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CHARACTERIZATION OF BOTH ANIONIC AND CATIONIC SURFACTANT-MODIFIED NATURAL ZEOLITE AND ITS APPLICATION FOR REMOVAL OF METAL-IONS FROM AQUEOUS MEDIUM

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Natural zeolite from Nor Koghb deposit (Armenia) was modified by anionic surfactant sodium dodecyl sulfate and cationic surfactant cetyltrimethylammonium bromide; and the modified samples were used for the removal of metal-ions from aqueous medium. The surface and textural characteristics of both natural and modified zeolites were studied by nitrogen adsorption/desorption isotherms and FTIR methods. The specific surface area, microporous surface area, volume of macro- and microporous both for natural and surfactant-modified zeolites were determined. It was shown that the surfactant-modified zeolites are effective adsorbents for the removal of metal-ions from aqueous medium. It was established that the optimal conditions of Co^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, and Pb^{2+} metal-ions adsorption are as follows: $m_{Me}{}^{2+}$=50 mg/l, $V_{solution}$=500 ml, m_{SMZ}=0.7 g, pH=6.5, T=298 K. Under these conditions, it is possible to remove the 88.27% Co^{2+}, 87.54% Fe^{2+}, 81.37% Ni^{2+}, 76.49% Cu^{2+}, 58.79% Zn^{2+}, 29.32% Mn^{2+}, 23.49% Pb^{2+} and 75% Cr(VI) from single-component system. In the multi-component system, the effectiveness of metal-ions removal is lower. From presented study, it is allowed that due to the low cost, industrial quantities availability of the natural Armenian zeolite and the high efficiency of their surfactant-modified samples as metal-ions removal sorbents, as well as easy and non-valuable process of modification, they can find wide application as effective adsorbents for purification of wastewaters.

Keywords: surfactant-modified zeolite, water treatment, metal-ions adsorption, competitive adsorption, zeolite characterization.

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Introduction

Many metals are emitted into the environment as waste raising pollution of water and soil. This problem is too vital for Armenia due to the intensive exploitation of metal-rich deposits during last decades and, as a result, spread tailings in large territories. Armenia is rich in alumosilicate clays, particularly there are few deposits of zeolite in industrial quantities. Among them, Nor Koghb is the largest one and the zeolite from Nor Koghb is characterized as clinoptilolite [1]. The Armenian zeolite is used as sorbent for removing pollutants from aqueous medium both in natural and modified forms. The modification of zeolite mainly has been done by acids and bases and it commonly have been used for removing of heavy, toxic and radioactive metals [2,3]. In addition, there are some studies about modification of natural Armenian zeolite by cationic and anionic surfactants [4]. However, these studies report no data of complete investigations of surface characteristics of modified samples and results of their application for removing pollutants, although they have been wildly used in the world as effective adsorbents in the period of the last decades. Particularly, it is shown that the zeolite, modified by the cationic surfactant cetyltrimethylammonium bromide (CTAB), is very efficient for removal of nitrate, anionic dyes, different oxyanionic heavy metals, chromium and arsenic, zinc and nickel, aniline and its derivatives from contaminated waters [5–8]. Zeolites modified by the anionic surfactant sodium dodecyl sulfate (SDS) have been used for removing ammonium and phosphorus, toxic and heavy metals, cationic dyes, organic and inorganic compounds [8–10]. It must also be noted that the modification of natural zeolite by surfactant is very easy to apply and the process is inexpensive, and therefore it does not significantly increase the cost of the sorbent. Thus, as a result of modification, both the sorbent and the sorption processes are more effective, economically beneficial and environmentally friendly for removing harmful pollutants from aqueous solutions. On the other hand, it is known, that after application of alumosilicate clays as sorbents for removing different pollutants, they are successfully used as additives in production of cement, bitumen and others (due to irreversible sorption) [8,11].

Based on the above mentioned, the adsorption capacity of Armenian zeolite (Nor Koghb deposit, Noyemberyan), modified by anionic surfactant SDS and cationic surfactant CTAB, have been studied in regard to the metal-ions both for single and competitive adsorption from aqueous medium and the surface characteristics of surfactant-modified zeolite (SMZ).

Experimental

Materials

Anionic surfactant sodium dodecylsulfate (SDS, $C_{12}H_{25}SO_4Na$, ASC reagent, ≥99.0%, Sigma-Aldrich), cationic surfactant cetyltrimethylammonium bromide (CTAB, $CH_3(CH_2)_{15}N(Br)(CH_3)_3$), BioXtra, ≥99.0%, Sigma-Aldrich), iron (II) chloride ($FeCl_2$, 98.0%, Sigma-Aldrich), cobalt (II) chloride ($CoCl_2$, purum p.a., anhydrous, ≥98.0% (KT), Sigma-Aldrich), copper (II) chloride ($CuCl_2 \cdot 3H_2O$, powder, 99.0%, Sigma-Aldrich), manganesse (II) chloride ($MnCl_2$, beads, 98.0%, Sigma-Aldrich), zinc (II) chloride ($ZnCl_2$, reagent grade, ≥98.0%, Sigma-Aldrich), nickel (II) chloride ($NiCl_2$, 98.0%, Sigma-Aldrich), lead (II) chloride ($PbCl_2$, powder, 98.0%, Sigma-Aldrich) and sodium chromate (Na_2CrO_4, 98.0%, Sigma-Aldrich) were used without further purification. All solutions were prepared by double-distilled water.

The clinoptilolite tuff (in this paper referred to as «zeolite») from Nor Koghb deposit (Noyemberyan, Armenia) was used as natural zeolitic material. Detailed mineralogical and petrographic study of the natural zeolite has been presented elsewhere [1]. Chemical composition and some characteristics of natural zeolite are given in Tables 1 and 2. Zeolite was air-dried, ground in ball mill and subsequently in pestle and mortar, so as to pass from 125 μm sieves and was stored at room temperature.

Methods

Preparation of surfactant-modified zeolite (SMZ)

Natural zeolite was modified by anionic surfactant SDS and cationic surfactant CTAB as it was described earlier [3].

Characterization of the natural and SM zeolites

Nitrogen adsorption/desorption isotherms were obtained using a NOVAe 2200 (Quantachrom) analyzer. The samples were outgassed under vacuum at 250°C for 5 h. The specific surface area was calculated by the BET method at $P/P_0 \approx 0.98$ and the size distribution of porous was calculated based on the adsorption and desorption isotherms. Mesoporous surface area and mesoporous volume were calculated by Barrett-Joyner-Halenda (BJH) model. The FTIR spectrum of both natural and SM zeolites were recorded using a Nexus spectrometer (Thermo Nicolet).

Table 1

Chemical composition of natural zeolite [1]

Constituent	SiO_2	Al_2O_3	CaO	K_2O	Fe_2O_3	MgO	Na_2O	TiO_2	FeO	P_2O_5	SO_3	H_2O	other
wt.%	67.80	11.67	4.23	1.67	1.23	0.91	0.72	0.28	0.17	0.13	0.10	3.01	7.58

Table 2

The characteristics of natural zeolite [1]

pH (refers to the aqueous suspension)	6.9
Moisture content, %	1.1
Organic matter content, %	2.3
Cation-exchange capacity, meq/100g	136.0
Specific surface area, m^2/g	19.6
Silt and clay, %	Clinoptilolite (major phase), quartz (minor phase), plagioclase (minor phase), smectite (trace phase)

Adsorption study

Batch experiments 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 were used for analysis.

The adsorption efficiency (%) was calculated from the batch experiments using the following formula:

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

where C_0 is the initial concentration of metal-ion, and C is the equilibrium concentration of the metal-ion.

Concentration of metal-ion in solution was determined by using PG-990 atomic absorption spectrophotometer. pH of solutions was determined by using HANNA HI 4522 technique. The presented data are the average values of twice repeated experiments.

Adsorption models

Adsorption data were analyzed by Langmuir and Freundlich models. Langmuir isotherm describes by the following relation:

$$\frac{C}{X} = \frac{1}{K_L \cdot X_m} + \frac{C}{X_m}, \quad (2)$$

where C is the equilibrium concentration of metal-ion in solution (mg/l), X is the amount of adsorbed metal-ion on per unit mass of adsorbent (mg/g), K_L is the constant which is related with adsorption energy (l/mg), and X_m is the maximum amount of adsorbed metal-ion on per unit mass of adsorbent (mg/g).

The liner form of Freundlich isotherm is as follows:

$$\ln X = \ln K_F + 1/n \ln C, \quad (3)$$

where K_F is the constant which shows the relative adsorption ability of adsorbent (l/mg), and n is the parameter which has value greater than unity and shows the intensity of adsorption.

Results and discussion

Characteristics of the natural and SM zeolites

The nitrogen adsorption/desorption isotherms of natural and SM zeolites are presented in Fig. 1 and the values of specific surface area of both natural and SM zeolites are given in Table 3. The value of specific surface area of natural zeolite determined by BET method is in good agreement with the literature data [1]. It is following from the obtained

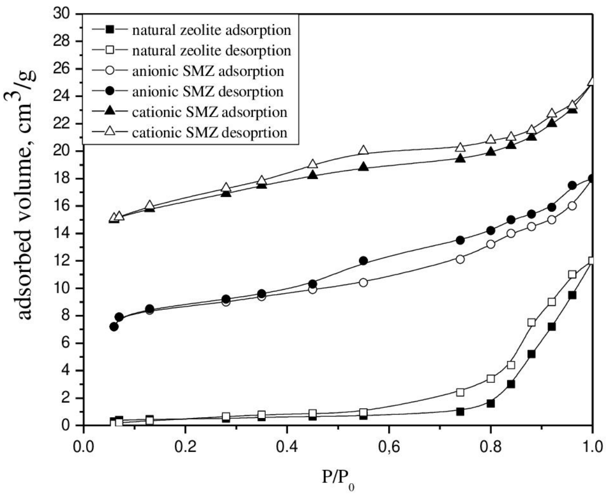


Fig. 1. N_2 adsorption/desorption isotherms of natural and SM zeolites

data that due to modification the specific surface area increases sharply.

Table 3

Specific surface area values of natural and SM zeolites*

Type of zeolite	Specific surface area, m^2/g	
	S_{BET}	S_{BJH}
Natural zeolite	19.4	13.7
Anionic SMZ	72.7	74.5
Cationic SMZ	93.6	89.7

* – Note: estimated uncertainties are ±0.2 m^2/g.

The changes in porous size distribution of zeolite due to modification are presented in Fig. 2. The microporosity (porous size <20 nm) of SMZ increases much more than macroporosity (porous size of 20–500 nm). The obtained values of mesoporous and microporous volume, as well as

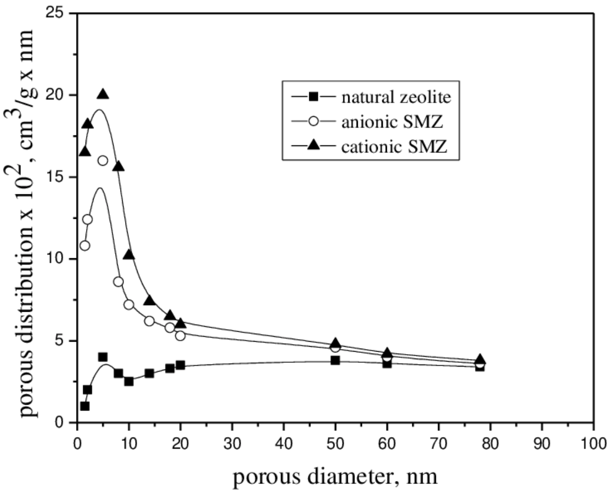


Fig. 2. Porous size distribution of natural and SM zeolites

Table 4

Values of characteristic parameters of natural and SM zeolites*

Type of zeolite	$S_{specific}$, m^2/g	$S_{external}$, m^2/g	S_{micro}, m^2/g	V_{meso}, cm^3/g	V_{micro}, cm^3/g
Natural zeolite	19.40	15.57	3.98	1.44	4.03
Anionic SMZ	72.70	18.00	54.70	3.54	17.90
Cationic SMZ	93.60	25.40	68.20	5.24	29.81

* – Note: estimated uncertainties are ±0.20 m^2/g for $S_{specific}$, ±0.20 m^2/g for $S_{external}$, ±0.20 m^2/g for S_{micro}, ±0.20 cm^3/g for V_{meso}, and ±0.20 cm^3/g for V_{micro}.

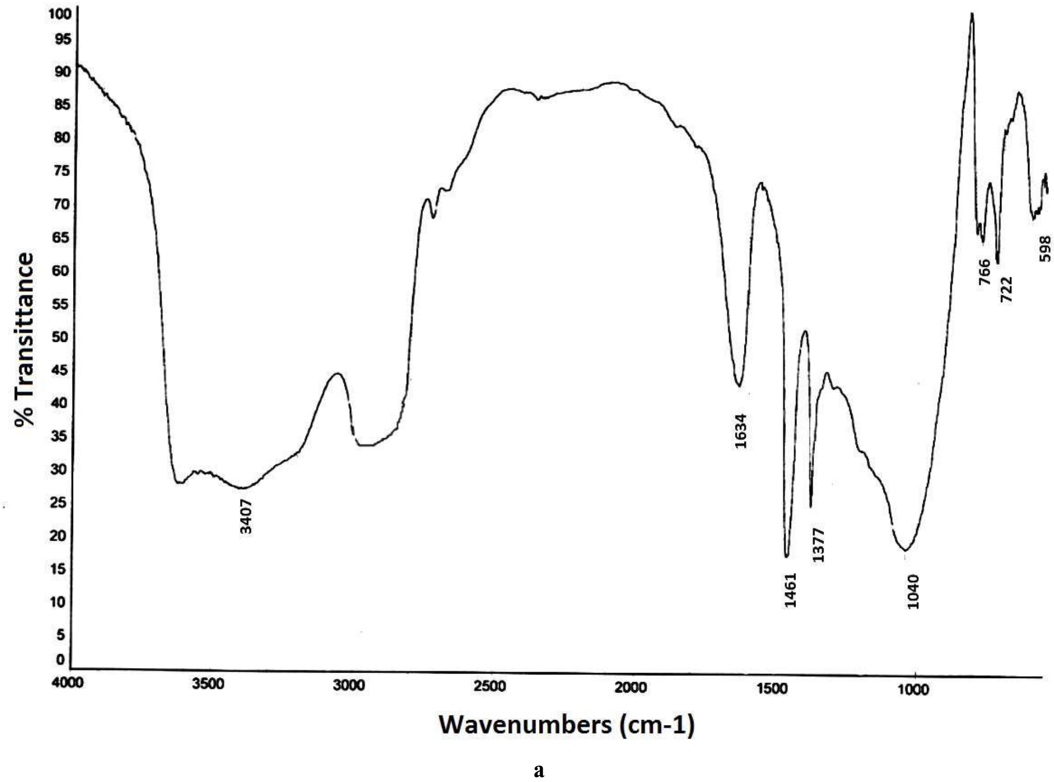
microporous surface, are given in Table 4. As it follows from the obtained data, both microporous specific surface area and microporosity increase due to modification.

The modification of zeolite by surfactant occurs mainly by layer formation on external surface and the modified surface has negatively-charged (in the case of modification by SDS) or positively-charged (in the case of modification by CTAB) exchange sites which increase adsorption ability of ions. It is accepted that the surfactants in concentrations higher than critical micelle concentration form bilayers on surface of zeolite due to the hydrophobic interaction between the tails [9].

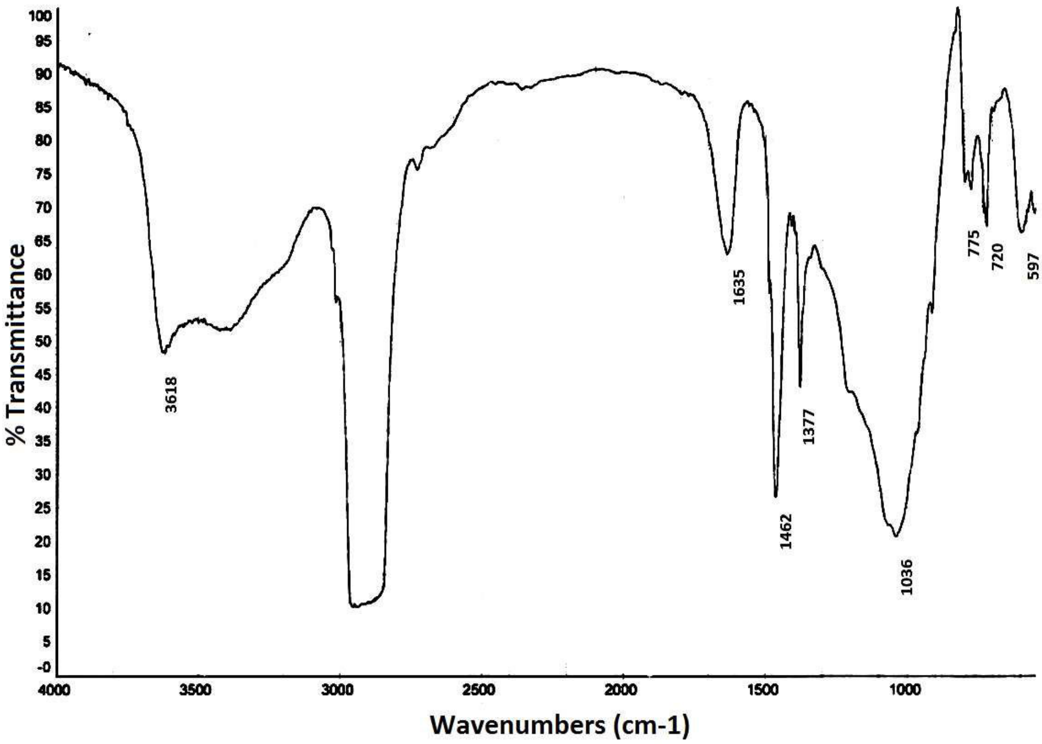
The FTIR spectra of natural and SM zeolites, given in Fig. 3, show the highest frequency of absorption for asymmetric and symmetric overlap of H–O–H with hydroxyl (O–H) groups of zeolite at 3000–3700 cm^{-1}. The peaks at 1630–1640 cm^{-1} show stretching and bending strength of the O–H groups in zeolites. The peaks at 900–1250 cm^{-1} and 700–850 cm^{-1} are associated with the asymmetric and symmetric vibration of O–Si–O and O–Al–O. It must be noted the spectral data of natural Armenian zeolite are in good agreement with the literature data [1]. The peaks at 2850–2920 cm^{-1} (Fig. 4 (b,c)) is asymmetric, and symmetric $-CH_2$ stretching vibration of SDS and CTAB indicates the successful modification of zeolite by SDS and CTAB [12,13].

Adsorption of metal-ions on anionic SMZ

The adsorption of metal-ions on anionic SMZ surface has been studied at 298 K varying metal-ion concentration from 50 to 400 mg/l at the constant values of other parameters. The results are shown in Fig. 4. The adsorption of Co^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, and Pb^{2+} metal-ions decreases with increase in the metal-ions concentration. It means that the adsorption of Co^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+},



a



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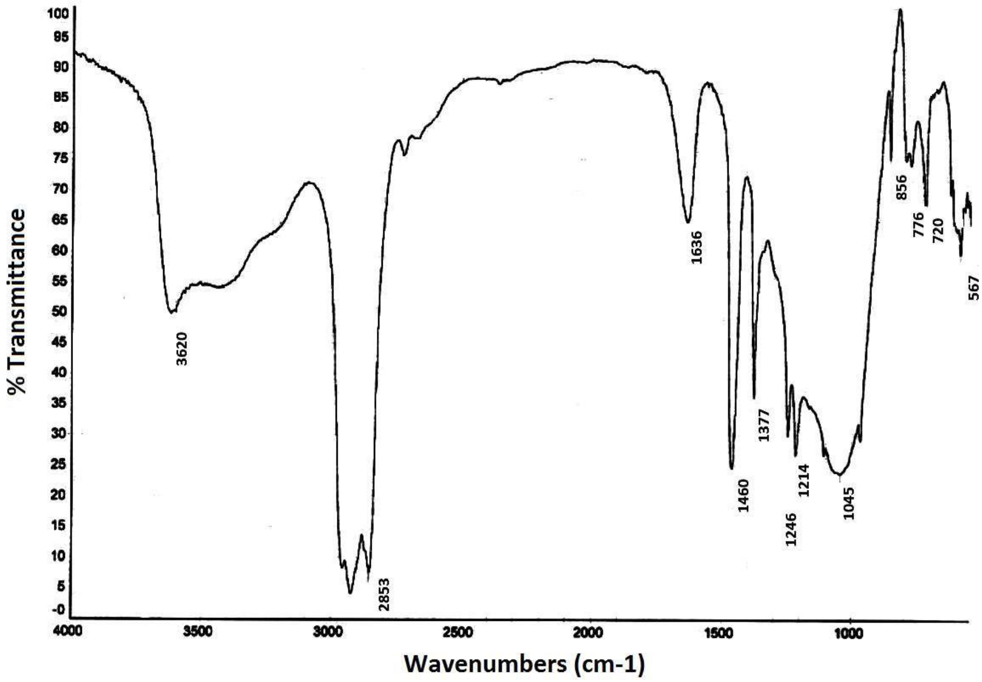

c

Fig. 3. FTIR spectra of natural – a, SDS-modified – b and CTAB-modified zeolite – c

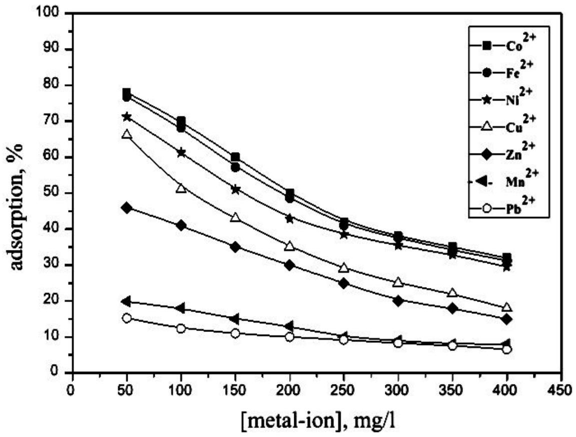

Fig. 4. Adsorption isotherms of metal-ions depending on metal-ions concentration. m_{SMZ}=0.2 g, $V_{solution}$=500 ml, pH=6, contact time 120 min, T=298 K

Mn^{2+}, and Pb^{2+} metal-ions is more effective in dilute solutions. The maximum exchanging degrees of metal-ions are as follows: Co^{2+} 77.96%, Fe^{2+} 76.87%, Ni^{2+} 71.23%, Cu^{2+} 66.10%, Zn^{2+} 45.96%, Mn^{2+} 19.84%, and Pb^{2+} 15.23%, the optimal initial metal-ion concentration being 50 mg/l.

Figure 5 shows the dependence of adsorption effectiveness on adsorbent amount. As can be seen, the adsorption effectiveness increases till 0.7 g of adsorbent amount, and then slightly decreases. Thus, the 0.7 g was used for the next experiments as the optimal condition.

Adsorption of metal-ions is very sensitive to the medium pH. As is seen from Fig. 6, the optimal value of pH for maximum adsorption of metal-ions is 6.5. At low pH values, the competitive adsorption occurs between H^+ ions and metal-ions which inhibit adsorption of metal-ions. At pH values of 7–8, a slight decrease of metal-ions adsorption is observed due to a decrease in the metal-ions concentration in the Me^{2+} form. At higher values of pH, the participation of $Me(OH)_2$ occurs.

The dependence of metal-ions adsorption on the metal-ion–adsorbent contact time was also studied. The adsorption of metal-ions sharply increases during the first 120 min, then adsorption effectiveness increases slightly from 120 to 195 min. After 195 min, the adsorption effectiveness remains practically unchanged. Thus, the value of 195 min can be chosen as the optimal time for shaking the aqueous mixtures anionic SMZ and metal-ions (Fig. 7). The adsorption effectiveness for optimal conditions is as follows: Co^{2+} 88.27%, Fe^{2+} 87.54%, Ni^{2+} 81.37%, Cu^{2+} 76.49%, Zn^{2+} 58.79%, Mn^{2+} 29.32%, and Pb^{2+} 23.49%.

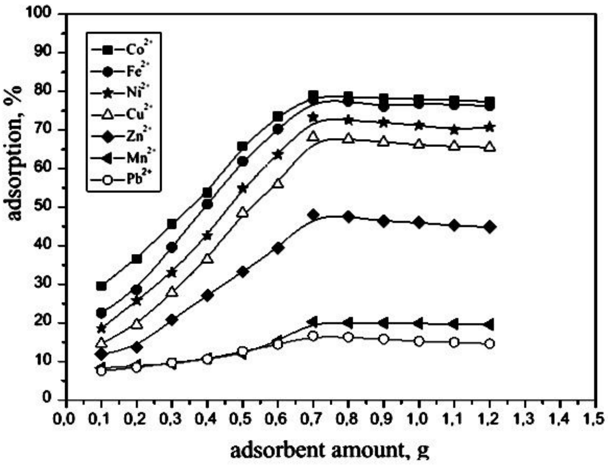

Fig. 5. Adsorption isotherms of metal-ions. $m_{Me^{2+}}$=50 mg/l, $V_{solution}$=500 ml, pH=6, contact time 120 min, T=298 K

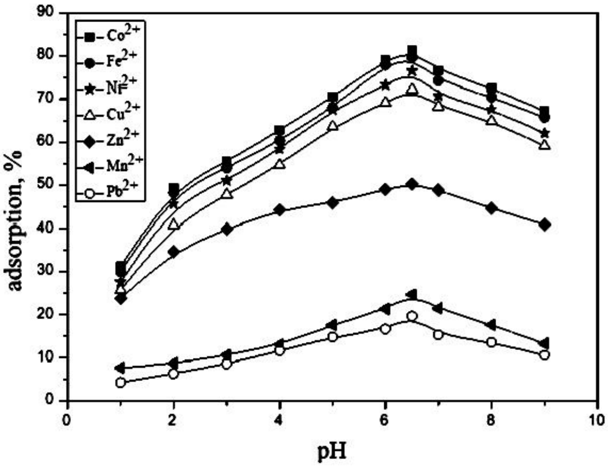

Fig. 6. Dependence of adsorption of metal-ions depending on pH. $m_{Me^{2+}}$=50 mg/l, $V_{solution}$=500 ml, m_{SMZ}=0.7 g, contact time 120 min, T=298 K

When comparing the obtained results with the

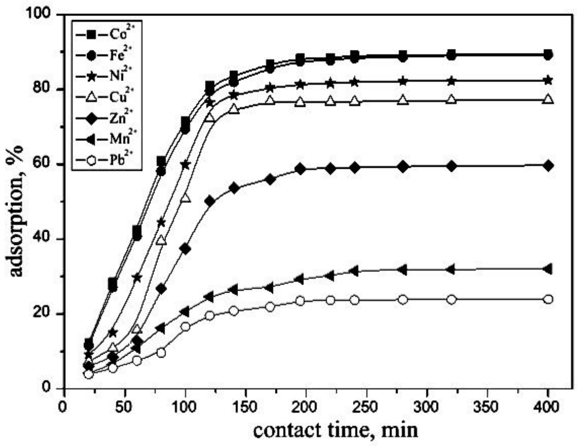

Fig. 7. Dependence of adsorption of metal-ions depending on sorbate-adsorbent contact time. $m_{Me^{2+}}$=50 mg/l, $V_{solution}$=500 ml, m_{SMZ}=0.7 g, pH=6.5, T=298 K

Table 5

Adsorption effectiveness of metal-ions from aqueous solution by using anionic SMZ, natural, acidic and basic treated zeolites of Armenia*

Metal-ion	Adsorption effectiveness, %			
	natural zeolite	anionic SMZ	acidic treated zeolite	basic treated zeolite
Co^{2+}	70.0	88.27	80.0	90.0
Fe^{2+}	–	87.54	–	–
Ni^{2+}	–	81.37	–	–
Cu^{2+}	–	76.49	–	–
Zn^{2+}	–	58.79	–	–
Mn^{2+}	80.0	29.32	–	90.0
Pb^{2+}	–	23.49	–	–

* – Note: estimated precision in adsorption effectiveness is better than ±2%.

literature data on adsorption effectiveness of metal-ions by Armenian natural zeolite (Nor Koghb deposit) and its acidic and basic treated samples (Table 5), it can be concluded that the anionic SMZ is more effective adsorbent for Co^{2+} than the natural Armenian zeolite and practically has the same effectiveness as basic treated zeolite; however, the adsorption effectiveness for Mn^{2+} is higher than that both in the case of natural and basic treated zeolites (Table 5).

Adsorption isotherms

The adsorption parameters calculated based on Langmuir model are given in Table 6 (R^2 is the linear dependence correlation coefficient). The studies have been done for 25–400 mg/l concentration range of metal-ions. The values of X_m show that the adsorption behavior of metal-ions is changed in the following order: $Co^{2+}>Fe^{2+}>Ni^{2+}>Cu^{2+}>Zn^{2+}>Mn^{2+}>Pb^{2+}$.

Table 6

Values of metal-ions adsorption parameters calculated by Langmuir model*

Metal-ion	X_m, mg/g	K_L, l/g	R^2
Co^{2+}	244.13	1.95	0.9875
Fe^{2+}	238.29	1.92	0.9920
Ni^{2+}	213.81	1.84	0.9846
Cu^{2+}	161.12	1.72	0.9919
Zn^{2+}	133.85	0.85	0.9893
Mn^{2+}	86.78	0.33	0.9863
Pb^{2+}	79.22	0.31	0.9938

* – Note: Estimated uncertainties are ± 2.00 mg/g in X_m and ± 0.05 l/g in K_L.

The studied metal-ions exist in aqueous solution as hexaaqueous complexes, that is each metal-ion is surrounded by six molecules of water and each metal-ion is moved through the channels of zeolite in form of complex. Adsorption depends on the density of cation charge and diameter of hydrated cation. The studied cations have the same charge (+2), therefore it can easily reveal the dependence of adsorption on diameter of metal-ions. It follows from data of Table 6 that among studied metal-ions the adsorption of Pb^{2+}, which has the biggest diameter, is minimum and the adsorption of Co^{2+}, which has the smallest diameter, is maximum.

Adsorption behavior of Co^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, and Pb^{2+} metal-ions is also analyzed by Freundlich model. The values of K_F and n are given in Table 7. The values of n are in the range of 2–10, which characterize adsorption as effective process. The values of 1/n<1 indicate that the adsorption of metal-ions on anionic SMZ is a favorable process.

Table 7

Adsorption parameters of metal-ions calculated by Freundlich model*

Metal-ion	$\log K_F$, (mg/g) $(L/g)^n$	1/n	R^2
Co^{2+}	1.35	0.30	0.9714
Fe^{2+}	1.33	0.32	0.9724
Ni^{2+}	1.17	0.40	0.9724
Cu^{2+}	0.98	0.36	0.9590
Zn^{2+}	0.93	0.43	0.9417
Mn^{2+}	0.81	0.50	0.9697
Pb^{2+}	0.77	0.31	0.9654

* – Note: estimated uncertainties are ±0.04 mg/g $(L/g)^n$ in $\log K_F$ and ±0.02 in 1/n.

Competitive adsorption of metal-ions on anionic SMZ

The competitive adsorption of Co^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, and Pb^{2+} metal-ions on anionic SMZ is also studied. The data presented in Table 8 shows that the adsorption efficiency of metal-ions by anionic SMZ sharply decreases in the multi-component system, which is quite predictable result

Table 8

Values of metal-ions competitive adsorption parameters calculated by Langmuir and Freundlich models*

Metal-ion	Langmuir model			Freundlich model		
	X_m, mg/g	K_L, l/g	R^2	$logK_F$, (mg/g) $(L/g)^n$	1/n	R^2
Multi-component system (Co^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, and Pb^{2+})	48.70	0.12	0.9633	0.45	0.782	0.9555

* – Note: estimated uncertainties are ±2.00 mg/g in X_m, ±0.05 l/g in K_L, ±0.04 mg/g $(L/g)^n$ in $logK_F$ and ±0.02 in 1/n.

because there is a strong competition between available adsorption sites on the surface of anionic SMZ.

Adsorption of Cr(VI) on cationic SMZ

Cr-containing compounds are widely used in dye industry, in metallurgy, for the preparation of galvanic surfaces and so on. The wastewaters of such industries are containing chromium ions in form of Cr(III) and Cr(VI). The Cr(VI) is more toxic than Cr(III), easily goes through cell membranes and has mutagen and cancerogenic effect [14]. Therefore, the removal of Cr(VI) from wastewaters and the prevention of its emission in environment is an actual problem [8,14]. According to the literature, at pH=6 the Cr(VI) ions exist in the aqueous solutions as $HCrO_4^-$(dichromate, 74%) and CrO_4^{2-} (chromate, 26%) [8]; in more acidic medium, Cr(VI) mainly exists as $HCrO_4^-$; and at pH higher than 9, it exists as CrO_4^{2-}. It is also shown that cationic SMZ is more selective towards CrO_4^{2-} than $HCrO_4^-$ [8].

The adsorption parameters of Cr(VI)-containing ions on natural and cationic SM zeolits are given in Table 9. It has been established that the use of cationic SMZ as adsorbent sharply increases the adsorption effectiveness of Cr(VI), which reaches 75% (Fig. 8).

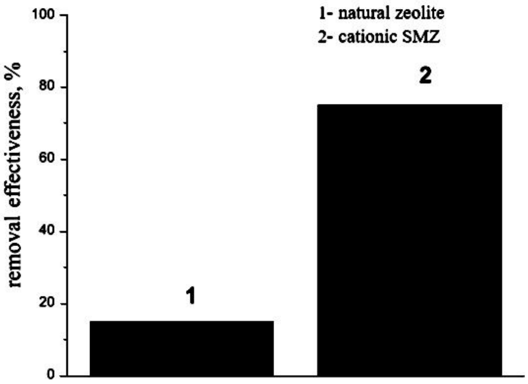

Fig. 8. The effectiveness of usage of natural and cationic SM zeolites for the removal of Cr(VI) from aqueous solution. [Cr(VI)]=100 mg/l, $V_{solution}$=500 ml, $m_{adsorbent}$=1 g, pH=5.0, T=298 K

Conclusions

It can be concluded from the presented data that the surfactant-modified natural zeolites from Nor Koghb deposit (Noyemberyan, Armenia) are effective adsorbents for the removal of metal-ions from aqueous medium both in the case of single- and multi-component adsorption. It was established that in the case of single adsorption the adsorption effectiveness on anionic SMZ is changed in the order $Co^{2+}>Fe^{2+}>Ni^{2+}>Cu^{2+}>Zn^{2+}>Mn^{2+}>Pb^{2+}$, the metal-ions adsorption process is better described by Freundlich isotherm and is multilayer. It was also shown that for Cr(VI) the cationic SMZ is effective adsorbent, the usage of which increases Cr(VI) adsorption by about 5 times as compared with natural zeolite.

The study of the textural and surface parameters of SMZ has shown the specific area and microporosity sharply increase due to modification, which, of course, increases the adsorption capacity of the modified samples. The FTIR studies established the formation of a external surface layer by surfactants and an increase of number of the charged sites (positive and/or negative) on surface of zeolite due to modification which determines the adsorption efficiency in regard to metal-ions in aqueous medium.

Table 9

Adsorption parameters of Cr(VI) on natural and cationic SM zeolites calculated by Langmuir and Freundlich models

Langmuir model			Freundlich model		
X_m, mg/g	K_L l/g	R^2	$logK_F$, (mg/g) $(L/g)^n$	1/n	R^2
63.1	0.22	0.8573	0.95	0.31	0.9850

* – Note: estimated uncertainties are ±2.00 mg/g in X_m, ±0.05 l/g in K_L, ±0.04 mg/g $(L/g)^n$ in $logK_F$ and ±0.02 in 1/n.

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ХАРАКТЕРИСТИКА ПРИРОДНОГО ЦЕОЛІТУ, МОДИФІКОВАНОГО АНІОННИМ І КАТІОННИМ ПАР, ТА ЙОГО ЗАСТОСУВАННЯ ДЛЯ ВИДАЛЕННЯ ІОНІВ МЕТАЛІВ ІЗ ВОДНОГО СЕРЕДОВИЩА

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Природний цеоліт з родовища Нор Кохб (Вірменія) модифікували аніонним ПАР додецилсульфатом натрію та катіонним ПАР цетилтриметиламоній бромідом, і модифіковані зразки використовували для видалення іонів металу з водного середовища. Поверхневі та текстурні характеристики як природних, так і модифікованих цеолітів вивчали за допомогою ізотерм адсорбції/десорбції азоту та методів FTIR. Визначено питому поверхню, площу мікропористої поверхні, об'єм макро- та мікропористості як для природних, так і для модифікованих ПАР цеолітів. Показано, що модифіковані ПАР цеоліти є ефективними адсорбентами для видалення іонів металів із водного середовища. Встановлено, що оптимальні умови адсорбції іонів металів Co^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Pb^{2+} становлять m_{Me2+}=50 мг/л, $V_{розчину}$=500 мл, m_{SMZ}=0,7 г, pH 6,5, T=298. K. За таких умов можна видалити 88,27% Co^{2+}, 87,54% Fe^{2+}, 81,37% Ni^{2+}, 76,49% Cu^{2+}, 58,79% Zn^{2+}, 29,32% Mn^{2+}, 23,49% Pb^{2+} і 75% Cr(VI) з монокомпонентних систем. У багатокомпонентних системах ефективність видалення іонів металу нижча. З результатів проведеного дослідження випливає, що через низьку вартість, доступність промислових кількостей природного вірменського цеоліту та високу ефективність їх модифікованих поверхнево-активними речовинами зразків як сорбентів для видалення іонів металів, а також легкість і дешевизну процесу модифікації, вони можуть знайти широке застосування як ефективні адсорбенти для очищення стічних вод.

Ключові слова: цеоліт, модифікований ПАР, водопідготовка, адсорбція іонів металів, конкурентна адсорбція, характеристика цеоліту.

CHARACTERIZATION OF BOTH ANIONIC AND CATIONIC SURFACTANT-MODIFIED NATURAL ZEOLITE AND ITS APPLICATION FOR REMOVAL OF METAL-IONS FROM AQUEOUS MEDIUM

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Natural zeolite from Nor Koghb deposit (Armenia) was modified by anionic surfactant sodium dodecyl sulfate and cationic surfactant cetyltrimethylammonium bromide; and the modified samples were used for the removal of metal-ions from aqueous medium. The surface and textural characteristics of both natural and modified zeolites were studied by nitrogen adsorption/desorption isotherms and FTIR methods. The specific surface area, microporous surface area, volume of macro- and microporous both for natural and surfactant-modified zeolites were determined. It was shown that the surfactant-modified zeolites are effective adsorbents for the removal of metal-ions from aqueous medium. It was established that the optimal conditions of Co^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, and Pb^{2+} metal-ions adsorption are as follows: $m_{Me}{}^{2+}$=50 mg/l, $V_{solution}$=500 ml, m_{SMZ}=0.7 g, pH=6.5, T=298 K. Under these conditions, it is possible to remove the 88.27% Co^{2+}, 87.54% Fe^{2+}, 81.37% Ni^{2+}, 76.49% Cu^{2+}, 58.79% Zn^{2+}, 29.32% Mn^{2+}, 23.49% Pb^{2+} and 75% Cr(VI) from single-component system. In the multi-component system, the effectiveness of metal-ions removal is lower. From presented study, it is allowed that due to the low cost, industrial quantities availability of the natural Armenian zeolite and the high efficiency of their surfactant-modified samples as metal-ions removal sorbents, as well as easy and non-valuable process of modification, they can find wide application as effective adsorbents for purification of wastewaters.

Keywords: surfactant-modified zeolite; water treatment; metal-ions adsorption; competitive adsorption; zeolite characterization.

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