USING OF MODIFIED ZEOLITES FOR PURIFICATION OF HEAVY METALS IONS FROM WASTEWATER

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ABSTRACT

Natural zeolites represent low-cost exchange and sorbent materials. The influence of different parameters, such as zeolite's mass to treat water volume, water's pH value, zeolite particles size and zeolite's modification has been investigated. The goal of the experiments was investigation of the ability of Bulgarian natural zeolite to remove heavy metal ions from wastewater.

Key words:zeolite, modification, industrial waste water

INTRODUCTION

Zeolite exchangeable ions are relatively harmless and makes them attractive native materials for removing undesirable heavy metal ions from industrial and processing effluent water. In addition, zeolite loaded with heavy metal ions can be easily regenerated.

Mine-supplied zeolite (2-0.8 mm) (run-off-mine) sample from Beli Plast deposit, Kardzhali, Bulgaria, was using for experiments. The goal of the experiments was investigation of the processes kinetics and influence of the obstructive ions upon the purification of waste water in different initial concentrations of heavy metals ions.

INVESTIGATION OF THE ABILITY OF BULGARIAN NATURAL ZEOLITE TO REMOVE Cu²⁺FROM WASTE WATER

A complex X-Ray Thermal analysis was made of initial and modified zeolites. The mineralogical composition is shown on Table 1.

Table 1. Mineralogical composition of initial and modified zeolites.

	Initial	NaZ	SMNaZ	SMHZ
	Z		250	250
Clinoptilolite	81%	83%	89%	93%
Albite	6%	3%	5%	-
Potassium feldspar	4%	6%	3%	-
Calcite	4%	-	1%	2%
Cristobalite	3%	3%	1%	3%
Tridymite	-	3%	-	-
Organic matter	-	-	Available	Available

The following abbreviations and ways of zeolite modifying are used:

Initial Z- Mine-supplied zeolite (2-0.8 mm) (run-off-mine) sample from Beli Plast deposit, Kardzhali, Bulgaria

NaZ - Na-zeolite single contact (i.e. NaZ) – Contacting the zeolite with 0.1M HCL for 5 hours. After 4 washes with tap water (about 40-45 % of mass of zeolite is lost) (since carbonates, clays etc. are leached). Further on in order to render the zeolite into Na form it was contacted in same manner with 1 M NaCl for 24h. All the conditioning was done before grinding.

SMNaZ 250 -25 grams from the dried zeolite representing the three initial forms described above (Na) were contacted with 100 ml of HDTMA solution with different concentration 250 % of the external CEC in 250 ml flasks for 24 hours under a shaking machine action.

SMHZ 250- 25 grams from the dried zeolite representing the three initial forms described above (H) were contacted with 100 ml of HDTMA solution with different concentration 250 % of the external CEC in 250 ml flasks for 24 hours under a shaking machine action.

Clinoptilolite was found to be the predominant material (Table 1).

Pretreatment with HCI increases to some extent Si/AI.

Treatment with NaCl causes an increase in Na⁺ and a decrease in Ca²⁺ concentrations in zeolite, leading to an increase of the ratios Na⁺/K⁺ and Mg²⁺/Ca²⁺ (Teppen, et. al., 1995; Sullivan, et. al., 1997).

Determination of Na⁺, Mg²⁺, Cu²⁺ and Pb²⁺ concentrations in treated solution was made with an ICP-AES analysis. Values of pH were measured with a Metrohm E 588 pH-mV-meter.

Each experimental result was obtained by averaging the data from two parallel experiments.

Adsorption procedure is carried out in following conditions:

Cations:	Cu2+, Pb2+ as nitrate salts.;
	No mixture, just one heavy metal.
Temperature:	20 °C
lon strength:	Cations 500ppm of Na+ and
	500ppm of Mg2+ as nitrate salts.
Concentration of BA:	5 g (dry weight)/l.
Particle size:	71-100 µm.
pH:	Not too far from neutrality
Treatment time:	10 min

The influence of a specific process parameter was determined by calculating Cu^{2+} extraction by zeolite and changing that parameter. Uptake efficiency was calculated using the equation (1):

Extraction, % = [(
$$C_o - C_{eq}$$
) / C_0] x 100, (1)

where C_{\circ} and C_{eq} are the initial and the equilibrium concentration of pollutant, mg/l.

Series of parallel experiments were made with initial contents of Cu²⁺ ions from 50 to 400 mg/l without obstructive ions and in the presence of ions with concentrations from 500 mg/l respectively of Na⁺, Mg²⁺ - Table 2.

The kinetic curve of sorption process is investigated in concentration of Cu^{2+} - 50 mg/l without and in the presence of obstructive ions Figure 3.

Table 2. Data for extent of the extraction of Cu²⁺ of NaZ with and without obstructive ions: Na⁺ - 500 mg/l and Mg²⁺ - 500 mg/l in different concentrations of Cu²⁺ in the initial solutions, mg/l

	Without obstructive ions			With obstructive ions				
Initial solution,	51,3	104,2	201,7	410,3	51,3	104,2	201,7	410,3
mg/I Cu								
Residual	6,7	8,4	26,0	172,0	29,2	76,6	158,0	255,0
concentration								
mg/I Cu								
Extraction, %	86,94	91,94	87,11	58,08	43,08	26,49	21,67	37,85
Capacity,	0,140	0,302	0,553	0,751	0,07	0,087	0,138	0,489
mMol/l								
Capacity, mMol/l	0,140	0,302	0,553	0,751	0,07	0,087	0,138	0,489

From the results obtained (Table 2) is obvious that in the absence of obstructive ions, a high extent of extraction of copper ions with NaZ is achieved.

At the same time a maximum of extraction (92 %) is observed in initial content of copper ions with concentration

100 mg/l, after which with increasing of the initial concentration up to 400 mg/l the extraction extent decreases to 48%. With increasing of the copper concentration in initial solutions without obstructive ions, capacity of the copper is increased too, reaching at 400 mg/l initial solution -0.751 mMol/g, which value is the maximum possible for this type of zeolites.

In the presence of obstructive ions – Na⁺ and Mg²⁺, the extraction extent decreases significantly (from 20 to 75% at different concentrations) (.Figure 1) With increasing of copper concentration in the initial solutions, a reverse dependence of the copper extraction is observed in relation to the same without obstructive ions. Higher values of extraction are obtained in copper initial concentrations 50 μ 400 mg/l, respectively 43 and 38%, and the lowest at 200 mg/l – 21,6%.



Figure 1. Dependence of the extraction extent from the copper ions concentration in the initial solution

With increasing of copper concentration in the presence of obstructive ions the capacity of copper is increased too(.Figure 2), but is significantly lower from the respective without obstructive ions, reaching at 400 mg/l initial solution –0,49 mMol/g.

Explanation of the dependence obtained, as well as the significant decrease of extraction extent, could be found in the presence of obstructive ions in comparatively high concentrations. On the one hand changing the solution ion power they influence upon the activity of the ions and compete the ion-exchange process of the copper ions with cations from the zeolite structure and causes change in the diffusive double layer of sorbent particles.

Experiments for determination of extraction kinetic curve at copper initial concentration -50mg\l, with and without presence of sodium and magnesium ions were carried out Figure 3.

As it can be seen on the Figure 3, the maximum extraction extent in both cases is achieved at treating time 10 min.

Low extraction extent - (below 50%) at the presence of obstructive ions - Na⁺ and Mg²⁺(above 500mg/l) at initial solutions with copper concentration above 50 mg/l does not give a reason for their effective using as BA for purification of industrial waste water.

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Figure 2. Dependence of the of zeolites capacity from the copper ions concentration in the initial solution



Figure 3. Kinetics of Cu²⁺ extraction. concentration of Cu²⁺-50mg\lwithout and in presence of Na⁺ and Mg²⁺ - 500mg\l

INVESTIGATION OF PROCESS KINETICS AND THE INFLUENCE OF OBSTRUCTIVE IONS AT Cu²⁺ AND Pb²⁺ CONCENTRATIONS BELOW 50 mg/l

Zeolites' cation selectivity in ion-exchange reactions is determined by the type of zeolite, distance between anionic sites, cationic radii and cationic hydration energy of ions to be removed. Data on radii and hydration energy for cations investigated are presented in Table 3.

Table 3.Radii and energy of hydration for some cat	ons:
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lon	lonic radius,	Energy of hydration,
	A	KJ/mol
Ca ²⁺	0,99	-1577
Cd ²⁺	1,03	-1807
Cu ²⁺	0,80	-2100
Mg ²⁺	0,65	-1921
Pb ²⁺	1,21	-1481

Natural water, consequently the main part of industrial wastewater, contains Na and Mg, but the average concentrations of them for example in Bulgarian water are 50-100mg\l and 20-50mg\l, respectively. That is why, the influence of Na and Mg presence on the extraction of Cu and Pb was investigated during the simultaneous addition of Na and Mg to Cu solution, in concentrations giving ratios of C _{Na+}/ C_{Me2+} = 1-8 and C _{Mg+}/ C_{Me2+} = 1.

The influence of Na⁺ presence (in different concentrations) on heavy metals removal is presented in Figure. 4 - 5.



Figure 4. Extraction of Cu²⁺ in the presence of Na⁺



Figure 5. Extraction of Pb2+ in the presence of Na+

As it can be seen from the figures, the higher is the ratio C $_{\text{Na+}/}$ C $_{\text{Me2+}}$, the more pronounced is the decrease in heavy metals' extraction.

The decrease in heavy metal's extraction in the presence of Na⁺ can be explained by competing ion-exchange of Na⁺. This results in the decrease of the sites of zeolite available to heavy metal ions.

Although the presence of Na+ in different concentrations has a negative influence upon the copper extraction, it is in a small

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extent in sodium concentrations close to the real (about 100 mg/l) in initial solutions in low copper concentrations - 10 and 50 mg/l. The extraction extent decreases from 90 % to 69 % in solutions with 10 mg/l copper and from 88 % to 69 % at 50 mg/l copper.

Still lower is their obstructive influence with regard to lead, where the extraction extent decreases from 95 % to 88 % in initial solutions with 10 mg/l lead and from 87 % to 82 % at 50 mg/l lead.

Table 4 presents the influence of Mg^{2+} in concentrations, equal to concentrations of corresponding heavy metal ions in solution on the extraction of heavy metal ions. These Mg^{2+} amounts are in range of concentrations most often met in natural water.

Table 4. Extraction of heavy metal ions in presence of Mg²⁺ in concentrations, equal to concentrations of corresponding heavy metal ions in solution.

Metal ion,	Extraction, %	Extraction, % from
Concentration		single metal ions
mg/l		solutions
Pb, 10	93,6	95,7
Pb, 50	88,0	94,5
Cu, 10	81,1	87,8
Cu, 50	84,2	88,2

As it can be seen from Table 4, magnesium influence in these concentrations is negligible and it decreases the extent of copper and lead extraction at their different concentrations from 3 up to 6 %.

The decrease observed for Cu^{2+} and Pb^{2+} extraction by zeolite in the presence of Mg^{2+} could be explained by the higher affinity of clinoptiolite to Mg^{2+} ions.

CONCLUSIONS

NaZ producing from natural zeolite from Kardjali deposit can be applied to remove Pb^{2+} and Cu^{2+} from wastewater in the presence of Mg²⁺ in concentrations similar to those found in natural water. Extraction of Cu^{2+} and Pb^{2+} by natural zeolite is decreased, if Na⁺ concentrations in wastewater are higher than concentrations of heavy metal ions to be removed. The decrease is less pronounced for solution containing Pb^{2+} in low concentrations. Requirements of Bulgarian standards for industrial wastewater can be met by a one-stage process for an initial Pb^{2+} or Cu^{2+} concentration of 10 mg/l, and by a two- stage process for an initial concentration of 50 mg/l.

Extraction of Cu²⁺ by zeolite from neutral wastewater has proved to be as effective as Cu²⁺ removal by precipitation of copper hydroxide. Contacting with 2 mol/l NaCl solution can easily regenerate loaded zeolites.

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