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# PURIFICATION OF WATERS FROM ANIONIC AND CATIONIC SURFACTANTS BY NATURAL ZEOLITES

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The adsorption of anionic sodium dodecylsulfate (SDS) and cationic cetyltrimethylammonium bromide (CTAB) from aqueous solution on zealots was studied. A series of batch experiments were performed to determine the sorption isotherms of surfactants to zeolite. Furthermore, the isotherm parameters, average percentage errors were calculated. Other factors influencing the adsorption capacity (contact time, adsorbent amount, and initial surfactant concentration) were also discussed. The experimental data fitted very well to the Langmuir and Freundlich equilibrium models. Among the surfactants, CTAB showed higher adsorption capacity onto solid compared with SDS (284 and 113 respectively).

***Keywords*:** adsorption of surfactants, zeolite, Langmuir and Freundlich models, sodium dodecylsulfate, cetyltrimethylammonium bromide.

**Introduction.** Surfactants mainly do not exist in nature: they are manufactured by chemical reaction. The applications of surfactants in science and industry are legion, ranging from primary processes such as the recovery and purification of raw material in mining and petroleum industries, enhancing the quality of finished products such as paints, cosmetics, pharmaceuticals and food products [1, 2]. Anionic surfactants occur in industrial sector, but also in household, e.g. in washing agents, household detergents and body care products. Cationic surfactants are used as anti-rust additives for metals, as fabric softeners, conditioners after hair washing, or disinfectants in cleaning agents [3]. As a consequence of widespread use, the concentration of surfactants can be relatively high in wastewaters coming from various industrial facilities. Because of the toxicity, their residual amounts can cause significant environmental problems to aquatic life [4–6]. Removal of these contaminants requires cost effective technologies, and a variety of techniques of wastewater treatment has been developed in the past decades. Currently, adsorption is believed to be a simple and effective technique for water and wastewater treatment and the success of the technique largely depends on the development of an efficient adsorbent. Adsorption of the surfactants on natural adsorbents, particularly on natural zeolites, is widely studied [7, 8]

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Natural zeolites are abundant and low cost resources, which are crystalline hydrated aluminosilicates with a framework structure containing pores filled with water, alkali and alkaline earth cations. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites were widely used as adsorbents in separation and purification processes in the past decades [9–11]. Later, the application of natural zeolites for water and wastewater treatment was introduced and is still a promising technique in environment cleaning processes.

After the original discovery of zeolitic minerals in volcanogenic sedimentary rocks, zeolitic tuffs have been found in many areas throughout the world.

In this paper the study of adsorption of anionic surfactant sodium dodecylsufate (SDS) and cationic cetyltrimethylammonium bromide (CTAB) on Armenian natural zeolite is presented.

**Experimental part.**

*Adsorptives.* The anionic surfactant SDS ("Aldrich", 99.8%) and the cationic surfactant CTAB ("Aldrich", 99.8%) were used without further purification. The sorption of surfactants was investigated at varying initial concentrations (100–3000 $mgL^{-1}$ for SDS and 100–500 $mgL^{-1}$ for CTAB). This concentration range also includes the critical micelle concentration (cmc) values of surfactants. The cmc of SDS and CTAB in water are 2361 $mgL^{-1}$ and 330 $mgL^{-1}$ respectively [12, 13]. All surfactant solutions were prepared by dissolving appropriate amount of surfactant in distilled water. The experiments were conducted at real pH values of solutions depending on the concentration (pH 6.8–7.1).

*Adsorbent.* The HEU-type zeolitic materials (in this paper referred to as "zeolite") were collected from Nor Kokhb deposit in Noyemberian region of Armenia. Detailed mineralogical and petrographic study of the Armenian zeolite has been carried out by Petrosov et al. [14, 15]. The Armenian HEU-type zeolitic materials have been characterized as typical heulandites type III zeolites, i.e. clinoptilolites. All materials are rich in zeolites (heulandite content 80%) contain minor quantities of quartz, plagioclase opal-CT smectite and mica.

*Table 1*

*Mineralogical composition and the characteristics of zeolite*

| pH | Moisture content, % | OMC, % | CEC, $meq \cdot 100g^{-1}$ | Specific surface area, $m^2 \cdot g^{-1}$ | Silt and clay, % |
|---|---|---|---|---|---|
| 6.9 | 1.1 | 2.3 | 136 | 19.6 | clinoptilolite (major phase), quartz (minor phase), plagioclase (minor phase), smectite (trace phase) |

*Table 2*

*Chemical composition of zeolite (mass %)*

| $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | FeO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $H_2O$ | $SO_3$ | Other |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 67.11 | 0.20 | 11.69 | 1.43 | 0.36 | 1.28 | 5.48 | 0.79 | 2.22 | 0.13 | 3.01 | 0.1 | 7.58 |

The mineralogical composition of the materials are studied and some characteristics of the mineral (organic matter content (OMC), cation-exchange-capacity (CEC), specific surface area) are given in Tab. 1 [14–16]. The materials

were air dried, ground in ball mill and subsequently in pestle and mortar, so as to pass from 125 $\mu m$ sieves and were stored at room temperature [16]. Chemical compositions of zeolite are given in Tab. 2. All experiments were carried out at double distilled water.

*Adsorption Studies*. Batch experiments were carried out at 298 ± 0.5 $K$ in a thermostat-controlled orbital shaker at an agitation speed of 150 rpm. The total of 50 $mL$ of the surfactant solutions was added to the given amount of adsorbent in stopped glass Erlenmeyer flasks.

Adsorption isotherms of SDS and CTAB were also obtained using the batch equilibrium technique. In all cases after shaking the samples were filtered through 0.45 $\mu m$ Whatman filter paper and used for analysis. The adsorbed amounts of surfactants were calculated using the following formula:

$$q_e = \left(C_0 - C_e\right)\frac{V}{W}, \tag{1}$$

where $q_e$ is the amount of surfactant adsorbed on the adsorbent; $C_0$ is the initial surfactant concentration; $C_e$ is the equilibrium concentration of surfactant solution; $V$ is the volume of surfactant solution used and $W$ is the weight of adsorbent used [17].

The removal efficiency $R$ was also calculated from the batch experiments, using the below-mentioned formula:

$$R = \left(C_0 - C_e\right)/C_0 \cdot 100\%. \tag{2}$$

*Analytical Procedure*. The concentrations of anionic and cationic surfactants were analyzed with the titration of aqueous samples by Hyamine 1622 solution and sodium dodecylethersulfate (SLES) solution respectively [18, 19]. All the experimental tests were carried out in duplicates and the average values were used in further calculations.

**Result and Discussion.** Finding the optimum contact time is very important for determining the maximum possible adsorbate removal. In this concern the 50 $mL$ of surfactant solution at the concentration 100 $mg{\cdot}L^{-1}$ was added to each Erlenmeyer flask and equilibrated with an adsorbent dosage of 0.1 $g$ for varying contact time.

Fig. 1 shows the effect of contact time on SDS and CTAB adsorption by zeolite. As can be seen, adsorption increased with the increase of contact time. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [20]. 48% removal of SDS was obtained within 50 *min* and this increased to 83% in 170 *min*. 76% removal of CTAB was obtained within 70 *min* and this increased to 98% in 130 *min* (see Fig. 1). Hence, 170 *min* was selected as the optimum contact time for SDS and 130 *min* for CTAB. The adsorption appears to be governed by two transport processes.

During the first stage, surfactants were rapidly adsorbed on hydrophobic zeolite through hydrophobic interactions in 50–70 *min*. On the second stage, slower migration of surfactants onto zeolite up to 170/130 *min* could be observed. Therefore, a large amount of surfactants was expected to be progressively adsorbed by the adsorbent matrices as the contact time increased [21]. The fast uptake of

adsorbates and the establishment of equilibrium over a short period indicate no strong chemical binding of the adsorbate with the adsorbent [22].

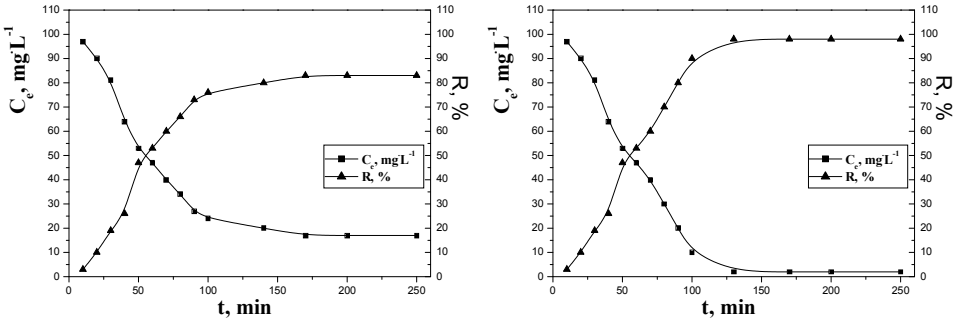


Fig. 1. Effect of contact time on SDS (a) and CTAB (b) adsorption on zeolite: $C_0 = 100 mg \cdot L^{-1}$, $T = 298 K$, 150 rpm, $W = 0.1\ g$.

*Effect of Adsorbent Amount on Adsorption*. Determining the optimum adsorbent amount is the second important stage of finding the maximum possible adsorbate removal. For this purpose, a series of 50 *mL* of surfactant solutions were shaken for optimum contact time at varying adsorbent amounts of 0.01–1.0*g*. The increase in adsorbent amount increased the percentage removal of both surfactants. The increase in the removal efficiency in response to the increase of adsorbent amount can be attributed to a greater surface area or increased number of sites available for adsorption [23]. 98% removal efficiencies (see Fig. 2) were obtained by the adsorbent amounts of 0.5 *g* and 0.07 *g* for SDS and CTAB respectively. These values were taken as the optimum amount for the other trials. The optimum adsorbent amount obtained for SDS was ~7 times greater than obtained for CTAB with a fixed initial surfactant concentration of 100 $mg{\cdot}L^{-1}$. This indicates that natural zeolite from Nor Kokhb deposite in Noyemberyan (Armenia) has a greater adsorption affinity to CTAB than SDS.

*Effect of Initial Concentration on Adsorption*. The sorption of surfactants was studied at varying initial concentrations: for SDS from 100 to 3000 $mg{\cdot}L^{-1}$ and for CTAB from 100 to 500 $mg{\cdot}L^{-1}$ for the consideration of the cmc values of surfactants. The amount of surfactants adsorbed per unit mass of the adsorbent increased with initial concentration, as expected. The amount of adsorbed surfactant on the adsorbent varied between 54.8–1921.3 and 82.8–241.9 $mg{\cdot}g^{-1}$ for SDS and CTAB respectively. The removal efficiencies of surfactants decreased with the increase of initial concentrations of surfactants. This decreasing trend was stronger for CTAB. The removal efficiency decreased from 93 to 82 % for SDS and from 97 to 67 % for CTAB as an effect of the increase of initial concentrations of surfactants.

*Adsorption Isotherms*. Adsorption isotherms are useful for selecting the most appropriate sorbent and also for predicting the performance of adsorption systems. They can be described by several mathematical relationships such as Langmuir and Freundlich models.

The Langmuir model suggests that sorption occurs on homogeneous surfaces by monolayer sorption (i. e., sorption onto a surface with a finite number of

identical sites) without interaction between sorbed molecules. This model isotherm is expressed by the following equations:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad \text{(non-linear form)}, \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad \text{(linear form)}, \tag{4}$$

where $Q^0$ is the maximum amount of adsorbate per unit weight of adsorbent to form a complete monolayer on the surface and $b$ is a constant related to the affinity of the binding sites [15, 22].

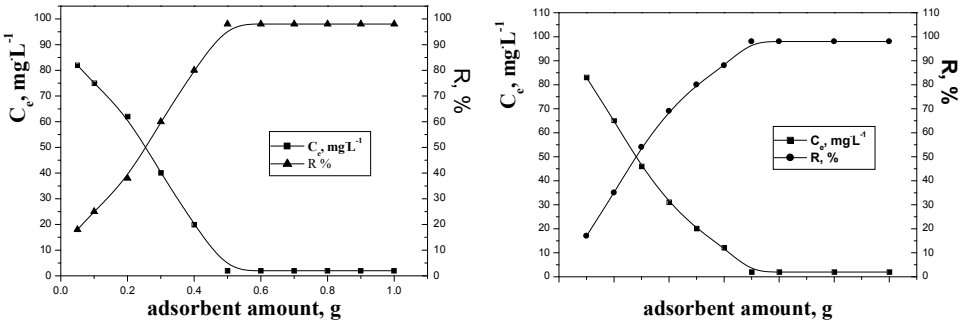


Fig. 2. Effect of adsorbent amount on SDS (a) and CTAB (b) adsorption by zeolite: $C_0 = 100 mg \cdot L^{-1}$, $T = 298 K$, 150 rpm, $t = 170\ min\ (a)$ and $t = 130\ min\ (b)$.

The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites and /or interactions between sorbet species that is multilayer sorption. This isotherm is widely used, particularly at the low to intermediate concentration range. It is expressed as

$$q_e = K_f C_e^n, \tag{5}$$

where $K_f$ and $n$ are non-competitive Freundlich constant characteristics of the system. $K_f$ and $n$ are indicators of adsorption capacity and adsorption intensity respectively [17, 24].

Giles et al. [25, 26] examined several liquid adsorption isotherms and classified them into four categories (S, L, H and C types) with subdivisions in each type. In the studied concentration ranges adsorption isotherms were regularly positive and concave to the concentration axis (Fig. 3). According to the slope of the initial portion of the curves, the isotherms of SDS and CTAB may be classified as L-type of the Giles classification. This indicates that no strong competition for the adsorption sites occurs between solvent molecules (here, distilled water) and adsorbate molecules (here, surfactant molecules).

The experimental equilibrium data of SDS and CTAB were compared with the theoretical equilibrium data obtained from adsorption models in Fig. 3. The experimental data was fitted with the Langmuir and Freundlich equations. The plots confirmed that the adsorption equilibrium data fitted well to the Langmuir

and Freundlich models in the studied concentration range. It was clear that the isotherms of SDS and CTAB are comparable.

The estimated parameters of the respective Eqs. (3)–(5) are shown in Tab. 3 along with the average percentage errors. The average percentage errors are calculated by the following equation [27]:

$$\varepsilon = 100\left(\sum_{i=1}^{N}\frac{q_{e,i,\exp} - q_{e,i,calc}}{q_{e,i,\exp}} : N\right)\ \%, \qquad (6)$$

where $N$ is the number of measurements and "exp" and "calc" show the experimental and calculated values respectively.

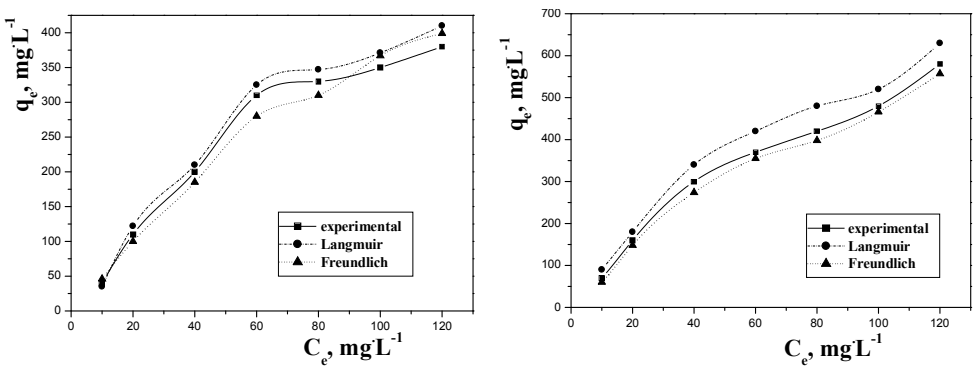


Fig. 3. Adsorption isotherms (Langmuir and Freundlich models) at 298 *K* of SDS (a) and CTAB (b) on zeolite.

As is seen from Tab. 3, higher correlation coefficients were obtained for SDS and CTAB on zeolite by the Langmuir and Freundlich models. At the same time, the percentage errors for two models exhibited good fit to the adsorption data of both surfactants in the studied concentration range.

*Table 3*

*Estimated parameters for Freundlich and Langmuir isotherm models at 298 K*

| Surfactant | Freundlich model | | | | Langmuir model | | | |
|---|---|---|---|---|---|---|---|---|
| | $K_f$ | $n$ | $R^2$ | $\varepsilon$, % | $Q^0$ | $b$ | $R^2$ | $\varepsilon$, % |
| SDS | 10.22 | 0.47 | 0.998 | 0.18 | 113 | 0.71 | 0.998 | 0.18 |
| CTAB | 21.58 | 0.57 | 0.998 | 0.23 | 284 | 0.04 | 0.998 | 0.23 |

It is known that surfactant adsorption is the result of several mechanisms at the solid-liquid interface, including ion exchange, ion pairing, hydrophobic bonding, hydrogen bonding, electrostatic attraction and dispersion forces. The nature of a solid surface, that is, hydrophobic or hydrophilic, and the electrical interactions play an important role in the kinetics of the adsorption of surfactant at the solid-liquid interface [28]. In double distilled water at pH 5, 6 and 7, the zeta potentials of zeolite were all zero. Therefore, the natural zeolite surface was uncharged in double distilled water among the broad pH range. In this context, it could be assumed that the electrostatic action might not significantly contribute to

the adsorption of surfactants. The adsorption of surfactants on hydrophobic zeolite relied mainly on surface-solute hydrophobic interactions.

**Conclusion.** The removal of surfactant from aqueous solutions by means of adsorption on natural zeolite from Nor Kokhb deposit in Noyemberyan (Armenia) was examined in our paper.

The adsorption isotherms of both surfactants were classified as L-type of the Giles classification, according to the slope of the initial portion of the curves. This suggests that surfactants were mainly adsorbed on zeolite and there is no competition from the solvent for adsorption sites.

It was found that the adsorptive behavior of both surfactants is in accordance with the Langmuir and Freundlich models. The values obtained for CTAB were approximately two times higher than those obtained for SDS. Natural zeolite has a greater adsorption capacity for CTAB. The optimum adsorbent amount for the maximum adsorbate removal is ~7 times greater for SDS than for CTAB. This may be explained by favorable adsorption for CTAB by natural zeolite.

The equilibrium time was reached at 170 *min* for SDS and 130 *min* for CTAB. The adsorption was controlled by two transporting processes; one fast (10–70 *min*) and one slow (after 100 *min*). The short equilibrium times of both surfactants showed no strong chemical binding of SDS and CTAB with the surface of zeolite.

Because of the uncharged zeolite surface at pH 5, 6 and 7, the electrostatic action might not significantly contribute to the adsorption of surfactants. The adsorption of surfactants on zeolite may be predominated by the hydrophobic interaction between the surfactants and zeolite surface. The longer alkyl chain makes CTAB more hydrophobic than SDS. Therefore, CTAB was adsorbed better than SDS on natural zeolite.

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