# REMOVAL OF PHOSPHATES ON LOW BASIC ANIONITE DOWEX MARATHON WBA

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## ABSTRACT

*The processes of determining the efficiency of Dawex Marathon WBA anionites in removing phosphates from water and creating waste-free processes for their regeneration were studied. In the course of an experimental study of sorption, model solutions of polluted water containing phosphates in a concentration of 40-100 mg dm$^{-3}$ were passed through the low-based Dawex Marathon WBA anionite in chloride form. The dependence of TDEC on pH and temperature was established when filtering through low-base anionite DOWEX MARATHON WBA in chloride form. An important aspect of the research was the determination of the principles of extracting phosphates in the form of mineral fertilizer during repeated use of regeneration solutions. The processes of anionite regeneration have been studied. Regeneration of anionite was carried out with two solutions, in parallel, namely - 10 % solutions of sodium chloride, 10 % solution of ammonium chloride. It should be noted that the degree of regeneration is 97 - 98 %.*

Keywords: *phosphates, ion exchange, regeneration, fertilizer, low-waste technology.*

## INTRODUCTION

Providing the population of Ukraine and industry with high-quality drinking and technical water, respectively, remains one of the key issues in the modern environmental, economic and social policy of our state [1 - 4].

Phosphorus is one of the common main elements of water pollution in the territory of Ukraine. It should be noted that phosphorus belongs to biogenic elements and is necessary for the growth of microorganisms and other organisms of various levels, including humans. It is also a nutrient resource that determines the productivity of autotrophic or other ecological systems and the primary productivity of water. Despite the fact that phosphorus compounds play an important role in the processes of photosynthesis and vital activity of living organisms, their excess in water bodies at correspondingly warm temperatures leads to eutrophication. Eutrophication is a complex process in fresh and marine water bodies, where the rapid development of certain types of microorganisms disrupts the balance of aquatic ecosystems [5 - 7].

The arrival of biogenic elements, which respectively includes phosphorus, occurs at the expense of industrial enterprises, wastewater from agricultural lands, animal complexes [8], communal and domestic sewage [9, 10] and natural phosphates [11, 12]. Thus, scientists [13] showed that the main sources of phosphorus entering water in the territories of the European Union are as follows: fertilizers - 16 %, industry - 7 %, background sources - 9 %, human and household waste - 24 %, detergents - 10 %, waste water - 34 %. Therefore, wastewater treatment is important to prevent excessive pollution of water with phosphorus compounds.

Also, everyone knows the fact that phosphorus compounds in the environment are mainly in the form of phosphates [11]. The advantages and disadvantages of the methods used to remove phosphates from water are presented in Fig. 1.

The most common methods of cleaning water from phosphates include the biological method [8]. But this method does not always allow you to achieve the required degree of dephosphorylation of water, in some cases it is impractical to use this method of water purification.

Of the large number of known methods for further purification of water from phosphates, reagent methods are most often used [14]. A big positive advantage of this method is the extraction of phosphates in the form of poorly soluble compounds of iron, aluminum and other salts, which avoids the formation of large volumes of liquid waste. But here, there is a drawback, namely that the separation of these sediments, in turn, complicates the technology of water purification and increases its cost. Thus, the economic impracticality and high energy consumption in the case of using reagent methods follows.

Over the last period of time, a number of works have been published on the removal of phosphates using reverse osmosis filters, that is, by the reverse osmosis method [15, 16]. Low-pressure reverse osmosis filters are effective, but unfortunately, at initial concentrations up to 350 mg dm$^{-3}$. The disadvantage of reverse osmosis is the formation of concentrates, which are quite difficult to dispose of. Even when phosphates are removed from them [17, 18], solutions containing ammonium, chlorides and other ions remain, which complicates its treatment before discharge into the sewer.

Therefore, it is obvious that ion exchange is much more promising in this case. Ion exchange allows not only to remove the necessary ions from water, but also to process regeneration solutions to obtain liquid fertilizers or other useful products and reuse purified eluates [19]. That is, ion exchange methods are on par with low-waste, or no-waste water purification technologies in the modern ecological world [20]. The implementation of low-waste technologies of ion-exchange purification involves, in fact, water purification, but without the formation of difficult-to-utilize waste. On the contrary, the obtained regeneration solutions can be used as relatively inexpensive phosphate fertilizers, which can be usefully and economically used in domestic agriculture [21, 22].

The purpose of this work was to evaluate the efficiency of Dawex Marathon WBA low-base anionite in the removal of phosphates from water and to create waste-free processes for their regeneration with the removal of phosphates in the form of mineral fertilizer.

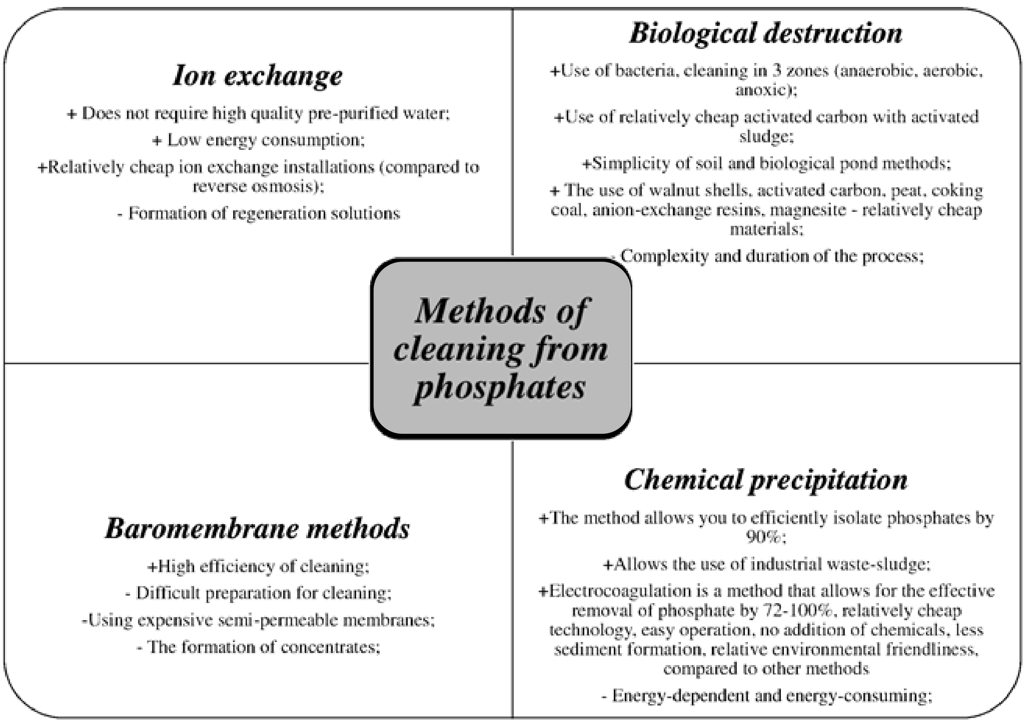


Fig. 1. Advantages and disadvantages of the methods used to remove phosphates from water.

## EXPERIMENTAL

One of the tasks was to determine the effectiveness of anionites in the removal of phosphates from water and to create waste-free processes for their regeneration with the removal of phosphates in the form of mineral fertilizer with the repeated use of regeneration solutions.

During the sorption process, model solutions containing phosphates in a concentration of 40 - 100 mg $dm^{-3}$ were passed through Dawex Marathon WBA anionite in chloride form (Table 1). Anionite was used in the $Cl^-$ form. Regeneration of anionite was carried out with 10 % solutions of sodium chloride and 10 % solution of ammonium chloride. During sorption, samples with a volume of 500 $cm^3$ were taken, while the flow of working solutions was 15 $cm^3$ $min^{-1}$. In the regeneration processes, the flow rate of regeneration solutions was 5 $cm^3$ $min^{-1}$, and the sample volume was 20 $cm^3$. The scheme of the installation is presented in Fig. 2.

When studying the sorption processes, the content of phosphates, chlorides and pH of the medium were determined. When regenerating ionite with NaCl solutions, the content of phosphates and chlorides was controlled, and when regenerating anionite $NH_4OH$, the alkalinity of the solution, pH, and phosphate concentration were controlled. The full exchangeable dynamic capacity (TDEC) and the degree of regeneration (A) of ionite were calculated according to the formulas:

$$TDEC = \frac{\sum_{i=1}^{n}(C_{in} - C_i)\cdot V_s}{V_i} \quad (1)$$

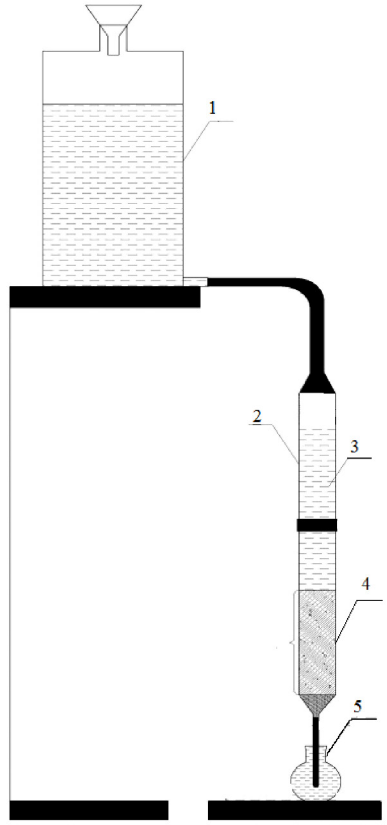


Fig. 2. Ion-exchange experimental installation filled with DOWEX MARATHON WBA ion-exchange resin: 1 - container with water containing phosphates; 2 - a column with a diameter of 19 - 30 mm; 3 - a layer of water, above the ionite; 4 - layer of ionite DOWEX MARATHON WBA; 5 - a flask for collecting purified water after filtering through ionite.

Table 1. Main features of Dowex Marathon WBA.

| № | Resin characteristics | Meaning |
|---|---|---|
| 1. | Ionic form | $OH^-$ |
| 2. | Dynamic exchange capacity | 1.0 g-eq $dm^{-3}$ |
| 3. | Full static exchange capacity | 1.3 g-eq $dm^{-3}$ |
| 4. | Mass fraction of moisture | 48-58 % |
| 5. | Coefficient of homogeneity | 1.1 |
| 6. | Mechanical strength, min. | 95 % |
| 7. | Bulk mass | 670 g $dm^{-3}$ |
| 8. | Maximum temperature | 60°C |
| 9. | Minimum layer height | 800 mm |
| 10. | Total consumption of water for washing | 2 - 5 vol/vol |
| 11. | Regeneration solution | 2 - 5 % NaOH 10 % NaCI / 1 % NaOH |
| 12. | General swelling | 20 % |

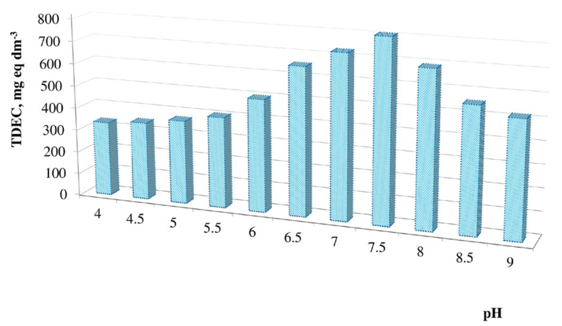


Fig. 3. Dependence of TDEC on pH on the passed volume of sodium phosphate solution with a concentration of 100 mg-eq dm$^{-3}$ through the low basic anionite DOWEX MARATHON WBA in chloride form.

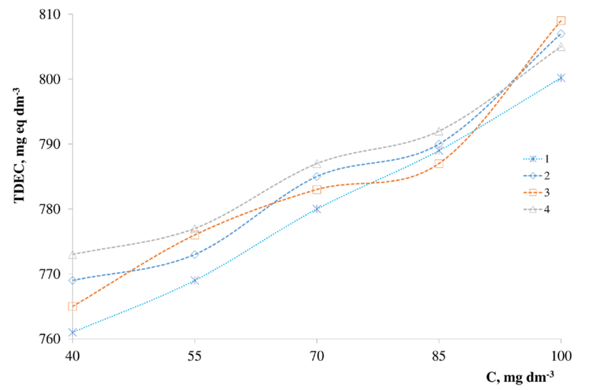


Fig. 4. Dependence of TDEC on temperature on the passed volume of sodium phosphate solution with a concentration of 100 mg-eq dm$^{-3}$ through the low basic anionite DOWEX MARATHON WBA in chloride form: 1 - 10°C; 2 - 20°C; 3 - 30°C; 1 - 40°C.

$$A = \frac{C_{in} - C_i}{C_{in}} \cdot 100\ \% \qquad (2)$$

where $C_{in.}$ - initial concentration of ions phosphates in the solution, mg-eq dm$^{-3}$, $C_{i.}$ - the concentration of ions phosphates in the i-sample after sorption, mg-eq dm$^{-3}$, $V_s$ - the volume of the sample, dm$^3$, $V_i$ - the volume of ionite, dm$^3$.

## RESULTS AND DISCUSSION

The increase in the phosphate content in water occurs due to natural and anthropogenic factors. Despite the fact that phosphorus compounds play an important role in the life processes of living organisms, their excess in the aquatic environment under appropriate conditions leads to eutrophication. Eutrophication is a complex process in fresh and sea waters, where the rapid development of certain types of microorganisms disrupts the balance of aquatic ecosystems. The primary cause of eutrophication is an excessive concentration of nutrients in water, among which phosphates occupy an important place. As a result of massive and unbalanced eutrophication, most of the flora and fauna of the reservoir can be destroyed, and the ecosystem of the reservoir can be drastically and catastrophically changed.

Also, it should be noted that PDE is currently optimal at neutral pH, namely 7.5. That is, the highest value of TDEC for phosphates of 807 mg-eq dm$^{-3}$ is reached at a neutral pH environment. We can say that at a pH lower than 7.5, low values of TDEC are observed, and at pH values above 7.5, there is also a decline in TDEC. For the optimal implementation of the process, it is necessary to adhere to a neutral pH of the environment (Fig. 3).

If we are talking about the influence of temperature on the processes of ion exchange through the low-basic anionite Dowex Marathon, then we can clearly state that TDEC will not be affected by temperature (10 - 40°C) (Fig. 4). Therefore, further studies were carried out at room temperature (20°C).

The efficiency of using Dawex Marathon WBA low-base anionite in the purification of water from phosphates is shown in Fig. 5a and Fig. 5b. Already from the first samples of the selected solution, the slippage of phosphates was noted. During the analysis, namely when taking samples, for the first time after filtering through low basic anionite, we observe the slippage of phosphates.

In the materials of previous studies, it was indicated about the low efficiency of using low basic anionite in the purification of phosphates, and we experimentally established the TDEC for phosphates and determined a high degree of regeneration. The ion exchange method is widely used to remove phosphates from water. Unlike nitrates, which are well sorbed on high- and low-basic anions in chloride form, phosphates are

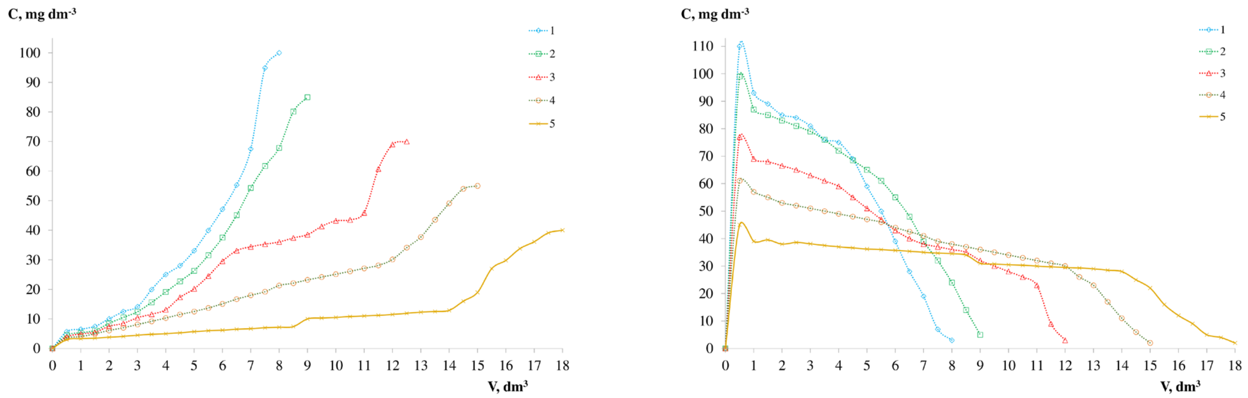


Fig. 5. Dependence of the initial concentration of phosphates (a) and chlorides (b) on the passed volume of sodium phosphate solution with a concentration of 100 (1), 85 (2), 70 (3), 55 (4), 40 (5) mg-eq dm$^{-3}$ through the low basic anionite DOWEX MARATHON WBA in chloride form.

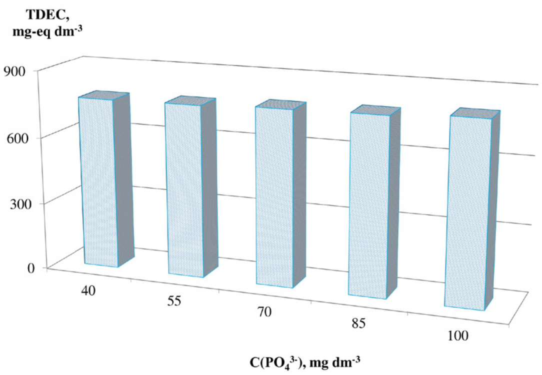


Fig. 6. Dependence of total dynamic exchange capacity (TDEC) from Dowex Marathon WBA anionite on their concentration anions the solution.

effectively sorbed mainly on high-basic anions in salt form. Previous studies show that sorption on low basic anionites depends on the reaction of the environment, and it is so. At elevated pH, the low basic anionite Dowex Marathon WBA practically does not sorb phosphates, from acidic solutions in its basic form it sorbs both sodium dihydrogen orthophosphates and orthophosphoric acid. We, on the other hand, found that from the first samples of the selected solution, phosphates had slipped through.

The full exchangeable dynamic capacity of anionite reached only 769 mg-eq dm$^{-3}$ at the initial sulfate concentration of 40 mg dm$^{-3}$. When the initial concentration is increased to 55, 70, 85, and 100 mg dm$^{-3}$, TDEC practically does not change and amounts to 773, 785, 790, and 807 mg-eq dm$^{-3}$, respectively (Fig. 6).

The low values of TDEC are primarily associated with a decrease in the sorption properties of ionite in a slightly alkaline environment and with a decrease in the degree of dissociation of phosphates in a neutral and slightly acidic environment. When using this ionite in its basic form, its phosphate capacity was even lower.

The regeneration processes of Dowex Marathon WBA anionite in the phosphate form have been studied in detail, but the issue of creating low-waste water purification technologies from biogenic elements remains open. Ionites are well regenerated with sodium chloride, but the eluates obtained after regeneration, which contain chlorides in high concentrations, are quite difficult to recycle. The discharge of such solutions into the sewers is also prohibited. Therefore, the processes of phosphate desorption, when using ammonia solution, were studied.

Dowex Marathon WBA's low-base anionite capacity recovers fairly well when regenerated with both NaCl and $NH_4OH$. At the same time, both phosphates and nitrates are desorbed quite effectively (Fig. 7).

The use of $NH_4OH$ is quite promising, as there is a possibility of further processing of the regeneration solution. Their pH can be easily adjusted by adding nitric or phosphoric acid or ammonia. After pH correction, these solutions can be used for the production of liquid fertilizers.

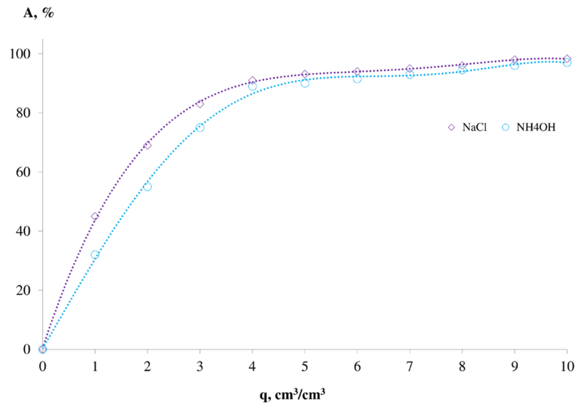


Fig. 7. Dependence of the degree of desorption of nitrates from Dowex Marathon WBA anionite in $PO_4^{3-}$ form on the passed volume of regeneration solutions.

As a rule, chlorides and sulfates are always present in natural and waste waters. With relatively low concentrations of anions - less than 45 - 50 mg $dm^{-3}$, as, for example, in the Dnipro or Desnian water, the use of the ion exchange method is quite acceptable. It follows from this that the natural waters of the central and western regions of our country can definitely be subjected to ion exchange purification, because the approximate content of chlorides and sulfates, which varies within these limits. Unlike the eastern industrial region.

Also, a large prospective part of the research is the study of aspects of water dephosphorization with the production of fertilizers as a result of the implementation of low-waste ion purification technologies.

## CONCLUSIONS

The effectiveness of the use of DOWEX MARATHON WBA low-base anionite in water purification from phosphates, as well as the basic principles of regeneration of this anionite, were investigated. Also, the prospect of processing regeneration solutions in the production of liquid fertilizers, thereby implementing low-waste technologies, has been established.

It was found that DOWEX MARATHON WBA anionite in chloride form had low values of total exchangeable dynamic capacity. The main advantage of low-base anionite is its high regeneration efficiency, especially in alkaline and weakly alkaline environments. TDEC was found to be optimal at neutral pH (7.5). Temperature was shown to have no effect on TDEC. It was established that the regeneration of anionite in the $PO_4^{3-}$ $Cl^-$ form is quite effective when using ammonia and sodium chloride for DOWEX MARATHON WBA. The degree of regeneration reaches ~ 97 %, respectively.

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