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Preparation and Characterization of NaA Zeolite Membranes and its Application for Removal of Heavy Metals

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Abstract: In this work, the characteristics of low cost NaA zeolite membranes for heavy metal removal from synthesised solutions are presented. These membranes were elaborated on a clay macroporous support which were prepared and characterized by XRD, SEM and N_2 permeation. The effects of synthesis parameters such as temperature T and time t on the proprieties of the NaA zeolite membranes were investigated. The best experimental conditions for synthezised membranes are obtained for T = 60 °C, t = 24 h and 117 L m^{-2} h^{-1} bar^{-1} for a water flux of membrane.

The tests for the removal of Pb(II), Zn(II) and Cr(VI), conducted on these NaA zeolite membranes, show respectively the rejection reached 99%, 99% and 12% after 1 hour of filtration at 7 bars of N_2 and at ambient temperature.

Key words: NaA zeolite, membrane, heavy metal, filtration, clay.

Introduction

In the last few decades, significant progress has been witnessed on zeolite supported membranes, due to their potential applications in separation and catalysis processes[1-5]. Synthesis concepts such as secondary growth on seeded support were developed and for more than 20 years, zeolite membranes, especially NaA zeolite membranes have been intensively investigated in wide range of applications due to their uniform pore structure and high thermal stability[6-11].

Nevertheless, these membranes have been seldomly reported for the removal of ions from aqueous solutions[12-16]. Li et al.[12] reported using MFI zeolite membranes supported by α-alumina in reverse osmosis. Malekpour et al.[13] used the NaA zeolite membrane for desalination of radioactive solution. Zhang et al.[14], in their experimental results, indicate that the developed multifunctional membrane can exhibit quick color change when in contact with cadmium ions in a solution even at relatively low concentrations.

However, such membranes are considered to be too expensive for such applications. Despite the considerable progress made in the development of organic and inorganic zeolite membranes prepared on porous or non-porous supports, few researchs have been conducted using zeolite membranes supported on clay[17-18]. These types of membranes can be a promising alternative to other ones, membranes due to the abundance of clay and its very low cost.

The goal of this work is to investigate the performance of NaA zeolite membranes supported by a cheaper clay macroporous support for the separation of some heavy metals cations such as Pb(II), Zn(II) and Cr(VI). These are considered the most toxic elements even

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at low concentrations. The clay mineral used is easily available in a large quantity in the region of Meknes in Morocco. Their porosity has been controlled by organic additives such as carbon.

Experimental Section

Synthesis of LTA membrane

Plane supports (40 mm in diameter, 2 mm in thickness, 0.42 µm median pores radius and about 35% porosity), based on clay, were elaborated by using organic additives as porosity agents following the experimental procedure given by Anbri et al.[17]. It can be noted that the clay was collected from the same site (in the region of Meknes in Morocco) of that used by these authors.

First, one side of the support was polished with 600 grit-sand paper to obtain a smooth surface. Next, it was washed with deionized water to remove lost particles created during polishing. Then, it was dried at 40 °C for 48 hours. Last, the polished face of the substrate was coated with a solution containing NaA zeolite nucleation seeds.

The synthesis mixture was prepared from an initial gel of the following composition[17]:

$$7.5Na_2O \ / \ 0.5Al_2O_3 \ / \ SiO_2 \ / \ 200H_2O$$

Sodium silicate solution: SiO_2 / 7.5NaOH / $102H_2O$ was prepared by dissolving sodium silicate ($Na_2Si_3O_7$, Aldrich) and sodium hydroxide in deionized H_2O.
A sodium aluminate solution: Al_2O_3 / 15NaOH / $197H_2O$ was prepared by dissolving sodium aluminate ($NaAlO_2$, Riedel-de-Haën) and sodium hydroxide in deionized H_2O.

The solutions were stirred in closed polyethylene bottles at room temperature until complete dissolution of the solid. After mixing the initial solution, the resultant mixture was placed in a polyethylene bottle and stirred vigorously for 15 min. The support was placed horizontally, and the bottle was covered with a cap.

The syntheses were performed at different temperatures (40, 50 and 60 °C) for 24 h. After each synthesis, the membranes were washed several times with deionized water and dried at 100 °C for 4 h.

Membrane characterization

The supported morphology of the supported NaA zeolite was examined using X-ray diffraction XRD (CuKα radiation: λ=1,5406Å) and scanning electron microscopy SEM (Hitachi S-4800).

N_2 permeation measurements

Single gas permeation was carried out to evaluate the quality of the membranes. Prior to gas permeation measurements, the membranes were dried at 110 °C for 24 hours to remove the water adsorbed in the zeolite channels. The dried disk-shaped NaA membrane was sealed in a permeation module with the zeolite membrane facing the high-pressure side[15]. The N_2 permeance of the membranes was measured by a soap-film flow meter under different pressures at room temperature. The permeance is defined as:

$$B = \frac{Q}{S.(P_1 - P_2)} \quad \textbf{(1)}$$

Where B is the permeance (mol Pa^{-1} s^{-1} m^{-2}), Q is the molar gas flow rate (mol s^{-1}), S is the effective membrane area (m^2), and P_1 and P_2 are the upstream and downstream pressure (Pa), respectively.

The permeance data were fitted to the following equation[19]:

$$B = \alpha + \beta P_{av}$$

where P_{av} is the arithmetic average of pressure on both sides of the membrane, and the constants α and β represent, respectively, the Knudsen and viscous flow contributions to the permeance. The ratio $100 \times \frac{\alpha}{\alpha + \beta}$ was used to measure the percentage of Knudsen flow.

Filtration of heavy metals

The filtration system is shown in Figure 5. The zeolite membrane was placed in a stainless steel cell sealed by o-ring facing the feed stream. A porous stainless steel disc was placed under the clay support to prevent cracking under high pressure. The feed pressure was maintained by nitrogen cylinder.

The experiments were carried out with different synthetic wastewater solution of $PbCl_2$, $ZnCl_2$ and CrO_3. Heavy metal concentrations were analyzed by atomic absorption spectroscopy (Varian type: 220 FS).

For initial experiments, die-hard-pure water (resistance 18 MΩ) was used as feed solution to measure the water flux F under different nitrogen pressure. The water flux (L h^{-1} m^{-2}) was calculated by the following equation:

$$F = \frac{V}{A.t} \quad \textbf{(2)}$$

where V is the volume (L) of water collected in time period t (h), and A is the effective membrane area, which is $9.07 \cdot 10^{-4}$ m^2 in this case.

For ionic solutions, rejection factors were obtained as:

$$R = \frac{C_f - C_p}{C_f} \times 100 \quad \textbf{(3)}$$

where C_f and C_p are ions concentrations in the feed and permeate solutions, respectively.

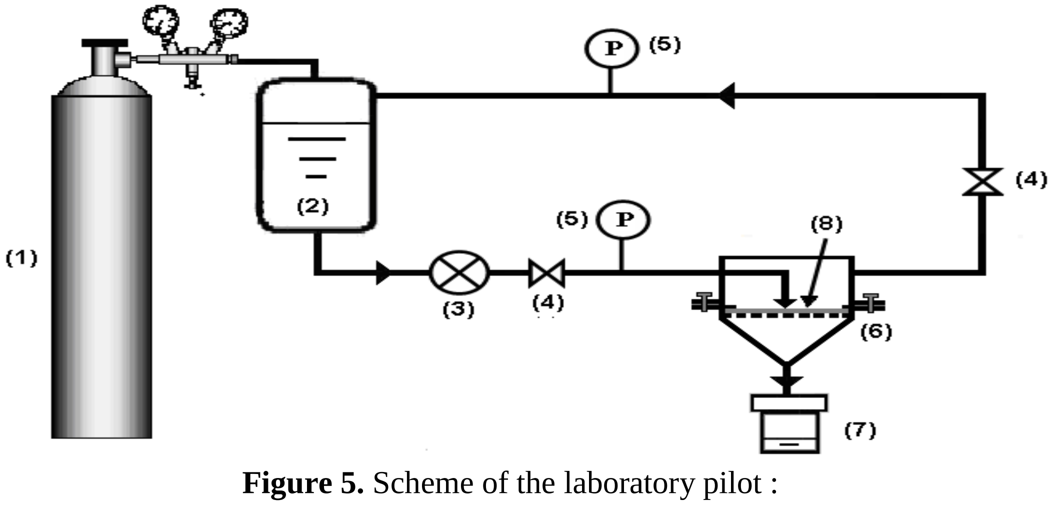


Figure 5. Scheme of the laboratory pilot :

(1) N_2 cylinder, (2) feed solution, (3) pumps, (4) valve, (5) manometer, (6) membrane cell, (7) permeate collector, (8) membrane.

Results and Discussion

XRD and SEM investigation

Figure 1 shows the XRD patterns of the raw substrate (a), the NaA zeolite crystal (b) and the as-synthesized NaA membranes (c) on the seeded substrate. The predominant clay mineral is as follow: Illite : d = 9,92 ; 4,97; 3,19 Å, Kaolinite : d = 7,14 ; 3,53 Å, Smectite : d = 4,47; 2,49 Å, Feldspath: d = 3,85 ; 3,03 ; 2,89 Å and quartz: d = 4,25 ; 3,9; 3,19 Å. These results are in good accord with the chemical composition of the clay support used (Table 1).

Table 1: Chemical composition of the clay support

Oxydes	SiO_2	CaO	Al_2O_3	SO_3	Fe_2O_3	MgO	K_2O
% en oxyde	43 ,60	14,46	13,20	0,04	5 ,18	2,52	2,30

The typical diffraction peaks of NaA crystals (10.1Å, 12.4Å, 16.1Å, 21.6Å, 24.0Å, 27.1Å, 29.9Å, 34.2Å and 54.3Å.) has been observed, suggesting the formation of NaA crystals on the surface of the clay substrate.

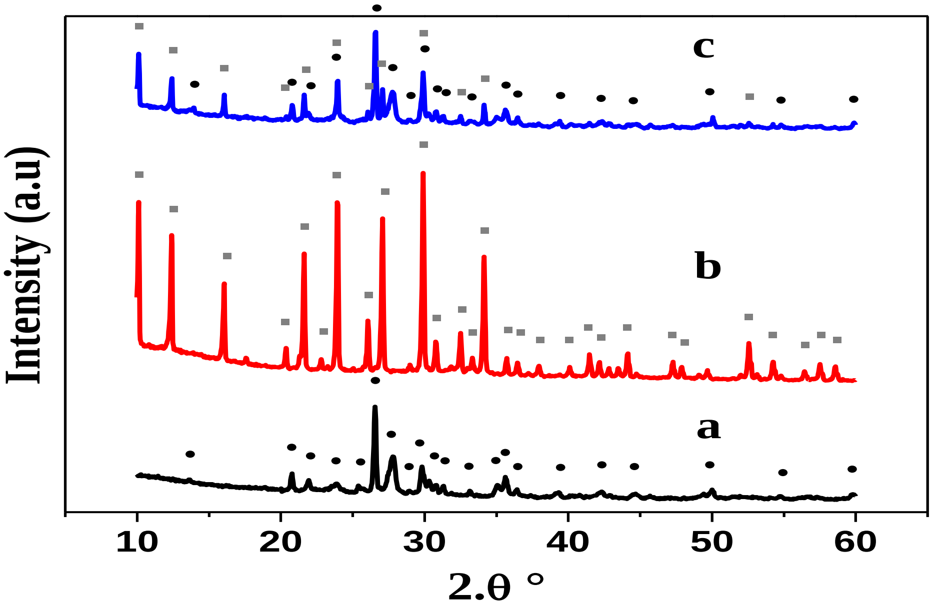
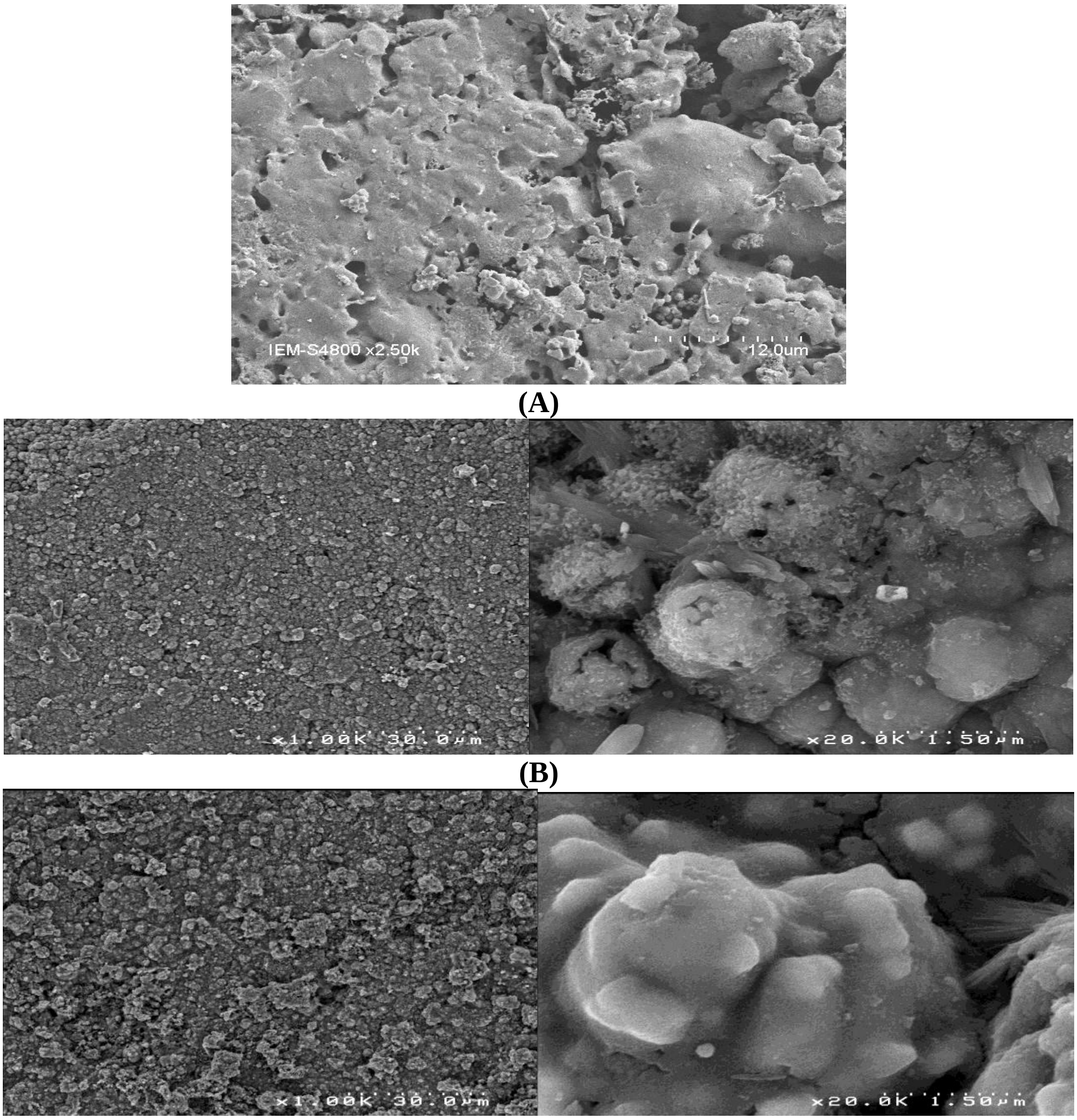


Figure 1. XRD patterns of: (a) substrate, (b) NaA zeolite crystals and (c) as-synthesized membrane (synthesis temperature of 60 °C), obtained after seeding the clay support; (●) support (■) NaA zeolite

Figure 2. shows the SEM micrographs of the as-synthesized NaA at different temperatures. For T = 40 °C and T = 50 °C the surface of the support is covered by a discontinuous NaA zeolite layer with no clear crystalline appearance (Figure 2. (B) and (C)). After a synthesis at 60 °C (Figure 2. (D)), the typical cubic morphology of zeolite LTA (Linde Type A) crystals almost covers the whole support surface. The size of the zeolite crystals ranges between 0.3 and 0.9 µm.

N_2 permeation measurements

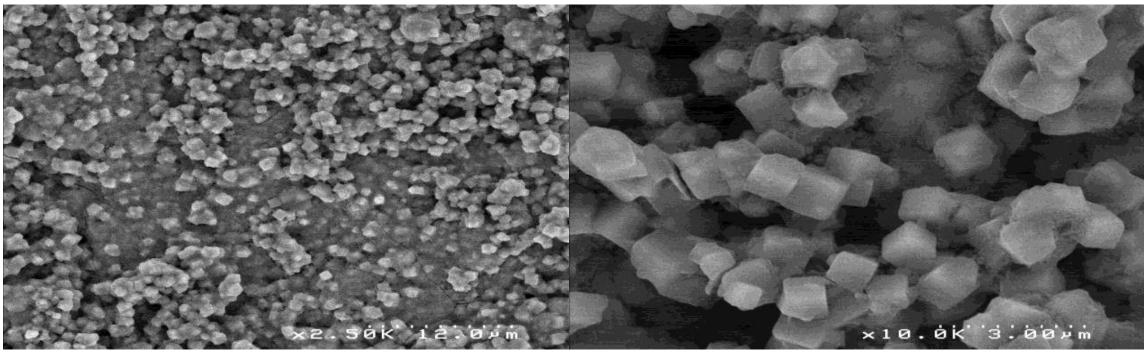
XRD and SEM indicate whether a continuous membrane is formed on the support; however, they provide no information on the permeation peformances of the zeolite membrane obtained[1,20]. The best way to evaluate the quality of the zeolite membranes is to perform gas permeation experiments[1]. N_2 permeation through three zeolite membranes, synthesized on clay support A with additive carbon (C), was measured at room temperature under different pressure difference (Figure 3). These three membranes have been named ACZA-T, where ZA is the zeolite type A and T is the synthesis temperature.



(A)

(B)

(C)



(D)

Figure 2. SEM micropgraphs (top view) of the as-synthesized NaA zeolite membranes obtained after seeding the clay support at different synthesis temperature : (A) support; (B) 40 °C; (C) 50 °C; (D) 60 °C

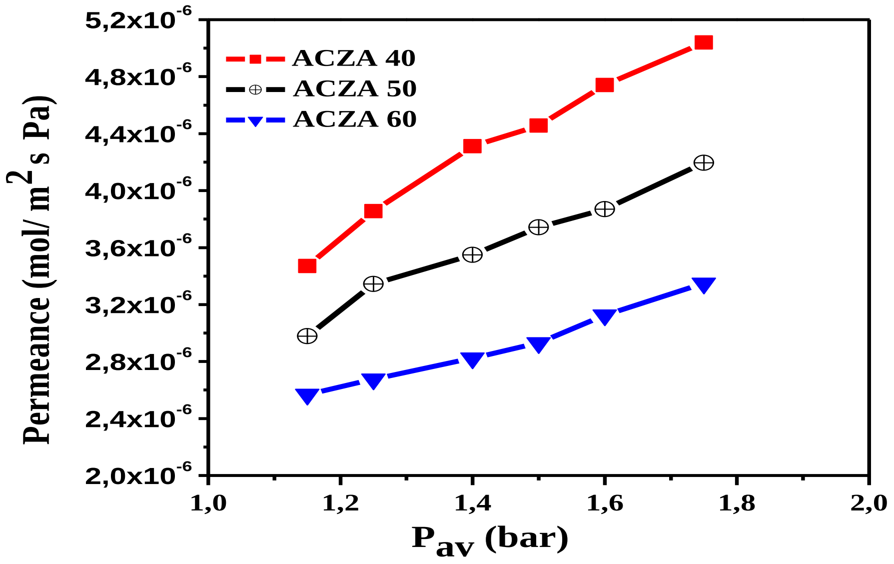


Figure 3. N_2 permeances of as-synthesized NaA zeolite membranes

Table 2. presents the N_2 permeation properties of the NaA zeolite membranes. It shows that the permeance of nitrogen decreased with the increase of the synthesis temperature and that the sample ACZA-60 presents the biggest Knudsen diffusion. This evolution can be related to the structure of crystallites formed at each synthesis temperature.

Table 2: The as-synthesized NaA membranes, their corresponding synthesis conditions and N_2 permeation properties

Membrane code	Synthesis conditions				N_2 permeance (10^{-6} mol/m^2 s Pa)	Knudsen diffusion
	seeding	Synthesis time (h)	Final synthesis temperature (°C)	Synthesis stage		
ACZA-40	Yes	24	40	1	3.6	17
ACZA-50	Yes	24	50	1	2.9	31
ACZA-60	Yes	24	60	1	2.0	50

Filtration tests of heavy metal

Prior to performing the solute rejection experiments, the water flux of ACZA-60 was measured by passing deionized water through the membrane. The result is illustrated in

Figure 4. The permeate flux varies linearly with the applied pressure, and the average permeability is equal to 117 L h^{-1} m^{-2} bar^{-1}.

Rejections of some heavy metallic cations such as Pb(II), Zn(II) and Cr(VI) as oxides were investigated for membrane ACZA-60 as a function of time at a given pH. Table 3 shows that Pb(II) and Zn(II) rejections increased rapidly to 99 % in 1h, while the rejection of CrO_3 stays low at comparables times.

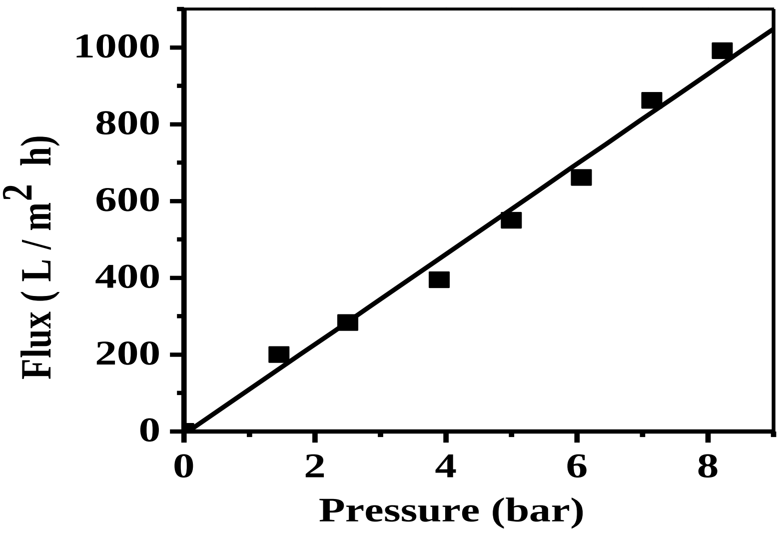


Figure 4. Water flux through the membrane ACZA-60 vs. working pressure

Since the isoelectric point (IEP) of NaA zeolite is 8.2[21] and since the pH of the treated solutions are lower than this value, the surface of the NaA zeolite membrane should be charged positively. For $PbCl_2$ and $ZnCl_2$, the majority of species in solution pH are Pb^{2+} and Zn^{2+}, respectively. The latters, because of their positive charge, will be repulsed by the membrane (in the same way charge), a fact which explains their big rejection (about 99% after 1 hour of filtration). As for the oxide of chromium being under hydrated form, it is dissociated in solution according to the following equation:

$$CrO_3 + H_2O \rightarrow 2H^+ + CrO_4^{2-}$$

On the other hand, it is known from the stability diagram for Cr (VI)–H_2O system, chromate anions, CrO_4^{2-} are dominant species at pH = 8 whereas acid chromates, $HCrO_4^-$ are the dominant ones at pH = 2. Therefore, the chromates species which are charged negatively reject small quantity of the Cr(VI). The increase in ion rejection with permeation may be explained by the partial fouling of the membrane and the ratio of $HCrO_4^-/CrO_4^{2-}$ species[22,23].

Table 3. Rejection of different heavy metals (P = 9 bar, feed concentration C = 10^{-4} mol L^{-1})

	Time (h)	**R (%)**
$PbCl_2$ pH = 5.6	**0.5**	**98**
	1	**99**
	1.5	**99**
	2	**99**
$ZnCl_2$ pH = 7.1	**0.5**	**91**
	1	**99**
	1.5	**99**
	2	**99**
CrO_3 pH = 3.3	**0.5**	**7.5**
	1	**12**
	1.5	**18**
	2	**21**

Conclusion

In sum, NaA zeolite membranes were successfully synthesized on a low cost seeded clay support made of the Meknès region (Morocco). Temperature played an important role in the formation of a continuous membrane. The best NaA zeolite membrane was obtained for a synthesis temperature of 60 °C (synthesis time of 24 h). Desalination of aqueous solutions with the obtained NaA zeolite membranes was investigated. The results indicated that zeolite membranes, especially LTA may be particularly useful for the separation of ions from solutions.

As it has been proved in this work, the results are promising, and since the type of support used for these membranes is not expensive, it seems worth pursuing further studies on desalination using these type of membranes.

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