

## Microfiltration process for tannery wastewater treatment from a leather industry in Fez-Morocco area

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### Abstract

Tannery wastewater contains large amount of chemical compounds including toxic substances. So an attempt was made to characterize physiochemical parameters of tannery wastewater and investigate the efficacy, and applicability of the microfiltration treatment utilizing a local clay tubular membrane. We carried out a treatment of industrial tannery effluent loaded by Fats, dyes and heavy metals. The physicochemical characterization of this sample before and after treatment showed a remarkable increase in removal rate from 60 min to 180 min of filtration; 54.8% after one hour and 73.28% after 3 hours for COD, 73.28% after 3 hours for BOD<sub>5</sub>, 26.48% after 3 hours of filtration for conductivity and a total elimination rate of Turbidity that was achieved 99% after 3 hours of treatment.

## 1. Introduction

The manufacture of leather is an important activity which satisfies the local and the international demand for leather shoes, drums.... the growth of this industry products is linked with the development of the populations, the increase in leather demand and these products. Two processes of tanning are used, the tanning with chromium and the vegetable tanning. Currently, at global scale, the most part of leather is produced by chrome tanning process. In addition, due to the complexity of the transformation of animal leather skin, tannery industries use lot of chemical agents (In particular: sodium hydroxide, sodium hypochlorite, potassium dichromate, lime, chlorides, sulfuric acid, formic acid, surfactants, sodium sulfide, sodium salts and ammonium, etc.) and produce enormous volumes of waste water and solid waste, approximately 35-40 liters of water is consumed per kilogram of treated skin [1]. The liquid effluents generated consist essentially from a mixture of biogenic substance skins (hair, lipids, proteins ...) and a large quantity of chemical content no-biodegradable and dangerous for the human life, which returns the treatment of tanneries wastewater a serious environmental problem.

Research shows that a large variety of methods may be used for the treatment of different effluents when preparing the leather skin. However, most of these methods present difficulties in industrial production partly due to the daily fluctuation of the pollutant concentration and the size of the used installations.

Several techniques are used such as precipitation or neutralization of some compounds, which necessitates the use of chemical products which still generates chemical waste, or the electrochemical method of chromium recovery which is a method requiring a large amount of electricity therefore expensive, or the adsorption technique. The membrane Processes used alone [2, 7-9] or in conjunction with conventional processes represent a competitive alternative to conventional water treatment [3, 4].

However, treatment by microfiltration of tannery effluents on mineral membranes has been, until now, the subject of few studies and research [5,9-11]. The benefits of mineral membranes such as facilitating their implementation and their good mechanical and chemical resistance, the availability of the raw material and their attractive cost compared with commercial membranes [5] are the cause of their increasing development in many industrial applications such as the treatment of industrial effluents [7, 12, 13].

The aim of this study is to characterize the wastewater generated by industrial tannery unit located in Fez region (Morocco) and its treatment with microfiltration ceramic membrane from local clay material.

## 2. Materials and methods

### 2.1. Tubular membrane:

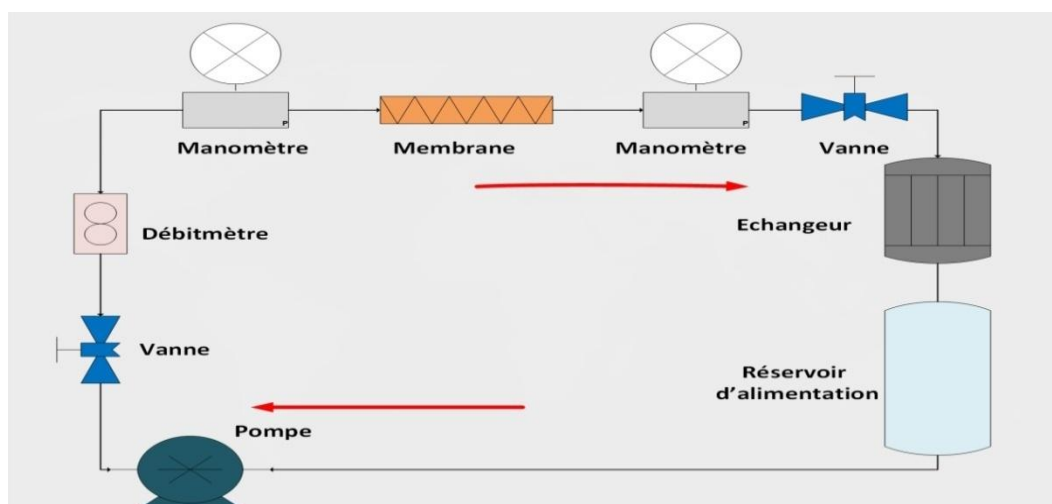
We used a natural clay microfiltration membrane formed by extrusion process of a ceramic paste in our Laboratory Centre. The physico-chemicals and structural characterizations of the used natural clay material are shown in our previous work [6]. The table 1 presents some characteristics of the used membrane.

**Table 1:** Characteristics of tubular membrane

Porosity (%)	28.8
Average pore diameter ( $\mu\text{m}$ )	1.5
Length (cm)	12
Internal diameter (mm)	12.6
External diameter (mm)	17.3
Thickness (mm)	2.35
External surface ( $\text{cm}^2$ )	65.22
Internal surface ( $\text{cm}^2$ )	47.5

### 2.2. Equipment:

The filtration pilot that we have used in the experimental section of this report, is a prototype designed and built within our laboratory. It is represented in Figure 1. The pilot operates in a closed buckle.



**Figure 1:** Microfiltration pilot plant schema

The filtration tests were conducted on a simple test bench equipped with an alimentation tray, a volumetric pump, a filtration membrane, a flow meter to measure the effluent flow rate in the circuit, a heat exchanger with double wall connected to an external water system in order to set the temperature of the trial, two pressure valves to set the transmembrane pressure and ensure purging of the installation.

## 3. Results and discussion

### 3.1. Characterization of effluent:

The Industrial effluent used come from a modern tannery in Fez region (Morocco) that does not have an effluent pretreatment installation. The physicochemical characteristics of the effluent are given in the table (2) below. As it can be seen in table 2, wastewater of tannery is characterized by high turbidity which is 119 NTU. This is due to the presence of great amount of suspended solids 5.14 g/l. the conductivity value of this effluent is 47.2 mS/cm which can be explained by the use of chemical salts in the tannery processes. The highest value of COD (3969.69 mg O<sub>2</sub>/l) may be due to the presence of high content of organic matter and hydrolyzed proteins.

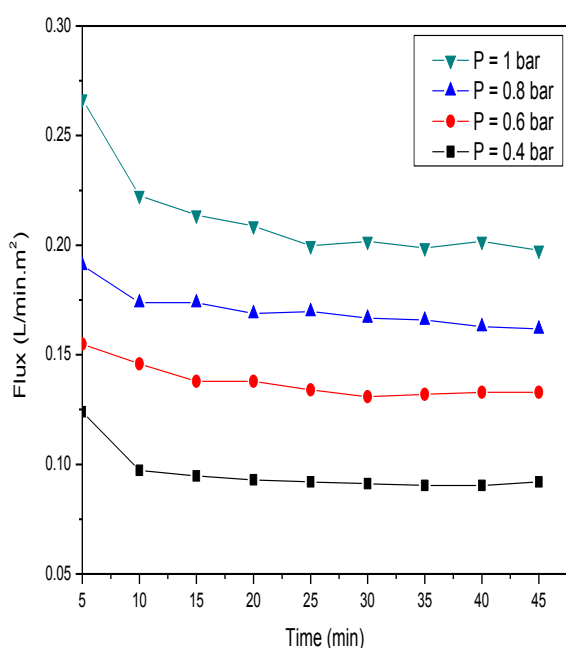
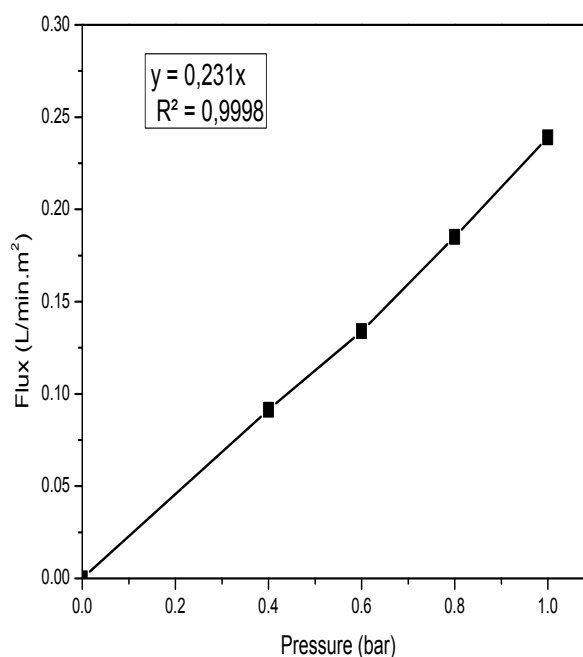
**Table 2:** Tannery effluent characterization

Parameters	Concentrations
pH	3.6
MES (g/l)	5.14
Conductivity (mS/cm)	47.2
COD (mg O <sub>2</sub> /l)	3969.69
Turbidity (NTU)	119
NO <sub>2</sub> <sup>-</sup> (mg/l)	23.62
PO <sub>4</sub> <sup>3-</sup> (mg/l)	12
BOD <sub>5</sub> (mg/l)	3096.36
SO <sub>4</sub> <sup>2-</sup> (mg/l)	4798.33
Cr (mg/l)	673.27

**N.B:** The variation in the grade of such effluent comes from the seasonal variation in the quality of treated skin, optimal dose of the used chemical products, type of industry and other parameters.

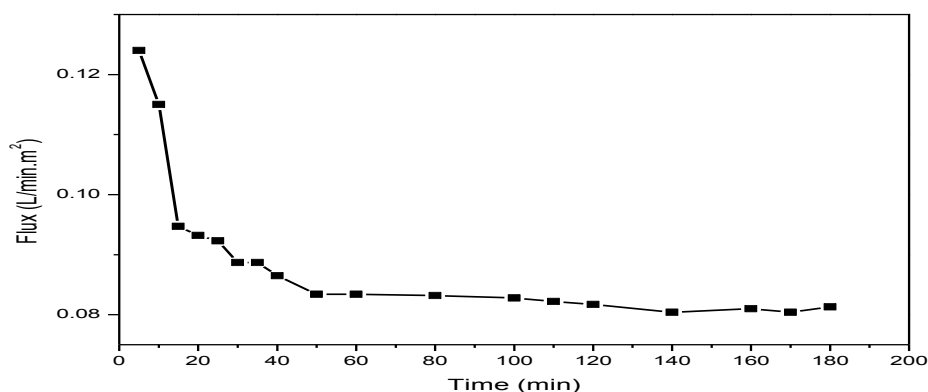
### 3.2. Determination of membrane permeability:

Clay microfiltration membrane was firstly characterized by its water permeability. The flux is measured at different transmembrane pressures (0.4, 0.6, 0.8, 1 bar). It can be observed in Fig 3, that the stabilization of the water flux through the membrane takes approximately 25 min. Experiments show also that the water flux through the membrane depends on the applied pressure. As can be seen in Fig 2, the value of membrane permeability determined using pure distilled water is about 0.231 L/min.m<sup>2</sup>.bar.

**Figure 3:** Distilled water flux vs operating time**Figure 2:** Variation of distilled water flux vs pressure

### 3.3. Filtration test:

The permeate flux variation of the effluent as a function of time at constant pressure (1 bar) is shown in Fig 4. It is observed that the permeate flux is approximately 0.09 L/min.m<sup>2</sup>, this value is low in comparison with the obtained one of distilled water 0.239 L/min.m<sup>2</sup>, which confirms the highly polluting charge of the as-treated effluent.



**Figure 4:** Permeate flux of effluent vs operating time (pressure = 1 bar)

A periodically measurements of conductivity, turbidity, COD, BOD<sub>5</sub> were be taken after 60 min, 120 min and 180 min of treatment. the evolution of these parameters with time can be observed in table 3. It is shown that the conductivity did not change significantly and the effect of membrane on conductivity is negligible because microfiltration process is not efficient to remove the soluble salts from effluent.

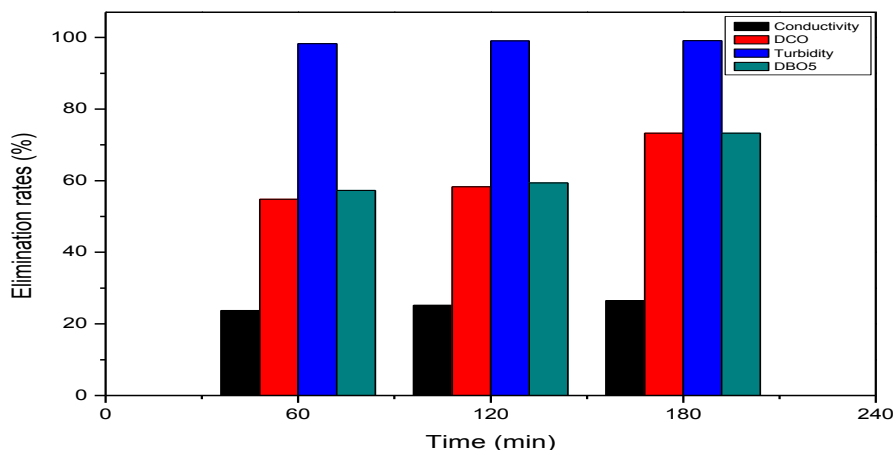
**Table 3:** Characteristics of effluent after treatment at 60 min , 120 min and 180 min

Parameters	After filtration		
	60 min	120 min	180 min
Conductivity (mS/cm)	36	35.3	34.7
COD (mg O <sub>2</sub> /l)	1654.545	1654.545	1060.606
Turbidity (NTU)	2.09	1.16	1.05
BOD <sub>5</sub> (mg/l)	1323.636	1257.454	827.272

Table 4 and Fig 5 shows the effect of microfiltration membrane on reduction of polluting loads presents on tannery wastewater, it can be seen that the removal percentage of turbidity is between 98.24 and 99.11%. According to these results, treatment by microfiltration decreases considerably the COD concentration by about 54, 58 and 73% for 60 min, 120 min and 180 min of treatment time respectively. Therefore, the microfiltration treatment can be a very promising technology in removing pollution from tannery wastewater. The obtained results for BOD<sub>5</sub> content confirm the microfiltration efficiency to decrease the Biochemical Oxygen Demand rate by about 57, 59 and 73% at 60, 120 and 180 min respectively.

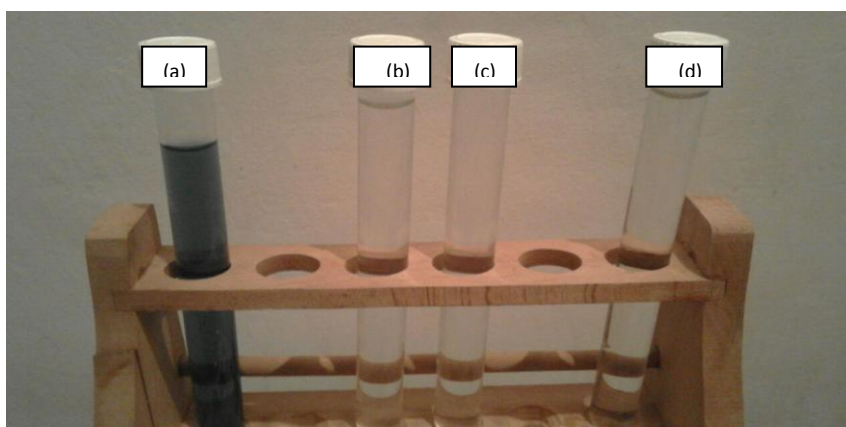
**Table 4:** Removal rates of all parameters after 60 min, 120 min and 180 min of treatment

Parameters	Elimination rates (%)		
	60 min	120 min	180 min
Conductivity	23.7288	25.2118	26.4830
COD	54.8090	58.3205	73.2823
Turbidity	98.2436	99.0252	99.1176
BOD <sub>5</sub>	57.2518	59.3892	73.3924



**Figure 5:** Comparison of elimination rates of each parameters

The color removal is one of the interest treatments because dye substances are considered as a very serious source of pollution, especially in tanneries. Fig 6 shows that the discoloration is complete by the use of tangential microfiltration, which improves considerably the quality of treated effluent.



**Figure 6:** Raw tannery effluent (a), Effluent treated at 60 min (b), at 120 min (c) and 180 min (d)

#### 4. Conclusion

In this work, we investigated the efficacy and applicability of microfiltration method using a local clay tubular membrane to treat the real tannery effluent.

All tangential microfiltration tests are operated at lower pressure (1bar), it is observed that the removal rates of COD, Turbidity, BOD<sub>5</sub>, and Conductivity are 73, 99, 73 and 26% respectively after 3 hours of treatment. These results confirm the capacity of the prepared low cost membranes to treat effectively the tannery wastewater. The use of microfiltration technology showed that these membranes have interesting retention properties and they can be more promising in removing pollution from numerous industrial effluents.

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