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Low waste technology for the removal of nitrates from water

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Abstract: As a rule, nitrates are present in all natural water bodies. Their increased concentrations are connected with the discharge of insufficiently treated wastewater from industrial and communal enterprises, agricultural and livestock complexes. Recent scientific publications concerning treatment methods for nitrates removal from natural water and wastewater were analyzed in order to create effective and low-waste technology for obtaining high quality water. It has been established that the ion exchange method is quite effective for removing nitrates from water. In the paper, the processes of ion exchange removal of nitrates from water on low-axis anionite in DOWEX Marathon WBA in Cl^- form were investigated. During the sorption of nitrates with a concentration of 186, 205, 223 and 2200 mg/dm^3, it was established that the full exchangeable dynamic capacity was 1.075, 1.103, and 1.195, 1.698 g-eq/dm^3, respectively. To regenerate anionite, solutions of ammonia as well as potassium chloride, ammonium chloride and potassium carbonate were used in this work. The choice of potassium and ammonium compounds is due to the prospect of further use of regeneration solutions for the production of liquid fertilizers.

Introduction

Recently, significant pollution of the water basin has been observed, which is an important environmental problem (Remeshevska et al. 2021). In many regions, especially industrial ones, the population consumes water with a high level of salts (Kaushal 2016). Anthropogenic activity leads to an increase in the level of mineralization of many water bodies, and low-water rivers are most negatively affected (Trus et al. 2022). In the water of wells and boreholes, nitrate concentrations far exceed the sanitary and hygienic standards. The concentration of nitrates in drinking water is limited by international standard Directive (Direttiva (UE), 2020/2184) and domestic standard of Ukraine (State sanitary norm and rules of Ukraine 2.2.4-171) to 45–50 mg NO_3^- per 1 dm^3. The lowest concentration of nitrates is usually in bottled water samples, the highest – in water from dug wells ~ 161.1 mg/dm^3 (National report on drinking water quality and drinking water supply in Ukraine in 2021). Water pollution with nitrates occurs as a result of both anthropogenic and natural factors, therefore, this environmental problem requires an immediate solution. Enterprises producing nitrogen fertilizers are among the biggest polluters of nitrates, which are widely used as mineral fertilizers in agriculture (Voutchkova et al. 2021, Zabłocki et al. 2022). Preventing leakage from the soil into deeper parts of the aquifer is a priority in sustainable aquifer management in water-scarce areas (Gutiérrez et al. 2018).

Discharge of insufficiently treated municipal wastewater cause the pollution of water bodies with nitrates. Nitrates complicate the problem of providing the population with quality water due to exceeding the permissible level (Hansen et al. 2016). Also, high concentrations of these pollutants lead to a significant negative impact on surface water, as they lead to increased eutrophication of water bodies, which causes disruption of the development processes of existing biocenoses and changes in ecosystem parameters. Constant use of water with high nitrate content leads to diseases of the blood and cardiovascular system (Ward et al. 2018).

A number of methods to treat water from nitrates, which differ in their essence, technical means, cost and degree of purification are developed. However, nitrates are quite difficult to remove due to their high solubility (Wiśniowska and Włodarczyk-Makuła 2020). What is more, current water purification methods have a number of disadvantages (Fig. 1).

Biodegradation technologies are commonly used to remove nitrates from water, but biological methods are quite slow and have limitations for the application in the preparation of drinking water due to bacterial contamination of water (Alguacil-Duarte et al. 2022).

During the electrochemical reduction of nitrates, their decomposition occurs with the formation of toxic substances

– nitrites and ammonia. In addition, this method is quite energy consuming (Song et al. 2022).

Membrane methods are quite effective in removing organic and inorganic pollutants from water (Bodzek 2019). Reverse osmosis and nanofiltration are most often used to remove nitrates from water. The use of high-pressure systems makes it possible to achieve water purification efficiency of 85%, but requires high energy consumption (up to 1.68 $kW \cdot h \cdot m^{-3}$). Also, the process efficiency significantly depends on the composition of the solution that is used for treatment. Water needs preliminary softening and removal of chlorides and sulfates from water. Ultrafiltration can also be used to remove nitrates. However, in this case, the ultrafiltration membrane does not provide the necessary level of water purification due to the size of the pores (0.005–0.1 μm). It is obvious that the obstacle to the wide implementation of baromembrane methods are the high requirements for preliminary water preparation and the unsolved conditions for effective processing of the concentrates that are formed at the same time (Boubakri et al. 2022). As a result of the process, a rather large volume of concentrated flow is formed (15–50% of the initial volume of water). Because it contains a very high concentration of dissolved substances, especially salts, additional treatment is necessary before discharging or recycling such solutions (Trus et al. 2020).

Quite often, sorption methods are used to remove nitrates. Moreover, natural materials are most often used as sorbents (Preetham and Vengala 2023). Usually, such adsorbents are quite ineffective in removing nitrates from water, moreover, methods of their further utilization have not been developed yet.

Technologies based on ion exchangers provide process control, are easily automated, and the process can be started in minutes and ensure stable operation regardless of temperature. Depending on the amount of water to be treated and its nitrate concentration, all or only a portion of the raw water stream can be treated and then mixed with the rest of the water stream, making it suitable for treatment plants of small to medium capacity. Therefore, ion exchange is a fairly promising method of water purification from nitrates, as it is a fairly simple and inexpensive method that does not require specific conditions for preliminary water treatment (Trus[a] et al. 2021, Nujić et al. 2017). It is important to select ionite and develop methods of ionite regeneration with processing of regeneration solutions.

Highly basic anions allow for effective removal of various anions from water, such as sulfates, chlorides, nitrates (Trus 2022, Trus[b] et al. 2021). Nitrates are quite effectively removed on highly basic anionites Purolite A520E and A500 resins, the efficiency of anion removal is 87.2 and 91.6%. It was confirmed by the experimental studies in a fixed bed adsorption column in laboratory scale (Vasilache et al. 2018). The main disadvantage of using highly basic anionite for nitrate extraction is low regeneration efficiency (Trus and Gomelya 2022). In the paper by Nujić et al. (Nujić et al. 2017) the removal of nitrates on low basic anionite Relite A490 was studied under static conditions, but it would be interesting to study the process under dynamic conditions. Therefore, the efficiency of nitrates removal with different concentrations on low basic anionite was investigated. To create an environmentally safe technology of ion exchange water purification, it is important to select reagents for regeneration that can be reused in this process or

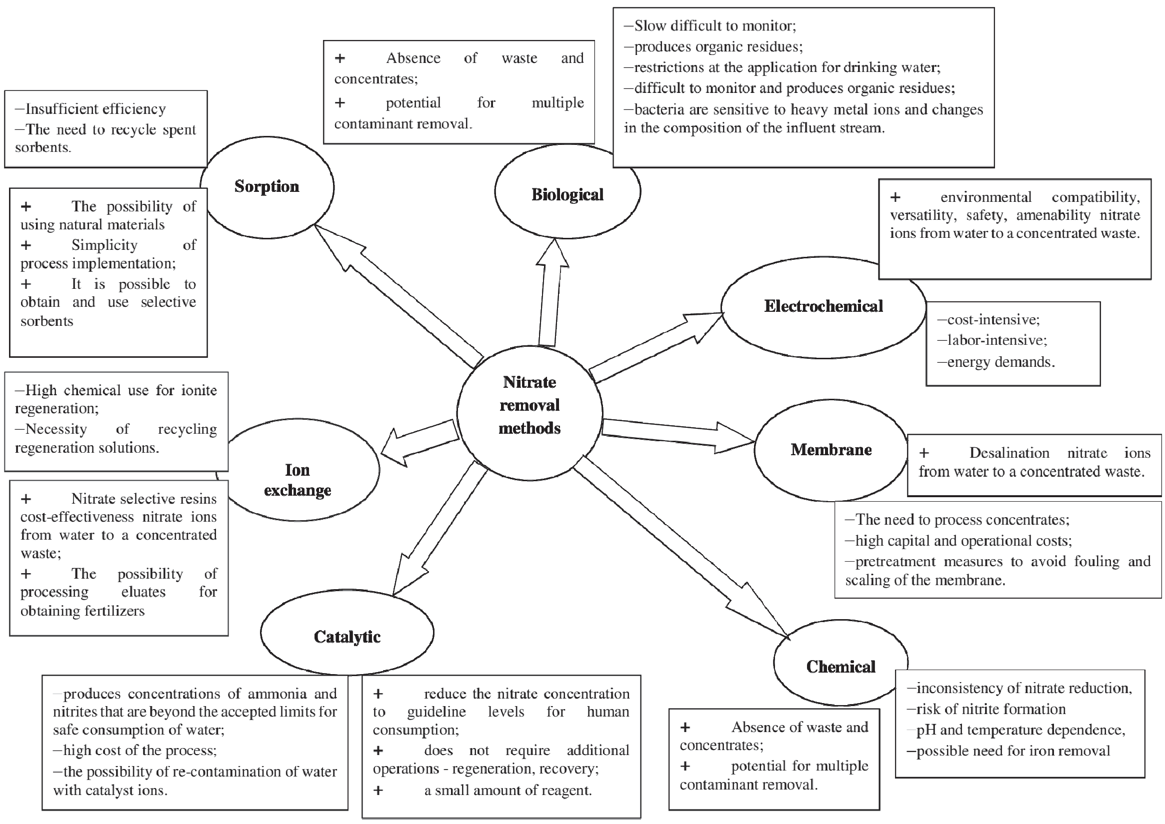

Fig. 1. Advantages (+) and disadvantages (–) of methods of removing nitrates from water

other productions. It is important to select reagent which can be processed with the obtaining of useful products and can be reused.

The purpose of this work was to study the processes of nitrates removal from water using a low-base anionite in the Cl^- form, to determine the conditions for effective regeneration and to obtain useful products from spent solutions. Thus, the technology for the ion exchange wastewater treatment, that excludes the discharge of regeneration solution, can be developed.

Experimental

The processes of water purification from nitrates were studied using the DOWEX Marathon WBA low-base anionite in Cl^- form (Fig.2).

Physico-chemical properties of DOWEX Marathon WBA (produced by Dow Inc.) anionite: ionic form – OH^-; active group – weakly basic, gel, macroporous, styrene--divinylbenzene; dynamic exchange capacity – 1.0 g-eq/dm^3; total exchange dynamic capacity – 1.3 g-eq/dm^3; mass fraction of moisture – 50–60%; grain size – 0.4–1.15 mm; the content of the working fraction was 95%; bulk mass – 620–650 g/dm^3; osmotic stability – 96%.

As a medium, model solutions with a nitrate concentration of 186, 205, 223 and 2200 mg/dm^3 were used. Distilled water was used to prepare model solutions. Nitrate concentrations in water were generally ~ 60 mg/dm^3, but in some individual wells they could be up to ~ 200 mg/dm^3. For a faster determination of the exchange capacity, a solution with a concentration of 2200 mg/dm^3 was used. The solution was passed through an anionite with a volume of 20 cm^3, at a filtration rate of ~3 m/h.

The following were used for regeneration: 10% KCl, NH_4Cl, K_2CO_3 and 5% NH_4OH. During regeneration, the filtration speed was ~ 0.3 m/h, samples were taken in 10 cm^3.

Determination of nitrate concentration was performed by potentiometric method using an ion-selective electrode. (HI 4113, Hanna Instruments SI).

The total exchangeable dynamic capacity (TEDC) of the ionite was determined by formula (1), based on the mass of sorbed ions on the anionite. The degree of ionite regeneration after passing *i* samples of the regeneration solution was calculated according to formula (2) as the ratio of the mass of desorbed and sorbed ions:

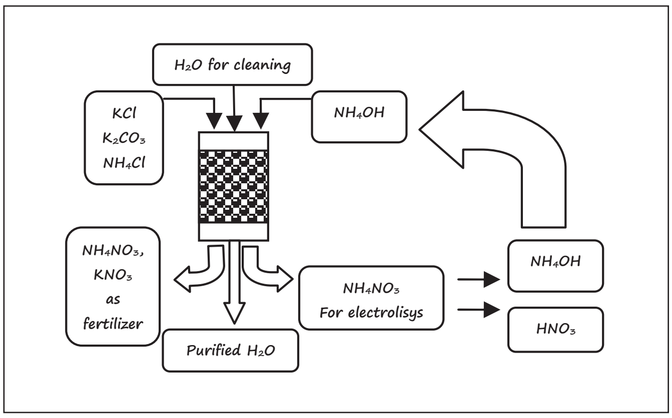

Fig. 2. Scheme of the nitrate extraction process

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

$$Z = \frac{\sum_{i=1}^{n} M_i^d}{M_s} \quad (2)$$

where $C_{in.}$ – initial concentration of ions in the solution, mg-eq/dm^3, $C_{i.}$ – the concentration of ions 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, where $M_i^{d.}$ – the number of desorbed ions with the i-sample of the regeneration solution, mg-eq/dm^3; $M_{s.}$ – amount of sorbed ions, mg-eq/dm^3.

Results and discussion

The concentration of nitrates in wastewater can be at the level of 1 mg-eq/dm^3. But with such a low concentration of nitrates in water, it is quite difficult to determine the exchange capacity of ionite, since the duration of the experiments increases significantly when passing such large volumes of water. Therefore, model solutions with a nitrate content of 186, 205, 223 and 2201 mg/dm^3 were used in the work.

When using Dowex Marathon WBA low-base anionite in Cl^- form for nitrate sorption from model solutions with a concentration of 186, 205 and 223 mg/dm^3, it was determined that the TEDC is 1.075, 1.103 and 1.195 g-eq/dm^3, respectively, which is a quite satisfactory as TEDS higher than 1 g-eq/dm^3 allows us to remove nitrates effectively (Fig. 3).

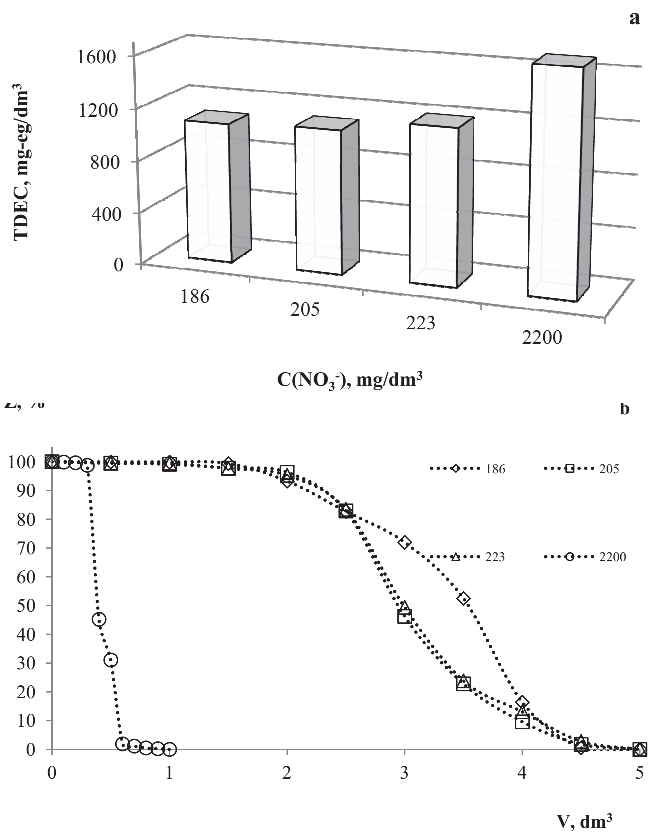

Fig. 3. Dependence of total dynamic exchange capacity (TDEC) (a) and nitrate removal efficiency (b) from Dowex Marathon WBA anionite on their concentration in the solution

When using saturated solutions with a $NaNO_3$ concentration of 35.5 mg-eq/dm^3, the full exchangeable dynamic capacity for low-base anionite reached 1.698 g-eq/dm^3. That is, the TEDC values are greater than when using anionite for sorption from dilute solutions. Under these conditions, the high exchange capacities of anionites during sorption of nitrates from concentrated solutions are due to over-equivalent sorption. This phenomenon is not of significant importance since the prospect of using anionites for sorption of nitrates from dilute solutions is real. At the same time, reaching the value of the working capacity of anions for nitrates at the level of 0.9÷1.0 g-eq/dm^3 can be a quite satisfactory result (Trus and Gomelya 2022). However, the relatively effective removal of nitrates from water on anionites does not provide a complete solution to the problem of removal nitrates from water with obtaining useful products.

For the regenerations of AV-17-8 anionite, solutions of potassium and ammonium chloride, potassium carbonate and ammonia were used (Fig.4). The choice of these reagents is explained by the fact that in the regeneration process ammonium or potassium nitrate is formed, which are mineral fertilizers and which can easily be used. The application of chlorides has also shown efficient results, while the efficiency of regeneration increased with an increase in the concentration of regeneration solutions and reached 87%. But the excess of chlorides in the regeneration solution makes it difficult to use such solutions as mineral fertilizers.

The functional groups of the low basic anionite Dowex Marathon WBA at pH >10 change to a non-dissociated form, so the anions are easily desorbed. This can explain a rather high degree of regeneration in the range of 87.9–97.3% of this anionite when using solutions of potassium carbonate, ammonia and ammonium chloride. Ammonia turned out to be the most effective regeneration solution: at its concentration of 5%, the degree of regeneration at q=5 cm^3/cm^3 (q is the ratio of the volume of regenerated solution to the volume of ionite) reached 93.1%, whereas at q=10 cm^3/cm^3 – 97.3%. One of the methods of processing this regeneration solution is electrochemical processing, which allows to separate excess ammonia or obtain solutions of ammonia and nitric acid. But this process has a significant drawback, since the low-base anionite does not absorb nitrates in the basic form due to the alkalinization of the solution. Therefore, to solve this problem and ensure effective sorption of nitrates from the solution, the anionite must be treated with hydrochloric acid to convert it into the Cl^- form.

The conducted research on water from an individual well (Petropavlivska Borschahivka, Kyiv region, Ukraine) with elevated nitrate content ($C(NO_3^-)$ = 205 mg/dm^3, $C(SO_4^{2-})$ = 40.5 mg/dm^3, $C(Cl^-)$ = 30.7 mg/dm^3) showed that TEDC was 0.937 g-eq/dm^3. The reduction of TEDC in nitrate-only water from 1.103 to 0.937 g-eq/dm^3 is due to the competing effects of sulfates and chlorides. Based on the results, it can be concluded that the volume of water for the treatment depends on the nitrates content and volume of ionite. It was calculated for the present conditions that 20 cm^3 of ionite allows to purify 2.5 dm^3 of water to standards below the maximum allowable concentration. This water meets the requirements for drinking water regarding the nitrate content. If it is necessary to obtain drinking water to adjust the content of hardness ions, it is advisable to use cation-exchange water softening.

In further studies, it is planned to study the competing effect of anions on the efficiency of nitrate removal on low basic anionite.

Conclusions

As a result of the conducted studies on the removal of nitrates from water, it has been shown that the low basic anionite Dowex Marathon WBA provides a degree of nitrate removal at the level of 90–97%. It was established that low basic anionite better sorbs nitrates in the chloride form, whereas nitrate sorption does not occur in the basic form.

During ion exchange treatment, TEDC was 1.103 g-eq/dm^3 for the model solution (with the initial nitrates concentration of 205 mg/ dm^3) and 0.937 g-eq/dm^3 for natural water (which contains 205 mg/dm^3 of nitrates, 40.5 mg/dm^3 of sulfates and 30.7 mg/dm^3 of chlorides).

The results of regenerations show that the efficiency of regeneration of low basic anionite Dowex Marathon WBA is satisfactory at the application of basic solutions – potassium carbonate and ammonia (92.0 and 97.3%, respectively). Salt

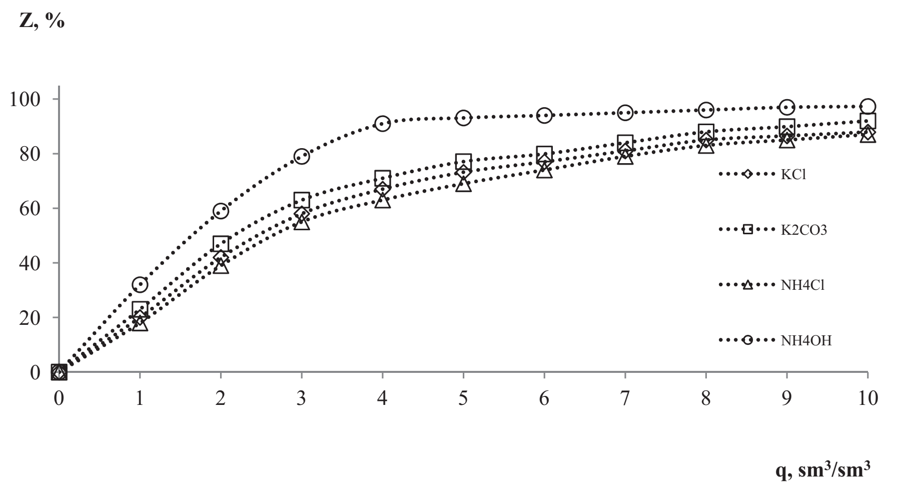

Fig. 4. Dependence of the degree of desorption of nitrates from Dowex Marathon WBA anionite in NO_3^- form on the passed volume of regeneration solutions

solutions can be processed by electrodialysis, but in this case, considering the possibility of using nitrates as mineral fertilizers, there is no need for electrodialysis. Therefore, it is advisable to use spent solutions containing potassium and ammonium nitrate in the production of liquid fertilizers.

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