Research Paper

Decolorization of Dyeing Effluent by Novel Ultrafiltration Ceramic Membrane from Low Cost Natural Material

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Graphical abstract

Highlights

• Novel antifouling low cost UF membrane
• Application to textile effluent treatment
• Almost a total retention of turbidity and color

Abstract

This paper is devoted to the application of new low cost ceramic ultrafiltration membranes material coming from the Tunisian ores (mud) which is usually considered as disastrous for the environment. A ceramic tubular support previously elaborated from mud was coated in the lumen side by slip casting method. After sintering at 650°C, the coated membrane shows homogeneous layer without cracks, with a pore diameter of 11 nm. The coating has the thickness of ~9 μm and water permeability of the prepared membrane is 90 L/h.m².bar. Then the prepared membrane has been applied for treating of dyeing wastewater under 5 bar pressure. The result was interesting with a permeate flux of 65 l/h.m², pollutants retention rate of 90% for COD and almost a total retention of turbidity and color, respectively. The membrane can then be regenerated by using a chemical washing.

1. Introduction

Textile industries are considered as a great consumer of water that cause producing huge quantities of effluents which is highly loaded with organic pollutants, salts and mainly synthetic dyes [1]. As a rough estimation in sequence to process a ton of textile, 230 – 270 tons of water has to be used [2–4].

Direct discharge of the dying wastewater in receiving medium can cause many ecological and environment problems inducing the eutrophication and anarchic algae proliferation in the aquatic systems [5]. It can have calamitous effects on potable water even in the deepest aquifers. So, the industries must find out appropriate solutions to effectively treat their effluents and eventually reuse them at the beginning their own production process. Although physicochemical and activated sludge treatments are typically used in textile wastewater treatment, whereas these kinds of treatment does not allow water reuse in any steps of the production process [6]. Since past few years, membrane processes have gained popularity and have considered as the most suitable technology to treat and reuse wastewater from various sources. Thus,

membrane technology has emerged as better alternative to conventional treatment systems since membranes offer a high efficiency in removal of pollutants. Moreover, it saves operation costs and water consumption by water recycling providing an important solution for environmental problems [7].

In many works, filtration processes that involve MF or UF have been operated to recover colloidal and dissolved suspended matters from textile wastewater. However they produce a permeate stream which still contains dissolved color. Promising results with respect to the color removal are using hybrid treatment integrating MF and UF or a combination of MF and NF processes. Indeed, NF has been classified as the most efficient for the decolorization and desalination of textile effluent because of its unique separation performance which includes size exclusion and electrostatic interactions resulting in treated effluent quality suitable for potential reuse [4, 8].

Hammami et al. [9] studied the enhancement of the removal of Acid

Orange 7 (AO7) dye by adding powder activated carbon (PAC) to ultrafiltration in hybrid process. The results signify that the flux persists almost constant during hybrid treatment while a strong decrease of flux was observed when simple UF was applied. In addition, an efficient decolorization was achieved by that processes, Masmoudi et al. [10] studied the combination of MF and NF for an effluent that is ready for reuse. The results showed almost 99% of color and turbidity removal, and also higher amount of COD decrease. Ellouze and Tahri [11] confirmed that the employment of microfiltration (MF) as the pretreatment step for NF is more effectual in terms of pollutants removal than Coagulation-flocculation followed by NF, especially regarding the color removal. Zahrim et al. [12] investigated the potential of combination of coagulation-flocculation step with NF to reduce the NF membrane fouling during the treatment of highly concentrated dyes solutions. Unlu et al. [13] tested different combinations of coagulation, MF, UF and NF and observed that MF/ NF system represents the optimum approach in the case of the treatment of indigo dyeing wastewater. Ellouze et al. [14] reported that NF and UF are suitable process which could be added to coagulation-flocculation to enhance the treated wastewater quality for reuse. In this case, more than 90% of color and turbidity were removed.

All these methods give acceptable results when coupled with NF, but there is an urgent demand to develop more effective and inexpensive methods which can be automatically followed and necessitate fewer chemicals and energy consumptions, and less installation spaces, as well.

The development of long life antifouling and cost effective UF membrane are thus expected to provide additional opportunity for membrane technology application in the fields of textile wastewater treatment.

Membranes can be made of polymeric or inorganic materials. As inorganic membrane, ceramic membranes have various advantages compared with polymeric membranes notably in term of chemical and biological stabilities as well as mechanical strength and separation efficiency [15, 16]. In addition, membrane surface presents a relatively homogenous pore size and high porosity resulting in obtaining high filtration performance.

In the domain of wastewater treatment, the usage of ceramic membranes remains limited because of their higher operational cost [17]. Therefore, many efforts have been done to produce cost effective and efficient membranes for various purposes. One of the challenges for future progress of inorganic membranes is the production of a low-cost membrane from natural materials such as clays [18-20], granitic sand [21], phosphates [22, 23] or graphite [24]. Such materials can be found in abundance in some countries and need lower firing temperature than that of pure metal oxide materials [25-27]. New ceramic membranes can further be made of some abundant products coming from industrial waste. Transformation of such product comes from fly ash or coal fired power station [28, 29].

Thus, local Tunisian mud coming from the phosphate industry transformation has been taken as the ceramic material in this study for the preparation of a novel and inexpensive ceramic membrane. This material is produced from the apatite washing step in the phosphate industry (Tunisia). It can cause risk for environmental impact due to its fullness in the Tunisian ores. This sub-product is collected by very small particles sizes of about a few tens of micrometers suitable for ultrafiltration membrane preparation after sieving.

In the literature, only our previous work [30] has been presented the upgrade of the phosphates industry sub-products in membrane elaboration. Indeed, a composite MF membrane consists a support from mud of the hydro cyclone laundries of phosphate, coated by a zirconia layer was elaborated for textile wastewater treatment. The results revealed mainly removal of 100% turbidity and a partial retention of COD. However, no retention of color was observed. Moreover, UF has a number of promising advantages over NF such as the production of a relatively high permeate flux, lower operating cost, and the capacity of adsorption of the present mud [31].

The main goal of this study was to develop a cost effective and novel antifouling UF membrane for cleaning industrial effluent generated in textile industry. The membrane has been prepared by deposition of mud's active layer directly on mud macro-porous support without intermediate layer. This allowed to decrease the membrane resistance and thus to enhance the ultrafiltration process performances.

2. Experimental

2.1. Membrane elaboration

2.1.1. Slip casting characterization and process

To make a slurry solution suitable for the slip casting, the composition of the slip should be carefully selected. According to the literature [19], the suitable composition of the slurry solution is given in Table 1. Moreover, to ensure the uniformity of the deposited layer on the lumen side of the macro-porous support, the constancy of the prepared suspension is required. This can be accomplished by the study of the rheological behavior (Viscosimeter: LAMY model TVe-05).

The UF layer from mud is prepared by a slip-casting process. The slurry solution is putted on the support with pore diameter of 1.07 μm and porosity of 39% [29], which is previously elaborated from the same material. The length and the inner/outer diameter are 150 mm and 6/9 mm, respectively. Figure 1 describes the slip-casting process which is composed by the following steps:
- Preparing suspension including the mineral powder and water.
- Adding (a 12-wt% aqueous solution of PVA) as binder and homogenization by magnetic shaking followed by ultrasound exposure.
- Slip casting of the suspension on the lumen side of the porous support for five minutes at room temperature. For the tubular membranes, the tube is closed from one end and filled with the solution. After a given casting duration, the excess is evacuated from the bottom.
- Drying during 24 h at room temperature.

2.1.2. Thermal treatment program

The firing temperature, fixed at 650 °C, is reached following the program registered in Figure 2. A temperature plate at 250 °C for 1 h is mandatory in order to completely eliminate the PVA, which is abundant in the slip. A rather slow temperature increasing rate (2 °C/min) is needed in sequence to avoid the formation of cracks on the layer.

2.2. Membrane characterization

The average pore diameter of the active layer was carried out by nitrogen adsorption/desorption isotherm using a Quantachrome instruments. The morphology of the surface and the thickness were characterized by Scanning Electron Microscopy (SEM) method.

Table 1
Composition of the slurry solution [19].

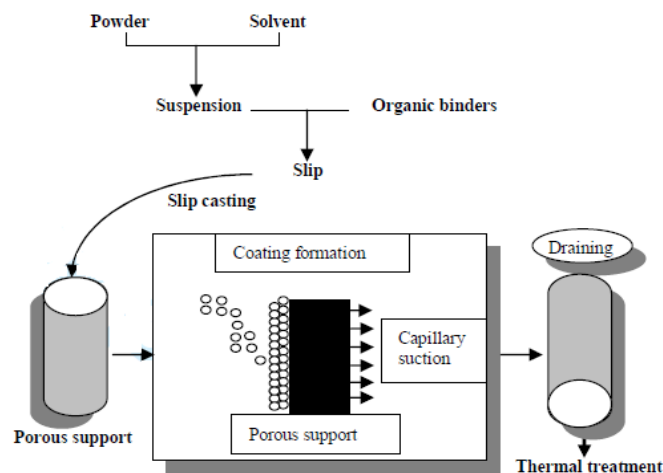| Component	Conditions	Proportion (Wt %)
Water	Deionised	65
Polyvinyl alcohol (aqueous solution)	12% aqueous solution	30
Mud of the hydrocyclone laundries powder	Particle size ≤ 63μm	5

Fig. 1. Slip casting process.

2.3. Ultrafiltration treatment

Crossflow ultrafiltration tests were determined using a lab-made single channel tubular membrane at 25 °C (see Figure 3). The operating pressure is applied using a nitrogen gas source directly linked to the feed solution. The pressure (TMP) varying in the range of 2 to8 bars was controlled by an adjustable valve at the concentrate side. The total active area of the membrane is 23.37 cm². Before experiments, the elaborated membrane was conditioned in ultrapure water for 24 h to get a speedy stabilization of permeate flux, then, the membrane permeability was determined.
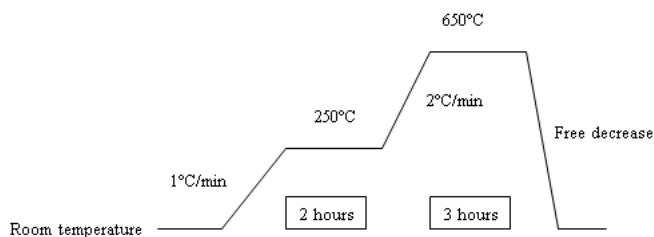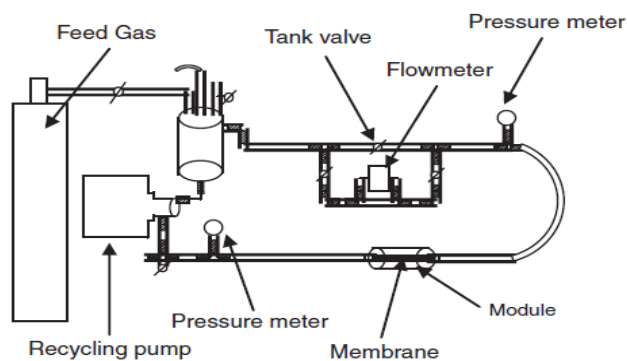
Fig. 2. Temperature–time schedule.

Fig. 3. Scheme of the experimental set-up.

Fig. 4. Rheologic behaviour of the slip mud.

The regeneration of the membrane was accomplished firstly by washing with fresh water for 15 min, then by using an acid-base treatment with a circulation of solutions of NaOH 2% at 80 °C and nitric acid 2% at 60 °C alternatively for 20 min. Finally, the membrane was rinsed with deionized water until neutral pH was reached. The efficacy of the cleaning protocol was verified by measuring the initial water permeability behind the cleaning cycle.

2.4. Effluent characterization

The membrane was used to treat a real effluent coming from Tunisian textile factory. Physico-chemical parameters of the effluent and of the permeate were then determined. Conductivity and pH were measured using a conducti-meter, Tacussel model 123 and a pH-meter, Metrohm 744. Turbidity was achieved using a turbidity meter (Hach RATIO 2100A) in accordance with standard method 2130B.

Color measurement was accomplished according to a standard multiple dilution method [32] and by comparing absorbance to a calibration curve. The decolorization was achieved by controlling the decrease of the absorbance peak at the maximum wavelength for the global effluent [33]. In the case of the wastewater used in this study, just one pick was observed at 420 nm UV–Visible spectrophotometer (Perkin Elmer Lambda 20 UV/VIS Spectrophotometer) was used in all experiments.

COD is estimated by the open reflux method. The protocol was applied in accordance with a method derived from the Standard AFNOR T90-101. The sample was refluxed in an acidic medium with a known quantity of potassium dichromate supplied from Sigma- Aldrich and the remaining dichromate was titrated with ferrous ammonium sulfate supplied from Sigma Aldrich. The COD values are obtained using a Fisher Bioblock Scientific reactor COD 10119 type COD meter.

3. Results and discussion

3.1. Membrane characterization

3.1.1. Slip characterization

The mud of hydrocyclone powder, sieved to 63 µm characterized in a previous study [30]. The composition is announced in Table 2. For a good adhesion on the macro-porous support, viscosity must be sufficient to facilitate the coating and to prevent fast absorption of the solvent. The viscosity of the slip was determined just before deposition on the support. The rheogram of the used slip was done by the curve of shear stress (τ) versus shear rate (D). According to Figure 4, the rheological study shows a plastic behavior of Bingham with a limiting shear stress of 11 Pa. A similar finding is reported by Masmoudi et al. [22].
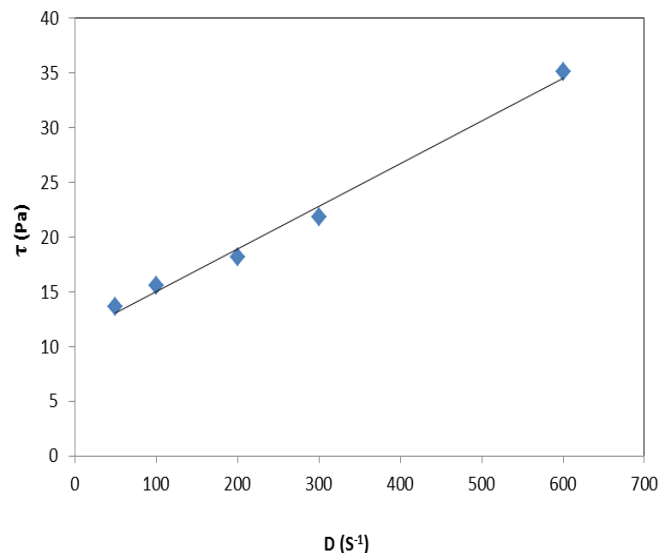
Table 2
Chemical analysis of the mud of the hydro cyclone laundries of phosphates powder.

Elements	Proportion (Wt %)
P_2O_5	8.40
CaO	19.98
SO_4	2.47
SiO_2	38.89
Fe_2O_3	1.09
F^-	1.30
COT	1.45
Al_2O_3	6.75
MgO	1.84
CO_2	6.06
LOI*	11.77

* Loss of ignition

3.1.2. Scanning Electron Microscopy analysis

The morphology, surface quality and the thickness of the active layer were examined by scanning electron microscopy. Figure 5 exhibits the cross-section and the surface views for different sintering temperatures. The temperature range from 600 °C to 700 °C was determined associated to the thermal analysis achieved by TDA-DSC in the literature [30].

All samples showed a typical asymmetric structure which reveals that the surface layer had a good adherence onto the support. By analyzing the surface texture of the different samples, it can be assumed that only the sample obtained at 650 °C was free of defects and without cracks. So the best layer was obtained at a sintering temperature of 650 °C with a thickness of ~9 µm.

3.1.3. Pore size determination

The casting deposition time and the sintering temperature are the cardinal parameters controlling the final pore diameter, the thickness of the layer and the morphology of the membrane. Based on these considerations, a casting time of 5 min and a sintering temperature of 650 °C were chosen. It can be observed in Figure 6 that the pore diameters are centered at 11 nm which approves that we achieved to prepare a UF layer.

This finding is very important since the UF active layer is directly deposited on the support without the need of an intermediate microfiltration layer, as it is usually observed in the literature [34, 35]. The reduction of the layer number should increase the filtration performance by limiting the membrane resistance.
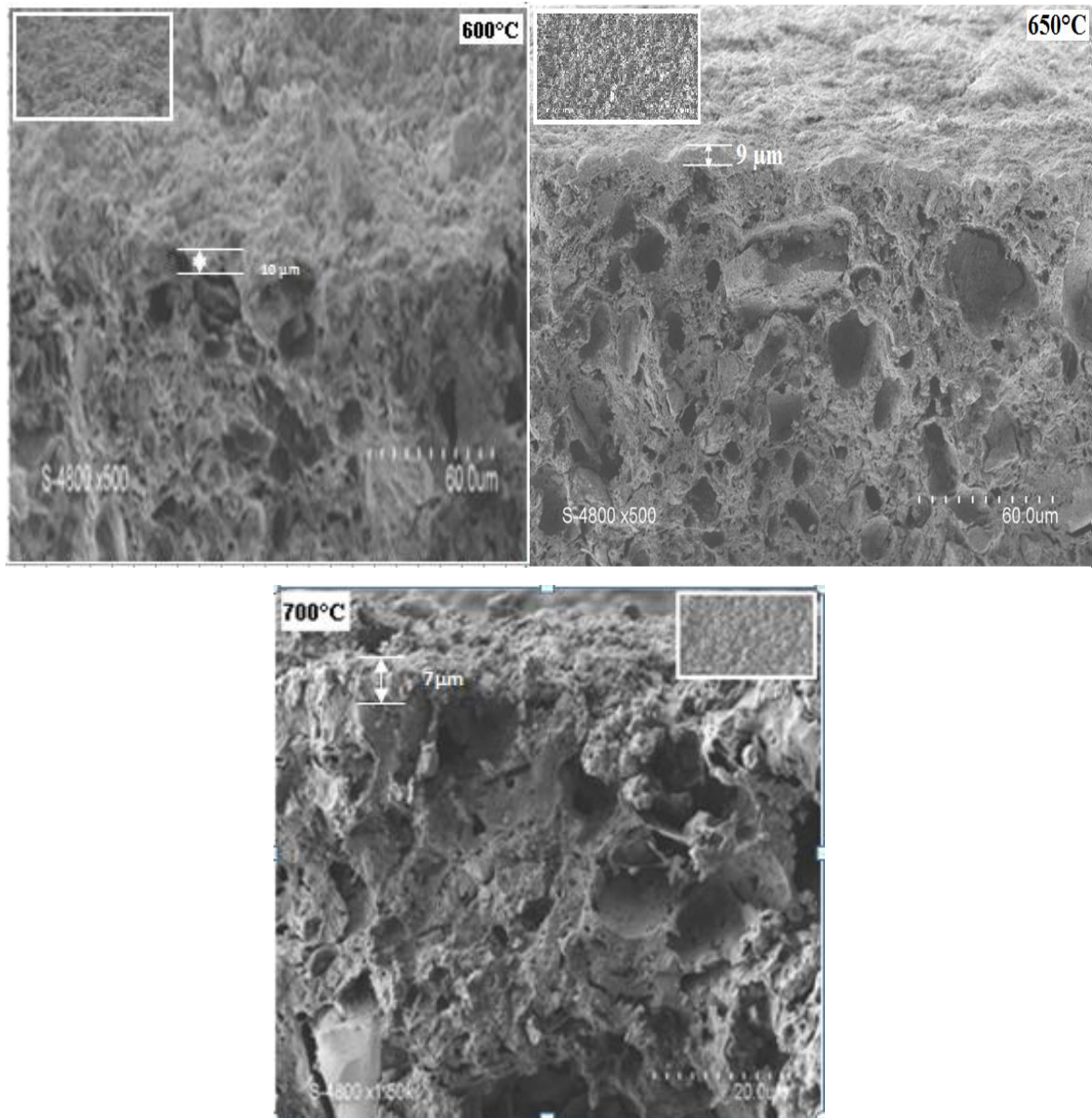
Fig. 5. SEM views of membrane texture at different temperatures.

3.1.4. Membrane permeability

The membrane permeability (L_p) was determined using pure deionized water. L_p is brought by the slope of the linear variation of the permeate flux J_w (L/h.m^2) with applied transmembrane pressure (bar) according to the well-known Darcy law:

$$J_w = L_p \ \Delta P \tag{1}$$

where

$$\Delta P = [(P_{inlet} + P_{outlet})/2 - P_f] \tag{2}$$

where P_{inlet} = inlet pressure; P_{outlet} = outlet pressure; P_f = filtrate pressure.

It can be noticed from Figure 7 that the flux decreased during a first period of 30–40 min and then became stable. The permeability of the UF membrane was determined from the stabilized water flux given at each pressure. It is around 90 L/h m^{2}bar which is comparable to that achieved by UF commercial membrane based on alumina [36].

3.2. Application to textile wastewater treatment

3.2.1. Wastewater characterization

The studied wastewater was produced from the various steps of the dyeing cycle using reactive dyes. Generally, the molecules of reactive dye are composed of a chromophore group and reactive chemical group forming covalent bond with the textile fiber. In our case, the used reactive dye has a blue color and with formula of $C_{37}H_{23}Cl\ N_{10}O_{22}S_7Na_6$.

The wastewater sample contains different chemical substances such as dyes, detergents, salts, auxiliaries (e.g. surfactants, emulsifiers) and caustic soda coming from the different washing baths related to dyeing, washing and bleaching operations. Table 3 represents that the raw effluent is heavily polluted in terms of pH, salinity, color and COD.

Table 3
Determination of the principal characteristics of textile industry wastewater.

Parameters	pH	Salinity (g/l)	COD (mg/l)	Turbidity (NTU)	Color[a]
Values	9.9	12.3	2869	880	2.32

[a]Integral of the absorbance curve in the whole visible range (400–800 nm).

3.2.2. Ultrafiltration treatment

The filtration performance is determined at a velocity of 2.5 m/s and a temperature of 25 °C. Figure 8-a gives the variation of permeate flux with

various transmembrane pressure (TMP). As could be observed, the permeate flux grows linearly with TMP until 5 bar and then becomes pressure independent. This can be attributed to the concentration polarization and fouling due to the interaction between membrane material and waste water solution [37]. It is salient to notice that fouling is not very important since the flux decline ratio between the initial values and the stabilized permeate flux obtained after 20 min of filtration, does not transcended 15% (see Figure 8-b). This behavior is a typical one for an UF membrane compared to MF membrane which shows generally a significant flux decrease [22, 29].
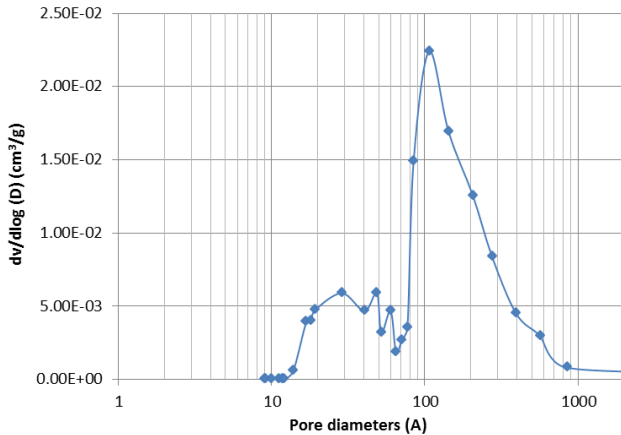
and might requires chemical cleaning [38]. Previous works concluded that reversible and irreversible fouling can contribute up to 18% and 26–46% of the permeate flux reduction, respectively [39].

In accordance to the resistance in series model, the fouling resistance can be described by the following equation:

$$R_T = R_m + R_{rev} + R_{irrev} \tag{3}$$

where R_T is the total filtration resistance which represents the distribution of the different resistances. R_T can be estimated from the following equation:

$$J = \Delta P / \mu R_T \tag{4}$$

where J is the stabilized permeate flux of the solution through the membrane (L.h^{-1}s^{-1}), R_T is the total membrane resistance (m^{-1}), and μ is the viscosity of the solution (Pa.s).

R_m is the inherent hydraulic resistance of clean membrane caused by the membrane itself. It is brought by the determination of pure water permeability. The R_{rev} corresponds to the reversible resistance due to the concentration polarization that can deleted by a simple rinsing with water after the filtration experiment. R_{irrev} corresponds to the irreversible resistance due to pore blocking and adsorption of substances onto the surface of membrane and pores that demands a chemical cleaning to be removed. After each run, the membrane was rinsed with pure water and then the water permeate flux was determined, giving the R_{irrev}. The R_{rev} value was calculated following the equation:

$$R_{rev} = R_T - (R_m + R_{irrev}) \tag{5}$$

The different resistances values calculated in this case are: R_T =2.759 10^{10}m^{-1}, R_{irrev} = 1.301 10^{10} m^{-1}, and R_{rev} =0.897 10^{10} m^{-1}. Thus, the fouling is rather irreversible: $R_{irrev} > R_{rev}$; i.e., the fouling resistance remaining after membrane rinsing. The total fouling resistance is almost double compared with the membrane resistance which is 1.370 10^{10} m^{-1} the irreversible fouling is almost similar with membrane resistance. These results show that the fouling is not so important which show the adaptation of the membrane materials to wastewater treatment.
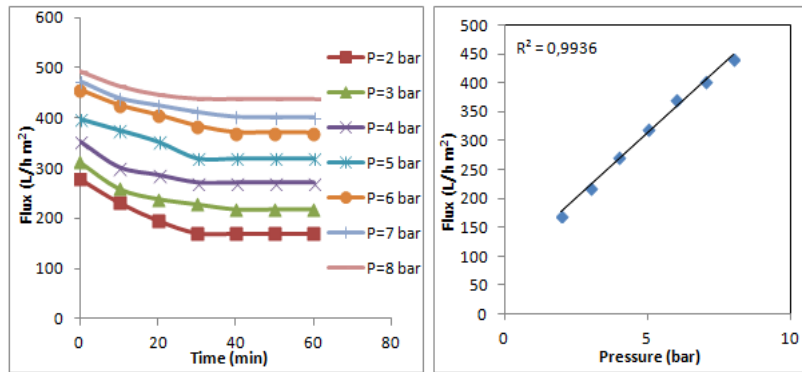

Fig. 6. Determination of the pore diameter of UFmud/mud.membrane.

3.2.3. Membrane fouling behavior

Membrane fouling was caused by inorganic or organic compounds, colloids, bacteria, or suspended solids. Fouling can lessened the permeate flux and impacted the retention of many compounds. It can be reversible or irreversible. Reversible fouling can be removed simply by water rinsing or changing some process parameters, while irreversible fouling is hard to revers

Fig. 7. Variation of water flux with time and pressure: determination of the membrane permeability.
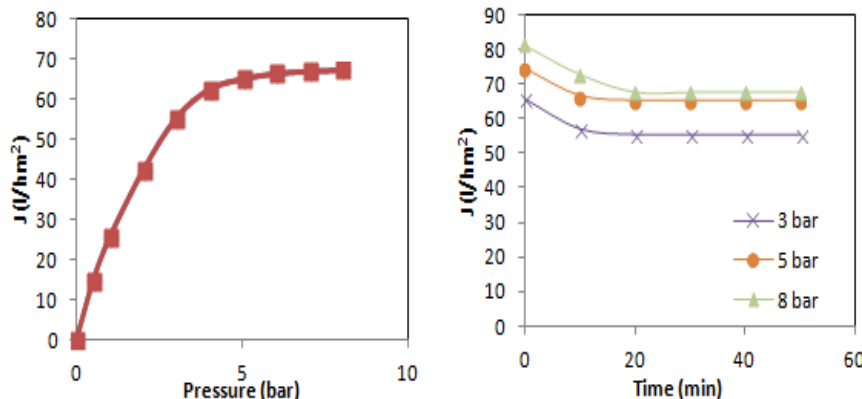

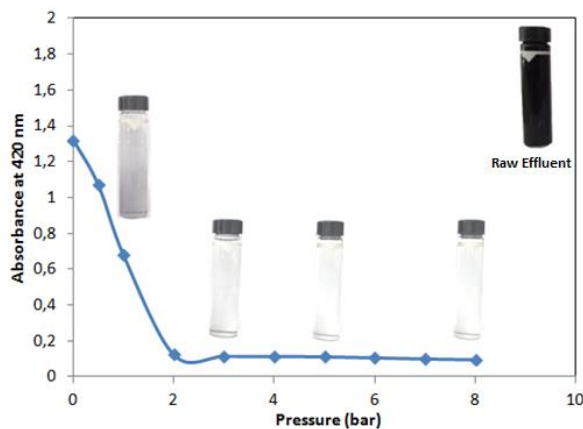**Fig. 8.** Variation of permeate flux with the pressure and time.

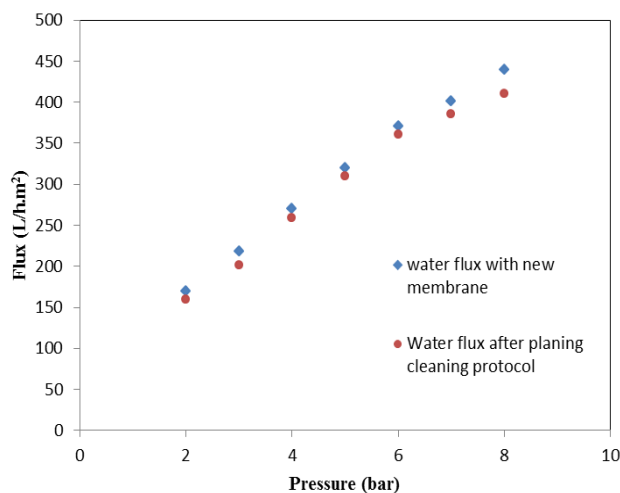**Fig. 9.** Evolution of color removal with pressure.

Fig. 10. Membrane regeneration.

The significant decolorization observed for a pressure higher than 5 bar (see Figure 9) confirms the character of irreversible fouling achieved from the model of series resistance. This behavior is correlated to the great retention of pollutants in terms of color and COD resulting in the formation of a gel layer on the surface of membrane.

Table 4 shows the average effluent characteristics after treatment by ultrafiltration process at 5 bar using the proposed membrane in this work compared with a commercial alumina membrane. In attendance of the elaborated UF membrane, almost a total retention of color, turbidity and polluting substances are achieved. Figure 9 presents the evolution of color removal with pressure. The increase of TMP resulted in a noticeable removal of color: for pressure above 2 bar, a great decrease of color of almost 95% was observed which confirms the previous results. The COD was found to get reduced by 90% with elaborated UF mud membrane whereas it was reduced by only 85% using the commercial membrane. For both membranes, there is not any significant variation of conductivity and pH between the feed and the permeate.

Compared with the alumina membrane, the performances obtained with the elaborated asymmetric mud membrane are quite good and slightly better than those for the commercial reference membrane made of alumina (see Table 4). Therefore, this study proves the industrial feasibility of UF textile wastewater treatment in attendance of the composite mud/mud UF membrane.

3.2.4. Membrane regeneration

The application of the UF membrane is constrained by the inevitable phenomena of irreversible fouling which causes the permeate flux decline and then exhibits a serious obstacle for the performance of membrane separation. For this, after each experiment, the membrane must be renovated following the protocol cited previously in paragraph *2.3*.

The effectiveness of the regeneration is checked by the determination of the membrane permeability which should be quite similar to that obtained with virgin membrane. Figure 10 shows almost total renovation of the membrane.

4. Conclusions

New asymmetric UF mud/mud membrane was prepared by deposition of only one layer onto the macro-porous support using a slip-casting process. The characterization by SEM analysis showed that the membrane is defect-free, with a thickness of 9 μm, a mean pore diameter of 11 nm and a permeability of almost 90 L/ h. m^2.bar.

The performance of this membrane toward the treatment of an industrial textile wastewater sample are determined in terms of the permeate flux and the pollutants removal. The stabilized permeate flux obtained after duration of 60 min is around 65L/h.m^2. The permeate from mud/mud UF membrane shows an increase of the performance in comparison to the commercial alumina UF membrane. The mud/mud UF membrane renovation was achieved using an alternative protocol based on acid-basic washing.

Finally, the results revealed that the mud of hydrocyclone laundries of phosphate is an appropriate material for the development of the UF membrane achieved by a deposition of one layer directly onto the support. The reduction of the layer number should increase the filtration performances by limiting the membrane resistance. This membrane can be capably applied to the industrial wastewater treatment.

Table 4
Determination of the Characteristics of permeate from mud/mud UF membrane and alumina membrane at a pressure of 5 bar.

Membrane used	pH	Conductivity (mS/cm)	COD (mg/l)	Turbidity (NTU)	Absorbance at 420 nm
mud/mud UF membrane	9.81	28.2	86	0.33	0.092
commercial UF membrane	9.78	29.8	122	0.82	0.11

Abbreviations

MF	Microfiltration
UF	Ultrafiltration
COD	Chemical Oxygen Demand
SEM	Scanning Electron Microscopy
TMP	Transmembrane pressure
PVA	Polyvinyl alcohol
Jw	Water flux
Lp	Water permeability
R$_m$	Membrane resistance
R$_{rev}$	Reversible resistance
R$_{irrev}$	Irreversible resistance

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