Modification of natural clinoptilolite for nitrate removal from aqueous media

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Abstract: Natural zeolitic tuff from the Zlatokop mine (Vranjska Banja deposit, Serbia) was investigated as the starting material to obtain a low cost adsorbent for the removal of nitrate from aqueous media. The tuff rich in zeolite, clinoptilolite, was modified with several oxides, iron(III), manganese(IV) and magnesium, by simple procedures in order to make the clinoptilolite surface accessible for binding nitrate ions. The obtained oxide-modified zeolite samples were characterized by scanning electron microscopy and energy dispersive X-ray analysis (SEM/EDS), powder X-ray diffraction (PXRD), infrared spectroscopy (FTIR) and by measurement of their specific surface area. The effects of the adsorbent dosage (0.5, 1.0, 1.5 and 2.0 g), temperature (25, 35 and 45 °C) and initial nitrate concentration (c_0, 100, 200 and 300 mg dm^{-3}) on the binding efficiency were also studied. For all adsorbents, the efficiency increased with temperature. The type of the oxide affected the adsorption mechanism. The Fe(III) oxide-modified zeolite exhibited the best binding ability. For this adsorbent, the adsorption kinetics were studied and it was found that they were best represented by the pseudo-second-order model.

Keywords: natural zeolite; clinoptilolite; oxide-modified zeolite; nitrate; adsorption.

INTRODUCTION

Many pollutants in water represent a serious problem for humans and the environment. Nitrates attract special attention because they readily leach from soil, have good solubility in water and accordingly, they are globally the most widespread contaminant.[1,2] Nitrate contamination of water is mainly caused by the excessive use of fertilizers, the increase in agricultural activities and by human and animal wastes. A high nitrate level in potable water is responsible for methemoglobinemia, commonly called the "blue baby syndrome". Moreover, nit-

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rates promote algal growth and eutrophication of water bodies and interact with organics forming carcinogenic nitrosamines.[3]

Various methods and technologies, such as adsorption, ion-exchange, biological denitrification, reverse osmosis and chemical reduction, have been tested and developed for nitrate removal.[4] Due to the fact that the majority are expensive, of low efficiency and/or have a problem with the management of the by-products, many investigations have been directed towards natural, environmental friendly, low cost materials which could be applied as filters in water purifications.

Owing to their adsorbent, ion exchange and catalytic properties, zeolites have attracted great attention. In particular, natural zeolites have been recognized as highly effective materials for the removal of different water contaminants.[5–8] Clinoptilolite, as the most abundant natural zeolite, could therefore be regarded as a cost-minimizing choice of adsorbent for developing countries such as Serbia. In Serbia, about 70 % of drinking water comes from groundwater sources and many of the springs suffer from high nitrate levels. Therefore, it is necessary to find a cost effective, efficient and easy to perform method for the removal of nitrates.

In this study, natural zeolite – clinoptilolite from the Zlatokop deposit in Serbia was examined as an adsorbent for nitrate removal from aqueous media. Since the aluminosilicate lattice of the zeolite is negatively charged, the zeolite has no adsorptive ability towards anionic nitrate ions and it has to be modified. Some of the reported modifications include coating of zeolite surface with surfactants[9] and low cost chitosan[10] or impregnation with different metal precursors.[11]

Taking into account that iron(III) and manganese(IV) oxide-modified clinoptilolite were reported as efficient adsorbents for different anionic species[12–14] and an MgO–biochar nanocomposite for the removal of phosphate and nitrate ions,[15] the modification of the natural clinoptilolite by oxides of iron(III), manganese(IV) and magnesium were investigated in order to obtain adsorbents for nitrates. Furthermore, the influence of different parameters on the adsorbent efficiency (adsorbent dosage, temperature and the initial nitrate concentration) were studied.

EXPERIMENTAL

Materials

In this study, a natural zeolite (Z) which contains about 73 % clinoptilolite phase, 14.6 % feldspar plagioclase and 12.8 % quartz[16] was used as the starting material. 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 (MnZ and MgZ)

The employed procedure was similar to that described by Camacho *et al.*[12] Z (10 g) was suspended in a glass beaker containing 10 cm^3 of 2.5 M MnCl$_2$ or MgCl$_2$ and 1.0 cm^3 of 1 M NaOH. The suspension was heated to dryness at 150 °C for 5 h and then the product was calcined at 500 °C for 1 h. Finally, the calcined products (MnZ and MgZ) were washed several times with distilled water and dried to a constant mass at 105 °C.

Preparation of the iron-modified zeolite (FeZ)

The modification was performed in a similar manner to that described by Stanic *et al.*[17] Z (10 g) was mixed with 50 cm^3 of 0.1 M FeCl$_3$ in an acetate buffer at pH 3.6, for 1 h at room temperature. Then 45 cm^3 of 4 % NaOH were added, the suspension was stirred for 1 h and finally mixed with 25 cm^3 of a 4 % NaCl solution. The suspension was then stirred for another hour at 50 °C. After filtering, the Fe-containing sample (FeZ) was heated to dryness, calcined and washed as described above.

Characterization

Powder X-ray diffraction (PXRD) patterns of Z and of the modified zeolite samples were recorded at room temperature on a APD2000 Ital Structure diffractometer with CuK$_α$ radiation ($λ$= 0.15418 nm) in the 2$θ$ range 5–50° with a step 0.04° s^{-1}. The thermal behavior of the samples obtained before the calcination step was examined by thermal analysis using a SDT Q600 simultaneous TGA–DTA instrument (TA Instruments). The samples were heated from room temperature to 800 °C at a heating rate of 10 °C min^{-1} under synthetic air.

The morphology and elemental composition of the samples were examined by energy dispersive X-ray spectroscopy (EDS) using a scanning electron microscope (SEM, Jeol, JSM-6610LV). For EDS, the samples were carefully prepared by embedding grains in an epoxy film, polishing the crystallites, cutting them with a fine-grid diamond cutter and coating them with carbon. In this manner, an intersection view of the crystallite grains was obtained that enabled detailed EDS analysis of the major mineral phases.

All samples were characterized by Fourier transform infrared spectroscopy (FTIR) using KBr pellets. The FTIR spectra were obtained on a Digilab-FTS 80 interferometer in the 400––4000 cm^{-1} range. The specific surface area was measured by the N$_2$-BET method (Micromeritics ASAP 2020).

Nitrate adsorption experiments

The adsorption experiments were realized by the batch method. The adsorption capacity of nitrates on MZ (M –Fe, Mn or Mg) samples was investigated as a function of the adsorbent dosage, temperature and the initial concentration of the nitrate solution. All nitrate solutions were prepared by dissolving KNO$_3$ in deionized water. The influence of different parameters on the removal efficiency was investigated as follows. The effect of adsorbent dosage was investigated at 25 °C by shaking different amounts of MZ (0.5, 1.0, 1.5 and 2.0 g) with 50.0 cm^3 of nitrate solution (c_0 = 100 mg dm^{-3}) for 24 h. The effect of temperature was studied with 1.0 g of MZ and 50.0 cm^3 of nitrate solution (c_0 = 100 mg dm^{-3}) at 25, 35 and 45 °C during 24 h. The influence of the initial nitrate concentration was studied at three different concentrations, 100, 200 and 300 mg dm^{-3}. 1.0 g of MZ was shaken with 50.0 cm^3 of the appropriate nitrate solution at 45 °C for 24 h.

Kinetic studies

For kinetic experiments, 1.0 g of each adsorbent was shaken in a thermostated water bath (Memmert, WBE 22) with 50.0 cm^3 of an aqueous solution of nitrate (c_0 = 300 mg dm^{-3}) at 45 °C, for contact times of 30, 240, 360, 600 and 1440 min.

In all the experiments, the suspensions were separated using 0.45 μm filter and the filtrate was analyzed. The amount of nitrate in the solutions was determined (Hach DR/2800) with NitraVer 5 reagents by the Cadmium Reduction Method (Hach method 8039) using a UV–Vis spectrophotometer. The amount of the adsorbed nitrate after time *t*, q_t, was calculated using the following formula:

$$q_t = \frac{c_0 - c_t}{m} V \tag{1}$$

where c_0 and c_t are concentrations of nitrate ions in the aqueous solution (mg dm^{-3}) before and after contact with the adsorbent, respectively, *V* is the volume of the solution in dm^3 and *m* is mass of the adsorbent in g.

RESULTS AND DISCUSSION

Physical and chemical properties of natural and the modified zeolites

The results of SEM analysis are given in Fig. 1. The shape and color contrast evident in Fig. 1a indicate that the zeolite sample consisted of different mineral phases, which were analyzed by EDS (Table I). It is evident that one of the phases is the most abundant and this was clinoptilolite with a Si/Al molar ratio of about 4.7.
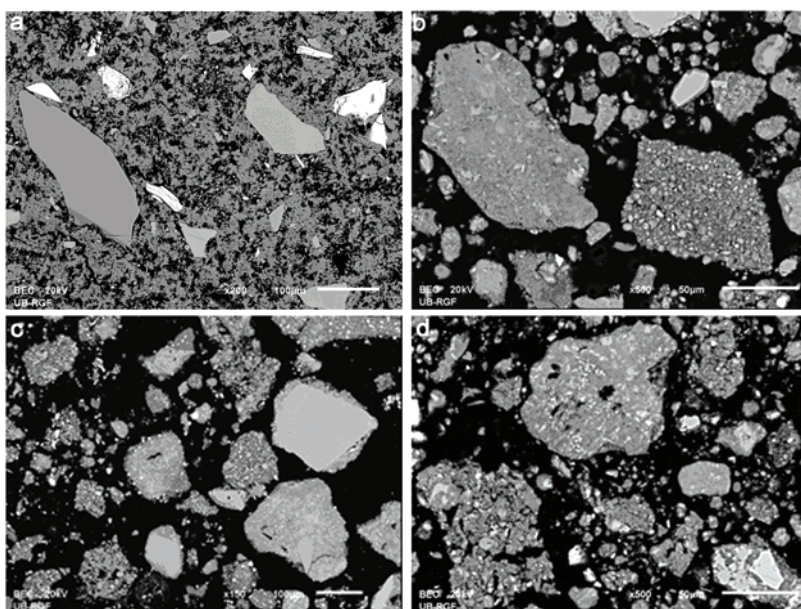

Fig. 1. SEM microphotographs of: a) natural zeolite and the modified products,
b) MgZ, c) MnZ and d) FeZ.

TABLE I. Elemental composition (mass %) of zeolite (Z) and the metal-modified zeolite samples

Element	Sample			
	Z	MgZ	MnZ	FeZ
Na	0.43	0.45	0.41	0.56
Mg	0.72	5.45	0.54	0.90
Al	6.39	6.16	6.07	6.65
Si	32.07	32.47	33.07	32.39
K	1.37	1.46	0.96	1.55
Ca	2.44	2.27	2.07	2.17
Fe	1.94	0.67	0.21	7.25
Mn	–	–	4.87	–

Figure 1b–d show that modification resulted in the appearance of white spots, mainly on the clinoptilolite phase, in all three modified products. EDS analysis indicated that the spots belong to different oxide phases. Furthermore, the results of EDS clearly showed that the modification did not proceed *via* an ion-exchange process. Namely, the content of exchangeable cations in clinoptilolite phase remained almost constant. Moreover, since the modification occurred in an alkaline medium, it seems likely that some complex hydroxo species were adsorbed at the clinoptilolite surface that then during the calcination were converted to the respective oxides. This was confirmed by PXRD and TG analyses.

The PXRD patterns of the MZ products (Fig. 2) showed that the crystallinity of the clinoptilolite lattice remained generally preserved during the modification. In addition, some new diffraction peaks appeared in the patterns of all samples, indicating the presence of novel crystalline phases. A new diffraction peak in the PXRD pattern of MnZ at $2\theta = 32°$ corresponded to Mn_3O_4.[18] In the pattern of FeZ, a new diffraction peak occurred at $2\theta = 36°$, suggesting the presence of Fe_2O_3,[19] whereas the diffraction peak at $2\theta = 42°$ in the pattern of MgZ indicates the presence of MgO.[20]

The results confirmed that the modification yielded products that contained different oxide phases. This was supported by the TG/DTG analyses. The analyses were performed on the metal-modified samples before their calcination in order to examine possible transformations of hydrous metal species into oxides at elevated temperatures.

The results of thermal analyses are presented in Table II and Fig. 3. The DTG curves (Fig. 3) of the samples displayed novel maxima and the corresponding mass losses differed from those for the parent Z sample. The changes were most conspicuous in the thermogram of the Mg-modified sample. In contrast to the TG curve of Z, which showed a rather continuous weight loss during heating, the weight loss of Mg-modified zeolite proceeded in several steps. Three strong maxima centered at 172, 238 and 441 °C could be assigned not only to the

water loss from the zeolite lattice (the first maximum), but also to transformation of the hydrous magnesium species to magnesium oxide, which was formed under 400 °C. Namely, the maximum centered at 441 °C was reported to correspond to the formation of MgO from Mg hydroxide.[20]
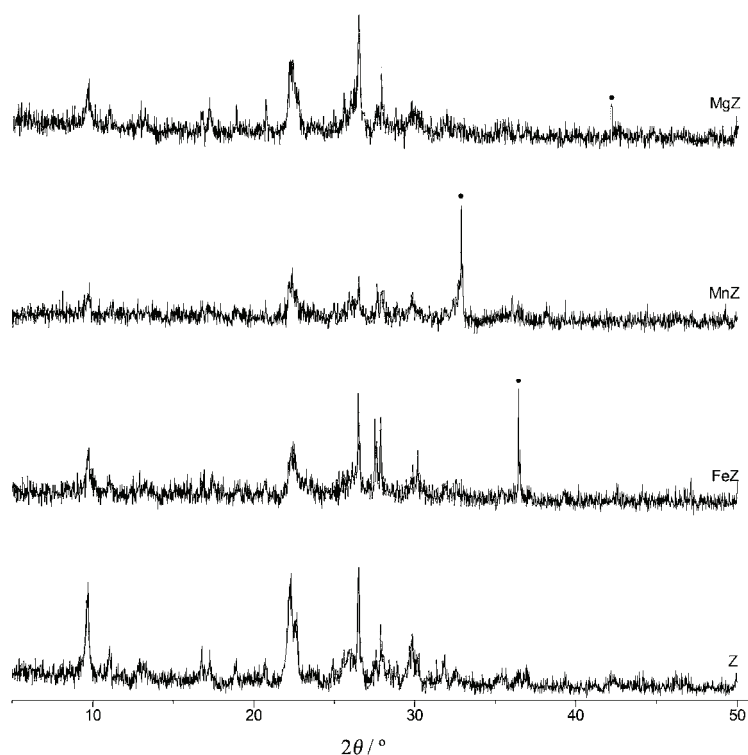

Fig. 2. Powder X-ray diffraction patterns of the zeolite samples.

TABLE II. Thermogravimetric results for the zeolite samples before calcination: natural zeolite (Z), Mg-modified zeolite (Mg-MZ), Mn-modified zeolite (Mn-MZ) and Fe-modified zeolite (Fe-MZ)

Parameter	Sample			
	Z	Mg-MZ	Mn-MZ	Fe-MZ
Total weight loss, %	14	21	17	12
Weight loss up to 300 °C, %	12	11	7	10

For the Mn- and Fe-modified samples, the differences were more pronounced below 300 °C. The maxima displayed below 140 °C most probably corresponded to the release of lattice water, whereas the further weight loss and the corresponding DGA events could be attributed to the dehydration of hydroxo species and formation of the corresponding oxides.
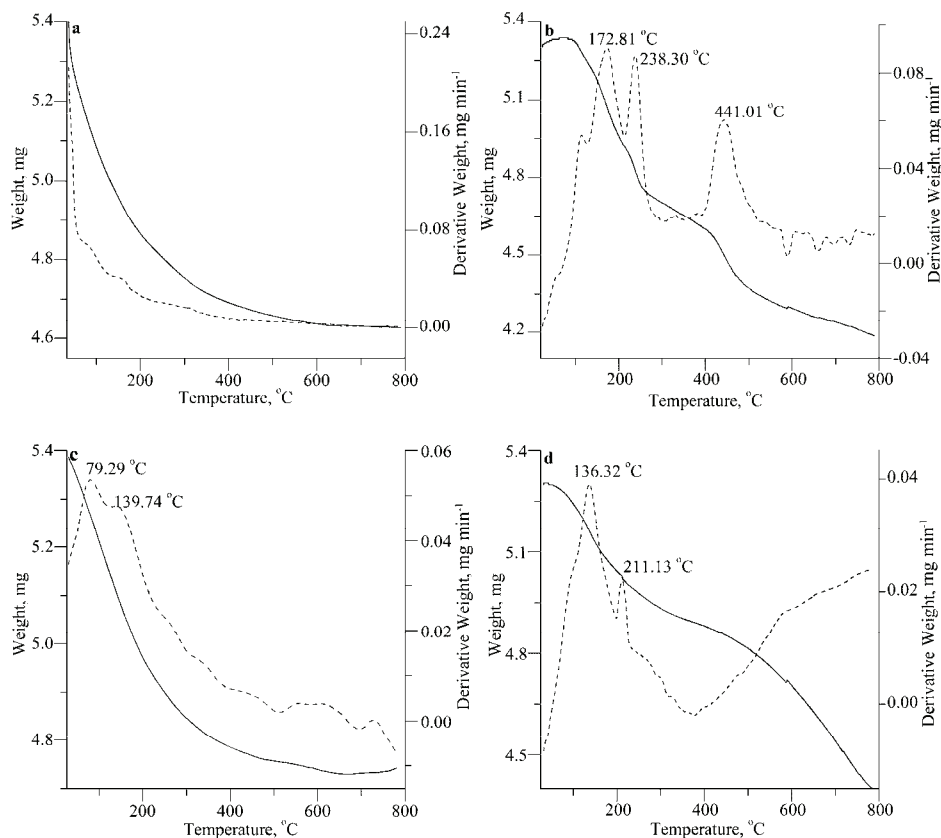
Fig. 3. TG/DTG curves of: a) Z and the zeolite samples modified by b) Mg, c) Fe and d) Mn; solid line: TG, dashed line: DTG.

In order to determine the specific surface area of the products, BET measurements were performed (Table III). The specific area for natural zeolite and modified samples differed mutually. The decrease in the specific area was most pronounced for MnZ, for which BET method gave a value of 17.5 m² g⁻¹. A similar phenomenon was previously reported for the modification of Mn-containing clinoptilolite.[12] The modification also led to a decrease of the specific surface area in MgZ and FeZ. Generally, the decrease should be attributed to the formation of oxide particles at the surface of the zeolites, which causes a partial blockage of the pore system of clinoptilolite.

TABLE III. Specific surface areas for the natural zeolite and the oxide-modified products: natural zeolite (Z), MgO-modified zeolite (MgZ), Mn_3O_4-modified zeolite (MnZ) and Fe_2O_3-modified zeolite (FeZ)

Sample	Z	MgZ	MnZ	FeZ
Specific surface area, m² g⁻¹	30.9	24.4	17.5	28.1

In order to check whether the modification procedure led to a change in the clinoptilolite surface and made it accessible towards nitrate ions, the samples (natural zeolite and modified ones) were treated with a nitrate solution for 24 h. The FTIR spectra of the products obtained after the treatment are shown in Fig. 4. In all spectra, a broad band at 3430 cm^{-1} and 1634 cm^{-1}, attributed to the vibrations of water molecules, and a broad vibration centered at 1069 cm^{-1}, corresponding to the zeolite lattice, are evident.[21] However, a vibration band at about 1380 cm^{-1} corresponding to the asymmetric stretching vibrations that are characteristic for the nitrate ion[22,23] could only be seen in the spectra of the modified samples. This indicates that the formation of MgO, Fe_2O_3 and Mn_3O_4 at the surface of clinoptilolite makes it available towards negatively charged nitrate ions.
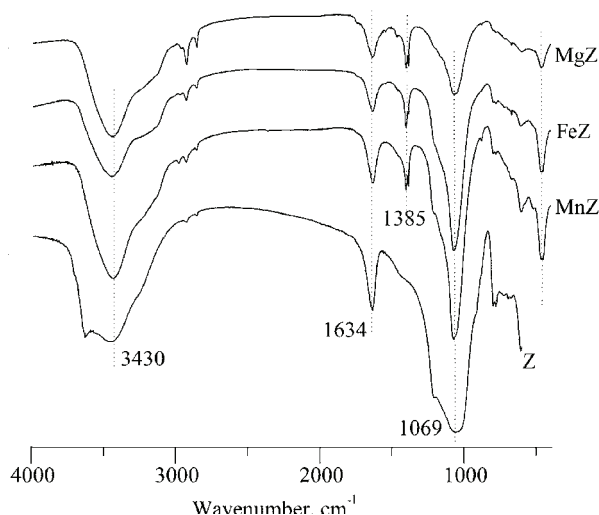

Fig. 4. FTIR spectra of Z and MZ samples after nitrate loading.

Effect of adsorbent dosage on the removal of nitrate by the different adsorbents

The removal of nitrate as a function of adsorbent dosage is shown in Fig. 5. Generally, increasing the adsorbent dosage increased the percent removal of nitrate, which could be attributed to the increase in adsorbent surface area of the adsorbents. For all samples, the percentage nitrate removal initially increased sharply with increasing adsorbent mass up to 1.0 g, above which the removal efficiency increased negligibly (*i.e.*, a two times increase in the mass of adsorbent at higher adsorbent masses increased the percentage of nitrate removal by only 10 %). Thus, a ration of 1.0 g of adsorbent per 50 cm^3 of liquid phase was chosen as the optimal for use in the further study.
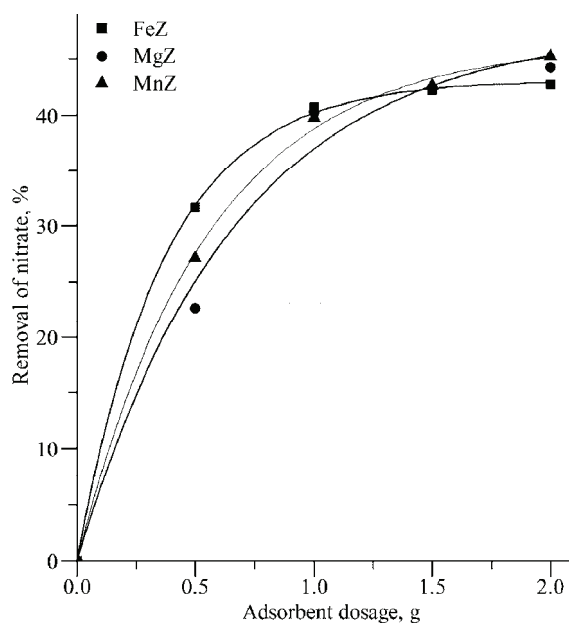
Fig. 5. Effect of the adsorbent dosage on nitrate removal by the different zeolite samples.

Effect of temperature on nitrate adsorption

The adsorption efficiency as a function of temperature was investigated at 25, 35 and 45 °C and the results are shown in Fig. 6. It is evident that concentration of the adsorbed nitrate (q_t) on adsorbent increases with increasing temperature for each MZ sample. Since the q_t values were highest at 45 °C, effect of initial concentration on nitrate removal efficiency was investigated at 45 °C.
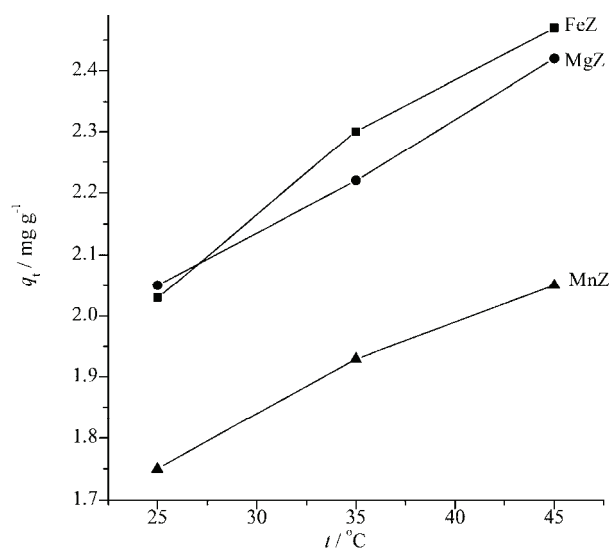

Fig. 6. Concentration of nitrate on different zeolite samples at different temperatures.

Effect of the initial concentration of nitrate on its removal efficiency

The results of the adsorption of nitrate by MZs at different initial concentration are presented in Fig. 7 as the amounts (q_t) of the nitrate adsorbed on MZ after a 24-h contact with nitrate solutions ($c_0 = 100$, 200 or 300 mg KNO$_3$ dm^{-3}) at 45 °C. The sharpest increase in removal efficiency with initial concentration was observed with FeZ. The nitrate concentration on FeZ increased from 2.5 ($c_0 = 100$ $=$ mg dm^{-3}) to 5.6 mg g^{-1} ($c_0 = 300$ mg dm^{-3}). The results indicate that nitrate removal efficiency depends on type of oxides present on the clinoptilolite surface.

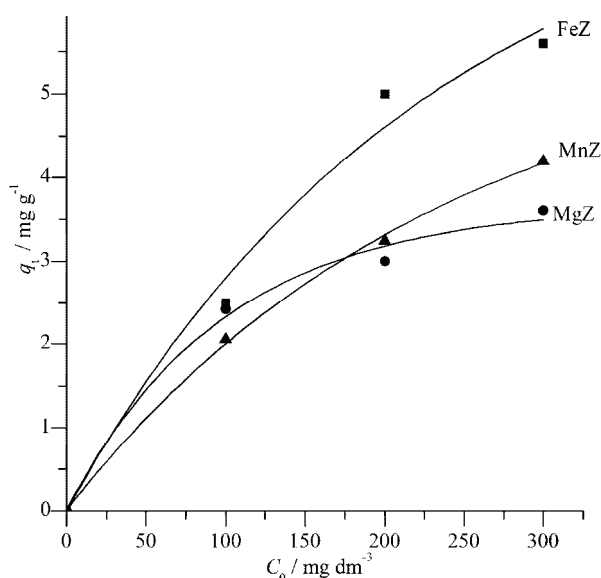
Fig. 7. Concentration of nitrate ions (q_t / mg g^{-1}) on different zeolite samples as a function of the initial nitrate concentration.

Adsorption kinetics

The study of nitrate adsorption on different adsorbents with time was performed at 45 °C for a solution with $c_0 = 300$ mg KNO$_3$ dm^{-3}. The results are shown in Fig. 8, from which it could be seen that the adsorption for MgZ and MnZ occurred in two steps. In the first step in the initial stage, the nitrate adsorption increased rather sharply (up to 400 min), which was followed by a second step in which the uptake of nitrate was rather gradual. The second step for FeZ proceeded in a different manner, indicating that the type of the oxide affects the adsorption mechanism. FeZ, as the most perspective adsorbent, was used in the further experiments for studying the kinetics of the process.

Two reaction-based kinetic models were applied in order to describe nitrate adsorption by FeZ. The first model is given by the Lagergren first-order rate equation:[24]

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (2)$$

where q_e (mg g^{-1}) is the adsorption capacity at equilibrium and k_1 (min^{-1}) is the rate constant of a first-order adsorption. In order to distinguish the kinetics equations based on the concentrations of solution from the adsorption capacities of solids, the Lagergren first-order rate equation is often called the pseudo-first--order rate equation.[25] Integrating the expression (2) between the limits $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$, one obtains:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (3)$$

A plot of log $(q_e–q_t)$ *vs.* t should yield a straight line if the experimental data conform to this kinetic model.
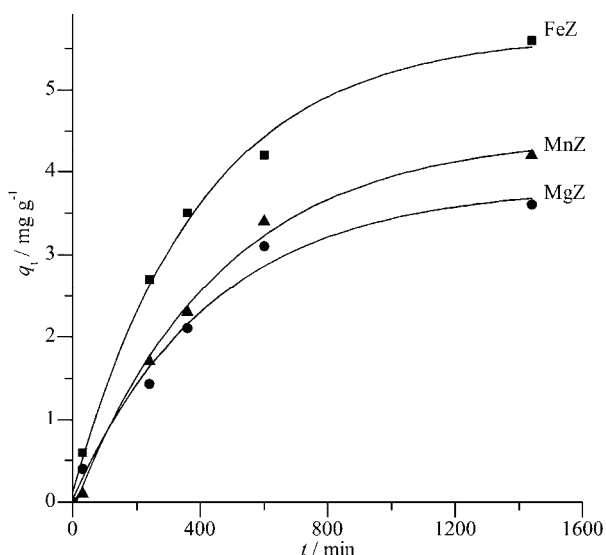

Fig. 8. Kinetics for the adsorption of nitrate ions on different zeolite samples.

The second reaction-based model that was applied in this study is described by the pseudo-second-order rate equation,[25] which is given as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (4)$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order adsorption. Integration between the same limits as above yields the following expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5)$$

The plot of t/q_t *vs.* t will give a straight line if the experimental data conform to this kinetic model, and the values of q_e and k_2 are obtained, respectively, from the slope and intercept of such a plot (Fig. 9).
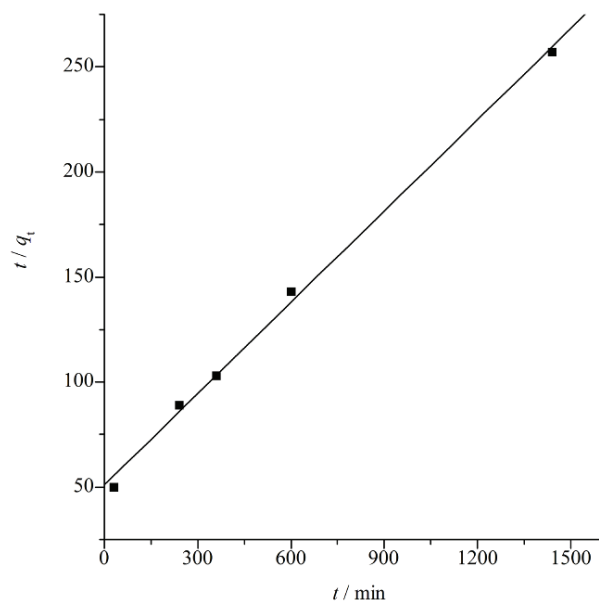

Fig. 9. Pseudo-second-order kinetic model for the adsorption of nitrate ions onto FeZ.

Application of the two models on the experimental data for the adsorption of nitrate on FeZ showed that the Lagergren first-order model gave rather poor agreement, the square of the linear regression correlation coefficient being lower than 0.90. Only the pseudo-second-order kinetic model gave satisfactory fits and the resulting parameters are listed in Table IV.

TABLE IV. Pseudo-second-order kinetic model parameters for Fe_2O_3-modified zeolite (FeZ) samples

q_e / mg g^{-1}	k_2 / g mg^{-1} h^{-1}	R^2
6.9061	0.0246	0.9973

CONCLUSIONS

The obtained results showed that the natural zeolite tuff from the Zlatokop deposit could be modified according to the described procedure into an adsorbent for nitrate ions present in aqueous solutions. The procedure is simple consisting of two steps: 1) a treatment of the natural zeolite in an alkaline solution of Mg, Mn(II) or Fe(III) and 2) calcination of the metal-enriched samples at 500 °C. The procedure yielded MgO-, Mn_3O_4- and Fe_2O_3-containing zeolite adsorbents. For all the obtained adsorbents, the removal efficiency increased with temperature, and the concentration of nitrate on the adsorbents increased with increasing ini-

tial nitrate concentration. For all adsorbents, 1 part of the solid in 50 parts of the liquid was found to be the optimal solid/liquid ratio. The best removal efficiency at 45 °C was exhibited by the Fe_2O_3-containing zeolite adsorbent, for which the adsorption kinetics was also studied. The results showed that the Fe_2O_3-containing zeolite removed nitrate ions in accord with a pseudo second order equation (with the rate constant of 0.0246 g mg^{-1} h^{-1}). From all the presented results, it could be concluded that the Serbian natural zeolite can be considered as a promising natural material for employment as a filter in a drinking water installation.

ИЗВОД

МОДИФИКАЦИЈА ПРИРОДНОГ КЛИНОПТИЛОЛИТА ЗА УКЛАЊАЊЕ НИТРАТА ИЗ ВОДЕНИХ РАСТВОРА

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Зеолитни туф из лежишта Златокоп (налазиште Врањска Бања) испитиван је са циљем добијања јефтиног адсорбента за уклањање нитрата из водених раствора. Како би се површина зеолита-клиноптилолита учинила прихватљивом за везивање нитрата, она је модификована: Fe(III)-, Mn(IV)- i Mg-оксидом. Карактеризација добијених адсорбената извршена је скенирајућом електронском микроскопијом са дисперзионом спектроскопијом, рендгенском дифракцијом праха и инфрацрвеном спектроскопијом као и мерењем специфичне површине. Такође, испитиван је утицај различитих параметара на ефикасност везивања нитрата за адсорбенте: масе адсорбента (0,5; 1,0; 1,5 и 2,0), температуре (25, 35 и 45 °C) и почетне концентрације нитрата у раствору (100, 200 и 300 mg dm^{-3}). Код свих адсорбената ефикасност везивања расте са температуром. Гвожђе-модификован зеолит показује најбољу ефикасност а кинетика везивања нитрата за овај адсорбент следи кинетику псеудо-другог реда.

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REFERENCES

1. T. S. Thomson, *Bull. Environ. Cont. Toxicol*. **66** (2001) 64
2. X. Jia, D. Larson, D. Slack, J. Walworth, *Eng. Geol.* **77** (2005) 273
3. M. Islam, R. Patel, *Desalination* **256** (2010) 120
4. A. Bhatnagar, M. Sillanpaa, *Chem. Eng. J.* **168** (2011) 493
5. H. Faghihian, R. S. Bowman, *Water Res.* **39** (2005) 1099
6. S. Jevtić, S. Grujić, J. Hrenović, N. Rajić, *Micropor. Mesopor. Mat.* **159** (2012) 30
7. N. Rajić, Dj. Stojaković, S. Jevtić, N. Zabukovec-Logar, J. Kovac, V. Kaucić, *J. Hazard. Mater.* **172** (2009) 1450
8. N. Rajić, Dj. Stojaković, M. Jovanović, N. Zabukovec-Logar, M. Mazaj, V. Kaucić, *Appl. Surf. Sci*. **257** (2010) 1524
9. J. Schick, P. Caullet, J. Paillaud, J. Patarin, C. Mangold-Callarec, *Micropor. Mesopor. Mat.* **132** (2010) 395

10. M. Arora, N. K. Eddy, K. A. Mumford, Y. Baba, J. M. Perera, G. W. Stevens, *Cold Reg. Sci. Technol.* **62** (2010) 92
11. F. Deganello, L. F. Liotta, A. Macaluso, A. M. Venezia, G. Deganello, *Appl. Catal., B* **24** (2000) 265
12. L. M. Camacho, R. R. Parra, S. Deng, *J. Hazard. Mater.* **189** (2011) 286
13. Z. Li, J.-S. Jean, W.-T. Jiang, P.-H. Chang, C.-J. Chen, L. Liao, *J. Hazard. Mater.* **187** (2011) 318
14. E. Bilgin Simsek, E. Ozdemir, U. Beker, *Water Air Soil Poll.* **224** (2013) 1614
15. M. Zhang, B. Gao, Y. Yao, Y. Xue, M. Inyang, *Chem. Eng. J.* **210** (2012) 26
16. Dj. Stojaković, J. Milenković, N. Daneu, N. Rajić, *Clay. Clay. Miner.* **59** (2011) 277
17. M. H. Stanić, B. Kalajdzić, M. Kules, N. Velić, *Desalination* **229** (2008) 1
18. Z. H. Wang, D. Y. Geng, Y. J. Zhang, Z. D. Zhang, *J. Cryst. Growth* **310** (2008) 4148
19. J. Zielinski, I. Zglinicka, L. Znak, Z. Kaszkur, *Appl. Catal., A* **381** (2010) 191
20. E. Alvarado, L. M. T. Martinez, A. F. Fuentes, P. Quintana, *Polyhedron* **19** (2000) 2345
21. O. Korkuna, R. Leboda, J. Z. Skubiszewska-Zieba, T. Vrublevs'ka, V. M. Gun'ko, J. Ryczkowski, *Micropor. Mesopor. Mat.* **87** (2006) 243
22. M. Islam, R. Patel, *J. Hazard. Mater.* **169** (2009) 524
23. M. Falk, *Vib. Spetrosc.* **1** (1990) 69
24. S. Lagergren, K. Sven. *Vetenskapsakad. Handl*. **24** (1898) 1
25. Y.-S. Ho, *J. Hazard. Mater.* **136** (2006) 681.