OIL-WATER SEPARATION, USING A HYDROPHILIC POLYSULFONE-POLYVINYLPYRROLIDONE ULTRAFILTRATION MEMBRANE

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RESUMEN

Se investigó la ultrafiltración para la separación de microemulsiones aceite/agua. Este procedimiento presenta el inconveniente de la reducción del flujo debido al ensuciamiento de la membrana. La hidrofilicidad de las membranas evita la adhesión de aceite en la superficie, mientras que la fuerza centrífuga evita la acumulación de aceite en las cercanías de la membrana, manteniendo flujos elevados. Los mejores resultados se obtuvieron con la membrana HL9 (4:18 Polivinilpirrolidona:Polisulfona), al aplicar 1000 r.p.m., la cual tuvo una recuperación del 85% de agua con una velocidad de flujo de 4553 L/m²·d y una reducción del flujo del 56%. El contenido de aceite se determinó por espectroscopía de infrarrojo, con transformadas de Fourier y accesorio de reflectancia total atenuada (HATR-FTIR).

ABSTRACT

Ultrafiltration for the separation of oil-in-water micro-emulsions was investigated. Membrane fouling is the major problem in ultrafiltration (UF) system. The present work proposes the rotary spinning ultrafiltration membrane system for the treatment of oil-in-water micro-emulsions. The best results were obtained using the membrane 9 (4:18 polyvnylpyrrolidone:polisulfone) with water recovering of 85% with 1000 rpm and a flux velocity of 4553 L/m²d, and 56% of flux decline. The oil-in-water micro-emulsions were measured using a HATR-FTIR.

INTRODUCTION

Oil-in-water emulsions are one of the main pollutants emitted into water by industry and domestic sewage (Daminger *et al.* 1995). The discharge of crude oily wastewater into the sea or rivers has been under increasingly careful scrutiny in recent years. In addition to oily wastes from the petrochemical, metallurgical and processing industries, it should be remembered that the production of crude oil is often accompanied, on average, by an equal volume of water. A production that separates most of the oil from water is usually used to give an initial separation of oil and water. The small quantity of remaining oil in the water must be reduced to an acceptable limit before the water can be discharged into sea or rivers or re-injected for water flooding (Zhen-Liang *et al.* 1999).

The particularly stable emulsions are generated during several mechanical operations such as grinding, rolling, alkaline degreasing and transportation (Koltuniewicz and Field 1996). The standard method for treatment of emulsified oily wastes is chemical de-emulsification followed by secondary clarification. The systems require the use of a variety of chemicals including sulphuric acid, iron and

alumina sulphates and proprietary chemicals such as polymers, waste pickle acid, etc. (Nazzal and Wiesner 1996; Koltuniewicz and Field 1996; Arnot *et al.* 2000).

Several new effective methods have been recently developed to solve the problem of oily wastes. Biotechnology offers a new approach based on biodegradation and biotransformation of fats and oily wastes (Koltuniewicz *et al.* 1995). One of the most effective methods of oil emulsion separation from water is microfiltration (MF) and ultrafiltration (UF) performed using ceramic membranes (Koltuniewicz *et al.* 1995). The performance of these membranes is enhanced by means of surface modifications to achieve maximum yield and separation effectiveness.

The primary limitation of conventional cross-flow UF system in the treatment of concentrated oily wastewaters is the low flux observed at high oil concentrations. Recirculating velocities are used in conventional UF systems to maintain a satisfactory flux by inducing hydraulic turbulence, which scours accumulated solute molecules from the membrane surface. However, as the oil is concentrated, it becomes difficult to maintain a high cross-flow velocity due to an increase in waste viscosity. This problem can be overcome by decoupling the hydraulic cleaning action from feed recirculation-pressurization. In the high-shear rotary ultrafiltration (HSRUF) system, disk membranes are rotated at speeds up to 1750 revolutions per minute (rpm) to generate the hydraulic turbulence necessary to scour solute molecules from the membrane surface. Pumping is required only to provide transmembrane pressure and a small amount of recirculation flow.

METHODOLOGY

Figure 1 shows the schematic view of our separation unit. The dispersion was transferred from the tank by pump to the membrane rotary system, and the rejected material was recirculated into the feed tank, while permeate was collected in a separated reservoir.

The emulsion was prepared as follows: Owing to the fact that the composition of the actual waste machine cutting fluid may vary from machine shop to machine shop, for the purpose of evaluating the functionalities of the innovative energy-saving design of the spinning membrane system, a synthetic waste machine oil was used to cut the fluid in this research. The new and undiluted machine cutting oil SOLG-A, from elf lubricants of México, was bought at a machine shop near the Research Center. The stock synthetic waste machine cutting fluid was prepared by diluting 1.0 g of the original commercial machine cutting oil into 1000 mL of deionized water.

Three membrane types were tested in the same manner, as previously reported (Espinoza-Gómez and Lin,
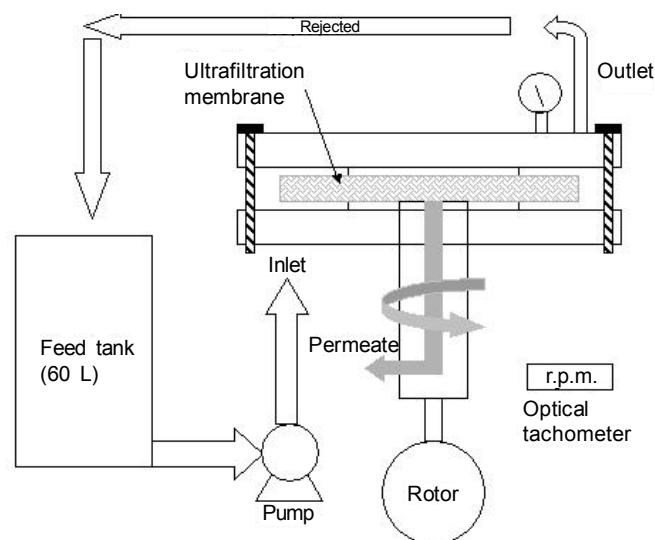

Fig. 1. Scheme of the ultrafiltration pilot plant

2001). The permeability of each of the membranes for pure water was tested after cleaning and before each run. The flux for pure water was easily restored to the original value through rinsing with distilled water.

The American Standard Test Method (ASTM) for oil, grease and petroleum hydrocarbons in water described in ASTM D 3921-85, Vol. 11.02. 1996 was adopted throughout our entire work. The oil content in the test solution was determined by Horizontal Attenuated Total Reflection IR (HATRIR), using an IR spectrophotometer (instrument model Perkin Elmer 1600 FTIR). A quantitative calibration curve, for oil content in oil-water emulsion, was constructed using standard solutions prepared from the new and undiluted machine cutting oil. **Figure 2** is an IR spectrum of the cutting oil; the peak at 2913 cm^{-1} was monitorated for the determination of oil content (**Fig. 3**). The oil content in the permeate sample solution was determined against this calibration curve as recommended by the ASTM.
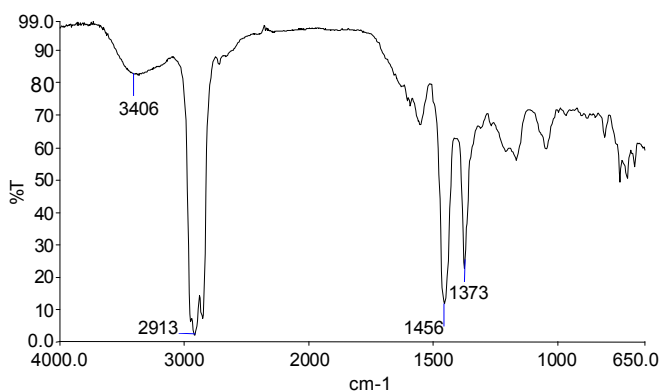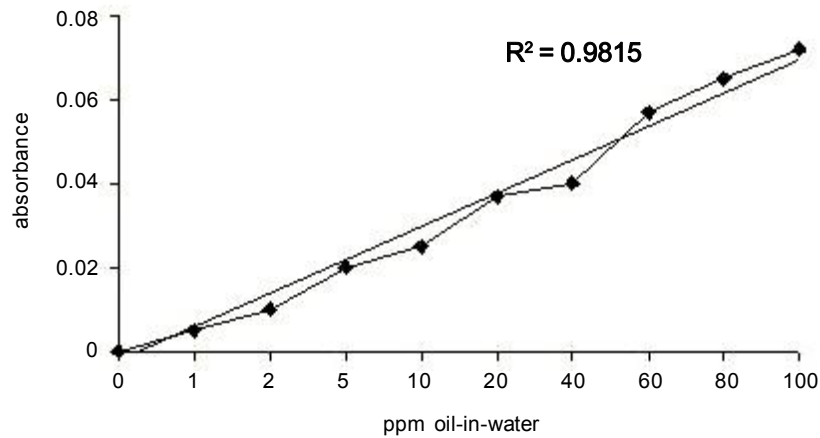

Fig. 2. IR spectrum of oil

Fig. 3. Calibration curve for the oil-in-water emulsion determination ($v=2930cm^{-1}$)

RESULTS

As illustrated in **Figure 4**, the conventional spinning membrane system suffers some energy waste. The process of permeate water flow behind the membrane disk to the central rotating hollow shaft, is hindered by the outward pushing centrifugal force during the spinning of the membrane filtration operation. Therefore the effective filtration pressure is cut short by the action of this centrifugal force, this amount of energy is being wasted during the filtration process.

The centrifugal force acting on this out-going permeate water flowing inside this tube creates a suction action to pull the permeate. This waste ends up in the product-water channel in front of the spinning hollow shaft. This in fact counteracts the centrifugal force, acting on the permeate that is flowing toward the spinning hollow shaft. The result of this is an increase in the effective filtration pressure across the spinning membrane. Thus for a given applied filtration pressure and at a given spinning velocity of the membrane disk, our energy-saving spinning membrane system (with tube), should have a
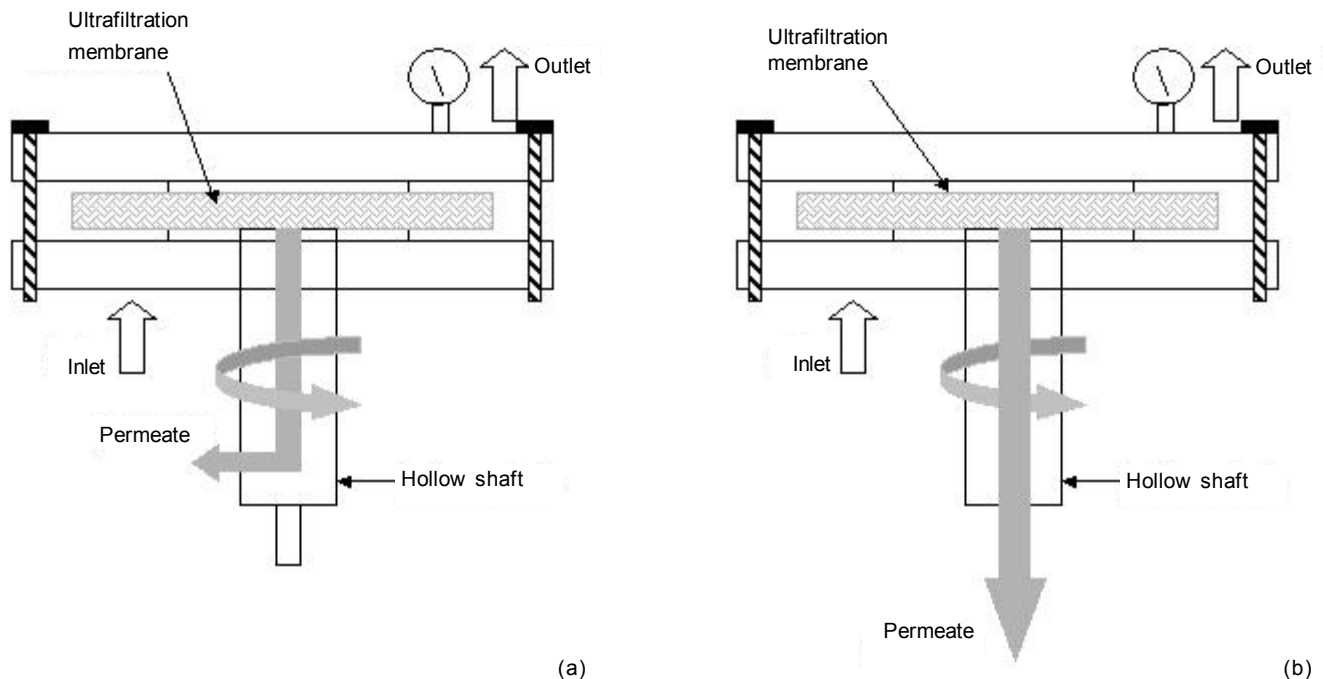

(a)   (b)

Fig. 4. Energy-saving membrane spinning system, (with tube) (a); and conventional spinning membrane (without tube) (b)
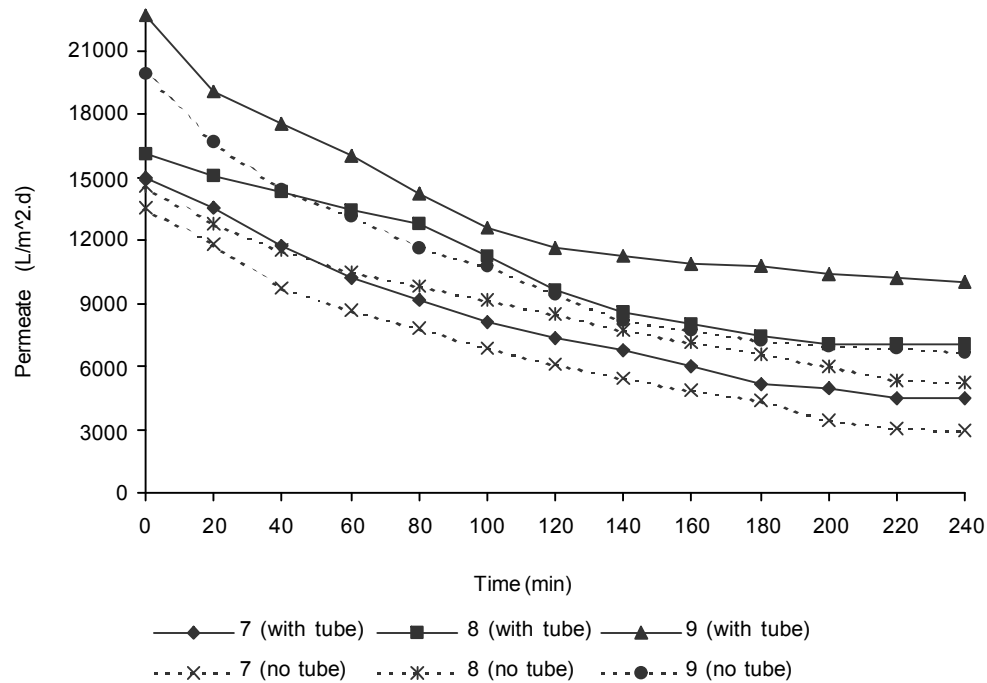
Fig. 5. Membrane permeates flux velocity for the spinning membrane disk system with and without the energy-saving device (1000 rpm oil-in-water in feed: 1000 mg/L)

higher permeate flux per time unit than the conventional spinning membrane system (without tube) (**Fig. 4**). Indeed the experimental results of oil-water emulsion separation demonstrate this energy-saving benefit. **Figure 5** shows the comparison on the membrane permeates velocities for the spinning membrane systems equipped with and without the energy-savings device (tube).

The permeate velocities for membranes 7, 8, and 9, were determined to be 19.3, 18.5, and 15.5 10^3 L/m^2.d respectively for the energy-saving design. For the conventional design, the corresponding permeates velocities were found to be 13.5, 10.9, and 6.7 10^3 L/m^2.d. These correspond to 43.0, 69.7 and 131% increase in permeates velocities for 7, 8, and 9 membranes respectively. The other membranes elaborated in this project, did not have good results in comparison with the three employed. The flow speed and the oil rejection were not significant.

The higher membrane permeates velocities achieved by our energy-saving spinning membrane system does not hinder the oil rejection by the membrane. **Figure 6** indicates that for the same membrane, the oil rejection was found to be higher for the spinning membrane system with our energy-saving design than for the conventional design.

The great force created by the spinning membrane disk gives the suspended solid or large soluble solute little chance to settle on the membrane surface. **Figure 7** shows the dependence among the permeate velocity, the

series of membranes (7, 8, and 9), and on membrane disk spinning velocity and filtration time. This spinning membrane filtration operation keep it's permeate velocity in a good level, throughout 6 hours of test run, while the stationary membrane filtration process suffers de-
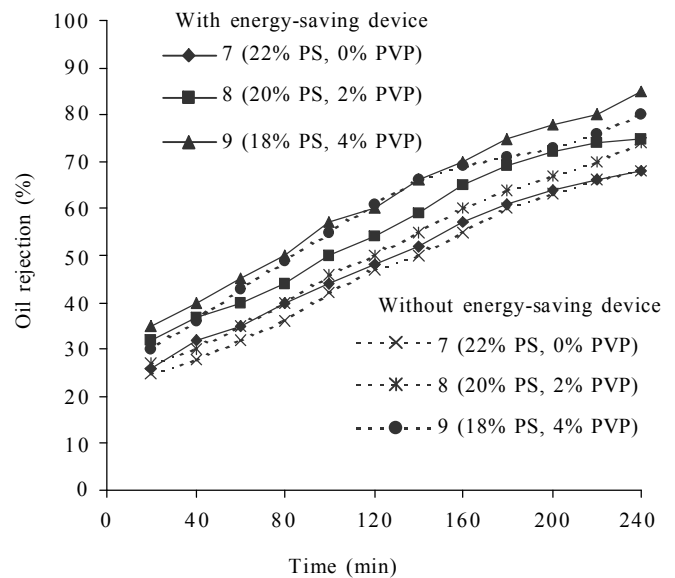

Fig. 6. Oil rejection (%) for the spinning membrane disc system with and without the energy-saving device (1000 rpm oil-in-water in feed: 1000 mg/L) (PVP: polyvinylpyrrolidone, PS: polisulfone)
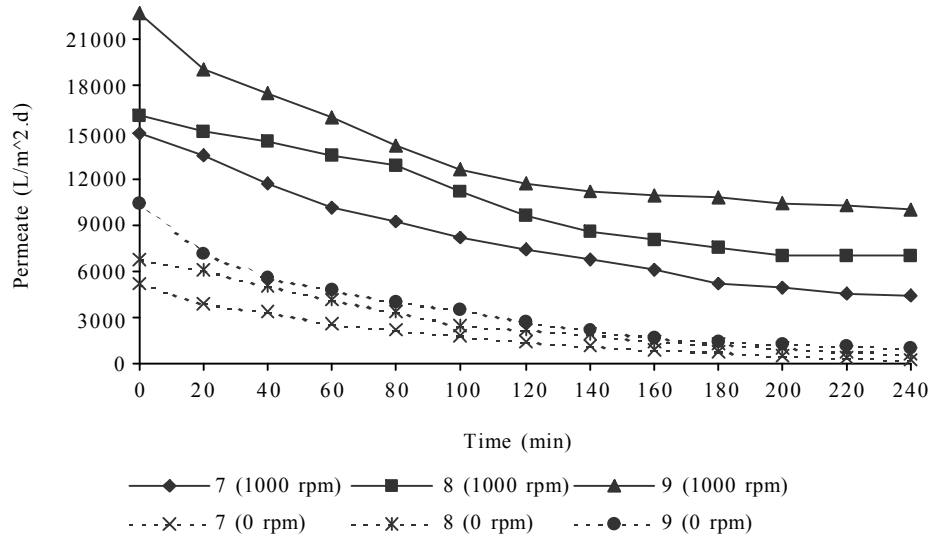
Fig. 7. Dependence of the permeate velocity on membrane series (7, 8 and 9), on membrane disc spinning velocity and filtration time (oil-in-water in feed: 1000 mg/L of oil-in-water)

crease in permeate velocity soon after the test run was started and continued to decrease with time. From these test runs, it can also be seen, that the negative surface charges density at the membrane surface do not affect the permeate velocity of the spinning membrane system. This is may be due to the fact that the great shear force created by the spinning membrane disk is so overwhelmed that the repulsive force existing between the fixed negative surface charge at the membrane and the negatively charged solute like oil-water emulsion in the feed, becomes insignificant.

However, for the stationary test runs (i.e., membrane disk spinning velocity = 0 rpm), the membrane, having higher negative surface charge density, indeed tends to have higher oil rejection from the oil-water emulsion feed. The oil rejection of the membrane series is in the order of 9>8>7 (**Fig. 8**). This is in line with the reduction in membrane surface charge density shown in **Figure 9.**
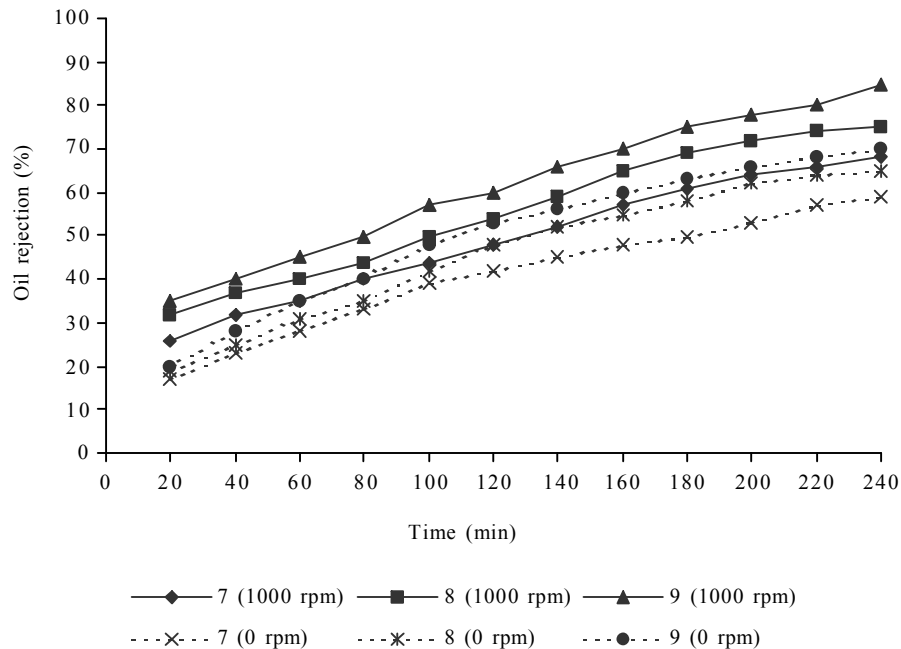

Fig. 8. Dependence of the oil rejection (%) on membranes series (7, 8 and 9), membrane disc spinning velocity and filtration time (oil-in-water in feed: 1000 mg/L)

Fig. 9. Composition of polyvinylpyrrolidone (PVP) polisulfone (PS) ultrafiltration membrane casting solution

In spite of more than thirty years of research and development works on membrane technology for industrial, environmental and domestic applications, membrane fouling is still a major obstacle facing us today. One of the major factors contributing to the membrane fouling process is the condition of the feed flow at the boundary region above the membrane surface. Turbulent flow decreases the thickness of the concentration polarization layer above the membrane surface, and also minimizes the chance of suspended solid or large solute in the feed to settle down at the membrane surface. In order to minimize the membrane fouling, the spinning membrane separation system should be a prime choice for many membrane separation processes. However the conventional spinning membrane disk separation system suffers one short coming: the effective filtration pressure of the spinning membrane system is cut short by the centrifugal force acting upon the permeate flowing towards to the spinning hollow shaft.

Our energy-saving design of the spinning membrane system clearly demonstrated the energy-saving benefit,

the increase of permeate velocity can be as high as 132% (using 9 membrane) over the conventional spinning membrane system. This innovative design for the spinning membrane system may have an impact on the wastewater treatment industries in the future.

ACKNOWLEDGEMENT

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