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Transfer of nitrate ions using a polymeric-surfactant membrane

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ABSTRACT

The polymer surfactant membranes used for the selective transport and separation of different species has emerged in recent years. In this work, a development of a novel class of surfactant membrane for performing nitrates ions elimination is reported. The influence of the composition of stripping solution on the separation of nitrate ions by Donnan dialysis using a polymeric membrane was studied. The membrane was prepared by dissolving a calculated amount of cellulose triacetate and poly-vinylpyrrolidone in chloroform after additive of polysorbate as surfactant. The obtained film after evaporation of the solvent is characterized by Fourier trans form infrared spectroscopy and thermo-gravimetric analysis. The degradation of the membranes occurs via two steps process whose main loss starts at 200°C is due to the thermal degradation of the polymeric chains. As application, cross ionic dialysis process was used, thus hydrogen ion from HCl medium give to the nitrate transference rather than Na^+ ion from saline medium. Transference percentage is approximately two times greater in HCl medium, and it reaches 41.5% when a synthetic membrane (SM) is used. The presence of chlorhydric acid in the strip compartment gives a rise to the nitrate transference from the feed compartment through synthesized or commercial membrane at ΔpH ~3.4 during 8 h. Some other parameters were studied, particularly time transference and composition of solution (water and saline medium). Furthermore it has been shown that SM has the same performance properties as commercial one.

Keywords: Polymer; Membrane; Removal; Nitrates; Dialysis

1. Introduction

Worldwide, the problem of nitrates contamination of drinking water supplies is severe and it is a problem of great importance in the world. Sources of nitrates contamination include the use of synthetic fertilizers, industrial and food processing operations and animal and human waste disposal. Since about 40 years the analyses carried out on surface water and underground waters revealed, in different countries, general and brutal increase of nitrate content.

The problems of nitrates in drinking water are well known and an excellent documentation of the

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nitrate–nitrite toxicity is given in [1]. Because of its link to several health hazards, limits have been set up regulating the maximum allowed level of nitrates in drinking water. The European Union allows a maximum of 50 mg/L nitrate in drinking water, but recommends a concentration of lower than 25 mg/L nitrate for treated water [2].

Contamination of drinking water by nitrate can be endangering health especially for infants. In babies younger than six months, nitrate can lead to methaemoglobinaemia, diarrhea and acidosis. NO_3^- can be reduced to NO_2^-, which combines with hemoglobin in the blood to form methaemoglobin, and leads to a condition commonly known as "blue baby syndrome" [3,4].

The elimination of nitrates from drinking water is a costly and difficult process. Among different methods used for this purpose, the ion exchange option has been applied for long times but relatively high cost [5], this technique has been taken over by microbiological denitrification only since last 25 years.

To remove nitrate from water several techniques are available: biological [6–10], chemical [11], catalytic or photo-catalytic [12–14] and physicochemical such as Donnan dialysis [15], electrodialysis [16–21], electrodeionization [22], reverse osmosis [23,24] and ion exchange [25–29].

The objective of this work is to study the influence of the dialysis parameters (flow rate, pH, nature of strip solution and membrane nature) on nitrate removal from ground water using an anion exchange membrane with a good selectivity towards nitrate. This in order to determine the optimum conditions to prevent the possible precipitation of bivalent salt in the concentrate compartment.

2. Experimental part

2.1. Chemicals

Potassium (I) nitrate, chloroform, cellulose triacetate (CTA 72,000–74,000 g/mol), poly-vinylpyrrolidone (PVP) and polysorbate used as surfactant were analytical grade reagents obtained from Fluka company. The aqueous phases were prepared by dissolving the different reagents in distilled water.

2.2. Membranes preparation

Polymer inclusion membranes were prepared according to the procedure reported by Sugiura et al. [30]. 0.2 g of CTA and 0.1 g of PVP were dissolved in 30 mL of chloroform and stirred for 4 h. Then, 0.1 mL of polysorbate was added under vigorous stirring during 2 h. The solution was transferred in a circular glass container, and the solvent was allowed to evaporate slowly during 24 h to obtain a polymer film with a smooth looking surface. The resulting membrane was extracted by addition of bi-distilled water and dried at 40°C.

2.3. Analysis

The concentration of nitrates at different time intervals was determined by specific ion method using Orion nitrate reference electrodes and specific Ion Meter. Cations were analysed by the atomic absorption spectroscopy technique using SpectrAA-110 Varian spectrometer. The other parameters (pH, temperature and conductivity) were determined following standard methods. Three independent experiments were realized to determine the different concentrations. The experimental standard deviation was determined to be ±5%. Fourier trans form infrared spectra were recorded on with Perkin-Elmer (Spectrum One) spectrophotometer. The thermo-gravimetric analyses (TGA) were achieved using a SETARAMTG96, thermal analysis instrument programmed from 30 to 600°C at rate of 10°C/min under the nitrogen atmosphere.

2.4. Transport

Transport experiments were carried out using a permeation cell in which the membrane film was tightly clamped between two compartments made of Teflon (Fig. 1). Both the source and receiving aqueous phases (1,000 mL each) were stirred at 800 rpm using a mechanical stirrer. The feed compartment

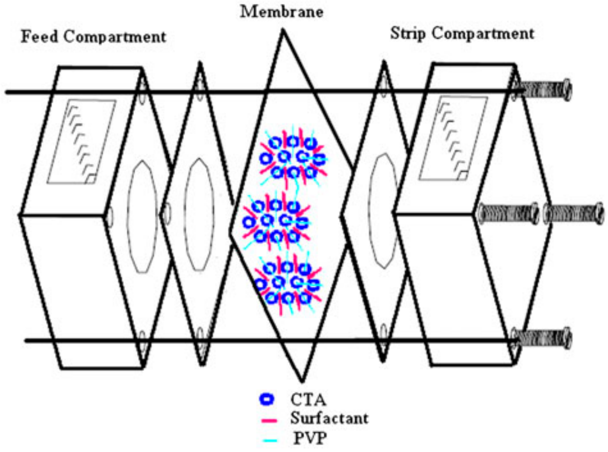

Fig. 1. Transport cell scheme.

contains the nitrate solution at a concentration of 200 ppm; the other compartment noted strip contains distilled water or HCl or NaCl. The experiments began when starting the stirring motors in the two compartments of the cell. The exposed membrane area was 49 cm^2. All the experiments were performed in a thermostat at 25°C.

3. Results and discussion

The membrane CTA—surfactant—polyelectrolyte was characterized using chemical techniques as well as TGA and FTIR.

3.1. Characterization by TGA

The TGA experiments were done using SETARAM TG96 equipment. Fig. 2 shows the TGA thermal behaviours of (CTA + PVP + surfactant) membrane. Based on this figure, the following observation can be made: The synthesized membrane breaks in two steps. The first step at 200–250°C represents the main thermal degradation of the polymeric chains. The second one starts at 350°C and represents the carbonization of the products to ash. This result confirms that the synthesized membrane shows a very good thermal stability.

3.2. Characterization by FTIR

Fig. 3 shows the spectrum of the CTA, polyelectrolyte (PVP), the surfactant (polysorbate) and CTA + PVP + polysorbate membrane, respectively. The main feature of these spectrums is an absorption band located around 1,755/cm, which is attributed to stretching vibrations of the carbonyl group. Bands at 1,237 and 1,011/cm correspond to the stretching modes of C·O bonds of carriers. Less intense bands at 2,922 and 2,890/cm are attributed to C·H bonds, and the wide band detected in the 3,472–3,100/cm region is attributed to the O·H bonds stretching modes. The obtained results showed that all the maximum values extracted from the spectrum of the CTA, PVP and polysorbate as references are presented in the modified membrane spectra in addition to those of the different molecules that also involve the same radicals.

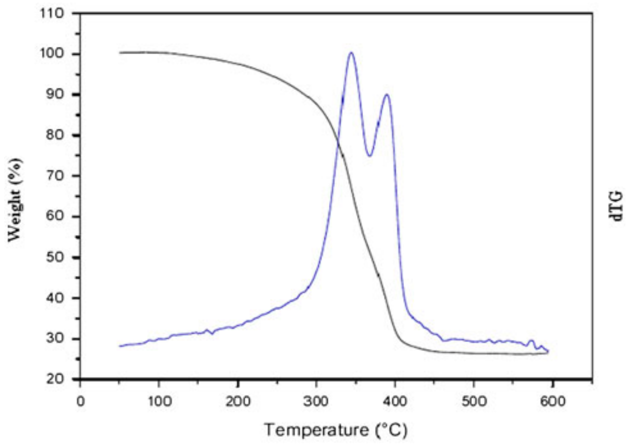

Fig. 2. Thermograms ATG/dTG of (CTA + PVP + surfactant) membrane. (10° C/min).

Table 1 collects the peak values and the corresponding radical of polymer + polyelectrolyte + urfactant membrane. This should suggest that no signs of covalent bond formation between the polymer, the polyelectrolyte and the surfactant, but only weak interactions between the different constituents of the membrane such as hydrophobic, Van der Waals and/or hydrogen bonds.

3.3. Membrane application

In Fig. 4, the transference amount of NO_3^- ion during time as a function of the nature of the composition of stripping solution is plotted.

In Table 2, the concentrations (mg/L) and the yield (%) of NO_3^- in the case of the three different medium are given.

It has been shown that the cross transference using chloride ions gives a higher transported amount of nitrate ions. Also, proton (H^+) seems to be better than sodium (Na^+) and causes its higher mobility. This is probably due to the great affinity of the modified membrane obtained in both sides, which enables chloride ions to pass from the strip to the feed compartment creating a potential gap that induces nitrate transference in the opposite direction. This behaviour agrees with our results found previously [31,32].

3.4. Variation of pH vs. time

In Fig. 5(a)–(c), the pH in the feed (compartment I) and strip (compartment II) vs. time using a synthetic membrane noted (SM) and a commercial membrane noted (CM) are represented. Results are given in the case of distilled water (a), HCl (b), and NaCl (c) in strip compartment.

It can be easily observed that the pH tendency is different in the different case. In water medium,

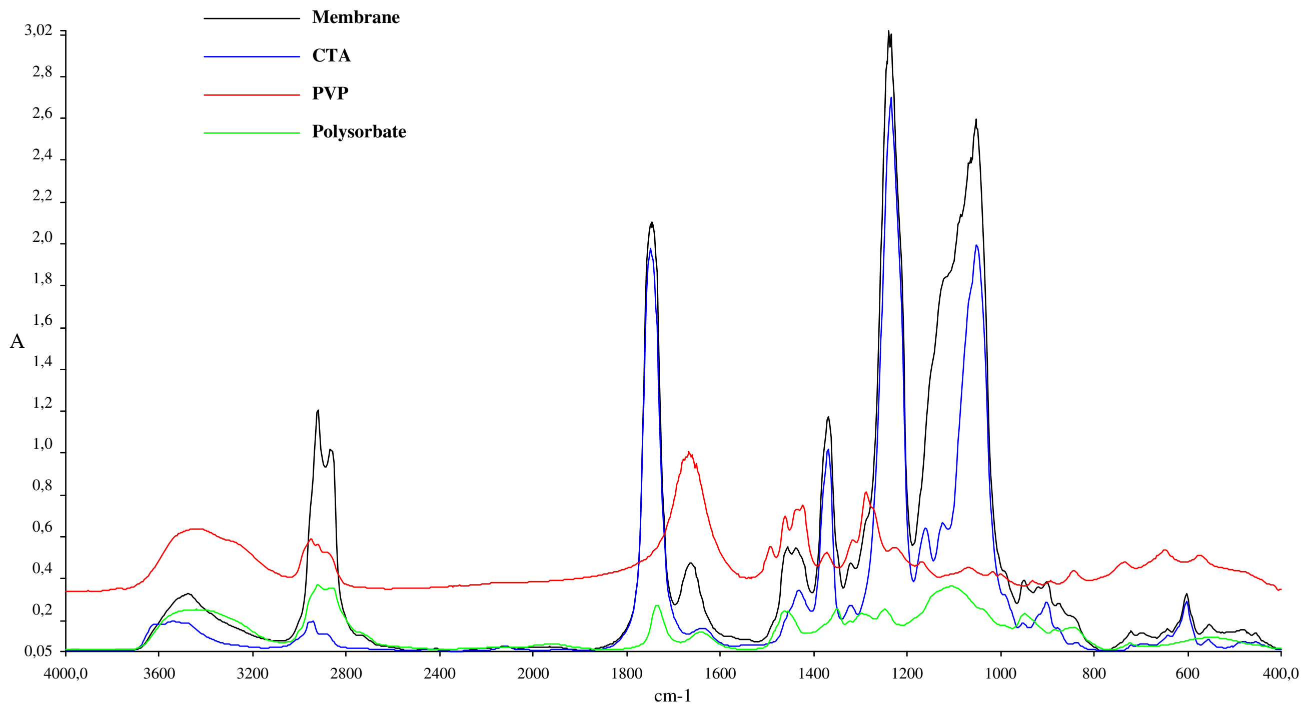

Fig. 3. FTIR spectrum of CTA, PVP, polysorbate and (CTA + PVP + polysorbate) membrane. Scans: 32 and resolution: 2/cm.

Table 1
Peak values and the corresponding radicals in different membranes elaborated

Membrane	Peak value/cm	Corresponding radicals
Cellulose triacetate (CTA)	3,476	O–H
	1,756	C=O
	1,239	C–O–C
	1,035	C–O–C
poly-vinylpyrrolidone (PVP)	2,954	C–H
	1,654	C=O
	1,493	C–N
Polysorbate (Surfactant)	3,449	O–H
	1,756	C=O
	1,249	C–O–C
(CTA + PVP + Polysorbate) membrane	3,476	O–H
	1,756	C=O
	1,559	C–N
	1,035	C–O–C

variation in pH value was only observed in the case of SM. This may be due to the low transference of nitrate ion contrarily to the case of CM. The presence of HCl in strip compartment decreases considerably with the value of pH in the feed solution using both membranes (commercial and synthetic). This result indicates that SM is very comparable to commercial one when HCl is used. However, a small variation of pH was observed in the case of NaCl in the stripping compartment.

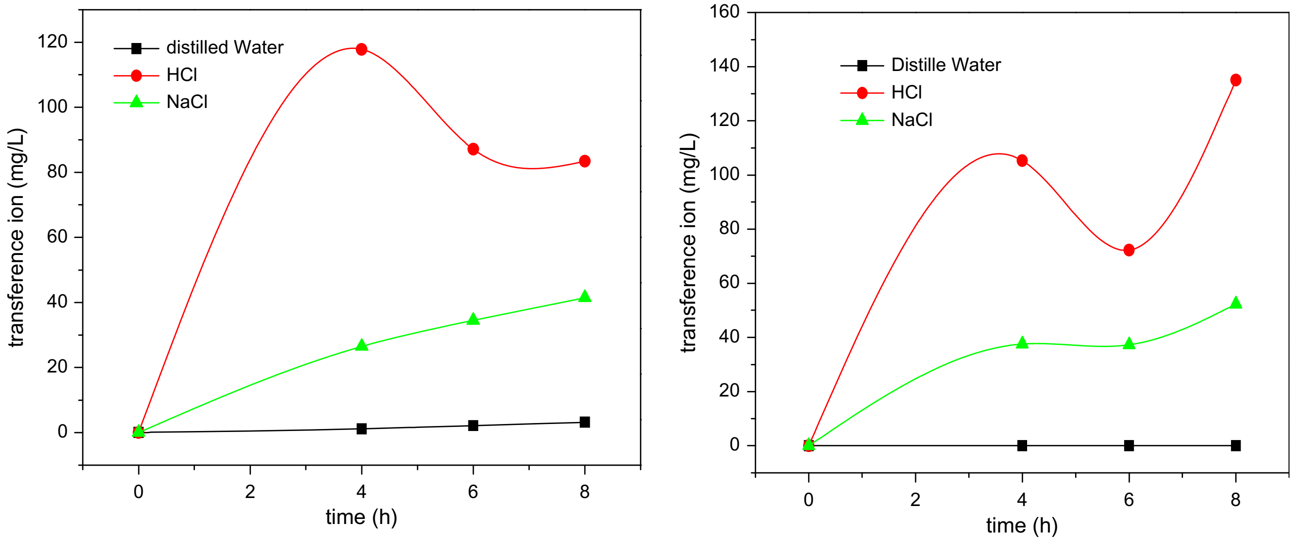

Fig. 4. Evolution of the concentration of nitrate ions in strip compartment: (a) SM. (b) CM. *T*: 25˚C, $[NO_3^-]_0$ = 200 mg/L, speed: 800 rpm.

Table 2
Yield and concentration of NO_3^- in strip compartment after 8 h of experiment

		Distilled water	NaCl	HCl
Synthetic membrane	Yield (%)	1.6	20.75	41.7
	Concentration (mg/L)	3.2	41.5	83.4
Commercial membrane	Yield (%)	0	26.15	67.5
	Concentration (mg/L)	0	52.3	135

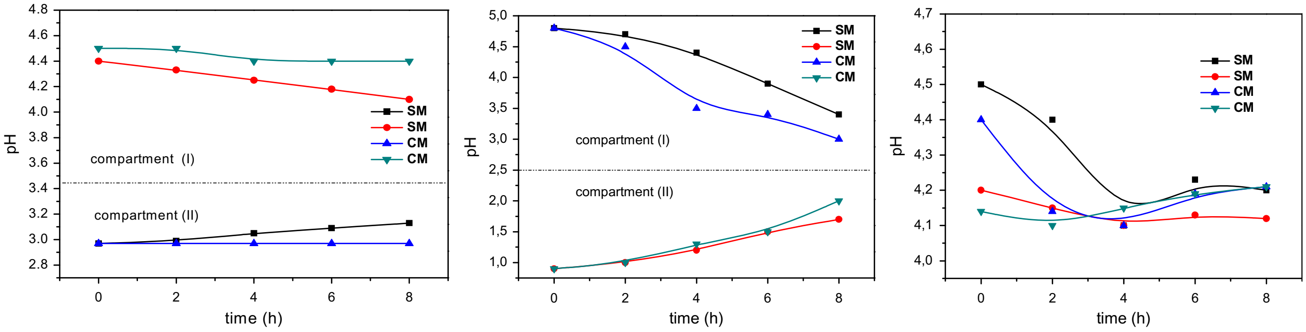

Fig. 5. pH against time for different membrane and medium. Strip compartment: Distilled water (a), HCl (b), and NaCl (c). SM: synthesized membrane, CM: commercial membrane. *T*: 25˚C, $[NO_3^-]_0$= 200 mg/L, speed: 800 rpm.

Fluxes are calculated after 8 h of ions transference in the case of the both membranes (synthesized and commercial) in the three different medium as follow:

The variation of the fluxes of nitrate ions across the synthesized and CMs vs. time using three different strip medium is reported in Fig. 6. An increase of the fluxes can be seen with HCl medium. Transference flux using the both membranes decreases in the sequence HCl > NaCl > D.W.

$$J_M = \frac{\Delta n}{S\Delta t}(\text{mol.cm}^{-2}.\text{s}^{-1})$$

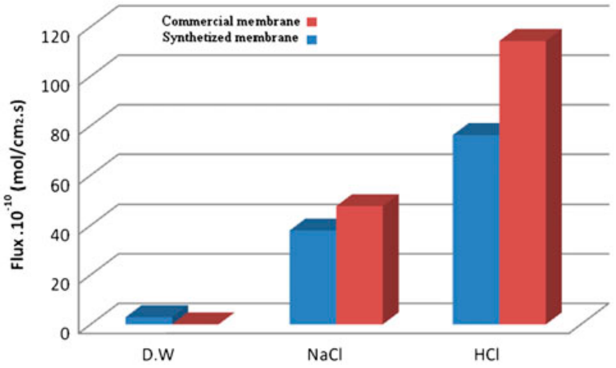

Fig. 6. Fluxes vs. time for different membrane and medium. *T*: 25°C, $[NO_3^-]_0$ = 200 mg/L, speed: 800 rpm.

4. Conclusion

A mixture of CTA and PVP and polysorbate membrane has been synthesized. This polymer + surfactant + polyelectrolyte membrane was characterized using chemical techniques as well as FTIR and TGA. The synthesized membrane degrades in two steps. The first step at 200–250°C represents the main thermal degradation of the polymeric chains. This result confirms that the synthesized membrane shows a very good thermal stability. The synthesized membranes present a dense and homogeneous structure.

As application, the study presented in this paper shows that the use of synthesized and CM as ionic exchanger permitted the transference of nitrate ions.

The membrane became more selective towards nitrate anion especially when the modification is realized by the addition of HCl in the strip compartment under the conditions of pH 4.5 in feed compartment and pH 0.9 in strip compartment during 8 h of transference.

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