Letter to Editor

Removal of Oil from Model Oily Wastewater Using the UF/NF Hybrid Process

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Abstract

Studies concerning the removal of oil from model wastewater using the hybrid process combining ultrafiltration and nanofiltration were performed. The separation and transport characteristics of the employed membranes were determined. The content of oil in wastewater was estimated by the determination of total organic carbon and oil concentration measurements using a Horiba OCMA-310. The investigations of oil wastewater treatment were carried out in two stages. The permeate obtained from the UF process (the first stage) generally contains less than 6 mg/dm^3 of oil, whereas in the NF process (the second stage) the complete removal of oil was achieved.

Keywords: nanofiltration, ultrafiltration, oily wastewater

Introduction

Oily wastewater generated by various industries which are discharged into the natural environment creates a major ecological problem throughout the world. Oily wastewaters originating from cooling and lubricating emulsions from the metal industry contain a considerable amount of mineral oil, which hardly undergoes biochemical decomposition. The traditional methods used for the separation of oily wastewater consist of a series of physical and chemical steps, namely: free oily removal, suspended solids removal, chemical emulsion break, dissolved air flotation, clarification and filtration [1]. The chemical methods are primarily based on the neutralization of detergents (emulsion stabilizers), and a change of pH solution [2]. Typical processes for the oily wastewater treatment performed by previous investigators included ultrafiltration (UF), UF combined with ion exchange and microfiltration (MF) [3]. Nanofiltration (NF) has become an established technology currently used for the treatment of the surface and ground water for the removal of color and the precursors of disinfection by-products, as well as in the treatment and concentration of wastewater of both industrial and municipal origin [4].

UF is a low-pressure membrane separation technique used for fractionation of selected components by size. UF separates dissolved solutes in the range of 0.005 to 0.1 μm, which corresponds to a molecular weight cut-off (MWCO) from 1,000 to 500,000 Da [2]. Depending on the molecular weight cut-off the selected membrane will concentrate high molecular weight species allowing the dissolved salts and lower molecular weight materials to pass through the membrane. The UF membranes are currently used in industry for the concentration and clarification of large process streams. Compared to UF, the NF membranes can reject smaller components with MWCO > 200 [5]. Therefore the complete reject of macromolecules, including bacteria, viruses and pyrogens can be achieved in the NF process [6]. A unique feature of the NF membranes is the negative electric charge located on/within the membrane, therefore, these membranes also exhibit ion-selectivity. The multivalent ions are separated by the

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NF membrane in a high degree, whereas the majority of the monovalent ions pass freely through the membrane. This phenomenon is associated with the Donnan effect [7,8]. The retention coefficient of the divalent cations is approximately three times larger than that for the monovalent cations [9].

The problem associated with application of the NF process is plugging (fouling) of the membrane surface caused by various solutes present in the feed. This causes a decline in the permeate flux; therefore, the pretreatment of a feed to reduce the turbidity (e.g. by UF process) [10,11] should be used to prevent fouling.

The objective of this work was to investigate the transport and separation of oil from model wastewater using the hybrid process ultrafiltration and nanofiltration.

Experimental

A combination of UF and NF processes was carried out using the tubular modules (UF membranes - made of polivinylidene fluoride, series FP 100 and NF – composite hydrophylic polyamide membrane, series AFC30, purchased from PCI). A scheme of the UF pilot plant is presented in Fig 1.

The process of cross-flow pressure-driven membrane filtration requires only the pumping of the feed stream tangentially to the appropriate membrane, i.e. parallel to the membrane surface. The membrane splits the feed into two streams: the permeate consisting of the components small enough to pass through the membrane pores and concentrate (retentate) consisting of the components large enough to be retained by the membrane. The process was operated in a closed system in which the permeate was recycled directly to the feed tank to ensure a constant feed concentration. The important operating variables are applied transmembrane pressure and the cross-flow velocity through the membrane module. The cross-flow velocity is the average rate, at which the fluid flows parallel to the membrane surface. The permeate flux depends on the applied transmembrane pressure. The investigations were carried out at the transmembrane pressures in the range of 0.1-0.4 MPa for UF process whereas in the range of 1.0-2.5 MPa (varied every 0.5 MPa) for the NF process.

The transport properties of the UF and NF membranes were investigated by the determination of the permeate flux on the basis of measurements of the permeate volume collected from a module during a unit of time (working area of the both membranes were equal to 0.9 m^2).

A permeate from the reverse osmosis (RO) pilot plant, tap water for both UF and NF membranes were used as a feed. The RO permeate is pure water, with the content of total organic carbon equal to 0.6 mg/dm^3 and electrical conductivity of 13 μS/cm. Thus, the application of RO permeate as a feed allowed us to determine the maximum permeate flux under given process conditions. Moreover, model solutions of oil (four series: 100-400 ppm of oil varied every 100 ppm) were applied for the UF process. The model solutions containing oil were prepared with the use of oil (slop oil) collected from bilge water treatment. These solutions were prepared using the RO permeate. The investigations of the removal of oil from model solutions were carried in two stages: in the first stage a model oil solution was used as the feed for the UF process, and in the second stage, the UF permeate was used as the feed for the NF process. The flow sheet of the system used in the investigations which comprise a combination of UF/NF processes is presented in Fig 2.

The feed temperature was kept at 25^{O}C for both processes. Samples of the permeate and feed were collected every hour for the determination of the retention coefficient, the concentration of oil (measured using a Horiba

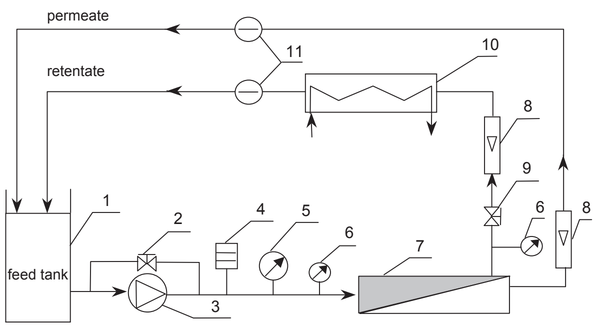

Fig. 1. Scheme of NF/UF pilot plant; 1 – feed tank, 2 – by-pass valve, 3 – pump, 4 - dampener, 5 – pressure gauge, 6 – manometer, 7 – module, 8 – rotameter, 9 – throttling valve, 10 – heat exchanger, 11 – control of temperature, conductivity.

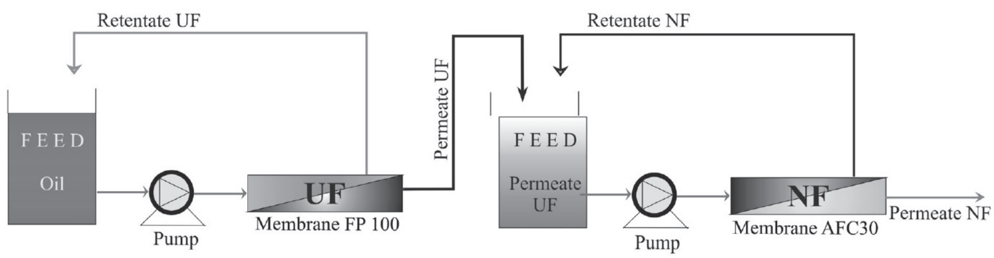

Fig. 2. Flow sheet of the UF/NF system for the removal of oil from wastewater.

OCMA-310) and total organic carbon (TOC) (measured using a Multi N/C Analyzer - Analytic Jena). The retention coefficient (R) was calculated using the following equation:

$$R = (1 - \frac{C_P}{C_N}) * 100\%$$

where: C_P – concentration of determined component in the permeate, C_N – concentration of determined component in the feed.

Results and Discussion

In Fig 3, the permeate fluxes (when the feed was, respectively, the RO permeate, tap water and model solutions of oil) as a function of transmembrane pressure are given. The curves exhibit practically a linear character and indicate that significant changes of the permeate flux were found as the transmembrane pressure increased. The maximum flux of the permeate was determined when RO permeate was used as a feed because in this case no plugging of the membrane was observed due to the composition of the feeding stream. The permeate flux obtained at a pressure of 0.4 MPa was equal to 98 dm^3/m^2*h and was 4 times higher than that at 0.1 MPa. However, a decline of the permeate flux by 20-40% in relation to maximum flux was observed when the feed was oily wastewater. The reason for permeate flux decline was associated with a growing concentration of oil in the respective series of feeds. The retention coefficients of the pollution indicators obtained in the UF process are presented in Fig. 4.

The retention of oil amounted to 95% and was found to be independent on the oil concentration in the examined feeds whereas the rejection of TOC was equal to 85%. In the second step of the studies the UF permeate was subjected to a further purification in the NF process.

After completing the first stage of studies the maximum permeate flux was again determined. A slight decline of the maximum permeate flux in relation to the starting permeate flux was observed; however, the complete recovery of the initial permeate flux was achieved after rinsing the membranes with the RO permeate.

A dependence of the NF permeate flux on the transmembrane pressure was shown in Fig. 5. As can be seen, the permeate flux increases with an increase of the pressure and the curves have a linear character. For the RO permeate used as a feed, the permeate flux was slightly higher than that for the UF permeates.

The retention coefficients of TOC and oil in the NF process at the selected transmembrane pressure amounting to 1.0 MPa were presented in Fig. 6. In the consecutive UF permeates used as the feed for the NF process the retention of oil determined as TOC and oil was over 99%. Similarly, as in the case of UF process, the maximum permeate flux was determined after completing the studies. A flux decline was not observed, which indicates that a membrane blocking (fouling) did not take place. A real content of oil in the feed and the permeates for both investigated processes was presented in Table 1.

The performed studies of two-stage treatment of model oily wastewater demonstrated a high effectiveness of treatment of oily wastewater already in the first stage with the application of the UF membrane. The application of the second stage of purification with the use of NF membrane demonstrated that the retention of oil was above 99%.

The membrane treatment of oily wastewater generally has the dual purpose of reuse and disposal. The NF permeate can be reused as process water since the quality of this permeate complies with requirements concerning the content of dissolved salts and almost all hardness was removed. Due to the complete removal of oil derivatives in the NF process zero oil discharge was achieved [12].

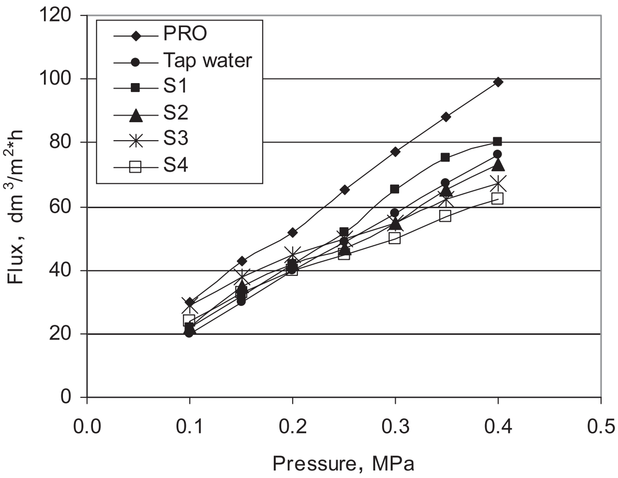

Fig. 3. Determination of the transport properties of UF membranes. The influence of the transmembrane pressure on the permeate flux. Feed: PRO – permeate RO, Tap water, S1 – 100 ppm of oil, S2 – 200 ppm of oil, S3 – 300 ppm of oil, S4 – 400 ppm of oil.

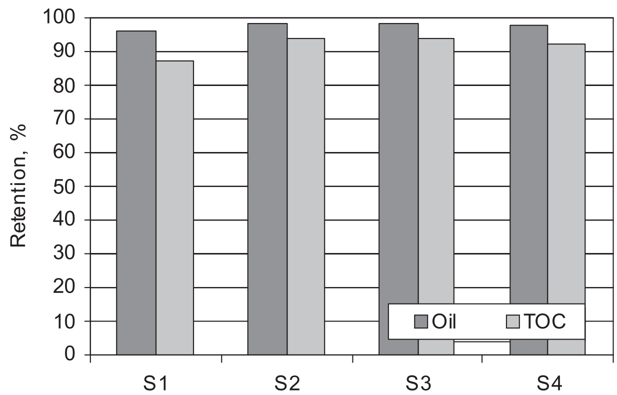

Fig. 4. Retention of oil and TOC in UF process for various feeds (at constant 0.2MPa transmembrane pressure). Feed: the content of oil in the feed: S1 – 100 ppm of oil, S2 – 200 ppm of oil, S3 – 300 ppm of oil, S4 – 400 ppm of oil.

Table 1. Retention coefficients of oil and TOC during the treatment of model solutions by UF and UF/NF processes.

Oil concentration, ppm (feed)	UF Permeate		NF Permeate	
	Oil concentration	TOC	Oil concentration	TOC
	ppm			
100	4.59	1.35	0.0	0.1
200	3.57	1.05	0.0	0.2
300	6.15	1.81	0.0	0.3
400	7.25	1.89	0.0	0.35

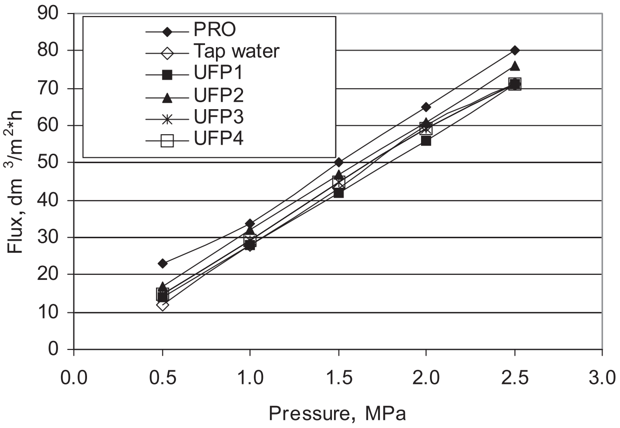

Fig. 5. The influence of transmembrane pressure on the permeate flux: Feed: UFP1 – UF permeate from series 100 ppm of oil, UFP2 – UF permeate from series 200 ppm of oil, UFP3 – UF permeate from series 300 ppm of oil, UFP4 – UF permeate from series 400 ppm of oil.

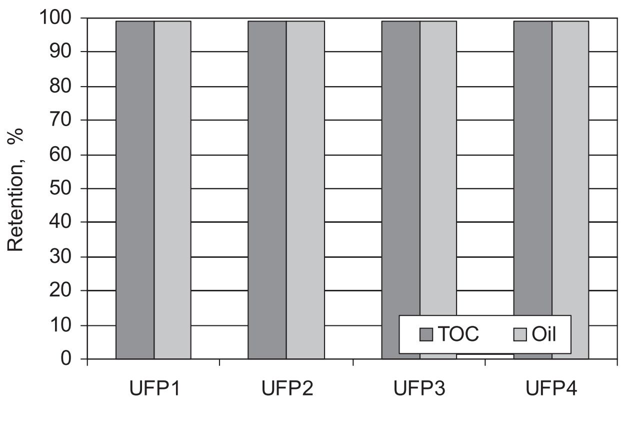

Fig. 6. Retention of oil and TOC in the NF process at constant pressure (1.0 MPa). Feed: UFP1 – UF permeate from series 100 ppm of oil, UFP2 – UF permeate from series 200 ppm of oil, UFP3 – UF permeate from series 300 ppm of oil, UFP4 – UF permeate from series 400 ppm of oil.

The use of the UF/NF integrated process for the treatment of oily wastewater simplifies the conventional system because the use of tubular UF modules does not require pretreatment and the obtained UF permeate complies with the requirements of feed for spiral-wound NF membranes [13,14].

Conclusions

1. The studies show that using UF, the oil pollutants determined as TOC were removed from the model wastewaters in 85%, whereas oil in 95%.
2. The application of the second stage of the model solution treatment (nanofiltration of the UF permeate) allowed complete removal of oil from treated solutions.
3. Both the UF and NF permeate comply with the standards concerning the discharge of oily wastewater into the environment (MARPOL – Convention below 15 ppm of oil in wastewater). Additionally, the permeate obtained in the NF process can be reused due to a practically total lack of oil.
4. Some soluble organic components (e.g. surfactants) go essentially untreated during the UF process but are removed in a significant degree (85%) during the NF process. Therefore, the need of further treat of UF permeate e.g. by biological method, is eliminated.

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