Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1095121

57 (2016) 17473–17482
August

Taylor & Francis
Taylor & Francis Group

Removal of NO_3^- by (cordierite/ZrO_2) membrane modified by microparticles

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Received 17 January 2015; Accepted 13 August 2015

ABSTRACT

This work aims at improving ceramic membrane selectivity by modifications of surface using inert solid biomaterials as adsorbents. Filtration experiments were performed with a ceramic tubular membrane cordierite/ZrO_2 (pore size 0.2 μm). This membrane has been modified by formation of a dynamic layer at the surface of the microfiltration membrane during the circulation of vegetal suspension. This study reports the results of the retention of NO_3^- by this new membrane system and we compare these results with those of the non-modified membrane (cordierite/ZrO_2). The influence of concentration was also studied. The images obtained by scanning electron microscopy of the surface and the transverse section of the modified membrane are commented. The results obtained are encouraging and show the possibility of using this process for the purification of polluted water by ions such as NO_3^-.

Keywords: Cordierite/ZrO_2/membrane; Incorporation; Microfiltration; Ultrafiltration

1. Introduction

Pollution of ground and surface waters by nitrates is a wide spread and serious problem. This pollution is caused by industries' rejections, human activity and especially by fertilizers used for intensive agriculture. The maximal admissible nitrate concentration for drinking water is fixed at 50 ppm. The classical processes used for nitrates' elimination in drinking water are ion exchange, biological denitrification and electrodialysis, but they are rather complex to execute and can also give rejections. Consequently, microfiltration associated with adsorption seems to be able to be used for the treatment of this pollution.

The goal of this work was to present the results obtained by the elimination of nitrates by means of a coupled adsorption/filtration low-cost process to achieve comparable results of reverse osmosis and nanofiltration.

Many studies have been consecrated to ameliorate the selectivity of the ceramic membranes, either by the synthesis of highly selective membranes, or by the modification of their surface by the formation of a polymer film, or by grafting, or deposition of a layer [1–4], looking at modifying the property of membrane in order to improve these performances.

The membrane filtration used in this study was obtained by incorporation of the microparticle through the cordierite/zirconia membrane; by circulation of the vegetable suspension (water/inert solid biomaterials

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(ISBMA)), several dried particles have been tested; the ISBMA used in this study is a dried form of *Carpobrotus edulis*.

The results of the retention of NO_3^- ions by this new membrane system from $C_i = 100$ mg/l are more important than those of the classic membrane (cordierite/ZrO_2) without any modification. The influence of C_i on NO_3^- retention was also studied.

2. Materials and methods

2.1. Materials

2.1.1. Microfiltration membrane (cordierite/ZrO_2)

Cordierite powders (0–125 µm) mixed with some organic additives were extruded to form, after firing, a porous tubular support for microfiltration membrane. The elaboration process was described by Loukili et al. [5] and Saffaj et al. [6] (Fig. 1): After drying at room temperature, the support was sintered at 1,275˚C for consolidation. Then, the zirconia ZrO_2 layer was deposited on the inner surface of the cordierite support by slip casting. The porosity of cordierite support is 40% and the pore size is in the range of 7 µm. The mechanical resistance of the support (15 MPa) is strong enough to consider its use for filtration application under pressure. After drying at room temperature, the ZrO_2 membrane was treated at 300˚C for 1 h before being sintered at 1,100˚C for 2 h. The pore diameter of microfiltration layer is 0.23 µm. Scanning electron micrographs of the microfiltration layer revealed a uniform thickness with an average value of 23 µm. The characteristics of cordierite support and zirconia microfiltration layer are summarized in Table 1.

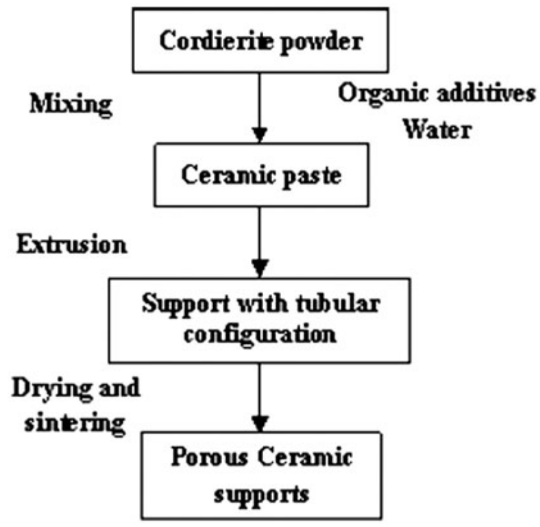

Fig. 1. Simplified diagram for elaboration of porous support by extrusion method.

2.1.2. Inert solid biomaterials

The ISBMA used in the present work were obtained from ground dried particles of *C. edulis* plant, which grow in the Agadir (Morocco) area. Several studies show that this plant can be used as adsorbents to fix metal cations (Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) and mineral ions (HPO_4^{2-}, $H_2PO_4^-$ and NO_3^-) with high efficiency [7–10]; this is explained by the presence of a chelating group (carboxylate, amino-group, etc.) in the vegetal residue [11–13]. These inert solid biomaterials are non-toxic and used in medical treatments [14]. From where the idea to associate the adsorbent performances of these ISBMA and the performances of microfiltration. The size of the biomaterial grains used in this study is lesser than 10 µm, in majority <2 µm (Fig. 2).

2.1.3. Modified membrane cordierite/ZrO_2/ISBMA

The modified ceramic membrane is elaborate while circulating a mixture of distilled water + ISBMA through the membrane cordierite/ZrO_2; after stability of flux, we obtain a modified membrane cordierite/ZrO_2/ISBMA (Fig. 3). The difference between the mass of the two membranes represents the amount fixed on the surface of zirconia. Fig. 4 shows the variation of flow during the fixing of ISBMA.

A comparison of fluxes in the absence and presence of ISBMA shows a progressive reduction in flux

Table 1
Characteristics of cordierite support and microfiltration layer

	Composition	Average pore diameter (µm)	Porosity (%)	Thickness (µm)	Mechanical strength (MPa)	Filtration area (cm^2)
Support	Cordierite (0–125 µm)	7	40	–	15	20
Microfiltration layer	ZrO_2 (8 m^2 specific area)	0.23	–	23	–	20

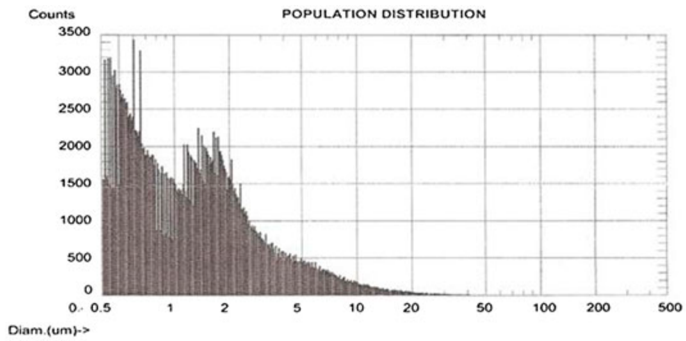

Fig. 2. *C. edulis* particle size distribution.

(20% in comparison with cordierite/zirconia membrane). The flow increases as a function of time; it is stabilized after 2 h of ISBMA circulation in suspension. The stability of flow would be an indicator of the occupation of the surface of layer by ISBMA and the formation of a new microlayer.

2.2. Methods

2.2.1. Solutions and pilot of filtration

The solutions were prepared from KNO_3 dissolved in bi-distilled water. We used a filter driver (Fig. 5) in the laboratory; it is a metal casing of stainless steel to receive a membrane length of 15 cm. A pump used to circulate the solution is discussed in the membrane mode tangential to limit clogging thereof. The fluid is recycled in the feed solution and the permeate through the membrane is collected and retained for the analysis of metal cation content. In our study, we circulated a volume of solution of 0.3l.

2.2.2. Analytical methods

The characterization of *C. edulis* plant was carried out using scanning electron microscopy (SEM), EDX spectrum and IR spectrum. The characterization of surface of the cordierite/ZrO_2 membrane and the modified membrane cordierite/ZrO_2/ISBMA was performed using SEM.

The levels of NO_3^- were determined by atomic absorption using a Varian spectrometer model. The pH solutions before filtration were measured using a pH meter.

Microfiltration, as any other membrane filtration process, is characterized by two parameters: solvent flow J (Volume/(Unit area. Unit time) and solute rejection, R, which is defined by:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

where C_p and C_f are the permeate (downstream) and feed (upstream) concentrations of solute respectively. Since the solvent flow determines the economic efficiency of the process, it is important to obtain as high a flow rate and a rejection factor as possible.

3. Results and discussion

3.1. Characterization of C. edulis plant

3.1.1. Morphology of C. edulis microparticles

SEM is widely used to study the morphological features of the particles. SEM photographs of *C. edulis* microparticles (Fig. 6) indicate the presence of grains and organic fibres in the structure. We can also observe the pores in structure.

3.1.2. Atomic composition of C. edulis

EDX spectrum (Fig. 7) shows the presence of O, C, Ca, Si, S, Al, Na and Mg in the dried *C. edulis*. The chemical composition of *C. edulis* plant is: 5.27% Ca, 4.00% Si, 29.05% C and 52.48% O. These have been known as the principal elements of *C. edulis* particles.

3.1.3. IR spectrum of C. edulis

The results of IR are quite helpful in the identification of various forms of minerals present in the biomaterial. The IR of *C. edulis* plant used in this study is shown in Fig. 8. This spectrum presents typical absorption bands found in the IR spectrum of the biomolecules (Fig. 9) [15]. IR spectra of these biomolecules show an absorption band at 3,300 cm^{-1} corresponding

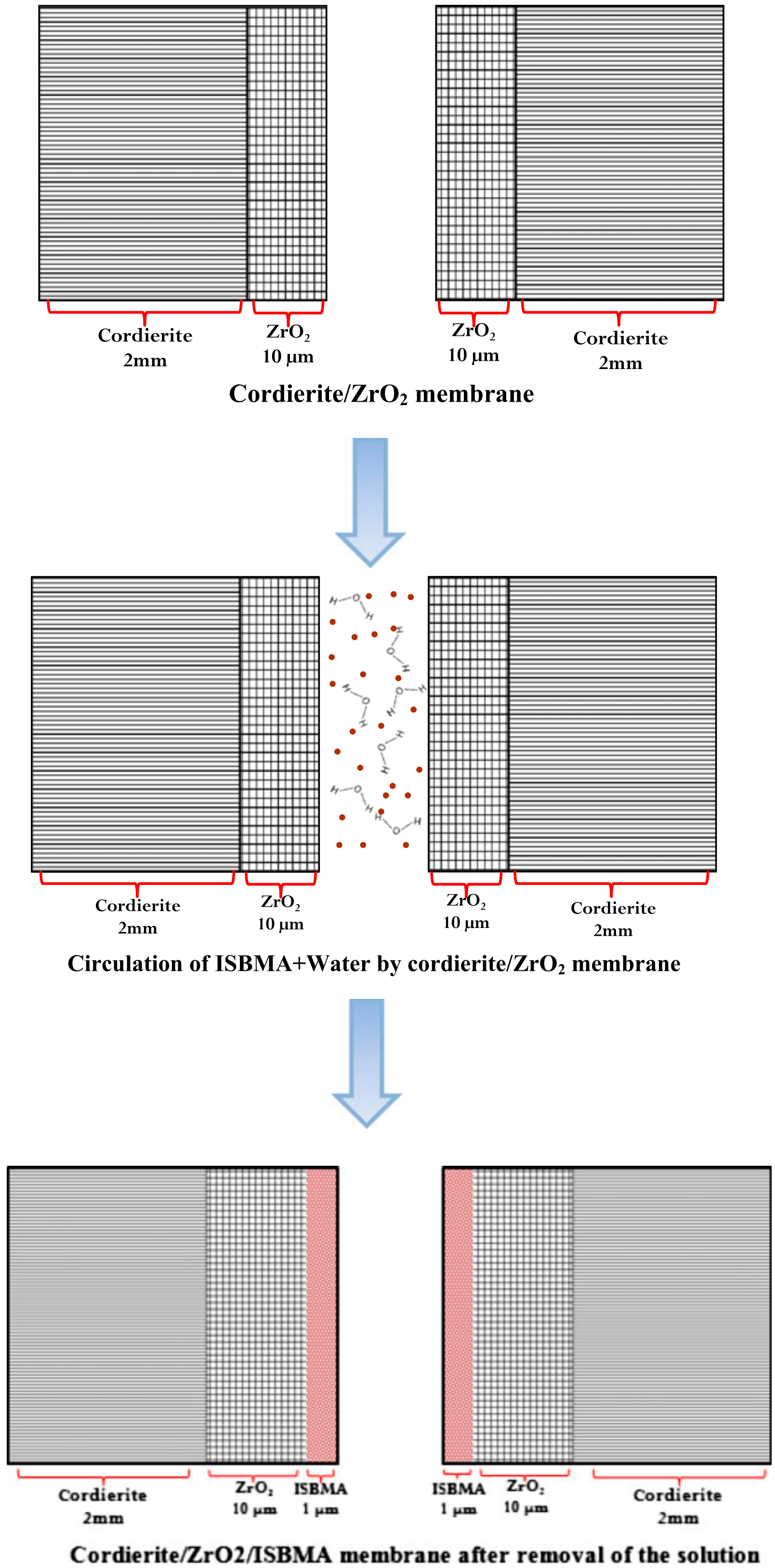

Fig. 3. Cordierite/ZrO_2/ISBMA membrane preparation.

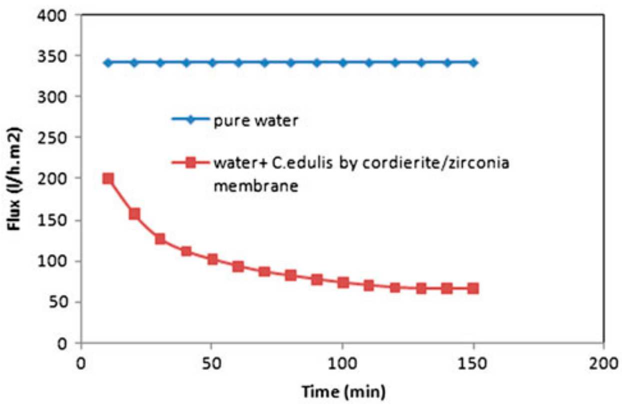

Fig. 4. Variation of flow of distilled water + ISBMA as a function of filtration time.

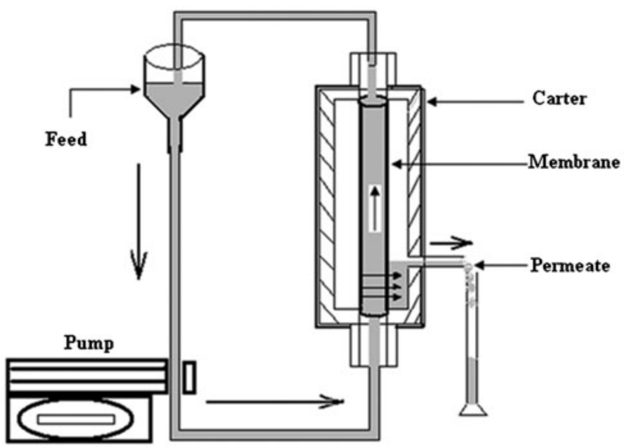

Fig. 5. Schematic of the pilot system.

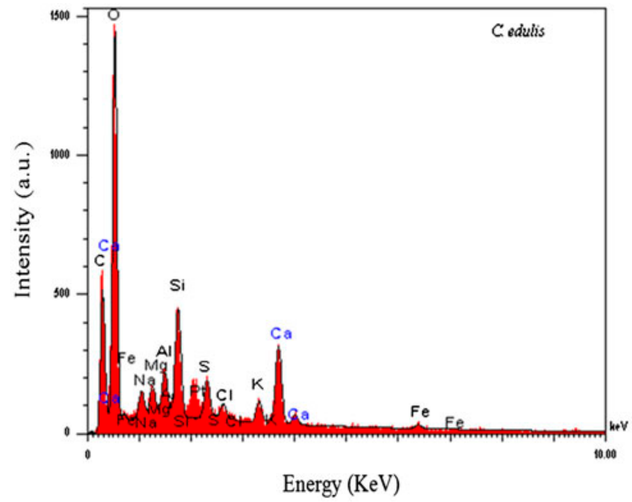

Fig. 7. EDX spectrum of *C. edulis* particles.

to hydroxyl (OH) and amine (NH) groups; the broad peak at 2,900 cm^{-1} can be attributed to the vibration absorption band of the –CH group. The peak located at 1,600 cm^{-1} is a characteristic of the carboxyl group. The peaks at 1,010 and 1,310 cm^{-1} can be assigned to alcohols. These chelating groups would play a major role in the efficient adsorption of *C. edulis* [16–18].

3.2. Characterization of the membrane cordierite/ZrO_2

The membrane of cordierite/ZrO_2 constituted the microfiltration membrane of zirconia, pore diameter = 0.2 m, deposited on a support of cordierite, pore diameter = 8 μm. This support ensures the mechanical strength of the membrane. The membrane is in the form of a tube of 15-cm length and 1-cm outside

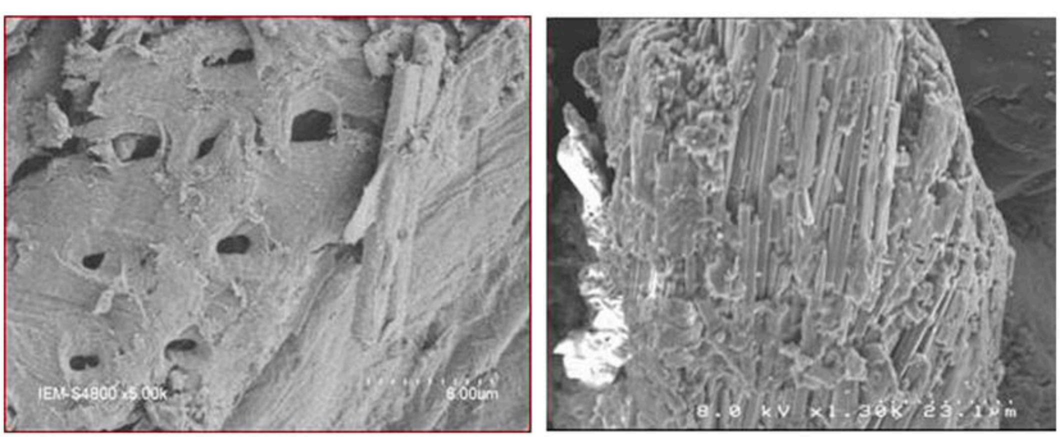

Fig. 6. SEM of *C. edulis* particles.

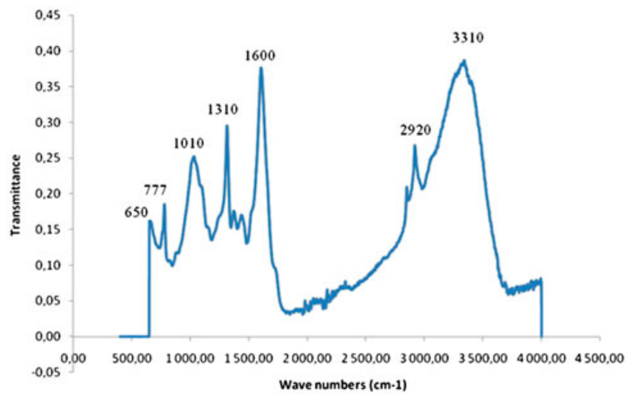

Fig. 8. IR spectrum of *C. edulis*.

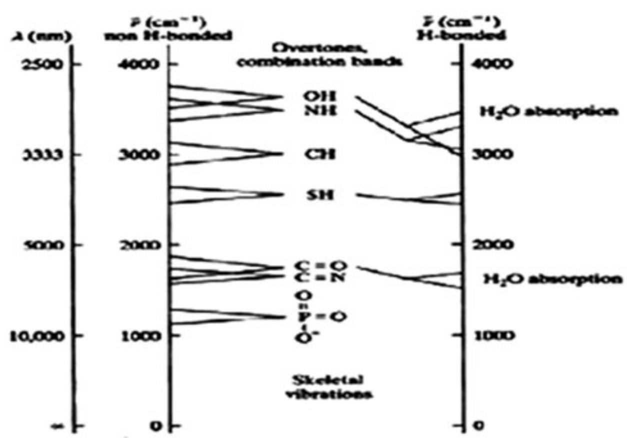

Fig. 9. Typical bands of the biomolecules.

diameter; and 0.5-cm diameter inner layer of microfiltration membrane is exceeded within the tube by a technique of casting slep a slip based on ZrO_2 and various additives to obtain a deposit of satisfactory quality. Examination by electron microscopy to view the support and microfiltration layer ZrO_2 thickness of 23 μm. Developed filter surface is approximately 15 cm^2 (Fig. 10). The flow of this membrane is about 350 l/h m^2.

3.3. Characterization of cordierite/ZrO_2/ISBMA membrane

The SEM of the surface and cross section of cordierite/ZrO_2/ISBMA membrane show the deposit of a thin layer (1–2 μm) on the surface of the zirconia membrane. The formation of this new dynamic membrane with a smaller pore size can be used to filter solutions of metal cations. The origin of this deposit can be attributed to the fixation of some soluble macromolecular compounds present in the suspension filtered in

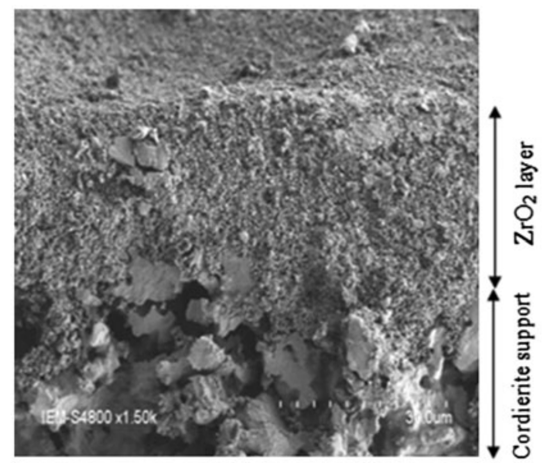

Fig. 10. Scanning electron micrographs of cordierite/ZrO_2 membrane.

contact with the zirconia membrane (Fig. 11). The flow of this membrane is about 60 l/h m^2.

The quantity of ISBMA inside the cordierite/ZrO_2 membrane is about 50 mg.

3.4. Filtration of NO_3^-

3.4.1. Effect of filtration time

This study was made at $C_i = 50$ mg/l with simple solutions of NO_3^- (solution of KNO_3). The experiments were done at $T = 25$°C (Fig. 12). The comparison of these rate eliminations with the process of filtration by cordierite/ZrO_2 membrane (without modification) shows that the retention of these metal ions by the cordierite/ZrO_2/ISBMA is more significant than the

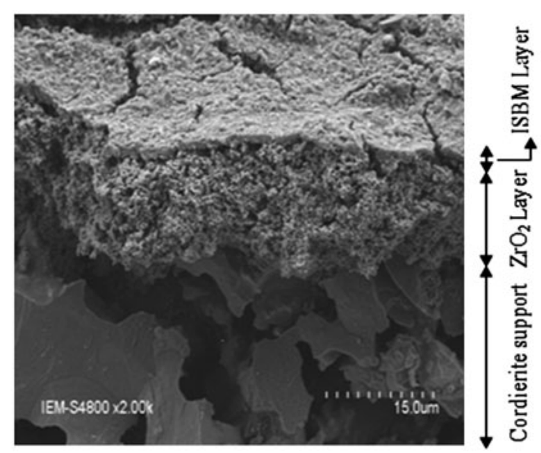

Fig. 11. Scanning electron micrographs of cordierite/ZrO_2/ISBMA membrane.

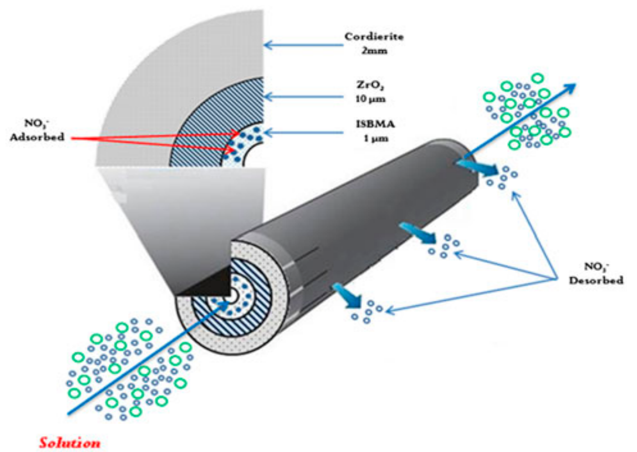

Fig. 12. Rejection of NO_3^- by cordierite/ZrO_2/ISBMA membrane.

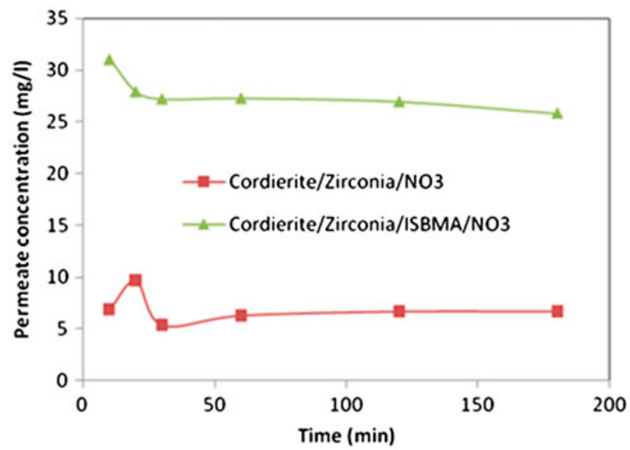

Fig. 13. Permeate concentration of NO_3^- as a function of time.

ceramic membrane cordierte/ZrO_2, which is four times more important. The results are illustrated in Fig. 13 and Table 2.

Many studies of the nitrate filtration with nanofiltration or ultrafiltration membranes have been described in the literature:

(1) P. Blanc synthesized in 1995 [19] several membrane-based hafnines, they have pore diameters from 1.4 to 2 nm. For membranes calcined at 450˚C, the retention rate obtained is in the order of 48% at pH 6.2 for $C_i = 10^{-3}$ mol/l $NaNO_3$.

(2) S. Alami Younssi has developed a membrane γ alumina in 1994 [20]. This membrane has a pore diameter = 0.8 nm when it is calcined at 450˚C. At $C_i = 10^{-2}$ mol/l of $NaNO_3$ and KNO_3, the rejection rate = 55 and 70% at pH 5.5, respectively, for $NaNO_3$ and KNO_3.

(3) G. Morel et al have investigated the filtration of nitrate ions by ultrafiltration membrane-based cellulose acetate modified by surfactants [21]: tetradecyl trimethyl ammonium bromide (TTAB), hexadecyl trimethyl bromide chloride (HTAC) and hexadecyl pyridinium chloride (HPC), retention rates obtained are in the order of 81, 94 and 90%, respectively, with TTAB, HPC and HTAC at an initial concentration of nitrate ions = 500 ppm. The results obtained by modified cordierite/zirconia/ISBMA membrane are significant than the conventional cordierite membrane/zirconia result. 50 mg/l NO_3^- is equivalent to 10^{-3} M, and we have about 52% retention. The percentage removal of nitrate ions, at low concentrations, is similar to the retention obtained with the nanofiltration membranes mentioned above.

3.4.2. Effect of initial concentration

The initial concentration varies from 100 to 200 mg/l. The modified membrane was prepared according to the method described previously.

Figs. 14 and 15 show the evolution of flux and permeate concentration of NO_3^- ions as a function of filtration time. It can be observed that the stabilization of the flux through the membrane takes approximately 60 min, and the retention of NO_3^- ions is stable with time from the first few minutes, except for $C_i = 200$ mg/l. The retention of nitrates is very significant and the performance remains stable in time. This may be caused by adsorption on the membrane surface during the experiment runs. The results can't interpret the natural adsorption, we can sign the

Table 2
Retention rate of NO_3^- through both membranes ($C_i = 50$mg/l)

	Cordierite/ZrO_2	Cordierite/ZrO_2/ISBMA
Permeate concentration (mg/l)	6.4	27.3
Retention rate (%) = $(C_p/C_i) \times 100$	12.8	54.6

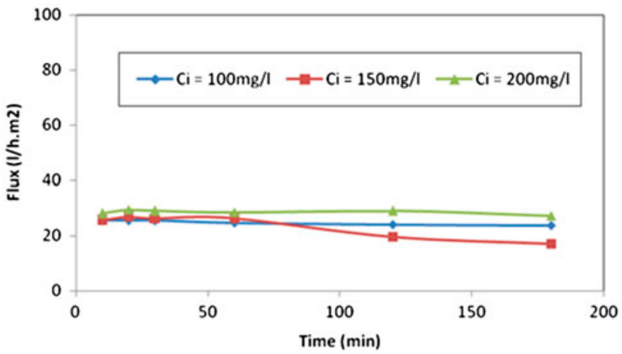

Fig. 14. Variation of flux of NO_3^- as a function of time and concentration.

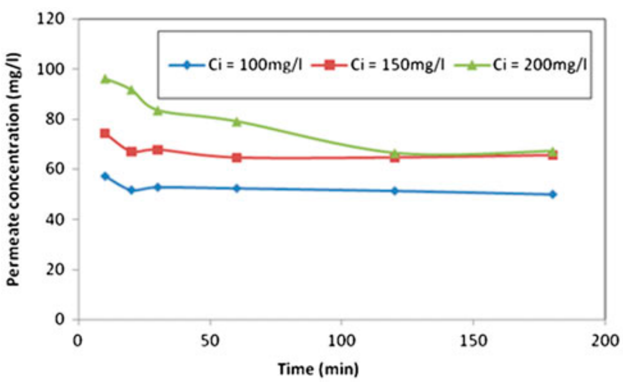

Fig. 15. Retention of NO_3^- as a function of time and concentration.

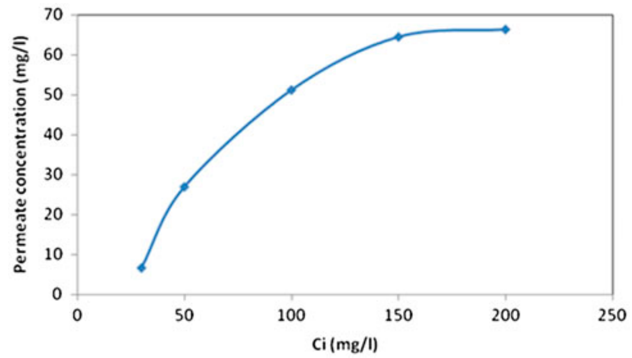

Fig. 17. Retention of NO_3^- as a function of concentration.

existence of equilibrium adsorption/desorption of NO_3^- from both sides of the membrane, got it the multiplicity of functional groups of ISBMA and we can suggest that the layer covering the zirconia is present as an exchange-ion membrane (Fig. 16).

Since the purpose of ultrafiltration membranes is to concentrate the effluent, it was important to have an idea of the influence of the concentration on the performance. In the microfiltration membrane (diameter of pore = 0.2 µm), concentration plays a significant role. For the NO_3^- solution, it can be observed in Fig. 17 that the retention increases as a function of C_i and it does not reach saturation.

Table 3 shows the retention of this ion at different initial concentrations after 60 min of filtration.

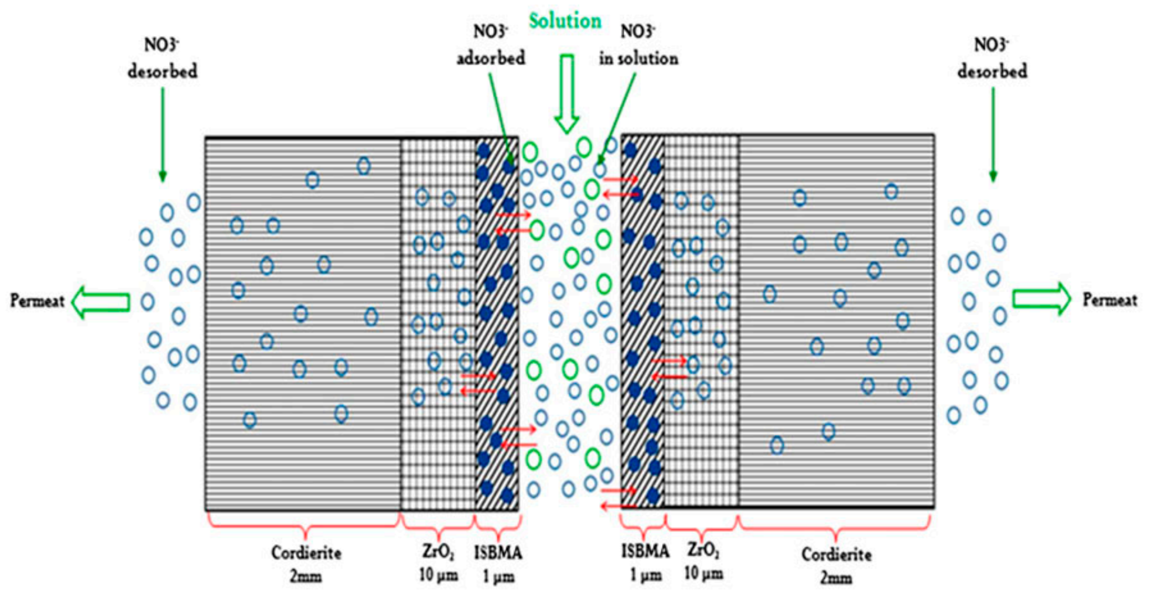

Fig. 16. Equilibrium of the cordierite/ZrO_2/ISBMA membrane.

Table 3
Retention rate of NO_3^- by modified membrane at different C_i (T = 1 h)

C_i (NO_3^-)	50 mg/l	100 mg/l	150 mg/l	200 mg/l
Retention rate (%)	54.6	52.2	43	39.5

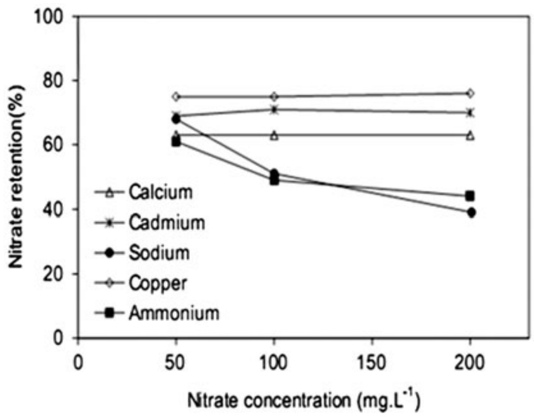

Fig. 18. Evolution of the rejection rate of NO_3^- as function of C_i for different salts.

Retention of NO_3^- by the cordierite/ZrO_2/ISBMA membrane is important; it decreases until 39.5% with the increase in the initial concentration. This confirms the results obtained by L. Paugam [22] who studied the effect of initial concentration on the retention of NO_3^- (Fig. 18) ions by a composite polyamide membrane. In this study, the rate of NO_3^- decreases with C_i, when the monovalent cation is associated ($NaNO_3$ and NH_4NO_3), an increase in the concentration decreases the ectrostatic interactions by screen effect. But when combining NO_3^- with a divalent cation (Ca $(NO_3)_2$, Cu $(NO_3)_2$ and Cd $(NO_3)_2$), the rejection rate is stable at initial concentrations.

4. Conclusion

The retention of NO_3^- ions by the cordierite/ZrO_2/ISBMA is more significant than the ceramic membrane cordierte/ZrO_2 (four times more important).

The study with cordierite/ZrO_2/ISBMA showed that the retention is stable with time and depends on the initial concentration (the retention increases with C_i).

ISBMA modifies the surface properties of cordierite/ZrO_2 membrane. We can conclude that the cordierite/ZrO_2/ISBMA will be tested for the treatment of wastewater contaminated with NO_3^-.

Acknowledgements

We would like to specially thank the "comité franco-marocain pour la recherche" which supported this work in the frame of AI N° MA/128/05.

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