

REMOVAL OF SURFACTANTS FROM AQUEOUS SOLUTIONS
BY USAGE OF BENTONITE

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Adsorption of anionic surfactant sodium dodecyl sulfate and cationic surfactant cetyltrimethylammonium bromide from aqueous solution on bentonite was studied. A series of batch experiments were performed to obtain sorption isotherms of surfactants on bentonite. Furthermore, the isotherm parameters were calculated. Other factors influencing the adsorption effectiveness (contact time, adsorbent amount and initial surfactant concentration) were also determined.

Keywords: adsorption of surfactants, bentonite, sodium dodecyl sulfate, cetyltrimethylammonium bromide.

Introduction. Surfactants are widely used in different branches of industry—oil, cosmetic, metallurgy, and in household goods [1, 2]. Anionic surfactants are contained in hygiene products and washing detergents. Cationic surfactants are used as anticorrosion additions to metals and as disinfected agents in cleaning liquids [3]. As a result of widespread use the concentration of surfactants in wastewaters is very high. Surfactants aren't destroyed biologically under natural conditions, thus their high content can arise huge ecological problems of aqueous environment [4–6].

Removal of surfactants from wastewaters requires efficient technologies. During last decades many technological processes had been developed and improved. Among them adsorption process is simpler and more effective. It has been established that the effectiveness of applied technology highly depends on the chosen adsorbent.

Bentonite is a natural clay, whose basic substance is montmorillonite [7, 8]. Bentonite is widely used in different technological processes, for removing organic pollutants [9], surfactants and dyes [10, 11], oil products [5] and metal-ions [12, 13].

In this paper the results of the study of anionic surfactant sodium dodecylsulfate (SDS) and cationic surfactant cetyltrimethylammonium bromide (CTAB) adsorption on bentonite are presented.

Experimental Part.

Adsorptives. Anionic surfactant SDS (“Aldrich”, 99.8%) and cationic surfactant CTAB (“Aldrich”, 99.8%) were used without further purification. The

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sorption of surfactants was investigated at varying the initial concentrations 100–3000 mg/L. All surfactant solutions were prepared by dissolving appropriate amount of surfactant in distilled water. The experiments were conducted at real pH values of solutions (pH 6.8–7.1).

Adsorbent. Bentonite from Sarigyugh deposit (Ijevan, Armenia) was dried in air, ground in ball mill and subsequently in pestle and mortar, so as to pass from 125 μm sieve and were stored at room temperature. The chemical composition of bentonite is given in Tab. 1 [14]. All experiments were carried out using double distilled water.

Table 1

Chemical composition of bentonite (mass %)

Moisture content	Loss at heating	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	TiO ₂	SnO ₂	P ₂ O ₅	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
6.38	6.73	62.3	14.22	2.26	–	0.3	0.04	0.09	1.54	3.13	–	2.15	1.3

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 glass-stoppered Erlenmeyer flasks. Adsorption isotherms of SDS and CTAB were also obtained using a batch equilibrium technique. In all cases after shaking the samples were filtered through 0.45 μm Whatman filter paper and were used for analysis. The adsorbed amounts of surfactants were calculated using the equation [15]

$$q_e = (C_0 - C_e) \frac{V}{M}, \quad (1)$$

where q_e is the amount of the surfactant adsorbed on the adsorbent; C_0 is the initial surfactant concentration; C_e is the equilibrium concentration of the surfactant; V is the volume of the solution used; M is the weight of adsorbent used, respectively. The removal efficiency was also calculated from the batch experiments, using the below mentioned equation:

$$R = \left[\frac{C_0 - C_e}{C_0} \right] \cdot 100\%. \quad (2)$$

Analytical Procedure. The concentrations of anionic and cationic surfactants were analyzed with the titration of aqueous samples by Hyamine 1622 solution and sodium dodecyl ether sulfate solution respectively [16, 17]. All the experimental tests were carried out in duplicate and the average values were used in further calculations.

Results and Discussion.

Effect of Contact Time on Adsorption. Estimation of the optimal contact time is one of the important parameters for effective removal of the surfactant. For this aim to 50 mL of surfactant solution with 100 mg/L initial concentration, 1 g adsorbent has been added and contact time was varied. The data of the effect of contact time on adsorption of SDS and CTAB are given in Fig. 1, a and b respectively. As it can be seen, the sorption of the surfactants increases with increase of contact time.

After 4 h removal of SDS is 36% and for CTAB after 3 h is 46% (Fig. 1). Thus, 4 and 3 h have been chosen as optimal contact times for SDS and for CTAB respectively.

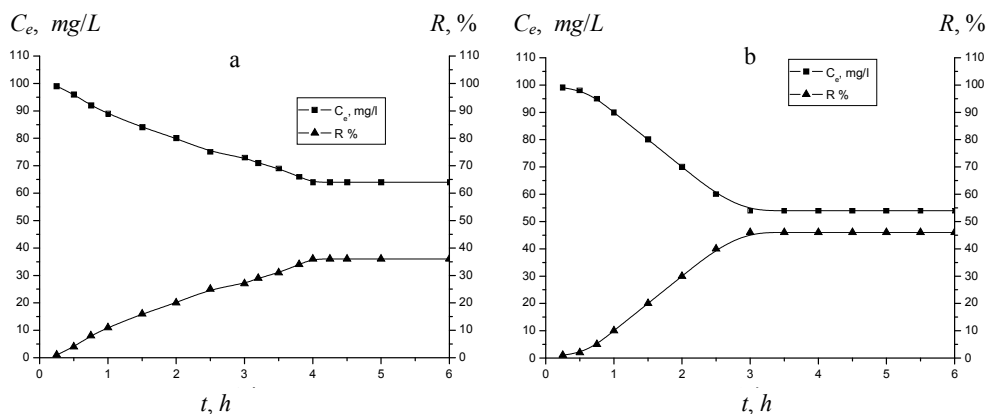


Fig. 1. Effect of contact time on sorption of SDS (a) and CTAB (b) on bentonite. $C_0 = 100 \text{ mg/L}$, $T = 298 \text{ K}$, 150 rpm , $M = 1 \text{ g}$.

Effect of Sorbent Amount on Sorption. Estimation of the sorbent optimal concentration is also one of the important steps for maximal removal of the adsorbate [18]. For this aim series of surfactants solutions (50 mL each) with initial concentration 100 mg/L have been shaking on magnetic shaker during optimal contact time with varying amount of sorbent from 0.5 to 5.0 g. The effectiveness of removal of surfactant increases with increasing amount of sorbent due to increase of quantity of available pores for sorption. 42% of SDS removal was detected at 1.5 g sorbent (Fig. 2, a) and 58% of CTAB at 1.7 g sorbent (Fig. 2, b). It is shown that bentonite has higher sorption effectiveness to CTAB in comparison with SDS.

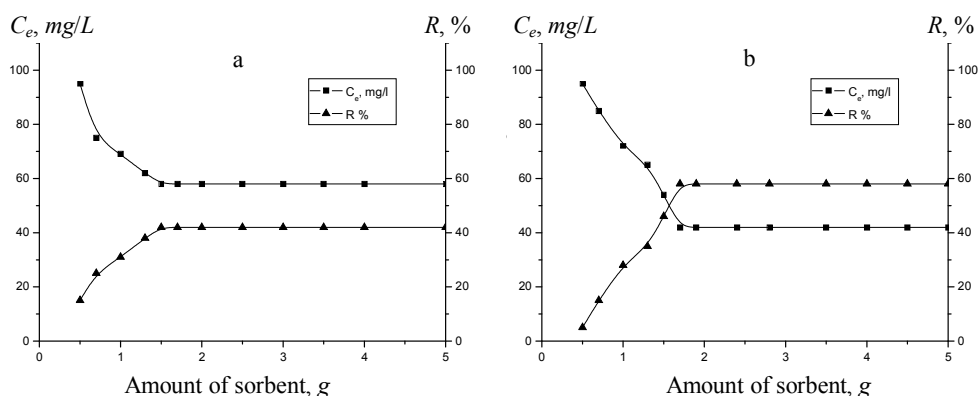


Fig. 2. Effect of sorbent amount on sorption of SDS (a) and CTAB (b) on bentonite. $C_0 = 100 \text{ mg/L}$, $T = 298 \text{ K}$, 150 rpm , $t = 4 \text{ h}$ (a) and 3 h (b).

Influence of Initial Concentration of Surfactant on Sorption. Sorption of the surfactant has been also studied depending on the initial concentration of the surfactant from 100 to 3000 mg/L. It was established that effectiveness of removal of the surfactant decreases with increasing initial concentration of the surfactant. A tendency of decreasing is more significant for CTAB. Effectiveness of sorption

for SDS with increasing initial concentration decreases from 42 to 32% and for CTAB from 58 to 45%.

Sorption Isotherms. Sorption isotherms are very useful for evaluating the effectiveness of the applied sorbent. In this view, sorption parameters have been analyzed both by the Langmuir and Freundlich models.

Langmuir's model suggests monolayer sorption on homogenous surface of sorbent and absence of interactions between adsorbed molecules. According to this model the adsorption isotherm is described by the following equations:

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

where Q^0 is the maximum concentration of adsorbate per mass of sorbent; b is the constant [15].

Freundlich model suggests a heterogeneous energetic distribution of active centers/or existence of interactions between adsorbed molecules (multilayer sorption). This model is successfully used at low and medium concentrations of adsorbate. Freundlich isotherm is described by the following equation:

$$q_e = K_F C_e^n, \quad (4)$$

where K_F (sorption capacity) and n (sorption intensity) are constants [15, 19].

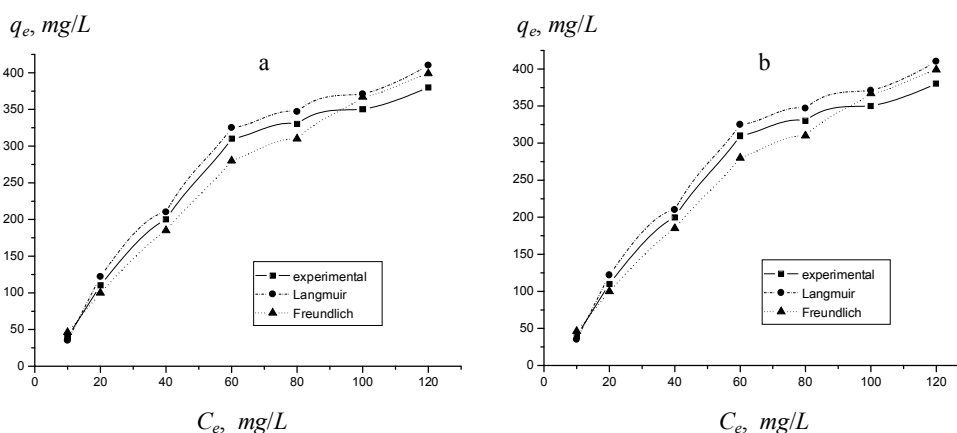


Fig. 3. Sorption isotherms of SDS (a) and CTAB (b) on bentonite at 298 K.

As it can be seen from Fig. 3, sorption isotherms of SDS (Fig. 3, a) and CTAB (Fig. 3, b) are analogous. Experimental data of SDS and CTAB equilibrium sorptions are comparable with theoretical data, which have been obtained based on the Langmuir and Freundlich sorption models in the studied concentration range. It means that sorption of the studied surfactants on bentonite can be successfully described by Langmuir model, thus sorption of the studied surfactants on bentonite is mainly monolayer.

The calculated values of the parameters of the Eqs. (3), (4) and values of the average percentage errors are presented in Tab. 2. The average percentage errors are calculated by the following equation [20]:

$$\varepsilon = \frac{\sum_{i=1}^N (q_{e,i,\text{exp}} - q_{e,i,\text{calc}}) / q_{e,i,\text{calc}}}{N} \cdot 100\%, \quad (5)$$

where N is the number of experiments; $q_{e,i,\text{exp}}$, $q_{e,i,\text{calc}}$ are experimental and calculated values of q_e .

Table 2

Values of Freundlich and Langmuir models at 298 K

Surfactant	Freundlich model				Langmuir model			
	K_F	n	$\varepsilon, \%$	R^2	Q^0	b	$\varepsilon, \%$	R^2
SDS	10.90	0.49	0.27	0.996	128.00	0.52	0.27	0.998
CTAB	19.30	0.41	0.41	0.998	251.00	0.40	0.29	0.997

According to Giles et al classification [21, 22], there are 4 types of sorption isotherms: S, L, H and C. Sorption isotherms of SDS and CTAB can be attributed to the L-type according to the Gills classification (Fig. 3). It indicates that there are no strong competition between solvent molecules (in this case water) and adsorbate molecules (in this case molecules/ions/micelles of surfactant), which also indirectly confirms that the sorption of the surfactants studied is described by the Langmuir model.

Conclusion. From studies of the sorption of surfactants on bentonite from Sarigyugh deposit (Ijevan) the following conclusion can be done:

Isotherms of the studied surfactants on bentonite surface are classified as L-type. It is assumed that there is no competition in sorption process between molecules/ions/micelles of the surfactant and solvent molecules (in this case water) and the molecules/ions/micelles of the surfactant are mainly adsorbed on bentonite.

It was established that the obtained values of Q^0 for CTAB are 1.5 times higher, than for SDS, i.e. the sorption capacity of bentonite is higher for CTAB.

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