# Determination of anionic surfactant adsorption capacity of expanded perlite from aqueous solution

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# DETERMINATION OF ANIONIC SURFACTANT ADSORPTION CAPACITY OF EXPANDED PERLITE FROM AQUEOUS SOLUTION

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## ABSTRACT

Surfactants are major constituents of detergent so that it is frequently present in domestic and industrial wastewater. The surfactants cause foams in rivers and surface waters, thereby reducing the oxygen penetration in water and posing environmental risks to aquatic organisms. They need to be removed from wastewater to avoid environmental damages. Adsorption is a conventional method for surfactant removal from the water environment. Perlite is an amorphous volcanic glass that has relatively high water content and is typically formed through the hydration of obsidian. It occurs naturally and has the unusual property of greatly expanding when heated sufficiently. Expended perlite have been used as an economical adsorbent in adsorption process due to its low cost and large surface area. The aim of this study was to determine an anionic surfactant adsorption capacity of expended perlite from aqueous solution. For these purposes, linear alkyl benzene sulphonic acid (LABSA) was used as a surfactant and the effects of pH, temperature, concentration of LABSA, amount of adsorbent and contact time on adsorption capacity of expended perlite were investigated. The adsorption kinetic was found to follow the pseudo second order kinetic model. The equilibrium adsorption data were well described by the Freundlich isotherm model. Finally, the thermodynamic parameters including, the change of Gibbs free energy ($\Delta G^{\circ}$), enthalpy ($\Delta H^{\circ}$) and entropy ($\Delta S^{\circ}$) of adsorption were calculated. The results showed that the adsorption of LABSA on expended perlite was feasible, spontaneous and exothermic at 15–45°C.

**KEYWORDS:**
Adsorption; Perlite; Surfactant; LABSA

## INTRODUCTION

Surfactants, or surface active substances, are used extensively in varieties of industrial cleaning processes as well as in consumer products. Surfactants have toxic effects on some aquatic organisms due to the ability to foam and need to be removed from water to avoid enviromental damages [1]. Human health is also affected when surfactants arrive into drinking water [2].

A number of techniques, namely chemical oxidation [3], ultrafiltration and ion-exchange [4], microbiology treatment [5], chemical coagulation-flocculation [6], adsorption and magnetic seperation [7] have been used to remove surfactants from aquatic environment. Among them, adsorption is considered as one of the most influential processes. Numerous alternative materials have been investigated to adsorb surfactants from aqueous solution such as alumina [8], activated carbons [1,9,10], magnetic alginate beads [7,11], silica gel [12] and perlite [13].

Perlite is an amorphous volcanic glass that has the unusual characteristic of expanding and becoming porous when it is heated. Perlite can be expanded up to 20 times its original volume when heated rapidly at 760-1100°C. Expanded perlite has special properties such as high porosity, chemical inertness, non-toxicity and low density [14]. Perlite is very cheap and easily available in Turkey markets. Perlite is receiving increasing attention as alternative adsorbents for removal of dyes and heavy metals from water [14-17].

In the present study, expanded perlite particles were evaluated for their potential to the removal of linear alkyl benzene sulphonic acid (LABSA) from aqueous solutions. The impact of adsorbent dosage, contact time, initial LABSA concentration and temperature on adsorption capacity were investigated. Additionally, the adsorption isotherms, kinetics and thermodynamics were deduced from the experimental results.

## MATERIALS AND METHODS

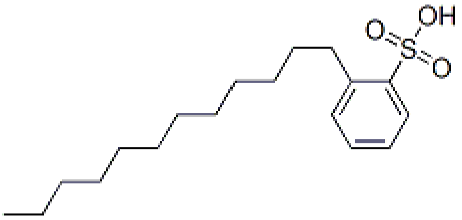
**Preparation of adsorbent and adsorbate.** Expanded perlite samples were obtained from İzmir, Turkey. The chemical composition of the perlite found in Turkey is given in Table 1 [18]. The expanded perlite was used as adsorbent without any chemical treatment. The expanded perlite samples were washed with deionized water to remove fine grains and water insoluble particles and dried for 24 h at 110°C. Then the dried perlite samples were mechanically sieved and segregated particles in the range of 0.85-1.6 mm.

**TABLE 1**
**Chemical composition of perlite.**

| Constituent | Percentage |
|---|---|
| $SiO_2$ | 71-75 |
| $Al_2O_3$ | 12.5-18 |
| $Na_2O$ | 2.9-4.0 |
| $K_2O$ | 4.0-5.0 |
| CaO | 0.5-2 |
| $Fe_2O_3$ | 0.1-1.5 |
| MgO | 0.03-0.5 |
| $TiO_2$ | 0.03-0.2 |
| PbO | 0.0-0.5 |
| $MnO_2$, $SO_3$, FeO, Ba, Cr | 0.0-0.1 |

The surfactant used as adsorbate in this study, LABSA, is an anionic surfactant with molecules characterized by a hydrophobic and a hydrophilic group. The molecular formula is $CH_3(CH_2)_{11}C_6H_4SO_3H$.

The structure of LABSA is shown as below:

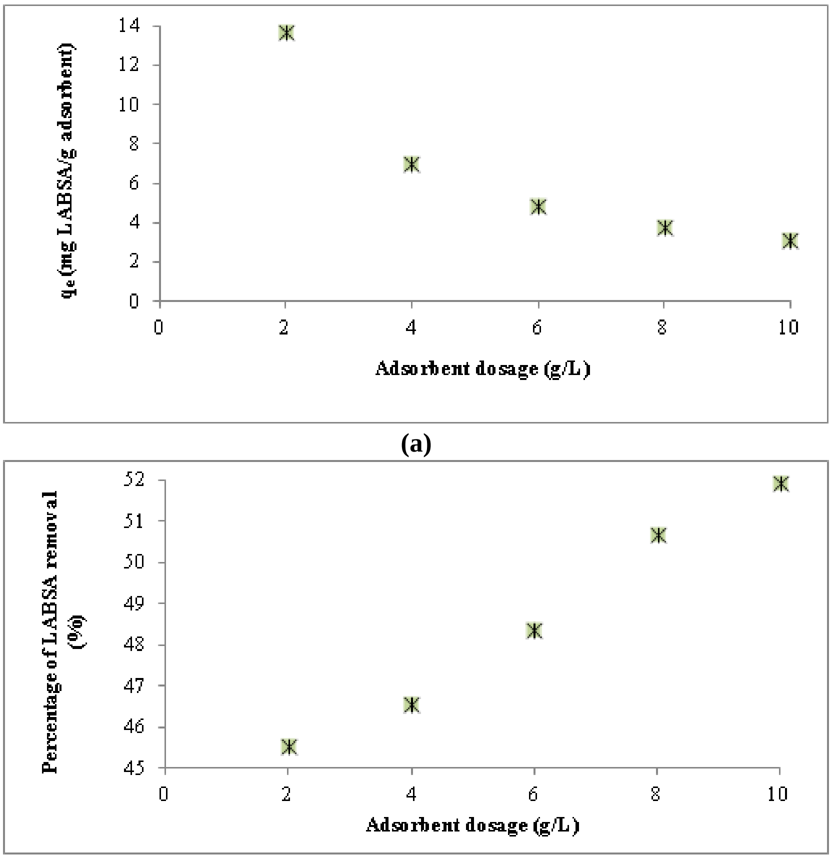


**Adsorption experiments.** Concentrations of LABSA were determined by measuring the absorbance characteristic wavelength using UV-spectrophotometer (JENWAY 7310). The percentage of LABSA removal (%) and amount of LABSA adsorbed per unit of adsorbent at a predetermined time t (qt) were calculated by Eq. (1) and (2), respectively [16]:

$$LABSA\ removal\ (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t) \times V}{W} \quad (2)$$

where $C_0$ is the initial concentration of LABSA (mg/L), $C_t$ is the concentration of LABSA at any time (mg/L), $V$ is the volume of the solution (L) and $W$ is weight of adsorbent (g).



**(a)**

**(b)**

**FIGURE 1**
**Effects of adsorbent dosage on the adsorption of LABSA onto expanded perlite (a) and LABSA removal (b) (LABSA concentration: 60 mg/L, pH: 9, agitation speed:100 rpm, temperature: 15°C, contact time: 180 min, volume of sample: 50 mL).**

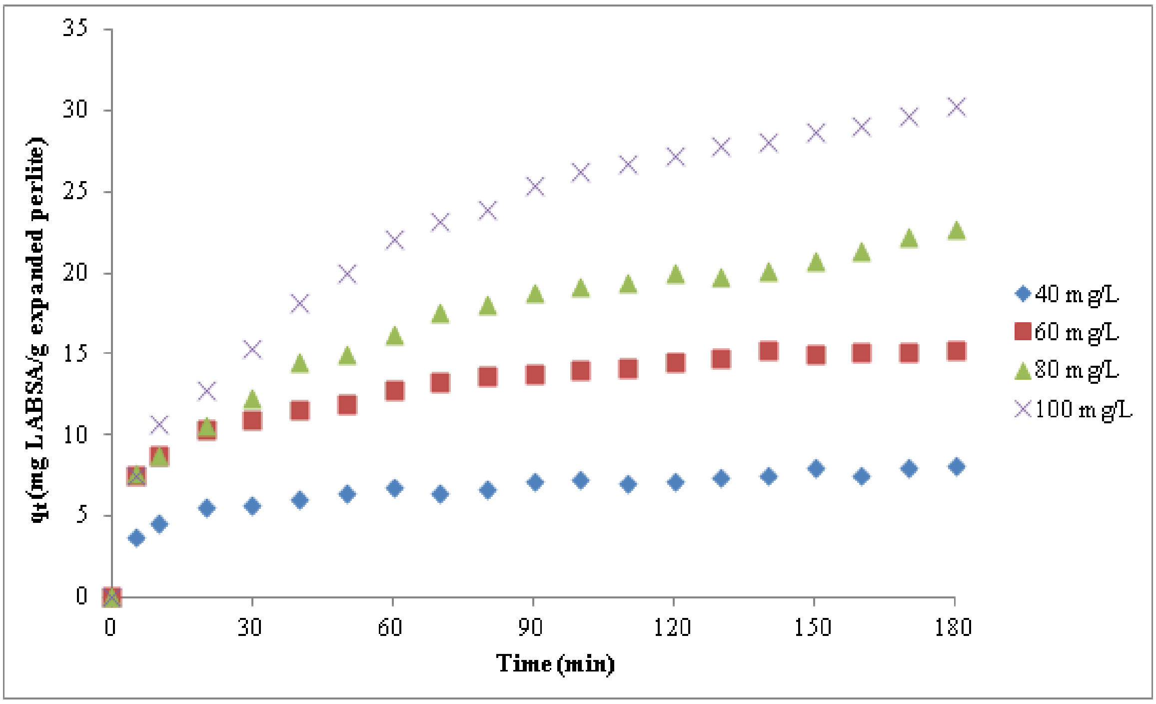


**FIGURE 2**
**Effect of contact time and initial LABSA concentration on the adsorption of LABSA onto expanded perlite (adsorbent: 2 g/L, pH: 9, agitation speed:100 rpm, temperature: 15°C).**

## RESULTS AND DISCUSSION

**Effect of adsorbent dosage.** The effect of adsorbent dosage (varying from 2 g $L^{-1}$ to 10 g $L^{-1}$) on the adsorption of LABSA onto expanded perlite and LABSA removal are presented in Figure 1. The amount adsorbed ($q_e$) decreased from 13.66 mg $g^{-1}$ to 3.12 mg $g^{-1}$ when the adsorbent dosage was increased from 2 g $L^{-1}$ to 10 g $L^{-1}$. The decrease of adsorption was due to the concentration gradient between adsorbent and adsorptive [19]. The percentage removal of LABSA from the solution increased from 45.5 to 51.9 as the adsorbent dosage increased from 2 g $L^{-1}$ to 10 g $L^{-1}$. The increase in removal of LABSA due to the availability of more surface area caused by increasing adsorbent dosage [19,20].

**Effect of contact time and initial LABSA concentration.** The effect of contact time on the amount of LABSA adsorbed was investigated at 40-100 mg $L^{-1}$ initial concentration of LABSA. It can be observed from Figure 2 that the LABSA adsorption increases with the increase of treating time and attained equilibrium within 180 minutes. The amount of LABSA adsorbed onto expanded perlite evidently increased with increasing initial LABSA concentration. Increased initial concentration enhanced the adsorption uptake of LABSA from 8.1 mg/g to 30.3 mg/g. This was caused by an increase in the mass gradient between the LABSA solution and expanded perlite particles [19].

**Adsorption kinetics.** Two kinetic models, commonly used in the literature, were applied to experimental kinetic data in order to investigate the behaviour of LABSA on expanded perlite. These models are Lagergren pseudo first order and pseudo second order equations.

The first model is the pseudo first order rate equation [21]:

$$\ln\,(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

where $q_e$ and $q_t$ refer to the amount of LABSA adsorbed (mg/g) at equilibrium and at any time, $t$ (min), respectively, and $k_1$ is the equilibrium rate constant of pseudo first order model (1/min). The plots of ln ($q_e - q_t$) versus $t$ were used to calculate the pseudo first order rate constant (Table 1).

The second model is the pseudo second order rate equation [21]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where $k_2$ is the rate constant of the pseudo second order adsorption model (g/mg.min). Figure 3 shows the curve-fitting plot of Eq. (4) ($t/q_t$ vs. $t$) and the parameters $k_2$, $q_e$ and $R^2$ values were determined (Table 2).

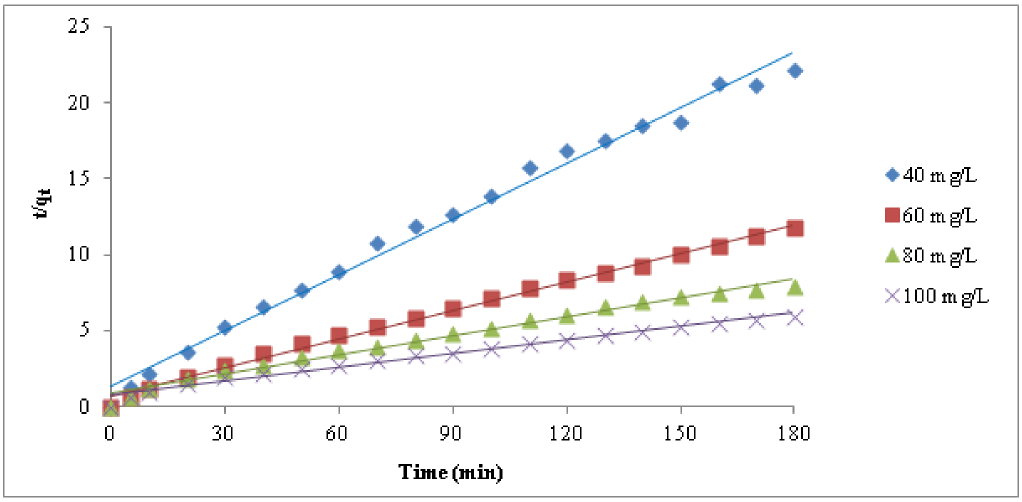


**FIGURE 3**
**The pseudo second order kinetic model for LABSA adsorption onto expanded perlite for different initial LABSA concentrations (adsorbent: 2 g/L, pH: 9, agitation speed:100 rpm, temperature: 15°C).**

**TABLE 2**
**Parameters of the Lagergren first order and pseudo second order models for adsorption of LABSA onto expanded perlite.**

| Initial LABSA concentration (mg/L) | $q_{e,exp}$ (mg/g) | Lagergren first order kinetic model<br>$q_{e,cal}$ (mg/g) | <br>$k_1$ | <br>$R^2$ $(min^{-1})$ | Pseudo second order kinetic model<br>$q_{e,cal}$ (mg/g) | <br>$k_2$ $(g.mg^{-1}$ | <br>$R^2$ $.min^{-1})$ |
|---|---|---|---|---|---|---|---|
| 40 | 8.13 | 4.39 | 0.0150 | 0.7412 | 8.19 | 0.0108 | 0.9902 |
| 60 | 15.22 | 9.02 | 0.0173 | 0.9650 | 15.92 | 0.0058 | 0.9952 |
| 80 | 22.68 | 18.02 | 0.0166 | 0.9254 | 23.75 | 0.0020 | 0.9827 |
| 100 | 30.31 | 27.00 | 0.0191 | 0.9794 | 33.22 | 0.0012 | 0.9818 |

The values of the correlation ($R^2$) for the pseudo first order model obtained are not high at the whole concentration range. Furthermore, large differences between experimental ($q_{e,exp}$) and calculated ($q_{e,cal}$) values of the equilibrium adsorption capacity were also observed. The pseudo second order model showed a better fit with experimental data, and the second order model showed a higher correlation coefficient ($R^2$) than that of first order model. Therefore, the adsorptions agreed with the pseudo second order model rather than pseudo first order model.

**Adsorption isotherm models.** Langmuir and Freundlich isotherm models were used to describe the equilibrium adsorption. The linear forms of Langmuir and Freundlich isotherm models are represented by Eq. (5) and (6), respectively [22]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (5)$$

$$\ln q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \qquad (6)$$

where $C_e$ is the equilibrium concentration of LABSA in solution (mg/L), $q_e$ is the adsorbed value of LABSA at equilibrium concentration (mg/g), $q_m$ is the maximum adsorption capacity (mg/g), $K_L$ is the Langmuir binding constant, which is related to the energy of adsorption, $K_F$ (mg/g $(L/mg)^{1/n}$) and $n$ are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

**TABLE 3**
**Adsorption isotherm constants for the adsorption of LABSA on the expanded perlite**

| Freundlich Adsorption Isotherm<br>$K_F$ | <br>$n$<br>[mg/g $(L/g)^{1/n}$] | <br>$R^2$ | Langmuir Adsorption Isotherm<br>$R^2$ |
|---|---|---|---|
| 0.0022 | 0.3838 | 0.9974 | 0.9306 |

Figure 4 shows the linear regression plots of the Langmuir (Fig. 4 (a)) and Freundlich (Fig. 4 (b)) isotherms, including the $R^2$ and fitted equation. The $R^2$ values of the plots indicated that the experimental data had higher agreement with the Freundlich model ($R^2$=0.9974) than with the Langmuir ($R^2$=0.9306). The parameters of Freundlich adsorption isotherm, evaluated from the linear plot, are presented in Table 3. According to the assumption of Freundlich model, adsorption takes place on heterogeneous sites and is not restricted to the formation of a monolayer [23].

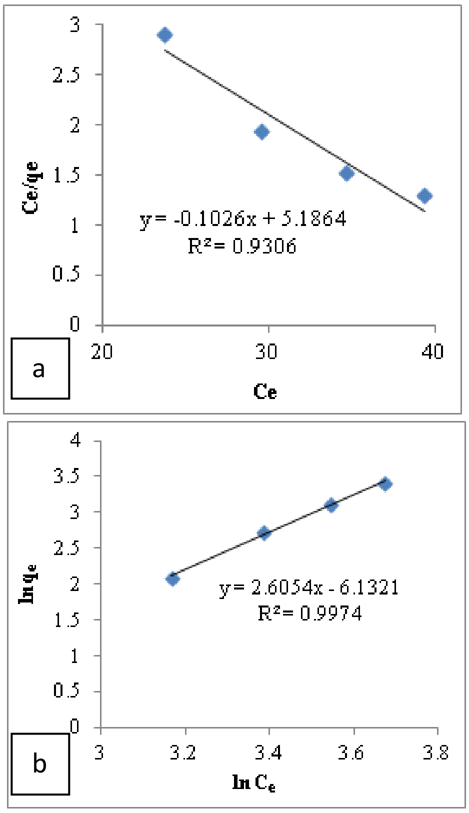


**FIGURE 4**
**Langmuir (a) and Freundlich (b) adsorption isotherms of LABSA on expanded perlite (adsorbent: 2 g/L, pH: 9, initial LABSA concentration: 40-100 mg/L, agitation speed: 100 rpm, temperature: 15°C).**

**Effect of temperature and adsorption thermodynamics.** The effect of temperature on adsorption of LABSA on expanded perlite was investigated by varying the temperature 298, 308 and 318 K. It was found that an increase in the adsorption temperature leads to a decrease in the LABSA removal efficiency.

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be calculated by using the following Van't Hoff equation [16]:

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (7)$$

$$K_C = \frac{q_e}{C_e} \qquad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (9)$$

where $R$ is the universal gas constant (8.314 J/mol.K), $T$ is the absolute temperature (in Kelvin) and $K_C$ is the equilibrium constant. The values of ΔH° and ΔS° can be calculated from the slope and intercept using the plotted graph of ln $K_L$ versus 1/T. The calculated constants are also illustrated in Table 4.

The negative value of ΔS° (-111.72 J/mol.K) suggests a decrease in the randomness at the solid/solution interface during the adsorption. The negtive values of ΔH° (-31.4 $kJ.mol^{-1}$) indicate the exothermic nature of adsorption process.

## CONCLUSION

This study shows that expanded perlite can afficiently remove surfactants from aqueous solutions. The equilibrium uptake was increased with increasing the initial concentration of surfactant in solution. Under the optimal conditions (pH:9; 298 K; 100 mg/L initial LABSA concentration), the experimental maximum adsorption capacity achieve 30.3 mg/g. The adsorption isotherm could be well fitted by Freundlich model, moreover, according to the results obtained from the comparison of kinetic models, the pseudo second order kinetic model had the best agreement with the experimental data.

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**TABLE 4**
**Thermodynamic parameters of LABSA adsorption by expanded perlite.**

| *T (K)* | *ΔG° ($kJ.mol^{-1}$)* | *ΔH° ($kJ.mol^{-1}$)* | *ΔS° ($J.mol^{-1}.K^{-1}$)* |
|---|---|---|---|
| 298 | 1.842 | -31.4 | -111.7 |
| 308 | 2.960 | | |
| 318 | 4.077 | | |

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