

Kinetics And Thermodynamic Studies Of Polycyclic Aromatic Hydrocarbons Uptake From Used Engine Oil

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ABSTRACT

In this work, base oil was recovered from used engine oil using solvent extraction with butanol, followed by adsorption of polycyclic aromatic hydrocarbon (PAH) unto activated carbon prepared from brewers' spent grain. Kinetic and thermodynamic studies for the adsorption process were studied. Kinetic data were fitted to eight models; Lagergren pseudo-first order, pseudo-second order, first-order, second-order, Elovich model, intra-particle diffusion, liquid film diffusion and pore (Banghams) diffusion model and it found out that the data fitted well to pseudo-second order model. Thermodynamic study showed that the process was endothermic in nature, feasible and spontaneous. The values of entropy obtained showed that the adsorption of PAH involved a dissociative adsorption mechanism. The activation and Gibbs free energies values confirmed the adsorption of PAH to be chemical reaction-based process.

KEYWORDS: *polycyclic Aromatic Hydrocarbons (PAHs), used engine oil, adsorption, butanol, kinetics, toluene, and thermodynamics.*

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I INTRODUCTION

Lubricating oils are viscous fluids used to facilitate relative motion of solid bodies by minimizing friction and wear between interacting surfaces [1]. Typical lubricating oil contains ninety percent base oil, most often petroleum fractions called mineral oils and less than ten percent additives [1]. There are many types of additive some of them contain metals and others are high molecular weight hydrocarbon. During automobile running, some of the above chemicals will be broken down or cracked into smaller molecules [2]. Waste lubricants are mainly generated from the transport sectors when they have lost their effectiveness during operation [3]. This is because it degrades after extended usage. Waste lubricant is a high pollutant material that requires responsible management. Waste lubricant from mineral sources are not biodegradable and contain materials produced in the degradation of base oils, such as polycyclic aromatic hydrocarbons (PAHS) with high viscosity, oxygen compounds (organic acids, ketones), resins, non consumed additives, waste metals from motors and lubricated machines, such as iron, lead, chromium, barium and cadmium, and other contaminants like water, non burned fuel, dust and various impurities which present risks to the environment [4]. Some of the particulate materials found in the waste oils can be removed by classical unit operations such as filtering and centrifugation. Waste engine oil may cause damage to the environment when dumped into the ground or into water streams including sewers. This may result in ground water and soil contaminant [5]. Regeneration of such contaminated materials will be beneficial in reducing engine oil cost. In addition, it will have significant positive impact on the environment [6]-[7]. Waste lubricating oil has been refined using many techniques such as chemical treatment, physical treatment by distillation and thin film evaporation and solvent extraction. Solvent extraction treatment has received considerable attention in recent years because it overcomes the problems associated with acid sludge produced from chemical treatment and its cost is one third of the cost of physical re-refining [3]. In spite of the advantages presented by solvent extraction process, a residual fraction (oxidation product) remains solubilized in the recovered oils, making its partial or total removal imperative for the final product to be commercially desirable [8]. Ramos et. al., [9] evaluated the adsorption of polynuclear crude oil fraction called asphaltene and resins on solid surfaces in aromatics solvents, verifying that some solid like activated carbon and silica presented good ability to concentrate those substances onto their surfaces. The similarity between crude oil polyaromatic fractions and the product from used lubricant oil oxidation makes the adsorption on solids a possible final step of their recovery process [10].

The aim of this study is to undertake kinetics, isotherm and thermodynamic studies for adsorption of polycyclic aromatic hydrocarbon unto activated carbon prepared from brewers' spent grain.

II MATERIALS AND METHODS

2.1 Preparation of PAHs-concentrated solid from the waste lubricant oil

This method was according to the work done by Assuncao et. al [10] with slight modification. Oil and butan-1-ol were mixed in a ratio of 1:3, followed by 30 min stirring and 1hr centrifugation, forming a biphasic system. The extract phase was discharged and the remaining refined phase was transferred to a filter paper, and then to a soxhlet extractor in which the organic material was extracted by continuous reflux with toluene. Toluene was then distilled and evaporated until a pastry material was obtained, which was then transferred to a new filter paper and washed in the soxhlet with pentane in order to extract the residual oil. This practice was continued until the refluxed solvent became clean. The pentane- containing solution was replaced with pure toluene in order to extract the remaining material from the filter paper. The obtained solution was subjected to distillation and evaporation so as to remove the toluene, yielding a solid which was placed in a dessicator for 24 h, before weighing.

2.2. Building of calibration curves for PAHs quantification

Solutions of the solid obtained as described above were prepared in toluene at different concentrations (0.5, 1, 2.5, 5g). UV model 1601 SCHIMADZU absorption spectrophotometer with a 1 cm glass cell was used to acquire absorbance of the solutions and calibration curve as a function of the concentrations was obtained. Absorbances were evaluated at the wavelength of 350nm, a value in the interval reported in the literature as being expressive for the absorption of polycyclic Aromatics Hydrocarbons (PAHs) [11].

2.3. Base oil recovery

Oil and butanol were mixed in a ratio of 1:3, stirred for 30 min and poured into a separating funnel, forming a biphasic system. The supernatant was put in contact with the adsorbent and, after equilibrium was reached, it was centrifuged for 10mins to remove the adsorbent. Lubricant oil was recovered from the supernatant by means of distillation. Solvent obtained was re-used as the process was repeated to obtain more yields.

2.4. Adsorption Kinetics

This method was according to the work done by Assuncao et. al [10] with slight modification. Solutions of the used oil plus solvent were prepared with oil/solvent ratio of 1:3 by weight. Each solution was homogenized using a magnetic stirrer at 2500rpm for 20 mins followed by settling under gravity for 24hrs for the formation of two phases, extract (supernatant) and the refined (lees). To evaluate the adsorption of the PAHs on the activated Carbon (adsorbent) after the phase separation, 20ml of the extract was put in contact with approximately 0.5g of adsorbents. Adsorption process was carried out for 3hrs at varying time intervals of 30mins, 60mins, 90mins, 120mins, 150mins, 180mins until saturation of the adsorbent was reached. The contents were centrifuged and the measurements of absorbance taken at the wavelength of 350nm. In order to access the amount of PAHs transferred to the adsorbent, the absorbance obtained was converted into concentration using the equation of the curve. After this, the critical and equilibrium concentrations of the PAHs in each extract and the volume of each sample were applied in the equation below for the calculation of the mass of PAHs adsorbed on the solid surface.

$$q_t \left(\frac{mg}{g} \right) = \frac{(C_i - C_t)V}{M} \quad (1)$$

Where q_t (mg/g) is the quantity of PAH adsorbed per unit mass of adsorbent, V (L) is the volume of solution used, C_i is the initial concentration of PAHs(mg/l) and C_t is the final concentration (mg/l) at different time intervals, m (g) is the mass of the adsorbent.

Kinetic data was fitted to pseudo-first order, Pseudo- second order, first order, second order, Elovich model, intra particle diffusion model, liquid Film Diffusion and Banghams Equation.

2.5. Thermodynamic Evaluation

Thermodynamic parameters of sorption such as Gibbs free energy change (ΔG°), Enthalpy change (ΔH°), Entropy change (ΔS°) and Energy of Activation were determined to assess the spontaneity, feasibility and heat change of the sorption process. The Gibb's free energy change of adsorption was calculated from the following equation

$$\Delta G = -RT \ln K_c \quad (2)$$

where R is the ideal gas constant (8.314 J/mol K), T (K) is the absolute temperature and K_c is the thermodynamic equilibrium constant that is expressed as

$$K_c = \frac{C_{ads}}{C_e} \quad (3)$$

where C_{ads} (mg/L) is the amount of PAH adsorbed at equilibrium, and C_e (mg/L) is the concentration of PAH in solution at equilibrium. The Gibb's free energy is also related to the enthalpy change (ΔG^0) and entropy change (ΔS^0) at constant temperature by the Van't Hoff equation as follows

$$\ln kc = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot of $\ln K_c$ versus $1/T$. R (8.314 J/mol K) is the ideal gas constant and T (K) is the absolute temperature at which the adsorption was conducted. Furthermore, the magnitude of activation energy (A) gives an idea about the type of adsorption which is mainly diffusion controlled process (not diffusivity of solute through micropore wall surface of a particle) or chemical reaction processes [12]. Energies of activation, A , below 42 kJ/mol indicate diffusion-controlled processes, and higher values give chemical reaction-based processes. Therefore, energy of activation, A , was calculated as per the following relation [13].

$$A = \Delta H^0 + RT \quad (5)$$

III. RESULTS AND DISCUSSION

3.1. Kinetic model analysis

Kinetic analysis helps in the prediction of the mechanism involved in sorption and identification of the rate limiting step of the process [14]. The pseudo-first order, pseudo-second order, intraparticle diffusion and liquid film diffusion models were applied to evaluate kinetic data. The calculated kinetic parameters and linear regression (R^2) are presented in Table 1. From the values of R^2 obtained for the pseudo first order, pseudo second order model, first order and second order, it is evident that the pseudo second order presented the best fit to the kinetic data for the removal of PAH with $R^2 = 1$. Also, from the experimental ($q_{e_{exp}}$) and the model calculated ($q_{e_{cal}}$) values, the $q_{e_{cal}}$ for the pseudo second order model was closer to the $q_{e_{exp}}$ than that of the pseudo first order model. The fit of the Pseudo-second order model implies the involvement of internal diffusion mechanism and considers that adsorption is of a chemical nature [15]. However, the Elovich equation was found to present the good fit to the sorption experiment as revealed by its highest R^2 value of 0.971. Researchers have found the Elovich model to be more suitable in the description of kinetic mechanism of sorption. The good fit of the Elovich model ($R^2 = 0.971$) to the sorption confirms clearly that physisorption is not the rate controlling mechanism. The R^2 value of 0.985 presented by the Bangham model showed a very little deviation from linearity indicating that the diffusion of PAH into the pores of the adsorbent cannot be ruled out as the rate controlling mechanism [16]. The plot was found to have a good correlation co-efficient (>0.98) indicating that kinetics confirmed to Bangham's equation and therefore the adsorption was pore diffusion controlled. This suggests that both film and pore diffusion were important to different extents in the adsorption process.

In order to identify the diffusion mechanism, the intraparticle diffusion and liquid film diffusion models were considered. The high R^2 value (0.983) presented by the intraparticle diffusion model suggest that the sorption process was controlled by intraparticle diffusion mechanism. However, the low values of R^2 (0.953) presented by the liquid film diffusion model indicate that the rate limiting step of sorption only partly involves film diffusion mechanism. Though intraparticle diffusion renders straight line with correlation co-efficients, $R^2 > 0.98$, the intercept of the line fails to pass through the origin which may be due to difference in the rate of mass transfer in the initial and final stages of adsorption [17] and indicates some degree of boundary layer control which implies that intraparticle diffusion is not only the rate controlling step. It has been reported that in a well agitated batch system, the external diffusion resistance is much reduced; hence intraparticle diffusion is more likely to be the rate controlling step [18]. In this study, the adsorption did not proceed in a settled condition at a given contact time but was under the influence of agitation, which is the reason why film diffusion should be the rate controlling mechanism rather than the intra-particle diffusion. However, the occurrence of the intercept suggests that neither intra-particle nor film diffusion is the sole rate controlling mechanism in the removal of PAH from used engine oil.

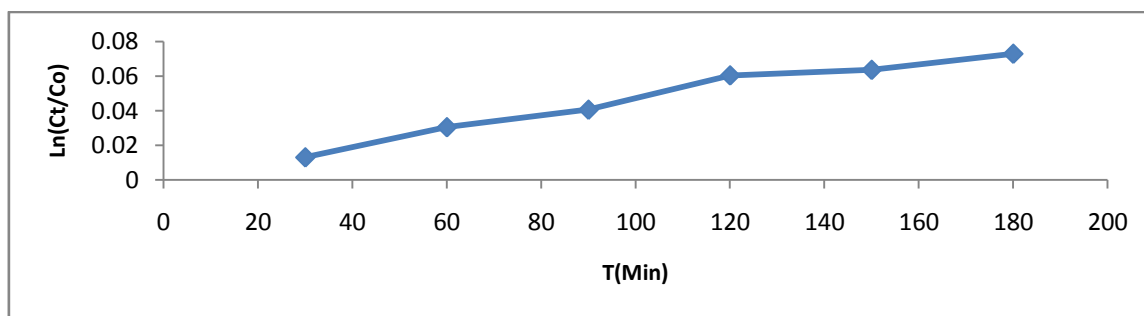
3.2. Thermodynamics modeling of PAH adsorption from used engine oil.

The variation in the amount of PAH adsorbed unto activated Carbon as a function of solution temperature is shown in TABLE 2.0. It was observed that the adsorption of PAH increased slightly as the temperature increased from 300 to 323 K. This indicates that a high temperature favors the adsorption process. The improved adsorption capability with increasing temperature suggests that the adsorption is an endothermic one. This trend may be due to the creation of more additional adsorption sites on the adsorbent surface with increase in temperature as a result of the dissociation of some of the surface components on the activated carbon that was used [19][20]. It may also be due to the tendency of PAH gaining more kinetic energy to diffuse from the bulk phase to the solid phase with a decrease in viscosity due to an increase in solution temperature [19]. In order to evaluate the feasibility of the adsorption process, thermodynamic parameters such as the standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were estimated. The negative values of ΔG^0 obtained at all temperatures indicate that the adsorption process is spontaneous in nature. It was also observed that the change in free energy increases with increase in temperature suggesting that higher temperatures make the adsorption easier. The positive value of ΔH^0 indicates an endothermic process which is supported by the increase adsorption of PAH with rise in temperature. The magnitude of ΔH^0 is very useful in describing the type

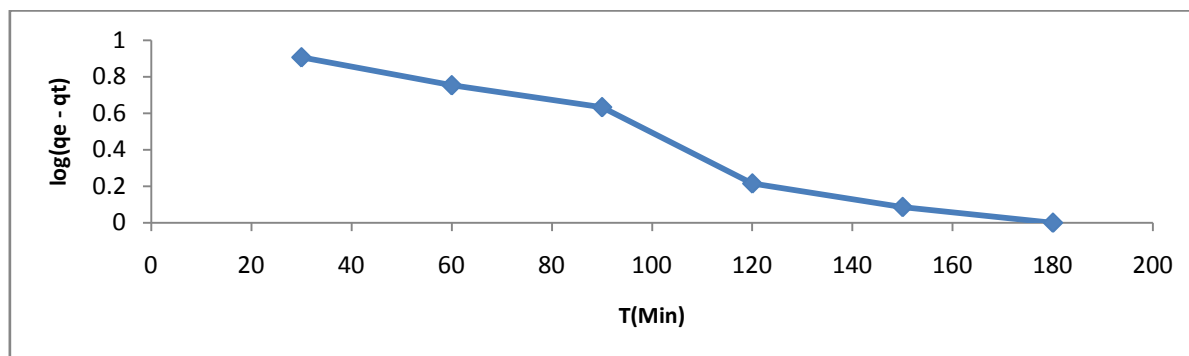
of adsorption. If the magnitude of ΔH^0 is in the range 2.1–20.9 kJ/mol, it denotes a physical adsorption process, while chemisorptions fall within the range of 80–200 kJ/mol [21]. From TABLE 2, the value of ΔH^0 obtained for PAH showed a chemical adsorption process unto the surface of activated Carbon used. This Chemical adsorption explains the reason why the kinetic data was best described by the pseudo-second order model (chemisorptions model). Furthermore, positive values of ΔS^0 indicate an increase in randomness at the solid/solution interface during adsorption while low values of ΔS^0 indicate that no remarkable change in entropy occurs [22]. Also, the magnitude of ΔS^0 reveals whether the adsorption reaction involves an associative or dissociative mechanism [19]. If the value of ΔS^0 is larger than 10 J/molK, it means that the adsorption conforms to a dissociative mechanism [23]. The values of ΔS^0 (TABLE 2) obtained show that the adsorption of PAH involves a dissociative adsorption mechanism, as the values obtained were far greater than 10 J/mol K.

Table 1: Kinetic modeling data

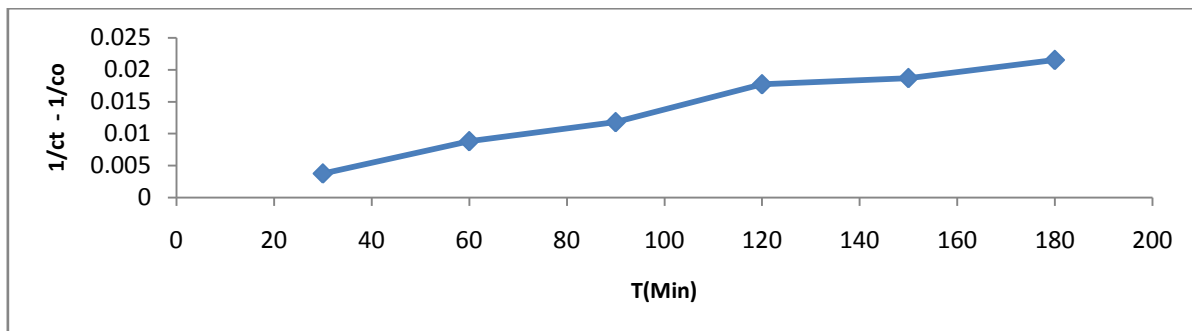
Kinetic models	Parameters	Values
1st order equation $-\ln(C/ Co) = K_1t$	R^2	0.964
	K_1	0
2nd order equation $1/C - 1/ Co = K_2t$	R^2	0.966
	K_2	0
Lagergren pseudo first order	R^2	0.956
	K_1	0.014
	$q_{e \text{ expt}}$	9.884
	$q_{e \text{ cal}}$	13.4
Pseudo second order	R^2	1
	K_2	0.000
	$q_{e \text{ expt}}$	9.884
	$q_{e \text{ cal}}$	9.9
Elovich Equation	R^2	0.971
	B	0.22
	A	0.207
Liquid film diffusion model	R^2	0.953
	K_{fd}	0.016
Intra- particle diffusion	R^2	0.983
	C	-3.732
	K_d	1.027
Banghams equation	R^2	0.980
	K_o	0.000457
	\bar{d}_b	0.943



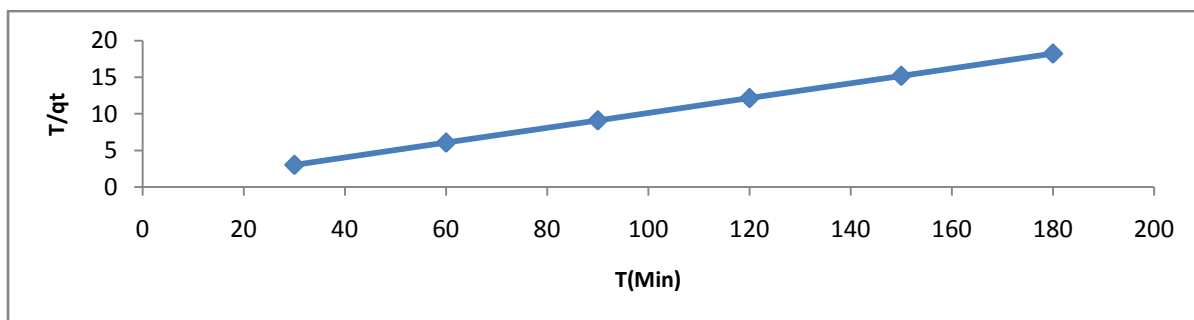
(a)



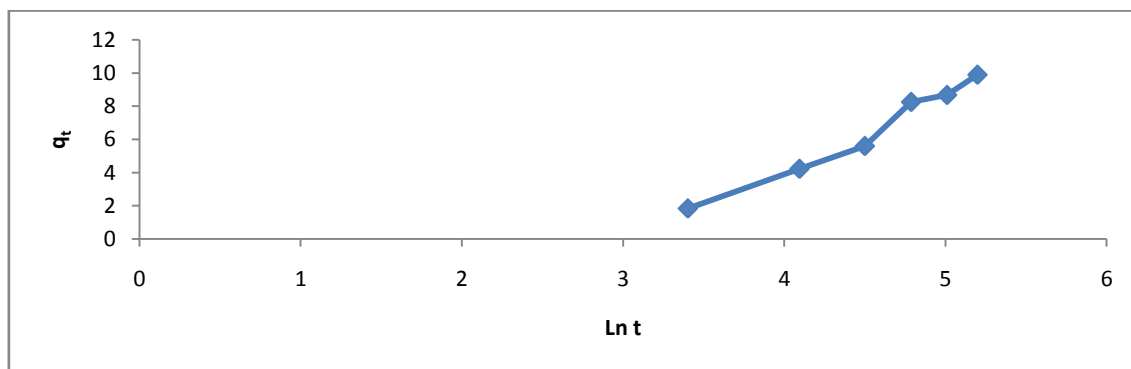
(b)



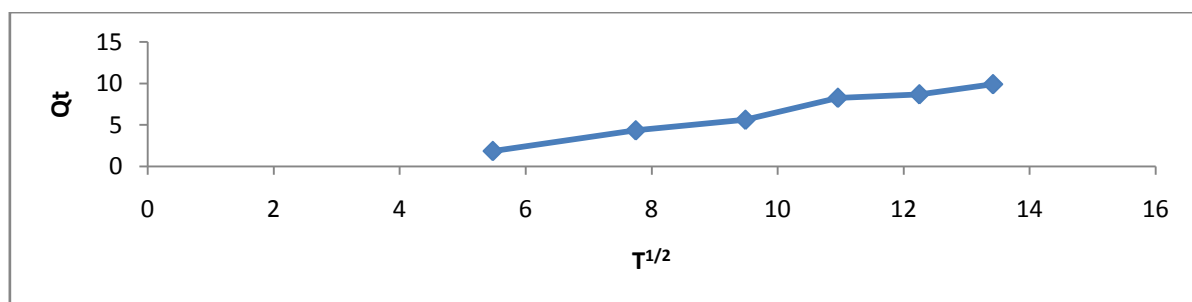
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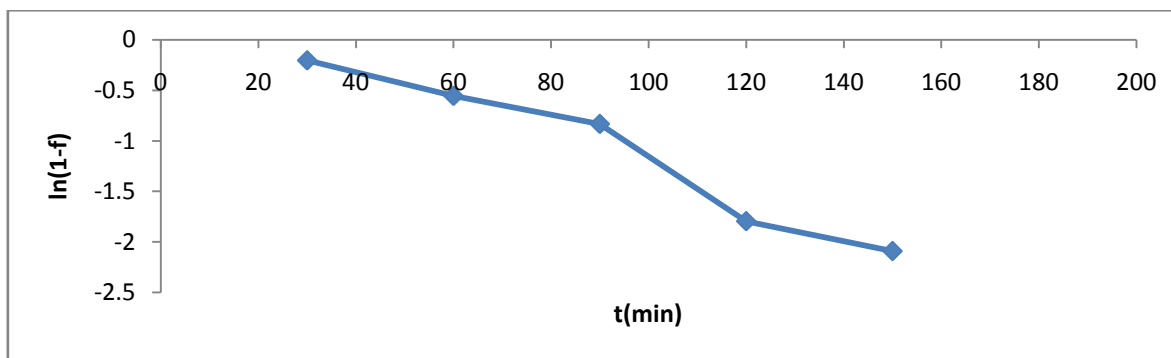
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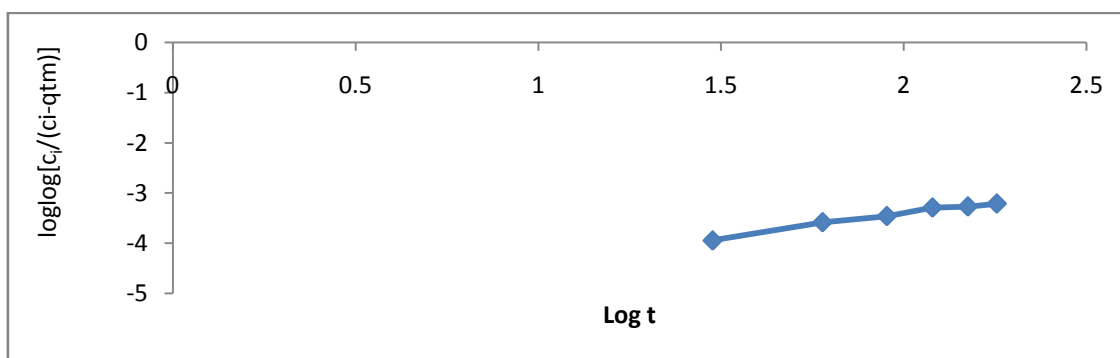
(e)



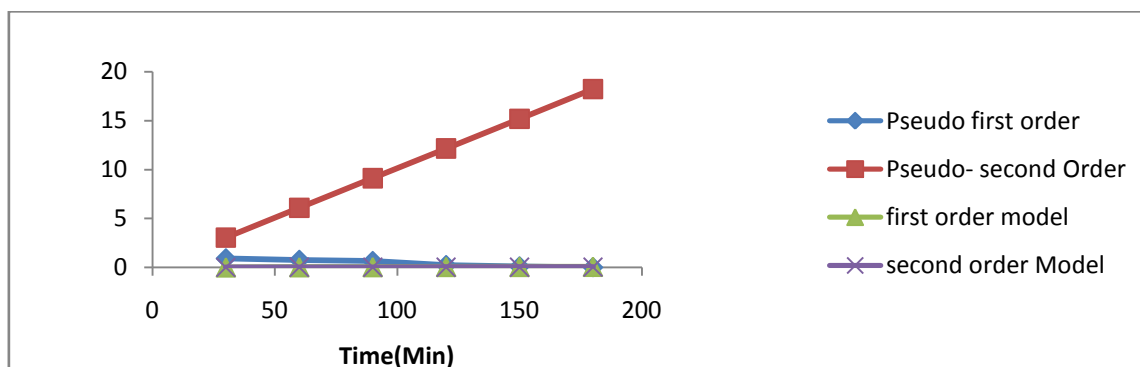
(f)



(g)



(h)



(i)

Figure 1.: kinetic plots for (A) first order model plot as a function of time. (B) Lagergren Pseudo-first order plot for the removal of PAH. (C) Second order kinetic model for the removal of PAH. (D) Pseudo-second order plot for the removal of PAH. (E) Elovich plot as a function of q_t against $\ln t$ for PAH removal from used engine oil. (F) Intra-particle Diffusion plot for 3:1 solvent/oil PAH removal from used engine oil. (G) Liquid film Diffusion Plot (H). Bangham's Kinetic Model (I) comparative plot of the kinetic order models as a function of time.

Table 2: Summary of thermodynamic parameters

Solvent: oil ratio	ΔH^0 (KJ/mol)	ΔS^0 (J/mol K)	A (KJ/mol)			$-\Delta G^0$ (KJ/mol)		
			303°K	313°K	323°K	303°K	313°K	323°K
3:1	48.45	126.71	50.96	51.05	51.13	38344.68	39611.78	40878.88

The positive value of ΔH° indicates the presence of an energy barrier in the adsorption process. Similarly, the ΔS° value is positive indicating increase in randomness during the adsorption process for the PAH. These positive value of ΔS° observed for the adsorption of the PAH indicate an increase in randomness at the solid/solution interface during their adsorption process. Energies of activation, A, below 42 kJ/mol indicate diffusion-controlled processes, and higher values give chemical reaction-based processes [13]. In this study, the activation energy (A) values were all greater than 42 kJmol⁻¹ indicating chemical reaction-based processes

IV. CONCLUSION

The research has successfully spent engine oil using solvent- adsorption process. From the properties obtained after application of adsorption methods, some desirable properties were enhanced though interest was on the removal of PAHs. The kinetic studies revealed that the pseudo-second order model gave the best fit which means that the adsorption process was chemical reaction base (Chemisorption). From the thermodynamic studies, the positive value of ΔH^0 indicated an endothermic process which was supported by the increase in adsorption of PAHs with rise in temperature. The magnitude of ΔH^0 which was in the range 51.38–70.519 kJ/mol confirmed chemisorptions. Activated carbon can be successfully applied in the removal of PAHs from spent engine oil. The occurrence of the intercept suggests that neither intra-particle nor film diffusion is the sole rate controlling mechanism in the removal of PAHs from used engine oil. The activation energy (A) values were all greater than 42 kJmol⁻¹ indicating chemical reaction-based processes

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