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

Felix Sughenen Atsar¹*, 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: *atsarsughen@gmail.com

Abstract
Adsorption of Pb, Cr, and Ni ions from spent lubrication oil (SLO) by sulfuric 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, asphaltene 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 adsorbent 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 Stuat 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 6 hours 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)

\[
\text{Adsorption} \% = \left( 1 - \frac{C_e}{C_o} \right) \times 100
\]

(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).

\[
q_e = \left( C_o - C_e \right) \times \frac{V}{M}
\]

(1.2)
where \( q_e \) (mg/g) is the equilibrium adsorption capacity, \( C_0 \) (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 \( \Delta G \), \( \Delta H \) and \( \Delta S \) were determined by using the following equations:

\[
\Delta G = \Delta H - T \Delta S
\]  
\[
\Delta G^\circ = -RT \ln K_d
\]

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

\[
\ln K_d = \frac{\Delta H}{RT} + \frac{T \Delta S}{R}
\]

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

\[
K_d = \frac{q_e}{C_e}
\]

By plotting a graph of \( \ln K_d \) versus \( 1/T \), the values \( \Delta H^\circ \) and \( \Delta S^\circ \) 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 | 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 lnK_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 $\Delta S$ 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 $\Delta H$ 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 Hegazi and Kumar with his co-researchers in their kinetic and thermodynamic
study of the adsorption of Pb ions from aqueous solution by adsorbents materials [19]-[24].

The negative values of ∆G indicate spontaneous adsorption of the metal ion unto SAMC. The experimental values of ∆G are below −40 kJ/mol which indicates that the adsorption is a physical process [17]. Generally, values of ∆G 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 ∆G values obtained in this study were negative for all the metals ranging from −2.095 to −6.255 KJ·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 ∆H_ads 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 unto 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, 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: Pb > Cr > 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 | $\Delta H$ (kJ·mol$^{-1}$) | $\Delta S$ (kJ·mol$^{-1}$·K$^{-1}$) | $\Delta G$ (kJ·mol$^{-1}$) |
|-------|-----------------|----------------|----------------|
|       | 301 k           | 306 k          | 311 k          |
| Pb    | 24.536          | 0.099          | −5.381         |
| Cr    | 41.873          | 0.154          | −4.517         |
| Ni    | 62.62           | 0.215          | −2.095         |

![Figure 4. Variation of removal percentage of heavy metals with contact time.](image)

#### 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)

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

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 Cr > Pb > 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):

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]  

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 $\theta q_t$ (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 |

pseudosecond-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 $q_t$ values were close to the experimental $q_t$ values in the case of pseudosecond-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.

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