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RESEARCH ON AMMONIUM NITROGEN AND PHOSPHATE REMOVAL FROM WASTEWATER USING NATURAL AND MODIFIED SORBENTS

Iryna FEDIV[1], Kateryna STEPOVA[2], Jonas MAŽEIKA[3*]

[1,2]Department of Environmental Safety, Lviv State University of Life Safety, Lviv, Ukraine
[3]Faculty of Mathematics and Informatics, Vilnius University, Vilnius, Lithuania
[*]E-mail: jonas.mazeika@mif.stud.vu.lt

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Abstract. The work deals with the issues of ammonium nitrogen and phosphate phosphorus removal from wastewater. Natural and modified sorbents: zeolite, glauconite, and bentonite were tested under laboratory conditions. The wastewater after biological treatment with an average ammonium nitrogen concentration of 5 mg/L and an average phosphate phosphorus concentration of 3.4 mg/L was used for experimental studies. Before the test, the phosphate phosphorus concentration in the wastewater was increased to 19.9 mg/L by the addition of potassium hydrophosphate salt. Glauconite (after 3 hours in a muffle furnace at a temperature of 550 °C) had the greatest ability to sorb phosphorus. Under the conditions of this study, the PO_4–P sorption efficiency was 58%. Ammonium nitrogen from wastewater was best sorbed by natural glauconite. Under the conditions of this study, the sorption efficiency of NH_4–N was 98%. The results showed that the adsorption process on glauconite could be used as an effective method for removing ammonium from wastewater.

Keywords: wastewater, phosphorus, ammonium, nitrogen, sorbents.

Introduction

Effluents from wastewater treatment plants contain high concentrations of inorganic nitrogen and phosphorus that may lead to the eutrophication of the water bodies that they discharge into (Zhang et al., 2008). One of the important goals of wastewater engineering and surface water management is to reduce the phosphate concentration in water and thus prevent eutrophication (Kauppinen et al., 2014). Chemical precipitation and biological nutrient removal are the two most commonly used methods for the removal of phosphate from municipal and industrial wastewater (Gupta & Ali, 2013). These processes essentially transfer a phosphate from the liquid to the sludge phase, which must then be transported and disposed of elsewhere. The main nitrogen removal processes are biological nitrification, denitrification, air stripping, chemical treatment, and selective ion exchange. Chemical precipitation and biological nutrient removal processes can reduce nitrogen and phosphorus content in municipal wastewater, however complete removal are unattainable by these methods due to thermodynamic and kinetic limitations (Herrmann et al., 2014; Mažeikienė et al., 2021). Frequently, only around 20% of phosphorus is removed from wastewater via soluble P consumption in biochemical processes. Chemical methods involve a high expenditure on the process and also these methods produce supplementary pollution (Bali & Gueddari, 2019). New methods and materials are being developed to eliminate P and N from wastewater refusing to use chemicals. Today, several substrates have been explored for nutrients removal, including minerals and rocks, soils, marine sediments, industrial byproducts, and man-made products (Eveborn et al., 2014; Rout et al., 2014; Huang et al., 2016; Karczmarczyk et al., 2019; Kauppinen et al., 2014). Extensive research studies were undertaken to explore the effectiveness of fixed-bed processes for phosphate removal. Municipal and industrial wastewater always contains sulfate and chloride anions which will compete with target phosphate for the sorption sites. Commercial anion exchangers, activated alumina, and zirconium oxides are some well-studied sorbents in this regard (Zhao & Sengupta, 1998). Interaction mechanisms between the phosphate and sorbent are categorized as hydrogen bonding, shape complementarity, and inner-sphere complexation, and their representative sorbents are organic-functionalized materials, molecularly imprinted polymers, and metal-based materials (Du et al., 2017). The critical shortcomings with these sorbents can be summarized as follows: poor selectivity toward phosphate over other competing species (sulfate, chloride, bicarbonate, organic), very low capacity in the neutral pH range, inefficient regeneration, loss in capacity due to dissolution of the sorbent or fouling by organic matter. The sorbent in the fixed-bed process should be durable and prefer phosphate over other dissolved competing species, which are commonly present in wastewater at much higher concentrations than phosphate. Orthophosphate is by far the most predominant phosphate species present in treated municipal and industrial wastewater. Phosphorus can be removed from aqueous solutions during physicochemical (adsorption and precipitation) processes (Huang et al., 2016).

Microwave synthesis is a promising method for cation exchange in the zeolite. Compared to conventional heating, microwave synthesis of zeolite significantly reduces the production time (50%), and both methods yield relatively the same BET surface area. It is important that the cation exchange capacity of zeolite treated by microwave irradiation is within 85% (Bukhari et al., 2015). Despite the good phosphate adsorption capacity of natural minerals modified with polyvalent metals such as Zr^{4+}, La^{3+}, Al^{3+}, or Fe^{3+}, there is a risk of toxic effects on aquatic species and deterioration of water quality due to the release of these metals, especially Al^{3+} and Fe^{3+}(Yin et al., 2016; Yang et al., 2014).

In this work, several natural and modified sorbents were tested to remove ammonium nitrogen and phosphate phosphorus from wastewater. The goal of the authors of the article was to find materials that would be environmentally friendly and remove nutrients from wastewater.

2. Materials and methods

2.1. Selected materials

Natural materials are collected in Ukraine, and their modification is carried out at Lviv State University of Life Safety, Ukraine. The following natural and modified sorbents were selected for sorption studies: 1) rock from the coal waste heap is soaked in a solution of 40 mg/L $FeCl_3$; 2) rock from a coal waste heap for 10 minutes under the influence of microwaves in a solution of 20 mg/L $CuCl_2$; 3) natural glauconite; 4) glauconite for 3 hours in a muffle furnace at a temperature of 550 °C; 5) glauconite 30 min under the influence of microwaves; 6) natural clinoptilolite.

2.2. 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. The experiments were performed in a laboratory at 18–20 °C. An aqueous solution containing PO_4–P phosphate phosphorus concentration of about 20 mg/L was prepared from wastewater after biological treatment and K_2HPO_4 salt. The amount of potassium hydrophosphate added is determined by molar mass (174 grams of salt contains 32 grams of phosphorus). To obtain ~20 mg/L PO_4–P concentration, 0.93 g of K_2HPO_4 was added to 10 liters of wastewater.

The pH of the produced solution was determined by measuring it with an Oxi 330/SET device. For each individual test, 6 cylinders 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. Stirring was continued for 30 minutes, after which each cylinder was sampled and filtered through 0.45-micron glass fiber filters (Figure 1).

Additional samples were taken after 90 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 effectiveness of removing nutrients E_i (%) from wastewater was calculated according to Equation (1):

$$E_i = \frac{C_0 - C_i}{C_0} \times 100\%, \quad (1)$$

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).

Figure 1. Materials and devices used in the experimental studies

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 Equation (2):

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

where: C_0 – initial concentration of PO_4–P or NH_4–N (mg/L); C_e – equilibrium phosphate or NH_4–N concentration (mg/L); V – a volume of PO_4–P or NH_4–N solution (L), and m – a mass of the adsorbent (g).

3. Results and discussion

The study used wastewater after biological treatment with an average ammonium nitrogen concentration of 5 mg/L and an average phosphate phosphorus concentration of 3.4 mg/L. The pH concentration in the delivered wastewater was 7.35. The concentration of phosphate phosphorus in wastewater treated by an individual sewage treatment plant varies greatly, so it was increased for experimental purposes to the maximum concentration that occurs in reality. The aqueous solution containing PO_4–P phosphate phosphorus concentration of about 20 mg/L was prepared by adding K_2HPO_4 salt.

Phosphate phosphorus concentrations in beakers with sorbents are presented in Figure 2. As can be seen from Figure 2, the lowest concentration of PO_4–P was in beaker 5, in which glauconite was added for 30 min under the influence of microwaves. The highest concentration (15.9 mg/L) was in beaker 6, which contained natural clinoptilolite.

Ammonium nitrogen concentrations in beakers with sorbents are presented in Figure 3. The figure shows that the highest concentration of ammonium nitrogen was in beakers 1 and 2, in which the modified rock from

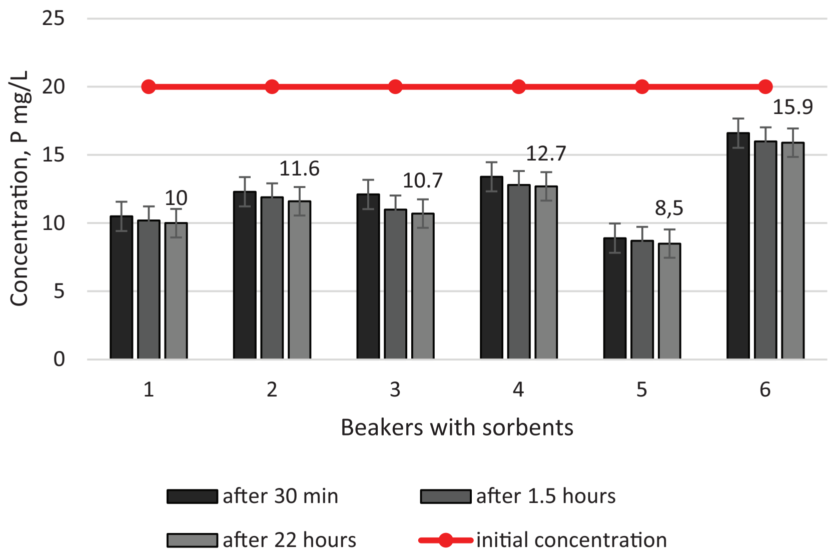

Figure 2. Phosphate phosphorus concentrations in beakers with sorbents

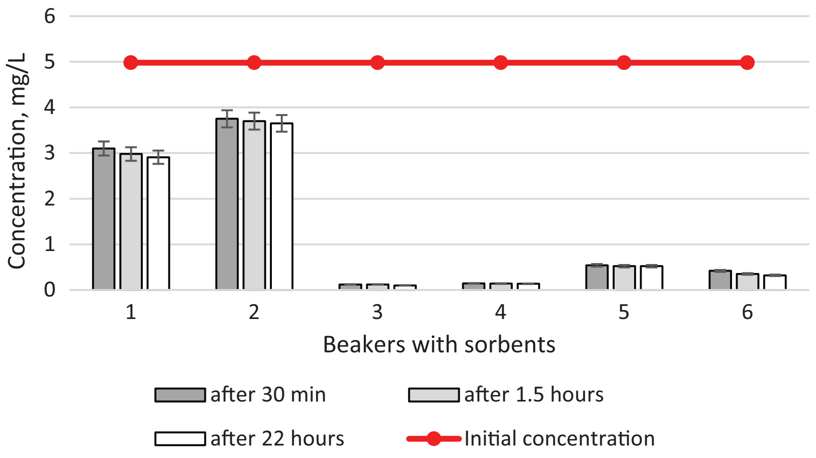

Figure 3. Ammonium nitrogen concentrations in beakers with sorbents

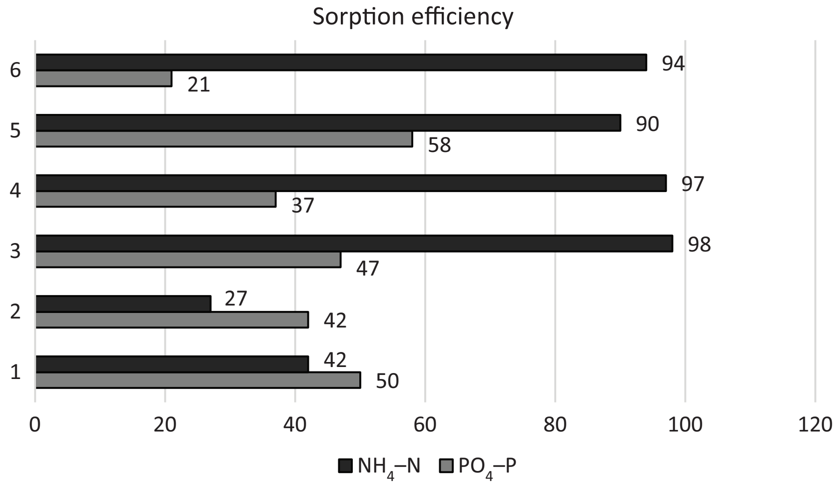

Figure 4. Phosphate phosphorus and ammonium nitrogen sorption efficiency

the coal waste heap was placed. The lowest concentration of NH_4–N was in beaker 3, which contained natural glauconite. After 22 h of stirring, the concentrations of PO_4–P and NH_4–N in the beakers decreased slightly, indicating that sorption was still taking place.

After calculating the sorption efficiency of PO_4–P and NH_4–N, the results are shown in Figure 4. From the results, it can be seen that in 3–6 glasses, in which natural and modified glauconite and natural zeolite were added, ammonium nitrogen sorption took place efficiently (90–98%). PO_4–P was most efficiently sorbed by glauconite placed in glass 5 for 30 min under the influence of microwaves and rock from the coal waste heap (soaked in a solution of 40 mg/L $FeCl_3$) in glass 1. Phosphorus sorption efficiency was 58 and 50%, respectively.

After measuring the pH in the glasses after 1.5 hours of mixing, the results obtained are shown in Figure 5. The first two sorbents (rock from the coal waste heap, soaked in a solution of 40 mg/L $FeCl_3$ and rock from a coal waste heap for 10 minutes under the influence of microwaves in a solution of 20 mg/L $CuCl_2$) slightly reduced the pH.

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).

In glasses 3–6, the pH increased, the most (up to 7.67) in glass 6. This can be explained by the fact that glauconite and zeolite increased the pH of the medium due to efficient NH_4–N sorption or ion exchange, where ammonium ions replace alkali metal ions. It is known that the amount of NH_4^+ adsorbed increased as pH increased (Kithome et al., 1999).

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 are presented in Table 1.

Glauconite after 3 hours in a muffle furnace at a temperature of 550 °C had the greatest ability to absorb phosphorus. It is assumed that calcination increased the surface area and porosity of glauconite grains, resulting in improved sorption properties. The sorption capacity of rock from the coal waste heap (soaked in a solution

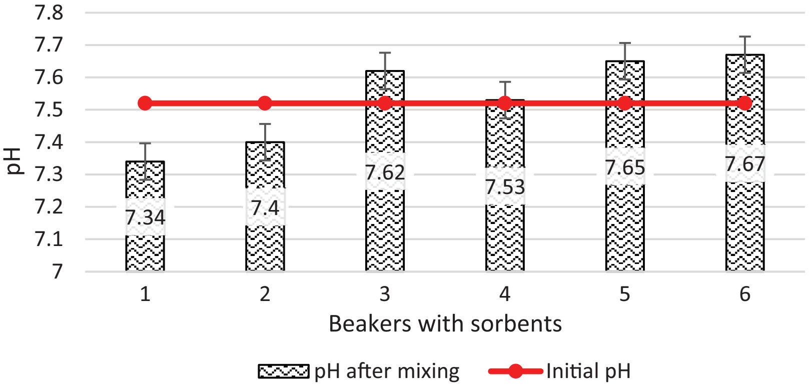

Figure 5. pH in beakers with sorbents

Table 1. The equilibrium relation between the q_e (mg/g) and the C_e (mg/L). Concentrations are averages obtained from 3 replicates

Sorbent	PO_4–P			NH_4–N		
	C_0	C_e	q_e	C_0	C_e	q_e
Rock from the coal waste heap is soaked in a solution of 40 mg/L $FeCl_3$	19.9	10.0	0.99	4.98	2.91	0.2
Rock from a coal waste heap for 10 minutes under the influence of microwaves in a solution of 20 mg/L $CuCl_2$	19.9	11.6	0.83	4.98	3.65	0.13
Natural glauconite	19.9	10.7	0.92	4.98	0.1	0.49
Glauconite after 3 hours in a muffle furnace at a temperature of 550 °C	19.9	12.7	0.72	4.98	0.14	0.48
Glauconite after 30 min microwave treatment	19.9	8.5	1.14	4.98	0.52	0.45
Natural clinoptilolite	19.9	15.9	0.4	4.98	0.32	0.47

of 40 mg/L $FeCl_3$) was 0.99 mg/g. The obtained ability of sorbents (to adsorb phosphorus) is relatively small. According to Liu et al. (2018), a magnetic Fe_3O_4 core-shell (MFC) had a high phosphate adsorption capacity of 45.45 mg/g at 30 °C. The MFC was prepared by the hydrothermal method and then functionalized with $La(OH)_3$ by depositing it on the MFC surface. The ability of the sorbents studied in this article to sorb PO_4–P is lower, but the previously observed property of iron to attract phosphorus is confirmed (Mažeikienė et al., 2021).

Natural glauconite had the greatest ability to sorb NH_4–N. According to Naghipour et al. (2018), using glauconite, the removal efficiency of NH_4^+ was 19.24 mg/g (77.08% at pH 7). All in all, the results showed that the adsorption process on glauconite could be used as an effective method for removing NH_4^+ from aqueous solutions. During the experiments described in this article, using glauconite, the removal efficiency of NH_4^+ was 0.49 mg/g (98% at pH 7.62). This result was influenced by the initial concentration of ammonium nitrogen in the wastewater, which was small (4.98 mg/L).

Conclusions

1. The tested sorbents reduced the concentrations of ammonium nitrogen (27–98% efficiency) and phosphate phosphorus (21–58% efficiency) in wastewater.
2. Glauconite (after 3 hours in a muffle furnace at a temperature of 550 °C) had the greatest ability to sorb phosphorus. Under the conditions of this study, the PO_4–P sorption efficiency was 58%.
3. Ammonium nitrogen from wastewater was best sorbed by natural glauconite. Under the conditions of this study, the sorption efficiency of NH_4–N was 98%.
4. The results showed that the adsorption process on glauconite could be used as an effective method for removing NH_4^+ from wastewater.
5. Modification of glauconite by incineration at 550 °C can improve its ability to sorb phosphorus from wastewater.

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AMONIO AZOTO IR FOSFATO FOSFORO PAŠALINIMO IŠ NUOTEKŲ, NAUDOJANT NATŪRALIUS IR MODIFIKUOTUS SORBENTUS, TYRIMAI

I. FEDIV, K. STEPOVA, J. MAŽEIKA

Santrauka. Darbe nagrinėjami amonio azoto ir fosfato fosforo šalinimo iš nuotekų klausimai. Natūralūs ir modifikuoti sorbentai: ceolitas, glaukonitas ir bentonitas – buvo išbandyti laboratorinėmis sąlygomis. Tyrimo metu buvo naudojamos biologiškai išvalytos nuotekos, kai vidutinė amonio azoto koncentracija buvo 5 mg/L ir vidutinė fosfato fosforo koncentracija – 3,4 mg/L. Prieš bandymą fosfato fosforo koncentracija nuotekose buvo padidinta iki 20 mg/l, pridedant kalio hidrofosfato druskos. Glaukonitas (išdegintas 3 valandas mufelinėje krosnyje 550 °C temperatūroje) turėjo didžiausią gebą sorbuoti fosforą. Šio tyrimo sąlygomis PO_4–P sorbcijos efektyvumas buvo 58 %. Amonio azotą iš nuotekų geriausiai sorbavo natūralus glaukonitas. Šio tyrimo sąlygomis NH_4–N sorbcijos efektyvumas buvo 98 %. Rezultatai parodė, kad glaukonito adsorbcijos procesas gali būti naudojamas kaip efektyvus amonio šalinimo iš nuotekų metodas.

Reikšminiai žodžiai: nuotekos, fosforas, amonis, azotas, sorbentai.