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## Comparative analysis of natural and synthetic surfactant adsorption by quartz minerals: An experimental study

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**Abstract:** The efficacy of surfactant flooding for enhanced oil recovery (EOR) can be considerably diminished by the adsorption of surfactant on reservoir rocks. The primary purpose of this study is to assess the equilibrium adsorption behavior of natural (Ziziphus Spina-Christi, ZSC) and to compare with that of synthetic (Sodium Dodecyl Sulfate, SDS) surfactants onto sandstone (quartz) minerals, which has been rarely reported in the available literature. Such a systematic investigation is beneficial for selecting a proper surfactant in EOR applications. For this purpose, electrical conductivity (EC), ultraviolet-visible spectrophotometry (UV-Vis), and Fourier transform infrared (FTIR) techniques were employed to measure the adsorption of surfactant on quartz minerals. From the results of this study, it can be pointed out that the maximum adsorption of SDS and ZCS on quartz minerals is approximately 3 mg/g and 25 mg/g, respectively. The adsorption rate of both surfactants increased with increasing surfactant concentration up to the critical micelle concentration (CMC). The Langmuir, Freundlich, and Temkin isotherm models were used to predict the experimental data. Based on the experimental findings, the Langmuir isotherm provides a good fit to the experimental data, with coefficients of determination ( $R^2$ ) of 0.9917 for ZSC and 0.9858 for SDS.

**Keywords:** Adsorption, Natural Surfactant, SDS, CMC, Quartz minerals, Adsorption isotherm models

## 1. Introduction

Oil and gas remain the world's primary energy suppliers, despite recent advancements in energy production from renewable sources [1]. As a result of increased extraction from oil reservoirs and a subsequent decrease in reservoir pressure, oil production gradually declines [2]. Consequently, the significance of enhanced oil recovery (EOR) approaches in enhancing oil recovery from reservoirs is highlighted by the growing energy demand [3]. Following the primary and secondary steps of oil recovery, approximately half of the original oil in place (OOIP) remains trapped underground [4-6]. Therefore, tertiary recovery methods (EOR) are used to recover the remaining oil [7,8]. Different EOR techniques can be divided into various groups [9-11]. Chemical EOR (CEOR) has garnered a lot of attention lately [12-21]. Surfactants are favorable chemical additives in EOR applications. By reducing the water/oil IFT and increasing the capillary number, surfactants play a vital role in EOR procedures [22,23]. Numerous studies have been conducted on the wettability alteration, and IFT decrease with anionic, cationic, and nonionic surfactants [24,25]. Several variables influence surfactant efficiency in EOR, including the type of surfactant, concentration, reservoir type, fluid properties, temperature, and salinity [26]. Surfactant

adsorption on reservoir rock surfaces occurs through several mechanisms, including electrostatic interactions, hydrophobic interactions, hydrogen bonding, and ion exchange, depending on the surfactant type and mineralogical composition of the rock [27]. In sandstone and quartz-rich systems, parameters such as salinity, pH, and temperature significantly influence these mechanisms by altering surface charge, electrical double layer thickness, and surfactant mobility [28]. In comparison to synthetic surfactants, natural surfactants are less costly and more environmentally friendly. The primary source of natural surfactants is saponins. The natural surface-active substances known as saponins are high-molecular-weight glycosides with detergent properties and the ability to create stable foam in water [29,30]. Recently, researchers have focused on the potential of both natural and synthetic surfactants in EOR applications. Ebrahimi et al. [20] examined the wettability reformation of calcite and dolomite rocks from oil-wet to water-wet conditions using the surfactant sodium dodecyl sulfate (SDS). They claimed that the SDS surfactant adsorbs onto rock surfaces, leading to a modification of the wettability of oil-wet rock surfaces to a water-wet state. The impact of the clay fraction's mineralogical composition on surfactant adsorption has been the subject of recent investigations by various authors [31-33]. Wu et al. [34] investigated static adsorption and dynamic adsorption of SDS with and without silica nanoparticles (SNPs). According to the results of this study, it was noted that the addition of SNPs reduces surfactant adsorption on rock.

Herawati et al. [35] studied the adsorption of an anionic alkyl ethoxy carboxylate surfactant on sandstone containing Ca-montmorillonite and kaolinite clays and its effect on wettability alteration. They demonstrated that surfactant adsorption is strongly dependent on clay mineralogy and electrostatic interactions, with higher adsorption resulting in enhanced water-wet conditions.

Belhaj et al. [36] studied the adsorption of an alkyl ether carboxylate and alkyl polyglucoside surfactant mixture on sandstone in the presence and absence of crude oil. They showed that adsorption increases due to surfactant partitioning into oil, emphasizing the importance of considering partitioning effects in surfactant flooding design. In another study, Belhaj et al. [37] investigated surfactant adsorption studies, considering laboratory testing, modeling, and simulation studies. They stated that numerous factors, including surfactant concentration, pH, salinity, temperature, and the mineral composition of the rock, can influence surfactant adsorption.

Belhaj et al. [38] conducted a comprehensive experimental and modeling study on the adsorption behavior of anionic and nonionic surfactants on sandstone under reservoir conditions. Their results demonstrated that surfactant adsorption is governed by heterogeneous mono- and multilayer mechanisms and is strongly affected by temperature, surfactant type, and competitive adsorption in binary systems. In addition, advanced modeling approaches, including adsorption isotherms and artificial neural networks, were shown to be effective tools for predicting surfactant losses and

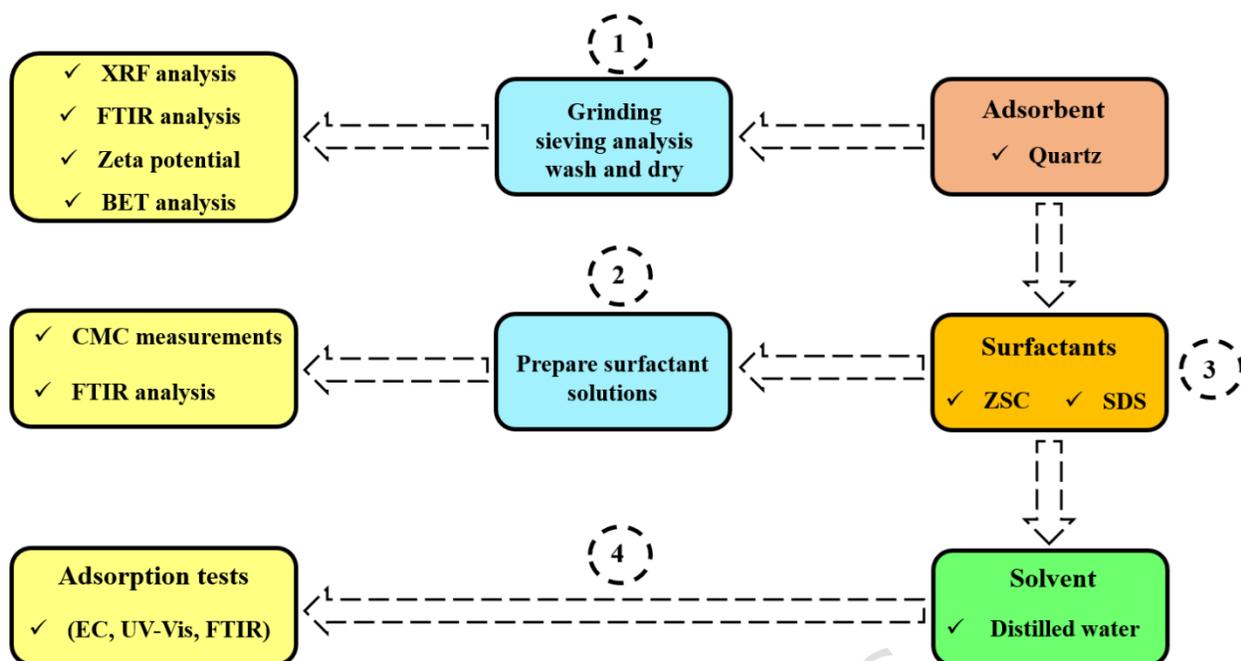
improving surfactant flooding design.

Lebouachera et al. [39] investigated the SDS adsorption on Algerian rock reservoirs. They suggested that reducing surfactant adsorption could lead to improved oil recovery. The adsorption of Ziziphus Spina-Christi (ZSC) surfactant on carbonate minerals was experimentally investigated by Ahmadi and Shadizadeh [40]. In another study, Zendehboudi et al. [41] investigated the equilibrium and kinetic behaviors of ZSC adsorption onto carbonate rock specimens. The findings of their study demonstrated that ZSC considerably reduces the oil-water IFT. The adsorption of surfactants on the minerals leads to the reduction of IFT, the improvement of wettability, and ultimately the mobility of the oil [42]. The adsorption of surfactant may be impacted by the characteristics of the rock surface [20]. Additionally, excessive salinity causes greater adsorption of surfactants [43,44]. The adsorption of surfactants on reservoir rocks reduces their concentration in the liquid phase, which can lead to a decrease in the effectiveness of the surfactant, potentially impacting processes such as oil recovery [45-48]. Surfactant adsorption directly influences its availability at the oil-water interface and therefore governs the extent of interfacial tension (IFT) reduction and wettability alteration in surfactant flooding processes [49-51]. Excessive adsorption on rock surfaces reduces the effective surfactant concentration in the aqueous phase, which can limit capillary number enhancement and ultimately diminish oil recovery efficiency [52,53]. To improve the optimum selection of surfactants for EOR operations, this study aims to perform a comparative analysis of the

adsorption of Ziziphus Spina-Christi (ZSC) surfactant (as a natural surfactant) and Sodium Dodecyl Sulfate (SDS) surfactant (as a synthetic surfactant) by sandstone (quartz) minerals. In this regard, various analysis methods, including electrical conductivity (EC), ultraviolet-visible spectrophotometry (UV-Vis), and Fourier transform infrared (FTIR) tests, are used. This study offers further understanding of the applicability of surfactant flooding in reservoir rock systems such as sandstone and contributes valuable data to the advancement of efficient and safe surfactant-based enhanced oil recovery methods. To the best of our knowledge, systematic equilibrium adsorption evaluation of ZSC on sandstone systems and its comparison with SDS under identical experimental conditions has rarely been reported in the literature. Therefore, such direct comparison under identical conditions provides new insights into the feasibility of replacing synthetic surfactants with environmentally friendly natural alternatives in EOR applications.

## **2. Materials and methods**

Figure 1 illustrates the schematic presentation of research steps. Experiments were conducted with two replicates, and the results presented are the average of the obtained data.



**Figure 1.** Schematic of the research steps.

## 2.1. Adsorbent

In this study, a quartz rock specimen is used as an adsorbent. A jaw crusher was used to disintegrate rock specimens into small pieces, and then they were ground using a rock pulverizer and sieved (Model Azmoontes SO410) through 60- and 80-mesh screens. Then, equal amounts were mixed in a 1:1 ratio and used as an adsorbent. After repeatedly washing the powdered rock specimens with distilled water (DW), they were allowed to settle and decant for 24 h to reduce clay content. Following the reduction of the clay content, the remaining wet quartz particles were dried for 24 hours at 100°C [54,55]. To determine the surface area for adsorption, a Brunauer-Emmett-Teller (BET) test (Model BELSORP Mini II) was performed. Before BET analysis, the quartz samples were degassed under vacuum at 150 °C for 8 h. Nitrogen adsorption-desorption measurements were carried out at 77 K using

Nitrogen (N<sub>2</sub>) as the adsorbate gas. The specific surface area was calculated using the BET method in the relative pressure range of 0.05–0.30, while pore volume and average pore diameter were determined using the Barrett-Joyner-Halenda method from the desorption branch of the isotherm. The BET analysis and other characteristics of the adsorbent specimen are shown in [Table 1](#), and the results of the X-ray fluorescence (XRF) test are presented in [Table 2](#).

**Table 1.** The BET analysis results of the adsorbent specimen.

Mineral	Particle size (µm)	Average pore diameter (nm)	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
Micro-quartz	170-250	6.0391	5.1874	1.1918

**Table 2.** The XRF results of quartz.

Element	Amount (%)	Element	Amount (%)
SiO <sub>2</sub>	79.31	P <sub>2</sub> O <sub>5</sub>	<0.01
Al <sub>2</sub> O <sub>3</sub>	9.9	SO <sub>3</sub>	0.18
BaO	0.04	TiO <sub>2</sub>	0.11
CaO	0.98	Cr <sub>2</sub> O <sub>3</sub>	0.01
Fe <sub>2</sub> O <sub>3</sub>	2.76	Cu	0.06
K <sub>2</sub> O	3.29	Pb	<0.01
MgO	0.38	Zn	<0.01
MnO	0.04	LOI*	0.79
Na <sub>2</sub> O	2.15		

Note: \*; loss on ignition.

## 2.2. Surfactants

The synthetic anionic sodium dodecyl sulfate (SDS) and the natural surfactant called Ziziphus Spina-Christi (ZSC) with high concentration of saponins were employed in this study. It should be noted that extracts

obtained from ZSC are complex natural mixtures rather than single purified compounds. Although saponins constitute the main surface-active components responsible for interfacial tension reduction, foaming, and adsorption behavior, the extract may also contain sugars, phenolic compounds, organic acids, and inorganic salts. Detailed compositional studies of ZSC leaf extracts have shown that they contain multiple structurally diverse triterpenoid saponins identified by chromatographic and spectroscopic methods, confirming the complex, saponin-rich nature of the extract used in this study [56]. Therefore, the term 'saponin-rich surfactant' is used throughout this study to reflect the dominant role of saponins while acknowledging the multicomponent nature of the extract. Triterpenoid saponins reported for ZSC generally possess molecular weights in the range of approximately 600–1200 g/mol, depending on the aglycone structure and sugar moieties [57,58]. It is worth noting that for the ZSC surfactant, all reported concentrations refer to the total extract concentration. The CMC, adsorption, and conductivity results therefore represent the effective macroscopic behavior of a saponin-rich natural surfactant system rather than that of a single purified compound. ZSC was selected because it is locally abundant, low-cost, non-toxic, and traditionally recognized as a rich source of triterpenoid saponins with strong surface activity [30,59]. In addition, its availability and ease of extraction make it an attractive candidate for practical, field-scale applications compared with many other plant-based surfactants.

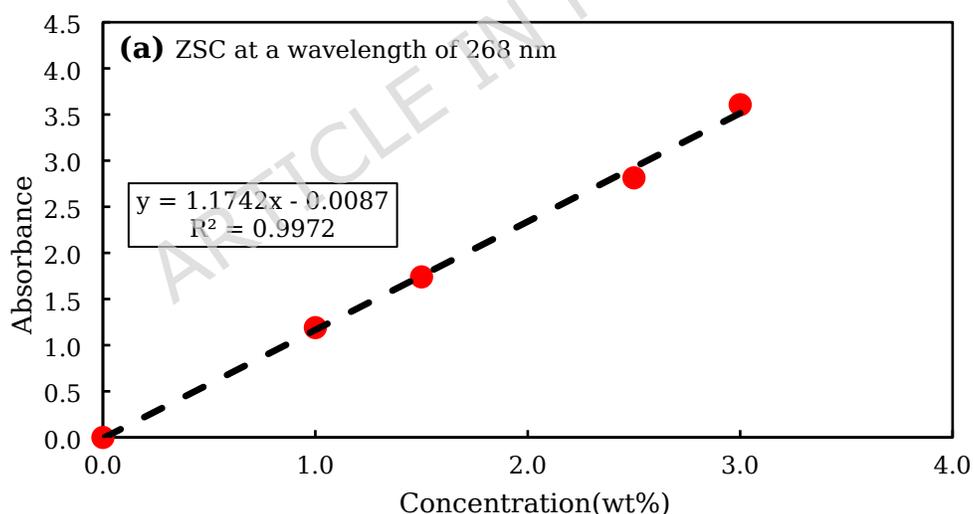
The molecular structure of SDS and ZSC surfactants was presented in [60,61]. Saponin is known as a biosurfactant [40]. SDS, with a density of 1.1 g/cm<sup>3</sup> and a purity of  $\geq 86\%$ , was purchased from Merck. Utilizing a magnetic stirrer (Model Alpha D-500), SDS surfactant solutions were prepared at concentrations of up to 2500 ppm in distilled water. The maceration method was used to extract cedar leaves (i.e., ZSC) [59]. For this purpose, 400 g of ZSC powder was mixed with distilled water and stirred for three days. It is worth noting that the process of soaking the cedar leaves at room temperature was performed. After 3 days, the concentrated extract was obtained by filtration and heating of the mixture [59]. The leaves of the cedar tree were used as the plant material in this study. They were commercially purchased from a local market. The material was initially a natural detergent product. The procurement of the plant material was made by the supervisor of the study. The species of the plant was identified by its commercial name and the features that the supplier provided. Since the plant material was obtained from a commercial source and no plants were collected from the wild, no collection permits were necessary, and no voucher specimen was deposited.

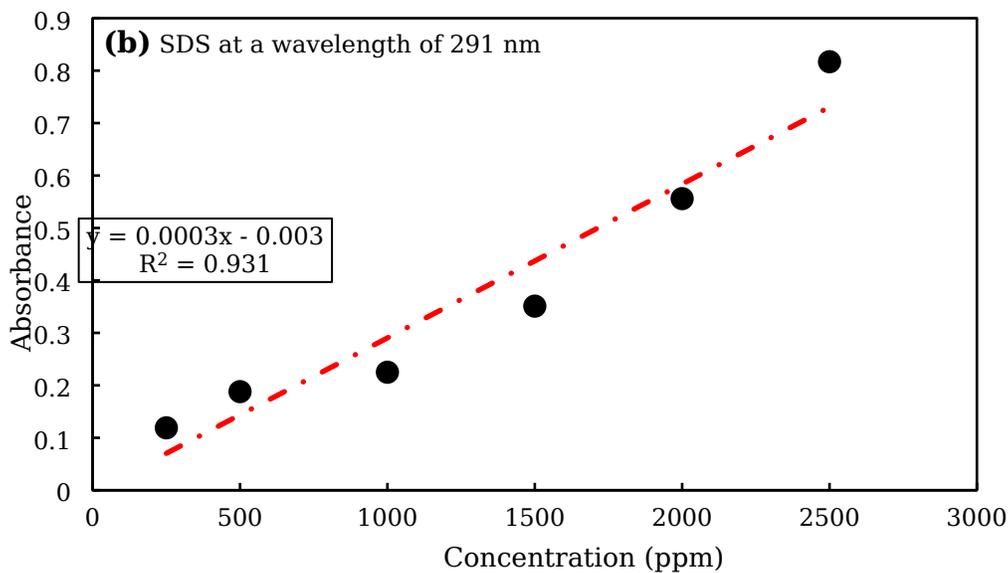
In this regard, test solutions were prepared with ZSC surfactant at concentrations of up to 4000 ppm. Adsorbent specimens and surfactant solutions with a ratio of 1:10 (i.e., 1 g of crushed quartz specimen and 10 mL of each solution) were mixed with a magnetic stirrer. The CMC of surfactants was determined by the EC procedure described in [62,63]. All experiments

were conducted at ambient pressure and temperature. All surfactant solutions were prepared using distilled water to establish controlled and comparable baseline conditions for comparative analysis. The influence of pH and ionic strength on surfactant adsorption is acknowledged and will be addressed in future studies under reservoir-relevant conditions.

### 2.3. Absorption calibration curve

UV-Vis spectrophotometry was used to determine the surfactants concentrations [19,64]. By plotting absorbance against concentration, a calibration curve was generated. Thus, this process ultimately resulted in the creation of calibration curves and the equations of the best-fit trend lines from the measured data points (Figure 2).





**Figure 2.** Calibration curve of surfactant specimens (a) ZSC and (b) SDS.

#### 2.4. FTIR analysis

Utilizing a Bruker TENSOR 27 spectrometer, FTIR tests were conducted with 32 scans and a resolution of  $4\text{ cm}^{-1}$  in the wavelength range of  $400\text{--}4000\text{ cm}^{-1}$ . To produce tablets, the different quartz samples were mixed with potassium bromide powder in a 1:100 ratio [65]. This analysis is a qualitative method used to identify functional groups and confirm adsorption [20,66,67]. It is worth noting that all spectra were subjected to baseline correction using the instrument software, and no normalization or difference spectra were applied.

#### 2.5. Adsorption study

Adsorption tests were performed to assess the amount of surfactant adsorbed onto quartz. The ratio of solid to liquid weight was 1:10. Known weights of quartz specimens (1 g) were added to 10 mL of ZSC and SDS surfactant solutions at different concentrations. Then, ZSC and SDS solutions

with quartz minerals were equilibrated in appropriate vessels with a magnetic stirrer [68,69]. It is worth noting that the maximum adsorption of SDS on quartz is obtained after 45 minutes, and in the case of saponin-rich extract/quartz, after nearly 83 minutes. However, in both cases, 150 minutes was selected as the adsorption time. After that, the specimens were centrifuged at 3800 rpm for 15 minutes. Then, supernatants were separated and examined for remaining surfactant concentrations. Surfactant adsorption was determined using equation (1) [55].

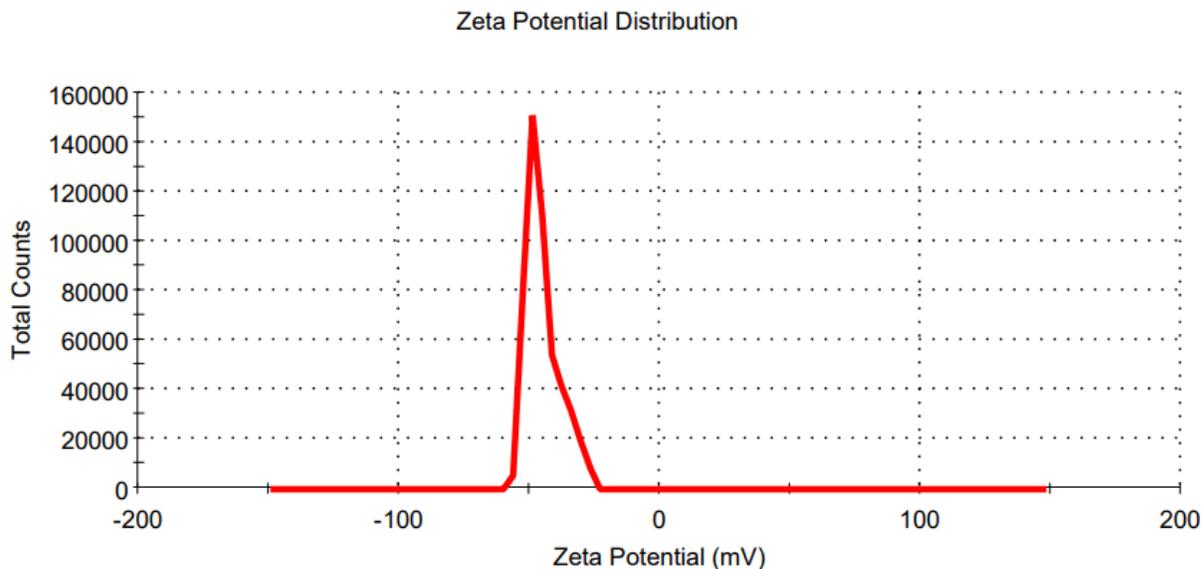
$$q = \frac{m_{\text{solution}} (c_0 - c)}{m_{\text{adsorbent}}} \cdot 10^{-3} \quad (1)$$

where  $q$  is the surfactant adsorption rate on adsorbent surfaces (mg/g-adsorbent),  $m_{\text{solution}}$  is the total mass of solution in the original bulk solution (g),  $c_0$  is surfactant concentration in the initial solution (ppm),  $c$  denotes surfactant concentration in aqueous solution after adsorption (ppm), and  $m_{\text{adsorbent}}$  is the total mass of the quartz minerals used (g).

### 3. Results and discussion

#### 3.1. Zeta potential determination

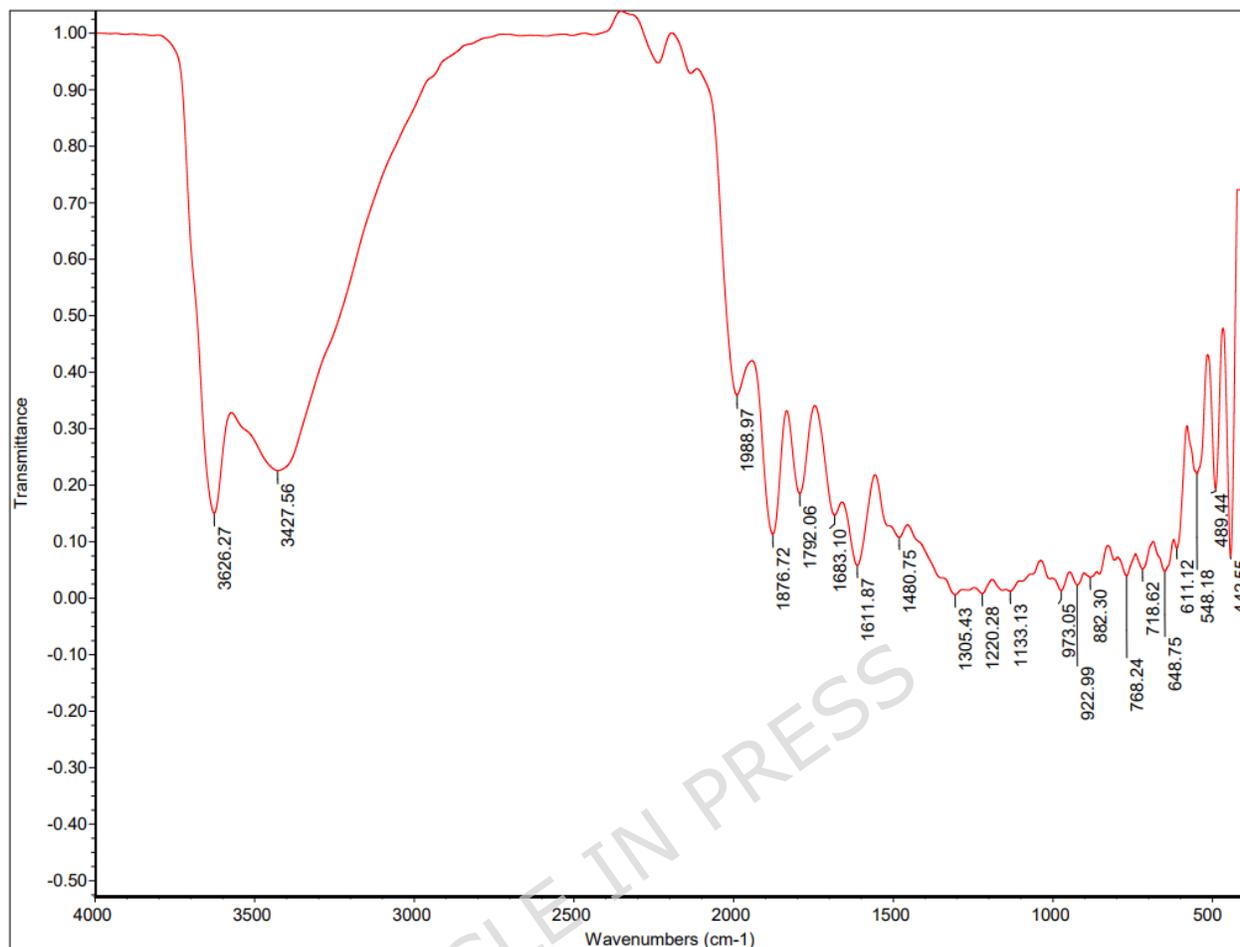
Figure 3 shows the results of the zeta potential analysis for the quartz used in this study. The maximum zeta potential for quartz is -45 mV. The surface charge for quartz is negative and is comparable to values reported in existing references for sandstone minerals [20,70].



**Figure 3.** Zeta potential analysis of pure quartz minerals.

### 3.2. FTIR analysis

Qualitative assessment of surfactant adsorption on adsorbent surfaces is performed using FTIR analysis (Figure 4). The absorption band at  $489.44\text{ cm}^{-1}$  corresponds to the asymmetric bending vibration of the Si-O bond [71]. The symmetric and asymmetric vibrations of the Si-O bond are represented by peaks located at  $768.24\text{ cm}^{-1}$  and  $1133.13\text{ cm}^{-1}$ , respectively [72]. The O-H bond was identified at a wavenumber of  $3626.27\text{ cm}^{-1}$  [73]. Therefore, the rock consists of pure silica as the primary component of quartz.

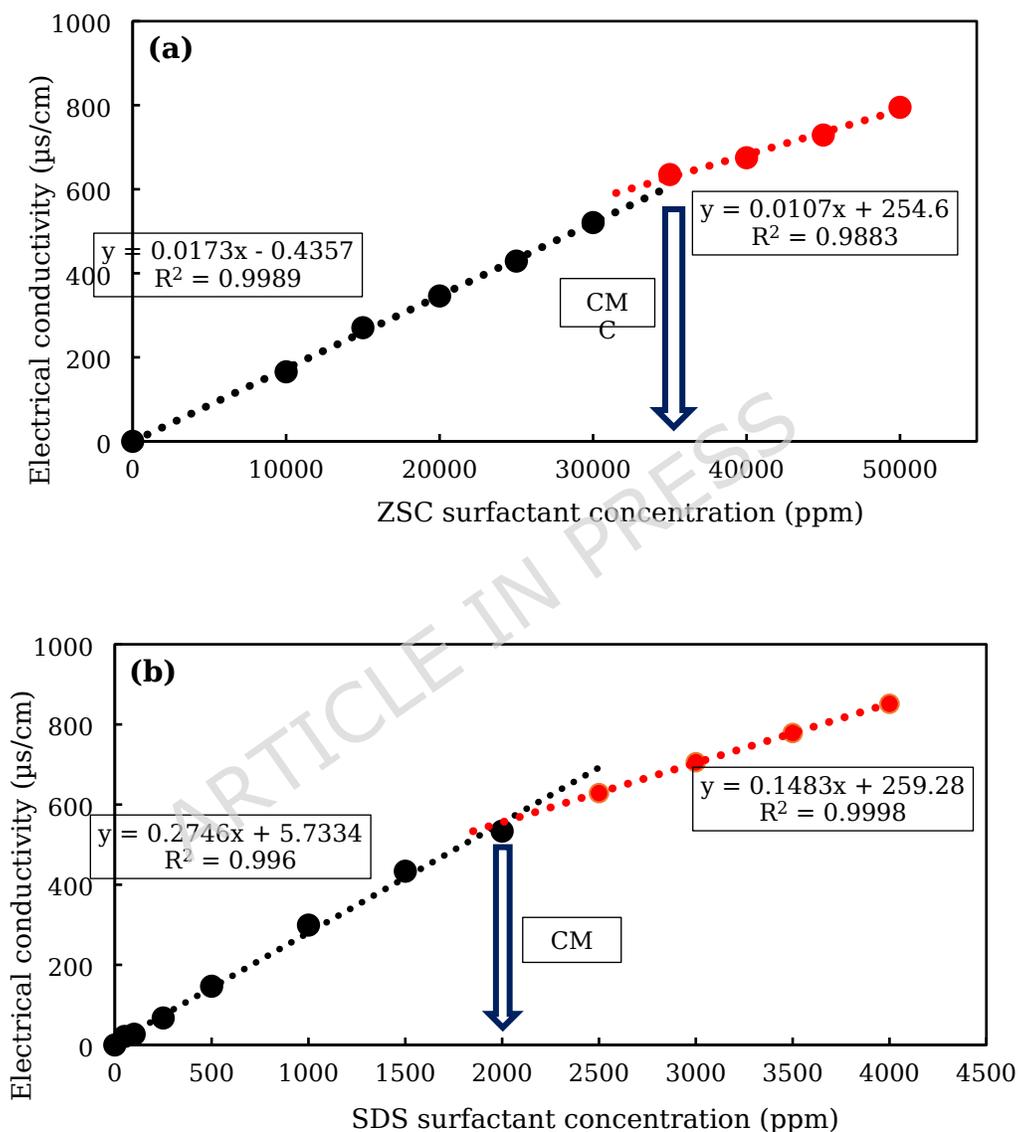


**Figure 4.** FTIR analysis of pure quartz.

### 3.3. Determination of CMC

When saponins are dispersed into aqueous solutions, they self-assemble into micellar aggregates [74]. A conductivity device was used to measure the conductivity of the solutions. To obtain the CMC, the data were plotted as a graph of conductivity versus concentration, and the value of CMC was determined from the inflection point in the curve [75]. According to the results presented in [Figure 5](#), the intersection of the two lines indicates the CMC concentration, which is about 2007 ppm for the SDS and around 36614 ppm for the ZSC surfactant. The relatively high CMC value obtained for ZSC

reflects the use of a crude saponin-rich extract. Therefore, the CMC of *Ziziphus Spina-Christi* should be interpreted based on total extract concentration rather than the intrinsic CMC of purified saponin molecules.



**Figure 5.** CMC determination: (a) ZSC and (b) SDS.

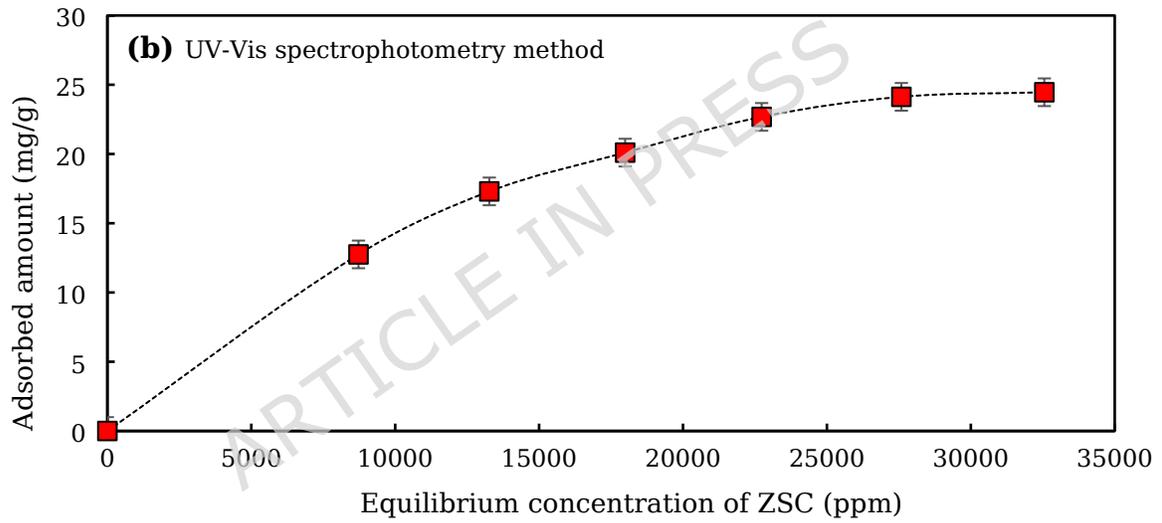
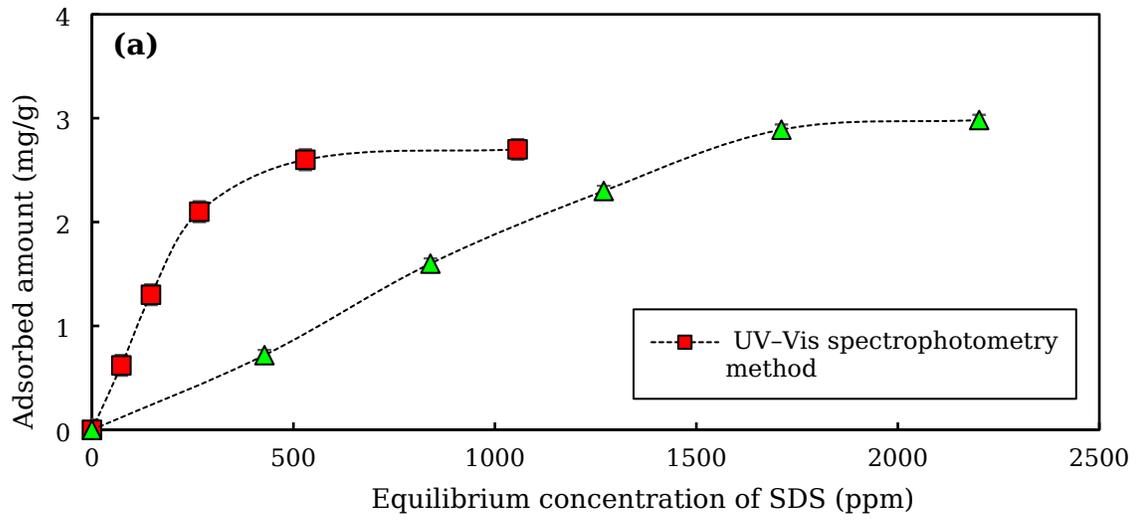
### 3.4. Adsorption tests

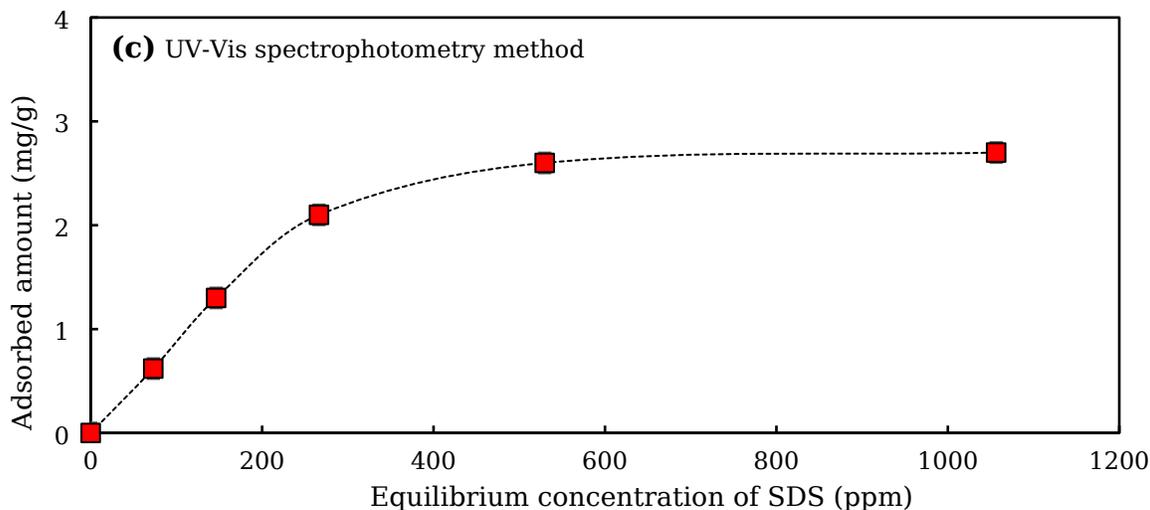
The amount of surfactant adsorption on the quartz minerals was measured

through adsorption studies using conductivity methods and UV spectroscopy at varying concentrations. Figure 6(a) illustrates the amounts of SDS as a function of the equilibrium surfactant concentrations using two analysis methods, and Figures 6(b) and (c) illustrate the amounts of ZSC and SDS using the UV-Vis spectrophotometry method. In the early steps, the rate of surfactant adsorption is high due to a high accessible adsorption surface [76]. Subsequently, when the available surface area is covered, this rate decreases [77]. At low concentrations of surfactant, surfactant can adsorb as monomers [78]. The measured negative zeta potential of quartz ( $-45$  mV) indicates that the mineral surface is negatively charged under the experimental conditions. Therefore, adsorption of anionic SDS occurs despite electrostatic repulsion and is mainly attributed to non-electrostatic mechanisms such as hydrophobic association and van der Waals interactions [20,52,79], whereas the amphiphilic saponin molecules in ZSC can additionally interact through hydrogen bonding with surface silanol groups, leading to higher adsorption [80–82]. In other words, the substantially higher adsorption of ZSC compared with SDS can be attributed to the multicomponent, triterpenoid-saponin structure of ZSC, which contains multiple hydroxyl groups and sugar moieties capable of strong hydrogen bonding and multisite surface attachment on quartz, in addition to hydrophobic association [83]. Although ZSC showed higher adsorption than SDS, this may limit its direct application in CEOR because of increased surfactant loss. However, previous studies have demonstrated that adsorption of natural and synthetic surfactants can be

significantly reduced by the addition of alkali or nanoparticles through competitive adsorption and surface charge modification [34,84]. At elevated concentrations, surfactant molecules begin to aggregate and form hemimicelles [78]. At surfactant concentrations above the CMC, most active sites on the surface are adsorbed by surfactant molecules, while additional surfactant forms micelles that are repelled by the adsorbed layer [46]. This trend is evident in [Figure 5](#), where the plot shows a steep slope up to the CMC, followed by a decrease in slope at concentrations above the CMC. In saponin-based substances, hydroxyl groups stick to surface particles via hydrogen bonds [80–82].

It is important to note that reservoir conditions differ significantly from ambient laboratory conditions. Elevated temperature and pressure, as well as high salinity, can alter surfactant adsorption behavior and interfacial properties. Temperature increases have been reported to reduce surfactant adsorption in many systems due to weakened binding interactions and changes in surfactant solubility, and surfactants that are not thermally stable may undergo degradation or loss of activity under reservoir conditions (e.g., high temperatures  $>100\text{ }^{\circ}\text{C}$ ) [85–87]. Pressure variations may also influence surfactant behavior, although their effects are typically smaller compared to temperature [88]. These factors should be considered in future studies for comprehensive evaluation under realistic reservoir environments.



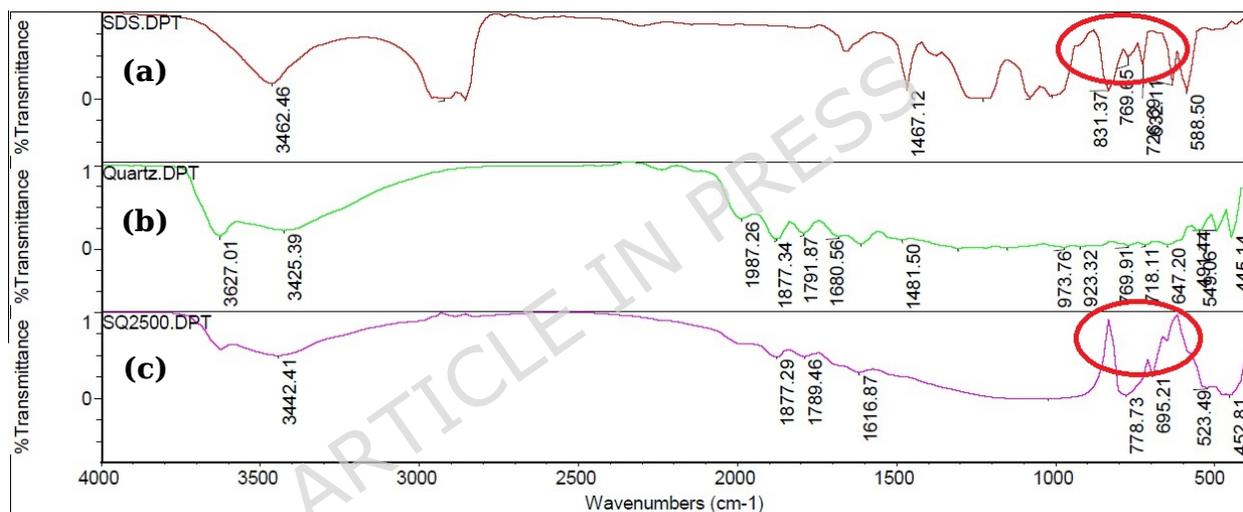


**Figure 6.** Adsorption isotherms of SDS and ZSC on quartz using two analysis methods.

### 3.5. FTIR analysis of adsorption

To detect the functional groups, the FTIR analysis was used. Figures 7 and 8 display the FTIR spectra of quartz adsorbent before and after adsorption with SDS and ZSC. The functional groups of the SDS surfactant are displayed in Figure 7(a). Additionally, Figure 7(b) illustrates pure quartz, while Figure 7(c) displays quartz after SDS adsorption. The FTIR spectrum bands for SDS demonstrated distinct peaks at the  $3462.46\text{ cm}^{-1}$  ( $-\text{OH}$  stretching),  $2900$ , and  $2841\text{ cm}^{-1}$  ( $-\text{CH}_2$  stretching and bending modes), the  $1208\text{ cm}^{-1}$  ( $\text{S}=\text{O}$  stretching), and the  $800$  and  $400\text{ cm}^{-1}$  (asymmetric C-H bending of the  $\text{CH}_2$  group) [39,89]. Note that the FTIR analysis for pure quartz was done earlier in Figure 4. In Figure 7(c), new peaks (red circle) have appeared in comparison to the pure quartz, indicating the adsorption of SDS onto the quartz adsorbent. In other words, after adsorption onto quartz, the spectrum is essentially a superposition of the quartz and SDS spectra. Crucially, there

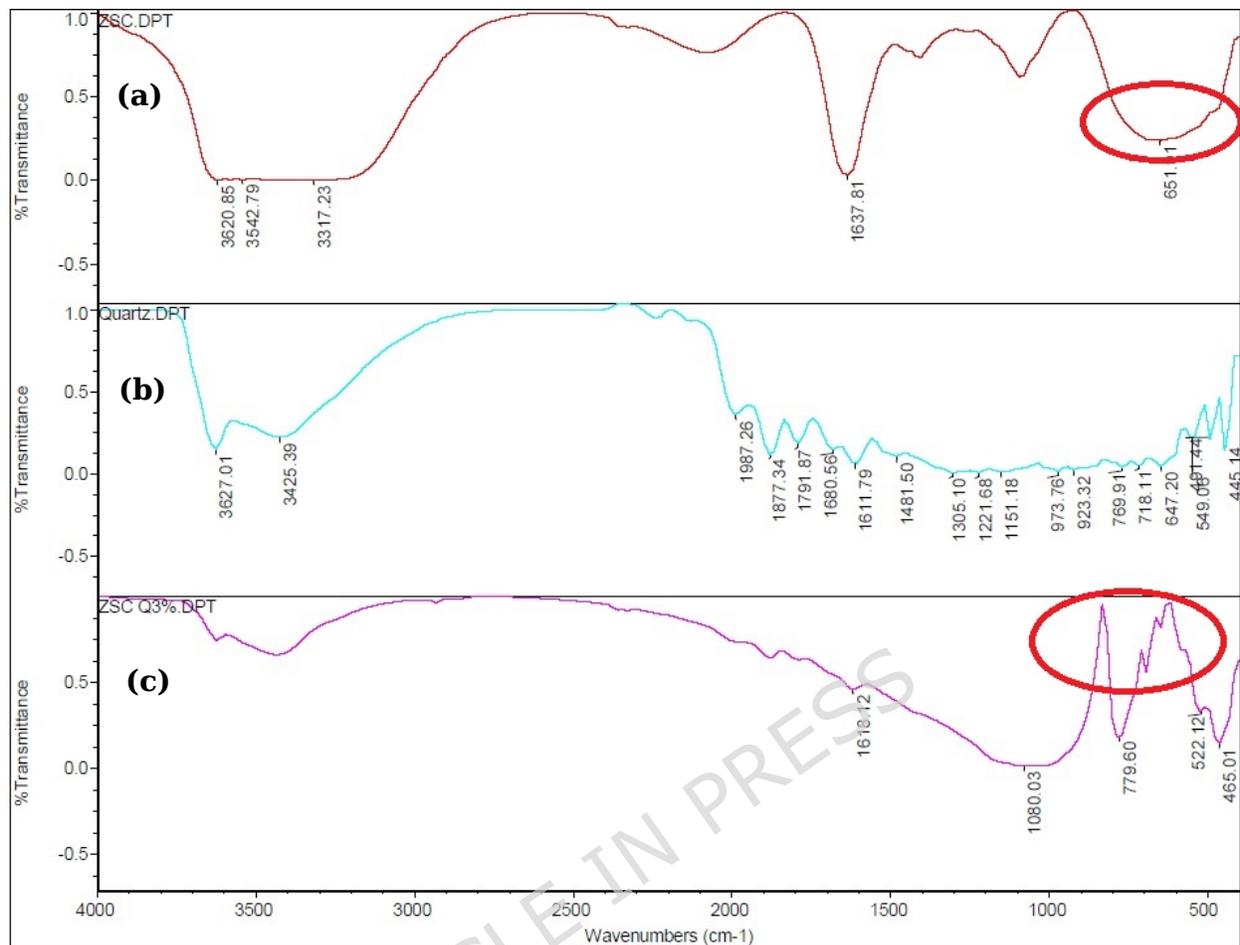
is no significant shift in the wavenumber of the key SDS functional group bands, particularly the S=O stretching band at  $\sim 1208\text{ cm}^{-1}$ . The absence of a notable change in the characteristic bands of the surfactant indicates that the chemical structure of SDS remains unchanged upon interaction with the quartz surface. The adsorption likely occurs via physical interactions such as electrostatic attraction between the anionic sulfate group ( $\text{SO}_4^{2-}$ ) of SDS and positively charged sites on the quartz surface (e.g.,  $\text{Si-OH}_2^+$ ), and/or van der Waals forces between the hydrocarbon tail and the surface [90].



**Figure 7.** FTIR analysis of (a) SDS surfactant, (b) pure quartz, and (c) quartz after SDS adsorption.

**Figure 8** displays the functional groups of pure quartz, ZSC surfactant, and quartz after ZSC adsorption. The ZSC/ FTIR spectrum at  $3317.23\text{ cm}^{-1}$  is attributed to the hydroxyl group. The band appearing at  $1637.81\text{ cm}^{-1}$  is attributed to the formation of oxygen functional groups like C=O stretching in carboxylic groups. The peak at  $651\text{ cm}^{-1}$  is caused by C-N-C. A peak at  $3542.79\text{ cm}^{-1}$  that is dominated by -NH stretching and illustrates the

existence of hydrogen-bonded -OH stretching from alcohol and phenols. The saponin's FTIR spectrum validates its efficacy as a surface-active species and is mostly in agreement with the literature [91,92]. Figure 8(c) indicates quartz after ZSC adsorption. In Figure 8(c), new peaks (red circle) have appeared compared to the pure quartz, indicating the adsorption of ZSC onto the quartz adsorbent. The changes in the hydroxyl (-OH) and amine (-NH) regions are particularly significant. Quartz surface is rich in silanol groups (Si-OH). The -OH and -NH groups in ZSC saponins can form strong hydrogen bonds with these surface Si-OH groups. While hydrogen bonding is a stronger specific interaction than van der Waals forces, it is generally still classified under physical adsorption [93]. However, if the interaction leads to the formation of a covalent-like bond, it could indicate chemisorption [93]. The current FTIR evidence does not conclusively indicate chemisorption (covalent bond formation).



**Figure 8.** FTIR analysis (a) ZSC surfactant, (b) pure quartz, and (c) quartz after ZSC adsorption.

### 3.6. Adsorption isotherm models

The large number of isotherm models provided by Kalam et al. [94] and Liu et al. [95] are typically used to modify surfactant adsorption curves. In this study, three well-known adsorption models were applied.

#### 3.6.1. Langmuir isotherm

The Langmuir isotherm model relies on three key assumptions: adsorption occurs in a single monolayer, all adsorption sites are uniform, and each adsorption site possesses the same energy. The Langmuir equation can be

represented as follows [39,41].

$$q_e = \frac{q_m k_l c_e}{1 + k_l c_e} \quad (2)$$

In this context,  $q_e$  represents the amount of adsorbed component (mg/g),  $q_m$  denotes the maximum amount of adsorbed component (mg/g),  $k_l$  refers to the Langmuir constant (L/mg), and  $c_e$  indicates the equilibrium concentration (ppm). Equation (2) can be expressed as follows in its linearized form:

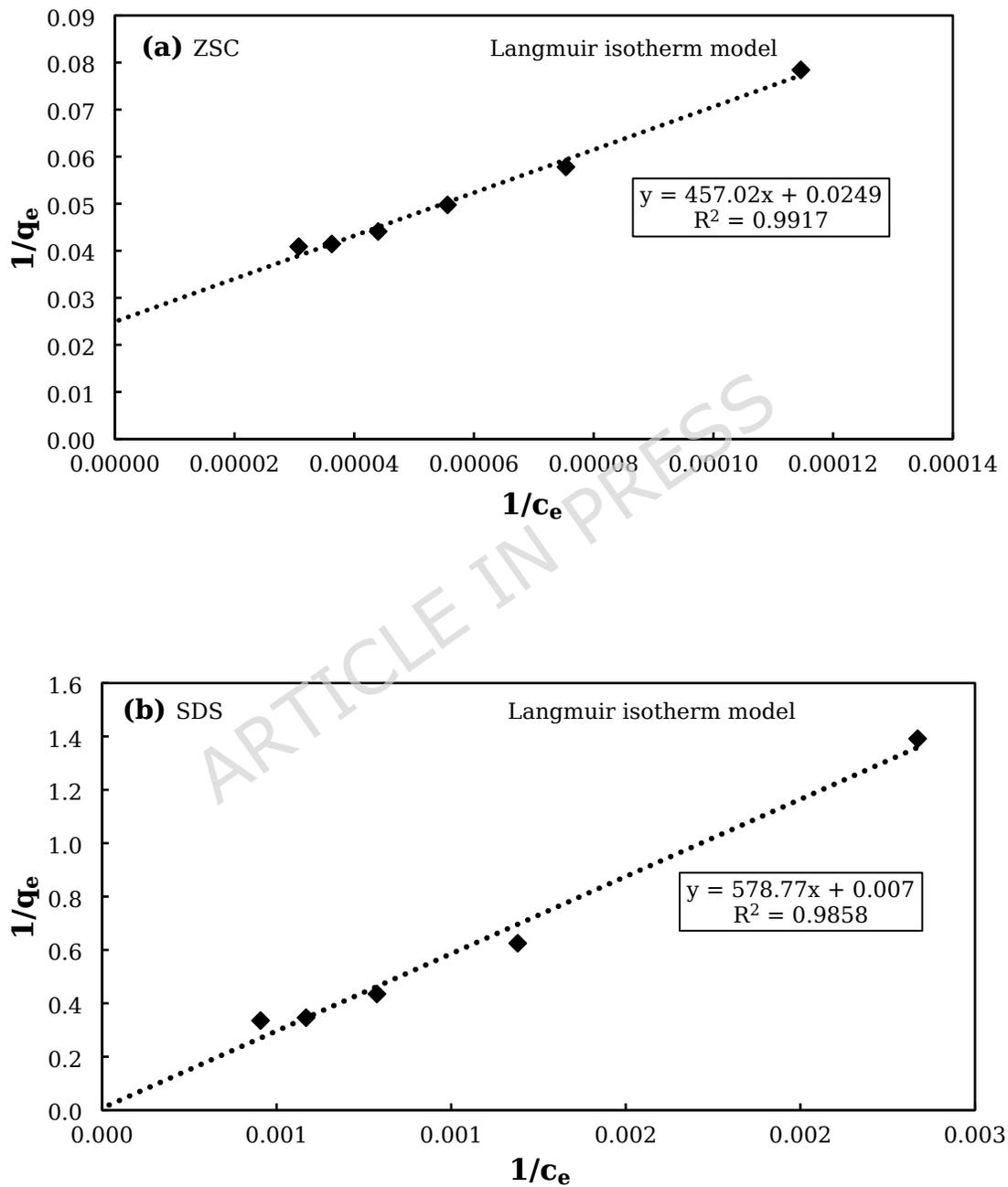
$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_l q_m c_e} \quad (3)$$

If the adsorption equilibrium values followed the Langmuir isotherm, a linear graph of  $1/q_e$  vs  $1/c_e$  will be generated. The slope and intercept of the straight line can be used to obtain the  $q_m$  and  $k_l$  amounts, respectively. The fitting of the ZSC and SDS adsorption isotherms using the Langmuir model is shown in Figure 9. The equilibrium parameter,  $R_L$  [39], can be used to express the key features of the Langmuir isotherm. It is defined as follows:

$$R_L = \frac{1}{1 + k_l c_0} \quad (4)$$

Here,  $c_0$  is the initial concentration of the surfactant solution, and  $k_l$  is the Langmuir constant. According to the  $R_L$  values, the isotherm type can be classified as unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or

irreversible ( $R_L = 0$ ) [39].



**Figure 9.** Langmuir adsorption isotherms fitting curves for (a) ZSC/quartz, (b) SDS/quartz.

### 3.6.2. Freundlich isotherm

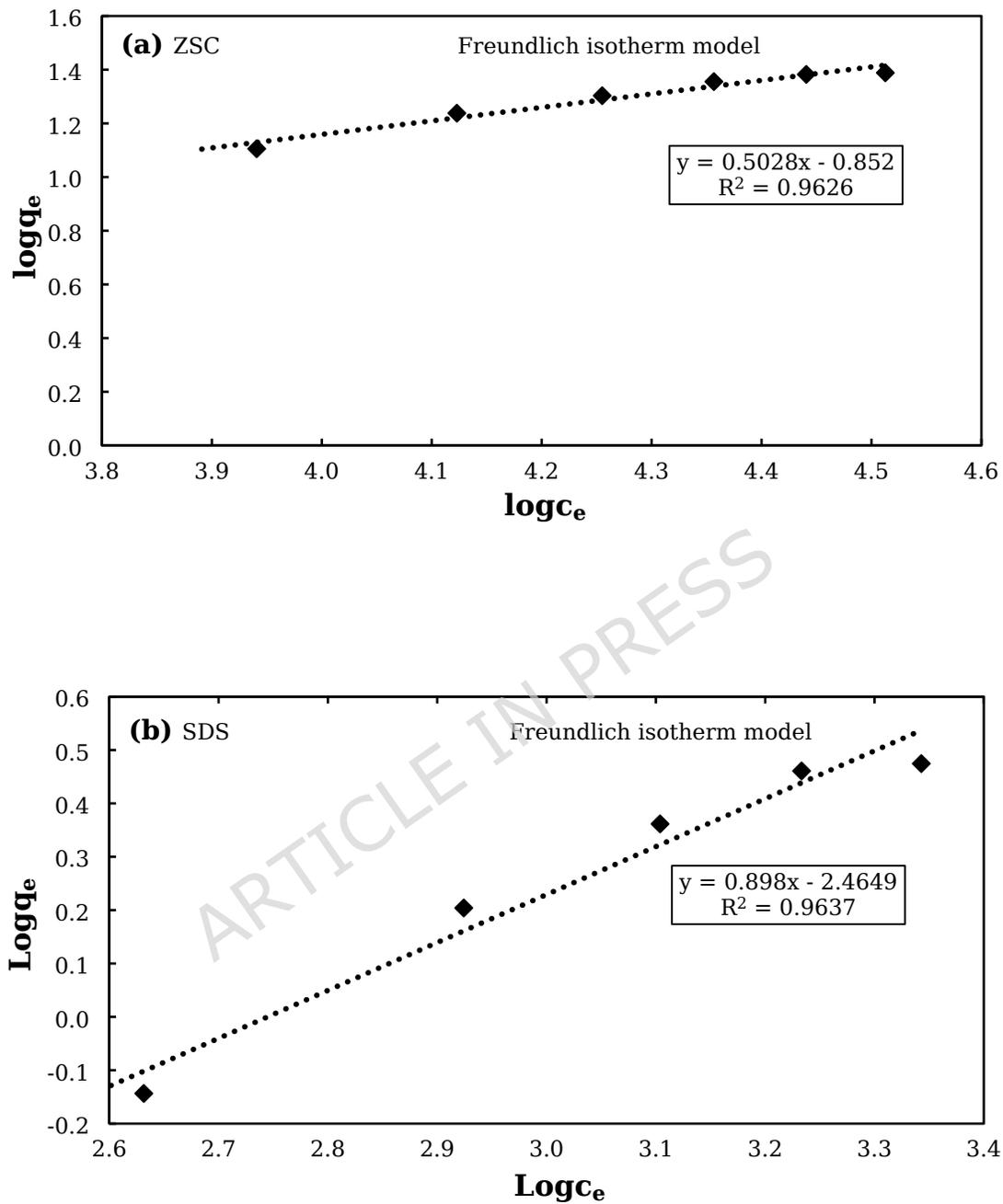
According to the Freundlich isotherm, multilayer adsorption occurs onto a heterogeneous surface [96,97]. This model is represented by the equation that follows [60]:

$$q_e = k_f c_e^{\frac{1}{n}} \quad (5)$$

where  $k_f$  represents the Freundlich isotherm constant and  $1/n$  represents the heterogeneity factor. Equation (5) can be displayed in its linear form as follows:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (6)$$

$k_f$  and  $n$  were obtained from the slope and intercept of the linear  $\log q_e$  versus  $\log c_e$  graph. The fitting of the ZSC and SDS adsorption isotherms using the Freundlich equation is shown in Figure 10.



**Figure 10.** Freundlich adsorption isotherms fitting curves for (a) ZSC/quartz, (b) SDS/quartz.

### 3.6.3. Temkin isotherm

The impact of the interaction between the adsorbent and adsorbate

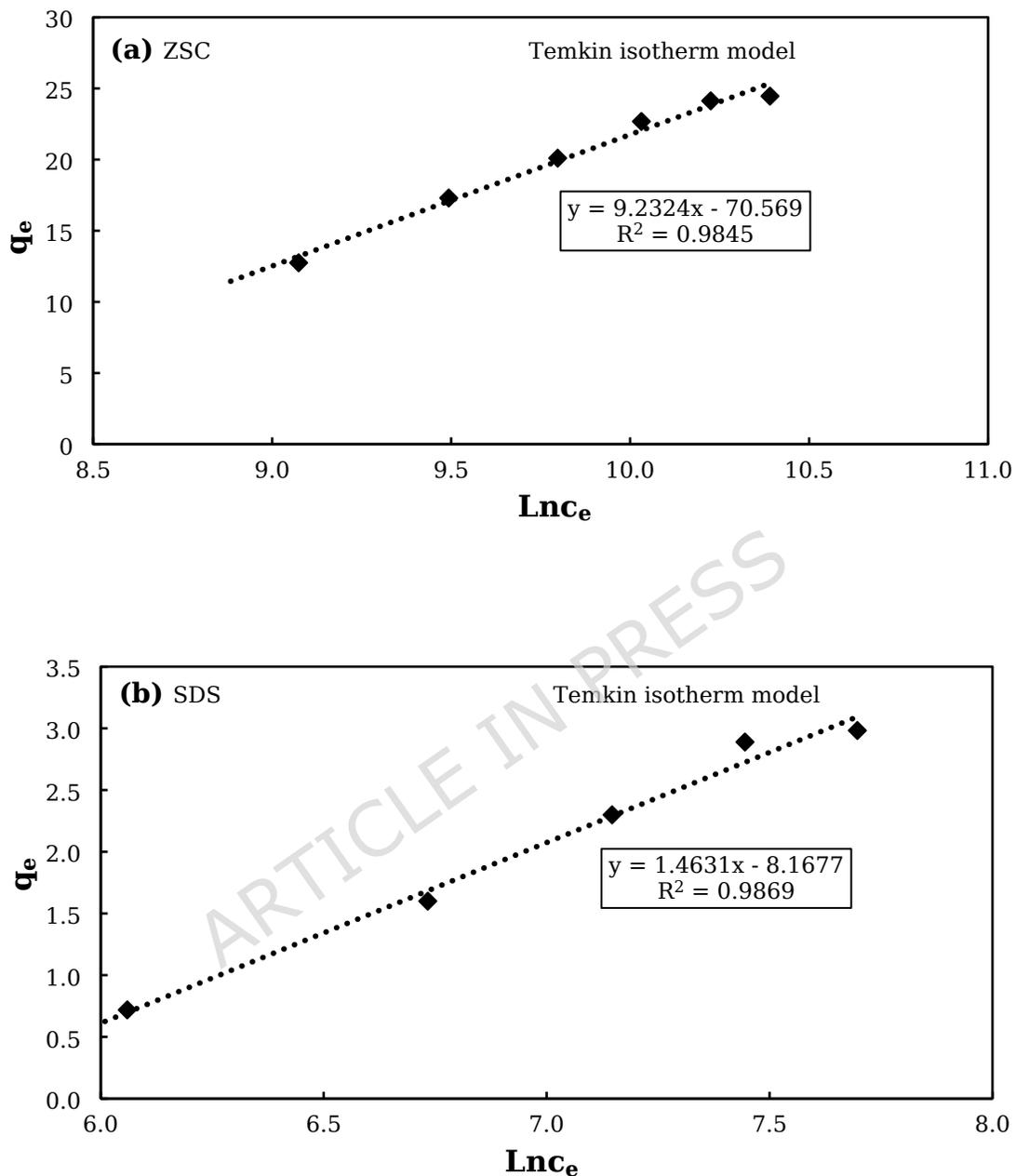
molecules is explained by the Temkin isotherm model [78]. The Temkin isotherm recommends that the adsorption heat decreases linearly with increasing coverage [60]. The Temkin equation is represented in the following form [41]:

$$q_e = \frac{RT}{b} \ln(k_t c_e) \quad (7)$$

The simple linear form of the equation above is as follows:

$$q_e = B \ln k_t + B \ln c_e \quad (8)$$

where  $B = RT/b$ ,  $b$  and  $k_t$  correspond to Temkin constants,  $T$  denotes the temperature, and  $R$  represents the gas constant. Therefore, linear plotting of  $q_e$  versus  $\ln c_e$  enables one to determine  $k_t$  and  $B$  from the intercept and slope, respectively. Reported ranges in adsorption literature indicate that adsorption energies below 8–40 kJ/mol are characteristic of physisorption dominated by weak van der Waals and electrostatic interactions, whereas chemisorption processes typically exceed 40 kJ/mol [97,98]. The fitting of adsorption data to the Temkin model is depicted in [Figure 11](#).



**Figure 11.** Temkin adsorption isotherms fitting curves for (a) ZSC/quartz, (b) SDS/quartz.

The parameters of Langmuir, Freundlich, and Temkin isotherm models and coefficient of determination ( $R^2$ ) values obtained by experimental data are reported in [Table 3](#) for the ZSC and SDS surfactants adsorption onto the

surface of quartz adsorbent. Parameter  $R^2$  is defined as follows [19]:

$$R^2 = 1 - \frac{\sum_{i=1}^N (q_{e,i} - q_{p,i})^2}{\sum_{i=1}^N (q_{p,i} - \bar{q}_{e,i})^2} \quad (9)$$

where  $q_{e,i}$  and  $q_{p,i}$  represent the experimental and predicted equilibrium adsorption values, respectively.

**Table 3.** Parameters of adsorption isotherm models of ZSC and SDS on quartz.

	Models	Parameter	Absorbent
			Quartz
ZSC	Langmuir	$k_l (L/mg)$	0.0878
		$R_L$	0.0011
		$R^2$	0.9917
	Freundlich	$k_f$	0.14
		$1/n$	0.5028
		$R^2$	0.9626
	Temkin	$b(J/mol)$	268.491
		$k_t (L/mg)$	$4.79 \times 10^{-4}$
		$R^2$	0.9845
SDS	Langmuir	$k_l (L/mg)$	0.2468
		$R_L$	0.0016
		$R^2$	0.9858
	Freundlich	$k_f$	0.0034
		$1/n$	0.8980
		$R^2$	0.9637
	Temkin	$b(J/mol)$	1694.2
		$k_t (L/mg)$	0.0038
		$R^2$	0.9869

The Langmuir model with  $R^2 = 0.9917$  showed the best fit to the experimental data, indicating a uniform monolayer adsorption of surfactant on the homogeneous surface of the adsorbent. The Freundlich model also provides a good fit to the data with an acceptable coefficient of determination ( $R^2 = 0.9626$ ) and indicates the presence of a heterogeneous surface in the adsorption process. While values of  $1/n$  greater than 1 represent weak

adsorption, values of  $1/n$  between 0.1 and 0.5 demonstrate strong adsorption, and values between 0.5 and 1 denote somewhat difficult adsorption. The value  $1/n = 0.5028$ , which is in the range of 0.5 to 1, indicates favorable adsorption conditions at different points on the adsorbent surface. Also, the value of  $k_f = 0.14$  indicates the intensity of adsorption at low concentrations. In the Temkin model, the value of  $R^2 = 0.9845$  also shows a good fit. The parameter  $b = 268.491$  J/mol in this model indicates that the adsorption mechanism is of a physical type, since this value is less than 8000 J/mol and therefore refers to physical bonds [99]. The value of  $k_t = 4.79 \times 10^{-4}$  L/mg indicates the relative binding strength between the adsorbent and the adsorbate. Accordingly, it can be concluded that although the Langmuir model has shown the highest accuracy, the Freundlich and Temkin models also provide useful information about the surface heterogeneity and multilayer adsorption, which is essential in a more comprehensive analysis of the adsorption behavior. In particular, the low value of the parameter  $1/n$  in the Freundlich model and  $b$  in the Temkin model can confirm that the adsorption process of ZSC on quartz is influenced by weak bonds between the surfactant and the rock surfaces and that multilayer physical adsorption has occurred on the heterogeneous surface. Also, considering the need to use higher concentrations of natural surfactants in industrial processes, the Freundlich and Temkin models can provide a more accurate description of the adsorption behavior in operational ranges.

According to [Table 3](#), the Langmuir model with a high coefficient of

determination ( $R^2 = 0.9858$ ) showed the best fit to the experimental data. This indicates that the adsorption of SDS on quartz surfaces occurs in a monolayer form. The value of  $R_L = 0.0016$  between 0 and 1, indicating the favorable nature of the adsorption based on the Langmuir model. This very low value of  $R_L$  indicates that the adsorption was very suitable and effective at the tested concentrations. The Freundlich model, with a relatively lower coefficient of determination ( $R^2 = 0.9637$ ), provided a poorer fit to the data than the Langmuir model. However, the value of  $1/n = 0.8980$ , which is close to 1, indicates that the adsorbent surface behaves relatively uniformly and the adsorption occurs under near-linear conditions. The very low value of  $k_f = 0.0034$  indicates that the adsorption intensity is very limited at low concentrations of SDS on quartz. In the Temkin model, a relatively high value of  $R^2 = 0.9869$  is obtained, indicating that this model also fits the data well. The value of  $b = 1694.2$  J/mol, which, considering the value of less than 8000 J/mol, can be concluded that the adsorption mechanism is physical. The value of  $k_t = 0.0038$  L/mg indicates a low strength of interaction between SDS and the quartz surface. Overall, the Langmuir model is the dominant model in describing the adsorption behavior of SDS on quartz due to its higher correlation and significant adsorption capacity. However, the Tamkin model can provide useful information regarding the physical nature of the adsorption process. The Freundlich model provides a weaker description of the adsorption process.

#### **4. Conclusions**

From the results of this study, it can be concluded that the adsorption of ZSC on quartz (approximately 25 mg/g) is about 8 times more than that of SDS on quartz (around 3 mg/g). The reason is that ZSC is neutral, and it therefore does not repel the negatively charged quartz surface. Based on the correlation coefficient ( $R^2$ ), the Langmuir model with  $R^2 = 0.9917$  for ZSC and  $R^2 = 0.9858$  for SDS is the most appropriate model. This study was conducted using pure quartz in order to isolate the fundamental adsorption behavior on the dominant sandstone mineral. It is acknowledged that many sandstone reservoirs contain clay constituents that may enhance surfactant adsorption through specific surface interactions. Therefore, the present results are most representative of quartz-rich systems, and future studies will extend this work to clay-bearing sandstones.

### **Data availability**

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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