

## Physico-Chemical Treatment Of Wool Scouring Effluent

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The proposed procedure to produce low polluting effluent consists of a combination of coagulation-flocculation and membrane separation process. The main role of the coagulation-flocculation process is the simultaneous enhancement of removal efficiency and increase the permeate flux by minimizing the membrane fouling. Membrane fouling has a significant impact on the cost, design, and operation of membrane technology. Experiments with wool scouring effluent were performed to find optimum conditions and to ensure the feasibility of the process. The optimum operating conditions for the coagulation-flocculation process were pH = 4 and 500 mg/L in ferric chloride. The high-quality permeate stream obtained, with 0.3 kDa polymeric membrane, allows the recycling of 90% of the water to the wool scouring process.

**Keywords:** Wool scouring; Coagulation; Flocculation; Membrane technology.

### Introduction

Wool scouring waste effluent is one of the most polluting in the textile industry. Minimization of water usage and production of relatively concentrated effluent streams are part of efficient scour management. Several treatments have been developed to purify wool scouring liquors: biological, chemical and physico-chemical processes. Some studies have improved the grease removal and digestion time of liquors by combining the anaerobic process with bioflocculation [3-4] and with physical treatment [5]. Chemical processes, such as chemical oxidation, are usually expensive because of the large amount of chemicals required, and their application has therefore been determined by economic factors. Physico-chemical treatments, an interesting option for grease removal since they are relatively cheap, are based on the coagulation-flocculation process of small particles followed by an adjusted settling time.

Membrane separation technology is an emerging cost effective method for treatment of wastewaters by concentrating the bulk of the pollutants into small liquid volumes for further disposal [7]. Fouling is the major obstacle in its successful implementation. Fouling is due to the adsorption-precipitation of organic and inorganic compounds onto membranes, leading to an increase in membrane cleaning costs and shortening of the life of the membrane. Membranes can be cleaned by acid and basic solutions, an aqueous-detergent cleaning solution, or an aqueous grease-degrading enzyme solution [8]. Membrane fouling can be minimized by combining various treatments, i.e. Hogetsu et al. [10] combined an anaerobic digester with ultrafiltration membrane.

The purpose of this paper is to contribute to the development of a better sustainable process to treat the wastewater coming from the wool scouring process.

## Experimental

### Materials

The initial spent wool scouring liquor was prepared by laundering 30 g of Australian Merino sheared raw wool, with 15.4% wool wax, in 400 ml of water at 50°C, containing 0.025% (w/v) of non-ionic surfactant (a technical branched fatty alcohol ethoxylated: C<sub>13-15</sub>EO<sub>7</sub>). The wool scouring liquor was characterized, following the *Standard Methods for Examination of Water and Wastewater* [11], by the grease content, total and dissolved solid content, and Chemical Oxygen Demand (COD). Total Organic Carbon (TOC) was determined by V-50 Shimadzu equipment (Kyoto, Japan). Table 1 shows the compositions of the untreated wool scouring liquor. Ferric chloride, supplied by Panreac Química S.A. (Castellar del Vallès, Spain), was used to coagulation-flocculation experiments.

### Experimental procedure

A four-paddle jar testing apparatus with six containers, supplied by Selecta (Barcelona, Spain), was used to find the operating conditions for the optimal coagulation/flocculation process. The procedure to find the operating conditions for the optimal coagulation/flocculation process involved the following steps: (1) The jar test apparatus containers were filled with 1 liter of the liquor and pH was adjusted to desired value by adding HCl 1M. (2) The coagulant-flocculant substance was added to each container and stirred at 150 rpm for 2 minutes to disperse it throughout the sample. (3) The stirring speed was then reduced to 50 rpm and mixing continued for 15 minutes to promote flock formation by enhancing particle collisions, which lead to larger flocks. (4) Finally, the mixers were turned off and the liquor was allowed to settle for 15 minutes. After that, the settled liquid was separated from the flocks by centrifugation.

The experimental set-up for membrane testing consisted of a thermostatic ( $25 \pm 0.5$  °C), 2 L feed vessel and a membrane cell for tubular ceramic membranes, supplied by Tami (Nyons, France), a membrane cell for flat sheet polymeric membranes (Sepa CF membrane cell), supplied by GE Infrastructure Water & Process Technology (Sant Cugat, Spain). The MWCO were ranged from 50 to 1 kDa, for tubular ceramic membranes, and 0.3 kDa (ref. DS DK) and 1.0 kDa (ref. DS5 DS) for flat polymeric membranes. The membrane system was operated in two modes: steady state mode and batch retentate-recycling mode.

## Results And Discussions

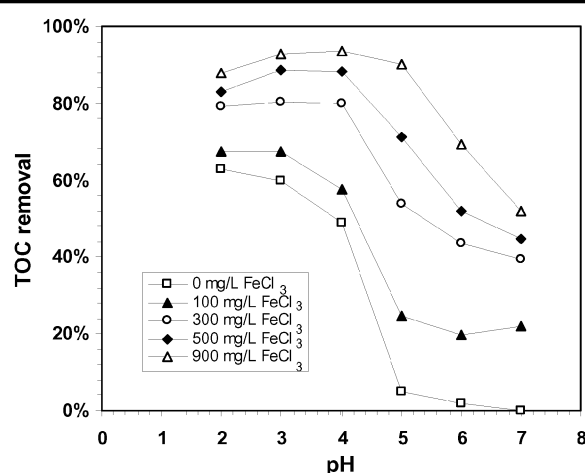
### Coagulation-flocculation process

Figure 1 shows TOC removal, in the coagulation-flocculation process, as a function of pH at different ferric chloride concentrations. Worth noting is the relatively high TOC removal reached at low pH in absence of ferric chloride. At a fixed ferric chloride concentration, TOC removal decreases gradually when pH increases. Simultaneously, TOC removal increases when the ferric chloride concentration also increases. Independently of the ferric chloride concentration, the main changes in TOC removal are found in the range pH = 4.0 – 6.0. At the same time, no significant changes in the TOC removal are found when pH drops below pH 4.0. A maximum value of 94% TOC removal was attained by combining the effect of ferric chloride concentration and pH (900 mg FeCl<sub>3</sub>/L at pH = 4). Below pH = 4 and high ferric chloride concentration, TOC removal slightly decreases, indicating a relative re-stabilization of particles. Although 94% of TOC removal can be reached with a high concentration of ferric chloride (900 mg FeCl<sub>3</sub>/L at pH = 4.0), cost-effective reasons indicate that around 500 mg FeCl<sub>3</sub>/L at pH = 4.0 was the most appropriate operating condition for the coagulation-flocculation process. Table 1 shows the composition of the wool scouring liquor before and after

treatment under these operating conditions, and the obtained sludge. The volume of the clarified liquor was the 90% of the initial wool scouring volume.

**Table 1** Composition of the initial and treated wool scouring liquors and the obtained sludge.

	Untreated wool scouring liquor	Treated wool scouring liquor	Permeate stream ( $V_P = 0.9 \cdot V_F$ )	Retentate stream ( $V_R = 0.1 \cdot V_F$ )
Grease content (mg/L)	7160	530	26	5066
Total solid (mg/L)	19160	5230	1060	42760
Dissolved solid (mg/L)	6890	4890	830	41430
Suspended solid (mg/L)	12270	340	230	1330
TOC (mg/L)	4375	488	76	4196
COD (mg/L)	37261	3193	383	28480



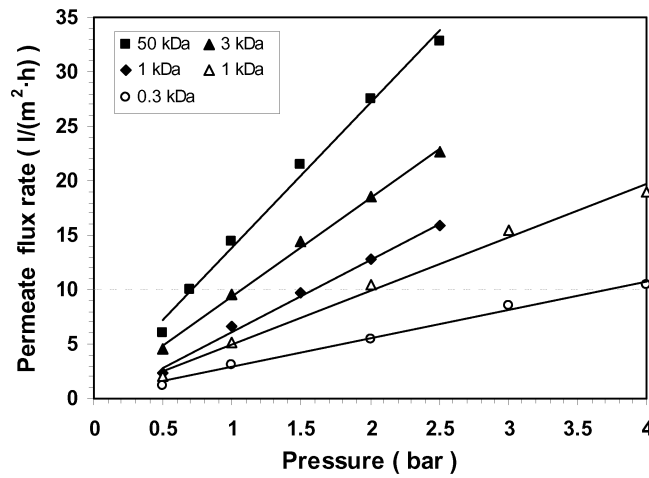
**Figure 1** Effect of pH on TOC removal at several ferric chloride concentrations.

### Membrane separation process

Wool scouring liquor coming from the coagulation-flocculation process described above can be purified with an additional membrane separation process. Figure 2 shows the permeate steady state flux rate for the different tested membranes at different transmembrane pressures. Linear dependence was observed for the permeate flux rate with transmembrane. Permeate flux rates for polymeric membranes were lower than rates achieved with ceramic membranes.

Membrane efficiencies were evaluated by determining TOC rejection,  $R = [1 - (C_P/C_R)]$  where  $C_P$  and  $C_R$  are the TOC at the permeate and retentate streams, respectively. High TOC rejection values indicate enhanced quality of the permeate stream. Figure 3 shows the effect of membrane MWCO on TOC rejection,  $R_{TOC}$ . When the membrane MWCO decreases, TOC rejection increases. Maximum TOC rejection of about 87% was

obtained with 0.3 kDa MWCO membrane ( $MWCO^{0.5} = 0.55$ ). The ceramic membrane of 1 kDa MWCO showed slightly higher TOC rejection than the polymeric membranes. In fact, the MWCO provided by the manufacturer is considered as an estimated value, since there are different methods to determine its value. MWCO is used as a measurement of membrane pore size when membranes are used to separate macromolecular chains. However, for particulate materials (like colloidal wool grease) pore size dimensions could be a more appropriate measurement. The dimension of the macromolecular chain (as given, for example, by  $\langle R^2 \rangle_o$ , the unperturbed mean-square end-to-end distance) is connected to the average molecular weight,  $M$ . Values of  $\langle R^2 \rangle_o/M$  based on small-angle neutron scattering (SANS) measurements for the most common macromolecules range from  $0.005 - 0.009 \text{ nm}^2 \cdot \text{Da}^{-1}$  [13]. The volume of the smallest sphere that completely contains the chain is about  $(\langle R^2 \rangle_o/3.6)^{3/2}$  and the diameter of sphere with the same volume is  $d_{sph} = ((6/\pi) \cdot (\langle R^2 \rangle_o/3.6)^{3/2})^{1/3}$ . Thus,  $d_{sph} = C \cdot M^{0.5}$ , where  $C$  ranges from  $0.046$  to  $0.062 \text{ nm} \cdot \text{Da}^{-0.5}$ . Hence,  $(MWCO)^{0.5}$  is a more appropriate gauge for characterizing the particulate sieving character of these membranes than  $(MWCO)^1$ . Therefore, a good estimation for membrane pore size,  $d_p$ , is  $d_p = 0.05 \cdot (MWCO)^{0.5} \text{ nm}$ .



**Figure 2** Effect of applied transmembrane pressure on the permeate steady state flux rate for the different tested membranes when tangential velocity was adjusted to 1 m/s. Filled symbols correspond to ceramic membranes and unfilled symbols to polymeric membranes. The flux was time independent after 60 minutes.

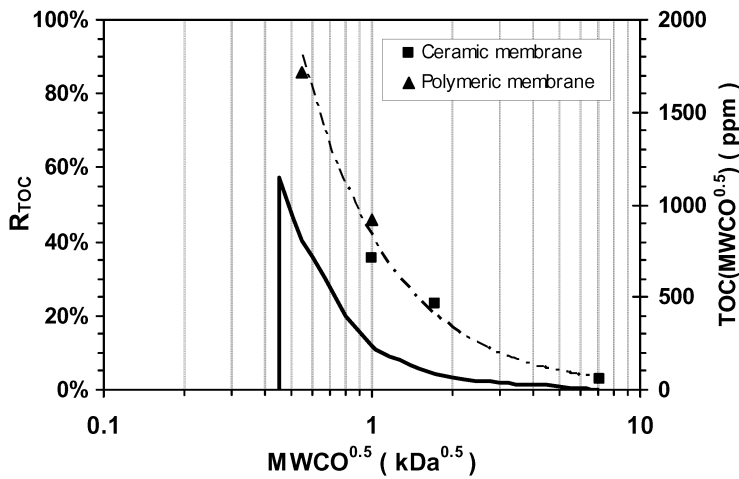
A TOC distribution function,  $TOC(\sqrt{MWCO})$ , was defined to give information about the colloidal particle size distribution and its contribution to TOC. The total TOC of the scouring liquor coming from the coagulation-flocculation process is  $(TOC)_o = \int_0^c TOC(\sqrt{MWCO}) \cdot d\sqrt{MWCO}$  and TOC rejection can be calculated with the following equation:

$$R_{TOC}(\sqrt{MWCO}) = 1 - \frac{\int_0^{\sqrt{MWCO}} TOC(\sqrt{MWCO}) \cdot d\sqrt{MWCO}}{(TOC)_o} \quad (1)$$

$TOC(\sqrt{MWCO})$  was deduced from  $R_{TOC}$  and plotted on Figure 3. It can be deduced that there is no significant contribution to TOC for  $\sqrt{MWCO} > \sqrt{4} = 2$ . Therefore, the diameters of the colloidal particles are below 1.5 nm (4 kDa MWCO).

The permeate flux, tested at 1 m/s of tangential velocity, declined due to membrane fouling. The fouling tendency in polymer membranes was lower than in ceramic, since the flux was only reduced in 18% after 9 hours without membrane cleaning. Workable fouling was found with a 0.3 kDa MWCO polymeric membrane at 1 m/s of tangential velocity.

Unsteady state experiments, operating in a batch retentate-recycling mode, were performed. The purpose of these experiments was to obtain a main volume of clear water and a minor volume of concentrated solution. The experiments were stopped when the permeate volume was 90% of the initial feed volume ( $V_P = 0.9 \cdot V_F$ ). TOC concentrations in the retentate did not increase much when the permeated volume was below 50% and 20% of the initial volume for the 1 kDa and 0.3 kDa MWCO membranes, respectively. However, the TOC concentrations in the permeate streams were almost constant during the entire procedure. Table 1 summarizes the final compositions of permeate and retentate streams obtained with a 0.3 kDa polymeric membrane. The high-quality permeate stream obtained allows the recycling of 90% of the water to the wool scouring process.



**Figure 3** TOC rejection,  $R_{TOC}$ , and TOC distribution function,  $TOC(MWCO^{0.5})$ . The dashed line corresponds to the effect of membrane MWCO on  $R_{TOC}$  (squares for ceramic membranes and triangles for polymeric membranes). The solid line corresponds to the TOC distribution function.

## Conclusions

The main conclusions arising from this study are as follows:

- The coagulation-flocculation process is very dependent on the pH and ferric chloride concentration. The optimum pH was found to be 4.0. The maximum TOC removal achieved by the addition of 900 mg/L of ferric chloride at pH = 4.0 was 94%. With a ferric chloride concentration of 500 mg/L at pH = 4.0, a suitable TOC removal of 89% was reached. Two tested polyamide flocculants were less effective in TOC removal than ferric chloride at pH = 4.0.
- After the coagulation-flocculation process, most of the colloidal material, which produces TOC, is removed by membranes (polymeric or ceramic) situated between 1.0 and 0.3 kDa MWCO. The high-quality permeate stream obtained, with 0.3 kDa polymeric membrane, allows the recycling of 90% of the water to the wool scouring process.

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