

## Purification of oily wastewater by ultrafiltration

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### Abstract

Investigations have been carried out for purification of oily wastewater by a combination of ultrafiltration/reverse osmosis processes. A tubular ultrafiltration system using cellulosic and non-cellulosic membranes was tested with typical oily wastewater collected from harbour and simulated emulsion without any pretreatment. Both membrane types produced a permeate with an oil content generally less than 10 mg/dm<sup>3</sup>. Rejection of chemical oxygen demand (COD) is 80% for ultrafiltration treatment. The permeate is generally of acceptable quality for direct sewer discharge. For further treatment of UF permeate, reverse osmosis was applied with tubular B1 PCI modules using cellulose acetate membranes. The rejection of COD after ultrafiltration/reverse osmosis treatment increased up to 98.5% and total dissolved solids (TDS) to 95.7%. Reverse osmosis treatment will permit reuse of the treated water as process water.

**Keywords:** Oily wastewater; Tubular membranes; Ultrafiltration; Reverse osmosis

### 1. Introduction

Oily wastewaters and oil-water emulsion are two of the main pollutants discharged to water environment. Oily wastewaters are generated by ships mainly in engine-rooms in amounts of millions of tons annually. Oil emulsion wastes, used in cooling and lubricating emulsions from the metal industry contain considerable amounts of mineral oil, which hardly undergoes biochemical decomposition. The common industrial practice to collect sewage from various sources in common storage tanks usually multiplies the problems [1–3]. Therefore, such wastes cannot be drained to the sewage system without previous treatment, even if they are very diluted. Generally, the total oil content of the mixed wastewater is 1–10% [4].

Emulsified oily wastewater can contain oil (mineral, vegetable or synthetic), fatty acids, emulsifiers (anionic and nonionic surfactants), corrosion inhibitors

(amines), bactericides and other chemicals designed to provide a long-lasting and effective fluid. Many fluids have very stable emulsion, which make chemical treatment difficult. Since the oil is chemically emulsified, normal separation processes (gravity, flotation, skimming) are not effective. The standard methods for treatment of emulsified oily wastewater is chemical de-emulsification followed by secondary clarifications, which requires the use of a variety of chemicals such as sulphuric acid, iron and alumina sulphates, etc. The water phase from chemical treatment has to be further purified to meet today's effluent standard for discharge systems.

To solve the problem with stable emulsion and oily wastewaters, new, effective methods have recently been elaborated. Biotechnology offers some new approaches, based on biodegradation and biotransformation of fats and oily wastes [5]. The most promising methods, based on membrane separation processes are: the dehydration of oil emulsion via pervaporation [6], reverse osmosis [7], ultrafiltration [8], membrane extraction for fat removal [9], and application of an

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electric field to coalesce the droplets [10]. To achieve maximum yield and separation effectiveness, the performance of these membranes has been enhanced by means of surface modification [11,12]. The separation of oil in wastewater from engine-rooms may be performed by ultrafiltration (UF), a pressure-driven membrane process which can separate, concentrate and fractionate macromolecular solutes and suspended species from water [1]. The ultrafiltration method of treatment produces a water phase which is generally of acceptable quality for direct sewer discharge into the sea, and an oil phase that can be incinerated. If further treatment of the permeate is required, there are several effective posttreatment methods. For example, stream discharge standards would normally require posttreatment of the permeate by: biological treatment, activated carbon, reverse osmosis and carbonaceous resins [4]. Reverse osmosis (RO) and activated carbon treatment will permit reuse of the treated water as process water.

The maximum attainable oil concentration ranges from 25 to 65% oil [1]. The oily concentrate can be further concentrated by centrifugation. The concentrated oil is usually not recyclable, but it can be burned to eliminate its pollution impact. For oily concentrates that cannot be incinerated, the cost of disposal is substantially reduced, as the concentrate represents only 5–10% (and many times even less of the original volume) [1].

There is a qualitative difference between the UF of oil emulsion and other colloidal suspensions. This is because the colloidal oil droplets have sizes that may vary with imposed shear, concentration, oil-surfactant ratio and interaction with the membrane [13].

Direct application of reverse osmosis for processing of oily wastewater would require some physical and chemical pretreatment, depending on the used module configuration. The simplest pretreatment would be for a tubular module, and can be done with an 'equalization tank', from which the free-floating oil and the settleable solids are removed. Application of ultrafiltration as a pretreatment stage before reverse osmosis should remove nearly all the oil and some COD.

In this paper, we report the ultrafiltration results of a typical oily wastewater from engine-rooms with large-diameter tubular modules without any pretreatment and further purification of a permeate by reverse osmosis. Fig. 1 shows a schematic layout of the integrated membrane processes.

## 2. Experimental

### 2.1. Fabrication of tubular UF membranes

Ultrafiltration experiments were carried out on the tubular membranes made of polyvinyl chloride (PVC), polyacrylonitrile (PAN) and cellulose acetate (CA), manufactured in our laboratory by the method of phase inversion [14]. PVC, powder of 99% purity, mol. wt = 82 000 and PAN, mol. wt = 93 800 was supplied by Nitrogen Plant of Tarnów and Anita Łódź (Poland), respectively. Cellulose acetate E-398-3 was produced by Eastman Kodak (USA). The solution of PVC and PAN in *N,N*-dimethylformamide (DMF) with a concentration of 12 wt% have been prepared at a temperature up to 323 K, subsequently they were filtered and deaerated. The cellulose acetate casting solution prepared at room temperature was composed of 17 wt% CA, 29 wt% formamide and 54 wt% acetone. All chemicals used in preparation of the casting solutions were of analytical reagent grade obtained from Merck (Germany) and Aldrich Chemical Company (USA).

In order to prepare the tubular membranes, a casting-bob method was used [15]. An apparatus for manufacture of tubular membranes was developed and constructed in our laboratory. The tubular membranes were formed by extrusion of a casting solution through an annular gap between the casting bob and membrane support lining a stainless steel tube with inner and outer diameters of 38 and 33 mm, respectively, and a length of 2000 mm. A leather-like material was applied as a membrane support because it has a suitable surface smoothness that secures a uniform coating without defects, a constant membrane thickness, and good adhesion between membrane and support. The leather-like material called nubuk was supplied by Pronit (Poland). In the fabrication process, a modified bob was used with an adjustable water

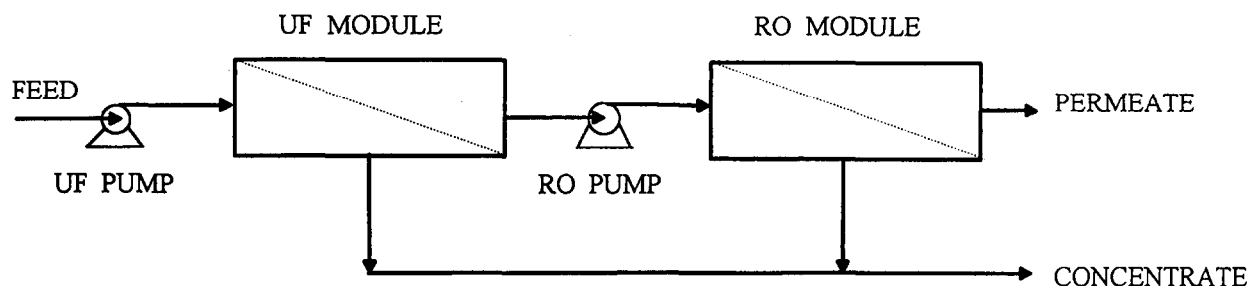


Fig. 1. Flow schematic of a unit combination of UF/RO processes.

probe and air-supply line, the combination of which offers a versatile mean of controlling both the rate of solvent removal from the freshly formed membrane surface and the rate of gelation of the entire membrane, which together control the overall porosity of the resulting membrane [15]. All membranes were bob-cast with a casting speed 4 cm/s, an annular gap width of 0.25 mm at room temperature and typically 50% relative humidity. The temperature of coagulation bath was 277 K in most experiments, but for CA 273 K was used as well. After gelation for 15 min, the membranes were rinsed with water for 8 h in order to remove the solvent. Membranes with different structure and pore size were obtained.

## 2.2. Membrane evaluation

Ultrafiltration tests for the evaluation of membrane performance were performed on stainless steel apparatus assembled as shown in Fig. 2. The flow rates and pressure were adjusted manually prior to each steady flow experiment, using in-line valves. Before these measurements were taken, the manufactured membranes had been conditioned by passing water through them for 8 h under a pressure of 0.2 MPa. During membrane conditioning and subsequent investigation of their transport and separation properties, deionized water (electrical conductivity  $\chi = 10 \mu\text{S}/\text{cm}$ ) obtained from reverse osmosis of tap water was applied. The water flux for each membrane was calculated

from measurement of a permeate volume per unit of time in the pressure range of 0.05–0.30 MPa.

The separation properties of these membranes were determined with test solutions having the following composition: deionized water 98.8 wt%, dextran 1.0 wt% and sodium azide 0.2 wt%. The addition of sodium azide permits the dextran solutions to be stored unaffected over a long period of time. Sodium azide, reagent grade and dextrans were supplied by POCh and Polfa, Poland, respectively. A series of retention measurements were carried out with dextran polymers with different molecular weights, ranging from 5000 to 110000, starting with the solute of the lowest molecular weight. The process was run with the test solution for 3 h in zero recovery, then feed and permeate samples were taken for analysis. The dextran concentrations in these samples were determined using a refractometer RL3, Poland. The retention  $R$  of membrane was calculated from a following equation:

$$R(\%) = (C_F - C_P) / C_F \times 100 \quad (1)$$

where:

$C_F$  and  $C_P$  are concentrations of dextran or value of the investigated parameters in the feed and permeate respectively.

UF performance (water flux and dextran retention) was determined at linear velocity of 4 m/s over the

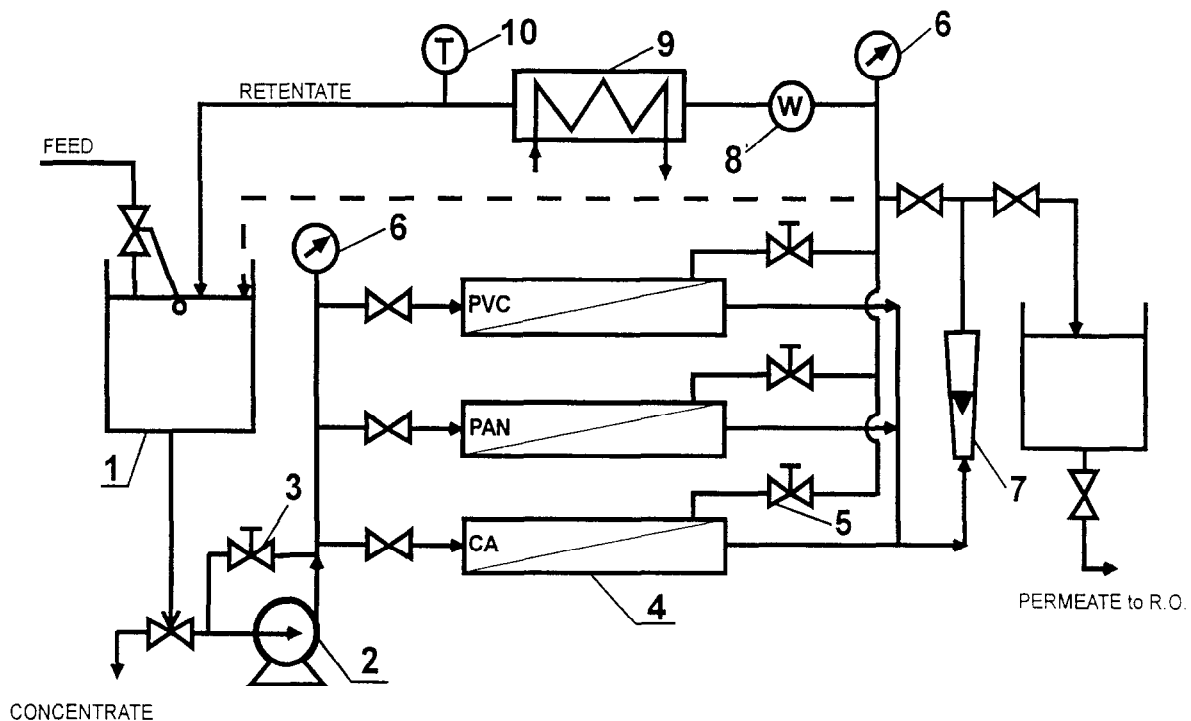


Fig. 2. Flow-sheet of ultrafiltration pilot plant. 1 — feed tank, 2 — pump, 3 — by-pass valve, 4 — tubular module, 5 — throttle valve, 6 — pressure gauge, 7 — rotameter, 8 — flowmeter, 9 — cooler, 10 — temperature control.

membrane surface, operating pressure of 0.1 MPa, and temperature of 298 K.

### 2.3. Experimental procedure

A continuous system for purification of oily wastewater with a combination of ultrafiltration/reverse osmosis was assembled according to the flowsheet shown in Fig. 1 and Fig. 2. Reverse osmosis pilot plant BRO Unit Mark II with B1 RO/UF module was supplied by PCI (England). Cellulose acetate membranes type T2/15W were inserted in the B1 module. Prior to the experiments, the initial water flux of each membrane at 298 K was measured with deionized water ( $\chi = 10 \mu\text{S}/\text{cm}$  at 298K).

Laboratory investigations were performed with emulsion obtained from a soreside settling tank used to collect the oily wastewater accumulated in Szczecin-Swinoujscie harbour.

Emulsified oil content in engine-room wastewater is usually in the range of 100–300  $\text{mg}/\text{dm}^3$ , but does not exceed the value of 1000  $\text{mg}/\text{dm}^3$  [16]. Oily wastewater was concentrated by UF in a semi-batch operation, whereby the clean permeate was drawn off continuously and further purified by reverse osmosis in the pressure range of 1–3.5 MPa at a temperature of 298K. The retentate containing the oil was recycled in an UF pilot plant with a recirculation velocity of 3 m/s, operating pressure of 0.15 MPa, and at a temperature of 310 K. Oily wastewater was added to the process tank to maintain a full level. At the end of the cycle, flow to the process tank was stopped and a batch concentration was performed on the solution in the process tank.

The effectiveness of the process was determined by measurements of the volume permeate flux as well as by means of feed and permeate sample analysis of the oil contents, chemical oxygen demand, total dissolved solids, pH and electrical conductivity. For each of these parameters, retention  $R$  was calculated from Eq. 1. All reverse osmosis measurements were performed starting after 2 h in order to avoid transient conditions. After product removal from the system, a standard cleaning procedure was applied. This includes rinsing with UF permeate — continued until both the retentate and permeate were totally clear, followed by circulation of a cleaning solution. The cleaning solution was composed of 0.5% Impurex (IMP Poland) dissolved in RO permeate. The cleaning was continued for 60 min at 315 K, with a recirculation velocity of 4 m/s and 0.10 MPa of operating pressure. Finally, the system was rinsed with RO permeate and water flux was then determined. This sequence was repeated with simulated emulsion prepared in the laboratory by adding a mixture of both diesel and engine oils at a ratio 1:1 to tap water and stirring with a rotary pump (2800 rev./min). To ob-

tain a stable emulsion, a single surfactant commonly used in shipyards was added. The concentration of oil and surfactant in the simulated emulsion was 5000  $\text{mg}/\text{dm}^3$  and 15  $\text{mg}/\text{dm}^3$ , respectively which corresponds to the average oil concentration in typical bilge waters.

### 2.4. Analytical methods

A number of analytical techniques were used to characterize the purification process of oily wastewater in the UF/RO system. The oil content in the feed and permeate was determined by extracting the oil with carbon tetrachloride and reading the concentration with an infrared spectrophotometer, UR 20 Carl-Zeiss (Germany), from a calibration curve [17]. The pH of feed and permeate streams was measured with a pH meter, Hanna Instruments (USA). Electrical conductivity of these streams was determined by means of a conductometer type OK-102 Radelkis (Hungary). Samples for chemical oxygen demand and total dissolved solids content of the feed and permeate were taken as necessary and analyzed by the procedure outlined in standard methods [18]. The oil droplet size distribution for both real and simulated emulsion was determined by microscopic methods. Analyses were conducted with a microscope (type — Biolar, Poland) with a magnification of  $\times 1000$ , fitted with a computer analyzed image (type Vist-Poland). Droplets of the examined emulsion were placed on the Bürker plate, which ensured equal thickness of the emulsion layer (0.1 mm) and overspread with cover glass. After 30 min all the oil droplets were counted in 13 vision fields in each quantity class.

## 3. Results and discussion

### 3.1. Transport and separation properties of PVC, PAN and CA membranes

The manufactured tubular membranes from PVC, PAN and CA were investigated by measuring their pure water flux and their retention for dextran molecules. In Fig. 3, the pure water flux values as a function of transmembrane pressure measured at 298 K with a deionized water ( $\chi = 10 \mu\text{S}/\text{cm}$ ) are given. In the case of PAN and CA membranes, the result was a linear dependence of water flux on pressure. However, in the case of PVC, membrane deviation from linearity has been observed, brought about by the compression of large pores due to pressure exceeding 0.1 MPa. In order to compare the characteristics of the investigated membranes as a reference condition, a transmembrane pressure of 0.2 MPa and a temperature of 298 K was taken. Under this reference condition, the water fluxes of the PVC, PAN and CA membranes are equal to 2.05, 1.52 and 1.22  $\text{m}^3/\text{m}^2\text{d}$ , respectively.

Retention measurements of these membranes were carried out in experimental set-up (Fig. 2) using dextran polymers with mol. wts of 5000, 15 000, 40 000, 70 000 and 110 000, respectively. The resulting retention curves for these membranes are given in Fig. 4. From the slope of these retention curves it has been noticed that the pore size distribution is rather narrow, e.g. in the case of a PVC membrane, the retention is 9% for dextran 5000 and 15% for dextran 15 000 and already 86% for dextran 70 000. The same type of relation holds for the PAN membrane, where the retentions are 15% and 38% for dextran 5000 and 15 000, respectively, and 91% for dextran 70 000. In the case of a CA membrane, the pore size distribution is similar, reaching a retention of 92% for dextran 70 000. The cut-off value which can be derived from these retention curves (90% retention) for PAN, CA and PVC membranes are 70 000 and 110 000, respectively.

### 3.2. The characteristic of oil-water emulsion

The curves shown on Fig. 5 present the oil droplet size and droplet size distribution for real and simulated emulsions, which were obtained as a result of the microscopic observation of samples on the Bürker plates. There are many small droplets in real emulsion. Most of them are smaller than 2  $\mu\text{m}$  in diameter. Bigger droplets appear less often. Almost all of them are in the same range. The analyses confirm that the character of real emulsion (124 ppm of oil) and simulated emulsion (5000 ppm of oil) does not change with respect to dilution. This is because the diameter of the droplets in these emulsions are very small and keep their size after dilution.

### 3.3. Ultrafiltration / reverse osmosis treatment of real oil-emulsion

A ship's wastewater was ultrafiltered in the range of

recommended process parameters for oil emulsions [4]. Table 1 presents the parameters of feed and permeates obtained from each membrane and pollution parameters reduction of UF and RO processes for real oil-emulsion. Purified real oil-emulsion was taken from the water phase of the ship's wastewater, formed under the influence of gravitational separation. This emulsion characterized low contents of oil (124 ppm) and chemical oxygen demand (346 mg  $\text{O}_2/\text{dm}^3$ ), but considerable amounts of total dissolved solids (3770 mg/ $\text{dm}^3$ ). Fig. 5 presents flux rate changes during UF treatment of real oil-emulsion on CA, PVC and PAN membranes ( $T = 310 \text{ K}$ ,  $p = 0.15 \text{ MPa}$ , linear velocity = 3 m/s). The highest flux rate, measured after 1 h, for PVC membranes was  $54 \text{ dm}^3/\text{m}^2 \cdot \text{h}$ . Substantially lower flux rates were obtained for PAN membranes ( $34 \text{ dm}^3/\text{m}^2 \cdot \text{h}$ ) and CA membranes ( $24 \text{ dm}^3/\text{m}^2 \cdot \text{h}$ ). Introduced values were conformable with the permeability of pure water for the same membranes, which for membranes of PVC, PAN and CA were, respectively:  $75 \text{ dm}^3/\text{m}^2 \cdot \text{h}$ ,  $47.9 \text{ dm}^3/\text{m}^2 \cdot \text{h}$  and  $37.9 \text{ dm}^3/\text{m}^2 \cdot \text{h}$ . During the process of purification of real oil-emulsion, the flux rate gradually slowed down (Fig. 6). Molecular weight cut-offs used in these investigations were 70 000 for membranes of CA and PAN and 110 000 for membrane of PVC (Fig. 4). The oil contents in UF permeate for membranes of PVC, PAN and CA were: 3.2 ppm, 2.6 ppm and 1.1 ppm, respectively (Table 1). These results show that a molecular weight cut-off of 70 000 is practically sufficient to obtain permeate with an oil content below 10 ppm. UF permeate with such oil contents can be drained directly to the sewage system without any posttreatment. The highest retention coefficient ascertained for oil, 97.9–99.1%, is much lower for COD 72.5–89.8%, and extremely low for TDS, 1.8–8.6%. All obtained UF permeates were limpid with a yellowish tinge, indicating the presence of some low-

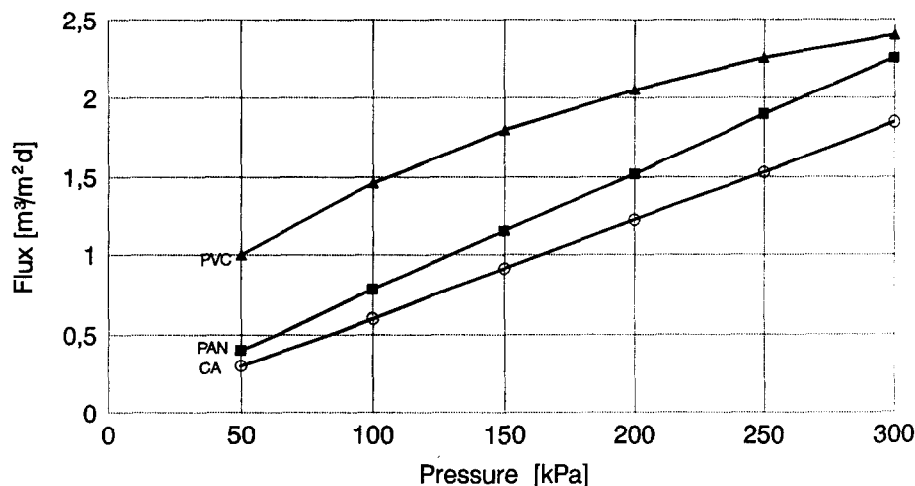


Fig. 3. Influence of transmembrane pressure on water flux for PVC, PAN, and CA membranes.

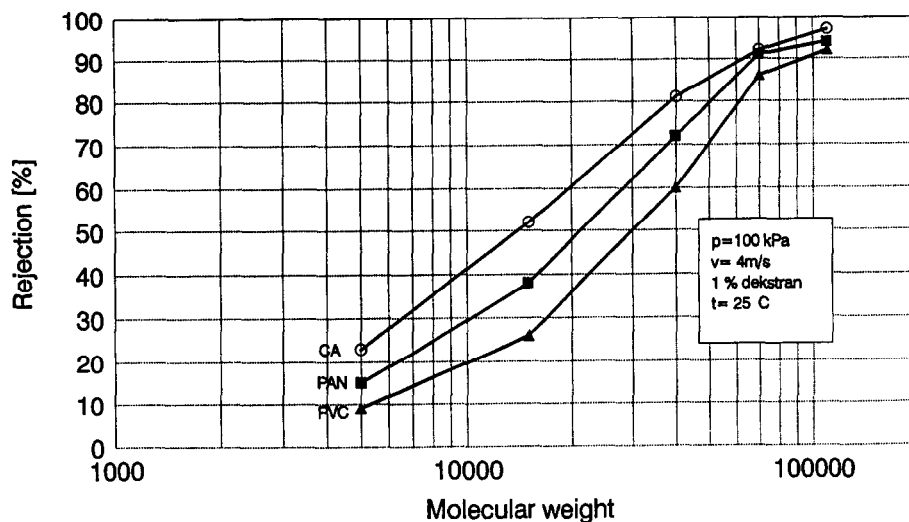


Fig. 4. Retention curves of UF membranes measured by refractive index for five different fractions of dextran.

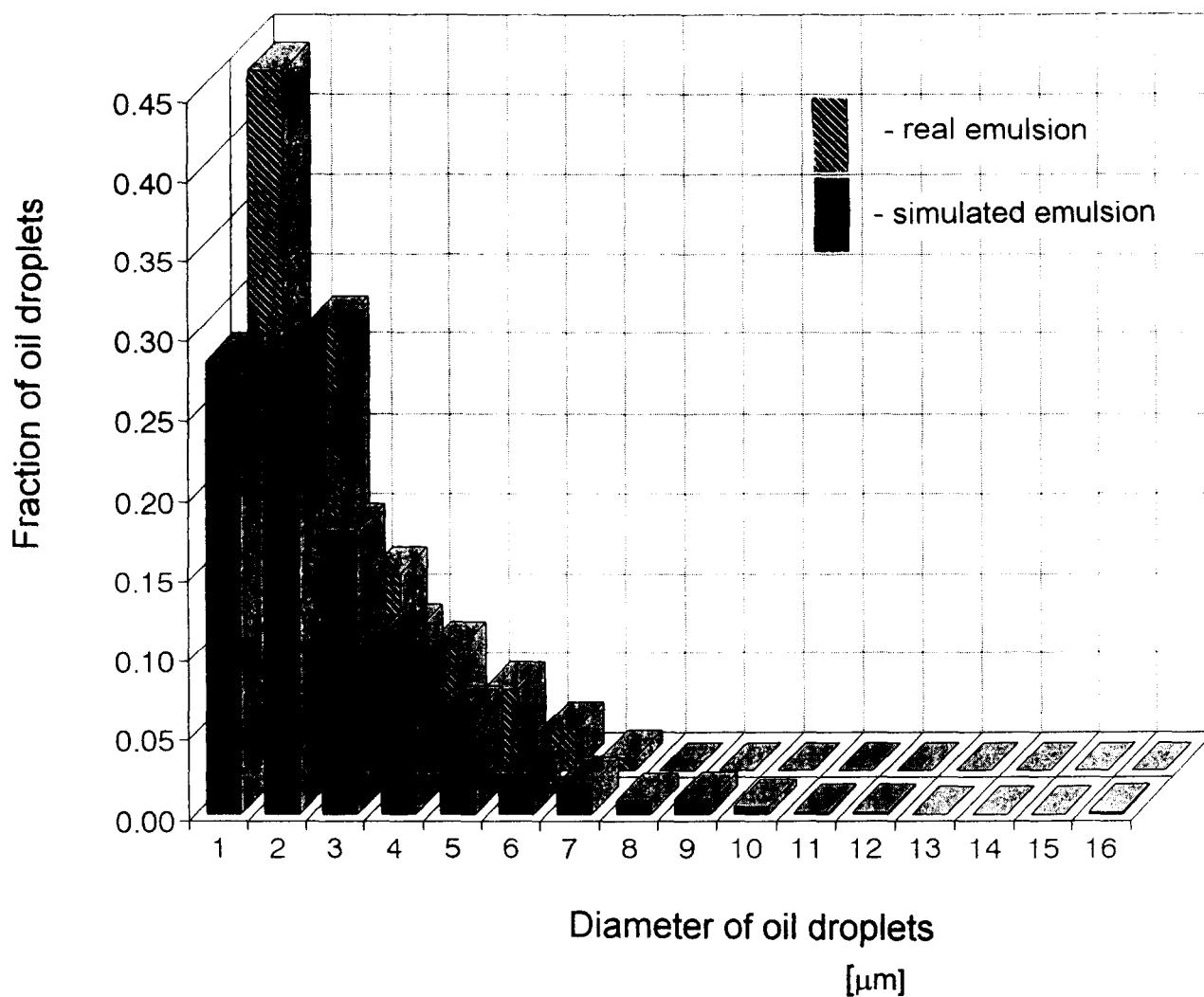


Fig. 5. Comparison of distribution and droplet sizes of oil in real and simulated emulsion.

Table 1

The parameters of feed and permeate and obtained pollution parameters reduction of UF and RO processes for real oil-emulsion ( $p = 0.15$  MPa,  $v = 3$  m/s,  $T = 310$  K)

Parameter	Unit	Ultrafiltration							Reverse osmosis		
		Feed	Permeate			Reduction (R) %			Feed	Per-meate	R %
			CA	PVC	PAN	CA	PVC	PAN			
Content of oil	mg/dm <sup>3</sup>	124	1.1	3.2	2.6	99.1	97.4	97.9	2.5	< 0.2	> 95
Chemical oxygen demand (COD)	mg O <sub>2</sub> /dm <sup>3</sup>	346	35	95	76	89.8	72.5	78.0	75.3	5.1	93.2
Total dissolved solids (TDS)	mg/dm <sup>3</sup>	3770	3510	3705	3445	6.9	1.7	8.6	3478	< 162	95.2

molecular compounds that will not be separated. Obtained results are conformable to UF membranes that have good fractionating and separating properties, but weak desalinating. When it is purposeful to utilize the UF permeate as process water, it is necessary to have posttreatment. In the second stage of purification, further trials were performed with RO treatment using PCI cellulose acetate membrane with nominal rejection for NaCl equals 90%. Fig. 7 presents dependence of flux and TDS rejection versus pressure for UF permeate purified by RO with PCI B1 module (CA membrane,  $T = 298$  K). The RO process was carried out in the pressure range of 1.0–3.5 MPa and a corresponding flux was obtained of 7–20 dm<sup>3</sup>/m<sup>2</sup>·h. Although in the second stage of purification, high retention coefficients of oil were obtained (> 95%), with COD = 93.2% and TDS = 95.2% (Table 1), RO permeate cannot be the process water because of the high values of TDS (162.5 mg/dm<sup>3</sup>). However, employment of composite RO membranes with a nominal rejection of 99% for NaCl permits the obtention of process water.

### 3.4. Ultrafiltration / reverse osmosis treatment simulated oil-emulsion

Simulated oil-emulsions were ultrafiltered at similar process parameters to real emulsions. Table 2 presents characteristic feed, permeate and pollution parameters in the reduction of UF and RO processes for simulated w/o emulsions. Simulated oil-emulsion prepared for investigations contains 5000 ppm of oil, which corresponds to the average contents of an oily ship's wastewater, containing both coarse dispersed emulsion as well as free floating oil [16]. The COD of oil emulsion was 12 100 mg O<sub>2</sub>/dm<sup>3</sup>, and TDS of 520 mg/dm<sup>3</sup>. The comparatively low value of TDS was probably a result of using fresh oils to prepare an emulsion. Simulated emulsions were ultrafiltered on the same membranes as the real emulsions (mol. wt cut-off = 70 000 for membranes of CA and PAN and 110 000 for membranes of PVC — see Fig. 4). The highest flux rate, measured after 1 h, was obtained for PVC membranes — 53 dm<sup>3</sup>/m<sup>2</sup>·h; it was lower for PAN membranes — 34 dm<sup>3</sup>/m<sup>2</sup>·h; and for CA membranes it was 10 dm<sup>3</sup>/m<sup>2</sup>·h. Obtained values illus-

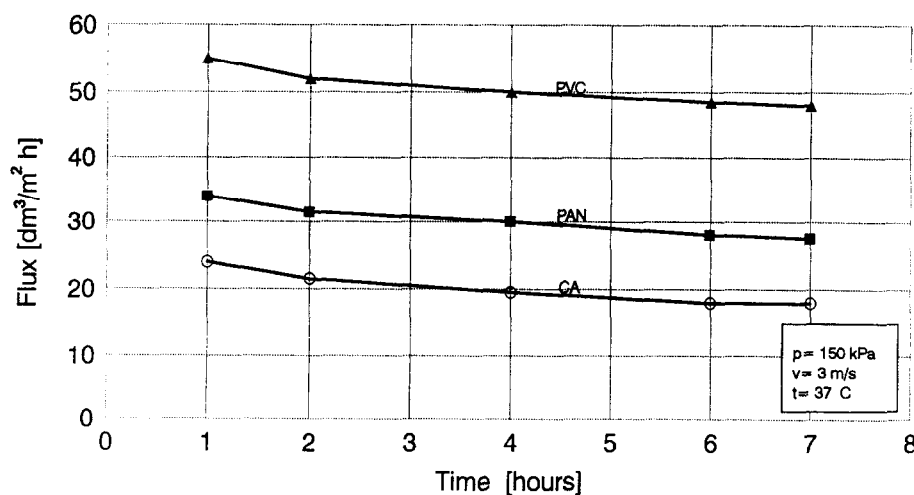


Fig. 6. Flux rate changes during ultrafiltration treatment of real oil-emulsion (124 ppm of oil) on PVC, PAN and CA membranes.

trate that oil concentrations in the range of 100–5000 ppm have not an essential influence on flux rate. The oil contents in UF permeate for membranes of PVC, PAN and CA were, respectively: 4.1 ppm, 4.2 ppm and 2.0 ppm. This test employed membranes that nearly completely separate oil from emulsion. The obtained UF permeate was colourless and in accordance with obligatory rules — such low oil contents can be discharged to the sewer. The highest retention coefficient was obtained for oil (99.9%), and was a little lower for COD (85.5–91.0%) and TDS (8.2–12.5). Obtained values confirm UF membrane properties — the oil concentration in the feed increases, but the oil content in UF permeate is still much the same. However, UF permeate has a low oil content, in comparison with the considerable values of COD (1089–1815 mg O<sub>2</sub>/dm<sup>3</sup>) and TDS (455–477 mg/dm<sup>3</sup>), and was therefore not suitable as process water. Also in that case, in order to get process water, it is necessary to employ additional RO treatment, using high efficiency

composite RO membranes, because employing RO in posttreatment by using the PCI B1 module with the T2/15W membrane at rejection coefficients for oil greater than 95%, for COD of 95.4%, and for TDS of 92.7%, does not produce process water.

#### 4. Conclusion

1. It has been observed that the obtained tubular membranes have relatively high pure water flux. It is appeared from the retention measurements that the relatively steep retention curves for polyacrylonitrile, polyvinyl chloride and cellulose acetate membranes could be obtained, indicating a rather narrow pore size distribution.
2. In the evaluation of these membranes for the separation of a real emulsion and simulated emulsion, the applied membranes with cut-offs of 70 000 for polyacrylonitrile and cellulose acetate

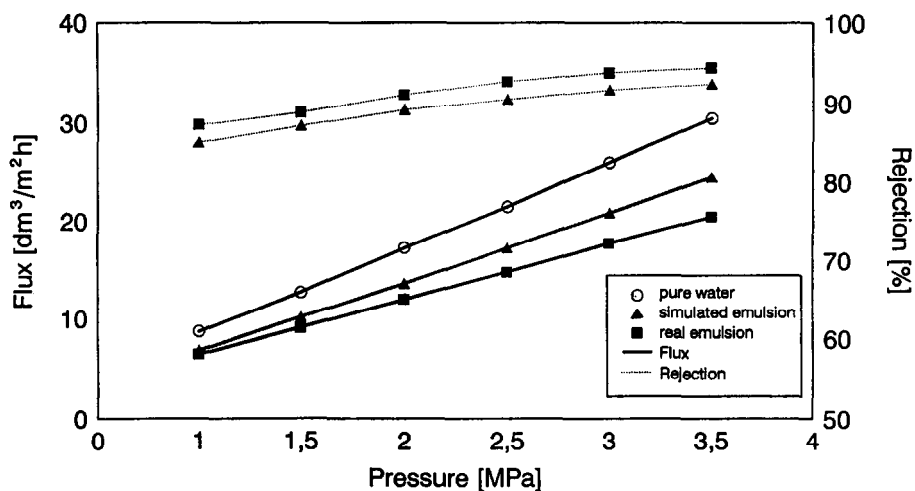


Fig. 7. Dependence of flux and TDS rejection versus transmembrane pressure for UF permeate purified by reverse osmosis with PCI B1 module (CA membrane type T2/15W,  $T = 298$  K).

Table 2

The parameters of feed and permeate and obtained pollution parameters reduction of UF and RO processes for simulated oil-emulsion ( $p = 0.15$  MPa,  $v = 3$  m/s,  $T = 310$  K)

Parameter	Unit	Ultrafiltration						Reverse osmosis			
		Feed	Permeate			Reduction (R) %			Feed	Permeate	R %
			CA	PVC	PAN	CA	PVC	PAN			
Content of oil	mg/dm <sup>3</sup>	5000	2.0	4.1	4.2	99.9	99.9	99.9	3.7	< 0.2	> 95
Chemical oxygen demand (COD)	mg O <sub>2</sub> /dm <sup>3</sup>	12 100	1089	1815	1330	91	85	89	1524	70.2	95.4
Total dissolved solids (TDS)	mg/dm <sup>3</sup>	520	477	461	455	8.2	11.2	12.5	469	34	92.7



membranes, and 110000 for polyvinyl chloride, give a permeate with an oil content of less than 10 mg/dm<sup>3</sup>. Most membrane manufacturers recommend treatment of oily wastewater using a membrane with a molecular weight cut-off of 50000, which can typically result in a permeate with an oil content of less than 10 mg/dm<sup>3</sup>.

3. These membranes exhibit high rejection coefficients of oil and COD for both real and simulated emulsions, reaching 99.9% for the oil and 91.0 % for COD. The rejection coefficient for TDS is low (maximum 12.5%), which is conformable to ultrafiltration membrane properties.
4. Obtained UF permeates are suitable to discharge into the sea, even in the special regions in accordance with obligatory international law. Application of reverse osmosis posttreatment, using RO membranes with a nominal rejection of 99% NaCl, allows UF permeate back into process water.
5. The results of dehydration of oil-water emulsion from the metal industry by ultrafiltration performed with PAN and PVC tubular membranes, described in [2], are similar to those obtained with the same type of UF membranes for bilge water as concerning the flux and separation coefficient of oil.

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