B. Buurman, I. Van Langer, E.J. Velthrost (1996). Manual for soil and water analysis, Backhugs Publishers, Laiden, Netherlands, pp 56 – 89.

[24] G.P. Gillman, E.A. Sumpter (1986). Modification to the compulsive exchange method measuring exchange characteristics of soils, *Aust. J. Soil Res*. 24: 61 – 66.

[25] D. Robati (2013). Pseudo-Second-order kinetic equations for modelling adsorption systems for removal of lead ions using multi-walled carbon nanotube, *Journal of nanostructure in Chemistry,* 3(55): 1 - 6.

[26] C. Ramesh, M. Yoji, S. Akinari, H. Takahiro (2011). Adsorption of trace levels of bromated from aqueous solution by organo-montmorillonite, *J. Applied Clay Science,* 51(3): 375 – 379.

[27] G. J. Fleer, T. Lyklema, In adsorption from solution at the solid/liquid interface; Rochester, C. H., Ed.; Academic: New York, 1983; p 470.

[28] S. Voronov, V. Tokarev, V. Datsyuk, V. Seredyuk, O. Bednarska, K. Oduola, H. Adler, C. Pushke, A. Pich, U. Wagenknecht *(*2000), Polyperoxidic Surfactants for Interface Modification and Compatibilization of Polymer Colloidal Systems. 2. Design of Compatibilizing Layers, *J. Applied Polym. Sci.*, 76, pp. 1217-1227.

[29] Y.S. Ho, G. McKay (2002). Application of kinetic models to the sorption of Copper (II) on to Peat, *Journal of Adsorption Science & Technology*, 20(8): 797 – 815.

[30] A.U. Itodo, F.W. Abdulrahman, L.G. Hassan, S.A. Maigandi, H.U. Itodo (2010). Intraparticle diffusion and Intraparticulate diffusivities of herbicide on derived activated carbon, *J. Researcher*, 2(2): 74 – 86.