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## New Approaches to the Use of Membrane Methods for Obtaining High-Quality Drinking Water

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### Abstract

A fundamentally new concept of providing the population with high-quality drinking water is proposed associated with the transfer of drinking water supply to cities and villages to the use of autonomous block installations for water purification in the sites of its direct consumption. Autonomous membrane installations for collective and individual use with biotesting and analytical control are developed. In these installations, preliminary water purification is carried out with the help of microfiltration tubular membranes made of lignocellulose (wood) and ceramic membranes made of clay minerals, which retain mechanical and colloidal impurities. The concentrations of these impurities after purification meet the drinking water standards. A technological scheme is developed for water purification from nitrate ions to drinking conditions with the production of mineral fertilizers through a rational combination of reverse osmosis and an improved electro dialysis process.

**Keywords:** membrane methods, drinking water, autonomous membrane installations, ceramic and lignocellulose membranes, complex purification of nitrate-containing waters

### INTRODUCTION

One of the global ecological problems of the XXI century is to provide high-quality drinking water to the population of the Earth. This problem becomes even more urgent with time because water quality in available sources of water supply is permanently worsening, while the population, industry and hence the amounts of water consumption are permanently growing.

According to the estimations of the World Health Organization (WHO), about 80 % of all diseases of the population are to some extent connected with the use of low-quality drinking water. The pollution of water bodies with industrial and communal waste waters is to a substantial extent due to inefficient technologies of water purification. In addition, unreasonable use of water resources is essentially dependent on the

quality of water preparation. Because of this, the development of new approaches to solving the problem of water purification is important and relevant [1].

In many countries, natural underground and surface waters are used to provide drinking water to the population. However, if the former waters require mainly decontamination, the latter waters may be used only after the corresponding water preparation. In this connection, one of the most important tasks in the preparation of high-quality drinking water is to select the processes that would allow flexible regulation of the technologies of water preparation for the purpose of optimizing their regimes.

Natural waters differ from each other in the qualitative and quantitative composition of pollutants, so it is reasonable to purify these waters with the help of autonomous installations com-

posed of separate functional blocks [2]. It is necessary to use such a combination of technological operations and processes that would provide the possibility of flexible optimization of the modes of water purification under the most complicated conditions, and each unit has a corresponding function. Depending on the quality of initial water, it is necessary to apply a set of units that would allow water purification to the drinking quality with minimal expenses.

Membrane methods in combination with other methods of water purification are of the great importance to the development of autonomous block units (ABU) of this kind. This is due to the high efficiency of membrane methods, simplicity of their instrumental arrangement and automation. Baromembrane methods (micro-, ultra-, nanofiltration and reverse osmosis) are widely used in world practice to obtain high-quality drinking water and to purify industrial waste waters [3–5]. Electrodialysis has been recently revitalized in connection with its use for simultaneous desalination and deep concentrating of salt solutions, which provides their efficient processing into valuable substances [6, 7].

#### **AUTONOMOUS BLOCK INSTALLATIONS FOR OBTAINING HIGH-QUALITY DRINKING WATER**

A fundamentally new concept has been proposed at the A. V. Dumanskii Institute of Colloid and Water Chemistry of the NAS of Ukraine (ICWC) on the basis of long-term experience in the area of water purification. This concept is connected with the transfer of drinking water supply for towns and settlements to water purification directly at the sites where it is consumed [2]. These complexes with relatively low productivity (1–5 m<sup>3</sup>/h) can be mounted in each locality of a city or in rural settlements similarly to the pump-room water supply complexes existing in Kiev, which are very popular. It is necessary to stress that this ideology does not require any changes in the city water pipe system.

The supply of high-quality drinking water to the population of the city is performed through the operation of 5–10 local installations, which will produce water only for drinking and for cooking. Similarly to Kiev, the population of other cities will be able to obtain high-quality drinking water directly from the installations, or through distribution networks if necessary. Drinking water supply to kindergartens, schools, hospitals and so

on may be provided by means of supply in large-volume bottles (20–50 dm<sup>3</sup>).

An important factor is that the drinking water obtained in autonomous installations would not enter water pipelines, so the absolute conservation of drinking water quality for consumers is guaranteed. The quality of drinking water is provided not only by the absence of its contact with overworn water supply systems but also by the use of chlorine-free technology of decontamination.

To solve this problem, water preparation ABU have been developed at the ICWC for collective and individual use with biotesting and the analytical control of drinking water quality [2]. The choice of the necessary methods of drinking water purification to the requirements of the modern national standards was performed in agreement with water composition; it is based on the flexible block principle, which provides the possibility to vary the number of blocks depending on the composition of initial water. The indicated problem has been solved using several methods, which are protected by Ukrainian patents. These methods are based on the combination of membrane methods – reverse osmosis or nanofiltration, which are presently among the most efficient and economic methods of water purification, with other physicochemical methods of water purification.

Much attention is paid to preliminary water preparation providing its further purification with the help of membrane methods to the requirements of modern national quality standards, from any kinds of pollution including substantial concentrations of so-called hardness salts, nitrates, fluorides, radionuclides and so on. Autonomous installations provide drinking water conditioning with respect to the content of useful ions, such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, which may be excessively removed from water by means of reverse osmosis or nanofiltration. On demand of consumer, autonomous units may be also supplemented with the blocks providing the treatment of wastes formed during water purification. The general view of autonomous complexes of different productivity is presented in Fig. 1, 2.

The quality of water purified through ABU is to be monitored using organism- and cell-level biotesting methods, which were developed at the ICWC. This allows us to evaluate the effect of pollutants on the human organism, on vital processes, and to obtain an integral evaluation of water quality. With the help of biotesting, we may determine the toxicity of water that does

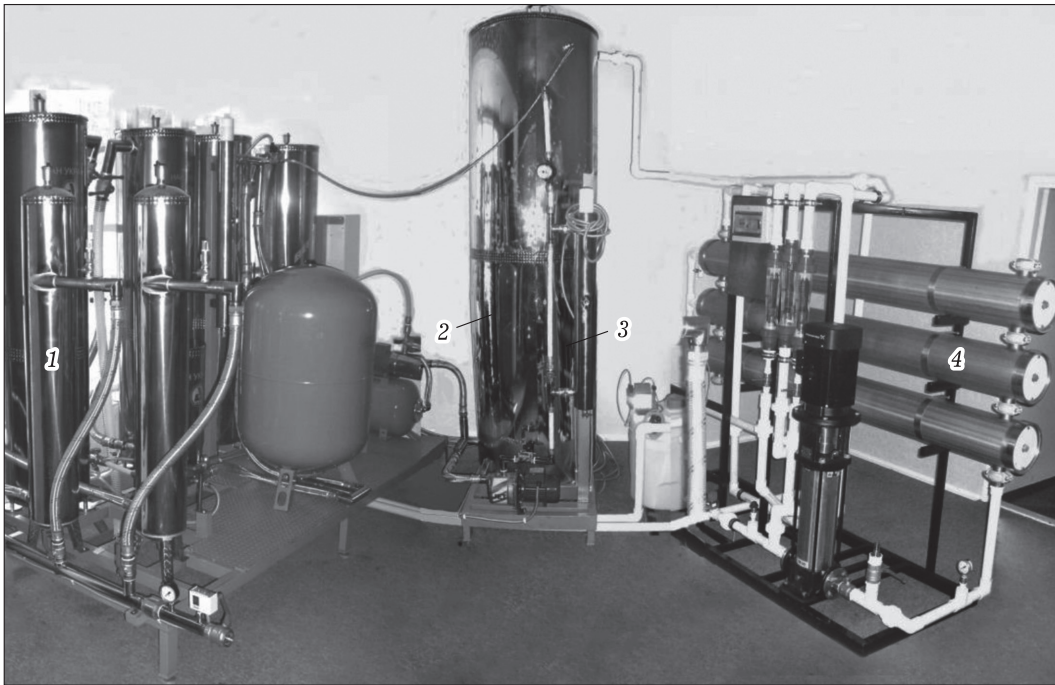


Fig. 1. Autonomous installation with the productivity of 5 m<sup>3</sup>/h for collective use:  
1 – unit of preliminary water purification; 2 – tank for purified drinking water; 3 – ultraviolet lamp;  
4 – reverse osmosis unit.



Fig. 2. Autonomous installation with the productivity of 0.5 m<sup>3</sup>/h for collective use:  
1 – unit of preliminary water purification; 2 – reverse osmosis unit; 3 – tank for purified drinking water;  
4 – ultraviolet lamp.

not contain hazardous impurities according to the results of chemical analysis.

To determine the standard parameters of the quality of drinking water under field conditions, each ABU may be equipped with a portable Akva-test laboratory developed at the ICWC. This laboratory illustrates a reasonable combination of low cost with broad functional possibilities; analysis procedures used in it provide the simplicity, convenience, high rate and ecological safety of analyses at the sampling site.

The cost of local installations with the productivity of 1–5 m<sup>3</sup>/h is 510–2040 thousand roubles. The net cost of water purified using these installations to WHO requirements is 3.6–3.8 roubles/m<sup>3</sup>. Local installations with the productivity of 1–5 m<sup>3</sup>/h are introduced in the Kiev, Kharkov, Donetsk and other Regions of Ukraine.

#### WATER PURIFICATION WITH CERAMIC MEMBRANES MADE OF CLAY MINERALS

It was proposed to use microfiltration tubular ceramic membranes made of clay minerals, developed at the ICWC, as the block of preliminary water purification in ABU [8]. They possess a set of advantages over microfiltration polymer membranes: increased strength; stability to the action of aggressive media, microorganisms and high temperature; simplicity of regeneration with the reverse flow of filtrate; availability of raw material. These membranes are cheaper than the membranes made of oxide ceramics, which are

widely used abroad to purify water and food liquids [9–11].

The tests of microfiltration ceramic membranes made of clay minerals with the maximal pore diameter of 1.05  $\mu$ m, as determined by the bubble point method [12], were carried out with the underground and surface natural waters from different sources. In the experimental installation with seven ceramic tubes (working length – 92 mm, inner and outer diameters – 11–12 and 6–7 mm, respectively), we used waters: 1) from a well (pH 7.4–7.5) at the territory of the technological division of the ICWC in Vyshgorod, Kiev Region; 2) from a lake (pH 7.3) in Gorbovich settlement, Kiev Region; 3) from the Dnieper (pH 7.9–8.3) near Kiev [13].

Figure 3, *a* shows the dependence of the retention capacity of membranes (retention coefficient  $R$ ) with respect to the compounds of iron, manganese, as well as suspended matter which is present in underground water (Vyshgorod, the Kiev Region) on the time ( $\tau$ ) of operation at the working pressure ( $P$ ) 0.2 MPa. It was established that the membranes under investigation even at the beginning of tests exhibited almost complete retention of the suspended matter (98.9–99.8 %) (see Fig. 3, *a*, curve 1). Retention coefficients for the compounds of iron and manganese increased from 94.2 to 99.3 % (curve 2) and from 32.8 to 67.2 % (curve 3), respectively, with an increase in  $\tau$  from 0.5 to 5.0 h. This phenomenon may be explained by the formation of an additional absorbing layer in the form of a dynamic membrane (DM) composed of hydroxo compounds of Fe (III)

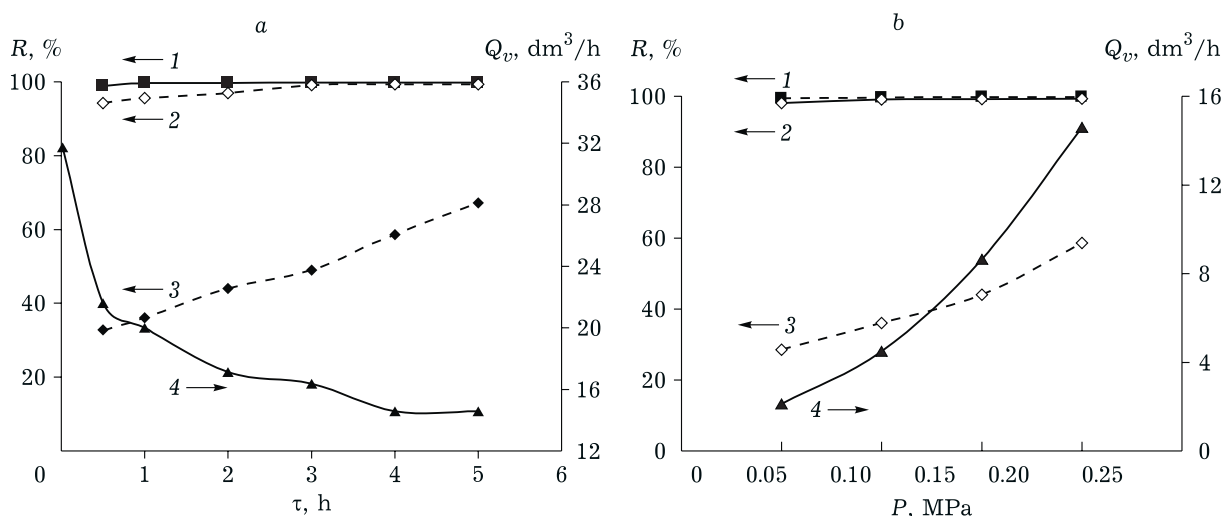


Fig. 3. Dependence of retention coefficient ( $R$ ) for suspended matter (1), compounds of iron (2) and manganese (3), and the productivity of the installation ( $Q_v$ ) (4) during purification of water from well (borehole) on: *a* – operation time ( $\tau$ ); *b* – working pressure ( $P$ ).



on the surface of ceramic tubes, which was confirmed by a sharp decrease in the productivity ( $Q_v$ ) of the set-up (Fig. 3, *a*, curve 4).

The dependence of membrane characteristics on working pressure ( $P$ ) during water purification for 4 h in the experimental installation is shown in Fig. 3, *b*. One can see that an increase in pressure from 0.05 to 0.2 MPa did not affect the completeness of the retention of suspended substances and iron compounds by the membrane (curves 1, 2). An increase in the retention coefficient of the membranes was observed for manganese compounds (curve 3), which may be connected with densification of the formed DM composed of the hydroxo compounds of Fe (III). It was established that the productivity of the installation increased with an increase in  $P$  (see Fig. 3, *b*, curve 4), which is explained by an increase in the driving force of the process. Relying on the obtained results, the working pressure equal to 0.2 MPa was chosen, which provided groundwater purification to the standard maximum permissible concentrations (MPC) for the above-listed pollutants in drinking water with the maximal productivity [14].

Results of the purification of natural waters from different sources in the installation with seven ceramic membranes ( $P = 0.2$  MPa and  $\tau = 4.0$  h) are presented in Table 1. One can see that simultaneously with a decrease in iron and manganese concentrations in initial natural waters, purification from organic impurities also occurred; their amount was determined by the content of total organic carbon (TOC). In underground water, TOC concentration decreased more than by a factor of 5, while purification of surface waters with increased TOC content resulted in a decrease in the concentration of organic impuri-

ties by a factor of 1.5. This feature of the retention by membranes with respect to TOC is due to the high content of iron ( $8.4 \text{ mg/dm}^3$ ) in the water from wells (boreholes), which caused the formation of DM from the hydroxocomplexes of Fe (III) on the surface of ceramic tubes. In surface waters, the concentration of iron compounds was only  $0.05\text{--}0.55 \text{ mg/dm}^3$ , which did not allow the formation of a dense DM layer, the retention of organic compounds by the membrane was lower. The content of suspended matter in underground water decreased from  $44.0$  to  $<0.3 \text{ mg/dm}^3$ . It should be noted that the ceramic microfiltration membrane provided retention of suspended substances down to the MPC level [14] during the treatment of all categories of natural waters. As a result of this process, DM was also formed on the surface of ceramic tubes.

It was established (see Table 1) that as a result of underground water purification the concentration of the compounds of iron decreased from  $8.4$  to  $0.02 \text{ mg/dm}^3$ , and manganese from  $0.58$  to  $0.24 \text{ mg/dm}^3$ , thus reaching the MPC level. In the samples of surface water, their content in the permeate after purification with ceramic membranes decreased only by a factor of 2. This may be due to insufficient concentration of the indicated ions to form a self-retaining DM composed of hydroxo compounds on the surface of the ceramic tube.

It is important to stress that the formation of DM promoted additional retention of accompanying anions, in particular,  $\text{Ca}^{2+}$  by  $13.0\text{--}24.0 \%$  (see Table 1). This level of the retention capacity for  $\text{Ca}^{2+}$  is characteristic of ultrafiltration membranes [13]. Under these conditions, the productivity of the installation reached  $15\text{--}16 \text{ dm}^3/\text{h}$ .

TABLE 1

Results of the analysis of natural waters before and after purification in the experimental installation with ceramic membranes (working pressure 0.2 MPa, permeate selection coefficient 80.0 %, process time 4.0 h)

Water sample	Total organic carbon, $\text{mg C/dm}^3$		Suspended matter, $\text{mg/dm}^3$		$\text{Ca}^{2+}$ , $\text{mg/dm}^3$		Mn (II), $\text{mg/dm}^3$		$\text{Fe}_{\text{tot}}$ , $\text{mg/dm}^3$	
	Before	After	Before	After	Before	After	Before	After	Before	After
Well, Vyshgorod, Ukraine	1.5	<0.3	44.0	<0.3	92.18	80.16	0.58	0.24	8.40	0.02
Lake, Gorbovichi village, Kiev Region, Ukraine	9.5	6.4	8.8	0.8	50.10	38.08	0.05	0.02	0.55	0.01
The Dnieper river, Kiev, Ukraine	9.6	6.4	1.7	0.5	40.08	32.06	0.04	0.02	0.05	0.02
MPC*	Not normalized	Not normalized	3.5	3.5	Not normalized	Not normalized	0.5	0.5	1.0	1.0

\* MPC according to DSanPiN 2.2.4-171-10 [14].

Analysis of the obtained results provides evidence that the membranes under investigation are characterized by the steric mechanism of action, based on the difference in the sizes of pores and the admixtures to be captured. During the purification of underground water, the microfiltration ceramic membrane made of clay minerals was modified with pollutants present in the waters, so that is attained ultrafiltration properties.

So, filtration of natural water through a ceramic membrane made of clay minerals promoted almost complete removal of particles that provided water turbidity; iron and manganese content decreased to the MPC level for drinking water. The concentration of TOC in the surface and underground waters decreased by ~30 and 80 %, manganese by 50 and 60 %, iron by 67.0 and 99.8 %, respectively. It was established that it is most reasonable to use the pressure 0.2 MPa and to form the DM for 1.5–2.0 h. The high efficiency of the purification of underground and surface waters with ceramic membranes made of clay minerals and the reasonableness of their practical use were demonstrated.

Microfiltration ceramic membranes made of clay minerals may purify water efficiently not only from mechanical and colloid impurities as it had been established previously, but also from ion admixtures. However, for this purpose, it is necessary to modify these membranes with definite compounds. The major regularities of fluorine removal by the ceramic membrane modified with hydroxo compounds of Al (III) were studied in [15], and the technological parameters of the membrane were determined.

The necessary conditions for this modification of the ceramic membrane were revealed preliminarily. It was established that during the filtration of a solution of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  salt with the initial concentration of Al (III) ions 65.0 mg/dm<sup>3</sup> and pH 6.0–6.5 for 90 min under the pressure of 1.0 MPa, the ceramic membrane exhibited almost complete retention of these ions. So high process efficiency may be explained by the steric mechanism of membrane performance, which is determined by the difference in the sizes of its pores and the particles of Al (III) hydroxo compounds formed at the indicated pH of the solution. The specific productivity ( $J_v$ ) of the membrane decreased from 0.16 to 0.11 m<sup>3</sup>/(m<sup>2</sup>·h) with an increase in process time from 10 to 60 min, which pointed to pore blockage in the ceramic membrane and the formation of the modifying layer on its surface. This layer is a DM composed of

hydroxo compounds of Al (III). After that,  $J_v$  of the membrane remained practically unchanged, which was the evidence of the finish of DM formation process.

Thus modified ceramic membrane exhibited a large retention coefficient ( $R$ ) for  $\text{F}^-$  ions (98–99 %) when their concentration ( $C_{\text{in}}(\text{F}^-)$ ) in the initial solution of NaF salt was equal to 10.3 mg/dm<sup>3</sup>,  $\text{pH}_{\text{in}}$  6.5, working pressure  $P = 1.0$  MPa,  $\tau = 90.0$  min, and concentration of the membrane-sustaining additive  $C_{\text{ad}}(\text{Al (III)}) = 11.0$  mg/dm<sup>3</sup>. It should be noted that a decrease in the concentration of  $\text{F}^-$  ions was observed both in the permeate and in the water under purification (retentate) to the level below the MPC of fluoride ions in drinking water (0.7–1.5 mg/dm<sup>3</sup>) [16]. The concentration of the hydroxo compounds of Al (III) in the permeate reached the MPC for drinking water (0.2 mg/dm<sup>3</sup>) during the entire purification process [16] and remained practically unchanged. The value of  $J_v$  for the membrane remained almost constant and was equal to 0.1 m<sup>3</sup>/(m<sup>2</sup>·h), which confirmed the dynamic mode of its operation.

The water defluorination process under investigation is likely to be due to the formation of aluminofluoride complexes like  $[\text{Al}(\text{OH})_n\text{F}_{6-n}]$ , with the composition depending on pH and the relations between the concentrations of Al (III) hydroxo complexes and fluoride ions [17]. It is generally accepted that Al (III) hydroxo complexes undergo polymerization in the aqueous medium and form very large sol particles together with aluminofluoride complexes.

The degree of  $\text{F}^-$  removal from water is critically affected by the electrokinetic charge ( $\xi$ -potential) of the formed sol particles, which determined their ability to coagulate, which in turn depends on the pH of the medium [17]. The most complete coagulation occurs at pH 6.3–6.6, when  $\xi$ -potential of sol particles approaches zero.

It is shown in Fig. 4 that variation of  $\text{pH}_{\text{in}}$  within the range 5.0–8.0 in NaF solution with  $C_{\text{in}}(\text{F}^-) = 10.3$  mg/dm<sup>3</sup>,  $P = 1.0$  MPa,  $\tau = 90$  min and  $C_{\text{ad}}(\text{Al (III)}) = 11.0$  mg/dm<sup>3</sup> had a substantial effect on the separating properties of the modifying layer composed of hydroxo compounds of Al (III). For instance, the maximal value of  $R$  for  $\text{F}^-$  ions (98–99 %) was observed at  $\text{pH}_{\text{in}}$  6.0–6.3, but at  $\text{pH}_{\text{in}}$  5.0 it decreased to 85.4 %, and at  $\text{pH}_{\text{in}}$  8.0 it was even lower and accounted for 57.3 % (see Fig. 4, *a*, curve 1). A noticeable decrease in  $R(\text{F}^-)$  at  $\text{pH}_{\text{in}} > 6.0$  may be explained by recharging of the particles of Al (III) hydroxo compounds. An increase in pore size in the modifying layer as a

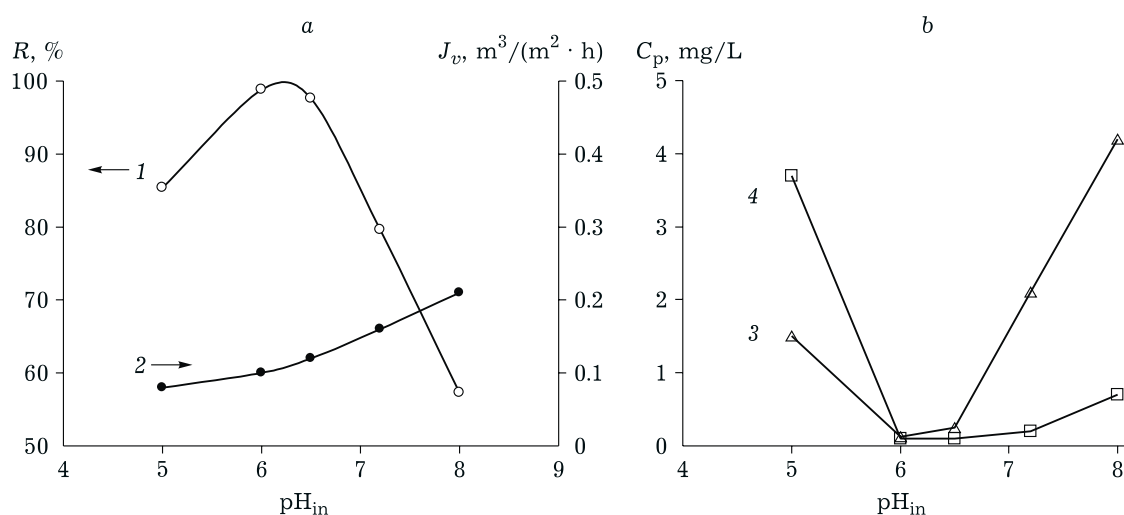


Fig. 4. Dependence on solution  $pH_{in}$ : a – retention coefficient ( $R$ ) for  $F^-$  ions (1) and specific productivity ( $J_v$ ) of the membrane (2); b – the concentration of ions ( $C_p$ )  $F^-$  (3) and  $Al(III)$  (4) in the permeate.

result of the growth of particles composed of  $Al(III)$  hydroxo compounds had significant importance under these conditions, which confirmed an increase in  $J_v$  of the membrane for  $pH_{in} > 6.0$  (see Fig. 4, a, curve 2).

An important role was also played by a decrease in the size of the particles of  $Al(III)$  hydroxo compounds which were able to pass together with adsorbed  $F^-$  ions through the pores of the modifying layer, which caused a decrease in  $R(Al(III))$  and  $R(F^-)$  at  $pH_{in} 5.0$ . The concentrations of these ions in the permeate varied under the indicated conditions in a similar manner (see Fig. 4, b, curves 3, 4). At  $pH_{in} 6.0-7.0$ , the concentrations of  $Al(III)$  and  $F^-$  ions in the permeate corresponded to their MPC in drinking water.

It was concluded on the basis of the studied regularities of this process that the use of the indicated membranes for water defluorination to the level of MPC of  $F^-$  ions in drinking water is reasonable in the case of their concentration in initial water up to  $22.0 \text{ mg/dm}^3$ ,  $pH_{in} 6.5-7.0$ , working pressure  $0.8-1.0 \text{ MPa}$ , selection coefficient ( $K$ ) of permeate up to  $80.0 \%$  and the concentration of the membrane-sustaining additive  $4.0-6.0 \text{ mg/dm}^3$ .

#### WATER PURIFICATION WITH LIGNOCELLULOSE (WOOD) MEMBRANES

Along with ceramic membranes made of clay minerals, attention to the use of wood as a cheap ecologically safe readily available and easily utilized material for the manufacture of membranes has increased during recent time [17–18]. It was

established [18] that the size of pores in wood corresponds to the size of pores in the microfiltration membrane. It is proposed to use membranes made of wood for water purification from mechanical and colloid impurities, in particular, to decrease the colour index and turbidity of water (by 70 and 90 %, respectively), and as single-use tools for decontamination [18, 19].

Microfiltration lignocellulose (wood) membrane with the maximal pore size of  $14.75 \mu\text{m}$  exhibiting high retention capacity to hydroxo compounds of  $Al(III)$  and aluminofluoride complexes was developed at the ICWC [20].

Investigations were carried out with an experimental baromembrane installation in the flow-recirculation mode. The working length, outer and inner diameters of the lignocellulose (wood) tubular membrane were 95, 11 and 5 mm, respectively. It is shown in Fig. 5, curves 1–3, that retention coefficient  $R(Al(III))$  reached 99.9 % with an increase in the time ( $\tau$ ) of the purification of the initial solution of  $AlCl_3 \cdot 6H_2O$  salt ( $C_{in}(Al(III)) = 29.5 \text{ mg/dm}^3$ ) at different  $pH_{in}$ , working pressure  $P = 1.0 \text{ MPa}$  and temperature  $18-20 \text{ }^\circ\text{C}$ . The value of  $R$  was larger for the higher pH of initial solution within the range of MPC for drinking water  $6.5-8.5$  [16]. It should be noted that the MPC of  $Al(III)$  in drinking water ( $0.2 \text{ mg/dm}^3$  [16]) was achieved in all experiments. This phenomenon may be explained by the fact that the size of the particles of  $Al(III)$  hydroxo compounds increased with an increase in pH of the initial solution, and the retention capacity of the membrane with respect to these compounds was higher than that with

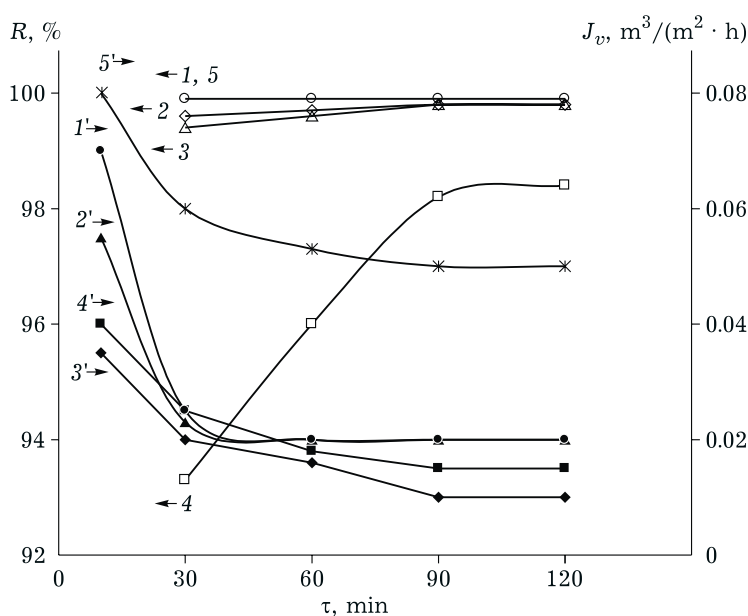


Fig. 5. Effect of the time ( $\tau$ ) of purification of the initial solution of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  at  $\text{pH}_{\text{in}}$  8.1 (1, 1'); 7.1 (2, 2', 5, 5'); 6.6 (3, 3'); 4.9 (4, 4') on retention coefficient ( $R$ ) of Al (III) (1–5) and on specific productivity ( $J_v$ ) of the membrane (1'–5') at  $P = 1.0$  MPa and  $C_{\text{in}}(\text{Al (III)})$ ,  $\text{mg}/\text{dm}^3$ : 29.5 (1–4, 1'–4'); 31.0 (5, 5').

respect to  $\text{Al}^{3+}$  ions. This is also the reason for lower  $R(\text{Al (III)})$  at  $\text{pH}_{\text{in}}$  4.9 (Fig. 5, curves 4) because in this case Al (III) hydroxo compounds form dimers, trimers and other smaller particles that are not so efficiently removed by the membrane [21].

It may be seen in Fig. 5, curves 1'–4', that under similar conditions the value of  $J_v$  for the membrane decreased to the level of  $0.01$ – $0.02$   $\text{m}^3/(\text{m}^2 \cdot \text{h})$ , at first sharply, and then slower. This is connected with pore blockage by Al (III) hydroxo compounds, which results in the formation of an additional retention layer in the form of a DM composed of these compounds on the surface of the wood tube. Higher  $J_v$  value was observed for DM formed at larger pH of the initial solution (see Fig. 5, curves 1', 2'). Evidently, this is due to the fact that larger particles of Al (III) hydroxo compounds formed DM with larger pore size. It should be noted that the higher is  $\text{pH}_{\text{in}}$ , the more intense was the formation of DM, which is also connected with the larger size of the particles of Al (III) hydroxo compounds. So, the mechanism of wood membrane operation is based on the same steric mechanism as the ceramic membrane.

Results shown in Fig. 5, curves 1'–4', provide evidence of the low specific productivity  $J_v$  of the wood membrane, which may be caused by substantial pore blocking and insufficient washing by the reverse flow of distilled water. Because of this,

a more efficient procedure was developed for membrane purification with a solution of citric acid. The essence of the procedure was as follows: after a definite series of experiments and regeneration with the reverse flow of distilled water, the membrane was subjected to preliminary treatment with the reverse flow of the solution of citric acid, followed by washing with distilled water. Results of these experiments are presented in Fig. 5 (curve 5') and provide evidence of an increase in the specific productivity  $J_v$  of the membrane by a factor of about 2.5.

It was demonstrated (Table 2) that with an increase in  $\text{pH}_{\text{in}}$  (from 6.0 to 8.0) of the solution containing both salts  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and NaF, at  $C_{\text{in}}(\text{F}^-) = 10.3$   $\text{mg}/\text{dm}^3$ ,  $C_{\text{in}}(\text{Al (III)}) = 30.0$   $\text{mg}/\text{dm}^3$ ,  $P = 1.0$  MPa and  $\tau = 2.0$  h, the concentration of  $\text{F}^-$  in the permeate ( $C_{\text{p}}(\text{F}^-)$ ) increased at first slowly, and then at a higher rate, from 0.73 to 3.81  $\text{mg}/\text{dm}^3$ . The value of  $J_v$  of the membrane increased from 0.04 to 0.06  $\text{m}^3/(\text{m}^2 \cdot \text{h})$ . An increase in  $C_{\text{p}}(\text{F}^-)$  may be explained by recharging of the particles of Al (III) hydroxo compounds and the formation of the negative charge on them, which resulted in a decrease in the adsorption capacity with respect to  $\text{F}^-$  anions. An increase in  $J_v$  of the membrane under the indicated conditions is caused by an increase in the size of the particles of Al (III) hydroxo compounds and the formation of the modifying layer with a large



TABLE 2

Dependence of the concentrations of  $F^-$  and Al (III) ions in permeate ( $C_p$ ) and specific productivity ( $J_v$ ) of the membrane on  $pH_{in}$  of the solutions of  $AlCl_3 \cdot 6H_2O$  (1) and  $Al_2(SO_4)_3 \cdot 18H_2O$  (2)

$pH_{in}$	$C_p(F^-)$ , mg/dm <sup>3</sup>		$C_p(Al(III))$ , mg/dm <sup>3</sup>		$J_v$ , m <sup>3</sup> /(m <sup>2</sup> · h)	
	1	2	1	2	1	2
6.0	0.73	1.75	0.15	0.22	0.04	0.04
6.5	0.84	1.83	0.10	0.13	0.04	0.04
7.2	1.23	2.17	0.05	0.12	0.05	0.06
7.5	2.12	3.08	0.06	0.11	0.05	0.06
8.0	3.81	3.92	0.05	0.11	0.06	0.07

pore size. This also promoted an increase in the retention capacity of the membrane with respect to Al (III) hydroxo compounds within  $pH_{in}$  6–8 (see Table 2). Taking into account the limits of  $pH_{in}$  range within which the concentration of  $F^-$  reached the MPC for drinking water, it was concluded that it is reasonable to conduct this process at  $pH_{in}$  6.5–7.2.

One can see in Table 2 that under similar conditions in the presence of  $Al_2(SO_4)_3 \cdot 18H_2O$  salt in solution (instead of  $AlCl_3 \cdot 6H_2O$ ) the membrane under investigation had larger  $C_p(F^-)$  and  $J_v$ . The concentrations of  $F^-$  and Al (III) ions in the permeate were higher and lower, respectively, than their MPC in drinking water. The obtained dependences are likely to be due to the larger size of particles of Al (III) hydroxo compounds formed in the solution of  $Al_2(SO_4)_3 \cdot 18H_2O$  salt.

#### INTEGRATED PURIFICATION OF NITRATE-CONTAINING WATERS WITH WASTE PROCESSING

At present, the problem of the removal of nitrate ions during drinking water preparation becomes increasingly important, which is due to the high toxicity of these ions and their wide occurrence in natural waters, where they arrive with atmospheric precipitation, household waste waters, waste waters from chemical, pharmaceutical, rubber, varnish-and-paint and textile plants, wastes from defence production and as a result of the use of mineral nitrogen fertilizers in agriculture. The content of  $NO_3^-$  in drinking water is regulated by the requirements of standards and should not exceed 50.0 mg/dm<sup>3</sup> [16].

There are universal and simple methods to purify water from nitrate ions because their salts belong to stable and well water-soluble compounds with the low ability to be precipitated or absorbed. The most promising methods to remove  $NO_3^-$  are membrane methods (reverse osmosis

and electrodialysis), which do not require the use of chemical reagents and thus decrease expenses for purification. The correct choice of membranes and the working parameters of membrane treatment of water allows optimization of the purification process, which provides almost complete removal of impurities and results in obtaining pure water. A concentrated solution (retentate) of nitrate ions is obtained through reverse osmosis. This solution may be further concentrated using other methods including electrodialysis, for the purpose of further processing to obtain valuable components.

In the ICWC, studies were carried out to determine the working parameters of the processes of water purification from nitrates using low-pressure reverse osmosis [22, 23] and deep concentrating by means of electrodialysis, thus obtaining valuable mineral fertilizers [24, 25].

It is shown in Table 3 that an increase in the selection coefficient ( $K$ ) of purified water (permeate) from 20 to 90 % and initial concentration of nitrate ions ( $C_{in}(NO_3^-)$ ) from 70.0 to 1000.0 mg/dm<sup>3</sup> the concentration of the latter in the permeate increased from 0.6 to 101.0 mg/dm<sup>3</sup>. These data provide evidence that the low-pressure reverse osmosis may be used successfully to purify water from nitrate ions to the drinking quality ( $\leq 50.0$  mg/dm<sup>3</sup> [14]) within concentration range  $C_{in}(NO_3^-) = 70-500$  mg/dm<sup>3</sup> at the permeate  $K$  below 90 %, while for  $C_{in}(NO_3^-)$  up to 1000.0 mg/dm<sup>3</sup> – at  $K$  below 60 %. For  $C_{in}(NO_3^-)$  up to 70.0 mg/dm<sup>3</sup>, their content in the purified water as low as 4.7 mg/dm<sup>3</sup> may be achieved, with  $K$  of the permeate up to 80 %, which corresponds to the toxicological parameters of the safety of drinking water chemical composition (5 mg/dm<sup>3</sup>) for non-central water supply (packed and non-packed) [16]. Under these conditions, the specific productivity ( $J_v$ ) of the membrane decreased from 0.124 to 0.085 m<sup>3</sup>/(m<sup>2</sup> · h) (see Table 3).

ТАБЛИЦА 3

Concentration of nitrate ions in permeate ( $C_p$ ) and specific productivity ( $J_v$ ) of TFC-75F membrane depending on the permeate selection coefficient ( $K$ ) for different  $\text{NO}_3^-$  concentrations in initial solutions ( $C_{in}$ ) and working pressure 1.5 MPa

K, %	$C_{in}(\text{NO}_3^-)$ , mg/dm <sup>3</sup>		250		500		1000	
	$C_p(\text{NO}_3^-)$ , mg/dm <sup>3</sup>	$J_v$ , m <sup>3</sup> /(m <sup>2</sup> ·h)	$C_p(\text{NO}_3^-)$ , mg/dm <sup>3</sup>	$J_v$ , m <sup>3</sup> /(m <sup>2</sup> ·h)	$C_p(\text{NO}_3^-)$ , mg/dm <sup>3</sup>	$J_v$ , m <sup>3</sup> /(m <sup>2</sup> ·h)	$C_p(\text{NO}_3^-)$ , mg/dm <sup>3</sup>	$J_v$ , m <sup>3</sup> /(m <sup>2</sup> ·h)
70	0.6	0.124	6.7	0.112	11.3	0.105	26.2	0.098
40	2.0	0.122	6.8	0.114	21.2	0.104	38.4	0.096
60	3.5	0.120	19.3	0.118	25.6	0.103	48.5	0.093
80	4.7	0.119	19.4	0.121	41.0	0.097	83.4	0.090
90	5.4	0.117	20.0	0.125	44.6	0.094	101.0	0.085

Worsening of the performance characteristics of the membrane with an increase in  $C_{in}(\text{NO}_3^-)$  and the selection coefficient of the permeate  $K$  is connected with an increase in the effect of concentration-caused polarization of the membrane on the process.

The regularities of the deep concentrating and purification of the solutions of nitrate ions resulting in obtaining potassium nitrate and ammonium nitrate as valuable mineral fertilizers by means of electro dialysis were also studied [24, 25]. These studies are necessary to determine the conditions for processing the solutions of nitrate ions that were formed after water purification by means of reverse osmosis. Investigations were carried out using ion-exchange membranes MK-40 and MA-40, and the model solutions of nitrate ions in which the concentrations corresponded to the indicated re- tentates.

The studies were carried out with the electro dialysis concentrating separator of EKR type developed at the ICWC and intended for desalination and deep concentrating of the solutions in the absence of precipitation on ion exchange membranes [26, 27]. A scheme of electro dialysis device of EKR type is shown in Fig. 6. Ion exchange membranes were MK-40 (cation-exchange, K) and MA-40 (anion-exchange, A). The area of each membrane was 1 dm<sup>2</sup>, the distance between the membranes was 1 mm.

The solution of  $\text{NaNO}_3$  was passed in recirculation mode through electrode chambers 1 of EKR-type electro dialysis device. Initial  $\text{NaNO}_3$  solution was supplied to desalination changes 2 also in the recirculation mode, while the solution of  $\text{KCl}$  ( $\text{NH}_4\text{Cl}$ ) was supplied to chamber 4. The concentrations of electrolytes in chambers 2 and 4 were equal (in g/dm<sup>3</sup>). Initial solutions were not supplied to the brine chambers 3 and 5, which ex-

cluded brine dilution. Only water of hydrate shells passed into these chambers through membranes, which provided a high concentration of brines.

During electro dialysis, a solution of  $\text{NaCl}$  salt was concentrated in chamber 3, while  $\text{KNO}_3$  ( $\text{NH}_4\text{NO}_3$ ) solution was concentrated in chamber 5. To eliminate electric current leakage through the collectors of brine chambers, the first brine (chamber 3) was let to flow spontaneously out of the polymer tube 6, and the second one (chamber 5) – from polymer tube 7.

The working current density optimal for electro dialysis was determined in experiments. The results of these experiments, which were carried out with the model solutions of  $\text{NaNO}_3$  and  $\text{KCl}$  with the initial concentrations of nitrate and chloride ions both equal to 2.0 g/dm<sup>3</sup> for 50 min with in current density 0.75–1.5 A/dm<sup>2</sup> provided evidence that higher productivity ( $Q$ ) was observed for chloride solutions than for nitrate solutions. Chloride ion may have transferred larger water volume in its hydrate shell and thus promoted brine dilution. The higher yield as a function of current for chloride ions is connected with their higher initial concentration (0.056 g-equiv/dm<sup>3</sup>) in comparison with the initial concentration of nitrate ions (0.032 g-equiv/dm<sup>3</sup>). With an increase in current density, the concentrations of  $\text{NO}_3^-$  and  $\text{Cl}^-$  ions in desalinated solutions decreased within the range 0.78–0.13 and 1.27–0.78 g/dm<sup>3</sup>, respectively, which is caused by an increase in the driving force of the process. At the current density of 1.0 A/dm<sup>2</sup> the concentration of  $\text{NO}_3^-$  in the brine was 138.6 g/dm<sup>3</sup>, at 1.25 A/dm<sup>2</sup> – 150.0 g/dm<sup>3</sup>, and at 1.5 A/dm<sup>2</sup> – 153.0 g/dm<sup>3</sup>. On the basis of the results obtained, the working current density of 1.25 A/dm<sup>2</sup> was chosen for the purification of solutions from nitrate ions and their concentrating by means of electro dialysis.

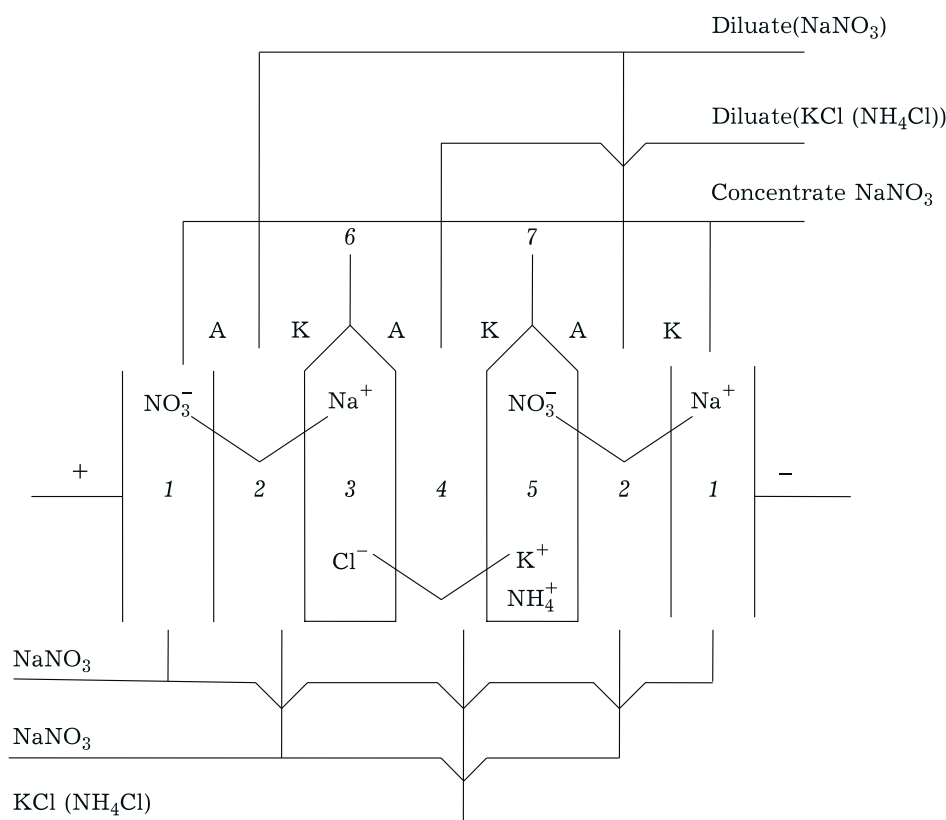


Fig. 6. Schematic of the experimental electrodiolysis concentrating-separating device of EKR type: 1 – electrode chambers; 2 – chamber for  $\text{NaNO}_3$  desalination; 3 – chambers for concentrating  $\text{NaCl}$ ; 4 – chamber of  $\text{KCl} (\text{NH}_4\text{Cl})$  desalination; 5 – chamber for concentrating  $\text{KNO}_3 (\text{NH}_4\text{NO}_3)$ ; 6 and 7 – outlets of  $\text{NaCl}$  and  $\text{KNO}_3 (\text{NH}_4\text{NO}_3)$  brines, respectively; A and K – anionite and cationite membranes, respectively.

On the basis of the studies, a principle flow diagram of integrated water purification from nitrate ions by means of low-pressure reverse osmosis was developed. It includes retentate processing by means of electrodiolysis for the purpose of obtaining drinking water and valuable mineral fertilizers [28]. According to this diagram (Fig. 7), nitrate-containing water is supplied sequentially to the coal filter (1), into the ultraviolet apparatus (2) and into microfilter (3) for preliminary purification from organic, biological, and colloid impurities, respectively. After preliminary purification, water is supplied to the low-pressure reverse osmosis apparatus (4). In this apparatus, water flow is separated into the permeate purified from nitrate ions, which is then supplied to the consumers, and retentate enriched with these ions. For the purpose of further concentrating and isolation of potassium nitrate (ammonium nitrate) in the mixture with potassium (ammonium) chloride and sulphate, the retentate from reservoir (5) is supplied to electrodiolysis apparatus of EKR type (6), where an auxiliary solution

of potassium (ammonium) chloride is supplied simultaneously as a separate flow from vessel (7). The resulting concentrated solution of potassium nitrate (ammonium nitrate) may be used as a mineral fertilizer.

Another concentrated solution containing  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  at first enters reactor (8) for purification from  $\text{Ca}^{2+}$  with the help of  $\text{Na}_2\text{CO}_3$ , and then it enters reactor (9) for the precipitation of  $\text{Mg}(\text{OH})_2$  due to the use of  $\text{NaOH}$ . The purified  $\text{NaCl}$  solution is used for electrochemical preparation of sodium hypochlorite (10).

The diluate from the electrodiolysis installation is directed to the reverse osmosis apparatus for additional purification to the necessary norm. The salt content of the diluate should be close to that of initial water in order to avoid complications in the operation of the reverse osmosis installation. Thus, the developed scheme involves the possibilities of these processes in the most efficient and economical manner: reverse osmosis is applied to obtain high-quality drinking water and partially concentrated retentate, while electrodi-

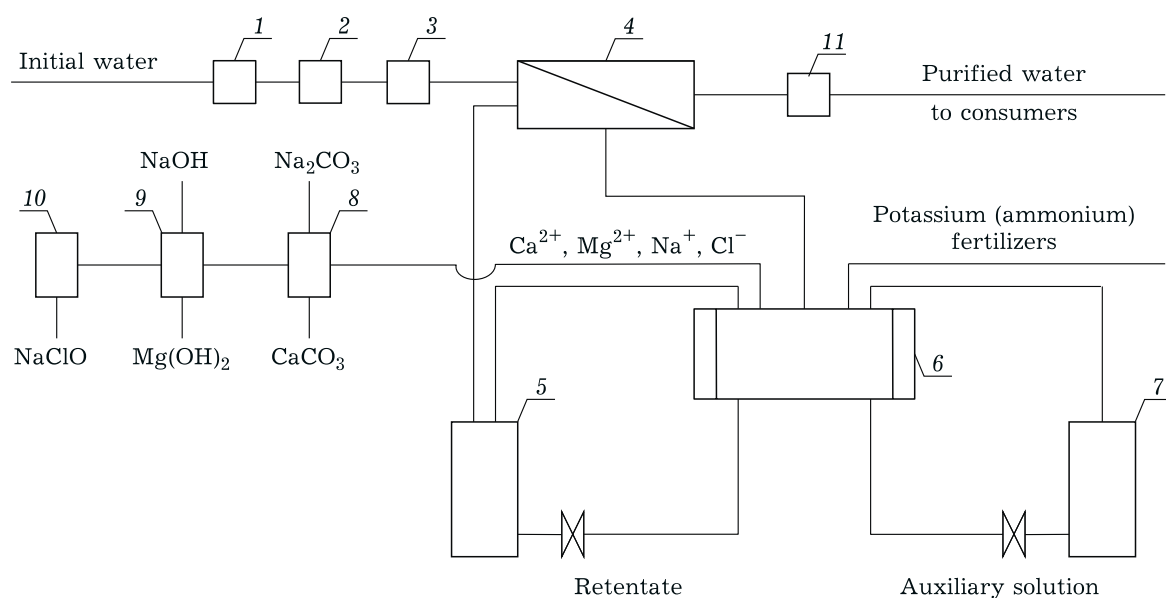


Fig. 7. Principle flow diagram of the purification of nitrate-containing water with waste processing: 1 – coal filter; 2 – ultraviolet apparatus; 3 – microfilter; 4 – low-pressure reverse osmosis apparatus; 5 – reservoir for retentate; 6 – electrodialytor-concentrator; 7 – vessel for auxiliary solution; 8, 9 – reactor; 10 – electrolyser; 11 – water conditioning unit.

alysis is used to obtain partially desalinated diluate and maximally concentrated brine.

## CONCLUSION

A fundamentally new concept was proposed at the A. V. Dumanskii Institute of Colloid and Water Chemistry of the NAS of Ukraine (ICWC) for high-quality drinking water supply to the population. The concept is connected with the transition of drinking water supply to the use of ABU in cities and settlement. These installations possessing relatively low productivity (1–5 m<sup>3</sup>/h) may be mounted in each urban locality or in rural settlements, they should produce water only for drinking and food preparation. In this case, the high quality of drinking water is provided not only by the absence of its contact with outdated centralized water supply systems but also due to the use of chloride-free decontamination technology.

To solve this problem, autonomous membrane installations for water preparation of collective and individual use with biotesting and analytical control were developed at the ICWC. The selection of necessary methods of water purification to the requirements of the national standard of quality is based on the flexible block principle, which allows one to vary blocks and arrange their positions depending on water composition.

In these installations, much attention is paid to preliminary purification of initial water. For this

purpose, it was proposed to use microfiltration tubular ceramic membranes made of clay minerals, developed at the ICWC. It was demonstrated that filtration of natural waters under the pressure of 0.2 MPa through these membranes allowed almost complete removal of the particles causing water turbidity; the content of iron and manganese ions decreased to the level of MPC in drinking water. Higher parameters of underground water purification in comparison with surface water are due to dynamic modification of the ceramic membrane by Fe (III) hydroxo compounds present in underground water, and the steric mechanism of action.

The ceramic membrane modified preliminarily by Al (III) hydroxo compounds, which it captured almost completely due to the steric mechanism, exhibited high retention capacity also to fluoride ions. This may be explained by the formation of aluminofluoride complexes and their adsorption by Al (III) hydroxide. It is proposed to use ceramic membranes for water defluorination to the drinking quality for the initial fluoride concentration up to 22.0 mg/dm<sup>3</sup>, pH<sub>in</sub> 6.5–7.0, working pressure 0.8–1.0 MPa, permeate selection coefficient up to 80.0 %, specific productivity 0.10–0.12 m<sup>3</sup>/(m<sup>2</sup>·h) and the concentration of modifying additive prepared from Al (III) hydroxo compounds 4.0–6.0 mg/dm<sup>3</sup>.

The high retention capacity to Al (III) hydroxo compounds was also exhibited by the lignocellulose (wood) membrane developed at the ICWC.



It was demonstrated that this membrane purified water from Al (III) hydroxo compounds to the MPC of Al (III) ions in drinking water in the case of their initial concentration up to 150.0 mg/dm<sup>3</sup>, pH 6.5–8.1, pressure 1.0 MPa, the selection coefficient of permeate up to 70 % and specific membrane productivity 0.03–0.06 m<sup>3</sup>/(m<sup>2</sup>·h). To increase specific membrane productivity, the procedure of periodic regeneration of the membrane with the solution of citric acid was developed.

A complex of investigations was carried out, and their results allowed developing the technological scheme of water purification from nitrate ions to the level of their MPC in drinking water. The scheme involves also waste processing through a combination of membrane-based and other methods of water purification. It was established that it is possible to purify water from nitrate ions to the standard level for drinking water in the case of their initial concentration up to 500.0 mg/dm<sup>3</sup>, pressure 1.5 MPa, permeate selection coefficient up to 90 % with the help of reverse osmosis membranes of TFC-75 F roll element. The possibility of deep concentrating of reverse osmosis retentate containing nitrates and preparation of mineral fertilizer with the help of improved electro dialysis was demonstrated.

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