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Original Research

Studies of Sustainable Desalination of Groundwater Using a Membrane Apparatus

Gani Iztleuov[1*], Abdugani Azimov[2], Marat Sataev [2], Alexandr Kolesnikov[3]**

[1]Department of Ecology, M. Auezov South Kazakhstan University, Shymkent 160012, Kazakhstan
[2]Research Laboratory Innovative water treatment systems, M. Auezov South Kazakhstan University, Shymkent 160012, Kazakhstan
[3]Department of Life Safety and Environmental Protection, M. Auezov South Kazakhstan University, Shymkent 160012, Kazakhstan

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Abstract

Today, all over the world, an important role in the sustainable provision of high-quality drinking water to the population is played by improving the quality of clean water, increasing the efficiency of water use, and ensuring the safety of both the population and countries. In these studies, experiments have been conducted to develop the design of a membrane apparatus capable of effective desalination of groundwater. According to the results of the study, the dependences of permeability and selectivity on the concentration of substances in water, pressure, and water flow velocity were determined. Based on the conducted experiments and the results obtained, a technological scheme and new results have been developed that can be used for sustainable desalination of groundwater and, accordingly, to ensure safe technology for membrane separation of nitrate, chloride, and sulfate salts, improve water quality, increase water use efficiency, and ensure freshwater reserves. The experimental results of groundwater purification in the developed membrane apparatus contribute to the purification of groundwater for chlorides up to 56%, for nitrates up to 99%, for sulfates up to 62%, and for dry residue up to 82%. The experimental results obtained comply with sanitary and hygienic requirements and are suitable for the sustainable use of groundwater as drinking water. It has been experimentally established that the dependence of the degree of regeneration on the rate of its drying is achieved within 1 hour of regeneration and is 99%.

Keywords: groundwater, pollution, desalination, membrane apparatus, regeneration

Introduction

One of the goals of sustainable development is to ensure the availability and rational use of water resources and sanitation for all. Important indicators for this goal of sustainability are the percentages of the population that uses safely managed drinking water, has access to safely managed sanitation, improves water quality, increases water use efficiency, and ensures freshwater supplies. Central Asia has huge freshwater resources; however, they are unevenly distributed throughout the country, as a result, many areas of Kazakhstan and Central

*e-mail: gani.iztleuov@auezov.edu.kz
Tel.: +7-705-256-6897
**e-mail: kas164@yandex.kz

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Asia (Fig. 1) lack water suitable for water supply to the population and for the irrigation of agricultural land [1, 2]. The two means of implementing these problems are to expand water and sanitation support to developing countries and to support local engagement in water and sanitation management [3, 4]. Central Asia (CA) is one of the most arid regions in the mid-latitudes and one of the major regions with shallow groundwater tables [5, 6]. Additionally, water conflicts in CA are among the most serious in the world, and the reduction in surface water resources may exacerbate these disputes, threatening regional progress [7, 8]. Several studies have reported the excessive salinity of the water downstream of the Amu Darya (ADR) and Syr Darya (SDR) rivers and described the sources of pollutants discharged into surface water [9]. In the arid regions of the globe, there is an acute shortage of freshwater supplies. Freshwater is a limiting resource on these lands, and groundwater withdrawal significantly exceeds replenishment [10, 11]. In another paper, based on the monitoring of underground water supply sources of pastures within various zones of the region, their structural elements and technical conditions are analyzed, and quantitative and qualitative parameters are presented [12, 13]. There is a publication on the problems of groundwater zoning by various indicators and problems of groundwater treatment [14, 15]

Natural brackish and salt water can find direct (without desalination) use instead of fresh water in industry, and agriculture under certain conditions, and for drinking water and household water supply under artificial desalination [16, 17]. The problem of artificial desalination has several interrelated aspects: technical, hygienic, economic, and hydrological-hydrogeological. The latter implies a reasonable solution to the following problems: where, from which source, in what quantity, and in what quality (composition) it is possible to obtain primary water for desalination [18, 19]. It should be noted that artificial desalination is fundamentally different from other measures to improve water supply that redistribute already existing freshwater resources. As a result of artificial desalination, new masses are formed, which are not only included in the balance sheets of water management, but also participate in the natural moisture cycle [20, 21]. However, for many areas of the world and for our country, in particular, desalination of the waters of the inland seas or salt lakes, especially groundwater with high mineralization, is important. To justify measures for the use of groundwater for improved mineralization, a certain amount of special hydrogeological information is required. However, historically, due to the requirements of the experiment, the attention of researchers was mainly attracted by fresh groundwater, which spread at relatively shallow depths. Recently, there has been an interest in deep-lying waters with high mineralization-salt solutions of industrial importance. Salt and brackish waters were studied not specifically and systematically, but randomly and randomly [22-25].

In Kazakhstan, there are local problems of groundwater pollution, which can develop into regional ones if emergency measures are not taken. Analysis of the state of forecast resources and proven groundwater reserves shows that the Turkestan region has significant resources [26, 27]. In the Turkestan region, groundwater plays an important role in providing the population and agriculture with high-quality drinking water. Groundwater in the territory of the Turkestan region is found in various hydrogeological conditions. Their protection against pollution is different and is determined mainly by the depth of groundwater occurrence, the presence, power, and composition of water-resistant sediments in the aquifer roof, the distance from the source of pollution, the filtration properties of water-resistant sediments, and the migration capacity of the polluting component [28-30].

The basis for the development of the topic was the deterioration of the quality of drinking water and the need to study the quality and environmental conditions to develop optimal technical and technological solutions and determine the recommendations of the regime and design parameters of equipment for their purification. Known membrane apparatus for filtering and water flow, containing a housing with inlet and outlet pipes,

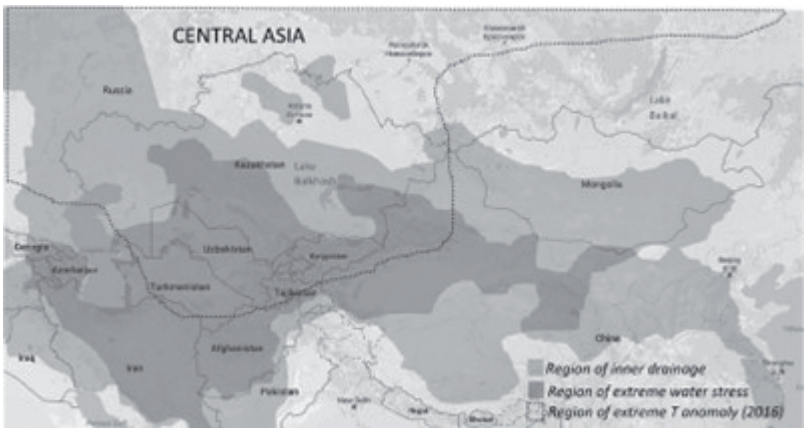

Fig. 1. Map of Central Asia, illustrating its extensive regions of inner drainage.

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fixed disc filter membranes, mesh elements mounted for rotation, and cylindrical elements of porous elastic material, freely located between the membrane and the mesh element with the possibility of rolling over the surface membranes [31].

A device for cleaning liquids is also widely used, containing a cylindrical body with a pipe for the inlet of the liquid being cleaned, located tangentially to the generatrix of the body, pipes for the output of purified and under-cleaned liquid, and a tubular membrane module containing a frame with drainage holes and an outer semi-permeable membrane, installed with a gap relative to the inner body walls. The lower end of the housing is cone-shaped. The tubular membrane module is equipped with elastic annular elements installed with the possibility of reciprocating movement when a predetermined value of the pressure drop across the membrane is reached [32].

This device has such disadvantages as rapid wear of elastic elements during rotation over the surface of the membrane and low productivity of the device.

This paper attempts to redress the imbalances in previous studies by developing and proposing a membrane apparatus that has such advantages as simplifying the design of the apparatus, increasing the efficiency of mixture separation, and increasing the duration of the membrane [33-38].

The objectives of this work were:

– development of a membrane device for desalination of underground waters;
– determination of effective conditions and modes of desalination of water;
– provide sustainable, safe, and affordable drinking water, improve water quality, increase water-use efficiency, and ensure freshwater supplies in the Turkestan region.

Experimental

Materials and Methods

Fabrication and Characterization of Membranes

For the desalination of underground waters, a membrane made of aromatic polyamide MGA-90 was used.

Technological and physicochemical characteristics of semi-permeable membranes are described in Tables 1 and 2.

Mass transfer at the surface of an ultrafiltration membrane is usually considered from the standpoint of the film theory, according to which laminar boundary layers appear at the phase interface, within which concentration gradients exist. The main resistance to mass transfer is concentrated in these layers. During the ultrafiltration process, solvents and low molecular weight solutes predominantly pass through the membrane. An increase in the concentration of retained substances in the boundary layer near the surface membrane properties is known as concentration polarization.

Tables 2-4 present the main characteristics of membrane desalination, energy consumption, overall dimensions of the device, and requirements for the quality of water supplied to the reverse osmosis plant.

Filtration Experiments

The description and view of the membrane installation used for desalination of groundwater are shown in Fig. 2 [38, 39]. The shape of the membrane unit is a cylinder (1), inside which membrane modules are installed, it consists of a tubular frame (2), inside which there are special tubes (3) for the passage of the liquid to be treated, in the outer layer of which semi-permeable membranes are located (4), a variable cover of the membrane unit (5), and purified water is connected to In the body of the membrane unit, there is a pipe (8) that pumps the salt water to be treated. Along this pipe, there is a filter (9) with large holes that filter the water to be treated. Completely untreated water is removed by a special pipe (10). At the top of the membrane unit, there is a special variable valve (11), in the center of the nozzle, there is a flexible elastic element (12), made in a cylindrical shape, which can rotate around its axis using an electric motor (13) made of porous material.

The membrane unit works with the following principle: water for desalination is filtered through a filter (9) with large holes, passing through a pipe (8) located tangentially in the membrane housing. The water to be purified is made in a ring movement in the membrane unit; the largest particles are sent to the periphery under the influence of physical forces and precipitate,

Table 1. Technological characteristics of semi-permeable membranes.

Membrane brand	Selectivity for NaCl, 5 g/dm^3, %	Permeability at p = 5 MPa, dm^3/(m^2 day)
MGA-90	90	350

Table 2. Main characteristics of membrane water purification

Productivity, m^3/hour	Working pressure, MPa	Filtrate-concentrate ratio in %
50	3	80/20

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Table 3. Main characteristics of energy consumption.

Power supply	Consumption power, kWt	Email pump power Maprotec, Grundfos, kW
380V/50Hz	3.0	20.0

Table 4. Main overall dimensions of the device.

Diameter, m	Height, m	Membrane type	Porosity, %	Pore diameter, µm
0.4	0.6	Osmonics	80	0.001

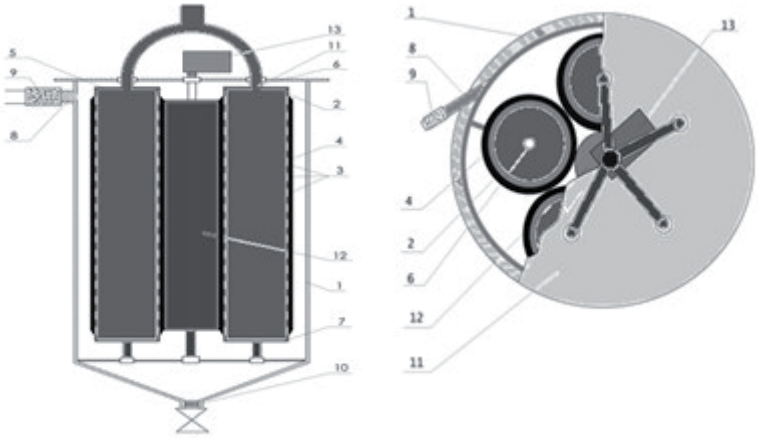

Fig. 2 .Top view of the membrane apparatus: 1-body of a cylindrical membrane drain, 2 - pipe for the passage of desalinated water 3-drainage holes, 4-semi-permeable membranes, 5-a valve cover, 6-a pipe for the discharge of desalinated water, 7-an empty bottom, 8 - a pipe for the introduction of desalinated water, 9-a large - pore filter 10-pipe, 11-a removable cover, 12-an elastic element, 13-an electric motor.

which contributes to the long-term preservation of the membrane's purification capacity. Salt water is purified from impurities and salts by passing through semi-permeable membranes, and through special drainage holes, 3 penetrating inside the membrane module, and special desalinated water is discharged through the outlet pipe (6). When the membrane unit is operated in filtration mode, the pipe (10) for the discharge of uncleaned liquid is closed.

When the apparatus is operating, there is a blockage of the membrane 4 surface, which leads to an increase in the pressure difference in the tubular-membrane module. When the magnitude of the pressure difference reaches the given one, the elastic roller element (12) is automatically activated by means of an electric motor (13).

When the elastic roller-shaped element (12) is activated, it comes into contact with the surface of the membrane, and (4) removes contaminants with a tangential water jet by washing, resulting in the membrane (4) being cleaned and washed, and the unrefined liquid is discharged through 10 pipes. In this way, the membrane cleaning, i.e., regeneration frequency, prevents its wear 4. The elastic element is made of porous elastic material, which does not damage the surface of the membrane and cleans mechanically. After the membrane unit for water desalination has been operating for up to 2.5-3 years, the membranes inside it are replaced with new ones.

For conducting research on membrane, treatment of nitrates, chlorides, and sulfates in groundwater, an experimental device was used, as shown in accordance with Fig. 2 and 3.

The experimental installation works as follows: water for primary production (1) is supplied from the tank by means of a pump (2) through a filter (3) of large cleaning to the membrane (4) device. Purified water (filtered) is sent to the container (5), and contaminants (concentrate) are sent to the container (6). When the pressure drop measure reaches the Tis value, an electric (7) motor drives the elastic camshaft element.

Characterization of the Water Sample

The permeate conductivity was measured with a MeterLab (CDM210). The measurements of the permeate mass and conductivity were automatically registered via MatLab 9.7 (Math Works, Natick,

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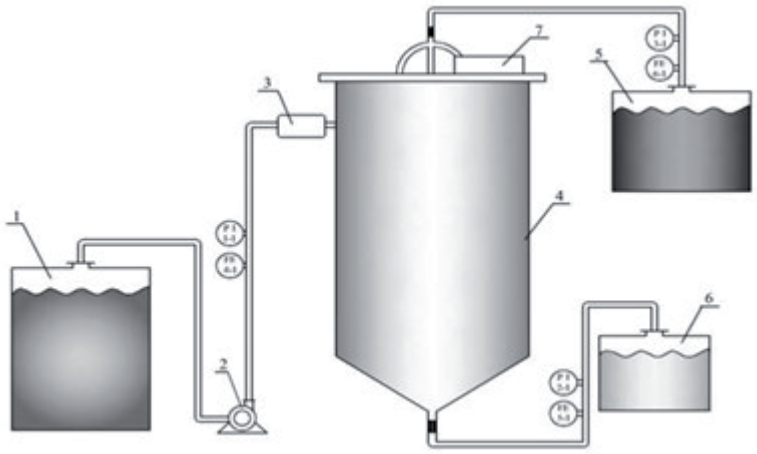

Fig. 3. Scheme of an experimental installation for desalination of groundwater
1-production water tank; 2-pump; 3-large cleaning filter; 4-membrane device; 5-container for treated water (filter); 6-container for contaminants (concentrate); 7-electric motor. a) chloride ions, b) sulfate ions, c) nitrate ions, d) duration of work, days.

MA, USA). Another important issue in the design of membrane installations is the accuracy and reliability of the method of measuring the salinity of the water flow. For continuous monitoring of the quality of the water flow, a conductometric method based on the measurement of its conductivity is used. Conductivity is a quantitative characteristic of dissolved components and can be determined by direct measurement of the flow of a water stream. The standard unit of conductivity in water treatment is micro-Siemens (mS or mmho). The conductivity of natural waters can range from 20 mS for meltwater to up to 70,000 mS for seawater. The concentration of relevant cations was measured by inductively coupled plasma spectroscopy (ICP) (PerkinElmer® Optima 8000 Optical Emission Spectrometer, Waltham, MA, USA) after calibration with standards from PlasmaCAL Q.C. No 4. (SCP Science, Clark, QC, Canada).

Results and Discussion

A feature of membrane desalination is the creation of mixed-type devices that allow for efficient performance during daily or seasonal events between the production of water and electricity. When using reverse osmosis, pretreatment of the main water must be considered to prevent contamination of the working membranes [40-57].

Table 5 presents the results of pilot tests, and Table 6 presents the main requirements for the quality of water supplied to the reverse osmosis plant. The results of groundwater purification in the membrane apparatus are given in percentages: chlorides 56%, nitrates 99%, sulfates 62%, dry residue 82%, and smell and flavor points of zero, which meet the sanitary and hygienic requirements and are suitable for sustainable use as drinking water in the Turkestan region. This corresponds in a similar way to previously conducted studies [40-57].

The selectivity of reverse osmotic membranes for chloride differs from the selectivity of other inorganic and organic solutes; therefore, when conducting experimental work on membranes, it is necessary to have information about the selectivity of membranes for various ions and substances.

Table 7 below provides selectivity data for the polyamide reverse osmosis membrane under study. The partition selectivity of the membrane is explained by one of two parameters: the (salt) retention (R) and the partition factor (α). For barometric processes, in particular, for the separation of aqueous solutions of salts, selectivity is defined as the (salt) retention in relation to the solute:

$$R = \frac{C_f - C_p}{C_f} \times 100\ \% \qquad (1)$$

Here, C_f is the concentration of the solute in the raw material;
Cp - is the concentration of the dissolved substance in the permeate (filtrate).

As can be seen from the table, the retention selectivity of divalent ions such as barium, magnesium, and sulfate is higher than that of monovalent ions such as potassium, sodium, and chloride.

Ions are arranged in the order of decreasing selectivity:

$Mg^{2+}>Ca^{2+}>Ba^{2+}>Na^{+}>K^{+}$ (total anion NO_3^{--})
$Mg^{2+}>Ca^{2+}>Ba^{2+}>Na^{+}>K^{+}$ (common anion Cl^{-})
$Mg^{2+}>Ca^{2+}>Ba^{2+}>Na^{+}>K^{+}$ (common anion SO_4^{2-})
$SO_4^{2-}> Cl^{-} > NO_3^{-}$ (total cation Mg^{2+})

These series correspond exactly to the series created on the basis of the heat of hydration and allow the distribution of the determined law to other solutions.

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Table 5. Results of pilot tests of groundwater purification in a membrane apparatus.

No.	Name	Content in water before cleaning	Contents in water after cleaning	MPC
1	Smell, points	2	0	2
2	Flavor, points	2	0	2
3	Turbidity, mg/dm^3	0	0	1.5
4	Color, deg	0	0	20
5	Dry residue, mg/dm^3	1120	200	1000
6	Total hardness, mEq/dm^3	10	7	7-10
7	Hydrogen index, pH	9	7	6-9
8	Oxidability, mg/dm^3	3	-	2
9	Chlorides, mg/dm^3	368	160	350
10	Sulfates, mg/dm^3	566	210	500
11	Fluorine, mg/dm^3	0.8	0.6	1.5
12	Nitrates, mg/dm^3	10.7	0.1	45
13	Coli index	-	-	less than 3
14	Total number of bacteria per1 l.	-	-	100

Table 6. Basic requirements for the quality of water supplied to the membrane installation.

No.	Options	Values
1	Turbidity	0.1 mg/l
2	Overall hardness	1.5 mol/l
3	Total iron (Fe)	0.1 mg/l
4	Oxidability	5 mgO_2/l
5	Free chlorine	0.1 mg/l
6	Salt content of treated water, g/l, no more	50
7	Suspended solids	4 mg/l
8	pH range	2.0-11.0
9	Sediment Density Index (SDI)	3.0

Based on the data given in the table, the dependence of the influence of worker pressure on the selectivity of ions of nitrate, chloride, and sulfate salts is given (Fig. 4a, b, and c.).

The operating pressure required for membrane desalination systems varies with the salinity of the base water. Due to the acceleration of the flow, the desalination efficiency increases with the increase in water temperature, but the efficiency of the working membranes is limited by the water salinity parameters.

Fig. 4d shows the effect of the selectivity of productivity on the duration of operation. The condition of the water, its temperature, as well as the number of days of use, significantly affect the service life of the membranes.

As can be seen from the graph, the efficiency and selectivity decrease as the operating time of the membrane device increases. The effective working period is 95 calendar days.

Based on the research information in the above table, the cations and anions of the studied solutions can be placed in the order shown in tables 8-10 depending on their individual properties.

As can be seen from the research results, the ion selectivity of the studied solutions does not affect the specific dependences of the sizes of the ions, the surface density of their charges, or the thermal hydration of the ions. The change in selectivity of ions is explained by the mismatch between their radius, surface density, and heat of hydration. Change in selectivity of divalent cations Ba^{2+}<Ca^{2+}< Mg^{2+}, the sequence of changes in the radius of univalent cations is K+< Na+, the sequence of changes in the radius of anions is $^{-}$< Cl^{-}< SO_4^{2-}.

The ratio of the velocities of the circumference of the surfaces of an elastic element with a ribbed surface and a tubular membrane model allows an increase in the degree of purification of the membrane revival by 1.2-1.7%. The required level of cleaning of membrane surfaces is not provided when the ratio of the surfaces of the circumferences of the chronic element with the wall surface and the surfaces of the tubular membrane model is less than 1.2 times, since the contact voltage on the surface of the sediment is significantly lower. With a ratio of more than 1.7 times the circumference of the surfaces of the elastic element with a ribbed surface and the surfaces of the model with a tubular membrane, the wear of the membranes increases slightly, and the energy consumption increases. With the ratio between

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Table 7. Data on the distribution of selectivity.

Basic salts mg/l	Cations					Anions			Salt selectivity φ, %
	K^+	Na^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	NO_3^-	Cl^-	SO_4^{2-}	
KCl	91						92		91.5
NaCl		92.1					92		92
$MgCl_2$			99.8				92		96
$CaCl_2$				99.6			92		95.8
$BaCl_2$					94		92		93
KNO_3	91					91.6			91.3
$NaNO_3$		92.1				91.6			92
$Mg(NO_3)_2$			99.8			91.6			95.7
$Ca(NO_3)_2$				99.6		91.6			95.6
$Ba(NO_3)_2$					94	91.6			92.8
K_2SO_4	91							93.3	92.1
Na_2SO_4		92.1						93.3	92.7
$MgSO_4$			99.8					93.3	96.5
$CaSO_4$				99.6				93.3	96.4
$BaSO_4$					94			93.3	93.6

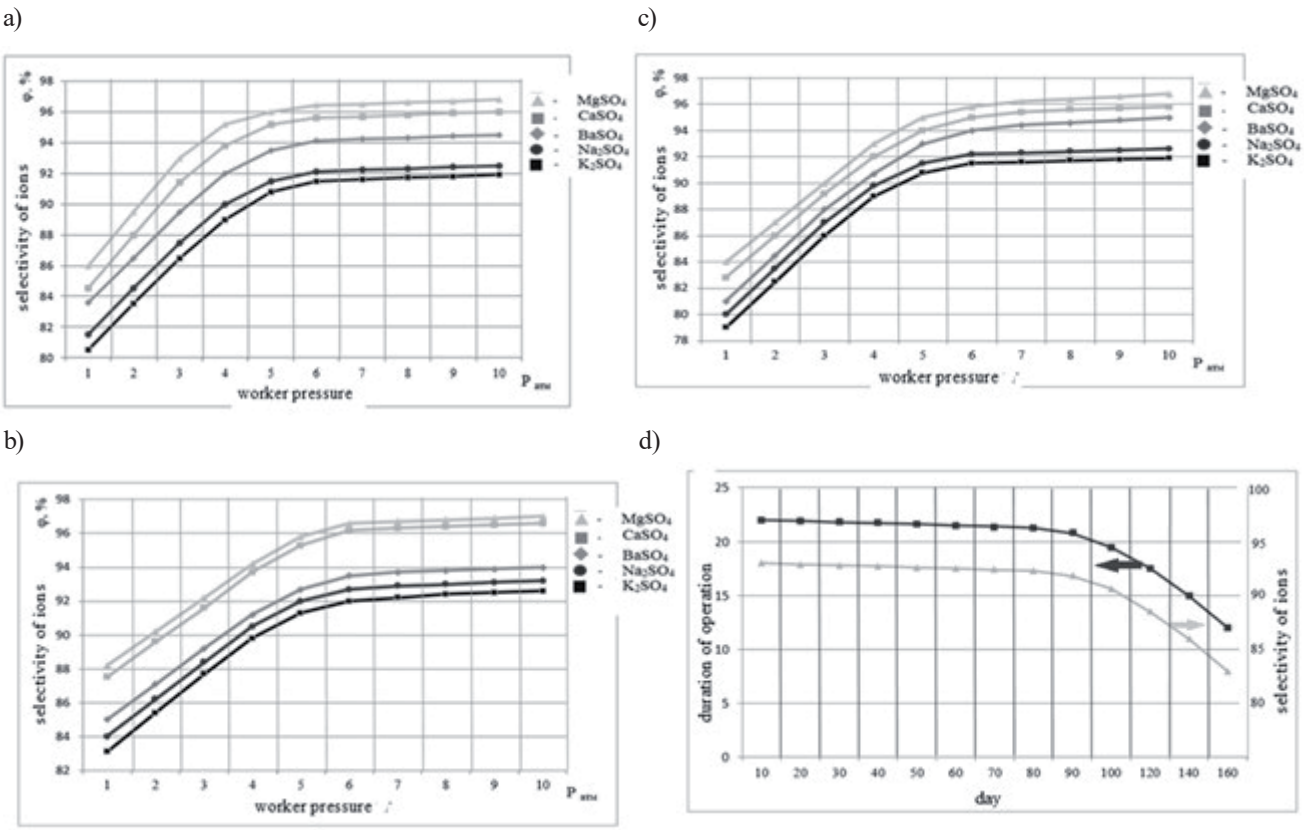

Fig. 4. The effect of worker pressure on the selectivity of salts (a,b,c) and the effect of productivity selectivity on the duration of work d) in days.

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Table 8. Properties of divalent cations.

No.	Ions	Ion radius,	Surface charge density of ions, Cl/²·	The hydrate number of ions	Thermal hydration of ions, kJ/mol	Specific hydration heat of hydration of ions, kJ/mol per unit of hydration number
1	Mg^{2+}	0.780	0.4193	4.41	1955	443.3
2	Ca^{2+}	1,090	0.2147	5.04	1616	320.6
3	Ba^{2+}	1,399	0.1304	4.7	1329	282.7

Table 9. Characteristics of monovalent ions.

No.	Ions	Ion radius,	Surface charge density of ions, Cl/²·	The hydrate number of ions	Thermal hydration of ions, kJ/mol	Specific hydration heat of hydration of ions, kJ/mol per unit of hydration number
1	Na^{+}	0.980	0.1328	3.12	423	135.5
2	K^{+}	1,330	0.0721	1.10	339	308.1

Table 10. Characteristics of some monovalent and divalent anions.

No.	Ions	Ion radius,	Surface charge density of ions, Cl/²·	The hydrate number of ions	Thermal hydration of ions, kJ/mol	Specific hydration heat of hydration of ions, kJ/mol per unit of hydration number
1	Cl^{-}	1.81	0.0389	0.91	351	385.7
2	NO_3^{-}	1.89	0.0357	0.83	310	373.4
3	SO_4^{2-}	2,3	0.0482	1.13	456	403.5

the chronic element with a ribbed surface located in the interval of 1.2-1.7 and the circumferential surfaces of the model surfaces with a tubular membrane, slightly higher shear stresses occur in the sediment, leading to its effective destruction and the next rinsing with a rinsing liquid.

This work eliminates imbalances in previous studies of the device, which had disadvantages such as rapid wear of elastic elements when rotating on the membrane surface and low device performance. The membrane device proposed by us has such advantages as simplifying the design of the device, increasing the efficiency of separation of the mixture, and increasing the duration of the membrane. According to the research results, it can be concluded that the use of an elastic roller element with a wall surface, as well as an installation for supplying washer fluid, reduces membrane wear and increases the efficiency of cleaning pores and membrane surfaces.

Conclusions

Based on the results of the conducted research, the following conclusions can be drawn:

- The design of the membrane apparatus has been developed, which makes it possible to increase the efficiency of desalination of groundwater and separation of the mixture and increase the duration of the membrane operation.
- The dependences of permeability and selectivity on the concentration of substances in water, pressure, and water flow rate are determined. At a rate of 0.8, sufficient permeability is provided for the installation of the membrane, where it is equal to 92 l/m^2h.
- The dependences of permeability on the volume of regeneration by an elastic roller are determined. After the fifth regeneration, the permeability is 70 l/m^2, which is sufficient for the effective operation of the membrane device.
- The dependence of the degree of regeneration on the rate of its drying showed that a high degree of regeneration, equal to 99%, is achieved in 1 hour of regeneration.
- It was found that an increase in the number of revolutions of the roller also leads to an increase in the degree of regeneration.
- Effective conditions and modes of groundwater desalination have been determined, such as improving the quality of drinking water and increasing the barrier role of structures in the event of severe man-made pollution of the water source.
- Based on the analysis of the influence of temperature, it was found that an increase in fluidity due to permeate is associated with a decrease in the viscosity of salt solutions, and ion selectivity varies

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in the order φBa2+<φCa2+<φMg2+, φK+< φNa+, φNO3 -< φCl - < φSO4 and depends on the specific heat of hydration.

– It has been established that in the complex problems of drinking water supply, the priority is improving the technology of water purification taken from surface sources.
– Deep water purification from most pollutants can only be carried out using a highly efficient membrane device.
– The results of groundwater purification in the membrane apparatus are determined in percentages: chlorides - 56%, nitrates - 99%, sulfates - 62%, dry residue - 82%, and the odor and taste index is zero, which meets sanitary and hygienic requirements and is suitable for sustainable use as drinking water in the Turkestan region.

Thus, the results obtained in the course of the above studies and their results can be used for sustainable desalination of groundwater, ensuring safe technology for membrane separation of nitrate, chloride, and sulfate salts in the development of membrane technologies, ensuring the availability of drinking water, improving water quality, increasing water use efficiency, and ensuring freshwater reserves in the Turkestan region of Kazakhstan.

The developed technological scheme and the design of the membrane installation can be used for sustainable groundwater purification, post-treatment of tap water at the place of consumption, and post-treatment of water at existing stations according to the traditional scheme, including coagulation, sedimentation, and filtration. Depending on the composition of the source water, it is possible to change the installation and the type of membranes used.

The practical significance of the developed membrane device design, which allows an increase in the efficiency of desalination and extends the life of the membrane, is protected by the following intellectual documents; in particular, the innovative patent of the Republic of Kazakhstan No. 85224, the innovative patent of the Republic of Kazakhstan No. 27720, and the patent of the Republic of Kazakhstan No. 31896.

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Conflict of Interest

The authors declare no conflict of interest.

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