

An Experimental Investigation of Pristine Barite Adsorption on Sodium Oleate and Sodium Palmitate

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Abstract: Characterization of the pristine barite mineral was established using a scanning electron microscope (SEM) and Fourier Transform Infra-Red (FTIR). Barite was applied for sodium oleate and sodium palmitate adsorption in aqueous solutions. Equilibrium adsorption data were fitted into two adsorption isotherms, three kinetic models and thermodynamic study. The concentration of the ion and pH in the solution proved to be a controlling factor in the adsorption process. Sodium oleate and sodium palmitate soaps adsorbed strongly onto the barite mineral at pH 9 and a temperature of 293K. They result was affected by the high bulk density and chemical resistance nature of barite indicated by successive increase in dosage amount. The effect of concentration and time typically gave a C-type adsorption isotherm. Adsorptive isotherm showed that sodium palmitate adsorption over natural barite was better described by the Langmuir adsorption isotherm while oleate desorption gave a good fitting with Freundlich isotherm. The adsorptive kinetics of sodium palmitate fitted well into pseudo 1st order and 2nd order kinetics. Intra particle diffusion was not the rate-determining step. Thermodynamic study showed a physio-sorption that was exothermic. Hence the findings showed that pristine barite absorbs at optimum pH and temperature of 9 and 293K.

Keywords: Barite, Adsorption, Sodium Palmitate, Sodium Oleate

1. Introduction

Surfactant adsorption by barite in aqueous solutions are of scientific interests; for purification and flotation processes. Adsorption study of BaSO₄ as anionic collector revealed hydrocarbon length of surfactants to be a major determinant in surface and thermodynamic properties of surfactants. Likewise, the adsorption effectiveness of the surfactant and BaSO₄ collector was predicted using modified Frumkin adsorption isotherm [1]. Researches have shown that pH, dosage amount and surface charges are important parameters during floatation processes. Common surfactants such as sodium laureate, sodium oleate, sodium dodecyl and sulfonate can modify the nature of adsorption [2, 3]. Barite also carries a negative charge at 0.3 point charges per 100 nm² arising from Ba²⁺ ions dissolution. Additionally, there is an observed change in the dissolution behaviour of barite (001) in the presence of NaCl solution concentration [4, 5].

Hence, it then means that BaSO₄ (adsorbent) surface charges can be modified by using surfactants in-place of adsorbates. In a similar study of barite formation in sea water. The results showed that barium concentration doubled and tripled in different samples wherein barite source was contributed by both unlabelled plankton and surrounding water [6]. Also, another study showed that there are natural isotope ratios and variations in Ba, and its pristine adsorption through silica gel surface favoured Ba heavier isotopes [7].

Therefore, additional factors modulate the relationship of BaSO₄ dissolution and its use as a collector. First-order kinetics elucidation of such factor showed the desorption of BaSO₄ was the rate-determining step rather than volume diffusion, while precipitation followed a second-rate law [8]. Interestingly, nucleation and growth study of barite showed that hydroxyl ions (high pH) affect the interaction between water molecules and barite building units, while carbonate ion in aqueous solution above a certain carbonate

concentration inhibits its growth [3, 9]. These enhancements by CO_3^{2-} and OH^- ions onto the barite structure, changes the surface characteristics and may provide evidence for other potential interactions by surfactants to a measurable degree [3, 8]. In another study, adsorption isotherm of anionic surfactants by barite was enhanced by non-ionic surfactants, while changes in the micelle composition is a factor driving the adsorption of anionic surfactants mixture on barite [10]. Experimental study also revealed that sodium dodecyl sulphate when used with sodium silicate can recover barite from calcite up to 95% [11]. Whereas, the adsorption of octyl hydroxamate on barite indicated a surface reaction and chemisorption mechanism [12].

On the contrary, the interaction of oleic acid with fluorite, calcite and barite showed that multilayers of metal oleate prevents dissolution of the minerals [13]. Hence chemisorption mechanism and monolayer coverage by surfactants are proposed to provide a meaningful interaction using adsorptive functions. Also, a typical detergent consists of surfactants, enzymes, builders and bleaching agents; the surfactant having the ability to adsorb at surfaces and interfaces in an oriented fashion [14]. Additionally, 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 [15]. Also, most surfactant head groups and hydrocarbon chains are influenced by the form of adsorption of the surfactant at any given surface in solution [16]. Thus, surfactants can modify surface properties of a system, causing preferential orientation for optimum interaction at the interface [14]. Therefore, this present study investigates for the first time, detailed adsorptive studies of barite adsorption over sodium oleate and sodium palmitate surfactants.

2. Materials and Method

2.1. Sample Collection and Characterization

Natural white Barite (BaSO_4) rock-like samples was obtained from rock and mineral display unit of the Department of Geology, Federal University of Technology Owerri and originated from Obubra L.G.A in Ikom Cross River state, Nigeria. The Obtained barite samples were characterized using scanning electron microscope (SEM) of PHENOM ProX Model and fourier transform infrared Spectroscopy (FTIR) of Perkin Elmer 8790 model instruments, were used to observe the microstructure and mineral absorption spectra of barite [17-21]. The concentration of adsorbates were determined using Perkin Elmer Lambda 850 UV/VIS Spectrophotometer [22].

2.2. Preparation of Adsorbent

Weighed barite samples of 50 g were first washed in triply distilled water and dried. The dried samples were ground to the desired size and sieved through a 50 μm mesh sieve. The obtained fine white powder was stored in a crucible. Oleic

acid, Lauric acid and sodium hydroxide used were analytical grade reagents of 98% purity. The concentration of soap samples was obtained from the calibration plots of the concentration against the absorbance.

2.3. Preparation of Adsorbate

Each of 50 g lauric acid and 50g of Oleic acid was each added to 50 mL of 30% sodium hydroxide solution contained in different 500 cm^3 Erlenmeyer flask, respectively. 30 mL of ethanol was added to each flask. The mixture was heated for 50 minutes at 100°C in a water bath with continuous stirring until it formed a creamy pasty soap. 50 cm^3 of hot saturated sodium chloride solution was slowly added to the pasty soap with vigorous stirring for 1 hr at 40°C to ensure uniform distribution. The mixture was allowed to cool for 24 hrs. The soap cake formed on the surface of the lye was removed and air dried before storing in labelled plastic containers [22].

2.4. Determination of Adsorption Parameters

2.4.1. Determination of pH

50 mL of sodium oleate and sodium palmitate each, having a concentration of 160 mg/L was weighed into two different 250 cm^3 Erlenmeyer flask and their pH kept at 7.0 using 0.1 M HCl. 0.5g of barite was added into each flask and vigorously agitated using a magnetic stirrer for 30 mins at 303 K and then centrifuged for 60 mins at 5,000 rpm. The reaction mixtures were filtered, and the filtrates analysed using Perkin Elmer Lambda 850 UV/Vis Spectrophotometer. The procedure was repeated for pH 3, 5, 9 and 11 respectively. A calibration curve of adsorption capacity against pH was prepared [23, 24, 25, 26].

2.4.2. Determination of Adsorbent Dosage

The adsorbent (barite) dosage of 0.5 g was weighed out in twofold into two different Erlenmeyer flask. 50 mL of sodium oleate and 50 mL of sodium palmitate having concentrations of 160 mg/L were kept at pH of 7.0, and was then transferred into each of the flask. The two flasks were vigorously agitated for 30 mins using the magnetic stirrer at 303 K and then centrifuged for 60 mins at 5,000 rpm. The solution was filtered, and the filtrates analysed for their respective concentration spectrophotometrically. The procedure was repeated for 0.1, 0.3, 0.7 and 1 g of the adsorbent [23-26].

2.4.3. Determination of Concentration

From the two stock solutions (160 mg/L) of sodium oleate and sodium palmitate, various soap samples were diluted to the required concentration in glass stopper volumetric flask with distilled water. The following soap concentrations were prepared: 30, 60, 90, 120 mg/L and each was kept in a glass bottle and labelled. 0.5 g of adsorbent was weighed into 250 cm^3 Erlenmeyer flask containing 50 mL of sodium oleate and another flask 50 mL of sodium palmitate at 160 mg/L concentrations each. The solution was vigorously agitated for 30 mins on a magnetic stirrer at 303 K and then further centrifuged for 60 mins at 5,000 rpm. The reaction mixture

was filtered and the filtrate analysed spectrophotometrically. The procedure was repeated for 30, 60, 90, 120 mg/L concentrations of both sodium oleate and sodium palmitate respectively [23-26].

2.4.4. Determination of Contact Time

0.5 g of barite adsorbent was weighed into two different flasks each. 50 mL of sodium oleate and sodium palmitate at a concentration of 160 mg/L was weighed into the flask and pH kept at 7.0. The solution was vigorously agitated for 30 mins on a magnetic stirrer at 303 K and then further centrifuged at 30 mins at 5,000 rpm. The reaction mixture was filtered and the filtrate from each of the flask analysed spectrophotometrically. The procedure was repeated for 60, 90, 120 and 150 mins for each of the adsorbates respectively [23-26].

2.4.5. Effect of Temperature

The temperature effect was studied for sodium palmitate and sodium oleate adsorption on barite surfaces. 0.5 g barite

adsorbent was weighed into two different flasks and 50 mL volume of adsorbates (sodium oleate and sodium palmitate) at 160 mg/L concentration each was added into the flasks and kept at 303 K with the pH kept at 7.0. The reaction mixture was agitated on a magnetic stirrer for 30 minutes and transferred to centrifuge for 60 mins at 5000 rpm. The solution was then filtered and the filtrates analysed spectrophotometrically to determine its concentration. The final procedure was repeated for 283, 293, 303, 313 and 323 K for both sodium oleate and sodium palmitate [23, 24, 25, 27].

2.5. Adsorption Functions

A number of literature and published works have provided reasonable and sound descriptions of adsorption isotherms and adsorption kinetics based on different materials and minerals analysed in their research works [27, 28, 29, 30, 31]. Hence, the selected adsorptive functions for this work will be briefly tabulated below.

Table 1. Adsorptive functions for barite adsorption of sodium oleate and sodium palmitate.

PARAMETER	FORMULAE	DESCRIPTION
Langmuir	$\frac{Ce}{qe} = \frac{1}{qmK_L} + \frac{Ce}{qe}$	Assumes a uniform energy of adsorption to describe a monolayer adsorption with homogenous layer of adsorbed solute at a constant temperature
Freundlich	$\log qe = \log K_f + \frac{1}{n} \log Ce$	Assumes exponential variations in energy sites of adsorbents involved with fall in heat of adsorption expressed in logarithm
Pseudo 1 st order	$\ln(qe - qt) = \ln qe - K_1 t$	The plots of $\ln(qe - qt)$ versus t give a straight line graph. The values of the rate constants K_1 and theoretical equilibrium adsorption capacities qe (theoretical) at different concentrations and temperatures can be calculated from the slopes and intercepts of the linear plots
Pseudo 2 nd order	$\frac{t}{qt} = \frac{1}{K_2 qe} + \frac{t}{qe}$	Based on the assumption that chemisorption is the rate-determining step. The plots of t/qt versus t give a straight line graph. Values of k_2 and qe calculated from the linear plots of t/qt vs. t for different initial concentrations and temperatures
Intra particle diffusion	$Q_t = K_i t^{1/2} + C$	It investigates the mechanism of adsorption by interpreting the straight line plot of qt versus $t^{1/2}$ as the adsorption process. If the line passes through the origin, it is the rate determining step in the adsorption process. But, if the plot is of multi linear plots, then several steps are involved in the adsorption process like film diffusion and intra particle diffusion.
Thermodynamic study	$\Delta G^\circ = -RT \ln K_c$ $\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$	Effects of temperature on the nature, feasibility and spontaneity of adsorption of soap molecules by natural barite will be explained by the thermodynamic parameters (ΔG° , ΔH° and ΔS°)

Langmuir: C_e is the equilibrium concentration of soap molecules (mg/L), q_e is the quantity of soap molecules adsorbed onto barite surfaces at equilibrium (mg/g) q_m is the maximum monolayer adsorption capacity of adsorbent (mg/g) and K_L is the langmuir adsorption constant. R_L determines the favourability of adsorption process and formula.

expressed as $R_L = (1/(1+K_L C_0))$.

Freundlich: q_e is the quantity of soap molecules adsorbed at equilibrium (mg/g), C_e is the concentration (mg/L) of soap solution at equilibrium; K_1 and n Freundlich constants incorporating the factors affecting the adsorption capacity and adsorption intensity.

Pseudo 1st order: q_e is the quantity adsorbed at equilibrium (mg/g) and qt is the quantity adsorbed at time t (mg/g). K_1 is the rate constant for the pseudo 1st order adsorption.

Pseudo 2nd Order:

Pseudo 2nd order: K_2 is the rate constant of the kinetic equation in $g/mg \text{ min}^{-1}$, q_e is the maximum sorption capacity in mg/g and qt (mg/g) is the amount of sorption at time t .

Intra-particle diffusion: qt (mgg^{-1}) is the amount of soap molecules adsorbed at time t and K_i ($mgg^{-1} \text{ min}^{-1/2}$) is the rate constant for the equation. C gives the expression for thickness of the boundary layer. A large value of C suggests great boundary layer.

Thermodynamics: R is gas constant ($8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$) and T is absolute temperature in Kelvin, R is the gas constant and K_c can be obtained from q_e/C_e . A plot of $\ln K_c$ versus $1/T$ gives a linear graph and ΔH° and ΔS° can then be calculated from the slope and intercept of the plot.

3. Results and Discussion

3.1. Sample Characterization

3.1.1. SEM Analysis

The sample micrograph of barite from Obubra can be seen in

the Figure 1 below at magnifications of 500x and 1500x. The scan revealed the different particle sizes (< 60 microns) of the barite mineral. Also, the scan showed that barite is a mixture of different minerals of chemical compositions traceable to their colour orientation from black to ash and grey. Likewise, at 1500x magnification, pore structure and sharp edges that will assist adsorption of soap molecules can be observed. Similarly,

the SEM micrograph also showed high surface area of samples useful in molecular adsorption [20, 21].

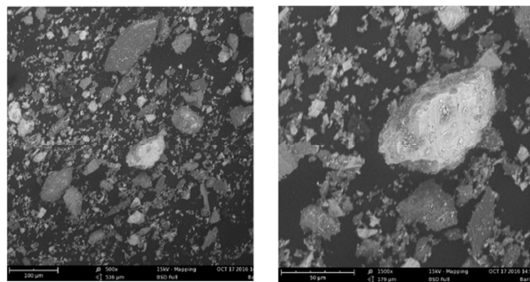


Figure 1. SEM image of Obubra barite at 500x and 1500x magnification.

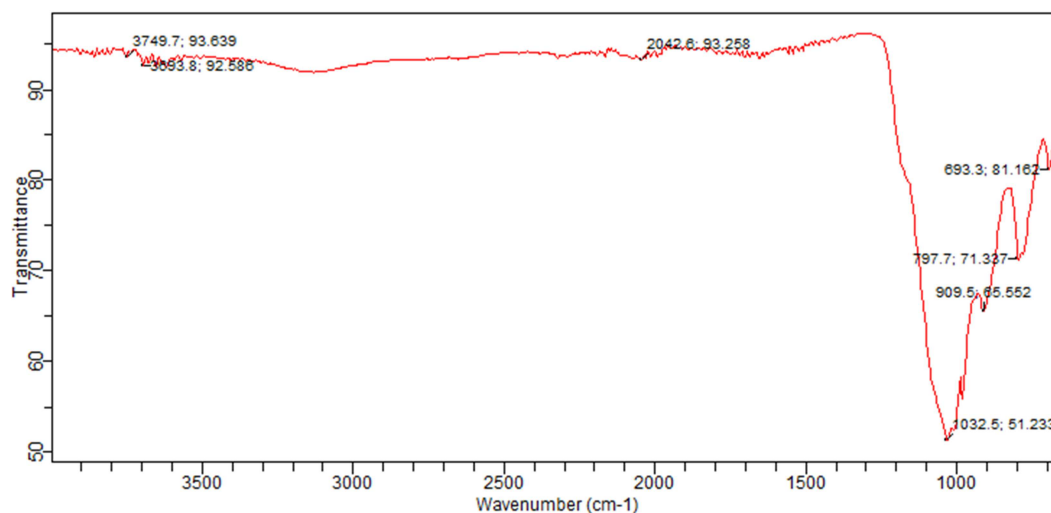


Figure 2. The FTIR spectra of Obubra barite sample.

Table 2. Vibrational frequency and assignment of Obubra barite sample.

Band (cm ⁻¹)	Strength	Assignments
3749.7	Medium	-OH Stretching
3693.8	Medium	-OH stretching
2042.6	Medium	Ba-S-O Stretching and bending vibrations
1032.5	Strong	Asymmetric stretching and bending vibrations
909.5	Strong	Triply asymmetric S-O stretching mode
797.7	Strong	stretching of SO ₄ ²⁻
749.7	Strong	Stretching of CO ₃ ²⁻
693.3	Strong	Ba-S-O ₁₂ polyhedral stretching vibration (sheet structure)

3.2. Adsorption Parameters

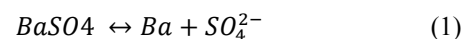
3.2.1. Effect of pH

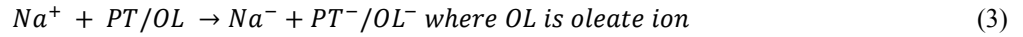
pH is one of the most important parameters controlling adsorption of metals in aqueous solutions. Figure 3(a) shows the effect of pH on barite removal efficiencies of sodium oleate and sodium palmitate. The studies were conducted for sodium oleate and sodium palmitate ions at varied pH over barite. The soap adsorption was significantly changed over the varied pH range. The soap adsorption was highest at pH 9 (15.00 mg/g and 14.40 mg/g) for sodium oleate and sodium palmitate, respectively. The lowest soap adsorption was recorded at pH 11 (12.33 mg/g and 11.57 mg/g) for sodium oleate and sodium palmitate, respectively. The equilibrium adsorption (q_e) was found to increase with increasing pH. At

3.1.2. FTIR Analysis

The FTIR spectra of Obubra barite sample is shown in figure 2 and interpreted in table 2. The spectra showed several significant bands: 3 medium bands with -OH and Ba-S-O stretching and bending. There were also 5 strong bands with asymmetric stretching. The result also showed that Ba is surrounded by 12 oxygens of 7 SO₄ tetrahedral. The peak at 749.7 and 797.7 suggests the presence of calcite and metallic oxide impurities such as Al-O and Si-O. The Ba-S-O suggests a sheet structure. Such bands discussed above have also been similarly reported in different research literatures [17, 18, 19, 21].

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. Also this study shows that critical micelles concentration of sodium oleate and sodium palmitate changes at high pH value of 11. The following equations could explain the rapid decrease in adsorption of sodium oleate or palmitate onto barite:





The reactions showed that the decrease in adsorption of sodium oleate/palmitate could also be explained in terms of solubility of BaSO_4 and Na oleate/palmitate in aqueous solution. Thus it can be inferred that agglomeration of Na-oleate/palmitate on barite surfaces decreases due to the

increase in solubility. Finally, there was a depression of adsorption at pH 11 which is comparable to studies by Offor et al. [24] and Alinnor et al. [26] that hematite and calcite natural ores are depressed by sodium oleate at pH 8.3 and 9 respectively.

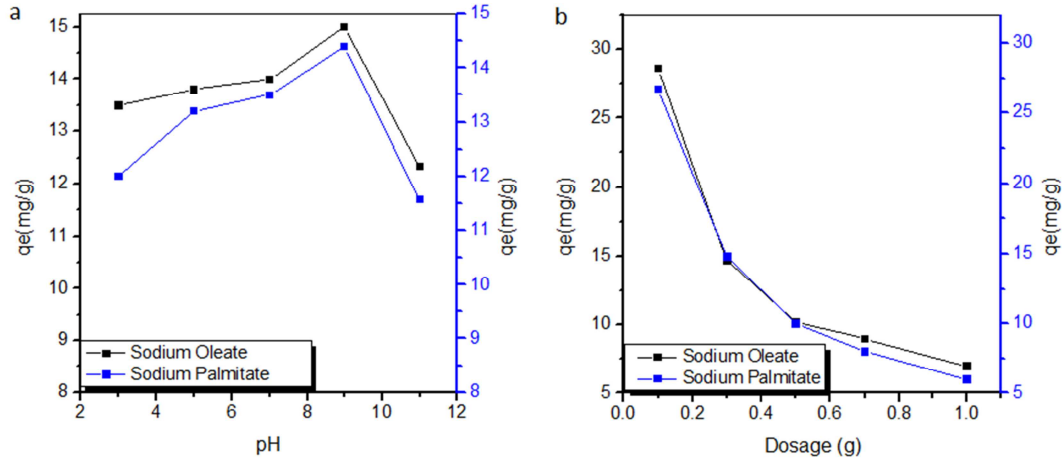


Figure 3. (a) Effect of pH on adsorption of soap molecules on natural barite; (b) effect of adsorbent dosage on adsorption of soap molecules on natural barite.

3.2.2. Effect of Dosage

The effect of the adsorption dosage of barite samples was studied by varying amounts of adsorbent while keeping other parameters constant. Figure 3(b) shows the effect of adsorbent dosage on soap adsorption. The adsorption capacity of soap adsorbed on barite samples was decreasing with the increasing adsorbent dosage. The adsorption decreased significantly as dosage increased from 0.1 to 1 g and then tends toward saturation at almost 95 % and 84 % for sodium oleate and sodium palmitate, respectively. The results showed that increasing dosage amount lead to to decrease in adsorption capacity owing to the high bulk density and chemical resistance nature of barite [19].

3.2.3. Effect of Contact time

The effect of contact time on the adsorption of sodium oleate and sodium palmitate from aqueous solution by barite is presented in figure 4(a). The initial concentration of soap in aqueous solution was 160 mg/L. A general increase in soap adsorption with contact time was observed at the initial stage until 100 minutes. 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 100 minutes for sodium oleate and sodium palmitate. The adsorption capacities got are 14.62 mg/g and 13.80 mg/g for sodium oleate and sodium palmitate respectively at agitation time of 100 minutes.

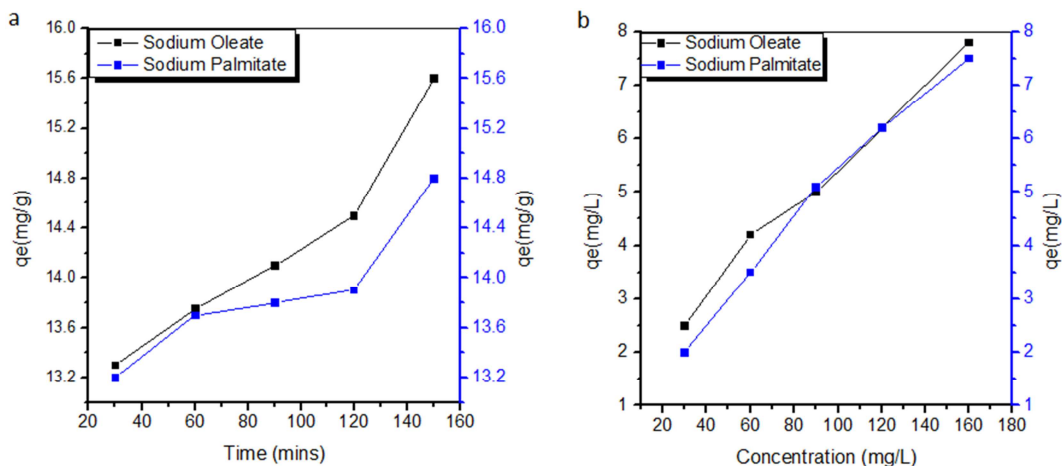


Figure 4. (a) Effect of time on adsorption of soap molecules on natural barite; (b) effect of concentration on adsorption of soap molecules on natural barite.

3.2.4. Effect of Concentration

The effect of the initial soap concentration on the adsorption of sodium palmitate and sodium oleate on barite adsorbent dosage of 0.50 g was plotted in a graph in figure 4(b). It would be seen that the adsorption at different concentrations was rapid initially, with a proximate linear graph. The amount of soap adsorbed at equilibrium (q_e) increased from 2.63 to 7.90 mg/g and 2.06 to 7.45 mg/g as concentration increased from 30 to 160 mg/L for sodium oleate and sodium palmitate, respectively. The initial concentration delivers an important driving force to overcome all mass transfer resistances of the barite between the aqueous and solid phases. The soap removal increased to 87 % and 80% for sodium oleate and sodium palmitate respectively as the soap concentration was increased from 30 to 160 mg/L. 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 (almost a linear relationship) [25]. 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 [28].

3.2.5. Effect of Temperature

The effect of temperature on sodium oleate and sodium palmitate adsorption from aqueous solution onto natural barite surface was investigated from temperatures of 283 K to 333 K. From figure 5 below, it showed that the adsorption of soap molecules increases with an increase in temperature. The increase in adsorption capacity of soap with temperature gave an endothermic process. The increase in adsorption with temperature can be attributed to (i) an increase in the number of active surface sites available for adsorption on the adsorbent or adsorbate of adsorbing species and, (ii) the decrease in the thickness of boundary layer surrounding the

adsorbate. At a higher temperature the possibility of diffusion of solute within the pore of the adsorbent may be enhanced leading to higher adsorption density 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 oleate had the higher adsorption capacity (14.30 mg/g) than sodium palmitate (13.56 mg/g) at the temperature of 323 K, and their adsorption gradually decreased again as the temperature increased to 333 K. This temperature effect is a case of H isotherm where the soap molecules exhibited higher affinity for the barite at 283 and 293 K before appearing nearly saturated to further increase [28].

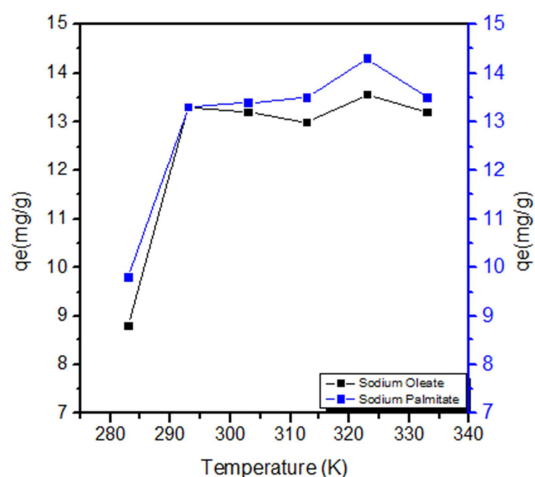


Figure 5. Effect of temperature on adsorption of soap molecules on natural barite.

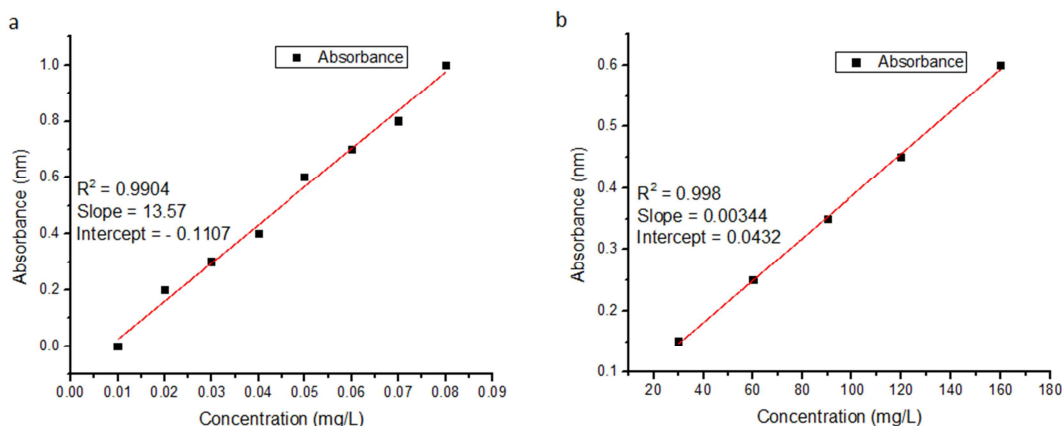


Figure 6. (a) Calibration curve for *p*-nitrophenol at 318 nm for Barite; (b) Isotherm Calibration curve graph for sorption onto Barite at 303 K.

3.3. Adsorptive Functions

Determination of specific surface area was done by

solution adsorption of *p*-nitrophenol. Calibration curve for *p*-nitrophenol at 318 nm for barite is shown below in figure 6(a) while isotherm calibration graph for sorption onto barite at 303 K is in figure 6(b). The surface area was calculated

from the Langmuir plot using the equation of surface area below [24, 26].

$$S.A = \frac{X_m A_m L}{N}$$

Where X_m is amount of solute adsorbed at monolayer per gram of adsorbent (mg/g).

A_m is cross-sectional area occupied by the adsorbate (m^2).

L is Avogadro number

N is coverage factor

The surface area of barite was calculated to be $2.00 m^2/g$. Hence, a similar surface area had been previously observed for barite to be $2.71 m^2/g$ [25].

3.3.1. Adsorption Isotherm

The Langmuir plot which shows monolayer coverage for the adsorption of sodium oleate and sodium palmitate is

presented in figure 7(a) and adsorptive functions shown in table 3. The graph had no negative slope, nor intercept, and adsorption increased as q_e (amount adsorbed at equilibrium) increased. Hence, a positive interaction between the natural barite and soap molecules. The residual plots showed no pattern or trend; a sign of good fitting. The R^2 (correlation coefficient) fitting of sodium palmitate (0.965) provided a better fit than sodium oleate (0.895). The K_L shows the binding strength of the soap molecules on the barite surface and showed corresponding higher value of 36.1 in palmitate than oleate at 15.7. The R_L which is the dimensionless constant was > 0 but < 1 in both soap molecules which showed a favourable reaction. Thus the palmitate adsorption over natural barite was better described by a Langmuir adsorption isotherm.

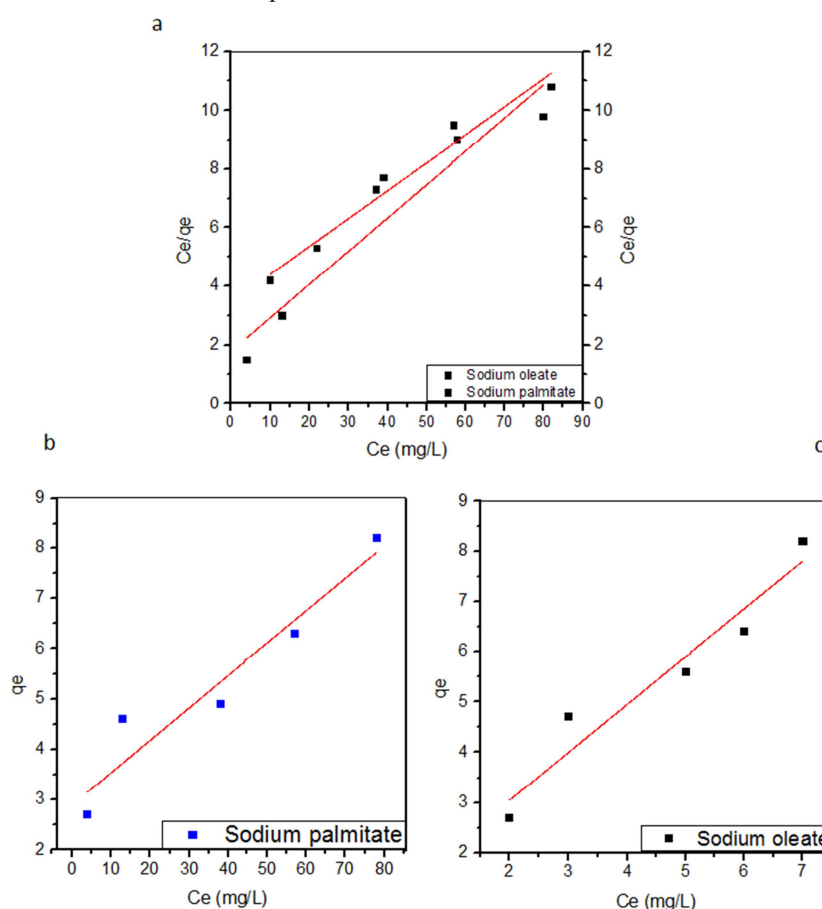


Figure 7. (a) Langmuir; (b) Freundlich for palmitate; (c) Freundlich for oleate on natural barite.

The Freundlich which explains the distribution of solutes between an aqueous solution and solid phases is presented in figure 7 (b) and (c). Residual plots were without pattern and trend. The graph gave a positive intercept and slope which describes energetically favourable reaction. These may occur because q_e (The q_e is known as the loading of adsorbate on the adsorbent, attained at equilibrium) increases as C_e is increased. The Freundlich constant K_F represents the adsorption capacity, was better at 3.04 in palmitate than 1.21 in oleate. The strength (energy) n , of the adsorption showed

that at 0.951 oleate presented a stronger binding force than palmitate at 0.0644. However, both 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 (0.914) gave a good fitting compared to palmitate at (0.896) with $1/n$ at 15.5 showing a slower mechanism. Thus it will be said sodium oleate was better described by the Freundlich adsorption isotherm.

3.3.2. Adsorption Kinetics

The graphs of pseudo 1st order is presented in figure 8 and parameters in table 3. Pseudo 1st order had $q_{e(cal)}$ larger than $q_{e(exp)}$. It shows that concentration of the adsorbed soap molecules in the experiment was much lower than the concentration of adsorbed soap molecules got by calculation. The K_1 which represents the rate constant was 0.0785 ($\text{g.mg}^{-1}\text{min}^{-1}$) in oleate and 0.169 ($\text{g.mg}^{-1}\text{min}^{-1}$) in palmitate and represents a small fraction of adsorption rate regarding time. Also, the slope and intercept as seen in table 3 were small absolute values which correlated with the rate constant. Also, the correlation coefficient of oleate was 0.944 while that of palmitate was 0.972. Although the R^2 were of good fitting, however, this adsorption study of soap molecules by natural barite shows that pseudo 1st order provided a good fitting in adsorption of soap molecules. This may be because of a surface area of natural barite containing pores sufficient to adsorb and keep the soap molecules on their surfaces as seen in Figure 1. Thus sodium palmitate was better described by

pseudo 1st order adsorption kinetics having a better R^2 and K_1 .

The graph of pseudo 2nd order function in figure 8(b) showed a positive correlation of adsorption capacity with time. They parameters are shown in table 3. The H ($\text{mg.g}^{-1}\text{min}^{-1}$) of the pseudo 2nd order that showed the initial adsorption rate of soap molecules by natural barite was the same in both adsorbates; an indication of suitability of experimental data. The adsorption rates constant K_2 was 2.57 ($\text{g.mg}^{-1}\text{min}^{-1}$) in oleate and 2.43 ($\text{g.mg}^{-1}\text{min}^{-1}$) in palmitate and showed a fast reaction kinetics. However, the $q_{e(cal)}$ from pseudo 2nd order was small in both adsorbates. Hence this shows a good agreement and the applicability of this kinetic function to evaluate adsorption of sodium palmitate and oleate over natural barite mineral. The correlation coefficients at 0.966 (palmitate) and 0.962 (oleate) gave a better fitting than pseudo 1st order kinetics. Thus palmitate experienced an improved adsorption kinetics.

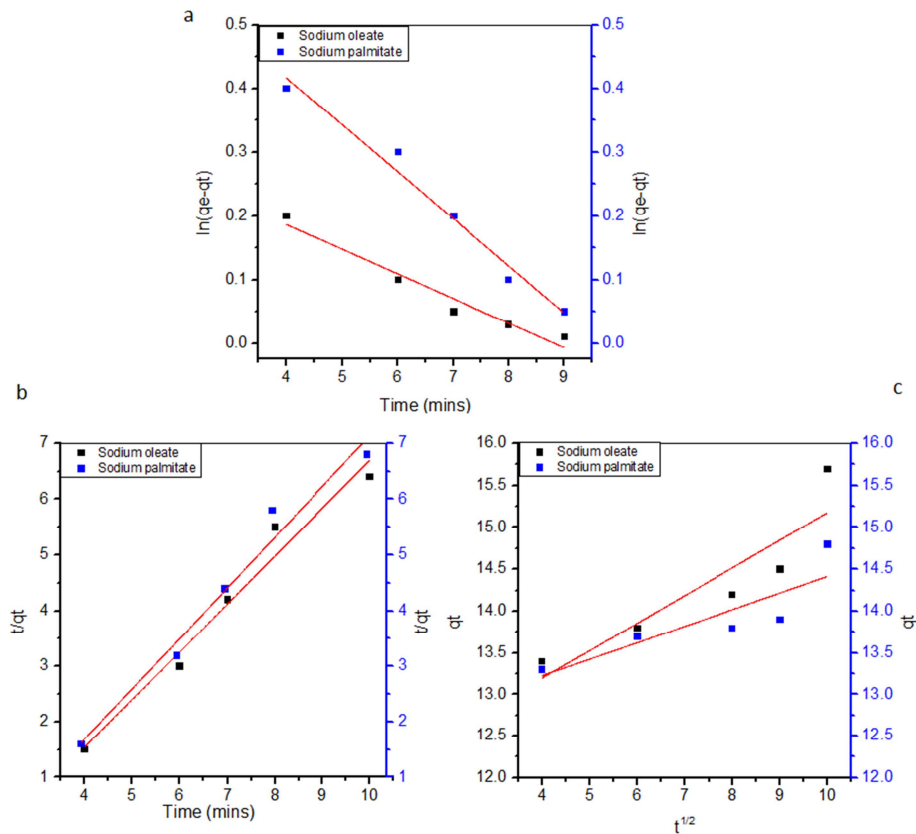


Figure 8. (a) pseudo 1st order; (b) pseudo 2nd order; (c) intra particle diffusion for adsorption of soap molecules over natural barite.

Table 3. Showing adsorptive functions and parameters of barite adsorption of soap molecules.

	Sodium oleate		Sodium palmitate	
Langmuir	$Q_m(\text{mg/g})$	0.558	$Q_m(\text{mg/g})$	0.291
	$K_L(\text{L/mg})$	15.7	$K_L(\text{L/mg})$	36.1
	R_L	3.97E^{-4}	R_L	1.73E^{-4}
	R^2	0.895	R^2	0.965
	$K_F(\text{mg/g})(\text{L/mg})^{1/n}$	1.21	$K_F(\text{mg/g})(\text{L/mg})^{1/n}$	3.042
Freundlich	n	0.95	n	0.0644
	$1/n$	1.05	$1/n$	15.5
	R^2	0.914	R^2	0.896

	Sodium oleate		Sodium palmitate	
Pseudo 1 st order	Q _e (exp)(mg/g)	-1.41	Q _e (exp)(mg/g)	-0.148
	Q _e (cal)(mg/g)	1.09	Q _e (cal)(mg/g)	5.14
	K ₁ (g.mg ⁻¹ min ⁻¹)	0.785	K ₁ (g.mg ⁻¹ min ⁻¹)	0.169
	R ²	0.944	R ²	0.972
Pseudo 2 nd order	H _(mg.g-1min⁻¹)	4.44	H _(mg.g-1min⁻¹)	4.44
	Q _e (cal)(mg/g)	1.16	Q _e (cal)(mg/g)	1.09
	K ₂ (g.mg ⁻¹ min ⁻¹)	2.57	K ₂ (g.mg ⁻¹ min ⁻¹)	2.43
	R ²	0.962	R ²	0.966
Intra-particle diffusion	K _{id} (mg/g/min)	0.331	K _{id} (mg/g/min)	0.198
	C (mg/g)	11.8	C (mg/g)	12.4
	R ²	0.766	R ²	0.663

The intra particle diffusion did not provide a good fitting with R² at 0.663 in palmitate and 0.766 in oleate. The boundary layer thickness (C) showed a considerable layered thickness at 11.8 in oleate and 12.4 in palmitate. The K_{id} known as the intra-particle rate constants were 0.331 and 0.198 been small values < 1; hence affected the rate constant. Thus the intra-particle diffusion was not the rate-determining step in the adsorption processes and their graph did not pass through the origin but had intercept C > 0 < 1. Hence, the mechanism was affected by some other adsorptive process in the system (multi-linear plots), albeit oleate is better described by intra particle diffusion than palmitate.

3.3.3. Thermodynamic Study

From the table 4 presented below, it shows that the reaction was spontaneous due to negative ΔG⁰ values. The decrease in ΔG⁰ negative values with the increasing temperature indicates that the higher temperature will favourably drive the adsorption process. Then again, ΔG⁰ was between 0 and -20 kJ/mol which shows a physio-sorption mechanism. The negative change in ΔH⁰ showed that the reaction was exothermic in nature accompanied by increasing randomness of soap molecules driven by the positive ΔS⁰ values that can be reversible. Hence a desorption study may be carried out by future researchers.

Table 4. Thermodynamic parameters for the adsorption of soap onto natural barite.

Adsorbents	ΔH ⁰ (kJ/mol)	ΔS ⁰ (J/mol/K)	ΔG ⁰ (KJ/mol)					
			283	293	303	313	323	333
Sodium oleate	-0.85	0.05	-2.93	-2.85	-2.75	-2.62	-2.57	-2.49
Sodium palmitate	-1.13	0.75	-3.21	-3.09	-2.97	-2.85	-2.72	-2.62

4. Conclusion

The research findings demonstrated that barite can be prepared for adsorption of sodium oleate and sodium palmitate surfactants. SEM micrograph revealed pores that where potential adsorption sites while the FTIR gave bond stretching that enhances adsorption. Thermodynamic study confirmed spontaneous reaction and exothermic in nature. The effect of pH and temperature showed that at optimum values, adsorption will be enhanced. Pseudo 2nd order kinetics gave the best overall of the adsorptive functions having R² for sodium oleate as 0.962 and sodium palmitate as 0.966 respectively. Thus the study has provided novel adsorptive insight into the interaction of sodium oleate and sodium palmitate with barite mineral, and should find useful applications in industrial purification and flotation processes.

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