THE USE OF A ZEOLITE FILTER MEDIA FOR THE REMOVAL OF AMMONIUM IONS FROM WASTEWATER BY FILTRATION

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Abstract. Experimental investigation of ammonium ions removal from artificially polluted wastewater using natural zeolite was carried out on pilot scaled filter at Water Management Department laboratory, Vilnius Gediminas Technical University. The purpose of this study was to test whether different fractions of zeolite that were obtained naturally (Sokyrnytskaya clinoptilolite, Ukraine) could influence either the removal of ammonium from wastewater and/or has possible uses as a filter media. For this study’s purpose, zeolite filter media was used as a natural sorbent for testing in a laboratory filter column of wastewater that was enriched with NH₄Cl and had substantial amounts of ammonium. This research demonstrated that different granulated natural zeolite particle sizes, promoted the significant removal of ammonium ions from artificially polluted wastewater.

Key words: zeolite, clinoptilolite, ammonium, sorption, filtration.

1. Introduction

Having joined the EU, Lithuania must follow EU legal requirements related to the protection of waters. Community policy concerning dangerous substances in European waters was introduced with the Council Directive on pollution caused by discharges of certain dangerous substances (Directive 76/464/EEC). The scope of the directive involves inland waters, internal coastal waters, territorial and ground waters. This directive established two lists of dangerous substances. List I contains certain individual substances which belong to the following families and groups of substances, selected mainly on the basis of their toxicity, persistence and bioaccumulation. List II includes other substances and categories of substances having deleterious effects on the aquatic environment, which can be confined to a given area and which depend on the characteristics and location of the water into which they are discharged [1]. List II also includes substances which have an adverse effect on the oxygen balance, particularly: ammonia, nitrates. Requirements of this legislative act are established in Lithuanian Minister’s of the Environment orders: “On the Approval of Wastewater Treatment Regulation” (17/05/2006, No. D1-236 and 8/10/2007, No. D1-515) [2], “On the Approval of Rules of Reducing Water Pollution with Dangerous Substances” (21/12/2001, No. 624), “On the Approval of the Description of Protection Requirements for Surface Water Bodies Were Freshwater Fish Can Live and Breed” (21/12/2005, No. D1-633). The mentioned legislative acts establish limit values of substances having a deleterious effect on the aquatic environment. When discharging wastewater to surface water bodies the maximum allowable concentration (MAC) of ammonium nitrogen in it may not exceed 5 mg/L [2]. The limit value of water quality indicator for surface water bodies were freshwater fish can live and breed (according to NH₄) is ≤ 1 mg/L (the same for salmon and carp ponds) [1].

According to statistics, around 1,000 tons of ammonium ions and salts enter Lithuania’s surface waters together with wastewater every year [3]. For example, 1.3 mln. m³ of untreated and 133.6 mln. m³ of inadequately treated household, municipal and industrial wastewaters were discharged into Lithuanian surface waters in 2002. 48.9 million m³ of surface (rainwater) wastewater, of which only 8% were treated to meet the standards of the maximum allowable pollution (MAP), also entered these water bodies [3]. In the domestic wastewater without treatment (with pH equal to 7.0-8.5) mineral nitrogen (ammonia and ammonium nitrogen) accounts for around 75% of the total nitrogen. Ammonium nitrogen accounts for 95% of mineral nitrogen [4]. As a rule, ammonium forms during decomposition of organic substances that contain nitrogen, and the amount of ammonium ions
(NH$_4^+$) increases at the presence of fresh faecal pollution. In the medium rich in oxygen nearly all ammonium is transformed into nitrates:

$$\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{H}_2\text{O} + 2\text{H}^+ + \text{NO}_3^- \quad (1)$$

Ammonium oxidation is a complex biochemical process, which is regulated and governed by certain groups of microorganisms. Due to the oxidation of ammonium and organic substances, first of all the amount of oxygen decreases in water polluted with organic substances and further oxygen may be taken from nitrates, i.e. the reduction of oxygen is replaced with the reduction of nitrates.

All these processes are important when wishing to remove nitric compounds from wastewater because upon entering the environment they cause the eutrophication processes of water bodies. Presently, the known methods of nitric compounds removal from wastewater are biological and chemical methods. Recently, attempts have been made to improve the operation of wastewater treatment plants by improving them and implementing full biological treatment (with an additional nitrogen and phosphorus removal). The biological technique is not always efficient because of the changing environmental conditions, while the chemical one requires big investment [5, 6]. Natural sorbents are recommended for the treatment of natural water and wastewater in scientific literature [7, 8, 9, 10]. The zeolite filter media can be recommended for NH$_4^+$ removal from wastewater. Previous investigations provided by Vilnius Gediminas Technical University (VGTU) Water Management Department’s scientists show that NH$_4^+$ can be removed from natural water by sorption using zeolite [11]. The removal of ammonium ions would prevent of nitrates formation into treated wastewater.

2. Object and techniques

Artificial wastewater for investigation was produced from chemically pure NH$_4$Cl and surface wastewater collected from the outlet pipe to the Vilnelė River by Užupis bridge in Vilnius city (shown in Fig. 1).

![Fig. 1. Surface wastewater outlet pipe to the Vilnelė River near Užupis bridge.](image)

The concentration of ammonium ions in the wastewater was increased by adding NH$_4$Cl, and in this way the solutions with the following concentrations of NH$_4^+$ (30 L or 60 L) were obtained: 100 mg/L (A), 50 mg/L (B), 20 mg/L (C). Wastewater for the investigation (30 L-60 L) was taken 6 times in November-December 2007 and transported to the VGTU Water Management Department’s laboratory where its temperature was measured, pH COD, SEC indicators as well as ammonium and nitrate concentrations. Ammonium (NH$_4^+$) and nitrate concentrations in the water were measured by spectrophotometer, using the MERCK ammonium and nitrate’s tests. During the research pH was measured by a WTW pH 323 pH – meter. The samples COD indicator was established using a reactor ECO 6 (VELP SCIENTIFICA), SEC indicator was measured with a conductivity meter Cond 315i. Subsequently, to obtain primary concentration of solution, the produced NH$_4$Cl solution was added to the wastewater.

A filter model was equipped at the Water Management Department’s chemical laboratory. It consisted of: a water reservoir (a plastic tank of 100 L), a pump supplying solution to filter column, (860 mm high, and diameter 40 mm), with 200 or 400 g zeolite filter media. Filter model’s photo is given in Figure 2.

![Fig. 2. Filter model: 1- water reservoir; 2-filter column; 3-zeolite filter media; 4-supportive layer; 5- filtration rate control valve; 6- sampling tap; 7-pump; 8-mixing valve](image)

To remove NH$_4^+$ from artificially polluted wastewater, 1.5-2.0 mm particle size natural zeolite
(selected on calibrated sieves) were used during the experiment. Zeolite rock from the Sokyrnytskaya deposit (the Transcarpathian region, Ukraine) containing 70-75 % of clinoptilolite was used in this study. The particles of natural zeolite were rinsed with distillate water and dried at 105 °C.

During the experiment, the steady filtration rate of 5 m/h, 7 m/h and 15 m/h were controlled. Samples from the primary solution and filtered water were taken at least every 30 minutes. The concentration of ammonium ions in them was measured.

3. Experimental results and discussion

Laboratory studies of surface wastewater samples (6) showed the following average indicators: NH₄⁺ concentration – 0.4 mg/L; NO₃⁻ concentration – 30.5 mg/L; pH – 7.5; temperature – 8.9 °C, COD – 35.1 mg O₂/L, SEC – 465 µS/cm (at 14.8 °C temperature). These results show that wastewater contains a small amount of ammonium ions but 30.5 mg/L concentration of nitrates. This can be explained by a comparatively small concentration of organic substances (a low indicator of COD) and the process of ammonium ion oxidation in the oxygen saturated medium.

After evaluating the obtained results further investigation was carried out in the laboratory using natural zeolite for the removal of ammonium ions from water solutions (wastewater with increased NH₄⁺ concentrations) by filtration. Upon adding NH₄Cl to surface wastewater for obtaining 100 mg/L NH₄⁺ concentration, SEC (specific electrical conductivity) in it increased to 1201 µS/cm (at 15 °C temperature). The results of ammonium ions removal from solutions are given in Figures 3-7.

![Fig. 3. Dependence of ammonium ion removal efficiency on filtration duration when solution A was filtered through 200 g zeolite filter media](image)

Data given in Fig. 3 show that when solution A (with the primary concentration of ammonium ions of 100 mg/L) was filtered through the zeolite filter media at 15 m/h filtration rate, at the beginning the efficiency of ammonium ions removal from solution was approximately 46%, and when filtering at the filtration rate of 7 m/h – approximately 65%. After 5 L of solution A were filtered through zeolite filter media, the efficiency of ammonium ions removal decreased till 31% and 45%, respectively. The change of ammonium ions concentrations in filtrates occurred according to logarithmic dependences as shown in Figure 4.

![Fig. 4. Change of ammonium ions concentration in the filtered water A when the filtration rate was 7 and 15 m/h](image)

As results given in Figures 3 and 4 show, the efficiency of NH₄⁺ removal from solution A is not sufficient when the solution is filtrated through 200 g 1.5-2.0 mm zeolite filter media at the filtration rate of 7 and 15 m/h. The selected size of filter media particle size is not sufficient to remove ammonium ions from the solution up to the MAC standards for the discharged wastewater (MAC for wastewater discharge to a wastewater collection system is 5 mg/L, and for discharge to the natural environment – 1 mg/L).

Further are presented the results of ammonium ions removal from solutions with lower primary concentrations, lower filtration rate or bigger amount of zeolite filter media.

Figure 5 presents the results of ammonium ions removal from solutions of different primary concentrations (100 and 50 mg/L), when the filtration rate is 7 m/h. When filtering solution B, was approximately 15 mg/L concentration of ammonium ions was recorded only during the first 10 minutes and subsequently it increased. As the Figure and Tables 3-4 show, the efficiency of ammonium ions removal after filtering 25 L of solutions (in filtered water) decreased from 65% to 22% (in the case of solution A) and from 69% to 18% (in the case of solution B). Consequently, the removal of ammonium ions is inefficient when the solution with the primary 50 mg/L concentration of ammonium ions is filtered through 200 g of 1.5-2.0 mm particle size zeolite at filtration rate of 7 m/h.
Fig. 5. Dependency of ammonium ions concentration in the filtered water of solutions A and B at the filtration rate of 7 m/h

Figure 6 presents the results of filtering the solution C (with the initial 20 mg/L concentration) through the zeolite filter media of different weight. The concentrations of ammonium ions in filtrates change according to the polynomial dependence $y = -0.0229x^2 + 0.8739x + 4.8974$ ($R^2 = 0.99$) when the solution is filtrated through the 200 g zeolite filter media, and according to the polynomial dependence $y = -0.0056x^2 + 0.3837x + 0.4505$ ($R^2 = 0.98$), when the solution is filtrated through the 400 g filter media (Fig. 6.).

Fig. 6. Dependency of ammonium ion concentration in filtered water of solution C at the filtration rate of 5 m/h through 200 and 400 g zeolite filter media

Research results show that after filtering 30 litres of solution (with the initial $NH_4^+$ concentration of 20 mg/L) through 200 g zeolite filler at the velocity of 5 m/h, filtrate contains $< 15$ mg/L concentration, which complies with the MAC when discharging wastewater to the collection system.

Figure 7 shows how $NH_4^+$ removal efficiency depends on the weight of zeolite filter media.

The obtained results were compared to previous research provided by VGTU Water Management Department’s scientists when smaller fractions of zeolite particles were used for the removal of ammonium ions from water solutions.

As the previous research shows [12], the filter media of zeolite particles of 0.315 – 0.630 mm efficiently removed $NH_4^+$ from aqueous solutions at the filtration velocity of 5 m/h and the initial $NH_4^+$ concentration of 15, 10 mg/L. The aim of this research was to remove ammonium ions from artificially polluted wastewater. The efficiency of $NH_4^+$ removal from artificially polluted wastewater was 96.5 – 99.9 %.
Table 1. Results of NH$_4^+$ removal from water under dynamic conditions

<table>
<thead>
<tr>
<th>Sampling time, h</th>
<th>NH$_4^+$, mg/l into reservoir</th>
<th>NH$_4^+$, mg/l filtered water</th>
<th>Removal effectiveness, %</th>
</tr>
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<tbody>
<tr>
<td>5$^{th}$</td>
<td>15.00</td>
<td>--</td>
<td>-</td>
</tr>
<tr>
<td>10$^{th}$</td>
<td>15.11</td>
<td>0.53</td>
<td>96.5</td>
</tr>
<tr>
<td>11$^{th}$</td>
<td>15.13</td>
<td>0.13</td>
<td>99.1</td>
</tr>
<tr>
<td>12$^{th}$</td>
<td>15.05</td>
<td>0.15</td>
<td>99.0</td>
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<tr>
<td>13$^{th}$</td>
<td>15.12</td>
<td>0.17</td>
<td>98.9</td>
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<td>12$^{th}$</td>
<td>15.04</td>
<td>0.11</td>
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<td>13$^{th}$</td>
<td>15.00</td>
<td>0.16</td>
<td>98.9</td>
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<td>14$^{th}$</td>
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<td>15$^{th}$</td>
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<td>15$^{th}$</td>
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<td>16$^{th}$</td>
<td>15.13</td>
<td>0.14</td>
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The second solution was made from the shallow well water in Salininkai garden plot, having the following parameters: ions concentration of 0.1 mg/L, SEC—668 µS/cm; pH – 7.25; t—15.2°C. After bringing the well water to the laboratory, the concentration of ammonium ions was increased till 10 mg/L by adding NH$_4$Cl. The obtained solution’s parameters: ammonium ions concentration— 10.05 mg/L, SEC—737 µS/cm, pH – 7.7, t—16.0°C. The prepared solution was filtrated through a filtering device (zeolite filler’s mass – 100 g) during 10 hours. A four times smaller amount of zeolite filler (100 g instead of 400 g during the first test under dynamic conditions) was used in order to have an increase in NH$_4^+$ concentration in the filtrated water. The filtration rate was 3 m/h. Average results of ammonium ions removal from solution are given in Figure 8.

Ammonium removal efficiency was decreasing following the polynomial dependency $y = -0.6451x^2 + 3.4331x + 90.449$, when $R=0.9456$. After all 30 L of the prepared solution were finished, the last filtrated water sample’s ammonium concentration was 5.35 mg/L, when effectiveness was 47.5 %. The comparison of results of two experiments of NH$_4^+$ removal from water by the dynamic technique obviously shows that a zeolite filter media (0.315-0.630 mm) removes ammonium ions from water and it can be used depending on the primary NH$_4^+$ concentration.

During subsequent experiments the comparison of the sorption of ammonium ions from aqueous solutions with different ionic strength was made at the filtration rate of 5 m/h via 0.6-1.5 mm zeolite filter media (solution 1 was produced from tap water and NH$_4$Cl, solution 2 – distilled water and NH$_4$Cl) and the primary concentration of ammonium ions of 2.0 mg/L. Water treated at Vilnius city Antaviliai water treatment plant was used for the experiment (solution 1). This water had the following most important quality indicators: pH ~ 7.6; SEC=514 µS/cm; Fe total~0.04 mg/L; NH$_4^+$~0.009 mg/L; Mn < 6 µg/L; Na ~ 13 mg/L; K~5 mg/L; dry residue ~ 306 mg/L. After the solution was prepared using this water with 2 mg/L concentration of ammonium ions (by adding standard NH$_4$Cl), its SEC indicator increased to 536 µS/cm (at 12.9 °C temperature). The second solution’s SEC indicator reached 22 µS/cm (at 19 °C temperature).

The results of this experiment are given in Figure 9. As the Figure 9 shows, during 6 hours of filtration the least change was recorded in the efficiency of NH$_4^+$ removal from the second solution (with distilled water), i.e. from 99.9 to 94.2 %. It is obvious that NH$_4^+$ removal

![Fig. 8. Ammonium removal efficiency decreasing depending on filtration run](image-url)
from solution made of tap water and NH₄Cl was not so efficient: 55-93%. Lower results were obtained when using tap water due to the fact that other positive ions contained in tap water also participated in ion exchange together ammonium ions.

Concluding the provided experiments it can be stated that the efficiency of ammonium ions removal from aqueous solutions depends on the zeolite particle size used for filter fillers, amount of filter media, filtration rate and other substances (impurities), the amount of ions contained in solutions and the conductivity (SEC indicator). It is obvious that finer fractions of zeolite grains (0.315-0.630 mm) remove NH₄+ from solutions more efficiently. To remove ammonium ions from wastewater to meet the MAC requirements, coarser fractions of zeolite (1.5-2.0 mm) can be used but it is necessary to select the affordable zeolite filter media amount considering the pollution of wastewater. The recommendation is to filtrate wastewater at the filtration rate of 5 m/h.

4. Conclusions

1. The results show that the efficiency of NH₄+ removal from solutions with the primary NH₄+ concentration of 100 and 50 mg/L is inadequate when solutions are filtrated through the 200 g filter media of zeolite particle media of 1.5-2.0 mm at the velocities of 7 and 15 m/h. The selected coarseness of particle size for the filter media is inadequate for the removal of ammonium ions from solutions in order to meet the MAC requirements to wastewater discharged to the natural environment or a wastewater collection system.

2. The results of subsequent experiments show that after filtrating 15 L of the same solution via 400 g weight zeolite filter media at the filtration rate of 5 m/h, the filtrated water contains < 5 mg/L concentration of NH₄+, which meets the MAC when discharging wastewater to the natural environment.

3. Therefore, the recommendation is to use the zeolite fraction of 1.5-2.0 mm for the removal of ammonium ions from wastewater at the filtration rate of 5 m/h. When removing ammonium ions from waste water it is necessary to evaluate the pollution of the wastewater and select the appropriate weight and zeolite particle size filter media.

References


