Efficiency of Reverse Osmosis and Ion Exchange in Water Purification from Nitrates

Mykola Gomelya¹, Tetyana Shabliy*¹, Iryna Makarenko¹, Anna Vakulenko¹

¹ Department of Ecology and Technology of Plant Polymers, Faculty of Chemical Engineering, Igor Sikorsky Kyiv Polytechnic Institute, Peremogy Avenu 37/4, 03056 Kyiv, Ukraine
* Corresponding author’s e-mail: dsts1@ukr.net

ABSTRACT

The process of extracting nitrates from water by the methods of reverse osmosis and ion exchange was investigated in the paper. In the formation of reverse osmosis, low-pressure membranes were used, and in ion-exchange processes, highly alkaline anionite AB–17–8 was applied in salt form. The dynamics of changes in the concentration of nitrates in the permeate and the concentration with an increase in the degree of permeate selection from 9 to 90% at initial nitrate concentrations of 18, 50 and 100 mg/dm³ were determined. The indicators of selectivity and productivity of membranes were calculated depending on the degree of permeate selection. It was shown that the low-pressure reverse osmosis membrane is characterized by low selectivity values at high productivity values in the selected part of the nitrate concentration. It was established that the ion exchange method is significantly more effective than reverse osmosis in removing nitrates from water. It ensures the reduction of nitrate content in purified water to a value of less than 1 mg/dm³ when the degree of their extraction is reached at the level of 99%. As the ionite is saturated with nitrates, the efficiency of their extraction decreases. Anionite sorbs nitrates effectively enough, being both in the chloride mixture and in the sulfate form. Nitrates are effectively desorbed by 2H solutions of sodium chloride and sodium or ammonium sulfate.

Keywords: nitrates, membranes, reverse osmosis, ion exchange, selectivity, productivity, permeate, concentrate, regeneration.

INTRODUCTION

Nitrates are often present in ground and surface water. Their source, as a rule, is agrochemical production, municipal wastewater and natural processes of nitrification [Giammarino et al., 2015; Goncharuk et al., 2013]. The permissible concentration of nitrates in drinking water is regulated by the requirements of normative documents [Dsan Pin 2.2.4.-400–10, 2010; Council Directive 98/83/EC, 1998]. For most countries, including Ukraine, it should not exceed 45 mg/dm³.

The difficulty in removing nitrates from water is that they are stable, highly water-soluble anions with a low ability to precipitate or adsorb. The choice of nitrate removal method is determined by specific conditions and situation [Yanhao et al., 2009].

To remove nitrates from water when using membrane processes, reverse osmosis [Goncharuk et al., 2013; Hayrynen et al., 2009], nanofiltration [Kombo, 2015; Epsztein et al., 2015] and electrodialysis [Osipenko et al., 2015] are used most often.

Quite often, sorption methods are employed to remove nitrates. Moreover, natural materials are usually used as sorbents [Xu et al., 2011; Dong-Wan et al., 2010]. Ion exchange is more widely used [Gomelya et al., 2016; Primo et al., 2009]. Biological methods of water purification are applied to clean large volumes of wastewater from nitrates [Pradhan et al., 2016; Ayyasamy et al., 2009]. Various methods of their recovery are also often employed in wastewater treatment to remove nitrates [Dehghani et al., 2016; Ghanbari et al., 2014]. All the considered methods have their advantages and disadvantages.
Methods of chemical and electrochemical reduction, biological methods of nitrate recovery should be used in wastewater treatment. They are inconvenient when preparing drinking water, often accompanied by secondary water pollution. Membrane methods of water purification and ion exchange are more convenient in this case. The main disadvantage of both methods is the formation of concentration or regeneration solutions, which are difficult to dispose. However, there are possible approaches that allow solving these problems.

The purpose of this work was to evaluate the effectiveness of water purification from nitrates using a low-pressure reverse osmosis membrane (Filmtec TW30–1812–50) and anion exchange resin AB–17–8, taking into account the possibility of processing liquid waste.

To achieve the goal, the following scientific tasks must be solved:

1. To evaluate the efficiency of nitrate removal from water on a low-pressure reverse osmosis membrane depending on the concentration of solutions and the degree of permeate selection.

2. To determine the efficiency of removal of nitrates on the AB–17–8 anionite in chloride and sulfate forms, to choose the methods of regeneration of anionite taking into account processing and use of spent regeneration solutions.

MATERIALS AND METHODS

Membrane processes for water purification from nitrates were carried out using cassettes with a low-pressure reverse osmosis membrane Filmtec TW30–1812–50. Sodium nitrate solutions with a nitrate concentration of 18, 50, 100 mg/dm³ were used as a medium. The initial volume of the solution was 11 dm³. This solution was pumped to a reverse osmosis filter with a cartridge containing a Filmtec TW30–1812–50 membrane. Permeate with a volume of 1 dm³ was taken into a measuring cylinder. The concentrate was returned to the container with the working solution. The pressure in the system was maintained by regulating the water supply by the pump and the concentrate flow was regulated by the tap. Then, 10 dm³ of water was passed, taking samples of 1 dm³. The nitrate concentration was determined in each permeate sample. For each permeate sample, the nitrate content in the concentrate was determined analytically and calculated mathematically. With the help of a stopwatch, the time during which 1 dm³ of permeate was selected was recorded.

The concentration of nitrates was determined by means of the potentiometric method using an ion-selective electrode AC0117A [MultiLab User Guide, 2019].

The selectivity of the membrane (R, %) was calculated according to the formula:

\[ R = \frac{C_o - C_p}{C_o} \cdot 100\% \] (1)

where: \( R \) – the selectivity of the membrane, %; 
\( C_o \) and \( C_p \) – the concentration of nitrates, respectively, in the original solution and permeate.

The concentration of nitrates in the i-th sample of the concentrate (\( C_{ki} \), mg/dm³) was calculated according to the formula:

\[ C_{ki} = \frac{V_o \cdot C_o - \sum_{i=1}^{n}(C_{ni} \cdot V_{ni})}{V_o - \sum_{i=1}^{n} V_{ni}}, \text{ mg/dm}^3 \] (2)

where: \( C_{ki} \) – the concentration of nitrates in the concentrate after taking the i-th sample of permeate, mg/dm³; 
\( C_o \) and \( V_o \) – concentration of nitrates in the original solution (mg/dm³) and volume of the original solution (dm³), respectively; 
\( V_{ni} \) – permeate sample volume, 1 dm³; 
\( C_{ni} \) – concentration of nitrates in the i-th permeate sample, mg/dm³; 
\( i \) – the number of permeate samples, \( n = 1–10 \).

Membrane productivity (transmembrane flux rate) (\( j, \text{ dm}^3/(\text{m}^2\cdot\text{h}) \)) was calculated using the formula:

\[ j = \frac{V_n}{S \cdot \Delta \tau}, \text{ dm}^3/(\text{m}^2\cdot\text{h}) \] (3)

where: \( j \) – the performance of the membrane, \( \text{ dm}^3/(\text{m}^2\cdot\text{h}) \); 
\( V_n \) – permeate sample volume, 1 dm³; 
\( S \) – membrane area, m²; 
\( \Delta \tau \) – sampling time, h.

Ion-exchange extraction of nitrates from water was carried out using anionite AB–17–8. Anionite was used in chloride and sulfate forms. Sodium nitrate solutions with a nitrate concentration
of 62 mg/dm³ and 125 mg/dm³ were used in the sorption processes. The ionite was converted into the chloride form with a 2H solution of sodium chloride, into the sulfate form with a 2H solution of sodium sulfate, and into the nitrate form with a 1H solution of sodium nitrate.

The consumption of sodium nitrate solution in the sorption process reached 15 cm³/min (3.18 m³/h) the consumption of solutions during regeneration reached 2 cm³/min (0.414 m³/h).

The volume of samples during the sorption process reached 1–2 dm³, during regeneration – 20 cm³.

The concentrations of nitrates and chlorides or sulfates were determined in the samples obtained in the sorption processes. The nitrate content was determined in the samples obtained during ionite regeneration. Determination of the concentration of nitrates was carried out via the potentiometric method using the ion-selective electrode AC017A [MultiLab User Guide, 2019], the concentration of chlorides was determined using the argentometric method of Mohr [Nabivanets et al., 1996], and sulfates were determined by means of the photometric method with barium ions [Lurie, 1984].

Full dynamic exchange capacity (FDEC, mg-eq/dm³) was determined by the formula:

\[ FDEC = \frac{\sum_{i=1}^{n} (C_0 - C_i) \cdot V_n}{V_i} \text{ mg-eq/dm}^3 \]  

where:
- \( FDEC \) – full dynamic exchange capacity, mg-eq/dm³;
- \( C_0 \) – the concentration of nitrates in the original solution, mg-eq/dm³;
- \( C_i \) – concentration of nitrates in the i-th sample after sorption, mg-eq/dm³;
- \( V_s \) – the volume of the water sample, dm³;
- \( V_i \) – the volume of ionite, dm³;
- \( n \) – the number of water samples.

The exchange dynamic capacity of ionite before breakthrough (EDC, mg-eq/dm³) was calculated using the formula:

\[ EDC = \frac{\sum_{i=1}^{m} (C_0 - C_i) \cdot V_n}{V_i} \text{ mg-eq/dm}^3 \]  

where:
- \( EDC \) – exchange dynamic capacity, mg-eq/dm³;
- \( C_0 \) and \( C_i \) – concentration of nitrates in the initial solution and filtrate, respectively.

The degree of nitrate extraction (A, %) was calculated according to the formula:

\[ A = \frac{C_0 - C_f}{C_0} \cdot 100\% \]  

where:
- \( A \) – degree of nitrate extraction, %;
- \( C_0 \) and \( C_f \) – concentration of nitrates in the initial solution and filtrate, respectively.

The degree of ionite regeneration (Zn, %) was calculated as the ratio of the mass of desorbed to the mass of sorbed ions:

\[ Z_n = \frac{\sum_{i=1}^{n} M_{di}}{M_s} \cdot 100\% \]  

where:
- \( Z_n \) – degree of ionite regeneration, %;
- \( M_{di} \) – the number of desorbed ions from the ionite i-th sample of the regeneration solution, mg-eq;
- \( M_s \) – amount of sorbed ions, mg-eq;
- \( n \) – number of samples.

RESULTS AND DISCUSSION

The results of the purification efficiency of aqueous solutions of sodium nitrate at nitrate concentrations of 18–100 mg/dm³ are presented in Fig. 1. and Fig. 2.

As it can be seen from Fig. 1, even when using a solution with a nitrate concentration of 18 mg/dm³, the efficiency of their removal on the Filmtec TW30–1812–50 membrane was low. When the degree of permeate selection increased from 9 to 90%, the nitrate content in the permeate increased from 12.5 to 20.5 mg/dm³. At the same time, the nitrate content in the concentrate increased to approximately 75 mg/dm³. With such low concentrations of nitrates in the concentrate and their relatively high values in the permeate, the decrease in working pressure due to the increase in osmotic pressure was insignificant and amounted to only 0.1 atm. with a degree of permeate selection of 90%. This indicator was slightly higher at initial nitrate concentrations of 50 and 100 mg/dm³ (Fig. 2). At a nitrate concentration of 50 mg/dm³, a decrease in operating pressure at a permeate selection rate of 90% was observed by 0.2 atm., for 100 mg/dm³ – by 0.3 atm. This is due to the low efficiency of nitrate retention on the membrane and a slight increase in their content.
in the concentrate. At an initial concentration of nitrates of 50 mg/dm$^3$, their content in the filtrate increased from 13 mg/dm$^3$ to 57 mg/dm$^3$ with an increase in the degree of permeate selection from 9 to 90%, and at an initial concentration of nitrates of 100 mg/dm$^3$, their content in the filtrate increased from 33 to 99.5 mg/dm$^3$. At the same time (Fig. 3), at a nitrate concentration of 18 mg/dm$^3$, the selectivity of the membrane was at the level of 38–73%, at 50 mg/dm$^3$, the selectivity was 67–81%, and at 100 mg/dm$^3$, it was within 57–78%.

It can be said that the selectivity of the membrane increases to a certain extent with an increase in the concentration of nitrates in the solution. However, in each case, when the degree of permeate selection was increased, the selectivity of the membrane first decreased, and then increased. The highest indicators of selectivity of the membrane were noted at the initial concentration of nitrates of 50 mg/dm$^3$. With further growth of the nitrate content in the water, this indicator decreased. Perhaps this is due to the phenomenon of concentration polarization on the membrane.

Considering the low level of nitrate concentrations in the water in the conducted experiments, the performance of the membrane was high (Fig. 3). A certain decrease of this indicator was observed when the concentration of nitrates in the water increased, which, in turn, caused a decrease in the working pressure (Fig. 1, Fig. 2). The obtained results, which testify to the low efficiency of the Filmtec TW30–1812–50 membrane in water purification from nitrates, agree well with the results obtained by the authors [Goncharuk et al., 2013; Balakina et al., 2013] when using reverse osmosis membranes of low pressure. In [Balakina et al., 2013], it was shown that when using the ESPA–1 membrane at nitrate concentrations in water of 200–1000 mg/dm$^3$ and at a degree of permeate selection of 10–90%, the concentration of nitrates in the filtrate reached 2.4–276.0 mg/dm$^3$. Somewhat better results were obtained when polycationites were used to bind nitrates during their removal from water by reverse osmosis [Ievleva et al., 2015]. However, this significantly complicates the technology, and makes it impossible to use reverse osmosis filters in everyday life.

When conducting the research on reverse osmosis purification of water from nitrates, the dynamics of changes in the pH of the medium in the filtrate and concentrate with increasing degree of permeate selection were determined (Fig. 4). In all cases, a certain decrease in pH in the permeate and an increase in pH in the concentrate were noted. This may be due to the higher selectivity of the membrane for sodium cations, compared to protons.

If the unsatisfactory results obtained in the purification of water from nitrates by membrane methods, including electrodialysis [Osipenko et al., 2015] are taken into account, it should be recognized that ion exchange removal of nitrates from water is more promising.
In previous works [Gomelya et al., 2016; Gomelya et al., 2015; Gomelya et al., 2016], it was shown that when using anionites, nitrates can be effectively extracted from water even in the presence of chlorides and sulfates. For example, work [Gomelya et al., 2015] showed that the AB–17–8 anionite has significant capacities for nitrates even in the presence of chlorides (Table 1).

However, in all cases, when studying nitrate sorption processes on anionites, solutions with nitrate concentrations of more than 200 mg/dm$^3$...
were used. Therefore, in this paper, the ion exchange extraction of nitrates on the AB–17–8 anionite in chloride and sulfate form was investigated at nitrate concentrations of 62 and 125 mg/dm³. The results are shown in Fig. 5.

As it can be seen from Figure 5, the efficiency of nitrate sorption at low nitrate concentrations in solutions is somewhat lower, compared to concentrated solutions. FEDC for nitrates for the initial concentration of 62 mg/dm³ reaches 830 mg-eq/dm³, for the initial concentration of 125 mg/dm³ it is 1138 mg-eq/dm³. At the same time, the exchange capacity for nitrates depends to a smaller extent on the form of the ionite (chloride or sulfate) and to a greater extent on the concentration of nitrates. The capacity before the breakthrough in this case reaches approximately 300 mg-eq/dm³ for an initial nitrate concentration of 62 mg/dm³, and 420 mg-eq/dm³ for an initial concentration of 125 mg/dm³.

The volume of filtrate with nitrate concentrations up to 1 mg/dm³ was taken into account when calculating the exchangeable dynamic capacity before breakthrough. In the case when 45 mg/dm³ of nitrates was taken as the control concentration, the dynamic exchange capacity at concentrations

Table 1. Dependence of ODE of the AB–17–8 anionite on the composition of solutions containing chlorides and nitrates [Gomelya et al., 2015]

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<th>Concentration, mg/dm³</th>
<th>EDC, mg-eq/dm³</th>
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<tr>
<td><strong>NO₃⁻</strong></td>
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of 62 mg/dm$^3$ reached 623 mg-eq/dm$^3$, and at concentrations of 125 mg/dm$^3$ it was 895 mg-eq/dm$^3$.

In all cases (Fig. 6), at concentrations of nitrates in solutions equal to 62 mg/dm$^3$ and 125 mg/dm$^3$, when using anionite in chloride and sulfate forms in the first samples of the selected filtrate, the degree of purification reached 97–99 %. As the ionite capacity was exhausted, this indicator decreased.

2H solutions of sodium chloride, sodium sulfate, and ammonium sulfate were used to regenerate anionite in nitrate form (Fig. 7).

As it can be seen from Figure 7, the best performance in the regeneration of anionite was provided by the sodium chloride solution. With a specific consumption of this solution of 5 cm$^3$ per 1 cm$^3$ of ionite (q=5 cm$^3$/cm$^3$), the degree of regeneration reached 93%. Solutions of sodium sulfate and ammonium sulfate provided high regeneration efficiency. This is important when using an ion exchange unit at water treatment plants of medium and large capacity. In this case, during the regeneration of anionite with ammonium sulfate, the spent regeneration solutions will mainly contain ammonium sulfate and nitrate, which are the basis to produce liquid fertilizers. These solutions will not contain chlorides, which is undesirable for liquid fertilizers. Under household conditions, anionite can be regenerated with sodium chloride solution, given its small volume.
In the preparation of drinking water and wastewater treatment, in many cases it is sufficient to use only an ion exchange unit to remove nitrates.

CONCLUSIONS

The processes of water purification from nitrates using a low-pressure reverse osmosis membrane have been studied. It was shown that the membranes of this type are characterized by low selectivity (40–80%) in the range of nitrate concentrations from 18 to 100 mg/dm³, they reduce the nitrate content in the permeate to 10–100 mg/dm³. Residual concentrations of nitrates increase both with increasing initial concentrations and with increasing the degree of permeate selection.

It was shown that highly basic AB–17–8 anionite in chloride and sulfate forms effectively sorbs nitrates from aqueous solutions at initial concentrations of 62 and 125 mg/dm³. Anionite is effectively regenerated by solutions of chloride and sodium sulfate, as well as ammonium sulfate. The use of the latter ensures the use of spent solutions for the production of liquid fertilizers.

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