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# STUDY OF METHODS FOR PHYSICO-CHEMICAL TREATMENT OF GROUNDWATER FROM NITRATES

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**Abstract**

Contamination of groundwater by nitrogen compounds is an urgent problem. In Belarus for the water supply of cities, towns, industrial enterprises use groundwater. There is a brief description of the operating conditions of underground water and their quality. It describes the impact of nitrates on human health. The most intensive pollution by nitrates at a depth of 10–15 m in the country side and in home gardens. Also at depths of 40–50 m recorded nitrate concentrations, that exceed the maximum permissible level (45 mg/l for of nitrates content). The article studies methods for removal of ammonium nitrogen, nitrates and nitrites from natural waters, presents the results of experimental studies of water purification from nitrates by ion exchange method for drinking water supply purposes.

**Keywords:** groundwater, nitrates, watertreatment, drinkingwatersupply, ionexchange, anion exchangers.

## ИССЛЕДОВАНИЕ МЕТОДОВ ФИЗИКО-ХИМИЧЕСКОЙ ОЧИСТКИ ПОДЗЕМНЫХ ВОД ОТ НИТРАТОВ

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**Реферат**

Загрязнение подземных вод соединениями азота является актуальной проблемой. В Беларуси для водоснабжения городов, поселков, промышленных предприятий используются подземные воды. Дана краткая характеристика условий эксплуатации подземных вод и их качества. Описано воздействие нитратов на здоровье человека. Наиболее интенсивное загрязнение нитратами присутствует на глубине 10–15 м в сельской местности и на приусадебных участках. Также на глубинах 40–50 м фиксируются концентрации нитратов, которые превышают уровень предельно допустимой (45 мг/л по содержанию нитратов). В статье изучены методы для удаления аммонийного азота, нитратов и нитритов из природных вод, представлены результаты экспериментальных исследований очистки подземных вод от нитратов методом ионного обмена в целях питьевого водоснабжения.

**Ключевые слова:** подземные воды, нитраты, водоподготовка, питьевое водоснабжение, ионообмен, аниониты.

### Introduction

Groundwater pollution with nitrogen compounds is the problem. In Belarus for the water supply of cities, towns, industrial enterprises use groundwater. Over the past few decades in the field of active agricultural production observed increase in groundwater salinity on the average from 190 (natural background) to 366 mg/l. The average mass concentration of nitrates of 140 mg/l [1], that exceed the allowable concentration of 3 times (45 mg/l) [2].

The presence in water mineral nitrogen (ammonia, nitrates, nitrites) leads to disease development hydrogen-nitrate methemoglobinaemia and different degrees of oxygen deficiency of the organism.

Nitrogen compounds get into groundwater from a variety of sources, natural or man-made. The main natural sources are: soil nitrogen, nitrogen-rich biological deposition and precipitation. The main sources of anthropogenic activities are nitrogen fertilizers, septic drainage water basins, livestock farms, places of business and discharge of industrial wastewater. This has led to a progressive deterioration of the groundwater. Concentrations of nitrates than the allowable concentration of 2–3 times, and sometimes reach 10–16 maximum permissible concentrations [3].

In 2015, the major pollution of ground and artesian waters of Belarus were ammonia nitrogen, nitrate and permanganate oxidation. The largest number of water samples with a high content of nitrate ions found in the basins of the Dnieper rivers (groundwater and artesian water), Western Bug and Pripyat (groundwater) [4].

Brest region has significant reserves of fresh water, and has a problem, as in many other regions of the country.

The most intensive pollution by nitrates at a depth of 10–15 m in the country side and in home gardens. Also at depths of 40–50 m recorded nitrate concentrations, that exceed the maximum permissible level (45 mg/l for of nitrates content).

The increase and accumulation of nitrogen compounds in natural waters of our country and beyond requires a removal of anthropogenic pressure, and improve the quality of drinking water through the use of innovative and cost effective water treatment methods [5].

### Analysis of the current state of water treatment technology from nitrogen compounds

Cleaning groundwater Methods of nitrogenous compounds are divided into physical, chemical and biological. As part of this classification, we analyzed the methods of physical and chemical water purification from nitrates, each of which has its own specific, advantages and disadvantages. Physico-chemical methods: chlorination, air venting, reverse osmosis, ion exchange, electrodialysis.

*Chlorination* allows mainly ammonium hydroxide to oxidize the nitrogen gas through the formation of chloramines. Big difference between the practical theoretical chlorine consumption due to the fact, that not only undergoes oxidation of ammonium hydroxide, but other substances contained in the water and are capable of oxidation. With this method of cleaning the treated water contains a sufficiently large amount of residual chlorine, for which you want to carry out dechlorination, the study showed the presence of the reaction products in the drinking water of toxic volatile halogenated organic compounds.

By means of *air stripping method* selection can be made from water dissolved volatile nitrogen compounds, such as ammonium hydroxide.

Upon contact of water with air dissolved volatile nitro-gen compounds pass into the gaseous form. Along with the benefits (direct transition of ammonium ion to gaseous ammonia), the method has disadvantages:

1) the process efficiency dependence on the temperature and the value of water pH, which should be high, as well as the air flow;

2) changes in the lime-carbon dioxide balance, because of which falls in the carbonate salts precipitate;

3) environmental pollution with nitrogenous compounds, they move from water to air.

*Reverse osmosis* is based on the use of special membranes of cellulose acetate and triacetate, aromatic polyamide and polyesteramide, having selective permeability. These materials are used in the form of modules, which create the maximum surface area per unit volume. The effect of nitrates removal is 85–95 % at 30 and a pressure of 60 bar. The method is characterized by high efficiency, compact installation, but it has the following disadvantages: a significant change in the source water quality, removal is not only harmful but also beneficial to health substances; the need for pretreatment of water in order to avoid contamination and fouling of membranes; the presence of concentrated waste, requiring disposal or recycling. The introduction of this method in practice is ham-pered by lack of selective membranes in the country.

Ion exchange method based on the use of ion exchange resins, which are obtained on the basis of styrene-divinylbenzene copolymer and have as trimethylammonium functional groups (type 1) or dimetilgidroksietilammony (type 2). When selecting the resins should be noted that one type of resin is chemically more stable, type 2 – is relatively more susceptible to degradation, primarily water, containing oxygen. However, type 2 resins have a higher capacity and the regeneration degree.

When using ion exchange solutions require disposal problem of spent regeneration solutions (brine of sodium chloride, hydrochloric acid, sodium hydroxide), and the search of materials with a high, in relation to the nitrogenous compounds, exchange capacity.

Electrodialysis can be used for the removal of nitrate and nitrite from the water potable purposes (effect of removing nitrate ions – up to 40–60 per cent). Implementation of the method on an industrial scale constrain the following disadvantages: the need for a thorough pre-treatment of water; insufficiently high selectivity membranes; presence of waste in the form of concentrated solutions that require additional costs for their elimination. This method is tested only in semi-production conditions.

Known biological methods of removing nitrogen compounds. Used biological processes of nitrification-denitrification. These processes are managed in special facilities, which develop and live microorganisms. Biological processes, which convert nitrogen compounds to nitrogen gas, occur in the presence of a substance capable of oxidation. Such material may be a gas (e.g., hydrogen), solid (sulfur) or liquid (carbon-containing organic compound).

Microbiological methods of nitrification and denitrification are designed for high productivity treatment plants, require specially trained technical staff and continuous monitoring of the process.

Study of the chemical properties of mineral nitrogen compounds, the theoretical analysis of pos-sible methods of removing them from the natural water, quality monitoring the groundwater in natural conditions showed, that under water autonomous objects preferable physicochemical methods, including ion-exchange and sorption [6].

**Investigation of clean groundwater from of nitrates by ion exchange**

Ion exchange method – one of the most common methods of water purification – traditionally used in those cases where the solution contains a small concentration of pollutants, or as a final purification step. For experimental studies of ion exchange were set tasks:

– determining the resource potential of the ion exchange unit;

– study changes in the salt composition of the treated water in the purification of nitrates in highly basic anion exchanger;

– study and optimization of the treatment process in various types of ion exchange resins;

– the choice of the mathematical model of the dynamics of ion exchange for water purification from of nitrates;

– study and optimization of the process of regeneration of ion exchange resins in the purification process involved.

For the study was used a mathematical method for the optimum planning.

As the pollution of underground water, in the first series of experiments used tap water with the addition of nitrates of 20 mg/l for nitrate nitrogen, which corresponds to a concentration twice the maximum allowed for drinking water.

The aim of research was: to receive an experimental statistical model of the ion exchange purification of groundwater from nitrates to predict the efficiency of the installation in any given mode of conducting the ion exchange purification process.

**Results and discussion**

The experimental results were processed on a computer using the program «STATGRAPHIGS-statistical Graphics System». Obtained experimentally-statistical process based on ion-exchange treatment the following variables: 1) loading height and the diameter of the filter; 2) temperatures of water, and 3) filtration rate [7, 8].

In a second series of experiments we used real ground water containing nitrate ions at concentrations up to 100 mg/l. With optimal parameters of the ion exchange process, a high effect of remov-ing of nitrates was confirmed, which was obtained in the first series experimental investigations at model water.

A stronger influence of values of filtration rate of treated water V, m/h, and the factor H/d on the cleaning effect was established (Figures 1, 2). When changing the velocity V, m/h, in the range V = 10 – 32 m/h and fixed values of the factor H/d, respectively, a decrease in the cleaning effect E = f(V) by 20–30 % is observed (Figure 1). At a fixed temperature parameter t, °C, the decrease of the effect (E = f(V) < 50 %) is also observed when the velocity V, m/h, increases, when the factor H/d has a value less than unity. This fact can be explained by the insufficient height of the fixed ionite layer compared to the filtration rate of the solution, when the exchange occurs in nonequilibrium conditions – the degree of ionite utilization decreases, the purification effect decreases.

As a result of increasing the value of the factor H/d, the degree of ionite utilization increases (Figures 2) and the effect of nitrate removal increases: in the range of values H/d = 0,1 – 5, a change in the effect E = f(H/d) up to 19 % is observed. At that, further increase of H/d factor in the interval H/d = 5,5 – 12 leads to decrease of E = f(H/d) up to 30 %, which is determined by layer resistance, tendency of narrow columns to wall effects and channel formation. For efficient use of ionite and ob-taining high purification effect, the velocity parameter V can be varied during operation of the ion exchange column, and the value of the factor H/d can be set initially.

In the region of optimal values, the partial solutions of the obtained experimental-statistical dependences allow estimating the change in the effect of water purification from nitrates taking into account the variation of the factors of ion-exchange column operation by linear regression equations (95 % significance):

– for the factor of treated water temperature t, °C, in the range t = 5–18°C,

$$E = 1{,}03 \cdot t + 78{,}46,\ \%; \quad (1)$$

– for the factor of filtration rate V, m/h, in the interval V = 10–32 m/h,

$$E = -0{,}69 \cdot V + 99{,}28,\ \%; \quad (2)$$

– for the H/d factor, in the interval H/d = 0,1 − 5,

$$E = 3{,}71 \cdot (H/d) + 77{,}77,\ \%. \quad (3)$$


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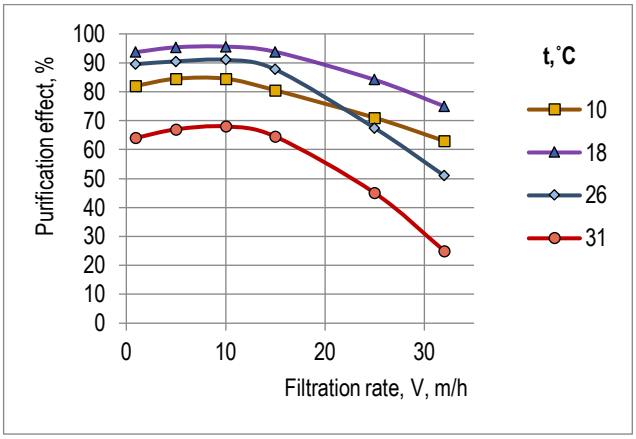


**Figure 1** – Dependence of nitrate removal effect on filtration rate

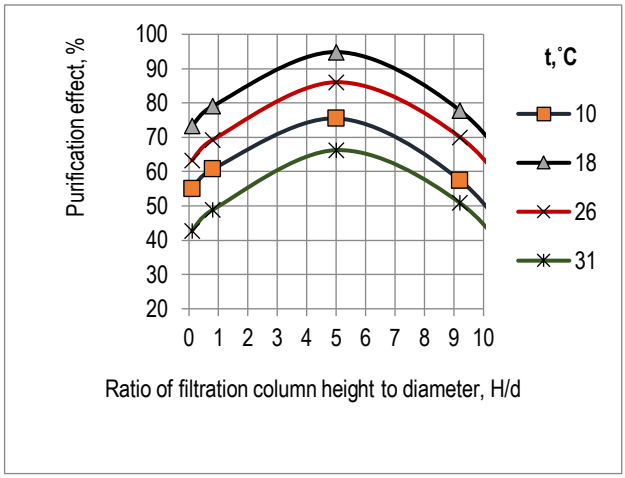


**Figure 2** – Dependence of nitrate removal effect on the H/d factor at a fixed rate value

Sulfate ions compete most with nitrate ions in the ion exchange process (Figure 3). In this case, groundwater ions of the studied region, absorbed by the strong-base anionite, are arranged in the order of affinity as follows:

$NO_3^-$ > $SO_4^{2-}$ > $HCO_3^-$ > $Cl^-$.

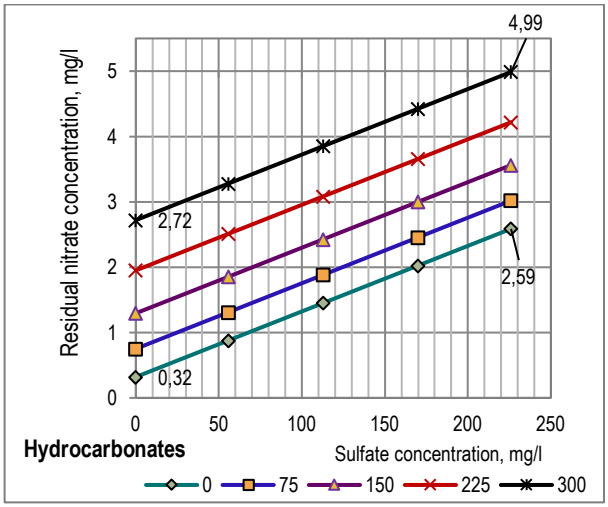


**Figure 3** – Influence of concentration of sulfates on nitrate removal from aqueous solutions of different anionic composition

In general, the change of anionic composition of water in the process of nitrate removal by ion exchange does not deteriorate its natural properties and corresponds to the quality and physiological fullness of drinking water.

**Conclusion**

Explore methods to remove ammonia nitrogen, nitrate and nitrite in natural water. The results of experimental studies of water purification from of nitrates by ion exchange for the purpose of drinking water. These equations allow to predict the efficiency of the ion exchange unit in any given mode of conducting the cleaning process.

The obtained experimental-statistical dependences of the process of purification of groundwater from nitrates by ion exchange method, describing the influence on the effect of nitrate removal filtration rate, temperature of treated water, the value of the ratio of filtration column loading height to its diameter, allowed us to determine the optimal values of these factors V = 13 m/h, t = 18 °C, H/d = 5, which provide the maximum purification effect, taking into account the anionic composition of water. It was found that the greatest influence on the process of ion-exchange purification of groundwater from nitrates is the concentration of sulfate ions in water.

**References**

1. Environmental protection in the Republic of Belarus. Statistical Collection; ed. by I. V. Medvedeva. – Minsk : National Statistical Committee of the Republic of Belarus, 2020. – 202 p.
2. State of the Environment of the Republic of Belarus: nat. report / Ministry of Natural Resources and Environment of Belarus, The Institute of nat wildlife. Academy of Sciences of Belarus // Beltamozhservice. – Minsk, 2010. – 150 p.
3. Environmental Bulletin. 2014 Minsk, 2015 / Editor: V. F. Loginov, Institute for Nature Management of NAS of Belarus, Minsk, Republic of Belarus.
4. Sanitary rules and normy 10-124 RB 99. Drinking water. Hygienic requirements for water quality of centralized drinking water supply systems. Quality control. Ministry of Health of the Republic of Belarus. – Minsk, 1999.
5. Technical Code 45-4.01-258-2012. Water industry. Building design standards Ministry of Architecture and Construction of Belarus. – Minsk, 2012.
6. Andreyuk, S. V. Research of methods of physical and chemical water purification from nitrates / S. V. Andreyuk // Collection of scientific articles of the International scientific-practical conference, Brest, 6–8 April 2016 : in 2 parts / Brest State Technical University ; ed. A. A. Volchek [et al.]. – Brest, 2016. – Part 2. – P. 159–163.
7. Andreyuk, S. V. The effectiveness of the study of the process of water purification from nitrates by mathematical planning / S. V. Andreyuk, B. N. Jitenev // Terrae agrariae, earum sustentabilitas et lineamenta evolutionis : collectio chartarum scientificarum innixa materiarum Conferentiae Internationalis Scientificae et practicae / comp. L. S. Novopolceva ; edited by I. S. Belyuchenko. – Krasnodar : Kuban State Agrarian University, 2020. – P. 321–323.
8. Andreyuk, S. V. Modeling of water preparation processes for technical and drinking water supply / S. V Andreyuk, M. A. Taratenkova // Biospheric compatibility: human, region, technologies. – 2021. – № 2. – P. 46–57.

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