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Determining the Efficiency of Reverse Osmosis in the Purification of Water from Phosphates

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ABSTRACT

Processes of water purification from phosphates using a low-pressure reverse osmosis membrane were studied. It was shown that the concentration of phosphates in the permeate largely depends on their initial concentration in the water and increases along with the degree of permeate selection. It was established that when using the Filmtec TW3–1812–50 membrane for phosphate concentrations up to 20 mg/dm^3, their concentration in the permeate does not exceed 2.5 mg/dm^3 with a degree of permeate selection up to 90% when cleaning solutions in distilled and artesian water. This value is below the permissible level for drinking water. When the concentration of phosphates increases to 100 and 1000 mg/dm^3, their content in the permeate increases sharply to the values significantly higher than the permissible level in both drinking and wastewater. When sodium orthophosphate was added to artesian water, the effectiveness of its purification on this membrane with respect to chlorides, sulfates, hardness ions, and hydrocarbons was high. This indicates that the cartridges with these membranes can be used both in industrial installations and in households for further purification of artesian and tap water to drinking water quality.

Keywords: phosphates, water treatment, water purification, reverse osmosis, permeate, concentrate, selectivity, productivity.

INTRODUCTION

Phosphorus belongs to biogenic elements, which is of special importance for the development of organisms, including agricultural production. Unlike compounds of carbon, oxygen or nitrogen, which can enter soils or water bodies from the atmosphere, phosphorus compounds are continuously introduced from soils or water bodies into the world's oceans and returned in very limited quantities.

At the same time, contamination of drinking or wastewater, water in natural reservoirs with phosphorus compounds is an undesirable phenomenon. Today, a significant number of natural water bodies suffer from an excessive phosphate content, a large part is carried there with wastewater, especially municipal wastewater contaminated with phosphate-based surfactants.

Despite the fact that a significant amount of phosphates is removed from water in the self-purification processes of reservoirs, there is always a possibility of their appearance in drinking water. This is possible because outdated water treatment methods are ineffective in removing phosphates. Therefore, it is important to evaluate the effectiveness of reverse osmosis, which is often used for further purification of water, also under domestic conditions, when removing phosphates.

Despite the large number of publications on water purification from phosphates, the bulk of wastewater is purified from phosphates, along with other biogenic elements, at regular biochemical treatment facilities [Ayrapetyan 2014; Gautam et al. 2014]. At the same time, biological methods are constantly being improved [Podorvan et al. 2014]. However, it is better to use biological methods in case of large wastewater consumption at the level of workshops, industrial enterprises, and entire cities. Another disadvantage of biochemical purification of wastewater from phosphates is insufficient efficiency. At the same time, insufficiently purified water is discharged into surface reservoirs, which causes several negative consequences, including a significant decrease in the quality of water in sources of drinking water supply.

A number of authors recommend using aluminum or iron coagulants for wastewater treatment [Tolkou et al. 2014.; Zhao et al. 2011]. Many works are devoted to the purification of water from phosphates on sorbents [Masindi et al. 2016; Zhang et al. 2013]. The disadvantage of coagulation processes is their insufficient efficiency [Petrychenko et al. 2018], and during sorption, significant volumes of waste sorbents are formed, which are difficult to dispose of. Therefore, a large number of electrocoagulation processes have recently been developed, which are characterized by high efficiency in the removal of phosphates from water in a wide range of concentrations [Nguyen et al. 2017; Franco et al. 2017]. Several works have been published that describe the processes of removing phosphates from water using steel slag [Barca et al. 2012; Han et al. 2016], using the method of magnetic separation [Xiong et al. 2008].

Most of the mentioned methods are aimed at binding phosphates into water-insoluble organic and inorganic compounds. The methods that allow them to be concentrated and reused are ion exchange [Gomelya et al. 2017] and baromembrane processes [Balakina et al. 2013; Seminska et al. 2015]. These processes make it possible to extract and process phosphates into useful products [Balakina et al. 2013; Sperlich et al. 2010]. However, if the technologies of water treatment or purification of drinking water are considered, then the advantage here is on the side of membrane methods, which are convenient to use both in industrial installations and in everyday life. However, the use of reverse osmosis for purification of drinking water from phosphates has not been sufficiently studied.

The purpose of the work was to study the processes of reverse osmosis purification of water from phosphates on a low-pressure membrane, to determine the dependence of the selectivity and productivity of the membrane on the initial concentrations of phosphates in the water and the degree of permeate selection.

To achieve the goal, the following tasks were solved:

- research on the processes of removing phosphates from model solutions on a low-pressure reverse osmosis membrane, determining the dependence of the efficiency and productivity of cleaning solutions on the concentration of phosphates and the degree of permeate selection;
- determination of the efficiency of further purification of phosphate solutions in artesian water, including its softening, extraction of phosphates, chlorides, and sulfates.

MATERIALS AND METHODS

When studying the baromembrane processes of water purification from phosphates, a cassette with a Filnitec TW30–1812–50 low-pressure reverse osmosis membrane was used (Table 1).

Membrane processes of water purification from phosphates were carried out using cassettes with a TW30–1812–50 low-pressure reverse osmosis membrane. Sodium orthophosphate solutions with phosphate concentration were used as a medium (H = 7.8 mg-eq/dm^3; A = 7.6 mg-eq/dm^3; [Ca^{2+}] = 6.0 mg-eq/dm^3; [Cl^-] = 31.0 mg/dm^3; [SO_4^{2-}] = 20 mg/dm^3; pH = 7.65).

These solutions were fed by a pump to a reverse osmosis filter. Permeate samples were taken, and the concentrate was returned to the working solution. The initial volumes of solutions are 10–11 dm^3. The pressure in the system at the level of 4 atm. was maintained by regulating the water

Table 1. Properties of a TW30–1812–50 reverse osmosis membrane

Indicator	Value
Productivity, dm^3/day (pressure 4-7 bar and a temperature 25 °C)	225-395
Permanent salt removal, %	98
Minimal salt removal, %	96
Maximum water supply, dm^3/min	7.6
Maximum pressure, bar	21
Maximum working temperature, °C	45
Maximum colloidal index	5
pH range (long-term operation)	2-11
pH range (30 min rinse)	1-13
The maximum concentration of free chlorine, mg/dm^3	<0.1
Size, mm	295x55

supply by the pump and the flow of the concentrate by the faucet. Then, 9–10 dm^3 of water were passed through, taking permeate samples with a volume of 1 dm^3. In each permeate sample, the concentration of phosphates and the pH of the medium were determined, in the case of using artesian water, in addition to the concentration of phosphates, the hardness, alkalinity of the water, the content of calcium, chlorides and sulfates were determined. When taking each sample of permeate in the concentrate, the content of phosphates and pH were determined, and when using artesian water, the hardness, alkalinity of the water, the content of calcium, chlorides and sulfates were also determined. In addition, for the concentrate, all indicators, except pH, were calculated theoretically.

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

$$R = \frac{C_0 - C_P}{C_0} \cdot 100\% \tag{1}$$

where: R – selectivity of the membrane, %;
C_0 and C_n – concentrations of the component in the original solution and permeate, respectively.

The content of the component in the i-th sample of the concentrate (C_{ki}, mg/dm^3) was calculated according to the formula:

$$C_{ki} = \frac{V_0 \cdot C_0 - \sum_{i=1}^{n}(C_{ni} \cdot V_{ni})}{V_0 - \sum_{i=1}^{n} V_{ni}}, \mathrm{mg/dm^3} \tag{2}$$

where: C_{ki} – the concentration of the component in the concentrate after the selection of the i-th permeate sample;
V_0 – the volume of the initial solution (V_0 = 10 or 11 dm^3);
V_{pi} – the volume of the permeate sample (1 dm^3);
C_{pi} – the concentration of the component in the ith permeate sample, mg/dm^3;
n – the number of permeate samples.

Membrane productivity (transmembrane flow rate) (j) (dm^3/(m^2·h)) was calculated using the formula:

$$j = \frac{V_n}{S \cdot \Delta\tau}, \mathrm{dm^3/(m^2 \cdot h)} \tag{3}$$

where: V_n – the permeate sample volume, dm^3;
S – membrane area, m^2;
$\Delta\tau$ – permeate sampling time, h.

The content of phosphates, chlorides, sulfates, calcium, alkalinity, hardness, pH of the medium were determined according to standard methods [Gomelya et al. 2017].

RESULTS

The results of water purification from phosphates on a low-pressure reverse osmosis membrane are shown in Figure 1 and Figure 2. As can be seen from Figure 1, the performance of the membrane significantly depends on the concentration of phosphates in the model solution. It is obvious that the decrease in membrane productivity with an increase in the concentration of phosphates in the initial solutions and with an increase in the degree of permeate selection is caused both by an increase in the osmotic pressure of the solutions along with the concentration of the component, and by the phenomena of concentration polarization on the membrane surface, the permeate selection to 70–90%.

The selectivity of the membrane was the highest at the minimum initial concentration of phosphates (18.5 mg/dm^3), contrary to the statement of the authors [Seminska et al. 2016]. An increase in the selectivity of the membrane was observed when the concentration of phosphates increased from 98 to 1100 mg/dm^3. What is interesting in this case is the ability of the membrane to effectively retain phosphates at low concentrations (Fig. 2), when the phosphate content in permeate did not exceed 2 mg/dm^3 even with a permeate selection rate of 90%. This is below the permissible level of phosphates in the bottom water [SSNR 2.24-171-10 2010; Directive 98/83/EC 1998]. The high efficiency of phosphate removal from water on a low-pressure reverse osmosis membrane was also observed by the authors [Seminska et al. 2016] at a favorable phosphate concentration of ~ 9 mg/dm^3.

Significantly higher concentrations were noted in permeate when the initial concentration of phosphates in the water increased to values of ~ 100 mg/dm^3. This can be seen in Figure 2 and according to the data given in [Seminska et al. 2015].

The concentration of phosphates in the permeate increases even more when their initial concentration in the model solution is increased to ~ 1000 mg/dm^3. In this case, the phosphate content in the permeate reaches 50–270 mg/dm^3. If it is

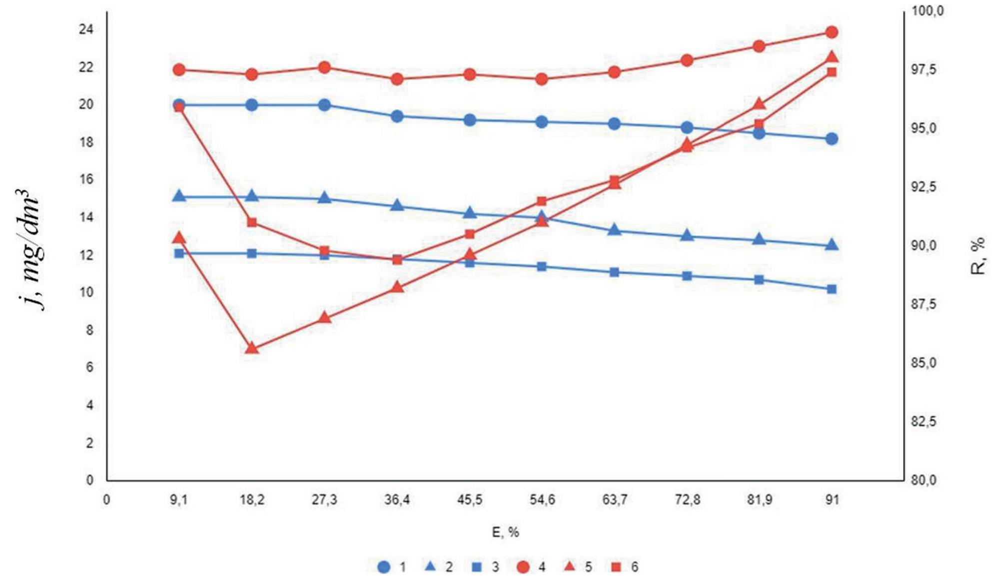

Figure 1. Change in productivity (1, 2, 3) and selectivity (4, 5, 6) of a low-pressure reverse osmosis membrane depending on the degree of permeate selection when filtering sodium orthophosphate solutions with phosphate concentrations, mg/dm^3: 18.5 (1; 4), 98 (2; 5); and 1100.5 (3; 6) at a system pressure of 4 atm. The volume of the solutions is 11 dm^3, the volume of the permeate sample is 1 dm^3

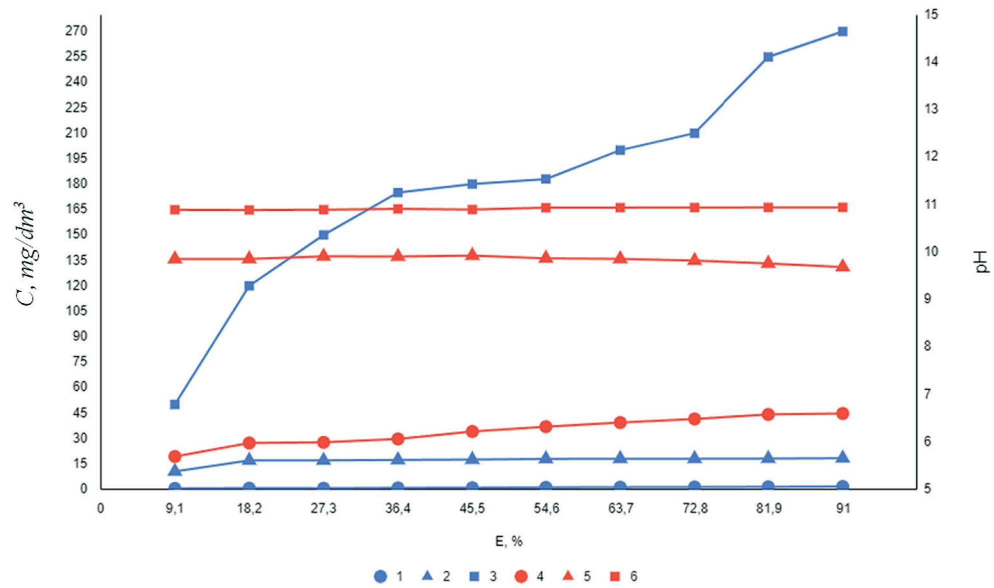

Figure 2. Changes in the concentration of phosphates (1; 2; 3) and the pH of the medium (4; 5; 6) in the permeate with an increase in the degree of permeate selection during filtration through a low-pressure membrane of sodium orthophosphate solutions with a concentration, mg/dm^3: 18.5 (1; 4); 98 (2; 5); 1100.0 (3; 6)

considered that at a phosphate concentration of up to 20 mg/dm^3, the pH of the solution does not exceed 7.523, then at a phosphate concentration of ~ 100 mg/dm^3, pH = 10.890 (Table 2, Figure 3). It is obvious that such an increase in pH significantly affects the hydration of phosphate anions in water and, accordingly, their ability to be retained by the membrane. When the pH increases due to the hydrolysis of sodium orthophosphate, the hydration conditions of partially hydrolyzed phosphate anions deteriorate. At neutral pH values of the medium, phosphate anions are the most hydrated, and therefore well retained by the membrane.

With increasing pH, this effect weakens, which leads to a decrease in the efficiency of water purification from phosphates. In addition, the concentration factor should not be underestimated, which leads to an increase in the influence of concentration polarization on the efficiency of phosphate removal [Seminska et al. 2015].

Table 2. Dependence of the content of phosphates in the concentrate on the degree of permeate selection during filtration through a low-pressure membrane of sodium orthophosphate solutions

E, %	C, mg/dm³		
0	18.5	98.0	1100.0
9.1	20.0	10.5	1205
18.2	22.1	17.0	1326
27.3	24.6	17.0	1472
36.4	28.0	17.3	1657
45.5	33.1	17.5	1903
54.5	38.8	17.9	2248
63.6	48.2	18.0	2759
72.7	63.9	18.0	3609
81.8	95.1	18.3	5286
90.9	188.0	18.3	10303

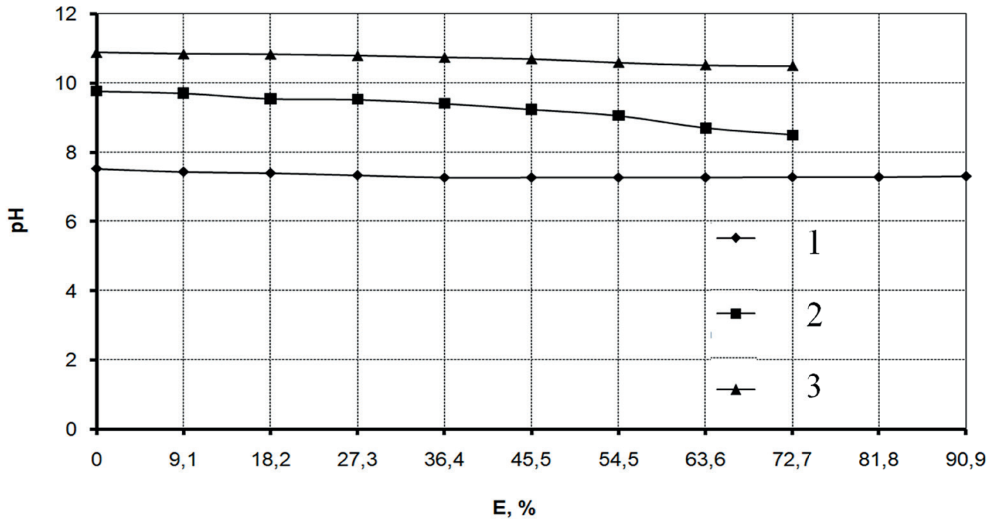

Figure 3. Dependence of the pH of the medium in the concentrate on the degree of permeate selection during filtration through a low-pressure membrane of sodium orthophosphate solutions with a concentration of mg/dm³: 18.5 (1), 98 (2) and 1100 (3)

If the effect of pH on the process of reverse osmosis removal of phosphates from water is evaluated, attention should be paid to the following. When the concentration of phosphates in water is up to 20 mg/dm³, a decrease in pH of the permeate and an increase in pH of the concentrate were observed (Fig. 2; Fig. 3). However, at concentrations => 100 mg/dm³, in contrast, an increase in permeate pH was observed compared to the concentrate, although the phosphate content in the concentrates in the second case increased to high values.

Obviously, at high pH values, when the content of hydroxyl anions was significant, their diffusion through the membrane was better, compared to phosphates. On the contrary, better diffusion of protons compared to sodium cations was observed in a neutral environment.

If reverse osmosis installations are considered as reliable means of improving the quality of drinking water, then in the case of water phosphate removal, they are quite promising, because the phosphate content in tap, artesian, ground and surface waters practically never exceeds a concentration of 10 mg/dm³. The conducted studies using phosphate solutions in artesian water showed the high efficiency of the method when purifying water not only from sulfates, but also from other water components (Fig. 4). Practically all the present components were effectively removed from the water and their concentrations in permeate were significantly lower than the permissible levels for drinking water.

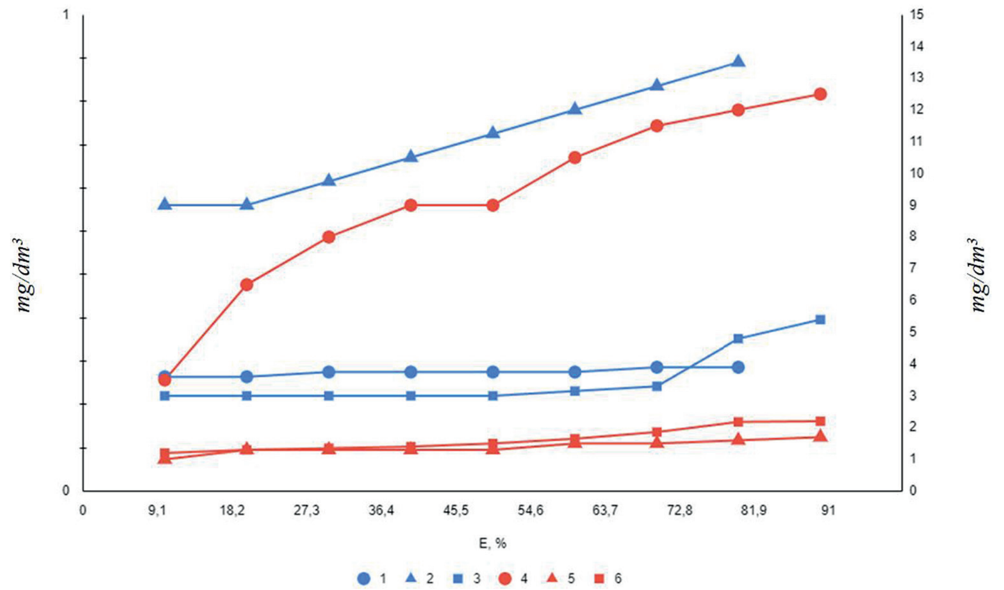

Figure 4. Dependence of hardness (1), alkalinity (2), concentration of calcium ions (3) (mg-eq/dm^3), chlorides (4), sulfates (5) and phosphates (6) (mg/dm^3) in the permeate obtained during filtration through a low-pressure reverse osmosis membrane of sodium orthophosphate solution in artesian water (H = 7.8 mg-eq/dm^3, A = 7.6 mg-eq/dm^3, Ca^{2+} = 6.0 mg-eq/dm^3, Cl^- = 31.0 mg/dm^3, SO_4^{2-} = 20 mg/dm^3; PO_4^{3-} = 22.5 mg/dm^3; pH = 7.65) from the degree of permeate selection

The performance of the membrane was sufficiently high (Fig. 5). The selectivity was relatively low only when removing chlorides, although, as it is known, it increases with increasing concentration [Seminska et al. 2015]. In addition, the permissible content of chlorides in drinking water is quite high. It should be noted that in this case - the calculated and determined concentrations of chlorides and sulfates in the water are relatively low, which allows the discharge of the concentrate into the sewer (Fig. 6). In this case, a slight acidification of the permeate compared to the concentrate was also observed, which is probably due to better diffusion of protons through the membrane, compared to sodium ions.

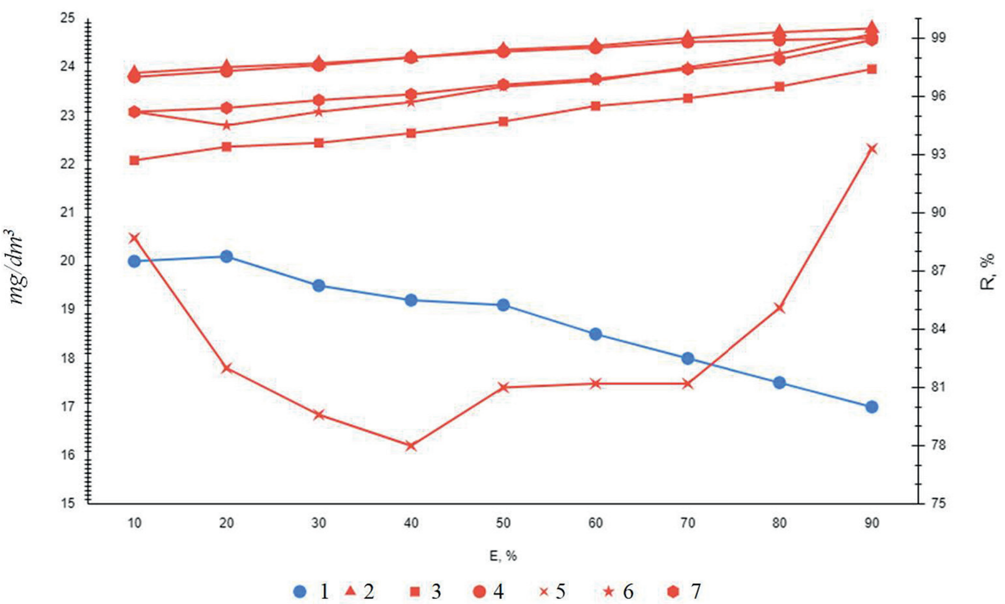

Figure 5. Change in performance (1) and selectivity (2; 3; 4; 5; 6; 7) of a low-pressure reverse osmotic membrane according to hardness (2), alkalinity (3), calcium ions (4), chlorides (5), sulfates (6) and phosphates (7) of the degree of permeate selection during filtration of sodium orthophosphate solution (C_{PO4}^{3-} = 22.5 mg/dm^3) in artesian water

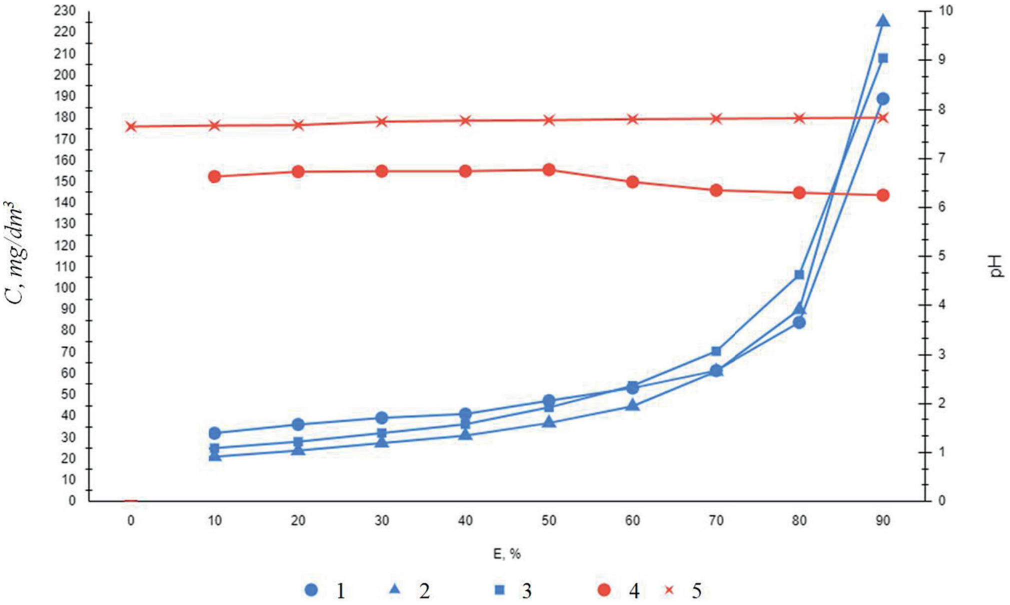

Figure 6. Changes in the content of chlorides (1), sulfates (2), phosphates (3) in the concentrate, the pH of the medium in the permeate (4) and concentrate (5) with an increase in the degree of permeate selection when filtering the sodium orthophosphate solution (PO_4^{3-} = 22.5 mg/dm^3) in artesian water through a low-pressure reverse osmosis membrane (final content values calculated for the concentrate, mg/dm^3: Cl^- – 190.7; SO_4^{2-} – 226.5; PO_4^{3-} – 210.4)

DISCUSSION

It is known that the bulk of municipal and industrial wastewater, with which 75% and 19% of phosphorus compounds enter natural water bodies, respectively [Seminska et al. 2015], is mainly treated at municipal wastewater treatment plants and wastewater treatment plants of large enterprises by using the biochemical method [Ayrapetyan 2014; Gautam et al. 2014]. This treatment method is characterized by high productivity (from hundreds of thousands to millions of m^3/day).

Therefore, it is advisable to use reagent, sorption, and ion exchange methods for further purification of such waters from phosphates. These methods do not require special preliminary water preparation, like reverse osmosis [Seminska et al. 2016; Seminska et al. 2017] and can be applied with significant water consumption. Ion exchange [Gomelya et al. 2017] allows catching phosphates and nitrates and using them as fertilizers. However, reverse osmosis has several advantages over the mentioned methods when it comes to the preparation of drinking water. Traditional methods of water treatment provide correction of turbidity, color of water, and its disinfection. However, they are not effective in removing chlorides, sulfates, nitrates, phosphates or reducing hardness and mineralization of water.

From the given results it is clear (Figs. 1, 2) that even when using low-pressure reverse osmosis membranes, phosphates can be effectively removed, provided that their initial concentration does not exceed 20 mg/dm^3. At the same time, it is known that even in wastewater, the phosphate content does not exceed 10 mg/dm^3. Therefore, it is obvious that reverse osmosis completely solves the problem of water purification or further purification to drinking quality.

Moreover, conducting experiments using a solution of phosphates in artesian water (Figs. 4; 5) showed that a low-pressure reverse osmosis membrane provides effective water softening, reducing its alkalinity, as well as removing not only phosphates, but also chlorides from water and sulfates. At the same time, the degree of permeate selection reached 90%. Only in the case of water softening (Fig. 7) was a tendency to sediment formation on the membrane due to carbonates of hardness ions at a degree of permeate selection >70% (Fig. 7). This can be judged by the difference between the determined values of hardness and alkalinity in the concentrate and the calculated values. The problem can be solved by adjusting the degree of permeate selection, when using antiscalants and periodic acid washing of the membrane surface.

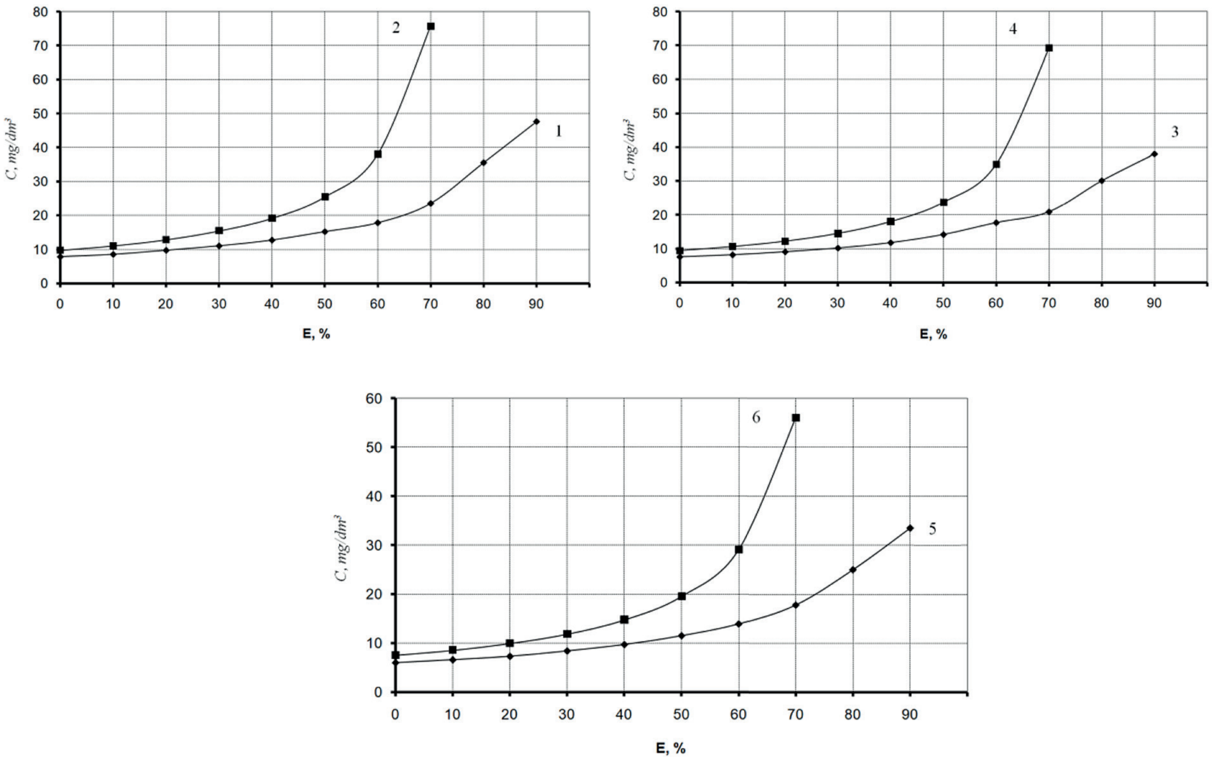

Figure 7. The effect of increasing the degree of permeate selection on the hardness (1; 2), alkalinity (3; 4) and concentration of calcium ions (5; 6) determined (1; 3; 5) and calculated (2; 4; 6) in the obtained concentrate when filtering sodium orthophosphate solution (PO_4^{3-} = 22.5 mg/dm^3) in artesian water through a low-pressure reverse osmosis membrane

In general, using the example of the TW30–1812–50 low-pressure reverse osmosis membrane, it was shown that at relatively low concentrations of phosphates in a neutral water environment, reverse osmosis provides effective purification of water from phosphates.

CONCLUSIONS

1. On the example of using model solutions of sodium orthophosphate in water, it was shown that a low-pressure reverse osmosis membrane provides high efficiency of removing phosphates from water at concentrations ≤ 20 mg/dm^3 while increasing the degree of permeate selection to 90%. At a concentration of phosphates ≥ 100 mg/dm^3, the efficiency of their removal from water decreases sharply, which may be due to salinization by water treatment.
2. It was established that a low-pressure reverse osmosis membrane provides effective purification of a sodium phosphate solution in artesian water with a phosphate concentration of ≤ 22.5 mg/dm^3 and a permeate selection rate of up to 90%. In this case, effective softening of water, reduction of its alkalinity, purification of chlorides and sulfates was achieved. With a degree of permeate selection >70%, deposition of carbonates of hardness ions on the membrane is possible.

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