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Experimental performance evaluation of polymeric membranes for treatment of an industrial oily wastewater

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ABSTRACT

In a comparative research, five polymeric membranes were employed to treat the oily wastewater of Tehran refinery using cross-flow membrane filtration. To do these experiments, the outlet wastewater of the API (American Petroleum Institute) unit of Tehran refinery was used as the feed. Five different membranes were used including two microfiltration (MF) PS (0.1 µm) and PS (0.2 µm) membranes and three ultra-filtration (UF) PAN (20 kDa), PS (30 kDa) and PAN (100 kDa) membranes. The performances of these membranes for treatment of the oily wastewater were evaluated and compared. The final permeation flux of oily wastewater was determined for each membrane (76.0, 73.1, 53.7, 32.1 and 96.2 L/m^2 h, respectively). The PAN (20 kDa), PS (30 kDa) and PAN (100 kDa) membranes showed higher rejection, lower permeation flux and higher permeation flux, respectively. The PAN (100 kDa) UF membrane was effective and suitable for treatment of the oily wastewater to achieve up to 94.1%, 31.6%, 96.4%, and 97.2% removal of TSS, TDS, turbidity and oil-grease content, respectively with a permeation flux of 96.2 L/(m^2 h).

In this work, Hermia's models were used to investigate the fouling mechanisms of polymeric membranes. The results show that cake filtration model can well predict the initial and final permeation flux of MF and UF membranes. After cake filtration model, the best permeation flux predicted to the experimental data was intermediate pore blocking model and worst predicted permeation flux was for complete pore blocking model. Chemical cleaning of polymeric membranes fouled with oily wastewater was investigated with metal chelating agent (EDTA), surfactant (SDS), and their combination. The results showed that combination of SDS and EDTA are able to clean the fouled polymeric membranes effectively. Mechanisms of the membrane fouling and chemical cleaning of them were also investigated.

1. Introduction

A recent research regarding generation of the oily wastewater in Iranian industries (e.g. Tehran refinery) indicates that there are over 100 plants in Iran discharging over 1000 m^3/day each. However, some industrial oily wastewaters may be less in volume but contain much higher concentration of pollutants. Industries like oil refinery, petrochemical, oil distribution and textile have high levels of oil-grease in their effluents. Oily wastewaters which are daily produced in Iran's oil industries have become a big threat for water sources and environment that must be solved urgently.

Conventional approaches to treat oily wastewaters include gravity separation, API unit and skimming, dissolved air flotation, de-emulsion coagulation and flocculation [1–3]. The gravity separation process followed by skimming is fairly effective to remove free oil from wastewater. API unit has been widely accepted as an effective, low cost, primary treatment step. However these methods are not effective for removing smaller oil droplets and emulsions. The oil that adheres to the surface of solid particles could be effectively removed sedimentation. Dissolved air flotation process uses air to increase the buoyancy of smaller oil droplets for the enhancement of separation rate. The emulsified oil in the influent of dissolved air flotation process is removed by de-emulsification with chemicals, thermal energy or both. Dissolved air flotation units typically employ chemicals to promote coagulation and to increase flock size to facilitate separation [1,4].

All these conventional systems based on physical and chemical principles indeed cannot give an absolute guarantee in terms of separation efficiency and effluent quality. However, high consumption of chemicals in coagulation makes these processes costly and even sometimes the chemicals not reacted are also found in the final wastewaters. Treatment of the oily wastewaters according to the environmental discharged standards (oil content less than 5 ppm) requires various oil treatment systems [5–7].

Membrane based separation processes, especially micro- and ultra-filtration processes are proving to be promising alternatives for conventional industrial separation methods, since they offer numerous

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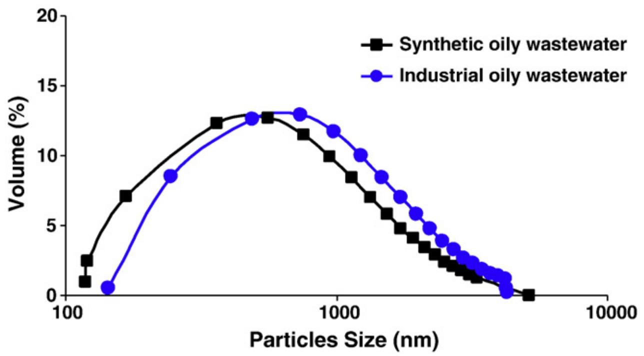

Fig. 1. Droplet size distribution of the synthetic (1000 ppm gas–oil) and industrial oily wastewaters.

advantages (e.g. high selectivity, easy separation, mild operation, continuous and automatic operation, economic and fast operation, as well as relatively low capital and running investment) [1,3,7]. Previous studies [8–13] showed that treatment of domestic, industrial, oil-in-water and oily wastewaters using MF and UF processes satisfied the environmental standards and reuse of the wastewater.

The major problem in application of polymeric membranes for treatment of oily wastewaters is membrane fouling. The fouling of polymeric membranes typically forms by inorganic and organic materials present in the wastewaters, adhering to the surface and pores of the membranes and resulting in deterioration performance (reduction of the permeation flux) with a consequent increase of energy and membrane replacement costs.

In this work, oily wastewater of Tehran refinery was treated by micro- and ultra-filtration processes employing polymeric membranes. In addition, cleaning of the fouled membranes was investigated using chemical agents such as chelating and surfactants. Finally, the fouling mechanisms in the present cases were assessed by fitting the experimental data to various filtration-fouling models.

2. Materials and methods

2.1. Feed

Synthetic and industrial oily wastewaters were used to investigate the performance of polymeric membranes. Oil-in-water emulsions were prepared by mixing commercial grade gas–oil (Tehran refinery, IRAN), deionized water and surfactant (Triton X-100 from Merck). The surfactant was dissolved in water 10 min before addition of gas–oil. Surfactant was added as emulsifier to the mixture to stabilize the emulsions. A blender was used to mix the mixtures at high shear rates (6000 rpm) for 30 min. The oil concentration of synthetic feed was 0.1% for all experiments. This was due to the similarity of size distribution of oil droplets between the synthetic emulsion containing 0.1% oil and the industrial oily wastewater.

The size of oil emulsion droplets in the feed was measured by a laser diffraction particle size analyzer, model LS 13320 manufactured by Beckman Coulter Co. Droplet size distribution of the emulsion (1000 ppm) is presented in Fig. 1. As observed, mean droplet size is 736.5 nm. Under these conditions, the emulsions were highly stable for employing in MF and UF experiments because within 12 h, no phase separation was observed.

Industrial oily wastewater is a two-phase dispersive system in which the continuous phase is water and the dispersed phase is oil-grease content, total suspended solid (TSS) and chemical substances such as detergents, salts and caustic soda. Their amounts depend on the type of the process that generates the effluent. The outlet of the API unit of Tehran refinery was used as the feed. The feed was taken daily and used immediately. Analysis of the feed taken from the industrial oily wastewater of the API separator unit is presented in Table 1. Droplet size distribution of the industrial oily wastewater is shown in Fig. 1. As observed, mean droplet size is 752.4 nm.

2.2. Membranes

The membranes used in this work were:

1) Polysulfone (PS), DOW Co. of Denmark, hydrophilic, MWCO 30 kDa
2) Polyacrilonitrile (PAN), Sepro membranes of USA, hydrophilic, MWCO 20 kDa
3) Polyacrilonitrile (PAN), Osmonics of USA, hydrophilic, MWCO 100 kDa
4) Polysulfone (PS), Alfa Laval of Denmark, hydrophilic, Pore sizes 0.1 μm
5) Polysulfone (PS), DOW of Denmark, hydrophilic, Pore sizes 0.2 μm

2.3. Analysis of the samples

The scanning electron microscopy (SEM) (Philips model XL30) was employed to analyze the samples. Samples for measurements of the feed and the permeate total suspended solids (TSS), biological oxygen demand (BOD_5), chemical oxygen demand (COD), oil-grease content, turbidity and total dissolved solids (TDS) were taken as necessary and analyzed according the procedure outlined in standard methods [14]. The turbidity was determined using Turbidimeter (Model 2100A HACH).

2.4. Experimental set up and operation

Fig. 2a shows experimental set up used in all the experiments. The oily wastewater treatment was operated in cross-flow batch concentration mode. In this manner, the feed crosses the cell adjacent to the membrane surface and the permeate passes through the cell vertical to the membrane surface. In other words, the feed was pumped to the cross-flow cell from the tank and the permeate was taken out of the loop and collected in an Erlenmeyer flask and measured using an electric balance, and the retentate was completely returned to the tank. This cycle was repeated continuously. There was a by-pass before the feed inlet to recycle extra feed to the tank. There were two valves in the bypass flow and the retentate flow to adjust the main flow rate and the desired operating pressure. The bypass flow had a significant influence on the feed temperature. Because of the bypass flow, the pump heated the feed and it was needed to control its temperature by cooling, so the feed tank was equipped with cooling water coil and heat exchanger. The cell consisted of two cubic parts

Table 1
Characteristics of the wastewater and the treated wastewater (micro- and ultra-filtration).

Parameter	Unit	Feed	Microfiltration		Ultra-filtration		
			PS 0.1 μm	PS 0.2 μm	PS 30 kDa	PAN 20 kDa	PAN 100 kDa
TSS	mg/L	68	8 (88.2%)	8 (88.2%)	Trace (100%)	Trace (100%)	4 (94.1%)
TDS	mg/L	2228	1580 (29.1%)	1584 (28.9%)	1560 (29.9%)	1424 (36.1%)	1524 (31.6%)
Turbidity	NTU	53	3.0 (94.3%)	3.4 (93.6%)	1.1 (97.9%)	0.4 (99.2%)	1.9 (96.4%)
Content of oil and grease	mg/L	78	3.9 (95.0%)	2.9 (66.3%)	2.2 (97.2%)	0.2 (99.7%)	2.2 (97.2%)