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ScienceDirect
DESALINATION
Desalination 196 (2006) 76–83
www.elsevier.com/locate/desal

# Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes

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Received 1 August 2005; accepted 9 November 2005

**Abstract**

A tubular UF module equipped with polyvinylidene fluoride membranes modified by inorganic nano-sized alumina particles was used to purify oily wastewater from an oil field. The membrane water permeations of the UF process were analyzed. Retentions of chemical oxygen demand and total organic carbon were more than 90% and 98%, respectively. The results indicate that after UF treatment, oil content was below 1 mg/L, suspended solids content was below 1 mg/L, and solid particle median diameters were less than 2 μm. The quality of the permeation water met the requirement by oilfield injection or drainage. Fouled membranes and washed membranes were analyzed by scanning electron microscopy, and fouled membranes were backwashed with different solutions. Results show that the addition of nano-sized alumina particles improved membrane antifouling performance, and the flux recovery ratio of modified membranes reached 100% washing with 1 wt% of OP-10 surfactant solution (pH 10).

*Keywords:* Oily wastewater; Ultrafiltration; Tubular membrane; Membrane fouling

## 1. Introduction

More and more oily wastewater has been generated from the development of oil fields, especially for those using water injection technology. It is necessary to purify this water so that it can be reused to save water resources and to protect the environment. Conventional oily wastewater treatment methods include gravity separation and skimming, dissolved air flotation, de-emulsification, coagulation and flocculation, which have several disadvantages such as low efficiency, high operation costs, corrosion and recontamination problems [1,2]. Also, these methods are not effective in removing smaller oil droplets and emulsions. All of these disadvantages have promoted the development of new processes for oily wastewater treatment.

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doi:10.1016/j.desal.2005.11.021

Membrane filtration is playing a more prominent role in the treatment of oily wastewater due to its advantages: no chemical additives are needed to break the emulsion, high COD removal efficiencies are achieved, and treatment facilities are quite compact and fully automated [3]. Many studies have been done on oily wastewater treatment with different membranes [4–11]. However, membrane fouling, which all membrane processes — especially for oily wastewater treatment, are subjected to, limits the industrialization of this membrane technology.

Membrane fouling is affected by surface hydrophilicity, i.e., improving hydrophilicity of the membrane can reduce membrane fouling to some extent. Therefore, different methods to hydrophilize the membrane surfaces have been investigated, such as blending a hydrophilic polymer with a hydrophobic polymer, grafting hydrophilic branches on hydrophobic polymer backbones and the deposition of hydrophilic films on hydrophobic materials.

The blend of polymers has the advantage of easy preparation by the phase inversion method. Ochoa and Masuelli [12] made membranes with different degrees of hydrophlicity of polyvinylidene fluoride (PVDF) and polymethyl methacrylate (PMMA). A higher hydrophilic character with an increase of PMMA in the casting solution and the appearance of larger macrovoids in the porous substructure were found without a substantial modification of the selective surface structure. Other hydrophilic polymers that can improve hydrophilicity of hydrophobic materials include polymethyacrylate (PMA), polyvinylacetate (PMAc), cellulose acetate (CA), etc.

In addition to the blending of organic polymers, recent studies have focused on blending inorganic and organic materials. It has been demonstrated that the addition of inorganic filler has led to an increase in membrane permeability and a better control of membrane surface properties [13–17]. Few studies were reported on treating oily wastewater with organic–inorganic composite membranes. In the present study, a tubular UF module equipped with PVDF membranes modified by inorganic nano-sized alumina particles was used to purify oily wastewater from an oil field. Cross-flow UF was used as the process. The performance of the membranes was characterized by their flux and antifouling properties. The quality of permeation water was evaluated by oil content and values of COD, SS, and TOC.

## 2. Experiments

### *2.1. Membrane production*

The PVDF used was a commercial product (FR904). Dimethylacetamide (DMAC, >99%, reagent) was used as the solvent. Alumina nano-sized particles (10 nm) were added to the PVDF solutions. Other additives were sodium hexaphosphate and polyvinylpyrrolidone (PVP). A mixture of distilled water and ethanol was used as the non-solvent for the polymer precipitation.

$Al_2O_3$–PVDF tubular membranes were prepared by the phase-inversion method. A casting solution was prepared by dissolving the PVDF (19%, by weight of the solution) in the solvent at room temperature and adding nano-sized $Al_2O_3$ particles (2%, by weight of PVDF) and other additives (1% sodium hexaphosphate, by weight of PVDF; 3% PVP, by weight of the solution) to the casting dopes while stirring. In order to obtain optimal dispersions of the particles in the polymer solutions, agitation was required for at least 24 h. The casting solutions were then kept in the dark for at leat 24 h to remove air bubbles. Inner pressure tubular membranes were prepared by using an epoxy resin porous tube as the supporter. An unmodified PVDF membrane was prepared in order to compare with $Al_2O_3$–PVDF membranes.

### *2.2. Cross-flow ultrafiltration*

The experimental set-up used in the cross-flow UF investigation is presented in Fig. 1. The