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Nevenka Rajić
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SURFACE MODIFICATION OF THE NATURAL CLINOPTILOLITE FOR ITS POTENTIAL USE FOR THE NITRATE REMOVAL FROM WATER MEDIA

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ABSTRACT

The natural zeolitic tuff, containing more than 70 % clinoptilolite (CLI), has been investigated as a starting material for obtaining a low cost adsorbent for the removal nitrate ions from water media. The clinoptilolite surface was modified by a simple method with iron(III), aluminum, manganese(IV) and magnesium oxide in order to make the negatively charged zeolite surface accessible for nitrate adsorption. Preliminary results indicate that the best adsorption capacity towards nitrate are shown by the zeolite samples containing magnesium and iron(III) oxide particles.

Keywords: clinoptilolite, zeolite modification, adsorption, nitrate removal

INTRODUCTION

The presence of some anionic species, such as nitrate and arsenate, in ground and surface waters represents a serious problem for humans and the environment. Nitrates are widely used in agriculture because of their good solubility in water and the plant nutrient value [1, 2]. The nitrate contamination of water is caused mainly by the use of excessive amounts of fertilizers but also by human and animal wastes. A high nitrate level in water is responsible for methemoglobinemia or “blue baby syndrome”. Nitrate ions also interact with organics forming carcinogenic nitrosamines. Finally, nitrates stimulate eutrophication resulting in a heavy algal growth [3].

Commonly used methods for the removal of nitrates from water include various processes [3, 4-6] such as biological denitrification, chemical reduction, reverse osmosis and adsorption. Most of the methods are not efficient enough and many efforts have been done in order to find a nitrate removal method that would be both cost effective and easy to perform.

Natural zeolites have been recognized as highly effective materials for the removal of different water contaminants. Their negatively charged aluminosilicate lattice not only attracts different heavy metal cations from aqueous solutions [7] but it can also exhibit an affinity towards anions by suitable modifications [8].

The aim of the present study was to prepare and characterize the zeolite-based materials by a simple procedure for using them in the removal of nitrate ions from aqueous media.

EXPERIMENTAL

The natural zeolite (CLI) used in this study was a clinoptilolite-rich tuff from the Zlatokop mine (Vranjska Banja deposit). Before modification, the zeolite samples (grain size 0,063-0,1 mm) were washed several times with distilled water to remove impurities and then dried at 60 °C.

Preparation of the manganese/magnesium-modified zeolite (Mn-CLI and Mg-CLI). The procedure used in this study was similar to that described by Camacho et al. [9]. The zeolite sample (10 g) was suspended in a glass beaker containing 10 cm³ of 2.5 M MnCl₂·4H₂O and

1.0 cm³ of 1 M NaOH. The suspension was heated at 150 °C for 5 h and Mn-CLI and Mg-CLI, recovered by filtration, were then calcined at 500 °C for 1h. After cooling to room temperature, Mn-CLI and Mg-CLI were stored in desiccators for further use.

Preparation of the iron/aluminum-modified zeolite (Fe-CLI and Al-CLI). The method used for modification was similar to that described by Stanic et al. [10]. 10 g CLI was treated with 50 cm³ of 0.1 M FeCl₃ in an acetate buffer at pH=3.6, during 1 h. Then 45 cm³ of 4 % NaOH were added, the suspension stirred for an hour and finally mixed with 25 cm³ of a 4 % NaCl solution. The suspension was then stirred for another hour at 50 °C, separated by filtration and the obtained samples were thermally treated: firstly dried at 105 °C and then calcined at 500 °C for 1 h.

The zeolite samples were characterized by powder X-ray diffraction (APD2000, Itai Structure), FTIR spectroscopy (Digilab-FTS 80) and thermal analysis (SDT Q600, TA Instruments). The morphology and elemental composition of the samples were studied using energy dispersive X-ray spectroscopy (EDX) by a scanning electron microscope (SEM, Jeol, JSM-6610LV). The specific surface area was measured by the N₂-BET method (Micromeritics ASAP 2020).

Nitrate adsorption experiments were carried out by batch method. The nitrate solution (C₀ = 400 mg dm⁻³) was prepared by dissolving KNO₃ in deionized water. 0.5 g of the M-CLI (M-Fe, Mn, Al, Mg) samples were suspended in 50 cm³ of the KNO₃ solution and shaken in a thermostated water-bath (Memmert, WPE 45) for 4 h at 25 °C. The amount of the adsorbed nitrate was determined using an UV-VIS spectrophotometer with NitraVer 5 reagent (Hach DR/2800).

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the obtained materials. It is evident that crystal structure of the clinoptilolite lattice remains generally preserved after modification. The XRD pattern of Mn-CLI displays a new diffraction peak at 2θ = 34°, which could be attributed to the formation of MnO₂ [11], whereas a new diffraction at 2θ = 36° in the Fe-CLI pattern could belong to Fe₂O₃ [12].

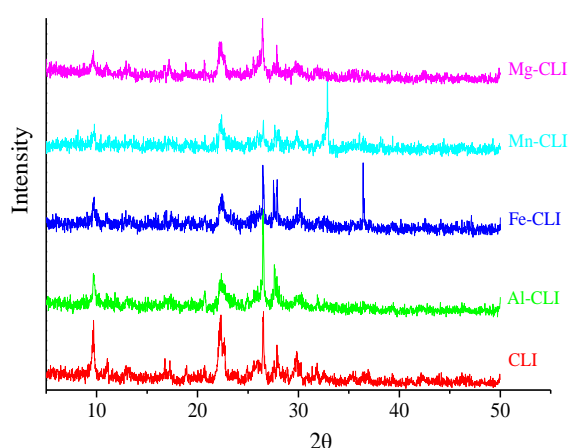


Figure 1: X-ray diffraction patterns of the CLI and M-CLI samples.

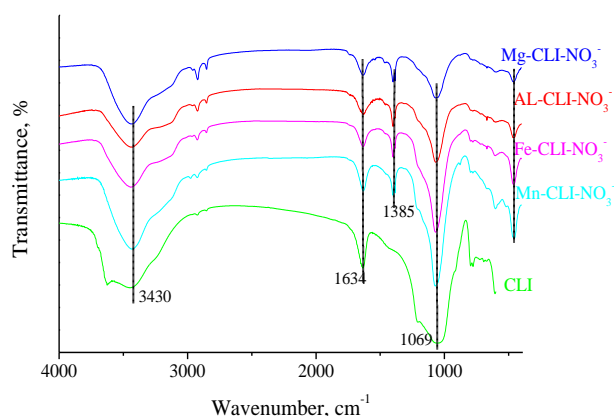


Figure 2: FTIR spectra of M-CLI samples after their treatment in nitrate aqueous solutions.

FTIR analysis (the spectra are given in Figure 2) indicates that all the modified zeolite samples, in contrast to the parent CLI, contain bound nitrate ions. A vibration band at about 1380 cm^{-1} appearing only in the spectra of the M-CLI samples can be attributed to asymmetric stretching vibrations that are characteristic for the nitrate ion.

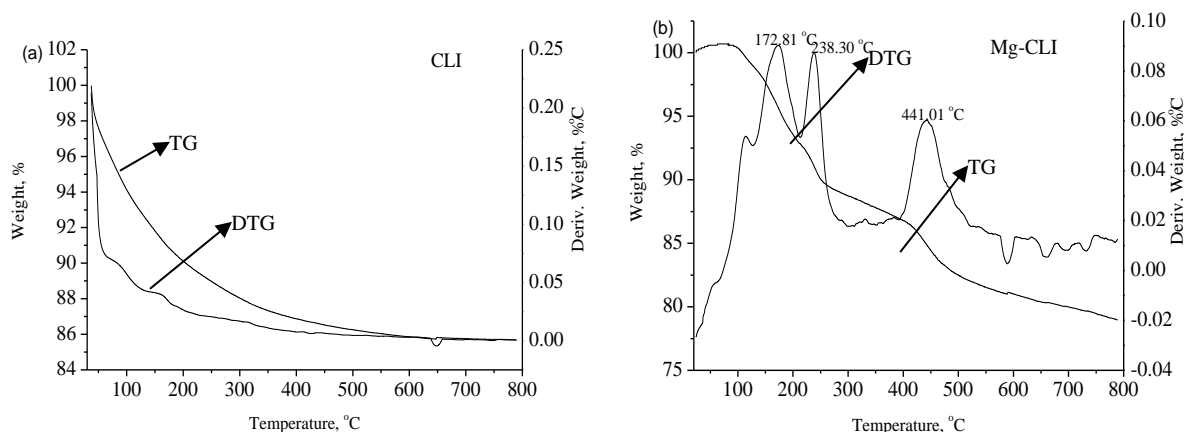


Figure 3: TG/DTG curves of CLI (a) and Mg-CLI (b).

Thermal analysis indicates that the modification changes the thermal behavior of zeolite samples. DTG curves of non-calcined M-CLI samples displayed novel maxima and the corresponding mass losses differ from those for the parent CLI sample. The changes are most conspicuous in the thermogram of Mg-CLI shown in Figure 3. In contrast to TG curve of the CLI sample which showed rather continuous weight loss by heating, weight losses of Mg-CLI proceed in several steps. Three strong maxima centered at 172.8, 238.3 and 441.0 °C can be assigned not only to the water loss from the CLI lattice (the first maxima) but also to a transformation of the magnesium hydroxo-species to magnesium oxide which is formed during the thermal treatment [13]. According to the literature data $\text{Mg}(\text{OH})_2$ transforms to MgO at 238 °C.

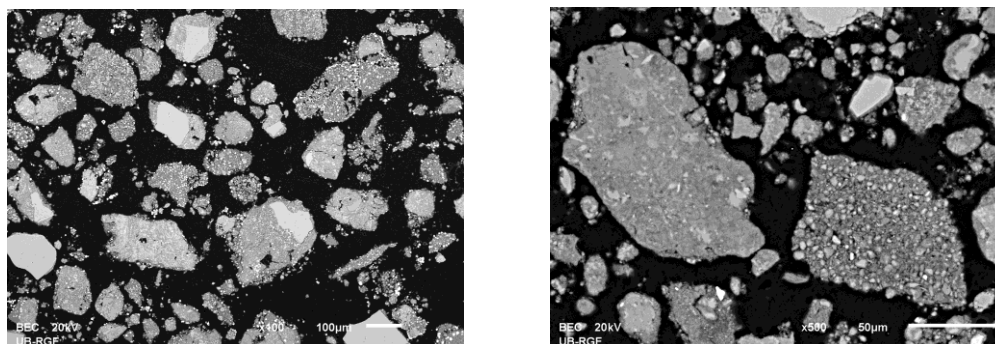


Figure 4: Representative SEM photos of the Mn-modified zeolite (left) and Mg-CLI (right).

SEM analysis confirmed the formation of novel oxide phases on the surfaces of the clinoptilolite phase in the samples. The SEM photos of Mn-CLI and Mg-CLI are presented as representative in Figure 4. The clinoptilolite phase is sprinkled with white spots, which the EDX analysis revealed to belong to the oxide phase. Elemental analysis showed that the metal content (Fe, Mn, Mg) in the samples varies from 4.10 to 7.3 wt. %. The results of the BET measurements are given in Table 1. It is evident that modification decreased the clinoptilolite specific area. This could be attributed to a partial blockage of the clinoptilolite pore system caused by oxide formation.

Table 1. Specific area of the zeolite samples and their adsorption capacity (mg g^{-1}) towards nitrate at 25 °C during 4 h ($C_0 = 400 \text{ mg dm}^{-3}$).

Sample	CLI	Al-CLI	Fe-CLI	Mn-CLI	Mg-CLI
Specific area [$\text{m}^2 \text{g}^{-1}$]	62.8	25.5	36.1	20.4	24.4
q_t [mg g^{-1}]	-	9.676	16.156	10.532	18.084

Preliminary results of the adsorption experiments confirmed that the M-CLI materials show the nitrate adsorption ability. Table 1 gives amounts (q_t) of the nitrate adsorbed on M-CLI after a 4 h contact with the KNO_3 solution at 25 °C. The highest adsorption capacity is found for Mg-CLI, which therefore seems to be an acceptable material for nitrate adsorption. Namely, the adsorption capacity (18 mg NO_3^- per g of zeolite) is comparable to the ion-exchange capacity of natural clinoptilolite towards some heavy metal cations (13 mg Cu^{2+} per g of the zeolite) [14].

CONCLUSIONS

This study shows that a simple two step procedure could be used for surface modification of the natural clinoptilolite by Mg-, Al-, Mn(IV)- and Fe(III) oxide species. Formation of these oxides was confirmed by XRD and SEM/EDX analyses. The modified zeolite samples have a good adsorption capacity towards nitrate ions from aqueous media, suggesting that the natural clinoptilolite, its modified form, could be a promising candidate for nitrate adsorption.

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