Treatment of Industrial Effluents by MF and UF Ceramic Membranes: Comparative Study using Commercial and Elaborated Tunisian Clay Membranes

Sabeur Khemakhem* and Raja Ben Amar

Abstract

Industrial effluents treatment was investigated using ceramic Microfiltration (MF) and Ultrafiltration (UF) tubular membranes. The comparison of performances between commercial ceramic membranes based on alumina material and elaborated ones based on Tunisian clay material was studied. MF and UF tests applied to cuttlefish effluent treatment were carried out respectively with 0.2 µm and 5 nm commercial membranes and 0.18 µm and 15 nm prepared membranes. The results show that for the two processes, the performances in term of permeate flux and quality of the treated wastewater using clay membranes was a little better than that obtained with commercial ones.

Keywords: Commercial membrane; Tunisian clay membrane; Cuttlefish effluent; ultrafiltration; microfiltration

Introduction

Interest in separation by the use of membrane processes has gradually increased during the last 20-25 years in many fields. The use of membranes increases the effectiveness of already existing processes and opens new possibilities for separation.

In the area of waste water treatment, membrane processes are often used in combination with other processes to treat very complex effluents which have often an important load of organic substances and salt. The membrane process would enhance the water treated quality in effluents which have often an important load of organic substances and often used in combination with other processes to treat very complex and opens new possibilities for separation.

Considering the manufacturers' rejection, the separation efficiency depends on the rejection value: 100% rejection would correspond to no permeation of the solute, whereas 0% rejection would imply a complete permeation. The rejection value is also denoted as 0% or 100% rejection. The rejection value is often reported as a simple average of the averages of the rejections obtained on a panel of solutes with different molecular weights. Thus, the rejection value can only be determined experimentally, as it can only be calculated if the rejection value is known for a panel of solutes with different molecular weights.

In the case of membrane processes, the rejection value is determined by two parameters, its selectivity (for some processes measured as percent rejection or retention) and the flow (often denoted as flux or permeate rate) [12]. Microfiltration (MF) is a pressure-driven membrane process for the separation of fine particles, microorganisms and emulsion droplets. The membranes used have a microporous structure which separates fine particles with a size in the range of 0.02–20µm. Therefore, MF is placed between ultrafiltration and coarse filtration, which is not a membrane operation. MF is the oldest membrane technology. It started at the beginning of this century and coarse filtration, which is not a membrane operation. MF is the oldest membrane technology. It started at the beginning of this century with the preparation of synthetic microporous membranes based on cellulose [13]. Ultrafiltration is currently used for the concentration of a wide range of protein products, including recombinant therapeutics, industrial enzymes, and a variety of food and beverage products [14,15]. Ultrafiltration membranes are normally rated by their nominal molecular weight cut-off, which is typically defined as the molecular weight of a solute that has a rejection coefficient of 90%. However, there is no standardization in this 90% value, and different manufacturers measure the rejection using solutes with very different physical properties and under very different operating conditions [16].

The aim of the present work was to compare filtration performance of two types of tubular ceramic membranes: commercial one based on alumina and elaborated Tunisian clay membranes. Experiments were carried out in order to reduce pollution load of the cuttlefish effluent generated from a sea product-freezing factory located in Sfax (Tunisia) which consumes a great amount of water for the washing baths (about 150 - 200 m³/day) which is generally discharged in the littoral. Before freezing, the cuttlefish must be washed to eliminate black colour caused by the ink (containing melanin) contained in the animal bag, resulting in highly coloured wastewater [17].

*Corresponding author: Sabeur Khemakhem, Laboratoire des Sciences de Matériaux et Environnement, Faculté des Sciences de Sfax, Route de Soukra Km 4, 3038, Sfax, Tunisie

Received April 29, 2011; Accepted May 18, 2011; Published June 14, 2011


Copyright: © 2011 Khemakhem S, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
Experimental

Materials

Two types of the commercial tubular membranes supported on the alumina were purchased from Pall EXEKIA (Figure 1). Tubular membranes with external/internal diameter of 10/7mm and the length of 150mm were used. The structure of alumina support is macroporous (average pore diameter equal 0.8µm). The microfiltration zirconia membrane has an average pore diameter of 200nm. The selective layer of the ultrafiltration membrane was prepared from titania with an average pore diameter of 5nm.

Two Tunisian clay membranes were prepared in our laboratory from the support to the finest layer. Tubular supports were elaborated with external/internal diameter of 9/7mm and the length of 150mm with an average pore diameters of 9.2µm. The microfiltration layer present an average pore size of 0.18µm and ultrafiltration membrane with 15nm diameter of pore.

Apparatus

Figure 2 shows the schematic diagram of the MF and UF pilot plant used for the treatment of the industrial effluent. The plant is equipped with a 5 litres feed tank. The transmembrane pressure was controlled by adjustable valves. It varies in the range of 0–3 bars. The temperature is controlled by a cooling device inserted into the feed tank. In our case, the flow velocity and the temperature of the solution are fixed respectively at 2.5 ms⁻¹ and 25°C. The tubular membrane (15 cm length, 6mm of diameter and 26 cm² filtering area) takes place in a stainless steel carter. The transmembrane pressure was regulated by means of nitrogen gas. The membrane was conditioned by immersion in pure deionized water for a minimum of 24 h before filtration tests. The duration of each test normally varied from 1 to 3 hours. Permeate samples were taken and analysed at each run. A thermal treatment was used for membrane regeneration.

The techniques used to analyse collected samples of feed, retentate and permeate are reported below:

- Turbidity: using a HACH <2100 N Turbidimeter> turbidimeter.
- Conductivity: using a «Consort K 911» conductimeter.

Wastewater

Wastewater samples were taken from the wastewaters produced by a sea-products freezing factory located in Sfax, Tunisia. In order to determine the physico-chemical characteristics of the effluent to be treated, the wastewater was monitored through daily sampling and analysis. A large number of analyses were conducted on each sample and the following parameters were measured: turbidity, COD, temperature, pH and conductivity. The COD values of raw effluent from the production process ranged between 6000 and 7000 mgL⁻¹ with an average concentration of 6042mgL⁻¹. The turbidity measured for the raw effluent presents a very high value which is in order to 700 NTU (Table 1).

Preliminary treatment of raw effluent

The general scheme wastewater treatment generally involves two main stages: (i) a primary clarification (or primary treatment) using physico-chemical methods such as a coagulation/flocculation process with a flotation or decantation step to remove mainly the suspended solids and colloids, and (ii) a decontamination step (or
The first step carried out in this part is a microfiltration. Permeate. For clay ultrafiltration membrane

The coagulation process is largely enhanced by the addition of aluminum salt (optimal quantity is 165 mg/L) to the effluent pretreated with, due to the increase of density of flocs (large particles) formed by the association of fine colloids which can be removed by prefiltration.

**Microfiltration**

Microfiltration experiments were carried out on the pilot units (Figure 2), functioning in mono-staged mode of tangential filtration. The transmembrane pressure (TMP) was controlled by an adjustable valve at the filter outlet. It varies in the range of 1-3 bar. Temperature was kept at 25 °C by a thermal exchange system. In crossflow microfiltration CMF, the fluid to be filtered flows parallel to the membrane surface and permeates through the membrane due to a pressure difference (Figure 3). The permeability of interest in microfiltration or ultrafiltration process is that with respect to the solvent Eq. (1):

$$L_p = \frac{J}{\Delta P}$$

(1)

Where $J$ is the volumetric filtrate flux (volume flow rate per membrane area) and $\Delta P$ is the transmembrane pressure driving force. $L_p$ is often referred to as the hydraulic permeability since water is the typical solvent, and the data are often normalized by the solvent viscosity to account for the effects of temperature.

Microfiltration permeate was always collected to measure the initial turbidity, COD, pH and conductivity. Before and after each experiment, membranes were cleaned by basic acid washing and the system was rinsed with distilled water before and after each washing. Permeability of membranes by distilled water was measured until the initial permeability was achieved.

**Ultrafiltration**

Ultrafiltration experiments were carried out on the same pilot units (Figure 2) and with same conditions used in microfiltration process. Ultrafiltration membranes are normally rated by their nominal molecular weight cut-off, which is typically defined as the molecular weight of a solute that has a rejection coefficient of 90%. Concentration was determined by ion chromatography and the rejection rates, denoted $R$, were calculated using Eq. (2):

$$R = \left(1 - \frac{C_0}{C_p}\right) \times 100$$

(2)

Where $C_0$ represents the initial concentration of the salted solution and $C_p$ the concentration of permeate. For clay ultrafiltration membrane a rejection rate of 90% is obtained for molecular weight larger than 185 kDa, this value will be considered as the cutoff of the synthesized membrane (Figure 4).

**Microfiltration associated with Ultrafiltration**

The first step carried out in this part is a microfiltration. Permeate obtained by microfiltration is collected in a large beaker. It is poured...
The effect of transmembrane pressures in microfiltration on COD and turbidity reduction. This porous membrane was prepared and characterized for its chemical and physical properties. Turbidity, COD, conductivity, and pH were measured as parameters to assess the membrane's performance. The obtained membranes showed a COD reduction of 38% and turbidity reduction of 93% after coagulation process. Alumina salt was used as a coagulant agent for COD reduction.

Results and Discussion

Coagulation performance

Table 1 shows a comparison between raw and pre-treated effluent by coagulation process. Alumina salt lowered COD by 38% and turbidity by 93%. Figure 6 shows the permeate flux versus the TMP for microfiltration membranes. This figure shows that the quality of permeate appears to be highly satisfactory in terms of turbidity and COD reduction for commercial and clay membranes. The permeate flux is about 93 l/h.m² for clay membranes and 87 l/h.m² for UF membrane. The obtained results refer to average samples taken at different periods of experiments. Table 2 shows that the quality of permeate seems to be highly satisfactory in terms of turbidity and COD reduction for commercial and clay membrane. The permeate flux is about 93 l/h.m² for clay membranes and 87 l/h.m² for UF membrane. The obtained results refer to average samples taken at different periods of experiments.

Microfiltration performances

MF test carried out by keeping constant the initial concentration of the raw effluent by returning both permeate and concentrate to the feed reservoir. This run was carried out to obtain preliminary information about the fouling tendency of the membrane through the study of the behaviour of the permeate flux as a function of operating time as well as of the transmembrane pressure (TMP).

Figure 6 shows the variation of permeate flux with TMP for microfiltration membranes. This figure shows that the permeate flux is linearly increased with increasing TMP for clay and commercial membrane. However, the performances in term of permeate flux are slightly better with the clay membranes. The MF permeate flux is about 93 l/h.m² for clay membranes and 87 l/h.m² for UF membrane. The obtained results refer to average samples taken at different periods of experiments.

Figure 7 shows the effect of transmembrane pressures in microfiltration on turbidity reduction. The obtained membranes can be used in the treatment of industrial effluents by preparing microfiltration and ultrafiltration membranes [22].

The preparation and characterization of the membrane

Clay powders mixed with some organic additives can be extruded into the tank of the filtration pilot. The microfiltration membrane is changed by an ultrafiltration membrane. It is then processed again by the ultrafiltration membrane. The same filtration conditions are followed for this type of procedure. In order to determine the physical and chemical characteristics of the obtained permeate after the two steps of microfiltration and ultrafiltration, permeate analysis was performed. A large number of analyses were conducted on each sample and the following parameters were measured: turbidity, COD, conductivity, and pH.

Preparation and characterization of the membrane

Clay powders mixed with some organic additives can be extruded to form a porous tubular support. After firing, the support showed an average pore diameter of 9 µm and a porosity of 49%. This porous ceramic tube was used as support to prepare microfiltration and ultrafiltration membranes [22].

The elaboration of macroporous ceramics was carried out by shaping of a ceramic paste, followed by the consolidation by sintering. The process of development is described in Figure 5. The preparation of the active layer based on clay too was performed by the slip casting method. A deflocculated slip was obtained by mixing a mineral powder, PVA (12 wt %), and water. The water permeability measured for the membranes calcinated at 900°C and with a mean pore size of 0.18 µm was 867 l.h⁻¹.m⁻².bar⁻¹. The obtained membranes can be used in microfiltration process [10]. Illite ultrafiltration top layer with 15 nm average pore size, have been deposit on the clay microfiltration layer previously prepared using aqueous colloidal suspensions. The top layer thickness was about 5 µm [11].

Results and Discussion

Coagulation performance

Table 1 shows a comparison between raw and pre-treated effluent by coagulation process. Alumina salt was used as a coagulant agent for COD and turbidity reduction. The COD values of raw effluent is 6042.40 mg.L⁻¹. After coagulation process, the COD values obtained is 3765.42 mg.L⁻¹. The turbidity values of raw effluent decreased from 700NTU to 49NTU after coagulation process. The results showed that coagulation process lowered COD by 38% and turbidity by 93%. Table 1 shows that the treated effluent can be potentially highly polluted even after treatment by coagulation, the degree of pollution well explained by the high values of COD and turbidity.

Microfiltration performances

MF test carried out by keeping constant the initial concentration of the raw effluent by returning both permeate and concentrate to the feed reservoir. This run was carried out to obtain preliminary information about the fouling tendency of the membrane through the study of the behaviour of the permeate flux as a function of operating time as well as of the transmembrane pressure (TMP).

Figure 6 shows the variation of permeate flux versus the TMP for microfiltration membranes. This figure shows that the permeate flux is linearly increased with increasing TMP for clay and commercial membrane. However, the performances in term of permeate flux are slightly better with the clay membranes. The MF permeate flux is about 93 l/h.m² for clay membranes and 87 l/h.m² for UF membrane. The obtained results refer to average samples taken at different periods of experiments. Table 2 shows that the quality of permeate seems to be highly satisfactory in terms of turbidity and COD reduction for commercial and clay membrane. The permeate flux is about 93 l/h.m² for clay membranes and 87 l/h.m² for UF membrane. The obtained results refer to average samples taken at different periods of experiments.
membrane by increasing transmembrane pressure and subsequently decreased rejection.

Ultrafiltration performances

In a general way, effluents showed a remarkable fouling character with respect to ultrafiltration membranes, as shown by comparisons with flux water. The nature of the permeate had a strong impact on ultrafiltration performances.

Figure 9 shows the evolution of permeate flux versus transmembrane pressure for each one of commercial ultrafiltration membrane and elaborated ultrafiltration clay membrane. For two types of used membranes the flux of permeate increased with transmembrane pressure applied. Flux of permeate obtained for clay membrane is higher than those recorded with commercial membrane. Indeed, permeate flux is 42 l/h.m² for clay membrane and 40 l/h.m² for commercial membrane.

Table 3 gives the main physicochemical parameters analyzed for permeate obtained by UF commercial membrane and UF clay membrane. These analyses show variability in the turbidity and COD values for two types of membranes. This variability depends essentially on the nature and performance of the used membranes.

For commercial membrane, the values of COD (from 1367 to 1830 mg L⁻¹ with TMP from 1 to 3 bar) and of turbidity (from 0.7 to 1.8 mg L⁻¹ with TMP from 1 to 3 bar). Percentage reduction of turbidity and COD as a function of TMP has been shown in Figure 10 and Figure 11. Both the turbidity and COD reduction have been found to increase with decrease in TMP, which could be attributed due to the higher rejection at lower TMP. Turbidity of permeate was found to get reduced by 98.26% for commercial membrane and 98.57% for clay membrane when UF was carried out at a TMP of 1 bar, whereas, COD was reduced by only 63.67% for commercial membrane and 70.9% for clay membrane a TMP of 1 bar. In fact, at all the TMP level, turbidity reductions were found to be more than the corresponding COD reduction on percentage basis. As the COD is caused by the presence of low molecular inorganic chemicals also, which might pass through the membrane, may give less % -COD. In term of quality, Figure 12 shows a noticeable elimination of suspended matter illustrated by the change of the effluent colour as well as the elimination of the turbidity.

Ultrafiltration performances combined with microfiltration

Table 4 shows average reduction of COD and turbidity retention compared to other process. In order to explain these differences, a physico-chemical analysis of permeate has shown important composition disparities between effluents resulting from this processes and the two other process used previously. Like other processes, percentage of reduction of COD and turbidity increased at height transmembrane process. The combination of ultrafiltration with microfiltration shows a very height performances to those obtained with microfiltration or ultrafiltration alone. The compatibility of this process proved to be excellent.
Membrane regeneration

After each experiment, the membrane must be regenerated. The efficiency of the using protocol is verified by the measurement of water flux. The regeneration of the membrane was carried out by firstly, thermal treatment at 300°C during 1h, and secondly, by leaving the membrane in distilled water. The used protocol appears sufficient because we obtained the value of the initial permeability of the membranes.

Conclusion

The purpose of this study was to evaluate the performance of the clay membranes developed in our laboratory, in the cuttlefish effluent treatment. A comparison with commercial membranes put into evidence the great importance from an economic point of view of membranes based on local material in the waste water treatment. Good performances were observed in term of permeate flux and pollution retention. For MF clay membrane, permeate flux reached 100 l/h.m² at a transmembrane pressure of 3 bars. This value corresponds to the range of permeate flux values usually recommended at an industrial scale.

References