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Additional Treatment of Nitrogen and Phosphorus Using Natural Materials in Small-Scale Domestic Wastewater Treatment Unit

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Abstract: The conventional wastewater treatment methods only remove up to 80% of total nitrogen (N) or phosphorus (P) from wastewater, so additional facilities are needed. This article describes a newly created other wastewater treatment unit (NCU) that increases the effectiveness of P and N removal of the small-scale biological wastewater treatment plant. This work aims to evaluate the capacity of simultaneous elimination from wastewater nitrogen (NH_4-N, NO_3-N) and phosphorus (PO_4-P) by adsorption. NCU was filled with the sorbent material zeolite (clinoptilolite) and OCS (Fe, Mn, Ca oxides coated sand). After treatment in the main plant, wastewater flows through the NCU without using electric power. A compact system consisting of a main treatment plant and the NCU worked for 4 months, as the harmonized European Standard EN 12566-7 recommended. The NCU unit reduced PO_4-P, NH_4-N, and NO_3-N concentrations in the effluent (74–98%, 52–99%, and 50–98%, respectively). In general, the small-scale system treated wastewater did not contain more than 1 mg/L phosphorus concentration and not more than 10 mg/L nitrogen concentration. This study demonstrates that treatment in NCU is an ecological and environmentally friendly method suitable for decentralized wastewater treatment.

Keywords: wastewater; oxides coated sand; phosphorus and nitrogen removal; adsorption

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1. Introduction

Nitrogen and phosphorus must be efficiently removed from wastewater, as their excess causes eutrophication of water bodies and deteriorates drinking water quality [1,2]. With the tightening of environmental requirements, focal attention is paid to the efficiency of urban wastewater treatment plants. Biological treatment is the principal method of domestic wastewater treatment plants (WWTPs). Recently, much attention has been paid to the optimization of biological processes. A nitrogen removal process based on simultaneous anammox and denitrification is being improved [3], and additives are being sought to improve dehydrogenation [4]. However, biological processes are often unstable: changes in the external environment can easily disrupt the microecology's dynamic balance and affect functional bacteria's activity in the biological nitrogen removal process [3]. Well-functioning WWTPs effectively remove organic matter from wastewater, but total nitrogen or phosphorus removal is at most 80% [5,6]. More remote areas also contain sensitive water bodies and receive P and N emissions from smaller WWTPs, but the potential adverse effects of these biogenic inputs are underestimated [1,7]. Planning of sewer systems typically involves limitations and problems [8]. However, decentralized wastewater treatment systems are a viable and necessary alternative for wastewater management, thus, minimizing environmental impacts and facilitating resource recovery [9]. Today, the main and additional wastewater treatment efficiency issues are relevant [10,11].

Physicochemical methods remove phosphorus from wastewater, but chemical solutions require additional treatment steps, as extraneous solids are formed during treatment,

leading to higher operational costs [12]. Adsorption is an excellent way to remove phosphorus from wastewater. Phosphorus is attracted and retained by porous materials containing Ca, Fe, Al, or Mg [13,14]. A wide range of Fe/Al/Ca materials has been tested to remove P from water efficiently and at high rates at the lab scale [15,16]. However, until now, the field scale applications of P filters have proven laborious and inefficient in their P removal [17]. When cleaning water or wastewater, it is important not to contaminate it with substances released from sorption filters. Sorption filters must be environmentally friendly and not take up much space. The potential of recycling the filter media is also an advantage.

Most of the total nitrogen in treated wastewater (90–95%) is ammonium nitrogen. Ammonia nitrogen is toxic for various aquatic organisms due to its high concentration in water, ultimately endangering the aquatic ecosystem [18]. In small-scale treatment plants, the treated wastewater is often infiltrated into the ground, so there is a risk of contamination of drinking water with nitrogen compounds. It has been observed that, due to the incomplete nitrification process, a concentration of >10 mg/L NH_4-N remains in wastewater treated by small-scale facilities [19]. The pH of domestic wastewater is primarily neutral, so ammonium nitrogen can be removed from wastewater by ion exchange [20]. Ammonium nitrogen is removed from wastewater by many natural and modified materials, especially zeolite, bentonite, and porous aluminosilicate minerals [21–23].

Organic and suspended matter in untreated domestic wastewater would quickly clog sorption filters, so these filters should be applied after biological wastewater treatment. During the biological treatment of efficiently functioning WWTPs, the concentrations of organic and suspended matter are reduced by 95–99%, so it is possible to additionally clean such wastewater by filtering through sorbent fillers [24].

Most research on nitrogen and phosphorus removal from water using sorbents has been conducted under laboratory conditions, preparing solutions with high initial concentrations and slowly filtering artificial wastewater [15,20]. This article presents the results of testing a newly created unit (NCU) prototype developed by the authors under natural conditions. NCU is a compact small-scale facility for additional wastewater treatment. This work aims at evaluating the capacity for the simultaneous elimination of nitrogen (NH_4-N, NO_3-N) and phosphorus (PO_4-P) contained in the wastewater by adsorption. The article's authors aimed to treat domestic wastewater with a small-scale system consisting of a main WWTP and additional unit so that no more than 1 mg/L of phosphorus and no more than 10 mg/L of nitrogen remained in the wastewater. The novelty of the work is that for the removal of phosphorus from wastewater, waste generated in the process of drinking water preparation (quartz sand with a layer of metal oxides) is used. A natural material (natural clinoptilolite) was chosen to remove ammonium nitrogen. Both filtering layers placed in the NCU are environmentally friendly and do not pollute the treated wastewater. The findings of the carried-out research are essential for dealing with the issues of phosphorus and nitrogen removal with ecological and environmentally friendly methods suitable for decentralized wastewater treatment.

2. Materials and Methods

Two materials were selected for the removal of nitrogen and phosphorus from treated wastewater.

The first selected material was zeolite (clinoptilolite). A zeolite containing 70–75% of clinoptilolite was used in this research from the Sokyrnytskaya deposit (located in the Transcarpathian region of Ukraine). The formula of clinoptilolite is $[AlSi_5O_{12}]_2(K_2, Na_2, Ca)(H_2O)_8$, so it seems to be the most attractive material for ammonium removal from water. The particle size of 0.7–1.2 mm (separated by calibrated sieves) of natural zeolite was used in this experimental investigation on removing nitrogen from wastewater.

The second selected material was quartz sand with a cover formed from Fe, Mn, and Ca oxides (OCS). Sand grain cover is a by-product originating from the deferrization of groundwater during drinking water production [25]. The OCS grains used in this research were obtained from the drinking water production facilities of Antaviliai in Vilnius,

Lithuania. In Lithuania, drinking water is prepared from underground water, which sinks at 30–250 m depth. It is clean water, the quality of which meets the requirements for drinking water, except for iron and manganese analytes. Iron and manganese in groundwater are in their reduced form (Fe^{2+}, Mn^{2+}), so the water must be aerated to precipitate. In preparing drinking water, it is fed from wells to aeration devices and filtered through sand filters that retain sediment. Sand grains are covered with scales of Fe, Mn, and Ca oxides; iron bacteria participate in this process. OCS in the cover layer is dominated by Fe (268 mg/g) as a P sorbing element [24]. Under non-reactive water treatment technology, quartz sand grains were covered with metal oxides for five years. The grain size of OCS was 0.7–1.2 mm. There was no further treatment of OCS before their use in this study. The author's previous research conducted under laboratory conditions showed that OCS grains attract PO_4-P and reduce phosphorus concentration in the liquids [26].

The zeolite and OCS grains were placed as filter media in a newly created unit (NCU) developed by the authors (Figure 1). Each material had a surface area of 0.8 m^2 and occupied a volume of 0.24 m^3.

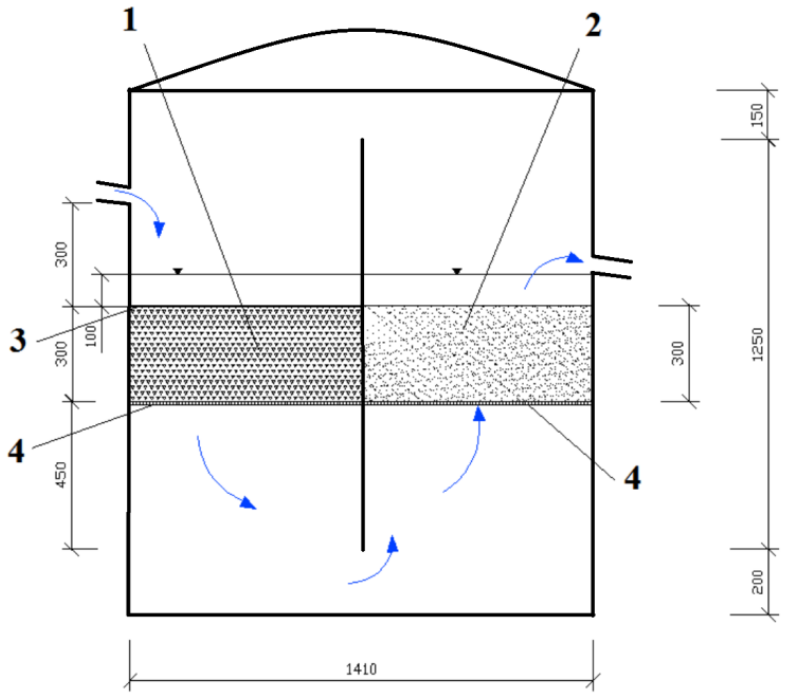


Figure 1. Scheme of the additional (NCU) wastewater treatment unit: 1—a layer of zeolite; 2—a layer of OCS; 3—geotextile; 4—perforated bottom. Dimensions are given in millimeters. Arrows indicate the direction of wastewater flow.

After the treatment in the main WWTP, wastewater flowed through the NCU downwards through the zeolite layer and then was forced upward through the OCS layer. A geotextile was laid over the zeolite layer to trap suspended solids.

The small-scale unit NCU was installed on a household plot after a compact domestic wastewater treatment plant with a flow rate of 0.9 m^3/d. The scheme of the main and additional wastewater treatment is presented in Figure 2.

The main wastewater treatment plant was selected based on activated sludge. The device has aerobic and anaerobic zones; nitrogen and phosphorus removal are also provided. This device (Figure 2 (1)) has recently (in 2018) been tested at the Construction Production Certification Centre (SPSC) following LST EN 12566–3:2005+A2:2013 "Small wastewater treatment systems for up to 50 PT—Part 3: Packaged and site assembled domestic wastewater treatment plant". The CE certificate states that organic and suspended substances are removed from wastewater with 95–97% efficiency and nitrogen and phosphorus with 80% efficiency.

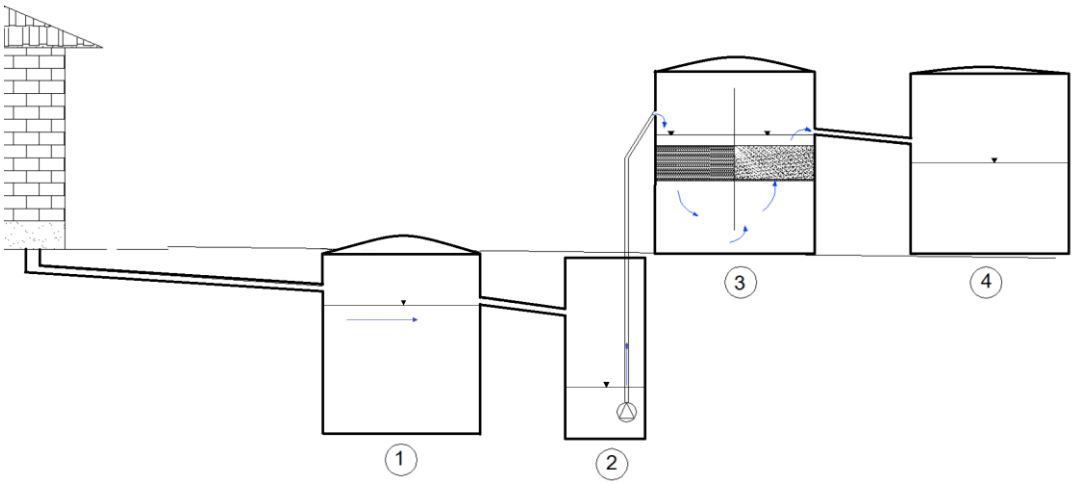


Figure 2. Scheme of the experiment: 1—biological treatment plant, 2—pumping station, 3—additional wastewater treatment unit (NCU), 4—treated wastewater tank.

The wastewater treated by the WWTP entered the pumping station (Figure 2 (2)), from which it was pumped to the testing NCU (Figure 2 (3)). After, NCU treated wastewater flowed into the collection tank (Figure 2 (4)). The entire wastewater flow (0.9 m^3/d) from the main WWTP flowed to the NCU, and the daily wastewater flow was distributed (Table 1).

Table 1. Structure of the daily effluent of the WWTP (according to the standard LST EN 12566–3:2005+A2:2013).

Duration, h	Percentage of Daily Volume, %
3	13
3	15
6	0
2	40
3	15
7	0

The created additional wastewater treatment unit had the same working volume as the main WWTP (1.5 m^3), so the residence time of the wastewater in it was one day. The average residence time of wastewater (treated in the main treatment stage) in the first (zeolite) and second (OCS) filter media was 6.4 h. The hydraulic surface load to both fillings was 1.13 $m^3/m^2/d$. The filtration speed through the filter media varied from 0 to 0.25 m/h.

The research lasted four months (July–October), as provided in the test methodology of the Construction Production Certification Centre, testing tertiary wastewater treatment facilities (which is recommended by the harmonized European Standard EN 12566-7). Treated wastewater samples (1 L each) were collected from the main domestic WWTP outlet pipe and the NCU outlet pipe once a week at the same time of day (around 3:30 p.m.). The wastewater temperature was measured on-site. The wastewater samples were taken to the laboratory for analysis. In the laboratory, the samples were allowed to warm up to room temperature, then their pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD_7), suspended solids concentration (TSS), nitrate nitrogen (NO_3-N), nitrite nitrogen (NO_2–N), ammonium nitrogen (NH_4-N), and ortho-phosphate phosphorus (PO_4-P) concentrations were measured. The values of these indicators were recorded by applying standard analytical methods (ISO 10523:2012; ISO 6060:2003; EN 1899-2:2000; EN 872:2005; EN 25663:2000; ISO 7150-1:1998; ISO 7890-3:1998; EN 27888:1999) at an accredited laboratory; indicators values varied by 5–15%. Each sample was tested three times, and

the average values of the results were presented. The effectiveness of removing pollutants (PO_4-P, NH_4-N, and NO_3-N) from wastewater was calculated according to Formula (1):

$$E_i = \frac{C_{1,i} - C_{2,i}}{C_{1,i}} \times 100, \quad (\%) \tag{1}$$

where: E_i—effectiveness of pollutant removal, %; $C_{1,i}$—concentration of pollutant before NCU, mg/L; $C_{2,i}$—concentration of pollutant after NCU, mg/L.

3. Results

The small-scale wastewater treatment system, consisting of the main WWTP and NCU, operated successfully throughout the test period (4 months). During the study period, the average pressure loss in the NCU unit was negligible (5 cm). As the filtration speed increased to 0.25 m/h, the pressure loss increased to 10 cm, then decreased again to 5 cm. After 4 months of NCU operation, the zeolite and OCS filter media's sorption (or ion exchange) capacity was not exhausted. The data of the wastewater analysis for the entire period are presented in Table 2.

Table 2. Chemical composition of wastewater before NCU (inflow) and after (outflow).

Indicator	Inflow	Outflow
pH	7.53 ± 0.3	7.56 ± 0.7
COD, mg/L	48 ± 20	47 ± 18
BOD_7, mg/L	6.8 ± 3.2	5.9 ± 2.8
NO_3-N, mg/L	1.3 ± 0.7	0.7 ± 0.6
NH_4-N, mg/L	11.8 ± 7.2	1.7 ± 1.08
PO_4-P, mg/L	3.4 ± 1.7	0.5 ± 0.2
TSS, mg/L	6.7 ± 3.0	5.2 ± 2.6

It can be seen from Table 2 that after biological treatment, a relatively high (on average 12 mg/L) concentration of ammonium nitrogen remains in the wastewater. It is nine times higher than the nitrogen concentration of nitrates. This is a problem for small wastewater treatment plants because too little oxygen is supplied to the plants while saving electricity. Blowers operate periodically (15 min on, 15 min off), so the aerobic environment required for ammonium nitrogen oxidation is not always ensured. The biological treatment plant (Figure 2 (1)) perfectly reduced the concentration of organic substances in the wastewater. BOD and COD residual concentrations are sufficiently low (corresponding to 98–95 percent of wastewater treatment efficiency). Activated sludge had a long life for good removal of organic matter from wastewater. Unlike large wastewater treatment plants, where the age of sludge is maintained for about 20 days, in individual facilities, the age is longer, as the excess of activated sludge is removed every 4–6 months.

During the research period, the pH of treated wastewater was neutral after biological treatment and only slightly increased after NCU treatment. The wastewater temperature varied between 13–26 °C during the summer–autumn period. COD, BOD7, and TSS concentrations before and after wastewater treatment in the NCU were similar, and their removal efficiency was only 2–22%. Low treatment efficiency can be explained by the fact that after biological treatment in the main plant (Figure 2 (1)), low concentrations of organic and suspended matter remained in the wastewater. The treated wastewater corresponded to the quality of the water bodies of the mesosaprobic zone according to the BOD indicator. It was impossible to further reduce the concentration of organic substances by adsorption methods. Changes in the concentrations of phosphate phosphorus, ammonium nitrogen, and nitrate nitrogen at the inlet and outlet of the NCU are presented in Figures 3–5.

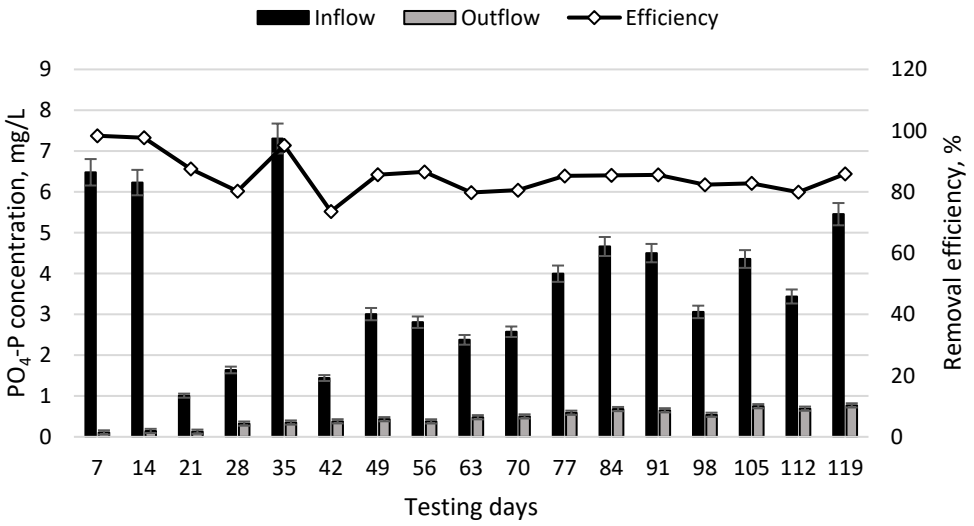


Figure 3. PO_4-P concentrations in treated wastewater and removal efficiency.

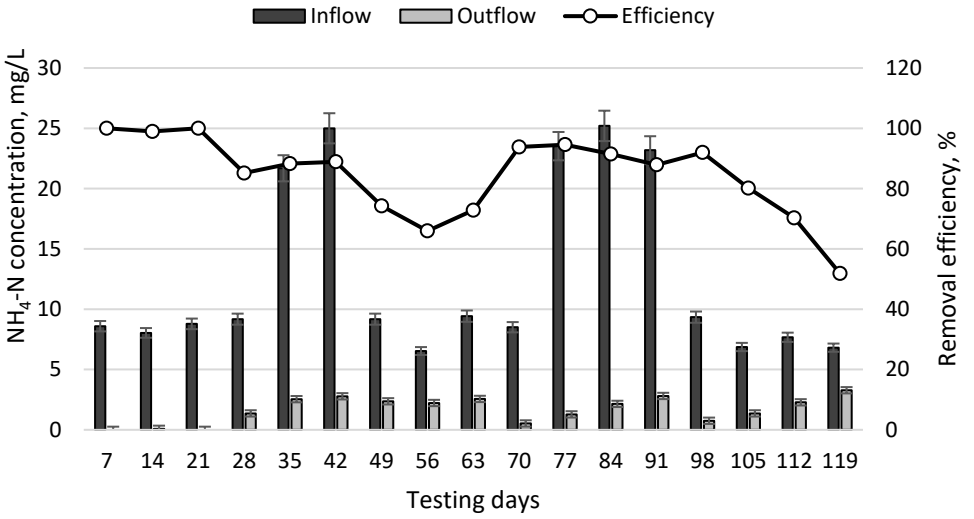


Figure 4. NH_4-N concentrations in treated wastewater and removal efficiency.

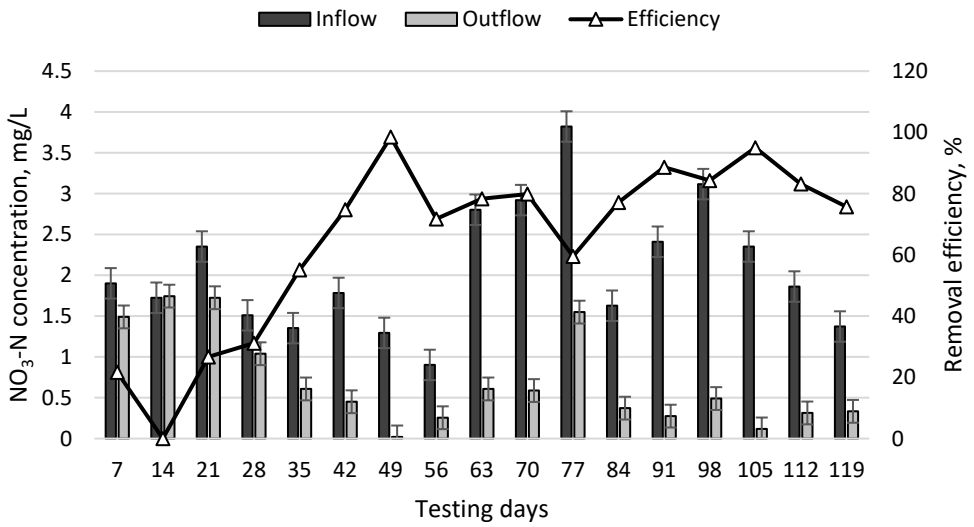


Figure 5. NO_3-N concentrations in treated wastewater and removal efficiency.

The concentration of PO_4-P at the inflow of the NCU varied considerably: from 1 to 7.3 mg/L (Figure 3). Such a fluctuation is characteristic of low-flow WWTPs. The sorbent

filter media OCS reduced the concentration of phosphate phosphorus; the concentration of only 0.1–0.77 mg/L remained at the outlet of the NCU. Phosphorus removal efficiency ranged from 74 to 98%. At the end of the research period, PO_4-P removal efficiency was still high (90%). Efficiency increased with increasing PO_4-P concentration at the NCU inlet. During experiments, 1 g of OCS filter media sorbed 1.05 mg of phosphorus. The sorption capacity of OCS was maintained after the 4-month research period. In an experimental and modelling study previously carried out by the authors, the maximum adsorption capacity of OCS (1.14 mg/g) obtained using the linearized Langmuir model was determined.

The concentration of NH_4-N at the inflow of the NCU unit was relatively high (5.6–25.3 mg/L) and also fluctuated greatly (Figure 4). The limit concentration of ammonium nitrogen when discharging wastewater into the natural environment is 2 mg/L (Regulation on Wastewater Management No. D1-236, 2006). As seen from Table 2, an average of ammonium nitrogen in wastewater after biological treatment was six times more than the allowable limit concentration. At the main WWTP, the blower was used, which operated periodically: blowing air for 15 min and not blowing for 15 min. Excess sludge from the main WWTP was not removed during the research period, so the concentration of activated sludge increased over time. It is assumed that the oxygen supplied by the air was sufficient for the complete nitrification process. Another reason for the incomplete nitrification process could be a change in the composition of the wastewater. Individual treatment plants receive wastewater with large fluctuations in flow rate and composition, and nitrifying bacteria are sensitive to such changes [27].

The NCU removed ammonium nitrogen from wastewater with 52–99% efficiency, and the concentration of 0–3.8 mg/L NH_4-N remained in the wastewater after NCU. The concentration of NH_4-N at the outlet of NCU was more constant, and the standard deviation from the mean was seven times lower than at the inlet. During research, 1 g of natural zeolite (clinoptilolite) retained 5.88 mg of ammonium nitrogen. The sorption capacity of the zeolite was not exhausted after the 4-month research period.

It should be noted that only a tiny (0.6–2.7 mg/L) concentration of nitrate nitrogen remained in the wastewater after biological treatment (Figure 5).

Nitrate nitrogen concentration was, on average, nine times less compared to ammonium nitrogen concentration. Nitrates are usually removed from wastewater during denitrification, with the formation of nitrogen gas. In the small WWTPs, the denitrification process became more active as the activated sludge biomass increased. Small concentrations of nitrates in wastewater treated by small-scale facilities have been detected before [19]. The NCU did not reduce nitrate concentrations at the beginning of the experiment (first 2 weeks). Later, a decrease in the concentration of nitrate nitrogen at the source of the NCU was observed. Nitrate removal efficiency increased to 50% after 4 weeks of NCU operation and continued to remain in the range of 50–98%. Denitrification could have started if the denitrifying bacteria entered a flooded tertiary wastewater treatment unit, creating a low-oxygen environment and thereby releasing nitrogen from nitrates.

4. Discussion

Up to now, extensive research has been performed to develop materials for efficient and cost-effective phosphate removal [16]. Phosphorus can be extracted from the solution by selectively attaching it to a solid phase. Scientists have identified chemisorption as the primary mechanism of phosphorus retention [28]. The negatively charged phosphate ions are attracted toward the surface of the adsorbent, as shown in the reaction given by [29]:

$$\text{M-OH}_2^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{M-H}_2\text{PO}_4 + \text{H}_2\text{O}, \quad (2)$$

where: M is one of the metal constituents (Fe, Al, Ca, Mg, Si, etc.) in the adsorbent.

It should be considered that using secondary materials, natural minerals (rich in iron, aluminum, or calcium), or engineered materials is the most suitable option [17]. Scientists conducted laboratory and simulation studies of the sorption capacity of OCS (secondary material) and determined that the sorption capacity is 1.14 mg PO_4-P/g sorbent [26]. Scien-

tists have investigated the applicability of iron-coated sand as phosphate sorption material to treat nutrient-rich greenhouse effluent and obtained adsorption capacity between 1.85 and 3.07 mg PO_4-P/g sorbent [28]. The differences in the results can be explained by the fact that the sorption capacity of iron-coated sand depends on the concentration of phosphorus and other substances in the treated wastewater, the size of sand grains, the thickness and composition of the coating layer; from the liquid flow (filtration) speed; ambient temperature and other parameters. During the operation of NCU, on average 1 g of OCS filler retained 1.05 mg of phosphorus, but the sorption capacity of OCS was not exhausted. The purpose and conditions of the study (to keep the NCU running for 4 months and PO_4-P concentration <1 mg/L) did not allow it to reach the higher capacity. It should be noted that the developed NCU can be buried in the ground, just like a biological treatment plant. Sewage can flow into it by itself, and the pumping station will not be needed. This scheme has yet to be tested but is planned to be implemented in the future.

Scientists researched phosphorus removal from goat farm wastewater [25]. Using a volume of 0.87 m^3 of iron oxide-coated sand in a fixed-bed reactor, 99% phosphorus removal efficiency was achieved. To achieve minimal costs, a 3.6 times lower volume of OCS was used, and nitrogen was also removed from the wastewater in the research by the authors of this article. The costs of producing, installing, and maintaining a P removal construction should be minimal. Available space for P removal construction is often limited. Therefore, the facilities must be compact. On the other hand, the P removal construction should be capable of processing peak flows, which contain the highest P loads. The OCS volume of 0.24 m^3 used in this study allowed us to achieve the main goal: <1 mg/L phosphorus concentration remained in the effluent. The concentration of phosphorus in the effluent could be lower if the height of the OCS layer was higher. Increasing the layer height is planned for future research. It should be noted that OCS is waste generated in the process of drinking water preparation. Filters media for drinking water preparation are usually replaced every 5–7 years. Therefore, the cost of OCS material would be its collection and delivery.

OCS used for wastewater treatment can be applied to soil improvement. Solid materials with sorbed P may be used as nutrient-bearing soil additions, according to [15]. Desorbing recovered P allows for the precipitation of a high-purity fertilizer. The authors found that the exhausted iron oxide-coated sand could be regenerated by using 0.5 M KOH after adsorption, and after regeneration, more than 80% adsorption capacity of P remained [25].

Natural zeolite, an abundant aluminosilicate mineral with a hierarchically porous structure, has a solid affinity to ammonium in solutions [23]. According to the fundamentals of an ion-exchange reaction with zeolite, a chemical process involving valence forces is described through the sharing or exchange of electrons between negatively charged zeolite sites and ammonium cations as expressed by using the following equation, given by [30]:

$$\text{Zeolite-}H_3O^+ + nNH_4^+ \leftrightarrow \text{Zeolite-}nNH_4^+ + H_3O^+ \quad (3)$$

In zeolite, H stands for the exchangeable ions, while n is the total amount of electric charges.

The exchange capacity of the zeolite depends on several factors, such as the negative charge of its framework structure and the size, concentration, and charge of the exchange ions [31]. Scientists indicate that the ability of natural zeolite to sorb ammonium nitrogen was measured as 16.0 mg/g at 1000 mg-N/L of ammonium [20]. During the operation of NCU, on average 1 g of zeolite filler retained 5.88 mg of NH_4-N, and zeolite sorption capacity was not exhausted within 4 months, but the main goal (that less than 10 mg/L of nitrogen remained in the treated wastewater). To increase the adsorption capacity of natural zeolite, it can be modified. In a previous study, the zeolite (clinoptilolite) was microwave irradiated in the solutions of Fe (III), Cu (II), or Ca(II) chlorides. The metal-modified zeolite exhibits a significantly higher (about three times) phosphate sorption capacity than natural zeolite [32].

The zeolites used for additional wastewater treatment (removing nitrogen from it) can be reused in agriculture because they can be employed as carriers of fertilizers due to their enhanced ion-exchange properties and adsorption capabilities. Having accumulated nitrogen, the zeolite may confer enhanced agricultural potential by preserving the physiological fitness of plants and soil [33]. The use of zeolites in increasing plant growth in many research studies has been demonstrated [34]. Clay minerals have no environmental toxicity and thus can ensure water quality safety [35]. Zeolite can also be regenerated. Guida et al. (2020) researched the regeneration of spent zeolite using 10% potassium chloride (KCl).

5. Conclusions

An additional wastewater treatment unit that can increase the efficiency of wastewater treatment was developed and investigated. After summarizing the results, the main goal set by the authors was achieved: the developed NCU prototype of the additional wastewater treatment plant worked efficiently during the 4-month research period, and the filtrate contained no more than 1 mg/L concentration of phosphorus and no more than 10 mg/L concentration of nitrogen.

During the research period, NCU reduced the amount of phosphorus compounds in the wastewater discharged into the natural environment by 86.3% and reduced the number of nitrogen compounds by 82%.

Low capacity (up to 1 m^3/d) NCU can be used after biological wastewater treatment to remove nitrogen and phosphorus compounds from wastewater without chemical reagents. In summary, the advantages of NCU are:

- Effectively removes nitrogen and phosphorus compounds from wastewater;
- Electricity is not required to ensure the flow of treated wastewater;
- The device is compact and does not take up much space;
- The filtering layers are made of natural materials.

The research results can be used to improve additional wastewater treatment and adapt it to treat larger volumes of wastewater. This study demonstrates that treatment in NCU is an ecological and environmentally friendly method suitable for additional wastewater treatment.

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Conflicts of Interest: The authors declare no conflict of interest.

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