

Selectivity and structural integrity of a nanofiltration membrane for treatment of liquid waste containing uranium

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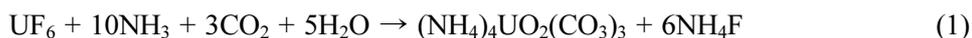
(Received May 17, 2012, Revised August 14, 2012, Accepted October 02, 2012)

Abstract. The performance of a nanofiltration membrane for treatment of a low-level radioactive liquid waste was investigated through static and dynamic tests. The liquid waste (“carbonated water”) was obtained during conversion of UF₆ to UO₂. In the static tests membrane samples were immersed in the waste for 24, 48 or 72 h. The transport properties of the samples (hydraulic permeability, permeate flow, selectivity) were evaluated before and after immersion in the waste. In the dynamic tests the waste was permeated in a permeation flow front system under 0.5 MPa, to determine the selectivity of NF membranes to uranium. The surface layer of the membrane was characterized by zeta potential, field emission microscopy, atomic force spectroscopy and infrared spectroscopy. The static test showed that the pore size distribution of the selective layer was altered, but the membrane surface charge was not significantly changed. 99% of uranium was rejected after the dynamic tests.

Keywords: nanofiltration; radioactive waste; uranium effluent treatment; polyamide; polymer stability

1. Introduction

The Brazilian Nuclear Fuel Factory (INB) is responsible for the production of nuclear fuel for PWR (Pressurized Water Reactor), adopted in Brazil for electricity generation. The production of uranium dioxide (UO₂) from the conversion of uranium hexafluoride gas (UF₆) is the most important stage in the nuclear fuel cycle. UF_{6(g)} is heated in an autoclave and vaporized in a vat containing demineralized water at 100°C, where it is mixed with two gases: carbon dioxide (CO₂) to prevent clogging of the injector nozzle of UF₆ gas and ammonia (NH₃), in order to avoid the reduction of U⁶⁺ to U⁴⁺ (Cunha. *et al.* 2011). The chemical reaction between these compounds produces ammonium tricarbonatouranate(VI), known as TCAU, a yellow solid insoluble in water. The global reaction is (Mellah *et al.* 2007)



After this process TCAU is dried in rotary vacuum filters. This process generates a liquid waste containing uranium known as “carbonated water” due to the presence of high concentration of CO₃²⁻ ions. This waste is originated from the washing of the gases produced at thermal hydrolysis of ammonium tricarbonatouranate(VI). This waste can contain up to 50 mg L⁻¹ of soluble uranium.

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This waste cannot be discarded without an adequate pre-treatment because it presents both chemical and radiological hazards.

The National Nuclear Energy Commission established rules related to radioactive waste management for several types of waste and treatments currently applied in Brazil (CNEN 1985). For liquid wastes, several well established processes are available, for example, chemical precipitation, evaporation, ion exchange resin, or a combination thereof. These processes certainly contribute to the treatment of liquid wastes; however, they may present some difficulties. For instance, the ion exchange resin technique, which has been widely used for uranium recovery from liquid wastes (Seneda *et al.* 2001, Ladeira and Morais 2005), generates a solid waste. When the resin cannot be regenerated it should be stored appropriately because of its radioactivity.

Nanofiltration (Nath 2008, Mulder 2000, Schäfer *et al.* 2005, Tannien *et al.* 2004, Dulama *et al.* 2008) is a membrane separation processes which uses the pressure driving force for separation. Nanofiltration has intermediate properties between ultrafiltration (0.2-0.7 MPa) and reverse osmosis (2.0-8.0 MPa). Nanofiltration membranes are usually obtained in two stages, namely: preparation of a microporous support and deposition of a thin film, usually by interfacial polymerization, creating a film thickness between 0.1-0.5 μm , responsible for the selectivity of the membrane. The nanofiltration process requires operating pressure in the range 0.5-2.5 MPa.

Nanofiltration process are widely used in seawater desulfation; purification of enzymes, concentration of fruit juices, among others, because they are able to reject negative multivalent ions, such as SO_4^{2-} and PO_4^{3-} , whereas monovalent ions like Cl^- are less rejected (0-70% - Schäfer *et al.* 2005). The separation process takes place through a combination of two mechanisms: ion size exclusion and ion charge exclusion (Nath 2008, Mulder 2000, Schäfer *et al.* 2005). Ion charge exclusion depends on the membrane surface charge, ionic strength and ion valence. The valence and ionic strength influence the charge density of the membrane and its isoelectric point (IEP).

The surface of the nanofiltration membrane is generally negatively charged below the IEP and positively charged above it. In general, the nanofiltration membrane is negatively charged in neutral and alkaline pH and positively charged at low pH (Tannien *et al.* 2004). The application of membranes for the treatment of radioactive wastes is relatively new and has been widely studied for treatment of low and intermediate level liquid radioactive wastes (LRWs) (Dulama *et al.* 2008, Macnaughton *et al.* 2004, Grazyna 2003, Pabby 2008, Raff and Milken 1999, Lin *et al.* 1987). Some articles have reported that treated wastes by reverse osmosis and nanofiltration processes attained uranium rejection in the range 80-99.5%.

The use of membrane processes for the treatment of radioactive waste requires an initial set of experiments before installation of such systems in a nuclear installation. The main requirement is to choose a membrane presenting chemical resistance and resistance to radiation, as the membrane will be continuously exposed to the radioactive waste. Polyamide nanofiltration membranes meet these requirements because they present many intermolecular crosslinkings (Chmielewski and Harasimowicz 1992, 1997). The pore size of the nanofiltration membrane is in the range 1-10 nm and is very resistant between pH 2-11. In the nuclear area, depending on the composition, nature of the ion and activity of the waste to be treated, changes in the performance of the membranes may occur, resulting in loss of their properties.

Some papers focused on the treatment of liquid radioactive wastes containing radionuclides such as ^{137}Cs , ^{241}Am , ^{238}U and ^{235}U using nanofiltration membranes (Ambashta and Sillanpää 2012). Rejection factors over 80% were obtained. However, membrane characterization before and after waste treatment is scarcely studied. Such study is essential in order to determine possible changes in

the membrane structure, especially when long-term permeation tests are performed. Therefore, it is necessary to study various parameters related to the operation before applying a membrane separation process to treat a given radioactive waste.

For this reason, this work aimed at evaluating the performance of a NF membrane to treat a radioactive liquid waste (“carbonated water”), in order to recover uranium for reintroduction in the nuclear fuel cycle. The transport properties (permeate flow, hydraulic permeability and selectivity) of the nanofiltration membrane were evaluated in two types of experiments: a) static tests and b) dynamic tests. In the static test the previously characterized membrane samples were immersed in the waste for a given time. After each time, the membranes were removed from the waste and their transport properties, chemical composition and morphology of the selective coating were evaluated. The dynamic test was performed by permeating the waste through a permeation cell to determine the influence of time on permeate flow and selectivity of the membrane to uranium.

2. Experimental

2.1 Radioactive waste sample

The sample of the waste specified as “carbonated water” was kindly provided by the Nuclear Fuel Factory (INB). Uranium was determined by arsenazo(III) method (Sawin 1961) using a FEMTO 800 XI spectrophotometer (wavelength = 650 nm); carbonate was determined by acid-base titration; ammonia (NH₃) was determined by the Nessler method (ASTM 1995); fluoride ion was determined an ion-selective electrode; pH was determined using a Digimed DM- 22 digital pHmeter.

2.2 Membrane samples

The nanofiltration membrane (NF) used in this study (“Developmental NF”) was kindly supplied by Dow/Brazil. It presents a selective layer of polyamide on a poly(ether sulfone) support and was identified in this work as NF0.

2.2.1 Transport properties of the membranes

2.2.1.1 Permeate flow and hydraulic permeability

For the experiments involving permeate flow, hydraulic permeability and selectivity, a system comprising a 350 mL dead-end permeation cell and a magnetic stirring was used. The maximum operating pressure was 0.5 MPa. The system was pressurized by dry compressed air, to carry the solution of the feed tank into the cell and permeating through the membrane. The effective area of membrane was 40 cm². The permeation cell used in this work has been described elsewhere (Ding and Bikson 2010).

Cuppons (circular membranes, diameter 76 mm) were used. Initially, the membrane was placed in water for an hour before being placed in the cell. The cell membrane was filled with distilled water at 0.5 MPa to compact the membrane. Compaction is the accommodation of the structure at the operating pressure. Compaction is achieved when three readings of the permeate flow at 20 min intervals are identical. The same procedure was carried at pressures of 0.4, 0.3, 0.2 and 0.1 MPa. The value of permeated flow (J_p) of the membrane was calculated through Eq. (1) (Mulder 2000).

$$J_p(Lm^{-2}h^{-1}) = \frac{Flow(Ls^{-1}) \times 3600(s/h)}{membrane\ area\ (m^2)} \quad (1)$$

Data obtained were used to build a curve of permeate flow versus pressure to determine the hydraulic permeability of the membrane, which is the slope of Eq. (1).

2.2.1.2 Selectivity for chloride and sulfate ions

After determining the hydraulic permeability, water was removed from the cell and the latter was filled with sodium chloride solution (1000 mg L⁻¹, pH 7), permeated under 0.5 MPa at 25°C. The first 50 mL were discarded. A new aliquot of 50 mL was taken away and reserved together with a sample of the feed chloride solution. For the rejection of sulfate, the cell was washed with water Milli-Q at 0.5 MPa. The cell was then filled with sodium sulfate solution (1000 mg L⁻¹, pH 7) at 0.5 MPa, repeating the same procedure described above. The concentrations of chloride and sulfate ions in the feed and permeates were determined by conductivity (Digmec DM-23 digital conductivity meter). The selectivity of the membrane was estimated by the rejection factor (R). It is defined as the fraction of solute retained by the membrane to a given concentration of feed solution, according to Eq. (2) (Mulder 2000).

$$R(\%) = \frac{C_f - C_p}{C_f} \times 100 \quad (2)$$

where C_f is the solute concentration in the feed and C_p is the solute concentration in the permeate. The conductivity readings of chloride and sulfate were inserted in the respective analytical curves for calculation of R.

2.2.2 Chemical resistance of the membrane to the waste

Two different tests were performed: static and dynamic.

2.2.2.1 Static test

The chemical resistance of the membrane was evaluated using the samples previously characterized as described in Sections 2.2.1.1 and 2.2.1.2. The membrane samples were immersed in 250 mL of the liquid waste in a closed system at 25°C. The membranes remained for 24 (NF24h), 48 (NF48h), or 72 (NF72h), in this liquid. After this period samples were removed and washed with water Milli-Q in order to determine permeate flow and selectivity of chloride and sulfate ions.

2.2.2.2 Dynamic test

The dynamic test was carried in a permeation cell system (Ding and Bikson 2010). Firstly, the permeated flow was determined at 0.5 MPa using the NF0 membrane. The cell was filled with 250 mL of waste under magnetic stirring at 0.5 MPa. An aliquot of 50 mL of the permeated waste was taken after 24, 48 and 72 h. The concentration of uranium in the permeate was determined by the arsenazo(III) method (Sawin 1961) using a FEMTO 800 XI spectrophotometer (wavelength = 650 nm).

2.2.3 Morphological, chemical structure and charge of the surface layer

2.2.3.1 Microscopy field emission (FESEM)

The membrane was prepared according to the following procedure: immersion in ethanol for 24 h; immersion in hexane for 24 h, drying at 25°C for 30 min, followed by drying at 60°C for 30 min.

This procedure intends to avoid the collapse of the porous surface due to the high surface tension of water. Then the sample was placed in the field emission microscope (JEOL JSM6710F), coated with a thin gold layer to make the sample conductive.

2.2.3.2 Fourier transform infrared spectroscopy (FTIR)

The objective was to identify possible changes of functional groups present in the membrane layer. The selective layer of each membrane was removed from the support using the following procedure: the membrane was placed in N,N-dimethyl acetamide (DMA) for a few minutes until complete dissolution of the support [poly(ether sulfone)], the selective layer was removed and washed with acetone and dried at 25°C. The samples were analyzed (KBr pellets) in a Thermo Scientific Nicolet 6700 spectrometer. Each spectrum was obtained as the average of 16 scans in the range 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} .

2.2.3.3 Zeta potential

The charge of the membrane surface is frequently characterized in terms of zeta potential, which is the potential at the shear plane between the solution and the membrane. The zeta potential curve and the isoelectric point (IEP) were determined from streaming potential measurements at different pH values (Nanda *et al.* 2010). The isoelectric point of the membrane indicates equality between positive and negative charges, where rejection of the membrane is minimal (Boussu *et al.* 2006).

The determination of zeta potential was carried out in a SURPAS equipment (Anton Paar), HCl 0.1 mol L^{-1} and NaOH 0.1 mol L^{-1} were employed in the titration and pH was set between 2.0 and 5.3. The relationship between the measurable streaming potential (ΔE) and the zeta potential (ξ) is given by the Helmholtz-Smoluchowsk equation (Mulder 2000, Nanda *et al.* 2010).

2.2.3.4 Atomic force microscopy (AFM)

The pore size distribution of the NF (Bowen and Doneva 2000) was determined by AFM (WiTec Raman Sensitivity). The silicon cantilever with nominal tip apex radius of 10 nm was used to scan the surface morphology of membranes at the contact mode. The images were obtained over an area of $2 \times 2 \mu\text{m}$ for three different surfaces for both before and after immersion of the membrane in the waste. An AFM image program was used for measurement the pore size distribution.

3. Results and discussion

3.1 Composition of the waste

The composition of radioactive liquid waste is shown on Table 1. Uranium concentration (8 mg L^{-1}) in this waste is fairly high and much above the limit established for disposal in the environment (0.02 mg L^{-1}) by the Brazilian Environmental Agency (CONAMA 2005). On the other hand, this waste can be regarded as a useful source for recovery of uranium because of its average amount produced in a batch process (1,300 L/day) at INB.

3.2 Characterization of the membrane before the static test

Permeate flow, hydraulic permeability and selectivity for chloride and sulfate ions were determined

Table 1 Concentration of chemical species in the waste (mg L^{-1})

U	F ⁻	CO ₃ ²⁻	NH ₄ ⁺	pH
7.0×10^0	5.2×10^2	9.8×10^4	7.0×10^4	9.4

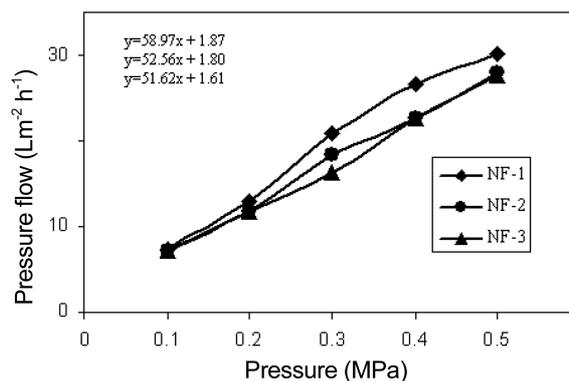


Fig. 1 Graph of the permeate flow versus pressure of NF0 cuppons

Table 2 Rejection factors and permeate flow of NFO cuppons before conditioning in the waste ($P = 0.5 \text{ MPa}$)

Membranes	Permeate flow ($\text{L m}^{-2} \text{ h}^{-1}$)	Rejection (%)	
		Cl ⁻	SO ₄ ²⁻
NF-1	25.8 ± 4.6	18.2 ± 9.8	97.9 ± 0.8
NF-2	27.3 ± 2.3	20.1 ± 7.0	98.6 ± 0.9
NF-3	24.6 ± 2.7	14.6 ± 8.5	98.4 ± 1.3

for three cuppons of NF0 membrane, identified as NF-1, NF-2 and NF-3. Fig. 1 shows the graph of permeate flow versus pressure. The slope is the hydraulic permeability of each cuppon, and the values found were 59, 53 and 52 $\text{L m}^{-2} \text{ h}^{-1} \text{ MPa}$ for NF-1, NF-2 and NF-3, respectively. These values fall in the range found in the literature for nanofiltration membranes ($10\text{--}66 \text{ L m}^{-2} \text{ h}^{-1} \text{ MPa}$). The hydraulic permeability of membrane can be correlated with the hydrophobic/hydrophilic character of the monomer used in the selective membrane layer. Nanofiltration membranes usually have a selective coating of polyamide, which presents higher affinity for water (hydrophilicity) (Mulder 2000, Schäfer *et al.* 2005).

The permeated flow and selectivity of the NF0 cuppons before immersion in the waste are shown in Table 2. The behavior of these cuppons is very similar. The selectivity of nanofiltration membranes is associated to the pore size distribution and amount of charge on the membrane surface. Most of the nanofiltration membranes has a negative surface charge in aqueous media (Tang *et al.* 2009, Rautenbach and Groschl 1990, Skozi *et al.* 2002, Veríssimo *et al.* 2006). The isoelectric point obtained for the NF0 membrane was at pH 2.5; at higher pH the membrane surface is negatively charged.

3.3 Characterization of the membrane after the static test

After immersion of the membranes for 24, 48 and 72 h in the waste, the permeate flow and selectivity of the membranes were determined. From data on Table 3, the permeate flow of the NF membranes was not significantly altered after immersion in the waste, being comparable to the values found in Table 2 (before the static tests). Zeta potential data (Fig. 2) show similar profiles for NF0 and NF24h membranes. The isoelectric point of the NF24h sample is slightly lower (pH 2.4) than for NF0 (pH 2.5).

AFM images (Fig. 3a) of the NF0 membrane showed a pore size distribution in the range 2-8 nm, and 3-12 nm for the NF24h sample (Fig. 3b). Therefore, immersion of the membrane in the liquid waste shifted pore size distribution to higher values. However, the permeate flow remained nearly the same for all times (Tables 2 and 3). This point requires further studies in order to understand this

Table 3 Rejection factors and permeate flow of membranes after conditioning in the waste for 24, 48 or 72 h ($P = 0.5$ MPa)

Membranes	Permeate flow ($L\ m^{-2}\ h^{-1}$)	Rejection (%)	
		Cl ⁻	SO ₄ ²⁻
NF24h	23.4 ± 2.7	8.0 ± 6.2	96.7 ± 1.3
NF48h	24.7 ± 3.3	12.4 ± 6.6	97.8 ± 1.7
NF72h	25.0 ± 2.7	10.5 ± 3.2	96.2 ± 2.8

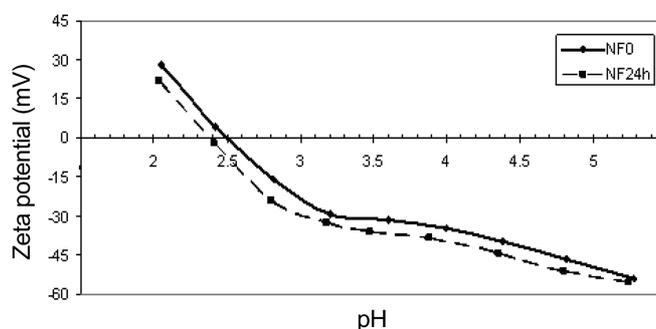


Fig. 2 Streaming potential measurements in the pH range 2.0-5.5 for NF0 and NF24h membranes

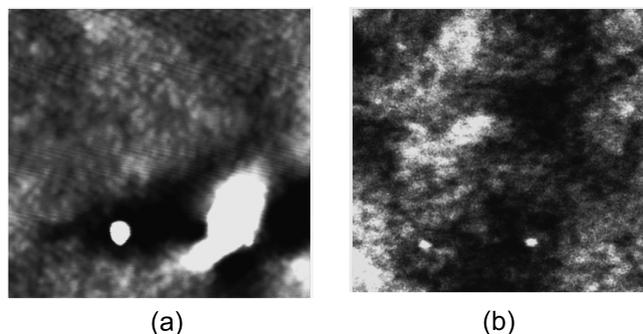


Fig. 3 AFM images of (a) NF0 and (b) NF24h membranes

phenomenon. The permeate flow of NF membranes also depends on the concentration polarization, but this phenomenon did not take place under our experimental conditions since the permeate flow was determined using water only (Section 2.2.1.1).

The radii of hydrated chloride and sulfate ions are 0.33 and 0.38 nm, respectively (Tanninen *et al.* 2006). After displacement of the pore size distribution from 2-8 to 3-12 nm (Fig. 3) a net decrease in chloride rejection (nearly 40%) was observed for all times after immersion of the membrane in the waste. Therefore, chloride (a monovalent anion) is essentially rejected by size exclusion. On the other hand, the rejection factor to sulfate ions (a divalent anion) only slightly decreased (Tables 2 and 3). In this case the rejection occurs mainly via charge exclusion (Chang *et al.* 2012), thus suggesting that the membrane charge was not significantly changed, as seen earlier (Fig. 2).

3.4 Evaluation of performance of NF membrane in a dynamic test using the waste containing uranium

As shown in the Table 1 the “carbonated water” waste contains high amounts of carbonate ions, which are a strong complexing agent for uranium, forming different complex ions, depending on pH (Raff and Wilken 1999). At pH 9.4 the dominant species is the four-valent anion complex $[\text{UO}_2(\text{CO}_3)_3]^{4-}$. From zeta potential data (Fig. 2), the NF membrane has a negative charge in the selective layer. As pH of the waste is 9.4, it is expected a high rejection of the membrane for uranium.

Table 4 presents the selectivity of the membrane for the uranium ion and the initial and final permeate flows. As expected, the NF membrane rejected 99% of uranium during the dynamic test.

The use of nanofiltration membranes is viable for the treatment and recovery of uranium from the “carbonated water” waste. However, it was observed a decrease of permeate flow (close to 60% after 72 h, Table 4). This decrease can be due to concentration polarization, a phenomenon inherent for all membrane separation processes. When a solution permeates through a selective membrane for a given solute, there is an increase of solute concentration in the interface membrane/solution and therefore an increase in osmotic pressure of the solution near the membrane, decreasing the driving force for the separation and therefore the permeate flow. The permeation cell used in this study (section 2.2.1.1) enhances the concentration polarization process (Mulder 2000, Schäfer *et al.* 2005). Further experiments are in progress using a cross-flow cell that simulates industrial membrane modules, thus avoiding concentration polarization.

3.5 Characterization of the membrane surface

3.5.1 FTIR data

The infrared spectra of NF membranes before and after conditioning for 24, 48 or 72 h in the

Table 4 Uranium rejection and permeate flows of the NF membrane after static tests

Uranium rejection (%)	Time (h)	Permeate flow* ($\text{L m}^{-2} \text{h}^{-1}$)
99.0	24	1.4
99.0	48	1.3
99.0	72	1.2

* Initial permeate flow: $2.5 \text{ L m}^{-2} \text{h}^{-1}$ (after 3 h)

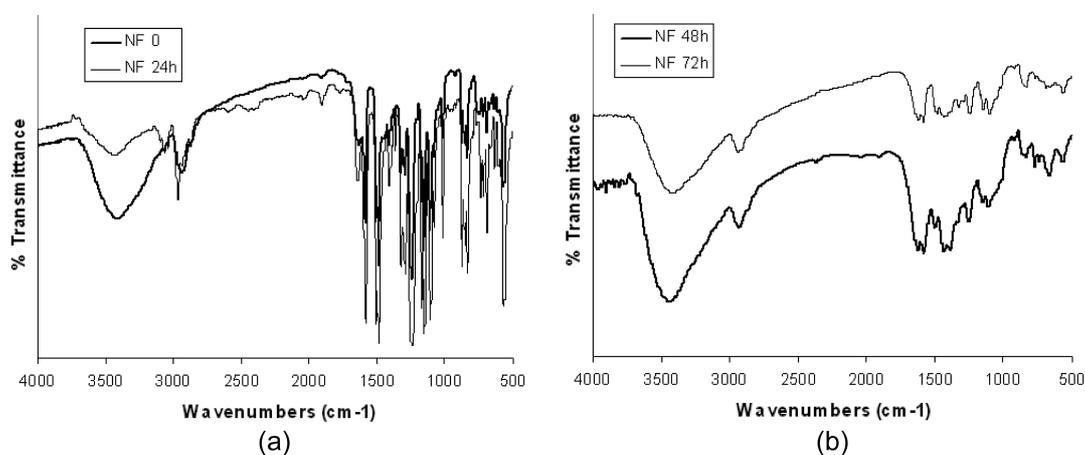


Fig. 4 FTIR spectra of the NF membrane before and after conditioning in the waste for 24, 48 or 72 h: (a) NF0 and NF24h and (b) NF48h and NF72h

radioactive waste are presented in Fig. 4. Overall, the profiles in the spectrum present the same characteristic polyamide bands. The spectra of NF0 and NF24h membranes (Fig. 4a) did not show significant differences. Characteristic bands of N-H, C-H aliphatic system ($3500\text{--}2900\text{ cm}^{-1}$), C=O and aromatic rings ($1700\text{--}1550\text{ cm}^{-1}$) were observed. The main difference was the decrease in intensity of the peak at 3436 cm^{-1} of the sample immersed in the waste. This change probably occurred due to some amide hydrolysis, resulting in absorption peaks in the range $3500\text{--}3100\text{ cm}^{-1}$, corresponding to a primary amine, as well as the increase of the intensity of the carbonyl peak at 1640 cm^{-1} .

The spectra of the NF48h and NF72h membranes (Fig. 4b) present the same profile, but the sample that stayed for 72 h in the waste showed a net reduction of the intensity of the bands, mainly in the region between $1750\text{--}600\text{ cm}^{-1}$, suggesting a possible interaction between the waste and the amide groups of the selective layer of the membrane.

3.5.2 Morphological characterization of the membrane

The morphological aspects of the NF24h membrane surface before and after immersion in the waste are presented in Fig. 5(a) and (b), respectively. This sample was chosen because it remained in the waste for less time. The idea is to observe if after 24 h some morphological change would occur. The micrographs confirm that after immersion for just only 24 h in the waste a change of the selective membrane layer was observed.

Fig. 5(a) shows the initial (NF0) membrane surface, which appears to be completely smooth without apparent porosity, even after magnification of $150,000\times$. Fig. 5(b) shows the membrane surface after immersion in the waste for 24 h. A granular structure can be distinguished, measuring around 30 nm, strongly suggesting a physical change in the selective layer. This contact with the waste can form free radicals or ions, which in turn may cause other reactions, resulting in breakdown of the molecule or the formation of new molecules by combining them (crosslinking) (Ramachandhran and Misra, 1982). Taking into account the differences in the IR spectra of NF0 and NF24h membranes (Fig. 4a), we can conclude that the selective layer presented a physical change together with some chemical change. However, these changes did not modify significantly the membrane surface charge, according to sulfate rejection (Tables 2 and 3) and zeta potential (Fig. 2) data. These

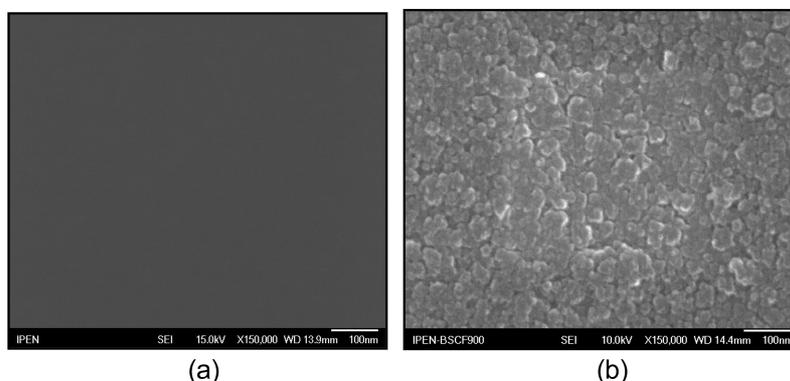


Fig. 5 Micrographs of the NF membrane surface: (a) before conditioning in the waste and (b) after 24 h in the waste (magnification: 150,000 \times)

changes likewise did not affect the membrane rejection for uranium in the dynamic test (Table 4).

4. Conclusions

The NF membrane tested in this work is promising for separation of uranium from the waste. 99% of the element was rejected even after a long-term test (72 h). This result is comparable to the best results found in the literature. The hydraulic permeability of the NF membrane of (52-59 L m⁻² h⁻¹ Mpa), indicates that the monomer used in the selective membrane layer presents a high hydrophilicity. The isoelectric points of NF0 and NF24h membranes are very close, the contact of the waste with the membrane did not alter significantly its surface charge.

The low rejection factors to chloride ions in static tests for the NF24h sample indicate that the porosity of the selective membrane layer was affected by the waste, as confirmed by AFM data: the pore size distribution of the NF24h membrane was shifted to higher values (3-12 nm) when compared to the original one (NF0, 2-8 nm). However, the permeate flow after immersion remained basically constant. The rejection of sulfate ions was essentially governed by an ion charge exclusion since the increase of pore size distribution of the NF24h membrane only slightly decreased it.

The micrographs of the NF24h membrane show that a physical change in the membrane surface took place after immersion in the waste. The IR spectra of the NF0 and NF24h samples presented the same bands, only a reduction in the intensity of the peak at 3436 cm⁻¹ of the NF24h sample was observed, probably due to some hydrolysis of the amide group. These changes did not modify significantly the membrane surface charge of both samples, the rejection to sulfate ions (static tests) and to uranium (dynamic tests).

Acknowledgments

We acknowledge INB for providing the waste. We are grateful to the Institute of Chemistry/UFRJ for FTIR analysis. We acknowledge PAM/COPPE/UFRJ for determination of zeta potential and AFM. We acknowledge Dow/Brazil for furnishing the membrane employed this work.

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