

Influence of Lignosulfonate Types and Electrolyte Concentrations on the Adsorption of Lignosulfonate onto Clay

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Abstract: Lignosulfonate has been reckoned as an effective sacrificial agent with the potential to minimize surfactant adsorption onto clay minerals. As such, this paper compares various types of LS at different electrolyte to determine their capability of adsorption onto kaolinite. The adsorption experiment by using depletion method had been conducted to investigate all genres of the LS. The best LS were then furthered investigated in equilibrium and kinetic condition. Adsorption at varying electrolyte values, such as NaCl (3wt%) and CaCl₂ (0.5wt%), displayed increment of sodium lignosulfonate (SLS) adsorption onto kaolinite along with escalating electrolyte. Effect of pH showed less effect on the adsorption. Moreover, adsorption isotherm models were taken up to investigate the mechanisms of LS adsorption, which exemplified not only SLS adsorption onto kaolinite was indeed favorable, but the adsorption data also best fitted and described by Freundlich isotherm models. As for kinetics adsorption, pseudo-second order appeared to be the best model that described SLS adsorption onto kaolinite. To conclude, this paper can provide insight benchmark to select the most effective sacrificial agent among the varies LS to minimize surfactant adsorption onto kaolinite.

Index Terms: adsorption, clay, lignosulfonate, equilibrium, kinetic

I. INTRODUCTION

The approach of surfactant-based enhanced oil recovery has been acknowledged as one of the most effective methods applied in Malaysia to discard any remaining oil found on surface area [1, 2]. In fact, deficiency of surfactant directly to adsorption of surfactant molecules onto reservoir rocks and clay minerals during chemical flooding seems to exhibit a direct impact upon the success of EOR [3]. Reservoirs found in Malaysia have been classified to possess high clay content. Several core samples taken from the West Malaysian oilfield recorded the presence of clay between 16% and 27% from the total rock mineralogy elements [4]. The types of clay mineralogy found in the field core had been illite/mica, kaolinite, chlorite, and illite/smectite. Nevertheless, the conventional method of using alkali to minimize surfactant

adsorption can, in the long run, cause damages to the formation and spark environmental issues [5]. Another effective method to decrease surfactant adsorption is by using sacrificial agent [6-9]. In fact, sacrificial agent has been proposed as an effective approach to reduce surfactant adsorption, especially for Malaysian reservoirs that demand further evaluation [10]. Besides, prior experimental works have revealed that lignosulfonate (LS), a waste product from paper mill, can be employed as a sacrificial agent to minimize surfactant adsorption. For instance, Hong and co-workers [11] in their laboratory tests, discovered a reduction for surfactant adsorption by 39% in Glenn Pool reservoir by using ammonium lignosulfonate (ALS). Meanwhile, Bai, et al. [9] and Syahputra, et al. [12] further obtained a 24-60% decrease in CD1045 surfactant adsorption onto Berea sandstone core and 15-29% decrease in adsorption onto Indiana limestone core samples respectively using calcium lignosulfonate.

Nevertheless, the suitability of numerous types of LS in the vast market has yet to be tested for kaolinite and information in the literature is scant to ascertain that LS is indeed a viable choice to serve as a sacrificial agent. Apart from this, most studies pertaining to reservoir rock that had incorporated LS, to date, are only associated with sandstone, dolomite, and limestone; but none for kaolinite, one of the rich clay minerals with high complexity of mineralogical composition and surface properties [3]. As such, this paper imparts a comprehensive investigation on the adsorption capacity of various types of LS onto kaolinite at varying electrolyte. With that, the goal of this study is to evaluate and to determine LS with the highest adsorption ability in kaolinite. The significant parameters embedded in this experiment were several types of LS, as well as varied LS concentrations, electrolyte and pH of the brine. As for methodology, the depletion method via UV-Visible (UV-Vis) had been employed to calculate the adsorption capacity. The adsorption data recorded from the experiments were analyzed so as to identify the best LS with the highest adsorption capacity onto kaolinite, aside from determining their fitting with Langmuir, Freundlich, and Temkin isotherm models. Hence, pseudo-first order, pseudo-second order, and intra-particle diffusion model were employed for kinetic adsorption so as to shed light on the adsorption process [13]. The findings yielded from the experimental

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work are discussed thoroughly and can be applied as a yardstick to select the most effective sacrificial agent towards reducing surfactant adsorption, particularly onto kaolinite.

II. METHODOLOGY/MATERIALS

A. Materials

Four different LS were tested in this study to determine their adsorption behaviour onto kaolinite, namely, 1) lignosulfonic acid sodium salt (SLS), 2) lignosulfonic acid calcium salt (CLS), 3) ammonium lignosulfonate (ALS), and 4) magnesium lignosulfonate (MLS). SLS and CLS (with 96% purity) were retrieved from sigma-Aldrich, Germany, while ALS and MLS (with 95% purity) were purchased from Greenagrochem, China. Whereas kaolinite was obtained from sigma-Aldrich and used directly without further cleaning and sieving processes. Besides, sodium chloride salt (NaCl) and calcium chloride salt (CaCl₂) from VCHEM were used to prepare the brine. Deionized water (DIW) from Smart2Pure water purification system by Thermo Scientific brand had been used to prepare the solutions in the experiments. Sodium hydroxide alkali (NaOH) and hydrogen chloride acid (HCl) were used to adjust the pH of the brine.

B. Experimental procedures

1) Lignosulfonate (LS)

The variance in LS exists due to the method of extracting the lignin material from woody materials [14, 15]. The related physical observations made on the properties among the varied LS are itemized in Table 1.

Table 1: Lignosulfonate properties

Properties	SLS	CLS	MLS	ALS
Appearance (color)	brown	brown	yellow brown	black
Appearance (form)	powder	powder	powder	powder
Moisture	3%-7%	3%-7%	max 7%	15%
Solubility in water	soluble	soluble	soluble	soluble
Solubility in NaCl (1-5wt%)	soluble	soluble	soluble	soluble
Solubility in CaCl ₂ (0.1-1wt%)	soluble	soluble	soluble	soluble
pH	4-7	~4	4-7	~9

2) X-ray fluorescence on Kaolinite

The kaolinite was characterized by using XRF to investigate the main component exists in the kaolinite. The XRF spectroscopic was done on the Bruker S4 PIONEER X-ray fluorescence spectrometer. An Ru target at 4 kW power was used. Table 2 shows the properties of the kaolinite.

Table 2: Kaolinite main properties

Chemical composition	Mass percentage (mass%)
SiO ₂	58.60
Al ₂ O ₃	37.20
Fe ₂ O ₃	0.55

3) Preparation of LS solutions

Four types of LSs were obtained in powder form. The LS

solutions were prepared by adding specific amounts of LS, based on the needed concentration, into 100ml of DIW in a volumetric flask. For all LS solutions, the amount of LS ranging from 0.001g – 0.15g had been used to prepare the solution concentration between 0.001wt% and 0.15wt% (10ppm to 1500ppm).

4) Critical micellar concentration (CMC) determination

In this experimental work, the aspect of critical micellar concentration (CMC) had been determined via electrical conductivity [16] by plotting the EC value against the LS concentrations [17]. As a result, two linear lines were noted from the graph and the intersection point was identified as the CMC value. Based on the UV-Vis method, the absorbance rate for each LS solution was determined and absorbance value versus LS concentrations had been plotted. CMC value was obtained at the point prior to the plateau region. Both CMC values from the two different methods were compared and cross-validated.

5) Calibration curve

The UV-Vis spectrophotometer Shidmadzu series 1800 was used to measure the concentration of the solutions before and after each adsorption test. In order to calculate the LS concentration, a standard calibration curve was established by fitting the best linear. As such, varied calibration curves were retrieved for different LS and ionic strength values.

6) Adsorption experiments

First to investigate the best LS in terms of adsorption capability under the influence of electrolyte (NaCl 1wt% and CaCl₂ 0.1wt%) and adjusted pH (range from 3 to 11), 10g of kaolinite was added into 50ml of LS solutions with varies concentration and in a 100ml glass bottle and was shook for 24 hours with a speed rotation of 150rpm and a constant temperature of 30°C, which was controlled by an orbital shaker, Sartorius Certomat. After shaken for 24 hours, the samples were left uninterrupted for another 48 hours. The LS solutions were then centrifuged using Centrifuge EBA 200, Hettich at 5000rpm for 20 minutes. Next, the equilibrium concentrations of the LS solutions had been determined by using the UV-Vis Shidmadzu 1800 series. All measurements were carried out and recorded in the average of three times. The amount of LS solutions adsorbed on kaolinite, q (mg/g), had been calculated by applying the mass balance equation, as given in equation 1 [18]:

$$q = \frac{(C_o - C_e)V}{m} \times 10^{-3} \tag{1}$$

where q=amount of LS solutions adsorbed (mg/g), C_o=Initial concentration of LS solutions (ppm), C_e=Equilibrium concentration of LS solution (ppm), V=volume of total solution (ml), and m=weight of kaolinite.

Then, LS with the highest adsorption capacity from the above experiment had to undergo several adsorptions test. The selected LS had been tested in the system containing zero salt (deionised water), NaCl 3wt% and CaCl₂ 0.5wt% in equilibrium and kinetic condition. Procedure to run the equilibrium adsorption

was similar as described above. Amount of LS solution adsorbed obtained from this experiment furthered fitting into the isotherms equilibrium model [17] to describe the process of adsorption. As for kinetic adsorption, 10g of kaolinite was added into 50ml of LS solutions with fixed concentration of 0.02wt% in a 100ml glass bottle and was shaken. The reading was recorded at the interval time set in prior until an equilibrium concentration was achieved and upon ending the experiments. The sample was later centrifuged for 20 minutes with a speed rotation of 4000rpm and the concentrations were determined using established calibration curve. The experiments took place at a constant temperature of 30°C. The amount of LS solutions adsorbed on kaolinite, q (mg/g), had been calculated by applying the mass balance equation, as given in equation 2:

$$q = \frac{(C_0 - C_t)V}{m} \times 10^{-3} \quad 2$$

where q=amount of LS solutions adsorbed (mg/g), C₀=Initial concentration of LS solutions (ppm), C_t=Concentration at any time taken of LS solutions (ppm), V=volume of total solution (ml), and m=weight of kaolinite. Amount of LS solution adsorbed obtained from the this experiment furthered fitting into the kinetic model [19] to discuss on the interaction between kaolinite and LS solution.

7) Adsorption isotherms equilibrium

The Langmuir equation, which was invented by Irving Langmuir in 1916, is as written in equation 3. This model assumes a completely homogenous adsorption surface.

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \quad 3$$

Where q_e=solid adsorbate concentration. Plotted graph of 1/q_e versus 1/C_e would reveal a straight line if the adsorption equilibrium data adhere to the Langmuir isotherm. The straight line from the graph can yield the values of q₀ and K_{ad} by taking slope and intercept respectively.

Freundlich (1906) developed an empirical model to characterize adsorption process. In the model, he presumes that an adsorbent with a heterogeneous surface has varied adsorption sites. However, due to the inability of the model to predict the saturations of adsorbent, infinite surface coverage is forecasted to specify multilayer adsorption of the surface. In precise, this model assumes multilayer adsorption on heterogeneous surface. The related mathematical equation is given as follows:

$$q_e = k_f C_e^{1/n} \quad 4$$

where, 1/n increment of solute concentration in the solution at equilibrium to the quantity of salute adsorbed (q_e). At a given temperature C_e^{1/n} / q_e remains constant and as well can be extracted by the slope and the intercept.

The Temkin model was developed by Aharoni and Tompkins after weighing in the impact of adsorbate interactions and adsorption processes. Based on the number of experimental works, increasing coverage appears to decrease adsorption heat. The adsorption is described by regular distribution of bonding energies. The mathematical

equation is presented in equation 5.

$$q_e = B \ln K_t + B \ln C_e \quad 5$$

Where, the constant is B, while K_t obtained from the slope and the intercept of the linear line graph. A summary of the equilibrium table had been presented in Table 3.

Table 3: Equilibrium adsorption models

Isotherm model	Equation	Description of parameters
Langmuir	$q_e = \frac{q_0 K_{ad} C_e}{1 + K_{ad} C_e}$	q _e = LS adsorbs (mg/g), q ₀ and K _{ad} = Langmuir constants signify the adsorption capability and energy of adsorption correspondingly C _e = LS equilibrium concentration (ppm)
Freundlich	$q_e = K_f C_e^{1/n}$	q _e = LS adsorbs (mg/g), K _f and 1/n = Freundlich constants linked to adsorption capability and adsorption intensity correspondingly C _e = LS equilibrium concentration (ppm)
Temkin	$q_e = B \ln K_t + B \ln C_e$	q _e = LS adsorbs (mg/g), B and K _t = Temkin constants related to distribution of bonding energies C _e = LS equilibrium concentration (ppm)

8) Adsorption kinetics model

Equation of pseudo-first-order rate appears to be a model that has been commonly used to calculate the adsorption rate of an adsorbate-adsorbent system. The differential mathematic equation is given as follows:

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad 6$$

where q_e (mg/g) refers to the adsorption rates at equilibrium, q_t (mg/g) denotes time t, while K₁ represents the constant rate with the unit of min⁻¹. By substituting equation 5 with the boundary conditions [q_t=0 at t=0; q_t=q_t at t=t], the equation becomes:



$$\ln(q_e - q_t) = \ln(K_1 q_e) - K_1 t \tag{7}$$

Linear graph of $\ln(q_e - q_t)$ versus t can be plotted and from the slope, value of K_1 can be found.

The pseudo-second order kinetics equation is commonly written in a differential form, as depicted in the below:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \tag{8}$$

Integration and rearrangement of equation 7 generates a linear expression that is generally relevant for solid/liquid adsorption kinetic process. The revised equation is presented in the equation 9.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

where K_2 (g/mg min) refers to the constant rate of the second-order, while the other units are similar to those found in the pseudo-first-order kinetic equation. Besides, graph t/q_t can be plotted versus t that yield the straight line can provide the equilibrium rate (q_e) and the constant rate (K_2). Meanwhile, the initial adsorption time (h) and the half-adsorption time ($t_{1/2}$) can be predicted by using equations 11 and 11, as denoted below:

$$h = K_2 q_e^2 \tag{10}$$

$$t_{1/2} = \frac{1}{K_2 q_e} \tag{11}$$

Lastly, the intra-particle diffusion model was employed to characterize and to explain the diffusion mechanism during adsorption. The related mathematical equation is given as follows:

$$q_t = K_i \times t^{1/2} + C \tag{12}$$

Plot of q_t versus $t^{1/2}$ can determine the K_i which is the constant diffusion rate from the slope of a linear while C refers to the intercept. Summary of the kinetic model shown in Table 4.

Table 4: Kinetic adsorption models

Kinetic model	Equation	Description of parameters
Pseudo-first order	$\ln(q_e - q_t) = \ln(K_1 q_e) - K_1 t$	q_e = LS adsorbs (mg/g), q_t = LS adsorbs at time t (mg/g), K_1 =constant rate for pseudo-first order (min^{-1}) and t = time
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$	q_e = LS adsorbs (mg/g), q_t = LS adsorbs at time t (mg/g), K_2 =constant rate for pseudo-second order (g/mg min) and t = time

Intra-particle diffusion	$q_t = K_i \times t^{1/2}$	q_t = LS adsorbs at time t (mg/g), K_i = constant diffusion rate and C = Constant from the intercept of the graph
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9) Error Estimation

The most frequent used for error estimation was squared coefficient regression (R^2). For this experiment, other important statistical parameter such as the absolute relative deviation and chi squared test (χ^2) used to discuss the accuracy of the model [13]. Reason to consider the ARD and χ^2 because sometimes the R^2 giving a very close results between the model and yet is hard to make decision which model is the best to choose. Thus, it is important to analyse the adsorption data using 3 error estimation functions. High R^2 and low ARD% and χ^2 values are the most satisfied scenario. Equation 13 and 14 below defined the ARD and χ^2 respectively. Value ARD% and χ^2 were small if the adsorption model similar with the experimental values and vice versa.

$$ARD\% = 100/n \sum_{n=1}^n \left| \frac{q_i^{exp} - q_i^{model}}{q_i^{exp}} \right| \tag{13}$$

$$\chi^2 = \sum_{i=1}^n \frac{(q_i^{exp} - q_i^{model})^2}{q_i^{exp}} \tag{14}$$

III. RESULTS AND DISCUSSION

A. CMC determination

CMC appears to be a significant parameter for surfactant flooding. Typically, an effective CMC that is designated to lower interfacial tension (IFT) is always below the CMC value, instead of portraying a higher value. As for this experiment, the CMC value for each LS had been determined to have a better control on the LS concentration. The related findings are presented in Table 5.

Table 5: CMC values for different type of lignosulfonate

Lignosulfonate Type	CMC value
Sodium Lignosulfonate (SLS)	0.04wt%
Calcium Lignosulfonate (CLS)	0.10wt%
Magnesium Lignosulfonate (MLS)	0.15wt%
Ammonium Lignosulfonate (ALS)	0.10wt%

B. Calibration Curve

The UV-Vis method was employed to measure the concentration of LS before and after the adsorption of the LS solutions onto kaolinite [20]. The calibration curve reflects the quantitative approach in determining concentrations by applying the Beer-Lambert law [8] with a fixed wavelength for each LS type. After that, the absorbance rates of the LS solutions were plotted against

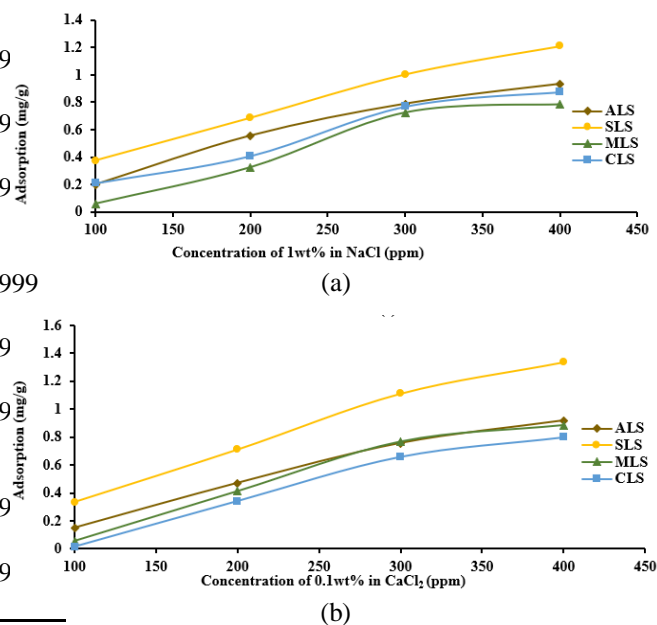


LS concentrations. A series of calibration curves are displayed in Table 6.

Table 6: Calibration curve at different LS type and electrolyte concentration

Lignosulfonate Type	Ionic Strength	Calibration	R^2
Sodium lignosulfonate (SLS) Wavelength 281nm	DIW	Conc=109.09*ABS-4.3127	0.998
	NaCl 1wt%	Conc=119.55*ABS-11.864	0.995
	NaCl 3wt%	Conc=113.34*ABS-4.2343	0.991
	CaCl ₂ 0.1wt%	Conc=121.52*ABS-11.538	0.996
	CaCl ₂ 0.5wt%	Conc=122.6*ABS-12.854	0.997
Calcium lignosulfonate (CLS) Wavelength 278.5nm	DIW	Conc=196.28*ABS+18.37	0.998
	NaCl 1wt%	Conc=208.9*ABS-15.924	0.998
	CaCl ₂ 0.1wt%	Conc=203.44*ABS+12.27	0.997
Magnesium lignosulfonate (MLS) Wavelength 275.5nm	DIW	Conc=287.49*ABS+3.388	0.999
	NaCl 1wt%	Conc=289.8*ABS+1.6342	0.999
	CaCl ₂ 0.1wt%	Conc=293.71*ABS-3.5739	0.999
Ammonium Lignosulfonate (ALS) Wavelength 273.5nm	DIW	Conc=174.14*ABS+1.744	0.999
	NaCl 1wt%	Conc=178.65*ABS+23.01	0.999
	CaCl ₂ 0.1wt%	Con=171.2*ABS-0.7511	0.999

which contains positives counter-ion Na⁺, NH₄⁺, Ca²⁺, and Mg²⁺ and while the kaolinite surface contains both negative and positive charge site [22]. In the monovalent inorganic environment, ions change the magnitude of the solid's surface by compression of the EDL without disturbing the sign of the surface potential charge [9]. While multivalent ions may adsorb to a surface of opposite charge and reverse the sign of the surface potential charge [9, 23]. In the system of monovalent 1wt% NaCl, the kaolinite surface remains negatively charge and anionic LS caused the repulsion electrostatic. SLS and ALS both having same ion counter had weaker repulsion electrostatic compared to ion counter in SLS and MLS, thus increased the adsorption. When the system become divalent with 0.1wt% CaCl₂, the zeta potential of the kaolinite surface increased positively [24]. The SLS and ALS had stronger attraction electrostatic compared to CLS and MLS, so the adsorption increased. Among SLS and ALS, SLS appeared the most favorable onto kaolinite.



C. Lignosulfonate (LS) adsorption capability at various LS, electrolytes and pH

In the electrolyte of 1wt% of NaCl, difference adsorption capability portrayed in the comparison of four LS. Sequence of SLS>ALS>CLS>MLS had been obtained (Fig. 1a). At the concentration of 400ppm of LS, amount of SLS adsorbed onto the kaolinite surface was 1.211mg/g followed by ALS 0.934mg/g, CLS 0.874mg/g and MLS 0.782mg/g. When the electrolyte changed to 0.1wt% of CaCl₂, sequence of SLS>ALS>MLS>CLS were observed and in the both systems, SLS appeared the most appealing LS in terms of adsorption capability (Fig. 1b). At the surface of solid particle and solution, there is unequal electrical charges. This situation created a potential across the interface and forms a phenomenon called electrical double layer [19]. Increasing concentration of electrolyte compresses the electric double layer (EDL) causing change in adsorption [21] based on the charges of the adsorbent (kaolinite) and the lignosulfonate solution. Lignosulfonate is an anionic polyelectrolyte with negative charge of functional group

Fig. 1: Influence of varying lignosulfonate concentration on kaolinite with, (a) concentration of 1wt% in NaCl, and (b) concentration of 0.1wt% in CaCl₂ (SLS is sodium lignosulfonate, CLS is calcium lignosulfonate, MLS is magnesium lignosulfonate and ALS is ammonium lignosulfonate)

The effect of pH in 1wt% NaCl on LS adsorption shows in Fig. 2. The LS adsorption was measured at 30°C with the concentration of LS fixed at 200ppm and pH concentration varies within the range of 3 to 11. The sequence of adsorption capacity under the influence of varying pH in 1wt% NaCl were obtained as follows: SLS> ALS> CLS>MLS. At the pH of 3, adsorption capability of SLS, ALS, CLS and MLS were obtained as 0.716mg/g, 0.588mg/g, 0.475mg/g and 0.271mg/g respectively. When the pH increased to 11, adsorption of SLS, ALS, CLS and MLS decreased to 0.660mg/g, 0.496mg/g, 0.436mg/g and 0.230mg/g respectively. The adsorption capability of the LS generally decreased with the increasing



pH. Similar trend observed on limestone and dolomite which reported by Bai and Grigg [25] and Bai, et al. [9]. Gogoi [26] on the other hand observed decreased of SLS adsorption onto sandstone rock from Naharkotiya oil field of Deohal with increased pH. This scenario can be clarified that the negativity of the LS solution increase with the increasing pH. Kaolinite, on the other are negatively charged in the high pH value. Hence, a repulsion occurs between kaolinite and the anionic LS, resulting in a reduced LS adsorption capability. The effect of salinity was observed to be more dominant than the pH effect on the LS adsorption onto kaolinite.

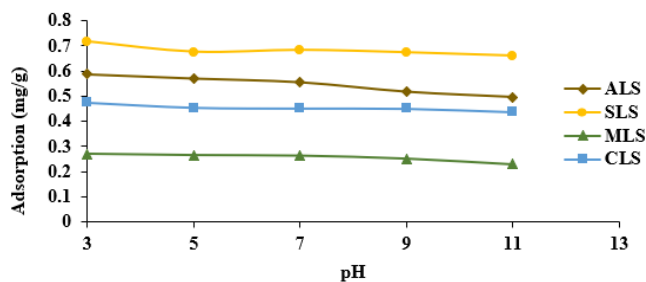


Fig. 2: Influence of varies pH with fixed LS concentration in 1wt% NaCl on kaolinite (SLS is sodium lignosulfonate, CLS is calcium lignosulfonate, MLS is magnesium lignosulfonate and ALS is ammonium lignosulfonate)

D. SLS best selected adsorption capability onto kaolinite in equilibrium and kinetic condition

1) Equilibrium adsorption model

Among the four tested LS on the adsorption capability onto kaolinite, SLS exhibited the best promising with high adsorption value. To further look into the behavior of SLS adsorption in equilibrium condition, three system which consisted of deionized water (DIW), 3wt% of NaCl and 0.5wt% of CaCl₂ were prepared. Fig. 3 shows the result of SLS amount of adsorbed versus SLS concentration in three different system. Results shown that increased of electrolytes, adsorption of SLS increased. Adsorption data obtained were used to analyze and describe the process of SLS adsorption onto the kaolinite.

For equilibrium model, 1/q_e against 1/C_e plot from Langmuir in Fig. 4a, for SLS adsorption on kaolinite in the electrolyte of 1wt% NaCl and 0.1wt% CaCl₂ yields a straight line. The Langmuir constant q₀ and K_L presented in Table 7 shows the adsorption capability for a complete monolayer and the energy of adsorption and affinity of the binding sites correspondingly.

A graph of Log q_e versus Log C_e from the Freundlich isotherm parameters different electrolyte is portrayed in Fig. 4b yields a straight line with linear correlation coefficients (R²) approaching 1. This signifies that the adsorption of lignosulfonate onto kaolinite is in adherence to the Freundlich isotherm. Freundlich constant values n and K_f are tabulated in Table 7 giving a clue of adsorption intensity and capability respectively.

The Temkin isotherm model is as illustrated in Fig. 4c, where a graph of q_e versus ln C_e is plotted. The Temkin model considers the effects of the interaction of the kaolinite and the LS. The isotherm constant, b known as the Temkin

constant, linked to the temperature of adsorption, while KT, empirical Temkin constant, referred to the equilibrium binding constant and the maximum binding energy. In general, the linear correlation coefficients (R²) in Temkin model was lower for SLS in the three different systems compared to the Langmuir and Freundlich isotherm models (Table 7). To summarize the discussion on the adsorption equilibrium isotherm, the adsorption of SLS onto kaolinite appeared to be possibly fitted the best with Freundlich isotherm model followed by Langmuir and Temkin isotherm model. These findings are aligned with the previous study reported in Grigg and Bai [27], Bai and Grigg [25] and Bai, et al. [9] studies.

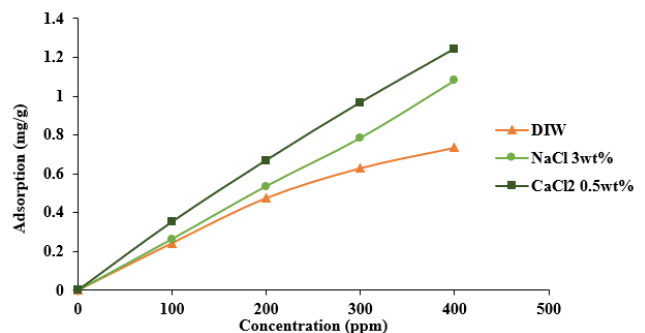


Fig. 3: SLS adsorption in different concentration and electrolyte

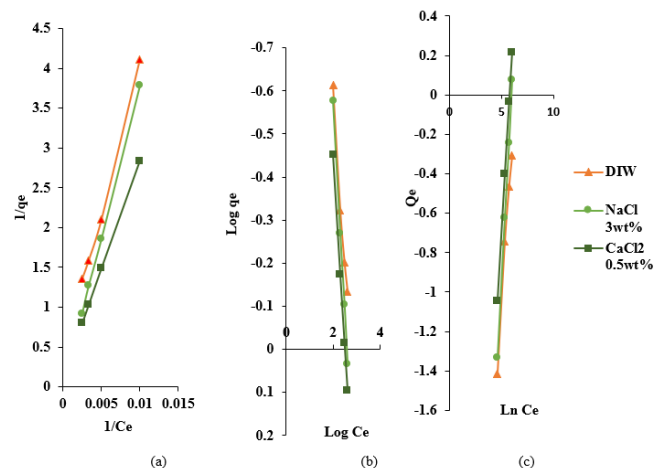


Fig. 4: SLS equilibrium model in DIW, 3wt% NaCl and 0.5wt% CaCl₂ (a) Langmuir (b) Freundlich (c) Temkin

Table 7: Isotherm parameter and error estimation for the adsorption of SLS onto kaolinite for isotherm model

Isotherm Model	Ionic Strength	Correlation	Isotherm parameters		Error Estimation		
			q ₀	K _{ad}	R ²	ARD	χ ²
Langmuir	DIW	1/q _e = 371.881/C _e + 0.3549	2.8177	0.000954	0.9959	0.25	0.0002
	NaCl 3wt%	1/q _e = 380.08/C _e + 0.017	58.824	0.000045	0.9998	0.65	0.002
	CaCl ₂ 0.5wt%	1/q _e = 270.96/C _e + 0.1308	7.6453	0.000483	1	0.03	0
Freundlich	DIW	q _e = 0.00616 ^{0.807}	0.0062	0.807	0.9861	0.05	0
	NaCl 3wt%	q _e = 0.00254 ^{1.0085}	0.0025	1.0085	0.9995	0.02	0
	CaCl ₂ 0.5wt%	q _e = 0.00531 ^{0.9119}	0.0053	0.9119	0.9999	0.03	0
Temkin	DIW	q _e = 0.807(lnC _e) - 5.0899	0.0018	0.807	0.9861	60	12.1
	NaCl 3wt%	q _e = 1.0085(lnC _e) - 5.9755	0.0027	1.0085	0.9995	44.9	8.6
	CaCl ₂ 0.5wt%	q _e = 0.9119(lnC _e) - 5.2384	0.0032	0.9119	0.9999	34.7	6.2

2) Kinetic adsorption model

Analysis of adsorption kinetics is significant due to the rate and the mechanisms of adsorption can be concluded from kinetic studies, which



highly relies on the interaction between solid and SLS solution [16, 28]. In kinetic adsorption, rapid adsorption process is observed at the beginning of the experiment while the adsorption process became slower as the equilibrium state is approached. Fig. 5 shows the SLS adsorption in the aqueous environment with DIW, 3wt% of NaCl and 0.5wt% of CaCl₂.

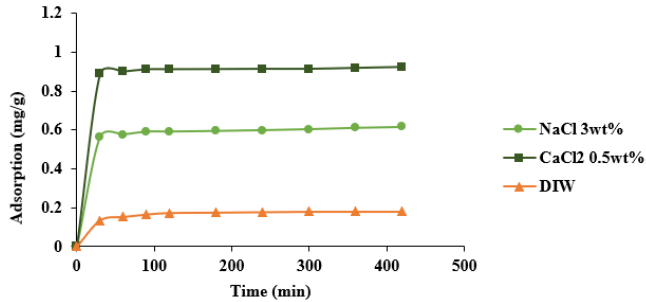


Fig. 5: Kinetics of SLS adsorption onto kaolinite at different electrolytes

To choose the most suitable model to describe SLS adsorption onto kaolinite, pseudo-first-order equation, pseudo-second-order equation, and inter-particle diffusion were analyzed. Fig. 6a illustrates the pseudo-first order approach in investigating the kinetic behavior of SLS adsorption onto kaolinite. The established parameters of the referred model are shown in Table 8. The calculated correlation coefficient (R^2) for SLS applying the pseudo-first order model displayed low R^2 . However, an entirely conclusive matching of the experimental data with the pseudo-second-order model which shown in Table 8 and were observed in Fig. 6b. The R^2 obtained by pseudo-second-order model is nearly 1. As for the inter-particle diffusion, if the inter-particle was the only one mechanism leading the process of adsorption, the q in the function of the $t^{1/2}$ will follow a straight line. Otherwise, other influences of mechanisms can occur. Correlation coefficient ($R^2 \ll 1$) calculated for all the targeted data seems low, hence the intra-particle diffusion model could not properly describe the SLS adsorption onto kaolinite (Fig. 6c). Table 8 shows the kinetics rate of the SLS onto kaolinite. To summarize, the kinetic models points out that the pseudo-second order had been more applicable to explain the adsorption of SLS onto kaolinite in different electrolyte. This observation is consistent with previous studies by Bai and Grigg [25] and Bai, et al. [9] where CLS adsorption on limestone and dolomites were observed to follow the pseudo-second order.

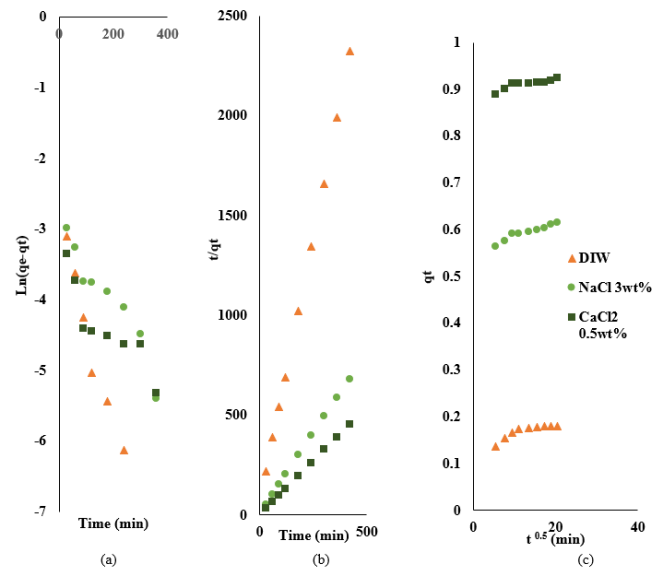


Fig. 6: SLS kinetic model in DIW, 3wt% NaCl and 0.5wt% CaCl₂ (a) Pseudo-first order (b) Pseudo-second order (c) Intra-particle diffusion

Table 8: Kinetics parameter for the adsorption of SLS onto kaolinite at different ionic concentration for kinetic model

Kinetic Model	Ionic Strength	Correlation	Kinetic parameters			Regression
			K_1	q_e	R^2	
Pseudo-first order	DIW	$\ln(q_e - q_t) = -0.0077t - 2.5163$	0.0077	10.488	0.9095	
	NaCl 3wt%	$\ln(q_e - q_t) = -0.0069t - 3.075$	0.0069	6.694	0.9371	
	CaCl ₂ 0.5wt%	$\ln(q_e - q_t) = -0.0051t - 3.7294$	0.0051	4.707	0.7968	
Pseudo-second order	DIW	$t/q_t = 2.1822t + 27.806$	0.1713	0.4583	0.9983	
	NaCl 3wt%	$t/q_t = 1.6186t + 7.9238$	0.3306	0.6178	0.9998	
	CaCl ₂ 0.5wt%	$t/q_t = 1.0826t + 1.8399$	0.637	0.9237	1	
Intra-particle diffusion	DIW	$q_t = 0.0044t^{0.5} + 0.3595$	0.0044	0.3595	0.9592	
	NaCl 3wt%	$q_t = 0.0029t^{0.5} + 0.5553$	0.0029	0.5553	0.9288	
	CaCl ₂ 0.5wt%	$q_t = 0.0018t^{0.5} + 0.8871$	0.0018	0.8871	0.7959	

3) Error Estimation

R^2 result obtained from the equilibrium model were very closed to each other. Thus, it was difficult to choose which model was best fitted for SLS adsorption. By calculating the ARD and x^2 , another set of error estimation can be alternative for decision making. Equations/correlations for each model had been established in Table 7. By substituting the equilibrium concentration into each model, q_i^{model} was calculated. Using the equation 13 and 14, the ARD and x^2 for each model can be generated, the ARD and x^2 for each model can be generated. In this study, ARD and x^2 for Freundlich was very low and close to the experiment data as compared to the Langmuir and Temkin. Additional error estimation again confirmed that the equilibrium SLS adsorption model was followed the Freundlich. As for kinetic adsorption, highest value for R^2 was obvious at pseudo-second order. Hence, ARD and x^2 were not calculated.

IV. CONCLUSIONS

Several types of LS solutions had been comprehensively investigated to determine the adsorption capability to adsorb onto kaolinite at varying electrolyte. This result is important to select to most viable sacrificial agent based on lignin for a later process of the EOR. Besides, several significant conclusions that can be drawn



from this study are: (1) Among the four tested LS solutions on the adsorption experiment, SLS appeared to be the best solution to achieve the highest adsorption capability; (2) Increment in electrolyte from NaCl 3wt% to CaCl₂ 0.5wt% in SLS solution led to higher adsorption; (3) Influence of electrolyte was more dominant compared to the pH (4) As for the adsorption isotherm model, Freundlich emerged as the best fitting model and parameters displayed that the adsorption was indeed favourable; (5) In terms of kinetic adsorption model, the pseudo-second order was discovered to be suitable in predicting SLS adsorption; and lastly, (6) Since LS is a type of lignin derived from waste product with nil effect upon the environment and possesses strong adsorption capability to adsorb into kaolinite, it appears to be viable and effective to serve as a sacrificial agent in surfactant flooding, especially to reduce or to eliminate surfactant adsorption onto kaolinite. With that, this study suggests that the outcomes retrieved can be further tested for EOR application.

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