РОЗДІЛ 2. ХІМІЧНА, РАДІАЦІЙНА ТА ЕКОЛОГІЧНА БЕЗПЕКА В УМОВАХ ВІЙНИ ТА ТЕХНОГЕННОГО НАВАНТАЖЕННЯ

CHAPTER 2. CHEMICAL, RADIATION, AND ENVIRONMENTAL SAFETY DURING WAR AND TECHNOGENIC STRESS

ADVANCED ADSORPTION MATERIALS BASED ON NATURAL MINERALS FOR WATER FILTRATION SYSTEMS IN EMERGENCY SITUATIONS

СУЧАСНІ АДСОРБЦІЙНІ МАТЕРІАЛИ НА ОСНОВІ ПРИРОДНИХ МІНЕРАЛІВ ДЛЯ ФІЛЬТРАЦІЙНИХ СИСТЕМ ОЧИЩЕННЯ ВОДИ В УМОВАХ НАДЗВИЧАЙНИХ СИТУАЦІЙ

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Abstract. This study investigates the efficiency of removing eutrophication agents—phosphate (PO_4^{3-}) and ammonium (NH_4^+) ions—from wastewater using natural sorbents: glauconite and clinoptilolite. The sorption capacities of natural, thermally treated, and metal-modified samples were compared. It was found that Fe- and Cu-modified samples demonstrated the highest efficiency for phosphate removal, while ammonium was better adsorbed by natural or Fe-modified clinoptilolite and thermally activated glauconite. The adsorption processes were analyzed using Langmuir-Freundlich isotherm models, allowing a detailed assessment of the interaction mechanisms between the sorbents and target ions. Experiments with real wastewater samples confirmed the applicability of these minerals in tertiary filtration systems. The findings highlight the practical value of glauconite and clinoptilolite as environmentally safe, cost-effective materials for the treatment of domestic and industrial wastewater containing eutrophication-inducing substances. Their use may significantly reduce nutrient loads entering natural water bodies and contribute to the preservation of aquatic ecosystems and environmental sustainability.

Keywords: wastewater, adsorption, eutrophication agents, clinoptilolite, glauconite.

Анотація. У роботі досліджено ефективність видалення евтрофікуючих агентів — іонів фосфатів (PO_4^{3-}) та амонію (NH_4^+) — зі стічних вод за допомогою природних сорбентів: глауконіту та клиноптилоліту. Проведено порівняння сорбційної здатності природних, термічно оброблених та металомодифікованих зразків. Встановлено, що для PO_4^{3-} найбільш ефективними є зразки, модифіковані іонами Fe та Cu, тоді як NH_4^+ краще поглинається природним або Fe-модифікованим клиноптилолітом, а також термічно обробленим глауконітом. Для опису процесів адсорбції застосовано ізотерми Ленгмюра-Фрейндліха, що дозволило оцінити характер взаємодії сорбентів з іонами. Експерименти з реальними стічними водами підтвердили доцільність використання мінералів у фільтраційних системах доочистки. Отримані результати вказують на практичну цінність глауконіту й клиноптилоліту як екологічно безпечних і доступних матеріалів для очищення стічних вод від евтрофікуючих речовин у побутовому та промисловому секторах.

Ключові слова: стічні води, адсорбція, еврофікуючі агенти, клиноптилоліт, грауконіт.

INTRODUCTION

In today's world, when environmental and humanitarian crises are tied together, making sure people have access to safe water is a big deal for countries. In particular, in the context of full-scale war in Ukraine, there is a growing need to develop and implement portable water purification systems that can be used in the field: for military units, displaced persons, populations in frontline areas, or in areas with destroyed infrastructure. Reliable and rapid purification of water from nitrogen and phosphorus, which cause eutrophication, is not only a environmental issue, but also an issue of survival and health.

Wastewater contains significant concentrations of ammonium (NH_4^+) and phosphates (PO_4^{3-}), substances that are nutritious for aquatic organisms but, in excessive amounts, cause ecosystem degradation. These substances cause algae blooms, reduce dissolved oxygen, worsen hydrobiological conditions, pollute water intakes, and can also negatively affect the human respiratory and digestive systems. During hostilities, access to centralized water disposal and treatment becomes difficult, which creates an additional burden on local ecosystems and requires immediate technical solutions.

One promising approach to solving this problem is the use of natural mineral sorbents, in particular glauconite and clinoptilolite, which are capable of binding ammonium and phosphate ions even in unstable conditions. These minerals have high ion exchange capacity, resistance to temperature variations, and can be used in mobile filtration units suitable for use in field conditions.

The aim of this study is to evaluate the effectiveness of natural, thermally treated, and metal-modified glauconite and clinoptilolite in the processes of NH_4^+ and PO_4^{3-} removal from wastewater. Particular attention is paid to the influence of pH, type of modification, and sorbent behavior in real wastewater. The results obtained can serve as a basis for the development of portable filtration systems that will provide fast and affordable water purification in areas where centralized treatment is absent or destroyed, both for military needs and for the civilians.

STATE OF WASTEWATER POLLUTION BY EUTROPHICATING AGENTS IN THE REGION

Wastewater pollution poses a serious environmental threat, as many of these products contain chemical compounds that can affect aquatic ecosystems and cause negative impacts on the aquatic environment. Wastewater from private households and many industrial and agricultural enterprises is characterized by high concentrations of ammonium and phosphates. However, nitrogen and phosphorus are also two important nutrients for plants and microorganisms, but their excess can have a negative impact on aquatic ecosystems, leading to eutrophication[443,444]. The presence of nutrients leads to the development of cyanobacteria (blue-green algae). Excessive algae growth impairs the operation of water intake structures and fisheries facilities, reduces hydraulic flow parameters, and water blooms also lead to a decrease in dissolved oxygen content, deterioration of conditions for the development of flora and fauna, and disruption of the normal functioning of natural ecosystems[445,446]. The high phosphate content in domestic wastewater is not only a pressing issue today, but has been a problem for the last decade. The average phosphate flow is

[443] J Liu, Y Feng, Y Zhang, N Liang, H Wu and F Liu, 'Allometric Releases of Nitrogen and Phosphorus from Sediments Mediated by Bacteria Determines Water Eutrophication in Coastal River Basins of Bohai Bay' (2022) 235 Ecotoxicology and Environmental Safety 113426 https://doi.org/10.1016/j.ecoenv.2022.113426

[444] J Huang, C-C Xu, BG Ridoutt, X-C Wang and P-A Ren, 'Nitrogen and Phosphorus Losses and Eutrophication Potential Associated with Fertilizer Application to Cropland in China' (2017) 159 Journal of Cleaner Production 171 https://doi.org/10.1016/j.jclepro.2017.05.008.

[445] DS Baldwin, 'Water Quality in the Murray–Darling Basin: The Potential Impacts of Climate Change' (2021) 1 Murray-Darling Basin, Australia 137 https://doi.org/10.1016/B978-0-12-818152-2.00007-3.

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33.9 thousand tons per year. Using the area of Ukraine's territorial waters, it has been calculated that 1.56 thousand tons of phosphorus enter Ukraine's coastal waters annually with atmospheric precipitation[4]. By comparison, the entire territory of Lithuania is located in an area sensitive to eutrophication, which is why relatively stricter requirements for wastewater treatment are applied. Amendments to Wastewater Management Regulation No. D1-236 (2016) of the Republic of Lithuania describe the process of removing phosphorus (up to 5 mg/l) and nitrogen (up to 25 mg/l) compounds in small treatment plants. The maximum permissible concentration of ammonium nitrogen in treated wastewater discharged into the natural environment is 5 mg/l. Ammonium nitrogen, commonly referred to as nitrogen in the form of free ammonia nitrogen (NH_3) and ammonium ions (NH_4^+), is present in natural waters. Its high content is observed in wastewater, such as domestic wastewater. Typically, the pH of domestic wastewater is <9, so NH4+ is the dominant form.

Compliance with MPCs (maximum permissible concentrations) for pollutants in wastewater is crucial for the environment and human health. According to the Rules for the Acceptance of Wastewater into Centralized Wastewater Disposal Systems, approved by Order No. 316 of the Ministry of Regional Development, Construction, and Housing and Communal Services of Ukraine dated December 1, 2017, with amendments dated January 6, 2022, Appendix 4 (Section IV, paragraph 2) contains the following requirements for the composition and properties of wastewater 2017, as amended on 06.01.2022, Appendix 4 (paragraph 2 of Section IV) contains the following requirements for the composition and properties of wastewater discharged into the centralized water disposal system for its safe disposal and treatment at the treatment facilities of the centralized water disposal system (Table 1):

Table 1

Maximum permissible value of index and/or concentration in the sample[447]

Wastewater quality indicators		Measurement unit	Maximum permissible value of the indicator and/or concentration in the wastewater sample
1.	Nitrogen (total organic and ammonium nitrogen)	mg/dm^{-3}	50,0
2.	Total phosphorus (P_{tot})	mg/dm^{-3}	5,0

Measuring phosphate and ammonium levels in waterways is an important part of environmental monitoring and water resource management to prevent negative impacts on the environment. In Lviv, water bodies located or originating in the city are monitored (Fig. 1) by the Administrative and Technical Management Municipal Enterprise (information from the Lviv City Council website). The media has repeatedly reported that the results of the analyses showed exceedances of the maximum permissible concentration for the following indicators: iron, ammonia, suspended solids, COD, BOD 5, phosphates, surfactants, and nitrates[448,449].

[447] Pro zatverdzhennia Pravyl pryimannia stichnykh vod do system tsentralizovanoho vodovidvedennia ta Poriadku vyznachennia rozmiru platy, shcho spravliaietsia za ponadnormatyvni skydu stichnykh vod do system tsentralizovanoho vodovidvedennia: Nakaz Ministerstva rehionalnoho rozvytku, budivnytstva ta zhytlovo-komunalnoho hospodarstva Ukrainy vid 1 hrudnia 2017 r. № 316, stanom na 23 liutoho 2024 r *https://zakon.rada.gov.ua/laws/show/z0056-18#Text*.

[448] 'Chym zabrudneni vodoymy Lvova. Rezultaty doslidzhennia' (Tvoie Misto – tvoie telebachennia, no date) *https://tvoemisto.tv/news/chym_zabrudneni_vodoymy_lvova_rezultaty_doslidzhennya_102225.html*.

[449] 'Rezultaty analiziv vody u vodoymakh Lvova perevyshchuiut hranichno dopustymi normy' (Lvivskyi portal, no date) *https://portal.lviv.ua/news/2017/04/10/rezultati-analiziv-vodi-u-vodoymah-lvova-perevishhuyut-granichno-dopustimi-normi*.

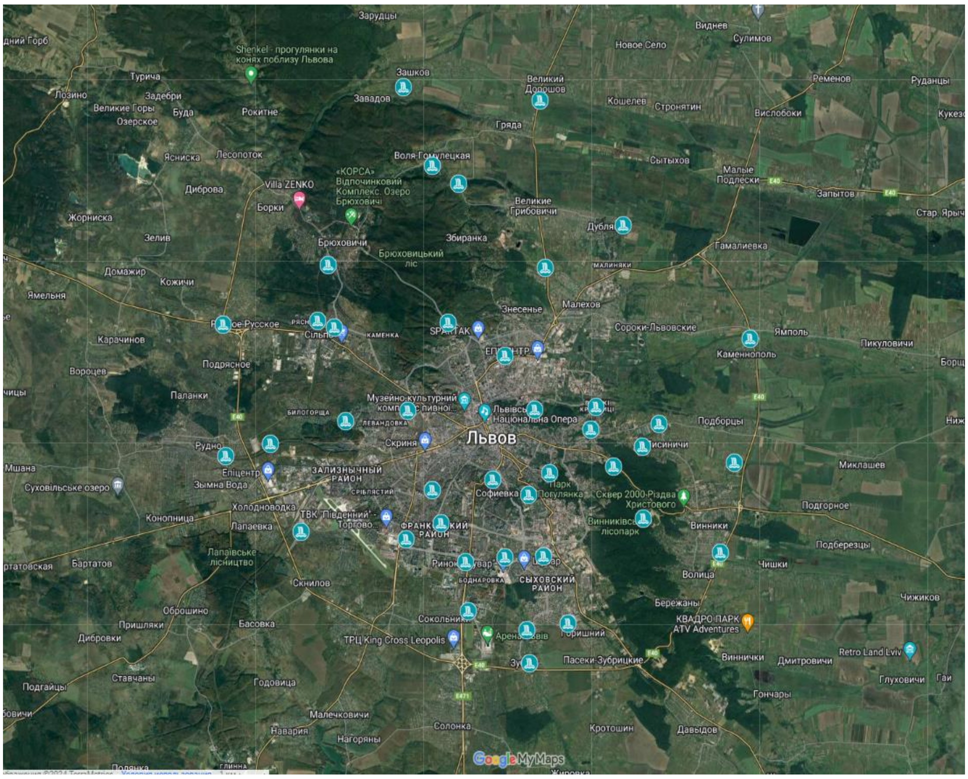

Figure 1. Water sampling points in Lviv (Google Maps)

As can be seen from the graphs based on data from the "Analysis of water from Lviv streams"[450] at sampling points (Figs. 2, 3, 4, 5) over the past 4 years, there has been a significant increase in the number of cases where the maximum permissible concentrations for phosphates and ammonia have been exceeded. This trend could have serious consequences for water resources and ecosystem health, requiring immediate action to prevent further deterioration of the situation.

In this context, installing systems for the post-treatment of household wastewater to remove eutrophicating agents is becoming an extremely important measure. These systems can effectively remove phosphates, ammonia, and other pollutants from wastewater, preventing them from entering water bodies and helping to preserve the ecological balance.

The installation of such systems will help reduce pressure on water resources, improve water quality for humans and animals, and preserve the biodiversity of aquatic ecosystems. In addition, it will raise public awareness of the importance of environmentally friendly practices in the use of water resources and ensure the health and well-being of local communities.

In general, the installation of tertiary wastewater treatment systems for households to remove eutrophicating agents is a step towards preserving the environment, ensuring ecological stability, and protecting the health of people and nature.

[450] 'Analiz vody lvivskykh potokiv (z 2008)' (Google Docs, no date) *https://docs.google.com/spreadsheets/d/1Si8xp5YFHfgBTRRafizeWsi69zwiukxOL1epHGmf-TY/edit#gid=1379203732*.

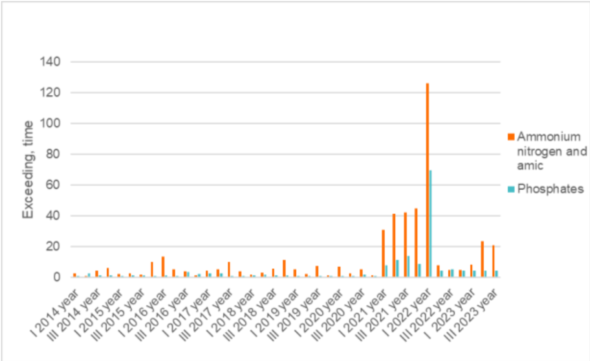

Figure 2. Sampling point 'Vodyanui' (coordinates: 49.810116, 23.930060)[8]

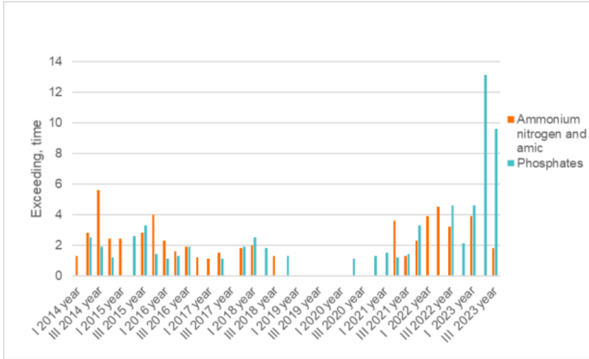

Figure 3. Sampling point 'the Zubra River' (coordinates: 49.794250, 24.040694)[8]

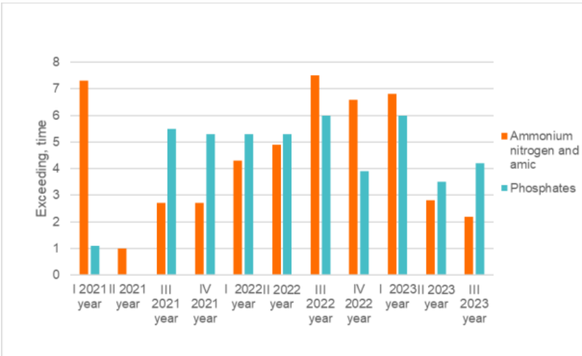

Figure 4. Sampling point 'Stream in the village of Mali Hrybovychi' (coordinates: 49.912313, 24.017428)[8]

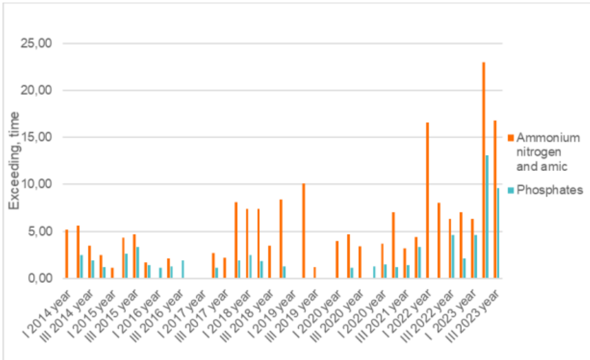

Figure 5. Sampling point 'Lysynichi' (coordinates: 49.843719, 24.117364)[8]

Thus, effective removal of phosphorus and nitrogen from wastewater is a key strategy in controlling eutrophication. The final stage of the technological processes should be post-treatment by adsorption[451].

Landfill fires and the mismanagement of hazardous waste in urban areas represent critical threats to chemical and biological safety, frequently leading to the contamination of water resources with toxic compounds. Under these conditions, deploying mobile filtration systems based on natural mineral sorbents offers an effective and adaptable solution for emergency water treatment[452,453,454].

CHARACTERISTICS OF EUTROPHICATING AGENTS

Excessive nutrient inputs into water bodies lead to eutrophication — toxic algae blooms, fish kills, and deterioration of drinking water quality[455]. This is a widespread problem in water bodies around the world, caused, in particular, by the irrational discharge of industrial and agricultural waste[456,457].

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451 K Stepova, I Fediv, A Mažeikienė, J Šarko and J Mažeika, 'Adsorption of Ammonium Ions and Phosphates on Natural and Modified Clinoptilolite: Isotherm and Breakthrough Curve Measurements' (2023) 15(10) Water 1933 https://doi.org/10.3390/w15101933.

452 VV Popovych and VP Kucheriavyi, 'Vplyv produktiv horinnia polihoniv tverdykh pobutovykh vidhodiv na orhanizm liudyny ta biotu' (2012) 20 Pozhezhna bezpeka: zbirnyk naukovykh prats 60.

453 VV Popovych, AI Buchkovskyi and NP Popovych, 'Lohistychna systema transportuvannia nebezpechnykh vidhodiv v umovakh mista' (2013) 8 Visnyk LDUBZhD: zbirnyk naukovykh prats 166.

454 VP Kucheriavyi and VV Popovych, 'Polihony tverdykh pobutovykh vidhodiv Zakhidnoho Lisostepu Ukrainy ta problemy yikh fitomelioratsii' (2012) 22.2 Naukovyi visnyk NLTU Ukrainy: zbirnyk naukovo-tekhnichnykh prats 56.

455 JY Huang, NR Kankanamge, C Chow, DT Welsh, TL Li and PR Teasdale, 'Removing Ammonium from Water and Wastewater Using Cost-Effective Adsorbents: A Review' (2018) 63 Journal of Environmental Sciences 174 https://doi.org/10.1016/j.jes.2017.09.009.

456 AR Ravishankara, JS Daniel and RW Portmann, 'Nitrous Oxide (N_2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century' (2009) 326(5949) Science 123 https://doi.org/10.1126/science.1176985.

457 E Stokstad, 'Air Pollution: Ammonia Pollution from Farming May Exact Hefty Health Costs' (2014) 343(6168) Science 238 https://doi.org/10.1126/science.343.6168.238.

Among nitrogen-containing substances, ammonium (NH_4^+) is the most common in wastewater, coming from both natural and anthropogenic sources[458]. Ammonium is toxic to fish even in low concentrations[459], and its transformation products — nitrates and nitrites — can cause methemoglobinemia in humans. Some of the ammonium evaporates in the form of ammonia (NH_3), which even in low doses (50–100 ppm) causes irritation to the eyes, skin, and respiratory tract[460,461]. In combination with SO_x and NO_x, ammonia forms secondary aerosols[12]. More than 200 million tons of NH_3/NH_4^+ are emitted annually[462], the main sources of which are fertilizer production, livestock farming, aquaculture, and industry. For example, about 60% of the nitrogen from the diets of animals on feedlots is lost in the form of ammonia[463].

As for phosphates, they are also an important nutrient, but their excess in water (above the MPC) causes environmental disturbances. The main sources of phosphorus are detergents (50–70%), human activity (30–50%), and industry (2–20%). Due to their impact on algae, the EU banned phosphate detergents in 2013[464].

Orthophosphate (>50%) is the most common form of phosphorus in water, while polyphosphate and organic phosphorus are found in smaller quantities. Traditionally, precipitation or biological treatment methods have been used to remove phosphates, but these have their drawbacks: instability, formation of harmful sediments, or high cost[18]. In this context, adsorption is gaining increasing attention as a simple, effective, and affordable technology that is being actively researched using inexpensive natural materials.

CHARACTERISTICS OF NATURAL SORBENTS

Clinoptilolite

Clinoptilolite is a natural volcanogenic-sedimentary mineral of the zeolite group with pronounced ion exchange, adsorption, and catalytic properties[465]. It belongs to the HEU (gelandite) group with a two-dimensional crystal structure[466], built from $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra with the inclusion of exchangeable cations[467].

One of the largest deposits in Europe is located near the village of Sokyrnytsia (Zakarpattia) region, which makes clinoptilolite an accessible material for wastewater treatment, especially from ammonium. To effectively remove phosphates, clinoptilolite is modified with Fe, Ca, or Cu cations, which ensure the sorption of negatively charged ions[468].

Ion exchange in zeolites occurs through the replacement of cations (Na^+, K^+, Ca^{2+}, etc.) from the solution. It depends on the pH, temperature, hydration capacity, and nature of the cations, as well as the

[458] VV Karabyn and YuM Rak, 'Khimichnyi sklad atmosfernykh opadiv v okolytsiakh m. Boryslava' (2016) 26 Zbirnyk naukovykh prats Instytutu heokhimii navkolyshnoho seredovyshcha 41.
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[468] OE Senderov and NI Khitarov, Tseolity, ikh sintez i usloviia obrazovaniia v prirode (Nauka 1970).

conditions of zeolite formation[469]. These properties determine the high selectivity, mobility, and efficiency of ion exchange even at room temperature. By changing the cations in the structure, it is possible to regulate thermal stability, sorption capacity, and catalysis.

Glauconite

Glauconite is a clay mineral with high sorption capacity for phosphates and heavy metals, used for water and soil purification[470]. Its formation is associated with marine transgressions, and its morphology varies from fecal granules to aggregates. It is also used in geochronology (K–Ar method).

Despite its lack of industrial value, glauconite has potential as an adsorbent for phosphates, with a surface area of 55 m^2/g, porosity of 0.032 cm^3/g, and pore radius of 1.99 nm[471]. Effective purification is achieved in just 1 minute at pH ~11. However, in its natural form, the mineral is prone to clogging filters. The solution is granulation, which increases strength, filter life, and preserves sorption capacity[472].

Further studies have shown that composite granulated sorbents with the addition of sunflower husks increase the purification efficiency to 78%[473]. Such sorbents are cheap, effective, and suitable for recycling. The use of glauconite in backfill filters opens up prospects for its reuse as a fertilizer together with clinoptilolite[474].

ADSORPTION OF EFTROPHIC AGENTS ON NATURAL SORBENTS

The adsorption of phosphate ions (PO_4^{3-}) on natural and modified clinoptilolites is best fitted by the Langmuir-Freundlich isotherm. For ammonium ions (NH_4^+), this model is also most suitable in the case of natural, Fe-modified, and microwave-irradiated samples. However, for thermally treated and Cu-modified samples, the Freundlich model shows a better fit.

The highest capacity for NH_4^+ was shown by the Fe-modified (4.375 mg/g) and thermally activated samples (2.879 mg/g). With regard to phosphates, metal-modified samples significantly exceed the natural sorbent: from 800.62 mg/g (Cu) to 813.14 mg/g (Fe), while for natural — 280.86 mg/g, and for calcined — 713.568 mg/g. Thus, clinoptilolite acts as an ion exchanger for NH_4^+ and an adsorbent for PO_4^{3-}.

For glauconite, the adsorption of both PO_4^{3-} and NH_4^+ is best described by the Langmuir-Freundlich model. The nature of the PO_4^{3-} isotherm indicates the presence of a microporous structure that promotes phosphate retention. In contrast, the NH_4^+ isotherm indicates the formation of a multimolecular layer on the outer non-porous surface, which indicates surface sorption of ammonium.

Thermo-treated glauconite had the lowest efficiency for phosphates (1.78 mg/g), but demonstrated a high capacity for ammonium (20.66 mg/g). Optimization of sorption properties is achieved through irradiation or metal modification: for NH_4^+ — 4.36 mg/g (irradiated), 3.67 mg/g (Fe), 4.11 mg/g (Cu); for PO_4^{3-} — 143.1 mg/g in a sample modified with iron salts[475,476].

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[476] K Stepova, I Fediv, A Mažeikienė, J Šarko and J Mažeika, 'Adsorption of Ammonium Ions and Phosphates on Natural and Modified Clinoptilolite: Isotherm and Breakthrough Curve Measurements' (2023) 15(10) Water 1933 https://doi.org/10.3390/w15101933.

INFLUENCE OF pH ON THE SORPTION PROCESS AND DETERMINATION OF THE ZERO CHARGE POINT

Figures 6 and 7 show the dependence of pH change in solutions upon contact with the studied samples on the initial pH value. The figure shows that the point of zero charge for copper-modified samples is at a pH of 3.5-4, and for iron-modified samples, it is at a pH of 6. When considering natural and thermally modified samples, the point of zero charge is at a pH of 8-8.4. From these data, it can be concluded that thermal modification of natural minerals leads to a shift of the zero charge point to a higher pH range, namely to values of 8-8.4. This means that modified samples have a more amphoteric nature, i.e., they can adsorb both cations and anions from solution in a wider pH range compared to natural samples. Such a shift can be useful for improving the adsorption properties of modified minerals in a wide range of environmental conditions, which may be important for their application in wastewater treatment in different areas with different pH characteristics.

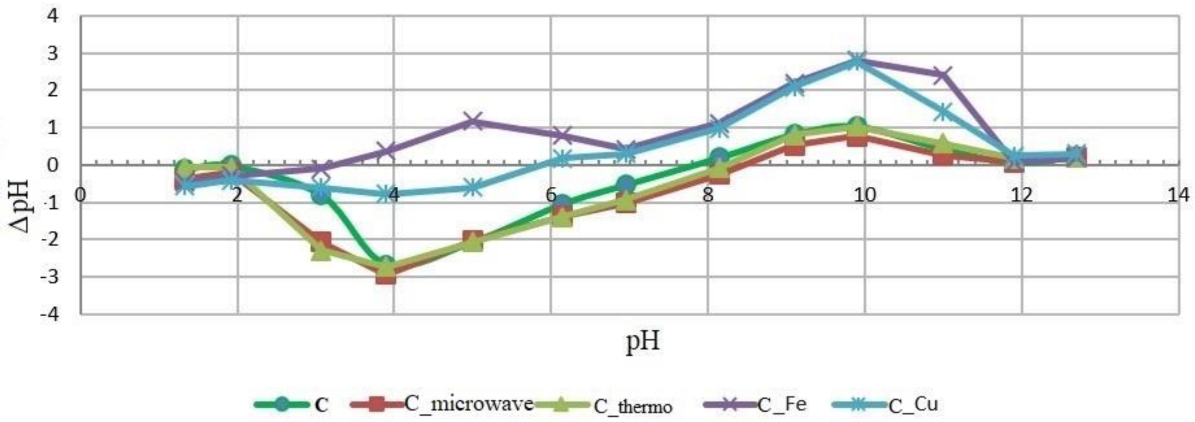


Figure 6. Diagram showing the determination of the point of zero charge for clinoptilolite samples

The low pH range (3.5-4 for copper and 6 for iron) for the modified samples may indicate that their surface becomes acidic when reacting with water. This means that in this pH range, they are effective for adsorbing cations from solution, as there will be more active positively charged groups on their surface. Such conditions may be useful for removing various cationic contaminants from water solution using modified minerals.

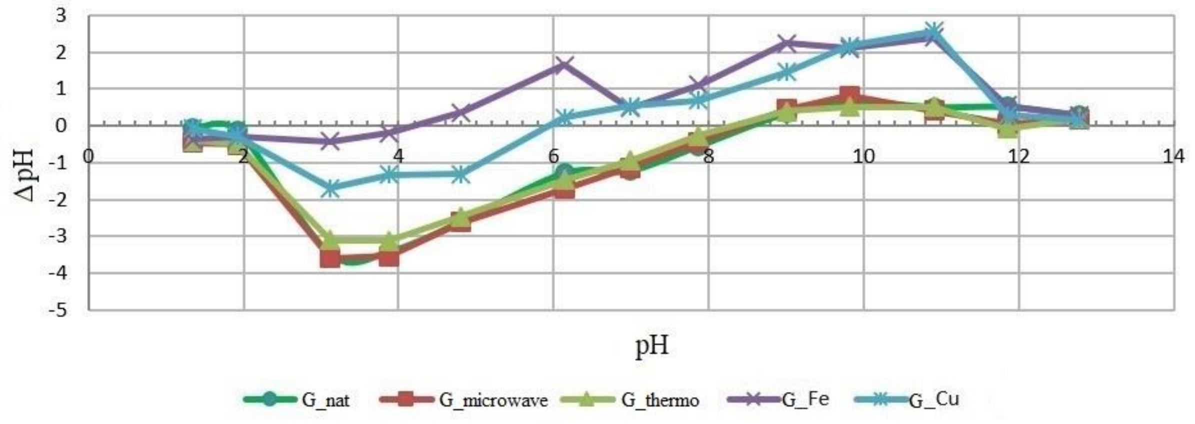


Figure 7. Diagram showing the point of zero charge for glauconite samples

Figure 8 shows that the adsorption efficiency of phosphate in a strongly acidic environment (pH = 2) is lowest for the natural glauconite sample. In contrast, Fe-modified glauconite shows an absorption efficiency of 15-23% across the entire pH range. The thermally modified sample also proved to be quite effective, almost at the level of natural glauconite, with the special property of greater absorption capacity at low pH values. The Cu-modified sample has the lowest efficiency.

During phosphate absorption, there is a significant difference in absorption capacity between clinoptilolite and glauconite (Fig. 9).

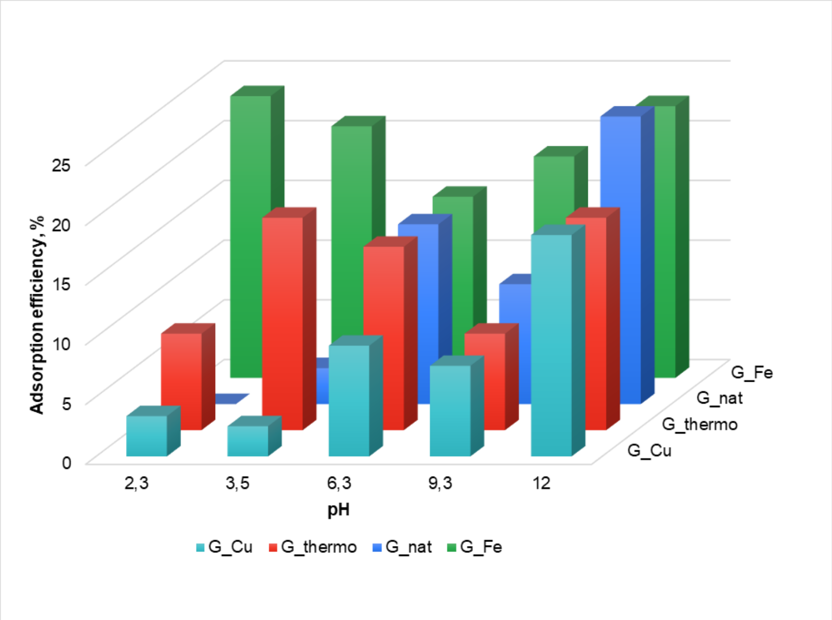


Figure 8. Graph showing the dependence of PO_4^{3-} adsorption efficiency on the initial pH of glauconite

The Cu-modified sample demonstrates the highest efficiency, which is 15%. At high pH, the absorption efficiency of Fe-modified clinoptilolite decreases compared to the natural sample, while heat treatment reduces the efficiency of clinoptilolite at pH = 2.

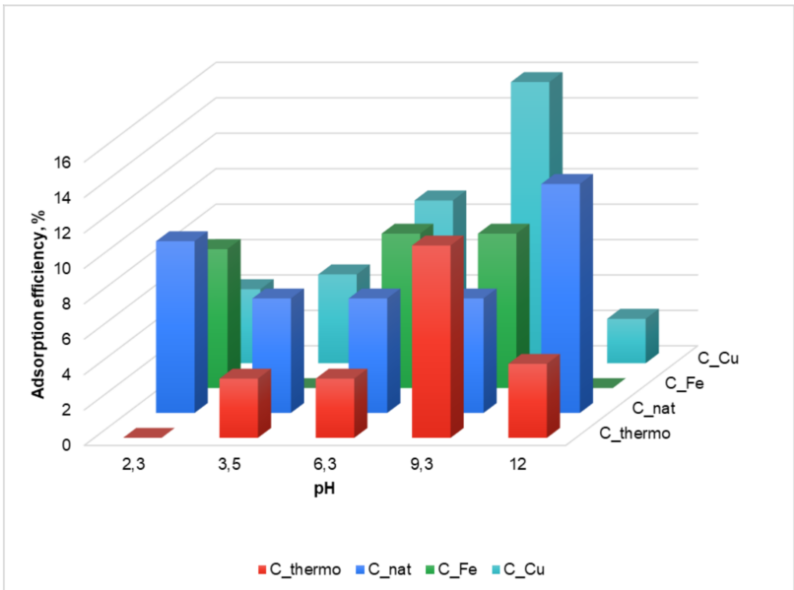


Figure 9. Diagram of dependence of PO_4^{3-} adsorption efficiency on the initial pH on clinoptilolite

Figure 10 shows that thermally treated and metal-modified clinoptilolite significantly reduces sorption efficiency at pH values between 2 and 9, while absorption efficiency at pH 12 increases compared to the natural sample. The highest absorption efficiency is 94% in the heat-treated sample. This may be due to changes in the structure and chemical properties of the material during heat treatment, as well as the effect of metal modifications on its sorption properties in different pH environments.

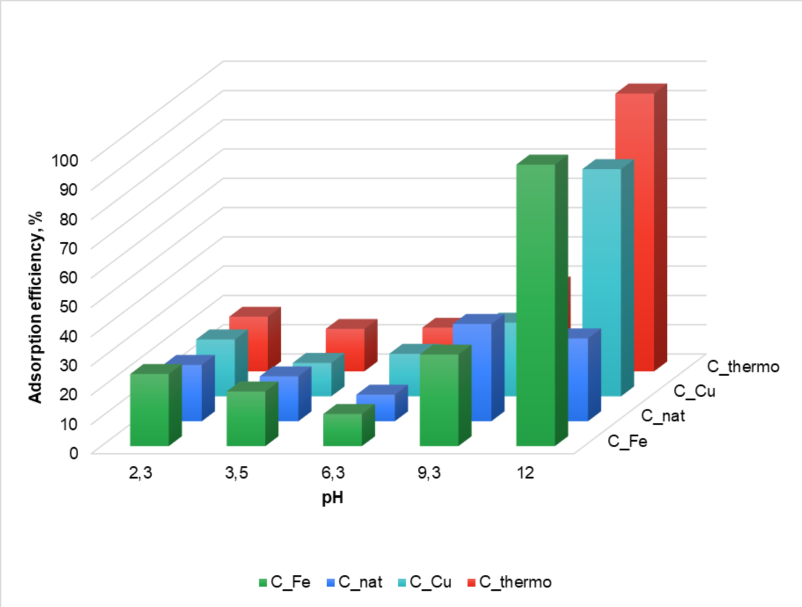


Figure 10. Diagram of dependence of NH_4^+ adsorption efficiency on the initial pH on clinoptilolite

In Figure 11, we can see that modification has a positive effect on NH_4^+ sorption in the pH range from 2.3 to 9.3, and at pH 12, all modified samples show 2 or more times the sorption efficiency on clinoptilolite.

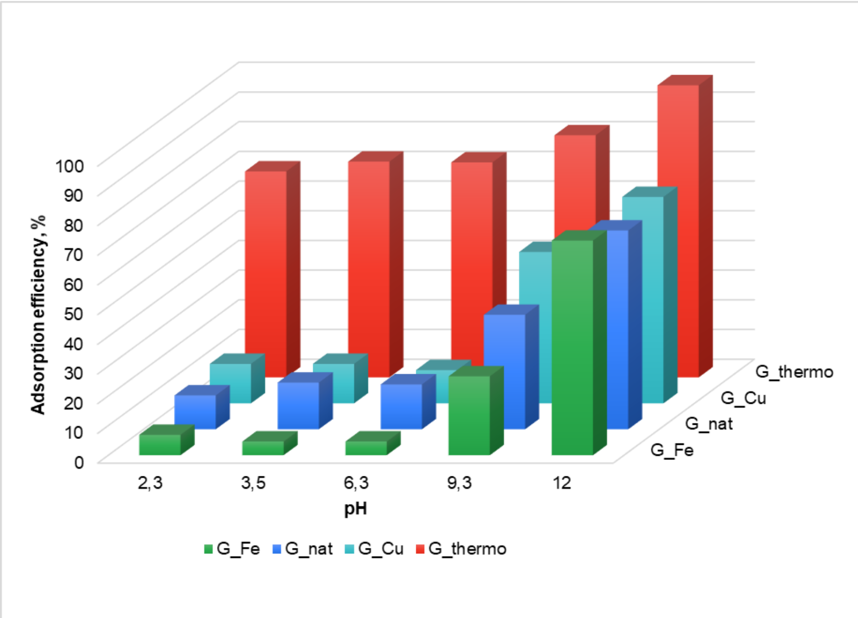


Figure 11. Diagram of dependence of NH_4^+ adsorption efficiency on the initial pH on glauconite

The glauconite samples (Fig. 3.14) show that thermal modification has a positive effect on sorption across the entire pH range, while metal-modified samples have a slight but noticeable increase in ammonium absorption efficiency.

ADSORPTION FROM REAL WASTEWATER SOLUTIONS ON THE TEST SAMPLES

The wastewater from the catering complex was collected upstream of the settling tank to test the sorbents in real conditions, and studies were conducted under static conditions to determine the maximum sorption capacity. The initial concentration of ammonium was 14.05 mg/L and that of phosphates was 49.75 mg/L. One gram of the sample was added to a 250 ml flask and filled with 100 ml of wastewater. As can be seen in Figures 4.6 and 4.7, the samples studied can be arranged in the following order depending on their maximum sorption capacity in relation to phosphates: copper-modified glauconite (3.45 mg/g) > heat-treated glauconite (1.79 mg/g) > natural glauconite (1.31 mg/g) > copper-modified clinoptilolite (1.24 mg/g). All clinoptilolite samples, except for copper-modified, did not absorb phosphates from wastewater, so it can be assumed that during sorption, organic substances can block the active centers of clinoptilolite, which reduces its ability to adsorb phosphates. Other ions (e.g., nitrates, sulfates, chlorides) may also be present in wastewater, competing with phosphates for active sites on the surface of clinoptilolite.

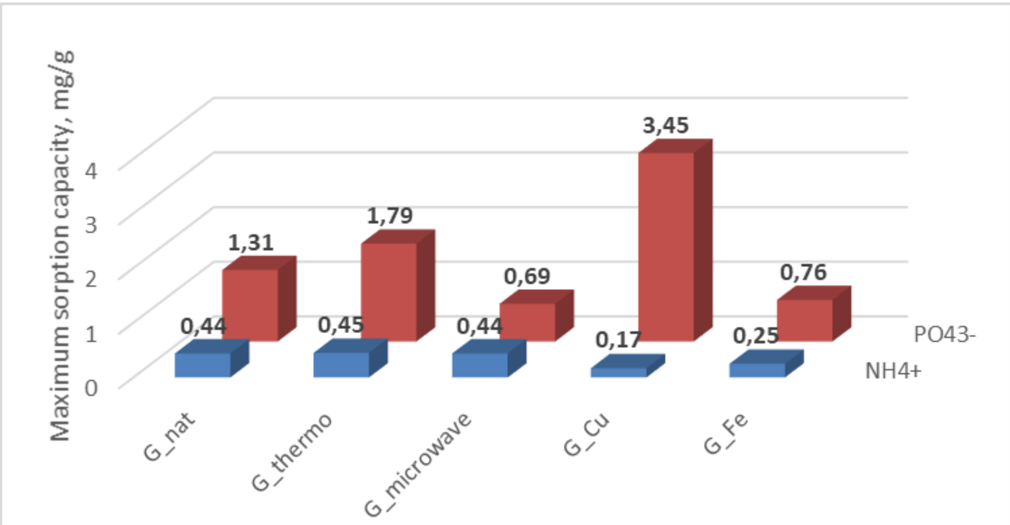
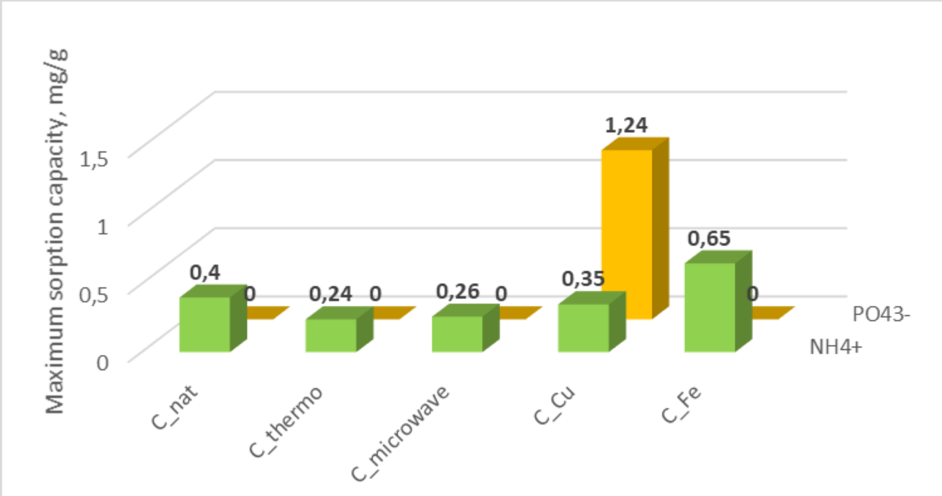


Figure 12. Sorption capacity of glauconite from real wastewater

Based on the results of experiments on the purification of real wastewater, presented in Figures 12 and 13, it was determined that the maximum sorption capacity of samples for ammonium can be arranged in the following order: Fe-modified clinoptilolite (0.65 mg/g) > thermally modified glauconite (0.45 mg/g) > natural glauconite (0.44 mg/g), irradiated glauconite (0.44 mg/g) > natural clinoptilolite (0.4 mg/g) > Cu-modified clinoptilolite (0.35 mg/g). It is obvious that thermal treatment and irradiation reduce the sorption capacity of clinoptilolite with respect to NH_4^+, but do not affect the sorption properties of glauconite. On the other hand, modification with metals leads to a decrease in the sorption capacity of glauconite with respect to ammonium (Fe-modified 0.24 mg/g; Cu-modified 0.17 mg/g). Therefore, in the case of NH_4^+ absorption, it is not advisable to modify natural glauconite, but the introduction of iron (III) ions into the clinoptilolite structure significantly improves its sorption properties with respect to ammonium.



Fugure 13. Sorption capacity of clinoptilolite from real wastewater

For comprehensive treatment of domestic wastewater from this particular catering establishment, we can offer a filter filled with copper-modified clinoptilolite, which has demonstrated the highest adsorption capacity for eutrophicating agents when they are present together, for use in a wastewater post-treatment system.

CONCLUSIONS

The results of the research confirm the relevance of the problem of excessive content of eutrophicating agents, in particular ammonium and phosphates, in wastewater, especially in conditions of environmental stress caused by military operations. The destruction of infrastructure, population displacement, and limited access to centralized water treatment systems all underscore the need to develop portable, autonomous post-treatment systems that can be used in the field for the needs of the military, rescuers, or residents of crisis areas.

The research revealed that natural sorbents — clinoptilolite and glauconite — are highly effective in removing ammonium ions and phosphates from wastewater. In particular, clinoptilolite modified with iron and copper showed high sorption capacity for PO_4^{3-}, while ammonium was better absorbed by natural or thermally activated clinoptilolite. Glauconite showed stable efficiency for phosphates without additional treatment, and thermal modification increased its ability to absorb NH_4^+.

The Langmuir-Freundlich model was used to characterize the sorption mechanisms in detail and determine the best conditions for the sorbents to work. Experiments with real wastewater showed that in complex multicomponent environments, the active centers of clinoptilolite can be blocked by organic substances or competitive ions. However, copper-modified clinoptilolite retains high efficiency for both types of pollutants, making it a promising material for dual-action filter cartridges.

These results suggest that glauconite and clinoptilolite, especially in modified or granulated form, are a good choice for making mobile filtration systems. Such systems can be implemented in the form of portable filters for purifying domestic or technical water in field conditions — at temporary bases, military accommodation points, mobile medical units, etc.

Thus, natural mineral sorbents are not only an environmentally safe and economically viable option, but also a strategic tool for ensuring water security in times of war, humanitarian crises, or emergencies. Further research should focus on studying the service life and regeneration of sorbents and their implementation in compact filtration modules for tactical and civilian use.