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SUSTAINABLE TECHNOLOGY OF WASTEWATER TREATMENT BY ENVIRONMENTALLY FRIENDLY MODIFIED NATURAL SORBENTS FOR REMOVAL OF NITROGEN AND PHOSPHORUS

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Abstract. The work deals with the issues of nitrogen and phosphorus removal from wastewater. Natural and modified sorbents: zeolite, glauconite, and bentonite were tested under laboratory conditions. The studies used effluent from biological wastewater treatment that contained an average concentration of 2.2 mg/L of ammonium nitrogen; 7.6 mg/L of nitrate nitrogen and 8.7 mg/L of phosphate phosphorus concentration. Wastewater (0.5 L) was mixed with sorbents (5 g) at a speed of 200 revolutions per minute, then nitrogen and phosphorus concentrations in the solution were measured. Natural glauconite and bentonite removed 58–60% ammonium nitrogen, while modified sorbents show higher 63–70% ammonium nitrogen removal efficiency, respectively. Clinoptilolite removed ammonium nitrogen from wastewater with 76% efficiency. The tested sorbents removed nitrate nitrogen with 14–15% efficiency and phosphate phosphorus with 19–45% efficiency.

Keywords: wastewater, sorbents, nitrogen, phosphorus, removal, efficiency.

Introduction

Nitrogen and phosphorus cause eutrophication in natural water. The removal of these compounds from wastewater has become an emerging worldwide concern (Boujelben et al., 2008; Cheng et al., 2019). An activated sludge process is commonly used in wastewater treatment, but it is often the case that the effluent from wastewater treatment plants has remaining phosphorus and nitrogen (Bali & Gueddari, 2019; Yamashita & Yamamoto-Ikemoto, 2014). Phosphorus compounds as an element of inadequately treated wastewater may enter natural water thus causing eutrophication and destroying the aquatic ecosystem (Bunce et al., 2018; Li et al., 2018). Ammonia nitrogen is toxic to various aquatic organisms (Tang et al., 2020). Municipal wastewater treatment plants need to be optimized to achieve greater efficiency in removing nitrogen and phosphorus from wastewater. On the other hand, wastewater treatment managers hope to minimize post-treatment operation and maintenance costs. The removal of ammonia nitrogen and phosphorus can be achieved through adsorption and precipitation processes (Boujelben et al., 2008; Hamisi et al., 2019). Therefore, post-treatment technologies will enable the use of waste materials or inexpensive natural materials (Marzec et al., 2017). The materials used to remove nitrogen and phosphorus compounds from the effluent after biological wastewater treatment must be insoluble, harmless, and not contaminate the water while treating it in the post-treatment stage (Cheng et al., 2019; Eregno & Heistad, 2019; Verma et al., 2017). New methods and materials are being developed to eliminate P from wastewater refusing to use chemicals (Mažeikienė & Šarko, 2022). The scientists applied a number of substrates for phosphorus removal, including minerals and rocks, soils, marine sediments, industrial by-products, and man-made products (Karczmarczyk et al., 2019; Rout et al., 2014). Ammonium is efficiently adsorbed by zeolites (Mažeikienė & Valentukevičienė, 2016; Doekhi-Bennani et al., 2021; Tang et al., 2020). Although natural sorbents are acceptable from an environmental point of view, their effectiveness of removing P from wastewater is not that high and frequently reaches only 30–50% (Šarko & Mažeikienė, 2020). Modification of natural materials can improve their sorption properties. The aim of this work is to investigate how effectively zeolite (clinoptilolite),

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bentonite, and glauconite (natural and modified) can sorb ammonium nitrogen and phosphate phosphorus from wastewater. The results will help to find the best sorbents or their combinations, which will be used for the development of sustainable wastewater treatment technology.

1. Materials and methods

1.1. Selected materials

For sorption studies, three natural sorbents were taken:

- bentonite, pH of aqueous extract – 10.5; bulk density – 1010 kg/m^3;
- glauconite, pH of aqueous extract – 8.6; bulk density – 1050 kg/m^3;
- zeolite (clinoptilolite), pH of aqueous extract – 7.75; bulk density – 947 kg/m^3.

Samples of natural sorption materials for synthesis were pre-washed, levigated, and dried at 80 °C until constant weight. After drying, the samples were sieved. A particle size fraction of 0.8–1.2 mm was chosen for research.

In order to improve the sorption properties of the samples, the following types of preliminary treatment were used: calcination at 550 °C for 3 hours, and microwave treatment for 30 min at 790 W.

The following natural and modified sorbents were chosen for sorption studies: 1) natural bentonite, 2) bentonite after 3 hours in a muffle furnace at a temperature of 550 °C, 3) natural glauconite, 4) glauconite after 3 hours in a muffle furnace at a temperature of 550 °C, 5) glauconite after 30 min microwave treatment at 790 W, 6) clinoptilolite after 30 min microwave treatment at 790 W.

1.2. Treated wastewater

The study used wastewater after biological treatment with an average ammonium nitrogen concentration of 2.22 mg/L, an average nitrate nitrogen concentration of 7.6 mg/L, and an average phosphate phosphorus concentration of 8.75 mg/L. After biological treatment in an individual WWTP, small concentrations of organic matter and suspended solids remained in the wastewater: BOD < 6 mg/L; TSS < 7 mg/L. The pH concentration in the delivered wastewater (average) was 7.35.

1.3. Experiments methodology

Closed batch experiments were used to estimate the first predictions of phosphate phosphorus (PO_4-P) and ammonium nitrogen (NH_4-N) retention. After the biologically treated wastewater was brought to the laboratory, it was allowed to warm to room temperature. Then the wastewater temperature, pH, ammonium, and phosphorus concentrations were measured. The experiments were performed in a laboratory at 18–20 °C. For each individual test, 6 beakers were used, loaded with 0.5 L aqueous solution and a certain mass of selected material (5 g), and mixed in an automatic mixer at 200 rpm. The sorbents were placed in the beakers in the following order:

Table 1. Distribution of sorbents in the beakers

Beaker No.	Sorbents
1.	Natural bentonite
2.	Bentonite after 3 hours in a muffle furnace at a temperature of 550 °C
3.	Natural glauconite
4.	Glauconite after 3 hours in a muffle furnace at a temperature of 550 °C
5.	Glauconite after 30 min microwave treatment
6.	Clinoptilolite after 30 min microwave treatment

Stirring was continued for 30 minutes, after which each cylinder was sampled and filtered through 0.45-micron glass fiber filters.

Additional samples were taken after 120, 180, and 1320 minutes (22 hours). PO_4-P and NH_4-N concentrations in the filtrates were determined using MERCK Spectroquant® tests, pouring test samples into cuvettes (Hellma), and measuring with a Genesys 10 UV-Vis spectrophotometer. The pH of the produced solution was determined by measuring it with an Oxi 330/SET device. The effectiveness of removing nutrients E_i (%) from wastewater was calculated according to Formula (1):

$$E_i = \frac{C_0 - C_i}{C_0}, \quad (1)$$

where: C_0 – PO_4-P or NH_4-N concentration before treatment, (mg/L); C_i – PO_4-P or NH_4-N concentration after treatment, (mg/L).

The study was repeated two more times to present the mean results of three experiments. The equilibrium relation between the adsorbed amount of the adsorbate q_e (mg/g) and the amount of the adsorbate in the solution C_e was determined using Formula (2):

$$q_e = \frac{(C_0 - C_e) \times V}{m}. \quad (2)$$

2. Results and discussion

Phosphate phosphorus concentrations in beakers with sorbents are presented in Figure 1.

From the Figure 1, it can be seen that the phosphorus concentration of phosphates decreased the most in beakers 3, 4, and 5, which contained natural and modified glauconite (Table 1). Phosphorus concentration decreased from 8.75 to 4.8–5.2 mg/L. Natural and modified bentonite and clinoptilolite reduced the phosphorus concentration in the beakers from 8.75 to 6.9–7.2 mg/L.

Ammonium nitrogen concentrations in beakers with sorbents are presented in Figure 2.

From Figure 2, it can be seen that the ammonium nitrogen concentration decreased the most in beakers 2 and 6, which contained modified bentonite and modified clinoptilolite (Table 1). Ammonium nitrogen concentration decreased from 2.22 to 0.54–0.67 mg/L. Natural and modified bentonite and clinoptilolite reduced the phosphorus concentration in the beakers from 8.75 to 6.9–7.2 mg/L. Other sorbents reduced the ammonium nitrogen concentration in the beakers from 2.22 to 0.9–0.94 mg/L.

Figure 3 shows the efficiency of reduction of phosphate phosphorus and ammonium nitrogen concentrations.

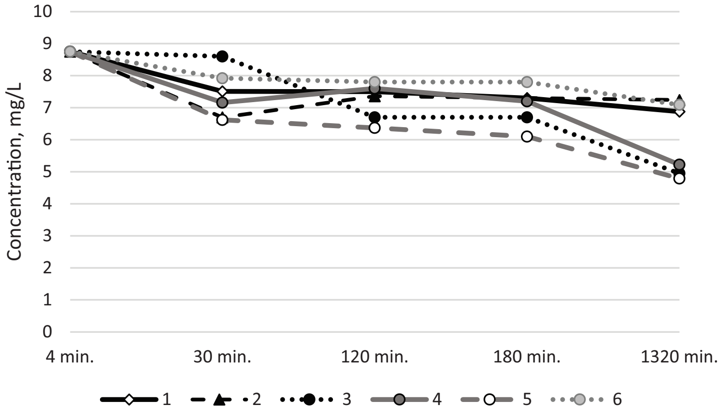

Figure 1. Phosphate phosphorus concentrations in beakers with sorbents (1 – natural bentonite; 2 – bentonite after 3 hours in a muffle furnace at a temperature of 550 °C; 3 – natural glauconite; 4 – glauconite after 3 hours in a muffle furnace at a temperature of 550 °C; 5 – glauconite after 30 min microwave treatment; 6 – clinoptilolite after 30 min microwave treatment)

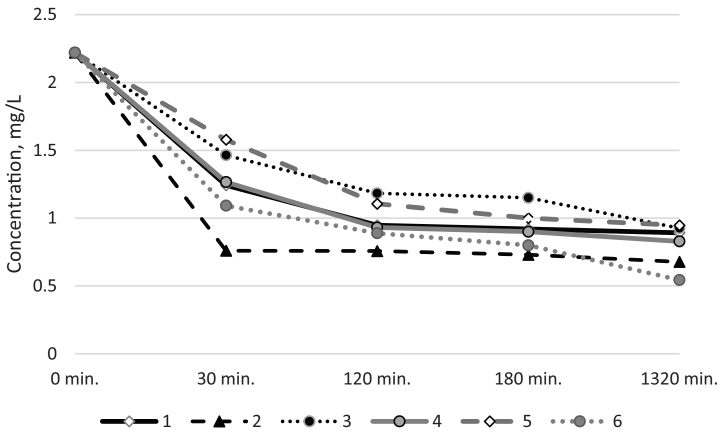

Figure 2. Ammonium nitrogen concentrations in beakers with sorbents (1 – natural bentonite; 2 – bentonite after 3 hours in a muffle furnace at a temperature of 550 °C; 3 – natural glauconite; 4 – glauconite after 3 hours in a muffle furnace at a temperature of 550 °C; 5 – glauconite after 30 min microwave treatment; 6 – clinoptilolite after 30 min microwave treatment)

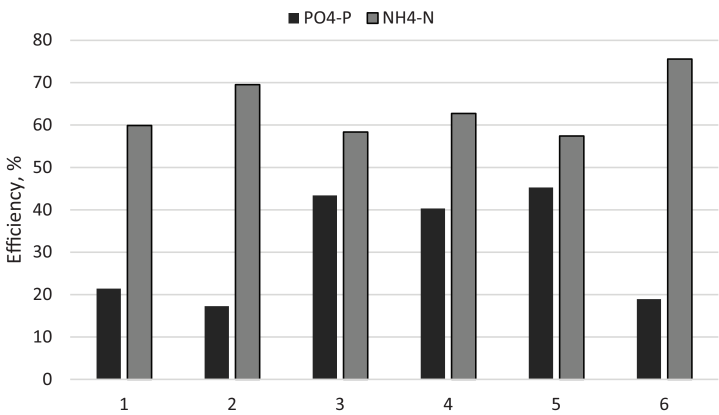

Figure 3. The efficiency of reduction PO_4-P and NH_4-N concentrations (1 – natural bentonite; 2 – bentonite after 3 hours in a muffle furnace at a temperature of 550 °C; 3 – natural glauconite; 4 – glauconite after 3 hours in a muffle furnace at a temperature of 550 °C; 5 – glauconite after 30 min microwave treatment; 6 – clinoptilolite after 30 min microwave treatment)

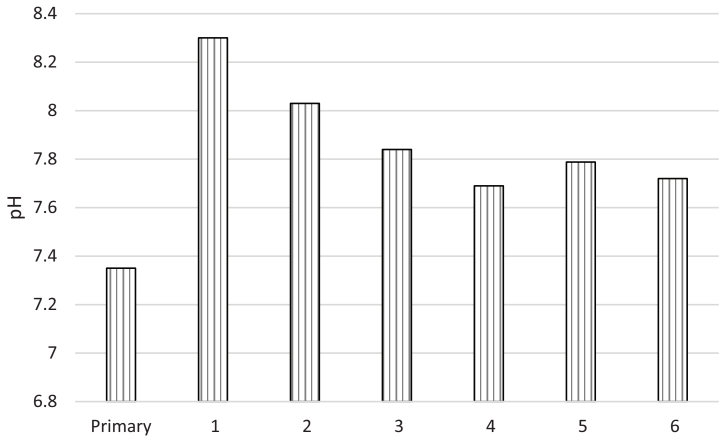

Figure 4. The results of the pH measurement (1 – natural bentonite; 2 – bentonite after 3 hours in a muffle furnace at a temperature of 550 °C; 3 – natural glauconite; 4 – glauconite after 3 hours in a muffle furnace at a temperature of 550 °C; 5 – glauconite after 30 min microwave treatment; 6 – clinoptilolite after 30 min microwave treatment)

From Figure 3, it can be seen that the concentration of ammonium nitrogen in the solution was most effectively reduced by microwave-modified clinoptilolite (75.6%), while the concentration of phosphate-phosphorus was most effectively reduced by microwave-modified glauconite (45.3%).

Figure 4 shows the results of the pH measurement.

It can be seen from Figure 4 that all 6 sorbents increased the pH in the media in the beakers. The pH indicator increased the most in glasses 1 and 2, where natural and modified bentonite was added. The least amount of pH (from 7.35 to 7.7) increased in beakers 4, 5, and 6, to which glauconite and clinoptilolite were added. Bentonite (especially natural) increases pH in the water medium from 7.35 to 8.3, which is unfavorable for phosphorus sorption. Because PO_4-P adsorption increases with decreasing pH, these adsorption processes would often be expected to be more influential at low pH, resulting in a "positive" pH dependence (i.e. increased PO_4-P solubility at higher pH). Phosphate adsorption decrease as the pH increases (Antelo et al., 2005).

The equilibrium relation between the adsorbed amount of the adsorbate q_e (mg/g) and the amount of the adsorbate in the solutions C_e (NH_4-N) and C_e (PO_4-P) are presented in Table 2.

Comparing the obtained ability of sorbents (to adsorb phosphorus) with the ability of other unmodified sorbents, it can be seen that the sorption capacity of some tested materials is similar or slightly larger; fragmented limestone waste – 0.398 mg/g (Mateus et al., 2012), ground burnt patties – 0.41 mg/g (Rout et al., 2014), red soil – 0.56 mg/g (Rout et al., 2015), kaolinite – 0.32 mg/g, and bentonite – 0.28 mg/g (Moharami & Jalali, 2013). According to Liu et al. (2022), the maximum ammonium adsorption capacity of natural zeolite was 26.94 mg/g. However, unlike in this study, this ability was achieved in the presence of high-concentration ammonium (1000~4000 mgN/L) in an aqueous solution (Liu et al., 2022). In this work, natural wastewater after biological treatment, containing a small concentration of ammonium nitrogen, was investigated. However, even 1–2 mg/L ammonium nitrogen concentration in biologically treated wastewater is too high to discharge the wastewater into the natural environment. The research results made it possible to identify materials that reduce the concentration of ammonium nitrogen in wastewater by 1 mg/L: these are modified and natural bentonite, glauconite, and clinoptilolite. The materials preliminarily studied in this work will be tested further by treating wastewater with various initial concentrations of nitrogen and phosphorus.

Table 2. The equilibrium relation between the adsorbed amount of the adsorbate q_e (mg/g) and the amount of the adsorbate in the solution C_e

Sorbent	PO_4-P			NH_4-N		
	C_0	C_e	q_e	C_0	C_e	q_e
1. Natural bentonite	8.75	6.88	0.19	2.22	0.89	0.13
2. Bentonite after 3 hours in a muffle furnace at a temperature of 550 °C	8.75	7.2	0.16	2.22	0.68	0.15
3. Natural glauconite	8.75	4.95	0.38	2.22	0.93	0.13
4. Glauconite after 3 hours in a muffle furnace at a temperature of 550 °C	8.75	5.22	0.35	2.22	0.83	0.14
5. Glauconite after 30 min microwave treatment	8.75	4.79	0.4	2.22	0.95	0.13
6. Clinoptilolite after 30 min microwave treatment	8.75	7.09	0.17	2.22	0.54	0.17

Conclusions

The research revealed the sorption capacity of natural and modified bentonite, glauconite, and clinoptilolite in relation to ammonium nitrogen and phosphate phosphorus from wastewater.

All three glauconite samples showed the highest sorption capacity in relation to phosphate phosphorus, decreasing its concentration from 8.75 to 4.8–5.2 mg/L. Natural glauconite and bentonite show ammonium nitrogen removal efficiency of 58–60 percent, while modified sorbents show higher ammonium nitrogen removal efficiency of 63–70 percent, respectively. Microwave-treated clinoptilolite revealed the highest adsorption capacity among other samples in relation to ammonium nitrogen, decreasing its concentration from 2.22 to 0.54 mg/L. Clinoptilolite removed ammonium nitrogen from wastewater with 76 percent efficiency. These results correlate with the results of pH measurement. Though all 6 sorbents ensure the pH increase, samples with lower pH reveal better adsorption capacity in relation to phosphate phosphorus compared to samples with higher pH.

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Contribution

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