MEMBRANE DISTILLATION USING SOLAR ENERGY – MEMBRANE MODIFICATION

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Abstract: *The desalination is an important technological process applied not only to obtain drinking water, but also for wastewater treatment from e.g. dyes, textile and mining industry. In this process, membrane processes such as reverse osmosis, pervaporation, electrodialysis and membrane distillation are quite commonly used. This work focuses on membrane distillation. The research was carried out in order to produce membranes absorbing solar radiation, to use this energy in the distillation process. Membranes were produced using the phase inversion method from polysulfone polymer at various proportions of ingredients to select the optimal blend composition. The fabricated membranes were investigated to assess wettability, maximum pore size and execute preliminary tests of the membrane distillation process.*

Keywords: WATER DESALINATION, RENEWEBLE ENERGY, MEMBRANE DISTILLATION, POLYSULFONE MEMBRANE, COOPER OXIDE

1. Introduction

According to current global estimations, approximately 2.7 billion people around the world do not have access to drinking water [1]. Prognosis of this situation is getting worse and worse, due to the climate changes and deteriorating quality of the inland waters, mainly due to the environmental pollution. It is estimated that by 2025, even 2/3 of world population may not have access to the drinking water [2]. At the moment, more than 14000 installations desalting sea water are actively working, giving total efficiency of about few billions liters per day. More than half of those type of systems are placed in the area of the Middle East and the Persian Gulf. They working principle is based on conventional electrical power and heating stations.

The use of the conventional fossil fuels for desalting sea water has two main drawbacks: increases costs of purified water as well as has negative influence on natural habitat [3]. Due to the fact that amount of available fossil fuels is constantly decreasing and geographical localization of the areas suffering from drinking water shortage in zones with high solar radiation, the application of the renewable sources of energy in the water desalting and purification process is getting more and more cost-effective.

Desalination of the water, according to the basic definition, is a process in which salty water is separated to fractions of fresh water (do not containing salt) and brine concentrate (fraction of higher salinity) [4]. Generally, desalination processes can be divided into three categories: thermal, membrane, and alternative. The last type includes freezing and ion exchange techniques. Thermal processes can be categorized further, including: multi-stage flash distillation (MSF) [5], multiple-effect distillation (MED) [6], vapour-compression evaporation (VC) [7], cogeneration [8], solar water desalination (SD) [9]. Cogeneration using off-heat from already existing installations is difficult, cause their localization not always cohere with places endangered by lack of access to drinking water.

Solar water desalination process needs large surface areas dedicated to collectors, that inhibits running the process in large scale. Energy consumption in the thermal processes is significantly exceeding reasonable values of the cost-effective methods. Therefore membrane-based techniques are getting more and more popular. Membrane processes belongs to the technology for splitting mixtures or solutions exploiting porous or non-porous membranes.

Water desalination processes are based mostly on following phenomena: reverse osmosis (RO), electrodialysis (ED) and membrane distillation (MD).

Reverse osmosis is a process running under pressure between 10 to 100 bar, exploiting a membrane which is able to filter low-mass compounds, or even ions. Investigations of the RO applied in the sea water desalination have been conducted for over 30 years, leading to very good process optimization and decreasing the energy consumption to the level of 2 kWh/m3. This value is very close to the theoretical energetically demand of 1_kWh/m3. Regardless, well-established technology and fine optimization of the process, RO has its drawbacks, e.g. susceptibility for concentration polarization and fouling from inorganic, organic and biological constituents, what influences permeate stream obtained in the process.

When the transport of cations and anions from solution occurs through semi-permeable ion-exchange membranes this technique is known as electrodialysis. The difference in electric potential is the driving force of this process [10]. This method is not that popular as MD, which in the recent years reached success in the water desalination. In contrary to RO settings, where high pressure on the side of the feed causes the process, the driving force of MD is temperature difference. It is possible to run MD at normal pressure, at the feed temperature below the boiling point. The very important asset of MD is possibility to operate at wide range of salt concentrations, because it has no effect on overall driving force of the process. And also obtained this way water is of the high purity and quality. Additionally, due to the thermal parameters of the process it is feasible to use off-heat or renewable sources of energy [10,11,12].

A direct absorption of the solar energy on the membrane is other alternative and innovative method. First research studies of this type conducted at Rice University in Huston reports on efficiency of the process at the level of 5dm3 of water from 1m2 of membrane within an hour, reaching desalination of 99.5%, when using modified membranes. Even though these results are not outstanding in comparison to other MD technologies gives the path for novel approaches for modifications of the MD processes.

The applied membrane has been modified by thin film coating of PVP containing carbon nanoparticles. This type of modification caused blackening of the membrane and increased absorption of the solar radiation [13].

2. Materials and methods

2.1. Chemicals

Polisulfone (PSU) Mn~22,000 (Sigma Aldrich), Ultrapure water (Milli-Q®,Millipore N,N-dimethylacetamide (DMA, 99.5%, Honeywell), Polyvinylpyrrolidone (PVP) K15 and K30 (Fluka), Copper(II) oxide nanopowder (Sigma Aldrich) were used to membrane preparation.

2.2. Solar Membrane distillation process

A schematic illustration of the experimental equipment is presented in Fig. 1. It consisted of a 3L thermostated feed tank

(stainless steel), linked to membrane module (with polycarbonate window) containing membrane (area: 11 cm2). The pump placed in feed tank allowed the feed (salinity water, temperature 50oC) flowing through the membrane unit with flow velocity of 4mm/s. The process was conducted in air gap membrane distillation configuration (air gap is interposed between the membrane cold surface and a condensation surface) in two series: without and with membrane illuminated by an artificial light source Helios 100 W Neodymium Bulb Daylight Lamp. Luminous flux density on the contactor surface ~70000 lux. The condensation surface was made of a copper plate and cooled by circulated water (temperature 8oC). The distillate samples were collected into a measuring vessel with simultaneous measurement of time.

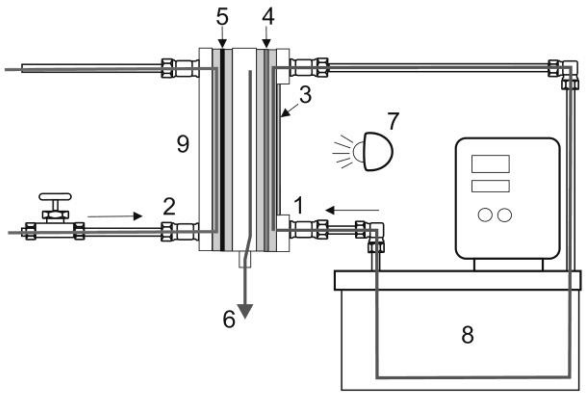

Fig. 1 *Schematic diagram of the laboratory solar membrane distillation setup. 1 – Feed inlet, 2 – cooling water inlet, 3 – polycarbonate window, 4 – membrane, 5 – cooling plate, 6 – distillate outlet, 7 – light source, 8 – feed thermostated tank, 9 – membrane module*

2.3. Membrane preparation

Flat, porous membranes were prepared by the phase inversion method. The, polysulfon was dissolved in DMA to achieve concentration in the range of 18-23%, and PVP was gradually added as blowing agent. The mixture was stirred continuously at 30 °C for 12 h until a transparent solution was obtained. The copper oxide was added to selected solutions to increase the absorption coefficient of light. The detailed composition of the membranes is given in the table 1. In order to carry out the phase inversion process the solution was cast onto a clean glass substrate at room temperature using a stainless steel knife. The knife rod was used to define solution height during casting, the knife height was 240 µm. The substrate was immersed into a ultrapure water bath (temperature 25 °C) in order to carry out subsequent phase inversion process. The resulting membrane was removed from water bath, and immersed into deionized water for 48 h.

Table 1: *Composition of solutions for different membranes*

Membrane	Polysulfone [g]	DMA [g]	PVP 15 [g]	PVP 30 [g]	Copper oxide [g]
1	1,15	5	0,0575	-	-
2	1,15	5	0,115	-	-
3	0,9	5	0,045	-	-
4	0,9	5	0,090	-	-
5	1,15	5	-	0,0575	-
6	1,15	5	-	0,115	-
7	0,9	5	-	0,045	-
8	0,9	5	-	0,090	-
9	1,15	5	0,0575	-	0,115
10	0,9	5	-	0,090	0,090

2.4. Salt concentration

The salt concentration in the collected samples was measured with a universal Elmetron CPC 501 device using a conductometric method and a type CD-2 electrode. The samples of distillate after the process was measured at 20°C using a previously prepared calibration curve.

2.5. Wettability

The contact angle was determined for all prepared membranes using goniometer Surftens-universal (Optik Elektronik Geratechnik). A droplet by volume 2 µl of deionized water was used as the probe. The measurement for each sample was conducted at ten different locations, and average value was reported.

2.6. Distillation flux

The distillation flux was calculated by Eq. (1):

$$J_v = \frac{V}{At} \tag{1}$$

where: V is the volume of the permeate obtained after time t, [m3], A s the area of the membrane [m2] and t is time taken to collect permeate volume V [h].

2.7. Salt rejection

For the purpose of evaluating the desalination performance, the following fundamental formula was used, giving the rejection coefficient (Eq. (2)):

$$R = \left(1 - \frac{c_p}{c_F}\right) \cdot 100\% \tag{2}$$

where: R is rejection coefficient [%], c_P is concentration of salt in the distillate [mg/kg] c_F is concentration of salt in the feed [mg/kg] 8mg/kg (corresponding to the salinity of Baltic Sea)

2.8. Maximum pore size

The bubble point test was used to determine maximum pore size. Maximum pore size was calculated using Eq. (3):

$$D = \frac{4\gamma \cos\theta}{P} \tag{3}$$

where: P [Pa] is the pressure, D [m] diameter of capillary or pore, θ [deg] is the contact angle between the liquid and capillary wall and γ [N/m] is the surface tension of the liquid.

2.9. Overall porosity

The overall membrane porosity was measured by the gravimetric method [14,15]. After the phase inversion, solvent (DMA) was exchanged in the membrane by the deionized water. Samples for overall porosity determination were further immersed in distilled water for another 72 h. Then they were wiped with blotting paper and weighed to determine the wet mass (mw, g). After being dried in vacuum dryer for 24 h at 40 °C, the dry mass of the samples (md, g) was measured. The overall porosity (ε, %) was calculated using Eq. (1).

$$\varepsilon = \frac{\frac{(m_w - m_d)}{\rho_w}}{\frac{(m_w - m_d)}{\rho_w} + \frac{m_d}{\rho_p}} \cdot 100 \tag{4}$$

where ρ_w is the density of water (0.997 g cm^{-3} at 25 °C) and ρ_p is the polymer density (1.24 g cm^{-3} at 25 °C).

3. Results

In Table 2 the results of investigations of the properties of polysulfone membranes produced during study and distillate flux obtained during membrane distillation (feed temperature: 50oC, with and without light) are presented. The resulting membranes were characterized by a low contact angle in the range of 52,2 to 68,3o and pore maximum pore size from 0,13 to 5,52 μm. The overall porosity of the as-prepared PSU membranes was about 90%. It slightly decreased for the membranes with PVP 30 as blowing agent.

Table 2: *Properties of the PSU membrane and comparison of the distillate flux of different membranes*

Membrane number	Wettability	Maximum pore size [μm]	Overall porosity	Distillation flux [dm^3/m^2h]	Salt rejection [%]	Distillation flux with solar energy [dm^3/m^2h]	Salt rejection with solar energy [%[	The fold increase in the light flux
1	67,6	0,17	90,1	9,25	97,78	9,87	99,60	1,07
2	73,8	0,13	88,6	10,00	95,25	11,54	93,24	1,15
3	51,9	0,22	91,4	90,89	6,53	114,62	5,41	1,26
4	56,4	5,52	91,3	269,30	7,59	346,32	8,58	1,29
5	68,3	1,58	89,2	9,87	98,71	10,10	98,87	1,02
6	64,9	1,14	87,1	10,77	98,98	11,58	98,47	1,08
7	66,8	2,64	89,1	28,46	28,38	37,03	15,78	1,30
8	48,0	2,66	89,2	26,93	32,61	35,46	31,55	1,32
9	66,0	2,13	90,5	7,34	92,74	10,21	92,01	1,39
10	52,2	1,10	87,9	19,75	47,19	29,32	30,03	1,48

Only five of the prepared membranes showed the ability to remove salts at the level above 90%, however, for these membranes the distillate flux did not exceed 11 $dm^3/(m^2h)$ for process without additional membrane illumination by an artificial light source. For all membranes, an increase in the distillate flux caused by the light's illuminating of the membrane was observed. The largest fold increase in the distillate flux was observed for the membrane with copper oxide and it is equal to 1,48. The addition of copper oxide increased the coefficient of light absorption.

4. Conclusions

The membrane distillation can solve problem with water demands in regions affected by a shortage of drinking water. Process of membrane desalination can only be carried out at elevated feed temperature, but this require substantial energy from conventional power plants. The research indicates that increasing of the light absorption coefficient of the membrane affects the increase of the distillate flux. The production of innovative membranes with such properties gives the potential possibility of conducting the membrane distillation process in geographical localization areas suffering from drinking water shortage with high solar radiation without the use of energy from conventional sources.

5. Literature

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