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REMOVAL OF AMMONIUM NITROGEN FROM WASTEWATER BY TERTIARY TREATMENT

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Abstract. Ammonium nitrogen present in treated wastewater effluent can cause eutrophication. Wastewater treatment plants do not always meet the strict requirements for the residual total nitrogen concentration – 10 mg/L in the treated wastewater. Additional wastewater treatment is recommended for higher nitrogen removal efficiency achievement. One of the ways to remove nitrogen compounds from wastewater is filtration through sorbents filter media. Zeolite is used to remove nitrogen compounds from water. Zeolite is known for its high surface area and high porosity. Zeolite adsorbs part of organic compounds and ammonium ions, so their concentration in the filtrate decreases. An ammonium nitrogen concentration was reduced by filtering wastewater through sorbents filter media during the experiment in real conditions. Concentrations of treated wastewater pollutants, filtration rate, efficiency of zeolite sorbent to remove ammonium nitrogen from the wastewater were measured and evaluated. Experiment results showed that ammonium nitrogen was effectively removed by zeolite sorbent (removal efficiency 66–99%), from wastewater by tertiary treatment.

Keywords: wastewater, removal of ammonium nitrogen, tertiary treatment, zeolite, adsorption.

Introduction

An excess of biogenic substances in natural water bodies causes eutrophication, during which the concentration of oxygen in the water decreases and the species composition of the biota of water bodies changes. The concentration of nitrogen compounds in water bodies is increased by the wastewater discharged into them, so wastewater treatment must be focused on the removal of biogenic substances (Pell & Wörman, 2011). Nitrogen concentration in wastewater is reduced by biological treatment, during the process of oxidizing ammonia into nitrites and nitrates, and then by denitrifying bacteria reducing nitrates into nitrogen gas (Radu & Racoviteanu, 2021). Biological treatment removes organic matter from wastewater with an efficiency of >90%, but the efficiency of nitrogen and phosphorus removal is often less than 80%. Inorganic nitrogen compounds that occur in wastewater after biological treatment are not only nitrate nitrogen, but also ammonium nitrogen (Šarko & Mažeikienė, 2022). Ammonium is an inorganic compound present in water at pH<9. Higher than allowed (1–2 mg/L) concentrations of ammonium nitrogen remain in wastewater when the nitrification process is not completed. Biological wastewater treatment can reduce the amount of nitrogen in domestic wastewater, but complete removal is not achieved by this method due to thermodynamic and kinetic limitations (Herrmann et al., 2014; Mažeikienė & Vaiškūnaitė, 2018). Concentrations of total nitrogen cannot be reduced to 90–100% by conventional wastewater treatment methods. Scientists are investigating the need for additional facilities when basic wastewater treatment does not achieve the required removal of biogenic materials (Battas et al., 2019; Gill et al., 2009). Various filters can be used as additional (tertiary) wastewater treatment facilities in which sorption or ion exchange processes take place (Abukhadra et al., 2020). Recently, researchers have been investigating the ability of different materials to sorb biogenic materials from wastewater: these materials are synthetic, natural, modified or waste materials that can be used as filter media (Cruz et al., 2018; Franchin et al., 2020; Kauppinen et al., 2014). Ammonium ion concentrations in water can be effectively reduced by filtering wastewater through zeolite material (Lin et al., 2013). Zeolites are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water and alkali metal cations. Due to their high cation exchange capacity and molecular sieving properties, natural zeolites are of particular importance for water and gas treatment, adsorption and catalysis (Inglezakis, 2005; Sun et al., 2022). The advantage of zeolites is that it is an inexpensive material that is readily

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available in large quantities in many countries around the world (Seruga et al., 2019). The exchange capacity of ammonium and cations depends on the presence of other cations in the wastewater and the initial concentration of ammonium. The process of ion exchange between the zeolite surface and the aqueous ammonium solution can be described by the equation:

$$\text{Ze-Mn}^{+} + \text{nNH}_4^{+} \leftrightarrow \text{Ze- nNH}_4^{+} + \text{Mn}^{+},$$

where Ze and mn represent the zeolite and free cations (depending on the zeolite), and n is the charge number. Exchangeable cations in zeolites are Ca^{2+}, Na^{+}, K^{+}, Mg^{2+} (Lin et al., 2013).

The sorption of zeolite (clinoptilolite – $[AlSi_5O_{12}]_2(K_2,Na_2,Ca)(H_2O)_8$) has been analysed in many laboratory studies, but there is a lack of data on how it is applied to real wastewater treatment in field conditions (Abukhadra et al., 2020). Most often, zeolites are used for water treatment, but treating wastewater is a more difficult task. Wastewater contains organic and suspended matter, also other ions that can interfere with the sorption of ammonium nitrogen. There is a lack of scientific literature on long-term sorption studies. The aim of this study is to reduce the concentration of ammonium nitrogen in biologically treated wastewater to 10 mg/L by applying filtration through zeolite filter media under field conditions. The results of the research will be useful for the development of new additional (tertiary) wastewater treatment facilities for the removal of biogenic substances from wastewater.

1. Materials and methods

1.1. System of wastewater treatment

The scheme of main and additional domestic wastewater treatment is shown in the Figure 1.

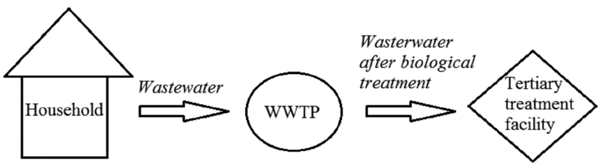

Figure 1. The wastewater treatment system

The wastewater treatment system, consisting of main wastewater treatment plant and tertiary treatment facility, was tested for 2 months during the summer of 2022. A low-flow main wastewater treatment plant (WWTP) with CE marking was chosen for the research. The WWTP's certificate states that organic and suspended solids are removed with 95–97% efficiency. The WWTP is installed underground next to an individual residential house, it is designed to treat 0.9 m^3/d of wastewater (6 PE). The WWTP is compact, its diameter is 1.4 m, and the height 2.2 m. The biologically treated wastewater enters a small pumping station, from which it is supplied by a submersible pump to a new tertiary treatment facility, which has a 30 cm high layer of zeolite filter media. Natural zeolite filler is used to remove ammonium nitrogen from biologically treated wastewater. Filling volume is 240 liters, fraction size 0.7–1.2 mm, weight 200 kg.

All wastewater flow from the main WWTP flows to the tertiary treatment facility, so it also has a flow rate of 0.9 m^3/d. During the day, the wastewater flow is distributed as follows: for 3 hours, biologically treated wastewater is supplied at a rate of 0.11 m/h (270 liters of wastewater flows); for 3 hours, biologically treated wastewater is supplied at a rate of 0.06 m/h (135 liters of wastewater flows); no wastewater flow for 6 hours; for 2 hours, biologically treated wastewater is supplied at a rate of 0.23 m/h (360 liters of wastewater flows); for 3 hours, biologically treated wastewater is supplied at a rate of 0.06 m/h (135 liters of wastewater flows); wastewater is not supplied for 7 hours. The tertiary wastewater treatment facility has the same working volume as the main wastewater treatment plant (1.5 m^3), so the wastewater remains in it for 1 day. The average residence time of wastewater (treated in the main treatment stage) in the filter media is 6.4 h.

The average residence time of wastewater in the filter media is calculated from the formula (1):

$$t = \frac{V}{\left(Q_d \div 24\right)}, \tag{1}$$

where: V is the volume of zeolite filter media, Q_d is the daily wastewater flow rate.

A geotextile is stretched over the zeolite filter media layer to trap potential particulates or suspended solids particles if they are carried out of the main wastewater treatment plant. Wastewater is filtered through the zeolite filter media as the liquid flows from top to bottom. After the tertiary wastewater treatment facility, the wastewater flows through a plastic pipe into the treated wastewater tank, from which it can be reused for irrigation or washing.

1.2. Chemical analysis of wastewater

Samples of treated wastewater (1 litre each) are taken from the outlet pipe of the main domestic wastewater treatment plant and from the outlet pipe of the tertiary sewage treatment plant once a week at the same time of day (around 3:30 p.m.), and their temperature is measured immediately. The samples are transported to the laboratory of the VILNIUS TECH Department of Environmental Protection and Water Engineering for analysis. In the laboratory, the samples are allowed to warm up to room temperature, then their pH, biochemical oxygen consumption (BOD_7), total suspended solids concentration (TSS), and ammonium nitrogen (NH_4-N) concentration are measured. Each sample is tested three times and the average values of the results are presented. The efficiency of pollutant removal is calculated from formula (2):

$$E_i = \frac{X_1 - X_2}{X_1} \times 100, \quad (2)$$

where: E_i – removal efficiency of the pollutant (%), X_1 – concentration of pollutant before treatment (mg/L); X_2 – concentration of pollutant after treatment (mg/L).

The wastewater temperature was measured with a SevenGo pro SG6 meter (Mettler Toledo, Switzerland). pH was determined potentiometrically LST EN ISO 10523:2012 (Lithuanian Department of Standardization, 2012), measuring with a WTW production pH-meter pH – 330i, Hamilton (Switzerland) and certified reference buffer solutions pH 7.00±0.01 and pH 9.21±0.02 was used for quality control of measurements. Biochemical oxygen demand in diluted wastewater was determined by the electrometric method, measuring with a WTW oximeter ino Lab OXI – 730 according to the methodology approved by LAND 47-1:2007 (Lietuvos…, 2007b). The concentration of suspended solids was assessed by the gravimetric method, filtering the wastewater through a glass fiber filter LAND 46-2007 (Lietuvos…, 2007a), weighed by a KERN (Germany) ABJ 220-4M type electronic laboratory scale. mERCK Spectroquant® tests were used to determine ammonium nitrogen concentration.

2. Results and discussion

During the entire research period, 57 m^3 of domestic wastewater was treated by the main and tertiary wastewater treatment facilities. Statistically processed data for the entire research period (2 months) are presented in Table 1.

From the data presented in Table 1, it can be seen that the pH of the wastewater is close to neutral and corresponds to the allowable value for wastewater released into nature (is in the range of 6.5–8.5). Wastewater pollution according to the BOD_7 parameter also meets the requirements and is ≤10 mg/L. During research period average concentration of BOD_7 before tertiary wastewater treatment was 6.7 mg/L, and after – 5.9 mg/L. Average concentration of TSS was ≤10 mg/L.

Table 1. Chemical analysis results of wastewater

Before tertiary treatment				
Indicator	pH	TSS, mg/l	BOD_7, mg/l	NH_4-N, mg/l
Average	7.61	5.9	6.7	11.5
Median	7.59	6.6	6.8	9.2
Standard deviation	0.22	1.5	2.2	6.9
Minimum value	7.30	2.5	2.0	5.6
Maximum value	7.97	6.9	10.0	25.1
Number of samples *n*	27			
After tertiary treatment				
Average	7.58	5.2	5.9	1.55
Median	7.47	5.9	6.2	2.22
Standard deviation	0.19	1.4	1.6	1.20
Minimum value	7.40	2.0	2.0	0.01
Maximum value	7.89	6.1	8.0	2.78
Number of samples *n*	27			

The Wastewater management Regulation of the Republic of Lithuania requires that for small biological wastewater treatment plants, the flow of which does not exceed 5 m^3 per day, the maximum allowable concentration norm for nitrogen compounds should be 25 mg/l. During research period average concentration of NH_4-N before tertiary wastewater treatment was 11.5 mg/L, and after – 1.55 mg/L, but maximum concentration of NH_4-N before tertiary treatment one week was 25.1 mg/L, so concentration of total nitrogen was even bigger.

During the research period, the concentration of ammonium nitrogen in the effluent from the main WWTP fluctuated. Fluctuation of pollutant concentrations in wastewater in low-flow (<5 m^3/d) treatment plants is common, as it depends greatly on the nature of economic activity, water consumption flow, and the use of chemical hygiene measures. The tertiary treatment facility reduced

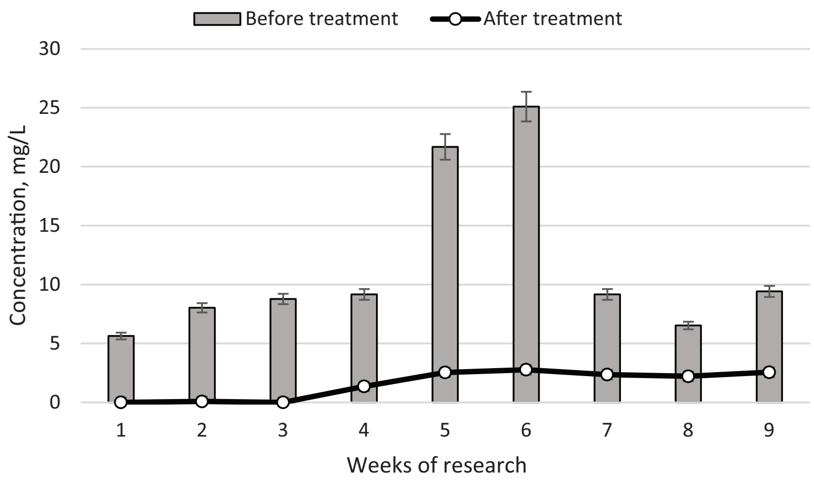

Figure 2. Variation of ammonium nitrogen concentrations before and after the tertiary wastewater treatment

ammonium nitrogen concentrations in the effluent, as can be seen in Figure 2.

Only 0.01–2.78 mg/L ammonium nitrogen concentration remained at the source of tertiary wastewater treatment, and the nitrogen removal efficiency reached 66–99% (Figure 3). Ammonium nitrogen removal efficiency decreased in week 7 because the initial N concentration in the wastewater decreased (Figure 2).

There is a weak correlation (coefficient of determination $R^2 = 0.33$) between the concentrations of ammonium nitrogen in the wastewater inflow and outflow from the tertiary wastewater treatment facility, as shown in Figure 4. Ammonium nitrogen concentrations fluctuated less at the outlet of the tertiary wastewater treatment facility than at the inflow. Over time, the efficiency of ammonium nitrogen removal from wastewater decreased (Figure 3).

Figure 5 shows the variation of wastewater pH and temperature in the wastewater entering and leaving the tertiary wastewater treatment facility during 9 weeks.

From the data in the Figure 5, it can be seen that the pH and temperature of the influent and the effluent were almost unchanged. It can be said that the zeolite filter media did not change the pH and temperature of the wastewater, but only reduced the concentration of ammonium nitrogen.

Ammonium nitrogen removal took place due to adsorption and ion exchange. Scientists Strusevičius, Gasiūnas, and Strusevičienė (2006) studied the removal of ammonium and nitrite nitrogen in constructed sand and plant filters by biological wastewater treatment. In their study, the effluent was distributed over the surface of the filter, gravitating through a 0.6–1.0 m thick layer of sand vertically down into collection pipes. During the research, it was found that the total nitrogen removal efficiency reached 24.4–38.1%, and the amount of ammonium nitrogen in the treated wastewater varied from 6 to 32 mg/1. Compared to this study, higher efficiency (66–99%) has now been achieved. Abukhadra et al. (2020) investigated

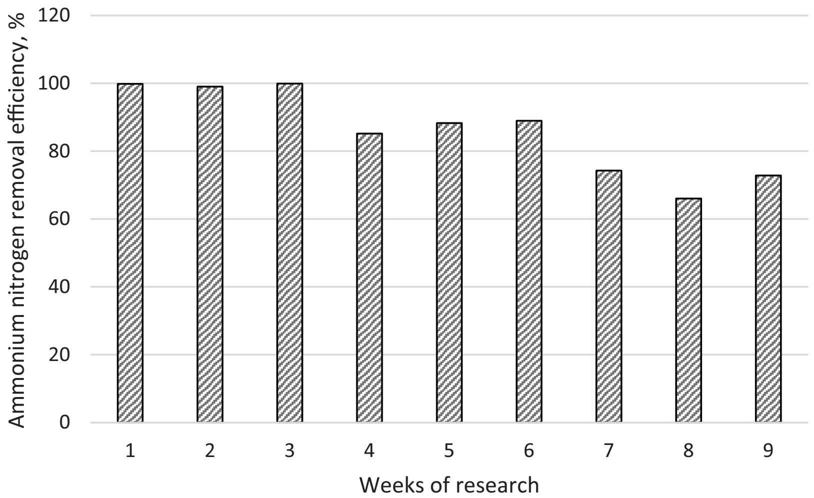

Figure 3. Efficiency of reduction of ammonium nitrogen concentration in the tertiary treatment facility

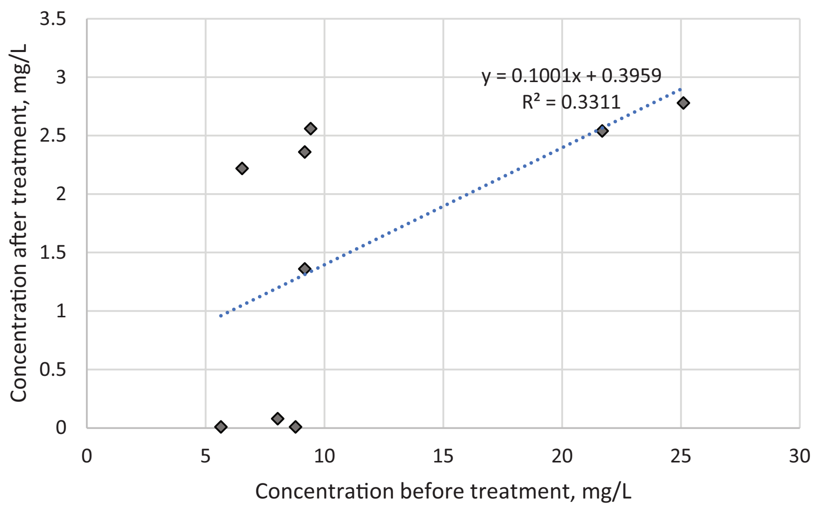

Figure 4. Dependence between ammonium nitrogen concentrations before and after the tertiary wastewater treatment

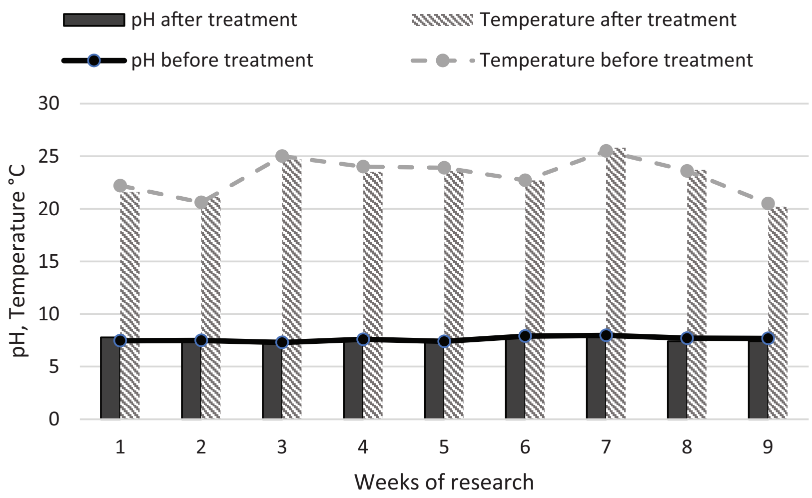

Figure 5. Temperature and pH in the wastewater entering and leaving the tertiary wastewater treatment facility

a synthesized bentonite/zeolite-P (BE/ZP) composite for wastewater and groundwater treatment. During the research, the important parameter was the pH value: the best results were achieved at pH = 6. Also, 150 mg/g sorption capacity and 74.5% ammonium removal efficiency were achieved (Abukhadra et al., 2020). Compared to the results of this article, the sorption capacity of the zeolite filler was not depleted within two months and an average efficiency of 86% was achieved. It should be noted that the synthesized composite of two types of silicates was characterized by higher porosity, larger surface area and higher ion exchange properties compared to separate zeolite materials (Canellas et al., 2019). Lin et al. (2013) noted that zeolites and porous aluminosilicate minerals have a strong attraction for ammonium in water. It should be noted that filters adsorbing ammonium ions can work for a longer time only when the concentrations of total suspended solids and organic matter in the wastewater before filtration are low (<10 mg/L), because suspended matter quickly clogs the filters (Mažeikienė & Šarko, 2022). The results of this research can be useful for the design of tertiary wastewater treatment facilities and the selection of sorbent materials.

Conclusions

During the research period (2 months), only 0.01–2.78 mg/L of ammonium nitrogen concentration remained in the wastewater after tertiary wastewater treatment.

Experiment results showed that ammonium nitrogen was effectively removed by natural zeolite (removal efficiency 66–99%), from wastewater by tertiary treatment, and an average removal efficiency of 86% was achieved.

The zeolite filter media did not change the pH and temperature of the wastewater.

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Contribution

Conceptualization, J.Š. and A.M.; data curation, J.Š. and A.M.; formal analysis, J.Š. and A.M.; investigation, J.Š. and A.M.; methodology, J.Š. and A.M.; resources, J.Š. and A.M.; supervision, J.Š. and A.M.; validation, J.Š. and A.M.; visualization, J.Š. and A.M.; writing–original draft preparation J.Š. and A.M.; writing–review and editing, J.Š. and A.M.

Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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