Chemical Engineering Journal 255 (2014) 403–410

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Comparison of ceramic and polymeric ultrafiltration membranes for treating wastewater from metalworking industry

Arnela Murić [a,1,*], Irena Petrinić [a,1], Morten Lykkegaard Christensen [b,2]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia
[b] Aalborg University, Department of Biotechnology, Chemistry, and Environmental Engineering, DK-9000 Aalborg, Denmark

HIGHLIGHTS

- It was found that the ceramic membrane operated effectively (i.e. higher fluxes).
- Fouling was reversible with ceramic membrane and irreversible with polymeric one.
- COD and lipophilic compounds were successfully removed by ceramic membrane (43% and 70%, respectively).
- Oil droplets did not coalesce in the permeate when the feed was in alkaline medium.
- The zeta potential of permeates was more negative than feeds in all cases.

ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form 23 May 2014
Accepted 4 June 2014
Available online 25 June 2014

Keywords:
Oily wastewater
Ultra Safe 620
Ultrafiltration
Fouling
Physicochemical analyses

ABSTRACT

Oily wastewater is one of the major pollutants that occur in the metal industry and is very harmful to the environment, especially to aquatic life. All conventional methods such as dissolved air flotation, coagulation, adsorption, used during oily wastewater treatment have their advantages but none is as effective as membrane technology, which offers many possibilities regarding the applications of different materials, modules and pressures. The aim of this study was a comparison between the ceramic and polymeric membrane modules for model solutions (1%, 2% and 4% solutions of hydraulic fluid Ultra Safe 620 in acidic and alkaline mediums). The model solution was filtered on a laboratory scale by using two plants equipped with ceramic (Al_2O_3/ZrO_2) and polymeric (PVC) membrane modules. The best result was obtained when using ceramic membranes where reversible membrane fouling was mainly presented, whilst in the case of polymeric membranes the irreversible membrane fouling was dominant. The physico-chemical analyses were performed by measuring pH, conductivity, turbidity, particle size and zeta potential, chemical oxygen demand, and lipophilic substances. Regarding substances' removals, the ceramic membranes were more efficient compared to the polymeric ones.

1. Introduction

The metalworking industry covers a broad area that includes extensive knowledge of metalworking fluids. Development in this area is very fast as, with good auxiliary means available, the work and the production is simpler, faster, cheaper, and of higher quality. Therefore, all kinds of auxiliaries are important and indispensable throughout the industry, but the industry also faces problems [1] such as the aqueous of the metal processing industries' waste streams containing a high content of waste oils and other inorganic materials – spent cutting-oils, which are one of the larger volumes regarding oily wastewater within metal-working industries. This waste stream cannot be discharged directly into the environment but has to be properly treated to attain the discharge requirements of discharged into public sewers and paid for environmental taxes. Thus, for each industry, it is from environmental and economic point of view important to seek and implement appropriate treatment for the generated wastewater.

In recent years more attention has been paid to discharge of oily wastewater, since they are the main polluter of aquatic environment [2]. Oil and grease in wastewater can exist in different forms: free, dispersed or emulsified. The differences are mainly based on the size of oil droplets in water. In an oil–water mixture, free oil is characterised with droplet sizes greater than 150 μm in size

* Corresponding author. Tel.: +386 40 576 647.
E-mail addresses: muric.arnela@gmail.si (A. Murić), irena.petrinic@um.si (I. Petrinić), mlc@bio.aau.dk (M.L. Christensen).
[1] Tel.: +386 2 2294 474; fax: +386 2 2527 774.
[2] Tel.: +45 9940 8464; fax +45 9635 0558.

http://dx.doi.org/10.1016/j.cej.2014.06.009
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and dispersed oil (mechanically emulsified) has a size range of 20–150 μm [3]. Oil-in-water emulsions (chemically emulsified) in the presence of emulsifier contain droplets smaller than 5 μm, which make the emulsion very stable. They may contain different oils (mineral, vegetable or synthetic), fatty acids, emulsifiers, corrosion inhibitors, bactericides and other chemicals [4].

Removal of oil from waste oil–water emulsions can be achieved by various well-known and widely accepted techniques. Implementation of any separation technique is entirely dependent upon the structure of wastewater. Due to the complex compositions of spent cutting-oil emulsions, conventional chemical destabilization methods (gravity, flotation, skimming, coagulation and flocculation) are ineffective for the treatment of oily wastewaters, and thus alternative methods need to be applied [5].

Membrane processes, such as microfiltration (MF) and ultrafiltration (UF), have become the standard technology for the treatment of oily waste water due to its ability to remove stable emulsified oil from wastewater. Most manufacturers recommend the use of membrane separation membranes limit of 20,000–50,000 Daltons for the treatment of oily wastewater.

The main problem in the application of membrane technology for purification of oily wastewater is membrane fouling, which can be reversible or irreversible. Reversible membrane fouling can be removed by strong shear forces in the rinse with reflux. Formation of a firm matrix blocked layer of solute during continuous filtration process changes reversible fouling into irreversible. Irreversible fouling is usually due to a strong connection of particles and membrane, which cannot be removed by physical cleaning, but only by the use of chemical agents.

Fouling not only reduces the flow, but also changes the ability of the membrane performance [6]. Membrane fouling can be caused by inorganic and organic matter present in the wastewater (foulant). Foulant is retained on the surface or in the pores of the membrane and thus impair performance (permeate flow reduction) with a consequent increase in required energy and membrane cleaning and/or replacement of membranes [7]. To reduce the fouling there is a number of classical techniques implementation including procedures for pre-treatment of oily wastewater. Numerous studies carried out around the world investigated the fouling reduction and cleaning of fouled membranes. However, fouling is usually impossible to avoid completely [8].

According to the literature, most researchers focused in the use of ultrafiltration and microfiltration membranes for the treatment of oily wastewater, where the oil droplets can be completely retained. As the oil droplets can be deformed, depending on the applied pressure, they can squeeze through the pores and thus contaminate the permeate. Lipp and colleagues reported on such contamination of the permeate [6]. Nazzal and Wiesner have found that the efficiency of breaking the emulsion was maximum if the transmembrane pressure being below the critical pressure [9]. Mueller and his colleagues have tested the performance of ceramic and polymeric microfiltration membranes in processing synthetic water containing 250–1000 mg/L of heavy crude oil droplets with a diameter of 1–10 mm and obtained permeate containing less than 6 mg/L of oil. The test was accompanied by strong membrane clogging and flux decrease [10]. Kong and Li investigated the effects of flow-rate on the input solution, operating pressure, membrane pore size and porosity during the separation of oil–water mixtures by the use of flat-sheet hydrophobic PVDF membrane [11]. Field and colleagues studied the impacts of different types of surfactants on the water flow through the hydrophobic microfiltration PVDF membrane [12]. Koltuniewiz and Field studied the effects of cross-flow velocity and transmembrane pressure on the permeate flow during the separation of oil–water emulsions using four different organic and inorganic membranes [13]. Ohya and colleagues reported that the cross-flow microfiltration changes the diameters of the membranes' pores when separating the oil–water emulsions. Zhao and his colleagues proposed the suspension of magnesium hydroxide on a ceramic support as a suitable material for the dynamic performance of membranes, where it reached more than 98% retention of oil from oil–water model emulsions within an alkaline medium [14]. Richard and his colleagues found that the charge distribution is an important factor in the stability of oil–water emulsions [15]. Alters showed that oil droplets in the emulsion are likely to be negatively-charged [16]. An electrical double layer was formed that caused repulsion between the oil droplets themselves, which in turn contributed to the emulsion stability [17]. Vijay and Harvey found that an increased volume of emulsifier resulted in somewhat smaller oil droplets and greater stability [18]. Li and Pozrikidis tested the effect of emulsifier on droplet deformation, finding that an increased quantity of emulsifier resulted in a reduction of surface tension, which is the main cause of deformation regarding oil droplets in miceles [18].

As some manufacturers and scientists already prefer ceramic membranes over polymeric ones in the field of oily wastewater treatment, it was decided to conduct a comparison of their efficiencies. This approach would be useful mainly for metal working and other industries, where large quantities of hydraulic fluids are used and oily wastewater generated.

2. Materials and methods

Diluted Ultra Safe 620 (*PETROFER*) was used as a model solution for oily wastewater. It contains in aqueous solution a combination of glycols of different chain lengths, and special additives for wear resistance and corrosion protection [19].

In order to perform cross-flow ultrafiltration ceramic (Al_2O_3/ZrO_2) and polymeric (PVC) membrane modules were used as laboratory-scale equipment. Their main characteristics are presented in Table 1.

Many authors have reported good performances of α-Al_2O_3, ZrO_2 membrane in oily wastewater treatment, due to higher mechanical and thermal stability, which was the reason for choosing this membrane. On the other hand PVC membrane was also used mainly because of its availability and low cost.

3. Experimental

Modelled oily wastewater was prepared: 1%, 2% and 4% solutions of Ultra Safe 620 in acidic and alkaline media, respectively. The model solution was treated by membrane filtration using cross-flow UF with polymeric and ceramic membranes. The membranes were not specially conditioned before usage.

Fig. 1 shows the process scheme of a cross-flow ultrafiltration plant using ceramic membrane. A B 1 tank was filled with ca. 15 L of model solution. At the same time, the pressure gauge (PI) and temperature gauge (TI) were activated. The valves VK 1, VK 2, and VK 3 were opened during the process. When the pressure was stabilised, valve VK 1 was slowly closed to increase the pressure and thereby enhance the permeate flow. The flow was measured manually by measuring the time needed to reach a certain volume of permeate. Permeate and retentate were returned to tank B 1 according to cross-flow configuration.

The ultrafiltration process using a polymeric membrane module was operated similarly to the one for ceramic membranes.

The experimental procedure was divided into cycles based on different pressures and pH values but the time of operating was 1 h at each test condition (for example 1 h of operating with 1% of US 620 at pH = 5 and inlet pressure of 3 bar). The operating temperature was approximately the same at the beginning of each cycle, at around room temperature. During operation the