Slovak Society of Chemical Engineering
Institute of Chemical and Environmental Engineering
Slovak University of Technology in Bratislava

PROCEEDINGS

46th International Conference of the Slovak Society of Chemical Engineering

Hotel Hutník I
Tatranské Matliare, High Tatras, Slovakia
May 20 - 23, 2019

Editors: Prof. Jozef Markoš, Dr. Mário Mihaľ

ISBN: 978-80-8208-011-0, EAN: 9788082080110

Gryta, M.: Separation of saline oily wastewater by membrane distillation, Editors: Markoš, J., Mihaľ, M., In *46th International Conference of the Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia, 2019.

Separation of saline oily wastewater by membrane distillation

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Keywords: membrane distillation, oily wastewater, bilge water, brine

Abstract

The presented work is associated with the investigations on the membrane distillation process for the treatment of saline oily wastewaters, such as bilge water. The polypropylene capillary membranes were applied for process study. During the separation of wastewaters the intensive membrane fouling was observed. The formation of deposits on the membrane surface accelerates the pores wettability. It was confirmed, that the degree of membrane wetting in the MD process influences on the purity of obtained distillate. However, the obtained degree of retention for the inorganic compounds amounted to 98% and more than 99 % for the organic compounds.

Introduction

The development of electrical power generation (water demineralisation), production of fresh water (Reverse Osmosis), geothermal energy, oil and shale gas (fracturing and processing water) and the global expansion of maritime transport (bilge water) and many other technologies generating saline wastewaters cause and promote environmental degradation due to the direct discharge of salt waste water into the environment. Membrane processes can most effectively be used in the treatment of such wastewaters, but the major problem constitutes the durability of membranes, particularly during the separation of brines containing various surface-active contaminants (e.g. oils and surfactants) [1-5].

The possibility of water evaporation from high concentration brine allows using the membrane contactors to desalinate hypersaline water or saline wastewater treatment [6-9]. A high concentration of salt in wastewaters makes their biological purification often impossible and the wastewater treatment plants usually do not treat this type of wastewater, which enhances a risk of illegal discharge into the environment. Integration of the membrane contactors with crystallization enables the elimination of salt discharge [10]. Unfortunately, the high salts concentration increases the scaling intensity of membranes, which additionally restricts e.g. the oily wastewater treatment by application of membrane contactors [6, 8, 11]. However, their application is very attractive in the case when wastewater treatment by traditional methods is difficult or expensive, especially for oily wastewaters such as bilge water or wastewater generated in the process of hydraulic fracturing [2, 3, 12, 13].

The porous non-wetted hydrophobic membranes are assembled in the membrane contactors [6, 7, 14]. However, the hydrophobic membranes are intrinsically prone to fouling by hydrophobic contaminants due to the strong hydrophobic-hydrophobic interaction [1, 2, 15, 16]. Therefore, the conventional hydrophobic membranes (made of PP, PTFE and PVDF) are usually applied for desalination of water with a relatively low concentration of hydrophobic contaminants [7, 17, 18]. Moreover, even for clean water, such as seawater, a progressive wetting of hydrophobic membrane is observed, which is attempted to eliminate by the application of superhydrophobic membranes [1, 11, 19-21], but very low surface energy of these membranes accelerates the membrane wetting if the hydrophobic contaminants will be present in the feed water. Therefore for this type of feed, the new composite hydrophilic/hydrophobic membranes or membranes with amphiphobic surfaces were proposed for water desalination [1, 16, 21-24]. However, the relatively high costs of the proposed new membranes are expected to be problematic because the industrial breakthrough of the contactors technology requires high performance and inexpensive membranes [25, 26].

In this work the relatively cheap polypropylene (PP) membranes [14, 27] were applied for evaluation of the membrane stability during membrane distillation (MD) used for the separation of actual oily wastewaters. A promising method that was reported [8] to mitigate fouling and scaling intensity is the application of low feed temperature, however, such option reduces the performance of processes realized in the membrane contactors. Therefore, a large membrane area should be used in order to achieve a high efficiency of the installation, which increases the capital investment costs [13]. This is an additional reason indicating, that the realization of industrial implementation requires the membranes as cheap as possible, namely, manufactured by a simple method from inexpensive raw materials [4, 25].

The capillary PP membranes were not-wetted during separation of bilge water [12, 28] and oilfield produced water [27]. However, the degradation processes have slow progress; therefore for observation of their effects on the PP membrane performance the continuous long-term studies were carried-out..

Experimental

The applied MD an experimental set-up was showed in Fig. 1. In the MD installation a role of energy source was performed by a magnetic stirrer equipped with a heating element (600 W, IKA, USA). Two submerged modules made from PP membranes Accurel PP (Membrana GmbH, Germany) were placed in the glass feed tank (4 L). The nominal diameter of the membranes pores was 0.2 μm and the open porosity was 73% (on the basis of the supplier data). In the MD1 module, four Accurel PP S6/2 (d_{in}/d_{out} = 1.8/2.6 mm) membranes with the length of 20 cm were assembled. The MD2 module was composed of a single membrane Accurel PP V8/2 HF (d_{in}/d_{out} = 5.5/8.6 mm) with the length of 25 cm. Each of the modules was connected to an individual distillate tank, cooled in a water bath (18°C). The initial volume of distilled water in the distillate tanks amounted to 1.5 L. The peristaltic pumps were used to obtain the volumetric flow rate of distillate (inside the capillary membranes) equal to 6 ± 0.2 mL/s (linear velocity of 0.59 m/s – MD1 module and 0.79 m/s – MD2 module). The composition of separated oily wastewaters was presented in Table 1.

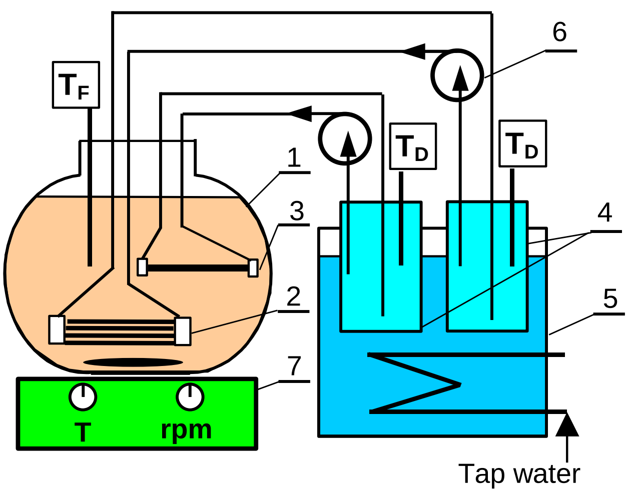

Fig. 1. The scheme of the experimental set-up. 1 – Feed tank, 2 – MD1 module, 3 – MD2 module, 4 – distillate tanks, 5 – cooling bath, 6 – pump, 7 – magnetic stirrer with heating and T – thermometers.

Table 1. The composition of studied oily wastewaters

Waste	Ions [mg/L]									Oil	pH
	Cl^-	Br^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	[ppm]	
OW1	5238	130	96	705	3356	25	142	1034	645	12.5	8.5
OW2	3383	128	59	876	1969	62	115	494	420	24.8	8.6

Results

The studies were performed with samples of wastewaters (Table 1) collected from deoiling installation at intervals of several days. The examined samples had the colour from light to dark brown and they exhibited a high turbidity. A sample filtration through a filter paper (5 μm) demonstrated that wastewater contained 0.064-1.9 g/L of suspended solids (s.s). The turbidity of shaken samples amounted to 27.7-154.3 NTU. These values decreased during the wastes storage, which indicated their sedimentation. The values in the range of 17-55 NTU were obtained after 5 days of storage, which indicated that sedimentation proceeds slowly. Slightly sediment sewage containing the least suspension, in addition, the resulting precipitate was unstable, caused a small swirl of liquid to increase the turbidity again.

The investigations of oil droplet size distribution demonstrated that formed emulsion have at least two ranges of oil droplet size (bimodal distribution). In the first range prevail the oil droplets with the diameters of 1-5 μm, whereas in the second range, in the range of 60-100 μm.

The MD process is carried out below the boiling point of water, what enables to utilization of low-grade heat sources of energy, and usually the feed temperature is in the range of 308-333 K. The application of such low feed temperature allows to significantly limit the membrane scaling [1, 6]. However, the feed temperature decreased rapidly during the feed flow in the MD module and a small yields were obtained for temperature below 318 K. for this reason, the efficiency of spiral-wound MD modules is at a level of 1-2 L/m^{2}h in the pilot plant installations. A solution of this problem is the application of submerged modules with the capillary membranes assembled inside the feed tank (Fig. 1), since in this case the entire surface of the capillaries is in a contact with the feed at the same temperature. As a result, the efficiency 2-3 fold large than those obtained for spiral-wound modules can be achieved at the feed temperature of 323 K. The additional advantage of using the submerged modules is a lack of forcing pressure of the feed, what should restrict the penetration of liquid into the pores (membrane wetting).

The Accurel PP V8/2 membrane have four times thicker walls (1.5 mm) in comparison with the membranes Accurel PP S6/2 (0.4 mm). The increase of wall thickness not only extends the diffusion path of vapour, but also favourable limits the heat losses through the membrane (temperature polarization). In this regard the efficiency obtained for the membranes with thicker walls were only two-fold lower than those obtained for Accurel PP S6/2 (Fig. 2).

The feeding of MD modules with real oily wastewater caused a decline of process efficiency to a level of 3 L/m^{2}h (S6) and 1.8 L/m^{2}h for V8 membranes (Fig. 3). In the case of MD a reason of such flux decline most often is associated with the pore wetting and membrane fouling. Moreover, a fast increases of distillate conductivity to a value of 220 μS/cm, is a confirmation of the aforementioned phenomena since the fouling is often a reason of the membrane wetting in the MD process. However, when the NaCl solution was again use as a feed after around 500 h of MD process operation, the distillate conductivity was reduced to a level of 10-15 μS/cm, and the permeate flux increased to almost initial; values (Fig. 3, period 490-650 h). Such results indicate that the treated oily wastewater did not cause the membrane wetting and the changes of process parameters shown in Fig. 3 resulted from other reason.

During the first period of studies was used wastewater OW1, the pH value of which amounted to 8.5 and this waste contained the NH_4^+ ions (Table 1). The IC analysis confirmed that a growth of distillate conductivity resulted, among others, from dissolution in the distillate of ammonia separated from the feed.

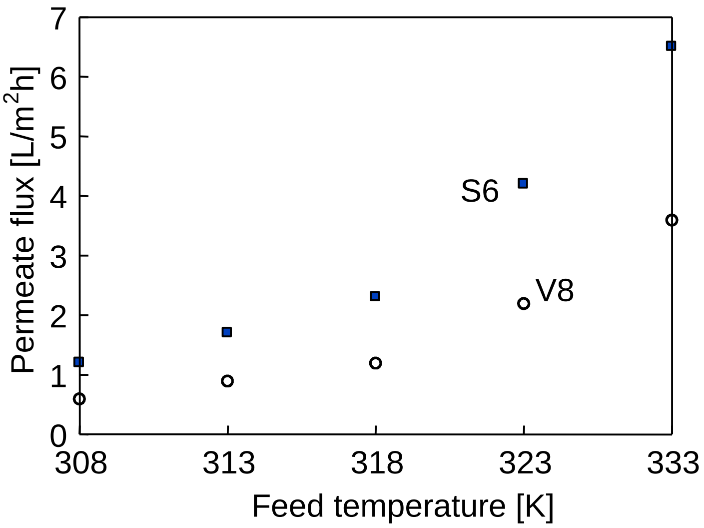

Fig. 2.The influence of feed temperature on the permeate flux obtained for Accurel PP S6/2 and Accurel PP V8/2 HF membranes. Feed: 5 g NaCL/L

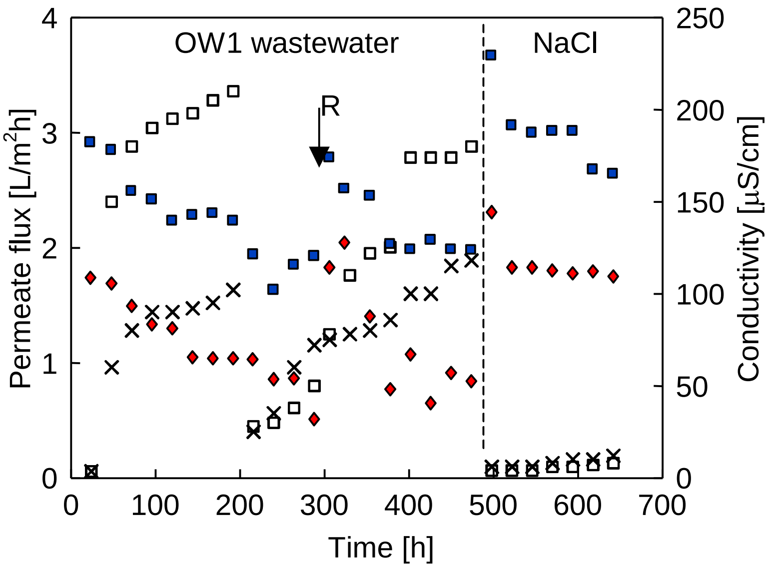

Fig. 3. The changes of the permeate flux (■, ♦) and distillate electrical conductivity (□, x) during MD process of oily wastewater. Membranes: ■, □ – S6; ♦, x – V8. R – modules rinsed with water

The MD investigations were carried out maintaining a relative constant volume of wastewaters in the feed tank (4L). However, despite of a continuous concentration of the feed and a periodical addition of fresh portion of wastewaters OW1 (Fig.4, points VCR), the pH values of feed were systematically decreased, what confirmed the separation of ammonium from the feed.

The results shown in Fig. 5 indicate that an increase of the membrane thickness limits the separation of ammonia since the concentration of NH_4^+ ions was 2-fold higher in the distillate obtained for Accurel PP S6/2 membranes. Moreover, the concentration of other ions such as Cl^- and Na^+ was lower. Such results indicate that the V8 membranes having significant thicker membrane wall were also more resistant for wetting.

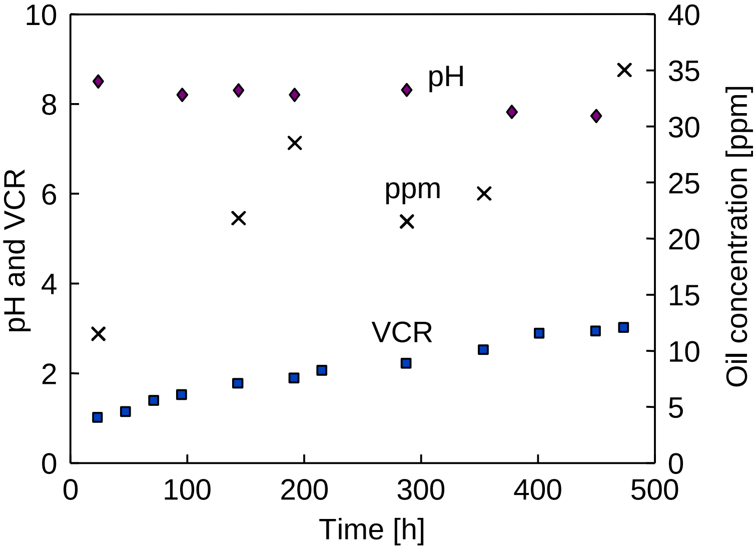

Fig. 4. The changes of pH and oil content in the feed, and the obtained values of VCR during separation of OW1 wastewater.

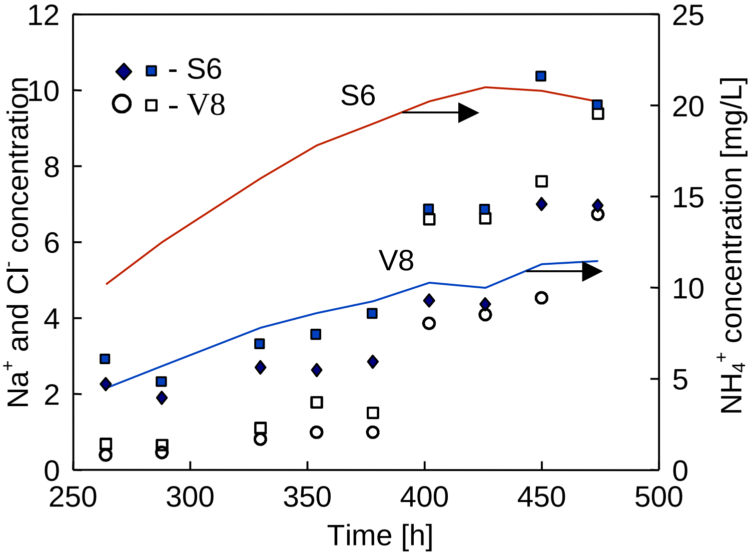

Fig. 5. The changes of ions concentration (■□ – Cl^-, ♦○ – Na^+, line – NH_4^+) in distillate during MD process

The results presented above indicated that observed decrease of MD efficiency during the separation of oily wastewaters (Fig. 3) most probably resulted from the membrane fouling. One of the components causing the fouling is the concentration of oils present in the treated wastewater. The water evaporation causes increasing oil concentration at the feed/membrane boundary, what limits the access of water to the membrane surface. As a result, the concentration of oily emulsions in the MD process is limited, since of the emulsion concentration at the order 1000 ppm the efficiency of MD process approaches zero [28]. However, the emulsion containing such a large amount of oil undergo breaking, what allows to separate the free oil in an additional device, e.g. decanter, connected to the MD installation.

In the studied case, wastewaters contained a small amount of oily substances (12-25 ppm). During the MD process due to a continuous concentration the oil concentration in the feed was systematically growing (Fig. 4), what enhances a negative effect of the oil presence, although its concentration was still a relatively low (30-40 ppm). For this reason, the oil concentration was not the main factor causing the membrane fouling. It was observed, that during the MD process, a brown deposit covered the membrane surface. After 300 h of investigations, the membranes were rinsed with tap water, and the majority of deposit was removed from the membrane surface. As a result, the module productivity increased to the initial level. However, the membranes were again covered by deposit after consecutive 50 h of process and their efficiency was stabilized at a level of 2 L/m^{2}h (S6/2) and 0.9 L/m^{2}h for the V8 membranes. The efficiency increased once again after changes the feed into an NaCl solution, what mainly resulted from a fact, that the membranes were again washed.

In the second stage of investigations were used oily wastewater OW2. This wastewater contained almost two times less of salt. However, the content of oil contaminations was higher (Table 1). The MD process efficiency obtained for such wastewaters was shown in Fig.6. Similarly as in the previous case the feeding of modules with wastewater caused the occurrence of membrane fouling and as a result, a decline of the process efficiency was observed.

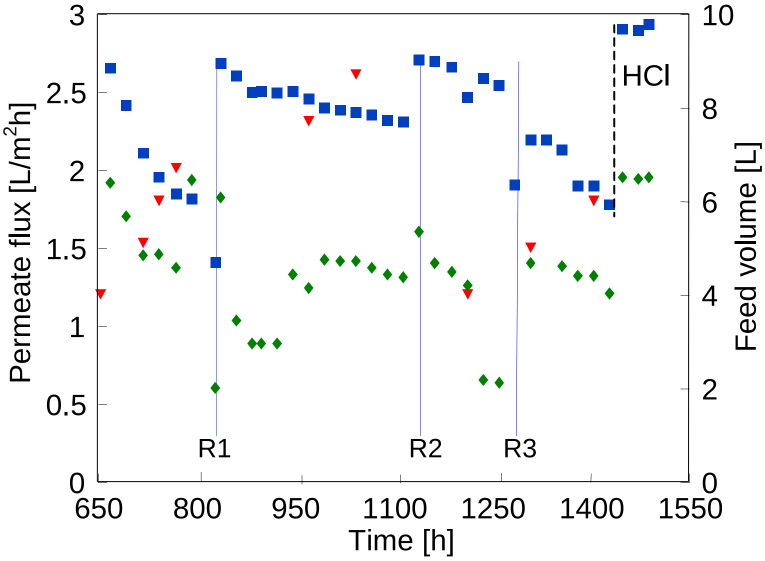

Fig. 6. The changes of the permeate flux (■– S6, ♦– V8) and total volume of OW2 waste dosed into feed tank during MD process of oily wastewater. R – modules rinsed with water.

During the first 180 h of the treatment of wastewaters OW2 by MD, the observed permeate flux decreased from 2.6 do 1.4 L/m^{2}h (S6 membranes) and from 1.9 to 0.6 L/m^{2}h for V8 membranes. The walls of feed tank made of glass allowed to observe the formation of brown deposit accumulated on the membrane surface, and at the end of this period (Fig. 6, from 790 h) after achieving 50% concentration, the intensity of deposit precipitation was significantly increased, and a layer of brown deposit was also formed on the tank walls. An increase in the intensity of deposit precipitation caused a greater reduction of the permeate flux (Fig.6, 830 h). The rinsing of membranes with distilled water allowed to remove the majority of deposits from the membrane surface and the process efficiency was increased to almost the initial values (Fig. 6, point R1). After further continuation of MD process during the consecutive 180 h, the process efficiency was again gradually decreased, although this decline of permeate flux was definitely slower, e.g. from 2.68 to 2.3 L/m^{2}h (S6). A similarly slower decline of process efficiency was obtained after performing the second cleaning of modules (Fig.6, point R2).

The initial volume of feed amounted to 4 L, and the permeate volume obtained during 24 h of MD process amounted to 0.4-0.6 L. The losses of feed volume were periodically supplemented by adding wastewater OW2 (Fig. 6, points V_F). The results presented in Fig. 6 indicate, that not only the feed concentration (degree of concentration) but also a volume of fresh wastewater had the influence of fouling intensity. The largest decline of efficiency was noted at the initial period, when a large volume of wastewater (4L) was heated to 328 K. A periodical dosage of smaller volumes of wastewater OW2 to thermally stabilized feed did not cause a significant reduction of the permeate flux. A similar effect was observed when the concentrated feed was removed from installation and was exchanged for a new portion of wastewater (4L) (Fig. 6, from 1214 h). Such result indicates, that the application of thermal pre-treatment of tested wastewaters could cause a decline of the membrane fouling during MD process.

The performed studies demonstrated that a brown organic deposit formed on the membrane surface could be removed by using a cyclic rinsing of the modules with water. However, the effectiveness of washing procedure was the smaller and smaller (Fig. 6, points R1-R3). A reason of such result was the occurrence of the membrane scaling besides the formation of sludge deposit. An IC analysis of the feed composition revealed that the concentration of the majority determined ions were systematically increased. Slight changes were found for the Ca^{2+}concentration, which could indicate the $CaCO_3$ precipitation. In this case a good solution is rinsing the membranes with HCl solution. The application of 5 wt% acid solution allowed to clean the membrane surfaces in a few minutes, and as a result, the permeate flux was increased to almost the initial values (Fig. 6, from 1450 h).

The OW2 wastewater similarly as OW1 also contained NH_4^+ ions, hence what enables the evaluation of ammonia to distillate when the pH of wastewater was equal to 8.2. The IC studies confirmed, that the significant amounts of the NH_4^+ ions were detected in the obtained distillate, what caused an increase in the electrical conductivity of produced distillate (Fig. 7). Similarly was in the case of wastewater OW1 definitely larger values of tested parameters were found for the S6 membranes. For these membranes a higher concentration of other ions such as Na^+ and Ca^{2+} was also determined. Such a result confirms that the membranes with thicker walls (V8) exhibited a higher resistance to wetting during the separation of tested saline oily wastewater.

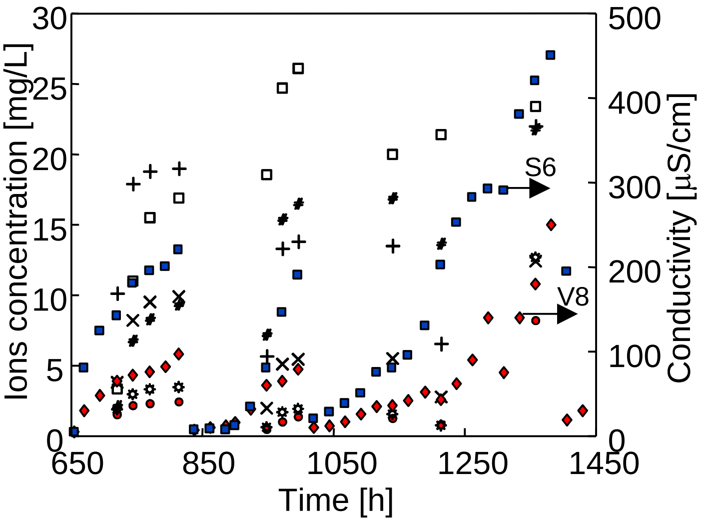

Fig. 7. The changes of ions concentration (+x-NH_4^+, *□ – Ca^{2+}, # ●-Na^+) and distillate electrical conductivity (■, ♦) during MD process of oily OW2 wastewater. Membranes: ■, □ + #– S6; ♦, x * ●–V8

The concentration of determined ions and the electrical conductivity of distillate were significantly increased during the concentration of the second portion of wastewater OW2 (Fig. 7, from 1240 h). This may indicate that the pore wetting was systematically increased during the studies carried out for 1500 h. A confirmation of this conclusion is a fact, that the ions concentration in the distillate obtained after 650 h of separation of wastewater OW1 (Fig. 3) was 2-fold smaller than that obtained for wastewater OW2 (Fig. 7), although the OW2 wastewater contained significantly less salts (Table 1). However, even for a high value of electrical conductivity of the order of 500 µS/cm, taking into account the feed conductivity amounting to 35-40 mS/cm, the obtained degree of solutes retention exceeded 98%.

The examination of oil content in the obtained distillate indicated for the complete retention of oil in the feed. The sensitivity of applied apparatus OCMA 310 amounts 0.05 ppm. A good separation of organic compounds was also confirmed by performed studies of the TOC content in the distillate. The concentration of organic carbon in the tested samples was varied in the range of 1-2 mg/L, when the TOC content in the fed was more than 450 mg/L TOC w nadawie.

Conclusions

The performed studies demonstrated that the MD process could be used for the treatment of saline wastewaters. The obtained degree of retention for the inorganic compounds amounted to 98% and more than 99 % for the organic compounds.

The formation of significant amounts of deposits on the membrane surface was observed during the MD process; hence, the process efficiency was reduced by 20-40% during 150-200 h of process operation. A decline of efficiency was limited by application of periodical rinsing of the membranes. Besides the formation of deposits of substances forming a layer of silt on the membrane surface the membrane fouling was also found. The deposit of precipitated salts mainly $CaCO_3$, was effectively removed by rinsing the MD membranes with a 5 wt% HCl solution.

Acknowledgments

The National Science Centre, Poland is acknowledged for the support of this work, grant number 2018/29/B/ST8/00942

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