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Kinetics and Thermodynamic Adsorption of Pb(II) and Cd(II) Ions from Used Oil onto *Thevetia neriifolia* Nutshell Active Carbon

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ABSTRACT

Active carbon was prepared from *Thevetia neriifolia* nutshell by carbonization at 480°C in N₂ and activation with CO₂ at 840°C for 3 h. The values of 822.2 mg g⁻¹, 0.113 cm³ g⁻¹ and 551 m² g⁻¹ were obtained for iodine number, micropore volume and BET surface area, respectively. First, second and Pseudo-second orders kinetic models described kinetic data at various temperatures for adsorption of Pb(II) and Cd(II) ions from used oil onto the carbon. Pseudo-second order kinetic model fitted better and was controlled by film diffusion. Enthalpy and entropy were found to be negative for Pb(II) and positive for Cd(II). Adsorption process was non-spontaneous for Pb(II) and spontaneous for Cd(II) metal ions. However, low enthalpy value makes the adsorption process energetically stable. Thus, the active carbon could be adopted as a potential adsorbent for remediation of environment.

Key words: Adsorption kinetics, metal ions, nutshell, active carbon, used oil

INTRODUCTION

Over the last two decades, the safety of our environment has been continuously threatened by increase in industrialization and human activities (Rivera-Utrilla *et al.*, 1988). There had been increase in the production of vehicles, heavy duty machineries that make use of oil as lubricant. Unfortunately, used oil types that are often disposed contain toxic metals. Some researchers have reported that virgin lubricating oils contain about 30% additives that include viscosity index improvers, pour point depressants, defoamers, antiwear and anti-friction compounds whose contents are mainly metals (Ciora and Paul, 2000). They have also described steps in removing ash and colour from used oils with aid of membrane filtration.

Despite the existence of various refining processes such as cracking, upgrading, hydro treatment, chemical treatment and addition of additives, United States Environmental Agency reported that 24% of used oil is still disposed. Certain heavy metals have been found present in used automobile engine oils (McKenzie, 1981) and are injurious to human health whenever their concentrations in the environment exceed certain limit. The management of these heavy metals is of global concern because heavy metals contaminate soils, water and air which in turn accumulate and affect plants and animals. Some major sources of these heavy metals include wastes from industries like electroplating, metal finishing, metallurgy, tannery operations, chemical processing, mine drainages, battery manufacturing leachates from land fills, disposal of automobile oils and domestic wastes (Reed *et al.*, 1994; Gallagher *et al.*, 1990).

The effects of heavy metals on human health are enormous due to their accumulation in living organisms which eventually reach humans via food chain (Viessman and Hamner, 1993; Bailey *et al.*, 1999). The oral uptake of cadmium through food and beverages tend to cause kidney failure, cancer and hypertension. Its acute intoxication through dust, results in dyspnea, cough, fever and chronic pneumonitis (Pier and Bang, 1980; Anderson, 2003; Dekhil *et al.*, 2011). The intake of lead poisoned food or its intoxication cause break down of central nervous system, kidney failure and affect red blood cells resulting into death (Silva *et al.*, 1993). It affects liver and bone marrow cause reduction of intelligence and stunted growth in children (Chang, 1990; Low *et al.*, 2000). Active sites of enzymes are also attacked by these heavy metals (Olayinka *et al.*, 2007).

Many techniques like reverse osmosis, chemical precipitation, ion exchange and electro-flotation had commonly been used for removal of heavy metals. Likewise, commercial active carbon had been used for adsorption and removal of heavy metals from effluent waste water and the environment. Some work on removal of colour and odour from lubricating oils had been reported (Ciora and Paul, 2000). Among the various methods of metal ion removal from the environment, adsorption with active carbon seem to be advantageous in that it combines large scale application, simple technology and cost effectiveness of cheap local agricultural raw materials. Moreover removal of trace quantities of metals or lowering of concentration of adsorbates in effluents (Bello *et al.*, 2011) is feasible when adsorption process is adopted.

The roles of active carbon include removal of heavy metals (Tekere and Imamoglu, 1999; Qadeer and Akhtar, 2005) decolourization of dyes (Gomez-Serrano *et al.*, 1998; Netzer and Hughes, 1984; Gokturk and Kaluc, 2008) and deodourization of effluents from industrial waste waters (Basar, 2006; Maleki *et al.*, 2007; Al-Jlil, 2009). Over the years, the use of active carbon has proved to be inevitable in the control of environmental pollution.

Since activities of human and industrial development are major sources of contamination of our environment (Igwe *et al.*, 2005), the use of automobiles and heavy duty machines in industries have contributed significantly to contamination of the environment. Improper disposal of used oils especially in Africa and some parts of third world countries abound. Lubricating oils play the role of reduction of friction between engine parts thereby protecting the engine parts from being corroded. If the oils are properly managed, they can be used again as base stock for new lubricating oils or as fuels for other machines.

As these heavy metals cause low life expectancy and high mortality rate, their adsorption from used oils becomes necessary. Active carbon prepared from *Thevetia neriifolia* (bush milk) nutshell which is a renewable source is utilized as the main precursor biomass in this study.

Therefore, this study investigated the applicability of *T. neriifolia* nutshell active carbon prepared by activation of its char for kinetic and thermodynamic studies in removal of Pb(II) and Cd(II) metal ions from digested used oil. The effect of temperature on adsorption of Cd(II) and Pb(II) metal ions from used oil as well as fitting of adsorption data into various kinetic equations was studied.

MATERIALS AND METHODS

Materials: The used automobile engine oil samples were collected at the mechanic site from Nigeria, during servicing of motor car. The brand of used engine oil investigated is AZ engine oil. Their corresponding virgin engine oil was bought directly from petrol filling station. The virgin and

used engine oils of AZ crown super high performance engine oil SAE 20 W 50-AP1 SG/CD were separately collected in tightly corked plastic containers and stored in the laboratory at room temperature.

Methods

Preparation of activated carbon: Active carbon utilised for the study was obtained from activation of *T. nerifolia* (oleander yellow) char with CO₂. The Char nutshell was prepared from *Thevetia nerifolia* nutshells via carbonization at 480°C in N₂ flowing at 1000 mL min⁻¹ followed by activation of 12 g of the char with CO₂ at flow rate of 500 mL min⁻¹ and temperature of 840°C for 3 h in horizontal tubular reactor furnace (Carbolite tube furnace, CTF 12/65/550 Model, Italy). Prior to activation, the air in the quartz tube was first evacuated by flow of N₂ gas at 500 mL min⁻¹ for 30 min (Nwosu *et al.*, 2009).

Characterization of activated carbon: The prepared Active Carbon (AC) was characterized using adsorption of iodine molecules to ascertain its iodine number and its BET surface area was obtained by aid of Gemmi 2375 Sorptometer. Its micropore and mesopore volumes were determined using n-hexane adsorption (Bayer *et al.*, 1995). FT-IR and Scanning Electron Microscopy (SEM) were carried out using a Nicolet Avatar 330 FT-IR spectrometer model (Thermo Electron Corporation, USA) and scanning electron microscopy instrument (model DSM 982, Germany) respectively.

Physicochemical properties of lubricating oils: The specific relative density of both used and virgin AZ oils was carried out using dried relative density bottles (McKenzie, 1981) while their viscosity was determined using Ostwald viscometer (Atkins and Paula, 2002). Wet and dry ash methods were adopted for determination of concentration of Pb(II) and Cd(II) metal ions. The dry ash method (Milner *et al.*, 1952) for determination of heavy metals involved the separate treatment of 2.5 g of each of the oil samples with 200 mL of concentrated H₂SO₄ acid in a crucible. It was thoroughly stirred and heated gradually on a thermostatic hot plate to dryness for about 5 h. The crucibles containing the dried oil samples were then transferred to a muffle furnace and held at 550°C for 1 h. They were then cooled in desiccators. The ash of each of the oils were then dissolved with 6 M HNO₃ in a 20 mL standard volumetric flask and made up to mark. The Pb(II) and Cd(II) metal ions were determined using Atomic Absorption Spectrophotometer (AAS).

The wet digestion method described by the Analytical methods Committee (1959) was also used. 15 mL of concentrated HNO₃ was added to 150 mL of the oil sample and heated for 10 min and cooled. Five milliliter each of concentrated HNO₃ and HClO₄ acids were added to the mixture and heated. The intermittent additions of 5 mL concentrated HNO₃ and 5 mL concentrated HClO₄ acids continued during the digestion process till clearer solutions of the oil samples were observed. The digested oil samples were then separately transferred to 1 L volumetric flask and made up to mark using methyl isobutyl ketone (MIBK) which formed the stock solution. A 250 mL of the stock solution was measured and made up to mark with MIBK solution in a standard 500 mL volumetric flask to obtain 50% oil: MIBK solution.

Kinetics and thermodynamic studies of adsorption: The kinetic and thermodynamic studies of adsorption of Pb(II) and Cd(II) were conducted using batch method (Kadirvelu and Namasivayam, 2003; Dekhil *et al.*, 2011; Maleki *et al.*, 2007). About 0.2 g of the CO₂-based active

carbon of *T. neriifolia* nutshell was added to 20 mL portions of 50% oil: MBIK solution in a plastic container and agitated at 150 rpm for various periods of 2-120 min on a thermostatic shaker. The kinetic studies were carried out at temperatures of 27 and 35°C; and at pH of 4.8 buffered by 2 mL of a mixture of equal volume of 1 M CH₃COONa and 1 M CH₃COOH (Johns *et al.*, 1999; Toles *et al.*, 1999). Aliquots of the supernatant solution were withdrawn and subjected to atomic absorption analysis for Pb(II) and Cd(II) using Buck scientific 205 Atomic Absorption Spectrophotometer with the aid of air acetylene flame. Plastic containers were used to ensure that no adsorption onto container occurred.

RESULTS AND DISCUSSION

Properties of activated carbon: The properties of the prepared *T. neriifolia* Active Carbon (AC) are shown in Table 1. Its percentage yield, bulk density, ash content and pH were found to be 21.63%, 0.50 g mL⁻¹, 1.33% and 4.3, respectively. The *T. neriifolia* CO₂-based AC exhibited iodine number value of 822.2 mg g⁻¹, micropore volume of 0.113 cm³ g⁻¹, mesopore volume of 0.017 cm³ g⁻¹ and BET surface area of 551 m² g⁻¹. The FT-IR of the prepared AC showed stretch vibrations of C = O in ketones and aldehydes in the range of 1700-1735 cm⁻¹. The C = O functional group may be attributable to aliphatic ketones, aldehydes and carboxyls formed (Petrov *et al.*, 2000). The C = O stretch vibrations which is corresponding to vibrations of C = O in carboxylic acids (-COOH) might be assigned stretching vibrations between 1637-1685 cm⁻¹. Its SEM micrograph revealed numerous pores and crevices all over the surface of the activated carbon (Fig. 1) (Dekhil *et al.*, 2011).

Properties of lubricating oils: Some properties of the virgin and used oils as well as their metal ion concentrations are presented in Table 2. It could be observed from Table 2 that the virgin oil with relative specific density of 0.950 exhibited a higher density than its corresponding used oil (0.923). The value (73.27 cp) of the virgin oil was found to be more viscous than its corresponding

Table 1: Properties of CO₂-based AC and ultimate analysis data of *T. neriifolia* nutshell

Properties of precursor nutshell		Properties of activated carbon	
Parameters	Values±SD	Parameters	Values
C (wt. %)	45.65±0.15	Bulk density (g mL ⁻¹)	0.50
H (wt. %)	6.05±0.12	Yield (wt. %)	21.63
N (wt. %)	0.16±0.08	Ash (wt. %)	1.33
S (wt. %)	0.00±0.00	Iodine number (mg g ⁻¹)	822.2
O (wt. %)	46.15±0.22	BET (m ² g ⁻¹)	551
Yield (wt. %)	34.60±0.21	Vmi, (cm ³ g ⁻¹)	0.113
Ash (wt. %)	0.38±0.02	Vme, (cm ³ g ⁻¹)	0.017

BET, Vmi and Vme: Brunaur Emmett Teller surface area, microporous volume and mesoporous volume, respectively

Table 2: Some properties and metal composition of used and virgin lubricant oil

Type of lubricant oil	Relative specific density	Viscosity (cp)	Metal ion concentrations (mg kg ⁻¹)	
			Pb(II)	Cd(II)
Commercial used oil	0.9501	73.27	810.4 (20.64 %)*	1.72 (0.03%)*
Commercial virgin oil	0.9230	70.27	5.24 (0.25 %)*	1.1 (0.30 %)*

*Indicate percentage of metal ion present among all the metal ions in lubricant oil investigated

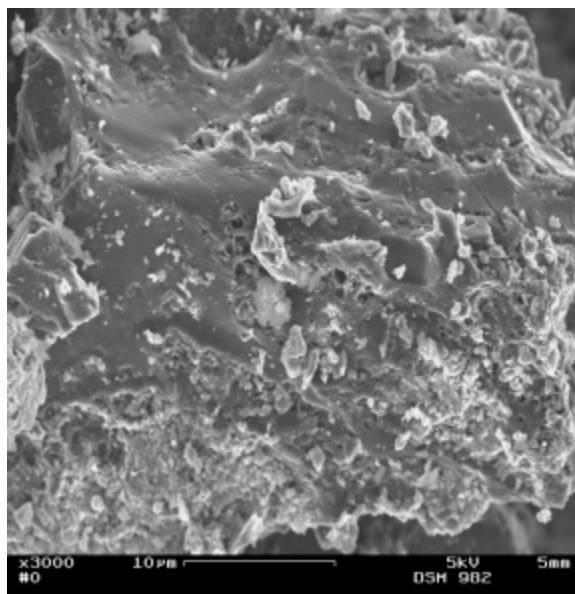


Fig. 1: Micrograph of *T. nerifolia* activated carbon

used oil brand (70.27 cp). The trend in specific density could be attributed to combustion of some components of the lubricating oil as it was heated up in various sections of automobile engine leading to contamination (McKenzie, 1981). Thus, the low viscosity of oils obtained from used oil became less viscous due to contamination of the oil with fuel and other impurities from the engine. Table 2 also showed that the concentrations of metal ions with values of 0.8104 and 0.0017 mg g⁻¹ for Pb(II) and Cd(II), respectively for used oils are higher than their corresponding concentrations in the virgin oil. Preliminary investigation of wear metals in lubricating oil revealed the presence of 16 metal ions in both used and virgin lubricating oil. Pb(II) constituted 20.64% and Cd(II) 0.03% for the used oil while 0.25 and 0.30% were obtained for Pb(II) and Cd(II), respectively in the case of the virgin oil. This is dangerous for the environment as there is possibility of its bioaccumulation that eventually gets to human and become injurious. The permissible WHO threshold limit value of Pb(II) ion in water is 0.01 mg L⁻¹ (Bulut and Baysal, 2006) which is less than Pb(II) value of 0.81 mg g⁻¹ found in the used oil. Similarly, the Cd(II) value found in the oils is greater than World Health Organization (WHO) and America Water Works Association (AWWA) drinking water guideline value of 0.005 mg g⁻¹ for Cd (Mohan and Singh, 2002).

Surface adsorption kinetic studies: The surface kinetic study for the adsorption of Pb(II) and Cd(II) were investigated at optimum pH of 4.8 using 0.1 M sodium acetate and 0.1 M acetic acid buffer (Toles *et al.*, 1999; Johns *et al.*, 1999). This is because Mohan and Singh (2002) and Brown *et al.* (2000) noted that Cd(II) ions do not easily hydrolyse at pH = 8 but existed in their hydroxo complex forms at pH>11. It was suggested that a pH lower than 8 is essential for adsorption to be significant while pH>3 is needed to avoid metal ions being exchanged with H⁺ ions that causes leaching of the metals from the adsorbent (Randall *et al.*, 1974; Coupal and Lalancette, 1976). In general, Brown *et al.* (2000) suggested that optimum pH for meaningful sorption of divalent metal ions from solution should range from 3.5 to 6.5. Thus, pH of 4.8 was chosen for adsorption process in this study in line with literature.

Four kinetic adsorption linear rate law expressions were applied to the adsorption data obtained in this study. The linear forms of the integrated rate law expressions are as follows:

- Pseudo-second order adsorption rate law given by Ho and McKay (1999a,b, 2000), Joseph *et al.* (2009) and Nyembe *et al.* (2010):

$$t/Q_t = 1/ksQ_e^2 + 1/Q_e (t) \quad (1)$$

- Second order adsorption rate law used by Ho and McKay (1998) for sorption of Pb(II) ion onto peat:

$$1/Q_t = k_2 t + 1/Q_0 \quad (2)$$

- First order adsorption rate law as reported by Periasamy and Namasivayam (1994, 1995) for removal of Cd(II) from wastes water and Pb(II) from aqueous solution:

$$\text{Log } C_t = \text{Log } C_0 - k_1/2.303 (t) \quad (3)$$

- The intraparticle diffusion equation as reported by researchers (Weber and Morriss, 1963; Gokturk and Kaluc, 2008) and is represented as:

$$Q'_t = K_p t^{1/2} + C \quad (4)$$

the symbol Q_e represent the derived maximum adsorption capacity (mg g^{-1}) of adsorbate for Pb(II) or Cd(II) metal ions on active carbon adsorbent and ks is pseudo-second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The Q_0 and Q_t symbols are initial and residual concentrations (mg g^{-1}) of metal ions respectively at various times, t (minutes). k_1 is the rate constant of first order adsorption (min^{-1}), k_2 is the rate constant of second order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$) while kp is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$) and C is the intercept. The linear plots of t/Q_t versus time, t obtained for the pseudo-second order adsorption process (Fig. 2-3) of Pb(II) and Cd(II) at two temperatures onto *T. neriifolia* CO_2 -based AC gave slope, intercept and correlation coefficients, R^2 from which their rate constants and maximum adsorption capacities were determined (Table 3).

The non-fitting of first order and second order kinetic adsorption data using residual concentrations revealed that the adsorption of Pb(II) and Cd(II) from used oil at pH 4.8 and at the temperatures of 27 and 35°C may not be feasible as their linear regression correlation coefficient; R^2 values were found to be less than 0.300 (graphs not shown) (Gokturk and Kaluc, 2008). From Table 3, it could be observed that the pseudo-second order rate constant, ks for Pb(II)

Table 3: Kinetic adsorption parameters of pseudo-second order sorption model

Metal ions	Temp. (K)	ks ($\text{g mg}^{-1} \text{min}^{-1}$)	Q_e (mg g^{-1})	R^2	B_F	S_R ($\text{mg g}^{-1} \text{min}$)	C_0 (mg L^{-1})
Pb(II)	300	0.122	5.319	0.979	9.63×10^{-1}	3.454	15.598
	308	0.327	1.605	0.742	9.64×10^{-1}	0.841	15.598
Cd(II)	300	1.558	0.615	0.922	9.87×10^{-1}	0.179	2.415
	308	2.179	0.629	0.940	9.87×10^{-1}	0.324	2.415

ks represent pseudo-second order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) Q_e : Maximum adsorption capacity (mg g^{-1}), R^2 : Correlation coefficient, B_F : Boltzmann factor, S_R : Initial sorption rate (mg/g min) and C_0 : represent initial concentration (mg L^{-1})

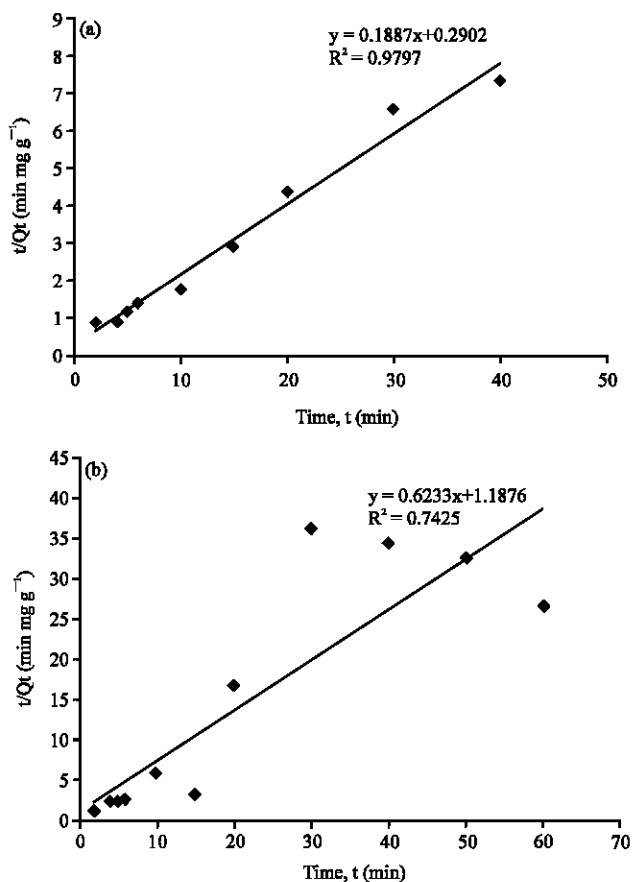


Fig. 2(a-b): Plot of t/Q_t versus time t for adsorption of Pb(II) at 27 and 35°C from used lubricating oil, (a) 27°C, (b) 35°C

increased from 0.122 to 0.327 $\text{g mg}^{-1} \text{min}^{-1}$ as temperature increased from 27 to 35°C. The linear regression correlation coefficients, R^2 equal 0.979 and 0.742 obtained for the Pseudo-second order rate constant at 27 and 35°C, respectively for Pb(II) were found to be high. The k_s for Cd also increased from 1.558 to 2.179 $\text{g mg}^{-1} \text{min}^{-1}$ when temperature was increased from 27 to 35°C with high correlation coefficients that fell within 0.922-0.940. The increase in pseudo-second order rate constant for Pb(II) and Cd(II) ions with increase in temperature could probably be attributed to the intrinsic nature of the metal ions in that they are divalent and have also gained kinetic energy as temperature increased and exhibited greater adsorption rate. The derived maximum equilibrium adsorption capacity, Q_e value for Pb(II) was small and decreased as temperature increased (Table 3) from 27 to 35°C because of matrix effect due to simultaneous adsorption of more than 16 metal ions contained in the used oil at same time (Nwosu *et al.*, 2008). The attachment of Cd(II) and Pb(II) metal ions onto the AC via physical adsorption process may be attributed to the aid of weak van der Waals forces. At higher temperatures, the adsorbed Pb(II) ions tend to detach, thereby reducing amount of adsorption capacity. This finding agrees with trend reported in literature that adsorption capacity reduces with increase in temperature for some divalent metal ions. This may be due to the weakening of sorption forces between the *T. neriifolia* AC sites and the metal ions as well as between the adsorbed metal ions of the sorbed phase (Viraraghavan and Dronamraju, 1995; Gokturk and Kaluc, 2008). In the case of Cd(II) ions, a slight increase in

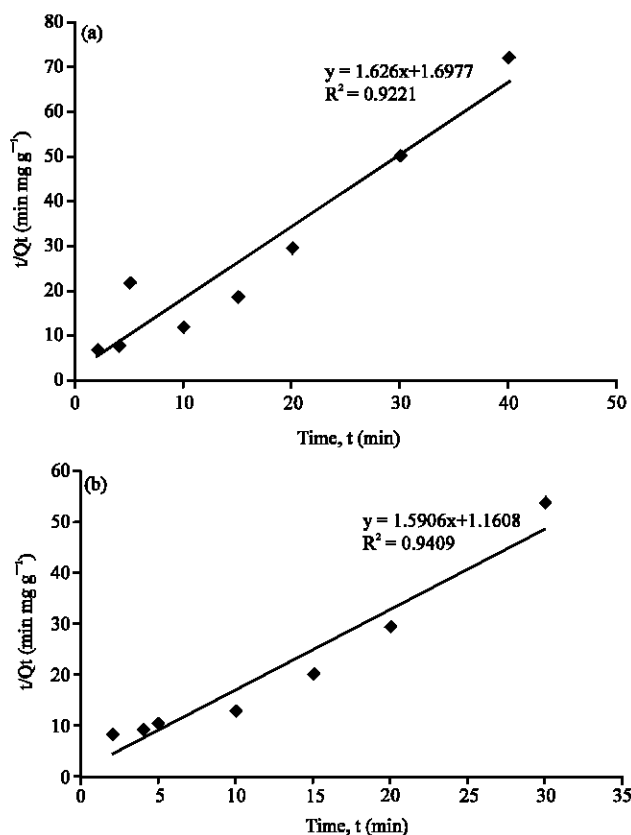


Fig. 3(a-b): Plot of t/Q_t versus time, t for adsorption of Cd(II) at 27 and 35°C from used lubricating oil, (a) 27°C, (b) 35°C

equilibrium adsorption capacity was observed with increase in temperature (Table 3) and is in agreement with finding of Bulut and Baysal (2006) and Raji and Anirudhan (1997). Moreover, Mohan and Singh (2002) asserted that adsorption in multi-component systems is complicated because of solute-surface and solute-solute interactions that are involved.

Despite the multi-component system of metal ions in used oils investigated, the pseudo-second order kinetic model of Pb(II) and Cd(II) ions fitted well for description of these metal ions that were selectively adsorbed onto the CO_2 -based AC (Joseph *et al.*, 2009). Since adsorption of Pb(II) ions are observed to follow exothermic process, ($\Delta H = -16.68 \text{ kJ mol}^{-1}$), then it could be expected that their adsorption rate would decrease with increase in temperature in line with the findings of some researchers (Atkins and Paula, 2002; Tsai *et al.*, 2004; Ho and McKay, 1999a; Singh, 1998). However, the adsorption of Cd(II) ion followed exothermic process as its ΔH value was found to be $-105.72 \text{ kJ mol}^{-1}$ and as such a slight increase in its maximum equilibrium adsorption capacity.

In another study, Murgulescu *et al.* (1981) and Mihaly-Cozmuta *et al.* (2005) referred $e^{-E_a/RT}$ factor in Arrhenius equation as Boltzmann factor, B_F . They defined it as fraction of active sites on adsorbent surface with adequate potential energy to adsorb adsorbates. The values of Boltzmann factor obtained for both Pb(II) and Cd(II) ions is within range of 10^{-1} (Table 3). From these values, it could be suggested that the CO_2 -based AC from *T. neriifolia* nutshells had equal potential to adsorb Pb(II) ion than Cd(II) metal ions. It further indicated that unoccupied active sites are equally available to both metal ions at conditions of sorption process considered (Murgulescu *et al.*, 1981; Mihaly-Cozmuta *et al.*, 2005).

Thermodynamic quantities of adsorption of Pb(II) and Cd(II) ions: The practical application of a process is dependent on values of thermodynamic parameters obtained. Equations 5, 6, 7, 8 and 9 were utilized for calculation of activation energy of adsorption (Ea), equilibrium constant (Kc), enthalpy change of adsorption (ΔH_{ad}), Gibbs free energy of adsorption (ΔG_{ad}) and entropy change of adsorption (ΔS_{ad}), respectively.

Thus, the equation that defines activation energy, Ea is:

$$\ln \frac{ks_1}{ks_2} = \frac{-E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad (5)$$

and equilibrium constant is defined as (Murgulescu *et al.*, 1981; Mihaly-Cozmuta *et al.*, 2005):

$$K_c = \frac{C_0 - C_e}{C_e} \quad (6)$$

while enthalpy change of adsorption is defined by Van't Hoff's equation (Atkins and Paula, 2002):

$$K_c = K_o - e^{\Delta H_{ad}/RT} \quad (7)$$

The determination of Gibbs free energy change (ΔG) and entropy change (ΔS) of adsorption were calculated with the aid of the following equations:

$$\Delta G = -RT \ln K_c \quad (8)$$

$$\Delta G = \Delta H - \Delta S \quad (9)$$

where, ks_1 , ks_2 , K_c , R , represent pseudo second order rate constant at 27°C (T_1), pseudo-second order rate constant at 35°C (T_2), equilibrium constant and gas constant respectively. C_0 and C_e are initial and equilibrium concentrations. ΔH , ΔS and ΔG indicate enthalpy change, entropy change and Gibbs free energy of adsorption, respectively.

From Eq. 5, activation energy, Ea values of the adsorption process was found to be 94.44 and 32.21 kJ mol⁻¹ for Pb(II) and Cd(II) metal ions respectively (Table 4). Hence energy barrier for Cd(II) adsorption is lower than that of Pb(II) ion. Furthermore, Morais *et al.* (1999) characterized low Ea energies (5-40 kJ mol⁻¹) as physical adsorption while higher Ea energies (50-800 kJ mol⁻¹) as chemical adsorption. The low value of Ea obtained for Cd(II) ions indicated low energy barrier for adsorption of Cd(II) and was found to be within range obtained by Nollet *et al.* (2003).

Table 4: Thermodynamics parameters using pseudo-second order rate constant

Metal ions	Temp. (K)	Kc	Ea (kJ mol ⁻¹)	ΔG_{ad} (kJ mol ⁻¹)	ΔH_{ad} (kJ mol ⁻¹)	ΔS_{ad} (kJ mol ⁻¹ K ⁻¹)
Pb(II)	300	0.6181	94.44	0.78	-16.68	-0.058
	308	0.1543		6.71		-0.076
Cd(II)	300	0.2981	32.21	-1.61	-105.72	-0.358
	308	0.4670		-2.55		-0.352

Where K_c , A_0 , E_a , ΔG_{ad} , ΔH_{ad} , ΔS_{ad} are symbols that indicate equilibrium constant, pre-exponential factor, activation energy, Gibbs free energy change, enthalpy change and entropy change of adsorption, respectively

Table 4 summarized the values of the thermodynamic quantities obtained for pseudo second adsorption kinetic data for Pb(II) and Cd(II) metal ions. Entropy change of adsorption of the metal ions, ΔS_{ad} which measured degree of randomness was found to be negative for Pb(II) ion and implied decrease in entropy and it was found to be negative for Cd(II) ion indicating decrease in entropy. In line with Mohan and Singh (2002), negative values of entropy change, ΔS_{ad} obtained for adsorption of Pb(II) ion onto the nutshell AC showed that no significant change occurred in the internal structure of the active carbon. Similar negative values have been obtained by other researchers (Gupta *et al.*, 1997a,b; Moham *et al.*, 2001). The positive entropy change obtained indicated that significant change in the internal structure of the active carbon surface might have occurred at the solid/solution interfaces. It also shows the affinity of the active carbon for the Cd(II) ion (Ajmal *et al.*, 2003; Bulut and Baysal, 2006). Moreover, the values of enthalpy change of adsorption, ΔH_{ad} obtained described the pseudo-second order adsorption kinetic model for Pb(II) and Cd(II) ions from used oil with multi-component metal ions as exothermic for Pb(II) ion and Cd(II) ion. The large negative value of enthalpy change of adsorption of -16.68 obtained for Pb(II) ion suggested that the process of adsorption for the Pb(II) metal ions onto the nutshell AC might tend towards chemical adsorption (Ozean and Ozean, 2005). Gibbs free energy change, ΔG is important indices for spontaneity of adsorption process. In general, Jaycock Parfitt (1981) assigned free energy change of adsorption, ΔG_{ad} values that ranged from -20 to 0 kJ mol⁻¹ as physisorption while chemisorption was assigned values that ranged from -80 to -400 kJ mol⁻¹. In this study, the spontaneity of adsorption process, ΔG_{ad} of Pb(II) were found to be 0.78 and 6.71 kJ mol⁻¹ at 27 and 35°C, respectively while -1.61 and -2.55 kJ mol⁻¹ were obtained for Cd(II) ions at 27 and 35°C, respectively. It could be suggested that adsorption of Pb(II) ions onto nutshell of *T. neriifolia* CO₂-based AC is non-spontaneous. However, the low values of ΔG_{ad} of Pb(II) indicated that its adsorption should preferably be carried out at lower temperature. Furthermore, adsorption of Cd(II) ions onto the nutshell AC indicated spontaneous and its adsorption process could be classified as physisorption. These findings agreed with other works reported in literature in support of non-spontaneity of adsorption process due to positive ΔG_{ad} values obtained (Ozean and Ozean, 2005).

Sorption mechanism: Sorption mechanism is important in industrial application especially after a particular kinetic model has been identified. According to Vadivelan and Kumar (2005), sorption mechanisms between solid-liquid solution systems follow certain stages:

- Movement of solutes to the exterior surface of adsorbent which implies boundary surface diffusion (external mass transfer or film diffusion)
- Movement of solute from external surface of the adsorbent which is intra particle diffusion

It has been noted that the plot of qt versus $t^{1/2}$ represents multi-linearity which characterizes two or more steps occurring in sorption process (Gokturk and Kaluc, 2008). If intraparticle diffusion is rate determining step in an adsorption process, then the plot of qt versus $t^{1/2}$ will give linear graph that will pass through the origin (Kannan and Sundaram, 2001; Bhattacharyya and Sharma, 2004; Chen *et al.*, 2003). Figure 4 depicts the linearity of plot of qt (amount adsorbed) versus $t^{1/2}$ (time)^{1/2} that does not pass through the origin within first 15 min. It implied that the adsorption process of Pb(II) metal ion at 27 and 35°C for 15 min was controlled by film diffusion (Vadivelan and Kumar, 2005). Figure 5 also showed that the mechanism of adsorption of Cd(II) ion onto

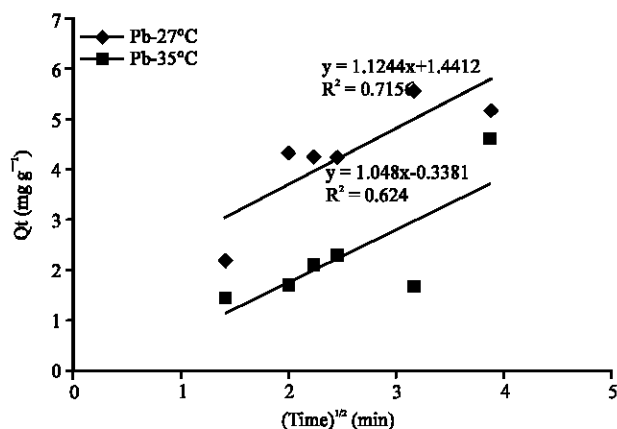


Fig. 4: Plot of Q_t versus $(\text{time})^{1/2}$ at various temperature for adsorption of Pb(II) ions from used lubricating oil

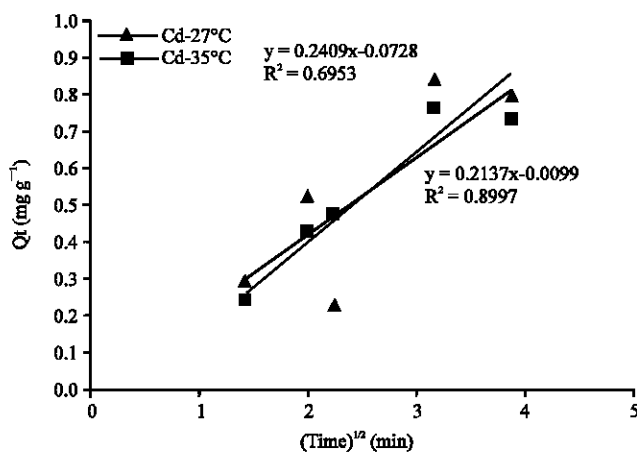


Fig. 5: Plot of Q_t versus $(\text{time})^{1/2}$ for adsorption of Cd(II) ions at various temperature from used lubricant oil

T. neriifolia nutshell CO_2 -based AC at 27 and 35°C followed film diffusion mechanism as plot of q_t against $t^{1/2}$ did not pass through the origin. Their correlation coefficient, R^2 obtained fell within the range of 0.624-0.899. However, some factors have been attributed to be responsible for rate determining step of adsorption of particular adsorbate (Moham *et al.*, 2001). The factors that assign rate determining step mechanism as film diffusion or external transport mechanism have been reported to be poor mixing, small particle size, dilute concentration of adsorbate and high affinity of the adsorbate for the adsorbent. The factors that include good mixing, large particle size, high concentration of adsorbate and low affinity of adsorbate for adsorbent are assigned intraparticle diffusion mechanism as the rate determining step. Consequently, the prepared active carbon has high affinity for the metal ions and as such followed film diffusion mechanism.

The first and second order rates of kinetic parameters with their linear regression correlation coefficient, R^2 of adsorption of these metal ions were also obtained (Data is not shown). It was found that none of these kinetic adsorption model fitted well as their correlation coefficients were very low ($R^2 = 0.5$). This is not unexpected as other works have supported pseudo- second order as

the best fit model for metal ion adsorption (Bulut and Baysal, 2006; Ozean and Ozean, 2005; Vadivelan and Kumar, 2005; Ho and McKay, 2000; Ho and McKay, 1999b; Joseph *et al.*, 2009). Moreover, this study has looked into real life situations in nature whereby the used oil contained more than 16 metal ions (Nwosu *et al.*, 2008). Thus, low values of correlation coefficient were obtained for first and second order kinetic rate equations. However, the correlation coefficients for pseudo-second order for the investigated metal ions were high enough for adsorption from a multi-component metal ions system as in used oil.

CONCLUSION

This study has revealed that the adsorption capacity of Pb(II) ions decreases with increase in temperature at pH of 4.8 while a slight increase in adsorption capacity was observed for the Cd(II) metal ion. The adsorption process for Pb(II) ion was found to be exothermic and that of Cd(II) was also exothermic. However, the free energy change of adsorption of Pb(II) ion at 27 and 35°C showed to be non-spontaneous while spontaneous adsorption process was obtained for Cd(II) ion. The adsorption process fitted well into pseudo-second order kinetic equation for both metal ions but did not fit well into first and second order kinetic equations. The mechanism of the pseudo-second order adsorption kinetics of Pb(II) and Cd(II) metal ions onto the CO₂-based nutshell AC was found to be controlled by film diffusion.

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