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Experimental Investigation of Greenzyme Adsorption on Sand Surface

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Abstract: *Greenzyme application in oil reservoir is an emerging enhanced oil recovery process but its adsorption on the rock surface may result in the loss and reduction of its concentration during flooding hence, rendering it less efficient in practical application. This paper presents experimental study on greenzyme adsorption on sand surfaces of different grain sizes at varied temperatures. The concentration depletion method that accounts for the difference in enzyme concentrations in solutions before and after contacting the sand surface was used to determine the enzyme adsorption on relevant surface. The results show that adsorption of greenzyme on sand surface increases with increase in its concentrations and when small sand particles are used. Increase in system temperatures however resulted in reduction of its adsorption on the sand surface irrespective of the sand size and the concentration. Finally, the experimental data were fitted with Langmuir and Freundlich adsorption models and the results show that adsorption of greenzyme on the sand surface is better modelled with Langmuir isotherm.*

Keywords: *Greenzyme, adsorption, temperature, Langmuir, Freundlich.*

1. INTRODUCTION

The hydrocarbon reservoir is a complex system that involves rock and fluids interactions at varied temperatures and pressures. Introduction of any external compound into the system can modify the natural occurrences in the system thereby, increasing the complexity of the system. The effect of any relevant compound on rock-fluid interactions can however be studied in systematic manner in order to improve the understanding of the system. Interactions between rock (solid) and fluids as related to reservoir have been studied through different methods such as adsorption, electrophoresis mobility, zeta potential measurements, adhesion and contact angle measurements for better understanding of the complex reservoir system [1]. Greenzyme application in oil reservoir is an emerging enhanced oil recovery (EOR) process that is used to improve oil production from both carbonate and sandstone rocks [2-4]. The adsorption of greenzyme from the aqueous solution in the porous reservoir rock is fundamental to its EOR process because its loss due to adsorption on the rock surface will reduce its concentration and also impair its effectiveness and may turn into an uneconomical venture.

In solid-liquid adsorption process, the nature of the solid surface plays significant role in adsorption process [5, 6]. Solid surfaces can broadly be classified into polar and non-polar surfaces. For non-polar surface, adsorption emanates from dispersion forces interaction between the solid and surface-active compound but when the solid surface is strongly polarised, adsorption will be based on ionic interaction such as ion exchange and ion pairing [5]. The phenomena by which surface active compounds (e.g. greenzyme) adsorb to solid surface from aqueous solution involve different mechanisms such as: ion exchange in which the previously adsorbed counter-ions on the solid surface are replaced by similar ions from solution; ion pairing which involves surface active compound adsorption on free counter-ions on solid surface through hydrogen bonding, through dispersive forces via Van der Waal and hydrophobic bonding which involves interaction between hydrophobic groups of the compound molecules and formation of aggregates on the solid surface [6-8]. The adsorption data are usually presented as isotherm which mathematically relates surface active compound equilibrium concentration in liquid phase to its adsorbed amount on the solid surface at a particular temperature with the aid of plot [6]. Adsorption may result from either physical interaction (physisorption) in which adsorption reduces with increase in temperature or chemical interaction (chemisorption) in which adsorption increases with increase in temperature [9].

Greenzyme is a surface acting enzymatic compound produced from the deoxyribonucleic acid (DNA) of selected oil-eating cultured microbes through a batch fermentation process [10, 11]. Adsorption of greenzyme has not been extensively studied because it is an emerging process, although a recent study by Udoh [12] investigated greenzyme adsorption on carbonate and sandstone rock surfaces. However, only a fixed rock size was investigated. Since the reservoir sand grains vary in size from one location to another, it is therefore important that greenzyme adsorption investigations be carried out on different particle sizes in order to improve the understanding of the process and viability of its application. Hence, this study is aimed at investigating the effect of sand particle size and temperature variation on adsorption of greenzyme on sand surface. In this study, the experimental data were also fitted with Langmuir and Freundlich adsorption models for better understanding of the observed adsorption process.

2. MATERIALS AND METHOD

2.1 Samples Preparation

The three sand particle sizes used in this study were obtained from 0.15, 1.75 and 2.36 mm mesh diameter apertures. The sand was first washed with methanol under continuous stirring for 30 minutes in order to remove dirt from the surface. Thereafter, the methanol was drained and each of the samples was rinsed with distilled water 40 times until a turbid free water was obtained. Then, the sand was dried at 90 ºC in the oven for 24 hours. The clean dried sand particles were used for the experiments. Six concentrations (10, 50, 100, 200, 500 and 1000 mg/L) of greenzyme in aqueous solutions were investigated with an additional solution to which no greenzyme (0 concentration) was added being used as a base.

2.2 Adsorption Test

The concentration depletion method [13] of adsorption test was adopted in this study. This involves measurement of greenzyme concentration in aqueous solutions before and after contacting the solutions with sand surface for a period of 24 hours. A series of batch experiments were carried out to determine the adsorption isotherms of greenzyme on the different sand particle sizes. 1 g of cleaned sand particles were added to a set of 10 ml greenzyme solutions in a 20 ml vials. The mixtures were then subjected to continuous shaking in an automatic mechanical shaker for 24 hours at relevant system temperatures (25, 50 and 75 ºC) for all experiments. Thereafter, the mixtures were cooled and the solutions were separated from the sand particles. The equilibrium concentration of the greenzyme in the solutions were determined by conductivity measurements of the solutions. The amount of greenzyme adsorbed on the sand surface Γ (mg/g), was calculated using Equation 1 [14]:

$$\Gamma = (C_0 - C_e)\frac{V}{m}, \quad (1)$$

where, C_0 and C_e are the initial and equilibrium concentration of greenzyme (mg/L) respectively, V is the volume of the greenzyme solution (L) and m is the mass (g) of the sand particle. All the experiments were carried out at three different temperatures of 25, 50 and 75 ºC.

3. RESULTS AND DISCUSSION

Figure 1 presents the adsorption isotherms of the greenzyme adsorption on the sand surface with different particle sizes at 25 ºC. At low concentrations, greenzyme adsorption increases with increase in its concentrations in the aqueous solution until adsorption plateau was attained when no significant change in adsorbed quantity occurred. Generally, increase in adsorption with increase in concentrations of greenzyme in the aqueous solutions was observed with all samples irrespective of the sand size but their respective adsorbed quantity varied based on the sand particle size. Also, all the isotherms have similar profile with only three of the clearly defined isotherm regions by Somasundaran and Krishnakumar [15], the isotherms did not have region I that indicates linear adsorption with increase in concentrations. The isotherms started with region II that indicates spontaneous adsorption of greenzyme on the sand surfaces at low concentrations. Increase in concentrations resulted in the aggregation of greenzyme molecules on the surface and in region III, the adsorption increases slowly with lateral interactions within the molecules. Finally, in region IV the adsorption limit was reached with the plateauing of adsorption on the respective surfaces. The sand with the smallest particle size (0.15 mm) was associated with the highest adsorption that plateaued at 0.72 mg/g, while the other sand particles have plateaued adsorption of 0.57 mg/g and 0.43 mg/g respectively. The observed increase in adsorption with reduction in the particle size can be attributed to the number of available adsorption sites on the surface of different sand particles. The smaller sized sand particles favoured compaction of more particles of sand in a fixed mass weight than the larger sized particles. Hence, more sites were available for greenzyme adsorption in small sand particles than the medium and large sand particles. This is consistent with the previous study by Udoh and Vinogradov [16] which showed that greenzyme required minimum number of molecules to form an aggregate thereby favouring its aggregation on the available sites. So, this results further show that the more available sites for greenzyme adsorption, the greater its adsorption on the surface.

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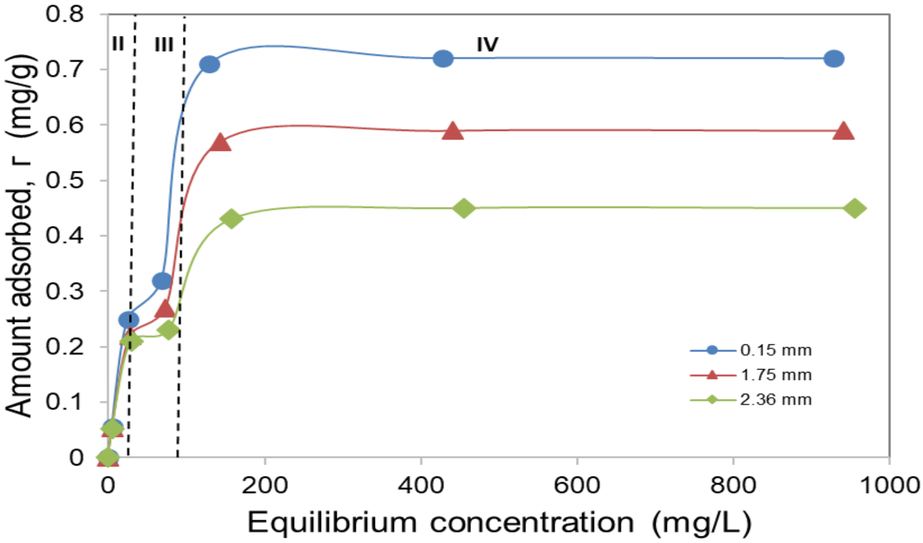

Figure 1: Adsorption isotherms of greenzyme on sand surface with particle sizes of 0.15 mm, 1.75 mm and 2.36 mm at 25 °C.

The results of greenzyme adsorption on the sand surfaces at 50 °C and 75 °C system temperatures are presented in Figure 2. Similar trend of increase in adsorption with increase in concentrations was also observed with high temperatures. The adsorption process however reduces with increase in temperatures for all the sand particle sizes. For the small sand particle size, the plateaued adsorption reduced from 0.72 mg/g to 0.62 mg/g and 0.59 mg/g with increase in temperature from 25 °C to 50 °C and 75 °C respectively. The plateaued adsorption on the medium sand particle size (1.75 mm) reduced from 0.57 mg/g to 0.28 mg/g and 0.27 mg/g with increase in temperature, while the large particle size adsorption reduced from 0.43 mg/g to 0.25 mg/g and 0.20 mg/g respectively.

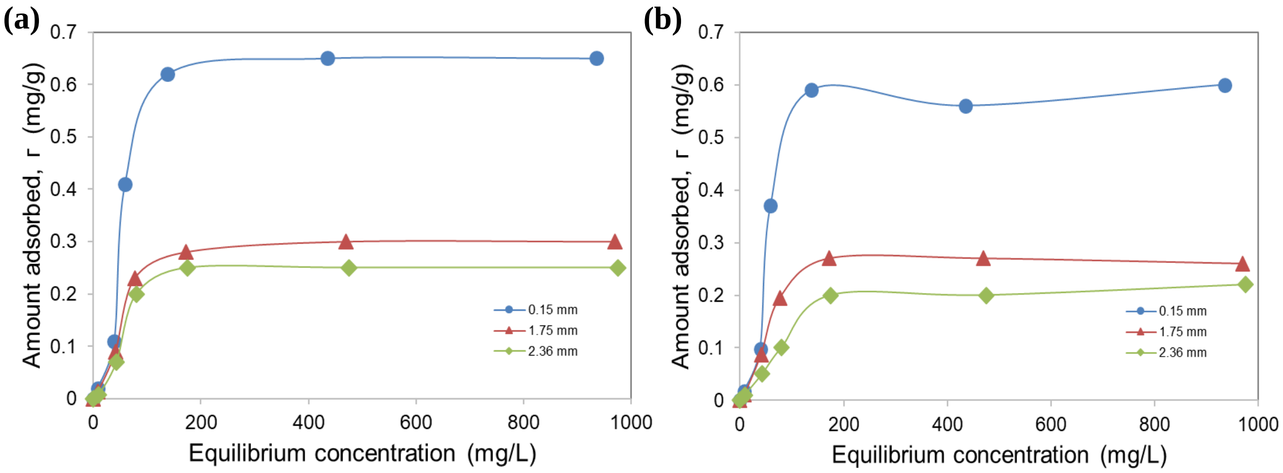

Figure 2: Adsorption isotherms of greenzyme on the sand surface of the three particle sizes: 0.15 mm, 1.75 mm and 2.36 mm at (a) 50 °C and (b) 75 °C.

Also, relating the adsorbed quantity at different concentrations to the system temperatures as presented in Figure 3, the results show that adsorption of greenzyme on the sand surface reduces with increase in the system temperatures irrespective of the concentration of greenzyme in the aqueous solution. An exception of an increase in adsorption with increase in temperatures was however observed with 100 mg/L concentration adsorption on the small sand particle (0.15mm). The reason for this variance is unknown but since this was just the only exception, it was presumed to be an insignificant effect. The generally observed increased adsorption with increase in the system temperatures can be related to the effect of higher kinetic energy as explained by Paria and Khilar [17]. Increase in the system temperature will result in increase in the kinetic energy of the molecules and the system entropy, this will invariably weaken interactions between the greenzyme molecules and the sand surface, thereby resulting in lower adsorption as the system temperature increases. This suggests that greenzyme adsorption on the sand surface is more of physisorption rather than chemisorption as described by Somasundaran and Krishnakumar [15]. The physisorption adsorption is mostly based on weak bonding such as Van der Waals forces and hydrogen bonding and greenzyme molecule is characterised by high H-O-H atoms that favour these kind of bonding [12].

The result of this study is consistent with previous studies [12,18-20] that also observed reduction in enzyme adsorption with increase in temperatures.

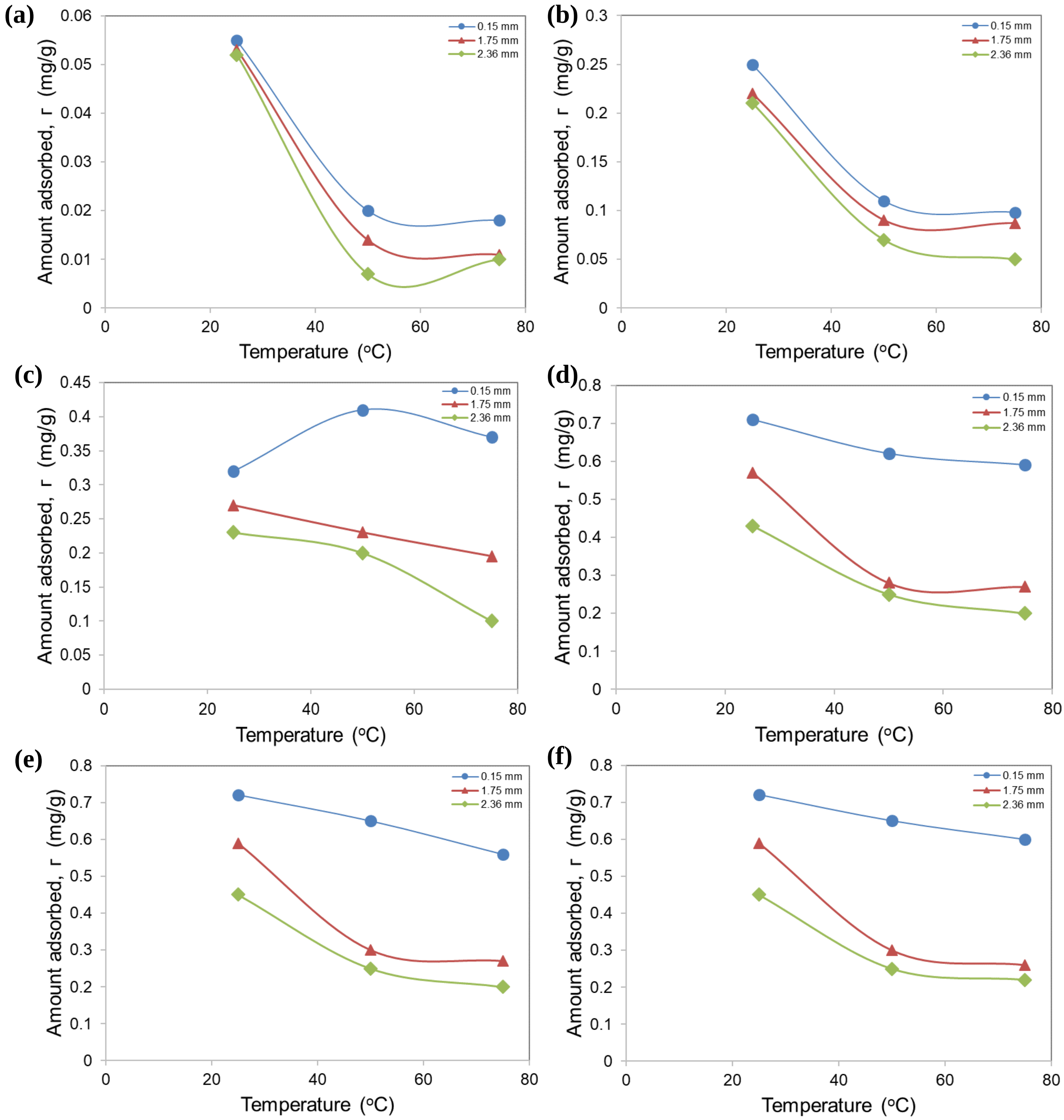

Figure 3: Greenzyme adsorption on three sand surfaces with grain size of 0.15 mm, 1.75 mm and 2.36 mm at different temperatures using (a) 10 mg/L, (b) 20 mg/L, (c) 100 mg/L, (d) 200 mg/L, (e) 500 mg/L and (f) 1000 mg/L.

In order to improve understanding of the observed adsorption process, the experimental data were fitted with the Langmuir and the Freundlich adsorption models, these two models are usually used to describe the equilibrium adsorption isotherm. The Langmuir adsorption model describes mono-layer coverage while the Freundlich model describes heterogeneous coverage [21]. The nonlinear Langmuir equation developed by Irving Langmuir [22] is expressed as:

$$\Gamma_e = \Gamma_{max} \cdot \frac{KC_e}{1 + KC_e}, \qquad (2)$$

this can be rearranged in the linear form as:

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

where, Γ_e is the amount of the adsorbed adsorbate at equilibrium (mg/g), Γ_{max} is the maximum adsorbed (mg/g), K_L is Langmuir equilibrium constant (L/mg) and C_e is equilibrium aqueous concentration (mg/L). Another important parameter in the Langmuir adsorption model is a non- dimensional constant (R_L) commonly referred to as separation factor of equilibrium parameter and it is expressed as [14]:

$$R_L = \frac{1}{1 + K_L C_0}, \quad (4)$$

where, C_0 is the initial concentration of the adsorbate in the aqueous solution (mg/L) and K_L is Langmuir equilibrium constant (L/mg). The R_L parameter gives an indication of the compatibility of the adsorption of the selected adsorbent on a given surface and there are four possible outcome of adsorption process based on the R_L value: when $0 < R_L < 1$, adsorption is favourable; when $R_L > 1$, adsorption is unfavourable; when $R_L = 1$, it indicates linearity of adsorption and when $R_L = 0$, adsorption is irreversible. The nonlinear Freundlich equation used is expressed as [14]:

$$\Gamma = K_F C_e^{1/n}, \quad (5)$$

where K_F and n are Freundlich constants related to adsorption capacity and intensity respectively. The Freundlich model assumes that the adsorbent adsorption takes place by multilayer sorption on heterogeneous surface. The adsorption intensity of any adsorbent is related to the constant (1/n). When $0.1 < 1/n < 0.5$, adsorption is said to be favourable; when $0.5 < 1/n \leq 1$, adsorption is easy and when $1/n > 1$, the adsorption is difficult or unfavourable.

Figure 4 shows the results of the Langmuir and Freundlich models data fitting of the experimental results of greenzyme adsorption on the sand surface of the different particle sizes. The summary of the values of the constants of the two models including the average values of the R_L are presented in Table 1. From all indications, the Langmuir model that describes monolayer adsorption process fits all the experimental data better than the Freundlich model, although the R^2 values from the two models are comparable. Furthermore, all the values of R_L obtained in this study were between 0.0396 and 0.9429, indicating that the adsorption of greenzyme on the sand surface is favourable. This therefore suggests that the adsorption of greenzyme on the sand surface of the different particle sizes is more of monolayer in nature rather than multilayer. Although the Langmuir model tends to fit the experimental data more perfectly when the adsorbed amount is below 0.2 mg/g, which is the range of adsorption values obtained at high temperatures. Also, even though the Freundlich model did not fit the experimental data like Langmuir model, the values of the adsorption intensity (1/n) suggest that the greenzyme adsorption on the sand surface was favourable at low temperature (25 °C) and easy at higher temperatures (50 °C and 75 °C). The results of this study is consistent with the previous study by Udoh [12] that showed that the adsorption of greenzyme on sandstone rock surface is monolayer in nature and it can be modelled with Langmuir isotherm model. Hence, the results of this study have shown that application of greenzyme in a reservoir with similar sand particles will be associated with some adsorption process, although the adsorbed quantity may not be much. Consideration however has to be given to this adsorption process in the design of greenzyme EOR application and other reservoir related applications. Hence, additional concentration to the minimum calculated concentration may be required during greenzyme injection for efficient performance to be attained. It is also worth noting that small adsorption of greenzyme on the reservoir rock surface is required for wettability alteration that can favour oil desorption from the rock surface in the reservoir [2, 23].

Table 1: Adsorption isotherm parameters of Langmuir and Freundlich models.

Isotherm models	**Parameters**	**Sand grain sizes**								
		0.15 mm			**1.75 mm**			**2.36 mm**		
		25 °C	50 °C	75 °C	25 °C	50 °C	75 °C	25 °C	50 °C	75 °C
Langmuir	Γ_{max} (mg/g)	0.687	0.582	0.332	0.463	0.218	0.192	0.375	0.161	0.139
	K_L (L/mg)	0.019	0.006	0.006	0.019	0.010	0.011	0.024	0.006	0.007
	R^2	0.993	0.915	0.913	0.969	0.760	0.763	0.880	0.667	0.600
	Ave R_L	0.340	0.522	0.530	0.339	0.436	0.430	0.305	0.518	0.514
Freundlich	Γ_{max} (mg/g)	0.609	0.718	0.654	0.604	0.340	0.309	0.091	0.300	0.220
	K_F (L/mg)	0.040	0.009	0.008	0.037	0.007	0.007	0.039	0.003	0.004
	R^2	0.863	0. 781	0.783	0.913	0.947	0.962	0.944	0.855	0.616
	1/n	0.485	0.724	0.732	0.461	0.629	0.650	0.406	0.735	0.670

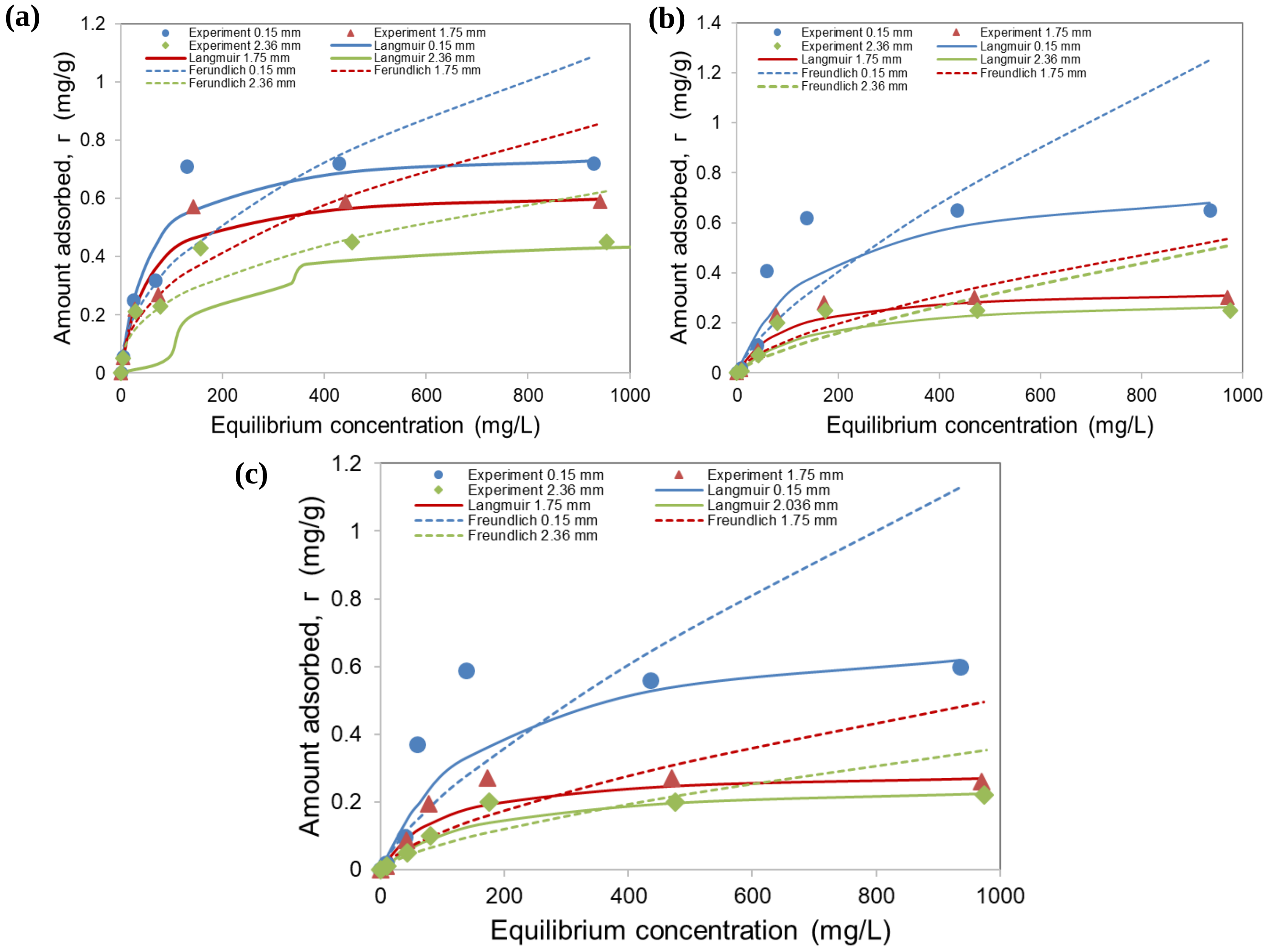

Figure 4: The Langmuir and Freundlich models data fitting of greenzyme adsorption on the sand of different grain sizes surfaces at: (a) 25 ºC (blue), (b) 50 ºC (red) and (c) 75 ºC (green). The experimental data (symbols), Langmuir model (_______) and Freundlich (--------).

4. CONCLUSION

The adsorption of greenzyme on the three sand particle sizes at three different temperatures from aqueous solutions was systematically investigated in this study. The results showed that with increase in greenzyme concentrations in the solution, its adsorption on the sand surface increased until the saturation point was reached. The sand with small particle size exhibited high adsorption efficiency at all temperatures investigated due to its high adsorption sites. Greenzyme adsorption however reduced with increase in system temperatures irrespective of the size of the sand particles. The results also showed that Langmuir isotherm model fitted the equilibrium adsorption of greenzyme on the sand surface, thereby suggesting the adsorption process as monolayer.

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