

Combined Filter for Water Treatment

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ARTICLE INFO

Article history:

Received: 19 February 2018;

Received in revised form:
20 March 2018;

Accepted: 31 March 2018;

Keywords

Natural zeolites,
Contaminated water,
Adsorbents,
Ion exchangers,
Combined filter.

ABSTRACT

The adsorption characteristics of Georgian natural and acid-modified forms of clinoptilolite and laumontite have been studied in order to determine possibilities of their application in treatment of water contaminated by metals. It was found that natural clinoptilolite washed by diluted acid is the most effective adsorbent for barium, cobalt and lithium, while strontium, manganese, nickel and lead can be captured by modified clinoptilolite, but zinc, iron and copper – by modified laumontite. A combined filter (quartz sand + washed clinoptilolite + laumontite + clinoptilolite, both treated with 1.0N HCl solution) is offered.

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Introduction

Treatment of water used for municipal and industrial purposes refers to the removal of impurities such as dissolved substances and suspended solids. Among all available water treatment technologies (coagulation, foam flotation, solvent extraction, electrolysis, etc.), adsorption is considered the best option because of convenience, ease of operation, and simplicity of design [1]. Activated carbon [2], clay minerals [3], biopolymers [4], some solid waste materials [1,5,6], and zeolites [7,8] have been widely used as adsorbents for adsorption of ions and organics in wastewater treatment.

Zeolites are aluminosilicates of general formula $M_{x/n}[Al_xSi_yO_{2(x+y)}]mH_2O$, where the metal M (usually Na, K, Ca, Mg) is in a ionic form M^{+n} , compensating the negative charge of the aluminum in crystal lattice. Each silicon and aluminum atom has covalent bonds with four oxygen atom, SiO_4 and AlO_4^- tetrahedrons are linked in their corners forming open, “framework” structure with cages and channels. For example, the most commonly used zeolite of the HEU type (clinoptilolite) forms a monoclinic crystal structure with the channels shown in Figure 1; “wide” channels formed by 10-membered rings have sizes 0.31 x 0.75 nm, “narrow” channels formed by 8-membered rings have sizes 0.28 x 0.47 and 0.36 x 0.47 nm. Presence of channels and cavities causes molecular-sieve, sorption and other properties of zeolites.

Natural or synthetic zeolites have been noted by scientists because of their unique adsorption properties – zeolites adsorb a variety of heavy metals and ammonia, and remove a wide range of pollutants. Natural zeolites outperform conventional granular media, are cost-effective, abrasion resistant, non-toxic and environmentally friendly, especially in the treatment of such special wastewater streams as acid mine drainage, landfill leachate, nuclear fallout, and urban runoff [9].

Among many natural zeolites identified in the world, clinoptilolite, mordenite, phillipsite, analcime and laumontite are very common.

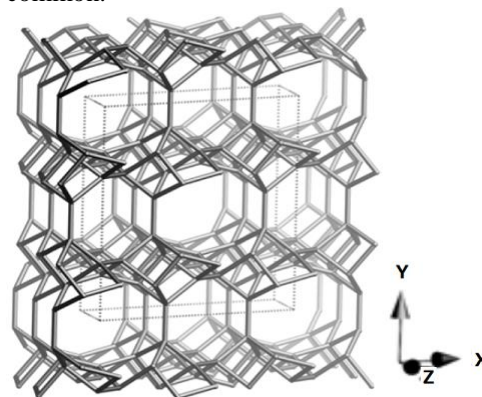


Figure 1. HEU framework viewed along [001].

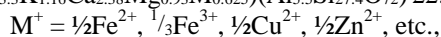
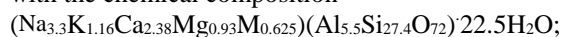
The results of the experimental study of adsorption of heavy metal ions by Na-clinoptilolite [10] suggest that the selectivity of zeolite is strongly influenced by the pH of the contact solution, as well as dehydration energy and diffusion coefficient of ions, and for the $pH > 4$ can be expressed by the series: $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Ni$. The ion exchange capacity of Ca,Na-laumontite from Georgia [11] is decreasing in the following series: $Cs^+ > Rb^+ > NH_4^+ > Li^+$, and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

The adsorption characteristics of any zeolite are defined by its chemical and structural properties (the Si/Al ratio, nature of compensating metal ions, their charge and location, etc.) that can be changed by several chemical treatments to improve separation efficiency of raw natural zeolite. So, acid washing of natural zeolite may remove impurities that block the pores/channels, and progressively eliminate metal ions to change into H-form characterized by lower ion exchange capacity, but does not introducing extraneous metals into water under purification.

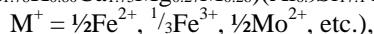
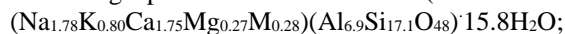
The purpose of our work was to investigate the feasibility of application of Georgian natural zeolites (clinoptilolite and laumontite) in treatment of natural waters and to offer a filter on their basis, providing water purification to the permissible level of toxic and polluting substances.

Experimental

Experiments have been carried out using zeolitic rock from the Hekordzula plot of Tedzami deposit, Eastern Georgia, containing up to 85% of clinoptilolite-heulandite with the chemical composition



and belonging to the Na,Ca-form of the HEU (UPAC chemical formula $[\text{Ca}_4(\text{H}_2\text{O})_{24}][\text{Al}_8\text{Si}_{28}\text{O}_{72}]$) type natural zeolites, and a tuff from the Tbilisi Botanical Garden plot containing up to 90% of laumontite (chemical composition



and belonging to the Na,Ca-form of the LAU (UPAC chemical formula $[\text{Ca}_4(\text{H}_2\text{O})_{16}][\text{Al}_8\text{Si}_{16}\text{O}_{48}]$) type natural zeolites.

Both zeolites have been characterized by the chemical composition determined by elemental analyses (Spectromom 381L plasma spectrometer, a Perkin-Elmer 300 atomic absorption spectrometer), as well as by X-ray diffraction patterns (DRON-4), IR spectra (Karl Zeiss UR-20 and Perkin-Elmer FTIR 10.4.2) in the wavenumber range 4000-400 cm^{-1} , water sorption capacity ($p/p_s=0.40$, 20-24°C) and thermal analysis (Paulik-Paulik-Erdei OD102) data.

Preparation of the clinoptilolite and laumontite H-forms from washed and dried granules raw material of 1.0-1.5 mm size) was carried out in a flask with HCl water solution (solid to liquid ratio 1:10), connected to a backflow condenser and placed in a sand bath. The content of the flask was boiled for 4 hours, separation of produced crystalline material was carried out by filtration, solid material was cleaned by water until pH 8.0-8.5, and dried at 90-100°C. Chemical composition of raw zeolites and treated by solutions with different HCl concentrations samples is given in Tables 1 and 2 according to the data of elemental analyses converted to the number of oxygen atom in the elementary cell defined by the UPAC formula.

Samples of natural water have been taken in industrial regions of Georgia, where water is characterized by high mineralization and can be contaminated by heavy toxic metals. Elemental analysis showed that water is characterized by high degree of mineralization (reaches a few grams per liter) and contains ions of iron, copper, manganese, lead, nickel, cobalt, zinc, etc., concentration of which is regulated by international and local legislation.

Table 1. Chemical composition of raw and treated clinoptilolite (number of atoms in the elementary cell containing 72 oxygen atoms).

Component	Raw zeolite	Concentration of HCl solution		
		0.025N	1.0N	5.0N
Si	27.4	28.5	31.6	34.2
Al	5.5	6.51	5.88	2.32
Na	3.31	1.95	0.90	0.12
K	1.16	0.96	0.56	0.24
Ca	2.38	1.18	0.78	0.22
Mg	0.93	0.53	0.25	0.06
Fe	0.25	0.15	0.05	0.02
Metals	0.07	0.05	0.01	<0.005
H ₂ O ⁺	22.5	20.45	18.3	14.2
Si/Al	4.98	4.38	5.37	14.7

Table 2. Chemical composition of raw and treated laumontite (number of atoms in the elementary cell containing 48 oxygen atoms).

Component	Raw zeolite	Concentration of HCl solution		
		0.1N	1.0N	3.0N
Si	17.1	17.4	18.2	18.8
Al	6.9	4.8	3.9	2.15
Na	1.78	0.8	0.6	0.05
K	0.80	0.65	0.35	0.15
Ca	1.75	1.2	0.65	0.23
Mg	0.27	0.10	0.025	0.020
Fe	0.08	0.05	0.02	<0.005
Metals	0.06	0.04	<0.005	<0.005
H ₂ O ⁺	15.8	15.1	13.2	11.8
Si/Al	2.48	3.625	4.66	8.74

To determine the absorptive capacity of the original zeolites and their modified forms we used model solutions of metal chlorides, the concentration of which in drinking water is regulated by World Health Organization's guidelines [12] and the Drinking Water Directive 98/83/EC [13], considering microbiological, chemical and indicator parameters in terms of the maximum admissible concentrations (MAC).

The concentration of model solutions corresponded to the MACs for metal ions and chlorine Cl⁻ (MAC = 250 mg/L or 7.05 meq/L); maximum permissible concentrations of strontium, cobalt and lithium not regulated in the European Union were taken from Russian Sanitary Rules and Regulations 2.1.4.1074.01 adopted in 2001.

Sorbents (raw and modified zeolites) in amount of 100 g each were loaded in a glass columns with an internal diameter of 30 mm, and the model solutions in amount of 1 liter each passed through the column with an average rate of 10 mL/min at room temperature without pumping. Determination of ions in solutions before and after passing the column was carried out on an ion chromatograph Shimadzu CDD-10Avp/10ASP.

Summarized results of experiments on model solutions are given in Tables 3 and 4.

Experiments on the combined filtration column described below have been carried out in following conditions: the collected water samples in amount of 4 liter each flew through the column at a rate of 5 mL/min at room temperature without pumping, the same ion chromatograph was used for measurements of ion concentration; the results of the experiment on one of the samples are given in Table 5..

Table 3. Content of ions (mg/L) in model solution and in filtrate passed through different clinoptilolites .

Ion	Before passing	Clinoptilolite			
		Raw	0.05N	1.0N	5.0N
Cl ⁻	250	245	245	240	250
Na ⁺	200	200	200	185	190
Ca ²⁺	100	98	98	95	96
Mg ²⁺	50	49	50	45	50
K ⁺	12	12	12	11	12
Sr ²⁺	7.0	5.9	4.3	3.2	6.8
Zn ²⁺	5.0	5.0	4.9	5.0	5.0
Fe ³⁺ +Fe ²⁺	3.0	2.9	2.6	1.15	2.95
Ba ²⁺	2.0	1.1	0.8	1.6	2.0
Cu ²⁺	2.0	1.6	1.5	1.7	2.0
Co ²⁺	0.1	0.06	0.04	0.07	0.09
Mn ²⁺	0.05	0.03	0.025	0.015	0.05
Li ⁺	0.03	0.01	0.01	0.02	0.03
Ni ²⁺	0.02	0.015	0.013	0.008	0.02
Pb ²⁺	0.01	0.003	0.002	<0.001	0.01

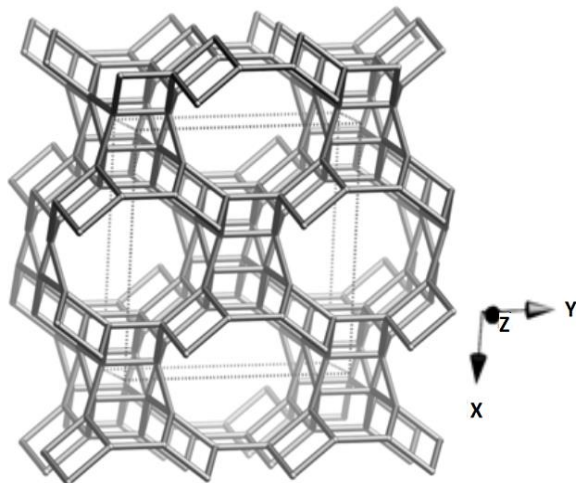
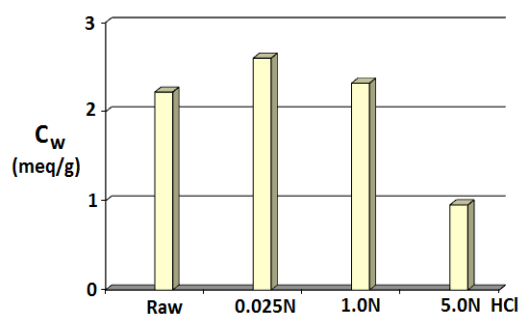
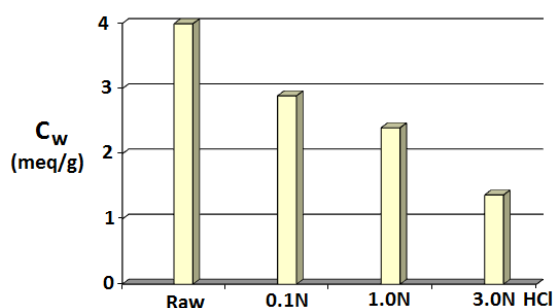
Table 4. Content of ions (mg/L) in model solution and in filtrate passed through different laumontites.

Ion	Before passing	Laumontite			
		Raw	0.1N	1.0N	3.0N
Cl ⁻	250	250	250	245	250
Na ⁺	200	200	195	180	190
Ca ²⁺	100	99	99	93	98
Mg ²⁺	50	50	49	44	48
K ⁺	12	12	12	11	12
Sr ²⁺	7.0	4.7	4.9	6.4	6.9
Zn ²⁺	5.0	4.6	4.0	3.1	4.8
Fe ³⁺ +Fe ²⁺	3.0	2.8	2.75	1.05	3.0
Ba ²⁺	2.0	1.3	1.7	1.9	2.0
Cu ²⁺	2.0	1.2	0.9	0.55	2.0
Co ²⁺	0.1	0.08	0.08	0.09	0.1
Mn ²⁺	0.05	0.04	0.03	0.04	0.05
Li ⁺	0.03	0.02	0.025	0.03	0.03
Ni ²⁺	0.02	0.016	0.012	0.015	0.02
Pb ²⁺	0.01	0.003	0.003	0.008	0.01

Results and Discussion

Laumontite has a higher aluminum content (for ideal structure Si/Al=2, for studied sample Si/Al=2.48) and theoretical weight ion-exchange capacity ($C_{ideal}=4.625$ meq/g, for sample 4.0 meq/g) than clinoptilolite (Si/Al_{ideal}=3.5, $C_{ideal}=3.08$ meq/g) and can be a more efficient ion exchanger, but it has different crystal structure (Figure 2) having only one type of channels formed by 10-membered rings with sizes of 0.4 x 0.53 nm.

According to data of elemental analyses given in Tables 1 and 2, the treatment of zeolites with diluted hydrochloric acid solutions (<0.1N) leads to a small reduction of the Si/Al ratio (from 4.98 to 4.3 for the clinoptilolite and from 2.48 to 2.2 for the laumontite), which is explained by the removal of impurities, but at higher concentrations (>0.2N) of acid there is an increase of the Si/Al ratio at the expense of leaching of aluminum. After treatment with a solution with a concentration of 1.0N the negative charge of the remaining aluminum approximately on 60% is compensated by the remaining ions of metals, and approximately on 40% by the H₂O⁺ ion, at higher concentrations up to 1.5N the content of hydronium ion increases. Acid treatment leads to a significant reduction in the content of comparatively light ions (Na⁺ and Mg²⁺), while the number of heavy ions (K⁺, Ca²⁺, Fe³⁺, etc.) decreases slightly. With the growth of acid concentration increases the degree of iron and impurity metals leaching, as well as the degree of dehydration of zeolite crystal structure.

**Figure 2. LAU framework viewed along [001].****Figure 3. Scientific weight capacity of raw clinoptilolite and its modified forms.****Figure 4. Scientific weight capacity of raw laumontite and its modified forms.**

Scientific weight capacity (C_w) of raw zeolites and their modified forms calculated for hypothetical H-forms of general formula $H^+(AlSi_xO_y) \cdot zH_2O$ is shown in Figures 3 and 4. For clinoptilolite washed by diluted acid C_w is close to the value for ideal structure, but with the increase of acid concentration decreases sharply; for laumontite C_w decreases monotonously.

XRD and FTIR data confirm preservation of the same microporous zeolite structures after treatment with solution of a certain concentration of acid, treatment with concentrated solutions (>2.0N) leads to the destruction of the crystalline structure and to the receipt of partially or completely amorphous material characterized by high silicon content.

As can be seen from the data in the Tables 3 and 4, amorphous materials (clinoptilolite treated with 5.0N HCl solution and laumontite treated with 3.0N HCl solution) are almost transparent to all ions, so their use as filters has no perspective. Sodium, calcium, magnesium and potassium present in the crystalline structure of zeolites practically do not take part in the process of ion exchange, although for the acid-treated forms there is a slight decrease in their concentration. Crystalline clinoptilolite and laumontite, both raw and modified, absorb all transition metals and lithium to varying degrees. So, the most effective adsorbent for barium, cobalt and lithium is washed clinoptilolite, its processed with the 1.0N HCl solution form well catches strontium, manganese, nickel and lead, but for absorption of zinc, iron and copper it is better to use the laumontite treated with 1.0N HCl solution.

Taking into account the obtained results, we offer a combined filter in which quartz sand plays the role of a preliminary barrier for large mechanical particles, while zeolites provides ion exchange with contaminating ions.

The combined filtration column (diameter 5 cm, length 20 cm) consisted of four layers each height of 5 cm: quartz sand washed with 1.0N HCl and heated at temperature of 200°C; granules (0.5-1.0 mm) of natural clinoptilolite washed with 0.025N HCl and dried at 200°C; granules (2-2.5 mm) of

laumontite treated with 1.0N HCl and heated at 200-250°C; granules (2-2.5 mm) of clinoptilolite processed in the same way.

Table 5. Ion content in water before and after cleaning with a combined filter .

Ion	Before filtration		After filtration	
	C (mg/dm ³)	C/MAC	C (mg/dm ³)	C/MAC
Na ⁺	448.(2)	2.24	102.(3)	0.51
Ca ²⁺	115.(1)	1.15	43.1(5)	0.43
Mg ²⁺	135.(1)	2.7	41.7(4)	0.83
K ⁺	8.30(6)	0.69	2.95(6)	0.25
Sr ²⁺	3.40(3)	0.48	0.386(8)	0.055
Zn ²⁺	0.06(1)	0.012	0.012(1)	0.0024
Fe (total)	2.23(5)	11.2	0.182(6)	0.9
Cu ²⁺	0.70(4)	0.35	0.253(6)	0.15
Co ²⁺	0.050(5)	0.5	0.020(3)	0.2
Mn ²⁺	0.31(0)	6.2	0.025(1)	0.5
Li ⁺	0.10(2)	3.3	0.025(1)	0.84
Ni ²⁺	0.060(4)	3.0	0.014(1)	0.67
Pb ²⁺	0.49(5)	25.0	0.0000	0
Cl ⁻	902.(4)	3.6	244.(5)	0.98
SO ₄ ²⁻	684.(1)	2.74	228.(7)	0.92
NO ₃ ⁻	0.15(1)	0.003	0.11(1)	0.002
NO ₂ ⁻	0.033(1)	0.066	0.033(1)	0.066
Br ⁻	1.130(5)		1.128(5)	
I ⁻	1.61(5)		1.60(5)	
HCO ₃ ⁻	463.(8)		0.0000*	
H ₂ PO ₄ ⁻	0.0042(2)		0.0010(1)	
HPO ₄ ²⁻	0.0478(5)		0.0000*	
PO ₄ ³⁻	0.0478(5)		0.0000*	
Total	2770(8)		665(2)	

* not detected

According to data of Table 5, the water sample passed through combined column had high mineralization (2.77 g/L) and increased content of non-toxic alkaline (sodium) and alkaline earth (calcium and magnesium) metals, as well as anions of chlorine and sulfate, the water also was contaminated with lead (>25MAC), iron (>11MAC), manganese (>6MAC), lithium (>3MAC), and nickel (>2MAC), the content of copper, cobalt, zinc and strontium was normal, barium was not detected.

After filtering all indicators came to normal, with the lead was absorbed completely, the content of iron and manganese decreased by 12 times, lithium and nickel approx. 4 times. In addition, the content of anions has changed – the concentration of chlorine and sulfate decreased, while the content of hydrocarbonate HCO₃⁻, as well as of phosphates HPO₄²⁻ and PO₄³⁻ reached zero. It can be assumed that the decrease in the content of these anions occurred due to the formation of insoluble salts, and disappearance of dissolved hydrocarbonate is associated with its interaction with the H⁺ ions located in crystal lattice with the subsequent release of carbon dioxide. All these processes, as well as the possible capture of colloids by modified zeolites led to a reduction of mineralization to 0.665 g/L (total measured positive charge decreased from 36.8(4) to 10.3(2), negative charge from 36.1(3) to 9.9(2) meq/L).

Conclusion

In summary, we offer a combined filter for the treatment of natural, sewage and waste water, consisting of washed natural clinoptilolite, as well as modified forms of clinoptilolite and laumontite, ensuring the purification of water from all contaminants. Establishing the duration of the effective operation of the filter and the method of its regeneration will be the subject of our further work.

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