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Removing polyphenols contained in olive mill wastewater by membrane based on natural clay and Hydrotalcite Mg-Al

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Abstract

The purpose of this work is to study the performance of a membrane based on Ghassoul and Hydrotalcite (GHTM) in the retention of polyphenols (organic pollutants). This membrane was elaborated and characterized in our laboratory and was used in the filtration of olive mill wastewaters (OMW) of semi-modern unit of the olives. The choice of these materials depends essentially on their interesting properties (low cost, abundantly in nature and the ease of the preparation).The diluted OMW (40%, 60% and 80%) were very acidic with a pH between 5.29-5.64 and had a high concentration of polyphenols from 30-60mg/L. However, after treatment the permeate revealed a significant decrease in polyphenols of61% and a complete disappearance of brown coloration for 80% OMW. The results show that the membrane developed is efficient to remove the polyphenols and reduce the turbidity, COD and BOD5 of OMW.

Keywords: Olive mill wastewater, Membrane, Hydrotalcite, Ghassoul.

1. Introduction

Olives containsabout 99% of polyphenols [1]. During the production of the olive a large part of polyphenols pass in the olive mill wastewaters (OMW) and a small part (about 1%) stay in the oil olive extract. Therefore the OMW poses an environmental problem for olive oil-producing countries as Moroccobecause thepolyphenols compounds are pollutants. Such these latter are able to exert acute toxic effects towards microorganisms [2, 3], plants [4, 5] and pluricellular organisms [6]. Several studies [7-13] have reported the elimination of polyphenols from olive mill wastewater using ultrafiltration (UF), nanofiltration (NF) and microfiltration (MF) with polymericand commercial membranes. These techniques are very expensive, for this reason in this work we have developed a ceramic membranes (GHTM) based on natural clay "Ghassoul" as flat support, and the Hydrotalcite $MgAlCO_3$as deposit for the membrane. On the other hand, the Ghassoul is abundant in Morocco and inexpensive,it is used as a natural shampoo or as a laundry product and the Hydrotalcite, from family of Layered Double Hydroxides 'LDH', is easy synthesizable.This study aims to assess the efficiency of the microfiltration membrane (GHTM) when treating a solution containing the most abundant polyphenols in OMW. To the extent of i) permeate flux; ii) remove of polyphenols and iii) determination of physicochemical parameters before and after filtration.

2. Material and methods

The reagents and Materials used in this study are:

The metal salts ($MgCl_2$, $6H_2O$) and ($AlCl_3$, $6H_2O$) with a content of 99%, sodium hydroxide (NaOH) in pellet form with a purity of 98%, sodium carbonate (Na_2CO_3) with a purity of 99.9%, and Folin-Ciocalteu reagent pure, silver sulfate, and mercury sulfate were provided by LobaChemie. The R quality nitrogen provided by the company 'Air Liquide Morocco' and Gallic acid 1-hydrate ($C_7H_6O_5$, MW=188, 14 with a purity of 98%) was provided by PanReac. The potassium dichromate and of 99, 7 % and sulfuric acid with a purity of 95% were provided by Sigma Aldrich.

pH was measured using a thermo-scientific type pH meter ,turbidity is measured by a turbid-meter (Turbo 550IR), and expressed in NTU (Nephelometric Turbidity Units) and the Absorbance is measured using SHIMADZU UV spectrometer.

2.1.OMW

Olive mill wastewaters, were supplied by system 2 phase, Fez-Meknes region (Morocco). Before use, liquid was barboting with nitrogen in order to avoid the degradation of polyphenols and filtered by centrifugation.

The choice of percentage dilution of OMW by water (40% OMW, 60% OMW and 80% OMW) was made to remove organic matter and to avoid the fouling of membrane.

2.2. Polyphenols ,COD and BOD_5 determinations

The concentration of polyphenols of the permeate was determined by a colorimetric method using Folin-Ciocalteu reagent [14]. The role of this one is to make it possible to reduce the molybdate and the tungsten by the polyphenols for giving a blue coloration. The calibration curves (Figure 1) were used with a standard stock solution which is prepared by dissolving 20 mg of Gallic-acid in 100 mL of distilled water then added to several diluted solutions prepared from an initial solution with a concentration from 0.4 to 0.05 g/L. After that, 0.4 mL of each solution was introduced into test tubes, the mixture (2 mL of Folin-reagent diluted 10 times and 1.6 mL of 7.5% of sodium carbonate) were added in tubes, stirred and incubated for 2 hours. Absorbance is measured at 760 nm using SHIMADZU UV spectrometer.This experience is repeated 3 times.

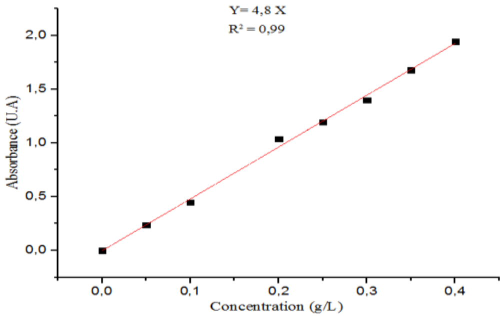

Figure 1. Gallic acid standard curve based on the collected data.

The determination of COD was carried out by the potassium dichromate. The principle of this method is based on a boiling oxidation (150°C for 2 hours) of the reducing materials by an excess of potassium dichromate in sulfuric acid (H2SO4) in the presence of silver sulfate as catalyst and mercury sulfate as complexing chlorides. The optical density of the sample is obtained by spectrophotometry at a wavelength of 585 nm. The COD values are measured using SHIMADZU UV spectrometer. BOD5 is determined according to the respirometric method in an enclosure thermostatically controlled at 20 °C (AFNOR T 90103) in the dark and for 5 days. The water samples were previously diluted, and their pH was adjusted to neutral pH.

2.3. Pilot of filtration

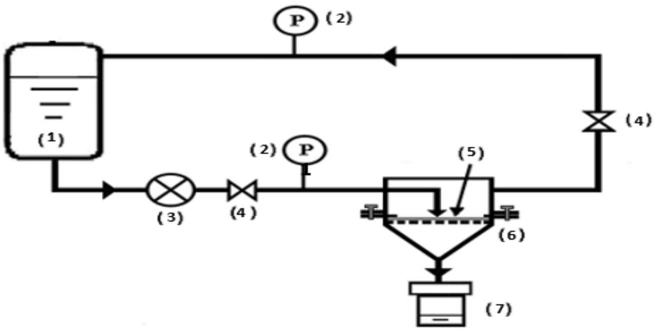

Figure 2. Pilot utilized for permeability and filtration tests of the different solutions of OMW

The pilot of the filtration (Figure 2) consist of a feed tank (1) with a volume of 10 L, pump (3), two valves (4),a stainless steel-flux cell able to accommodate a flat-sheet membrane (6) and membrane (5) with a diameter of 3.7 cm. Permeate (7), two manometers (2) located before and after the flat-sheet membrane were used to measure the inlet and outlet pressure furthermore, thus the transmembrane pressure (TMP) and a cooling framework, sustained with faucet water, was used to keep the temperature constant of the feed arrangement at 25±1 °C. Microfiltration 'MF' experiments were carried out at five pressures (1, 2, 3, 4 and 5 bar) and a constant temperature 25 °C to determine the permeability [15].

2.4. Membrane

The membrane was developed in our laboratory according to the process described by Qabaqous et al. [16,17]. This process requires two steps: The first step is the preparation of the support. For this purpose, the clay of Ghassoul 'Gh-B' is blended with 3% of commercial activated carbon with a total mass of 4g then put in the oven at 900 °C. The support demonstrates a porosity of 38%. The second step, the magnesium-aluminium Hydrotalcite 'HT-$MgAlCO_3$'

with a molar ratio equal to 3 (Mg/Al=3) is synthetized by co-precipitation method. After, the obtained precipitated was used as depot on the surface of the support [16]. The obtained membrane was referenced (GHTM).

2.5.Measurement of membrane water permeability

The permeate flux of different samples was determined at different pressureand various times at constant temperature (25 °C) by: $J_f = \frac{V}{A \times t}$,where J_f is the flux(L.h^{-1}.m^{-2}), V is the volume (L) of water collected in time period t (h) and A is the surface of the membrane, which is 8.04x10^{-4} m^{2} in this case.

2.6. Procedure of filtration

The filtration was carried out for all samples at different times from 30 min to 180minbased on previous experiences[18] using the pilot designed in the laboratory (Figure 2) and the polyphenols containing in the permeate were analyzed by the Folin–Ciocalteu method [14]. The elimination yield of polyphenols was determined by:

$$R = \frac{C_0 - C_f}{C_0} \times 100$$

Where C_f and C_0 arethe final and initial concentrations of polyphenols respectively after and before filtration. In this case, C_f and C_0 are expressed by g/L.

2.7. *SEM analysis*

Apparatus of Quanta 200 from FEI Company, available in UATRS, CNRST, Rabat Morocco, is used to determine the morphology of membrane before and after filtration.The scanning electron microscope used is environmental-type (ESEM).

2.8. Characterization of different dilutions of OMW before and after filtration by GHTM membrane

The physicochemical characterizations of different dilutions of OMW (40%, 60%, and 80%) before and after filtration by membrane (GHTM) were carried out by measuring the following parameters: acidity (pH), Turbidity, polyphenols (PP), chemical oxygen demand (COD) and biological oxygen demand (BOD_5).

3.Results and discussion

3.1. *OMW permeability*

Figure 3 shows that the initial permeate flux was about 46-84 (L/m^2.h) for different dilutions of OMW. This flux decrease rapidly within the first 60 min followed by a slower decrease until reaching a steady-state at 120 min for both dilution (40% and 60% OMW) and at 150 min for OMW diluted at 80%. This time difference is due to the fact that dilution at 40% and 60% contain too much organic matter. Load and high polyphenols concentration compared to the OMW diluted 80%. However, this stabilization due to the fouling of the membrane pores by the particles having approximately the same size as the mean pore diameter and due to the formation of a deposit layer [19] (Figure6B). The flux of three samples (60, 70 et 47L/m^2.h) is great compared to the work of Akdemir et al. [10] which found a low flux equal to 25.9 L/m^2.h. This latter study was based on treatment of olive mill wastewater by ultrafiltration polymericmembrane. The mechanical resistance of the membrane was verified by determining the permeability of diluted OMW (80%, 60% and 40%) according to the pressure (1-5 bar). Figure 4 represents the linear variation of the permeate flux J_f (L/h.m^2) by varying the transmembrane pressure for different solutionsof OMW. The same variation of the permeate flux with pressure for our membrane was observed. The J_f value of 80% OMW is more important than

the 60 and 40% OMW and the slope of flux versus pressure rises with the increase pressure for all dilutions of OMW. Observation with the naked eye by increasing the pressure up to 5 bar causes no cracking of the membrane.We can conclude that the membrane (GHTM) has a good mechanical resistance. The increase in pressure up to 5 bar without damaging the membrane is a good result compared to the work of Turano et al. which could only make the pressure up to 3 bar during the study of the treatment of OMW by integrated centrifugation–ultrafiltration system with a commercial membrane [12].

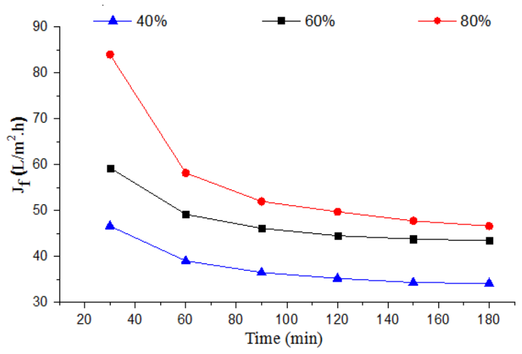

Figure 3. Evolution of the permeate flux in the microfiltration (GHTM) of OMW (operating conditions: T =25°C, P = 1 bar).

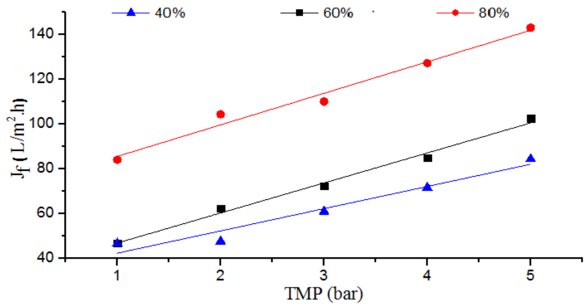

Figure 4. Different dilutions of OMW in MF process as a function of the applied TMP values.

3.2. Filtration of different dilutions of OMW using GHTM membrane

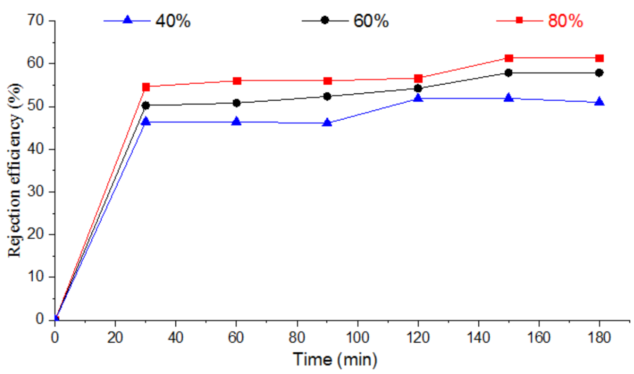

Figure 5. Retention yields of polyphenols (%) as function of time for different dilutions of OMW by GHTM membrane.

Elimination yield of polyphenols as function of time are given in Figure5. Removal polyphenols improved with increasing time and stabilized after 120 min. This stabilization due to the clogging of the membrane by the presence of deposit polyphenols onto its surface (Figure 6B).As has been observed by Qabaqous et al. in the retention of heavy

metal (Cr, Pb, Zn, Cd) by similar membrane (GHTM) [16] .The remove of polyphenols presented a similar evolution of all diluted OMW. However, OMW 80% gives a great yield forremoving polyphenols (61%) compared to OMW 60% (57%) and OMW 40% (51%) at 1 bar pressure. These values are satisfactory and effective compared to results obtained in the study of filtration of OMW made by Macro stoller, which found the rejection yield of polyphenols is 55% at a pressure filtration equal to 5 bar [9].The membrane process is very important compared to adsorption method of polyphenols onto Ghassoul clay and $MgAlCO_3^{2-}$ Hydrotalcilte 'HT3'. The adsorption tests of polyphenols by Ghassoul and Hydratalcite consist to mix 50 mg of Ghassoul or Hydrotalcite with 50 ml of OMW 80% in the time interval 20 min-3h. The adsorption amount of polyphenols at the equilibrium (t=2 h) is 161 mg/g and 140 mg/g and the elimination yields of polyphenols were 53% and 34% for Ghassoul and Hydrotalcite respectively, weaker that this obtained with the GHTM membrane (61%) (Figure 5). Therefore, it can be concluded that the membrane process is more effective than the adsorptionphenomena. On the other hand, a naked eye test was also performed; it shows that the brown colorof initial solution due to non-dissolved organic matter (tannins, sugars, organic acids, and phenolic compounds, polyalcohols, pectins and lipids) becomes colorless after filtration on the GHTM membrane (Figure 6A)due to the retention of these species. This result testifies to the efficiency of the membrane to filter the solution of OMW especially that diluted 80 times and to retain the polyphenols (Figure 6B).

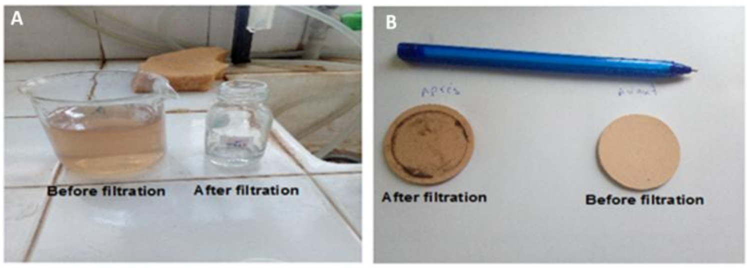

Figure 6. Membrane and 80% OMW solution before (A) and after microfiltration tests (B).

3.3. SEM

Figure 7 shows the SEM of the membrane GHTM before and after filtration of 80% OMW solution. The morphology of the membrane before filtration presents the formation of Hydrotalcite layer in the form of laminated sheets on the surface of the support (Figure 7A).This deposit of Hydrotalcite layer reduces the size of support pores and the surface of membrane become denser. After filtration (Figure 7B) we observe also the presence of the deposit of polyphenols from OMW on the membrane (red circle), which confirms that the polyphenols have been retained by the GHTM membrane (Figure 7B).

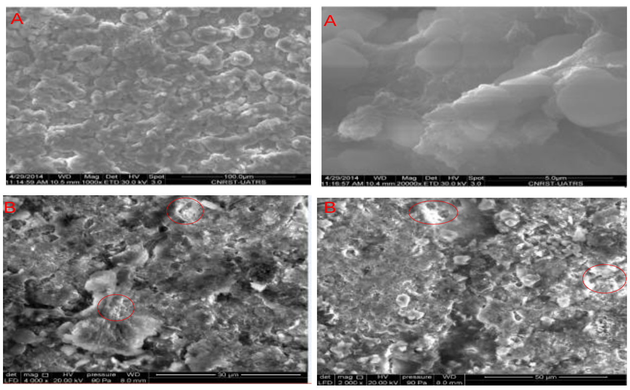

Figure 7. Morphology of GHTM membrane (A) before and (B) after the filtration test of 80% OMW.

3.4.Physical and chemical parameters of different dilutions of OMW before and after filtration on GHTM.

The values of the different physicochemical parameters (pH, Turbidity, chemical oxygen demand 'COD', biological oxygen demand 'BOD_5' and Polyphenols 'PP') of three dilutions (80%, 60%, and 40%)of OMW before and after filtration are summarized in Table 1.

Table 1.Physical and chemical parameters of different dilutions of OMW before and after filtration on GHTM**.**

	Before filtration			**After filtration**		
Samples OMW	40%	60%	80%	40%	60%	80%
pH	5.58	5.63	5.64	7.8	7.76	7.45
Turbidity (NTU)	50	30	22	1,40	2,1	5,30
COD (g/L)	4.80	2.89	1.47	3.20	2.43	0.23
BOD5(g/L)	2.20	1.36	0.52	1.4	0.92	0.12
PP (g/L)	0.60	0.40	0.30	0.27	0.16	0.11

3.5. Evolution of pH

The pH evolution of different dilutions of OMW filtered by a membrane (GHTM) shows an increase in pH value from acidic pH (5.58 ± 0.05) to neutral pH (7.45 ±0.35). These increases may be due to alkalinity of the membrane and it could be the result of the fixation of the organic acids responsible for the acidic pH of OMW but can be also due to the strong capacity of the membrane neutralized polyphenols from OMW transformation of phenols into phenolate and ion formation $C_6H_5O^-$ [20]. The result is in agreement with works of Meftah et al. [21] and Achak et al. [22] who obtained the increasing of pH for three units afterapplicationsthe OMW onto moist soil and infiltration-percolation on a sand filterrespectively.

3.6. Reduction of turbidity and polyphenols

Table 1 shows an important reduction of the turbidity after filtration on membrane for different dilutions of OMW. Turbidity concentration decreases from 22 NTU to 5.30 NTU for 80% OMW, from 30 NTU to 2.1 NTU for 60% OMW and from 50 NTU to 1.40 NTU for 40% OMW after 2hof filtration. This reduction remains always important until the clogging of the membrane. This result is in agreement with Tamer Coskum and al. who work on treatment of olive mill wastewaters by nanofiltration and reverse osmosis with commercial membranes based on polyamide, cellulose, and polyethersulfone [14]. On the other hand, the analysis shows a diminution of concentration of polyphenols from 0.6 to 0.3 g/L after dilution of OMW from 40% to 80% respectively and as well a significant decreasing of polyphenols after filtration on membrane GHTM. For example, for 80% OMW the PP in the retentate passes from 0.3 to 0.11 g/L. This decrease explains the retention of the polyphenols and the formation of the deposit of organic matter onto the membrane and the discoloration of OMW 80% solution (Figure 6A and 6B) which isalso confirmed by SEM (Figure 7).

3.7. Reduction of COD and BOD_5

In both cases the dilution of OMW (80%, 60% and 40%) leads the diminution of COD and BOD_5. This reduction is even greater after passage of the OMW solutionson the GHTM membrane for all dilutions (Table 1). After filtration, the COD is decreased by about 33%, 16% and 84%, and the BOD_5 is decreased by about 37%, 33% and 78% for 40%, 60% and 80% OMW diluted respectively during 2 hours of filtration. This which is due to the diminution of the

turbidity and the discoloration of OMW solution.These result are in agreement with those of Oladoja and Santi, which found the reduction of DCO from 427 mg/L to 4.5 mg/L by using different clay deposits in Nigeria as adsorbents [23].

4. Conclusion

The elaboration of the membrane based on natural clay Ghassoul and Hydrotalcite was carried out successfully to remove polyphenols from olive mill wastewater. The investigated process based on first treatment by splashing with nitrogen, centrifugation and all dilutions of OMW (40%, 60%, 80%). These solutions are treated by a microfiltration membrane (GHTM) a help filtration pilot. The result shows the yield for the remove of polyphenol species is 61% of 80% OMW and a complete disappearance of color. For 40% OMW and 60% OMW, this value decreases to 51% and 57% respectively because of the fouling of the membrane. The physicochemical parameters (Turbidity, COD, and BOD_5) have decreased after filtration of all solutions of OMW (40%, 60%, and 80%). The diminution is about of 33%, 16% and 84% for COD and 37%, 33% and 78% for BOD_5 respectively. Which this shows that the organic matter (polyphenols) is retained by GHTM membrane. The retention of polyphenols has been confirmed by SEM and the discoloration of the solution 80% OMW. Therefore, the membrane-based onto Hydrotalcite deposit on a support Ghassoul clay allows the retention of polyphenols from OMW and can be constituted the future process for removing these species.

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