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Study on the removal of nitrate in groundwater from Căpuş, Cluj county by natural zeolite of Mirşid and granular activated carbon

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ABSTRACT

This paper focuses on a comparative study regarding the performance of natural zeolite from Mirşid (NZM) and granular activated carbon (GAC), respectively, for treatment process of contaminated groundwater from Căpuş, Cluj region for nitrate removal. The effect of pH, conductivity, contact time, and nitrate concentration have been studied. The Langmuir and Freundlich models were used to fit the experimental data and these showed good correlations with the Freundlich model, providing a better description of the equilibrium (higher R^2 value). Textural analysis was employed in order to determine the specific surface area, and pore size distribution of the used activated carbon and natural zeolite. The adsorbents (GAC and NZM) were characterized by using Fourier transform infrared spectroscopy and x-ray powder diffraction.

Keywords: Groundwater; Granular activated carbon (GAC); Natural zeolite of Mirşid (NZM); Nitrates (NO_3^-); Adsorption

1. Introduction

Groundwater is the source of drinking water for many people around the world, especially in rural areas. Groundwater can become contaminated naturally or because of numerous types of human activities. Residential, municipal, commercial, industrial, and agricultural activities can all affect groundwater quality [1].

Contamination of groundwater can result in poor drinking water quality, loss of water supply, high clean-up costs, high costs for alternative water supplies, and/or potential health problems [2].

Nitrate (NO_3^-) concentration is one of the most important water quality parameter. The European Union Directive on drinking water quality (98/83/EC) established the maximum contaminant level (MCL) of 50 mg/L [3]. On the other hand, the US Environmental Protection Agency (EPA) has set a (MCL) goal (MCLG) for nitrates at 10 mg/L, because EPA believes this level of protection would not cause any of the potential health problems described above. The presence of nitrates can pose serious health risks, especially for infants and pregnant women [4]. The

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removal of nitrate from drinking water has gained renewed attention due to the potential harm by nitrate to human health [5]. Council Directive 91/676/EEC was drawn up with the specific purpose to protect waters against pollution caused by nitrates from agricultural sources, and is therefore typically labeled the Nitrates Directive [6,7].

In the rural areas of the Cluj region, the main sources of drinking water are groundwater aquifers; therefore, excessive nitrate concentrations in groundwater may be a health hazard for consumers.

Adsorption is the most suitable process for drinking water treatment. Different adsorbents have been tested for lead removal in materials such as: fruit stones [8], pyrolyzed coffee residues [9], pine bark [10], nutshells, [11] and olive stones [12] and GAC for fluoride removal [13] and nitrate removal, respectively, [14] were studied.

Activated carbon is a porous adsorbent with a high surface area, a great adsorption capacity, and an effective regeneration. Carboxylic, carbonylic, lactonic, phenolic, aldehydic, and other organic functional groups are located at the edges of the hexagonal carbon layer planes and are responsible for surface reactivity of activated carbon [15].

Commercial activated carbons are mostly prepared from coal, wood, peat, and coconut shells [16]. However, the demand for novel and more efficient adsorbents initiated a research on low-cost, locally available, and renewable materials as potential alternative precursors in activated carbon production.

Natural zeolites are naturally occurring crystalline aluminosilicates. The fundamental building block of the zeolite is a tetrahedron composed of four oxygen atoms surrounding a relatively small silicon or aluminum atom. Since aluminum has one less positive charge than silicon, the framework usually has a net negative charge and is balanced by the exchangeable cation (K^+, Na^+, Mg^{2+}, and Ca^{2+}) [17]. Therefore, ion exchange capability of natural zeolite makes it favorable for water treatment to remove unwanted ions, mainly cations [18,19]. In the case of anions, a surface functionalization has been applied in order to allow the retention of anions [20,21]. Besides, the cheap naturally zeolite is attractive. Clinoptilolite is one of the commonly known natural zeolites and is widely utilized in pollution control [22,23]. Dıaz-Nava et al. [24] reported a natural modified zeolite (clinoptilolite from Mexico) treated with NaCl, $CaCl_2$, $La(NO_3)_3$, and $Eu(NO_3)_3$ for water defluoridation.

The aim of the current study is a comparative study regarding the performance of natural zeolite from Mirşid (NZM) and granular activated carbon (GAC), respectively, for nitrate removal from groundwater from Căpuş, Cluj region. We tried to show that in some cases the retention of nitrate is possible even if the surface of zeolites suffered no modifications.

2. Materials and methods

2.1. Chemical and sorbent materials

The activated carbon utilized in the experiments was dried at 120°C for 2 h to minimize interferences by soluble organic residues in the material, develop the porosity, and increase the surface area. The carbon surface chemistry depends upon the activation conditions and the treatment temperatures; activation also refines the pore structure. GAC 1–3 mm, made from peat grey was purchased from Carl Roth GmbH + Co (Karlsruhe, Germany). The characteristics of GAC are presented in Table 1.

The NZM containing 68% clinoptilolite was collected from the Salaj region located in the northern part of Romania, and was provided by the Chilioara Mining Company, Mirşid. The zeolite characteristics are shown in Table 2. The zeolite sample of Mirşid

Table 1
The characteristics of GAC

Parameters	Batch results
Molecular weight	12.01 g/mol
Methylene blue adsorption	11 g/100 g
Density	270 kg/m^3
Ash	7%
Moisture	2%
pH-value	Alkaline
Iodine value	700
Particle size > 3.15 mm	3%
Particle size < 0.7 mm	1%

Table 2
The characteristics of NZM

Parameters	From (%)	To (%)
SiO_2	61.96	67.17
TiO_2	0.15	0.32
Al_2O_3	12.46	15.12
Fe_2O	0.98	2.05
MnO trace	–	0.05
MgO	1.3	1.96
CaO	3.03	4.35
Na_2O	0.70	1.11
K_2O	0.78	1.32
H_2O at 100°C	4.05	4.74
H_2O at 1,000°C	7.50	69.56

Table 3
The characteristics of groundwater from Capus city, Cluj region

Parameters	Nitrate (mg/L)	pH	Conductivity (μS/cm)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)
Groundwater	59.73	7.32	879	108.74	27.59	29.91

(NZM) was crushed and sieved to a particle size fraction of 125–250 μm.

The experimental tests were performed on groundwater from Căpuş city, Cluj-Napoca region, with the characteristics presented in Table 3.

2.2. Instruments

Conductivity and pH were measured using WTW multimeter inoLab 740. The nitrate concentration in the groundwater was measured using the UV–vis spectrophotometer PerkinElmer Lambda Bio 40 in accord with International Standard ISO 7390-3 (1988) [25].

FTIR spectra for GAC before and after water treatment were determined on Spectrum BX, Perkin Elmer, USA spectrophotometer.

The diffraction data (for GAC before and after water treatment) were collected in the $2\theta = 10–85^\circ$ angular domain with a Bruker D8 Advance diffractometer, using CuKα$_1$ radiation ($\lambda = 1.5406$ Å) (40 kV; 40 mA). In order to increase the resolution, a Ge 111 monochromator was used to eliminate the Kα$_2$ radiation. Data collection was performed at room temperature with the programs DIFFRAC and XRD Commander.

The BET isotherms were recorded using a Sorptomatic 1990 apparatus (Thermo Electron Corporation). Each sample was degassed at 200˚C for 3 h at a pressure of 1 Pa prior determination, in order to remove the physisorbed impurities from the surface.

2.3. Experimental

The adsorption experiments were carried out by contacting 2 g of GAC and NZM with 50 ml of groundwater in the sealed 100 ml Erlenmeyer flasks. The suspensions were magnetically stirred at 300 rpm at different temperatures (20, 30, and 40˚C). After the specified time, the suspensions were filtered through filter paper. Groundwater nitrates in the filtrates were determined by UV–vis spectrophotometer PerkinElmer Lambda Bio 40.

In order to obtain an accurate measurement, the quality control samples were analyzed to check the reliability of measurements after three samples were analyzed. Once the relative standard deviation exceeded 5%, analysis was repeated and the results were recorded.

The quantity of adsorbed NO_3^- on the GAC was calculated by the difference between the initial and final concentrations at equilibrium with the following equation:

$$q_e = \frac{v(c_i - c_e)}{m} \tag{1}$$

where q_e is the NO_3^- adsorbed (GAC and NZM) at equilibrium (mg of nitrate ion/g of adsorbed), c_i is the initial concentration of NO_3^- in the groundwater (mg/L), c_e is the equilibrium concentration of NO_3^- ions in the groundwater (mg/L), ν is the initial volume of the used groundwater (*L*), and m is the weight of the used GAC (g). The removal efficiency (adsorption percent %) was calculated using the following equation:

$$\%\,\text{Removal efficiency} = \frac{c_i - c_e}{c_i} \times 100 \tag{2}$$

3. Results and discussion

3.1. pH and conductivity of the treated groundwater

The effect of temperature on the pH and conductivity was studied making a series of adsorption experiments at temperature ranges from 20 to 40˚C. Generally, the pH of a solution is recognized as a very influential parameter that governs the adsorption process. It was established that pH affects the surface charge of the adsorbent [26]. In the present study, an increase in the pH (Fig. 1) of treated groundwater can be observed, especially for the first 30 min, reaching a maximum, and then after about 45 min the value of pH remains almost constant. The value of the final pH corresponds to the accepted values according to the legislation for drinking water [27].

Electrical conductivity (EC) is an important parameter in groundwater quality assessments for drinking and irrigation, since it is related to the concentration of charged particles in the water. Electrical conductance mostly depends on major anions and cations in

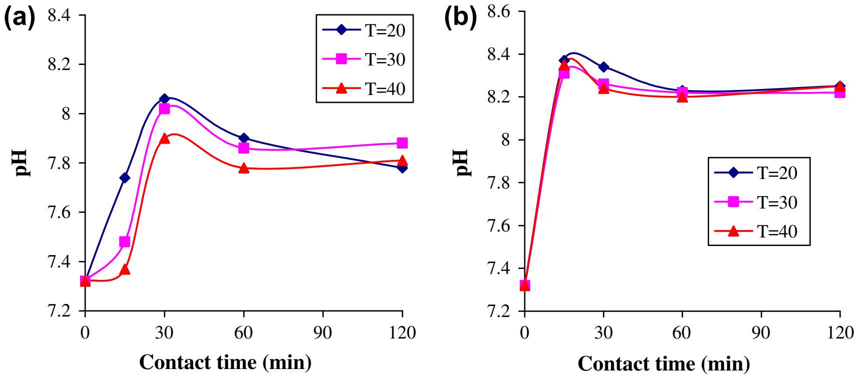

Fig. 1. The pH of treated groundwater as a function of adsorption time at different adsorption temperatures (20, 30, and 40°C), 300 rpm, for NZM (a) and GAC adsorber (b).

water. The major cations in natural groundwater are calcium (Ca^{2+}), sodium (Na^{+}), potassium (K^{+}), and magnesium (Mg^{2+}). EC provides a good indication of the changes in the composition of water, especially in its total dissolved solids.

The USA Salinity Laboratory system uses EC together with the sodium, magnesium, and calcium concentrations in the water. According to this system, water with EC level between 100 and 250 mS/cm has low, between 250 and 750 mS/cm has medium, and above 750 mS/cm has high salinity hazard [28]. It can be seen in Fig. 2 that the electric conductivity of the treated groundwater decreased with the increase of adsorption time, over several temperature ranges in the both cases (GAC and NZM). In the GAC adsorber, the decrease of electric conductivity is higher than in the case of the NZM adsorber. It means that the quantity of ions decreased after the adsorption process [29]. After 30 min, the slope of the decreasing curve is much smaller. The decrease of electric conductivity reduced the number of the anions and cations present in the water after the adsorption process; however, the concentration of calcium (Ca^{2+}), potassium (K^{+}), and magnesium (Mg^{2+}) in drinking water is not limited by the legislation in Romania. The MCL for drinking water is 200 mg/L for sodium (Na^{+}). Similar results were obtained by M. Al-Anber and Z.A. Al-Anber from adsorption of Fe^{3+} on the natural zeolite [29].

3.2. *Effect of temperature and the contact time on the nitrate concentration*

The nitrate concentration of the treated groundwater (Fig. 3) decreased as the adsorption time increased over several temperature ranges, but lower temperatures increased the adsorption capacity of nitrate ions on both GAC and NZM. GAC has higher adsorption capacity for nitrate as compared to natural zeolites of Mirşid.

3.3. *Effect of the temperature on the percent removal of nitrate*

The value for percent removal of nitrate was calculated after 30 min of contact time. It can be seen that the removal efficiency increased at 20°C, and then

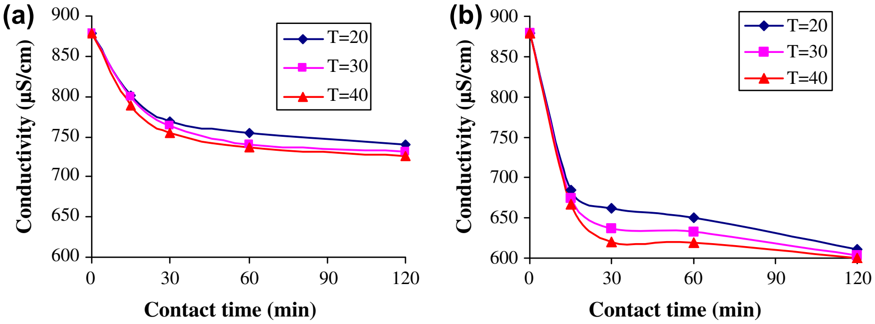

Fig. 2. The conductivity of the groundwater vs. the adsorption time at different adsorption temperatures (20, 30, and 40°C), 300 rpm, for NZM (a) and GAC adsorber (b).

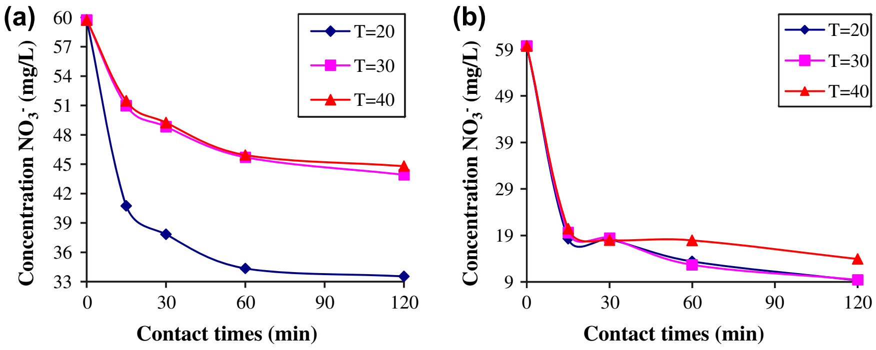

Fig. 3. The concentration of nitrate from treated water as a function of adsorption time at different temperatures (20, 30, and 40°C), 300 rpm, for NZM (a) GAC (b) adsorber.

declined in the range of 30–40°C in the same adsorbers. This may be due to the weakness of the adsorptive forces between the active site of the adsorbent and the adsorbate species and also between the adjacent molecules of the adsorbed phase [30]. Studying Fig. 4 can conclude that the absorption process almost completed after 30 min of contact time.

3.4. Adsorption isotherm

Fitting the data to different isotherm models is an important step to find the suitable model that can be used for performance evaluation of the adsorption process. Adsorption isotherm studies were conducted at 20°C by varying the quantity of the adsorbent: 1, 1.5, 2, 2.5, and 3 g, which were mixed with 50 ml groundwater for 30 min at 300 rpm, which is the equilibrium time for the GAC, the NZM, and the nitrate reaction mixture.

The Langmuir adsorption model [31] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. The Langmuir adsorption isotherm has been successfully used in many monolayer adsorption processes [32]. The expression of the Langmuir model is given below:

$$\frac{c_e}{q_e} = \frac{1}{Q_{max} K_L} + \frac{c_e}{Q_{max}} \tag{3}$$

where q_e is nitrate concentration on the adsorbent (GAC and NZM) at equilibrium (mg of nitrate ion/g of GAC and NZM); Q_{max} (mg/g) and K_L (1/mg) are the Langmuir constants. These constants are found from the slope and intercept of c_e/q_e vs. c_e linear plot so that $Q_{max} = 1/\text{slope}$; and $K_L = \text{slope}/\text{intercept}$ is obtained as shown in Fig. 5.

The correlation coefficients, R^2 (0.9856 for GAC and 0.9860 for NZM) indicated that the adsorption

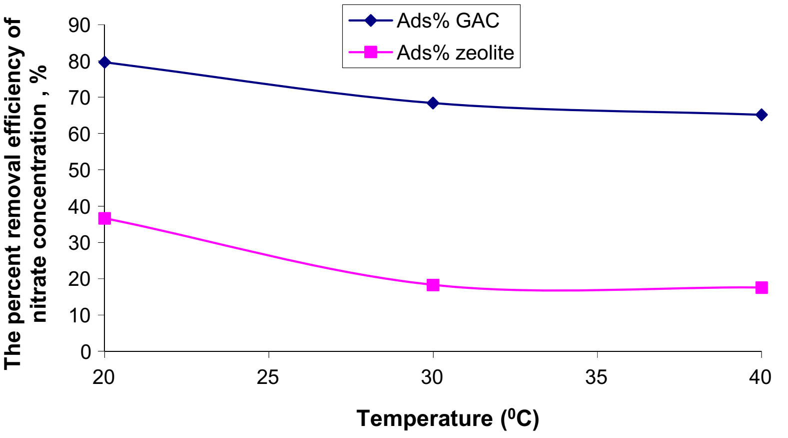

Fig. 4. The value for percent removal of NO_3^- after 30 min contact time.

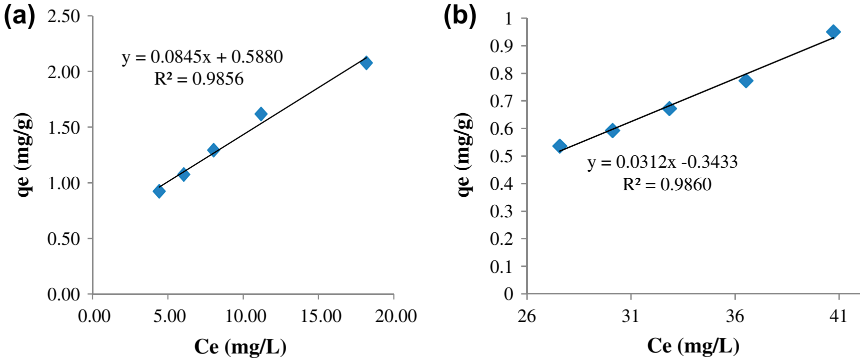

Fig. 5. Langmuir isotherm model plot of nitrate on GAC (a) and on NZM (b), 300 rpm, 20˚C, and 30 min contact time.

data of nitrate on the adsorbents (GAC and NZM) are well fitted to the Langmuir isotherm, supporting the formation of monolayer coverage of nitrate ions at the surface of GAC and NZM.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [33] The parameter is defined by: $R_L = 1/(1 + K_L C_0)$, where K_L is the Langmuir constant and C_0 (mg/L) is the initial nitrate concentration. The parameter R_L indicates the shape of the isotherm as given in Table 4 [32]:

It was found that for the 59.73 mg/L of nitrate concentration studied, the R_L values are 0.1043 for GAC and 0.0909 for NZM, which are between 0 and 1, indicating that the isotherm is favorable.

The linear form of the Freundlich model is also given by:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln c_e \tag{4}$$

where K_F (L/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. From the slope and intercept of the straight portion of the linear plot obtained by plotting ln q_e against ln c_e, the values of Freundlich parameters were obtained.

Table 4
The dimensionless equilibrium parameter for studied isotherms

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The obtained value of Freundlich model correlation coefficient was $R^2 = 0.9967$ in the case of GAC, but when NZM was used, $R^2 = 0.9919$ (Fig. 6). It was clear that the R^2 of the Freundlich isotherm was a little higher than that of the Langmuir isotherm model for adsorption of nitrate on GAC and on NZM. Therefore, the Freundlich isotherm model could better describe the adsorption equilibrium data.

Larger values of K_F mean larger capacities of adsorption. The constant $1/n$ is a function of the strength of adsorption. Larger values of $1/n$ mean that the adsorption bonds are weak because the value of q_e experiences large changes for small changes in c_e. Smaller values of $1/n$ mean that the adsorption bond is strong [34].

A straight line with a slope $1/n$ and an intercept ln K_F is obtained. This reflects the satisfaction of the Freundlich isotherm model for the adsorption of nitrate ions. The ln K_F is an indicator of adsorption capacity and the slope, $1/n$, is a criterion for adsorption intensity. In this study, the values of $1/n$ for GAC was 0.5899 and for NZM was 1.4575, where value less than 1 suggested that the adsorption conditions were favorable for GAC. The monolayer adsorption capacities of the adsorbents possess high adsorption capacity and hence it could be employed as a low-cost adsorbent for the removal of nitrate from groundwater.

The apparent Gibbs free energy (ΔG^0) is the fundamental criterion for the feasibility and spontaneity of the adsorption process. A reaction occurs spontaneously at a given temperature if ΔG^0 is negative. The standard Gibbs free energy change (ΔG^0) for the adsorption of nitrate by GAC can be calculated using the following thermodynamic equation (classical Van't Hoff equation) [35]:

$$\Delta G^0 = -RT \ln K_L \tag{5}$$

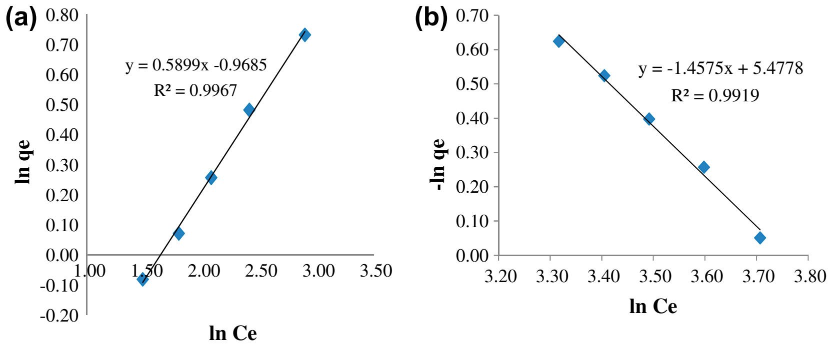

Fig. 6. Langmuir isotherm model plot of NO_3^- on GAC (a) and on NZM (b), 300 rpm, 20°C, and 30 min contact time.

where T is the absolute temperature and R is the gas constant (8.314 J/ mol.K). The value of standard Gibbs free energy change calculated at 20°C was found to be −20.46 kJ/mol for GAC and −16.01 kJ/mol in case of NZM. The negative sign for ΔG^0 indicates that the system reached a more stable energy level after ion exchange and the spontaneous nature of nitrate adsorption on the GAC/NZM [36,37].

3.5. BET characterization

The specific surface area is a significant factor to affect the adsorption property of GAC and NZM. BET-specific surface areas and pore distributions for the adsorbents are presented in Table 5. GAC had the largest specific surface area, pore volume, and mesopore volume. The adsorption of nitrate groups resulted in drastic decline in the surface area and pore volume values; however, it was to the same extent (GAC and NZM) as that was mostly used in case of GAC. As it can be seen in Table 5, the specific surface area and pore specific volume decreased after adsorption, illustrating that the pores have been irreversiby occupied following the adsorption process.

Table 5
Surface area and pore specific volume values of the activated carbon and natural zeolite

Adsorbent	Specific surface area (m^2/g)	Pore specific volume (cm^3/g)
GAC initial	782.81	0.5829
GAC after adsorption	609.48	0.5196
NZM initial	91.00	0.1226
NZM after adsorption	80.29	0.1074

3.6. FTIR spectroscopy

FTIR data was collected for qualitative characterization of the surface functional groups of the activated carbon samples and is presented in Fig. 7(a). In the IR spectrum of GAC after experiment are present the characteristic bands of NO_3^- group, with the stretch vibration at 1,419 cm^{-1} and the out-of-plane vibration at 871 cm^{-1} [14].

The FTIR spectrum of clinoptilolite (NZM) is presented in Fig. 7(b). The fact that zeolites are significantly hydrated is illustrated by the discrete water absorption by the O–H stretching bands in the 3,600 and 1,600 cm^{-1} region. Other bands that appear near the 1,020 cm^{-1} band arise from the asymmetric stretching vibration modes of internal Al(Si)–O bonds in AlO_4 tetrahedra (Al and Si). The 790 cm^{-1} bands are assigned to the stretching vibration modes of O–Al (Si)–O groups and the bending vibration modes of Al (Si)–O bonds, respectively [38,39].

Compared to FTIR spectrum of initial zeolite, the FTIR spectrum of zeolite after adsorption of nitrate ions was similar to initial zeolite; this was due to the small content of nitrate ions in zeolite. So, the peaks of the nitrate ions were masked by those from zeolite.

3.7. XRD analysis

Clinoptilolite was the major crystalline phase detected on the x-ray diffraction pattern of NZM, as shown in Fig. 8 (PDF 39-1383). According to PDF 39-1383, Mirşid Zeolite has a monoclinic structure, space group C2/m (12). The patterns acquired from clinoptilolite were found to be identical to that reported in literature [40]. The XRD pattern of the NZM showed a characteristic peak at 2θ = 20.27, corresponding to the $Ca(NO_3)_2$ (PDF 07-0204). According to Csicsery [41], the pore size of zeolites ranges from 4 to 10 Å, depending on the cations in the structures. The size of

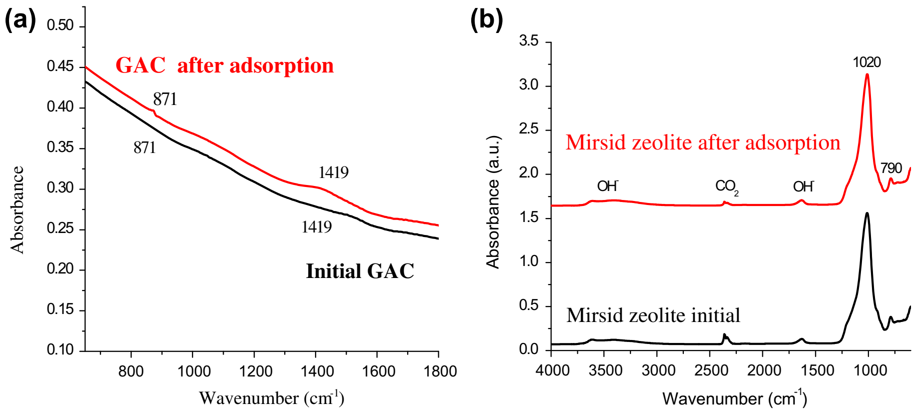

Fig. 7. FTIR-spectra of GAC (a) and NZM (b) before and after the groundwater adsorption treatment.

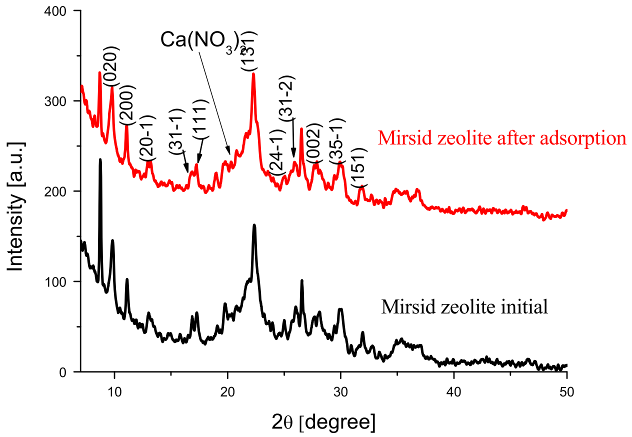

Fig. 8. X-ray powder diffraction patterns for initial NZM and after absorption.

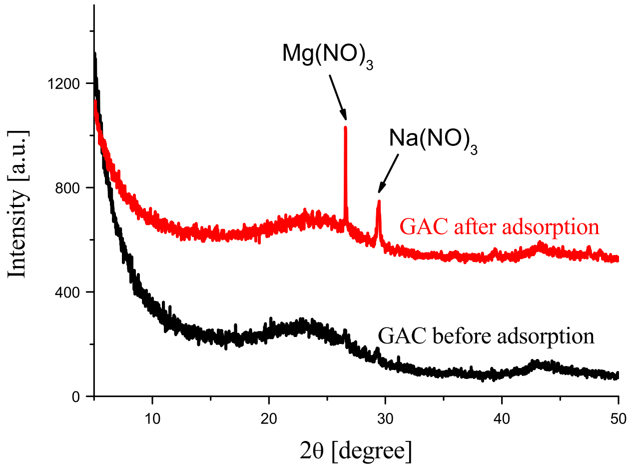

Fig. 9. X-ray powder diffraction patterns for initial GAC and after adsorption.

nitrate ions is around 3.3 Å [42] and they can enter into the zeolite network. As a consequence, the mechanism of nitrate retention could be explained by the size selectivity.

Fig. 9 shows the x-ray diffraction pattern for initial GAC and after treatment. It can be seen that, for the XRD pattern of initial GAC only two halous are present which are characteristic for amorphous samples. After absorption, some weak diffraction maxima appear. The peak at 29.47° belongs to $NaNO_3$ (PDF 89-2828) and peak at 2θ = 26.67° belongs to $Mg(NO_3)_2$ (PDF 19-0765), both of which are present in the sample after treatment [14].

4. Conclusion

In the present study, the potential usage of low-cost, natural adsorbents, GAC and NZM (clinoptilolite), was investigated by the adsorption method for removal of nitrate ions from groundwater with respect to different experimental parameters including mixing ratio, contact time, pH, and temperature. GAC has higher adsorption capacity for nitrate as compared to NZM.

The classical Langmuir and Freundlich adsorption isotherms were applied to evaluate the experimental data and it was found that the experimental data could fit the Freundlich isotherm better in the both cases (GAC and NZM).

Using the BET method, it was shown that the adsorption capacity and the volume of pores of both GAC and NZM decreased after adsorption. Specific surface area decreased from 728.81 to 609.48 m^2/g in the case of GAC and from 91 to 80.29 m^2/g in the case of NZM. FTIR spectra revealed that the GAC presents nitrate peaks, but in the case of NZM, there are not supplementary peaks. XRD studies showed that after adsorption, sharp peaks corresponding to natrium and magnesium nitrate appear in GAC diffraction patterns, while in the case of NZM, there is a small supplementary peak corresponding to calcium nitrate, at 20.27°.

The results of this study illustrate that the adsorption of nitrate performed by GAC and NZM showed that both GAC and NZM can be used for nitrate removal from groundwater of the Căpuş Cluj region.

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Nomenclature

BET — BET specific surface area, m/g
c_e — equilibrium concentration of NO_3^-, mg/L
c_i — initial concentration of NO_3^- in the groundwater, mg/L
EC — electrical conductivity, μS/cm
GAC — granular activated carbon
K_F — Freundlich constant, L/g
K_L — Langmuir constants, 1/mg
m — weight of the used GAC/NZM, g
MGL — maximum contaminant level goal
n — Freundlich constant
NZM — natural zeolite from Mirsid
q_e — NO_3^- adsorbed at equilibrium, mg of nitrate ion/g of adsorbed
Q_{max} — Langmuir constant, mg/g
R — gas constant, 8.314 J/ mol K
R_L — dimensionless equilibrium parameter
T — absolute temperature, K
ΔG^0 — Gibbs free energy
ν — initial volume of the groundwater, L

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