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HEAVY METAL ADSORPTION BY ARMENIAN NATURAL ZEOLITE FROM NATURAL AQUEOUS SOLUTIONS

Sh. V. KHACHATRYAN [*]

Chair of Regional Geology, Petrology and Mineral Deposits YSU, Armenia

Copper, zinc, chromium, mercury, manganese, arsenic, lead and cadmium removal from natural aqueous solutions by Armenian natural zeolites was examined by using batch type and dynamic type methods. The percentage of adsorption was determined for the adsorption system as a function of contact time and number of cycle. Two types of selective series of heavy metal ions have been carried out. According to the studies, the selectivity sequence can be given as Cu>Pb>Mn>Cd>Fe>Zn>Cr>Ni>As≥Hg and Cu>Pb>Cd>Zn>Fe≥Mn≥Ni≥As>>Cr>Hg in dynamic type and batch type methods.

Keywords: heavy metals, natural zeolite, adsorption kinetics, selectivity.

Introduction. Heavy metals are considered hazardous pollutants due to their toxicity, even at low concentration. Increasing level of heavy metals in natural water bodies poses a serious threat to all living species including humans. Therefore, it is essential to reduce the heavy metal concentration in effluents and wastewater before it is discharged into the water bodies [1]. Numerous processes exist for removing dissolved heavy metals, including ion-exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis [2, 3].

Ion exchange and adsorption is one of the few promising alternatives for this purpose, especially using low-cost natural sorbents such as clay materials, zeolite, biomass, perlites and diatomits [4, 5]. In this regard naturally occurring zeolites hold great potential to be used as packing material in subsurface reactive barriers intercepting ground water plumes, and for fixed bed reactors designed to remove heavy metals from industrial wastewater [6].

Zeolites are hydrated aluminosilicate minerals with a cage-like structure. The structures of zeolite consist of three-dimensional framework of SiO^{4+} and AlO^{4+} tetrahedral [7]. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Al^{3+} for Si^{4+} raises a negative charge in the lattice. The negative net is balanced by the exchangeable cation (sodium, potassium and calcium). These cations are exchangeable with certain cations in solutions such as lead, cobalt, zinc and manganese. The fact that zeolite exchangeable ions are relatively innocuous

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[*] E-mail: sh_khach@ysu.am

(sodium, calcium and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters.

Clinoptilolite is the most abundant mineral among zeolites belonging to the HEU-type zeolite group [7, 8]. One of the earliest applications of a natural clinoptilolite was in removal and purification of cesium and strontium radioisotopes [9, 10]. The high selectivity for toxic metals such as Pb, Cd, and Zn makes clinoptilolite a promising material for treatment of mine wastewaters. Inglezakis et al. studied the ion exchange of Pb^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+} on natural clinoptilolite and showed that equilibrium is favorable for Pb^{2+}, unfavorable for Cu^{2+} and of sigmoid shape for Cr^{3+} and Fe^{3+} [11]. Mieret et al. described the interactions of Pb^{2+}, Cd^{2+} and Cr^{3+} competing for ion-exchange sites in natural clinoptilolite [12]. Selectivity series have been given as $Ba^{2+}>Cu^{2+}$, $Zn^{2+}>Cd^{2+}$, $Sr^{2+}>Co^{2+}$ by Blanchard et al. [13], as $Pb^{2+}>Cd^{2+}>Cs+>Cu^{2+}>Co^{2+}>Cr^{3+}>Zn^{2+}>Ni^{2+}>Hg^{2+}$ by Zamzow et al. [14] and as $Co^{2+}>Cu^{2+}>Zn^{2+}> Mn^{2+}$ by Erdem et al. [15].

The clinoptilolite samples from different regions show different behavior in ion-exchange processes. In this study the adsorption properties of Armenian natural zeolite with respect to some heavy metal cations in the Lake Sevan were investigated.

Materials and Methods. Natural zeolite sample was obtained from North-East region of Armenia. It was ground to approximately 200-mesh size powder. The given amount of the material was washed with deionised water three-four times to remove any dust and other water-soluble impurities. The sample was then dried in an electric oven at 150–200°*C* for 2–3 *h* before using for adsorption purpose.

Chemical analyses have been carried out on fused glass discs and pressed powder pellets with wavelength-dispersive XRF technique on a PHILIPS PW 2400 machine. Mineralogical specification was estimated by X-ray diffraction using Seifert FPM diffractometer (CuK, α-radiation, voltage 40 *kV*, intensity 40 *mA*, Ni-filter, diaphragm 1,1,05).

The results of XRD analyses show that the dominant mineral of tuff from Noyemberyan Deposit is well-crystallized clinoptilolite (heulandite 80–85%) with typical reflections: *d* (020) – 8.93–9.01 Å; *d* (200) – 7.9 Å; *d* (201) – 6.7–6.8 Å; *d* (131) – 3.97–3.98 Å; *d* (151) – 2,97 Å. As impurities the tuff contains quartz, albite, illite, barite and volcanic glass. The sample composition was determined analytically (Tab. 1).

Table 1

Chemical composition of the zeolite material

Composition	Weight, %
SiO_2	68.03
TiO_2	0.21
Al_2O_3	11.92
Fe_2O_3	1.77
MnO	0.01
MgO	0.83
CaO	2.65
Na_2O	1.96
K_2O	2.26
H_2O	10.25
P_2O_5	0.06
SO_3	0.05

In the experiments static and dynamic methods have been used. In static conditions adsorption tests were conducted in 250 *mL* glass tubes. A zeolite sample of 50.0 *g* was mixed in 100 *mL* water, mechanical shaking at a speed of 250 *rpm* for a period of 1 month. After the agitation for an equilibrium period, the supernatant solution was filtered through 0.45 *μm* micro porous membrane filter.

In dynamic conditions water treatment experiments in the glass column of 20 *mm* diameter and of 5 *mm* height have been conducted. The water with the rate of 0.1 *mL*/*min* passed through a column filled by zeolite. The past solution was collected and analyzed.

The exact concentration of metal ions in water was verified by AAS ATI UNICAM 929 atomic absorption spectrophotometer. The flame type was airacetylene. The degree of metal removal (%) from the investigated solutions was calculated by the following formula:

$$\text{Uptake} = \frac{(C_0 - C)}{C_0} 100\%,$$

where C_0 and C are the initial and final concentration ($mg\ L^{-1}$).

Results and Discussion. Metal ions' removal efficiencies for tested zeolite sample are shown in Tab. 2 and 3. As it is shown in the Tables, zeolites have selectivity related to the copper, lead, manganese, cadmium and zinc. In Tab. 2 the results, which have been achieved after 10 cycles of purification, are shown. It is obvious that zeolites selectively uptake copper and lead.

Table 2

Contents of metals in the sample before and after its contact to an adsorbent in dynamic conditions: $m_{\text{sorbent}} = 5\ g$, $V_{\text{water}} = 50\ mL$, *speed put of a solution = 0.1 mL/min*

Metals	Concentration of metal ions, *mg*/*L*		The rate of purification, %
	without contact to an adsorbent	after contact	
Cu	0.020	0.011	45.0
Pb	0.012	0.007	41.6
Mn	0.090	0.060	33.3
Cd	0.020	0.014	30.0
Fe	0.280	0.230	27.7
Zn	2.200	1.800	18.1
Cr	0.030	0.025	16.6
Ni	0.010	0.008	15.0
Hg	0.010	0.009	10.0
As	0.010	0.009	10.0

In Tab. 3 are shown the results of batch type method purification. The results achieved after 48 *h* of zeolite–water system contact. It is evident that zeolites have effective sorption of copper and lead.

In batch type method of purification the selectivity of ions differs from dynamic type purification: Cu> Pb> Cd> Zn> Fe≥ Mn≥ Ni≥ As> Cr> Hg (Tab. 3). It can be seen, that water treatment under dynamic and static conditions are not the same. It is clear that water purification in dynamic and batch type methods are taking place by different mechanisms. This difference of series may be attributed by reversible ion-exchange processes.

During purification in zeolite–water system the equilibrium does not achieve due to suspension of organic and mechanical materials in the sample, which obturate the zeolite cavity and prevent easy ion-exchange processes.

According to the literature, natural an treated zeolites are able to sorb up to 79% copper from modal water solution [16], however, in multi ion system sorption of ions gradually decreases with increasing number and concentration of ions in the solution.

Table 3

Contacts of metals in water before its contact to a clinoptilolite in a static mode during 1 month: $m_{\text{sorbent}}= 50$ *g,* $V_{\text{water}}= 100$ *mL, d=1–2 mm*

Metals	Concentration of metal ions in water, *mg/L*		The rate of purification, %
	without contact to an adsorbent	after contact	
Cu	0.020	0.012	40.0
Pb	0.012	0.008	33.3
Cd	0.020	0.016	20.0
Zn	2.260	1.930	13.6
Fe	0.280	0.260	11.1
Mn	0.090	0.080	11.1
Ni	0.010	0.009	10.0
As	0.010	0.009	10.0
Cr	0.030	0.028	6.6
Hg	0.010	0.010	0.0

Conclusion. Armenian zeolites can be used as effective sorbents for purification of drinking and waste waters. The content of many ions have been decreased in natural aqueous solutions during dynamic and static methods of purification. More than 40% of lead and cobalt ions have been sorbed by zeolites. According to the literature, zeolites can remove more than 80–90% of Cu, Pb and Co. In this case such high results have not been achieved, because of competitions of cations during sorption processes. The results show that dynamic type of sorption is more effective, than static type method. It was easier to remove from the water Cu, Pb, than Ni, Cr and Hg, As. Uptakes of 41.6% for Pb and 45% for Cu were obtained.

These results show that natural zeolites hold great potential to remove heavy metal species from drinking water. It has been sown that dynamic type method purifies water more effectively than batch type.

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