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EXPERIMENTAL STUDY OF TERTIARY TREATMENT OF WASTEWATER USING ZEOLITE

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Abstract. Small individual household wastewater treatment plants not always operate well. Consequently, the concentrations of ammonium nitrogen and phosphate phosphorus are exceeded. The aim of the work was to examine the zeolite as a wastewater tertiary treatment material and propose environmentally friendly ways to solve fresh water problem.
During experiment zeolite filter material was tested. In the article is analyzed zeolite filtering efficiency of nutrient removal from wastewater. Zeolite filler most effective was against ammonium nitrogen (99.9–10.1%) and relatively less effective against phosphate phosphorus (51.2–4.9%).

Keywords: tertiary treatment, wastewater, phosphorus and ammonium removal, zeolite.

Introduction

Degradation of water ecosystems is a major problem in most countries of the world. Industrial and agricultural manufacturing is responsible for a huge production of wastewater, which must be treated to prevent pollution of water ecosystems (Omernik, 1977; Schlesinger, 1991; Vitousek, Mooney, Lubchenko, & Melillo, 1997).

While the presence of aromatics and heavy metals in wastewater have adverse effects on the environment and living beings, the presence of excessive amounts of innocuous nutrients, such as nitrogen (N) and phosphorus (P), can also upset the balance of aquatic ecosystem through eutrophication. Eutrophication is a process of rapid plant/algae growth in natural water bodies due to nutrient overloading; this leads to oxygen depletion resulting in deterioration of water quality and endangering of aquatic life.

Conventional techniques for N and P removal from wastewater are based on physical and chemical methods. These techniques are not economical and do not facilitate nutrients recycle and reuse (Wu, Yang, & Lin, 2005).

Disposal of improper treated wastewater often pose risk to the environment and ecology. Using advanced technology to mitigate risk by refine wastewater treatment is a key issue in meeting legislative guidelines, e.g. EU Water Framework Directive. Municipal wastewater treatment typically comprises preliminary treatment, primary treatment and secondary treatment. Preliminary treatment includes a series of screens and grit removal to prepare wastewater for subsequent treatment. Primary treatment involves the separation of readily-removable suspended solids through gravity sedimentation. Following these two basic processes, wastewater is then subjected to secondary treatment in which biological and/or chemical processes are involved to remove dissolved constituents. The secondary treatment was previously considered as a complete process, with its effluent being discharged into the receiving environment after disinfection with chlorine gas. However, as environmental regulations are getting stringent and introduction of EU Water Framework Directive in 2000, secondary sewage effluent was no longer a guarantee for discharge. Advanced tertiary treatment is therefore, required for further decreasing the residual constituents in secondary sewage effluent (Choi, 2015; Praveen & Loh, 2015).

There also exist important researches, where activated carbon is used. However, activated carbon is less economically viable as an adsorbent due to the costly activation and regeneration of the spent carbon and disposal of regenerant wastes. As a result, over recent years there has been growing interest in using low-cost natural minerals for treating wastewater (Xu, Bernards, & Hu, 2014). In this article are analysed three types of filter materials, which can be used for wastewater tertiary treatment. Its aim was to determine which of them is the most effective this way.

Zeolites are crystalline hydrated alumino-silicates, which are known to have an affinity for ammonium (NH_4^+) and other cations (Pansini, 1996). Overseas studies have established that zeolites have the potential to remove NH_4^+ from municipal, industrial, and aquacultural wastewaters. The capacity of zeolites to remove NH_4^+ from wastewaters has been found to vary, depending on the type of zeolite used (e.g., mordenite, clinoptilolite, erionite, chabazite, and phillipsite), zeolite particle size, and wastewater anion-cation composition. This capacity is also governed by the extent of aluminium (Al_3^+) substitution for silicon (Si_4^+) in the zeolite framework. Each Si_4^+ substitution by Al_3^+ generates a negative charge. The greater the substitution, the higher the negative charge, and hence the greater the number of cations (e.g., NH_4^+) required for balancing the negative charge (Nguyen & Tanner, 2010).

2. Methods and materials

2.1. Wastewater samples and domestic wastewater treatment plant (WWTP)

In the work was applied one of Lithuania's most popular low-capacity domestic wastewater treatment plant (WWTP) – AT-6, which operating principle is based on the basis of the active sludge. The AT-6 cleaning unit is completed in one container. After flowing out from the plant, water is secondary treated.

2.2. Samples

Wastewater samples were taken from the AT-6 wastewater treatment plant (WWTP), which is located in Vilnius city (gardening community) next to the dwelling house. The device is operated by a family (four members) for four years. The design capacity of this unit is 0.54 m^3/d, the design load per day with organic pollutants is 0.24 kg/d. Purified wastewater is discharged into an infiltration well.

Investigations conducted on February 13, 2018 – May 15, 2018. The treated wastewater samples were taken from the outflow pipe of the AT-6 type, once a week at the same time of day (about 7:30 am) temperature was measured on place. Samples were transported to the VGTU laboratory of the Department of Environmental and Water Engineering. Wastewater samples were allowed to warm up to room temperature at the laboratory, then their pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), concentration of suspended matter (SM), nitrate nitrogen (NO_3-N), nitrite nitrogen (NO_2-N), ammonium nitrogen (NH_4-N) and orthophosphate phosphorus (PO_4-P) concentrations. Measurements are made by metrologically verified meters. Each sample was tested three times (I – after 40 minutes. II – after 1.5 hours, and III – after 4.40 hours of filtration).

Examination of sewage contamination was reduced by filtering through granular excipients. At VGTU laboratory of Environmental Protection and Water Engineering Department was installed filtrating columns stand (Figure 2.1).

Figure 2.1. Filtrating column stand

A composite sample was prepared from the treated wastewater, which was evenly distributed to the filtration columns. Throughout all fillers, the effluent was filtered at 0.7 m/h (1.1 l/h flow), the filtration rate was determined by the volumetric method. During the experiments, samples of the filtrate were taken from the filtrating column at the same time. The filtrated samples were measured following some same parameters as in the initial wastewater composite sample. The efficiency of the removal of pollutants is calculated according to the formula:

$$E(X)_i = \frac{x_{1,i} - x_{2,i}}{x_{1,i}} \cdot 100\%, \quad (2.1)$$

here: $E\ (X)_i$ – the efficiency of the respective pollutant, %; $X_{1,i}$ – concentration of the respective pollutant before treatment, mg/l; $X_{2,i}$ – the concentration of the respective pollutant after treatment, mg/l.

In the work were used following fillers (aggregates) to filter wastewater, which was taken from domestic wastewater treatment plant – AT- 6.

2.3. Zeolite

The zeolite was selected as is natural, ecological sorbent, passable treated water characteristics (Miladinovic & Weatherley, 2008; Mažeikienė, Valentukevičiene, Rimeika, Matuzevičius, & Dauknys, 2008).

Figure 2.2. *Zeolite granules*

Zeolite is a crystalline hydrated alumino-silicate with a framework structure containing pores occupied by water, alkali and alkaline earth cations. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites (being cheap materials, easily available in large quantities in many places of the world) show special importance in water and gas purification, adsorption and catalysis (Miladinovic & Weatherley, 2008).

The particle size of 0.6–2.0 mm (separated by calibrated sieves) of natural zeolite were used into this experimental research on removal of ammonium ions from wastewater (Figure 2.2). Clinoptilolite rock from the Sokyrnytskaya deposit (the Transcarpathian region, Ukraine) containing 70–75% clinoptilolite was used in this research. Natural zeolite granules were washed with distillated water for undesirable turbidity removal and dried into laboratory oven, 105 °C of temperature. The weight of the material was 442 g (0.5 l volume).

2.6. Phosphate determination

Laboratory samples were taken after filtration through zeolite filler. Samples were placed into the 50 ml marked glass flasks and were added the following reagents by us (Figure 2.3). Every flask was filled with filtered wastewater (1–20 ml). After 1 ml of ascorbic acid and 2 ml of ammonium molybdate solution (I) were added. Last step of the mixing was to fill the flask with distilled water up to 50 ml and put for 10–30 minutes at the room temperature (20–25 °C). After passing this time we used to put these mixed samples into the spectrophotometer (λ = 880) and measure concentration. The obtained result is applied in the formula:

$$\rho_p = \frac{(A - A_0) * V_{\max}}{f * V_s}, \quad (2.2)$$

where: ρ_p – phosphate phosphorus concentration, A – the absorbance value of the test portion, A_0 – the absorbance value of the blank sample. $V_{\max}$ – volume, to which disseminated test portion, ml. f – calibration curve inclination, mg/l. V_S – The volume of the test portion taken for analysis, ml.

Figure 2.3. Tested samples

2.7. Ammonium determination

During the process of ammonium determination, wastewater sample are places in the 50 ml volume flask. Basically, an amount of the wastewater sample was 1 ml. After putting of sample in the marked flaks, we used to add 39 ml of distilled water (to be filled 40 ml). Then, there were added 4 ml of colour reagent and mixed well. Second reagent is sodium dichloroisocyanurate solution and it was necessary to add 4 ml and mix well again. After all these procedures, we used to put the mixed samples at the room temperature (20–25 C) for 1 hour and then we used to make the last step of the practical work – measuring the concentration of the sample with spectrophotometer (λ = 660) and the obtained result is applied in the formula:

$$\rho_a = \frac{(A - A_0)}{f \cdot V_s}, \qquad (2.3)$$

where: ρ_a – ammonium concentration, A – the absorbance value of the test portion, A_0 – the absorbance value of the blank sample. f – the calibration curve inclination, mg/l. V_S – the volume of the test portion, taken for analysis, ml.

3. Results and discussion

As it is shown on the Figure 3.1, after filtration series by zeolite, we have received quite good results of removing ammonium nitrogen from wastewater samples. Especially good quality of tertiary treatment was shown in the first weeks of the filtration. After filtration 24 liters of wastewater, seems that zeolite is starting to weaken and its efficiency decreased, but it is a fact that zeolite after some time, takes a "break" and its efficiency slowly decreasing. The highest level of removal efficiency of NH_4-N, was after filtration 4 liters of wastewater (first week) – 99.9% of removing ammonium. Minimal value of efficiency was reached after the last test (10.1%),

Each data which is given after filtration, is calculated as an average value of three results.

According to Nguyen research, effects of two zeolite particle size ranges (0.25–0.50 mm and 2.0–2.83 mm) on NH_4^+ removal performance were also investigated (Nguyen, 2010). Results obtained from the batch adsorption experiments indicated that both zeolites tested, regardless of their particle sizes, were equally effective (87–98%) at NH_4^+ removal from domestic wastewaters. Comparing to our experiment when maximum efficiency was 99.9%, average – 69.1%.

The sorbic capacity of zeolite was effective for the whole period of experiment and it was exhausted after 56 liters of wastewater filtration.

Trend of the efficiency is decreasing respectively. The accuracy of the fit is interpreted using the R-squared value. As the R-squared value approaches 1, the accuracy of the fit approaches 100%. R-squared value on chart is 0.9989 (polynomial), which shows that results of the experiment highly coincide with the polynomia l trendline.

The efficiency of the phosphorus removal after filtration by zeolite, was not significant (Figure 3.2). It was caused because of the natural features of zeolite and characteristic, as zeolite is not capable to absorb a big amount of PO_4-P from wastewater. In fact, in the beginning of the experiment, there ware similar predicts about phosphorus removal by zeolite, because, according to its features zeolite is not specialized to remove phosphorus from the wastewater.

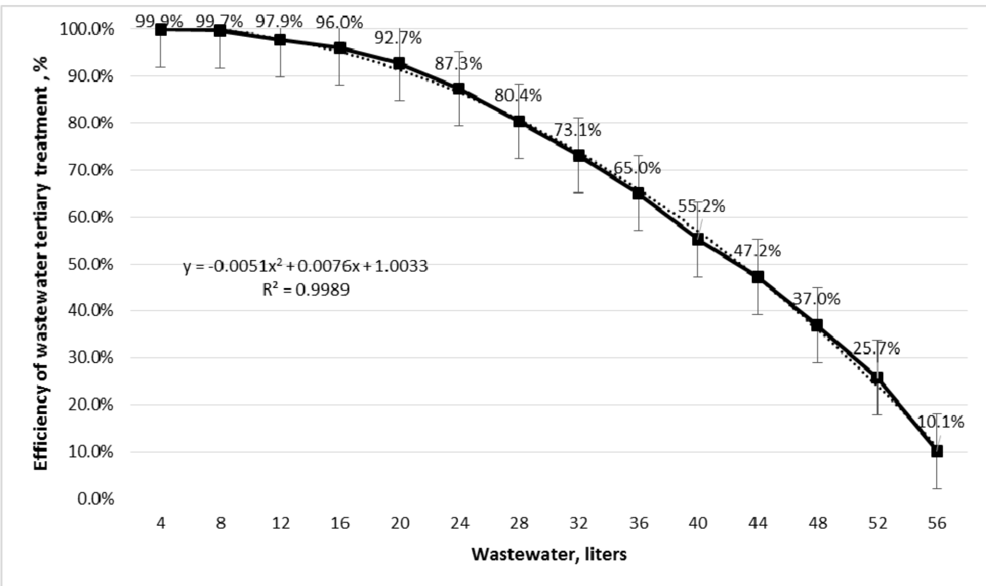

Figure 3.1. Removal efficiency of NH_4-N

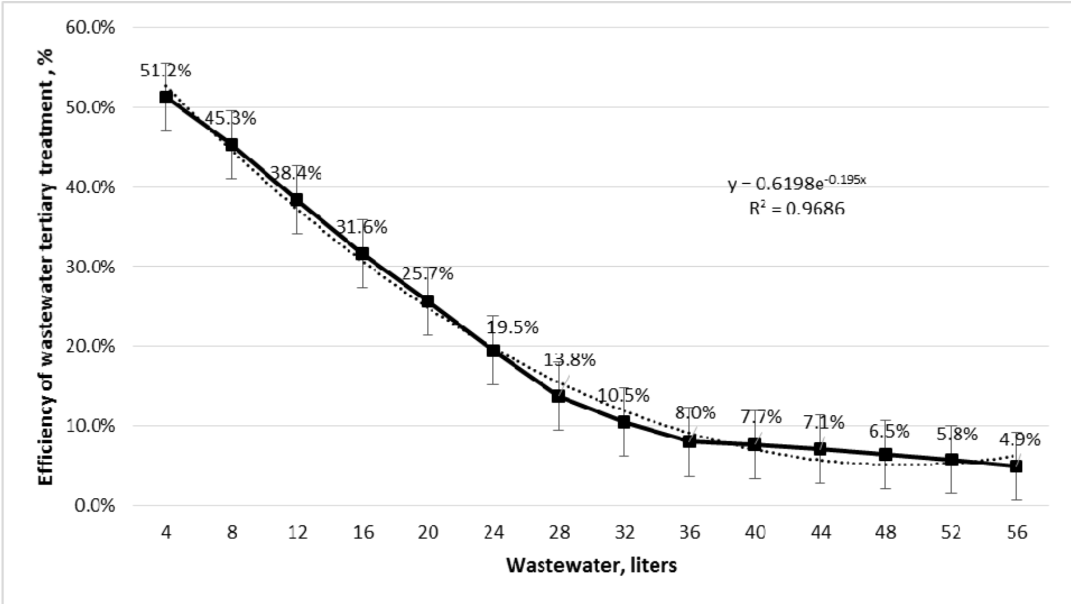

Figure 3.2. Removal efficiency of PO_4-P

Maximal efficiency of phosphorus removal from wastewater was after first day of test (51.2%), when zeolite filler was new and clear. Minimal value of efficiency was reached after the last test (4.9%), when zeolite filler has absorbed 41.09 mg/l of phosphorus and it was not able to absorb more, since zeolite got weakened and its granules saturated with another pollutants of wastewater (sludge, suspended solids and etc.). Trend of the efficiency is decreasing respectively. The accuracy of the fit is interpreted using the R-squared vale. As the R-squared value approaches 1, the accuracy of the fit approaches 100%. The R-squared value on chart is 0.9947 (polynomial), which shows that results of the experiment highly coincide with the polynomial trendline.

Figure 3.3 shows the comparison of removal efficiency of phosphorus and ammonium after filtration by zeolite, where it is clear how much effective is zeolite against ammonium than against phosphorus. More exactly, the average efficiency of ammonium removal from wastewater by zeolite filler was 69.1%, and phosphorus removal – 19%, which shows that the average efficiency of ammonium removal exceeds phosphorus removal by 50.1%.

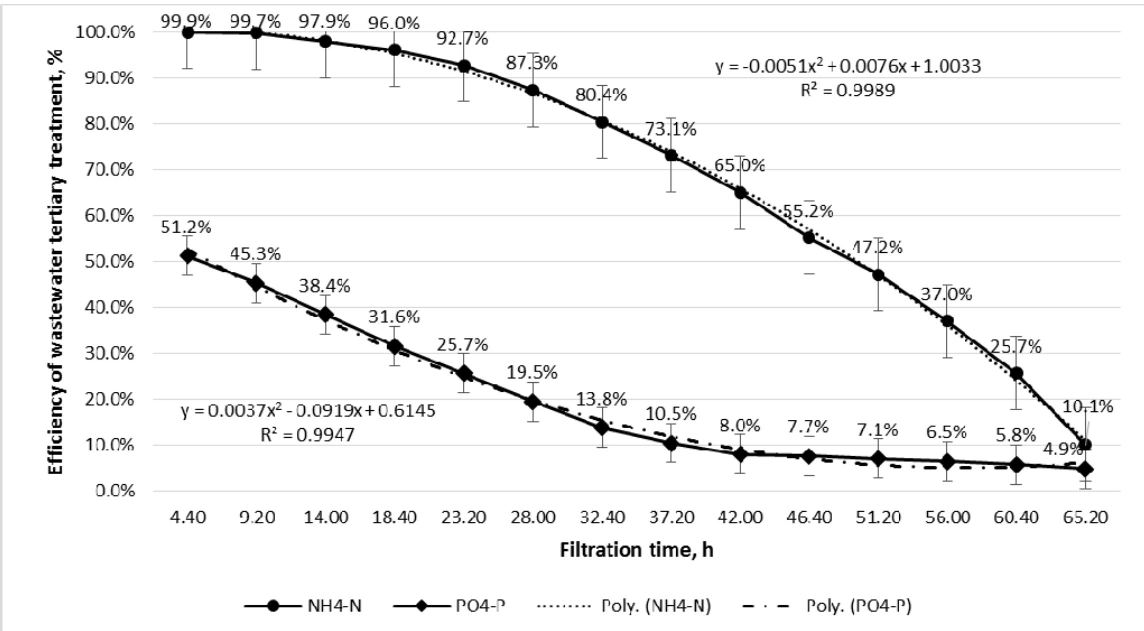

Figure 3.3. Efficiency of wastewater tertiary treatment, according to filtration time (h)

Table 3.1. Results of nutrient removal from wastewater

	Nutrient removal after using zeolite filter material, mg/l.														
Days	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**	**XIII**	**XIV**	**Sum**
Filtration time (h)	4.40	9.20	14.00	18.40	23.20	28.00	32.40	37.20	42.00	46.40	51.20	56.00	60.40	65.20	65.20
NH_4^+-N	69.93	69.79	68.53	67.2	64.89	61.11	56.28	51.17	45.5	38.64	33.04	25.9	17.99	7.07	677.04
PO_4-P	7.68	6.8	5.76	4.74	4.31	2.25	2.22	1.28	1.2	1.2	1.06	0.98	0.87	0.74	41.09

According to Table 3.1, where we see the amount of removed phosphorus and ammonium (in mg/l) during the wastewater treatment experiment using zeolite, we can say that end of our wastewater tertiary treatment experiment 442 g (0.5 l volume) of zeolite filler could absorb 677.04 mg/l of ammonium and 41.09 mg/l of phosphorus after filtration of 56 liters of wastewater in 14 days (65.20 hours), from 13th of February to 15th of May, 2018.

Conclusions

This study successfully tested zeolite as a wastewater treatment material.

Zeolites filler is capable to absorb a big amount of nutrients, its efficiency of ammonium nitrogen removal at the beginning of the study was 99.9%, in the middle of the study – 73.1% and the end of the study – 10.1%. The efficiency of the phosphorus removal after filtration by zeolite, was not significant. That was caused because of the natural features of zeolite and characteristic. The average efficiency of ammonium removal from wastewater by zeolite filler was 69.1%, and phosphorus removal – 19%, which shows that the average efficiency of ammonium removal exceeds phosphorus removal by 50.1%.

Finally, 442 g (0.5 l volume) of zeolite filler could absorb 677.04 mg/l of ammonium and 41.09 mg/l of phosphorus after filtration of 56 liters of wastewater in 14 days (65.20 hours),

According to results of the research, we can recommend zeolite filler to be used as a filter material to remove ammonium from wastewater, since its filtration level is satisfying.

Also, it is important fact, that after filtration zolite filter material become waste, but it can be secondary applied as a building material, also zeolite in the production of asphalt, reduces the installation temperature of the asphalt mix, which reduces emissions, especially in winter, also saves energy and makes it easier to use asphalt mix. Zeolite prolongs the process of laying the asphalt. The use of zeolite increases the bio-gas production using organic solids in wastewater treatment plants, and this can have huge economic benefits. Of course, there must be considered the pollution quality and the duration of using of filter material (zeolite), only after the individual assessment of pollution quality, it can be recommended for the reuse.

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TRETINIO NUOTEKŲ VALYMO, NAUDOJANT CEOLITĄ, EKSPERIMENTINIS TYRIMAS

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Santrauka

Individualaus buitinių nuotekų valymo įrenginiai ne visada dirba efektyviai. To pasėkoje fiksuojami amonio azoto ir fosfatų fosforo koncentracijų išvalytose nuotekose viršijimai. Darbo tikslas buvo ištirti ceolitą, kaip nuotekų tretinio apdorojimo medžiagą ir pasiūlyti šiai problemai spręsti aplinkai draugiškas technologijas, kad nepilnai išvalytos nuotekos nepakenktų aplinkai.

Eksperimentų metu buvo tiriamas ceolitas. Straipsnyje analizavome ceolito užpildo efektyvumą, valant maistingas medžiagas iš nuotekų. Ceolitas buvo efektyvesnis už amonio azotą (99,9–10,1 %), bet mažiau efektyvus už fosfatų fosforą (51,2–4,9 %).

Raktažodžiai: tretinis valymas, nuotekos, fosforo ir amonio valymas, ceolitas.