

Досліджено процеси іонообмінного вилучення з води амонію та нітратів. Визначено вплив умов сорбції нітратів та амонію на ефективність очищення води, досліджено процеси регенерації катіонітів та аніонітів з подальшою утилізацією відпрацьованих регенераційних розчинів. Запропоновано принципову технологічну схему, що забезпечує очищення води від сполук азоту з переробкою відпрацьованих регенераційних розчинів

Ключові слова: переробка відходів, регенерація, амоній, нітрати, іонний обмін

Исследованы процессы ионообменной очистки воды от аммиака и нитратов. Определено влияние условий сорбции нитратов и аммония на эффективность очистки воды, исследованы процессы регенерации катионитов и анионитов с дальнейшей утилизацией отработанных регенерационных растворов. Предложена принципиальная технологическая схема, которая обеспечивает очистку воды от соединений азота с переработкой отработанных регенерационных растворов

Ключевые слова: переработка отходов, регенерація, аммоний, нитраты, ионный обмен

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LOW-WASTE ION EXCHANGE TECHNOLOGY OF EXTRACTION OF NITROGEN COMPOUNDS FROM WATER

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1. Introduction

Today, the ecological state of natural water reservoirs in Ukraine largely depends on the effectiveness of the cleaning of communal wastewater and efficient use of water in the industry, including energy, and also providing the population with heat and electricity.

Ukraine has a limited supply of fresh water and has almost lost the clean surface water that would meet the requirements of the water quality for domestic supply. The surface waters of rivers, lakes, underground water, and pressure artesian water are used for the drinking water supply, but many of them have lost their quality due to excessive contamination by the wastewater. Often the technogenic pressure on aquatic reservoirs exceeds their ability of self-cleaning.

Most of all, the contamination of water reservoirs leads to a significant increase in the level of mineralization of reservoirs, a significant increase in the hardness of water. A rather complex and acute problem is the water pollution by nitrates and ammonium. Nitrogen compounds enter the water objects with precipitations, as a result of the solid waste decomposition, with household sewage wastewater, sewage of the food industry and other sectors of production, from the wastes of military facilities, as well as the result of using fertilizers in agriculture. The increase of the content

of nitrates in surface water reservoirs is not only due to the discharge of wastewater [1] and other anthropogenic factors, but also due to their accumulation in the soil and underground waters as a result of natural processes. This is proved by the data on the determination of nitrates in underground waters [2].

2. Analysis of scientific literature and the problem statement

Today to remove nitrogen compounds from water they use adsorption [3, 4], biological [5, 6], baro-membrane [7–9], electrochemical [10–12], ion-exchange [14, 15] methods of water purification and the methods of catalytic chemical recovery [13].

However, the considered methods have a number of significant shortcomings. Sorption removal of ammonium on mineral sorbents has low effect due to the low capacity of sorbents [3]. Not really effective is the removal of nitrates on the sorbents [4]. Biological processes of the purification of water from nitrates are rather slow [5]. When extracting ammonium compounds by this method, sufficient aeration of the water is required, which leads to increased concentrations of nitrites and nitrates [6]. During the application of nanofiltering, the degree of extraction of nitrates from water does not exceed 50 % [7]. The method of reverse osmosis is

also characterized by low efficiency when cleaning the water from nitrates [8]. In addition, the authors [9] showed that the presence of sulfates and chlorides in water reduces the efficiency of the reverse-osmosis purification of water from nitrates. Even combining the processes of reverse osmosis with the electro dialysis does not always give the possibility to reduce the nitrates content to acceptable levels and does not solve the problem of the utilization of concentrates [10]. The problem of utilization of concentrates is not solved by the improvement in the processes of electro dialysis [11]. Extraction of nitrates from water by electro dialysis is the energy-consuming technology [12]. The application of photo catalysis recovery of nitrates using reducing agents is quite expensive and is accompanied by the secondary pollution of water [13].

Much easier and more reliable at extracting nitrates from water is the application of ion exchange [14]. However, the extraction of ammonium from water in the presence of the ions of hardness on the cationites is almost impossible, and during the extraction of nitrates on the anionites, the effectiveness of the cleaning process greatly depends on the content of chlorides and sulphates. In addition, regenerative solutions are often contaminated with chlorides, which significantly worsens the possibilities of obtaining liquid fertilizers out of them [15].

3. The purpose and objectives of the study

The aim of this work was to design a low-waste ion exchange technology of purification of water from nitrogen compounds based on the methods of regeneration of ionites which ensure the recycling of exhausted regenerative solutions into liquid fertilizers.

To achieve the set goal, the following tasks were solved:

- research of the processes of the sorption of nitrates on a low-base anionite in the salt and the main form, determination of the conditions of effective regeneration taking into account the recycling of regenerative solutions;
- research of the processes of cationic water softening to ensure effective extraction of ammonium nitrogen from water and creation of low-waste processes of regeneration of cationites;
- design of conceptual technological scheme of water purification from nitrogen compounds, which includes recycling of exhausted regenerative solutions.

4. Materials and methods of research

4.1. Materials and equipment used in the experiment

In this work we used sub-acid cationite Dowex Mac-3, highly-acid cationite KU-2-8 and low-base anionite Dowex Marathon as the ion-exchange materials.

We used distilled, tap and artesian water as well as the simulation solutions on its base as the media (Table 1).

Experimental research of the extraction of nitrogen compounds was carried out by the method of ion exchange. The concentration of ammonium and nitrate ions in water was determined photometrically and spectrophotometrically. The concentration of chloride ions was analyzed by titration by solution of silver nitrate in the presence of chromates, the concentration of sulfate was determined by the method of titration by the solution of barium chloride.

Table 1

Characteristics of water

Parameter	Tap water	Artesian water
Hardness, mg-eqv/dm ³	4.2	4.8
Alkalinity, mg-eqv/dm ³	4.2	–
The concentration of calcium ions, mg-eqv/dm ³	3.4	3.7
Magnesium ion concentration, mg-eqv/dm ³	0.8	1.1
The concentration of chloride ions, mg/dm ³	23	19
The concentration of sulfate ions, mg/dm ³	39	27
pH	7.82	7.72

4.2. Methods of experiment

The processes of sorption of compounds on the ion-exchange materials were conducted under dynamic conditions. The ionite was in the column with a diameter of 19 mm, in the volume of 10–20 cm³. The solution was filtered through the ionite with the flow of 10–15 cm³/min, selecting the samples of volume of 0.1–1.0 dm³. After the passage of the water through the cationites, the samples were analyzed for the content of ammonium ions, their acidity and pH of the medium were defined. We determined the acidity of the water, the content of chlorides, sulphates, nitrates and pH of the medium after the anion-exchanging filter.

The regeneration of cationite was carried out by the 5 and 10 % solutions of nitric acid. The samples' volume totalled 20 cm³. In the samples we determined the content of ammonium and residual acidity.

The anionite was regenerated by the 10 % solutions of sodium chloride, ammonium chloride and a 4 % solution of ammonia. The samples' volume equaled that of the anionite – 10 cm³. The samples were analyzed for the concentration of nitrates.

The degree of regeneration was calculated as the ratio of total mass of desorbed ammonium or nitrates to the mass of the adsorbed substances.

5. Results of the study of the extraction of ammonium ions and nitrates by the ion-exchange method

It is known from the scientific literature on the ion-exchange water purification from nitrates [14, 15] that the high- and low-base ionites in a Cl⁻ form rather well adsorb nitrates from water.

In this case the exchange capacity of anionites on the nitrates reached 870–1180 mg-eqv/dm³. Good results were obtained during the regeneration of anionites by the sodium chloride and ammonia chloride solutions. The regeneration degree amounted to 60–70 %. However, even in the case of using ammonia chloride, the possibilities for the processing of exhausted regenerative solutions into liquid fertilizers are limited due to the high content of chlorides. Therefore, by using the prospect of effective regeneration of low-base anionite by ammonia solutions, we studied the processes of sorption of nitrates on the low-base anionite in the main form of acidic solutions (Fig. 1, 2).

Acidic solutions have been selected because after H⁺-cationization and the allocation of carbon dioxide from the water in a degasser, the weak solutions of acids – hydrochloric, sulphuric and nitric – go to the ion-exchange filters. The ratio of acids content depends on the ratio of chlorides, sulphates and nitrates in the source water.

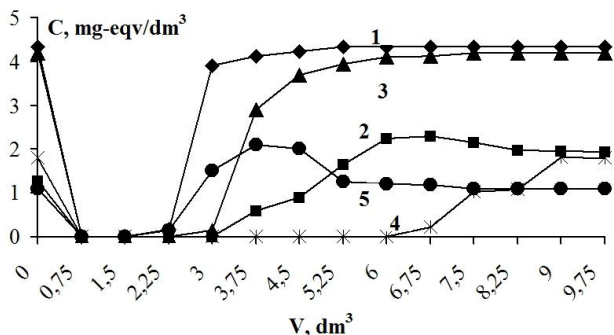


Fig. 1. Output concentrations of nitrates (1, 2, 3), sulfates (4) and chlorides (5) during sorption on a low-base anionite Dowex Marathon ($V_i=10\text{ cm}^3$) from the solution of nitric acid ($[\text{HNO}_3]=4.33\text{ mg-eqv/dm}^3$) (1), a mixture of nitric and sulfuric acids ($[\text{HNO}_3]=1.98\text{ mg-eqv/dm}^3$, $[\text{H}_2\text{SO}_4]=1.79\text{ mg-eqv/dm}^3$) (2, 4), a mixture of nitric and hydrochloric acids ($[\text{HNO}_3]=4.20\text{ mg-eqv/dm}^3$, $[\text{HCl}]=1.1\text{ mg-eqv/dm}^3$) (3, 5) ($\text{FEDC}_1=1697\text{ mg-eqv/dm}^3$, $\text{FEDC}_2=827\text{ mg-eqv/dm}^3$, $\text{FEDC}_3=1416\text{ mg-eqv/dm}^3$, $\text{FEDC}_4=969\text{ mg-eqv/dm}^3$, $\text{FEDC}_5=340\text{ mg-eqv/dm}^3$)

As can be seen in Fig. 1, nitrates are well sorbed from acidic solutions on the low-base anionite in the main form. The ionite has the highest capacity when using a solution of nitric acid or its mixture with hydrochloric acid. FEDC (full exchange dynamic capacity) on nitrates reaches 1446–1697 mg-eqv/dm³. This is due to the fact that in the first case there are no competing ions for nitrate anions and in the case of chlorides, the selectivity by nitrates is higher, which also contributes to the sorption of nitrates. In the case of a mixture of nitric and sulfuric acids, both nitrates and sulphates sorb. In this case the presence of sulfates in regenerative solutions does not affect the quality of liquid fertilizers during their processing. And the chlorides are replaced by nitrates from the anionite [15].

Good results were obtained when extracting the nitrates from water after its treatment on highly-acid cationite KU-2-8 in acidic form (Fig. 2). FEDC on nitrates reaches 1544 mg-eqv/dm³. Rather good results were obtained after processing the water on sub-acid cationite and low-base anionite ($\text{FEDC}=1377\text{ mg-eqv/dm}^3$).

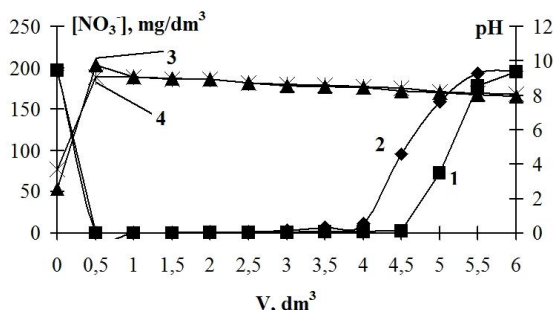


Fig. 2. Dependence of the concentration of nitrates (1, 2) and pH (3, 4) solutions, obtained after H^+ - cationization of artesian water on the cationite KU-2-8 (1, 3) ($\text{H}=0.28\text{ mg-eqv/dm}^3$, $\text{K}=2.93\text{ mg-eqv/dm}^3$, $[\text{HNO}_3]=197\text{ mg-eqv/dm}^3$, $[\text{HCl}]=19\text{ mg/dm}^3$, $[\text{H}_2\text{SO}_4]=27\text{ mg/dm}^3$, $\text{pH}=2.54$), and Dowex Mac-3 (2, 4) ($\text{H}=1.21\text{ mg-eqv/dm}^3$, $\text{K}=1.26\text{ mg-eqv/dm}^3$, $[\text{HNO}_3]=197\text{ mg/dm}^3$, $\text{pH}=3.68$) and after filtration through a low-base anionite Dowex Marathon in the main form ($V_i=10\text{ cm}^3$) ($\text{FEDC}_1=1544\text{ mg-eqv/dm}^3$, $\text{FEDC}_2=1377\text{ mg-eqv/dm}^3$)

High-capacity of anionite on nitrates in this case is due to the fact that during the passage of water through the cationite in acidic form, the principal amount of hardness ions (Fig. 3) is extracted from water and the water acidification occurs.

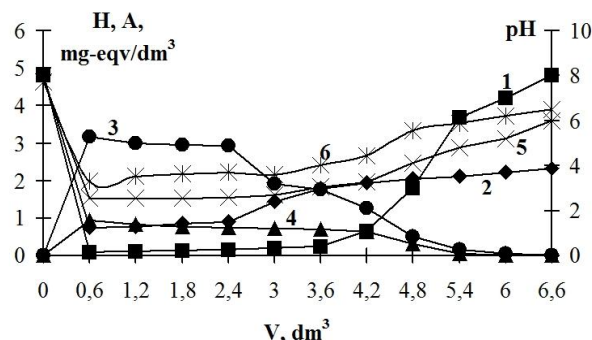


Fig. 3. Dependence of hardness (1, 2), alkalinity (3, 4) and pH (5, 6) of artesian water ($\text{H}=4.8\text{ mg-eqv/dm}^3$, $\text{A}=4.6\text{ mg-eqv/dm}^3$, $[\text{Ca}^{2+}]=3.7\text{ mg-eqv/dm}^3$, $[\text{Mg}^{2+}]=1.1\text{ mg-eqv/dm}^3$, $[\text{NO}_3^-]=197\text{ mg/dm}^3$, $[\text{Cl}^-]=19\text{ mg/dm}^3$, $[\text{SO}_4^{2-}]=27\text{ mg/dm}^3$, $\text{pH}=7.72$) on the volume passed through the cationite KU-2-8 ($V_i=10\text{ cm}^3$) (1, 3, 5) and Dowex Mac-3 ($V_i=10\text{ cm}^3$) (2, 4, 6) in acidic form ($\text{FEDC}_1=2207\text{ mg-eqv/dm}^3$, $\text{FEDC}_2=2145\text{ mg-eqv/dm}^3$)

In the case of the cationite KU-2-8, initially the main mass of cations adsorbs and nitric, hydrochloric and sulfuric acids remain in the solution. Coal acid breaks down into water and carbon dioxide, which is displaced out of the water. On the sub-acid cationite in acidic form, the coal acid is mainly displaced out of the water, while chlorides, sulphates and nitrates remain in the form of salts. However, the acidity of the solution reaches 1.2–1.56 mg-eqv/dm³, which increases the efficiency of sorption of nitrates on the low-base anionite in the main form.

Application of the low-base anionite Dowex Marathon in the main form allows not only increasing the capacity of anionite on nitrates, compared to the anionite in chlorine form (Fig. 4), but also giving the opportunity to solve the problem of regeneration of anionite and the recycling of regenerative solutions.

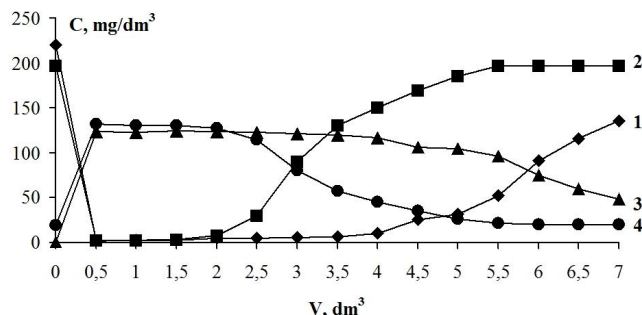


Fig. 4. Dependence of the concentration of nitrates (1, 2), and chlorides (3,4) on the passed volume of the solution of sodium nitrate in distilled water ($[\text{HNO}_3]=220\text{ mg/dm}^3$) (1, 3) and artesian water ($[\text{HNO}_3]=197\text{ mg/dm}^3$) through the anionite Dowex Marathon ($V_i=10\text{ cm}^3$) in Cl^- -form ($\text{FEDC}_1=1184\text{ mg-eqv/dm}^3$, $\text{FEDC}_2=968\text{ mg-eqv/dm}^3$)

As can be seen in Fig. 5, anionite regeneration in NO_3^- -form by sodium chloride is carried out rather effectively. When using ammonium chloride, the degree of regeneration reach-

es 93 %, but the regeneration solution contains chlorides and it is not applicable for the production of mineral fertilizers. When using a 4 % solution of ammonia, we reached full regeneration of anionite. With the specific consumption of regeneration solution of 5 cm³ to 1 cm³ of ionite, we achieved a degree of regeneration at the level of 93 %. While neutralizing the excess ammonia by nitric acid, the exhausted regenerative solution will contain only ammonium nitrate and will be suitable for the production of mineral fertilizers.

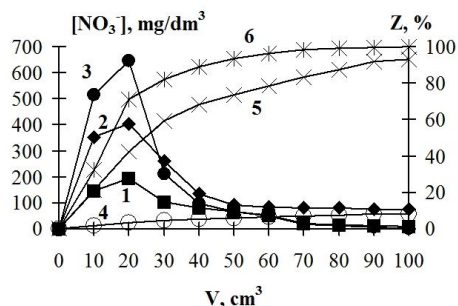


Fig. 5. Impact of the discharge of 10 % solutions NaCl (1, 4), NH₄Cl (2, 5) and 10 % solution NH₄OH (3, 6) (anionite Dowex Marathon in NO₃⁻-form (V_i=10 cm³)) on the output concentration of nitrates (1, 2, 3) and the degree of ionite regeneration (4, 5, 6)

It should be noted that the pretreatment of water on acidic cationites allows not only increasing the efficiency of extraction of nitrates on anionites from it, but also providing effective removal of ammonium from water.

It is known that cationites have a much higher selectivity on the hardness ions compared to singly charged cations including ammonium. However, with the discharge of water through cationites in acidic form, during the first stage of cationization the main mass of ions of calcium and magnesium is extracted from it, and during the second stage of cationization, the ammonium ions adsorb well. This is confirmed by the results given in Fig. 6.

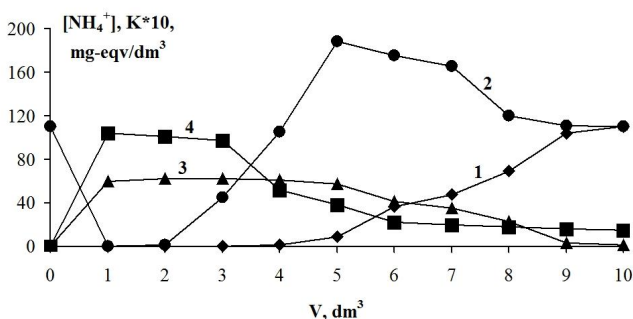


Fig. 6. Dependence of the concentration of ions of ammonium (1, 2) and acidity (3, 4) on the volume of the solution of ammonium chloride in distilled ([NH₄Cl]=6.2 mg-eqv/dm³) (1, 3) and tap water ([NH₄Cl]=6.2 mg-eqv/dm³, H=4.2 mg-eqv/dm³, A=4,2 mg-eqv/dm³, pH=7.82) (2, 4) passed through cationite KU-2-8 in acidic form (V_i=20 cm³) (FEDC₁=2009 mg-eqv/dm³, FEDC₂=175 mg-eqv/dm³)

So, in the absence of ions of hardness, the capacity of cationite KU-2-8 on ammonium reaches 2009 mg-eqv/dm³. During the sorption of ammonia from the tap water with hardness of 4.2 mg-eqv/dm³, the capacity of ionite on ammo-

nium reaches only 175 mg-eqv/dm³. Under these conditions, ammonium ions after sorption on the initial stage are gradually replaced from the cationite by ions of hardness with further filtering of the water.

For the desorption of ammonium ions from the cationite it is advisable to use the solutions of nitric acid. This allows using exhausted regenerative solutions for the production of mineral fertilizers.

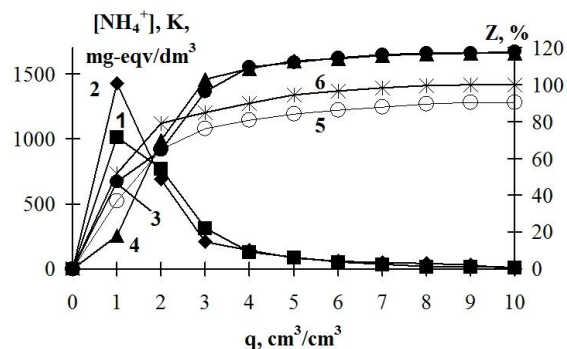


Fig. 7. Dependence of the concentration of ions of ammonium (1, 2), the acidity of the solution (3, 4) and the degree of ammonium desorption from the cationite KU-2-8 (V_i=20 cm³) (5, 6) on the specific consumption of the solution of nitric acid (q, cm³/cm³) by the concentration of 5 % (1, 3, 5) and 10 % (2, 4, 6)

As can be seen in Fig. 7, regeneration of cationite in the ammonium form by the solutions of nitric acid runs quite effectively. The efficiency of the process increases with the increase in the concentration of acid.

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

From the given results one can see that the efficiency of extraction of nitrates from water grows with its pre-treatment from hardness ions on the cationites in acidic form. In this case the acidification of solutions occurs and the sorption of nitric, sulfuric or hydrochloric acids occurs on the anionite, which undergoes quite effectively when using anionite in the main form. The main reaction of the process is the neutralization, which is characterized by high speed and irreversibility.

Another feature of the process is the high efficiency of the regeneration of low-base anionite by main reagents. With the high values of pH, the low-base anionite transfers from ammonium form into amine form, in which functional groups lose the positive charge that promotes effective desorption of sorbed anions. Therefore, when using the solutions of ammonia one can achieve complete regeneration of the anionite.

Exhausted regenerative solutions contain nitrates and excess ammonia, which simplifies their recycling into liquid fertilizers based on ammonium nitrate. The extraction of ions of hardness when filtering water through cationites in acidic form allows effectively extracting ammonium ions and nitrates from the water. Cationite of the second stage of cationization, on which ammonium ions are sorbed, is advised to regenerate by the solutions of nitric acid and to recycle the exhausted regenerative solutions into liquid fertilizers also on the ammonium nitrate base.

Based on the obtained results, the conceptual technological scheme of water purification from the compounds of nitrogen and its simultaneous mitigation was designed (Fig. 8).

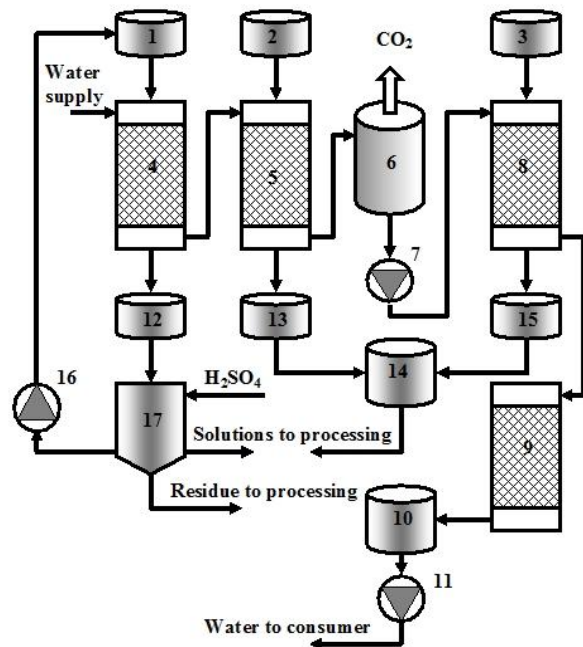


Fig. 8. The conceptual technological scheme of demineralization of water that contains nitrogen compounds:
 1, 2, 3 – reservoirs with regenerative solutions of, respectively, hydrochloric, nitric acids, and ammonia;
 4, 5, 9 – cation-exchanging filters; 6 – degasifier;
 7, 11, 16 – pumps; 8 – anion-exchanging filter;
 10 – treated water reservoir; 12, 13, 15 – reservoirs of exhausted regenerative solutions; 14 – neutralizer; 17 – reactor

According to the proposed scheme, water passes in sequence through sub-acid cation-exchanging filter, filled with resin Dowex Mac-3 in acidic form (4), and highly-acid cationite KU-2-8 in acidic form (5). During the first stage, the ions of hardness are mainly extracted, during the second stage the remains of the ions of hardness and ammonium ions are extracted. The carbonation is extracted from acidified water in a degasifier (6). Later on, the water of the nitric acid (possibly, sulfuric acid and hydrochloric acid impurity) is released on the filter (8), filled with a low-base anionite Dowex Marathon in the main form. In this case neutralization of the water occurs, as well as its purification from nitrates. In the presence of sulfates, they also sorb on the anionite. Chlorides, if they are present in the water, are replaced by sulphates or nitrates from the anionite, the selectivity of which on the anionite is larger than that of nitrates.

It should be noted that this technology is effective for water purification with a low content of chlorides and sulphates. As a rule, fresh surface or underground waters contain chlorides or sulphates in low concentrations. That is, often there are the waters in which the content of chlorides and sulphates does not exceed 50 mg/dm^3 with the concentrations of nitrates over 100 mg/dm^3 . In the case of the need of obtaining drinking water, to adjust the hardness ions content in it, it is advisable to pass it through sub-acid cationite Dowex Mac-3 in calcium-magnesium form during the last stage (9). Then hydrogen chloride, washed out

of the anionite, will wash out the ions of hardness from the cationite during the adjustment of the pH level to 7. When the content of chlorides in water is at the level of $1.0\text{--}1.5 \text{ mg-eqv/dm}^3$, the hardness of the treated water will reach 1.5 mg-eqv/dm^3 that meets the requirements for drinking water. There is no need to specifically lead the cationite to a calcium-magnesium form, as the ionite enters this form during the first stage of the cationization. Applying it during the last stage will facilitate its regeneration and will reduce the consumption of the reagent for the regeneration.

The regeneration of cationite is advised to conduct by hydrochloric acid by the technology described in the paper [16]. By this technology, exhausted solution of hydrochloric acid is treated with sulfuric acid with the allocation of insoluble calcium sulfate in the reactor (17), while the clarified solution is used for the regeneration of cationite. The solution can be used until its saturation with magnesium salts to a concentration of approximately 2000 mg-eqv/dm^3 . After that it is sent for the recycling, which includes evaporation with obtaining technical magnesium chloride suitable for use. Cationite in the ammonium form (5) regenerates by nitric acid. Exhausted acid solution goes to the neutralizer (14), which also receives the main regeneration solution, formed after the regeneration of anionite in nitrate form by the ammonia solution (8). After neutralizing this mixture, aqueous solution of ammonium nitrate is produced that is used for the manufacture of liquid fertilizers. Flushing waters after the washing of cationite in the filter (5) are used to prepare the solution of nitric acid in the reservoir (2). Flushing waters after the washing of anionite in the filter (9) are used to prepare the solution of ammonia in the reservoir (3). The filter (9) after the washout of ions of hardness applies instead of one of the filters during the stage of sorption (5), and one of the filters (5) in calcium-magnesium form is used in its place instead.

7. Summary

1. The processes of sorption of nitrates of acidic and neutral solutions on a low-base anionite Dowex Marathon were researched. It is shown that the application of the anionite in the main form provides effective extraction of nitrates from sub-acid solutions with high efficiency of the regeneration of anionite by the solutions of ammonia, which significantly simplifies their further processing.

2. It was found that the extraction of the hardness cations from water on the cationites in acidic form provides effective extraction of ammonium ions from the water. The application of nitric acid for the regeneration of cationite allows using exhausted regenerative solutions for the production of liquid fertilizers.

3. The conceptual technological scheme of a low-waste technology of water purification from nitrogen compounds was designed, based on the use of a two-stage cationization on the sub-acid and highly-acid cationites in acidic form and extraction of the anions on a low-base anionite in the main form, the feature of which is that it ensures the extraction of ammonium from water in the presence of ions of hardness and nitrates in the presence of chlorides and sulphates. The technology provides the recycling of exhausted regenerative solutions into liquid ammonium nitrate-based fertilizers.

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