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Research Article

Adsorption of Sodiumoleate on Barite in Aqueous Solution: A Kinetics and Thermodynamic Study

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Abstract

Concern has been raised about the necessity of separating barite from other minerals. When barite needs to be separated from other minerals, sodiumoleate, also known as napoleate, works well as an adsorbate. The purpose of this work is to examine the impact of temperature, pH, and contact duration on different Na-oleate adsorption methods onto barite. The change in the oleate concentration was used to determine the adsorption of sodium oleate on barite. In a batch adsorption experiment, sodium hydroxide and NaOH solution were combined with oleic acid in different flasks to create sodium oleate. To flasks containing Na-oleate, 1g of purified barite was added. A mechanical shaker was used to shake the specimen flasks and their contents for one hour. After stirring, the contents of each flask were given another 30 minutes to settle. Filter paper was used to filter the contents of the flask. Following filtering, the concentration of each filtrate was red-marked from the calibration graph by measuring the surface tension of each filtrate using a traveling microscope. The investigation's findings demonstrate that the first-order reaction kinetics are followed by the initial rate of Na-oleate adsorption onto barite. This study indicates that adsorption of Naoleate onto calcite increases at low pH values than higher pH. The amount of Na-oleate adsorbed onto calcite increases gradually as temperature increases from 303K to 313K. Beyond optimum temperature 322K, adsorption of Na-oleate on barite decreases rapidly. This study indicates optimum contact time of 80 min on adsorption process of Na-oleate onto calcite. Also this study indicates that adsorption of Na-oleate onto barite is pH dependent. Barite-oleate formation first increases with increasing Na-oleate concentration. At low pH 4, adsorption of Na-oleate onto barite increases, whereas adsorption decreases at high pH 9. Result also demonstrates that pseudo 2nd order offered an excellent fitting in the adsorption of oleate on barite, furthermore, the Langmuir adsorption isotherm favors the interaction between oleate ions and barite more than the Freundlich's isotherm, with the Langmiur isotherm's correlation coefficient (0.9728) being greater than the Freundlich's isotherm (0.9626). The trend of decreasing ΔG^O negative values as temperature rises suggests that a higher temperature will more effectively promote oleate adsorption on barite.

Keywords

Barite, Contact Time, Langmuir, Freundlich, Sodiumoleate, Gibbs Free Energy

1. Introduction

Approximately 90% of Nigeria's foreign exchange profits come from the oil and gas industry, which is a major contributor to the country's economy [5]. Solid minerals such as bauxite, hematite, barite etc. are one of the main sectors where the need to diversify the economy has been highlighted on several occasions.

An essential and crucial raw element for the petroleum industry is barite. Because of its poor water solubility, high specific gravity, and inertness to acids, it is utilized as drilling mud [12]. Low-grade wastes need to be beneficiated in order to be effectively used, whereas high-grade barite generated from the mines may be used immediately for the production of barium compounds, pigments, and paper coating applications.

Barite is typically beneficiated by physical separation techniques like crushing, screening, log washing, jigging, heavy media separation, tabling and spiral concentration, magnetic separation, and in some cases by flotation. Beneficiation strategies primarily depend on the grade of the ore, nature of gangue, and liberation size [10].

A great deal of researches has been done on the agglomeration of barite in the presence of Na-oleate [10, 12] but little is known about the kinetics and thermodynamics of sodium oleate adsorption on bauxite, where the adsorption parameters are determined by surface tension from traveling microscopes. It is against this backdrop that this study investigated the adsorption kinetics and thermodynamics of sodium oleate on barite in aqueous solution.

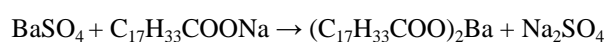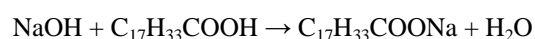# 2. Materials and Methods

2.1. Sample Collection and Analysis

The natural Barite ($BaSO_4$) was obtain and anyzed by the National Geosciences Research Laboratories, Nigerian Geological Survey Agency, Kaduna South. X-ray diffraction (XRD) using an XRD-6000 X-ray powder diffractometer made by Shimadzu (Japan) was used to determine the phase composition of the mineral. The x-ray diffraction spectrum of Barite as presented in figure 1 which was analyzed in accordance with [9]. The reagents employed were sodium hydroxide and oleic acid, both of which were analytical grade and 98% pure, obtained from Judical Chemicals International, FCT. Abuja Nigeria.

2.2. Preparation of Adsorbent

About 30 grams of the mineral in lump was crushed and ground in a mortar. The sample was subsequently washed with distilled water. The sample was dried in an electric oven at 110 ℃. After drying, the sample was separated into particle sizes by passing through 50 μm mesh sizes. After separation, the barite was stored in a plastic container.

2.3. Preparation of Adsorbate (Sodiumoleate)

To a 500 cm^3 Erlenmeyer flask containing 50 ml of a 30% sodium hydroxide solution, 50g of oleic acid was added. In the flask, 30 ml of ethanol were added. To make a creamy, pasty soap, the mixture was heated to 100 ℃ for 50 minutes while being constantly stirred in a water bath. After a rigorous one-hour stirring period at 40 ℃, 50 cm^3 of a hot saturated sodium chloride solution was gradually added to the pasty soap, making sure to mix evenly. Before being stored in a plastic container with a label, the soap cake that had developed on the lye's surface was taken off and allowed to dry naturally. [4, 10]. The chemical reaction process can be written as shown below;

$$NaOH + C_{17}H_{33}COOH \rightarrow C_{17}H_{33}COONa + H_2O$$

$$BaSO_4 + C_{17}H_{33}COONa \rightarrow (C_{17}H_{33}COO)_2Ba + Na_2SO_4$$

2.4. Adsorption Parameters

2.4.1. Calibration Graph

At a pH of 7, the surface tensions of 0.0001, 0.0003, 0.0005, 0.0007 and 0.0009 mol/dm^3 of sodium oleate were determined with the traveling microscope by measuring the rise of the solution along a narrow capillary tube, with which the calibration graph of surface tension (in $dyncm^{-1}$) against concentration is plotted as seen in figure 2.

2.4.2. Effect of pH on Adsorption of Sodiumoleate

100ml of 0.0001, 0.0003, 0.0005, 0.0007 and 0.0009 mol/dm^3 Na-oleate was measured into five Erlenmeyer flasks whose pHs where pre-adjusted to 5. 1.0g of barite was measured into each beaker at 301K and agitated in a mechanical vibrator for 1 hour and allowed to settle for thirty minutes. The contents were filtered using Whatman No.4 filter paper and the surface tension of each filtrate was determined. The concentration of oleate in the filtrates were read-off from the calibration graph and the amount of oleate adsorbed determined. The procedure was repeated at pH of 7, 9 and 11 respectively from which the graph of oleate adsorbed against pH is plotted as shown in figure 3.

2.4.3. Effect of Initial Concentration

Different sodium oleate initial concentrations of 0.0001, 0.0003, 0.0005, 0.0007 and 0.0009 mol/dm^3 of pH 7.0 were prepared into Erlenmeyer flask. 1.0 gram of barite was added to each flask at 301K, agitate vigorously in a mechanical vibrator for 1 hour and allowed to settle for thirty minutes. The contents were filtered using Whatman No.4 filter paper and the surface tension of each filtrate was determined with which the concentration of filtrate obtained from the calibration graph. The amount of oleate adsorbed was plot against initial concentration as presented in figure 4.

2.4.4. Effect of Contact Time

1.0g of barite was weighed into five Erlenmeyer flask containing 0.0009 mol/dm^3 sodium oleate solution having pHs of 7.0 each. The contents at 301K were agitated for 30, 60, 90, 120 and 150 minutes respectively. For each procedure, the sample was allowed to settle for further thirty minutes before the surface tension was determined and the concentration obtained from the calibration graph. A graph of amount of oleate adsorbed against contact time is presented in figure 5.

2.4.5. Effect of Temperature

1.0g of barite was weighed into an Erlenmeyer flask containing 0.0009 mol/dm^3 sodium oleate solution having pHs of 7.0. The content at 303K was agitated for 1hr. The content was allowed to settle and the surface tension of the content

determined. The concentration of the filtrate was read-off from the calibration graph. The procedure was repeated at 313K, 323K and 333K respectively.

3. Results and Discussion

3.1. Results

3.1.1. X-ray Diffraction

Figure 1 presents the x-ray diffraction peaks of barite with chemical formula $Ba_{4.00}S_{4.00}O_{16.00}$. The crystal system is orthorhombic with a calculated density of 4.47g/cm^3. Less wide peaks may be seen in the raw barite ore pattern, which suggests that the particles are coarser-grained and have bigger crystallite sizes.
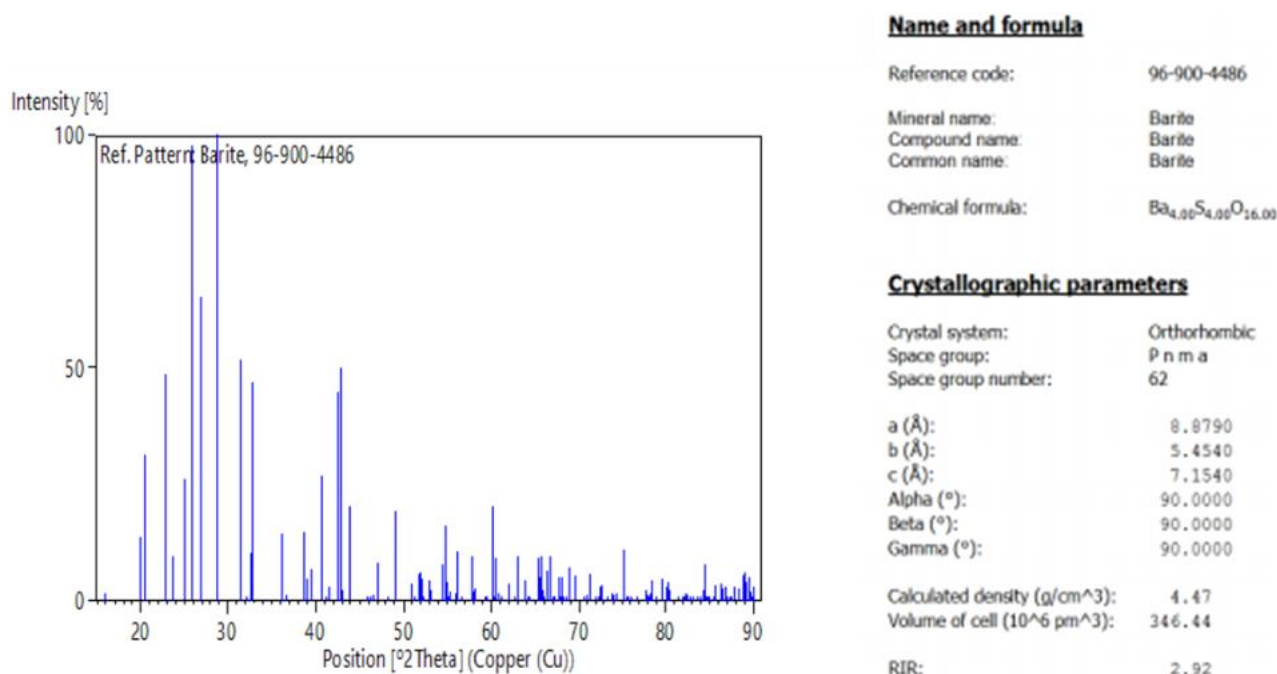

Figure 1. XRD spectrum for Barite.

3.1.2. Calibration Graph

The calibration curve presented in Figure 2 illustrates how the surface tension of sodiumoleate rises as the concentration increases. Some scholars have noted this relationship [7, 8], and this study uses it as a method to calculate the amount of oleate adsorbed at equilibrium in the corresponding solutions.
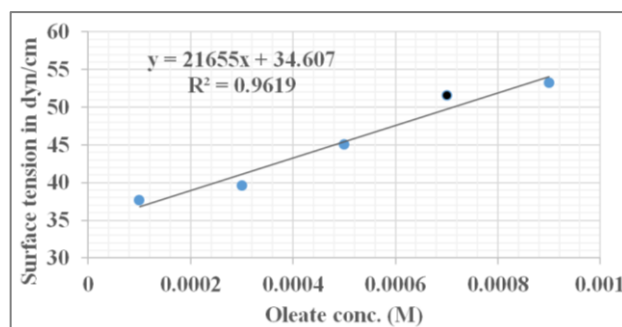

Figure 2. Calibration graph of surface tension against sodiumoleate concentration.

3.2. Discussion

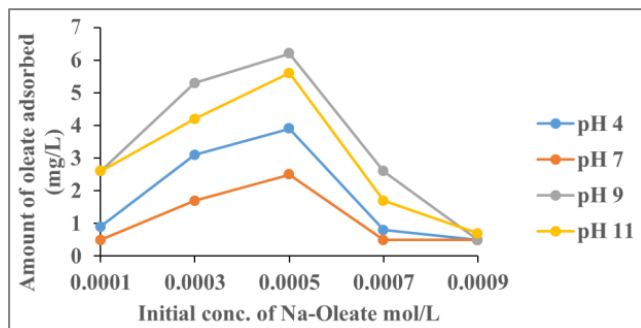### 3.2.1. Effect of pH on Adsorption of Sodiumoleate on Barite

Figure 3. Effect of pH on adsorption of oleate on barite.

Figure 3 displays the graph showing how pH affects the adsorption of oleate on barite in aqueous solution. One of the key factors influencing adsorption is pH [3]. It was discovered that when pH increased, so did the equilibrium adsorption. Higher pH levels can cause barite particle surfaces to become negatively charged, which strengthens the positively charged soap cations by electrostatic contact. At pH 9 and pH 11, the highest concentration of Na-oleate that showed the greatest adsorption onto barite was $7x10^{-3}$ mol/dm^3. The adsorption of Na-oleate onto barite quickly diminishes above this maximum adsorption concentration.

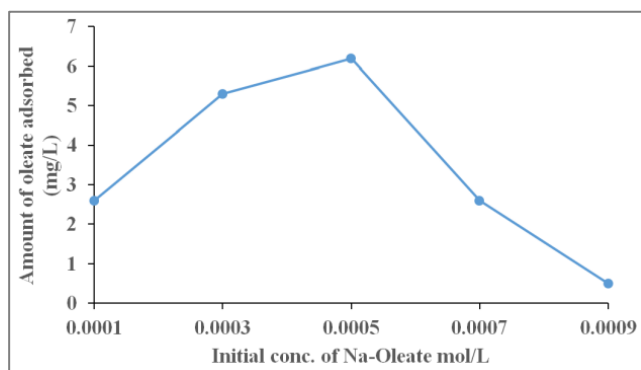### 3.2.2. Effect of Sodium Oleate initial Concentration

Figure 4. Effect of sodium oleate initial concentration.

Figure 4 shows the impact of the initial sodium oleate concentration for the adsorption oleate on the barite adsorbent. It would be evident that the adsorption, with a near-linear curve, was initially quick at various concentrations. As concentration increased, so did the quantity of soap adsorbed at equilibrium (qe). One may argue that the initial concentration provides a significant driving force to get beyond all of the

barite's mass transfer resistances between the aqueous and solid phases. This makes sense in light of the findings of Nwoko *et al.* [10], who found that an increase in concentration produced a sufficient surface for the interaction of the soap molecules with the barite.

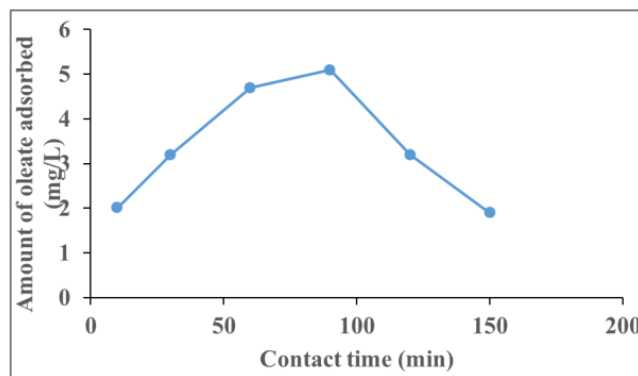### 3.2.3. Effect of Contact Time

Figure 5. Effect of contact time.

The effect of contact time on the adsorption of sodium oleate from aqueous solution by barite is presented in figure 5. 0.0009mol/L of sodiumoleate was the initial concentration at a pH of 7.0. From the initial stage to 90 minutes, there was a general increase in oleate adsorption with contact time. For equilibrium to be established during the adsorption process, the contact time is crucial. The study's findings indicate that the maximum sodium oleate adsorption capacity was reached after 90 minutes. The quantity of Na-oleate adsorbed onto calcite diminishes after the optimal duration of 80 minutes. This suggests that Na-oleate has saturated the surface of calcite, meaning that Na-oleate begins to desorb from the surface of barite after 80 minutes.

3.2.4. Effect of Temperature

Figure 6 illustrates the temperature dependence of sodium oleate adsorption from aqueous solution onto barite surface. It indicates that the temperature increases along with the adsorption of soap molecules. This temperature-dependent increase in adsorption can be explained by two factors: an increase in the number of active surface sites available for adsorption on the adsorbent or adsorbate of adsorbing species, and a decrease in the thickness of the boundary layer surrounding the adsorbate. The results of Nwoko *et al.* [10] and Alinnor & Enenebeaku [1] also support this, showing that temperature increases the ion diffusion rate in the external mass transport process, that chemical reactions predominate at high temperatures, and that these lead to faster adsorbate species reaction kinetics. The temperature at which adsorption is most effective was found to be 322 K, or 49 ℃. Na-oleate's adsorption onto barite quickly reduced above this optimal temperature. An increase in solubility may be connected to a decrease in oleate's adsorption onto barite at
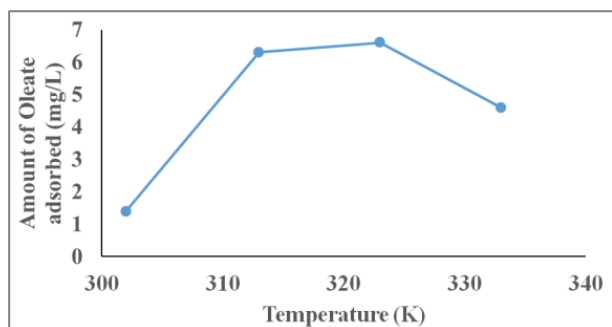
higher temperatures [1].

Figure 6. *Effect of temperature.*

4. Adsorption Isotherms

In this study, the Langmuir and Freundlich isotherms were employed for the determination of the nature of interaction between the oleate ions and barite.

4.1. Langmuir Adsorption Isotherm

According to Yu & Liangm in Agbaghare & Agbaghare [3] the Langmuir model can be presented by the equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}}C_e \qquad (1)$$

Where: q_{max} is the monolayer adsorption capacity of the adsorbent, i.e. the maximum amoumt adsorbed; K_L is the Langmuir adsorption constant; C_e is the equilibrium metal ion concentration in the solution and q_e is the equilibrium metal ion concentration on the adsorbent. Values of q_{max} and K_L are calculated respectively from the slope and the intercept of plot of $\frac{C_e}{q_e}$ against C_e [3] as shown in the figure 7:
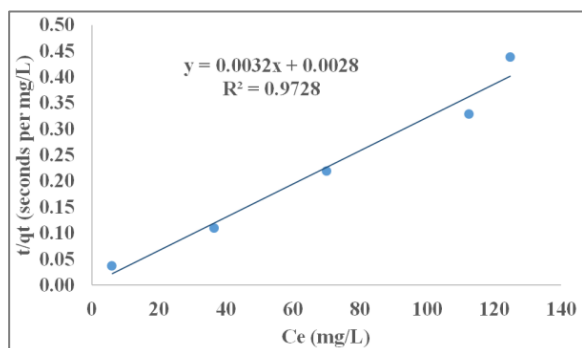

Figure 7. *Langmuir Isotherm for oleate adsorption onto barite in aqueous solution.*

A favorable interaction between the barite and oleate molecules is demonstrated by the monolayer coverage of the

sodium oleate adsorption in the Langmuir plot. There was no negative slope or intercept on the graph, and adsorption rose as q_e increased. The absence of pattern or trend in the residual plots indicated a successful match. A fitting correlation value of 0.9728 is also observed for the adsorption of oleate on barite. The resultant barite has a 125 mg/L (q_{max}) monolayer adsorption capacity. The K_L, which was more than 0 but less than 1, indicates a positive reaction and shows the binding strength of the oleate molecules on the barite surface.

4.2. Freundlich Adsorption Isotherm

The equation of the Freundlich adsorption model as expressed in Agbaghare & Agbaghare [3] is represented below;

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (2)$$

Where: K_F is a constant related to the adsorption capacity (Freundlich constant); $\frac{1}{n}$ is an empirical parameter related to the adsorption intensity. Values of $\frac{1}{n}$ and K_F are calculated from the slope and the intercept of plot of $\log q_e$ vs. $\log C_e$ as shown in the figure 8 below:
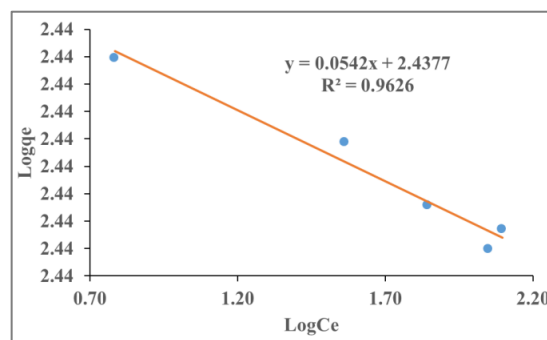

Figure 8. *Freundlich isotherm of oleate adsorption on barite in aqueous solution.*

Figure 8 displays the Freundlich, which describes how solutes are distributed between aqueous solutions and solid phases. There was no trend or pattern in the residual plots. The graph's positive slope and intercept indicate an energetically favorable response. These could happen as a result of qe rising when Ce rises. Adsorption capacity is represented by the Freundlich constant K_F, which is 2.4344. Similarly, the oleate adsorption correlation coefficient (R^2) provided a well-fitting R^2 value of 0.9626 with 1/n at 0.0542.

4.3. Comparison of Langmuir and Freundlich Isotherms

By contrasting the correlation coefficients, each model's applicability is ascertained. According to Agbaghare and Agbaghare [3], the goodness of fit increases with a greater

correlation coefficient (R^2). Table 1 indicates that the Langmuir adsorption isotherm favors the interaction between oleate ions and barite more than the Freundlich's isotherm, with the Langmiur isotherm's correlation coefficient (0.9728) being greater than the Freundlich's isotherm (0.9626). Furthermore, supporting this is the value of 1/n (0.0542), which shows co-

operative adsorption when it is above one (1) and a regular Langmuir isotherm when it is below one (1). [6]. Therefore, it can be observed that the value of 1/n was within the range of 0 and 1, suggesting that the adsorbents developed are suitable for the adsorption of the metal ions in the study's circumstances.

Table 1. Adsorption Isotherm Parameters.

Langmuir Adsorption Isotherm			Freundlich Adsorption Isotherm		
R^2	q_{max} (mg/L)	K_L (l/mg)	R^2	1/n	K_F (mg/l)
0.9728	125	0.35	0.9626	0.0542	2.4344

5. Adsorption Kinetics

The pseudo-first and pseudo-second order equations were used for explaining the kinetic parameters for the adsorption of oleate on barite. Mathematically, the equations are explained below.

5.1. Pseudo 1st Order

$$\ln(q_e - q_t) = lnq_e - K_1t \qquad (3)$$

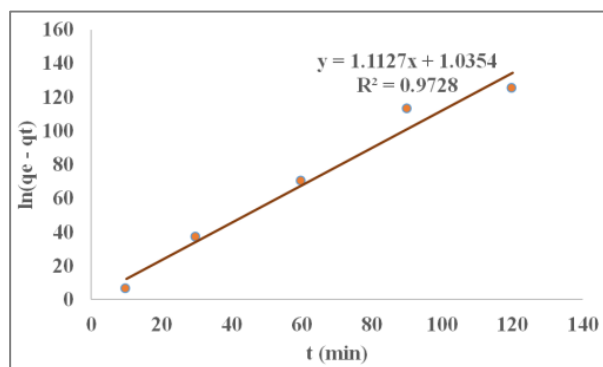The plots of $\ln(q_e - q_t)$ versus t give a straight line graph with slope K_1 and intercept lnq_e.

Figure 9. Pseudo first order plot.

5.2. Pseudo 2nd Order

$$\frac{t}{q_t} = \frac{1}{K_2q_e} + \frac{t}{q_e}t \qquad (4)$$

The chemisorption step is assumed to be the rate-

determining step in the pseudo-second order. The plot of $\frac{t}{q_t}$ versus t gives a straight line graph. Values of K_2 and q_e calculated from the slope, $\frac{t}{q_e}$ and intercept, $\frac{1}{K_2q_e}$.
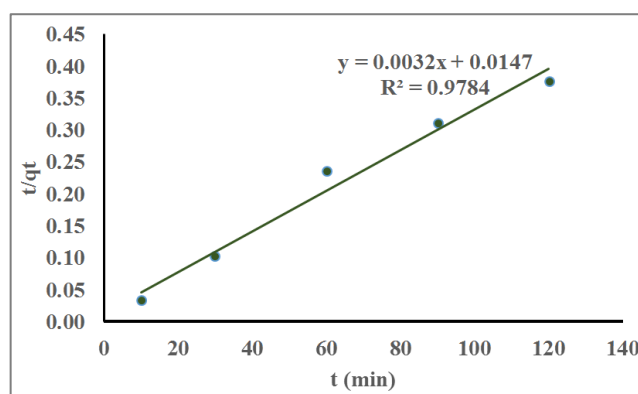
Figure 10. Pseudo second order plot.

Table 2. Comparison of Pseudo first and second order.

Pseudo-First order		Pseudo-Second order	
R^2	K_1	R^2	K_1
0.9728	1.1127	0.9784	1.8386

The correlation coefficients and rate constants for pseudo first and second order, respectively, are shown in Table 2. The rate constants for pseudo first and second order that were determined, denoted by the letters K_1 and K_2, were 1.8386 and 1.1127 (mgL⁻¹min⁻¹), respectively. For the pseudo-first and second orders that were obtained, the oleate correlation coefficients were 0.9728 and 0.9784, respec-

tively. This adsorption research of soap molecules by natural barite demonstrates that pseudo 2nd order offered an excellent fitting in the adsorption of oleate on barite, despite the fact that the R^2 values were of good fitting. This might be as a result of the natural barite's surface having enough pores to both adsorb and retain the soap molecules on it. [10, 11]

6. Thermodynamic Studies

Temperature-related changes in the kind, viability, and spontaneity of oleate ion adsorption on barite will be described by Gibbs free energy (ΔG^O). The Gibbs free energy values at standard condition for the adsorption of oleate on barite at different temperatures is presented in table 3 below;

Table 3. Values of ΔG^o at various temperatures.

T (K)	303	313	323	333
ΔG^O	-3.15	-3.25	-3.36	-3.46

The values were obtained from the equation [2];

$$\Delta G^O = -RTlnK \qquad (5)$$

Due to the negative ΔG^O values, Table 3 indicates that the reaction was spontaneous. The trend of decreasing ΔG^O negative values as temperature rises suggests that a higher temperature will more effectively promote oleate adsorption on barite. Conversely, the value of ΔG^O fell between 0 and -20 kJ/mol, indicating a physio-sorption process. [10, 11].

7. Conclusion

The results of the study showed that barite may be synthesized for sodium oleate adsorption. Thermodynamic analysis verified the spontaneous reaction, and temperature and pH effects demonstrated that adsorption will be maximized at ideal levels. The best overall adsorptive function was produced by pseudo second order kinetics, with an R2 of 0.9784 for sodium oleate. Because of this, the study has offered fresh insights into how sodium oleate interacts with barite in aqueous solution. These insights might be helpful in processes related to flotation and beneficiation as well as industrial purification.

Abbreviations

XRD   X-ray Diffraction

XRPD   X-ray Powder Diffractometer

Conflicts of Interest

The author declares no conflicts of interest.

References

[1]   Alinnor, I. J. & Enenebeaku, C. K. (2014). Adsorption characteristics of sodium oleate onto calcite. *International Research Journal of Pure & Applied Chemistry* 4(1): 88-96.

[2]   Daniel, E. (2024). Electrochemical cell and Arrhenius law: a hypothetical dimension. *Journal of Advanced Research in Applied Chemistry & Chemical Engineering 7(2), 1-8.*

[3]   Daniel, E. & George, O. (2024). Kinetic analysis of the sorption removal of copper (II) from aqueous solution by plantain peel. Journal of Advanced Research in Applied Chemistry & Chemical Engineering 7(2), 1-7.

[4]   Asuquo, J., Anusiem, A., and Etim, E. (2012). Effect of pH on the Adsorption of Metallic Soaps of Shea Butter Oil onto Hematite in Aqueous Medium. *International Journal of Modern Chemistry*, 2(2), 74-83.

[5]   Audu, D., Maigari, A. S., Ahmed, I. H., & Isah, Y. (2022). Resource assessment and possible industrial applications of bauxite occurrences in Parts of the Mambila Plateau, Nigeria. *European Journal of Environment and Earth Sciences*. 3(2), 9-23.

[6]   Fiyadh, S. S., AlSaadi, M. A., Jaafar, W. Z., AlOmar, M. K., Fayaed, S. S., Mohd, N. S., Hin, L. S. & El-Shafie, A. (2019). Review on heavy metal adsorption processes by carbon nanotubes. *Journal of Cleaner Production*. 230, 783-93.

[7]   Hernánz, F. B. & Gálvez, A. B. (1995). Modification of surface tension in aqueous solutions of sodium oleate according to temperature and pH in the flotation bath. *Journal of Colloid and Interface Science*. 173(1), 8-15.

[8]   Katarina, T. & Robert, P. (2001). The influence of ph and temperature on the equilibrium and dynamic surface tension of aqueous solutions of sodium oleate. Journal of Colloid and Interface Sc. 239(1) 209-216.

[9]   Jacobsen, S. D., Smyth, R. J. & Downs, R.T. (1998). *The Canadian mineralogist*, 36, 1053-1060.

[10]   Nwoko, C. A., Nkwoada, A. U., Okoji, J. & Opah, S. (2018). An Experimental Investigation of Pristine Barite Adsorption on Sodium Oleate and Sodium Palmitate. American Journal of Physical Chemistry 7(4), 63-72.

[11]   Yu, L. and Liang, S. (2008). From Langmuir Kinetics to First- and Second-Order Rate Equations for Adsorption 24(20), 11625–11630.

[12]   Zhijie, C., Zijie, R., Huimin, G., Yupeng, Q. & Renji, Z. (2018). Effect of modified starch on separation of fluorite from barite using sodium oleate. *Physicochemical Problem on Mineral Process.* 54(2), 228-237.