Politechnika Lubelska

Water Supply and Wastewater Disposal

Designing, Construction, Operation and Monitoring IV

MONOGRAFIE

edited by
Beata Kowalska
Dariusz Kowalski

Lublin 2022

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Effect of stabilization treatment of water on the quality of its reverse osmotic desalination

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Abstract

Nowadays, the problem of a sharp increase in water mineralization in surface water is quite acute. An important and urgent task is to provide high-quality drinking water to the population and industry, especially in areas with limited water resources. Therefore, softening and reducing salt content is important in preparing water. To create low-waste processes of water desalination, the selectivity of the reverse osmosis membrane towards chlorides, sulfates, hardness ions depending on the degree of permiate selection was determined. When purifying water using membrane technologies, there is a problem of formation of deposits and fouling on the membranes, which reduces the flow of filtrate and increases the transmembrane pressure. Therefore, the influence of pre-treatment of water on the ultrafiltration membrane and stabilization treatment of water on weakly acid cation exchange resin in acid form on the quality of reverse osmosis desalination of mineralized waters is studied.

Keywords: desalination, membrane, pollutant, productivity, selectivity

1. Introduction

In this study, the optimum parameters of membrane desalination of model solutions were determined and the required efficiency was achieved. Methods for stabilizing treatment of water before barometric desalination were developed to improve the efficiency of membranes.

Nowadays, the problem of salinization of water is very common in Ukraine due to natural and anthropogenic factors, and industrial regions suffer the most. The high level of mineralization is occurred due to the presence of coal, iron ore and uranium mines. Great contribution to the salinity of water objects is made by the discharge of mine water, saline wastewater, water from cooling systems and brine infiltration of many slime storages (Buzylo et al., 2018; Liu et al., 2019).

Wastewater from Ukrainian mines is characterized by a high content of suspended solids (up to 0.1 g/dm^3), increased mineralization (salt content up to 3 g/dm^3), increased alkalinity (4–16 mmol/dm^3) and total hardness (7–16 mval/dm^3), due to which more than 3 million tons of mineral salts and substances are discharged into water reservoirs and rivers annually. This leads to a deterioration in the quality of surface and groundwater due to increasing salinity up to 2–2.9 g/dm^3, increasing the content of heavy metals and siltation of water reservoir and lake.

Unfortunately, modern methods of saline water treatment do not solve the problem, but only aggravate the situation in densely populated areas with well-developed industries (Gomelya et al., 2016).

The solution to this problem is the introduction of innovative complex water desalination technologies at the utilities and industrial enterprises (Kinnunen et al., 2018). It will helps to use water that has an increased mineralization, which will ensure a significant reduction of discharges of mineralized sewage and will lead to improvement of the quality of groundwater.

In water treatment systems, the use of membrane technologies is gradually expanding, which leads to replacement of traditional filtration methods: with the application of sand, of rotary drum and mesh filters, etc. For microfiltration, ultrafiltration and nanofiltration are distinguished according to classification of membrane filters, three groups of filters. For the mentioned filters order the transmembrane pressure increases from 0.5–3 to 15–50 bar, at the same time the pore size decreases.

The main advantages of baromembrane methods of water purification are high reliability of barrier filtration, compactness of equipment, possibility of full process automation, minimal use of reagents, low energy consumption. The disadvantages include: high cost of equipment, formation of deposits on the membranes, certain requirements for the quality of source water.

Membrane technologies have high efficiency and can be used at different stages of water treatment (Amaya-Vías et al., 2019), as well as together with other methods of purification (Kim et al., 2018).

In regions with a lack of fresh water, membrane technologies are widely used to desalinate highly mineralized waters (Haan et al., 2018).

Depending on the quality of the water and the requirements for the treated water, membrane separation methods are regarded as quite promising and most appropriate that can be used for water treatment and wastewater treatment in a technologically grounded combination (Ambiado et al., 2017; Gomelya et al., 2014).

The aim of this paper was to study the processes of desalination of mineralized waters by the membrane method for the creation of innovative technologies of water treatment for ecologically safe water supply systems.

2. Materials and Methods

In this work, water desalination was studied using cartridges with low-pressure reverse osmosis membrane Filmtec TW30-1812-50 and the properties of the membrane is described in Table 1.

Table 1. Properties of the reverse osmosis membrane Filmtec TW30−1812−50

Parameter	**Value**
Productivity, dm^3/day at a pressure of 4–7 bar and temperature 25°C	225−395
Stable salt removal, %	98
Minimal salt removal, %	96
Maximum water supply, dm^3/min	7.6
Maximum operating pressure, bar	21
Maximum operating temperature, °C	45
Maximum colloidal index	5
Ph range (long-term work)	2−11
Ph range (flushing up to 30 min)	1−13
Maximum concentration of free chlorine, mg/dm^3	<0.1
Size, mm	295 × 55

The model solution was used through experiments: hardness – 9.0 mval/dm^3, alkalinity – 5.0 mmol/dm^3, SO_4^{2-} – 620.0 mg/dm^3, Cl^- – 100. mg/dm^3, pH = 8.9.

After filtering the solution through the weakly acid cationite Dowex MAC-3 in acid form, it had the following characteristics: hardness – 3.9 mval / dm^3, acidity – 0.6 mmol/dm^3, Cl^- – 100.0 mg/dm^3, SO_4^{2-} – 620.0 mg/dm^3, pH = 3.9.

Filtration through an ultrafiltration membrane was used to reduce turbidity of the water, which reduced the turbidity and color of the water.

Filtration through weakly acid cation exchange resin in H^+ form was used for stabilization water treatment.

For desalination of water, samples of 10 dm^3 were used. The degree of selection of permeate was changed from 10 to 90%.

The concentrations of chlorides, sulfates, hardness and alkalinity were determined in initial solutions and in permeates. The selectivity (%) and productivity (dm^3/m^2 h) of the membrane were calculated:

$$R = \frac{C_0 - C_n}{C_0} \cdot 100, \tag{1}$$

$$J = \frac{\Delta V}{S \cdot \Delta t}. \tag{2}$$

where: C_0, $C_{n.}$ (mg/dm^3; mval/dm^3) – concentration of pollutant in initial solution and in treated solution, respectively, ΔV – volume of treated solution (dm^3), that passed through the membrane S (m^2) for the time of selection Δt (h).

3. Results and Discussion

In order to prevent the sediment deposition on membranes in barometric methods, it is necessary to provide an effective stabilizing treatment of water. It is believed that water with a turbidity of 0.5 mg/dm^3 and a color of up to 20 degrees meets the requirements for water supplied to reverse osmosis systems. An effective lighting and discoloration of water is important at baromembrane water purification. Therefore, to reduce the load on the reverse osmosis membrane, increase the process productivity, increase the period of operation of reverse osmosis membranes, we proposed to conduct pre-treatment with the application of ultrafiltration membranes to purify water from suspended solids.

In the work, the effect of the mechanical water purification on the productivity and selectivity of the reverse osmosis membrane of low pressure Filmtec TW30−1812−50 was determined.

The membrane Filmtec TW-30-1812-50 provides an effective water desalting at pressures up to 1 MPa (in this case, P = 0.3 MPa) with high process efficiency. Despite the fact that through a cassette with a reverse osmosis membrane only 10 dm^3 of model solution was passed, its pre-lighting significantly influenced the productivity of the membrane. When passing water through the ultrafiltration membrane, the turbidity and color of the water is reduced to ~ 0–0.1. The operation of the ultrafiltration device is at a dead end. The duration of the filter cycle is 2 hours, the duration of washing is 40–60 seconds, while the amount of washing water is 1–2%. During filtering an increase in membrane productivity on 12–20% is observed.

As shown in Fig. 2–4, the efficiency of removal of sulfates and chlorides as well as ions of hardness from water depends on the pre-purification stage of water treatment. During the desalination of the model solution, the highest final concentrations were fixed in the permeate for chlorides. The sulfates and hardness ions residual concentrations were rather low. The residual content of ions in concentrates depend on the initial concentration of ions in solution as well as on the membrane effectiveness of detention.

In concentrates, the increase in concentrations of all cations and anions that were controlled in this process were observed. The highest concentrations correspond to hardness ions and to sulfates (hardness – 34–75 mval/dm^3, SO_4^{2-} – 490–550 mg/dm^3, Cl^- – 75–83 mg/dm^3).

Since the efficiency of water purification from any ions depends not only on the residual concentrations of ions, but also on their initial concentration, then the efficiency of the water purification process from any ions is better to evaluate by the values of the membrane selectivity (Fig. 1).

During filtering, the Filmtec TW30-1812-50 membrane was characterized by the lowest selectivity of 89–95% in relation to chlorides; the selectivity towards sulfates and ions of hardness reached the values 98.8–99.7% (Fig. 2–4).

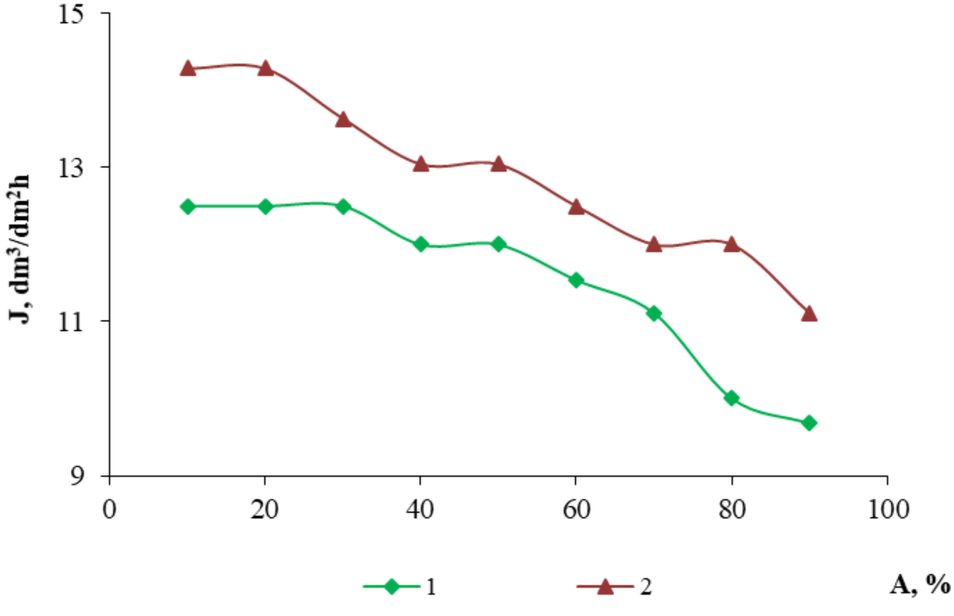

Fig. 1. Dependence of the productivity of the reverse osmosis membrane Filmtec TW-30-1812-50 on the degree of selection of permeate during desalination of unfiltered (1) and filtered model solution (2)

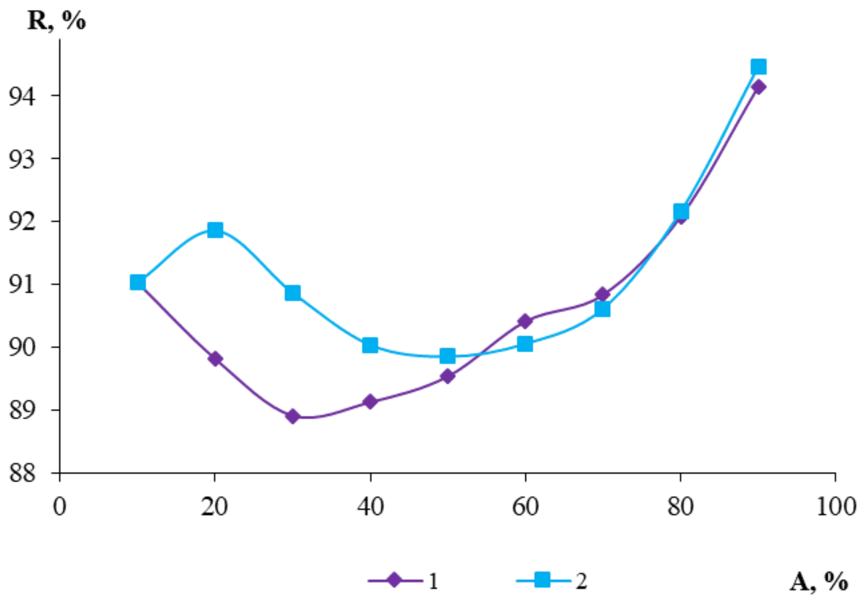

Fig. 2. Dependence of the selectivity of the reverse osmosis membrane on chlorides (pH = 8.6 (1), pH = 3.9 (2))

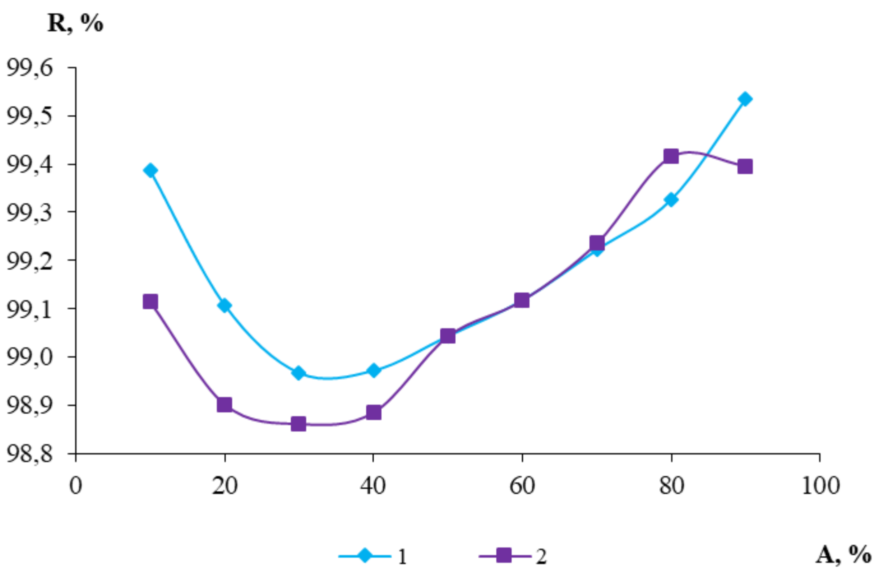

Fig. 3. Dependence of the selectivity of the reverse osmosis membrane on sulfates (pH = 8.6 (1), pH = 3.9 (2))

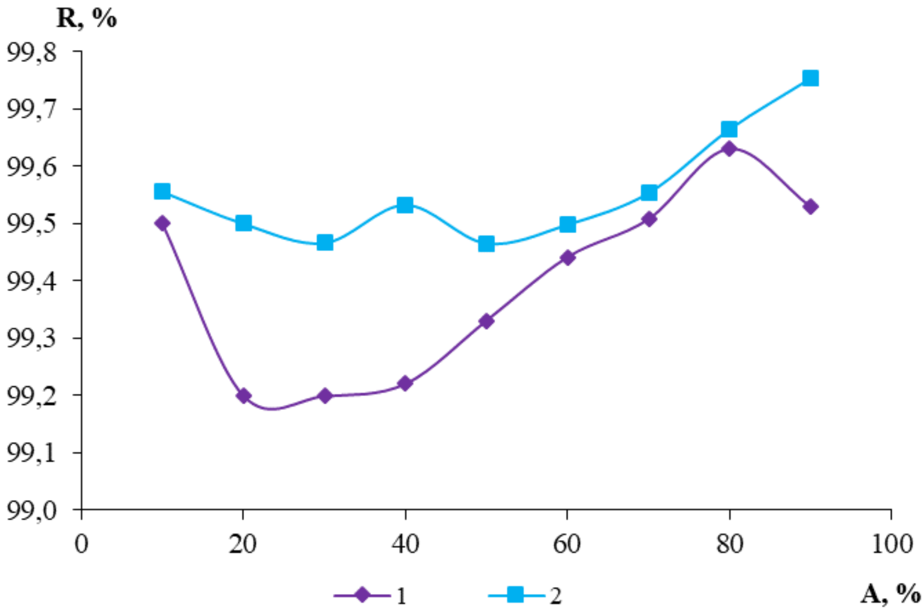

Fig. 4. Dependence of the selectivity of the reverse osmosis membrane on ions of hardness (pH = 8.6 (1), pH = 3.9 (2))

Thus, initial lighting of water leads to a decrease in water turbidity from 0.5 mg/dm^3 to 0.1 mg/dm^3 and to increase in membrane productivity up to 1.2–2.0 times.

Another complicated problem of reverse-osmosis water purification is its preparation before membrane treatments. During treatment of water with membrane technologies, there is a problem of formation of deposits on the membranes, resulting in a decrease in the flow of filtrate and increased transmembrane pressure (Gryta, 2018). Therefore, along with effective lighting and discoloration, the problem of its stabilization to prevent sediment deposition on membranes is acute. The main reason for deposition of sediments is the deposition of calcium carbonate on the surface of the membrane. The main methods of preventing sedimentation of poorly water-soluble salts on membranes are based on the dosing of inhibitors into the row water and chemical washing (Gomelya et al., 2017). By accurately dosing the inhibitor, regulation of the pH, water flow and transverse flow rate, membrane contamination can be significantly reduced. Sodium hydroxide, ethylenediaminetetraacetic acid complexing agent (EDTA), sodium dodecyl sulfate, hydrogen peroxide, sodium chloride, etc. are used as reagents for chemical cleaning of membranes. The efficiency can be increased by sequential use of two reagents or a mixture of reagents.

For water pretreatment with a high content of non-carbonate hardness it is rational to use antiscalants. In the preliminary preparation of water with high hardness, the use of the method of ion-exchange water softening at the stage of preliminary preparation is expedient when the content of hardness ions in the water is less than 20 mval/dm^3 (Trus et al., 2019).

In the application of weakly acid cationite Dowex MAC-3 in the H^+ form there is a decrease in the alkalinity of water is observed (Trus et al., 2020; Trokhymenko and Gomelya, 2017). In this case, the alkalinity of water decreased to zero values, and the pH reached 3.9; and such water can not lead to the formation of carbonate deposits on the membrane.

During the application of Dowex MAC-3 cation exchange resin in acid form, partial softening of water and its almost complete decarbonization due to partial acidification are taken place. The processes follow the reactions:

$$2Kt^-H^+ + Ca(HCO_3)_2 = (Kt^-)_2Ca^{2+} + 2H_2CO_3,$$

$$2Kt^-H^+ + Mg(HCO_3)_2 = (Kt^-)_2Mg^{2+} + 2H_2CO_3,$$

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O,$$

where: Kt^- – fragment of cation exchange resin.

In the work, the effect of stabilizing treatment of water on weakly acidic cake Dowex MAC-3 in the H^+ form on the efficiency of water desalination in a reverse osmosis membrane Filmtec TW 30-1812-50 was determined. The model solution after filtration through weakly acidic cake Dowex MAC-3 in acid form had the following characteristics: hardness – 3.5 mval/dm^3, acidity – 0.6 mmol/dm^3, Cl^- – 100.0 mg/dm^3, SO_4^{2-} – 620.0 mg/dm^3, pH = 3.9.

The results of the evaluation of the productivity of the reverse osmosis membrane are shown in Fig. 5.

As can be seen from Fig. 3, the productivity of the membrane at a working pressure of 0.30 MPa a little depends on the pH of the solution. Acidification of the solution with partial softening improves the productivity of the reverse osmosis membrane. It happens primarily due to the partial demineralization of the solution on the ion exchange filter and due to the absence of carbonate deposits on the membrane. During filtering of 10 dm^3 of water, there is no significant deposition of sediments on the membrane, so the effect of the pH of the medium on the performance is insignificant. At longer tests and larger volumes of water, the membrane's productivity after stabilization treatment of water will stay high during the time of use.

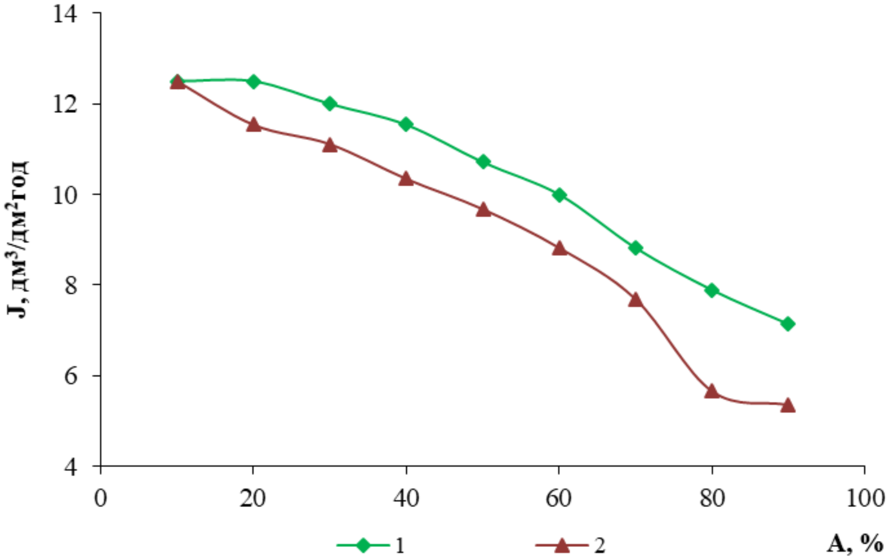

Fig. 5. Dependence of the productivity of the reverse osmosis membrane on the degree of selection of permeate during desalting the filtrate after the cation filter Dowex MAC-3 in acid form pH = 3.9 (1) and model solution pH = 8.6 (2)

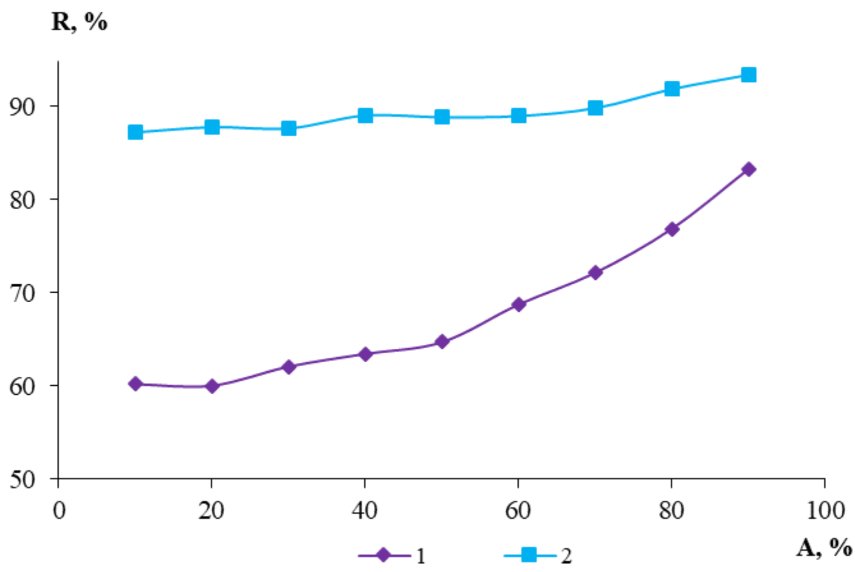

Fig. 6. Dependence of the selectivity of the reverse osmosis membrane towards chlorides on the degree of selection of permeate during desalination of solutions (pH = 3.9 (1), pH = 8.6 (2))

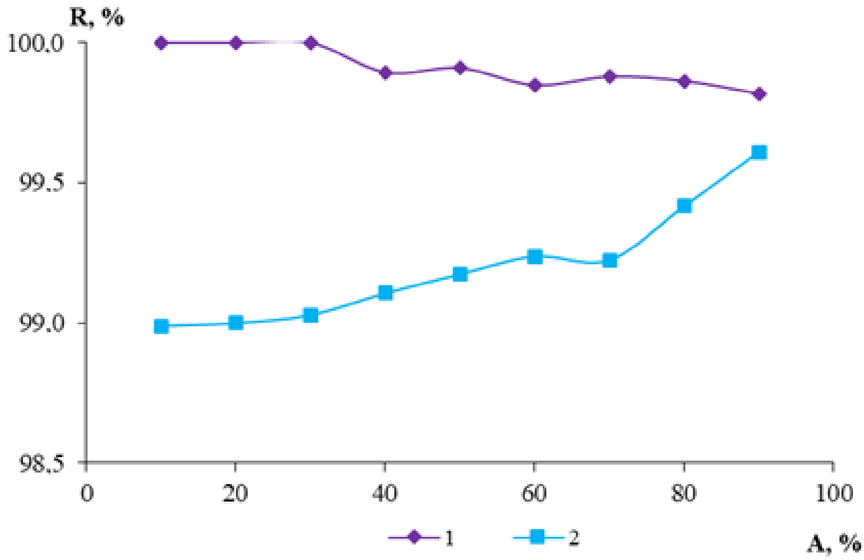

Fig. 7. Dependence of the selectivity of the reverse osmosis membrane towards sulfates on the degree of selection of permeate during desalination of solutions (pH = 3.9 (1), pH = 8.6 (2))

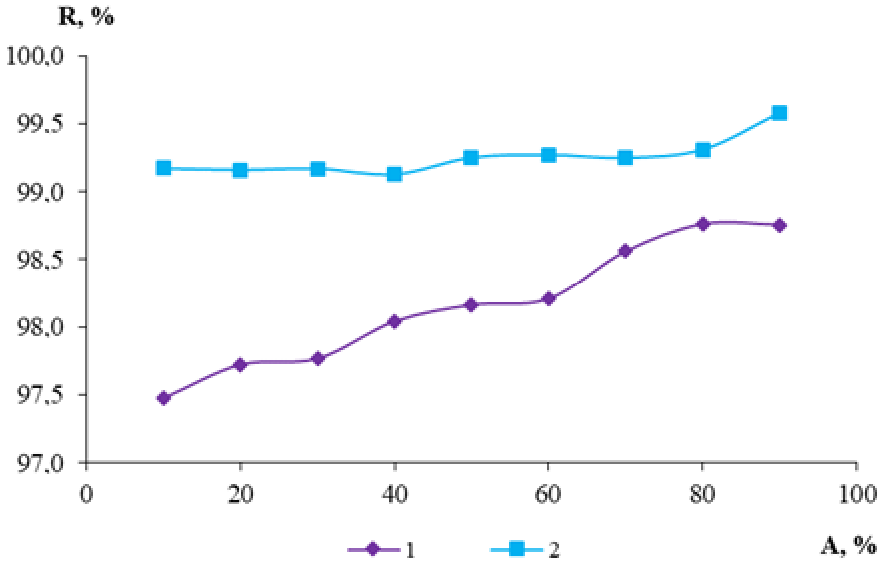

Fig. 8. Dependence of the selectivity of the reverse osmosis membrane towards ions of hardness on the degree of selection of permeate during desalination of solutions (pH = 3.9 (1), pH = 8.6 (2))

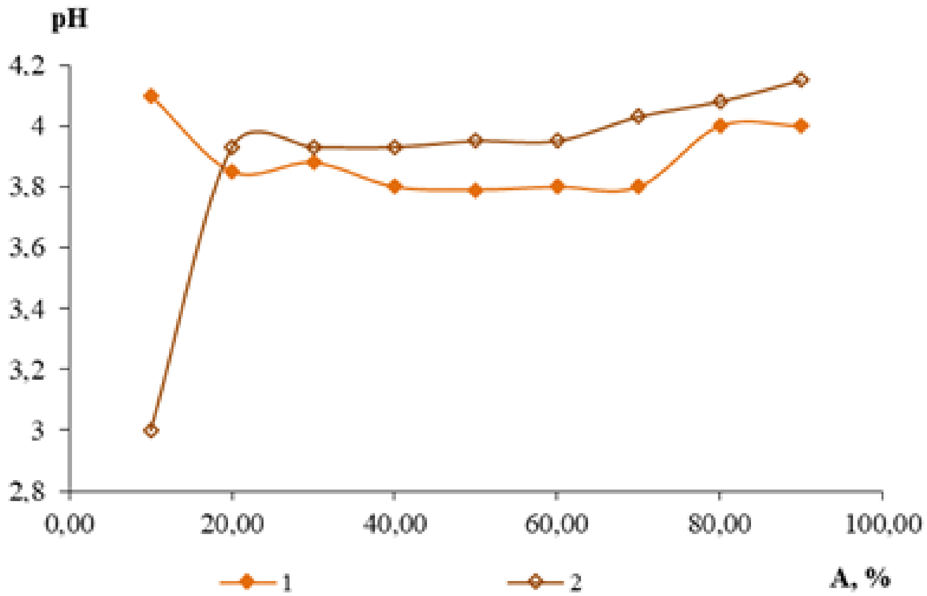

Fig. 9. Dependence of pH on the degree of selection of permiate during desalinating of solution with pH = 3.9 (1 – pH of permiate, 2 – pH of concentrate)

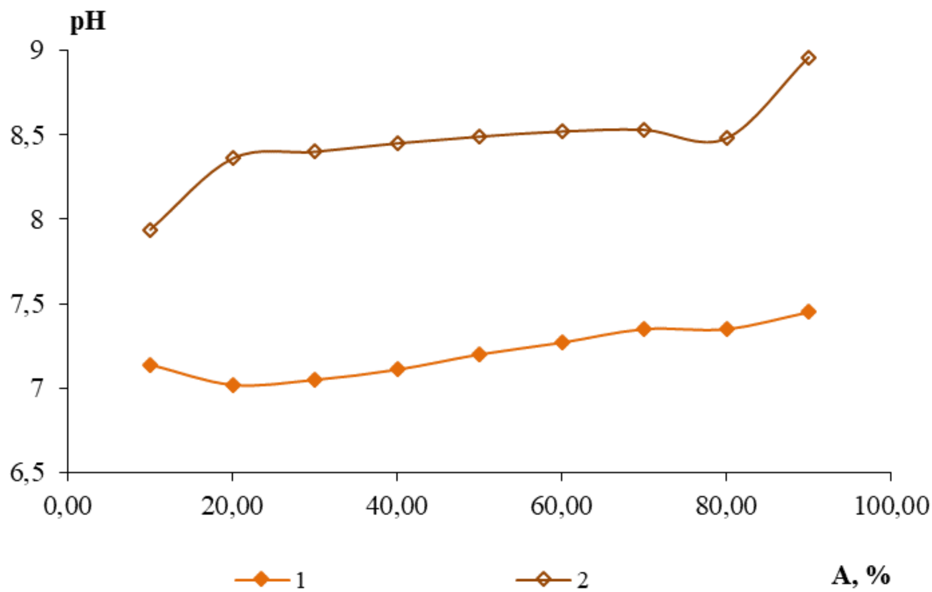

Fig. 10. Dependence of pH on the degree of selection of permiate during desalination of the model solution with pH = 8.6 (1 – pH of permiate, 2 – pH of concentrate)

However, the selectivity of the membrane depends on the pre-treatment of water on cation exchanges. As can be seen from Fig. 6–8, as the pH of the medium was decreased, a slight increase in the selectivity of the membrane by sulfates and a significant decrease in its selectivity by chlorides was observed. Acidification of water leads to a decrease in the selectivity of the reverse osmosis membrane by chlorides by 10–30%. The selectivity of the membrane practically does not depend on working pressure and stays high towards sulfates and ions of hardness (98–99%), regardless of the pH and degree of selection of permeate.

It should be noted that during filtering of solutions, which were pre-treated on the cation exchange resin in acid form, the pH of treated water and of concentrate were close in values (Fig. 9). During filtration of the original model solution, a decrease in the pH of the solution in the permiate to 7.02–7.45 was observed (Fig. 10). The pH of the concentrate reached values of 8.36–8.96. This is due to the difference in membrane selectivity for hardness ions and hydrocarbonates.

As a result of reverse osmosis desalination, highly mineralized concentrates are formed, which are characterized by a high content of chlorides, sulfates and hardness ions. The process of processing such concentrates was developed in (Trus et al., 2017; Gomelya et al., 2014).

4. Conclusions

The optimal parameters of membrane desalinization of solutions providing high water quality were determined in the work.

The methods of stabilization treatment of water before barometric desalination was developed to increase the efficiency of the productivity and the operation time of the membranes.

Proposed method of integrated treatment of mineralized waters allows to create low-waste technologies of waters desalting.

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