

Removal of heavy metals and COD containing leachate by ceramic membranes

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ABSTRACT/RESUME

Abstract: This work focused on the development of new ceramic membranes, made with locally available kaolin mixed with aluminum oxide, and their application in the treatment of polluted liquid effluents. Qualitative analyzes were performed on different leachates from the landfill of Tiaret (west of Algeria). Cross flow filtration performed with modified ceramic membranes leads to complete rejection of some heavy metals as Pb along with nitrite and nitrate rejection rates higher than 96 %. Moreover, the chemical oxygen demand was found to decrease by more than 90 % with the two types of membranes developed in this work.

I. Introduction

Waste management is a global problem. Despite an increasing effort in recent years, the problem remains far from being resolved. Each year Algeria generates 10 to 12 million tons of household waste [1] and landfill is widely used in waste management. After the deposition step the waste is subjected to degradation processes involving complex biological and physicochemical reactions [2]. Water infiltrates and produces leachate and biogas containing organic or inorganic compounds that are responsible for organic and metallic pollution [3], with the release of many toxic substances for the environment (including the atmosphere, groundwater and streams).

If leachates are not secure, they are likely to pollute groundwater or surface water [4]. That is why leachates must undergo a purification treatment before being discharged into the environment [5, 6]. More and more stringent regulations require implementing highly efficient separation techniques such as membrane processes (microfiltration, ultrafiltration, nanofiltration or reverse osmosis) [7, 8]. Indeed, the main limitation of traditional treatments is the difficulty to adapt to the variation of raw effluent features [9, 10]. This work aimed at

developing new ceramic membranes with good ability for leachate treatment.

II. Materials and methods

II.1. Membrane synthesis

The membranes synthesized in this work were mono-channel tubular membranes with a length L of 30 cm and an external diameter of 1,6 cm. Two types of membranes were developed. The first one was made of a mixture of kaolin and alumina Al₂O₃ (5 % in weight) and it will be labelled SMS (simple membrane symbol) hereafter. The second kind of membrane, labeled AMS (active membrane symbol), was obtained by adding a thin layer of alkoxide Tretoxiide alumina onto the SMS membrane (which then served as a support layer for the AMS membrane). The alkoxide active layer was prepared by sol-gel method and was cast at 750 °C. This membrane can be regenerated manually through gentle scraping or chemically using hydrochloride acid pH = 3 or sodium hydroxides solution pH = 10 [20].

II.2. Quantitative chemical analysis

The kaolin chemical analysis revealed that membranes were essentially composed of silica and

alumina Table 1. The results were obtained by X-ray fluorescence measurements.

II.3. Membrane morphology and structure

The morphology and microstructure of AMS membrane were characterized by Scanning Electron Microscopy (HITACHI - 4500 S). The pore size of the support was determined by mercury porosimetry (Micrometrics Autopore II 9215).

II.4. Differential Scanning Calorimetry

The thermogravimetric analysis TGA and differential scanning calorimetry DSC of the SMS membrane were carried out with a DSC-TGA 2960 TA instrument at the temperature ranging between 0 and 1000°C at a rate of 5 °C/min under air.

II.5. Cross flow filtration

The filtration performance of both SMS and AMS membranes was tested with a crossflow filtration unit Figure 1 at a transmembrane pressure TMP of 5 bar. The feed solution 20 L was circulated onto the membrane surface at a flow rate of 500 L/h. The permeate solution was recycled to the feed tank so as to keep the feed solution constant over the whole filtration experiment.

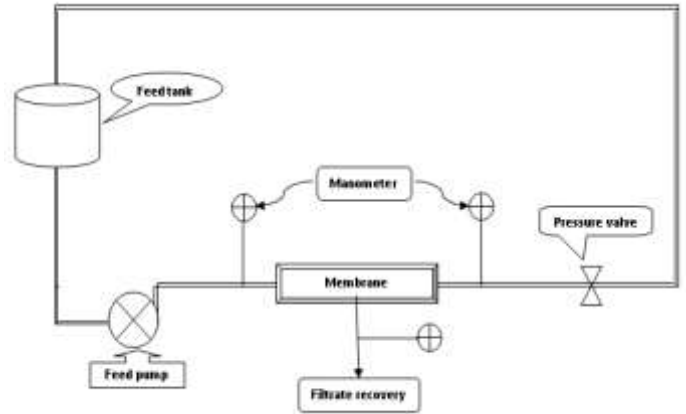


Figure 1. Schematic of the cross-flow filtration unit [21-23].

II.6. Analysis of leachates

Several leachates were collected in the city of Tiaret. Dates of collection were chosen according to the rainfall maximum in February: February, April and May. The main features of these leachates are given in Table 2.

Table 1. Chemical composition of the kaolin used to synthesize the SMS membrane and the support layer of the AMS membrane

Oxide	Weight percentage (%)	Oxide	Weight percentage (%)
SiO ₂	49,5 %	Na ₂ O	< 0,1
Al ₂ O ₃	35,5 %	CaO	< 0,1
TiO ₂	< 0,3	MgO	< 0,4
K ₂ O	1,55	WL: weight loss	11,8

Table 2. Physicochemical characteristics of the collected leachates.

	leachate L1	leachate L2	leachate L3	Standard releases
pH	8,94	8,80	8,90	6,5-8,5
COD (mgO ₂ /L)	14400	28800	7680	120
NO ₃ ⁻ (mg/L)	13,42	16,57	11,65	/
NO ₂ ⁻ (mg/L)	23,15	28,90	18,67	/
Iron (mg/L)	145	210	125	3
Zinc (mg/L)	7,8	9,30	7,10	3
Cadmium (mg/L)	0,78	0,92	0,69	0,2
Nickel (mg/L)	9,3	11,90	7,40	0,5
Lead (mg/L)	1,45	1,80	1,22	0,5

III. Results and discussion

III.1. Membrane characterization

III.1.1. Phase identification

Figure 2(a), (b) and Figure 3 show the XRD patterns of raw and thermally treated powders used to synthesize the SMS membrane. Kaolinite, muscovite and quartz were found to be the major

minerals in the raw materials. After heat treatment at 1150 °C the peaks associated with kaolinite and muscovite disappeared and mullite appeared due to the transformation of metakaolinite. The peaks of quartz confirmed the thermal stability of this phase. The peaks of amorphous silica and alumina in comparison with those of α -Al₂O₃ and γ -Al₂O₃ presented the polymorph structure.

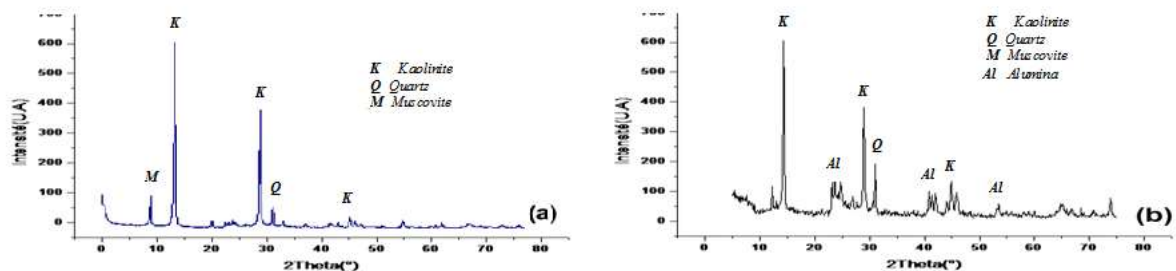


Figure 2. X-ray diffractogram of (a) kaolin raw powder and (b) the mixture of kaolin and 5% Al₂O₃.

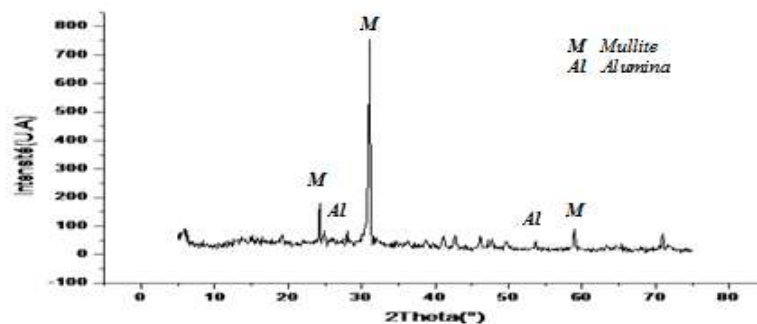


Figure 3. X-ray diffractogram of the mixture of kaolin and 5% Al₂O₃ heated to 1150°C.

III.1.2. Thermal analysis

Figure 4 shows the differential thermal analysis of the SMS membrane. A mass loss of 0,5 % is observed between 65 °C and 450 °C caused by the removal of residual physically adsorbed water, the mass loss of 0,8 % between 460 °C and 520 °C, the mass loss is due to the transition alpha quartz to beta quartz.

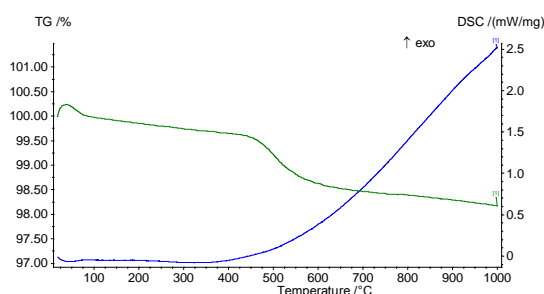


Figure 4. Thermal analysis (DSC and TGA) for the SMS membrane

III.1.3. Microstructure

The morphology of the AMS membrane surface and cross-section is shown in Figure 5(a). The figure shows that the AMS membrane surface of support uniformly structured and well covered by the alumina particles. This porosity corresponds to transformation of the new crystalline phase for the first mullite to second mullite with 0,1 μm pore size Figure 6 prepared following the colloid filtration technique and a thin film functional layer carried out according to the sol-gel preparation method Figure 5(b).

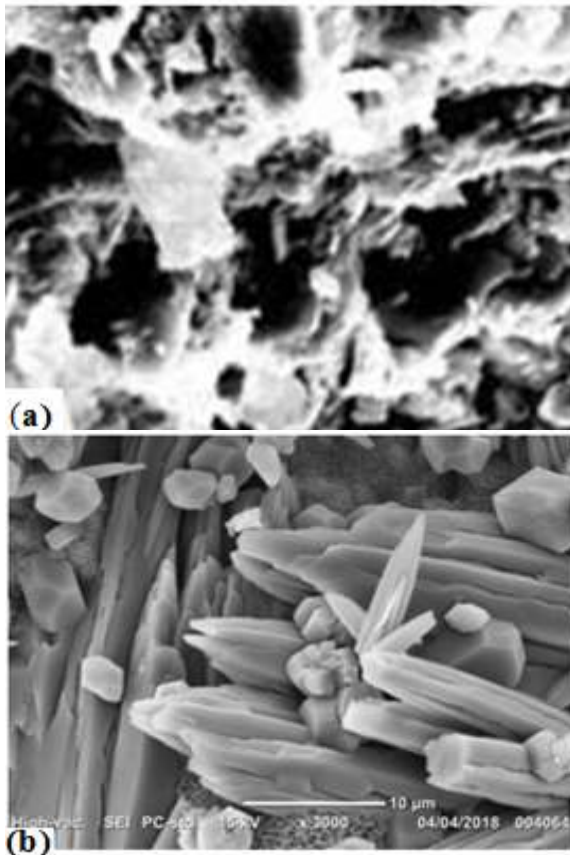


Figure 5. SEM images of the AMS membrane (kaolin and 5% Al₂O₃); (a) surface; (b) cross-section. Amplification: × 3000.

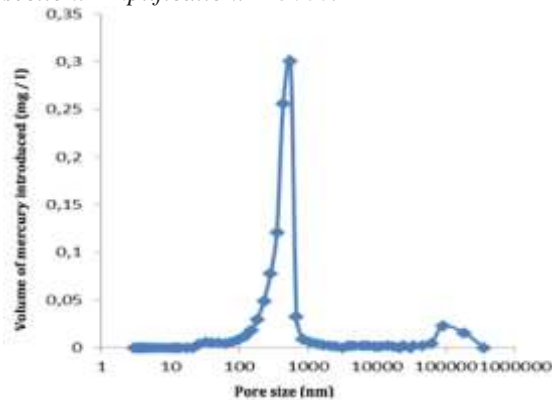


Figure 6. Pore size of the AMS membrane.

III.2. Filtration tests

III.2.1. Water flux

The time dependence of SMS and AMS membranes tap water flux is shown in Figure 7. A relatively stable water flux was obtained with both membranes. The different fluxes obtained for the SMS and AMS membranes resulted from their different porosity and morphology [11-13].

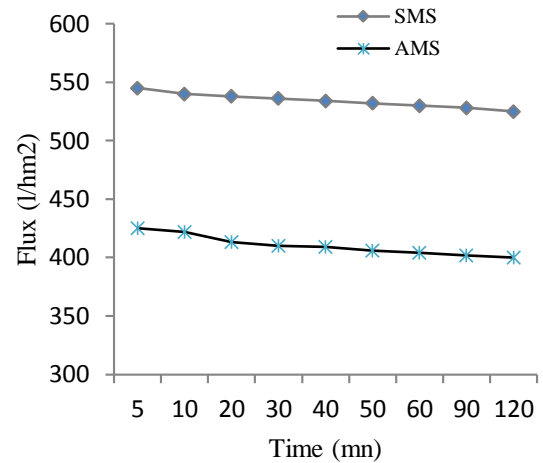


Figure 7. Variation of the tap water flux as a function of time through SMS and AMS membranes.

III.2.2. Permeate flux during leachate filtration

The variation of permeate fluxes measured for the different leachates L1, L2 and L3 is shown in Figure 8. Similarly, to what was observed with tap water, the monolayer membrane SMS had a higher permeate flux than the double layer membrane AMS, whatever the leachate. For both membranes a flux decline was observed over time as a result of membrane fouling. However, a more stable flux, and then a less severe fouling, was obtained with the AMS membrane.

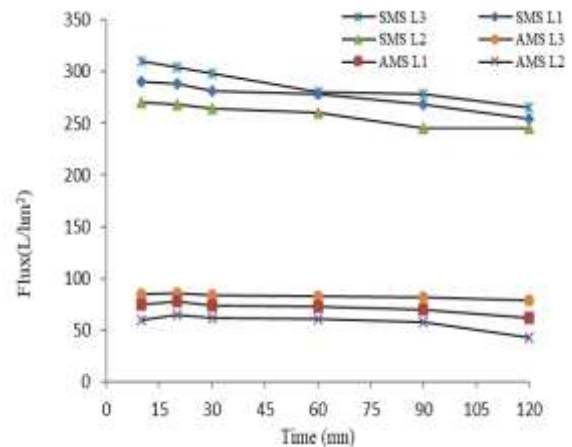


Figure 8. Variation of permeate flux (TMP 5 bar) versus time for the different membranes (AMS and SMS) and leachates (L1, L2 and L3).

III.2.3. Evolution of leachate COD

The measurement of the chemical oxygen demand COD during leachates treatment gives information about organics removal. The results obtained for the different membranes are shown in Figure 9.

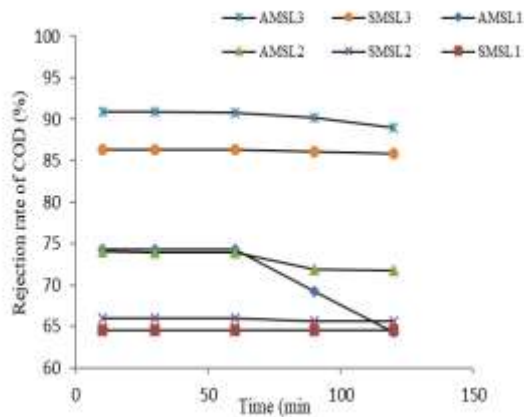
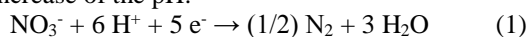


Figure 9. Variation of COD as a function of time through the various membranes AMS and SMS for the different leachates L1, L2 and L3.

III.2.4. Nitrates and nitrites rejection

Nitrates and nitrites rejections are shown in Figure 10 and Figure 11.

Both membranes were found to be highly efficient for nitrates and nitrites removal with rejection rates higher than 95 %. It is worth noting that leachates had a relatively high pH (see Table 2) and rather low levels of nitrites and nitrates. This could be explained by the occurrence of a denitrification reaction [15] in which the consumption of protons necessary to reduce nitrates or nitrites to molecular nitrogen and / or nitrogen oxide gas, results in an increase of the pH:



In the drainage phase, the residence time in the vessel is between 1,7 and 4,2 months, which allows the above reaction to occur. However, the absence of oxygen in the storage tank creates favorable implementation conditions for denitrification and the residence time of leachate in the tank, the longer the denitrification is, the more important it will be [16-19].

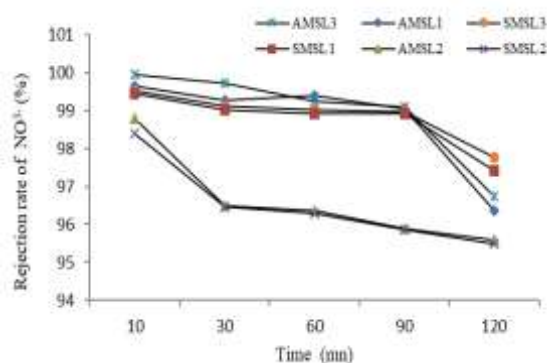


Figure 10. Nitrates rejection as a function of time.

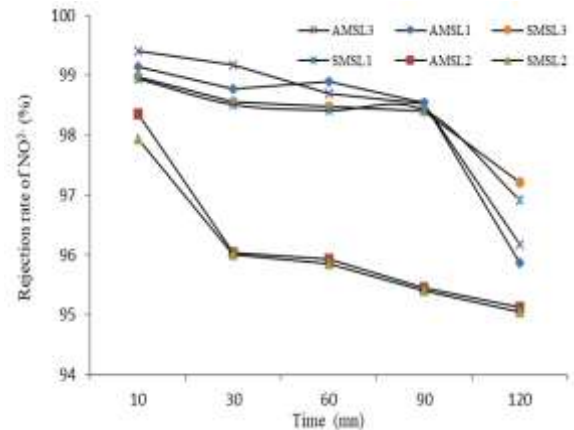


Figure 11. Nitrites rejection as a function of time.

III.2.5. Lead rejection

Lead rejection by both membranes is shown in Figure 12. Both membranes were found to have promising performance for heavy metal removal since lead rejection rates were higher than 95%. This indicated the key role of the combination between kaolinite and alumina, allowing an enhancement on the lead rejection. The continuous decreases of the rejection rates in time are caused by the reduction of the solute concentration in the vicinity [24, 25]. Consequently, this reduction can be attributed to purely steric rejection mechanisms, which lead to limit the rejection rates.

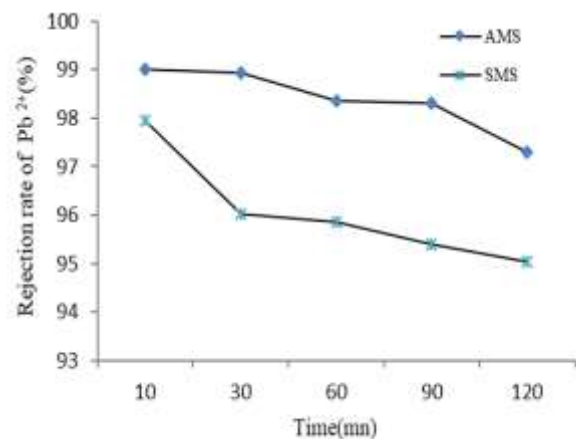


Figure 12. Lead rejection as a function of time for leachate L3.

IV. Conclusion

This study aimed at evaluating the performance of two recently developed ceramic membranes for leachate treatments. Promising results were obtained since both membranes exhibited high nitrite, nitrate, COD and lead rejections. Indeed, a decrease of COD by about 70 % and 90 % was observed with monolayer and bilayer membrane,

respectively. Regarding nitrite, nitrate and lead, rejection rates higher than 95 % were obtained with both membranes.

This work therefore demonstrated the possibility to use local materials for developing low cost and high-performance ceramic membranes.

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