REMOVAL OF NITRATES AND AMMONIUM IONS FROM WATER USING NATURAL SORBENT ZEOLITE (CLINOPTILOLITE)

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Abstract. Experimental investigation of nitrogen compound (nitrates and ammonium ions) removal from water using natural zeolite was carried out in the laboratory of Water Management Department in VGTU. Shallow-well water samples were taken from a few place situated in Vilnius city and Vilnius district, nitrate concentration was enhanced adding Na NO_3 into the samples. Nitrate removal from water solutions was carried out under static conditions: solutions with nitrate concentration of 74–288 mg/l were mixed during one hour with 5 g of 0.315 mm particle-sized zeolite in an automatic mixer when mixing intensity was 100 min.$^{-1}$; after 30 min. sedimentation nitrate concentration was measured in all the samples. Ammonium ion removal from water solutions (made of shallow-well and tap water with NH_4Cl) was carried out under static and dynamic conditions (water solutions with 10–15 mg/l of ammonium ion concentration were filtered through 0.315–0.63 mm particle-sized filter medium).

Experimental results show that shallow-well water (with nitrate concentration of 74–288 mg/l), after one-hour mixing with 5 g of 0.315 mm particle-sized zeolite and after 30 min. sedimentation, nitrate concentration stayed the same without any reduction. The same shallow-well water (with 1–10 mg/l ammonium ion concentration) mixed with 5 g of 0.315–0.63 mm particle-sized zeolite showed ammonium ion removal efficiency of 72–86 %. For ammonium ion removal from tap water and NH_4Cl solution (primary concentration was 15 mg/l) under dynamic conditions, filtering through 400 mm high, 0.315–0.63 mm particle-sized zeolite filter medium, when filtration rate was 5 mg/l, NH_4^+ removal efficiency was 95–99.9 %. Ammonium ion removal from shallow-well water and NH_4Cl solution (primary concentration was 10 mg/l) under dynamic conditions, filtered through 95 mm high, 0.315–0.63 mm particle-sized zeolite filter medium, when filtration rate was 3 mg/l, NH_4^+ removal in filtered water samples decreased with exponential dependency. The obtained results show that zeolite particles are not suitable for nitrate sorption from water solutions, but 0.315–0.63 mm particle-sized zeolite can be a very useful sorbent for NH_4^+ removal from water because of the above mentioned reasons, therefore, further investigations are needed in this area.

Keywords: zeolite, clinoptilolite, nitrates, ammonium, sorption, filtration.

1. Introduction

Nowadays approximately one third of Lithuania's population (usually in rural areas) uses water sources from shallow wells where the water quality has become a crucial issue. Shallow excavated well water form shallow groundwater horizons and are less protected from surface pollution. This work shows the pollution of shallow-well water according to nitrates and organic matter, and to a lesser degree other substances (Rutkovienė *et al.* 2001; Aškinis, Strusevičius 1997; Klimas 2005; Juodkazis, Kučingis 1999). The Public Health Center data show that during 1986–1989 more than 40 % of analysed shallow wells were polluted by nitrates and microorganisms. During 1991–1996 LR Health Protection Ministry Survey provided research data show that near 50 % of samples are inadequate to requirements. Following existing data approximately half million of people in Lithuania use water with inadequate hygiene norm requirement quality

(HN 24:2003). In some regions of Lithuania this is especially in moraine loam areas – flat middle of Lithuania, north west (Akmenė–Mažeikiai section) and Suvalkija (Šakiai–Vilkaviškis–Marijampolė–Kalvarija section) – where nearly all of them have polluted shallow well water. The biggest part of polluted shallow wells is in the Eastern–Eastern/Southern part of Lithuania (Giedraitienė, Juodkazis 1999; Mičiudienė *et al.* 1995).

Nitrates and similar substances assimilating into organism can be provocative to methaemoglobinaemia, interrupt thyroid activities and cause cancer risk (nitrosamines). Nitrates are extremely dangerous to pregnant females, newborn babies and in the first months of babies (Gandolli *et al.* 1994; Jakučionytė *et al.* 2001).

Provided research results data (Rutkovienė *et al.* 2003) show that during warm seasons (spring, summer) a positive temperature of shallow wells results in conditions for ammonium nitrogen transformation into nitrates with nitrate concentration increase. When nitrite concen-

tration is higher than the limits (50 mg/l), other quality indicators, like ammonium concentration, increase simultaneously. Maximum pollution load of nitrates in shallow water wells occurs during spring, and the quantity of organic substances and ammonium increases during summer (Rutkovienė *et al.* 2003). Water treatment was not related to ammonium removal because of till 2003 the hygiene norm requirements of the biggest permissible level for ammonium concentration was four times higher (2 mg/l) compared with today's requirements (HN 24:2003). When requirements for drinking water quality became stricter, ammonium removal during water treatment became an up-to-date issue. One of possible methods to remove nitrogen compounds from water is sorption, i.e. by using natural cost-effective sorbents (zeolite, opoka, clinoptilolite).

Zeolites are crystalline hydrated aluminum silicates with a framework structure containing pores that are occupied by water and by alkali and alkaline earth cations. Due to their high cation-exchange ability as well as molecular sieve properties, natural zeolites (cheap materials, easily available in large quantities in many parts of the world) show special importance in water and gas purification, adsorption and catalysis (Inglezakis 2005). Zeolites have also an advantage over filter materials with significant permeability and are widely used for water purification by filtration (Sakalauskas, Valentukevičienė 2003; Brannvall *et al.* 2006). Clinoptilolite, a natural zeolite with the representative unit-cell formula $[AlSi_5O_{12}]_2(K_2,Na_2,Ca)(H_2O)_8$ seems to be the most attractive material for ammonium removal from drinking water and wastewater – due to its ammonium–ion selectivity and good performance in ammonium sorption under low temperatures (Inglezakis 2005; Sheta *et al.* 2003).

The ammonium cation–exchange capacity varies depending on the presence of other cations in the aqueous phase and initial ammonium concentrations (Sheta *et al.* 2003; Inglezakis *et al.* 2003). Amounts of NH_4^+ adsorbed by clinoptilolite increase with increasing initial concentration in an aqueous solution, and NH_4^+ adsorption and desorption by zeolite are particle–diffusion–controlled processes (Lebedynets *et al.* 2004). The pH level of an aqueous solution must be at or below 7 (Inglezakis 2005; Sprinskyy *et al.* 2005). Cation– exchange capacity of clinoptilolite tends to increase with the increasing relative content of alkaline metal cations and it is independent on alkaline earth cation content. The exchange efficiency is influenced significantly by chemical and physical pretreatment techniques and loading or regeneration of zeolite. Sodium chloride solution treatment seems to be the best method of clinoptilolite preparation and regeneration (Sheta *et al.* 2003; Inglezakis *et al.* 2003; Sprinskyy *et al.* 2005) even though the efficiency of ammonium removal increases with decreased zeolite particle size (Inglezakis 2005; Sprinskyy *et al.* 2005).

The aim of the present work is to investigate the features of nitrates and ammonium-ion sorption from shallow-well water and synthetic aqueous solutions by using natural zeolite Transcarpathian clinoptilolite under static and dynamic conditions.

2. Materials and methods

Clinoptilolite rock from the Sokyrnytsya deposit (the Transcarpathian region, the Ukraine) containing 70–75 % of clinoptilolite was used in this study. The zeolite (clinoptilolite) samples were ground in a metal mortar and divided into fractions (in mm) 0–0.315, 0.315–0.63 by mechanical sieves. Each fraction was washed with pure water to remove turbidity and was dried at a temperature of 105 °C. First fraction of zeolite (mesh size of 0.315 mm) was used for nitrate (NO_3^-) adsorption from a water solution under static conditions. During the experimental procedure natural shallow-well water was artificially polluted with known nitrate concentration water. Shallow-well water quality was evaluated and analyzsed from February 2006 till May 2006. The total number of analysed samples was 12 when nitrate concentrations, water conductivity (SEL) and pH were analysed. An artificially-polluted with $NaNO_3$ solution, shallow wells water was enriched by nitrate concentration. Standard solution dosing was selected for nitrate concentrations in the water: 50 mg/l, 100 mg/l, 150 mg/l and 200 mg/l. When natural shallow-well water was used, the obtained primary nitrate concentration was bigger in the samples. After the measurement of nitrate concentration, SEL and pH, 5 g of zeolite (0.315 mm mesh size) were added to each sample. Samples with the solution and zeolite were mixed by an automatic mixer for 1 h, 100 min.$^{-1}$. After mixing by an automatic mixer and 30 min. sorbent sedimentation of mixed solutions, the rest was filtered through Whatman No. 5 filter. Measurements were carried out with the following analyses: solution nitrate concentration, pH and SEL. Nitrate concentration was measured by using a spectrophotometer, completed by a *MERCK* nitrate test. Electric conductivity (SEL) was measured with a portable conductive meter *Cond 315i*. During the investigation pH data were measured by a *WTW pH 323* pH-meter.

Then a prepared zeolite fraction (0.315–0.63 mm) was used for ammonium (NH_4^+) adsorption from water solutions. Natural shallow-well water was used from Vilnius, Salininkai summer house site. Artificially-polluted water (NH_4Cl was added to natural water), with primary ammonium pollution: 1, 2, 5, 10 mg/l. Adsorption analyses were carried out from May 2006 to October 2006 under static and dynamic conditions. First case study solutions (volume 500 ml) with 5 g zeolite were mixed with a laboratory mixer for 1 h, 100 min^{-1}. When mixing was finished, a 30 min sedimentation procedure was provided. After filtration through a paper filter Whathman No 5, ammonium concentration was measured. Ammonium (NH_4^+) concentration in water was measured by a spectrophotometer, using the MERCK ammonium test.

When ammonium was removed from the water solutions under dynamic conditions, a laboratory pilot-scaled filter model was used, including a water reservoir (50 l volume); a filter column (height 500 mm, diameter 34 mm), with 0.315–0.63 mm mesh-size zeolite filter medium. Preliminary investigation was carried out during May–June 2006 when filter medium height was 400 mm

of zeolite. The weight of dried-zeolite-filter medium was 410 g, ammonium concentration in the water solution was approximately 15 mg/l; then the filtration rate was estimated as being approximately equal to 5 m/h. Further investigation was carried out (August–October) by using a 100 mm heigh zeolite-filter medium. The weight of this filter medium was 100 g, primary ammonium concentration was approximately 10 mg/l, and the filtration rate estimated was 3 m/h. Ammonium concentration, pH data of solution into reservoir and filtrated water was measured by applying the following methods by using the above equipment.

3. Experimental results

The water quality data of shallow water wells situated in Nemenčinė settlement of Vilnius district is provided in Table 1.

Table 1. Water quality data of investigated wells

Sampling day	NO_3, mg/l	Air temperature, t °C	SEL, µS/cm	pH
6 Feb.2006	84.40	−17.22	1324	7.44
13 Feb. 2006	84.66	−11.33	1328	7.42
20 Feb. 2006	87.56	−0.78	1359	7.41
27 Feb. 2006	88.10	−9.67	1365	7.45
6 Mar. 2006	88.91	−6.44	1366	7.42
20 Mar. 2006	93.40	−3.76	1375	7.53
27 Mar. 2006	89.00	+0.33	1366	7.14
3 Apr. 2006	8.03	+4.67	1276	7.20
10 Apr. 2006	76.23	+6.22	1207	7.03
24 Apr. 2006	49.59	+9.11	916	6.61
2 May 2006	55.80	+11.67	917	7.03
9 May 2006	44.73	+12.11	877	7.48

Nitrate concentration, electric conductivity and pH of all the water samples were measured five times, and the statistically estimated data are provided in the investigation results. Nitrate concentration in water from the investigated wells ranged between 44.73 and 93.40 mg/l, and 10 from 12 samples were found to exceed the legal limit of 50 mg/l. Some systematic changes of the water quality were obtained: nitrate concentration in well water was raised from 6 February 2006 because of organic compounds that had accumulated and decayed during summer. During the beginning of April 2006, when the temperature became positive, nitrate concentration decreased. This phenomenon can be explained because the plants used for vegetation nitrogen had been activated for vegetation purposes. It is also possible that a large amount of snow melted water (penetrated into this well) that was not polluted with nitrates has impact on concentration decreasing.

Electric conductivity (SEL) of the investigated water well changed in a way very similar to that of nitrate concentrations. Maximum SEL – 1375 µS/cm (200 Mar. 2006) is at the same maximum with nitrate concentration – 93.4 mg/l (20 Mar. 2006), and in the same way the minimum ranges were: SEL – 877 µS/cm (9 May 2006) and nitrate concentrations – 44.73 mg/l (9 May 2006).

The strong dependency of $R^2 = 0.984$ between nitrate concentration and electric conductivity following the equation $y = 11.629 \cdot x, + 328.14$ is provided in Fig. 1.
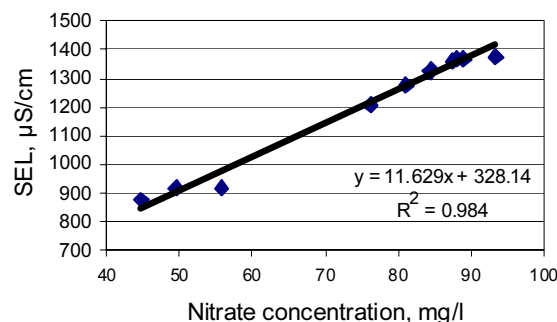

Fig. 1. Dependency of SEL on nitrate concentration

Our investigation results show that SEL data can be helpful in evaluating possible nitrate concentration in well water under the same conditions.

The analysed water pH data were similar to those from usual natural water sources, and slightly alkali pH > 7. Some changes between 6.61 to 7.53 were not dependent on the analysed water nitrate concentrations and SEL.

The aim of the next part of our investigation was to study possibilities of nitrate concentration reduction by using powdered zeolite. The investigated well water solution with artificially added $NaNO_3$ statistically evaluated data (before mixing and after mixing with added powdered zeolite) are shown in Table 2.

Table 2. Adsorption measurement data

No.	NO_3^-, mg/l		SEL, µS/cm		pH	
	Before adding zeolite	After mixing with zeolite	Before adding zeolite	After	Before	After
1	74.31	70.23	980	998	7.2	7.6
2	128.61	129.16	1073	1086	7.2	7.7
3	177.79	187.26	1161	1185	7.3	7.7
4	228.02	216.19	1253	1272	7.3	7.7
5	287.46	280.36	1346	1361	7.3	7.6

After mixing of water with zeolite and sedimentation, raised pH and SEL of solutions can be explained, that zeolite contains a large amount of calcium and magnesium carbonates ($CaCO_3$, $MgCO_3$) with hydrolyze possibilities into water.

Nitrate concentration range, when using powdered zeolite, is shown in Fig. 2.

The investigation results show a low (approximately of 5 %) nitrate reduction from the first, fourth and fifth samples, but nitrate concentration rose in two samples. Repeated experiments show that the used zeolite fraction cannot be used for nitrate removal.
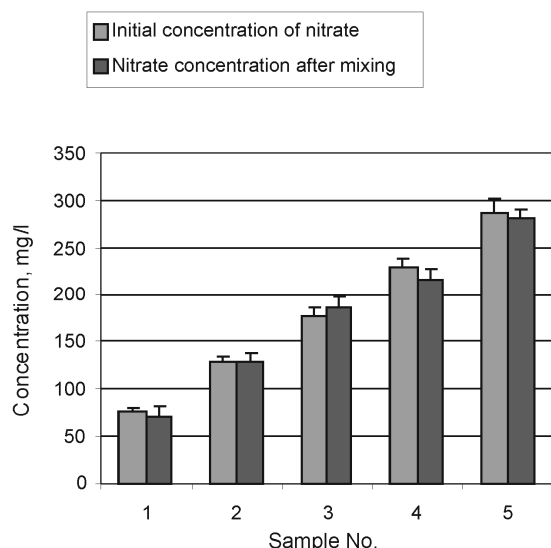
Fig. 2. Variation range of nitrate concentrations

The next step in the investigation was aimed at ammonium removal from water. Ammonium concentration is limited in drinking water to 0.5 mg/l [HN]. Primary NH^+_4 solutions were prepared from supplied tap water and artificially polluted by NH_4Cl. Primary solutions were prepared, when ammonium concentrations were approximately 5, 10 and 15 mg/l, and mixed with 0.315–0.63 mm mesh-size zeolite fraction. From 16 Oct. 2006 till 19 Oct. 2006 the investigation was continued by using natural shallow-well water. Well water had ammonium concentration of 0.1 mg/l, SEL – 668 µS/cm, pH – 7.25, t – 15.2 °C. When the solution of well water and NH_4Cl was prepared with 10, 5, 2, 1 mg/l of ammonium concentration (each with a volume of 500 ml), 5 g of zeolite were added (0.35–0.6 mm particle size) and a 1 h mixing procedure was applied in the laboratory mixer 120 min^{-1}. When each mixing and sedimentation procedure was 0.5 h, SEL and pH and measurements of NH_4^+ concentration were carried out. The same measurements were repeated after two hours. The results are shown in Table 3.

Statistically estimated measurement data are shown in the table above. Our investigation results show a decrease of concentration in all the samples. Zeolite particles were adsorbed by NH^+_4 with the best efficiency from a sample that had the minimum primary ammonium concentration of 5.1 mg/l.

Ammonium concentration was decreased by approximately 4.15 mg/l in the first sample, when the removal efficiency was approximately 81 %. Two samples had a lower NH^+_4 removal efficiency because the primary concentrations were higher. The zeolite (mesh size of 0.315–0.63 mm) quantity of 1 g removes approximately 0.4–0.6 mg of ammonia, and the zeolite sorption capacity for ammonium in this study was approximately equal to 0.5 mg/g. The pH was not influenced during the experiment because of a small rate of increase in all the samples (approximately 7.1–7.2 before mixing with zeolite, and 7.4–7.6 after mixing). Solution pH increases after mixing with zeolite because calcium and magnesium carbonate compounds hydrolyze.

Table 3. Results of NH^+_4 removals from water under static conditions

Samples	NH_4^+, mg/l	pH	SEL, µS/cm	Removal efficiency, %
Tap water and NH₄Cl solutions				
Before mixing				
1	14.93	7.2	–	–
2	10.04	7.1	–	–
3	5.10	7.2	–	–
After mixing and 0.5 h sedimentation				
1	9.13	7.7	–	38.84
2	3.89	7.6	–	61.25
3	0.95	7.7	–	81.37
Well water and NH₄Cl solution				
Before mixing				
1	10.23	7.2	733	–
2	4.92	7.2	701	–
3	1.88	7.2	682	–
4	0.90	7.3	676	–
After mixing and 0.5 h sedimentation				
1	3.20	7.7	706	64.81
2	1.23	7.8	683	75.00
3	0.53	7.7	665	71.80
4	0.11	7.9	653	77.78
After 2 h sedimentation				
1	3.41	7.7	707	–
2	1.28	7.7	682	–
3	0.54	7.8	663	–
4	0.12	7.9	654	–

Well water and artificially NH_4Cl polluted solution pH increase after adding zeolite in the same manner as in the previous experiments. SEL data decrease because ammonium concentration decreases. Ammonium removal efficiency in the samples was 65–78 %. Measured data after 30 min. and 2 h mixing was slightly different, but ammonium adsorption was still the same. Following the investigation results, it was found that 5 g of zeolite could remove ammonium to a required limit of 0.5 mg/l in a water volume of 0.5 l, when primary concentration was 1.0–2.0 mg/l.

The next stage of experiments was carried out under dynamic conditions. Tap water and NH_4Cl were used for preparing 30 l of solution (primary ammonium concentration was approximately 15 mg/l), after filtration through a filtration column (the zeolite-filter medium height was 400 mm) with a filtration rate of 5 m/h. The results of ammonium removal from solutions, that were statistically estimated, are shown in Table 4.

According to the results in Table 4, all the 13 samples (taken every half of an hour) had primary ammonium concentrations from 15.00 to 15.16 mg/l. This deviation resulted from the influence of external factors. The precision of measurements with a spectrophotometer *GENESYS* is 0.5 %. Ammonium concentration of 0.53 mg/l after the first filtration was inadequate hygiene norm requirements for drinking water (HN 24:2003). After stabilization of 1 h filtration process, NH^+_4 concentration of filtered water was from 0.11 to 0.17 mg/l, i.e.

less than the required 0.5 mg/l concentration. The efficiency of NH_4^+ removal from water was 96.5–99.2 %.

Table 4. Results of NH_4^+ removal from water under dynamic conditions

Sampling time, h	NH_4^+, mg/l into reservoir	NH_4^+, mg/l filtrated water	Removal efficiency, %
9^{30}	15.00	--	-
10^{00}	15.11	0.53	96.5
10^{30}	15.13	0.13	99.1
11^{00}	15.05	0.15	99.0
11^{30}	15.12	0.17	98.9
12^{00}	15.04	0.11	99.2
12^{30}	15.00	0.16	98.9
13^{00}	15.11	0.12	99.2
13^{30}	15.16	0.13	99.1
14^{30}	15.14	0.14	99.1
15^{00}	15.05	0.15	99.0
15^{30}	15.13	0.14	99.1
16^{00}	15.00	0.13	99.1

The next stage of the investigation was carried out by using shallow-well water, when primary ammonium concentration was 0.1 mg/l, SEL – 668 µS/cm, pH – 7.25, t – 15.2 °C. Ammonium concentration was increased in the laboratory to 10 mg/l with added NH_4Cl. Solution data were measured: ammonium concentration – 10.05 mg/l, SEL – 737 µS/cm, pH – 7.7, t – 16.0 °C. The prepared solution was filtered through a filtration column (the zeolite-filter medium height of 95 mm) for 10 hours. Four times less amount of zeolite-filter medium (100 g instead of 410 g of the first experiment under dynamic conditions) was used to get an increased concentration of NH_4^+ in filtered water. Filtration rate was 3 m/h. The statistically estimated results of ammonium removal from solution are shown in Fig. 3.

Ammonium concentration of water before filtration and that of water filtered through a zeolite-filter medium were measured 11 times, and each sample was analysed three times.
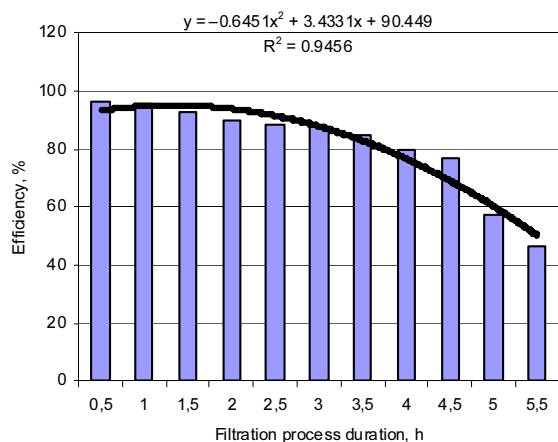

Fig. 3. Decrease of ammonium removal efficiency depending on filtration process

Following the results, the primary ammonium concentration remained the same, and NH_4^+ concentration of filtered water met the hygiene norm requirements only in the first two filtration hours. Ammonium removal efficiency was decreasing following polynomial dependency $y = -0.6451x^2 + 3.4331x + 90.449$, when $R = 0.9456$. After the 30 l of the prepared solution ended, ammonium concentration of the last filtrated-water sample filtered was 5.35 mg/l, when the efficiency was 47.5 %.

Comparison of experimental investigation results of two methods of NH_4^+ removal from water under dynamic conditions shows that zeolite-filter medium (0.315–0.63 mm mesh size) removes ammonium from water and can be used for drinking-water treatment. The optimum height needs to be found, depending on the primary NH_4^+ concentration.

However, such processes still need to be proved by more extensive studies, but the obtained investigation results could be applied as a basic scenario.

4. Conclusions

1. The investigated shallow wells (in Vilnius city and Vilnius district, Nemenčinė town) show that its water quality, following nitrate concentration, is over the limits of the hygiene norm of 50 mg/l in 10 from 12 samples.

2. Seasonal increase/decrease data were obtained for nitrogen compounds in well water. Nitrate concentration was increasing during autumn and winter seasons because of occurring organic matter decomposition processes.

3. The experiments show that the used zeolite fraction cannot be used for nitrate removal.

4. After one hour of mixing tap water and NH_4Cl, (when ammonium concentration was from 5 to 15 mg/l) by adding 5 g of 0.315–0.63 mm mesh-sized zeolite fraction, and after 30 min. of solution sedimentation, ammonium concentration was decreased from 81 to 39 %.

5. After one hour of mixing shallow-well water and NH_4Cl (when ammonium concentration was from 1 to 10 mg/l), by adding 5 g of 0.315–0.63 mm mesh-sized zeolite fraction, and after 30 min. of solution sedimentation, the ammonium removal efficiency was 65–78 %.

6. Ammonium removal from solutions of supplied tap water and NH_4Cl (when primary concentration was 15 mg/l) under dynamic conditions, filtered through 400 mm heigh, 0.315–0.63 mm mesh-sized zeolite-filter medium, when filtration rate was 5 m/h, NH_4^+ removal efficiency reached 95–99 %. Ammonium removal from solutions of shallow-well water and NH_4Cl (when primary concentration was 10 mg/l) filtered through 95 mm height at filtration rate of 3 m/h, NH_4^+ removal efficiency reached approximately 96 %.

7. The obtained results show that 0.315–0.63 mm mesh-sized zeolite fraction can be useful as an adequate sorbent for NH_4^+ removal from water.

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NATŪRALIOJO SORBENTO CEOLITO (KLINOPTILOLITO) NAUDOJIMAS NITRATAMS IR AMONIO JONAMS ŠALINTI IŠ VANDENS

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S a n t r a u k a

VGTU Vandentvarkos katedros laboratorijoje vykdyti eksperimentiniai azoto junginių (nitratų bei amonio jonų) šalinimo iš vandens, naudojant gamtinius ceolitus, tyrimai. Iš kelių Vilniaus mieste ir rajone esančių šachtinių šulinių paimti vandens mėginiai. Nitratų koncentracijos juose padidėjo pridėjus $NaNO_3$. Nitratai šalinti iš vandeninių tirpalų statiniu būdu, tirpalus (kuriuose nitratų koncentracija siekė 74–288 mg/l) 1 h maišant su 5 g 0,315 mm stambumo ceolito grūdelių frakcija automatinėje maišyklėje 100 aps./min intensyvumu ir po 30 min nusodinimo išmatuojant juose nitratų koncentraciją. Amonio jonų šalinimas iš vandeninių tirpalų (kurie buvo pasigaminti iš šachtinio šulinio ir vandentiekio vandens pridedant NH_4Cl atliktas statiniu ir dinaminiu būdu (filtruojant vandens tirpalus, kuriuose amonio jonų koncentracijos siekė 10–15 mg/l, per 0,315–0,63 mm ceolito grūdelių užpildo sluoksnį).

Eksperimentų rezultatai parodė, kad, maišant šachtinio šulinio vandenį (kuriame nitratų koncentracijos buvo 74–288 mg/l) vieną valandą su 5 g 0,315 mm grūdelių stambumo ceolito frakcija, po 30 min tirpalams nusistovėjus, nustatyta, kad nitratų koncentracija juose nesumažėjo. Tokiu pat būdu maišant šachtinio šulinio vandenį (kuriame amonio jonų koncentracijos buvo 1–10 mg/l) su 5 g 0,315–0,63 mm grūdelių stambumo ceolito frakcija, nustatyta, kad amonio jonų šalinimo efektyvumas mėginiuose siekė 72–86 %. Šalinant amonio jonus iš vandentiekio vandens ir NH_4Cl tirpalo (pradinė koncentracija 15 mg/l) dinaminiu būdu, filtruojant per 400 mm aukščio 0,315–0,63 mm stambumo ceolito grūdelių užpildą 5 m/h greičiu, NH_4^+ šalinimo efektyvumas siekė 95–99,9 %. Šalinant amonio jonus iš šachtinio šulinio vandens ir NH_4Cl tirpalo (pradinė koncentracija 10 mg/l) dinaminiu būdu, filtruojant per 95 mm aukščio 0,315–0,63 mm stambumo ceolito grūdelių užpildą 3 m/h greičiu, NH_4^+ koncentracija filtrato mėginiuose mažėjo pagal eksponentinę priklausomybę. Gauti rezultatai parodė, kad ceolito grūdeliai netinka nitratų sorbcijai iš vandeninių tirpalų, bet 0,315–0,63 mm stambumo ceolito grūdelių frakcija galėtų būti ypač tinkamas sorbentas NH_4^+ šalinti iš vandens, todėl būtų tikslinga atlikti daugiau tyrimų šioje srityje.

Reikšminiai žodžiai: ceolitas, klinoptilolitas, nitratai, amonis, sorbcija, filtravimas.

ПРИМЕНЕНИЕ НАТУРАЛЬНОГО СОРБЕНТА ЦЕОЛИТА (КЛИНОПТИЛОЛИТА) ДЛЯ ОЧИСТКИ ВОДЫ ОТ НИТРАТОВ И АММОНИЯ

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Р е з ю м е

Экспериментальные исследования очистки воды от азотосодержащих соединений (нитратов и аммония) с применением природного цеолита были проведены в лаборатории кафедры водоснабжения Вильнюсского технического университета им. Гедиминаса. Для этой цели использовалась вода из нескольких шахтных колодцев, находящихся в г. Вильнюсе и его районе, концентрация нитратов была увеличена, дозируя $NaNO_3$. Очистка водных растворов от нитратов производилась статическим методом, растворы (концентрация нитратов составляла 74–288 мг/л) в течение часа смешивали с 5 г цеолита (фракция – до 0,315 мм) автоматической мешалкой при интенсивности 100 об/мин. После 30 мин отстаивания определялась концентрация нитратов. Очистка от аммония водных растворов, полученных из воды шахтных колодцев и водопроводной воды с добавлением NH_4Cl, производилась статическим и динамическим методами (водные растворы, в которых концентрация аммония достигала 10–15 мг/л, фильтрировались через загрузочный материал из цеолита с фракцией 0,315–0,63 мм).

Результаты эксперимента показали, что концентрация нитратов в растворах не уменьшилась, когда воду из шахтных колодцев, в которых концентрация нитратов достигала 74–288 мг/л, смешивали в течение часа с 5 г цеолита, фракция которого составляла 0,315 мм, и отстаивали в течение 30 мин. При смешивании воды из шахтного колодца, в котором концентрация аммония достигала 10–15 мг/л, с 5 г цеолита, фракция которого составляла 0,315–0,63 мм, эффективность очистки от аммония достигала 72–86 %. При очистке водопроводной воды с раствором NH_4Cl от аммония, концентрация которого составляла 15 мг/л, в динамических условиях, фильтруя через загрузочный материал высотой в 400 мм и фракцией 0,315–0,63 мм со скоростью 5 м/ч, эффективность очистки достигала 95–99,9 %. При очистке воды из шахтных колодцев с раствором NH_4Cl от аммония (концентрация составляла 10 мг/л) в динамических условиях, фильтруя через загрузочный материал высотой в 95 мм со скоростью 3 м/ч, концентрация NH_4^+ в фильтрате уменьшалась с закономерностью экспонентной функции. Полученные результаты показали, что загрузка цеолита не способствует сорбции нитратов из водных растворов, в то время как цеолит с фракцией в 0,315–0,63 мм может быть приемлемым сорбентом для очистки воды от NH_4^+, поэтому целесообразно проведение дополнительных исследований.

Ключевые слова: цеолит, клиноптилолит, нитраты, аммоний, сорбция, фильтрирование.

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