1. Introduction

Phosphorus belongs to the biogenic elements and is essential for the growth of organisms. This is a nutrient resource that determines the productivity of autotrophs of various environmental systems and primary productivity of water reservoirs. It is known that compounds of carbon, oxygen, or nitrogen can penetrate soils or water from the atmosphere. In contrast, the phosphorus compounds are regularly taken away from soil and water areas into the oceans and returned to the land ecosystems in very limited volumes along with organic matter or detritus.

Despite the fact that phosphorus compounds play a decisive role in the processes of photosynthesis and life of living organisms, their excess in the aquatic environment under certain temperatures leads to eutrophication. Eutrophication is a complex process in fresh and marine waters where rapid development of certain types of microalgae upset the balance of aquatic ecosystems. The primary cause of eutrophication is the excessive concentration of nutrients in water, among which the phosphates occupy an important place.

The inflow of biogenic elements occurs through industrial enterprises, wastewater from agricultural land, animal farms, household wastewater and natural factors. The main sources of inflow of phosphorus to the water areas of the European Union are fertilizers – 16 %, industry – 7 %, background sources – 9 %, human and domestic waste – 24 %, detergents – 10 %, wastewater – 34 % [1–3].

Given the above, it can be concluded that the main source of contamination of water reservoirs with the compounds of phosphorus is agricultural and domestic wastewater. That is why it is a relevant issue to purify the wastewater from phosphorus compounds. In addition, in some cases it is inappropriate to apply this method of purification because of low effectiveness of water dephosphating.

2. Literature review and problem statement

Technologies of water purification from biogenic elements most commonly employ a biological method [1, 4]. The shortcoming of this method is the complexity and duration of obtaining the required biomass in order to decompose the phosphorus compounds. In addition, in some cases it is inappropriate to apply this method of purification because of low effectiveness of water dephosphating.

Reagent methods are most commonly used in order to additionally clean water from phosphates [5]. The advantage of the method is the removal of phosphates in the form of low-soluble compounds of iron, aluminum and other salts, which makes it possible to avoid the formation of significant amounts of liquid waste. However, the separation of the given sediments complicates, in turn, the technology of post-purification of water, thus increasing its cost.

A number of articles have been recently published about the removal of phosphates using the inverse osmotic filters [6].

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4. Materials and methods for examining the removal of phosphates from water by the method of ion exchange

4. 1. Materials and equipment used in the experiment

In present work, we used the strong-base anionite AV-17-8 and the weak-base anionite Dowex Marathon WBA (Fig. 1) as the ion-exchanging materials. We employed the distilled water and tap water in the city of Kyiv, Ukraine.

![Fig. 1. Anionites used in the present work: a – weak-base Dowex Marathon WBA; b – strong-base AV-17-8](image)

Experimental research into removal of phosphates was carried out using the ionic exchange and the reagent method.

4. 2. Technique of conducting the experiment on the removal of phosphates from water on different anionites

We carried out the processes of phosphate sorption on the ion-exchanging materials under dynamic conditions. The ionite of volume 20 cm\(^3\) was put in a column of diameter 19 mm. The solution was filtered through the ionite at the flow rate of 10–15 cm\(^3\)/min., separating the samples of volume 0.1–1.0 dm\(^3\). The samples were analyzed for the content of phosphates, chlorides, sulfates; we determined their pH and residual alkalinity by known methods [11].

The concentration of phosphates was defined by a spectrophotometric method using tin chloride. The method is based on the hydrolysis of polyphosphates that transfer into orthophosphates, with the formation of a phosphorus-molybdenum complex. The complex of blue color is analyzed at wavelength 690–720 nm.

The sulphates were determined by the method of titration with the barium chloride solution. We added ethyl alcohol to the sample, 2 drops of the 0.2 % nitrochrome solution, and then titrated it with the 0.02 H barium chloride solution until changing the color of the solution from purple to blue.

pH index was defined by the method of potentiometry. The method is based on measuring the difference in potentials, which arise between the surface of the pH-selective membrane of a glass electrode, by a standard solution of acid inside the electrode and by the examined solution.

In order to determine the alkalinity, we added 3–4 drops of methyl orange to the sample and titrated with the 0.1 M solution of HCl until the coloration changed from yellow to orange (pH=4).

Determining the hardness was performed by the titration method. For this purpose, we added 5 cm\(^3\) of buffered solution to the sample, 5–7 drops of the indicator eriochrome black, and titrated with the 0.05 H trilon B solution until a change in the coloration from violet to blue in the equivalent point.

The regeneration of anionites was carried out by the solutions of ammonium chloride and sodium chloride of concentration 10 and 15 %. The anionite AB-17-8 was transferred to the basic form by the 4 % solution of alkali. At the regeneration of anionite, the volume of samples was 20 cm\(^3\), the flow rate reached 1–3 cm\(^3\)/min. Regeneration solutions were analyzed for the content of phosphates, chlorides and sulphates. The degree of regeneration was calculated as the ratio of total mass of desorbed phosphates or sulphates to the sorbed mass of the corresponding anion.

In order to remove phosphates from the used regeneration solutions based on ammonium chloride, they were treated with the calculated amount of magnesium chloride. The sediment of phosphate ammonium magnesium was removed on the filter "blue ribbon". The filtrate was analyzed for the content of phosphates and magnesium ions.

5. Results of research into removal of phosphates on anionites

Results of the sorption of phosphate anions are shown in Fig. 2. The figure demonstrates that the strong-base anionite AB-17-8 quite effectively sorbs phosphate anions when used both in the salt and in the basic form. In this case, we observed a certain growth in the full dynamic exchange capacity (FDEC) of anionite by phosphates when used in the basic form, compared with the Cl⁻-form.
Especially significant here is the growth of dynamic exchange capacity of anionite by phosphates until the breakthrough. For the anionite in the Cl-form from 290 mg-equiv/dm³ to 995 mg-equiv/dm³ for the ionite in the OH-form. This is due to the alkalization of medium when applying the ionite in the OH-form. This leads to the increase in pH of the medium to 9.38–10.63 (Fig. 2, curve 5), which in turn provides a more complete dissociation of phosphates in water. In addition, during the desorption of chlorides from anionite in the Cl-form, the concentration of chlorides reaches 70–100 mg/dm³, which is why they may create a certain competition to the phosphate-ions. Selectivity of the anionite AV-17-8 by hydroxide-anions is lower than that by chlorides, which also contributes to increasing the capacity of anionite on the OH-form by phosphates.

Less effective proved to be the use of the weak-base anionite Dowex Marathon WBA while purifying water from phosphates. Fig. 3 shows that we observed the breakthrough of phosphates already in the first samples of the separated solution. The full dynamic exchange capacity of anionite amounted to 641.5 mg-equiv/dm³ only. This is due primarily to a decrease in the sorption properties of ionite in a weakly alkaline environment to a decrease in the degree of dissociation of phosphates in the neutral and weakly acid medium. When using this anionite in the basic form, its capacity by phosphates was even lower. Therefore, further research was carried out using the strong-base anionite AV-17-8.

The data shown in Fig. 2 refer to the solution of phosphates in distilled water, where there are no competing ions. Chlorides and sulphates are as a rule always present in natural and wastewaters. That is why we determined the efficiency of sorption of phosphates on the strong-base anionite AV-17-8 in the Cl- and OH-form.

Fig. 4 shows that the capacity of anionite by phosphates in this case is significantly lower compared with the distilled water. For the anionite in the chloride form, the full dynamic exchange capacity (FDEC) amounted to 1480 mg-equiv/dm³, while the dynamic exchange capacity before the breakthrough (DEC₁gap) reached 689 mg-equiv/dm³ only.

Such a decrease is due primarily to the presence of sulphates in the solution. This anionite obviously has a higher selectivity by sulphate-anions, which are the anions of a strong acid. Phosphoric acid is the acid of medium strength, which is why the charge of phosphate-anions depends on the pH of the medium. At pH exceeding 7.2, a phosphate group is mostly in the basic state of a two-charge cation, of the HO-P(O)(O)₂⁻ type. However, the degree of dissociation of the given anions is lower compared to sulphates, which is why the selectivity of ionite by sulphates is larger.

Fig. 4 shows that sulphate-ions are completely removed from water regardless of the form of ionite and regardless of the volume of the passed water. In this case, dynamic exchange capacity by sulphates reached 646 and 713 mg-equiv/dm³. This is caused by the low concentration of sulphates in water. At higher concentrations of sulphates in water, FDEC of anionite by sulphates amounts to 1590 mg-equiv/dm³, while DEC₁gap = 1330 mg-equiv/dm³ [11].

In this case, reducing the capacity by phosphates on anionite in the basic form is predetermined not by the form of ionite but the higher concentration of sulphates in water. Increasing the pH to 9.5–10.0 when using anionite in the basic form is not sufficient for complete dissociation of phosphate-anion with the formation of a three-charge anionite of the NO₃⁻ form. This anion is formed at pH exceeding 7.2, a phosphate group is mostly in the basic state of a two-charge cation, of the HO-P(O)(O)₂⁻ type. However, the degree of dissociation of the given anions is lower compared to sulphates, which is why the selectivity of ionite by sulphates is larger.
taining sulphates at concentration 570 mg/dm³ amounted to 98 % when cleaning only 2 dm³ of water.

The same results were obtained when using the anionite in the chloride form. In this case, the degree of removal of phosphates amounted to 99–100 % when purifying 6 dm³ of the phosphate solution in distilled water. When cleaning 4 dm³ of the phosphate solution in tap water, the degree of removal reached 99 %. The content of sulphates in tap water amounted to 36.7 mg/dm³. In another case, results of cleaning the tap water from phosphates were higher than the previous ones mainly due to the lower concentration of sulphates.

In general, no results of the ion-exchange water purification can be considered positive without solving the problems on the regeneration of anionites and recycling of the used regeneration solutions.

Fig. 6 shows that the desorption of phosphates from the anionite AV-17-8 occurs quite effectively when using the solutions of sodium chloride and ammonium chloride at concentration 10 and 15 %. It is worth noting that the given solution provides as well effective regeneration of anionite in a mixed sulphate-phosphate form (Fig. 7). The full desorption of phosphates was achieved at qᵢ = 6 cm³/cm³, and the degree of desorption of sulphates at the same consumption of the solution amounted to 82 %. The degree of desorption of 95 % was achieved at specific consumption of the regeneration solution of 10 cm³/cm³.

Application of ammonium chloride for the regeneration of anionite, which is in the phosphate form, has a significant advantage. The regeneration solution that was formed has to be brought to pH=9. Subsequent addition to this solution of magnesium chloride in stoichiometric amount (Table 1) may contribute to achieving almost complete removal of phosphate from the solution.

<table>
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<th>No. of entry</th>
<th>[PO₄³⁻], mol/mol</th>
<th>Consumption of Mg²⁺, mg-equiv/dm³</th>
<th>C(PO₄³⁻), mg/dm³</th>
<th>Mg²⁺, mg-equiv/dm³</th>
<th>pH</th>
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<td>3530</td>
<td>0.92</td>
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</tr>
<tr>
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<td>3520</td>
<td>0.77</td>
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<td>3</td>
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<td>4</td>
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</tr>
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<td>1.120</td>
<td>252.7</td>
<td>3353</td>
<td>0.54</td>
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</tr>
</tbody>
</table>

In this case, phosphates are removed from the regeneration solution in the form of phosphate magnesium ammonium (struvite) (MgNH₄PO₄), insoluble in water. The solution cleared of phosphates may subsequently be reused in the process of anionite regeneration.

6. Discussion of results of the ion-exchange purification of water from phosphates

The results presented indicate that at low concentrations of sulphates in water the strong-base anionite is fully applicable for the removal of phosphates from water. It should be emphasized that in the wastewater at the Bortnitska aeration station in 2015 the average concentration of sulphates reached 53.4 mg/dm³, which is quite acceptable for their ion-exchange removal from water. Thus, Fig. 3 shows that at concentration of sulphates 57 mg/dm³, FDEC by phosphates in the tap water amounted to 930 mg-equiv/dm³ while $\text{Dec}_{\text{mg}} - 261$ mg-equiv/dm³. On the other hand, if one takes into account that TLV of phosphates to be discharged to the river Dnipro, after water purification at the Bortnitska aeration station is 7.5 mg/dm³, and in drinking water is...
which, as shown in Fig. 5, also provides effective desorption. It is expedient to perform by the solution of sodium chloride, Dnipro or Desna, the application of the ion exchange method for pre-treatment to easily remove from water a large amount of valuable component. Thus, at concentration of phosphates ~60 mg/dm$^3$ (60 g/m$^3$), while discharging the wastewater at the Bortnitsa aeration station with flow rate ~80000 m$^3$/per day, it will be possible to remove ~42 tonnes of phosphates on a daily basis. This is an important indicator under conditions of scarcity and high prices for the phosphate fertilizers. Anionite in the phosphate form is rather easily regenerated by the ammonium chloride solution, from which phosphates are deposited almost quantitatively when adding magnesium chloride in the form of struvite (MgNH$_4$PO$_4$) (reaction 1):

$$(\text{NH}_4)_2\text{PO}_4 + \text{MgCl}_2 \rightarrow \text{MgNH}_4\text{PO}_4 \downarrow + 2\text{NH}_4\text{Cl}. \quad (1)$$

In this case, in order to bring pH to 9, we used a solution of ammonia (Table 1). The deposition of struvite took place at molar ratio (NH$_4$)$_2$PO$_4$ and MgCl$_2$: 1:1 almost completely without a significant amount of magnesium left in the solution. That is why such solution is expedient to use for repeated regeneration of anionite in the phosphate form.

It should be emphasized that the ion exchange in this case has a number of benefits compared to the reverse osmosis when cleaning the water from phosphates. It does not require high quality of water pre-treatment, less energy-intensive, while the ion exchange units are significantly cheaper than those employing the reverse osmosis and there are no problems in recycling the concentrates.

The problem is complicated in the case when phosphates exist in water. At high concentrations of phosphates, water purification from phosphates is advisable only in the context of complete demineralization of water. At relatively low concentrations – 15–50 mg/dm$^3$, for example, in the rivers Dnipro or Desna, the application of the ion exchange method is fully acceptable. However, the regeneration of anionite is expedient to perform by the solution of sodium chloride, which, as shown in Fig. 5, also provides effective desorption of phosphates. When treating the sodium chloride solution that contains phosphates with ammonium chloride and magnesium chloride, when bringing the pH with alkali to 9, it is possible to easily remove struvite out of it (reaction 2).

$${\text{Na}_3}\text{PO}_4 + \text{NH}_4\text{Cl} + \text{MgCl}_2 \rightarrow \text{MgNH}_4\text{PO}_4 \downarrow + 3\text{NaCl}. \quad (2)$$

However, this solution, in addition to phosphates, will contain sulphates, which are also well desorbed from the anionite AV-17-8 [11].

According to data of the same authors, the restoration of regeneration solution containing sulphates occurred during its treatment with calcium chloride with the sedimentation of gypsum, applicable for processing to be used as building materials. It is better to remove the residue of calcium at treating the solution with soda with the sedimentation of calcium carbonate. Upon clarification by settling and filtering, the solution is suitable for reuse in the regeneration of the anionite AV-17-8 in the sulphate-phosphate form.

References

1. Introduction

The level of water pollution of such rivers as the Rhine, Danube, Elbe, gave the reason, in the twentieth century, to call them “gutters of Europe”. On 17 March, 1992, under the aegis of the United Nations Economic Commission for Europe, in Helsinki (Finland), the “Convention on the Protection and Use of Transboundary Watercourses and International Lakes” (“Water Convention”) was adopted.

This Convention serves as a mechanism for strengthening national measures and international cooperation aimed at achieving environmentally sound management and protection of transboundary surface and ground waters. It includes legislative norms for punishing and encouraging enterprises, which discharge industrial waste water (IWW) and sludge into rivers.

Industrialists have been interested in the fulfillment of the commission’s instructions. For this purpose, new technologies were developed to reduce volumes of industrial waste water, flows of toxic filtrates from ponds of industrial waste water and sludge into the water basin.

A sufficiently effective way to prevent infiltration of industrial waste water is to arrange protective anti-filtration screens from polymer films (Fig. 1).