# LOW-WASTE TECHNOLOGY OF WATER PURIFICATION FROM NITRATES ON HIGHLY BASIC ANION EXCHANGE RESIN

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## ABSTRACT

*The contamination of groundwater and surface water with nitrates is a global environmental problem today. Elevated concentrations of nitrates lead to eutrophication of water bodies, resulting in problems with water supply. Purification of water from nitrates should be carried out by ion exchange methods, which are quite simple and inexpensive. In addition, they are not subject to harsh conditions of pre-treatment of water. Anion exchange resin AV-17-8 provides the degree of extraction of nitrates at the level of 90 - 92 %. Methods for efficient regeneration of anion exchange resin to obtain products suitable for further use have been developed. When using sodium chloride, the degree of desorption was 98.1 %, for sodium sulfate and potassium chloride it was 89.9 % and 72.11 %, respectively. Regenerative solutions of potassium nitrate should be used to produce liquid fertilizers. The technological scheme of ion exchange purification of water from nitrates with regeneration of ion exchanger by solutions containing potassium compounds is suggested. This will allow further use of regeneration solutions for production of liquid fertilizers.*

*Keywords: nitrate removal, anion exchange resins, sorption, regeneration, drinking water, eutrophication.*

## INTRODUCTION

Pollution of the water reservoirs is a very important environmental problem, which is currently becoming increasingly acute [1, 2]. Due to anthropogenic impact, a significant number of reservoirs have a high level of mineralization, the greatest negative impact is on low-water rivers [3]. There is a decrease in water quality in terms of the presence of heavy metals, organic, surfactants, nutrients [4 - 6]. As a result, in industrial regions, the population consumes water with a quite high level of salts.

One of the very serious problems that need to be addressed immediately is water pollution with nitrates due to both anthropogenic and natural factors [7, 8]. An increase in the concentration of nitrates in water bodies is observed all over the world [9, 10]. Since nitrates are widely used as mineral fertilizers in agriculture, nitrogen fertilizer plants are one of the biggest polluters [12]. Large quantities of nitrates enter the reservoirs during the discharge of treated municipal wastewater [13]. Nitrates complicate the problem of water supply due to exceeding the permissible level. Also, high concentrations of these pollutants lead to a significant negative impact on water reservoirs, as they lead to increased eutrophication, which causes disruption of the development of existing biocenosis and changes in ecosystem parameters. In addition, high levels of nitrates have a negative effect on human health [14, 15]. It should be noted that elevated concentrations of nitrates have many dangers, besides methaemoglobinemia, this includes colorectal cancer, neural tube defects and thyroid disease [16, 17].

The choice of a specific method of extracting nitrates from water is determined by the cost, technical means, and degree of purification, as well as the final purpose of the purified water [18, 19].

Existing methods of water purification have a number of disadvantages [20, 21].

Water purification processes used at municipal water treatment plants, such as coagulation, filtration, chlorination, are not effective for removing nitrates [22 - 24].

Biological methods of nitrate removal from water are based on the denitrification process. Denitrification is the process of microbiological reduction of nitrates to nitrites and subsequently to gaseous oxides and molecular nitrogen [25, 26]:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

It should be noted that the biological decomposition of nitrates is quite slow, in addition, this method has limitations when used for drinking water, because the bacterial contamination of water takes place [27, 28].

Electrochemical membrane methods are quite effective in the practice of water purification [29]. Various electrolytic methods for removing nitrates from water are constantly being researched and tested [30 - 32]. During the electrochemical reduction of nitrates [33], they are decomposed with the formation of toxic substances - nitrites and ammonia. Furthermore, this method is quite energy consuming.

An obstacle to the widespread introduction of membrane methods is the high requirements for the pre-treatment of water and the unresolved conditions of efficient processing of concentrates that are formed [34 - 36].

Another common method used to remove nitrates is sorption on synthetic and natural sorbents [37 - 39]. When choosing a sorbent, it is necessary to consider various parameters: cost, efficiency, availability, environmental safety of waste sorbents [40, 41].

Therefore, a very promising method of purification of water from nitrates is ion exchange [42 - 44]. It is a simple and inexpensive way, which does not require harsh pre-treatment conditions [45, 46]. The use of ion exchange reduces the concentration of nitrates to acceptable levels [47]. But the issues of effective regeneration of ion exchangers and processing of eluates are unresolved. Therefore, it is important to develop a comprehensive technology for mineralized water treatment [48, 49].

The aim of this work is to study the processes of water purification from nitrates on a highly basic anion exchange resin, as well as to determine the conditions of effective regeneration and methods of utilization of spent regeneration solutions in fertilizers.

## EXPERIMENTAL

The processes of water purification from nitrates were studied using a highly basic anion exchange resin AV-17-8 in $Cl^-$ and $SO_4^{2-}$ forms. Model solution with nitrate concentration of 3.2 mg-eq/dm$^3$ and artesian water from Kyiv (hardness = 4.1 mg-eq/dm$^3$, calcium ion concentration = 2.1 mg-eq/dm$^3$, magnesium ion concentration = 2.0 mg-eq/dm$^3$, alkalinity = 3.4 mg-eq/dm$^3$, sulfates = 9.0 mg/dm$^3$, chlorides = 117.0 mg/dm$^3$, nitrates, = 194.0 mg/dm$^3$, pH = 8.4, mineralization = 345 mg/dm$^3$) were used.

The solution was passed through an anion exchange resin with a volume of 20 cm$^3$, with a water flow rate of 10 - 15 cm$^3$/min. During regeneration, 10 cm$^3$ samples were taken. The consumption of regeneration solution is 1 - 2 cm$^3$/min.

The total dynamic exchange capacity (TDEC) of the resin was determined by the formula based on the mass of absorbed ions on the anion exchange resin.

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$$DEC = \frac{\sum_{i=1}^{m}(C_{in} - C_i) \cdot V_s}{V_i}$$

where $C_{in}$ - initial concentration of nitrates in solution, mg-eq/dm$^3$; $C_i$ - the concentration of nitrates in the i-th sample after sorption, mg-eq/dm$^3$; $V_s$ - sample volume, cm$^3$; $V_i$ - volume of resin, cm$^3$;

The degree of regeneration of the resin after passing *n* samples of the regeneration solution was calculated by the formula as the ratio of the mass of desorbed and absorbed ions:

$$Z_n = \frac{\sum_{i=1}^{n} M_d^i}{M_s} \cdot 100\%$$

where $M_d^i$ is the number of desorbed nitrates with the *i*-th breakdown of the regeneration solution, mg-eq/dm$^3$; $M_s$ is the number of sorbed nitrates, mg-eq/dm$^3$.

## RESULTS AND DISCUSSION

The maximum permissible concentration of nitrates in accordance to Directive 98/83/CE and the State Sanitary Norms and Rules "Hygienic requirements for drinking water intended for human consumption" (DSanPiN 2.2.4–171–10) is 50 mg/dm$^3$. The concentration of nitrates in water can be at the level of 60 - 250 mg/dm$^3$, which significantly exceeds the permissible standards. This necessitates the development of environmentally friendly methods of water purification from nitrates.

As it can be seen from Fig. 1, the anion exchange resin has satisfactory efficiency when used in $Cl^-$ form in the process of extracting nitrates from water. Sorption of nitrates on the anion exchange resin AV-17-8 in sulfate form was quite effective. At a nitrate concentration of 3.2 mg-eq/dm$^3$, the AV-17-8 anion exchange resin in $Cl^-$ form had a total exchange dynamic capacity of 1.027 g-eq/dm$^3$, and in $SO_4^{2-}$ form 0.992 g-eq/dm$^3$. This can be explained by the higher selectivity of ion-exchanger for sulfates, compared with chlorides. When using anion exchangers for sorption of nitrates from dilute solutions, the value of the working capacity of anion exchangers for nitrates is at the level of 0.8 - 0.9 g-eq/dm$^3$, which can be quite a satisfactory result.

However, the relatively efficient extraction of nitrates from water on the anion exchange resin does not provide a complete solution to the problem of isolating nitrates from water to obtain useful products.

Solutions of chloride and sodium sulfate were used to regenerate the AV-17-8 anion exchange resin. The results on the use of solutions of sulfate and sodium chloride are shown in Fig. 2. When using 10 % solutions of sodium chloride and sulfate, quite satisfactory results were obtained.

The best results were obtained when using a solution of sodium chloride. At a specific consumption of the regeneration solution of sodium chloride of 6 volumes per 1 volume of ion exchanger, the degree of desorption at the level of 87.1 % was reached, while for sodium sulfate this value is only 57.9 %. With increasing $q$ to 10 cm$^3$/cm$^3$, the desorption rate was 98.1 % for sodium chloride and 89.9 % for sodium sulfate. In this case, the concentration factor provided higher regeneration efficiency with NaCl solution. This is due to the fact that the 10 % NaCl solution contains 1.71 g-eq of salt per 1 dm$^3$, and the 10 % $Na_2SO_4$ solution contains only 1.41 g-eq/dm$^3$ of salt.

The best results are obtained when using chlorides, while the efficiency of regeneration increases with increasing concentration of regeneration. In further studies for the regeneration of the anion exchange resin

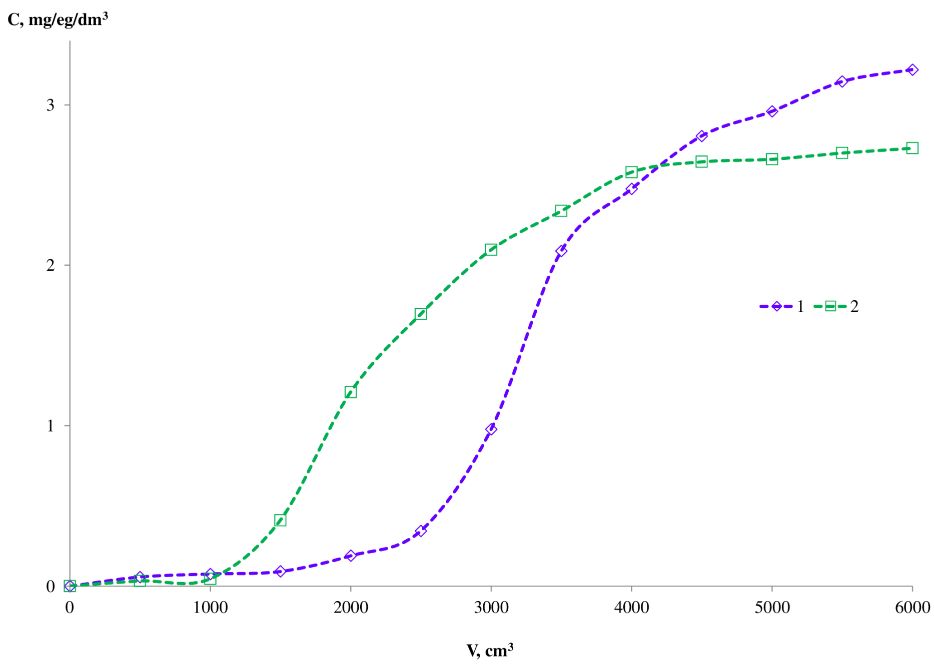


Fig. 1. Initial curves of sorption of nitrates on the anion exchange resin AV-17-8 in $Cl^-$ (1) and $SO_4^{2-}$ (2) forms when filtering $NaNO_3$ solutions with a concentration of 3.2 mg-eq/dm$^3$.

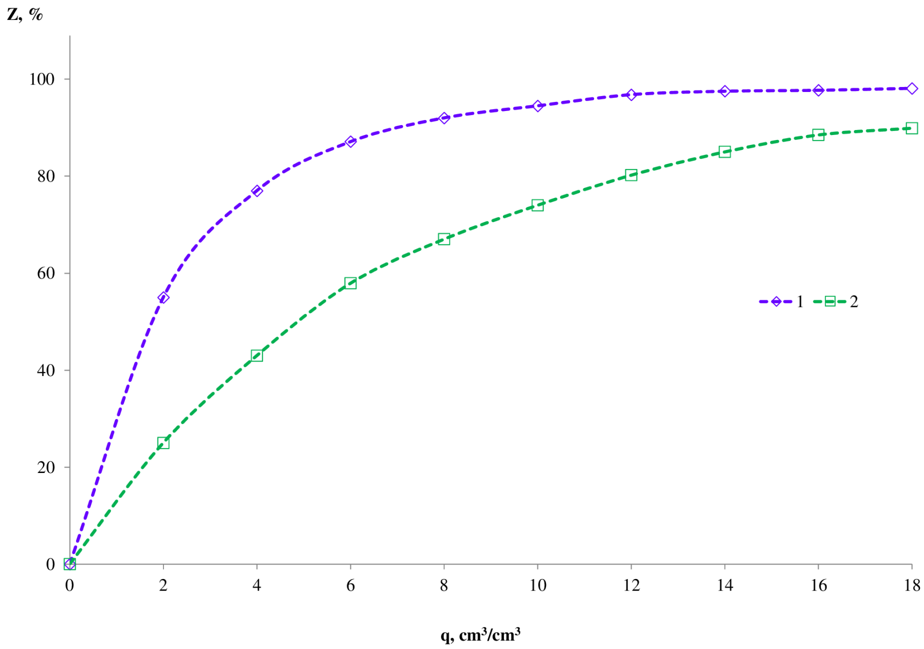


Fig. 2. Dependence of the degree of regeneration of the anion exchange resin AV-17-8 in $NO_3^-$ form on the specific consumption of 10 % solutions of sodium chloride (1) and sodium sulfate (2).

AV-17-8, solutions of potassium chloride of different concentrations were used (Fig. 3).

The choice of this reagent is due to the formation of the potassium nitrate, which is a mineral fertilizer that can be easily used, in the process of regeneration. Ionite regeneration was insufficiently effective when using potassium chloride with a concentration of up to 6 %. At $q$ = 10 $cm^3/cm^3$, the degree of desorption was 45.11 % for 6 % KCl and increased to 58.61 % and 72.11 % for 8 % and 10 % potassium chloride, respectively.

Regenerative solutions of potassium nitrate should be used in the production of liquid fertilizers.

In general, these results are satisfactory. The main disadvantage of this process is the low efficiency of the anion exchange resin, so in further studies it is necessary to check the efficiency of nitrate extraction on low-basic anion exchangers.

Based on the obtained results on the efficiency of ion exchange water purification from nitrates, a basic technological scheme of water purification is proposed.

Quite often the artesian waters, which meet the requirements for drinking water quality in all respects, are characterized by a significant excess of permissible concentrations of nitrates. At the same time, nitrate concentrations may reach 1 - 3.5 mg-eq/$dm^3$, and sometimes have even higher values. Therefore, for the organization of water supply of the population from artesian sources it is necessary to develop effective methods of water purification from nitrates.

Studies have shown that nitrates are effectively absorbed on highly basic anion exchange resin in chloride and sulfate form. Since the maximum permissible concentrations of sulfates and chlorides are higher than the permissible concentration of nitrates, the anion exchange resin can be used in sulfate or chloride form. As a rule, the content of sulphates or chlorides in artesian freshwater does not exceed 70 mg/$dm^3$, so when sulfates or chlorides enter the water when displacing the nitrates from the anion exchange resin, their concentration will not exceed the permissible levels.

If the final purpose is not only the release of nitrates, but also their separation from chlorides and sulfates, the most important indicator is not the full exchange dynamic capacity, but the exchange capacity of the resin for nitrate before leakage. EDC before and after the passage of nitrates at a concentration of 50 mg/$dm^3$ was determined. This indicator was chosen as the maximum allowable value of the concentration of nitrates in drinking water. It was found that during the ion exchange purification of artesian water on the highly

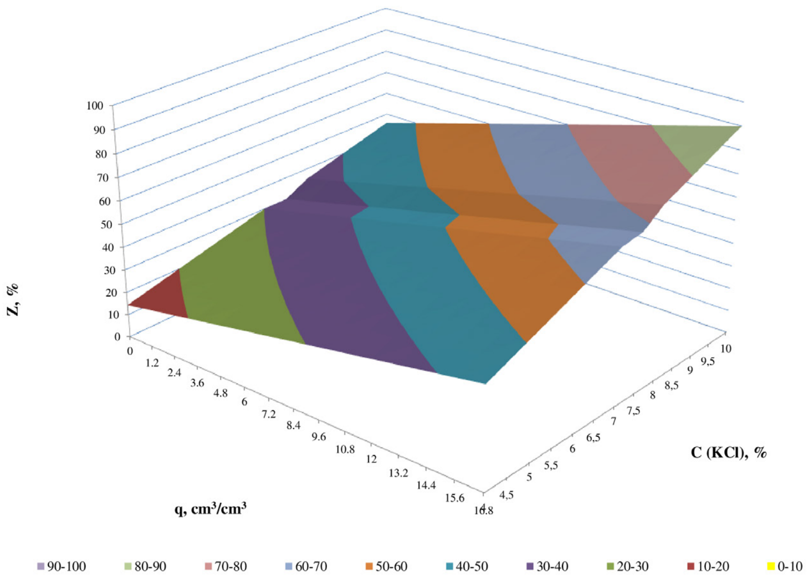


Fig. 3. Dependence of the degree of regeneration of the anion exchange resin AV-17-8 in $NO_3^-$ form on the specific flow rate and concentration of potassium chloride.

basic anion exchange resin AV-17-8 in the chloride form, the EDC before the $NO_3^-$ < 50 mg/dm$^3$ leakage was 0.74 g-eq/dm$^3$. EDC after the leakage of $NO_3^-$ < 50 mg/dm$^3$ was 0.99 g-eq/dm$^3$. Regeneration of the resin was performed with 10 % potassium chloride. With a specific consumption of regeneration solution of 16 cm$^3$/cm$^3$, the degree of desorption was 89.97 %.

The basic technological scheme of purification of artesian water from nitrates is presented in Fig. 4. After the receiving tank, the water enters the ultrafiltration unit. Then the extraction of nitrates from water occurs due to the sorption on the highly basic anion exchange

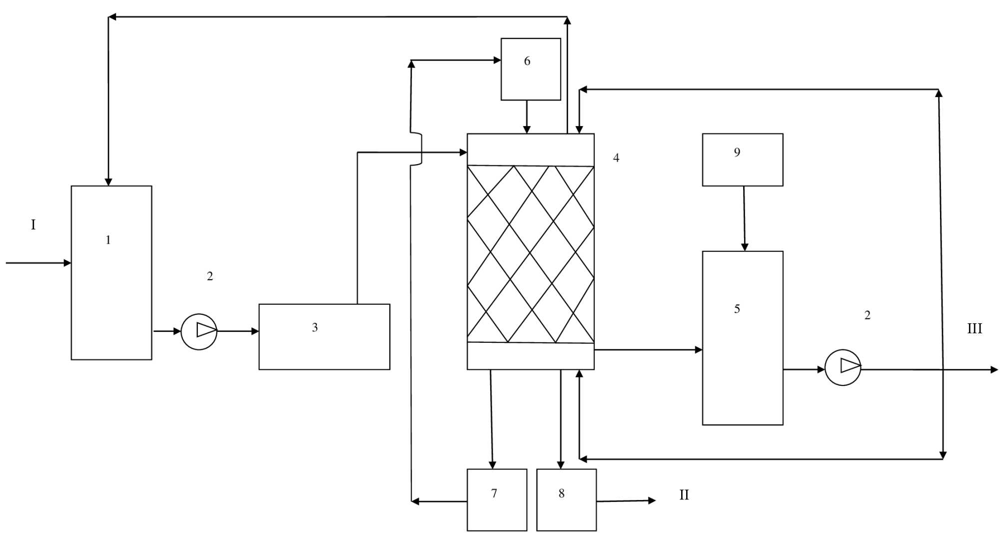


Fig. 4. Schematic technological scheme of purification of artesian water from nitrates: I - water supply from the well; II - supply of the solution for production of liquid fertilizers; III - water supply to the consumer; (1 - receiving tank; 2 - pumps; 3 - ultrafiltration unit; 4 - anion exchange filter filled with highly basic anion exchange resin AV-17-8; 5 - clean water tank; 6 - consumable tank with regeneration solution; 7 - receiving tank with flush water; 8 - tank with spent regeneration solution; 9 - ozonator installation).

resin AV-17-8. Regeneration of the anion exchange resin should be carried out with a solution of potassium chloride, which provides a very effective desorption of nitrates. Spent regeneration solutions should be used in the production of liquid fertilizers. The flush water is used to prepare regeneration solutions. After the ion exchange resin is depleted, it enters the receiving tank and is reused. This allows one to create low-waste technologies for the purification of artesian water from nitrates.

## CONCLUSIONS

As a result of the research on the removal of nitrates from water, it was shown that the highly basic anion exchange resin AV-17-8 provides the removal degree of nitrates at the level of 90 - 92 %. It was established that the sorption efficiency of highly basic anion exchange resin is higher in chloride form than in sulfate form.

During regenerations, it was found that the regeneration efficiency of the highly basic anion exchange resin AV-17-8 is higher when using chloride solutions and increases with increasing concentration of regeneration solutions.

A low-waste technological scheme of nitrate extraction, which allows obtaining purified water and liquid fertilizers that are suitable for further use, was proposed.

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