

USE NATURAL ZEOLITIC TUFF FROM IGROŠ VIDOJEVIĆ DEPOSIT FOR GROUND WATER SOFTENING PROCESS

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ABSTRACT

Natural zeolitic tuff from the locality Igroš near Brus (Serbia) consisting mostly of clinoptilolite (about 90%) has been investigated as a sorbent for the reduction of the Mg²⁺ concentration in ground water. The zeolitic tuff removes Mg²⁺ from water solutions by an ion exchange process, which has been proved by an energy dispersive X-ray analysis (EDS). The extent of ion exchange was influenced by the initial Mg²⁺ concentration. Kinetics study revealed the Lagergen's model of the pseudo-second order. Intra-particle diffusion of Mg²⁺ influenced the ion exchange, but it is not the rate-limiting step.

Key words: clinoptilolite, ion exchange, water softener, kinetics, ground water.

INTRODUCTION

Spring waters from mountainous regions formed largely by dolomite rock such as the area of the city Raška (Southwest Serbia) contain up to 200 mg Mg dm⁻³ and therefore it is not acceptable for public use (allowed concentration being 50 mg Mg dm⁻³). The spring water from abandoned mines Potkop near the town of Raška has a stable physico-chemical quality according to experimental data from Raska water-supply, with negligible low level of microbiological pollution of this water may be suitable for use in water supply system .

It has been recently reported that a synthetic zeolite obtained from waste pumice is effective sorbent for the reduction of the water hardness [1]. With this in mind, we have investigated the clinoptilolite rich zeolitic tuff from Igroš Vidojević in order to consider it as a water softener in an installation for obtaining potable water. Until now, this zeolite deposit has not been studied in detail.

EXPERIMENTAL

Natural zeolite (Z) was obtained from the large sediment accumulation Igroš Vidojević in Brus (Serbia). Grain size in the range 1-2 mm was chosen for the experiments. In order to improve the tuff's sorption capacity, the as-received sample was pre-treated with an aqueous NaCl solution (2.0 mol dm⁻³) and obtained product was denoted as Na-Z. In all sorption and kinetic experiments a (solution volume)/(zeolite sample) ratio of 100 cm³ : 1 g was used.

The sorption isotherm was determined at 298K using a batch method. Na-Z was placed in MgCl₂ solution of chosen concentration of 20 to 100 mg Mg dm⁻³. The solutions were prepared by dissolving MgCl₂·6H₂O (Aldrich, p.a.) in deionized water. The suspension of Na-Z and the chosen Mg solution was shaken at about 100 rpm in a thermostated water bath (Memmert WPE 45) for a time period from 20 min to 24 h. The solid was afterwards separated by filtration and Mg concentrations in solution were determined by AAS using Varian Spectra AA 200; at least five measurements were done for each determination. EDS (using a scanning electron microscope JEOL JSM-6610LV) was also performed for the detailed analysis of major mineral phases in metallographically prepared zeolite samples. Moreover, the X-ray powder diffraction (XRPD) patterns were recorded at room temperature on an Ital Structure diffractometer using CuK α radiation.

During the investigation process of desorption of the Mg-loaded sample (Mg-Z) was performed as follows: Mg-Z containing 2.5 mg Mg g⁻¹ was suspended in a 2 mol dm⁻³ solution of NaCl and then left for 24 h in a thermostated water bath at 298K for 24 h. After filtration the Mg content in the filtrate was analyzed by atomic absorption spectroscopy (AAS). In order to check the possibility of a multiple reuse of Na-Z the experiment was done in six adsorption/desorption cycles.

RESULTS AND DISCUSSION

The presence of the clinoptilolite, feldspar, and quartz phases in Na-Z was confirmed by the XRPD analysis. A typical pattern is shown in Figure 1. The XRPD analysis also confirmed that the pre-treatment of the zeolitic tuff in NaCl solution did not influence crystallinity of the mineral phases.

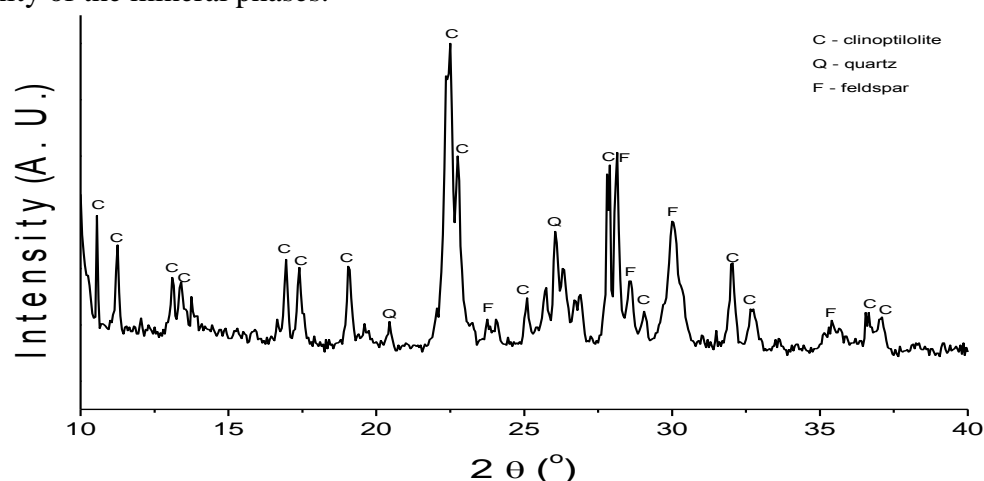


Figure 1. XRPD pattern of Na-modified zeolitic sample

The average elemental compositions of the clinoptilolite phase in the as-received (Z), Na-modified (Na-Z) and Mg-loaded samples (Mg-Z) found by EDS are given in Table 1.

Table 1. Results of EDS analyses of the as-received (Z), Na-modified (Na-Z) and Mg-loaded Na-Z (Mg-Z) in wt. %

	Z (%)	Na-Z (%)	Mg-Z (%)
Na ₂ O	0.123	4.084	2.644
CaO	4.376	1.538	1.872
K ₂ O	1.032	0.831	0.706
MgO	1.324	1.039	1.867
SiO ₂	67.86	67.04	67.55
Al ₂ O ₃	11.93	11.97	11.60
H ₂ O	13.35	13.50	13.76

It is evident that the zeolitic tuff from Igroš locality contains Ca-rich clinoptilolite. Treatment of Z in NaCl solution led to an increase of Na content. The increase is accompanied by an ion exchange process. Mg sorption by Na-Z is also ion-exchange in which Mg²⁺ ions present in water solution mainly replace Na⁺ cations from the clinoptilolite lattice.

Effect of initial concentrations on the Mg loading

Sorption curves are presented as the time functions for variable initial concentrations in Figure 2. It can be noticed that it could be taken that the equilibrium time is approx. 180

minutes, which points out to a relatively slow sorption process. A possible reason could be the fact that small Mg^{2+} ion has a large hydration volume, which prevents its entrance into the zeolite channels [1].

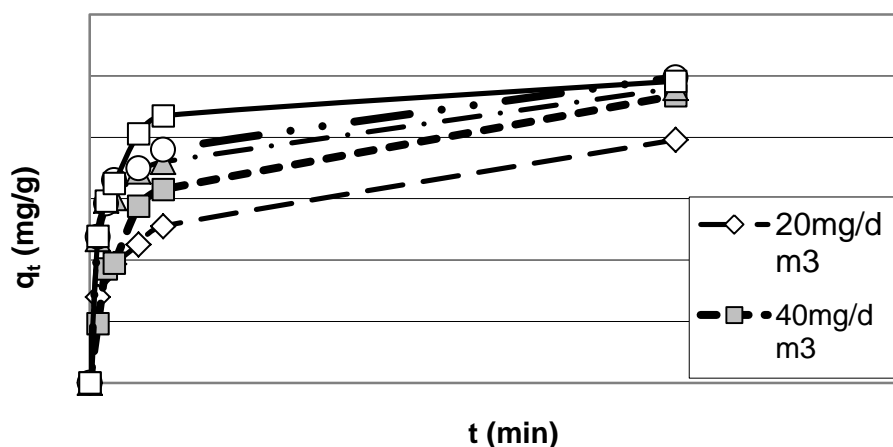


Figure 2. Sorption kinetics for Mg on Na-CLI for different initial Mg concentrations; q_t is the amount of the sorbed Mg (mg per 1 g of Na-Z) after time t .

Kinetics study

Two basic kinetic models were applied to describe the obtained experimental data. First is the Lagergren model for the first order rate of the sorption process [2] and the other model which has also been used in the present study could be described by an equation of the pseudo-second order [3]. Calculated parameters are given in Table 2.

Table 2. Parameters calculated from the kinetic models for pseudo-first and pseudo-second order reactions applied to the uptake of Mg^{2+} by Na-Z at variable initial concentrations of the solutions; q_e is the amount of the sorbed Mg at equilibrium.

Mg (mg dm ⁻³)	Lagergren model of the pseudo-first order		Lagergren model of the pseudo-second order		
	$k_1(\text{min}^{-1})$	R^2	$k_2(\text{g mg}^{-1} \text{min}^{-1})$	$q_e(\text{mg g}^{-1})$	R^2
20	4.61×10^{-4}	0.764	8×10^{-3}	2.05	0.9951
40	6.91×10^{-4}	0.776	6×10^{-3}	2.44	0.9960
60	4.61×10^{-4}	0.620	1.3×10^{-2}	2.45	0.9984
80	6.91×10^{-4}	0.631	1.2×10^{-2}	2.54	0.9985
100	4.61×10^{-4}	0.474	1.8×10^{-2}	2.49	0.9996

It is evident that the model for the pseudo-second order process is in a better agreement with the experimental data. Also, it can be seen that the zeolitic tuff exhibits rather low affinity towards Mg^{2+} ions (approx. 2.5 mg Mg g^{-1}).

Diffusion effects

In order to investigate the effect of diffusion on the sorption process the data were interpreted via the Weber–Morris model for mass transfer [4]. Fig. 3 shows that the plots are straight lines. They have been analyzed by linear regression and it was found that the intercept

I (eq. 4) is greater than zero (not given in the text). This indicates that in the present study the intra-particle diffusion is present but it is not the rate limiting step.

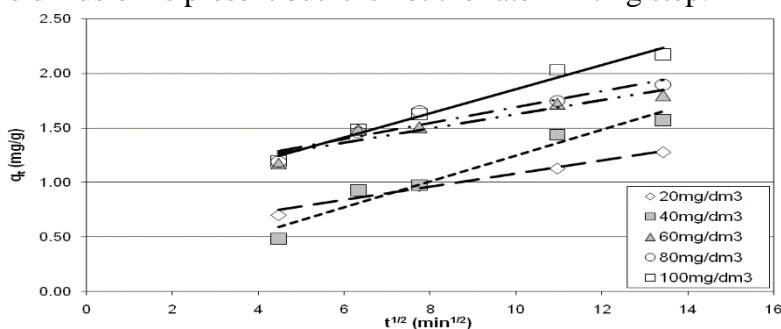


Figure 3. Intra-particle diffusion kinetic plots for the sorption of Mg on Na-Z for different initial Mg concentrations; q_t is the amount of the sorbed Mg in mg per 1 g of Na-Z.

Regeneration of the exhausted clinoptilolite

The possibility of regeneration of the exhausted zeolite and its reuse was investigated by multiple adsorption/desorption cycles. Amounts of the Mg uptake per cycle is given in Figure 4. It can be noticed that a complete desorption of Mg from Mg-containing zeolite is possible.

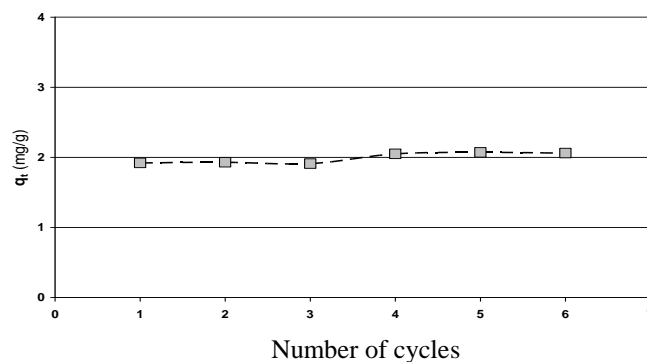


Figure 4. Amounts of Mg uptake (mg g^{-1}) after several adsorption/desorption cycles

CONCLUSIONS

The zeolitic tuff from the locality Igroš near Brus (Serbia) exhibits rather low affinity towards Mg ions (max. 2.5 mg Mg per 1 g zeolite). It removes Mg from water solution by an ion exchange process which follows the pseudo second order kinetics. In spite of low capacity of the zeolite tuff it could be considered for use as a softener in smaller plants for drinking water. Considering its low price, availability and the possibility of its complete regeneration, the zeolitic tuff from the locality Igroš is a beneficial material.

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