

Kinetics and Thermodynamic Studies: Adsorption of Pb, Cr and Ni Ions from Spent Lubrication Oil (SLO) Using Acid Modified Clay

Felix Sughnen Atsar^{1*}, Donald Kukwa¹, Raymond Ahule Wuana², Beatrice Arwenyo³

¹Department of Chemistry, Benue State University, Makurdi, Nigeria

²Department of Chemistry, University of Agriculture, Makurdi, Nigeria

³Department of Chemistry, Gulu University, Gulu, Uganda

Email: *atsarsughnen@gmail.com

How to cite this paper: Atsar, F.S., Kukwa, D.T., Wuana, R.A. and Arwenyo, B. (2021) Kinetics and Thermodynamic Studies: Adsorption of Pb, Cr and Ni Ions from Spent Lubrication Oil (SLO) Using Acid Modified Clay. *American Journal of Analytical Chemistry*, 12, 109-120.

<https://doi.org/10.4236/ajac.2021.125009>

Received: February 15, 2021

Accepted: May 16, 2021

Published: May 19, 2021

Copyright © 2021 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Adsorption of Pb, Cr, and Ni ions from spent lubrication oil (SLO) by sulphuric acid modified clay (SAMC) was investigated considering the effect of contact time and temperature of the adsorption system. The removal percentage of the heavy metals was found to be temperature and contact time-dependent. Adsorption of the heavy metals increases with an increase in temperature and contact time with 95.0% - 100% adsorption recorded at the temperature of 331 K with the equilibration time of 12 hours. The thermodynamic and kinetics investigation of the adsorption process showed that the adsorption of these metals by the modified adsorbent is a spontaneous and endothermic physical adsorption process that followed the pseudo-second-order kinetic model.

Keywords

Adsorption, Heavy Metals, Sorption Mechanism, Pseudo-Second-Order Kinetic Model

1. Introduction

Advances in science and technology have brought tremendous progress in many spheres of human development, but these developments have also contributed to the degradation of the environment all over the globe due to indiscriminate discharge of hazardous waste into the ecosystem without proper treatment or disposal option.

Spent lubricating oil (SLO) is one of the common hazardous waste materials

generated globally. In developing countries, SLO ends up in the environment due to a lack of recycling facilities. It is hazardous because it contains high values of ash, carbon residue, asphaltenic materials, metals (arsenic, lead, cadmium, copper, zinc, chromium, manganese, etc.), water, and other dirty materials which are produced in the process of lubrication action [1] [2] [3].

In Nigeria, about 20 million gallons of spent lubrication oil are generated annually from the mechanic workshop, industrial areas, and domestic's places and is disposed of by either incineration, discharge into water channels, suppressing of dust during road construction, etc [4]. Unfortunately, the spent lubrication oil ends up directly in the environment, therefore, contaminating the soil with heavy metals which can drain into both surface waterways and leach into the groundwater [3] [4] [5]. Since it is very difficult to prevent spent lubrication oil from getting into our environmental media regarding the non-environmentally friendly disposal options currently practiced, SLO can be alternatively treated with adsorbent materials to remove and immobilized the heavy metals before disposal.

The absorption of contaminant from environmental media has since been adopted as a sustainable practice especially in the treatment of wastewater. This is due to their low cost, easy availability, environmental sustainability, low energy requirements, and processing technology, etc. Researchers have continued to study and develop agricultural biomass and by-products as adsorbent materials like saw dust, biochar's, activated charcoal, and clay for the removal of heavy metals and organic dyes from aqueous environments [6].

Adsorption technique was also used in the treatment of SLO for the removal of petroleum-based contaminants as reported by Lidia Bandura [7]. Similarly, the decolorization and neutralization spent Lube oil as a recycling process using clay materials was reported by Oladimeji, T. E. and Khaled Okiel [8] [9]. The investigation showed that only products of the oxidative degradation of base oil, such as organic acids, esters, ketones were adsorbed by the clay material.

Nabil, M. A. *et al.* and Udonne carried out an investigation on the removal of heavy metals from spent lubricating oil using different low-cost adsorbents materials. Their studies reviewed that the adsorption of heavy metals from SLO was higher in acid-activated bentonite than any other adsorbent material used in the process. Though a greater percentage of the heavy metals were removed in the process, no or little attention was given to the adsorption mechanism [6] [10].

In this study, the aim is to investigate the adsorption mechanism and sorption kinetics of Pb, Cr, and Ni by sulphuric acid modified clay in the sorption treatment of SLO.

2. Materials and Methods

2.1. Adsorbent Collection and Pre-Treatment

2.0 kg of clay sample from the Benue valley were collected by making a pit in the clay deposit along the University of Agriculture Makurdi—Gbajimba Road in

Makurdi Local Government area of Benue State (N07°45'11.3" and E008°57'12.2") at a depth of 30 cm using a stainless-steel digger and a stainless-steel shovel like the sampling method reported by Osabor [11].

2.2. Lubrication Oil

Eight (8) liters of unused lubricating oil of Total brand with a commercial-grade labeling of 10W-30 were obtained from Total filling station in Port Harcourt City of Rivers State and divided into two equal volumes of four (4) liters each. The first 4 Liters were kept and labeled Unused Lubricating Oil (ULO) while the remaining 4 Liters were introduced into the automobile engine of Nissan Pathfinder car and allowed to operate for a period of three months. After which, the lubrication oil from the engine was evacuated and labeled as Spent Lubricating Oil (SLO) after pretreatment by filtration. The filtered SLO was properly covered in plastic bottles and kept for further analysis.

2.3. Adsorbent Preparation

The beneficiated clay was air-dried for two weeks thereafter which 100 g of the air-dried clay (size 0.2 mm) was equilibrated with 150 mL of sulphuric acid (1.0 M) in a 500 mL Teflon beaker, stirred with a glass rod for 30 minutes, and shaken for 1 hour with rotary shaker. The mixture was oven dried for 6 hours at a temperature of 80°C until a paste-like material was formed and allowed to cool, washed severally with distilled water until a neutral pH was reached. The modified clay was then air-dried, sieved, and labeled as Sulphuric Acid modified clay (SAMC)

2.4. Batch Adsorption Experiment

0.5 g of SAMC was mixed with 50 mL of the SLO in a 100 mL Erlenmeyer bottle and the mixture was shaken thoroughly using an electrical shaker SF1 Stuart for 3 hours and heated in a thermostatic water bath at the temperature of 301 K for duration of 12 hours. The slurry was centrifuged using D800 centrifuge at a speed of 4000 rpm for 20 min, decanted, and filtered using a plastics funnel and glass wool. The filtrate (treated spent lubricating oil) was ashed in a muffle furnace at 600°C for 6hours and digested with 10 mL 0.02 M Nitric acid and analyzed for the presence of Pb, Zn, and Ni using the flame atomic absorption Spectrophotometer Phoenix-986. The removal efficiency of the clay for all the metal ions was calculated as adsorption percentages using Equation (1.1)

$$\text{Adsorption (\%)} = \frac{C_o - C_e}{C_e} \times 100 \quad (1.1)$$

where, C_o and C_e are the initial and final metal ion concentrations, respectively.

The equilibrium capacity of adsorption was calculated respectively using the formula described by Mohammed *et al.* [12] as represented by Equation (1.2).

$$q_e = (C_o - C_e) \times \frac{V}{M} \quad (1.2)$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_o (mg/L) and C_e (mg/L) is the initial and equilibrium metal concentration, respectively, V is the volume (L) and M is the amount of the adsorbent (g) and the values tabulated.

2.5. The Effect of Temperature

The effect of temperature was investigated by varying the temperature at 301 K, 306 K and 311 K at a constant contact time of 12 hours.

2.6. Thermodynamic Modeling

The thermodynamic parameters such as ΔG , ΔH and ΔS were determined by using the following equations:

$$\Delta G = \Delta H - T\Delta S \quad (1.3)$$

$$\Delta G^\circ = -RT \ln K_d \quad (1.4)$$

Substituting Equations (1.3) into (1.4), transition state equation is obtained in Equation (1.5)

$$\ln K_d = \frac{\Delta H}{RT} + \frac{T\Delta S}{R} \quad (1.5)$$

The standard thermodynamic equilibrium constant, K_d (L/g) is defined by

$$K_d = \frac{q_e}{C_e} \quad (1.6)$$

By plotting a graph of $\ln K_d$ versus $1/T$, the values ΔH° and ΔS° were estimated from the slope and intercept, respectively.

2.7. Kinetic Studies

The effect of contact time on the adsorption of heavy metals from SLO was conducted in batch adsorption mode using SAMC as described above but with different equilibrating time of 4, 6, 8, 10 and 12 hours. The adsorption percentage and equilibrium capacities in each case were estimated by applying Equations (1.1) and (1.2), respectively.

3. Results and Discussions

3.1. Effect of Temperature

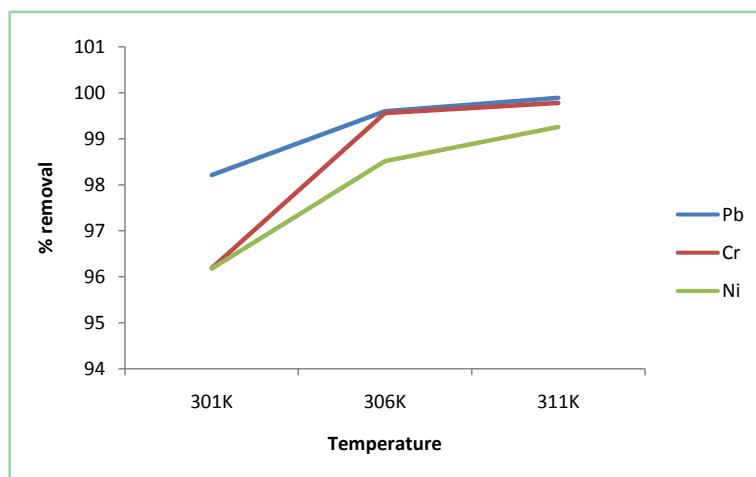
Temperature has important effects on the adsorption processes similar to other chemical reaction processes. As the temperature increases, the rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of the adsorbent particles increases [13] [14].

The Sorption of Pb, Zn and Ni unto SAMC obtained from the study showed that adsorption of heavy metals increases with increase in temperature values starting from 301 K to 311 K (Table 1).

At the maximum temperature of 311 K, almost 100% removal efficiency was achieved for Pb and Cr, by using 0.5 g of SAMC for the adsorption process (Figure 1)

Table 1. Variation of adsorption capacity with temperature using SAMC.

Metal ion	301 K			306 K			311 K		
	C_e (mg/L)	q_e (mg/g)	% Removal	C_e (mg/L)	q_e (mg/g)	% Removal	C_e (mg/L)	q_e (mg/g)	% Removal
Pb	0.003	0.025	98.21	0.002	0.023	99.60	0.001	0.011	99.98
Cr	0.004	0.023	96.19	0.003	0.021	99.56	0.001	0.016	99.97
Ni	1.010	2.313	96.18	0.920	2.300	98.52	0.420	2.271	99.26

**Figure 1.** Variation of temperature with percentage removal of heavy metals by SAMC.

The increase in adsorption of heavy metals by the adsorbent as the temperature increases is an indication that the adsorption process is endothermic in nature. The results also show a decrease in the adsorbed amount per unit mass of the adsorbent (equilibrium capacity, q_e) as the temperature increased like the result reported by Mohammed *et al.* [12].

3.2. Thermodynamics of the Adsorption

The adsorption thermodynamics study of Pb, Zn and Ni by SAMC was done by calculating Standard Gibb's free energy (ΔG°) from Equation (1.3) while the slope and intercept of the plot of $\ln K_d$ against $1/T$ (Equation (1.5)) were used to deduced Standard Enthalpy (ΔH°) and Standard Entropy (ΔS°) respectively as seen in **Figure 2** and **Figure 3**.

Thermodynamics parameters are not only used to predict the feasibility of a chemical reaction, but they also provide information as to whether the reaction is endothermic, exothermic, or at equilibrium [15] [16]. The negative values of ΔG and positive values of ΔS which determine the disorderliness of the adsorption of solid-liquid interface and the driving force of the reaction is a clear indication that, the adsorption of these metal ions by SAMC is feasible [17].

The positive values of ΔS could be because of redistribution of energy between the adsorbate and the adsorbent [17]. Before adsorption occurs, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free heavy metal ions to ions interacting

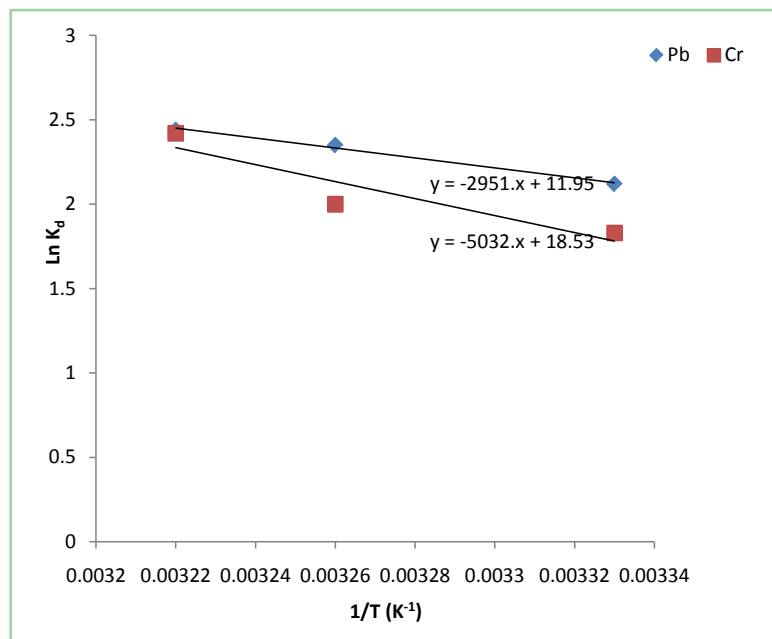


Figure 2. Plot of $\ln K_d$ against $1/T$ for the Pb and Cr ions.

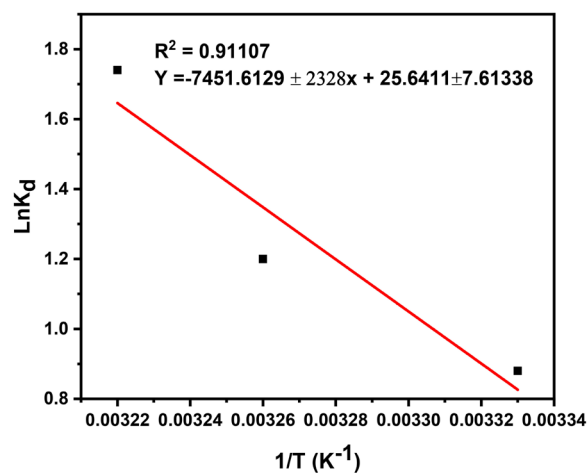


Figure 3. Plot of $\ln K_d$ against $1/T$ for the Ni ion.

with the adsorbent will be higher than in the adsorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will increase with increasing adsorption by producing a positive value of ΔS and randomness will increase at the solid-solution interface during the process of adsorption [17] [18].

The result also supports the suggestion that the adsorption capacity of SAMC for the ions increases with increasing temperature. One possible explanation of positive ΔH is that these ions are well solvated. For the ions to be adsorbed, they must lose part of their hydration sheath. This dehydration process of the ions requires energy. This energy of dehydration supersedes the exothermicity of the ions getting attached to the surface. Similar results were also established by He-gazi and Kumar with his co-researchers in their kinetic and thermodynamic

study of the adsorption of Pb ions from aqueous solution by adsorbent materials [19]-[24].

The negative values of ΔG indicate spontaneous adsorption of the metal ion onto SAMC. The experimental values of ΔG are below -40 kJ/mol which indicates that the adsorption is a physical process [17]. Generally, values of ΔG up to -20 kJ/mol are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption) while those more negative than -40 kJ/mol involves charge sharing or transfer from the adsorbate to the adsorbent surface to form a co-ordinate type of bond (which indicates chemisorption) [24]. Physical adsorption is a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution.

The ΔG values obtained in this study were negative for all the metals ranging from -2.095 to -6.255 $\text{KJ}\cdot\text{mol}^{-1}$ as seen in **Table 2** which shows that the adsorption process is a physical process. According to Mondal D.K. and Kumar R. [21] [22] [24], the principal test for distinguishing chemisorption from physisorption is the magnitude of ΔH_{ad} values less negative than -25 kJ/mol are normally considered as signifying physisorption, and values more negative than about -40 kJ/mol are taken to represent chemisorptions. The results also showed that the adsorption of Ni ion onto SAMC is more endothermic and spontaneous compared with that of Pb and Cr because of its higher value of ΔH and ΔS (62.62 and 0.215, respectively.)

3.3. Effect of Contact Time

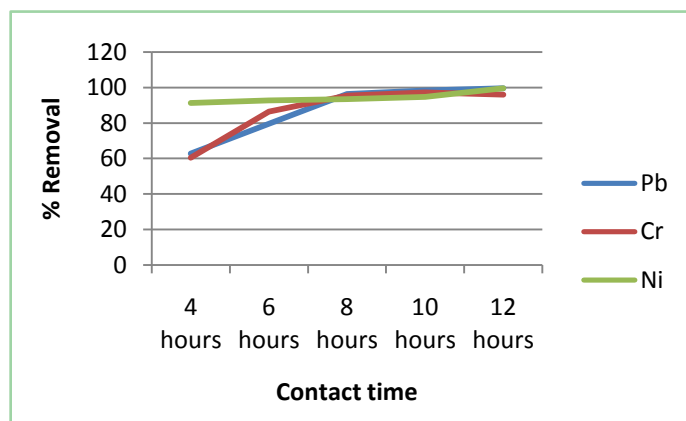
The results obtained by using SAMC as the adsorbent materials showed that SAMC adsorbed appreciable amount of all the metals at the minimal equilibration interval of 4 hours and the percentage of metal removal increases proportionally to increase in contact time. At equilibration time, more Pb and Ni were adsorbed by SAMC compared with the amount of Cr ions adsorbed within this time.

The increase in the removal percentages of the heavy metals with increase in contact time for SAMC adsorbent was observed to follow the order: $\text{Pb} > \text{Cr} > \text{Ni}$ (**Figure 4**). Basically, the removal rate of adsorbate is rapid especially with Pb and Cr ions, but gradually decreases with time until it reaches equilibrium. The percent of metal removal was relatively high in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals [24].

It is also relevant to point out that, since the active sites in the system (adsorbent materials) have a fixed number and each active site can adsorb only one ion in a monolayer, the metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for decreasing availability of active sites intensifies by the metal ions remaining in solution [24]. However, absorption of over 90% was reached for all the metals without the adsorbent material being saturated.

Table 2. Thermodynamic parameters for the adsorption process.

Metal	ΔH (kJ·mol ⁻¹)	ΔS (kJ·mol ⁻¹ ·K ⁻¹)	ΔG (kJ·mol ⁻¹)		
			301 k	306 k	311 k
Pb	24.536	0.099	-5.381	-5.758	-6.253
Cr	41.873	0.154	-4.517	-5.287	-6.057
Ni	62.62	0.215	-2.095	-3.170	-4.245

**Figure 4.** Variation of removal percentage of heavy metals with contact time.

3.4. Kinetics Models

To investigate the mechanism of the sorption of heavy metals from SLO using SAMC as the adsorbent material used in this study, kinetics models were used to test the experimental data obtained in the study. The kinetic parameters for the adsorption process were studied for contact times ranging from 4 to 10 hours by monitoring the percent removal of the heavy metals by the adsorbent at this time interval. The kinetic models used include the pseudo first order and the pseudo second order models.

3.4.1. The Pseudo First Order Kinetics (Lagergren)

The linear form of this equation is given by Equation (1.6)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t, \quad (1.6)$$

where q_e and q_t are the amount of metal ions adsorbed at equilibrium time and any instant time (t) respectively. A plot of $\log(q_e - q_t)$ against t gives a straight line where k_1 and the theoretical q_e can be deduced from slope and intercept, respectively. The parameters for the Lagergren first order models were generated from the kinetic investigation data obtained from the experiment and tabulated in **Table 3**.

Kinetic studies for all the heavy metal ions adsorbed by SAMC was done by plotting their respective estimated $\log(q_e - q_t)$ value against their corresponding equilibration time, t in hours. The experimental data as tested on the pseudo first order model showed that, the removal of Pb, Cr and Ni from SLO using

Table 3. Calculated values of $\log(q_e - q_t)$ for sorption of heavy metals from SLO using SAMC at 301 K.

	4 HOURS	6 HOURS	8 HOURS	10 HOURS
Pb	-2.03152	-2.22185	-3.00000	-3.39794
Cr	-2.04096	-2.39794	-3.00000	-3.22185
Ni	-0.96658	-1.13077	-1.24413	-1.58503

SAMC fitted into the first order model. The conformity between experimental data and the model values was expressed by the correlation coefficient factor, R^2 . A relatively high R^2 value indicates that the model successfully described the kinetics of the adsorption process [24]. From the plots, the regression correlation coefficient obtained showed that Cr, Pb and Ni had R^2 values of 0.972, 0.953 and 0.943 respectively. As reported by Olayinka *et al.* [26], regression correlation coefficient values lower than 0.5 implied the non-applicability of the pseudo first order kinetics model to experimental data. The suitability of this experimental data to the Lagergren first order kinetic model was observed to follow the order of $\text{Cr} > \text{Pb} > \text{Ni}$ (Figure 5).

3.4.2. The Pseudo Second Order Kinetic Model

The experimental data for the removal of Pb, Cr and Ni from SLO using 0.5 g of SAMC at the temperature of 301 K was tested with the pseudo second order kinetic model expressed in Equation (1.7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (1.7)$$

A plot of t/q_t against equilibration time, t produced a straight line with a positive slope and an intercept where theoretical value of q_e and rate constant for the pseudo-second-order kinetic, k_2 can be deduced, respectively. The values t/q_t were calculated from the experimental data are presented in Table 4.

The pseudo second order kinetic model for the heavy metal ions adsorbed by the SAMC in the investigation showed that the sorption of all the metal ion on this adsorbent also fitted into the model as their R^2 values exceed 0.5 [21]. However, the adsorption of Ni unto this adsorbent implies a perfect applicability of the pseudo second order kinetic model to the experimental data with a correlation coefficient of 0.999 followed by Pb and Cr with 0.972 and 0.921, respectively.

Comparing the correlation coefficient, R^2 obtained from the two kinetic models, it was observed that the sorption of Ni, and Pb by SAMC at 301 K was fitted better in the pseudo second order model while adsorption of Cr, by SAMC at a temperature of 301 K is better described by the pseudo first order kinetic model (Table 5). Similar results were also reported for the adsorption of Zn, Pb, Fe and Cu on different adsorbents by many researchers [21] [22] [23] [24] [25].

From the calculated values of the rate constants obtained from pseudo second order and pseudo-first-order models showed that, the rate constant for the

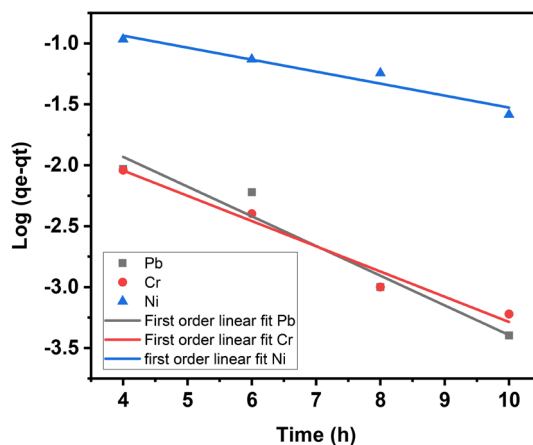


Figure 5. First order plot for the metal adsorption.

Table 4. Calculated values of t/q_t (ming/mg) at different contact time for the sorption of heavy metal by SAMC at 301 K.

Metal ions	4 hours	6 hours	8 hours	10 hours
Pb	254.77	301.50	333.33	406.50
Cr	287.76	301.50	363.63	446.42
Ni	1.81	2.68	3.54	4.37

Table 5. Correlation coefficient values for pseudo first and pseudo second order kinetic models for the adsorption of metals from SLO by SAMC.

Metal ions	Pseudo first order			Pseudo second order		
	R ²	Equation of graph	K ₁ (min ⁻¹)	R ²	Equation of graph	K ₂ (g/mg min)
Pb	0.953	$y = -0.243x - 0.955$	0.5596	0.972	$y = 24.35x - 135.5$	3.8626
Cr	0.972	$y = -0.207x - 1.214$	0.4767	0.921	$y = 26.90x - 161.4$	4.4833
Ni	0.943	$y = -0.098x - 0.542$	0.2257	0.999	$y = 0.427x - 0.108$	1.6882

pseudo-second-order kinetics was higher than that of the first-order kinetics for the adsorption of all the metal ions on SAMC as is seen in Table 5. The theoretical q_e values were close to the experimental q_e values in the case of pseudo-second-order kinetics. These observations suggest that the sorption system is the second-order model, based on the assumption that the rate determining step may be the sorption which provides the best correlation of the data [24]. This implied that the mechanism of adsorption of these ions on SAMC followed the second order kinetics.

4. Conclusions

From the result of the experiment conducted, the following conclusions were reached;

- The percentage removal of these heavy metals increases with increase in contact time and temperature at the experimental stated conditions

- The removal of these heavy metals from SLO using SAMC follows a pseudo-second-order model hence it is a second order reaction.
- Then adsorption of heavy metals (Pb, Cr, and Ni) unto SAMC from SLO is a physical adsorption process that is spontaneous and endothermic in nature

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Sánchez-Alvarracín, C., Criollo-Bravo, J., Albuja-Arias, D., García-Ávila, F. and Pelaez-Samaniego, M.R. (2021) Characterization of Used Lubricant Oil in a Latin-American Medium-Size City and Analysis of Options for Its Regeneration. *Recycling*, **6**, 10. <https://doi.org/10.3390/recycling6010010>
- [2] Kashif, S.-ur-R., Zaheer, A., Arooj, F. and Farooq, Z. (2018) Comparison of Heavy Metals in Fresh and Used Engine Oil. *Petroleum Science and Technology*, **36**, 1478-1481. <https://doi.org/10.1080/10916466.2018.1496105>
- [3] Stout, S.A., Litman, E. and Blue, D. (2018) Metal Concentrations in Used Engine Oils: Relevance to Site Assessments of Soils. *Environmental Forensics*, **19**, 191-205. <https://doi.org/10.1080/15275922.2018.1474288>
- [4] Zitte, L.F., AWAadu, G.D.B. and Okorodike, C.G. (2016) Used-Oil Generation and Its Disposal along East-West Road, Port Harcourt Nigeria. *International Journal of Waste Resources*, **6**, 195.
- [5] Akaninwor, J.O., Wegwu, M.O. and Iba, I.U. (2007) Removal of Fe²⁺, Zn²⁺ and Mg²⁺ from Polluted Water Samples Using Thioglycolic Modified Oil-Palm Fiber. *African Journal of Biochemistry Research*, **1**, 11-13.
- [6] Nabil, M.A., Essam, A.U., Zubaidy, A.L. and Mehrab, M. (2010) Waste Lubricating Oil Treatment by Adsorption Process Using Different Adsorbents. *World Academic of Science, Engineering and Technology*, **2**, 62-69.
- [7] Bandura, L., Wozuk, A., Kołodynska, D. and Franus, W. (2017) Application of Mineral Sorbents for Removal of Petroleum Substances: A Review. *Minerals*, **7**, 37. <https://doi.org/10.3390/min7030037>
- [8] Oladimeji, T.E., Sonibare, J.A., Omoleye, J.A., Adegbola, A.A. and Okagbue, H.I. (2018) Data on the Treatment of Used Lubricating Oil from Two Different Sources Using Solvent Extraction and Adsorption. *Data in Brief*, **19**, 2240-2252. <https://doi.org/10.1016/j.dib.2018.07.003>
- [9] Okiel, K., El-Sayed, M. and El-Kady, M.Y. (2011) Treatment of Oil-Water Emulsions by Adsorption onto Activated Carbon, Bentonite and Deposited Carbon. *Egyptian Journal of Petroleum*, **20**, 9-15. <https://doi.org/10.1016/j.ejpe.2011.06.002>
- [10] Udone, J.D. (2011) A Comparative Study of Recycling of Used Lubricating Oil Using Distillation Acid and Activated Charcoal with Clay Methods. *Journal of Petroleum and Gas Engineering*, **2**, 12-16.
- [11] Osabor, V.N., Okafor, P.C., Ibe, K.A. and Ayi, A.A. (2009) Characterization of Clays in Odukpani, South Eastern Nigeria. *African Journal of Pure and Applied Chemistry*, **3**, 79-85.
- [12] Mohammed, W.A., Fawwaz, I.K. and Akl, M.A. (2009) Adsorption of Lead, Zinc and Cadmium Ions on Polyphosphate-Modified Kaolinite Clay. *Journal of Envi-*

- ronmental Chemistry and Ecotoxicology*, **2**, 1-8.
- [13] Renu, M.A. and Singh, K. (2017) Heavy Metal Removal from Wastewater Using Various Adsorbents: A Review. *Journal of Water Reuse and Desalination*, **7**, 387-419. <https://doi.org/10.2166/wrd.2016.104>
- [14] Saka, C., Şahin, Ö. and Küçük, M.M. (2012) Applications on Agricultural and Forest Waste Adsorbents for the Removal of Lead(II) from Contaminated Waters. *International Journal of Environmental Science and Technology*, **9**, 379-394. <https://doi.org/10.1007/s13762-012-0041-y>
- [15] Ye, H., Zhu, Q. and Du, D. (2017) Adsorptive Removal of Cd(II) from Aqueous Solution Using Natural and Modified Rice Husk. *Bioresource Technology*, **101**, 5175-5179. <https://doi.org/10.1016/j.biortech.2010.02.027>
- [16] Saad, A.A. (2010) Removal of Heavy Metals from Industrial Water by Adsorption Using Local Bentonite Clay and Roasted Date Pits in Saudi Arabia. *Trends in Applied Science Research*, **5**, 138-145. <https://doi.org/10.3923/tasr.2010.138.145>
- [17] Fu, F.L. and Wang, Q. (2011) Removal of Heavy Metal Ions from Wastewaters: A Review. *Journal of Environmental Management*, **92**, 407-418. <https://doi.org/10.1016/j.jenvman.2010.11.011>
- [18] Kyzas, G.Z. and Kostoglou, M. (2014) Green Adsorbents for Wastewaters: A Critical Review. *Materials (Basel)*, **7**, 333-364. <https://doi.org/10.3390/ma7010333>
- [19] Alalwan, H.A., Kadhom, M.A. and Alminshid, A.H. (2020) Removal of Heavy Metals from Wastewater Using Agricultural Byproducts. *Journal of Water Supply: Research and Technology—AQUA*, **69**, 99-112. <https://doi.org/10.2166/aqua.2020.133>
- [20] Hegazi, H.A. (2013) Removal of Heavy Metals from Wastewater Using Agricultural and Industrial Wastes as Adsorbents. *HBRC Journal*, **9**, 276-282. <https://doi.org/10.1016/j.hbrcj.2013.08.004>
- [21] Kumar, U. and Bandyopadhyay, M. (2013) Sorption of Cadmium from Aqueous Solution Using Pretreated Rice Husk. *Bioresource Technology*, **97**, 104-109. <https://doi.org/10.1016/j.biortech.2005.02.027>
- [22] Kumar, R., Laskar, M.A., Hewaidy, I.F., *et al.* (2019) Modified Adsorbents for Removal of Heavy Metals from Aqueous Environment: A Review. *Earth Systems and Environment*, **3**, 83-93. <https://doi.org/10.1007/s41748-018-0085-3>
- [23] Liu, B.J., Wang, D.F., Yu, G.L. and Meng, X.H. (2013) Adsorption of Heavy Metal Ions, Dyes and Proteins by Chitosan Composites and Derivatives—A Review. *Journal of Ocean University of China*, **12**, 500-508. <https://doi.org/10.1007/s11802-013-2113-0>
- [24] Mondal, D.K., Nandi, B.K. and Purkait, M.K. (2013) Removal of Mercury(II) from Aqueous Solution Using Bamboo Leaf Powder: Equilibrium, Thermodynamic and Kinetic Studies. *Journal of Environmental Chemical Engineering*, **1**, 891-898. <https://doi.org/10.1016/j.jece.2013.07.034>
- [25] Navarathna, C.M., Karunanayake, A.G., Gunatilake, S.R., Pittman, C.U., Perez, F., Mohan, D. and Mlsna, T. (2019) Removal of Arsenic(III) from Water Using Magnetite Precipitated onto Douglas Fir Biochar. *Journal of Environmental Management*, **250**, Article ID: 109429. <https://doi.org/10.1016/j.jenvman.2019.109429>
- [26] Olayinka, O.K., Oyedeji, O.A. and Oyeyiola, O.A. (2009) Removal of Chromium and Nickel Ions from Aqueous Solution by Adsorption on Modified Coconut Husk. *African Journal of Environmental Science and Technology*, **3**, 286-293.