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Solutions separation by natural membrane evaporation

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Keywords: solutions separation and concentration, oily wastewater, membrane distillation

The development of cheap water evaporation methods can facilitate the management of various waste solutions. In this work an idea of solutions concentration by water evaporation from the surface of capillary membranes, whose bundles are loosely distributed inside large chambers was presented (Fig. 1). For this purpose, the membrane evaporation was realized by using the capillary module without a housing (module shell). This design allows the process to be carried out with low gas flow (close to natural convection) and for high gas flow velocities (forced convection). In such a system, the solar energy transferred to the air surrounding the installation is used to evaporate the water. During the tests the feed was flowing inside the hydrophobic polypropylene membranes, whereas the water evaporated through the non-wetted membrane pores into the air surrounding the module. The capillary length was 1 m, which allowed to obtain conditions like those in industrial modules. The paper considers how the process parameters and the feed composition affect the efficiency and fouling of membranes.

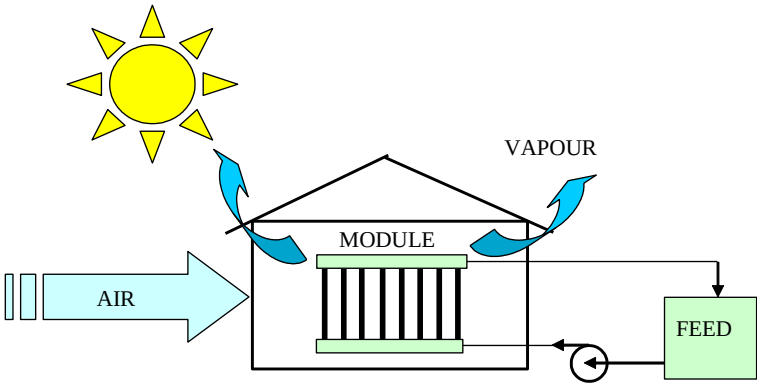

Fig.1. The idea of solution concentration by the natural membrane evaporation

The performed studies confirmed that the process of natural membrane evaporation can be used for concentration and separation of salt solutions. In this case, air parameters, i.e. temperature and relative humidity, have a significant impact on the process efficiency. The evaporation rate increased with increasing air temperature and decreasing the RH value. These results indicate that the natural evaporation process is advantageous to carry out in areas with a dry and hot climate.

Oil fouling and scaling was found during separation of saline oily wastewater. Although this did not cause a significant decrease in the efficiency of the process, the SEM studies showed that in this case it is advantageous to combine the installation with a salt crystalization system, which will reduce the amount of deposit formed on the membrane surface.

Acknowledgments

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Abstract

The development of cheap water evaporation methods can facilitate the management of various waste solutions. In this work an idea of solutions concentration by water evaporation from the surface of capillary membranes, whose bundles are loosely distributed inside large chambers was presented. For this purpose, the membrane evaporation was realized by using the capillary module without a housing (module shell). This design allows the process to be carried out with low gas flow (close to natural convection) and for high gas flow velocities (forced convection). In such a system, the solar energy transferred to the air surrounding the installation is used to evaporate the water. During the tests the feed was flowing inside the hydrophobic polypropylene membranes, whereas the water evaporated through the non-wetted membrane pores into the air surrounding the module. The capillary length was 1 m, which allowed to obtain conditions like those in industrial modules. The paper considers how the process parameters and the feed composition affect the efficiency and fouling of membranes.

Introduction

The membrane evaporation process can be realized by applying porous or non-porous membranes. The dense membranes are used for liquid separation and water desalination by pervaporation (PV). For non-porous uncharged polymeric membranes, the solution-diffusion model usually describes the desalination PV mechanism. According to this model, the water molecules are preferentially adsorbed and diffuse through the polymeric material of the dense hydrophilic membrane, while salt is rejected [1].

In the case of porous membranes, the evaporation mechanism is strongly affected by the hydrophobicity of membranes. The pores of the hydrophobic membranes are non-wetted, in opposition to the hydrophilic membranes, where the feed evaporates from the wetted surface. However, such evaporation of water caused a rapid crystallization of salts on the membrane surface [2], hence, the hydrophilic membranes can be only used for the separation of feed without solutes. When the hydrophobic membranes are applied, the evaporation of water proceeds at the feed/membrane interface and a cross-flow of nonsaturated feed prevents the precipitation of solutes, even for a high concentrated brine [3]. However, an additional resistance is created for vapour diffusion across the membrane pores in this case, which causes a decrease of the evaporation rate from the feed/membrane interface [4].

The driving force for the water evaporation is created by a difference between the partial pressure of water vapor (in equilibrium with a liquid feed), and its value in the air surrounding the membranes (Fig. 1). The obtained permeate flux is proportional to the driving force, which is usually expressed by the application of mass transfer coefficient (K_m) [5, 6]:

$$J = K_m (P_F - P_{Air}) \quad (1)$$

where: K_m – membrane mass transfer coefficient, P_F- water partial pressure at membrane surface, P_{AIR} – water vapour pressure inside surrounding air.

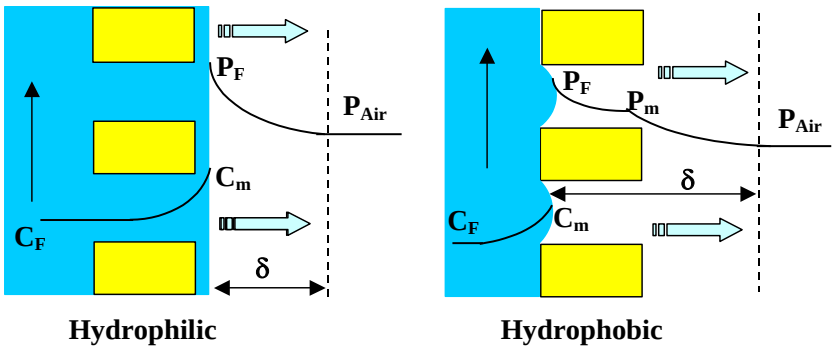


Fig. 1. Water evaporation through wetted (hydrophilic) and non-wetted (hydrophobic) membranes. P –partial pressure, δ -thickness of the viscous boundary layer, C – feed concentration

The value P_{Air} is associated with air humidity, expressed e.g. by relative humidity (RH), thus, increasing a value of the humidity also decreases the evaporation rate. For this reason the process efficiency is limited in the modules with housing, since a value of the relative humidity of the air in the module rapidly increases even for high air flow rates [4, 6].

The water evaporation into air flowing inside module housing is realized using sweeping gas membrane distillation (SGMD). In the SGMD variant the feed is pre-heating, and most of the energy consumption results from the drop in the feed temperature in the module. In the solution proposed in the present study, water evaporates from the surface membranes in the open-module, using the energy from the environment around the installation. The air heated by the sun flows between the capillaries and transfers the energy to the membranes surface. The energy consumption in the process will be mainly due to the operation of the fans. However, even large fans with a capacity of several thousand m^3/h consume much less energy compared to the heat of water vaporization [7]. The idea of the solution concentration by the membrane evaporation process is presented in Fig. 2.

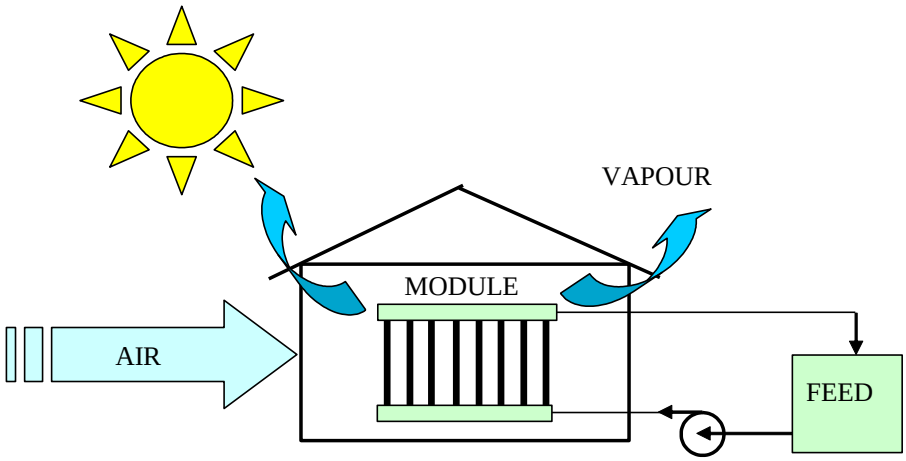


Fig.2. The idea of solution concentration by the natural membrane evaporation

Evaporation is an energy intensive process, therefore, the transport of heat to the interface is the rate-limiting step for the evaporation of liquids into an inert gas. During the natural membrane evaporation, the temperature in the gas phase near the liquid–gas interface is higher than that of the liquid (Fig. 3). If the feed is not heating, the energy for evaporation (Q_V) can only be taken from the gas phase (Q_A), therefore, the water temperature is quickly aligned to the constant value due to a larger thermal conductivity and the temperature gradient in liquid is negligible [8].

The feed composition has a significant influence on the scaling and fouling intensity. Therefore, studies on the influence of the feed composition on the process efficiency and membrane fouling during solution concentration by membrane evaporation also were performed.

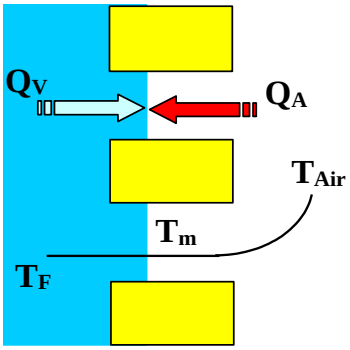


Fig.3. Membrane evaporation of water without feed heating - temperature profile at feed–air interface. T – temperature, Q – heat.

Experimental

The studies of solutions concentration by membrane evaporation were carried out using an installation presented in Fig. 4.

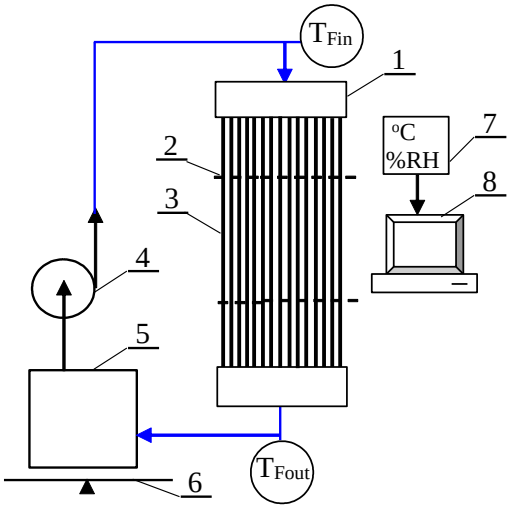
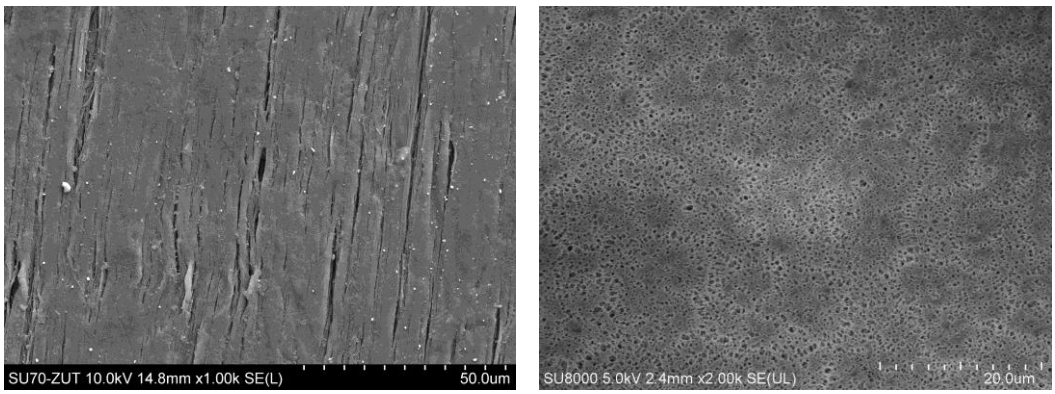


Fig. 4. Experimental set-up. 1- membrane module, 2 – capillary membrane, 2 – polypropylene net, 4 – peristaltic pump, 5 – feed tank, 6 – balance, 7 – hygrometer, 8 – computer, T_{Fin}, T_{Fout} – thermometers

The commercial hydrophobic polypropylene capillary membranes (K1800-A and K1800-B) manufactured for microfiltration (EuroSep, Poland), were used for the studies of membrane evaporation process. Two modules were made (M#1 and M#2), each with 14 membranes glued on both ends inside the PVC tube (1/2”diameter). The capillary membranes have the internal diameter of 1.8 mm and outer diameter of 2.6 mm, and the effective length of 1 m. The total membranes area calculated for the lumen side amounted to 0.079 m^2. The membranes were positioned rectangularly in every third mesh of two polypropylene nets. A distance between each capillary membrane was about 1 cm. The membranes used were characterized by similar porosity (about 70%), however, the surface porosity of K1800-A membranes (M#1) was lower than observed that for K1800-B membranes (Fig. 5).

The feed flowed inside the capillaries (lumen side) during the evaporation experiments. A peristaltic pump was used, and the volume flow rate of feed was equal to 3 ± 0.2 ml/s (linear velocity 0.08 m/s).

The NaCl solutions, oil in water emulsion and oily wastewater were used as a feed. The oily wastewater was supplied from harbour wastewater treatment facility (Table 1). The oil concentration in examined samples was determined by means of the oil analyzer HORIBA OCMA 310.



A) B)

Fig. 5. SEM images of membrane surface. A) K1800-A (M#1), B) K1800-B (M#2)

Table 1. Composition of oily wastewater [mg/L]

	Cl^-	Br^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	oil
Feed	5366	132	104	1203	3456	154	1053	658	38
Retentate M #1	8121	224	396	1474	5145	233	1098	761	29
Retentate M #2	9821	254	287	1874	6245	284	1278	958	31

The electrical conductivity and total dissolved solids (TDS) of solutions were measured with a 6P Ultrameter (Myron L Company, USA). This meter was calibrated for measurements as NaCl equivalent using TDS/Conductivity standard Solution (Myron L Company). The air temperature and relative humidity were measured by electronic hygrometer AZ8829 (AZ-Instruments, Poland) connected with computer software TRLOG v.3.4.

The waste composition (anion and cation concentrations) was determined using an ion chromatography method with conductivity detector (850 Professional IC, Herisau Metrohm – Switherland, equipped with Metrohm A Supp5-250 and Metrosep C2-150 analytical columns).

Results

The feed temperature has a significant impact on the intensity of water evaporation. In the case of natural evaporation the liquid temperature is well known as wet-bulb temperature [9]. The heat is transferred not only by feed/air interface but also through the wall of membrane, which is in a direct contact with the surrounding air. Therefore, the feed temperature can be higher than the expected wet-bulb temperature. It has been determined that the feed temperature (T_F) during NaCl solution evaporation established at a level of 25 ^oC and it was 1-1.5 degree lower than the air temperature (Fig. 6). For the feed temperature T_F indicated above the permeate flux changed in the range 1.5-2 LHM. The data presented in Fig. 6 were calculated as average for each day. Fluctuations of permeate flux with time mainly resulted from the changes in ambient air temperature and relative humidity. During the tests, due to the evaporation of water, the NaCl solution was concentrated, and its concentration increased from 50 to 113 g/L. The increase in concentration led to a reduction in the vapor pressure and, as a result, the permeate flux should slightly decrease, which is confirmed by the results obtained during the first 100 h of the process run. In the following hours, however, despite the increasing salt concentration, the evaporation efficiency also increased. The reason for this was a decrease in the relative humidity (RH) value which increased the driving force.

The driving force for water evaporation is a difference of the vapour pressure between gas inside the membrane pores and in the air surrounding installation (Fig. 1). For this reason (Eq. 1), a decrease of air humidity from 60 to 45% led to an increase in the yield of membrane evaporation from 1.4 to 2.2 LHM. Similarly, large increase in the yield were noted for natural evaporation from a porous surface, where an declines of RH from 70 to 30% caused, that the evaporation rate of water (25 ^oC) increased 2-fold and almost 3-fold for 35 ^oC [10].

This relationship is also confirmed by the results obtained during the second series of NaCl concentration tests. The increase in the feed concentration to 75 g/L caused a systematic decrease in the permeate flux, which was increased by the increase in the RH value up to 40% (Fig. 7). After the period in which the feed was concentrated to 100 g/L, air humidity decreased from 35 to 28%, which resulted in over 10% increase in the efficiency of the process. In the following hours of the process run, both the temperature and the air humidity were relatively constant. Under these conditions, the changes in efficiency were determined by the feed concentration, hence, during its separation for concentrations above 100 g/L, a systematic slight decrease in permeate flux was observed.

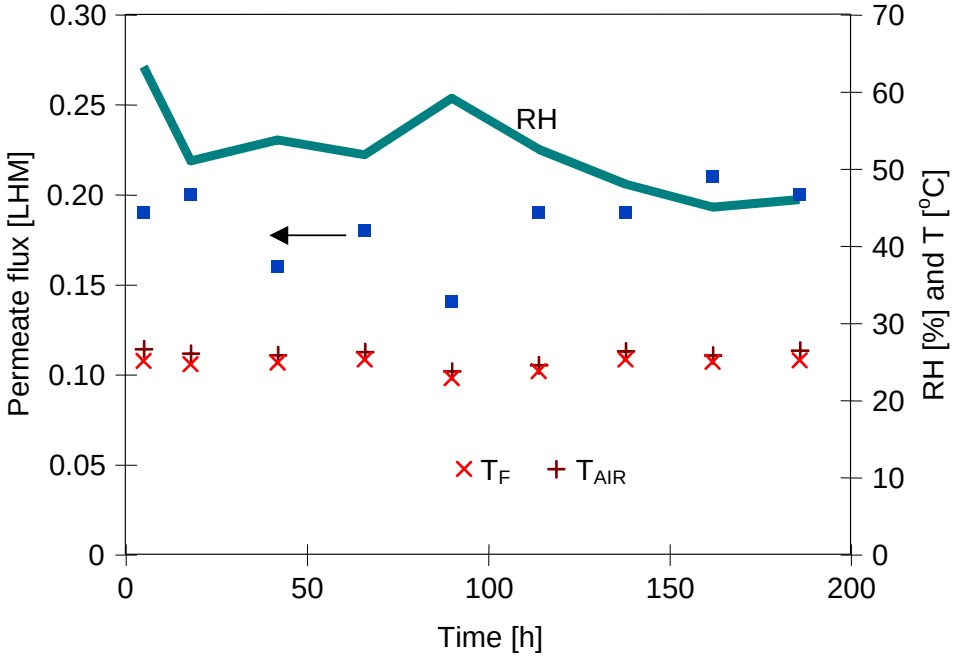


Fig. 6. The influence of feed temperature and relative humidity on the permeate flux. Feed: NaCl solutions (50-113 g/L)

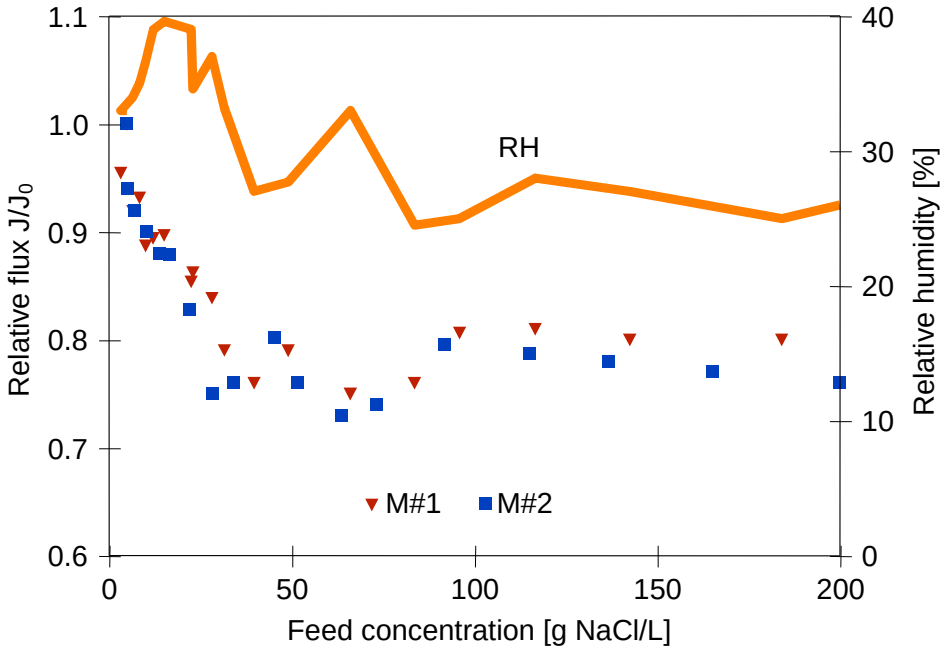


Fig. 7. The changes of permeate flux during the feed concentration

The membranes in the M#1 module had a lower surface porosity (Fig. 4A), which resulted in a slight decrease in their performance (Fig. 8). Therefore, for the same process time, the measured salt concentrations in the feed for the M#1 module were lower compared to those obtained for M#2 (Fig. 7). Due to the greater permeate flux, the value of polarization in the M#2 module was greater and, as a result, the reduction of the J/J_0 value for this module was also greater.

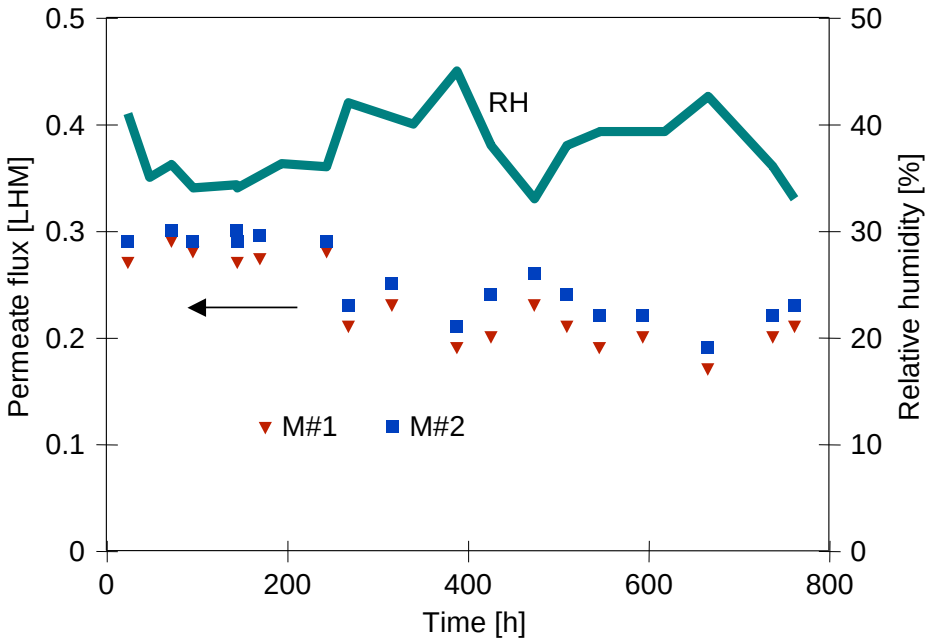


Fig. 8. Changes of the permeate flux during separation of oil in water emulsion

The presence of oil in the feed can cause significant fouling in the case of hydrophobic membranes. In order to determine its intensity, studies on the concentration of a salt solution (5 g/L) containing 50-57 mg/L of oil were carried out. During the tests, distilled water and emulsion concentrate were periodically added to the feed (2 L), which allowed to limit changes in salt and oil concentration in the feed. For the first 200 hours, the process efficiency remained at a similar level, then it decreased from 0.3 to 0.2 LHM, which was mainly due to an increase in RH from 35 to 45%. After 490 h of the process, the RH value decreased to 32%, but the permeate flux did not rise to the initial level. This result indicates that during the long operation of the module (500 h), oil was adsorbed on the membranes surface, which made it difficult for the water to evaporate.

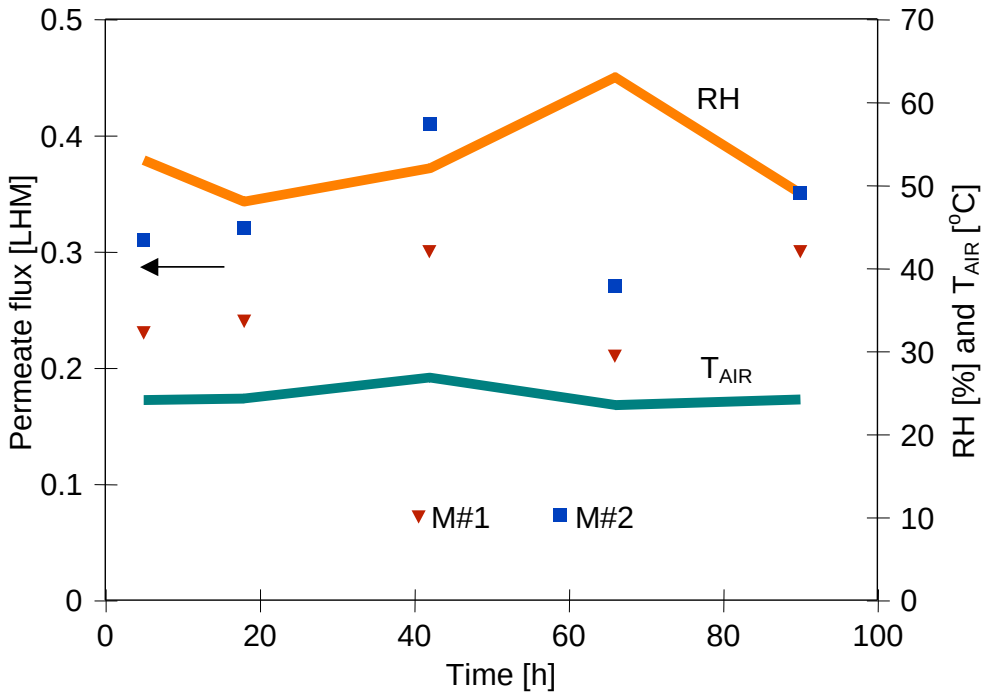
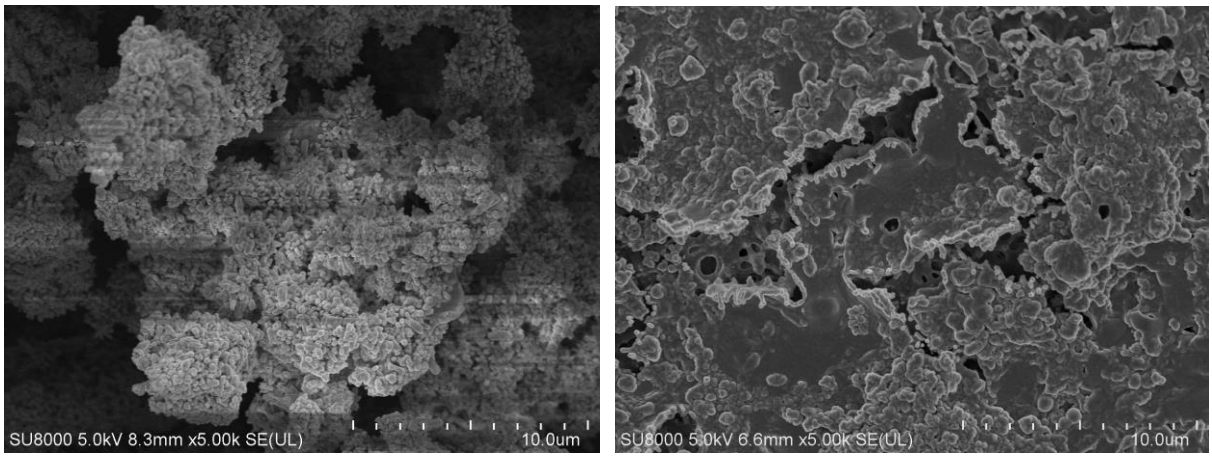


Fig. 9. Changes of the permeate flux and process parameters during separation of oily wastewaters

In addition to oil, oily wastewater also contains various salts that may cause scaling during the concentration of the feed. The occurrence of this phenomenon was confirmed by the studies conducted on the wastewaters, containing mainly bilge water. The analysis of the retentates composition showed a decrease in the content of Ca^{2+}, Mg^{2+} and SO_4^{2-} (Table 1), which indicates the precipitation of carbonates and sulphates. The formation of deposits on the membranes surface was confirmed by SEM examinations of the membranes samples after the end of the process (Fig. 10). The formation of this precipitate did not significantly reduce the permeate flux, and the observed changes in process performance resulted mainly from changes in the RH value (Fig. 9). However, these results were obtained during 90 hours of the process run, therefore, it should be admitted that in the long run, much greater drops will occur as a result of membrane scaling. This negative phenomenon can be reduced by combining the evaporation process with a salt crystallization system [3].



A) B)

Fig. 10. SEM images of membrane surfaces with deposits formed during separation of oily wastewaters. A) module M#1, B) module M#2

Conclusions

The performed studies confirmed that the process of natural membrane evaporation can be used for concentration and separation of solutions. In this case, air parameters, i.e. temperature and relative humidity, have a significant impact on the process efficiency. The evaporation rate increased with increasing air temperature and decreasing the RH value. These results indicate that the natural evaporation process is advantageous to carry out in areas with a dry and hot climate.

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