Valorization of Clays in the Removal of Organic Pollutants by Adsorption and Membrane Filtration: A Comparative Study

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Keywords: Clay, Ceramic Membrane, Membrane Filtration, Adsorption, Phenol

Abstract. Within the framework of the valorization of a clay from the Draa-Tafilalet region and following the study of the retention of phenol in aqueous solution which was carried out previously by adsorption on a clay, we have proceeded in this present work to the elimination of phenol by filtration on a mineral membrane already elaborated on the basis of the same clay and characterized by several tests in a previous work. A phenolic solution of known concentration was treated by tangential filtration using a laboratory-scale micro-pilot, with a filtering surface area of approximately 0.0072 m^2. To make a comparative study of the retention of phenol by the two techniques mentioned above, the membrane was first characterized by the water permeation test, and then the tests of filtration which were carried out at a circulation pressure of between 0.5 and 1 bar at room temperature. Secondly, the results obtained were compared with those obtained by adsorption. The results obtained showed that the filtration process is very effective at a pressure of around 0.5bar. A comparison of the results obtained for the yield of phenol elimination by adsorption and by filtration revealed that the adsorption technique can reduce the concentration of phenol by up to 97%, while the filtration technique also recorded a very high percentage of around 90%.

1. Introduction

Today, the world's water problem is not only about the quantity available but also the quality of water [1]. The increase in human and industrial activity is leading to a significant amount of wastewater being discharged, polluting and damaging aquatic environments and ecosystems[2,3]. For a long time, considerable endeavors have been dedicated to devising and adopting processes that are both more effective and economically efficient in treating liquid effluents [4–6]. These processes include adsorption and membrane technology.

Membrane technology is widely used in many separation processes, for example, the food industry, the chemical industry, seawater desalination, industrial effluent treatment, etc. Because of the mechanical, thermal, chemical, and long-life performance that mineral membranes can offer, they are more popular with professionals than organic membranes [1]. Membranes are available in a variety of shapes, including flat and tubular, etc...., with varying diameters. Membrane filtration is a process that works by applying a pressure difference that allows the solvent to pass through a membrane with pores of a specific size to retain the solute. Tangential filtration stands out as the frequently employed method due to its cost-effectiveness in terms of energy. It possesses the added benefit of postponing and restricting the accumulation of deposits on the membrane, through the fouling phenomenon generated by the tangential flow of fluid across the membrane surface. The formation of deposits on the membrane leads to fouling of the pores, and this phenomenon causes variations in permeability and selectivity. To combat fouling, various cleaning techniques have been used, such as periodic backwashing that improves permeability, when the filtration rate is high the backwashing is even more obvious [7,8]. Photocatalytic materials are also used because of their effectiveness in combating fouling, for example, TiO_2 They have a photocatalytic capacity to decompose organic matter, microorganisms, and pollutants, reducing their adsorption on the surface of the membrane. [9,10]. Chemical cleaning of the membrane is also used and is still manner necessary regularly, their conditions depend on both the nature of the fouling and the membrane.

Adsorption is one of the easily implementable technologies; it is commonly used for water treatment. Activated carbon stands out as a commonly utilized adsorbent due to its elevated capacity for adsorbing organic contaminants[11,12]. However, its usage for treating substantial quantities of contaminated water is restricted by its elevated cost. Various researchers have explored the quest for economical and efficient alternative adsorbents, preferably sourced from natural substances and local waste [13,14]. Clays, owing to their abundance and cost-effectiveness, rank among the frequently employed inorganic materials.

This bibliographic review aims to present the studies undertaken in the field of organic pollutant elimination. The adsorption of phenol by clay was the subject of our most recent work research [15].

The membrane cost is contingent on both the raw material prices and the energy consumption during the sintering process [16]. One significant hurdle in membrane processes involves utilizing or developing membranes crafted from materials that impart novel properties to the membrane processes. [17]. Due to its low cost, natural abundance, and the benefit of densification at comparatively lower sintering temperatures in comparison to the mentioned oxides [18]. The development of membranes based on natural clay has been the subject of our previous work [17].

The primary aim of this study is to use clay in the treatment of a phenolic solution using the adsorption technique and filtration on an M_8 membrane that we developed previously in a work that has already been published [17]. In this work, a study was carried out on reducing the concentration of phenol in an aqueous solution by tangential filtration using a laboratory-scale micro-pilot. The filtering surface area is approximately 0.0072 m^2, and the results were compared with those obtained using the adsorption technique in the previous work.

2. Materials and Methods

2.1 Raw materials

The clay used for the development of the membranes was collected in the Draa-Tafilalet region, it is characterized by several analysis techniques, namely X-ray fluorescence, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric and differential thermal analysis (TGA/DTA). The choice of this clay is due to its abundance in nature [17].

2.2 Manufactured membranes

The M_8 membranes were shaped by extrusion, and were characterized by several tests: porosity test, chemical resistance test, mechanical strength test, and scanning electron microscopy test[17].

2.3 Test water permeation

The permeation test was carried out on drinking tap water using a laboratory-scale filtration pilot Fig.1. The pilot has been fitted with an adjustable-flow electric pump (P) with a maximum pressure of 3 bar, a pressure gauge (m), a safety valve (V), a membrane module (M), a pressure regulator (R), a filtered water (permeate) recovery tank (B) and a drinking water feed tank (FW).

Materials Research Proceedings 40 (2024) 284-293 https://doi.org/10.21741/9781644903117-30

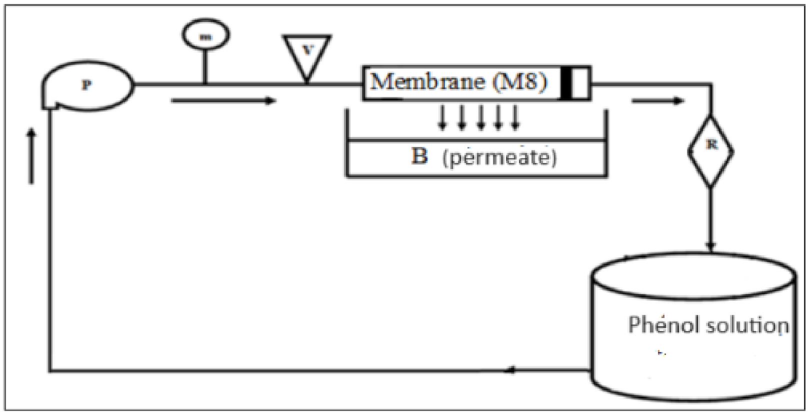

Fig 1: Micro-pilot of tangential filtration

The permeate flow rate is calculated using the following equation:

$$D = \frac{V}{t*S}\ (L/h.m^2) \quad (1)$$

D ($L/h.m^2$) is the Permeate volume flow rate, t (hour) is the time, V (Liter) is the Volume, and S (m^2) is the Filter surface area.
The calculation for the filtering surface of each membrane is as follows:

$$S = 2.\pi.r.l = \pi.D_{int}.l\ \ (m^2) \quad (2)$$

With, l (m) and Dint (m) are the length and inside diameter of the membrane respectively.

2.4 UV-visible spectrophotometric properties of phenol

Before beginning the study of the elimination of phenol by membrane filtration, the first approach consists of determining the UV-visible spectrophotometric properties of phenol, i.e. determining the λ_{max} for which the absorbance is maximum and verifying the validity of the Beer-Lambert law. To determine λ_{max} of phenol, measurements were made on a series of daughter solutions prepared by dilution of the mother solution. Measurements of absorbance as a function of wavelength (200-700nm) enabled us to deduce λ_{max}. The curve shown in Fig.2 represents the variation in absorbance as a function of wavelength.

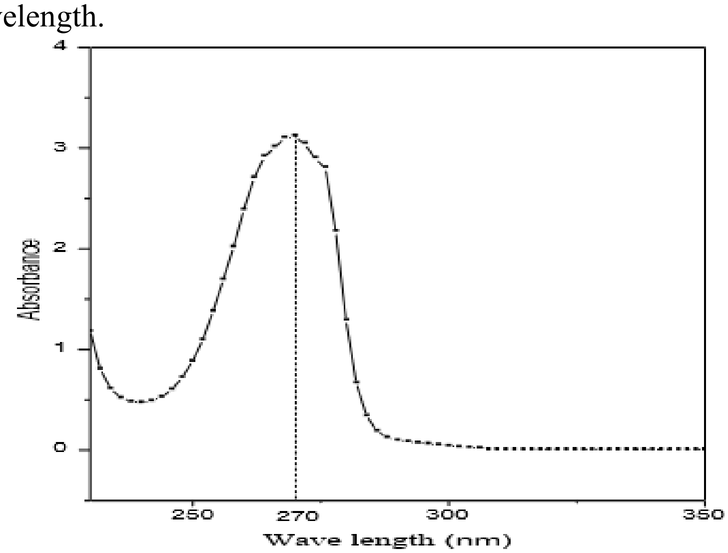

Fig 2: Determination the λ_{max} of phenol

2.4.1 Calibration curve

Taking previous results into account, we drew the calibration curve for phenol in order to determine the range of concentrations for which Beer-Lambert's law is respected (obtaining a straight line). The calibration was carried out using solutions of different concentrations, prepared from a stock solution. Table 1 gives the absorbance values as a function of the solutions at different concentrations prepared by dilution. Fig. 3 shows the calibration curve in the form of a straight line and verifies Beer-Lambert's law.

***Table 1**: absorbances after dilution*

C (mg/l)	10^{-4}	4.10^{-4}	8.10^{-4}	10^{-4}	2.10^{-3}	6.10^{-3}
Absorbance	0.233	0.675	1.166	1.378	2.72	3.518

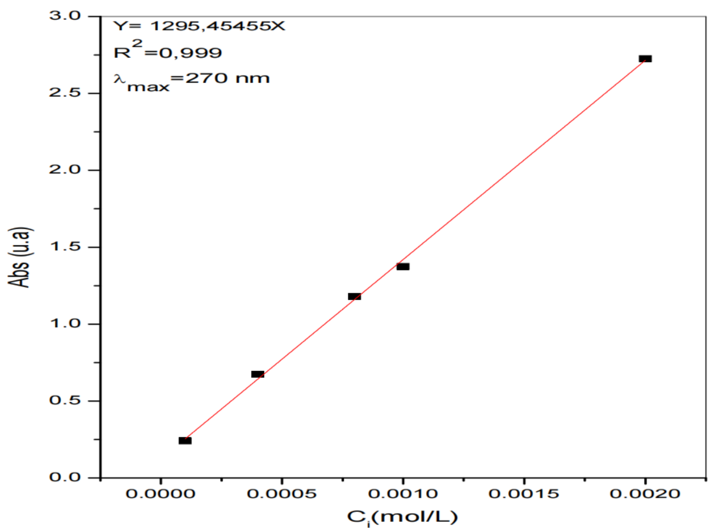

Figure 3: Phenol calibration curve

2.5 Treatment of the phenolic solution

The first stage consists of preparing a phenolic solution of known concentration. The second stage involves filtering the previous solution Fig 4. The concentration of the filtrates obtained is determined by visible UV. The efficiency of this membrane was evaluated by the flow rate of the permeate and the elimination yield as a function of time.

Fig 4: Treatment of the phenolic solution

3. Results and Discussion

3.1 Water permeation test

3.1.1 Variation in flow rate as a function of time D=f (t)

Fig. 5 shows the variation in flow rate as a function of time for M_8 treated at 1000°C [16], with a circulation pressure of 1 to 2 bar. Examination of the results obtained shows that the water permeation flow rate values are higher at the start of filtration for different pressure values from 1 to 2 bar. The M_8/1000°C/1bar flow rate = 37.9 L/h.m^2, M_8/1000°C/1.5bar flow rate = 13.15 L/h.m^2 and M_8/1000°C/2bar flow rate = 15.36 L/h.m^2. This is due to the pores being partially blocked by suspended solids or colloids present in the drinking water used. After a filtration time equal to 68, 97 and 90 min respectively for a pressure equal to 1 , 1.5 and 2 bar, we observe a stabilisation of the flow rate, which is explained by the concentration polarisation phenomenon. In other words, during the circulation of water at a given pressure, all the species present create an accumulation of matter at the water-membrane interface. Concentration polarisation refers to the formation of a very thin layer of water, whose concentration is greater than that of the feed solution (tap water). This layer remains immobile and thus reduces the apparent size of the pores, a phenomenon that has been well explained by several researchers [19].

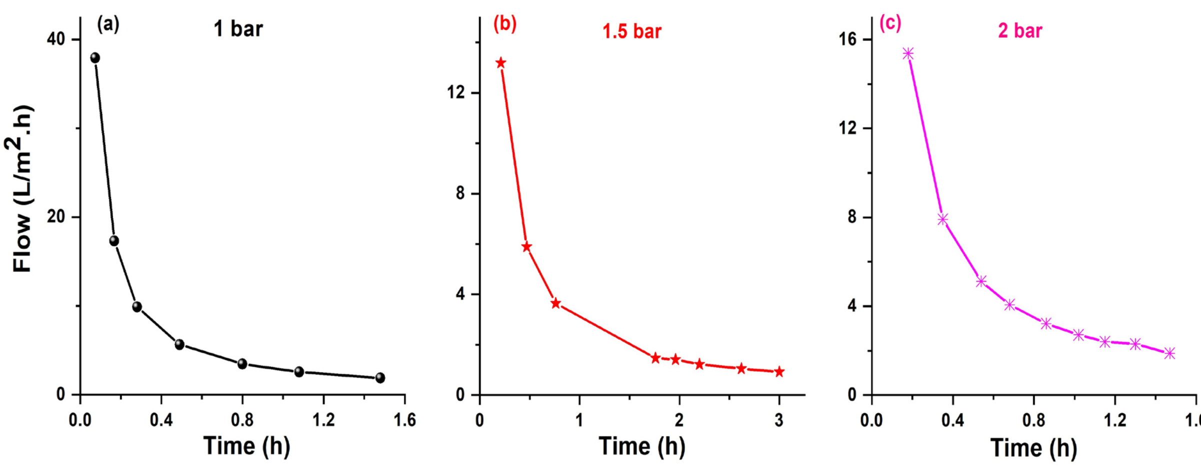

Fig 5: *Evolution of membrane water permeability flow rate as a function of Time*

3.1.2 Variation in flow rate as a function of pressure D=f(P)

The variation in flow rate as a function of pressure is shown Fig. 6. The decrease in flow rate at P=1.5 bar can be explained by the low driving force of the feed flow created by this pressure to remove the material accumulated at the water-membrane interface during filtration at P= 1bar. This material forms what is known as a deposit (rearrangement of suspended particles and colloids present in the water), so during filtration there will be an increase in deposit resistance. In the case of P = 2bar, there is an increase in deposition, unlike the case of 1.5 bar, which is due to the partial shearing of the layer formed during the previous filtrations.

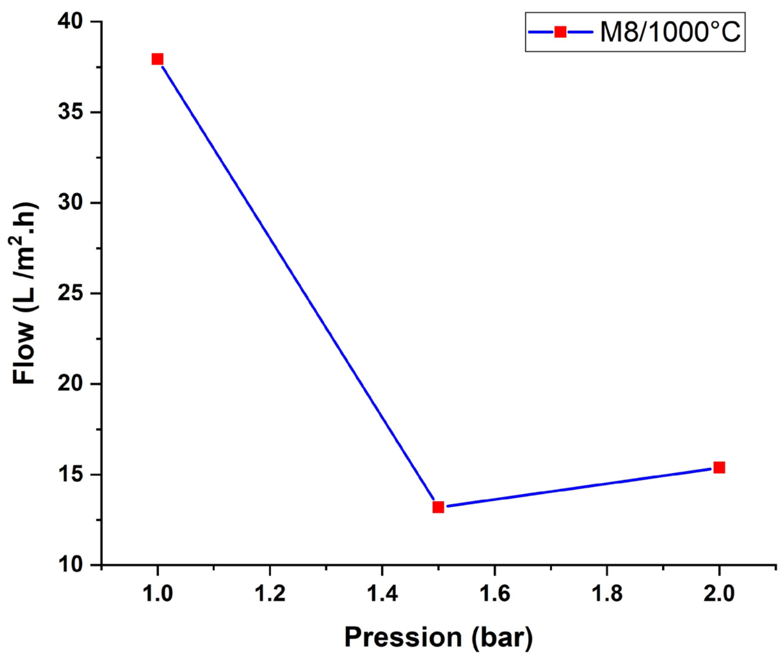

Fig 6: Flow rate evolution of membrane water permeability as a function of pressure

3.2 Polluted solution treatment tests

3.2.1 Changes in permeate flow rate as a function of time

For all the 0.5 and 1 bar pressure values, the permeate flow rate for this membrane decreased as a function of time and stabilized after 31 and 75 min of filtration respectively at 2.21 L/m^2.h and 5.16 L/h.m². The decrease in permeate flow rate is due to the progressive blocking of the pores by the retained phenol molecules on the external surface of the pores and on the internal surface of the membrane, leading to the phenomenon of concentration polarization.

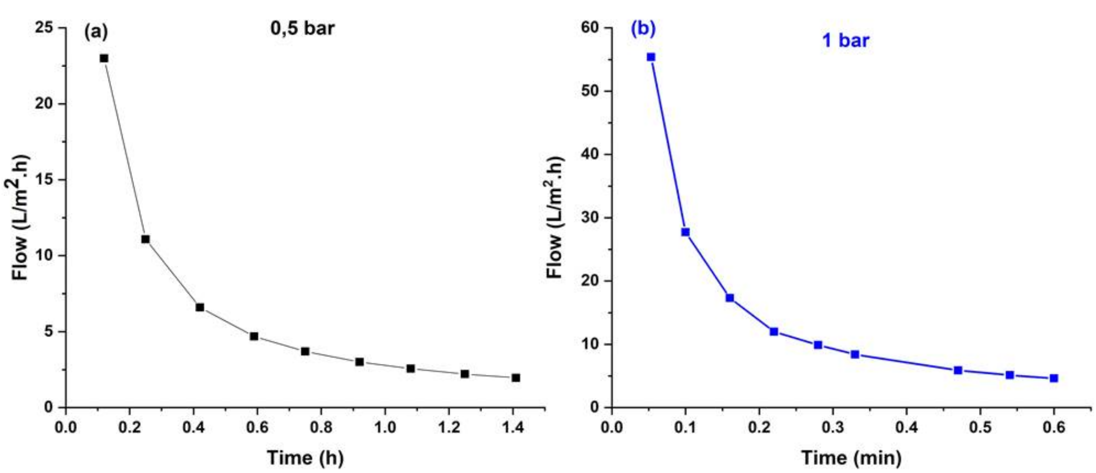

Fig 7: Evolution of membrane permeability flow rate as a function of time

3.2.2 Phenol retention efficiency

The visible UV spectrum of the phenol stock solution (510-4mol/L) shows a characteristic band at λ= 270 nm (Fig.2). The absorbance of permeates obtained after filtration at circulation pressures of 0.5 and 1bar, corresponding to the same value of λ, were determined by UV visible analysis.

Materials Research Proceedings 40 (2024) 284-293 https://doi.org/10.21741/9781644903117-30

To determine the concentrations of permeates we plotted the calibration curve (Fig.3) using standard phenol solutions of different concentrations. The retention efficiency of phenol as a function of time was calculated by equation 3:

$$R(\%) = \frac{C_i - C_{res}}{C_i} * 100 \quad (3)$$

C_i: initial concentration (mol/L)
C_{res}: concentration of phenol in the permeate (mol/L)
Analysis of the results obtained after filtration at P= 0.5bar shows that the yield of the reduction in the concentration of phenol in aqueous solution can reach 90% (Figure 8). The low absorbances of the permeates at λmax compared with the absorbance of the stock solution confirm these results (Fig. 9 and 10).

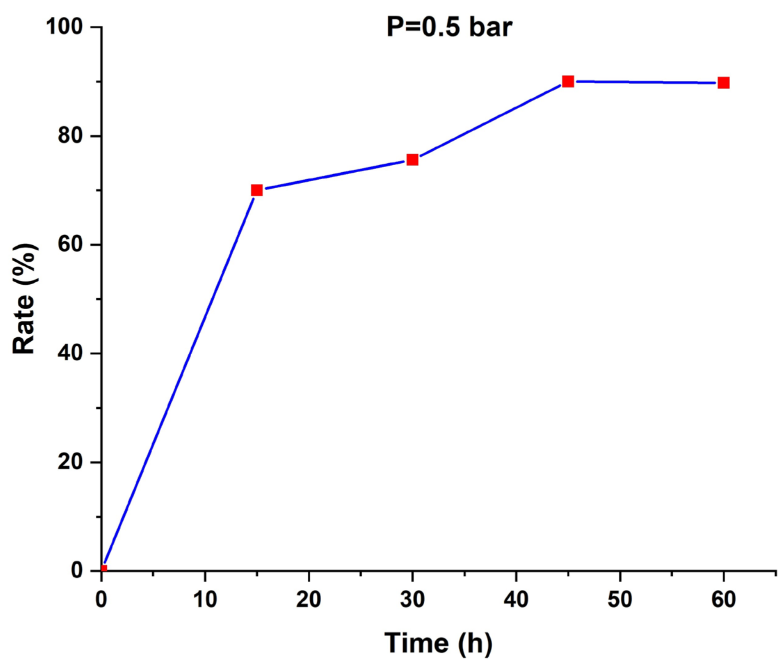

Fig 8: Evolution of phenol elimination yield in aqueous medium as a function of Ttime

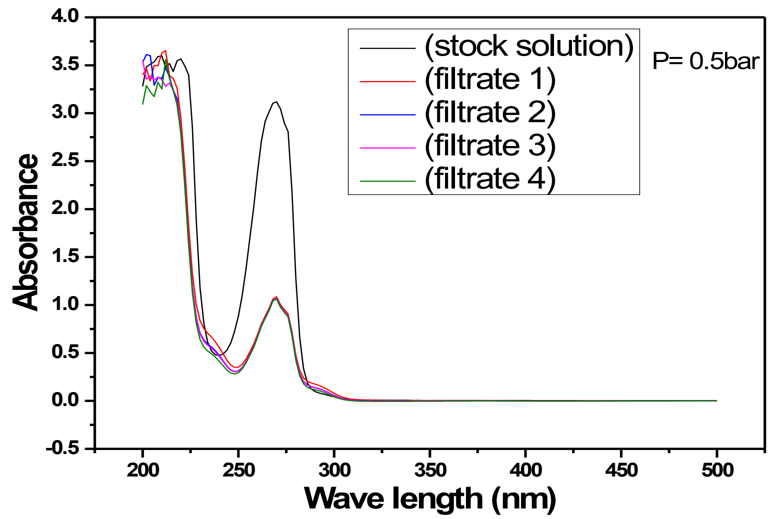

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Fig 9: Illustration of UV analysis of the stock solution and permeates at P=0.5 bar

However, at P=1bar no elimination was recorded. Indeed the curves obtained by the UV analysis, illustrating the variation in the absorbances of the permeates are superimposed with that of the stock solution (Fig.2) which shows that there is no elimination at P=1bar.

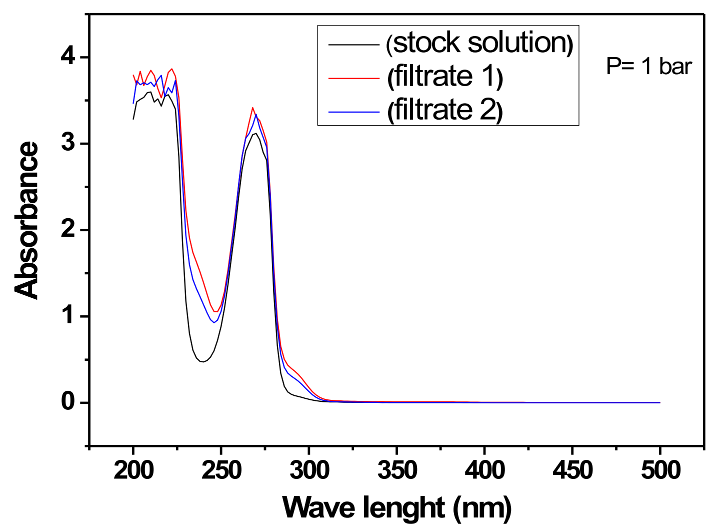

Fig 10: Illustration of UV analysis of the stock solution and of the permeates at P=1bar

3.3 Comparative study of phenol retention by adsorption and filtration

A comparison of the results obtained for the yield of phenol elimination by adsorption and filtration revealed that the yield of phenol retention by filtration on the M_8 membrane recorded a very high percentage of around 90%, while that obtained by adsorption on ART clay was only 51.8%[15].

Conclusion

In this study, we showcased the potential of developing cost-effective mineral membranes utilizing Moroccan clay. Additionally, this research has provided insights into various phenomena associated with the treatment of liquid effluents overall, with a specific focus on phenol elimination through filtration.

Examining the findings reveals that M_8 membranes, sintered at 1000°C, demonstrate favorable permeability and exceptional performance in phenol removal. This underscores the versatility of clays, suggesting their utility not only as raw materials for constructing building materials but also as effective adsorbents for retaining pollutants in aqueous environments. Consequently, we can deduce that the filtration membranes devised in the laboratory hold promise for widespread application in the treatment of liquid effluents.

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