Kinetic and Thermodynamics of Adsorption of Heavy Metals from Spent Automobile Engine Oil onto Activated Carbon from Thevetia peruviana

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Abstract

The presence of heavy metals was analysed from oil samples employing the dry ashing method. The specific densities and viscosities of the spent and virgin AZ oil samples were determined and found to be 0.9230, 0.9501 and 70.27, 73.27cP respectively. Kinetic and thermodynamic studies of the adsorption of lead (Pb) and chromium (Cr) from the spent oil was also investigated. The spent oil samples were digested and mixed with methyl isobutyl ketone (MIBK), agitated with activated carbon produced from *Thevetia peruviana* (bush milk) shells at various contact times of 2, 4, 5, 10, 15, 20, 30, 40, 50, 60, 90 and 120 minutes. Kinetic studies revealed that for lead (Pb), the rate constants were found to be 0.044, 0.060 and 0.067 ppm/min at 27°C, 35 °C and 45 °C, respectively, while higher values or rate constants of 0.126, 0.127 and 0,168 ppm/min were observed at 27 °C, 35 °C and 45 °C, respectively, for chromium (Cr). For the thermodynamic studies the Gibb's free energy (Δ**G**) values were; –1.29, -1.61 and –1.82 KJmol^{-1}at 27 °C, 35 °C and 45 °C, respectively, indicating spontaneity. However, the Gibb's free energy (Δ**G)** for chromium showed +0.050, -2.13 and -2.14 KJmol^{-1}at 27 °C, 35 °C and 45 °C, indicating non-spontaneity at 27 °C. The positive values of Δ**S** for both metals with Pb (21 - 30 Jmol^{-1}) and Cr (695 – 1867 Jmol^{-1}) indicated that the metals were dissociatively adsorbed onto the adsorbent while for the **E$_a$** values, Cr (8 – 61 KJmol^{-1}) had higher than with Pb (6 – 35 KJmol^{-1}) further explaining the non-spontaneity of the process for Cr at some reaction condition.

Key words: Activated carbon, heavy metals, kinetic, thermodynamic, AZ oil

Introduction

Managing heavy metals in the environment is greatly of global concern. This is because they contaminate the abiotic factors of the environment like the soil, water and air, which in turn become toxic to the biotic factors (plants and animals) of the environment. Wastes from industries that carry out processes like electroplating, metal finishing, metallurgy, tannery operations, chemical processing, mine drainages, battery manufacturing, leachates from land fills, contaminated ground waters from hazardous waste sites, disposal of automobile oils and domestic waste are some of the main sources of these heavy metal in the environment (Meal *et al,* 1990; Reed *et al*, 1994; Leke *et al,* 2011; Bhat and Khan, 2011; Leke *et al,* 2012; and Safarzadeh *et al,* 2018). Since these heavy metals are toxic to life, the need for their safe handling, removal or recovery from their sources before disposal to the environment has attracted the attention of the research world. Heavy metals like lead (Pb), chromium (Cr), iron (Fe), copper (Cu), mercury (Hg) cadmium (Cd) and so on cause diseases like brain damage, malfunctioning of the central nervous system (CNS), abnormal growth and development of plants and animals (Leke *et al,* 2012; Henry *et al,* 2015). Adsorption has been a process employed over the years for the removal and/or recovery of heavy metals from their sources especially from wastewater in trying to safe handle them in the environment (Gloaguen and Morvnor, 1997; Bulut and Baysal; 2005; Leke *et al,* 2012). This process makes use of suitable substances (adsorbents) that hold onto them the heavy metals thereby separating them, from the matrix that contain them. Adsorbents employed for the adsorption of heavy metals include activated carbon, kaoline clay, zeolite and silica gel (Greankoplis, 1995; Mohammad and Nwaedozie, 2011; Leke *et al,* 2012).

Agricultural by-products have also found application as adsorbents for the removal of trace amounts of toxic heavy metals from the environment (Igwe *et al*, 2005). This could be due to economic reasons as agricultural by-products can be acquired at relatively little cost. However, activated carbon has been more widely employed in adsorption over the years.

Spent automobile engine oil can be defined as any oil that has been refined from crude oil or synthetic oil, which has been used by automobiles and is considered spent as a result of use, and has become contaminated by physical or chemical impurities (USEPA, 1992).

Studies of the environment over the years have revealed contamination of water bodies, the soil and air by heavy metal through human activities (Igwe *et al,* 2005). Since automobiles are in common use by man, due to the demand for them, spent oils from automobiles have become a major source of heavy metals contaminants in the environment. Improper disposal of these oils to the environment cause them to contaminate the water and soil. These heavy metals from the oil get to the soil and to water, which find their way into the food chain by the plants taking them up either from the water or directly from the soil or air. Animals consume these toxic heavy metals subsequently and this is hazardous to health. This has the propensity to cause low life expectancy and high mortality rate of humans in third world countries like Nigeria. Thus proper treatment of spent automobile oils is required before disposal.

In view of this, adsorption onto activated carbon from plants appears to be the most interesting method on a large-scale application, simple technology and cost effectiveness (Kadirvelu and Namasivayam, 2003; Igwe and Abia, 2007; Mohammad and Nwaedozie, 2011; Leke *et al,* 2012). This implies that to fashion an effective model of adsorption, these factors would have to be studied to ascertain good performance. A study of the extent of adsorption of a substance with respect to time at various temperatures becomes important for kinetic and thermodynamic studies of adsorption of two heavy metals from the oils under investigation. This research was aimed at studying the trends of adsorption of two heavy metals (Pb and Cr) from spent engine oils onto activated carbon prepared from *Thevetia peruviana* (bush milk) shells with respect to time and temperature.

Materials and methods
Sample Collection

The spent automobile engine oil samples were collected from various mechanic sites during the periodic change of engine oils from motor cars in Makurdi (North Central), Illorin (North Cental) and Ibadan (South West), all in Nigeria. The corresponding virgin oils were bought directly from the gas station. The oils investigated are,

- AZ crown super high performance engine oil SAE 20W/50-API SG/CD
- Total quartz 5000 ultra-high performance multigrade engine oil. 20W/50-API SL/CF
- Lubcon XV 50 premium quality motor oil. SAE 50 API SF/CC.

The activated carbon prepared from the nutshell of *Thevetia peruviana* commonly known as bush milk plant was supplied from Industrial Chemistry Laboratory, University of Ibadan.

Sample Preparation and Preservation

The oil samples were tightly corked in their plastic container and stored in the laboratory. The activated carbon was washed in 0.1M HCl, thoroughly rinsed in deionised water and dried in an oven at 105 °C for about 1 hour. It was cooled and stored in desiccators.

Apparatus and Reagents

Apparatus and/or instruments used were common laboratory apparatus and instrument except otherwise mentioned in the experimental. Reagents used in the experiment include: 98.4% methyl pentane-2-one (MIBK), 99.6% glacial acetic acid, 97% sulphuric acid, 70% nitric acid, 70% perchloride acid and 98% sodium acetate. All these reagents were used as manufactured by BDH.

Experimental
Determination of Specific Density and Viscosity

Determination of specific density of the various oil samples was carried out using the method as reported by Murrell and Jenkini (1994). The specific density experiment was carried out at laboratory temperature measured to be 27 °C. Kinematics viscosity measured in centipoise (cP), is a measure of the resistance to flow of a substance under the influence of gravity. It is determined using the Ostwald viscometer as reported by Atkins and Paula (2002). Viscosity experiments were carried out and reported at a laboratory temperature also measured to be 27 °C.

Determination of Heavy Metal Ions

In the determination of heavy metals ions, the oil samples were first digested. The method for the determination of metal ions in the oils are the dry-ash and the wet digestion methods (Gorsuch, 1970). The dry ash methods of oil sample digestion was explored in the experimental of this research.

Dry Ash Method

This method of heavy metals determination from oil is as recommended by Milner *et al* (1952). About 2.5 g of the oil samples were treated with equal volume of concentrated sulphuric acid in a crucible thoroughly stirred and heated gradually on a thermostatic hot plate to dryness for about 3-5 hour. The crucible containing the dried oil sample subsequently transferred to a muffle furnace and ignited at 550 °C until all traces of carbon were removed. This was indicated by the absence of charcoal black colour. The ashing process in the muffle furnace at 550 °C took about 50-60 minutes. The crucible, containing the ash was then removed after cooling to about 200 °C and placed in a desiccators. The ash was then treated with 6 ml HNO_3 in a 20 ml volumetric flask and made up to mark with deionised water. The heavy metals present were determined using Atomic Absorption spectrophotometer.

Kinetics Studies of Adsorption

29 ml each was measured out of the 50% oil: MIBK solution prepared. About 0.2 g of the activated carbon was measured and mixed with each of the 20 ml measured. This was shaken for different time durations of 2, 4, 5, 10, 15, 20, 30, 40, 60, 90 and 120 minutes, on a thermostated shaker. After each contact time specified, a container was removed from the shaker and configured for about 5 minutes. It was then decanted into a sample bottle leaving behind the activated carbon. The solutions analysis for determination of the metal ions present.

The pH of the samples was kept constant at 4.8 before shaking by introducing a pH buffer prepared by mixing 30 ml of the 1M Acetic acid produced with 30ml of the 1M sodium acetate earlier prepared. The kinetic experiment was performed at 27 °C, 35 °C and 45 °C.

Determination of Kinetic Parameters

The kinetic rate constant for Lead (Pb) and chromium (Cr) for the three (3) different temperatures were calculated using the pseudo second order equation expressed as (Low *et al* 2000, Ho and McKay, 1999):

$$t/Q_t = 1/k + 1/C_e.t$$

Where t is contact time, Q_t is concentration/quantity adsorbed at time t, C_e is Concentration/quantity adsorbed at equilibrium, K_c is rate constant.

The equilibrium constant K_c is also calculated using the formula reported by Panayotova (2001), Bekta and Kara (2001) and Komarneni (1985):

$$K_c = {}_{eeo}CCC-$$

Where K_c is Equilibrium constant (non-dimensional), C_o is Initial concentration of Pb or Cr, C_e is Concentration of Pb or Cr equilibrium

Determination of Thermodynamics Parameters

The thermodynamic parameters of the adsorption lead (Pb) and chromium (Cr) on the activated Carbon adsorbent were calculated using the following formulae (Okonjo *et al*, 2005).

$$\Delta G = - R T \ln Kc$$

$$\Delta G = \frac{2.303 R T_1 T_2}{T_1 - T_2} \log \frac{K_{CT1}}{K_{CT2}}$$

$$\Delta G = \Delta H - T \Delta S$$

$$Ea = \frac{R T_1 T_2}{T_1 - T_2} \ln \frac{k_1}{k_2}$$

Where ΔG is Gibb's free Energy (Kjmol[-1]), ΔH is Enthalpy (Kjmol[-1]), ΔS is Entropy (Kjmol[-1]), R is Gas Constant (J Mol.k[-1]), T is Temperature (K), Kc is Equilibrium constant (a dimensional), k is Rate Constant

Results and Discussion
Specific Density and Viscosity of the Oils

Table, shows variation of data of specific density as well as viscosity of automobile virgin and spent oils.

Table 1: Specific Densities and Viscosities of the virgin and their corresponding spent automobile oils.

Oil Sample	Specific Density	Viscosity (cP)
Virgin Lubcon oil Performa (VLOP)	0.9428	79.27
Virgin Lubcon oil NATTA (VLOT)	0.9408	76.77
Spent Lubcon oil-Toyota (ULOT)	0.9252	67.77
Virgin Lubcon oil-Nissan (ULON)	0.9322	64.27
Virgin Total oil (VTO)	0.9523	72.77
Spent Total Oil-Toyota (UTOT)	0.9269	66.77
Virgin AZ Oil (VAZO)	0.9501	73.27
Spent AZ Oil Mercedes (UAZOM)	0.9230	70.27

The specific density for the virgin oils range 0.9408 - 0.9523 while the spent oils are 0.9230, 0.9252, 0.9269. 0.9322, for the UAZOM), (ULOT), (UTOT) and (ULON), respectively. It can be observed that the virgin oils are denser than their corresponding spent oils. However, the differences are quite small. This trend could be attributed to the fact that during combustion in an automobile engine, the oil in the engine is heated up through the various sections it passes. Consequently, some components of the oils are spent up. The oils are thus expected to be exhausted and become less dense as compared to their virgin ones. However, impurities from the various engine components, which these oils pass through, wear out and contaminate the oil. A similar trend has been reported by McKenzie (1981).

The results of the viscosity of the various oils as shown also in table 1 indicate that the virgin oils are more viscous as compared to their corresponding spent oils. Louis (2005) attributed low viscosity of oils to contamination of the oils by fuels and other impurities from the engines of automobiles. This adulteration accounts for the lowering of the viscosity of the oils after use in engines. For instance, the virgin Lubcon oil (VLO) has a viscosity of 79.27cP while that of spent Lubcon Oil-Toyota (ULOT) is 67.77cP.

Metal Content of the Oil Samples

This method showed a general increase in the metal ion concentration in the spent oil as compared to their corresponding virgin oils as normally expected. The spent AZ oil (UAZOM) showed the most prominent increase in concentration of Lead (Pb) and chromium (Cr) relative to their virgin oils. McKenzie (1981) attributed the cause of contamination of oil by Lead (Pb) as a result of furl and bearing wear while chromium as a result of piston-wear. These two metal ions were chosen for the kinetic and thermodynamic studies of the spent AZ oil (UAZOM).

The various data obtained for the kinetic studies of Lead (Pb) and chromium (Cr) at 27 °C (laboratory temperature), 35 °C and 45 °C were as shown in tables.

Table 1: Kinetic Studies of the adsorption of Lead (Pb) with respect to time at 27 °C.

t (mins)	R	C_o (ppm)	C_t (ppm)	Q_t (ppm)	t/Q_t (min/ppm)	Q_t (%)
0	1.014	15.598		-	-	-
2	1.011	15.598	15.552	0.046	43.48	0.29
4	0.967	15.598	14.875	0.732	5.533	4.64
5	0.943	15.598	14.506	1.092	4.58	7.00
10	0.945	15.598	14.537	1.061	9.43	6.89
15	0.036	15.598	14.398	1.200	12.50	7.69
20	-	15.598	-	-	-	-
30	0.939	15.598	14.444	1.154	26.00	7.40
40	0.931	15.598	14.321	1.277	31.32	8.19
50	0.935	15.598	14.383	1.215	41.15	7.79
60	0.889	15.598	13.675	1.928	31.12	12.36
90	0.862	15.598	13.260	2.338	38.49	14.99
120	0.831	15.598	12.783	2.815	42.63	18.05

Table 2: Kinetic Studies of the adsorption of Lead (Pb) with respect to time at 35°C.

t (mins)	R	C_o (ppm)	C_t (ppm)	Q_t (ppm)	t/Q_t (min/ppm)	Q_t (%)
0	1.014	15.598		-	-	-
2	1.011	15.598	15.552	0.046	43.48	0.29
4	-	15.598	-	-	-	-
5	0.001	15.598	15.398	0.200	25.00	1.28
10	0.936	15.598	14.398	1.200	12.00	7.69
15	0.938	15.598	14.429	1.169	12.83	7.49
20	0.919	15.598	14.137	-1.461	13.700	9.37
30	-	15.598	-	-	-	-
40	0.903	15.598	13.890	1.708	23.40	10.95
50	0.877	15.598	13.491	2.107	23.73	13.51
60	0.867	15.598	13.337	2.261	26.54	14.50
90	0.865	15.598	13.306	2.209	39.27	14.69
120	0.799	15.598	12.291	3.307	36.29	21.20

Table 3: Kinetic Studies of the adsorption of Lead (Pb) with respect to time at 45°C.

t (mi1ns)	R	C_o (ppm)	C_t (ppm)	Q_t (ppm)	t/Q_t (min/ppm)	Q_t (%)
0	1.014	15.598	-	-	-	-
2	1.004	15.598	15.444	0.154	12.99	0.99
4	1.003	15.598	15.429	0.431	11.60	2.07
5	0.986	15.598	15.167	0.169	23.67	1.08
10	0.993	15.598	15.279	0.323	30.96	2.07
15	0.997	15.598	15.029	0.564	26.60	3.65
20	0.950	15.598	14.613	0.985	20.30	6.31
30	0.940	15.598	14.460	1.138	26.36	7.30
40	-	15.598	-	-	-	-
50	0.869	15.598	13.367	2.234	22.41	14.30
60	0.863	15.598	13.275	2.323	25.41	14.89
90	0.847	15.598	13.025	2.573	34.98	16.47
120	0.795	15.598	12.229	3.369	35.62	21.60

Table 4: Kinetic Studies of the adsorption of Chromium (Cr) with respect to time at 27ºC

t (mi1ns)	R	C_o (ppm)	C_t (ppm)	Q_t (ppm)	t/Q_t (min ppm)	Q_t (%)
0	0.531	8.168	-	-	-	-
2	0.501	8.168	7.707	0.461	4.34	5.64
4	0.493	8.168	7.584	0.584	6.85	7.17
5	0.493	8.168	7.338	0.830	6.02	10.16
10	0.472	8.168	7.261	1.907	5.24	11.10
15	0.466	8.168	7.168	1.000	15.00	12.24
20	0.461	8.168	7.092	1.076	18.59	13.17
30	0.433	8.168	6.661	1.507	19.91	18.45
40	0.396	8.168	6.092	2.076	19.27	25.42
50	-	8.168	-	-	-	-
60	0.3562	8.168	5.483	2.685	22.35	32.87
90	0.390	8.168	5.999	2.169	41.49	25.55
120	0.386	8.168	5.938	2.230	53.81	27.30

Table 5: Data Kinetic Studies of Chromium (Cr) at 35ºC.

t (mi1ns)	R	C_o (ppm)	C_t (ppm)	Q_t (ppm)	t/Q_t (min/ppm)	Q_t (%)
0	0.531	8.168	-	-	-	-
2	0.501	8.168	7.707	0.461	4.34	5.56
4	0.498	8.168	7.661	0.507	7.89	6.21
5	0.494	8.168	7.599	0.569	8.79	6.97
10	0.493	8.168	7.584	0.854	17.12	7.15
15	0.486	8.168	7.476	0.692	21.68	8.47
20	0.483	8.168	7.430	0.738	27.10	9.04
30	0.4614	8.168	7.097	0.071	28.00	13.11
40	-	8.168	-	-	-	-
50	0.411	8.168	6.415	1.753	28.52	21.46
60	0.417	8.168	6.417	1.751	36.27	21.44
90	0.398	8.168	6.122	2.046	43.99	25.05
120	0.371	8.168	5.707	2.461	48.76	30.13

Table 6: Data Kinetic Studies of Chromium (Cr) at 45 ºC.

t (mi1ns)	R	C_o (ppm)	C_t (ppm)	Q_t (ppm)	t/Q_t (min/ppm)	Q_t (%)
0	0.531	8.168	-	-	-	-
2	0.503	8.168	7.737	0.431	4.64	5.28
4	0.501	8.168	7.707	0.461	8.68	5.64
5	0.488	8.168	7.507	0.661	7.56	8.09
10	0.476	8.168	7.322	0.846	11.82	10.36
15	0.441	8.168	6.784	1.384	10.84	16.94
20	0.432	8.168	6.645	1.523	13.13	18.65
30	0.429	8.168	6.699	1.469	20.42	17.98
40	0.413	8.168	6.353	1.815	22.04	22.22
50	0.400	8.168	6.153	2.015	24.81	24.67
60	0.398	8.168	6.122	2.046	29.33	25.25
90	0.314	8.168	4.830	3.338	27.00	40.87
120	0.312	8.168	4.800	3.368	35.63	41.23

Where t is time, R is Instrument Reading, C_o is Initial concentration at t = 0, C_t is Concentration at t = t, Q_t is Amount Adsorbed at time, t

From the data of the kinetic studies of the two (2) metals here considered, shown in   Table 2 – 7, the initial concentration of lead (Pb) and chromium (Cr) were found to be 15.59 ppm and 8.16 ppm respectively in the spent oil under investigation. The results of agitation with the adsorbent at various contacts time at three different temperatures (27 ºC, 35 ºC and 45 ºC) reveals the following:

Effect of Temperature on Adsorption

The amount of lead (Pb) and chromium (Cr) adsorbed was observed to increase with increase in temperature. For instance after 120 minutes, the amount of lead (Pb) adsorbed increased from 2.815 ppm at 27 ºC to 3.307 ppm at 35 ºC and to 3.369 ppm at 45 ºC. This represents an increase in percentage adsorption from 18.05% to 21.20% and to 21.60% respectively. Similarly, after 120 minutes, the

amount of chromium (Cr) adsorbed increase from 2.230 ppm at 27°C to 2.461 ppm at 35°C and to 3.368 ppm at 45°C representing 27.30% to 30.13% and to 41.25% respectively. Raji and Aniradhan, (1997) have attributed such increase adsorption of metal ions with increasing temperature to be due to desolvation of sorbing species and/or changes in pore sizes of the adsorbent. This also indicates that the adsorption process is endothermic in nature. Al-Ashah and Duvrijak (1998) have also reported the rate of adsorption as being temperature dependent.

Effect of Contact time on Adsorption

Adsorption was generally observed to increase with contact time of the oil with the adsorbent both for lead (Pb) and chromium (Cr) at

the three (3) temperatures considered as shown by the results in the tables. The effect of the change of the concentration as a result of varying contact time was the basis on which the Kinetics of this process was studied.

Kinetic Parameters

Plotting t/Q_t against t for the data in tables 2 to 7, for Lead (Pb) and chromium (Cr) at 27 °C, 35 °C and 45 °C, a straight line graph is obtained with $1/k$ as the intercept on the t/Q_t axis and $1/C_e$ as the slope. From these graphs, the rate constant k for lead (Pb) and chromium (Cr) at each temperature was calculated. This kinetic parameters obtained from the plots are as shown in the tables 7 and 8 below:

Table 7: Rate and equilibrium constants calculated for lead (Pb) adsorption.

Temperature T(K)	Rate Constant k (ppm/min)	Equilibrium Constant (Kc)
318	0.067	1.992
308	0.060	1.876
300	0.045	1.675

Table 7: Rate and equilibrium constants calculated for chromium (Cr) adsorption.

Temperature T(K)	Rate Constant k (ppm/min)	Equilibrium Constant (K_c)
318	0.168	2.244
308	0.127	2.091
300	0.126	0.981

From the kinetic parameters for the Pb and Cr (Table 7 and 8), it is observed generally that the higher the temperature, the higher the rate constant **k** of the adsorption process and the higher the equilibrium constant **K**$_c$. Atkins and Paula (2002)

presented similar trend of results for reactions with similar conditions.

The thermodynamic parameters for the adsorption of the Lead (Pb) and chromium (Cr) on the activated carbon are shown in the tables below;

Table 8: Thermodynamic Parameters for Lead (Pb) adsorption.

Temperature (K)	Gibb's Free Energy ΔG (KJmol^{-1})	Enthalpy ΔH (KJmol^{-1})	Entropy ΔS (Jmol^{-1})	Activation Energy E_a (KJmol^{-1})
318	-1.82	4.86	21.0	6.54
308	-161	10.9	40.6	34.34
300	-1.29	7.6	29.7	24.74

Table 1: Thermodynamic Parameters for Chromium (Cr) adsorption.

Temperature (K)	Gibb's Free Energy ΔG (KJmol^{-1})	Enthalpy ΔH (KJmol^{-1})	Entropy ΔS (Jmol^{-1})	Activation Energy Ea (KJmol^{-1})
318	-2.14	218.8	695.0	55.5
308	-2.13	1022.4	3325.0	8.2
300	+0.05	562.3	1867.0	60.9

From the thermodynamic parameters given in the Tables 9 and 10 above, the values of $\Delta G^0 < 0$ implies spontaneity of the adsorption process. While the positive values of ΔG at 27°C for Chromium indicates non-spontaneity of the process at the temperature.

The positive values of ΔH^0 indicates an increase randomness at the solid/solution interface during the adsorption of the metal ions on the activated carbon implying an affinity of the activated carbon for the Lead (Pb) ions and chromium (Cr) ions under consideration. The ΔH values of 4.86KJ/mol, 10.90KJ/mol and 7.60KJ/mol at 45°C, 35°C and 27°C respectively for lead (Pb) indicates physisorption processes while for chromium, ΔH values of 218.83KJ/mol, 1022.4KJ/mol and 562.3KJ/mol at 45°C, 35°C and 27°C respectively indicates chemisorption processes (Atkins and Paula, 2002). This also suggests that there were some structural changes at the adsorbent – adsorbate interface for chromium (Ajmal *et al* 2003). The positive values of ΔS for both the Pb and Cr metals are indicative of a dissociative adsorption process. While the comparatively higher values of ΔS for the Cr are an indicator for the Cr as being more dissociatively adsorbed.

Activation energy E_a being an indicator of the energy barrier to be overcome for the adsorption process to take place, shows that the process was basically feasible with values ranging from 6 – 61 kJmol^{-1} and could indicate transition from a physisorption to a chemisorption process.

Conclusion

Results from this research showed that the adsorption of lead (Pb) and chromium (Cr) ions from spent AZ Oil (UAZO) onto activated carbon from *Thevetia peruciana* is affected by temperature and contact time. Thus, the higher the temperature, the higher the rate of adsorption, also the longer the contact time, the higher the rate of adsorption. The adsorption process followed a pseudo second order model from kinetic studies. The processes for lead (Pb) were physisorption while those for chromium (Cr) were chemisorption. The adsorption processes were all spontaneous with negative values of Gibb's free energy (**ΔG**) at the three temperatures for lead (Pb) and chromium (Cr) except at temperature, 27°C (Laboratory temp) for chromium (Cr) where **ΔG** was positive indicating a non-spontaneous process. The metals were also dissociatively adsorbed onto the adsorbent in the processes as demonstrated by their +ve **ΔS** values with their **E_a** within the same range of 6 – 35 kJmol^{-1} for the Pb while Cr had 8 – 61 kJ mol^{-1}

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