

*Досліджено процеси сорбції фосфатів на слабоосновному та сильно-основному аніонітах. Встановлено вплив форми аніоніту АВ-17-8 на його ємність по фосфатах у модельних розчинах та у водопровідній воді. Вивчено вплив сульфатів на селективність іоніту по фосфатах. Визначено ефективний метод вилучення фосфатів із регенераційних розчинів хлориду амонію, що робить їх придатними для повторного використання*

*Ключові слова: іонний обмін, аніоніт, селективність, фосфат-іони, сульфат-іони, хлорид амонію, відновлення іоніту*

*Исследованы процессы сорбции фосфатов на слабоосновном и сильноосновном анионитах. Установлено влияние формы анионита АВ-17-8 на его емкость по фосфатам в модельных растворах и в водопроводной воде. Изучено влияние сульфатов на селективность ионита по фосфатам. Определены эффективный метод удаления фосфатов из регенерационных растворов хлорида аммония, что делает их пригодными для повторного использования*

*Ключевые слова: ионный обмен, анионит, селективность, фосфат-ионы, сульфат-ионы, хлорид аммония, восстановление ионита*

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# STUDY OF USING THE ANIONITES IN LOW-WASTE PROCESSES OF WATER PURIFICATION FROM PHOSPHATES

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## 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 are 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 upsets 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 phosphates, as well as solving the problem on selecting the best method of purification. This method should provide effective and low-waste removal of phosphate-ions from water.

## 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].

Paper [7] noted that the low-pressure inverse osmotic filters are effective when the starting concentrations of phosphates do not exceed  $350 \text{ mg/dm}^3$ . The main shortcoming of this method is the use of expensive semipermeable membranes. It is demonstrated in article [8] that insufficiently effective mechanical cleaning of water prior to the baromembrane processes reduces the performance of membranes and negatively affects their selectivity. This requires highly-efficient pre-treatment of water in order to prevent the formation of sediments on the membranes. In addition, another drawback of the inverse osmosis is the formation of concentrates, which are quite difficult to recycle. Paper [9] proposed removing the phosphate-ions from concentrates in the form of insoluble sludge. However, there remains the solution containing ammonium, chlorides and other ions, complicating its treatment before discharge into sewers.

The most promising is to explore removing the phosphates by the method of ion exchange, which will make it possible to remove the required ions from water. In the future, it is possible to obtain liquid fertilizers or other useful products from the regeneration solutions [10]. This will allow the reuse of cleaned eluates, which will make the purification process more efficient and will reduce costs.

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### 3. The aim and tasks of research

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The aim of present work was to determine the effectiveness of anionites when removing phosphates from water and to devise waste-free processes for their regeneration with the removal of phosphates in the form of mineral fertilizer at repeated use of the regeneration solutions.

To accomplish the set aim, the following tasks were to be solved:

- to examine the processes of phosphate sorption from their model solutions and solutions in tap water on strong-base and weak-base anionites in the salt and the basic form;
- to explore the processes of anionite regeneration by the salt solutions of sodium chloride and ammonium chloride;
- to determine conditions for the removal of phosphates from the regeneration solutions, in order to enable their reuse.

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

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#### 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.

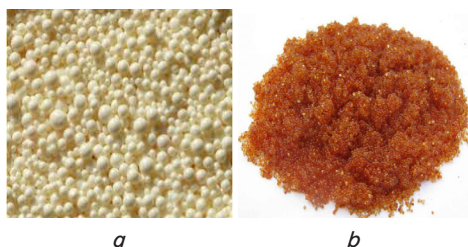


Fig. 1. Anionites used in the present work: *a* – weak-base Dowex Marathon WBA; *b* – strong-base AV-17-8

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  $20 \text{ cm}^3$  was put in a column of diameter 19 mm. The solution was filtered through the ionite at the flow rate of  $10\text{--}15 \text{ cm}^3/\text{min}$ ., separating the samples of volume  $0.1\text{--}1.0 \text{ dm}^3$ . 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  $690\text{--}720 \text{ nm}$ .

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 % nitchromazo 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 ( $\text{pH}=4$ ).

Determining the hardness was performed by the titration method. For this purpose, we added  $5 \text{ cm}^3$  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  $20 \text{ cm}^3$ , the flow rate reached  $1\text{--}3 \text{ cm}^3/\text{min}$ . 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.

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### 5. Results of research into removal of phosphates on anionites

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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.

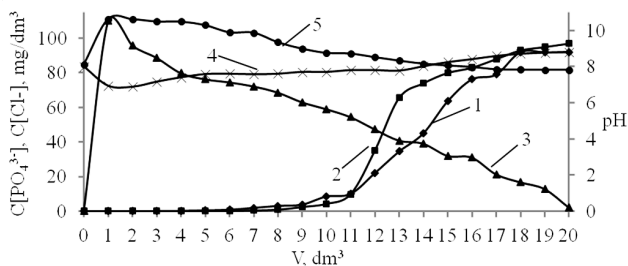


Fig. 2. Dependence of the starting concentration of phosphates (1; 2), chlorides (3), pH-medium (4; 5) on the volume of passed solution of sodium phosphate ( $C(\text{PO}_4^{3-})=92 \text{ mg/dm}^3$  (1; 3; 4),  $97 \text{ mg/dm}^3$  (2; 5);

Alky=1.5 mg-equiv/dm<sup>3</sup>; pH=8,00) through the anionite AV-17-8 ( $V_i=20 \text{ cm}^3$ ) in the Cl<sup>-</sup> (1; 3; 4) and OH<sup>-</sup> (2; 5) form. ( $\text{DEC}_{1\text{gap}}=290 \text{ mg-equiv/dm}^3$ ,  $\text{FDEC}_1=1888 \text{ mg-equiv/dm}^3$ ;  $\text{DEC}_{2\text{gap}}=995 \text{ mg-equiv/dm}^3$ ,  $\text{FDEC}_2=1950 \text{ mg-equiv/dm}^3$ )

Especially significant here is the growth of dynamic exchange capacity of anionite by phosphates until the breakthrough. For the anionite in the Cl<sup>-</sup> form from 290 mg-equiv/dm<sup>3</sup> to 995 mg-equiv/dm<sup>3</sup> for the ionite in the OH<sup>-</sup> form. This is due to the alkalization of medium when applying the ionite in the OH<sup>-</sup> 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<sup>-</sup> form, the concentration of chlorides reaches 70–100 mg/dm<sup>3</sup>, 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 in the OH<sup>-</sup> 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/dm<sup>3</sup> 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<sup>-</sup> and OH<sup>-</sup> 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/dm<sup>3</sup>, while the dynamic exchange capacity before the breakthrough ( $\text{DEC}_{\text{gap}}$ ) reached 689 mg-equiv/dm<sup>3</sup> 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)<sub>2</sub> 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/dm<sup>3</sup>. 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/dm<sup>3</sup>, while  $\text{DEC}_{\text{gap}}=1330 \text{ mg-equiv/dm}^3$  [11].

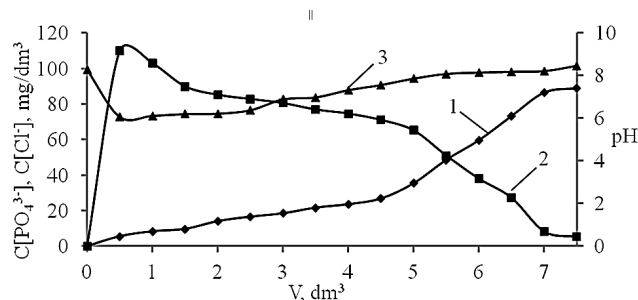


Fig. 3. Dependence of the starting concentration of phosphates (1), chlorides (2) and pH of the medium (3) on the volume of the solution of sodium phosphate ( $C(\text{PO}_4^{3-})=90 \text{ mg-equiv/dm}^3$ ) passed through the weak-base anionite Dowex Marathon WBA in the chloride form ( $V_i=20 \text{ cm}^3$ ). ( $\text{FDEC}_1=641.5 \text{ mg-equiv/dm}^3$ )

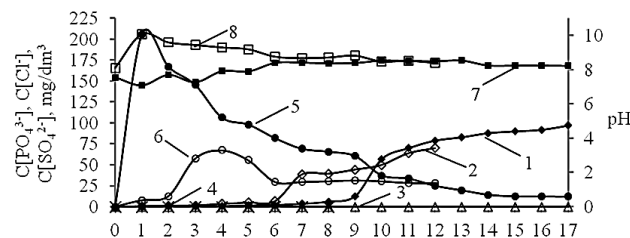


Fig. 4. Dependence of the concentration of phosphates (1; 2), sulphates (3; 4), chlorides (5; 6), pH of the medium (7; 8) on the volume of tap water (Hardness=3.1 mg-equiv/dm<sup>3</sup>; Alky=4.9 mg-equiv/dm<sup>3</sup>;  $C(\text{PO}_4^{3-})$ , mg/dm<sup>3</sup>: 105 (1; 3; 5; 7), 83 (2; 4; 6; 8);  $C(\text{Cl}^-)$ , mg/dm<sup>3</sup>: 12.07 (1; 3; 5; 7), 28.4 (2; 4; 6; 8);  $C(\text{SO}_4^{2-})$ , mg/dm<sup>3</sup>: 36.7 (1; 3; 5; 7), 57 (2; 4; 6; 8)) passed through the anionite AV-17-8 in the Cl<sup>-</sup> (1; 3; 5; 7) and OH<sup>-</sup> (2; 4; 6; 8) form ( $V_i=20 \text{ cm}^3$ ) ( $\text{FDEC}_1=1480 \text{ mg-equiv/dm}^3$ ;  $\text{DEC}_{1\text{gap}}=689 \text{ mg-equiv/dm}^3$ ;  $\text{FDEC}_2=930 \text{ mg-equiv/dm}^3$ ;  $\text{DEC}_{2\text{gap}}=262 \text{ mg-equiv/dm}^3$ ;  $\text{DEC}_{3\text{gap}}=646 \text{ mg-equiv/dm}^3$ ;  $\text{DEC}_{4\text{gap}}=713 \text{ mg-equiv/dm}^3$ )

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 (O)P(O)<sub>3</sub>. This anion is formed at pH ≥11.9. Thus, the capacity of anionite by phosphates was defined mostly by the concentration of competing sulphate-anions.

Fig. 5 shows that the degree of removal of phosphates on anionite in the OH<sup>-</sup> form from the distilled water was at the level of 99–100 % when purifying 8 dm<sup>3</sup> of water on 20 cm<sup>3</sup> of ionite; while the degree of removal from the tap water con-

taining sulphates at concentration 570 mg/dm<sup>3</sup> amounted to 98 % when cleaning only 2 dm<sup>3</sup> of water.

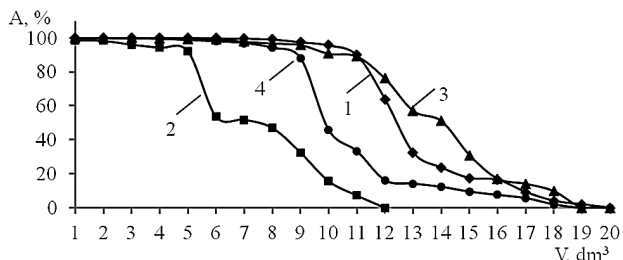


Fig. 5. Dependence of the degree of removal of phosphates on the anionite AV-17-8 ( $V_i=20\text{ cm}^3$ ) in the  $\text{OH}^-$  (1; 2) and  $\text{Cl}^-$  (3 and 4) form from the model solutions ( $C(\text{PO}_4^{3-})$ ,  $\text{mg}/\text{dm}^3$ : 97 (1), 92 (3)) and tap water ( $C(\text{PO}_4^{3-})$ ,  $\text{mg}/\text{dm}^3$ : 83 (2), 105 (4)) on the volume of the filtered solution

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 dm<sup>3</sup> of the phosphate solution in distilled water. When cleaning 4 dm<sup>3</sup> 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/dm<sup>3</sup>. In another case, results of cleaning the tap water from phosphates are 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  $q_n=6\text{ cm}^3/\text{cm}^3$ , 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  $10\text{ cm}^3/\text{cm}^3$ .

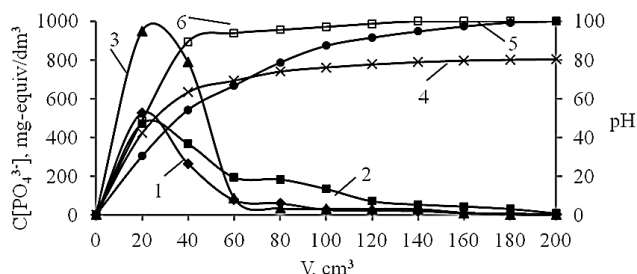


Fig. 6. Dependence of the starting concentration of phosphates (1; 2; 3) and the degree of their desorption (4; 5; 6) on the volume of the passed solution of sodium chloride at concentration 10 % (1; 4) and 15 % (2; 5), and the ammonium chloride solution at 10 % concentration (3; 6) through the anionite AV-17-8 in the  $\text{PO}_4^{3-}$ -form ( $V_i=20\text{ cm}^3$ )

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.

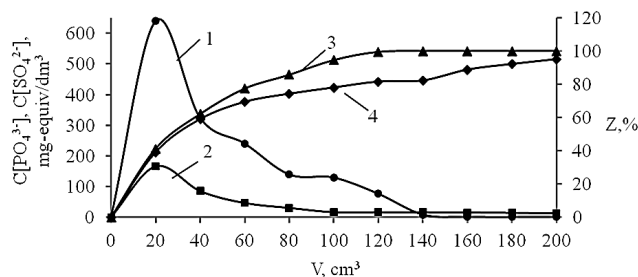


Fig. 7. Dependence of the starting concentration of phosphates (1) and sulphates (2), the degree of desorption of phosphates (3) and sulphates (4) on the volume of the 10 % ammonium chloride solution, passed through the anionite AV-17-8 in the  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  form ( $V_i=20\text{ cm}^3$ ) ( $M_{\text{Ci}}(\text{PO}_4^{3-})=31.09\text{ mg-equiv}/\text{dm}^3$ ,  $M_{\text{Ci}}(\text{SO}_4^{2-})=12.92\text{ mg-equiv}/\text{dm}^3$ )

Table 1

Dependence of the residual concentration of phosphates, magnesium and pH of the medium on the consumption of magnesium chloride when treating the ammonium phosphate solution ( $C(\text{PO}_4^{3-})=0.1053\text{ mol}/\text{dm}^3$ ) that contains 80 g/dm<sup>3</sup> of ammonium chloride at initial pH 8.0(I) and 9.0 (II)

No. of entry	$[\text{PO}_4^{3-}]$ , $[\text{Mg}^{2+}]$ , mol/mol	Consumption of $\text{Mg}^{2+}$ , mg-equiv/dm <sup>3</sup> cm <sup>3</sup>	$C(\text{PO}_4^{3-})$ , mg/dm <sup>3</sup>		$\text{Mg}^{2+}$ , mg-equiv/dm <sup>3</sup> cm <sup>3</sup>		pH	
			I	II	I	II	I	II
1	1:1.00	210.6	3550	0.92	74.21	0.15	5.10	8.69
2	1:1.05	221.3	3520	0.77	83.45	1.45	5.09	8.66
3	1:1.07	225.3	3300	0.56	83.95	8.36	5.09	8.67
4	1:1.10	231.66	3200	0.47	87.81	15.45	5.08	8.65
5	1:1.15	242.2	3180	0.57	96.52	24.32	5.05	8.66
6	1:1.20	252.7	3533	0.54	110.72	31.44	5.05	8.65

In this case, phosphates are removed from the regeneration solution in the form of phosphate magnesium ammonium (struvite) ( $\text{MgNH}_4\text{PO}_4$ ), 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/dm<sup>3</sup>, which is quite acceptable for their ion-exchange removal from water. Thus, Fig. 3 shows that at concentration of sulphates 57 mg/dm<sup>3</sup>, FDEC by phosphates in the tap water amounted to 930 mg-equiv/dm<sup>3</sup> while  $\text{DEC}_{\text{gap}} = 261\text{ mg-equiv}/\text{dm}^3$ . 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/dm<sup>3</sup>, and in drinking water is

3 mg/dm<sup>3</sup>, then the dynamic exchange capacity at the breakthrough limit of 7.5 mg/dm<sup>3</sup> will reach 871 mg-equiv/dm<sup>3</sup>, and at 3 mg/dm<sup>3</sup> – only 600 mg-equiv/dm<sup>3</sup>.

At low concentrations of sulphates in water, it is a simple task to create a low-waste technology of removing the phosphates from water. In the given case, when using the strong-base anionite in the chloride form, it is possible to effectively purify water from phosphates at lowering their concentrations to 0.1–3.0 or 0.1–7.5 mg/dm<sup>3</sup>. This will make it possible to easily remove from water a large amount of valuable component. Thus, at concentration of phosphates ~60 mg/dm<sup>3</sup> (60 g/m<sup>3</sup>), while discharging the wastewater at the Bortnitska aeration station with flow rate ~800000 m<sup>3</sup>/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<sub>4</sub>PO<sub>4</sub>) (reaction 1)

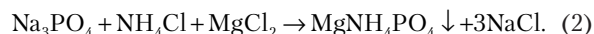


In this case, in order to bring pH to 9, we used a solution of ammonia (Table 1). The deposition of struvite took place at molar ratio (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> and MgCl<sub>2</sub> 1:1 almost completely without a significant amount of magnesium left in the solution. That is why such 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 sulphates exist in water. At high concentrations of sulphates, water purification from phosphates is advisable only in the context of complete demineralization of water. At relatively low concentrations – 15–50 mg/dm<sup>3</sup>, 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).



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.

## 7. Conclusions

1. We examined the processes of sorption of phosphates on the weak-base and strong-base anionites. It is shown that the exchange capacity of the anionite Dowex Marathon WBA on phosphates is low and its use for the removal of phosphates is not advisable. The strong-base anionite in the chloride and the basic form provided effective removal of phosphates from the model solutions. The full dynamic exchange capacity of anionite by phosphates grew from 1888 mg-equiv/dm<sup>3</sup> to 1950 mg-equiv/dm<sup>3</sup> in the transition from the salt to the basic form. It was found that in the tap water, capacity of the anionite AV-17-8 by phosphates practically does not depend on the form of ionite and significantly depends on the concentration of sulphates.

2. We studied the processes of regeneration of the anionite AV-17-8 in the phosphate and phosphate-sulphate form. It is demonstrated that the full desorption of phosphates at high degrees of desorption of sulphates can be achieved when using the solutions of sodium chloride or ammonium chloride at concentration 10–15 %.

3. It is shown that phosphates are effectively removed from the solution of ammonium chloride when treating it at pH≥9 with a stoichiometric amount of magnesium chloride. The regeneration solution, restored in this way, is applicable for reuse.

## References

1. Cornel, P. Phosphorus recovery from wastewater: needs, technologies and costs [Text] / P. Cornel, C. Schaum // *Water Science & Technology*. – 2009. – Vol. 59, Issue 6. – P. 1069. doi: 10.2166/wst.2009.045
2. Prokopchuk, O. I. Fosfaty u vodnykh ekosystemakh [Text] / O. I. Prokopchuk, V. V. Grubinko // *Naukovi zapysky Ternopil's'koho natsional'noho pedahohichnoho universytetu imeni Volodymyra Hnatyuka*. Ser. Biolohiya. – 2013. – Issue 3 (56). – P. 78–85.
3. Van der Perk, M. Soil and water contamination [Text] / M. Van der Perk. – CRC Press, 2013. – 428 p.
4. Grady Jr, C. L. Biological wastewater treatment [Text] / C. L. Grady Jr, G. T. Daigger, N. G. Love, C. D. Filipe. – CRC Press, 2011. – 1022 p.
5. Khentse, M. Ochistka stochnykh vod [Text] / M. Khentse, P. Armoes, Y. Lia-Kur-Yasen. – Moscow: Mir, 2009. – 480 p.
6. Baker, R. W. Membrane technology and applications [Text] / R. W. Backer. – Wiley, 2012. – 588 p. doi: 10.1002/9781118359686
7. Seminskaya, O. O. Main regularities of reverse-osmotic water purification of phosphates [Text] / O. O. Seminskaya, M. N. Balakina, D. D. Kucheruk, V. V. Goncharuk // *Journal of Water Chemistry and Technology*. – 2016. – Vol. 38, Issue 1. – P. 39–44. doi: 10.3103/s1063455x16010070
8. Trus, I. M. Vplyv poperednogo mekhanichnogo doochyshchennia vody na efektyvnist zvorotnoosmotychnogo oprisnennia vody [Text] / I. M. Trus, M. D. Gomelia, V. M. Radovenchik // *Visnyk Skhidnoukrainskogo natsionalnogo universytetu imeni Volodymyra Dalia*. – 2013. – Issue 9 (198). – P. 197–202.

9. Bhuiyan, M. I. H. Phosphorus recovery from wastewater through struvite formation in fluidized bed reactors: a sustainable approach [Text] / M. I. H. Bhuiyan, D. S. Mavinic, F. A. Korch // Water Science and Technology. – 2008. – Vol. 57, Issue 2. – P. 175. doi: 10.2166/wst.2008.002
10. Gomelya, M. Low-waster ion exchangetechnology of extraction of nitrogen compouds from woter [Text] / M. Gomeya, G. Trohymenko, T. Shablii // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 3, Issue 10 (81). – P. 18–23. doi: 10.15587/1729-4061.2016.72328
11. Trus, I. N. Razdelenie khloridov I sulfatof pri ionoobmennom obezsolivanii vody [Text] / I. N. Trus, N. D. Gomelia, T. A. Shablii // Metalurgicheskaia i gornorudnaia promyshlennost. – 2014. – Issue 5. – P. 119–122.

*Розглянуто питання оцінки факторів, що впливають на забруднення поверхневих і ґрунтових вод промислових територій. Проаналізовано негативний вплив накопичувачів промислових стічних вод і шламів на стан водного басейну. Визначено об'єкти та суб'єкти впливу, наведені технологічні схеми очищення стоків і охарактеризовані види шкоди навколишньому природному середовищу з боку накопичувачів промислових стічних вод*

*Ключові слова: захист водного басейну, очищення стічних вод, важкі метали, утилізація шламів*

*Рассмотрены вопросы оценки факторов, влияющих на загрязнение поверхностных и грунтовых вод промышленных территорий. Проанализировано отрицательное воздействие накопителей промышленных сточных вод и шламов на состояние водного бассейна. Определены объекты и субъекты влияния, приведены технологические схемы очистки стоков и охарактеризованы виды ущерба окружающей природной среде со стороны накопителей промышленных сточных вод*

*Ключевые слова: защита водного бассейна, очистка сточных вод, тяжелые металлы, утилизация шламов*

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# ASSESSMENT OF THE POLLUTION DEGREE OF THE DNEPR RIVER AND DEVELOPMENT OF MEASURES FOR ITS DECREASE

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## 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 pro-

tection 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).