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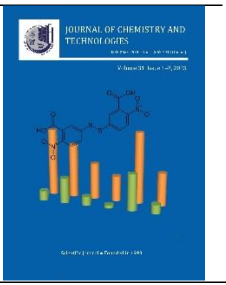

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LOW-WASTE TECHNOLOGIES OF ION-EXCHANGE EXTRACTION OF PHOSPHATES FROM SOLUTION

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Abstract

Excessive supply of biogenic substances with wastewater from industrial enterprises, in particular phosphorus, causes excessive eutrophication of natural water bodies, which leads to the qualitative depletion of water resources. The most promising method of water purification from phosphates is ion exchange. The process of sorption of phosphates on highly basic anionite in chloride and alkaline form is investigated in the present work. The processes of influence of competing anions on the efficiency of phosphate extraction were studied. It was established that the selectivity of the AV-17-8 anionite increases in the series of chlorides-phosphates-sulfates. It is shown that for regeneration of anionite in phosphate and phosphate-sulfate form it is advisable to use solutions of 10 % NH_4Cl, 15 % NaCl, 6 % Na_2CO_3, 7% KOH, 6 % $(NH_4)_2SO_4$. Methods for extracting phosphates from regeneration solutions have been developed making them suitable for reuse. To create waste-free processes, a method of extracting phosphates from water using AV-17-8 anionite and its regeneration has been proposed, which will allow extracting phosphates in the form of mineral fertilizers and repeatedly using regeneration solutions.

Keywords: anionite; phosphates; sorption; magnesium chloride; regeneration solutions; struvite.

МАЛОВІДХОДНІ ТЕХНОЛОГІЇ ІОНООБМІННОГО ВИЛУЧЕННЯ ФОСФАТІВ ІЗ РОЗЧИНУ

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Анотація

Надмірне надходження зі стічними водами промислових підприємств біогенних речовин, зокрема фосфору, спричиняє надмірну евтрофікацію природних водойм, що призводить до якісного виснаження водних ресурсів. Найбільш перспективним методом очищення води від фосфатів є іонний обмін. У роботі досліджені процеси сорбції фосфатів на високоосновному аніоніті в хлоридній та лужній формах. Досліджено процеси впливу конкуруючих аніонів на ефективність вилучення фосфатів. Встановлено, що селективність аніоніту АВ-17-8 збільшується в ряду хлориди-фосфати-сульфати. Показано, що для регенерації аніоніту в фосфатній та фосфатно-сульфатній формах доцільно використовувати розчини 10 % NH_4Cl, 15 % NaCl, 6 % Na_2CO_3, 7 % KOH, 6 % $(NH_4)_2SO_4$. Розроблені методи вилучення фосфатів із регенераційних розчинів, що робить їх придатними для повторного використання. Для створення безвідходних процесів було запропоновано спосіб вилучення фосфатів із води на аніоніті АВ-17-8 та його регенерацію, що дозволить вилучати фосфати у вигляді мінеральних добрив та багаторазово використовувати регенераційні розчини.

Ключові слова: аніоніт, фосфати; сорбція; хлорид магнію; регенераційні розчини; струвіт.

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Introduction

Surface reservoirs are the main source of water supply in Ukraine. The development of industry and urbanization lead to an increase in water consumption, and finally this causes increasing the level of household wastewater discharge [1–3].

The increase in the level of phosphates in the environment occurs as a result of natural and anthropogenic factors [4–7].

Increasing anthropogenic load on ecosystems occurs as a result of the development of industry, agricultural industry and also the growth of the planet's population. Finally the discharge of wastewater from industrial enterprises and agricultural lands that use phosphate fertilizers, animal complexes and municipal sewage leads to an excessive influx of phosphates into surface and underground water bodies. In addition, the industrial production of fertilizers and detergents, as well as their improper use, also lead to the pollution of water bodies with phosphates [8, 9].

Weathering and dissolution of rocks containing orthophosphates (apatites and phosphorites) and their arrival on the catchment surface in the form of ortho-, meta-, pyro- and polyphosphate ions (fertilizers, surfactants, etc.), biological processing of animal and plant residues are the main natural factors of phosphorus level increase [10; 11].

The State Water Agency has prepared information about discharges of phosphates into surface water object as a part of return wastewater based on the data from the state water use accounting in 2019. So, in 2019, 5.708 tons of phosphates were dumped into water object of Ukraine. The largest polluter of water object is the housing and communal economy that makes up 5354 tons. The industry is significantly inferior in this respect, however, it is still the second in the anti rating with 319.5 tons. They are followed by: agriculture –10.1tons; trade and catering – 8.3 tons; transport – 5.1tons and health care – 4.1 tons [12].

Phosphorus compounds play a decisive part in the processes of photosynthesis and vital activity of living organisms, but their excess in the aquatic environment leads to eutrophication. As a result, a rapid development of certain types of microalgae takes place, which leads to a disturbance in the balance of aquatic ecosystems. Therefore, an important task is the creation of effective low-waste technologies for water purification from phosphates.

In water purification technologies from biogenic elements, physical, biological, chemical – reagent, membrane and ion exchange methods are most often used [13–15].

The use of reagent methods for further purification of water from phosphates allows removing phosphates in the form of poorly soluble compounds of iron, aluminum and other salts, which avoids forming the significant volumes of liquid waste. However, the development of methods for extracting these sediments not only complicates the technology of water purification, but also increases its cost [16; 17]. Separation of sediments in the process of further purification involves additional expenditures. Firstly, this needs the special reagents that would precipitate phosphates and, secondly, the technical component, as an additional line in the cleaning process. As a result, this means the necessity in additional technological equipment.

Electrocoagulation technology has some drawbacks that can limit its effectiveness. For example, the electrodes should be replaced periodically, since they dissolve in the solution due to the oxidation process, so, it is necessary to select the reactor designs and the operating parameters of the process [18].

The use of the biological method is impractical due to the complexity of the process, the insufficient efficiency of removing phosphates from water, and the length of time it takes to obtain the necessary biomass for the decomposition of phosphorus compounds [19–24].

In the case when biological indicators deteriorate due to changes in operating conditions, the adsorption method can be used in addition to the biological purification of water from phosphates. To reduce the concentration of phosphates in water, it is proposed to use phosphogypsum based on biochar? [25], synthetic zeolites obtained from fly ash and modified with lanthanum as sorbents [26].

It is rational to use adsorbents based on agricultural waste [27; 28]. They are potential adsorbents for the removal of phosphates from wastewater, but there is the need for improved practical application of these adsorbents on a commercial scale and the development of effective and environmentally safe modification methods [29].

Reverse osmosis filters are used in water purification technologies from biogenic elements. The process of reverse osmosis water purification is effective at initial concentrations of phosphates up to 350 mg/dm^3. However, the use of expensive semipermeable membranes does not allow this process to be widely implemented. To avoid deposits on the membranes, it is necessary to develop methods of effective pre-treatment of water, since this leads to a decrease in the performance and selectivity of the membranes [30–32]. The formation of concentrates is one of the significant disadvantages of reverse osmosis, because it is quite difficult to dispose of them [33–35]. While removing phosphate ions in the form of an insoluble precipitate from concentrates, high concentrations of pollutants (ammonium, chlorides and other ions) remain in the solution, so the issue of processing these solutions before discharge into the sewer remains unresolved.

The ion exchange method is less energy-consuming, it does not require high-quality pre-treatment of water, and it does not lead to the formation of concentrates that must be disposed of. These are advantages in comparison to reverse osmosis methods. In addition, ion exchange installations are much cheaper compared to reverse osmosis [36–38]. While using the ion exchange method during purifying water from phosphates, these ions can be removed from the solution, and it is expedient to obtain liquid fertilizers or other useful products from regeneration solutions [39–42]. The reuse of purified eluates allows reducing water purification costs and switching to low-waste technologies.

The global food security is a priority for the future development agenda of the United Nations. It is imperative that any politics at the international, national and local levels aimed at achieving food security and protecting aquatic ecosystems include measures to address key sustainability issues for the global phosphorus fertilizer resource [43].

The present paper reviews the state-of-the-art of nutrient recovery, focusing on frontier technological advances and also economic and environmental innovation perspectives [44].

Although full-scale P recovery methods are technologically feasible, economic feasibility, legislation and national politics are the main reasons why these methods are not yet used worldwide [45].

Therefore, this work is aimed at creating low-waste phosphorus extraction technologies for its further use.

Thus, it should be noted that the rationality of the ion method is a novelty since this leads to minimal economic costs and waste-free production. After water purification all spent eluates do not need to be disposed of, wasting economic and energy resources, but they are sent to receive useful fertilizers.

Materials and methods

Model solutions were used to study the ion exchange removal of phosphates, the characteristics of which are presented in the Table 1.

Table 1

Characteristics of model solutions

Solution	Water type	C(PO_4^{3-}), mg/dm^3	H, mg-eq/ dm^3	C(SO_4^{2-}), mg/dm^3	C(Cl^-), mg/dm^3	Form AV-17-8
1	Distilled water	95	–	–	–	Cl^-
2	Tap water	95	3.7	36.0	11.8	Cl^-
3	Tap water	105	3.7	60.0	28.0	Cl^-
4	Tap water	115	3.7	96.0	35.0	Cl^-
5	Distilled water	95	–	–	–	OH^-
6	Tap water	95	3.7	60.0	28.0	OH^-

Extraction of phosphates from water was carried out on AV-17-8 anionite in Cl^- (solutions 1 – 4) and OH^- form (solutions 5, 6).

During sorption, samples with a volume of 1000 cm^3 were taken, while the consumption of working solutions was 10–15 cm^3/min. The content of phosphates, nitrates, chlorides, sulfates, alkalinity and pH of the medium were determined in the samples.

During regeneration, samples with a volume of 20 cm^3 were taken, while the flow rate of regeneration solutions was 5 cm^3/min. 10 % ammonium chloride solution, 15 % sodium chloride solution, 6 % sodium and ammonium sulfate solutions, and 7 % potassium hydroxide solution were used to regenerate AV-17-8 anionite. While regenerating ionite with solutions of NH_4Cl, NaCl, $(NH_4)_2SO_4$, the content of phosphates, chlorides or sulfates was controlled, and while regenerating anionite with hydroxide and soda, the alkalinity of the solution, pH, and phosphate concentration were controlled.

The exchange dynamic capacity before leakage (DEC), the total exchange dynamic capacity (TDEC), and the degree of regeneration (A) of ionite were calculated.

Precipitation of phosphate ions with magnesium chloride was carried out in containers with a volume of 250 cm^3 from the spent regeneration solutions based on ammonium chloride. At the same time, phosphates were deposited in the form of struvite – magnesiumammonium phosphate. The initial concentration of phosphates was 30 g/dm^3, the content of ammonium chloride was 50–80 g/dm^3, then the pH of the solution was adjusted to values of 8÷9 with NaOH solution. Magnesium chloride was added to the obtained solutions in different ratios according to the phosphate content and left for 4 hours for the sediment to settle completely. After that, the sediment was separated on a "blue tape" paper filter, and the residual content of phosphates and magnesium was determined in the filtrate.

Results and Discussion

While using in the basic form, a certain increase in the total exchangeable dynamic capacity of the anionite for phosphates was noted, in comparison to the Cl$^-$ form. While filtering through anionite in the OH$^-$ form, the medium is alkalinized, that leads to an increase in pH. This ensures a more complete dissociation of phosphates in water. In the OH form an increase in the capacity of the AV-17-8 anionite for phosphates is noticed, what can be explained by the lower selectivity of the anionite for hydroxide ions compared to chloride ions. Since the concentration of chlorides reaches ~ 100 mg/dm^3 during desorption from anionite in the Cl$^-$ form, chlorides can create a certain competition with phosphate ions.

While filtering solutions with an initial concentration of phosphates of 95 mg/dm^3 prepared in distilled water, the growth of the DEC of the anionite by phosphates before the breakthrough is particularly significant – from280 mg-eq/dm^3 for anionite in the Cl$^-$ form to 1003 mg-eq/dm^3 for ionite in OH$^-$ form. This dependence is typical for solutions which do not contain competing ions. However, chlorides and sulfates are usually present in natural and wastewater. At high concentrations of these anions, removal of phosphates from water is appropriate only in the context of complete demineralization of water. If the concentrations of sulfates and chlorides are relatively low, up to 50 mg/dm^3, as, for example, in the Dnipro or Desnian water, the use of the ion exchange method is appropriate.

Therefore, in subsequent studies, the efficiency of phosphate sorption in the presence of sulfate anions on the highly basic anionite AV-17-8 in Cl$^-$ and OH$^-$ form was investigated. In this case the capacity of anionite for phosphates decreased significantly, compared to distilled water due to the presence of sulfates in the solution.

Since sulfate anions are strong acid anions, and phosphate ions are medium acid anions, their charge depends on the pH of the medium. Phosphoric acid is of the medium strength one, its charge depends on the pH of the medium. At pH > 7.2, the phosphate group appears mainly in a dissociated state forming anions of the HO-P(O)(O$^-$)$_2$ type, the degree of its dissociation is lower than that of sulfates. Therefore, AV-17-8 has a higher selectivity for sulfate anions, which are completely removed regardless of the form of the ionite and the volume of water passed through.

For anionite in the Cl$^-$ form, the TDEC was 1501, 1010, 715 mg-eq/dm^3, and the DEC reached only 702, 235, 97 mg-eq/dm^3 for solutions with the initial phosphate concentration of 95, 105 and 115 mg/dm^3, respectively.

For anionite in the OH$^-$ form, the TDEC was 917 mg-eq/dm^3, and the DEC reached only 255 mg-eq/dm^3 for a solution with an initial phosphate concentration of 95 mg/dm^3.

Complete dissociation of the phosphate anion to form a three-charged anion of the type (O)P(O$^-$)$_3$ occurs at pH ≥ 11.9, in the process of ion exchange, while using anionite in the OH$^-$ form, the pH increases only to 9.5–10.0. Therefore, the decrease in the phosphate capacity of AV-17-8 anionite in its basic form is caused by a higher concentration of sulfates in water, and not by the ionite form. So, in this case, the phosphate capacity of AV-17-8 was mainly determined by the concentration of competing sulfate anions.

Therefore, an increase in the concentration of sulfates in the solution leads to a decrease in the TDEC of the AV-17-8 anionite with respect to phosphates. During desalination of water containing sulfates and phosphates, these anions are initially removed simultaneously, but after displacement of the main mass of chlorides, sorbed phosphates are displaced by sulfates, since ionite has a higher selectivity for sulfates. Therefore, the concentration of phosphates in the last sample exceeds the concentration that was in the original solution.

Table 2

Permissible values of MPC for phosphates for different water sources (mg/dm^3)

drinkable water	water supply (tap water?)	flowing water	ponds and lakes	return water	wastewater entering biological treatment facilities
3.5	0.4	0.1	0.05	0.03	10.0

Therefore, the creation of a low-waste technology for extracting phosphates from water is expedient at low concentrations of sulfates in water. In the case while using highly basic anionite in chloride form, it is possible to purify water effectively from phosphates while reducing their concentrations to 0.1–10.0 mg/dm^3. This method allows extracting a large amount of a valuable component from water. Since the average concentration of sulfates is ~ 50 mg/dm^3 in the waste water of the Bortnitskaya aeration station, the ion exchange methods are suitable. Thus, with a concentration of phosphates of ~ 40–90 mg/dm^3 (60 g/m^3) during the discharge of wastewater at the Bortnitskaya aeration station with a consumption of ~ 1,100,000 m^3/day, it will be possible to remove ~ 44–99 tons of phosphates, which is important in conditions of shortage and high prices of phosphorus fertilizers.

So, the Fig. 1 shows that the present method can be used for purifying to a certain limit, until phosphates begin to slip through the residual samples again saturating the ionite. The method is more suitable for low-concentration phosphate solutions.

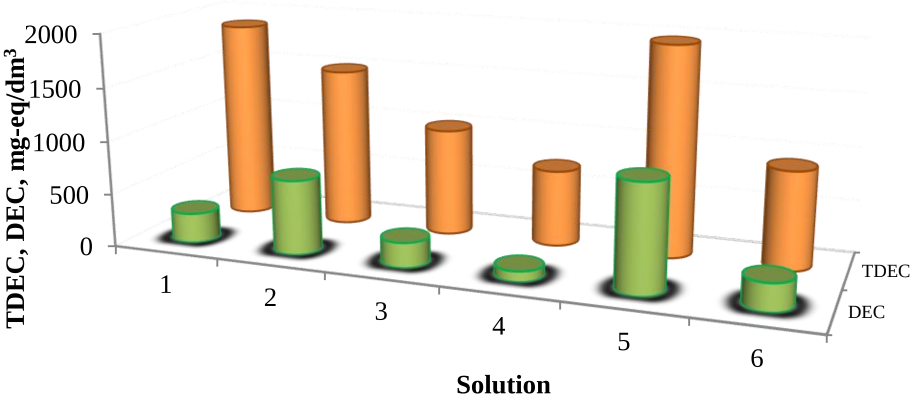


Fig. 1. The dependence of the exchange dynamic capacity of the anion exchange AV-17-8 before leakage (DEC) and its total dynamic exchange capacity (TDEC) for phosphates in Cl$^-$ (1–4), OH$^-$ (5, 6) form of ion exchanger on the composition of the solution

To create a low-waste technology of ion exchange water purification, it is necessary to develop effective methods of anionite regeneration and disposal of spent regeneration solutions. Solutions of NH_4Cl, NaCl, Na_2CO_3, KOH, $(NH_4)_2SO_4$ were used to regenerate AV-17-8 anionite (Fig.2).

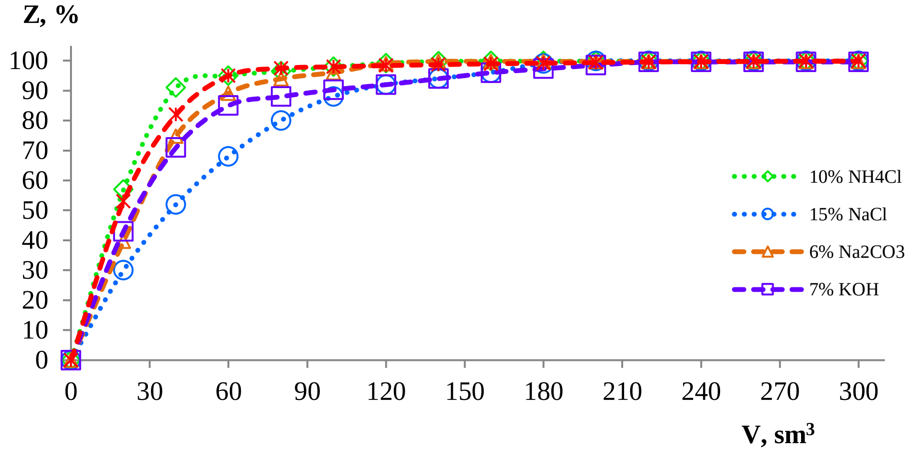


Fig. 2. Dependence of the degree of phosphate desorption from AV-17-8 anionite on the specific consumption of regeneration solutions

The increase in the cost of phosphorus fertilizers, the shortage of high-quality phosphate rocks, and the increase in surface water pollution make necessary accelerating the recovery and reuse of phosphorus from various waste sectors [46–48]. Crystallization of struvite is a potential method of phosphorus recovery through the production of slow-release fertilizers, since the availability of phosphorus resources is currently limited and, according to forecasts, phosphorus will soon be depleted [49, 50].

In the case of presence nitrates in the solution planting struvite is impractical. So, alkaline solutions were investigated for the regeneration of ionite, since when the spent solutions are neutralized with nitric or phosphoric acid, they can be fully used in the production of liquid fertilizers – nitrogenand phosphorous.

Phosphates are desorbed quite effectively while using a 6% soda solution. At a specific consumption of regeneration solution of 4 cm^3 per 1 cm^3 of AV-17-8 anionite, the degree of desorption reaches 93.9%. Nearly complete removal of phosphates occurs when the specific loss increases to 7 cm^3/cm^3. Ionite in the phosphate form is effectively regenerated with a solution of potassium hydroxide. In terms of regeneration efficiency, these solutions are not inferior to ammonium chloride.

The use of ammonium sulfate solution ensures high efficiency of phosphate desorption. The regeneration solution containing phosphates, sulfates, ammonium, nitrates is suitable for the production of liquid fertilizers.

In the case of high concentrations of sulfates in the water its purification from phosphates is appropriate only in the context of complete water demineralization. In the presence of sulfates in water in relatively low concentrations up to 50 mg/dm^3 the use of the ion exchange method is quite acceptable. For the regeneration of anionite, it is advisable to use a 10% solution of sodium chloride. NaCl provides quite effective desorption of phosphates. The degree of phosphate desorption is 95.0%. At a specific consumption of the regeneration solution of 3 cm^3 per 1 cm^3 of anionite, it increases to 99.8-99.9 at a consumption of 6-7 cm^3/cm^3. To reuse the sodium chloride solution containing phosphates, it was treated with ammonium chloride and magnesium chloride while bringing the pH to 9 with alkali, which allows struvite to be precipitated from it and a NaCl solution to be obtained.

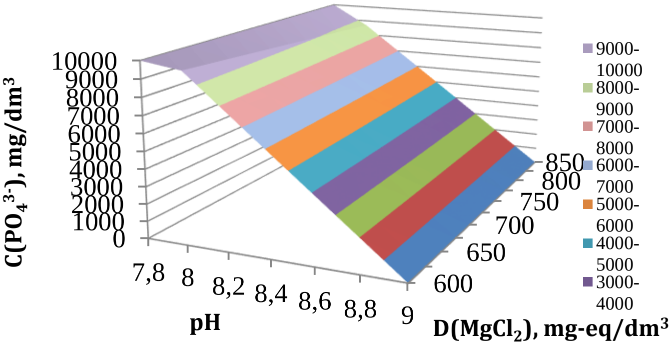
$$Na_3PO_4 + NH_4Cl + MgCl_2 \rightarrow MgNH_4PO_4\downarrow + 3\ NaCl \qquad (1)$$

However, this method makes possible to obtain a solution that will contain phosphates, as well as sulfates, since the latter desorb quite well from the AV-17-8 anionite [36]. Therefore, to restore the regeneration solution containing sulfates, it is better to use calcium chloride treatment that will allow planting gypsum from the solution, which is suitable for processing into building materials. While treating the solution with soda, the remaining calcium will be precipitated in the form of calcium carbonate. The regeneration solution, after clarification by settling and filtering, is suitable for repeated use in the regeneration of AV-17-8 anionite in sulfate-phosphate form.

Anionite in phosphate form is effectively regenerated by ammonium chloride solution. In the process of regeneration of anionite 10% NH_4Cl, ammonium phosphate is formed, which is a valuable mineral fertilizer, so it is important to achieve its complete desorption. At a specific consumption of the regeneration solution of 8 cm^3 per 1 cm^3 of anionite, phosphates are completely desorbed. The advantage of this method is the possibility of extracting water-insoluble magnesium ammonium phosphate (struvite ($MgNH_4PO_4$)) from the regeneration solution, as well as the reuse of the solution in the processes of desorption of phosphates from anionite (reaction 2).

$$(NH_4)_3PO_4 + MgCl_2 \rightarrow MgNH_4PO_4\downarrow + 2NH_4Cl \qquad (2)$$

The efficiency of removing phosphates from the ammonium chloride solution largely depends on the pH and it increases with increasing pH up to 9.0. When the solution was adjusted to pH 9.0 with ammonia, almost complete removal of phosphate from the solution was achieved. Precipitation of struvite in the form of sediment occurred most effectively when magnesium chloride was added in a stoichiometric amount (Fig. 3, Fig. 4).



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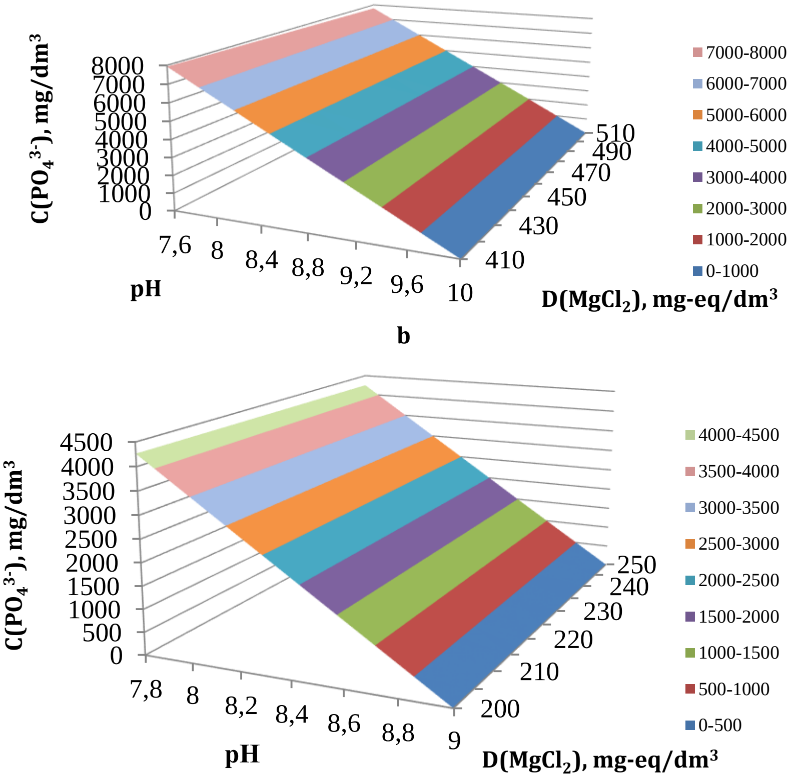

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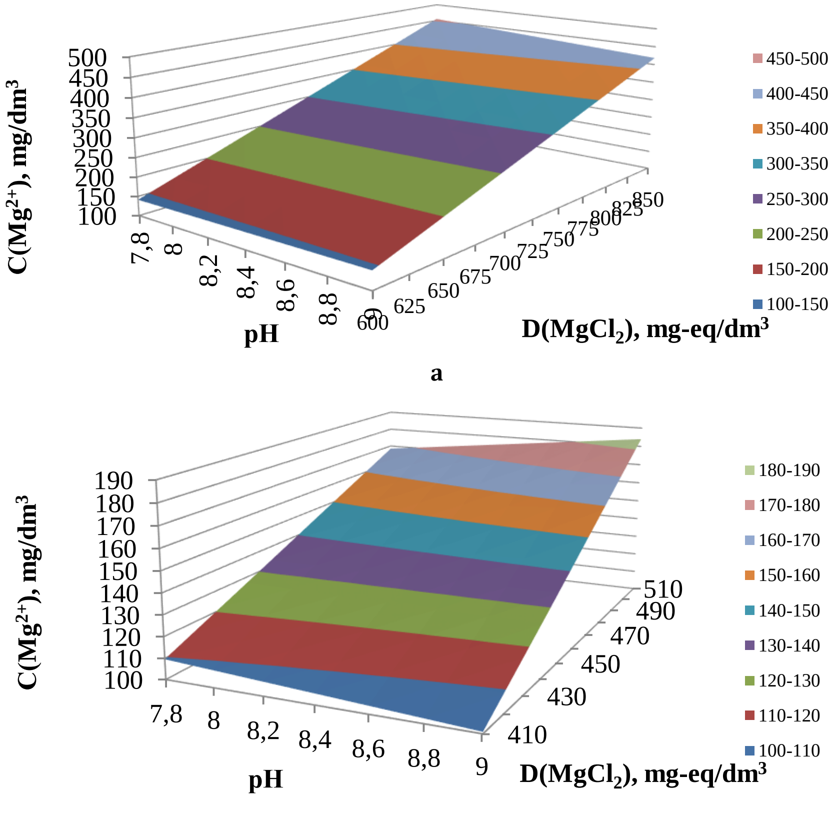
Fig. 3. The dependence of the residual concentration of phosphates on the consumption of magnesium chloride during the treatment of an ammonium phosphate solution containing 50 (a), 60 (b) and 80 (c) g/dm³ of ammonium chloride



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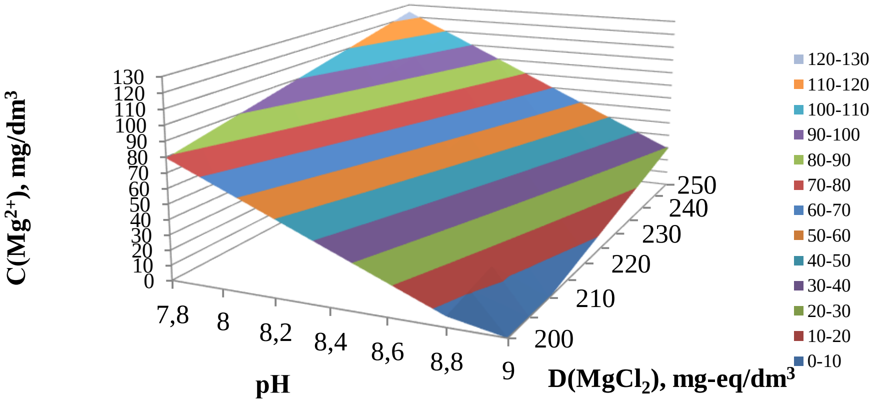

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Fig. 4. The dependence of the residual concentration of magnesium on the consumption of magnesium chloride during the treatment of an ammonium phosphate solution containing 50 (a), 60 (b) and 80 (c) g/dm^3 of ammonium chloride

At a 1:1 molar ratio of $(NH_4)_3PO_4$ and $MgCl_2$, nearly total precipitation of struvite occurs. At the same time, almost no magnesium remains in the solution, so this solution should be used for repeated regeneration of anionite in phosphate form.

The efficiency of removing phosphates from the solution depends on the pH of the medium. Phosphates were planted inefficiently at pH 8. Increasing pH to 9 allows reducing residual phosphate concentrations to < 1 mg/dm^3. While treating solutions with magnesium chloride at pH=9, with an increase in the concentration of ammonium phosphate in the regeneration solutions, an increase in the residual concentrations of magnesium ions is observed to fairly high values. This makes their reuse impossible, as it will lead to the formation of sediments in the anionite pores. Increasing the pH to 9÷10 allows simultaneous effective removing the both phosphates and magnesium ions from the solution.

Conclusions

To create waste-free processes, the method of extracting phosphates from water using AV-17-8 anionite and its regeneration was proposed, which will allow extracting phosphates in the form of mineral fertilizers and repeatedly using regeneration solutions.

While evaluating the efficiency of ion exchange extraction of phosphates on highly basic anionite, it was established that AV-17-8 sorbs phosphate anions quite effectively while using in both Cl^- and OH^- forms.

It was established that highly basic anionite in chloride and basic form is suitable for removing phosphates from water. It is shown that the capacity of the anionite practically does not depend on the form of the ionite. It strongly depends on the presence of competing ions, in particular sulfates, therefore, the method is appropriate only for concentrations of sulfates < 50 mg/dm^3.

It was established that complete desorption of phosphates from anionite can be achieved using solutions of 10 % NH_4Cl, 15 % NaCl, 6 % Na_2CO_3, 7 % KOH, 6 % $(NH_4)_2SO_4$. The spent regeneration solutions are promising for the production of liquid fertilizers.

Treatment of the ammonium chloride solution with a stoichiometric amount of magnesium chloride makes it possible to restore and reuse the regeneration solution and obtain struvite. Increasing the pH of the solution from 8 to 9÷10 makes it possible to increase the efficiency of phosphate precipitation from the solution in the form of struvite. Increasing the consumption of magnesium practically does not affect the process, so, the efficiency of phosphate precipitation improves, but not significantly.

References

[1] Mitchenko, T., Kosogina, I., Kyrii, S. (2019). The local solutions for water security in Ukraine. *Physical and Cyber Safety in Critical Water Infrastructure*, 99–105. doi: 10.3233/NICSP190044

[2] Trus, I., Gomelya, N., Halysh, V., Radovenchyk, I., Stepova, O., Levytska, O. (2020). Technology of the comprehensive desalination of wastewater from mines. *Eastern-European Journal of Enterprise Technologies*, 3/6 (105), 21–27. https://doi.org/10.15587/1729-4061.2020.206443

[3] Remeshevska, I., Trokhymenko, G., Gurets, N., Stepova, O., Trus,I., Akhmedova, V. (2021). Study of the Ways and

Methods of Searching Water Leaks in Water Supply Networks of the Settlements of Ukraine.*Ecol. Eng. Environ. Technol.*, *22*(4), 14–21. https://doi.org/10.12912/27197050/137874

[4] Zhang, X., Yi, Y., Yang, Z. (2020). Nitrogen and phosphorus retention budgets of a semiarid plain basin under different human activity intensity. *Science of The Total Environment*, *703*, 134813. https://doi.org/10.1016/j.scitotenv.2019.134813

[5] Zhao, Z., Qin, W., Bai, Z., & Ma, L. (2019). Agricultural nitrogen and phosphorus emissions to water and their mitigation options in the Haihe Basin, China. *Agricultural Water Management*, *212*, 262–272.https://doi.org/10.1016/j.agwat.2018.09.002

[6] Wang, M., Wang, Y., Li, Y., Liu, X., Liu, J., & Wu, J. (2020). Natural and anthropogenic determinants of riverine phosphorus concentration and loading variability in subtropical agricultural catchments. *Agriculture, Ecosystems & Environment*, *287*, 106713. https://doi.org/10.1016/j.agee.2019.106713

[7] Bunce, J. T., Ndam, E., Ofiteru, I. D., Moore, A., & Graham, D. W. (2018). A review of phosphorus removal technologies and their applicability to small-scale domestic wastewater treatment systems. *Frontiers in Environmental Science*, 6, 8. https://doi.org/10.3389/fenvs.2018.00008

[8] Azam, H. M., Alam, S. T., Hasan, M., Yameogo, D. D. S., Kannan, A. D., Rahman, A., & Kwon, M. J. (2019). Phosphorous in the environment: characteristics with distribution and effects, removal mechanisms, treatment technologies, and factors affecting recovery as minerals in natural and engineered systems. *Environmental Science and Pollution Research*, *26*(20), 20183-20207.https://doi.org/10.1007/s11356-019-04732-y

[9] Mekonnen, M. M., & Hoekstra, A. Y. (2018). Global anthropogenic phosphorus loads to freshwater and associated grey water footprints and water pollution levels: A high-resolution global study. *Water resources research*, *54*(1), 345-358.https://doi.org/10.1002/2017WR020448

[10] Wang, Y., Li, Y., Liu, X., Liu, F., Li, Y., Song, L., ... & Wu, J. (2014). Relating land use patterns to stream nutrient levels in red soil agricultural catchments in subtropical central China. *Environmental Science and Pollution Research*, *21*(17), 10481-10492.https://doi.org/10.1007/s11356-014-2921-9

[11] Clément, F., Ruiz, J., Rodríguez, M. A., Blais, D., & Campeau, S. (2017). Landscape diversity and forest edge density regulate stream water quality in agricultural catchments. *Ecological indicators*, *72*, 627-639.https://doi.org/10.1016/j.ecolind.2016.09.001

[12] https://www.davr.gov.ua/news/pro-skidi-v-poverhnevi-vodni-obyekti-fosfativ-u-skladi-zvorotnih-stichnih-vod-na-osnovi-danih-derzhavnogo-obliku-vodokoristuvannya-u-2019-roci

[13] Bacelo, H., Pintor, A. M., Santos, S. C., Boaventura, R. A., & Botelho, C. M. (2020). Performance and prospects of different adsorbents for phosphorus uptake and recovery from water. *Chemical Engineering Journal*, *381*, 122566.https://doi.org/10.1016/j.cej.2019.122566

[14] Peng, L., Dai, H., Wu, Y., Peng, Y., & Lu, X. (2018). A comprehensive review of phosphorus recovery from wastewater by crystallization processes. *Chemosphere*, *197*, 768–781. https://doi.org/10.1016/j.chemosphere.2018.01.098

[15] Li, K., Liu, Q., Fang, F., Luo, R., Lu, Q., Zhou, W., ... &Ruan, R. (2019). Microalgae-based wastewater treatment for nutrients recovery: A review. *Bioresource technology*, *291*, 121934. https://doi.org/10.1016/j.biortech.2019.121934

[16] Cichy, B., Kużdżał, E., &Krztoń, H. (2019). Phosphorus recovery from acidic wastewater by hydroxyapatite precipitation. *Journal of environmental management*, *232*, 421–427. https://doi.org/10.1016/j.jenvman.2018.11.072

[17] Shewa, W. A., &Dagnew, M. (2020). Revisiting chemically enhanced primary treatment of wastewater: a review. Sustainability, *12*(15), 5928. https://doi.org/10.3390/su12155928

[18] Hashim, K. S., Idowu, I. A., Jasim, N., Al Khaddar, R., Shaw, A., Phipps, D., Aljefery, M. H. (2018). Removal of phosphate from River water using a new baffle plates electrochemical reactor. *Methods X*, *5*, 1413–1418. https://doi.org/10.1016/j.mex.2018.10.024

[19] Yu, S., Liu, S., Yao, X., & Ning, P. (2022). Enhanced biological phosphorus removal from wastewater by current stimulation coupled with anaerobic digestion. *Chemosphere*, 133661. https://doi.org/10.1016/j.chemosphere.2022.133661

[20] Chan, C., Guisasola, A., Baeza, J. A. (2020). Living on the edge: Prospects for enhanced biological phosphorus removal at low sludge retention time under different temperature scenarios. *Chemosphere*, 258, 127230. https://doi.org/10.1016/j.chemosphere.2020.127230

[21] Gebremariam, S. Y., Beutel, M. W., Christian, D., Hess, T. F. (2011). Research advances and challenges in the microbiology of enhanced biological phosphorus removal—a critical review. *Water Environment Research*, *83*(3), 195–219. https://doi.org/10.2175/106143010X12780288628534

[22] Guisasola, A., Chan, C., Larriba, O., Lippo, D., Suárez-Ojeda, M. E., &Baeza, J. A. (2019). Long-term stability of an enhanced biological phosphorus removal system in a phosphorus recovery scenario. *Journal of Cleaner Production*, *214*, 308–318. https://doi.org/10.1016/j.jclepro.2018.12.220

[23] Izadi, P., Izadi, P., Eldyasti, A. (2020). Design, operation and technology configurations for enhanced biological phosphorus removal (EBPR) process: a review. *Reviews in Environmental Science and Bio/Technology*, *19*(3), 561–593.https://doi.org/10.1007/s11157-020-09538-w

[24] Zou, H., Wang, Y. (2016). Phosphorus removal and recovery from domestic wastewater in a novel process of enhanced biological phosphorus removal coupled

with crystallization. *Bioresource technology*, *211*, 87–92. https://doi.org/10.1016/j.biortech.2016.03.073

[25] Wang, B., Lian, G., Lee, X., Gao, B., Li, L., Liu, T., Zheng, Y. (2020). Phosphogypsum as a novel modifier for distillers grains biochar removal of phosphate from water. *Chemosphere*, *238*, 124684. https://doi.org/10.1016/j.chemosphere.2019.124684

[26] Goscianska, J., Ptaszkowska-Koniarz, M., Frankowski, M., Franus, M., Panek, R., Franus, W. (2018). Removal of phosphate from water by lanthanum-modified zeolites obtained from fly ash. *Journal of colloid and interface science*, *513*, 72–81. https://doi.org/10.1016/j.jcis.2017.11.003

[27] Halysh, V., Trus, I., Nikolaichuk, A., Skiba, M., Radovenchyk, I., Deykun, I., Vorobyova, V., Vasylenko, I., Sirenko, L. (2020). Spent Biosorbents as Additives in Cement Production. *Journal of Ecological Engineering*, *21*(2), 131–138. https://doi.org/10.12911/22998993/116328

[28] Halysh, V., Trus, I., Gomelya, M., Trembus, I., Pasalskiy, B., Chykun, N., Trokhymenko, G., Remeshevska I. (2020). Utilization of Modified Biosorbents Based on Walnut Shells in the Processes of Wastewater Treatment from Heavy Metal Ions. *Journal of Ecological Engineering*, 21(4), 128–133.10.12911/22998993/119809

[29] Pokhrel, M. R., Poudel, B. R., Aryal, R. L., Paudyal, H., Ghimire, K. N. (2019). Removal and recovery of phosphate from water and wastewater using metal-loaded agricultural waste-based adsorbents: a review. *Journal of Institute of Science and Technology*, *24*(1), 77–89. https://doi.org/10.3126/jist.v24i1.24640

[30] Trus, I., Gomelya, M., Levytska, O., Pylypenko, T. (2022). Development of Scaling Reagent for Waters of Different Mineralization. *Ecol. Eng. Environ. Technol.*, 4, 81–87. https://doi.org/10.12912/27197050/150201

[31] Trus, I., Gomelya, M., Skiba, M., Pylypenko, T., Krysenko, T. (2022). Development of Resource-Saving Technologies in the Use of Sedimentation Inhibitors for Reverse Osmosis Installations. *J. Ecol. Eng.*, *23*(1), 206–215. https://doi.org/10.12911/22998993/144075

[32] Trus, I., Radovenchyk, I., Halysh, V., Skiba, M., Vasylenko, I., Vorobyova, V., Hlushko, O., Sirenko, L. (2019). Innovative Approach in Creation of Integrated Technology of Desalination of Mineralized Water. *Journal of Ecological Engineering*, *20*(8), 107–113. https://doi.org/10.12911/22998993/110767

[33] Wang, X. X., Wu, Y. H., Zhang, T. Y., Xu, X. Q., Dao, G. H., Hu, H. Y. (2016). Simultaneous nitrogen, phosphorous, and hardness removal from reverse osmosis concentrate by microalgae cultivation. *Water research*, 94, 215–224. https://doi.org/10.1016/j.watres.2016.02.062

[34] Luo, W., Hai, F. I., Price, W. E., Guo, W., Ngo, H. H., Yamamoto, K., Nghiem, L. D. (2016). Phosphorus and water recovery by a novel osmotic membrane bioreactor–reverse osmosis system. *Bioresource technology*, *200*, 297–304. https://doi.org/10.1016/j.biortech.2015.10.029

[35] Li, X., Shen, S., Xu, Y., Guo, T., Dai, H., & Lu, X. (2021). Application of membrane separation processes in phosphorus recovery: A review. *Science of The Total Environment*, *767*, 144346.https://doi.org/10.1016/j.scitotenv.2020.144346

[36] Trus, I., Gomelya, M., Skiba, M., Vorobyova, V. (2021). Promising method of ion exchange separation of anions before reverse osmosis. *Archives of Environmental Protection*, 47(4), 93–97. https://doi.org/10.24425/aep.2021.139505

[37] Trus I. (2022). Optimal conditions of ion exchange separation of anions in low-waste technologies of water desalination. *Journal of Chemical Technology and Metallurgy*, 57(3), 550–558. https://dl.uctm.edu/journal/node/j2022-3/14_21-57_br_3_pp_550-558.pdf

[38] Trus I., Gomelya M. (2022). Low-waste technology of water purification from nitrates on highly basic anion exchange resin. *Journal of Chemical Technology and Metallurgy*, 57(4), 765–772. https://dl.uctm.edu/journal/node/j2022-4/14_21-93_br4_2022_pp765-772.pdf

[39] Beaudry, J. W., Sengupta, S. (2021). Phosphorus recovery from wastewater using pyridine-based ion-exchange resins: Role of impregnated iron oxide nanoparticles and preloaded Lewis acid (Cu^{2+}). *Water Environment Research*, *93*(5), 774–786. https://doi.org/10.1002/wer.1469

[40] Guida, S., Rubertelli, G., Jefferson, B., Soares, A. (2021). Demonstration of ion exchange technology for phosphorus removal and recovery from municipal wastewater. *Chemical Engineering Journal*, *420*, 129913. https://doi.org/10.1016/j.cej.2021.129913

[41] Pinelli, D., Bovina, S., Rubertelli, G., Martinelli, A., Guida, S., Soares, A., Frascari, D. (2022). Regeneration and modelling of a phosphorous removal and recovery hybrid ion exchange resin after long term operation with municipal wastewater. *Chemosphere*, *286*, 131581. https://doi.org/10.1016/j.chemosphere.2021.131581

[42] Williams, A. T., Zitomer, D. H., Mayer, B. K. (2015). Ion exchange-precipitation for nutrient recovery from dilute wastewater. *Environmental Science: Water Research & Technology*, *1*(6), 832–838. https://doi.org/10.1039/C5EW00142K

[43] Chowdhury, R. B., Moore, G. A., Weatherley, A. J., & Arora, M. (2017). Key sustainability challenges for the global phosphorus resource, their implications for global food security, and options for mitigation. *Journal of Cleaner Production*, *140*, 945–963. https://doi.org/10.1016/j.jclepro.2016.07.012

[44] Robles, Á., Aguado, D., Barat, R., Borrás, L., Bouzas, A., Giménez, J. B., Seco, A. (2020). New frontiers from removal to recycling of nitrogen and phosphorus from wastewater in the Circular Economy. *Bioresource technology*, *300*, 122673. https://doi.org/10.1016/j.biortech.2019.122673

[45] Desmidt, E., Ghyselbrecht, K., Zhang, Y., Pinoy, L., Van der Bruggen, B., Verstraete, W., ... &Meesschaert, B. (2015). Global phosphorus scarcity and full-scale P-

recovery techniques: a review. *Critical Reviews in Environmental Science and Technology*, *45*(4), 336–384. https://doi.org/10.1080/10643389.2013.866531

[46] Sarvajayakesavalu, S., Lu, Y., Withers, P. J., Pavinato, P. S., Pan, G., Chareonsudjai, P. (2018). Phosphorus recovery: a need for an integrated approach. *Ecosystem health and sustainability*, *4*(2), 48–57. https://doi.org/10.1080/20964129.2018.1460122

[47] Amann, A., Zoboli, O., Krampe, J., Rechberger, H., Zessner, M., &Egle, L. (2018). Environmental impacts of phosphorus recovery from municipal wastewater. *Resources, Conservation and Recycling*, *130*, 127–139. https://doi.org/10.1016/j.resconrec.2017.11.002

[48] Kataki, S.; West, H.; Clarke, M.; Baruah, D. C. (2016). Phosphorus recovery as struvite: Recent concerns for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential. *Resources Conservation and Recycling, 107*, 142–156. https://doi.org/10.1016/j.resconrec.2015.12.009

[49] Li, B., Huang, H. M., Boiarkina, I., Yu, W., Huang, Y. F., Wang, G. Q., Young, B. R. (2019). Phosphorus recovery through struvite crystallisation: Recent developments in the understanding of operational factors. *Journal of environmental management*, *248*, 109254. https://doi.org/10.1016/j.resconrec.2015.12.009

[50] Corre, K. S. Le, Valsami-Jones, E., Hobbs,P. & Parsons, S. A. (2009). Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review.*Critical Reviews in Environmental Science and Technology*, *39*(6), 433–477.https://doi.org/10.1080/10643380701640573