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Elaboration and characterization of new ceramic disk membranes from natural zeolite and Tunisian crude clay for H_2S retention

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Abstract

The aim of this study is the elaboration of a low-cost membrane from natural Turk zeolite and crude Tunisian clay in order to be utilized in agas retention process. The reason of preparation for the support and membrane than the characterization of the crude material is in order to find the super condition of the ceramic preparation. After drying and firing at 900° C, the elaborated support presents an average pore diameter about 0.49µm for zeolite and 0.55 µm for Kaolin. The coated layer resulting in the ultrafiltration (UF) membrane was performed by a slip-casting method using a suspension made of a mixture of the mud powder, water and polyvinyl alcohol solution (PVA), then heated at 850 ° C. The UF membrane average pore diameter measured by mercury porosimetry method was of 77 nm for zeolite and 62 nm for kaolin. The different characterizations were performed to determine the surface morphology by scanning electron microscopy and the porosity with mercury porosimetry. The chemical composition was determined by fluorescence –X. One application of these supports and membranes is the decreasing contents of H_2S from the chimney of chemical group of Tunisia. The retention rate result of hydrogen sulfide was 100 % using these ceramics.

1. Introduction

Hydrogen sulfide (H_2S) is one of the large common particules that can be found in coal gasification and petrochemical plants, wastewater treatment plants etc [1]. It is a major air pollutant when it is emitted in atmosphere because H_2S is a malodorous gas also a corrosive gas, and a source of acidic rains. There are several commercial treatment techniques that can be used for hydrogen sulfide removal, such as adsorption by activated carbon [2,3], condensation [4], wet absorption, catalytic combustion or incineration and chemical oxidation [5-8]. Retention by ceramic support-based zeolites, clay and other inorganic materials is supposed to be one of the most reliable methods.

The new research is generally addressed to the reducing of these gases by means of suitable filtering materials. The ceramic membranes are very competitive in terms of chemical, mechanical and thermal strength (resistance); these membranes have earned, in these years, a substantial place in chemical engineering technology being in a lot range of applications [9-11]. The development of inorganic membranes could carry on to an important technological application that would add economic importance to the used of the membrane processes in the environment [12-14].

This study describes the preparation of both microporous support and ultrafiltration layer using zeolite and clay (Kaolin) to prepare a new asymmetric ceramic ultrafiltration membrane. The efficiency of this membrane was appraised through the application to the treatment of industrial gases.

2. Theory and Experimental

For this work, the supports were prepared from Turk zeolite and Tunisian crude clay. The particle size of kaolin and zeolite does not achieve the optimum mechanical resistance of the ceramic support; therefore we crushed each 100 g of powder for 20 minutes with the assistance of an agate mill than calibrated with 100 µm.

Plastic pastes are mixed from ceramic powder of zeolite with organic additives and water. For sintering two temperatures have been determined: the first temperature is 250°C to eliminate the organic additives and the second is 900°C for the sintering.

The material utilized for the ultrafiltration layer preparation is the same powders that we use it for support preparation. The deposition of the slip on the ceramic support was performed by slip casting method using a deposition time from 10 up to 15 min. After drying at room temperature for 24 h, the zeolite membrane was sintered at 850° C for 2 h, after deboning at 250 °C for 1 h.

The prepared ultrafiltration-layer has been applied to remove the hydrogen sulfide exhausted from the chimney of chemical group of Tunisia.

3. Gas retention experiment

Before using the support and membrane for gas retention, we immerse these materials for 24 hours in water to stabilize the surface and the size of pore. For gas retention, we packed the materials into a column (length 30 cm & diameter 26 mm). The hydrogen sulfide used for application was taken directly from a purge fixed at the chimney of phosphoric units. H_2S were passed through regulators with and then mixed before passing into the filtering column (**Fig.1**). The flow rate of mixed gases was exactly 2 l/min. After passing into the column, the exit gases were analyzed by bubbler reaction during the time of adsorption. The tests were terminated at a breakthrough concentration of 150 l for mixture of gases.

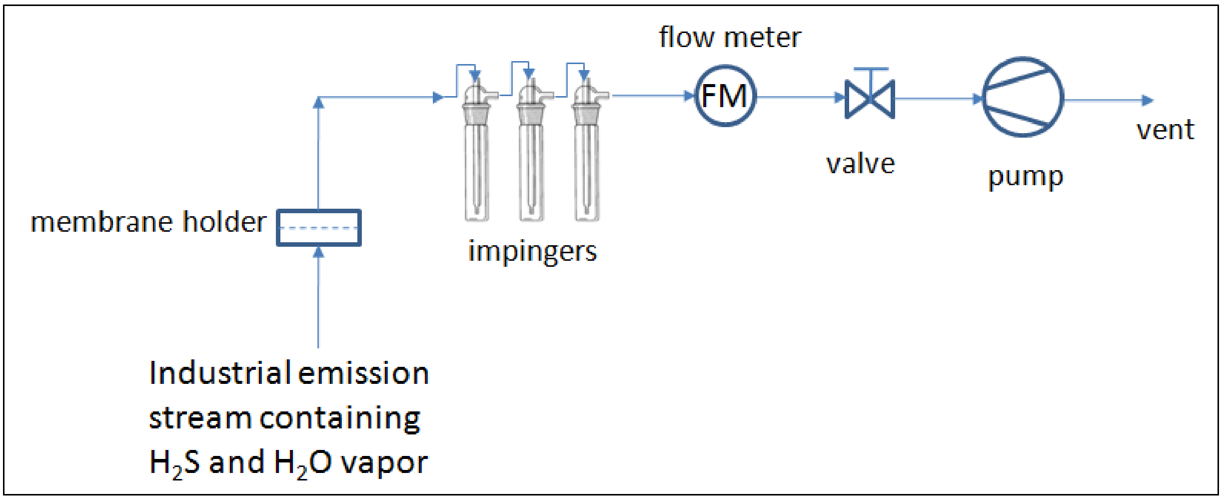

Figure 1: Experimental set-up for H_2S filtration tests

The concentration of H_2S was then calculated from amount of sulfide of cadmium formed by iodometric method as given by Eq (1) [15].

$$H_2S_{(g)} + Cd(CH_3COO)_{2(l)} \rightarrow CdS\downarrow_{(r)} + 2CH_3COOH_{(1)} \quad (1)$$

The H_2S removal percentage determined from hydrogen sulfide inlet and outlet concentration as given by Eq (2):

$$\%H_2S\ removal = \frac{H_2S\ inlet - H_2S\ outlet}{H_2S\ inlet} * 100 \quad (2)$$

4. Materials characterizations

4.1. Fluorescence X

The chemical composition was determined by using fluorescence X (Society of Cement Gabes-Tunisia).

4.2. X-ray diffraction

The diffraction patterns presented in this study were pulverized samples on a Debye-Scherrer configuration diffraction assembly. The beam emitted by the X-ray source is filtered by a dissymmetrical monochromator to obtain a convergent monochromatic beam of wave length $\lambda CuK\alpha 1 = 1.5405Å$.

4.3. Scanning electron microscopy

The scanning electron microscope (SEM) makes it possible to produce images of the surface of objects in three dimensions with a very high resolution (order of the nanometer). The principle is that an electron beam scans the surface of the sample to be analyzed and some interactions can take place. A detector captures parameters related to these interactions which are interpreted to construct a topography of the sample to be analyzed. The equipment used in the laboratory is a high-resolution, field-effect Hitachi S4800 microscope.

4.4. Mercury porosimetry

This technique relies on the penetration of mercury into a support's pores under high pressure. The intrusion volume has been recorded as a function of the applied pressure and then the pore size has been determined.

4.5. Mechanical strength:

The mechanical strength tests were carried out by the three-point bending method (LLOYD Instrument) to check the resistance of the disk support at different temperatures. The sample size was 45 mm / 12 mm / 2 mm and the distance between the two points was 30 mm.

5. Result and discussion

The composition of the zeolite and kaolin powder are shown in **Table 1** and **2**. It reveals that the major component is silica respectively 73.33 % and 52.43 %. This result was performed by X-ray diffraction analysis in figures **2** and **3** of original Turk zeolite indicated high content of quartz; the major crystalline phase identified was quartz (SiO2).

Table 1: Chemical composition of zeolite by fluorescence-X

SiO_2	Al_2O_3	$CaCO_3$	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SO_3	TiO_2	ZnO
73.33	12.13	6.5	3.65	1.67	1.46	1.22	0.31	0.01	0.03	0.01

Table 2 : Chemical composition of clay by fluorescence-X

SiO_2	Al_2O_3	$CaCO_3$	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SO_3	TiO_2	ZnO
52.43	18.17	1.20	1.10	11.12	3.01	2.83	0.51	0.62	0.03	0.01

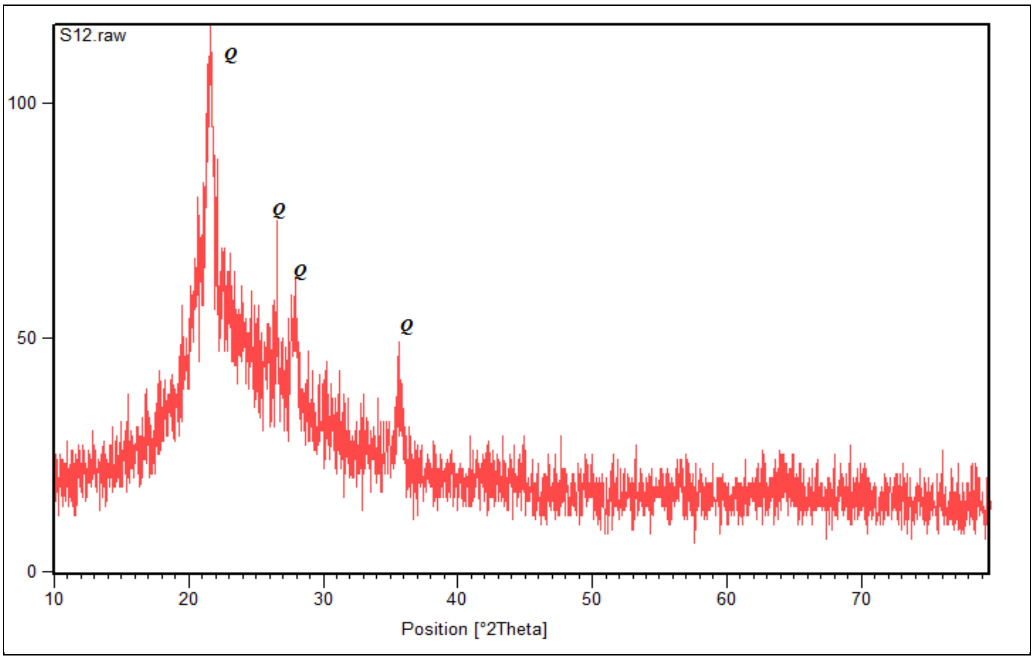

Figure 2:X-ray diffraction of zeolite powder

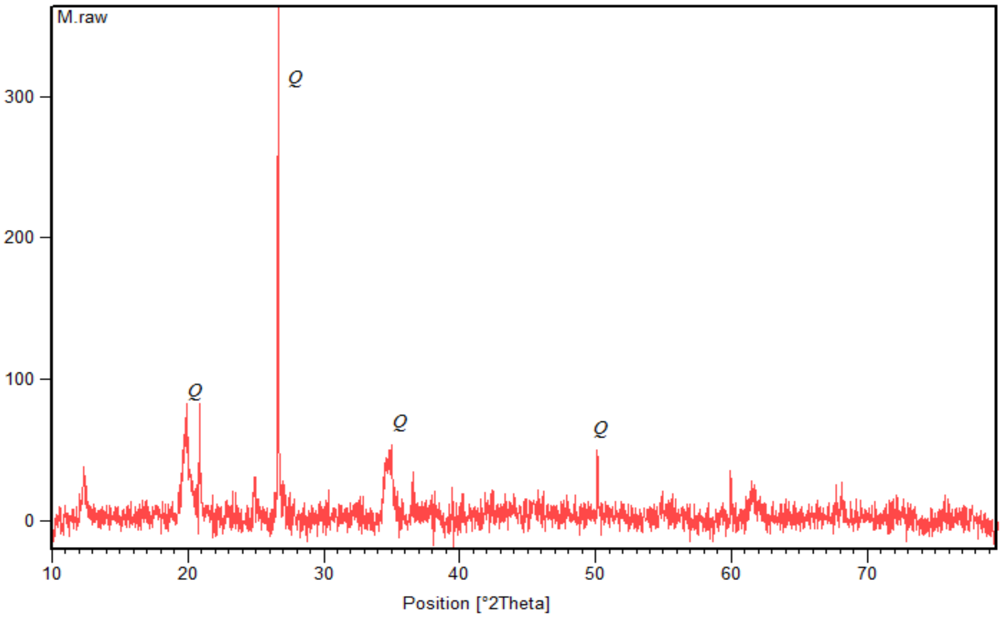

Figure 3: X-ray diffraction of kaolin powder

We have observed that the obtained zeolite and clay supports present the highest mean pore diameter for the highest mechanical strength: The zeolite support fired at 900° C and characterized by mercury porosimetry showed mean pore diameters and porosity of about 049 µm. The pore diameters determined for the ultrafiltration layer were centered near 0.07 µm (**Fig 4**). While the clay support fired at 900°C and characterized by mercury porosimetry showed mean pore diameters about 0.55 µm. The pore diameters measured for the ultrafiltration layer were centered near 0.062 µm (**Fig 5**)

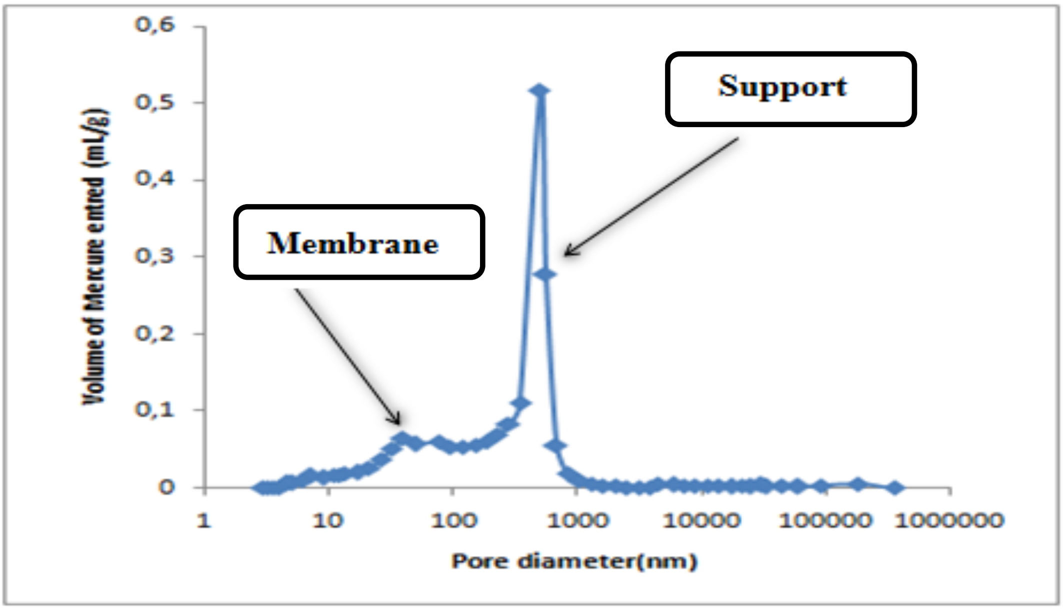

Figure 4: Pores diameters of Zeolite membrane

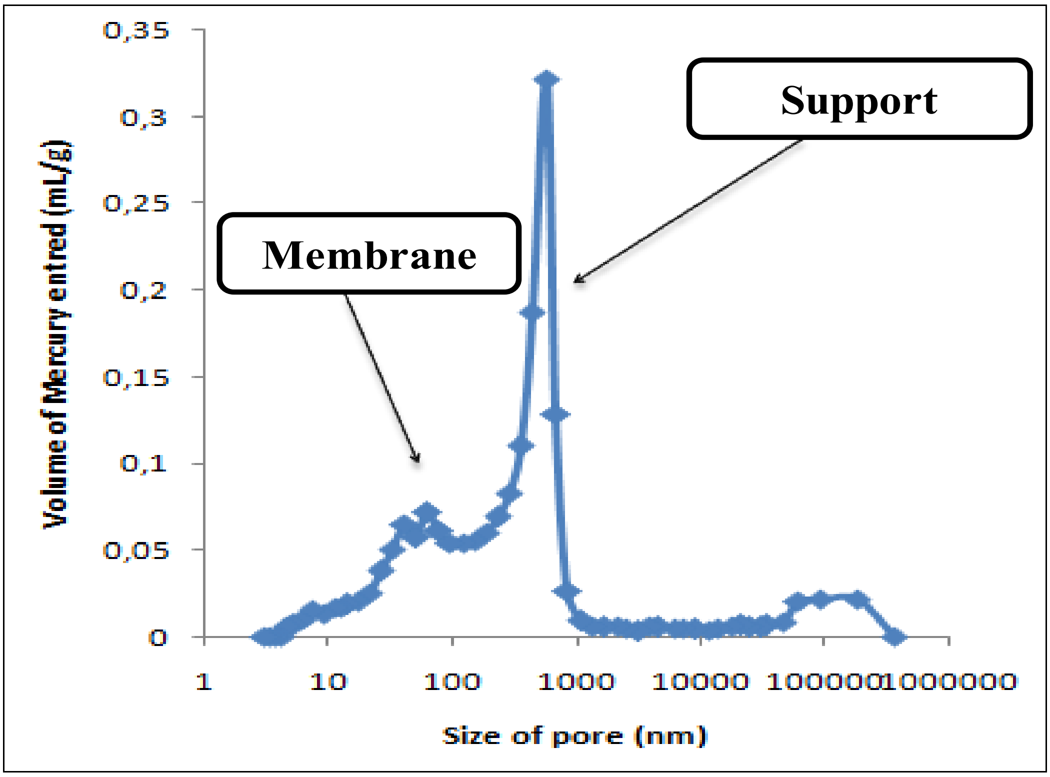

Figure 5: Pores diameters of kaolin membrane (MA)

The scaning microscopy images of the resulting membranes are shown in **Fig. 6** and **7**. This figure gives information on the morphology of the elaborated membrane surface. A defect free zeolite membrane was only attained for membrane thickness less than 25 µm. The thickness of the clay ultrafiltration layer is uniform with an average value of about 30µm, and moreover, the surface of the grafted ultrafiltration layer is homogenous without defects and nomicrocracks.

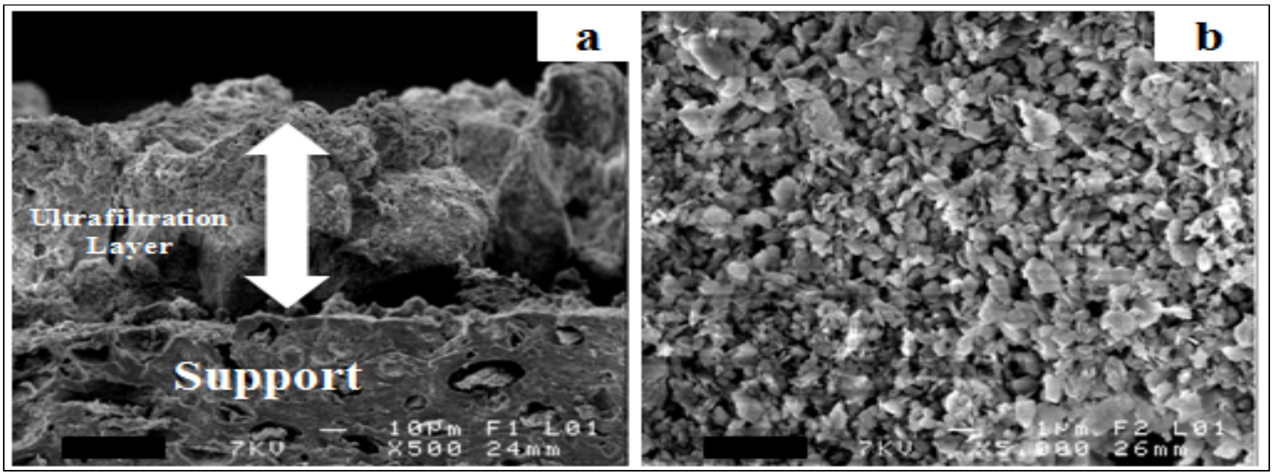

Figure 6: SEM images of Zeolite membrane (a: membrane thickness, b: membrane surface)

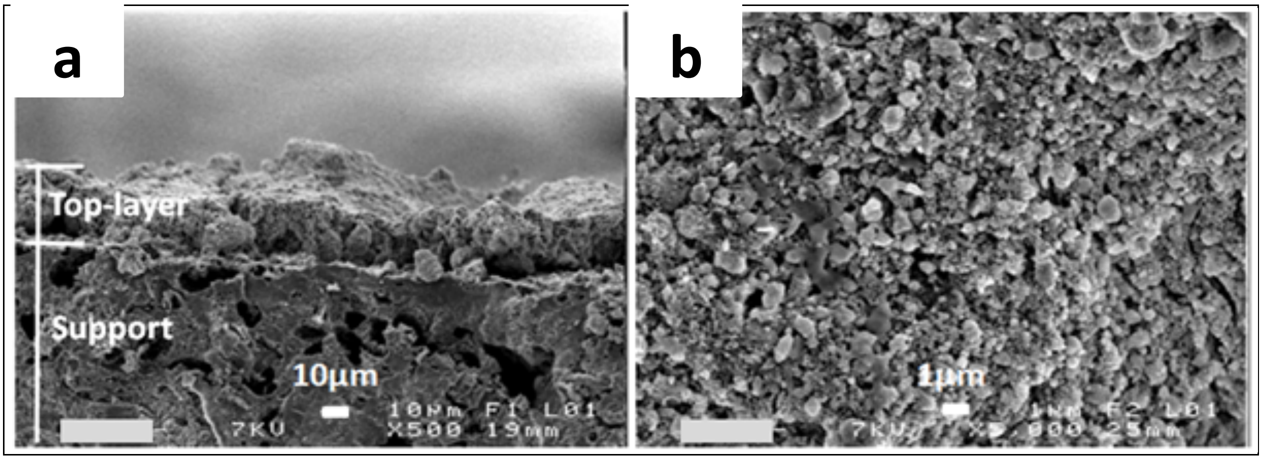

Figure 7: SEM images of kaolin membrane (a: membrane thickness, b: membrane surface)

For the zeolite membrane's mechanical resistance, the figure**7** shows the variation in flexural strength with respect to the sintering temperature using three-point bending tests. The increase in the sintering temperature is accompanied by a densification phenomenon and consequently by an increase in the flexural strength (from 6.67 MPa at 850 ° C. and 18.02 MPa at 950 ° C.) . The sintered material at 900 ° C. reached a flexural strength of 12.65 MPa, which represents a good mechanical strength of membrane (**Fig 8**). For the kaolin membrane's mechanical strength, It is noted that the increase in modulus of the stress at break (σ) in three-point bending with temperature reflects a progressive increase in the mechanical strength of the material (**Fig 9**). The ceramic is consolidated by densification and becomes more and more rigid. This test reveals an elastic deformation (linearity) and joins the observed observations on the porous texture of the material. Indeed, the densification causes an increase in the maximum stress before the rupture and a gain in the rigidity of the material. The supports calcined at 900 ° C. possess a mechanical strength of the order of 11.4 MPa.

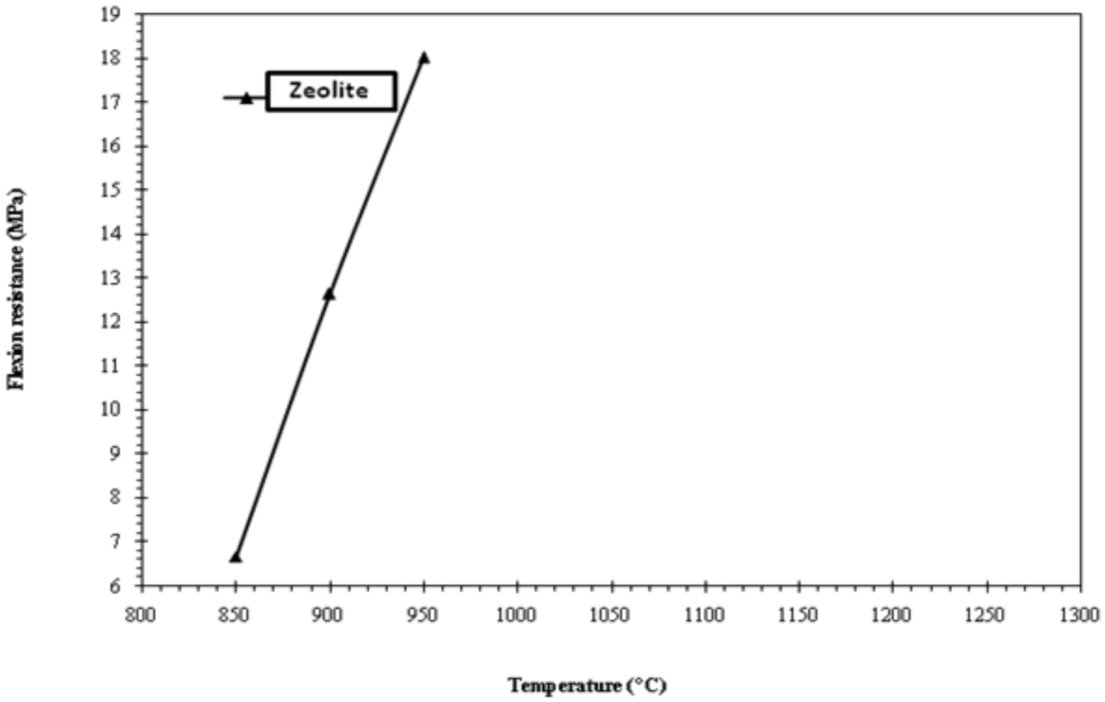

Figure 8: Mechanical strength of sintered Zeolite at three temperatures

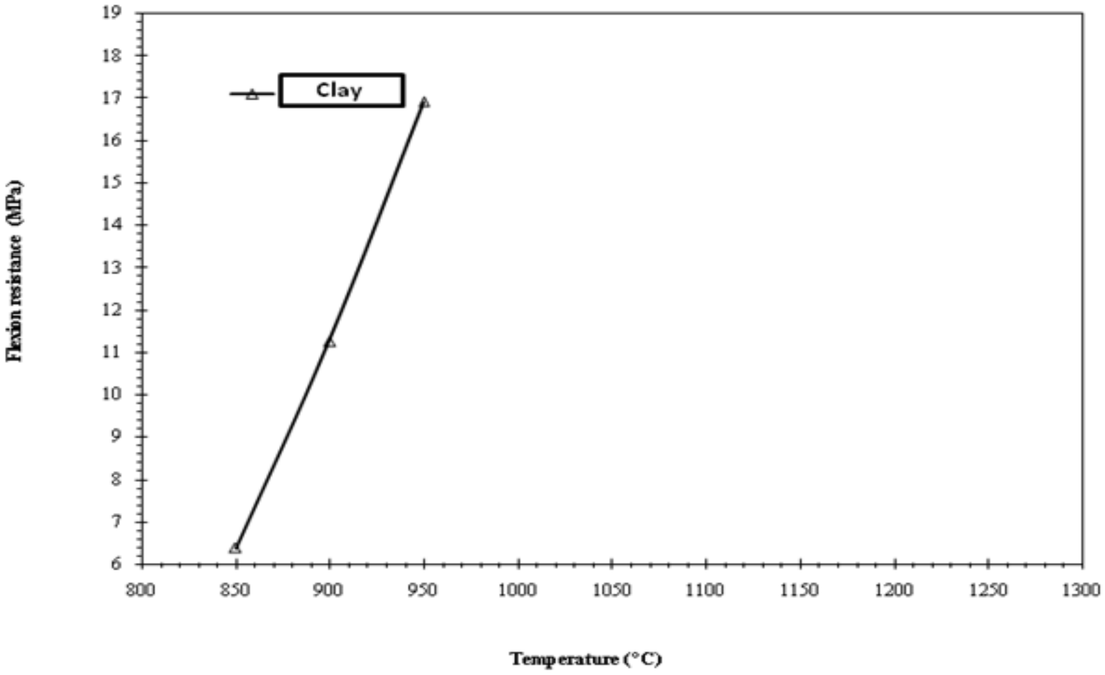

Figure 9: Mechanical strength of sintered clay at three temperatures

In the presence of vapor water at the retention process column, the passage of H_2S's molecules will be reduced until the diameters of the pores will be smaller than the size of H_2S molecules. So, we can talk about the presence of two hypotheses:

1) The presence of a mechanism of transformation of the H_2S molecule to another intermediate molecule for a larger size and retained by the smallest pores present at the membrane (**Fig 10**). Bonds are established between the hydrogen atoms of water molecules and the sulfur atom of the molecule of hydrogen sulphide in view of the presence of intermolecular hydrogen.

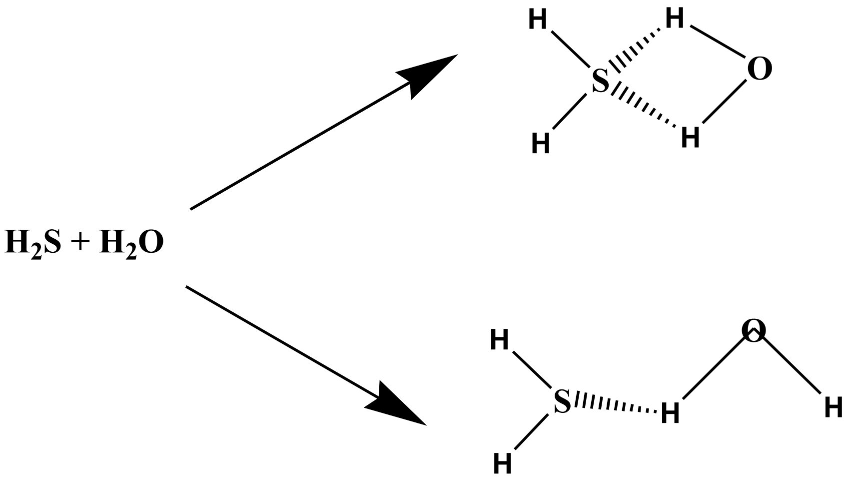

Figure 10: Estimation of the mechanism of the H_2S molecule reaction with water vapor

2) Structure and porous surface chemistry should also have an effect on the oxidation of hydrogen sulphide. Nevertheless, with the presence of vapor water, a significant improvement in the adsorption capacity of H_2S is noticed, with an increasing passage time of less than 140 min for the clay-based support and zeolite. Furthermore, the sample of elaborated membranes also shows an increased capacity, more than 50 min for retention. They are not so effective for the reaction with the H_2S molecule like water cations. The HS-formed ions react with water to give sulfide ions on the ceramic surface. The hydrogen ions released in this reaction are capable of neutralizing the charge of the layers. Exposure of samples to air for a sufficient period of time may lead to the oxidation of sulphides to sulfur due to the instability of sulphides. The reaction between H_2S and water vapor is given by equation (1). The H_2O molecule present in clay-based ceramic and zeolite in a heterogeneous catalytic system have a potential for the removal and decomposition of H_2S, as it can be regenerated by contacting with oxygen. The oxidation mechanism on H_2S and regeneration can be shown in the equations (3)-(5). The overall reaction (3) of the elemental sulfur formation from H_2S can be written as the following three equations:

$$H_2S\ (g) + H_2O\ (1) <===> H_3O^{+}\ (aq) + HS^{-}\ (aq) \quad (3)$$

$$HS^{-}(aq) + H_2O\ (1) <===> H3O^{+}\ (aq) + S^{2-}\ (aq) \quad (4)$$

$$H_2S\ (g) + 2\ H_2O\ (1) <===> 2\ H_3O^{+}\ (aq) + S^{2-}\ (aq) \quad (5)$$

Hydrogen sulfide is soluble in water and acts as a weak acid. It initially dissociates into the hydrosulfide ion, HS^{-}, and then the sulfide ion, S^{2-}. As sulfurous hydrogen can give as another mechanism the production of SO_2 or sulfur compounds. During gas elimination test, the time of retention will be vary depending on the initial size of the support pores and membranes. The figures **11** and **12** shows that the membranes have the time of retention rather ultrafiltration faster than the carrier thanks to the deposit layer to the support's surface. The first two curves show that the time for total retention of H_2S is in the average of 120 min for zeolite support but in the curve of ultrafiltration membrane is about 45min (**Fig 11 a.b**). While the second two curves show that the time for total retention of hydrogen sulfide is in the average of 125 min for clay support but in the curve of ultrafiltration membrane is about 55 min (**Fig 12 a.b**). So, we can see that the water will quickly minimize and stabilize the diameters of pores and consequently the H_2S molecules will be filtered; results obtained are in good agreement with obtained previously [16-18].

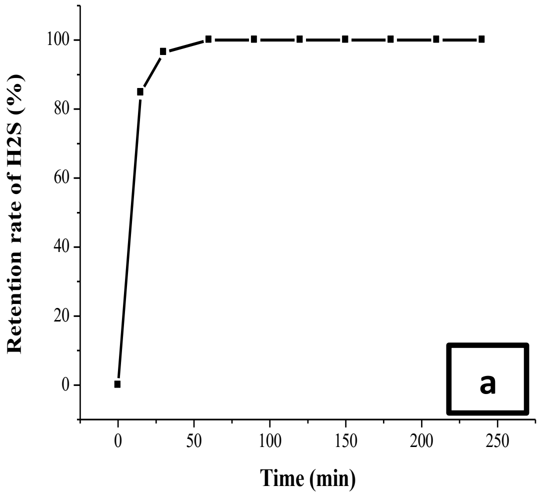

Figure 11: Retention test of Hydrogen sulfide by zeolite ceramic (a: support, b: membrane)

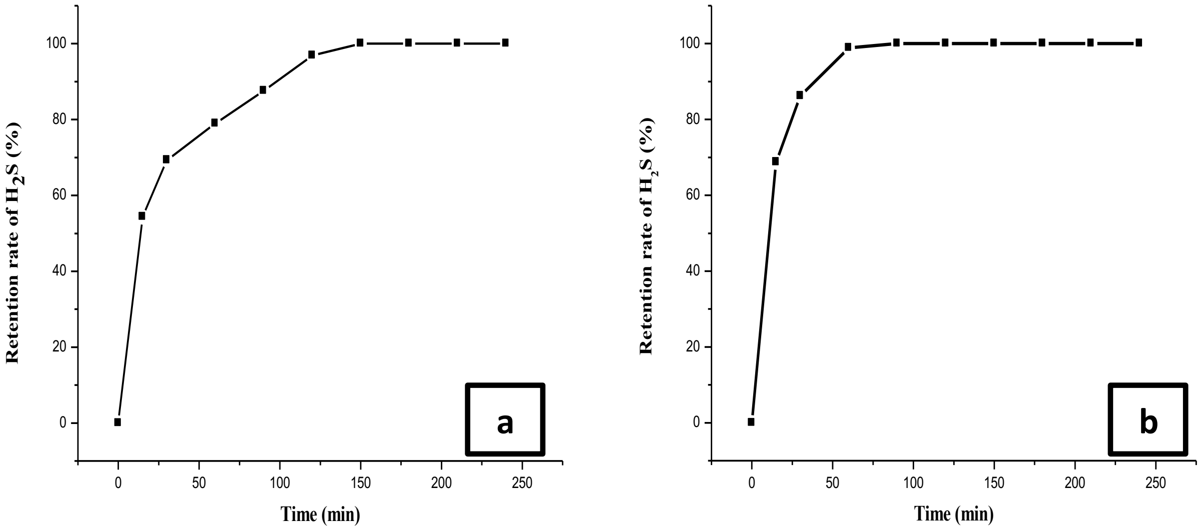

Figure 12: Retention test of Hydrogen sulfide by clay ceramic (a: support, b: membrane)

6. Conclusion

In this work, a new process has been developed in view of the manufacture of an ultrafiltration ceramic membrane based on Turkish zeolite and the Tunisian clay. This membrane has an excellent mechanical resistance. It can therefore be used as a support for the deposition of any layers for nanofiltration. The membrane obtained was characterized in terms of porosity, texture and mechanical strength. The porosity and pore size values of the microporous support can be controlled by varying the powder particle size of the materials used. The ultrafiltration layer deposited on the support is produced by the slip casting process using a slurry of clay powder or zeolite to a PVA solution. The sizes of the support pores could be vigilantly controlled by the choice of the particle diameters of the materials. The desired pore sizes of the ultrafiltration layer (<0.1 µm) were obtained by optimization of the calcination temperatures. The ceramic membranes with pore sizes gave 0.07 µm for the zeolite and 0.06 µm for the clay. We have carried out a series of industrial applications for the reduction of the H_2S content using the inorganic supports and membranes thus prepared. These membranes have a high capacity to retain this gas in a time not exceeding 55 min with 100% of the percentage but the support remains about 125 min to 140 min to reach 100% retention. This difference results from the pore size between the ultrafiltration membrane and the support.

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