STUDIES THE IMPACT OF LOW-FREQUENCY ACOUSTIC FIELD UPON CATION EXCHANGE CAPACITY OF NATURAL ZEOLITE

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ABSTRACT

The work is dedicated to investigation of the influence of low-frequency acoustic treatment upon natural clinoptilolite. More precisely upon their sorbtion properties regarding some commonly meet heavy metal cations in the mine waste waters. A comparison is made between the cation exchange capacity, the coefficient of distribution and the recovery of no treated and treated with low-frequency sound zeolite towards the ions of Cu, Fe and Zn from model solutions in sulphate forms. The influence of the ions concentration upon the same indexes is investigated.

INTRODUCTION

Bulgaria is a country with limited availability of natural waters because of that with special stays a question for the water presrevation and conservation from different damaging effects. From the other hand, the water is the vulnerablest component towards contamination of environment and exerts strong influence on related flora and fauna. That's why the preservation of the water supplies is connected besides with the rational usage but with purification of domestic waste waters and especially industrial waters before their over again using or joining with river courses.

One of the wide used methods for waste waters purification is adsorptional. In the last 10-15 years the interest in the zeolites as natural adsorbent for waste waters purification is exceptionally great. In this context they are a new raw material and the field of application for waste waters purification to a certain extent are unknown for technologists and

SUMMARY FOR THE ZEOLITES

1. Zeolite rocks

The zeolites today are accepted as main rock formed minerals in modified piroclastic sediments. Because of lack of unified system in the usage of names for one and the same rocks (Alexiev and Djourova, 1975) develop exemplary classification according which under zeolites rocks are marked all sediment rocks containing over 10% the zeolites. Until 1980 year 40 variety of natural and over 100 modified zeolites are established. A deposits with economically significant concentrations form eight zeolite minerals - clinoptilolite, shabazite, mordenite, filipsite, erionite (low interest because of cancer behavior), ferierite and analcimite.

2. Chemical composition and property of the zeolites.

The zeolites represent crystal aluminium silicate minerals containing metal cations and water. The crystal lattice is composed of silicate and aluminate tetrahedryties bounded in between at different manner and united by common peaks. These tetrahedrites form three-dimensional complex crystal structures with disposed in fixed order microcavities and channels with dimensions from several to several of microns. The generalized formula of zeolite chemical composition is:

 $M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$

where: M is the cation of alkali or alkali-earth element with valence n, x vary between $2\div10$, and y between $2\div7$.

The alkali and alkali-earth cations are disposed in microcavities and are relatively low fixed to the lattice, that's why they could be exchanged with others.

The zeolites are divided according to crystal pore size into wide-, middle- and narrow porosity i.e. "the free diameter" of the channels appears to be the basic controlling factor at entering of "outside" units. The commensurability of equivalent diameter of the zeolite crystal pores with dimension of series molecules define the ability for their selective adsorptions and with this property they are related to the group of the molecular sieves.

Based upon the correlation Si:Al the zeolites are divided into high-, middle- and less silica which determine their stability at different pH values.

They possess high termostability, like internal pore-cavity structure break over 1000° C.

The natural zeolites have high mechanical strength $(3\div4.5 \text{ at Mos})$ and although behind quartz in this regard they may be successful utilized as filtration materials.

3. Occurrence of the zeolite rocks in our country.

Over 1000 deposit are known in different parts of the world-USA, Russia, Japan, Cuba, Romania, Italy, Mexico, Hungary, Bulgaria and etc.

In our country zeolite rocks are established for the first time eastern from Kardjali town, at railway station "Jelezni vrata". Now in this region are situated the considerablest deposits: "Jelezni vrata", "Beli plast", Beli bair", "Goloburdo", "Most", "Liaskovez" and "Perpelik". Clinoptilolite is a basic mineral in this deposits. Mordenite is found in regions around Malko Popovo village and filipsite around Obrochishte village.

4. Zeolite usage for industrial waste waters purification.

The purification of waste waters is one of the most widely distributed technological processes, that's way research interest is so big for the usage of natural zeolites as materials for filtration (Tarasevich, Kravchenko et al. 1985; Tarasevich et al. 1982), ion exchanging (Stoev, 1991; Poliakov et al. 1979), adsorption (Komarneni, 1985; Papachristou et al. 1993) and catalyzes (Xiao et al. 1998; Corma et al. 1994) materials.

The clinoptilolite shows high acid resistance and sufficient stability to the action of the basis (Poliakov et al. 1979; Barrer et al. 1964), from the other hand it softens the purified water Kovacheva et al. 1995).

During the last years for increasing of zeolite ion exchange capacity they are modified with solutions of different substances containing ions which settle in crystal pores and possess higher affinity to the waste water ions (Papachristou et al. 1993; Bowman et al. 1994).

It is getting clear that the usage of zeolite and the search of methods for increasing their sorbtional capacity is very actual direction for waste waters purification.

EXPERIMENTAL

The investigations are aiming to study the effect of physical impact upon the sorbtion properties of the zeolites and more precise low-frequency acoustic field with the objective to increase cation exchange capacity of natural zeolite.

1. Zeolite characterization and indexes.

For accomplishment of experiments was used a zeolite from enterprise "Bentonite"-Kardjali town with following characteristics:

1.1.Chemical composition - table 1

Table 1.	Zeolite	chemical	composition
	200110	ononnou	composition

Indexes	Average content, %
SiO ₂	66.16
Al ₂ O ₃	11.41
Fe ₂ O ₃	0.80

TiO ₂	0.15
MgO	0.85
MnO	0.06
CaO	2.81
Na ₂ O	0.22
K2O	2.90
H₂O⁺	7.49
P ₂ O ₅	0.02

1.2. Content of impurity elements - table 2

Table Z. Impunity elements in the Z	i able 2.	its in the zeolit	es
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Elements	Contents, g/t
Pb	62÷102
As	6.0
Cd	2.0
Hg	0.2

1.3. Zeolite quantity indexes

a) Clinoptilolite content- 70%;

b) Sum of exchange ions K, Na, Ca, Mg (defined by NH₄ with usage of NH₄Cl), i.e. total exchange sorption capacity (TESC)-min 100 mgeq/100g;

c) Humidity- max 10%.

2. Determination of TESC as regard to Cu, Fe and Zn ions from model sulphate solutions

The sorptional indexes during achievement of total equilibrium between sorbent and the investigated elements from the solutions were determinated.

2.1. *Methods of experiments.* Three samples of 5g zeolite, class 0.8-2.5 mm are placed in Bunsen flask and each one of them is filled with model solution with concentration 1g/l of CuSO₄, ZnSO₄ and FeSO₄ in liquid:solid ratio 10:1. The contact between the solution and zeolite is realized through shaking machine CITRON at 150 min⁻¹ during 1.5 h, after that the flasks are left for reaching equilibrium for 72 h.

The initial and remaining concentration of Cu, Fe and Zn ions from model solutions is determinated by spectrometer with inductive coupled plasma, ICP in mg/l.

2.2. Determination of TESC, recovery " ε " and coeficient of *distribution* " κ ". The indicated sorbtional indexes are determined by the following formulaes:

$$\mathsf{TESC} = \left(\frac{c_1 - c_2}{m \cdot 1000}\right) V;$$
$$\varepsilon = \left(\frac{c_1 - c_2}{c_1}\right) \cdot 100, \%; \ \kappa = \left(\frac{c_1 - c_2}{c_1}\right) \cdot \frac{V}{m};$$

where:

c1- initial concentration of the element in solution, mg/l;

c₂- remaining concentration of the element in solution, mg/l;

V- volume of solution, ml;

m- weight of dry sorbent, g; TESC- total exchange sorption capacity, mgelm/g sorbent;

ε- recovery of the element, %;

κ- distribution coefficient.

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2.3. *The obtained results.* The obtained sorption indexes of zeolite regarding the investigated elements are shown at table 3.

Table 3. Zeolite sorptional indexes regarding Cu, Fe and Zn ions from model solutions.

Indexes		Elements	nents		
	Cu	Zn	Fe		
c1, mg/l	245.3	340.0	264.0		
c ₂ , mg/l	13.0	44.2	18.6		
TESC, mgelm/g	2.32	2.96	2.45		
ε, %	94.70	87.00	92.95		
к	178.7	66.9	131.9		

3. Comparison between cation exchange capacity (CEC) of untreated and treated zeolite with low-frequency sound, regarding Cu, Fe and Zn ions from model sulphate solutions.

3.1. *Methods of experiments.* A zeolite with 5g weight is placed in glass with distilled water with volume 200 ml and is subjected to low frequency acoustic treatment at amplitude 0.4 mm and frequency 30 Hz for time 15 min. The apparatus for creating of low frequency field is described in details (Kovatcheva et al. 1995), main part of the system is the acoustic emitter immersed into cup with distilled water. For comparison untreated zeolite is put in glass with distilled water with the same volume for the same time. After that both zeolites are filtrated and are put in 50 ml model solution with concentration 1 g/l of CuSO₄, ZnSO₄ or FeSO₄. The adsorption is realized with help of shaking machine CITRON at 150 min⁻¹ time from 5 to 45 minutes.

The concentration of investigated elements in the model solutions is determined as was mentioned above by ICP, in mg/l.

3.2. The obtained results

a) CEC of untreated and treated zeolite regarding Cu ions The concentrations, recovery and distribution coefficient of Cu²⁺ are shown in table 4 and CEC in figure 1.



Figure 1. Cation exchange capacity of untreated and treated zeolite with sound regarding Cu ions from CuSO₄ solution.

As we seen from table 4 and fig.1 the sorbtional indexes of treated with sound zeolite up to 30^{-th} minute are higher in comparison to untreated zeolite regarding Cu ions. Highest sorption is achieved up to 10^{-th} minute, as the acoustic treatment of zeolite increases CEC with 1.3 times and reaches 75.43% from TESC of Cu ions towards 59.48% for untreated zeolite.

Table 4.	Sorbtional	indexes	of	untreated	and	treated	zeolite
regarding	g Cu ²⁺ from	model so	luti	ion.			

Sorbtion	C2,			0/			
time, min	m	g/i	ε,	70	κ		
	without sound	with sound	without sound	with sound	without sound	With sound	
	Initi	al concen	tration c ₁ =	245.3 mg	/I		
5	125	88.0	49.04	64.13	9.62	17.88	
10	107	70.0	56.38	71.46	12.92	25.04	
15	95	73.5	61.27	70.04	15.82	23.37	
20	105	91.3	57.19	62.78	13.36	16.87	
30	103	92.0	58.01	62.5	13.81	16.66	
45	89	91.3	63.72	62.78	17.56	16.87	

b) CEC of untreated and treated zeolite regarding Fe ions The concentrations, recovery and coefficient of distribution of Fe²⁺ are shown in table 5 and CEC in figure 2.

Again the sorbtional indexes of treated with sound zeolite are higher up to $30^{\text{-th}}$ minute in comparison to untreated zeolite regarding Fe ions. Highest sorbtion is achieved up to $15^{\text{-th}}$ minute as the acoustic treatment of zeolite increases CEC with 1.2 times and reaches up to 77.40% from TESC of Fe ions towards 63.30% for untreated zeolite.

Table	5.	Sorbtional	indexes	of	untreated	and	treated	zeolite
regard	ling	Fe ²⁺ from	model so	luti	on.			

Sorbtion time, min	C M	2, g/l	ε,	%	к			
	without sound	with sound	without sound	with sound	Without sound	with sound		
	Initial concentration c ₁ =264.0 mg/l							
5	128.0	82.6	51.52	68.71	10.63	21.96		
15	109.0	74.8	58.71	71.67	14.22	25.29		
30	94.6	87.0	64.17	67.05	17.91	20.34		
45	75.1	79.4	71.55	69.92	25.15	23.25		
60	74.5	86.0	71.78	67.42	25.44	20.7		
90	66.8	91.3	74.7	65.42	29.52	18.92		

c) CEC of untreated and treated zeolite regarding Zn ions The concentrations, recovery and coefficient of distribution of Zn²⁺ are shown in table 6 and CEC in figure 3. The obtained results again show that the sorption of Zn ions by acoustically treated zeolite is higher up to 30^{-th} minute in comparison to untreated. Highest sorption is obtained up to 15^{th} minute with treated zeolite while the same values are reached at 60^{-th} minute for untreated. CEC of the treated zeolite is 1.2 times higher in 15^{-th} minute in comparison to untreated and 64.2% of TSEC is obtained in comparison to 55.4\% for untreated.



Figure 2.. Cation exchange capacity of untreated and treated zeolite with sound regarding Fe ions from FeSO₄ solution.

Table 6. Sorbtional indexes of untreated and treated zeolite regarding Zn^{2+} from model solution.

Sorbtion time, min	c m	2, g/l	ε,	%	к			
	without sound with sound		Without sound with sound		Without sound	with sound		
	Initial concentration c1=340.0 mg/l							
5	204.0	190.0	40.00	44.12	6.67	7.89		
15	176.0	150.0	48.24	55.88	9.32	12.67		
30	168.0	160.0	50.59	52.94	10.24	11.25		
45	163.0	164.0	52.10	51.76	10.86	10.73		
60	150.0	154.0	55.88	54.71	12.67	12.08		
90	155.0	151.0	54.41	55.59	11.94	12.52		

4. Comparison between sorption indexes of untreated and treated zeolite regarding Cu, Fe and Zn ions when their concentration decreases in the model sulphate solutions.

4.1. Methods of experiments. The methods of the experiments are the same as in point 3.1. at adsorption time 30 minutes.

4.2. The obtained results. The sorptional indexes are shown in table 7 at decreasing of the Cu²⁺, Fe²⁺ and Zn²⁺ concentration.

The results from table 7 show identical tendencies for the three elements. With decreasing of the element concentration in initial model solutions, their recovery increases as well as

the distribution coefficient, but the value of CEC decreases. This tendency is similar for treated zeolite. This fact confirms that the natural zeolite as sorbent is suitable for purification of low and medium contaminated waste water.



Figure 3. Cation exchange capacity of untreated and treated zeolite with sound regarding Zn ions from ZnSO₄ solution.

CONCLUSIONS

On the basis of the investigation work the following conclusions are made:

1. It is confirmed that the clinoptilolite zeolites could be successfully utilized for purification of Cu, Fe and Zn ions from low and medium contaminated waste waters.

2. The possibility for intensification of the sorptional ability of zeolite is established by their treatment with low frequency sound.

3. The positive influence of acoustic field upon the sorption indexes is within the framework of 30-45 minute after treatment and filtration.

4. The reached CEC for 15 minute sorption with treated zeolite towards the three investigated elements Cu, Fe and Zn is around 1.2 times higher in comparison to untreated as well as for distribution coefficient 1.55 times. It is reaching for treated zeolite 75.43%, 77.40% and 64.2% from TESC against 59.48%, 63.30% and 55.40% for untreated respectively for Cu, Fe and Zn ions.

5. Less time is required for reaching same CEC values for treated zeolite in comparison to untreated. The CEC value is reached for 10-15 minutes sorption from treated zeolite towards 30 and more minutes for untreated i.e. the time of sorption is reduced two and more times.

6. The CEC values decrease with decreasing of the studied concentrations of Cu, Fe and Zn ions in model solutions. This remains the same when treated zeolite is used, but the sorptional indexes are higher.

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able 7. The zeolite sorbtion indexes depending on the concentration of Cu ²⁺ , Fe ²⁺ and Zn ²⁺ in model sulphate solutions.									
c ₁ , mg/l	C2,	mg/l	ε,	%	CEC, mgelm/g		k	κ	
	without sound	with sound	without sound	with sound	without sound	with sound	Without sound	with sound	
	towards Cu ions								
245.3	103.0	92.0	58.01	62.5	1.42	1.53	13.81	16.66	
122.65	38.0	31.0	69.02	74.72	0.85	0.92	22.28	29.56	
61.33	15.0	12.0	75.54	80.43	0.46	0.49	32.89	41.11	
30.67	2.2	0.9	92.83	97.07	0.28	0.30	129.41	330.78	
	_		to	wards Fe ions	-	-		-	
264.0	109.0	74.8	58.71	71.67	1.55	1.90	14.22	25.29	
132.0	25.7	20.7	80.53	84.32	1.06	1.11	41.36	53.77	
66.0	12.4	11.3	81.21	82.88	0.53	0.55	43.23	48.41	
33.0	2.56	1.47	92.24	95.55	0.30	0.32	118.91	214.50	
			to	wards Zn ions					
340.0	168.0	160.0	50.59	52.94	1.72	1.80	10.24	11.25	
170.0	49.9	33.22	70.65	80.47	1.20	1.40	24.10	41.20	
85.0	15.5	13.30	81.76	84.35	0.69	0.72	44.84	53.91	
42.5	5.97	3.07	85.95	92.78	0.37	0.40	61.19	128.44	

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Recommended for publication by Department of Mineral Processing, Faculty of Mining Technology