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A Comparative Kinetics and Thermodynamics Sorption Analysis on The Impact of Molecular Architecture of Palmitate, Oleate And Laureate Adsorption on Barite in Aqueous Solution

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Abstract: This study comparatively investigated the sorption of sodium laureate, sodium palmitate and sodium oleate on barite in aqueous solution taking into consideration the effect of molecular architecture (hydrocarbon chain length and degree of unsaturation) on the sorption mechanism. The effects of initial concentration, pH, adsorbent dosages, temperature and contact time for each of the adsorbates were investigated and the results obtained were analyzed using Langmuir and Freundlich isotherms and Pseudo first and Second orders. Adsorption of sodium laureate, sodium palmitate and sodium oleate on barite increases with increase in contact time, pH, temperature and initial concentration while increase in adsorbent dosage decreases spontaneously in all cases. Values of the correlation coefficients, shows that Langmuir isotherm is best for describing the adsorption of sodium laureate and sodium oleate onto barite in aqueous solution as compared to the Freundlich isotherm. For sodium palmitate, the Freundlich isotherm is best for describing the adsorption. From the R^2 values of pseudo-first and pseudo-second orders, it can be observed that pseudo-second order is the best fit kinetic model for describing the adsorption of all three soap molecules on barite. Specifically, in terms of correlation, Napalmitate>Naoleate>Nalaureate. The adsorption capacity q_e values for the pseudo-second order are 1.02, 2.05 and 1.13 for each of the soap similar to the K_2 respectively. It has been confirmed in this study that molecular architecture of fatty acids (specifically sodium laureate, palmitate and oleate) significantly influences their adsorption behavior on barite surfaces in aqueous solutions. Chain length promotes stronger hydrophobic interaction, while unsaturation introduces (cis-double bonds) structural kinks that reduce packing density. Palmitic acid, due to its long, saturated chain, exhibits the highest adsorption affinity and stability, while oleic acid offers a balance of surface activity and molecular flexibility. Lauric acid, though more soluble, demonstrates lower adsorption potential due to its short chain and weaker interactions. The positive change in ΔH^o showed that the reactions were endothermic and the increasing randomness of soap molecules is driven by the positive values of ΔS^o with the highest form of randomness in pamitate>oleate>laureate. The values of the standard free energy are beyond 0 and -20 kJ/mol, asserting that the adsorption is physico-chemical sorption mechanism, reflecting the influence of physico-chemical interactions between the soap molecules and barite. This can also be asserted to the molecular architecture which favours the adsorption of the three acids in order of palmitate>oleate>laureate due to the influence of chain length and degree of saturation. The finding of this study underlines the importance of understanding the interaction between different surfactants and barite surfaces, which can have implication in mineral.

Keywords: sodiumlaureate, sodiumpalmitate, sodiumoleate, barite, adsorption, molecular architecture

I. Introduction

Nigeria's oil sector is the most important part of its economy, accounting for over 80% of the federal government's revenue and more than 95% of export earnings. Barite ($BaSO_4$) is a widely used industrial mineral, particularly in the oil and gas industries, as a weighting agent in drilling fluids.[1] Barite is separated from its ore by physical separation techniques like crushing, screening, jigging (which involve the use of a jig machine) this jig machine uses a pulsating water flow to separate barite from gangue minerals based on their density. Barite is denser and settles faster, so it sinks to the bottom of the sorting tank, while the lighter gangue minerals float on top, other method of physical separation is flotation gravity separation, heavy medium separation, in some cases magnetic separation. [2,3] The main purpose of beneficiation is to remove gangue from the ore. Labidi et al. and other researchers asserted that due to the amphipathic nature of soap molecules, Langmuir and Freundlich equations are suited for long-chain fatty acids (sodium oleate and sodium palmitate) adsorption on the barite surface been an ionic crystal. They further emphasized that most surfactant head groups and hydrocarbon chains are influenced by the form of adsorption of the surfactant at any given surface in solution.[4,5,6] Thus, surfactants can modify surface properties of a system, causing preferential orientation for optimum interaction at the interface. Soap molecules bear hydrophobic or hydrophilic parts which can be adsorbed selectively on the surface of the desired mineral particles to reduce wetting by water thereby enhancing their floatability.[7] Several experimental studies revealed that soap molecules when used can recover up to 95% of mineral ore in so doing establishing that the concentration, flotation or beneficiation of minerals can be carried out by the experimental adsorption of salts of fatty acids as adsorbate on mineral surfaces as adsorbents.[1,4,6,8]

Soap molecules adsorption on barite in aqueous solutions are of scientific interests for optimal beneficiation and flotation processes. Nwoko *et al* and Prieto et al affirmed that the adsorption of soap molecules on barite revealed that hydrocarbon length of surfactants

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is a major determinant in surface properties of surfactants, yet attention by researchers has mostly been drown to individual assessment of sodium/potassium salts of fatty acids adsorption, with paucity of information on effect of hydrocarbon chain length on the adsorption reaction which is assessed in this study for sodium laureate, sodium palmitate and sodium oleate.[6,9] Additionally, the adsorption kinetics of fatty acids also depends on the molecular architecture and the degree of unsaturation of the fatty acids.[10] Prominent soap molecules of oleic, lauric, steric and palmitic acids have been utilized by many researchers[1,4,6] in the assessments of the adsorption of the soap molecules on mineral ores with little or no information on the effect of molecular architecture on the adsorption capacity of salts of fatty acids molecules, which is considered in this study for sodium laureate (saturated), sodium palmitate (saturated) and sodium oleate (unsaturated).

II. Methodology

Adsorbent Collection and Preparation

The natural Barite obtained from the National Geosciences Research Laboratories, Nigerian Geological Survey Agency, Kaduna South and FTIR characterization was done at Agilent Technologies, Kaduna. 100g of the mineral in lump was crushed and ground in a mortar, washed with distilled water. dried in an electric oven at 110 degrees and sieved using 50 µm mesh and preserved in a plastic container following the methodology of Nwoko et al. [6]

Preparation of Adsorbates (NaLaureate, NaPalmitate and NaOleate)

To two 500ml beakers containing 50ml of a 30% NaOH, 30g of lauric and palmitic acids added respectively. To the same flask, 30 ml of ethanol was also added to make each sample creamier and pastier. The mixtures were heated to 60 and 98 degrees Celsius respectively in a water bath with constant stirring. 50 ml of NaCl was added gradually until homogeneous clear mixtures were obtained and allowed to cool for 24 hours to form sodiumlaureate and sodiumpalmitate soap cakes.[11] 200ml of liquid oleic acid was added to a 500ml beakers containing 30% NaOH. 20 ml of ethanol was also added to make it creamier and pastier. The mixture was heated to 60 degrees Celsius respectively in a water bath with constant stirring. 20 ml of NaCl was added gradually until a homogeneous clear mixture is obtained and allowed to cool for 24 hours to form a sodiumoleate soap cake. [6,12]

Adsorption Studies

Variation of initial concentration

To five 250ml Erlenmeyer flasks containing 1.5g/250ml, 3.5g/250ml, 5.5g/250ml, 7.5g/250ml and 9.5g/250ml sodium laureate, 1.5g barite was added and the pH adjusted to 4.5 at room temperature. The samples were stirred in rotary shaker for 30 minutes, allowed to settle, and filtered. The concentration of sodiumlaureate was measured using UV-spectrophotometer. [1,6] The same procedure was repeated for sodium palmitate and sodium oleate.

Variation of pH

To five 250 ml Erlenmeyer flasks containing 2.8g/250ml each (0.05M/11.1g/L) of sodium laureate of pH 3.5, 5.5, 7.5, 9.5 and 11.5, 1.5g barite was added to each of the five flask at room temperature. The samples were stirred in rotary shaker for 30 minutes, allowed to settle, and filtered. The concentration of sodiumlaureate was measured using UV-spectrophotometer.[6] The same procedure was repeated for 0.05M (or 3.5g/250 ml or 13.9g/L) sodium palmitate and 0.05M (or 3.8g/250ml, or 15.2g/L) sodium oleate.

Variation of adsorbent dosage

To five 250 ml Erlenmeyer flasks containing 2.8g/250ml each (0.05M/11.1g/L) of sodium laureate of pH 4.5; 1.5g, 3.5g, 5.5g, 7.5g and 9.5g of barite were added to each of the five flasks respectively at room temperature. The samples were stirred in rotary shaker for 30 minutes, allowed to settle, and filtered. The concentration of sodiumlaureate in each sample was measured using UV-spectrophotometer. [1,6] The same procedure was repeated for 0.05M (or 3.5g/250 ml or 13.9g/L) sodium palmitate and 0.05M (or 3.8g/250ml, or 15.2g/L) sodium oleate.

Variation of temperature

To five 250 ml Erlenmeyer flasks containing 2.8g/250ml each (0.05M/11.1g/L) of sodium laureate of pH 4.5; 1.5g of barite was added to each of the five flasks respectively at 30, 40, 50, 60 70^{o}C temperatures in a water bath. The samples were stirred in rotary shaker for 30 minutes, allowed to settle, and filtered. The concentration of sodiumlaureate in each sample was measured using UV-spectrophotometer. [1,6] The same procedure was repeated for 0.05M (or 3.5g/250 ml or 13.9g/L) sodium palmitate and 0.05M (or 3.8g/250ml, or 15.2g/L) sodium oleate.

Variation of Contact Time

Similarly, five 250 ml Erlenmeyer flasks containing 2.8g/250ml each (0.05M/11.1g/L) of sodium laureate of pH 4.5; 1.5g of barite was added to each of the five flasks respectively at room of 29^{o}C temperature in a water bath. The samples were stirred in rotary shaker for 10, 20, 30, 60 and 90 minutes, allowed to settle, and filtered. The concentration of sodiumlaureate in each sample was

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measured using UV-spectrophotometer.[1] The same procedure was repeated for 0.05M (or 3.5g/250 ml or 13.9g/L) sodium palmitate and 0.05M (or 3.8g/250ml, or 15.2g/L) sodium oleate.

III. Results and Discussion

Effect of initial concentration

The effect of initial concentration of sodiumlaureate, sodiumpalmitate and sodiumloleate adsorption on barite is presented in figure 1.

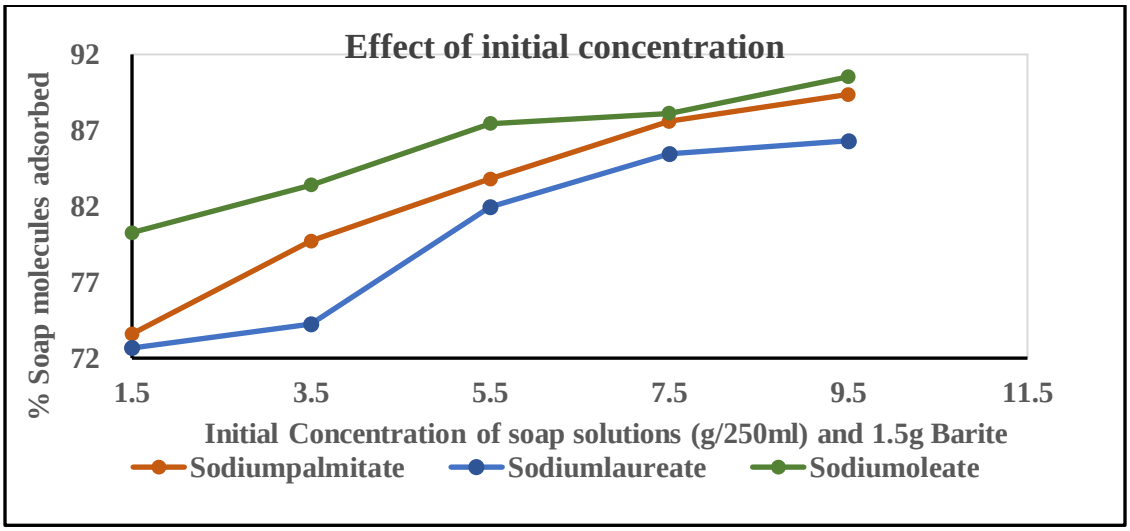

Figure 1. Effect of initial concentration

The percent of soap molecules of laureate, palmitate and oleate adsorbed onto barite with variation of initial concentration is presented in figure 1. Generally, it can be seen that the adsorption of the soap molecules onto barite increase with increase in adsorbates concentrations. The soap removal increased to 86 %, 88% and 90.1% for sodium laureate, sodium palmitate and sodium oleate respectively as the soap concentration was increased from 1.50g to 9.50g/250ml. Hence, it can be understood that increase in concentration provided an enough interface for soap molecule interaction with the barite. It is also suggested that increase in concentration of soap molecules increases barite ore surface charge and driving more adsorption to take place.[13] The effect of concentration and time, typically gave a C type- adsorption isotherm which means that the concentration of the soap molecules remaining in solution and adsorbed on the barite is almost at same concentration.[14]

Effect of pH

The effect of pH on the adsorption of sodium laureate, sodium palmitate and sodium oleate is presented in figure 2

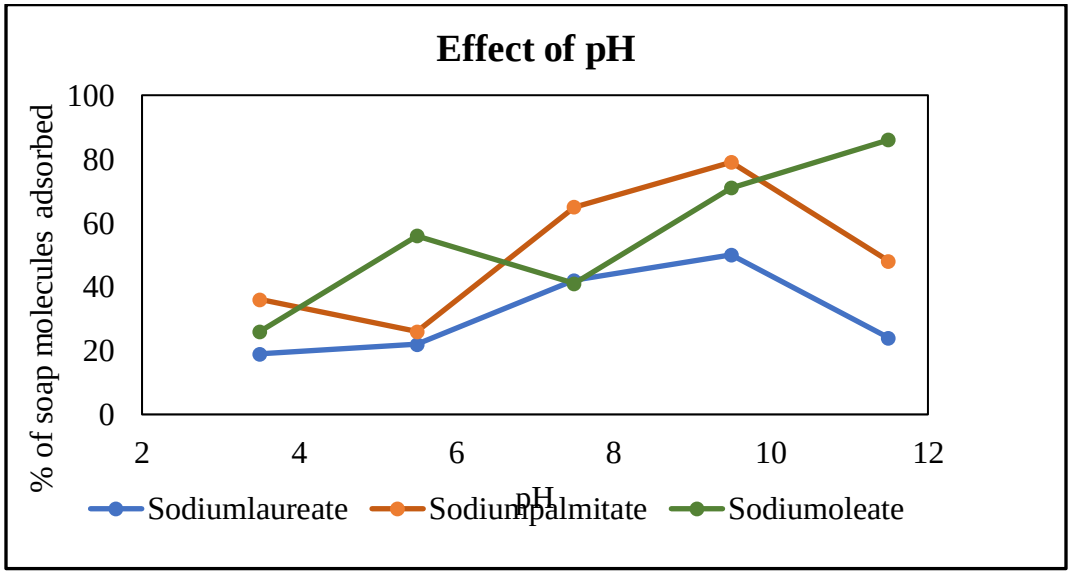

Figure 2. Effect of pH

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The soap molecules adsorption was significantly changed over the varied pH range. The adsorption is highest between pH 8 and 10 for sodium laureate and sodium palmitate respectively while sodium oleate is highest at pH 11 and decrease above pH 10.5 for sodium laureate and sodium palmitate. Also, there was a depression of adsorption at pH 9.5 which is comparable to studies by Nwoko et al., Offor et al. and Alinnor et al. that barite, hematite and calcite or natural ores are depressed by soap solutions between pH 8.3 and 11. [6,11,13] At higher pH, the surface of barite particles may get negatively charged, which enhances the positively charged soap cations through electrostatic interaction. The decrease in the formation of barite oleate at higher alkaline pH values may probably be attributable to an increase in electrostatic repulsion between the micelles and the negative barite surface.

Effect of adsorbent dosage

Figure 3 presents the effect of adsorbent dosage on the adsorption of sodium laureate, sodium palmitate and sodium oleate on barite in aqueous solution.

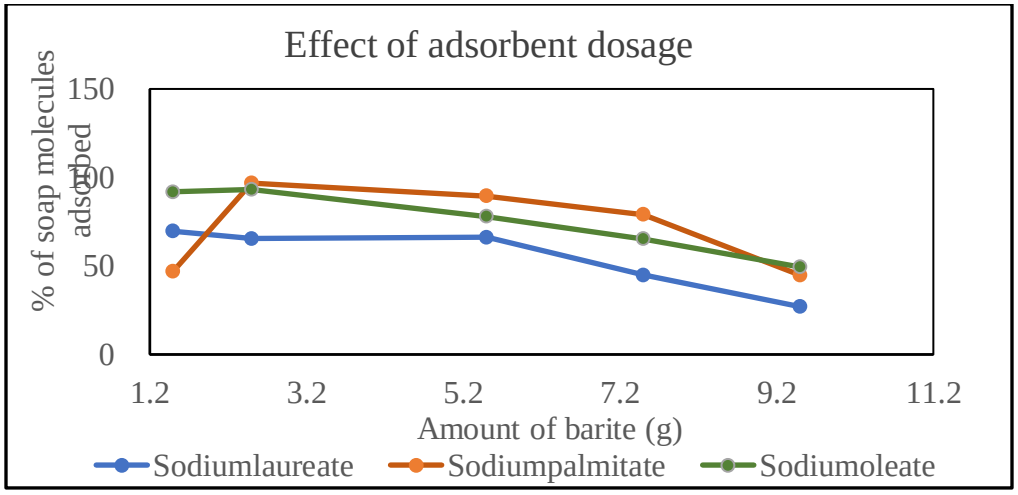

Figure 3. Effect of adsorbent dosage

The percentage adsorption decreased significantly as dosage increased from 1.2 to 9.2 g for sodium laureate and sodium oleate respectively while adsorption increased from 1.2 to 1.5 g for sodium palmitate and starts decreasing from 1.5 to 9.5 grams. The results showed that increasing dosage amount led to decrease in adsorption capacity owing to the high bulk density and chemical resistance nature of barite.[15] This is also similar to the studies carried out by Nwoko et al. [6]

Effect of temperature

The effect of temperature on adsorption of sodium laureate, sodium palmitate and sodium oleate is presented in the figure 4.

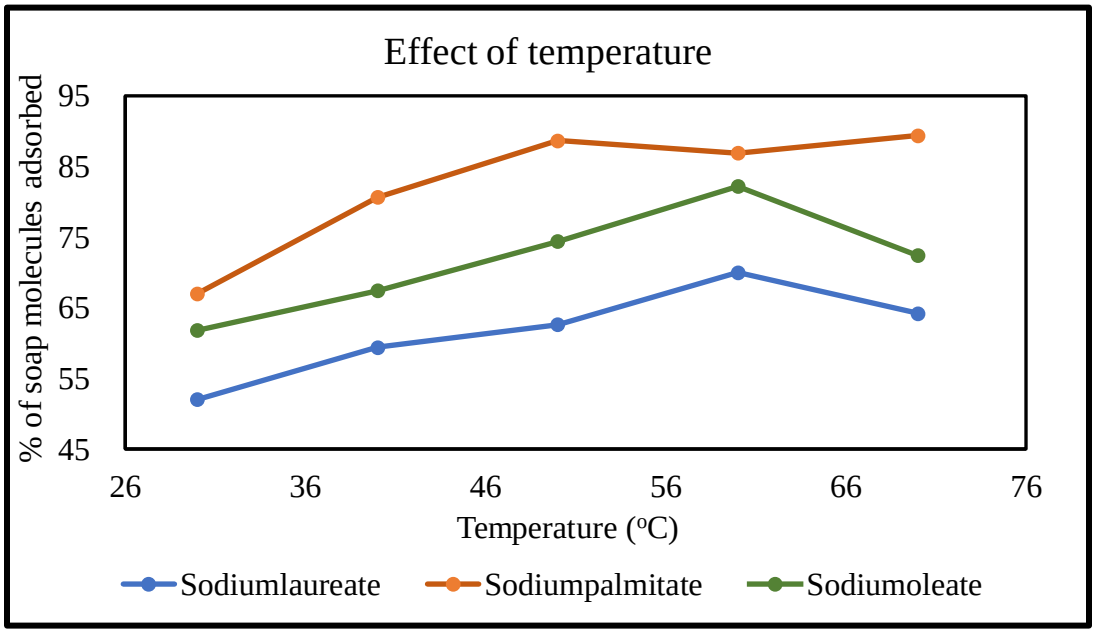

Figure 4. Effect of temperature

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The effect of temperature on sodium laureate, sodium oleate and sodium palmitate adsorption from aqueous solution onto natural barite surface was investigated from temperatures of 29 °C to 70 °C. From the figure. it showed that the adsorption of soap. The increase in adsorption with temperature can be attributed to an increase in the number of active surface sites available for adsorption on the adsorbent. At a higher temperature the possibility of diffusion of soap molecules within the pore of the adsorbent may be enhanced leading to higher adsorption density and since diffusion is an endothermic process, greater adsorption will be observed at high temperature. Thus, the diffusion rate of ion in the external mass transport process increases with temperature. The observation of temperature effect of soap adsorption on barite therefore confirms that chemical reaction is dominant at high temperature and it causes faster reaction kinetics of the adsorbate species. This means, the particle will travel at a faster rate to the surface to get adsorbed. However, it was observed that sodium laureate and sodium oleate adsorption gradually decreased again as the temperature increased from 60 to 70 °C. The decrease in adsorption with increase in temperature may also be attributed to weak attractive forces between the soap molecules and barite and partly due to enhancement of thermal energies of adsorbate; thus, making the attractive forces between the soap molecules and barite insufficient to retain the molecules at binding sites. This could lead to desorption or cause the laureate and oleate ions to bounce off surface of barite instead of colliding and combining with it.

Effect of contact time

The effect of contact time is presented for the adsorption of sodiumlaureate, sodiumpalmitate and sodiumoleate on barite is presented in figure 5.

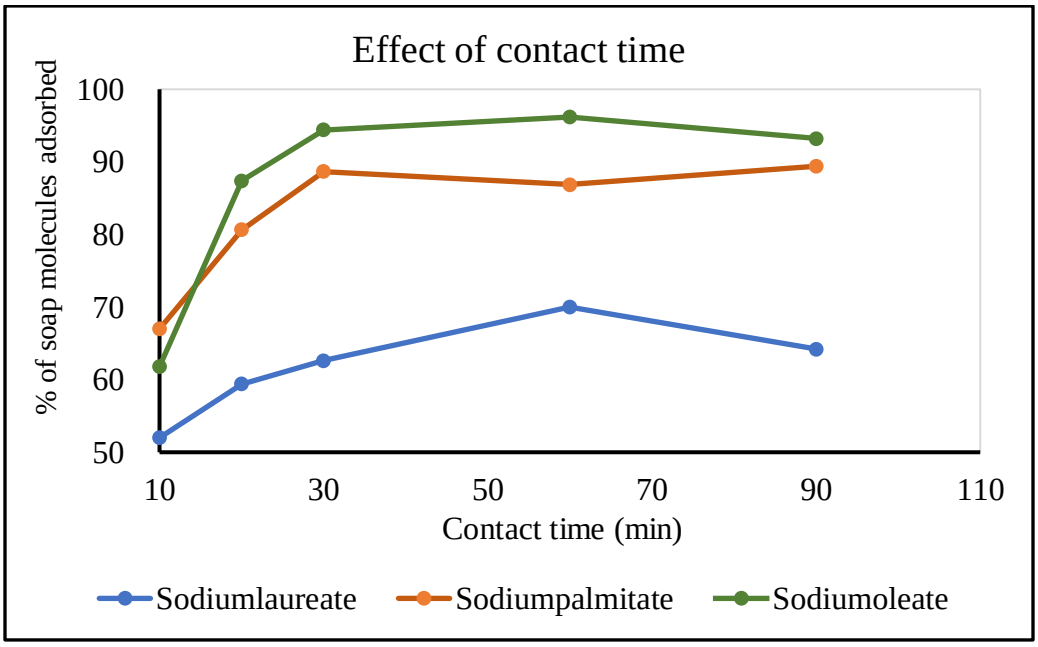

Figure 5. Effect of contact time

A general increase in soap adsorption with contact time was observed at the initial stage for all soap molecules until 60 to 70 minutes which is similar to the findings of Itodo et al. [16] The contact time is essential for the establishment of equilibrium during the adsorption process. From the result of this study, the maximum adsorption capacity was obtained at 60 minutes for sodium oleate and sodium laureate and 90 minutes for sodium palmitate. The adsorption capacities got are 23.2 mg/g, 29.8 mg/g and 32.1 mg/g for sodium laureate, sodium palmitate and sodium oleate respectively.

Adsorption Isotherms

Langmuir adsorption isotherm

The Langmuir model can be presented by the equation below[8].

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

Where:q_{max} is the monolayer adsorption capacity of the adsorbent, i.e. the maximum amount adsorbed; K_L is the Langmuir adsorption constant; C_e is the equilibrium palmitate concentration in the solution and q_e is the equilibrium palmitate concentration on calcite. Values of q_{max} and K_L are calculated respectively from the slope and the intercept of the plot of $\frac{C_e}{q_e}$ against C_e as shown in figures 6(a), 6(b) and 6(c) respectively.

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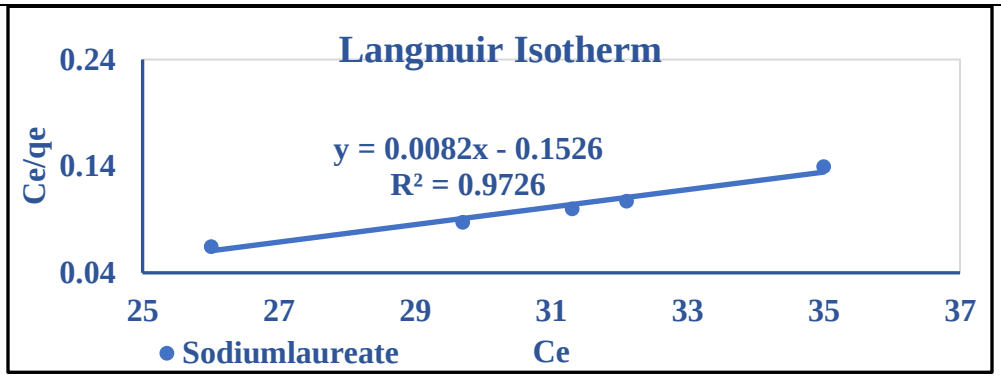

Figure 6(a). Langmuir isotherm for sodium laureate adsorption

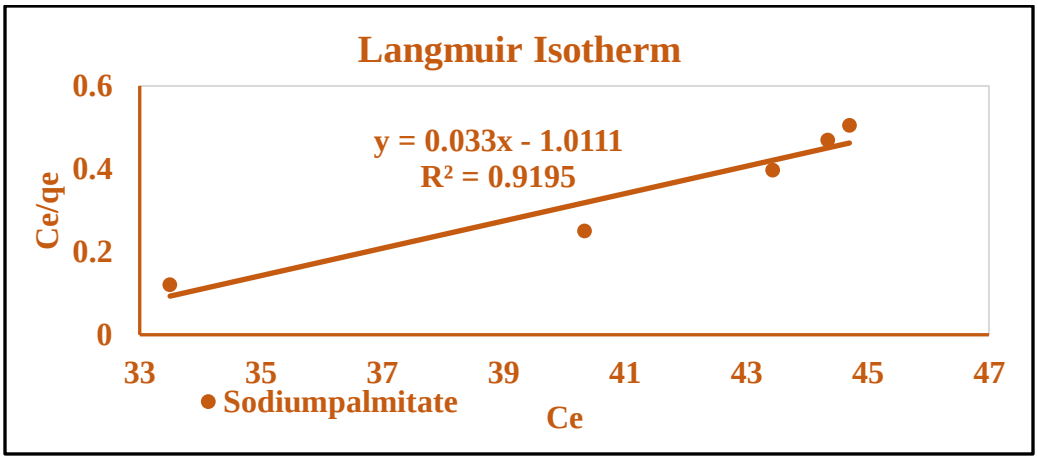

Figure 6 (b): Langmuir adsorption isotherm for sodium palmitate adsorption

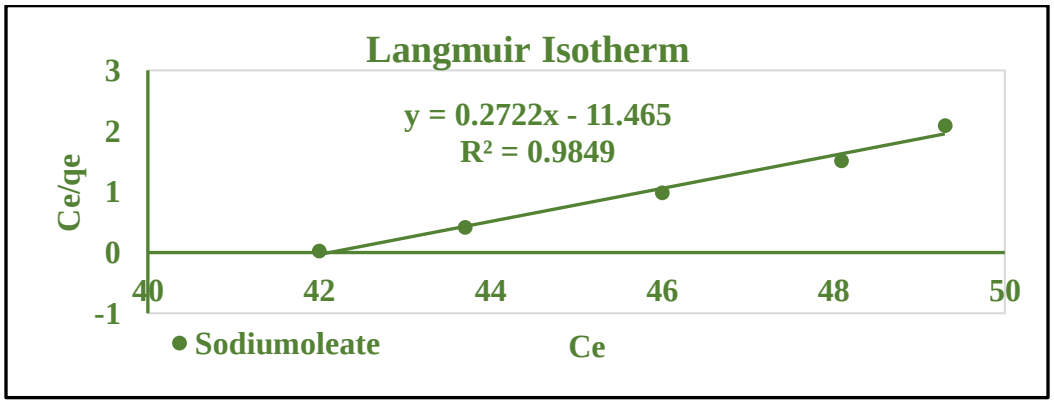

Figure 6(c): Langmuir isotherm for sodium oleate adsorption

The Langmuir plot which shows monolayer coverage for the adsorption of sodium laureate, sodium palmitate and sodium oleate indicated that none of the graphs had negative slope, nor intercept, and adsorption increased as qe (amount adsorbed at equilibrium) increased in each case. Hence, a positive interaction between the natural barite and soap molecules. The residual plots showed no pattern or trend; a sign of good fitting in each case and the correlation coefficient (R^2) fitting of sodium oleate (0.9849) provided a better fit than sodium palmitate (0.9195) and sodium laureate (9726). The high K_L values of 12.2, 30 and 36.7 for sodium laureate, sodium palmitate and sodium oleate respectively shows the binding strength of the soap molecules on the barite surface in each case with sodium oleate having the highest value indicates a more favorable adsorption in oleate. The R_L values of 0.024, 0.033 and 0.054 for sodium laureate, sodium palmitate and sodium oleate being a dimensionless constant was > 0 but < 1 in all three soap molecules indicating a favorable adsorption reaction.[6] Thus, the sodium oleate adsorption over natural barite was better described by a Langmuir adsorption isotherm.

Freundlich adsorption isotherm

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. [17,18] The equation of the Freundlich adsorption model is expressed as:

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

Where K_F is a constant related to the adsorption capacity (Freundlich constant) and $\frac{1}{n}$ is an empirical parameter related to the adsorption intensity. Values of K_F and are calculated from the slope and the intercept of the plot of $\log q_e$ vs. log as shown in 7(a), 7(b) and 7(c) for sodium laureate, sodium palmitate and sodium oleate adsorption on barite in aqueous solution respectively.

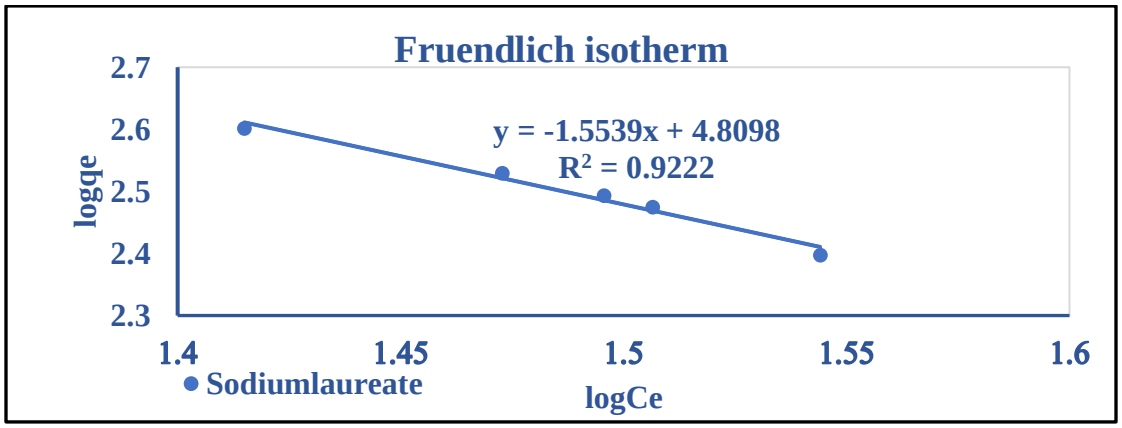

Figure 7(a). Freundlich isotherm for sodium laureate adsorption

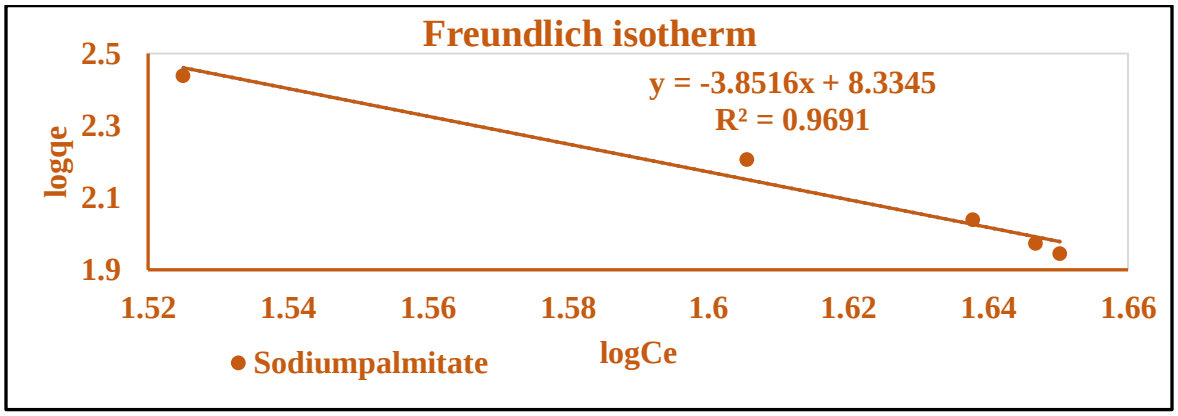

Figure 7(b). Freundlich isotherm for sodium palmitate

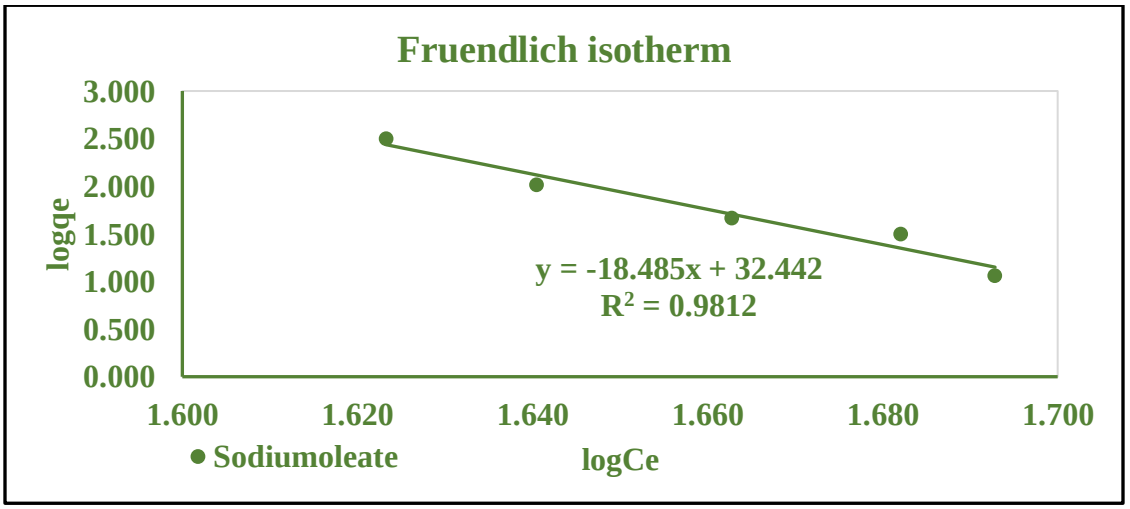

Figure 7(c). Freundlich isotherm for sodium oleate adsorption

The Freundlich isotherm explains the distribution of solutes between an aqueous solution and solid phases. All the graphs gave a positive intercept and slope which describes energetically favorable reactions. These may occur because the loading of adsorbate on the adsorbent, attained at equilibrium (q_e) increases as (C_e) is increased. The Freundlich constant K_F represents the adsorption capacity, was better at oleate (2.84) than in palmitate (2.02) and laureate.1.23. The strength (energy) n, of the adsorption showed

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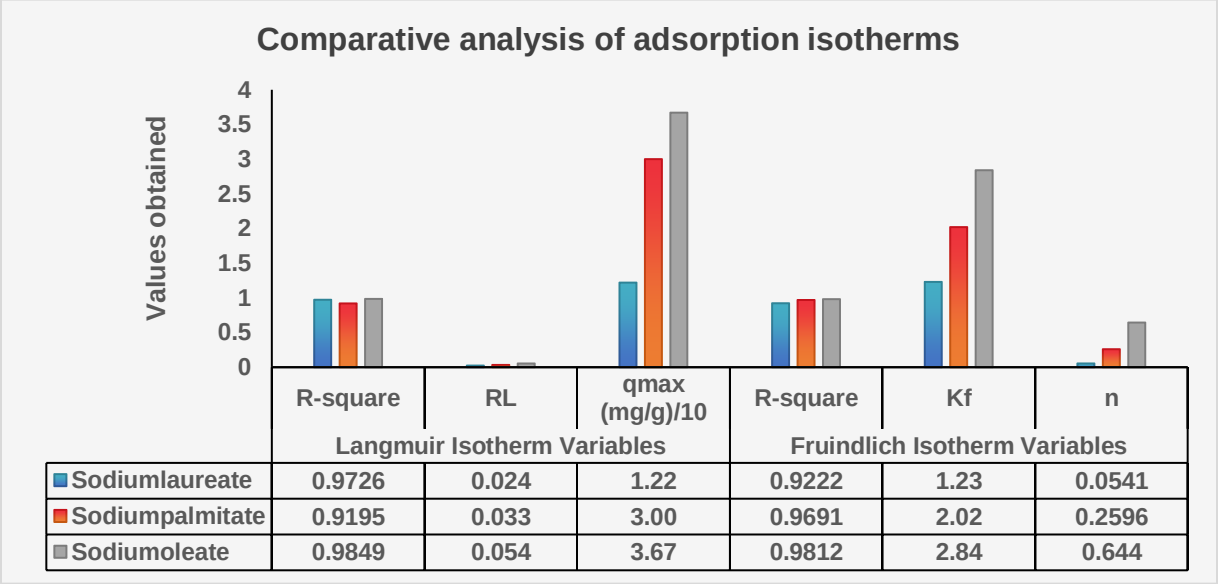
that at 0.6441 oleate presented a stronger binding force than palmitate at 0.2596 and laureate at 0.0541. However, all three showed a slow adsorption mechanism suggesting that an increase in temperature may drive the reaction towards faster adsorption equilibrium. Likewise, the correlation coefficient of oleate (0.9812) gave a good fitting compared to palmitate at 0.9691 and laureate at 0,9222. Thus, it will be said sodium oleate was better described by the Freundlich adsorption isotherm and this is similar to the observation noted by Agbaghare, Nwoko *et al* and Zhijie et al. [1,6,19]

Best fit adsorption isotherm from the study

Figure 8 presents the variable values that are used to identify the best fit adsorption isotherm model between Langmuir and Freundlich isotherms for each of sodium laureate, sodium palmitate and sodium oleate respectively.

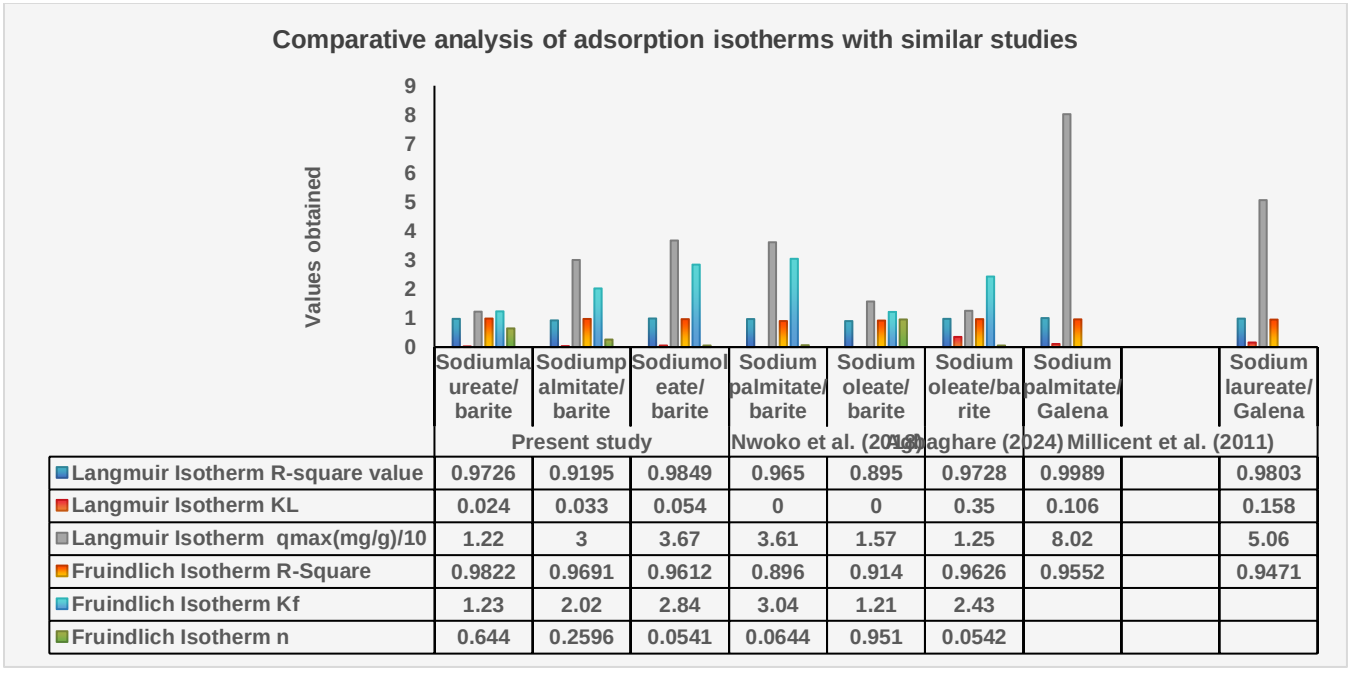


	Langmuir Isotherm Variables			Fruindlich Isotherm Variables		
	R-square	RL	qmax (mg/g)/10	R-square	Kf	n
Sodiumlaureate	0.9726	0.024	1.22	0.9222	1.23	0.0541
Sodiumpalmitate	0.9195	0.033	3.00	0.9691	2.02	0.2596
Sodiumoleate	0.9849	0.054	3.67	0.9812	2.84	0.644

Figure 8. Comparative analysis of adsorption isotherms

From the values of the correlation coefficients, it can be observed that Langmuir isotherm is best for describing the adsorption of sodium laureate and sodium oleate onto barite in aqueous solution as compared to the Freundlich isotherm. For sodium palmitate, the Freundlich isotherm is best for describing the adsorption other than Langmuir isotherm model.

Comparative Analysis of adsorption isotherms with similar studies



	Present study			Nwoko et al. (2016)		Agbaghare (2024)			Millicent et al. (2011)
	Sodiumlaureate/ barite	Sodiumpalmitate/ barite	Sodiumoleate/ barite	Sodium palmitate/ barite	Sodium oleate/ barite	Sodium oleate/barite	Sodium palmitate/ Galena		Sodium laureate/ Galena
Langmuir Isotherm R-square value	0.9726	0.9195	0.9849	0.965	0.895	0.9728	0.9989		0.9803
Langmuir Isotherm KL	0.024	0.033	0.054	0	0	0.35	0.106		0.158
Langmuir Isotherm qmax(mg/g)/10	1.22	3	3.67	3.61	1.57	1.25	8.02		5.06
Fruindlich Isotherm R-Square	0.9822	0.9691	0.9612	0.896	0.914	0.9626	0.9552		0.9471
Fruindlich Isotherm Kf	1.23	2.02	2.84	3.04	1.21	2.43			
Fruindlich Isotherm n	0.644	0.2596	0.0541	0.0644	0.951	0.0542			

Figure 9. Comparative analysis of adsorption isotherms with similar studies

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Other studies carried out by Agbaghare, Nwoko et al., and Millicent et al. also attested based on their findings that the best fit adsorption isotherm for describing most adsorption process rests on either Freundlich or Langmuir isotherm among others. [1,6,20] From figure 9, Fruendlich isotherm suited the description for the adsorption of laureate and palmitate than oleate in the present study while oleate adsorption is best described by the Langmuir. This is similar to the findings of Nwoko et al. [6] whereby oleate adsorption onto barite is best described by Langmuir unlike palmitate adsorption which is best described by Freundlich. Agbaghare and Chen et al. in their studies also confirmed that the Langmuir Isotherm is the best fit model describing oleate adsorption on barite. [1,8]

Kinetics Models

The pseudo-first and pseudo-second order equations were used for explaining the behavior for the adsorption of laureate, palmitate and oleate on barite.

Pseudo-first order

The pseudo-first order equation is given by

$$\ln(q_e - q_t) = lnq_e - K_1 t \quad (3)$$

and figure 10(a) is a plot of $\ln(q_e - q_t)$ versus t.

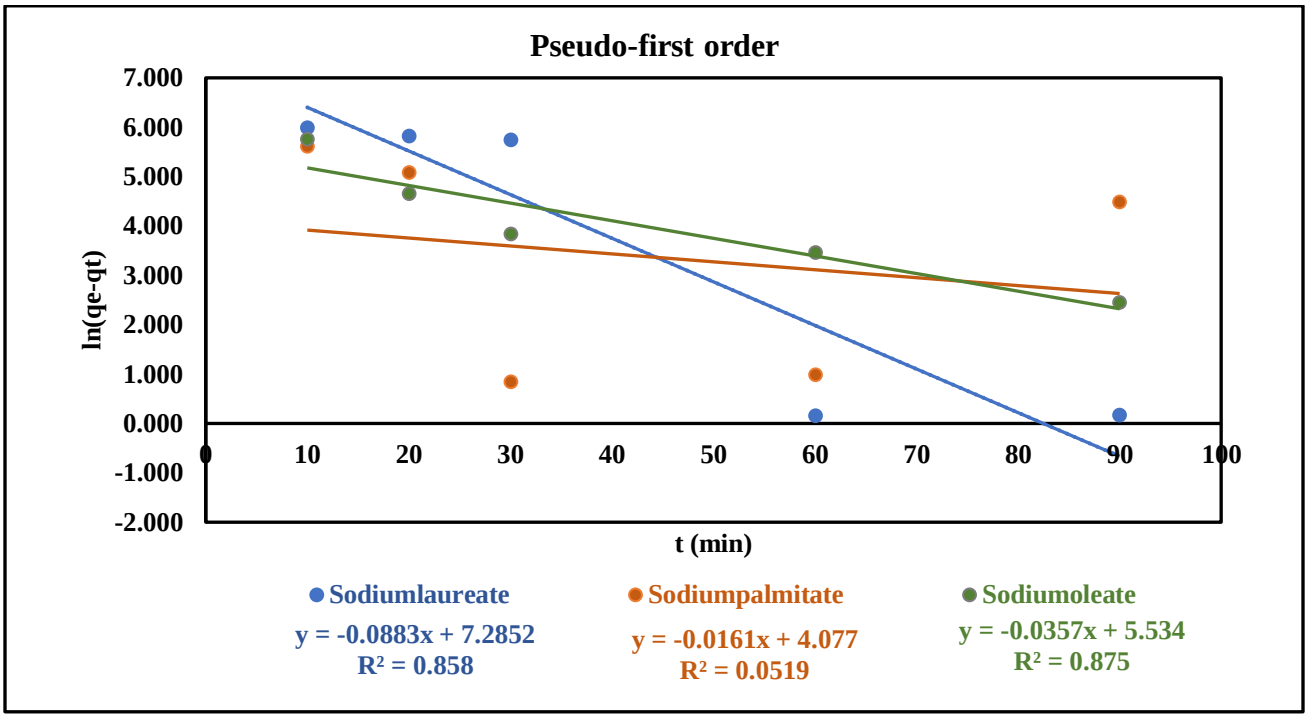

Figure 10(a): Pseudo-first order for laureate, palmitate and oleate adsorption on barite

The correlation coefficients for pseudo-first order kinetic adsorption of laureate, palmitate and oleate on barite are 0.858, 0.0519 and 0.875 indicating a low correlation, making it not efficiently suitable model for describing the adsorption process for the three soap solutions.

Pseudo-second order

The pseudo-second order equation is represented by the equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} t \quad (4)$$

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.[21] Values of K_2 and q_e calculated from the slope, $\frac{t}{q_e}$ and intercept, $\frac{1}{K_2 q_e}$.

Figure 10(b) shows the pseudo-second order plots for sodium laureate, sodium palmitate and sodium oleate adsorption on barite. The correlation coefficients (R^2 values) for laureate, palmitate and oleate adsorptions are 0.9781, 0.9834and 0.9531 respectively indicating high correlation.

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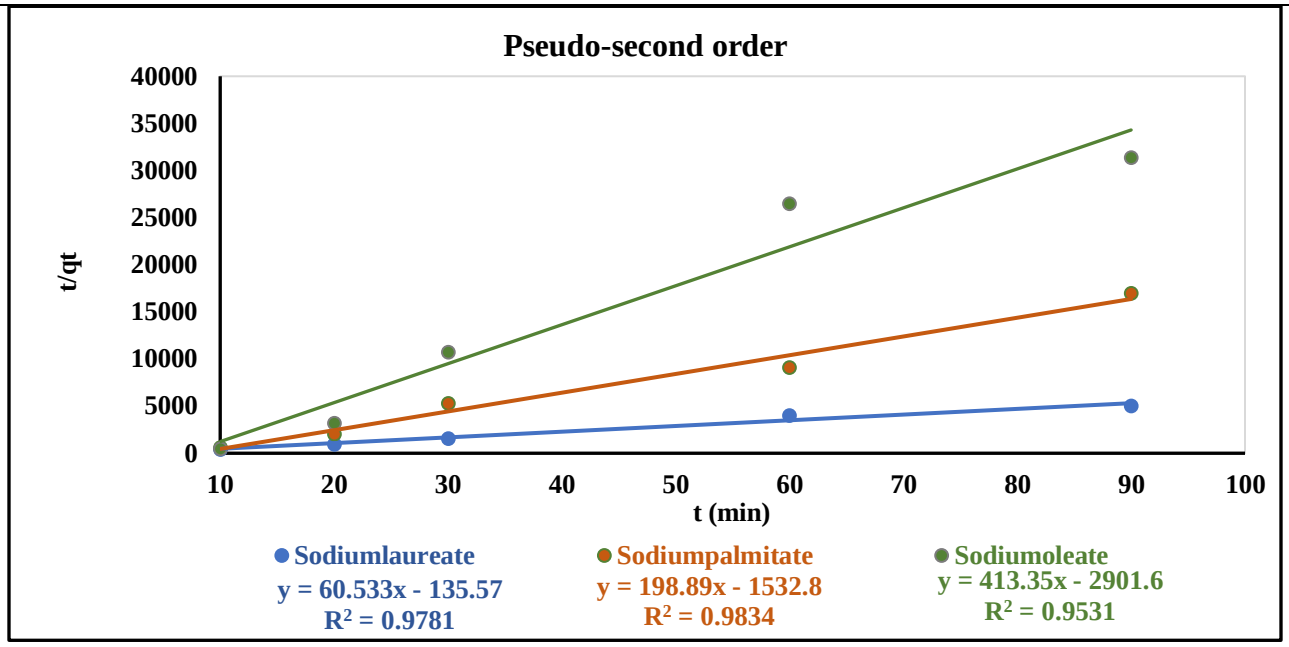
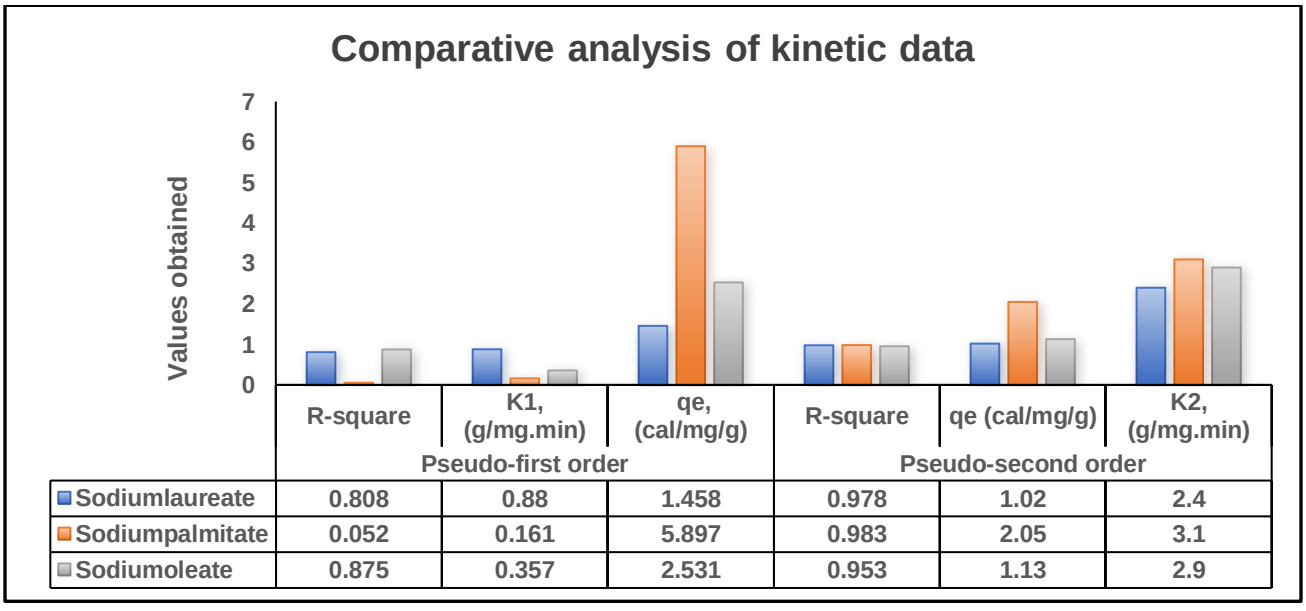


Figure 10(b). Pseudo-second order for laureate, palmitate and oleate adsorption

This also entails that the rate of adsorption of sodium laureate, sodium palmitate and sodium oleate is proportional to the available sites on the barite. The values of K_2 and q_e calculated from the slope, $\frac{t}{q_e}$ and intercept, $\frac{1}{K_2 q_e}$ are presented in table 10.

Best fit Kinetic Model

Figure 11 presents the variable values that is used to identify the best fit adsorption kinetic models between pseudo-first and second orders for each of sodium laureate, sodium palmitate and sodium oleate respectively.



	Pseudo-first order			Pseudo-second order		
	R-square	K1, (g/mg.min)	qe, (cal/mg/g)	R-square	qe (cal/mg/g)	K2, (g/mg.min)
Sodiumlaureate	0.808	0.88	1.458	0.978	1.02	2.4
Sodiumpalmitate	0.052	0.161	5.897	0.983	2.05	3.1
Sodiumoleate	0.875	0.357	2.531	0.953	1.13	2.9

Figure 11. Comparative analysis of kinetic data

From the R^2 values of pseudo-first and pseudo-second orders, it can be observed that pseudo-second order is the best fit kinetic model for describing the adsorption of all three soap molecules on barite. Specifically, in terms of correlation, Napalmitate>Naoleate>Nalaureate. The adsorption capacity q_e values for the pseudo-second order are 1.02, 2.05 and 1.13 for each of the soap similar to the K_2 respectively.

Comparative Analysis with Similar Studies

Figure 12 presents the variable values that is used to identify the best fit adsorption kinetic models with similar studies.

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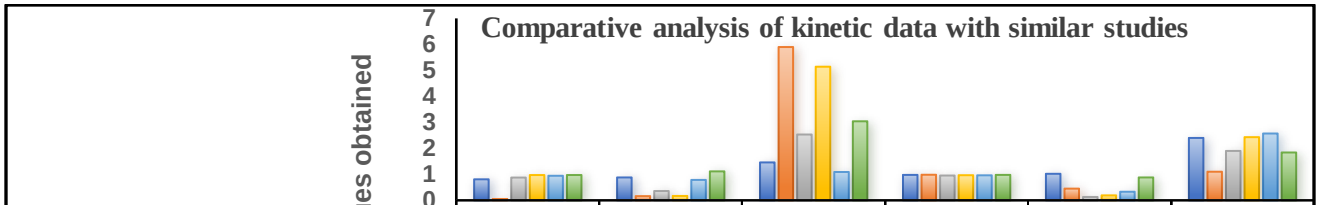

	Pseudo-first order			Pseudo-second order		
	R-Square	K1 (g/mg.min)	qe (cal/mg/g)	R-Square	qe (cal/mg/g)	K2, (g/mg.min)
Present study Sodiumlaureate/ barite	0.808	0.88	1.458	0.978	1.02	2.4
Present study Sodiumpalmitate/barite	0.052	0.161	5.897	0.983	0.45	1.1
Present study Sodiumoleate/ barite	0.875	0.357	2.531	0.953	0.13	1.9
Nwoko et al. (2018) Sodium palmitate/ barite	0.972	0.169	5.14	0.966	0.19	2.43
Nwoko et al. (2018) Sodium oleate/ barite	0.944	0.785	1.09	0.962	0.33	2.57
Agbaghare (2024) Sodiumoleate/barite	0.973	1.113	3.04	0.978	0.88	1.84

Figure 12. Comparative analysis of kinetic data with similar studies

This present study demonstrates that pseudo second order offered a better fitting in the adsorption of laureate, palmitate and oleate on barite, more than pseudo first order fitting and this also justified by the correlation coefficient values obtained for the second order and the reports of Agbaghare and Nwoko et al. [1,6] as presented in figure 11.

Thermodynamics Study

Effects of temperature on the nature, feasibility and spontaneity of adsorption of sodiumlaureate, sodiumpalmitate and sodiumoleate on barite is described by the thermodynamic parameters (ΔG°, ΔH° and ΔS°) using the equations:

$$\ln Kc = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (5)$$

R is gas constant (8.314 $Jmol^{-1}K^{-1}$) and T is absolute temperature in Kelvin and Kc can be obtained from qe/Ce.[6] A plot of ln Kc versus 1/T gives a linear graph and the values of ΔH° and ΔS° calculated from the slope and intercept of the plot respectively for sodiumlaureate, sodiumpalmitate and sodiumoleate are illustrated in figure 13 and table 1.

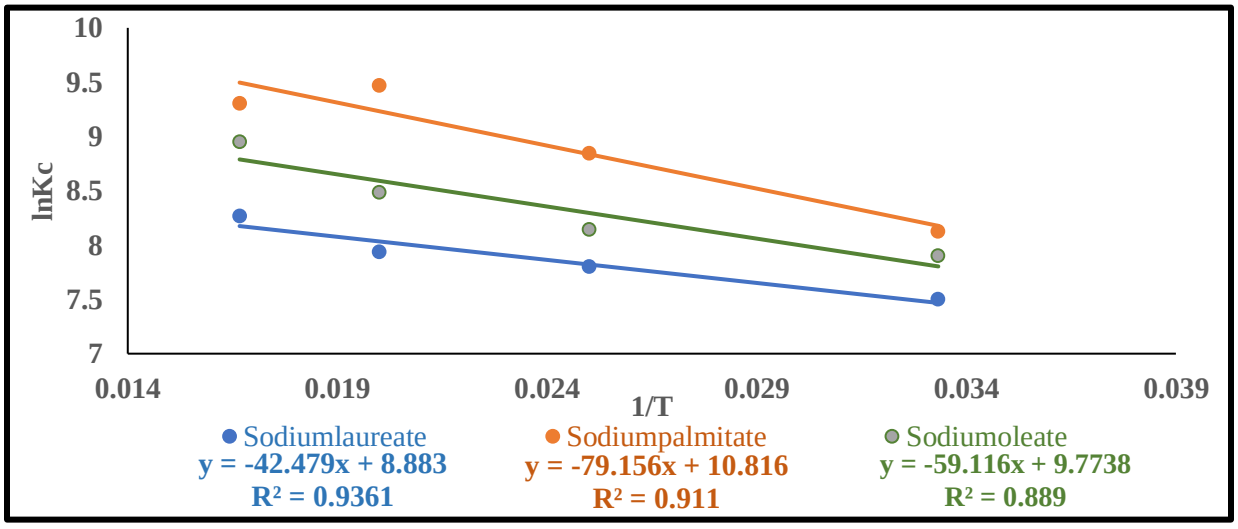

Figure 13. Plot of lnKc against 1/T

Standard Enthalpy (ΔH^o)

The standard enthalpy for sodiumlaureate (SL), sodiumpalmitate(SP) and sodiumoleate (SO) are obtained from the slope of the respective linear graph equations (y = -42.479x + 8.883; y = -79.156x + 10.816 and y = -59.116x + 9.7738) whereby: $-\frac{\Delta H^o_{SL}}{R}$ = -42.479, $-\frac{\Delta H^o_{SP}}{R}$ = -79.156 and $-\frac{\Delta H^o_{SO}}{R}$ = -59.116 giving ΔH^o_{SL}, ΔH^o_{SP} and ΔH^o_{SO}values of 353.178 J/mol (+ 0.353 kJ/mol), 658.118 J/mol (+ 0.658 kJ/mol) and 491.502 J/mol (+ 0.492 kJ/mol) respectively. The positive change in ΔH^o showed that the reactions were

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endothermic in nature unlike that observed in Millicent and Anusiem[20,21] and Nwoko et al.[6] This is justified by the influence of heat on the adsorption of soap molecules on barite.

Standard Entropy (ΔS^o)

The standard entropy for sodiumlaureate (SL), sodiumpalmitate(SP) and sodiumoleate (SO) are obtained from the slope of the respective linear graph equations (y = -42.479x + 8.883; y = -79.156x + 10.816 and y = -59.116x + 9.7738) whereby: $\frac{\Delta S^o_{SL}}{R}$ = 8.883, $\frac{\Delta S^o_{SP}}{R}$ = 10.816 and $\frac{\Delta S^o_{SO}}{R}$ = 9.7738 giving ΔS^o_{SL}, ΔS^o_{SP} and ΔS^o_{SO} values of 73.9 J/mol (0.074 kJ/mol), 89.9 J/mol (0.090 kJ/mol) and 81.26 J/mol (0.081 kJ/mol) respectively. The increasing randomness of soap molecules is driven by the positive values of ΔS^o with the highest form of randomness in pamitate>oleate>laureate.

6.3 Standard Free Energy (ΔG^0)

The standard free energies for sodiumlaureate, sodiumpalmitate and sodiumoleate at 303K, 313K, 323K and 333K were computed using the equation (6):

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (6)$$

The values are presented in table 1.

Table 1: Thermodynamic parameters laureate, palmitate and oleate adsorption

Adsorbate	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)	ΔG^0 (kJ/mol)			
			303K	313K	323K	333K
Sodiumlaureate	+0.353	+0.074	-22.069	-22.809	-23.549	-24.289
Sodiumpalmitate	+0.658	+0.090	-26.612	-27.512	-28.412	-29.312
Sodiumoleate	+0.492	+0.081	-24.051	-24.861	-25.671	-26.481

From the table 1, it shows that the reaction was spontaneous due to negative ΔG^o values. The decrease in ΔG^o negative values with the increasing temperature indicates that the higher temperature will favourably drive the adsorption process. Furthermore, the values of ΔG^o were not between 0 and -20 kj/mol (as observed in Nwoko et al.) [6] which shows a physio-sorption mechanism rather, they are beyond 0 and -20 kJ/mol, asserting that the adsorption is physico-chemical sorption mechanism, reflecting the influence of physico-chemical interactions between the soap molecules and barite.[21-24] This can also be asserted to the molecular architecture which favours the adsorption of the three acids in order of palmitate>oleate>laureate due to the influence of chain length and degree of unsaturation.

Effect of Molecular Architecture

Effect of molecular architecture on sodium laureate adsorption on barite

It is known that short chain length leads to high water solubility and weaker hydrophobic interaction with the mineral surface.[24] This was reflected in the effects of initial concentration, pH, adsorbent dosage, temperature and contact time adsorption of sodium laureate on barite in the present study, whereby sodium laureate adsorption was lowest and weaker in all cases unlike the observed cases in sodium palmitate and sodium oleate adsorption. Furthermore, the weak electrostatic attraction between the carboxyl group and Ba^{2+} surface ions formed fewer stable monolayers compared to longer-chain acids giving rise to lower adsorption affinity and surface coverage of sodium laureate on barite.[24]

Effect of molecular architecture on sodium palmitate adsorption on barite

Longer chain enhances van der Waals interactions, promoting stronger adsorption and tighter molecular packing.[25,26] This was clearly reflected in the effect of pH, adsorbent dosage and temperature where palmitate adsorption is higher than laureate and oleate adsorption while moderate in initial concentration and contact time. Additionally, low solubility of sodium palmitate in water, which favors monolayer formation at the palmitate–barite interface, demonstrates high surface affinity by displacing water molecules on the barite surface effectively resulting to highest adsorption density and stable film formation.[25,27]

Effect of molecular architecture on sodium oleate adsorption on barite

The molecular structure of oleate which contains a cis-double bond has the ability of introducing a kink in the hydrocarbon chain thereby causing reduction in molecular packing density, resulting in less compact adsorption monolayers.[5] This also reflected in oleate adsorption onto barite in the effect of pH, adsorbent dosage and temperature where sodium palmitate adsorption density supersedes that of sodium oleate. Nonetheless, the long chain of oleate still supports moderate hydrophobic interaction with the barite surface resulting higher and moderate adsorption on barite in the effect of initial concentration and contact time respectively. Moderate adsorption strength, with potential for dynamic and reversible surface modification.[27]

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IV. Conclusion

The comparative kinetic sorption analysis of sodium palmitate, oleate, and laurate on barite in aqueous solution has provided a valuable insight into the adsorption behavior of these fatty acids. Through systematic experimentation, it has been established that the adsorption kinetics of these surfactants on barite surface are influenced by various factor such as concentration, pH, temperature, adsorbent dosage and contact time. It has been confirmed in this study that molecular architecture of fatty acids (specifically sodium laureate, palmitate and oleate) significantly influences their adsorption behavior on barite surfaces in aqueous solutions. Chain length promotes stronger hydrophobic interaction, while unsaturation (cis-double bonds) introduces structural kinks that reduce packing density. Palmitic acid, due to its long, saturated chain, exhibits the highest adsorption affinity and stability, while oleic acid offers a balance of surface activity and molecular flexibility. Lauric acid, though more soluble, demonstrates lower adsorption potential due to its short chain and weaker interactions. The positive change in ΔH^o showed that the reactions were endothermic and the increasing randomness of soap molecules is driven by the positive values of ΔS^o with the highest form of randomness in pamitate>oleate>laureate. The values of the standard free energy are beyond 0 and -20 kJ/mol, asserting that the adsorption is physico-chemical sorption mechanism, reflecting the influence of physico-chemical interactions between the soap molecules and barite. This can also be asserted to the molecular architecture which favours the adsorption of the three acids in order of palmitate>oleate>laureate due to the influence of chain length and degree of saturation. The finding of this study underlines the importance of understanding the interaction between different surfactants and mineral surfaces, which can have implication on mineral processing,

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