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# Treatment of effluents coming from beamhouse section of tannery by microfiltration through Cordierite/Zirconia and Alumina tubular ceramic membranes

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## Abstract
This study was conducted to evaluate the applicability of microfiltration in treating effluent coming from beamhouse section of tannery. Two tubular ceramic membranes were tested: A Zirconia $ZrO_2$ membrane ($M_1$) deposited on a macroporous support made from Cordierite and a commercial Alumina membrane ($M_2$). The pore diameter of microfiltration layer is 0.23 µm for the first membrane ($M_1$) and 0.2 µm for the second ($M_2$). The average membrane permeabilities determined using pure distilled water are 1136 l/h.m².bar and 1033 l/h.m².bar, respectively. Microfiltration using Cordierite/$ZrO_2$ membrane proved to be effective in removing the turbidity and the dark colour of the effluent and in reducing COD and TKN with almost the same efficiencies than that obtained with Alumina membrane: Tangential microfiltration process was seen to remove turbidity from the feed completely; the removal percentage of suspended solids from the effluent is between 98.5 and 100%. This technique operated at lower pressure (1 bar) showed significant reduction of COD (60-65%) and TKN (57-59%). The filtration's effect on conductivity was negligible. The combination of microfiltration with other techniques should be carried out to achieve the treatment.

*Keywords:* Treatment; Tannery; Beamhouse effluent; Tangential microfiltration; Ceramic membrane.

## 1. Introduction
The operations involved in the transformation of hides into leather generate both liquid and solid pollution loads at various processing stages. The environment is under increasing pressure from solid and liquid wastes emanating from the leather industry. Through the application of clean technologies (water savings, recycling of most pollutant baths) and solid wastes revaluation techniques, the mass balance for tanneries can be significantly improved [1-3]. The tanning process can be divided into three main phases: beamhouse, tanning and finishing. The beamhouse process normally accounts for about 40% of wastewater volume in a tannery [4]. In general, the beamhouse phase includes soaking (first process used to rehydrate and wash the hides or skins), liming (treatment with sulphides and lime milk for unhairing), washing (rinse with water and sodium bisulphide), deliming (lime removal with mineral or organic acids or acid salts), bating (enzymatic treatment to complete the removal of epiderm residues and more or less completely destroy the elastic fibers) and pickling (acidification in order to permit the penetration of tanning material) [5]. In the tanning industry, most of the operations require considerable water consumption, high concentration of tanning substances and others chemical species. Tannery effluents are characterized by high concentrations of pollutants and a great variety of composition which results from changeability of technological processes conducted in tanneries. There are considerable dissimilarities in the concentration range of pollutants in tannery wastewaters as given by different authors [6-8]. Generally, all of the organic pollution is associated with the beamhouse

processes. Suspended or settleable pollution is related to beamhouse or tanning operations, while toxic pollution is due in particular to sulphides and chromium salts [2,3]. Accordingly, physical, physicochemical and biological methods can be applied to purification of tannery effluents [6-9].

In order to minimize the pollution of tannery wastewaters, some authors propose the adoption of membrane technologies. For example, Cassano et al. [10] have experimentally studied the treatment of the unhairing, pickling and chromium tanning effluents by membranes (UF, RO and their combination). The use of nanofiltration for pickling and chromium tanning effluents was evaluated by Galiana-Aleixandre et al. [11] to minimize the sulphate ions concentration in the global wastewaters. For water reuse, Fababuj-Roger et al. [12] have evaluated a tannery wastewater treatment consisting of a physical-chemical process, filtration, ultrafiltration and reverse osmosis. Catarino et al. [5] have studied the decontamination of tannery wastewaters using different unit operations to select the best treatment sequences. Textile membrane filtration, microfiltration and ultrafiltration were complemented by screening, flocculation or flotation operations. The use of membrane technology showed to be promising in removing organic pollutants and allowing the reuse of water and chemicals in the tannery process [5].

In the goal to develop the use of low cost membranes for potential environmental application, we present in this work the performance of two microfiltration membranes for the treatment of tannery wastewaters coming from the beamhouse section. A Zirconia membrane deposited on macroporous support made from cordierite was used. The performances of this elaborated membrane were compared with those of a commercial ceramic membrane made from Alumina.

## 2. Experimental

### *2.1. Microfiltration membranes*

Cordierite powders (0–125 µm.) mixed with some organic additives were extruded to form, after firing, a porous tubular support for microfiltration membrane (Fig. 1). The elaboration process was described by Loukili et al. [13] and Saffaj et al. [14]: After drying at room temperature, the support was sintered at 1275°C for consolidation. Then, the Zirconia $ZrO_2$ layer was deposited on the inner surface of the cordierite support by slip casting. The porosity of cordierite support is 40% and the pore size is in the range of 7 µm. The mechanical resistance of the support (15 MPa) is strong enough to consider its use for filtration application under pressure. After drying at room temperature, the $ZrO_2$ membrane was treated at 300°C for 1h before being sintered at 1100°C for 2 h. The pore diameter of microfiltration layer is 0.23 µm. Scanning electron micrographs of the microfiltration layer revealed a uniform thickness with an average value of 23 µm (Fig. 2). The characteristics of Cordierite support and Zirconia microfiltration layer are summarized in Table 1.

The performances of the elaborated membrane were compared with those of a commercial ceramic membrane, made from Alumina, with a pore diameter of 0.2 µm.

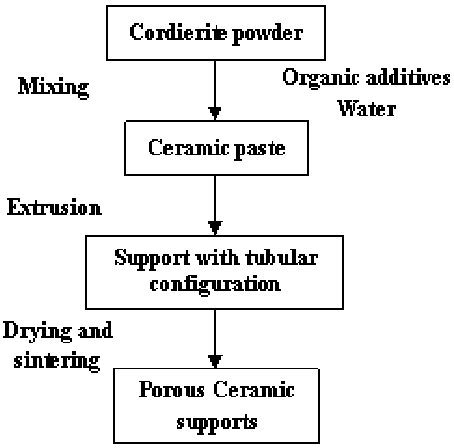


**Fig. 1.** Simplified diagram for elaboration of porous support by extrusion method.

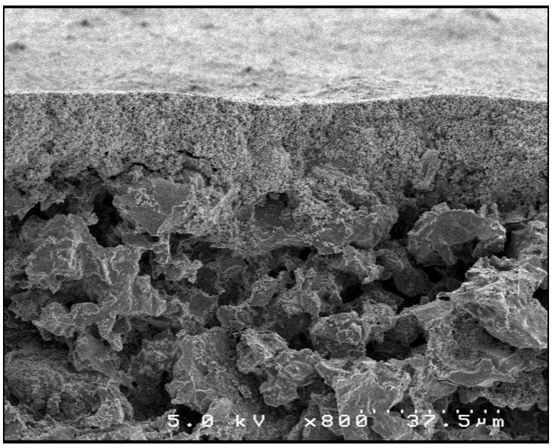


**Fig. 2.** SEM micrograph of Cordierite/$ZrO_2$ membrane (Cross section view).

**Table 1**
Characteristics of cordierite support and microfiltration layer.

| | Composition | Average pore diameter (µm) | Porosity (%) | Thickness (µm) | Mechanical strength (MPa) | Filtration Area ($cm^2$) |
|---|---|---|---|---|---|---|
| Support | Cordierite (0-125 µm) | 7 | 40 | - | 15 | 20 |
| Microfiltration layer | $ZrO_2$ (8 $m^2$ specific area) | 0.23 | - | 23 | - | 20 |

## *2.2. Filtration pilot*

Tangential filtration tests were performed on laboratory scale filtration pilot using a recycling configuration (Fig. 3). It was equipped with an adjustable out-flow pump, a thermostatic feed tank and a membrane module of 15 cm length. The filtration area developed by the membrane is 20 $cm^2$. Effluent was fed into the membrane module by means of gear rotate pump. Inlet flow rate was measured by the flow meter. A valve was used to control the pressure in the system, it varies between 0 and 2 bar.

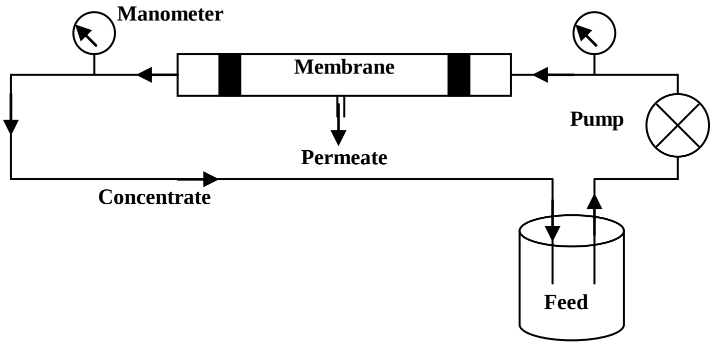


**Fig. 3.** Microfiltration pilot plant scheme.

## *2.3. Pollution analysis*

The feed and permeate concentrations were obtained by the use of standard methods (AFNOR). The main analyzed parameters were Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN), turbidity, pH, conductivity, suspended matter (SM) and sulphur. Determination of multielement was carried out using ICP (Ultima 2, Horiba Jobin Yvon, France). Turbidity was measured using TN-100/T-100 device. The pH and conductivity of the feed and permeate solution were measured directly by the use of a Fisher Scientific Accumet Basic AB15 pH Meter (USA) and a Conductivity Meter Model 101 (Orion Research, Cambridge, MA, USA), respectively. The pollutants rejection R was determined by the classical relation: R % = (1-$C_p$/$C_f$).100 where $C_p$ is the concentration in permeate and $C_f$ the concentration in the feed.

## 3. Results and discussion

## *3.1. Characterisation of tannery effluent*

The characteristics of the effluent used in this study are shown in Table 2. As it can be seen, wastewaters coming from beamhouse section of tannery are characterized by high conductivity value (22.2 $ms.cm^{-1}$) which may be due to the excess of non-used salts. The great value of pH (~12) can be explained by the use of chemical products such as lime, sodium sulphide and sodium hydrogen sulphide. These compounds are basic in nature and increase consequently the pH of the effluent. Their use in beamhouse section of tannery generates wastewaters with high concentration of sulphur (5529.02 mg/l), sodium (5682.77mg/l) and calcium (1514.7 mg/l). Chemical Oxygen Demand (COD) is the amount of oxygen required for the oxidation of organic matter presents in the effluent. The highest value of COD (40320 mg/l) may be due to the presence, in effluent, of high content of organic matter and soluble hydrolysed proteins (KTN=3570 mg/l). Turbidity (132 NTU) is due to the considerable amounts of suspended solids (4.32 g/L) which are responsible of the colour of beamhouse effluent.

### 3.2. Determination of membrane permeability

The membranes are conditioned by immersion in pure deionized water for a minimum of 24 h before filtration tests. MF membranes were first characterized by their water permeability. For each membrane, fluxes are measured at different transmembrane pressures (0.5, 1 and 1.5 bar). It can be observed that the stabilization of the water flux through the membrane takes approximately 30 minutes (Fig. 4). Experiments show also that the water flux through the membrane depends on the applied pressure. The average membrane permeability determined using pure distilled water is 1136 l/h.m².bar for the Cordierite/$ZrO_2$ and 1033 l/h.m².bar for the Alumina commercial membrane (Fig. 5). It remains almost constant during all the filtration experiments. As it can be seen, permeability is a function of the nature of membrane and of its porosity.

**Table 2**
Effluent characterization.

| Parameters | Values |
|---|---|
| pH | 12.03 |
| Conductivity (ms) | 22.2 |
| Turbidity (NTU) | 132 |
| COD (mg $O_2$/l) | 40320 |
| KTN (mg/l) | 3570 |
| Calcium (mg/l) | 1514.7 |
| Sodium (mg/l) | 5682.77 |
| Sulphur (mg/l) | 5529.02 |
| Suspended matter (g/l) | 4.32 |

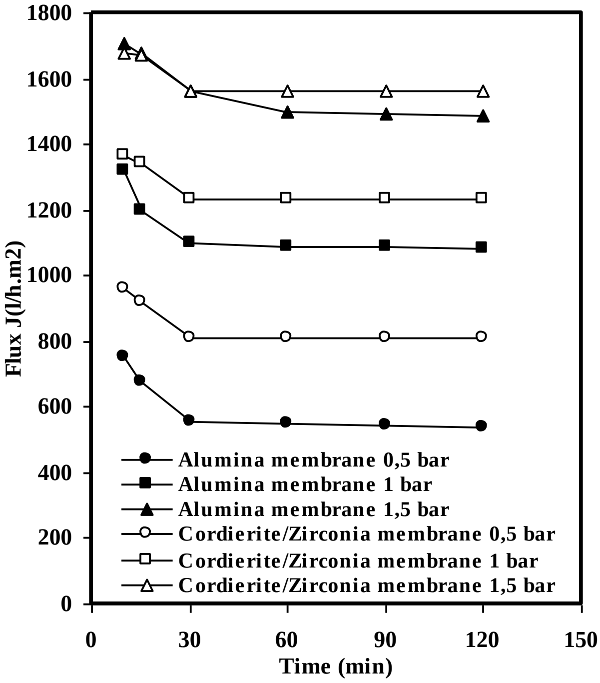


**Fig. 4.** Water flux vs. operating time.

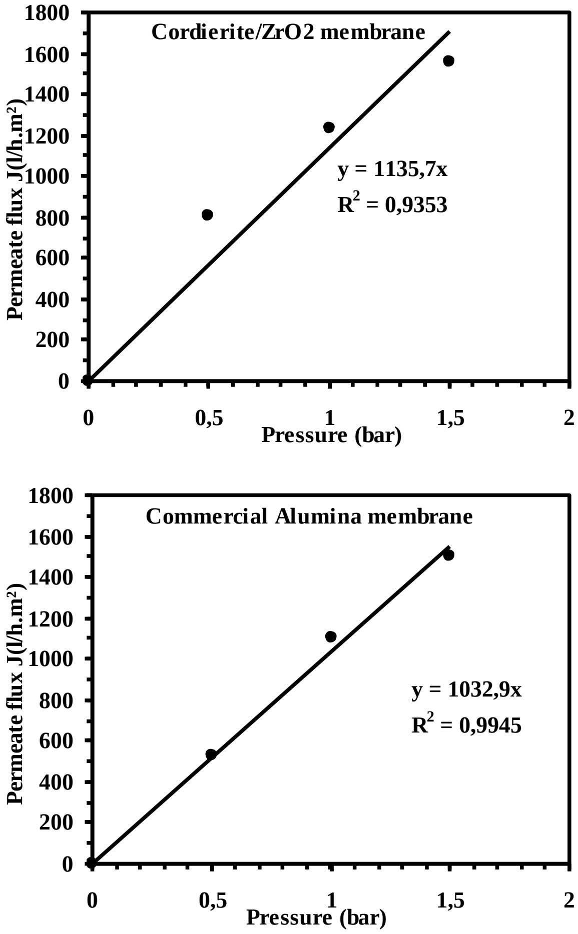


**Fig. 5.** Variation of water flux as a function of working pressure.

### 3.3. Filtration test

The variation of permeate fluxes of effluent as a function of time is shown in Fig. 6. For the two membranes, all microfiltration experiments were carried out at $\Delta P = 1$ bar. Permeate fluxes are low in comparison with those obtained with distilled water. This can be explained by the contaminants effect which changes the dynamic proprieties of water such as viscosity and density. Flux stabilizes at a permeate flux of about 200 l/h.$m^2$ and 150 l/h.$m^2$ with Cordierite/$ZrO_2$ membrane and Alumina membrane, respectively.

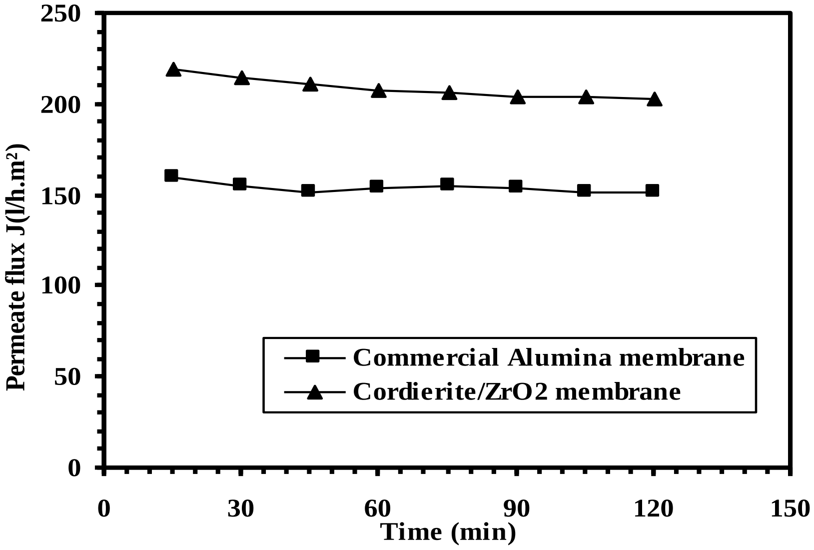


**Fig. 6.** Permeate flux of effluent as a function of operating time.

For all microfiltration experiments, pH and conductivity were periodically determined. The evolution of these parameters in relation to time can be observed in Fig. 7. Obtained results show that pH value remains constant during all the filtration tests. The effect of membrane on conductivity is negligible because microfiltration process is not efficient to remove the soluble salts from the effluent.

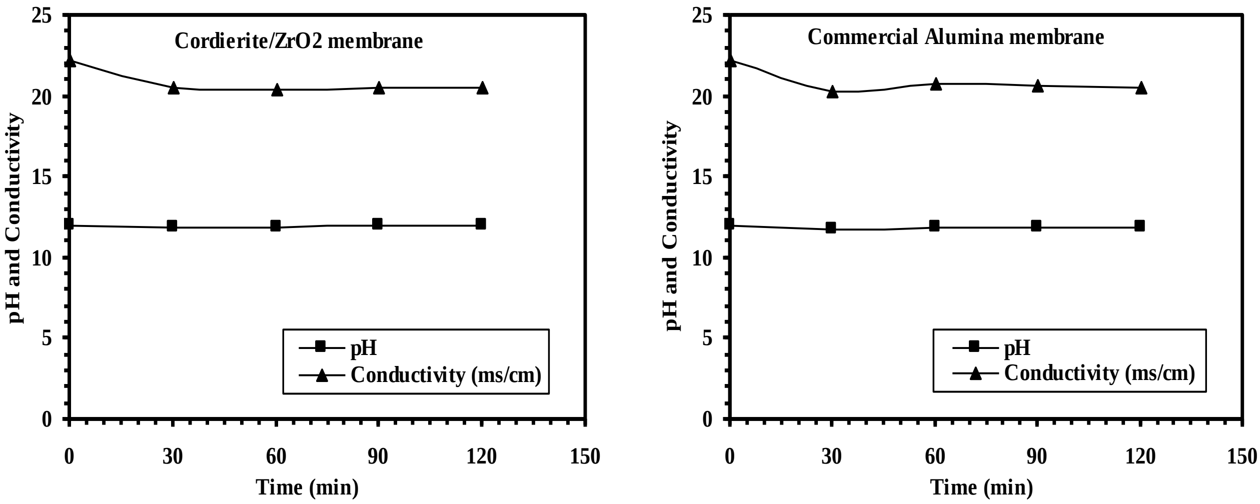


**Fig. 7.** Variation of pH and conductivity with the operating time.

Analyses of beamhouse wastewaters by ICP (Table 3) detect high concentration of sulphur, sodium and calcium followed by remarkable contents of potassium and magnesium, and low amounts of some elements such as aluminum, zinc, iron, copper, etc. The decrease of some elements concentration in permeate is due probably to the sorption of quantity of salts on suspended solids and their rejection together by microfiltration membranes. To improve effluents quality by removing soluble salts, other techniques should be used to achieve treatment of the effluents such as combination of microfiltration with nanofiltration or reverse osmosis.

In order to show the effect of microfiltration membranes on reduction of pollutants in beamhouse wastewaters, turbidity, COD and KTN were analyzed. As it can be seen in Fig. 8, the microfiltration process was seen to remove turbidity from the feed completely. The removal percentage of turbidity is between 98.5 and 100% for the two membranes which allow complete elimination of colloidal particles or suspended solids from effluent. According to the results shown in Fig. 9, treatment by microfiltration decreases considerably the COD concentration. The reduction of COD content can reach 60 and 65% for Cordierite/$ZrO_2$ and commercial Alumina membranes, respectively. Remained percentage in permeate may be due to the soluble COD of the wastewaters which correspond mainly to hydrolyzed proteins resulting from unhairing process. Obtained results reveal also that microfiltration decreases KTN content from 3570 mg/l to 1523 mg/l in the case of Cordierite/$ZrO_2$ membrane and from 3570 mg/l to 1470 mg/l in the case of commercial Alumina membrane. The KTN rejection is 57.34% and 58.82%, respectively (Fig. 10). Results show clearly that rejection percentage of KTN is directly proportional to COD removal.

**Table 3**
ICP analysis of effluent and permeates.

| | Concentration (mg/L) | | |
|---|---|---|---|
| Element | Effluent | Permeate of cordierite/$ZrO_2$ membrane | Permeate of alumina membrane |
| Al | 13.520 | 8.24 | 6.912 |
| As | 0.16 | 0.15 | 0.10 |
| Ca | 1514.7 | 1442.68 | 1391.05 |
| Cd | 0.452 | 0.250 | 0.200 |
| Co | 0.120 | 0.08 | 0.08 |
| Cr | 0.08 | 0.08 | 0.08 |
| Cu | 1.056 | 0.984 | 0.868 |
| Fe | 1.196 | 0.638 | 0.450 |
| K | 113.74 | 101.28 | 96.235 |
| Mg | 50.390 | 41.360 | 39.143 |
| Mn | 0.172 | 0.08 | 0.08 |
| Mo | 7.697 | 4.023 | 4.148 |
| Na | 5682.77 | 5405.63 | 5363.81 |
| Ni | 0.608 | 0.572 | 0.348 |
| S | 5529.02 | 5386.45 | 5354.35 |
| Zn | 3.372 | 3.276 | 2.412 |

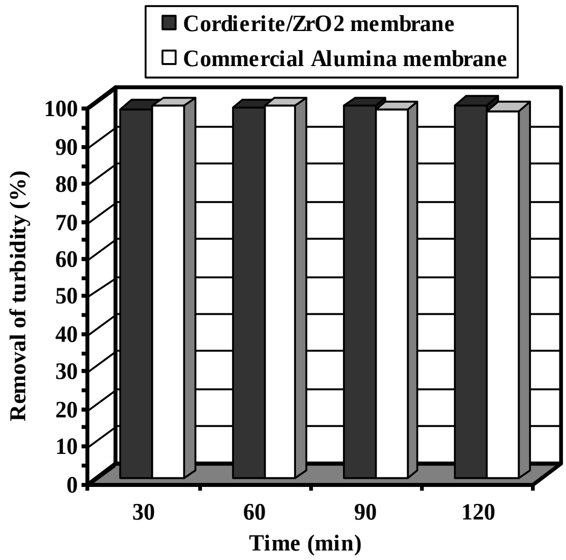


**Fig. 8.** Removal of turbidity as a function of operating time.

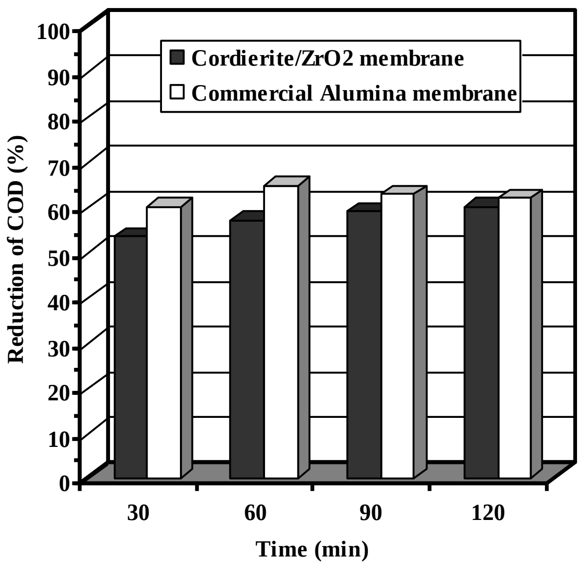


**Fig. 9.** Reduction of COD with the operating time.

As it can be seen, microfiltration using Cordierite/$ZrO_2$ membrane proved to be effective in removing turbidity and colour (Fig. 11) and in reducing COD and TKN with almost the same efficiencies than that obtained with alumina membrane. Therefore, the use of microfiltration treatment technology showed to be promising in reducing pollution level of beamhouse wastewaters but complementary treatment is necessary to remove or reduce residual COD and KTN in permeate.

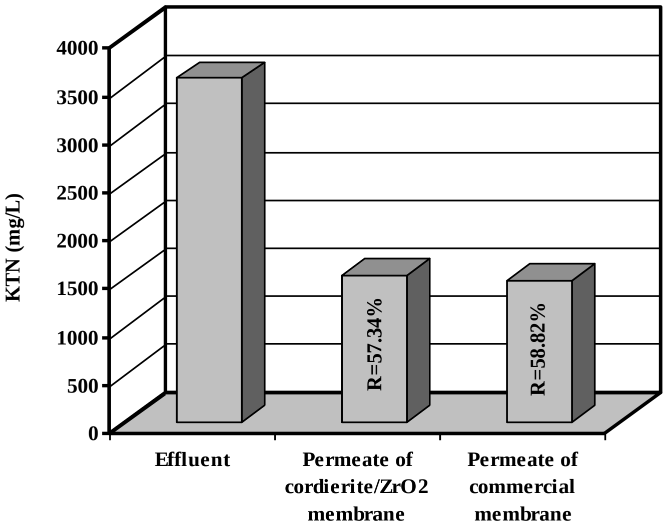


**Fig. 10.** Reduction of KTN content by microfiltration process.

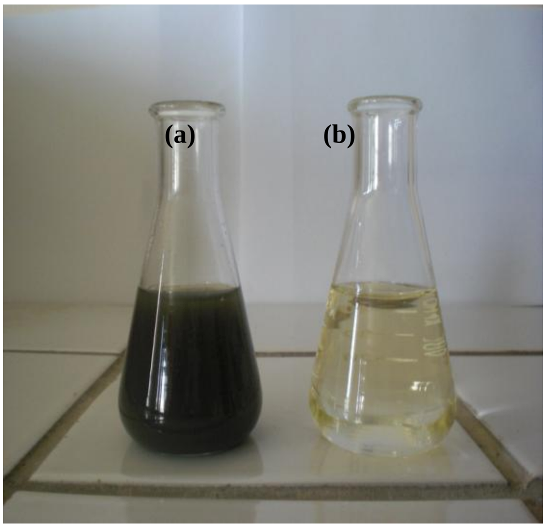


**Fig. 11.** Effluent before (a) and after (b) treatment using cordierite/$ZrO_2$ microfiltration membrane.

## 4. Conclusion

In this work, we have shown that microfiltration ceramic membrane can be successfully used for the treatment of wastewaters coming from beamhouse section of tannery. Microfiltration process is able to improve the quality of effluent by removing suspended matters and reducing COD and KTN contents. Zirconia and Alumina membranes reduced the feed concentration of COD by 60-65% and that of TKN by 57-59%. Microfiltration was seen to remove turbidity from the feed completely. So, the process showed to be promising in reducing tannery pollution.

The main objectives of our later works are the isoelectric precipitation, as complementary treatment, to remove hydrolyzed proteins remained in permeate; the recovery of sulphide, the removal of residual salts and the reuse of treated water.

## References

1. Panswad, T., Chavalparit, O., Sucharittham, Y., Charoenwisedsin, S. *Wat. Sci. Tech.*, 31 (9) (1995) 73-81.
2. Carré, M.C. Vulliermet, A., Vulliermet, B. Environment and tannery. Centre Technique du Cuir (C.T.C), France, 1983.
3. Aloy, M., Folachier, A., Vulliermet, B. Tannery and pollution. Centre Technique du Cuir (C.T.C), France, 1976.
4. U.S. Environmental Protection Agency (US-EPA), Guidance Manual for Leather Tanning and Finishing Pretreatment Standards (1986) 2-3.
5. Catarino, J., Mendonça, E., Picado, A., Lança, A., Silva, L., Norberta de Pinho, M. *Can. J. Civ. Eng.*, 36 (2) (2009) 356-362.
6. Ates, E., Orhon, D., Tunay, O. *Wat. Sci. Tech.*, 36 (1997) 217-223.
7. Naumczyk, J., Rusiniak, M. *Polish Journal of Environmental Studies*, 14 (6) (2005) 789-797.

8. Bartkiewicz, B. Industrial wastewater purification; PWN: Warszawa (2000) 271-279, (In Polish).
9. Tsotsos, D. *Wat. Sci. Tech.*, 18 (1986) 69-76.
10. Cassano, A., Molinnari, R., Romano, M., Drioli, E. *J. Memb. Science.*, 181 (2001) 111-126.
11. Galiana-Aleixandre, M.V., Iborra-Clar, A., Bes-Piá, B., Mendoza-Roca, J.A., Cuartas-Uribe, B., Iborra-Clar, M.I. *Desalination*, 179 (2005) 307-313.
12. Fababuj-Roger, M., Mendoza-Roca, J.A., Galiana-Aleixandre, M.V., Bes-Piá, A., Cuartas-Uribe, B., Iborra-Clar, A. Desalination, 204 (2007) 219-226.
13. Loukili, H., Persin, M., Alami Younssi, S., Albizane, A., Bouhria, M., Saffaj, N., Larbot, A. Removal of textile dyes from waste water by ceramic ultrafiltration membrane. Proceedings of the Congress: Water Resources in Mediterranean Basin WATMED2 (2005) 1-8.
14. Saffaj, N., Alami-Younssi, S., Albizane, A., Messouadi, A., Bouhria, M., Persin, M., Cretin, M., Larbot, A. *Separation and Purification Technology*, 36 (2004) 107-114.

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