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Comparative Study on Adsorption of Biologically Generated Surface Active Agents on Carbonate and Sandstone Rock Surfaces

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Abstract

Surfactant adsorption at rock-fluid interface is fundamental to wettability alteration that is relevant to enhanced oil recovery process but the extent of this adsorption can also impact the economic viability of the surfactant application in the process. In this paper, adsorptions of two biologically generated surfactants (rhamnolipid and greenzyme) on carbonate and sandstone rock surfaces have been studied and reported. The rocks' main components and physicochemical makeup were determined with the use of X-ray diffraction and scanning electron microscopy. The compositional analyses of sandstone and carbonate rocks show the dominant components as quartz and calcite respectively. From the adsorption investigations, rhamnolipid tends to show higher surface activity than greenzyme. It also shows stronger affinity for sandstone rock surface than carbonate while greenzyme shows stronger affinity for carbonate surface. Furthermore, decrease in adsorptions of rhamnolipid and greenzyme with increase in temperature and decrease in salinity was observed in all the systems. Finally, the adsorption models suggest rhamnolipid adsorption process to be mono-layer in nature, while greenzyme adsorption tends to be mono-layer at low adsorption and heterogeneous at high adsorption.

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Keywords

Adsorption, Biosurfactant, Rhamnolipid, Greenzyme, Carbonate, Sandstone

Introduction

Surfactant adsorption at rock-fluid interface is fundamental to wettability alteration that is relevant to enhanced oil recovery (EOR) process. However, the extent of this adsorption on porous reservoir rocks can also impact the economic viability of their application in the process because high adsorption of surfactants may limit their efficiency in practical EOR applications due to concentration reduction during flooding process (Green and Willhite, 1998; Sheng, 2011). Adsorption is a dynamic process that involves an interaction between the adsorbed substance (adsorbate) and the substance on which adsorption takes place (adsorbent). In a solid-liquid interaction, interfacial adsorption involves molecular compositional changes of the system in which surfactant molecules are transferred from bulk solution to the interface (Myers, 1999). Adsorption may result from either physical interaction otherwise known as physisorption or chemical inter- action known as chemisorption, the difference between these two is usually based on their temperature dependence. In physisorption process, adsorption reduces generally with increase in temperature while in chemisorption process, adsorption increases with temperature (Somasundaran and Krishnakumar, 1997). The phenomena by which surfactant adsorbs to solid surface from aqueous solution involves different mechanisms such as: ion exchange,

ion pairing, hydrogen bonding, Van der Waal force and hydrophobic interaction (Norde, 1996; Nakanishi *et al.*, 2001; Rosen, 2004). Surfactant adsorption however, is a complex process that is greatly influenced by environmental factors such as solid composition, aqueous solution composition, ionic strength, pH as well as the nature and concentration of surfactants (Azam *et al.*, 2013).

Chemical surfactants are commonly used in EOR processes due to their high surface activity but they however constitute environmental threat because of their non-degradable nature. Hence, biologically generated surfactants (biosurfactants) are now being considered as possible substitutes for their chemical counterparts (Van Hamme *et al.*, 2006). Biosurfactants also have the following advantages: biodegradability, renewable sources, environmental friendliness and adaptability to extreme reservoir conditions such as high temperature and salinity (Banat, 1995). However, high cost of massive production of biosurfactants has been the major disadvantage (Banat, 2014), but studies have shown that biosurfactants can be generated from waste products and engineering of cheap renewal natural substrates (Banat *et al.*, 2010; Muller and Hausmann, 2011). In fact, some biosurfactants production process has reached an advanced stage and are being commercialised, but they are still highly under utilised (Sineriz *et al.*, 2001). The objective of this work therefore, is to investigate biosurfactant adsorption on natural sandstone and carbonate rock surfaces under varied brine salinity and temperature relevant to hydrocarbon reservoirs using rhamnolipid (sugar based) and greenzyme (protein-enzyme based) as case study.

Most previous studies on adsorption of rhamnolipid and proteins have been in environmental, medical and food sciences. For instance, Keomany and Asnachinda (2014) studied adsorption of rhamnolipid on aluminum oxide for the purpose of organic removal of solute from aqueous solution in which adsorption process was attributed to admicelle partitioning effect. Noordman *et al.*, (2000) on the other hand, studied adsorption process of rhamnolipid on two sandy soil for the purpose of soil remediation and the observed adsorption process was associated with hydrophobic interaction driven by interfacial process rather than partitioning process. Furthermore, Chen (2016) has reported insignificant impact of calcium ion on rhamnolipid adsorption and demonstrated how rhamnolipid adsorption process is similar to that of non-ionic surfactants. Norde and Anusiem (1992) however studied adsorption process of five proteins on silica and hematite surfaces and they observed two trends of adsorption process as: protein restructuring in which had sorption takes place irrespective of the surface charges and electrostatic attraction between opposite charges. Koutsoukos *et al.*, (1983) also studied adsorption of two proteins on hematite surfaces and observed similar trend to what Norde and Anusiem (1992) reported. Meylheuc *et al.*, (2001) studied the effect of rhamnolipid on stainless steel for the purpose of inhibiting adhesion of pathogenic strain on its surface. Also, Addessoand Lund (1997) reported adsorption of protein on stainless steel, titanium and Teflon in relation to fouling heat exchanger. While Shibata and Lenhoff (1992) studied proteins adsorption on modified quartz surface under conditions applicable to liquid chromatography.

There is however no previous study on the comparative adsorption of either rhamnolipid or greenzyme on both sandstone and carbonate rock samples. Sandstone and carbonate rocks are samples of reservoir rocks with carbonate holding more than 50% of oil world reserves and sandstone is the most commonly studied reservoir rock (Sheng, 2013). In this study, static adsorption of rhamnolipid and greenzyme on sandstone and carbonate rock surfaces have been experimentally investigated and reported. The experimental data were also fitted with Langmuir and Freundlich adsorption models for better understanding of the observed adsorption process.

Materials and Methods

Three brine solutions comprising of high salinity (HS), medium salinity (MS) and low salinity (LS) were used to investigate the salinity effects on adsorption of these biosurfactants. Table 1 presents the compositional breakdown and concentration of these brine solutions. The HS is an example of formation brine in hydrocarbon reservoir, while MS is an example of seawater that is sometimes injected into the reservoir and the LS water is an example of injection water usually used for EOR process. The absorbents used for all the experiments were outcrop rock samples that mimic reservoir rocks. Clashach sandstone from Scotland and Estaillades limestone from France were used as a representative of sandstone and carbonate rock respectively. The main composition of these rock samples as determined by X-ray diffraction and scanning electron microscopy analyses are presented in Table 2. The two biologically produced surfactants used in this study are rhamnolipid of Agae Technology USA and greenzyme from Biotech Processing Supply, Dallas Texas.

Methods

Specific surface area determination

The specific surface areas of the rock samples available for adsorption of biosurfactants were measured based on N_2 physisorption with Micromeritic flowPrep 060 using Brunauer-Emmet-Teller (BET) method (Rouquerol *et al.*, 2013). The rock samples were grinded into powder and sieved using 300 μm mesh size and below and then subjected to heat treatment at 200ºC for 4 h. Finally, the adsorption and desorption of N_2 at its boiling point of -196ºC were carried out over a relative pressure range of 0.01-1.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses

The Bruker D8 Advance Powder Diffractometer was used to carryout X-ray diffraction (XRD) analysis on the powdered sands to Ne and carbonate in order to determine the main components in rock samples. While the Topcon ABT 60 Scanning Electron Microscope was used to capture the polished carbon coated rock samples elemental compositional distribution.

Biosurfactants analysis

The compositional analysis of functional groups of rhamnolipid and greenzyme were determined with Fourier Transform Infrared (FTIR) method. This is based on absorbance spectroscopy in which infrared absorbance of biosurfactant molecules was measured and used as quantitative measure of their compositional functional groups. These functional groups give an indication of the strength of their hydrophilic and hydrophobic groups which are fundamental to their hydrophilicity and hydrophobicity effects in interfacial interactions.

Adsorption test

The concentration depletion method (Hlady, 1999) which involves comparison of biosurfactants concentration in aqueous solutions before and after contacting them with rock surfaces was used to determine the biosurfactant equilibrium concentration, based on absorbance measurement described by Gogoi (2009). A series of batch experiments on static adsorption of rhamnolipid and greenzyme on the rock surfaces were carried out using 1g of grinded rock in 10mL aqueous solutions. Different concentrations of aqueous solutions of rhamnolipid and greenzyme were prepared and each rock sample was mixed with the aqueous solutions. The mixtures were then subjected to continuous mixing on a VWR incubating orbital shaker for 24 h at the temperature of interest (25, 50 and 65ºC) for all experiments. Thereafter, the mixtures were cooled and centrifuged at 13,000 rpm for at least 15 min and the supernatants were extracted for analysis (Azam, 2013).
The Jenway 6850UV-Vis spectrophotometer was used to measure the absorbance of samples over a wavelength range of 250-650 nm. For greenzyme, the maximum peak obtained from the scan at 265 nm was used to generate a calibration curve with deionised water being used as reference. However, for rhamnolipid, the method used by Rahman *et al.*, (2002) for crude rhamnolipid was adopted because of the difficulty encountered in identifying a well- defined peak. This involves addition of 1 ml of rhamnolipid aqueous solution to 4.5 ml of diluted sulfuric acid (6:1 v/v), the mixtures were properly mixed and then subjected to 100ºC heating for 10 min. The mixtures were cooled to room temperature after which 0.1 ml of freshly prepared thioglycolic acid was added and the samples were incubated for 3 h in darkness. An absorbance scan was then carried out on the samples and the maximum peak obtained at 378 nm was used to generate the calibration curve.

This procedure was applied to all the supernatant extracted after adsorption before absorbance measurements. For brine solutions with high concentrations, dilution factors of 20-50 were applied before measurements. The amount of rhamnolipid and greenzyme that adsorbed on the rock surface was determined from the difference between their respective initial and equilibrium concentrations using Equation 1 (Rosen, 2013).

$$\Gamma_e = \frac{(C_0 - C_e)V}{mS_a}, \quad (1)$$

Where Γ_e is adsorbed amount per unit area (mg/m^2), C_0 and Ce is the initial and equilibrium concentration (mg/ml) respectively, V is volume of the solvent used (ml), m is mass of rock samples (g) and S_a is the specific surface area of rock samples (m^2/g). The effect of temperature and salinity on adsorption of rhamnolipid and greenzyme on carbonate and sand stone rock surfaces were also investigated by increasing the system temperature and using brine solutions. For salinity effect investigations, high and medium salinity were used for greenzyme, while only low salinity was used for

rhamnolipid due to precipitation effects observed with high salinity brine.

Results and Discussions

Specific surface area determination

Figure 1 shows the adsorption and desorption of nitrogen used to determine the specific surface areas of the rock samples. The isotherms are type IV with hysteresis loop at relative pressure of 0.8-1.0 and 0.9-1.0 for sandstone and carbonate respectively, which shows that they are both mesoporous (Wu *et al.*, 2014). The measured BET specific surface area of sands to ne sample was found to be 1.1279m^2/g while that of the carbonate was 0.8221m^2/g. These specific surface areas define the available space for the adsorption of rhamnolipid and greenzyme during the adsorption process.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses

The compositions of the sand stone and carbonate rock samples as determined from XRD analysis are reported in Table 2. Silica has the highest fraction in sandstone while calcite has the highest fraction in carbonate. The compositional distribution of the rocks minerals and pore structure as imaged by SEM are presented in Figures 2a and 2b. Since sandstone and carbonate rocks have different composition, it is expected that they will experience different surface reaction when exposed to the same fluids. The surface chemistry of the sandstone and carbonate rock samples may therefore be greatly influenced by silica and calcite respectively.

Compositional analysis of rhamnolipid and greenzyme

Figure 3 shows the combined FTIR spectra of rhamnolipid and greenzyme, the spectra were examined with regard to -OH vibrations (3,600-3,200 cm^{-1}), -CH_2 vibrations (3,000-2,800 cm^{-1}), -C=O vibrations (1,750-1,600 cm^{-1}), and the fingerprint section (900-1460 cm^{-1}). They both have similarities and differences based on their source as evidenced in the fingerprint section. The main vibrational peaks used to determine the hydrophilic group was due to hydroxyl functional group (-OH) at 3,351 cm^{-1} which is common to both of them with greenzyme having a more pronounced absorbance than rhamnolipid. This suggests that greenzyme has more hydrophilic groups than rhamnolipid. Also common to both is the stretching bonds of CH_2 and CH_3 groups at 2925 & 2927 and 2854 & 2857cm^{-1}respectively, indicating the presence of alkanes which is more pronounced in rhamnolipid than greenzyme. This may suggest that rhamnolipid has more hydrophobic group than greenzyme.

Furthermore, the presence of carboxylic acids groups as shown by C=O at 1637 & 1638 $cm^{-1}$is also common to both and it is usually referred to as amideI in proteins (Yu, 2006; Kong, and Yu, 2007) and carboxylate an ion stretching in rhamnolipid (Gogoi *et al.*, 2016). However, in the fingerprint section between 900-1460 cm^{-1}, the differences in both are evident. rhamnolipid have a pronounced C-H, C-O and CH_3 at 1400, 1124, 1051 cm^{-1}showing the presence of carbonyl group (carbohydrate) as rhamnose (Leitermann *et al.*, 2008). Greenzyme however has wagging amino group of NH_2, CN and CH_3 stretching at 1482, 1183 and 1032 cm^{-1}known as amide II and amide III in the fingerprint section (Yu, 2006; Wolpert and Hellwig, 2006). These results are consistent with studies done on FTIR investigation of cultured rhamnolipid and protein as reported in the literature e.g. (Wolpert and Hellwig, 2006; Kong and Yu, 2007; Barth, 2007; Leitermann *et al.*, 2008; Zhangand Yang , 2015; Noramiza *et al.*, 2016).

This shows that they both have similar molecular composition consisting of carbon, hydrogen, oxygen with greenzyme having an addition of nitrogen. This also suggests the possibility of greenzyme being more hydrophilic in nature than rhamnolipid as indicated by higher H-O-H vibrations due to hydrogen bonding, while rhamnolipid tend to have a higher hydrophobic nature than greenzyme as suggested by the stronger presence of -CH_3, -CH_2 in their spectrum. Also, Traube's rule states that "in dilute aqueous solutions of surfactants belonging to anyone homologous series, the molar concentrations required to produce equal lowering of the surface tension of water decreases three fold for each additional CH_2 group in the hydrocarbon chain of the solute" (Attwood, and Florence, 2012). Furthermore, Ozdemir *et al.*, (2004) also noted that pure mono-rhamnolipid (R1) has less hydrophilic nature than di-rhamnolipid (R2) due to the absence of the second rhamnosyl group which indicates its lower hydrophilicity. They also observed that R1 molecules have more surface activity than R2 that has higher hydrophilic group.

Adsorption isotherm

Adsorption data are usually presented as isotherm which mathematically relates surface active agent equilibrium concentration in liquid phase to its adsorbed amount (per

unit area) on the solid surface at a particular temperature with the aid of plot (Hlady, 1999; Rosen, 2004). Figure 4 shows the adsorption isotherms of rhamnolipid and greenzyme on sandstone and carbonate rock surfaces. At low concentration, their respective adsorption increases with increase in concentration until the adsorbed plateau was reached, when no significant change in adsorbed quantity was observed.

A closer look at the adsorption isotherms of rhamnolipid and greenzyme, show that adsorption isotherms of rhamnolipid have the four clearly defined regions of isotherm described by Somasundaran and Krishnakumar (1997) while greenzyme isotherms only have three regions. The adsorption isotherms of rhamnolipid are however similar to isotherm commonly obtain for biosurfactants and chemical surfactants e.g. (Paria, and Khilar, 2004; Dubey *et al.,* 2008; Rizwan *et al.,* 2013; Keomany and Asnachinda, 2014) and greenzyme isotherms are similar to the commonly reported proteins isotherms e.g. (Norde, 1996; Addesso and Lund, 1997; Hlady, 1999; Norde *et al.,* 2008).

The rhamnolipid isotherm show that at relatively low concentration in region I, adsorption of rhamnolipid was characterized by electrostatic interaction between the hydrophilic head of rhamnolipid and rock surfaces but with the increase in concentration, further adsorption was based on hydrophobic interaction between hydrophobic tail of adsorbed rhamnolipid and that of the solution molecules resulting information of admicelle at the surface in region II.

Further adsorption with increase in concentration resulted in growth of admicelles to micelles due to increased hydrophobic interaction in region III, until adsorption plateau was attained in region VI. The rhamnolipid adsorbed quantity on sandstone and carbonate were found to be 4.40 $mg/m^2$and 4.21 mg/m^2respectively. Beyond these points there was no significant difference in adsorbed amount, rhamnolipid however adsorb more on sandstone than carbonate.

The greenzyme isotherms on the other hand did not have region I characterized by linear increase in adsorption with increase in concentration. The adsorption isotherms began with region II associated with sudden increase in adsorption. This indicates spontaneous adsorption of greenzyme on the rock surfaces with a non-uniform distribution of its molecules on the surface side-way at low concentration as suggested by Norde (1996). At higherconcentration,adsorptiontakesplaceintwosequence, thefirstsequenceisfastandinvolvesdirectproteinsadsorptio nto the surface without any conformational changes while the second sequence is slow and involves conformational changes from side-one to end-one type promoting hydrophobic interaction which leads to increased adsorption and surface layer thickness (Dietschweiler and Sander, 2007). This occurred in region III through region VI where adsorption limit was reached with the plateau adsorption of 2.01 $mg/m^2$for carbonate surface. However, for sandstone surface, region VI did not plateau with in the experimental time and the adsorbed quantity on this surface was found to be 0.32mg/m which is much less than that of the carbonate.

This observed difference in surface behaviour of the greenzyme on the two rock surfaces can therefore be related to conformational changes it underwent during adsorption process as observed with proteins adsorption by Xia (2001). Dietschweiler and Sander (2007)also reported similar effect in adsorption of hard and soft proteins on both negatively and positively charged surfaces in which most of the proteins showed reversed adsorption on both surfaces. Lysozyme for instance had the lowest adsorption on negatively charged surface and highest on positively charged surface and this was attributed to reduction in proteins stability due to increased net charges on the molecules.

On a general note, rhamnolipid exhibited higher adsorption on both rock surfaces than greenzyme, which is an indication of its higher surface activity potential. However, the cause of higher adsorption of rhamnolipid on the sand stone surface relative to its carbonate counter part is not very clear. As this observation is contrary to what is expected of anionic surfactant because in pH range (7.87-8.26) observed for aqueous rhamnolipid mixture with rock samples, the rock surface of sandstone is negatively charged while that of carbonate is positively charged (Somasundaran, and Agar, 1967; Jaafar *et al.,* 2014).

So, based on electrostatic cattraction, an ionic surfactant normally should adhere more on positively charged carbonate than negatively charged silica. The observed variance with this rhamnolipid can be related to weak nature of the carboxylic component in rhamnolipid (Chen *et al.,* 2013). From previous studies, rhamnolipid behave more like non-ionic rather than anionic (Yuan *et al.,* 2007; Chen *et al.,* 2013) and non-ionic surfactants adsorb on any surface in different oriented position through hydrogen bonding (Rosen, 2004).

Effect of salinity on adsorption of rhamnolipid andgreenzyme

Figure 5 shows the results of greenzyme and rhamnolipid adsorption on carbonate and sandstone surfaces undervariedsalinityconditions.Theadsorptionsofgreenzy meandrhamnolipidonbothrocksurfaceswerefound to be higher with the introduction of electrolyte in aqueous solutions. The greenzyme adsorption on sandstone and carbonate surfaces increased from 0.32 to 0.55 mg/$m^2$and 2.01 to 2.05 mg/m^2respectively with the use of 0.75 M salinity while its adsorption increased to 0.91 mg/$m^2$and 2.75 mg/m^2 respectively with 3 M salinity usage. For rhamnolipid, adsorption increased from 4.40 to 4.59mg/m^2 on sandstone and from 4.21 to 4.42mg/m^2 on carbonate with the use of 8.3 mM salinity. For better understanding, the adsorbed amount on the rock surfaces were directly related to the solutions ionic streng that varied concentration of greenzyme and rhamnolipid as shown in Figures 5b and 5d. It is obvious that adsorption of rhamnolipid and greenzyme increases with increase in salinity irrespective of their concentration.

This observed increase in the adsorption of greenzyme and rhamnolipid on both rock surfaces with the addition of electrolytes is attributable to compression of electric double layer resulting from decrease in electrostatic repulsion induced by presence of electrolyte ions in their aqueous solutions (Norde, 1996; Yuan *et al.*, 2007), which is consistent with other studies (Kirchman *et al.*, 1989; Itohetal., 1994; Yuan *et al.*, 2007; Norde *et al.*, 2008).

Norde *et al.*, (2008) noted that increase in electrostatic repulsion at rock-fluid interface weakens protein structural stability on the rock surface and invariably reduces its adsorption. Yuan *et al.*, (2007) observed increased adsorption of rhamnolipid with increase in aqueous salinity, while Kirchman et al., (1989) also observed higher protein adsorption in seawater than in low ionic strength buffer solution. The increased adsorption in aqueous sea water observed was attributed to compression of double layer due to the presence of cations that promote attraction between the same charges.

Table.1 Composition of brine solutions

Ions	HS(M)	MS(M)	LS(M)
Na^+	1.463	0.550	0.0061
Ca^{2+}	0.420	0.014	0.0002
Mg^{2+}	0.091	0.045	0.0005
Cl^-	2.485	0.620	0.0069
$SO4^{2-}$	0.002	0.024	0.0003
Ionic strength	3.000	0.750	0.0083

Table.2 Composition of Clashach sandstone and Estaillades limestone

Sandstone	
Components	**Amount (wt.%)**
SiO_2	92
$KAlSi_3O_8$	5
FeTiO	< 0.5
TiO_2	< 0.5
ZrO_2	< 0.5
$Al2O_3$	< 0.5
others	< 1
Limestone	
Components	**Amount (wt.%)**
$CaCO_3$	95
$MgCO_3$	4
$CaSO_4$	1

Figure.1 Nitrogen adsorption-desorption isotherm on: (a) carbonate rock (b) sandstone

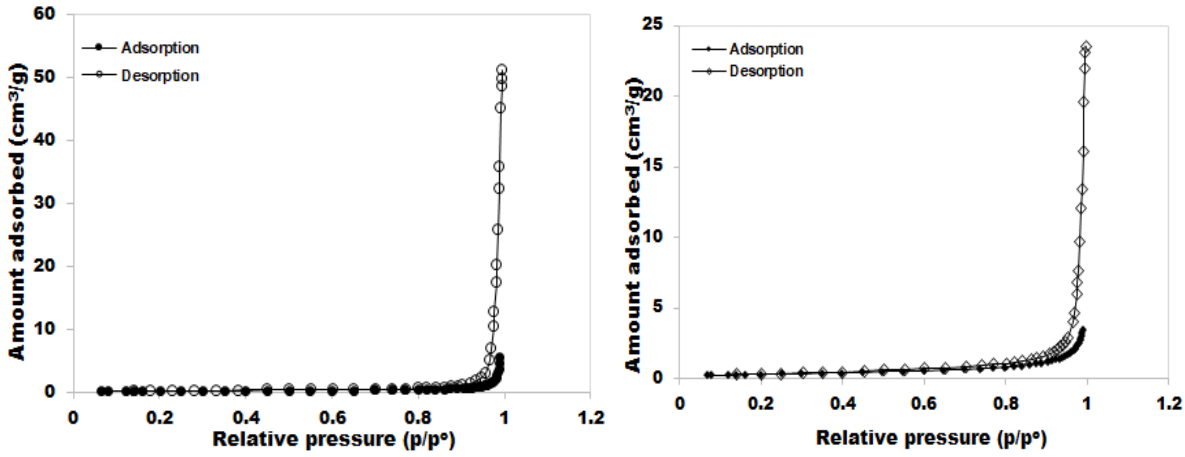


Figure.2 Scanning electron microscopy (SEM) analysis of: (a) sandstone (b) carbonate

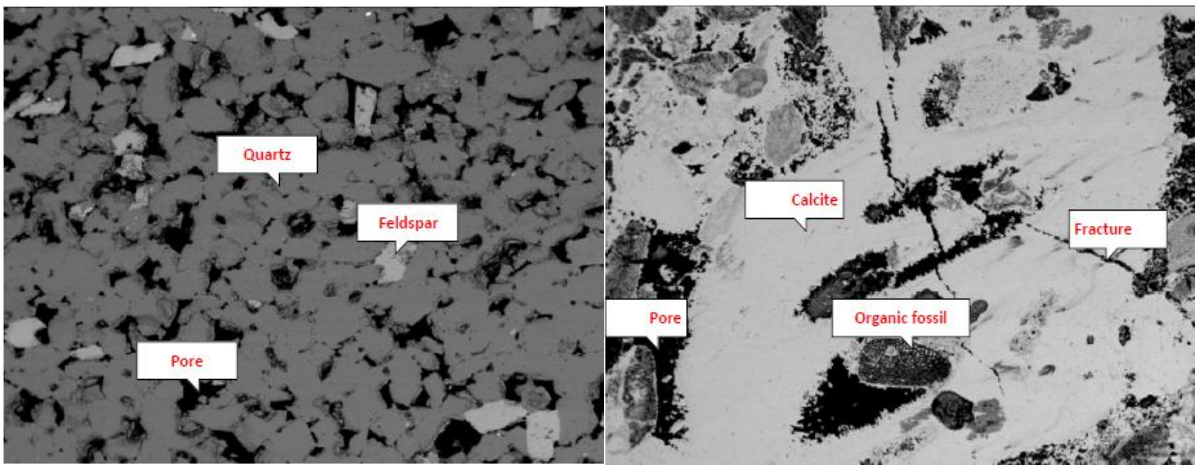


Figure.3 FTIR spectra of rhamnolipid and greenzyme with the peaks label notation for greenzyme written first, followed by rhamnolipid's notation. Where only one peak is labeled, the other sample's notation is omitted (-), it shows no absorbance

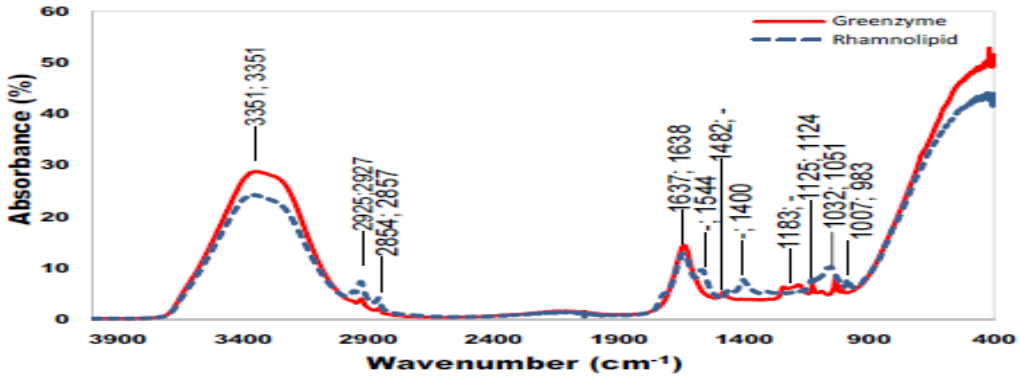


Figure.4 Plots of adsorption isotherm of (a) rhamnolipid on sandstone (b) rhamnolipid on carbonate (c) greenzyme on sandstone (d) greenzyme on carbonate

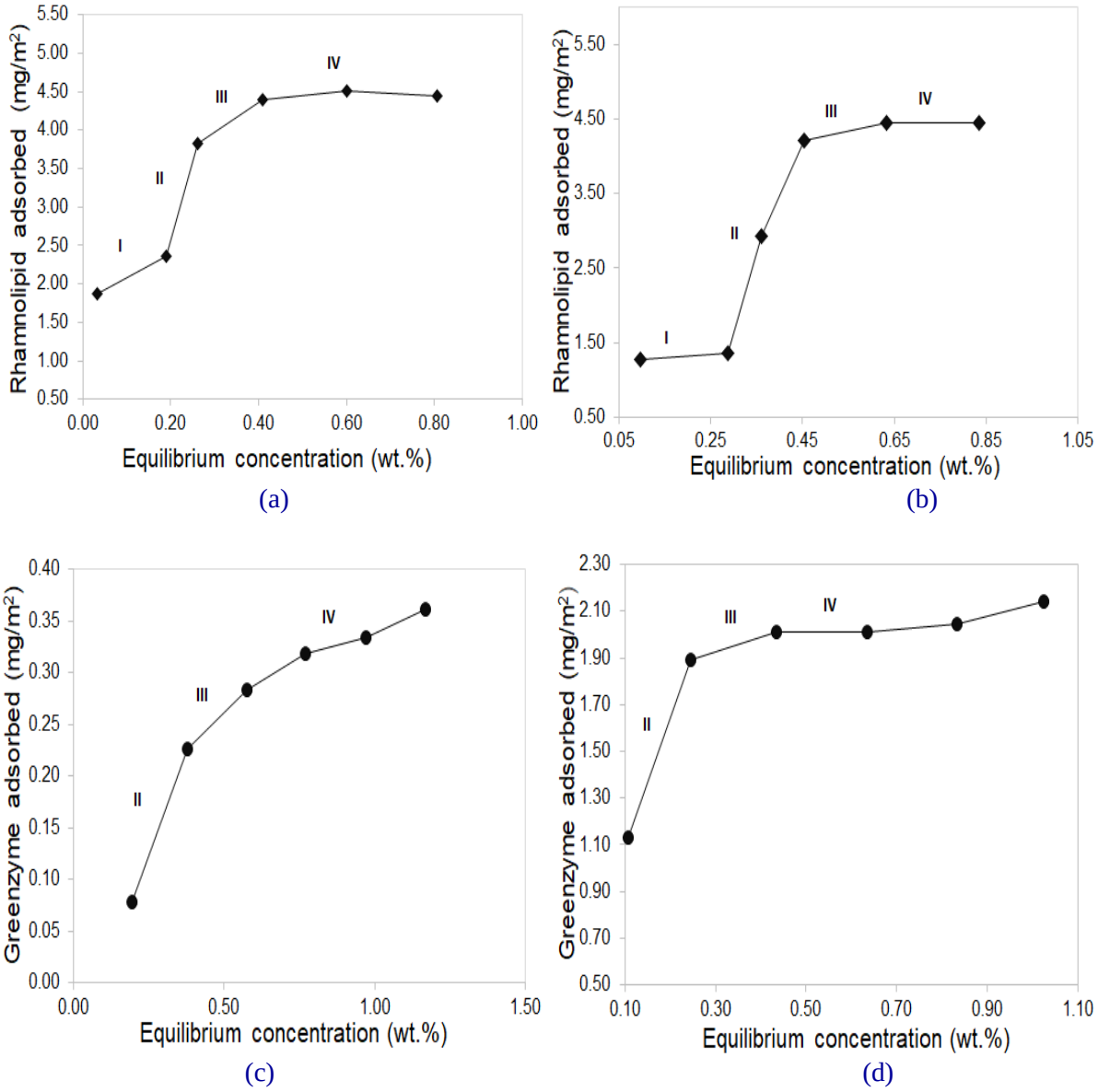
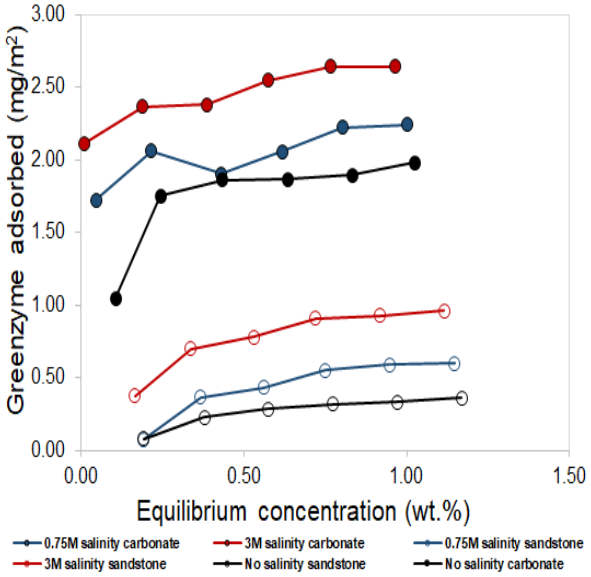
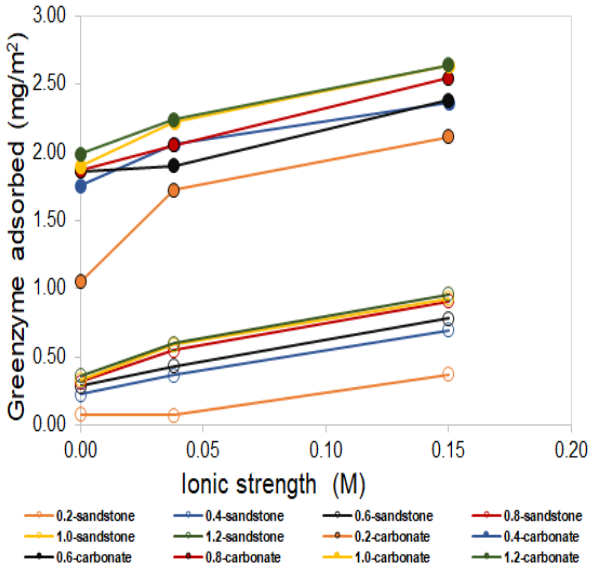


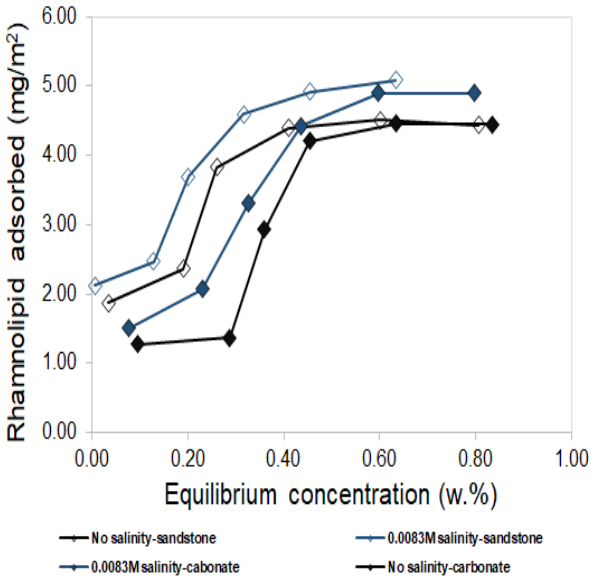
Figure.5 Salinity effects on adsorption of greenzyme and rhamnolipid: (a) greenzyme adsorption isotherms under different salinity conditions, (b) effect of solution ionic strength on greenzyme adsorption on rock surfaces, (c) rhamnolipid adsorption isotherms under different salinity conditions and (d) effect of solution ionic strength on rhamnolipid adsorption on rock surfaces



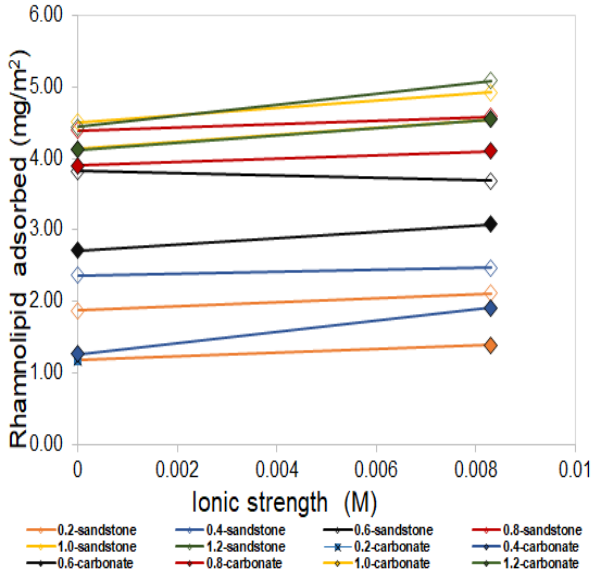
(a)



(b)



(c)



(d)

Figure.6 Temperature effects on: (a) adsorption isotherms of greenzyme on carbonate and sandstone rock surfaces,(b)adsorption isotherms of rhamnolipid on carbonate and sandstone rock surfaces, (c) adsorption of greenzyme on carbonate, (d) adsorption of greenzyme on sandstone, (e) adsorption of rhamnolipid on carbonate, (f) adsorption of rhamnolipid on sandstone

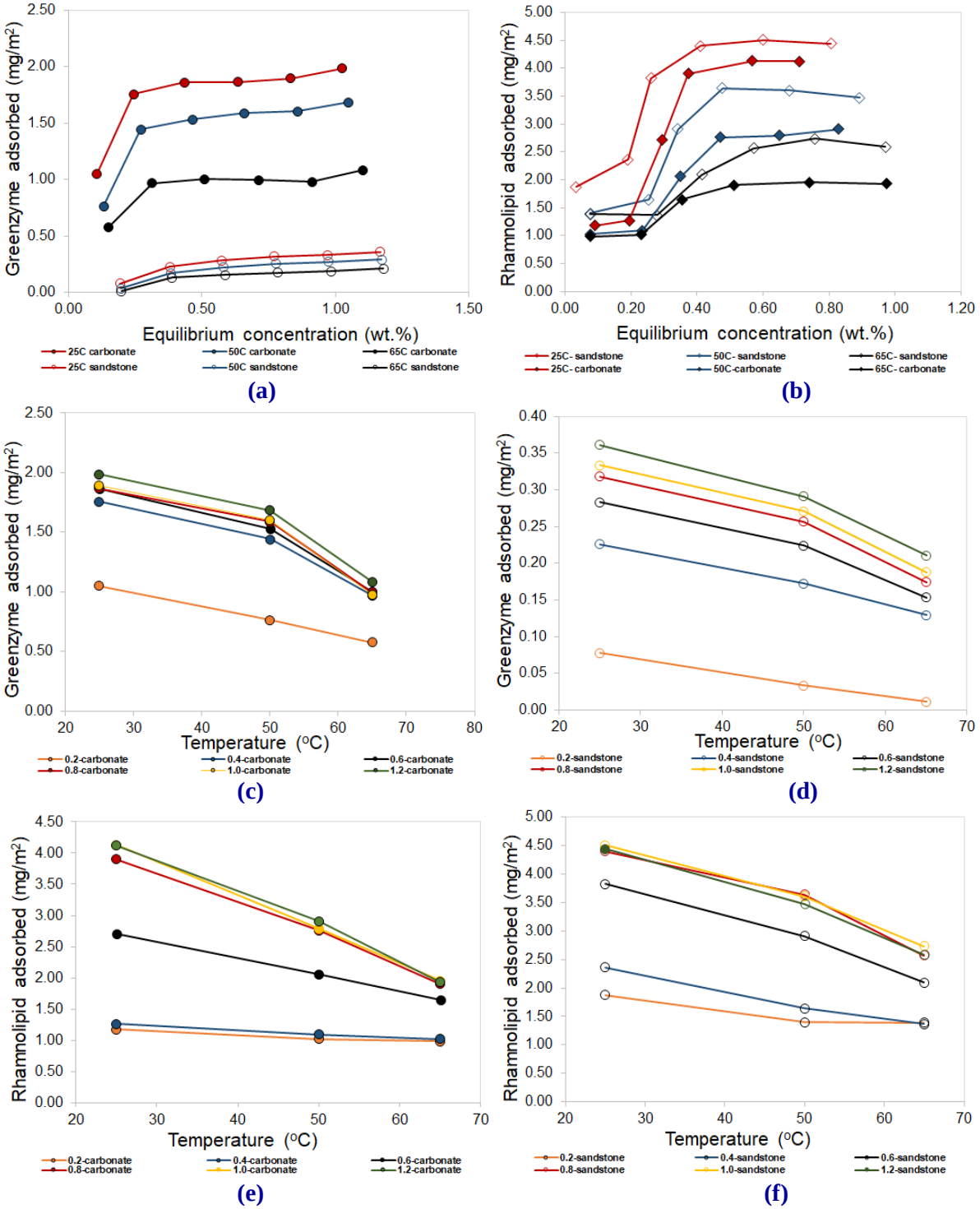


Figure.7 The Langmuir and Freundlich models data fitting of greenzyme: (a) salinity effect on sandstone, (b) salinity effect on carbonate, (c) temperature effect on sandstone and (d) temperature effect on carbonate

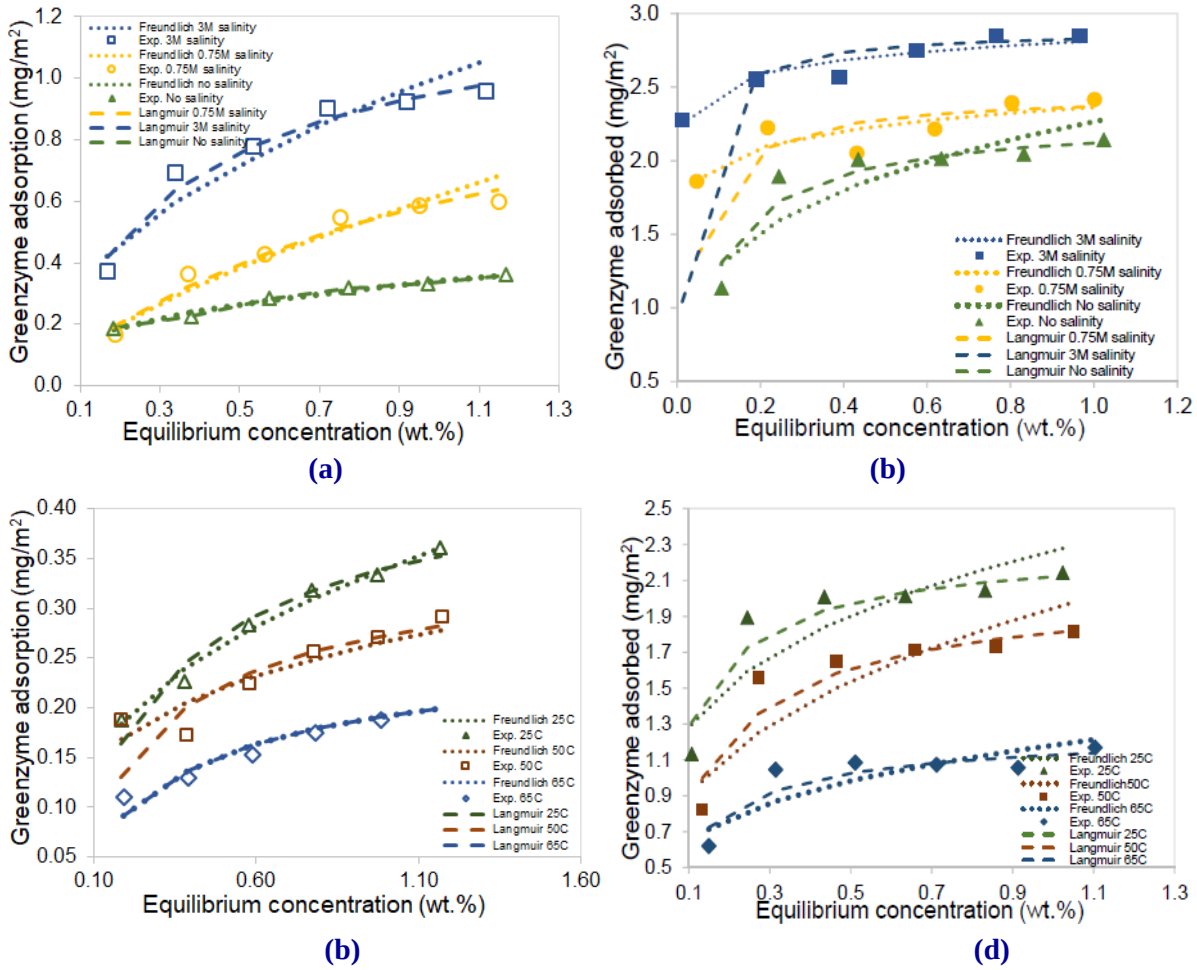
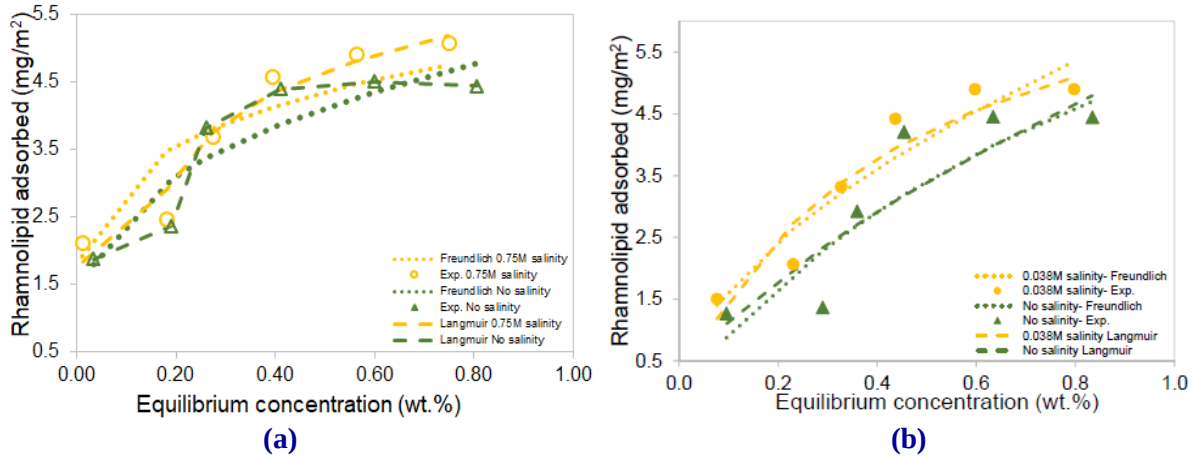
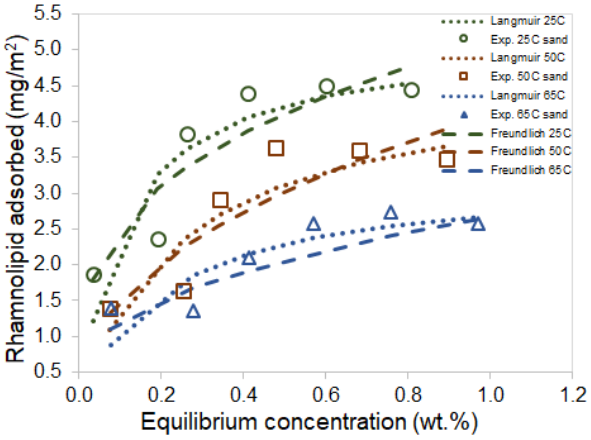
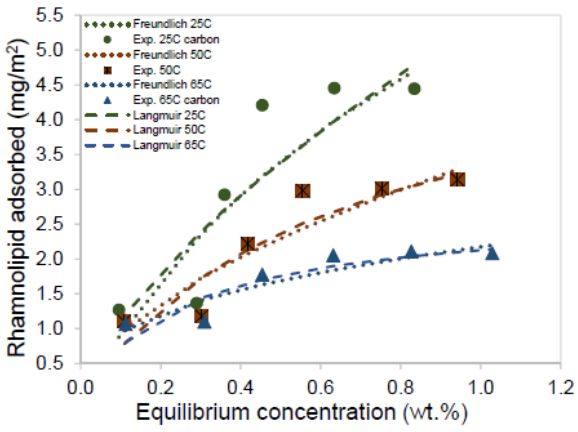


Figure.8 The Langmuir and Freundlich models data fitting of rhamnolipid: (a) salinity effect on sandstone, (b) salinity effect on carbonate, (c) temperature effect on sandstone and (d) temperature effect on carbonate





(c)



(d)

Nakanishi *et al.*, (2001) also noted that increase in ionic strength may influence hard protein adsorption on adsorbent but soft protein tends to adsorb on different surfaces irrespective of their electro- static nature due to their conformational nature. Itoh *et al.*, (1994) however demonstrated how adsorption of protein can be altered by modifying the carboxyl and amino acid groups. Increased adsorption was observed when the carboxyl (negatively charged) was reduced while no adsorption was observed when the aminoacid group (positively charge) was reduced. Hence, modification of the natural proteins through enzymatic process may have enhanced the solubility and stability of the greenzyme in all the solutions.

Effect of temperature on adsorption of rhamnolipid and greenzyme

Figure 6 shows the results of temperature effects on adsorption of greenzyme and rhamnolipid on sandstone and carbonate rock surfaces. Adsorption of greenzyme and rhamnolipid on both rock surfaces decreased with increase in temperature. Temperature increase from 25 ^{o}C to 50 ^{o}C and 65 ^{o}C, resulted in reduction of greenzyme adsorption on sandstone surface from 0.32 to 0.26 and 0.17 mg/m^{2}respectively while on carbonate surface, it reduced from 2.01 to 1.65 and 1.07 mg/m^{2}respectively. Rhamnolipid adsorption also reduced from 4.40 to 3.64 and 2.57 mg/m^{2}on sandstone and from 4.21 to 2.98 and 2.05 mg/m^{2}on carbonate.

This observation can be related to a higher kinetic energy effect with increased temperature as explained by Paria and Khilar (2004). Increased temperature leads to increased kinetic energy of their respective molecules and the system entropy, which invariably results in weaker interaction between their molecules and the rock surface.

It also results in decrease in their stability on the surface as the temperature increases hence, low adsorption was observed with increased temperature. This is an indication that their adsorption process was physisorption rather than chemisorption as described by Somasundaran and Krishnakumar (1997). The physisorption adsorption is basically due to weak bonding such as Vander Waals forces and hydrogen bonding hence, the adsorption of greenzyme and rhamnolipid on the rock surfaces can be related to interactions between their polar ends (mainly through hydrogen and hydroxide) and the rocksurface.

Previous studies have also shown that rhamnolipid behaves as non-ionic rather than anionic due to the weak nature of its carboxylic component (Yuan *et al.*, 2007; Chen *et al.*, 2013) and non-ionic surfactants adsorb on surfaces in different oriented positions through hydrogen bonding (Rosen, 2004).

Reduction in adsorption with increase in temperature has also been reported by Yuan *et al.*, *(*2007), Maleki *et al.*, (2012)and Hagiwara et al., (2015) and the observed reduction in adsorption with increase in temperature was also associated with reduced mobility of the molecules and exothermic sorption at increased temperature. However, the effect of temperature on greenzyme and rhamnolipid adsorption can also be influenced by thermodynamic of the adsorption process specific to their system. Some studies have recorded increased ad-sorption e.g. (Norde and Lyklema, 1978; Wahlgren and Arnebrant, 1991; Dubey, 2005) while some others have

observed decreased adsorption e.g. (Mitra and Chattoraj, 1979; Yuan *et al.,* 2007; Ladan, 2008; Maleki *et al.,* 2012; Hagiwara *et al.,* 2015), yet others have observed both effects (Dillman and Miller, 1973) and even non effect (Addesso and Lund, 1997) with increased temperature. This suggests that different biosurfactants show different thermal characteristics based on their source bacteria (Kuznetsov and Oppenheimer, 2012).

Adsorption thermodynamic model

For better understanding of the observed adsorption processes, the nature of adsorption of rhamnolipid and greenzyme on carbonate and sand stone rock surfaces were modeled with the Langmuir and the Freundlich adsorption models using the experimental data fitting. The Langmuir adsorption model describes mono-layer coverage while the Freundlich model describes heterogeneous coverage (Wu *et al.,* 2014). The nonlinear form of Langmuir equation is given as (Langmuir, 1917):

$$\Gamma_e = \Gamma_{max} \cdot \frac{\alpha C_e}{1+\alpha C_e}, \quad (2)$$

rearranging Equation 2 gives the linear form:

$$\frac{C_e}{\Gamma_e} = \frac{1}{\alpha \Gamma_{max}} + \frac{C_e}{\Gamma_{max}}, \quad (3)$$

where C_e is bulk concentration at equilibrium, α is Langmuir equilibrium constant, Γ_{max} is the maximum adsorbed density at equilibrium and Γ_e is surface density. The nonlinear Freundlich equation used is (Bera *et al.,* 2013):

$$\Gamma_e = K C_c^{\frac{1}{n}}, \quad (4)$$

and the linear form is given as:

$$ln\Gamma_e = lnK + \frac{1}{n} C_e, \quad (5)$$

where *k* and *n* are Freundlich constants related to adsorption capacity and intensity respectively.

Figures 7 and 8 show results of data fitting of different adsorption isotherms of greenzyme and rhamnolipid on carbonate and sandstone rock surfaces. All the adsorption of greenzyme on sandstone both in the presence of electrolytes and at increased temperature, are well fitted by Langmuir model which suggest that the adsorption of greenzyme in these system is monolayer. Also, the adsorption of greenzyme on carbonate surface in the absence of salt and at increased temperature tend to fit more with Langmuir model but its adsorption in the presence of electrolytes at low temperature fit more with Freundlich model which suggest heterogeneous coverage. All the greenzyme adsorption that fit well with the Langmuir model have lower range than those fitted by the Freundlich model, suggesting low greenzyme adsorption to be mono-layer while its high adsorption is multi-layer.

On the other hand, all adsorption of rhamnolipid were well fitted with Langmuir model, thereby suggesting rhamnolipid adsorption process on both rock surfaces to be mono-layer in nature. Noordman *et al.,* (2000) also de- scribed adsorption of rhamnolipid as mono-layer based on adsorption isotherm, although the data were not fitted with any model. This implies that adsorption of rhamnolipid and greenzyme on carbonate and sandstone surfaces can alter their respective wetting state depending on the fluid composition. Also, application of rhamnolipid and greenzyme in enhanced oil recovery will be associated with some retention due to their adsorption on the rock surface.

Conclusions

Compositional analysis of rhamnolipid and greenzyme was used to identify the strength of their hydrophilic and hydrophobic groups, which suggested higher hydrophobic groups in rhamnolipid and higher hydrophilic groups in greenzyme. The results of adsorption study have shown that rhamnolipid and greenzyme have the tendency to adsorbed on both carbonate and sandstone due to their surface activity effect with rhamnolipid having higher adsorption relative to greenzyme on both rock surfaces but with greater affinity for sandstone while greenzyme shows more affinity for carbonate surface. The observed high adsorption of rhamnolipid on both rock surfaces is attributable to its high surface activity. Also, decreased adsorption of rhamnolipid and greenzyme with increase in temperature and decrease in salinity was observed and the adsorption model suggested all rhamnolipid adsorption to be mono-layer while greenzyme adsorption was found to be mono-layer at low adsorption and multi-layer at high adsorption. This implies that the EOR application of rhamnolipid and greenzyme will be associated with some retention due to their adsorption on the rocksurface. This can also lead to rock surface wettability alteration which invariably will influence rock-fluid interactions.

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