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EFFICIENCY OF APPLICATION OF SURFACTANT-MODIFIED NATURAL ZEOLITE FOR REMOVAL OF METALS FROM AKHTALA AND SHNOGH RIVERS WATERS

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The sorption (removal) efficiency of anionic surfactant modified natural zeolite from Nor Koghb deposit in relation to metal contaminants of water samples from Akhtala and Shnogh Rivers has been studied. It is shown that suggested anionic surfactant modified zeolites exhibit high sorption capability for metal adsorption from multi-component natural aquatic systems.

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***Keywords*:** metals removal, surfactant-modified zeolite, adsorption effectivity, batch adsorption, natural Nor Koghb zeolite.

Introduction. The pollution of the natural aquatic systems by harmful contaminants is one of the most worrying problems in the modern world, because it leads to negative effects on the quality of the environment, life and quantity of animals in aquatic systems, as well as on the quality of human life globally [1–4]. To remove the contaminants from aqueous systems, different technologies are used – adsorption, membrane filtration, using chemical compounds, biochemical methods, etc. [5–7]. One of the easiest, highly effective and non-expensive technologies is adsorption, especially if there are local deposits of the natural alumosilicate clays. Armenia is rich in zeolites, there are a number of deposits of high-quality zeolite, among which the largest is Nor Koghb deposit in Noyemberyan district. The zeolite from Nor Koghb deposit is characterized as clinoptilolite with high sorption capability [8–10]. However, it is possible to increase the sorption capability of the natural zeolite by physical and chemical modification. One of the ways to modify natural zeolite is the modification by surfactants [11–15]. During last years, the modification of zeolites from Nor Koghb deposit by surfactants and their characteristics have been intensively studied [16–20]. The surfactant modified zeolites (SMZ) have been effectively used for removal of metal-ions from model aqueous systems, both from mono-component and multi-component [16]. But, of course, SMZ can be suggested as effective sorbents only after testing for the removal of metal-ions from wastewater. Particularly, it would be ideal to use them to remove metal-ions from tailings or industrial wastewater. But, unfortunately, the owners of the mining factories, as well as tailings, whom we asked, refused to provide us with

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samples for studies. In this case, for practical testing of the effectiveness of SMZ for the removal of metals from aqueous medium, water samples of Rivers Shnogh and Akhtala were used. According to [21, 22], the water quality in the estuary of the both Akhtala and Shnogh Rivers is characterized as V class with a high content of harmful metals.

This paper presents the results of adsorption effectiveness studies of Nor Koghb zeolites modified by anionic surfactant sodium dodecyl sulfate in relation to metals from water samples taken from the Shnogh and Akhtala Rivers.

Materials and Methods. The clinoptilolite tuff (in this paper referred to as "zeolite") from Nor Koghb deposit (Noyemberyan, Armenia) was used as a natural zeolitic material. Detailed mineralogical and petrographic study of Armenian zeolite has been presented in [8, 23, 24]. Zeolite was air dried, ground in ball mill and subsequently in a pestle and mortar, so as to pass through 125 μm sieves, and stored at room temperature.

Anionic surfactant sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4Na$, ASC reagent, ≥ 99.0%, "Sigma-Aldrich") was used without further purification. Water samples from Akhtala and Shnogh Rivers were taken by accredited laboratory of "Hydrometeorology and Monitoring Center" SNCO of MoE of RA. The water samples were taken in the estuary of the rivers. A water sample from the Akhtala River was taken at the end of March 2022, and from the Shnogh River – at the end of June 2023.

The modification of natural zeolite by anionic surfactant SDS was carried out by the method presented in [25]. The surface as well as textural characteristics were completely studied and presented in [16].

Batch experiments of adsorption study were carried out at 298 ± 0.5 K in a thermostat controlled orbital shaker at an agitation speed of 250 *rpm*. After shaking the samples were filtered through 0.45 μm Whatman filter paper and used for analysis.

The adsorption effectiveness (%) was calculated from the batch experiments using the formula below:

$$\text{adsorption} = \frac{C_0 - C}{C_0} \cdot 100\%, \quad (1)$$

where C_0 is the initial concentration of the metal, C is the equilibrium concentration of the metal. The concentration of metal in the solution was determined using PG-990 atomic absorption spectrophotometer, pH of solutions was determined using HANNA HI 4522 technique.

Results and Discussion. The initial concentration of metals in water samples taken from Akhtala and Shnogh Rivers was determined in an accredited laboratory of "Hydrometeorology and Monitoring Center" SNCO of MoE and by us in parallel. After purification of water sample using SMZ, the concentrations of metals in multi-component system of Akhtala River water sample sharply decrease (Tab. 1), showing the high adsorption ability of SMZ in relation to metals. The effectiveness of the removal of Cu from multi-component water sample of Shnogh River using SMZ as an adsorbent is 29.3%. As it can be seen from Tab. 1, due to the adsorption process, the concentration of Cu in Shnogh River water sample decreases about 1.4 times.

Table 1

Values of metal content in the water sample of Akhtala and Shnogh Rivers before and after sorption; $V_{solution}$= 500 mL, m_{SMZ} =1 g, contact time= 260 min, pH 5.0, T=298 K

Metal	Concentration of metal, *mg/L*	
	before sorption	after sorption
	in water sample of Akhtala River	
Mn	1.24000	1.03500
Zn	0.32300	0.22300
Cu	0.15600	0.10400
Ni	0.00519	0.00320
Fe	0.23900	0.12100
Co	0.01600	0.00781
	in water sample of Shnogh River	
Mn	0.11900	0.10000
Zn	0.00370	0.00274
Cu	0.15700	0.11100
Ni	0.00671	0.00458
Fe	0.86000	0.48100
Co	0.00203	0.00101

To evaluate the effectiveness of SMZ in removing metals from multi-component water samples of Akhtala River, the results were compared with the data of usage of natural (non-modified) zeolite. The experimental results for the same conditions, given in Tab. 2, show that the removal effectiveness (adsorption efficiency) of SMZ is much higher and, therefore, the modification of zeolite was justified.

Table 2

Adsorption efficiency (%) of metals in multi-component system of Akhtala River water sample using natural and anionic SM zeolites;. $V_{solution}$ = 500 mL, m_{SMZ} = 1 g, contact time = 260 min, pH 5.0, T = 298 K

Metal	Adsorption efficiency, %	
	natural zeolite	anionic SMZ
Mn	10.4	16.5
Zn	13.6	31.0
Cu	11.1	33.3
Ni	13.8	38.3
Co	14.2	51.2
Fe	14.0	49.4

Conclusion. From the presented data it can be concluded that anionic SMZ is an effective sorbent for removing metals from multi-component natural aquatic systems and can be suggested as effective purification agent for sorption of metal contaminants from aqueous media of different type in general.

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Լ. Շ. ԹԱՆԳԱՄՅԱՆ

ՄԱԿԵՐԵՎՈՒԹԱՅԻՆ ԱԿՏԻՎ ՆՅՈՒԹՈՎ ՄՈԴԻՖԻԿԱՑՎԱԾ ԲՆԱԿԱՆ ՑԵՈԼԻՏԻ ԿԻՐԱՌՄԱՆ ԱՐԴՅՈՒՆԱՎԵՏՈՒԹՅՈՒՆԸ ԱԽԹԱԼԱ ԵՎ ՇՆՈՂ ԳԵՏԵՐԻ ՋՐԵՐԻՑ ՄԵՏԱՂՆԵՐԻ ՀԵՌԱՑՄԱՆ ՀԱՄԱՐ

Ուսումնասիրվել է Նոր Կողբ հանքավայրի ցեոլիտի, մոդիֆիկացված անիոնային մակերևութային ակտիվ նյութով, սորբցիայի արդյունավետությունը Ախթալա և Շնող գետերի ջրերի նմուշներից մետաղ-աղտոտիչների հեռացման համար: Ցույց է տրված, որ առաջարկվող մակերևութային ակտիվ նյութով մոդիֆիկացված ցեոլիտը ցուցաբերում է բարձր կլանողունակություն բազմաբաղադրիչ բնական ջրային համակարգերից մետաղների կլանման համար:

Л. Ш. ТАНГАМЯН

ЭФФЕКТИВНОСТЬ ПРИМЕНЕНИЯ МОДИФИЦИРОВАННОГО ПОВЕРХНОСТНО-АКТИВНЫМ ВЕЩЕСТВОМ ПРИРОДНОГО ЦЕОЛИТА ДЛЯ УДАЛЕНИЯ МЕТАЛЛОВ ИЗ ВОДЫ РЕК АХТАЛА И ШНОХ

Изучена эффективность сорбции (удаления) природного цеолита из месторождения Нор Кохб, модифицированного поверхностно-активным веществом, по отношению к металлам-загрязнителям для образцов воды рек Ахтала и Шнох. Показано, что предложенный модифицированный поверхностно-активным веществом цеолит проявляет высокую сорбционную способность для сорбции металлов из мультикомпонентных природных водных систем.