



Research Paper

Cellulose Acetate Nanofiltration Membranes for Cadmium Remediation

Ibtissem Ounifi ^{1,2,*}, Claudia Ursino ³, Sergio Santoro ⁴, Jalila Chekir ¹, Amor Hafiane ¹, Alberto Figoli ^{3,*}, Ezzedin Ferjani ⁵¹ Laboratory, Water, Membrane and Environmental Biotechnology, Centre of Research and Water Technologies, Technopark of Borj-Cedria, BP 273, 8020 Soliman, Tunisia² Faculty of Sciences of Tunis, University of Tunis - El Manar, 20 Toleda street, Tunis 2092³ Institute on Membrane Technology (ITM-CNR), Via P. Bucci 17c, 87036 Rende (CS), Italy⁴ Department of Environmental Engineering (DIAM), Università della Calabria, Via Pietro Bucci, Cubo 44/A, 87036 Rende (CS), Italy⁵ Higher Institute of Sciences and Technology of Environment of Borj-Cedria Bp 2050 Borj-Cedria, Tunisia

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Highlights

- CA-NF membranes were successfully prepared via NIPS applied for cadmium removal
- Cd²⁺ removal was evaluated using three type of cadmium salts: CdCl₂, Cd(NO₃)₂ and CdSO₄
- The effect of several operating conditions such as feed pressure and composition, was studied
- CA-NF membranes rejection was up to 98%

Abstract

In this work, cellulose acetate (CA) nanofiltration (NF) membranes were prepared via non-solvent phase inversion technique (NIPS). Polymer concentration was varied from 22 to 25 wt% in order to study its effect on the membrane properties. The fabricated membranes were characterized in terms of morphological analysis using scanning electron microscopy (SEM), contact angle, water content, water permeability and salts retention such as Na₂SO₄, CaCl₂ and NaCl. Membranes performances were evaluated for cadmium Cd²⁺ removal using three types of cadmium salt: CdCl₂, Cd(NO₃)₂ and CdSO₄. The effects of several operating parameters such as the pH of the feed solution (2-12), trans-membrane pressure (0-14 bar), feed concentration (10⁻⁴-10⁻² mol.L⁻¹) and ionic strength were also studied and investigated. Results evidenced that the prepared CA-NF membranes consists of a sustainable remediation of Cadmium contamination for safe water supply.

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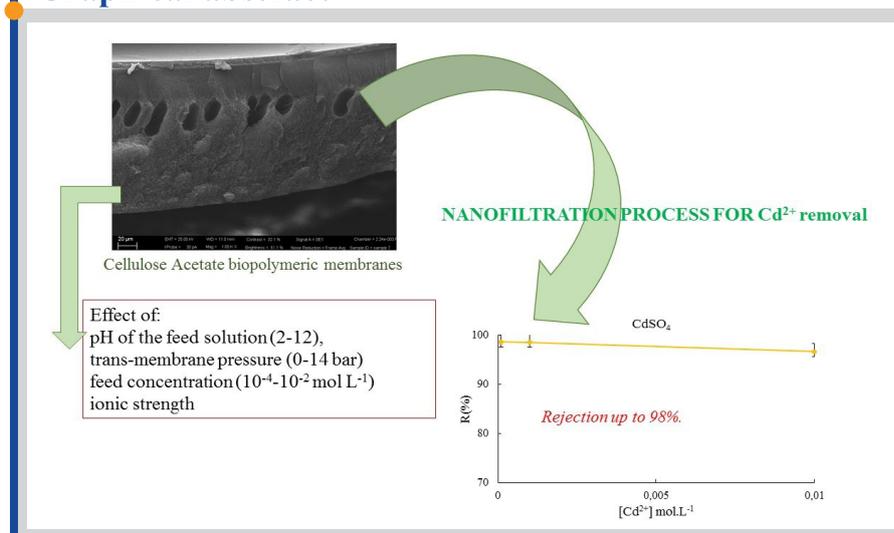
1. Introduction

The contamination of water supplies by traces of heavy metals is a global issue causing serious environmental and health concerns and, as a consequence, an increasing of demand for water remediation technologies [1-3].

Cadmium (Cd) is widely distributed throughout the Earth's crust, particularly abundant in zinc and lead ores, and is presented in anthropogenic

sources such as fertilizers, industrial effluents (i.e. smelting, dye manufacturing, electroplating industries) and sewage sludge [4]. However, chemical fertilizers and herbicides are considered the main anthropogenic cause of the introduction of Cd in the environment: metal retention of soils is very limited, thus Cd contaminates groundwater entailing pollution of the water-soil-plant-animal-human chain [5].

Graphical abstract



* Corresponding authors: ibtissemounifi@yahoo.com (I. Ounifi); a.figoli@itm.cnr.it (A. Figoli)

Cd is considered as one of the most toxic heavy metals, classified as a human carcinogen impacting lungs, liver and kidney [6]. Moreover, Cd is characterized by a long environmental persistence, biologically and thermodynamically non-degradable, it bio-accumulates quickly with a half-life of 10-35 years causing metabolic disruptions and a progressive chronic intoxication [6-8].

The World Health Organization (WHO) set the maximum allowable concentration of Cd (II) to 3 $\mu\text{g}\cdot\text{L}^{-1}$ for drinking water [9]. Cd generally occurs as divalent Cd^{2+} cation [10,11] and treatment processes for contaminated water streams include: coagulation/flocculation [12], electrochemical treatment [13] and absorption [14]. These techniques present several limitations such as high operational cost, slow operation duration, secondary pollutant generation, non-reusability, and incompatibility for large-scale application [15]. Moreover these methods required generally a second treatment of separation/filtration to remove the secondary products [16]. Membrane technology offers the advantage of the one-step effective purification combined with low energy consumption and scalability [17-20]. Nanofiltration (NF) has come a long way since first inception in the late 1980s gaining interest as an effective and feasible method for the removal of traces of ions from water [21]. For instance, thin-film composite (TFC) polyamide (PA) membrane (Perma-TFC-NF-300) demonstrated a rejection of 98.94% for Ni^{2+} and 82.69% for Cd^{2+} respectively for an initial feed concentration of 5 ppm [22]. Previous studies observed a maximum rejection of 85% for Cd^{2+} ($[\text{Cd}^{2+}] = 10^{-3} \text{ mol L}^{-1}$) for NF polyamide thin-film composite membranes (TFC) evidencing the key role played by the Donnan exclusion mechanism [23]. Commercial TFC-NF membranes (NF-HL by Osmonics and NF-90 by Filmtec) were successful employed in Cd^{2+} removal from aqueous solutions and industrial effluents [24]. Designed hollow-fiber made of polybenzimidazole (PBI) and polyethersulfone (PES)/polyvinylpyrrolidone (PVP) showed excellent rejections of ions from wastewater reaching values of 95% and 93% for Cd^{2+} and Pb^{2+} respectively [25]. Outstanding rejection (above 99%) for Pb^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} and As^{5+} and water permeability ($3.6 \text{ L m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ at 10 bar) were obtained using TFC-NF developed by grafting poly (amidoamine) dendrimer (PAMAM) grafted on interracial polymerized layer of polyethersulfone (PES) membranes [26].

Recently different strategies have been proposed to decrease the footprint of membrane preparation using low toxicity chemicals, minimizing the number of steps in membranes production to reduce waste, and minimizing energy in preparing casting solutions paving the way for an environmental friendly NF [27].

Herein, in this work, cellulose acetate (CA), an inexpensive hydrophilic biopolymer [28], was chosen as polymer for preparing NF membranes via non-solvent induced phase inversion technique (NIPS). The effect of the CA concentration on the properties of CA NF membranes was investigated by morphological analysis via scanning electron microscopy (SEM), contact angle, water permeability and salts retention, (NaCl , Na_2SO_4 and CaCl_2). The obtained membranes were tested for Cd^{2+} removal from water studying the effect of the co-ions (SO_4^{2-} , NO_3^- , and Cl^-), NF conditions (feed pressure) and feed composition (contaminant and salt concentrations, pH).

2. Materials and methods

2.1. Materials

Cellulose acetate ($\text{MW } 30,000 \text{ g}\cdot\text{mol}^{-1}$), acetone, formamide, cadmium salts (CdSO_4 , $\text{Cd}(\text{NO}_3)_2$, and CdCl_2), sodium salts (NaCl , and Na_2SO_4) and CaCl_2 were purchased from Sigma Aldrich and used without any further purification.

2.2 Polymeric dope solution preparation

CA dope solutions were prepared by adding the polymer at different concentrations (22-25 wt%) in a blend of acetone and formamide (2:1). The solution was magnetically stirred until the complete dissolution of the polymer (24 h). Subsequently the stirring was stopped for 1 h in order to favor degassing.

2.3. Preparation of CA flat membranes

CA membranes were prepared by casting the polymeric solution on a suitable smooth glass using a casting knife of 200 μm . After casting, the membranes were immediately immersed in a coagulation bath of distilled water (4 °C) for 1 h. The nascent membranes were subsequently immersed for 10 min in distilled water at 85 °C, in order to remove residual traces of solvent. The CA NF membranes prepared in this work were summarized in Table 1.

Table 1

Summary of the CA NF membranes prepared.

| Membrane name | Solution composition (wt %) | | |
|---------------|-----------------------------|---------|-----------|
| | Polymer | Acetone | Formamide |
| NF-22 | 22 | 52 | 26 |
| NF-23 | 23 | 51,33 | 25,67 |
| NF-24 | 24 | 50,66 | 25,34 |
| NF-25 | 25 | 50 | 25 |

2.4. Scanning electron microscopy (SEM)

The morphology of CA membranes was analysed using a scanning electron microscope (Zeiss EVO MA 100, Assing, Italy). In order to observe the membrane cross sections, membranes were first frozen in liquid nitrogen and then submitted to fracture. All samples (cross sections top and bottom surfaces) were sputter-coated with a thin gold film prior to SEM observation.

2.5. Contact angle

The hydrophilic/hydrophobic nature of the membranes was evaluated by an optical camera using an Attention Theta T200 blood pressure monitor (Biolin Scientific, Sweden). The software used was "One Attention Software". The measurements were performed using ultrapure water drop (5 μL). For all membranes, at least 3 measurements were taken and the average value and the corresponding standard deviation were then calculated.

2.6. Porosity

Membranes porosity ($\epsilon\%$), defined as the ratio between volume of voids present in the membrane and the overall membrane volume, was measured by gravimetric method as reported in literature [29,30] consisting in weighting the membrane in dry and wet (kerosene for 24 h) conditions. The porosity was calculated following to this formula (1):

$$\epsilon(\%) = \left\{ \frac{(\text{W}_w - \text{W}_d)/\rho_i}{(\text{W}_w - \text{W}_d)/\rho_i + \frac{\text{W}_d}{\rho_P}} \right\} \quad (1)$$

where ϵ is membrane porosity (%), W_w is the weight of the wet membrane, W_d is the weight of the dry membrane, ρ_i is the kerosene density ($0.82 \text{ g}\cdot\text{cm}^{-3}$) and ρ_P is the CA density ($1.28 \text{ g}\cdot\text{cm}^{-3}$). For each membrane, three measurements were performed; then, the average values and corresponding standard deviation were calculated.

2.7. Water content

Samples for the equilibrium water content (EWC) were immersed in water for 24 h and weighted (m_w) [31]. Then, the samples weighted again (m_d) after drying overnight at 75 °C [31]. Finally, the EWC was calculated according to the following equation [32]:

$$\text{EWC} = \frac{m_w - m_d}{m_w} \times 100 \quad (2)$$

2.8. Nanofiltration (NF) experiments

Membranes performance was studied in terms of water flux, salts rejection (CaCl_2 , NaCl and Na_2SO_4 , $10^{-3} \text{ mol}\cdot\text{L}^{-1}$) and cadmium salts permeability (CdCl_2 , $\text{Cd}(\text{NO}_3)_2$ and CdSO_4).

All experiments were performed using a dead-end stainless-steel cell supplied by Millipore. The total volume was 350 mL and the diameter 7.1 cm. The effective membrane area was 38.54 cm^2 . CA membrane were previously conditioned in distilled water for 4 h at 25°C and then used to NF test. The effects of the feed concentration (0, 10^{-2} , 10^{-3} , $10^{-4} \text{ mol}\cdot\text{L}^{-1}$) and the chemistry of different cadmium salts (CdCl_2 , $\text{Cd}(\text{NO}_3)_2$ and CdSO_4) were studied and evaluated. Experiments were carried out with pressurized N_2 on the feed compartment generating a trans-membrane pressure (TMP) ranging from 2 to 16 bar. The permeate was collected at atmospheric pressure and the resulting

flux was calculated according the equation:

$$J = \frac{Q}{A\Delta t} \quad (3)$$

where J is the pure water flux ($L.m^{-2}.h^{-1}$), Q is the amount of permeate (L), A is the effective membrane area (m^2) and Δt is the operations time (h). The concentration of Na_2SO_4 , $NaCl$ and $CaCl_2$ in feed and permeate solution was determined using conductivity method (Consort C832). For Cd^{2+} solutions, feed and permeate concentrations were determined using Flame atomic absorption spectroscopy (Analytik Jena AG - AAS vario@ 6). Retention rate was calculated according the following equation:

$$R\% = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

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

3. Results and discussion

3.1. Membrane characterization

CA membranes morphology was examined by scanning electron microscopy (SEM), the obtained images of cross section, top and bottom surface were reported in Figure 1. In all cases CA NF membranes showed an asymmetrical morphology consisting of a dense layer supported on a porous sub-structure characterized by the presence of macrovoids, whereas both the surfaces appeared uniform, smooth and dense. The presence of a denser skin on the top surface is attributed to the volatile nature of acetone. In fact, once the polymeric solution is cast, the CA concentration on the surface locally increased as a consequence of the acetone evaporation generating a dense gel resulting in a dense skin [33]. Subsequently the cast solution is immersed in the coagulation bath where the rate of solve/non-solvent exchange is delayed by the presence of the dense layer. The consequence is a L-L phase separation of the polymeric solution with the formation of conical voids containing mainly solvent and the non-solvent [34].

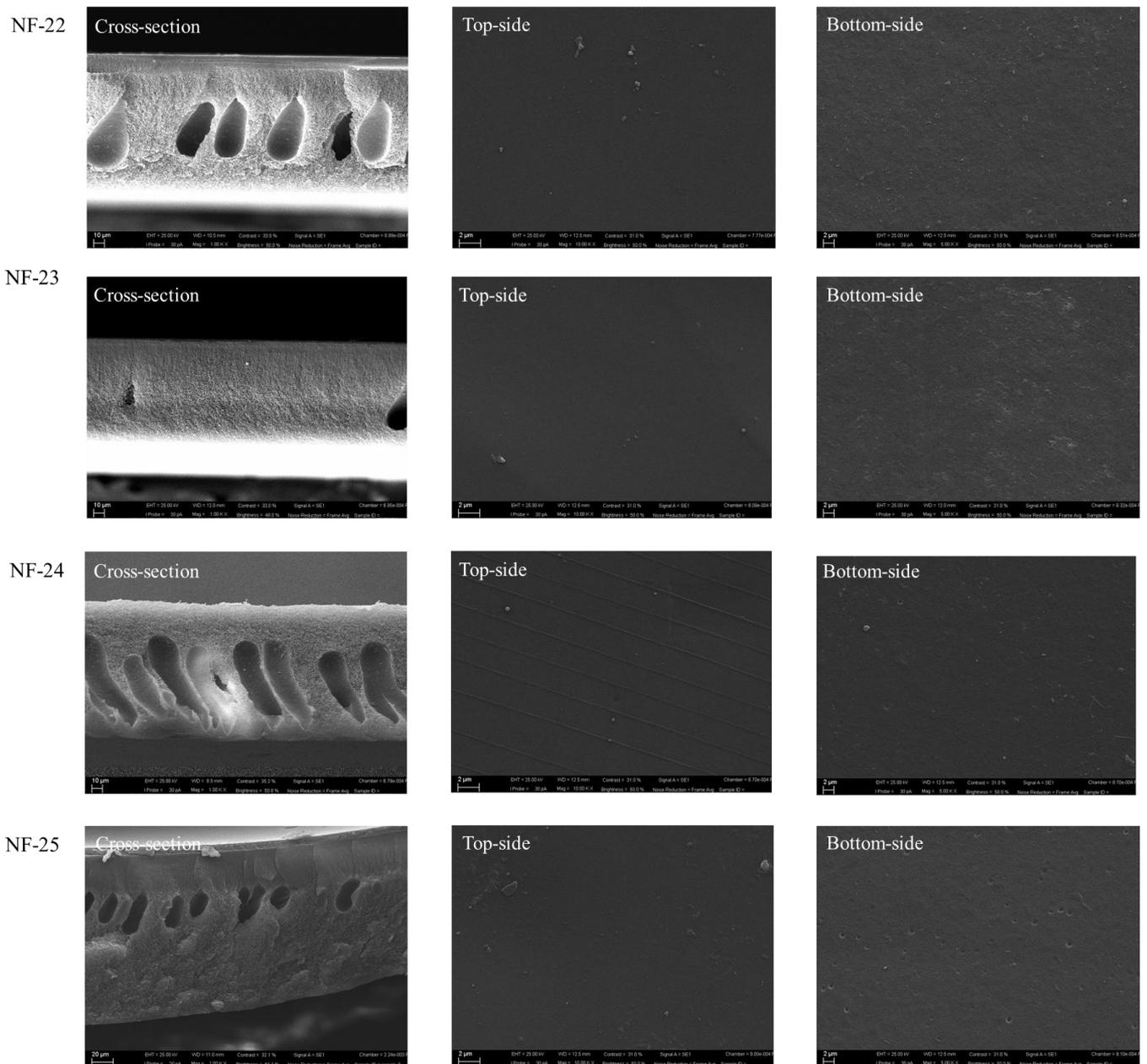


Fig. 1. SEM images of the CA NF prepared membranes (Magnification of 1000 KX for cross section and 10000 K X and 5000KX for top and bottom side, respectively).

Figure 2 summarized the effect of CA concentration on the properties of CA NF membranes in terms of water content (%), porosity (%) and contact angle. The porosity of NF CA membranes is dramatically affected by the CA concentration in the polymeric solution: a linear decreasing of the porosity from ca. 50% to 12% was observed by increasing the polymer concentration from 22wt.% to 25wt.% (Figure 2a). As we know, the polymer is the principal component of the membrane, thus the improvement of its concentration leads to a decreasing of the porosity of the polymer structure in the native membrane. Moreover the polymer concentration affects the viscosity of the casting solution increasing the resistance of solvent/non-solvent diffusion during the NIPS: the result is a larger time provided to polymer chains to organize resulting in a more compact membrane structure [35]. The consequence is a lowering of the space available for water uptake with the improvement of the CA concentration in the dope solution as observed by evaluating the decreasing of EWC (Figure 2a). Figure 2b shows the contact angle average for the prepared NF membranes evidencing their hydrophilic character, according with the nature of the polymer. In particular, contact angle decreases from 76° for NF-22 membrane to 47° for NF-25 membrane. The effect of CA concentration on surface contact angle is attributed to the membrane morphology and, in particular, on its impact on membrane porosity and roughness. The improvement of the polymer concentration reduces the membrane porosity and consequently the membrane roughness causing a decreasing in contact angle. In fact, the apparent contact angle (θ^*) of a sessile droplet on the membrane depends on the chemical texture of the surface as well its roughness (r) as proposed by Wenzel in the following equation:

$$\cos(\theta^*) = r\cos(\theta) \quad (5)$$

where θ is the ideal contact angle for a perfectly smooth surface ($r=1$) [30,36,37].

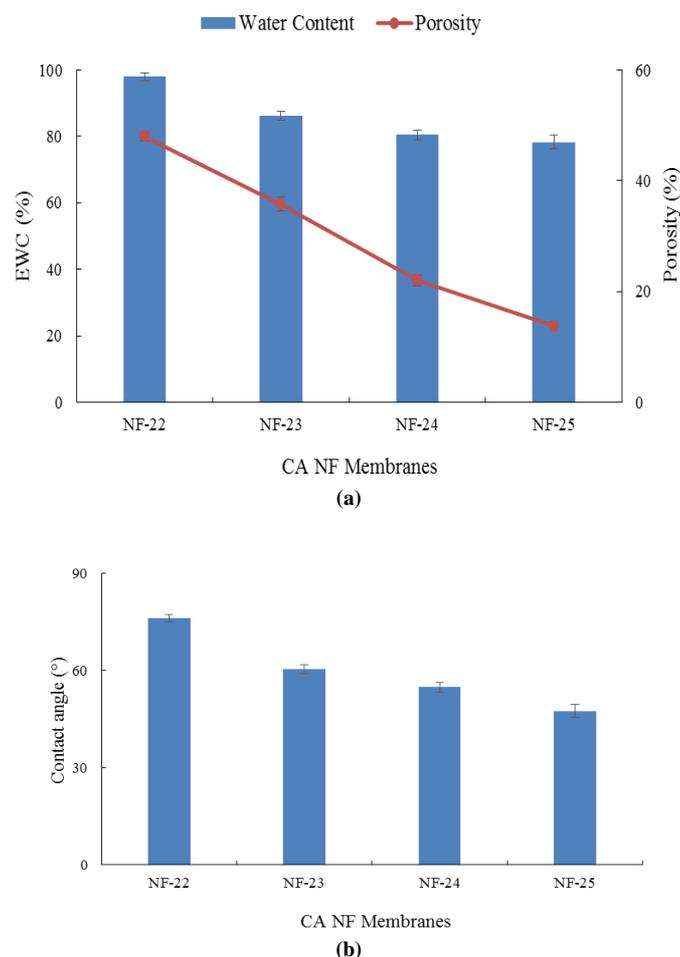


Fig. 2. a) Water content (%) and porosity (%); b) Contact angle of the CA NF prepared membranes.

3.2. Water permeability and salt retention measurements

CA NF membranes performance was evaluated in terms of the water flux and salt rejection. As is possible to observe in Figure 3, water flux linearly increased by increasing the feed pressure (ΔP) and decreased with the CA concentration due to the effect of the porosity on the membrane permeability. In fact the trans-membrane flux for pressure driven processes is well described by the Hagen-Poiseuille equation and it is proportional to the driving force and the membrane porosity. The water permeance lies in the range of 9.9 L.m⁻².h⁻¹.bar⁻¹ for NF-22 to 6.80 L.m⁻².h⁻¹.bar⁻¹ for NF-25 membrane.

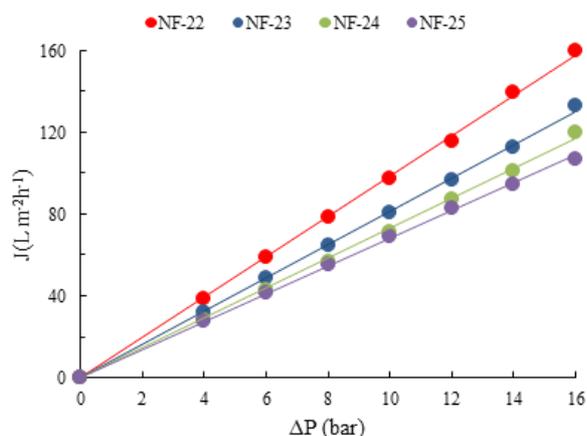


Fig. 3. Water Flux of CA NF membranes.

CA NF membranes were initially tested for salts rejection ($R\%$) using NaCl, Na₂SO₄, and CaCl₂ at 10⁻³ mol.L⁻¹ at $\Delta P=4$ bar and the results were summarized in Table 2.

Table 2

Rejection results of NF-22, NF-23, NF-24 and NF-25 XA membranes at $\Delta P=4$ bar, $C_{\text{feed}}=10^{-3}$ mol.L⁻¹, pH=6.8 and T=25 °C.

| CA NF Membrane | NF-22 | NF-23 | NF-24 | NF-25 |
|-----------------------------------------|-------|-------|-------|-------|
| R(NaCl) (%) | 41.46 | 42.98 | 48.20 | 50.66 |
| R(CaCl ₂) (%) | 65.23 | 66.06 | 66.84 | 69.71 |
| R(Na ₂ SO ₄) (%) | 72.18 | 76.67 | 79.85 | 81.35 |

Results evidenced an improvement of the rejection coefficient of the salts with the CA concentration in the polymeric solution employed for membrane preparation. This result is due to the fact that the membrane with high polymer concentration (NF-25 membrane) presented lower porosity and denser structure making the membrane more selective.

In all the cases, the retention sequence was: R (Na₂SO₄) > R (CaCl₂) > R (NaCl), thus the removal of monovalent salts (i.e. NaCl) is less efficient in comparison to bivalent salts (i.e. CaCl₂ and NaCl). This behavior is commonly related to steric hindrance mechanism: bivalent ions are sterically retained because of their larger hydrated size [38]. In fact, as highlighted in Table 3 monovalent ions presented a lower hydrated radius than bivalent ions. A similar contribute is related to the dehydration phenomenon: ions at the boundary layer on membrane surface can temporarily strip the surrounding water shells fitting easily into the pores [39]. The hydration energy (HE) depends on both the ionic size and charge: usually higher ionic charge and smaller ionic size result in higher hydration energy [40]. As reported in literature, the rejection increases by improving the hydration energy (HE) and decreasing the diffusion coefficients [41]. Herein, the values presented in Table 4 reveal that the diffusion coefficients of the divalent ions (Ca²⁺, SO₄²⁻) are lower than those of the monovalent ions (Na⁺, Cl⁻). On the other hand, the hydration energy for SO₄²⁻ (1047 kJ.mol⁻¹) and Ca²⁺ (1615 kJ.mol⁻¹) were much higher than Na⁺ and Cl⁻ which are 454 kJ.mol⁻¹ and 325 kJ.mol⁻¹ respectively [35].

Table 3
Hydration energies, hydrated radius and diffusion coefficients (*D*) of ions and electrolytes used in this work.

| Ions | Na ⁺ | Ca ²⁺ | Cl ⁻ | SO ₄ ²⁻ | NaCl | CaCl ₂ | Na ₂ SO ₄ | References |
|-----------------------------------------------------|-----------------|------------------|-----------------|-------------------------------|------|-------------------|---------------------------------|------------|
| HE (kJ.mol ⁻¹) | 454 | 1615 | 325 | 1047 | – | – | – | [42] |
| Hydrated radius (nm) | 0.358 | 0.412 | 0.332 | 0.379 | – | – | – | [43] |
| D (10 ⁹ m ² s ⁻¹) | 1.333 | 0.718 | 2.032 | 1.065 | 1.61 | 1.45 | 1.23 | [44] |

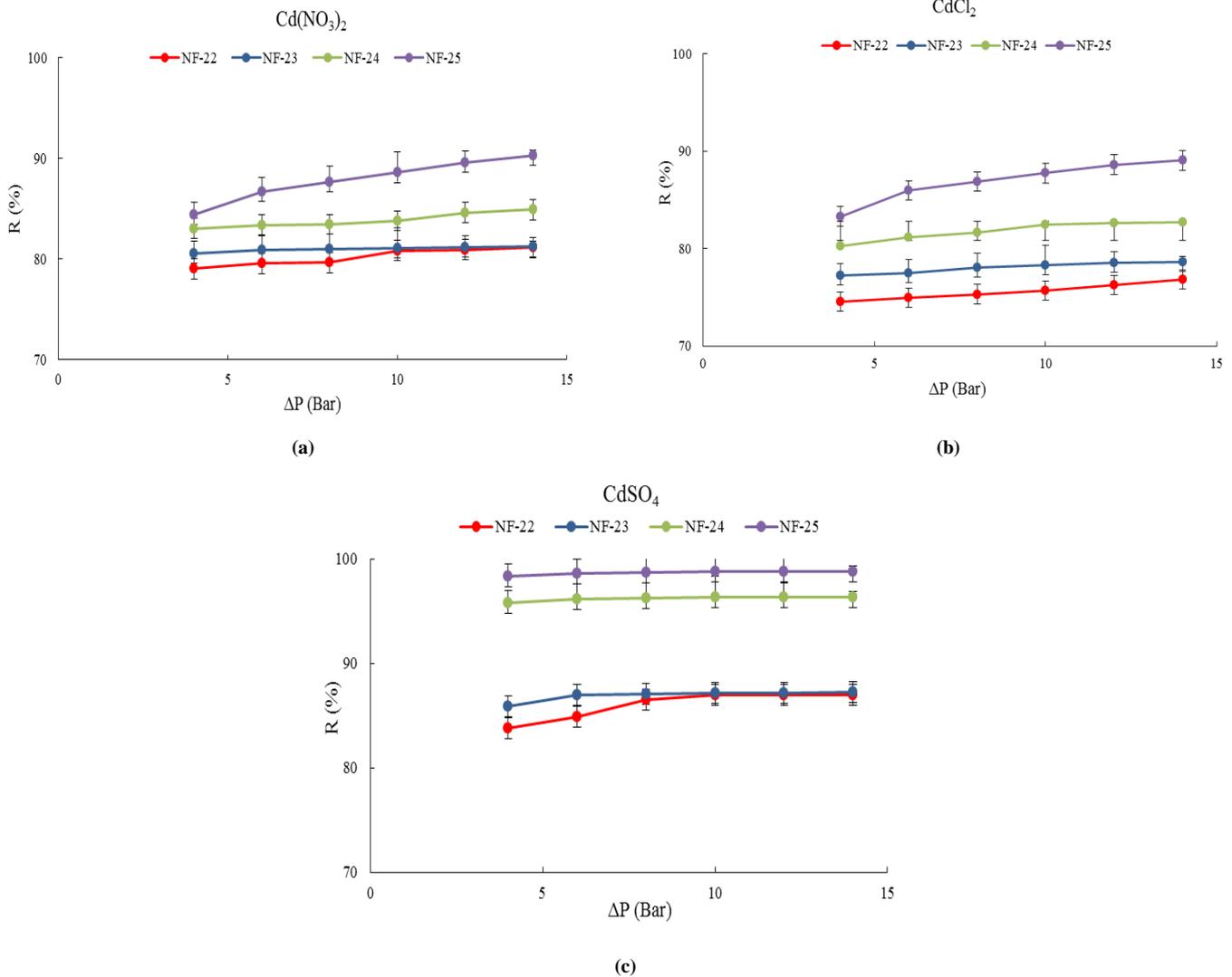


Fig. 4. Cadmium salts retention a) Cd(NO₃)₂; b) CdCl₂; c) CdSO₄; as a function of trans-membrane pressure, T = 25 °C, [Cd²⁺] feed = 10⁻³ mol L⁻¹.

3.3. Cadmium removal from aqueous solutions

Cadmium retention was studied using three types of cadmium salts: CdCl₂ (10⁻³ mol.L⁻¹), Cd(NO₃)₂ (10⁻³ mol.L⁻¹) and CdSO₄ (10⁻³ mol.L⁻¹), in order to evaluate the effect of the co-ion nature and its valency. The experiments, summarized in Figure 4, were performed at 25 °C and pH= 6.8 varying the feed pressure from 4 to 14 bar.

In all cases, CA NF membranes showed the following salt rejection sequence: R (CdSO₄) > R (Cd(NO₃)₂) > R(CdCl₂). Size exclusion mechanism describes the higher cadmium associated with the divalent anion (SO₄²⁻) with respect to monovalent anions (Cl⁻ and NO₃⁻), characterized by lower hydration radii. Moreover sulphate ions present superior hydration energy (EH) enhancing the rejection of the salt. Similar results were observed in the rejection of CdCl₂ and Cd(NO₃)₂, due to similarity in terms of hydration energies and hydrated radii of chloride and nitrate anions (Table 4).

Figure 4 evidenced a positive effect of the feed pressure on the rejection

of Cd due to the different mechanism of transport: a diffusive transport takes place at low pressure, whereas increasing the pressure convective transport became more important leading to higher rejection [45].

The effect of feed concentration (varied from 10⁻⁴ mol.L⁻¹ to 10⁻² mol.L⁻¹) on Cd²⁺ rejection is depicted in Figure 5. In particular, it can be noticed that the concentration of the salts negatively affected their rejection. The reason is an improvement of the salt permeability with their concentration in the feed due to fact that the effective pore size became larger. Higher salt concentration means high amount of salt inside the membrane, causing the increasing of the average pore size due to the stronger repulsive interaction between ions with same charge inside the pores [46]. Moreover the increasing of the contaminant concentration favors the formation of a layer of cations on the CA surface. As a consequence anions easily permeate through CA NF membranes and Cd²⁺ is less rejected because of the electro-neutrality principle [24].

Table 4
Hydration energies of ions and cadmium salts used in this work.

| Ions | NO ₃ ⁻ | Cl ⁻ | SO ₄ ²⁻ | Cd ²⁺ | References |
|--------------------------------------------|------------------------------|-----------------|-------------------------------|------------------|------------|
| Hydration energies (kJ.mol ⁻¹) | 310 | 325 | 1047 | 1815 | [37] |
| Hydrated radius (nm) | 0.335 | 0.332 | 0.379 | 0.426 | [43] |

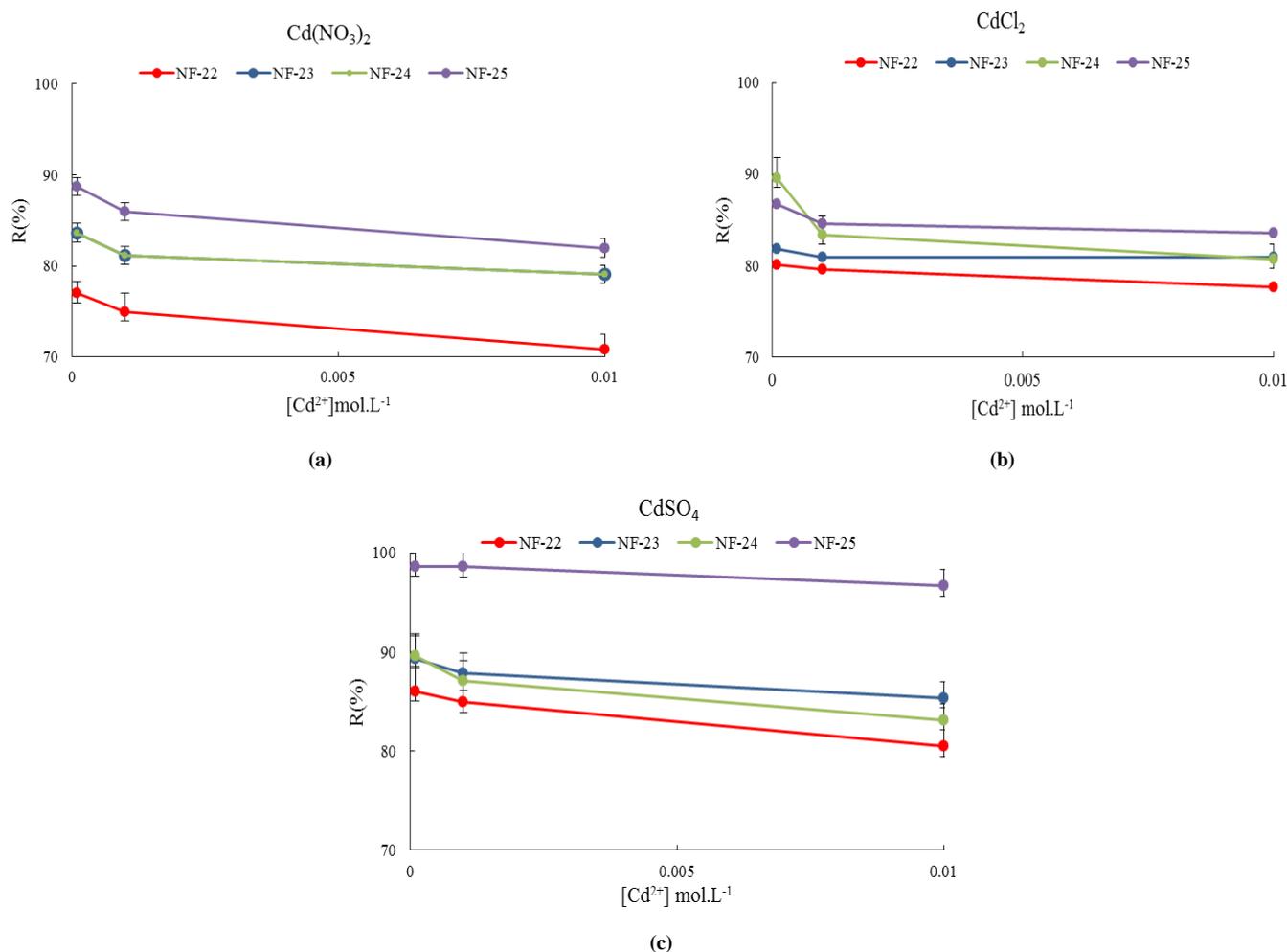


Fig. 5. Cadmium salts retention a) Cd(NO₃)₂; b) CdCl₂; c) CdSO₄; as a function of feed concentration, T = 25°C at pH=6.8.

The effect of ionic strength on cadmium removal was studied in terms of NaCl concentration ranging from 0 to 10⁻² mol.L⁻¹ with [Cd²⁺] = 10⁻³ mol.L⁻¹ and pH=6.8. As shown in Figure 6, Cd²⁺ retention decreases with increasing NaCl concentration. In particular, at higher salt concentration (NaCl 0.01 mol.L⁻¹) the cadmium retention decreases from 88.50 % to 80.87 % for CaCl₂ and from 87.70 % to 78.76% for Cd(NO₃)₂ from 98.83 to 93.04 for CdSO₄ for NF-25. This behavior is related to the electrostatic interaction between the NaCl and the CA, Na⁺ interact with the negative charge of CA related to the presence of hydroxyl and carboxylic groups, neutralizing the negative sites of the membrane reducing the electrostatic force of repulsion causing the decreasing of the rejection of Cd²⁺ [24]. In fact the increasing of the electrolyte in the feed weakened the average distance, Debye length, of the electrostatic interactions between the ions and the charges of the membrane facilitating the permeation of ions [47].

The influence of pH feed solution for the cadmium salts rejection presented in Figure 7. The pH was varied from 2 to 12, whereas cadmium salts concentration, pressure and temperature were fixed at 10⁻³ mol.L⁻¹, 9 bar and 25°C, respectively. The performance of NF process in terms of rejection of salts is strongly dependent on the pH of the solution and the isoelectric point of the membrane, generally around to a pH of 4.2 for CA membranes [48]. This explains the behavior of CA membranes in treating Cd

contaminated solutions at different pH:

- at pH=2, the membrane was charged and consequently high retention cadmium values were observed because of the repulsion forces between the ions and the membrane surface;
- at pH≈4, the neutralization of the charge of the membrane causes a reduction of R%;
- at pH>5, the presence of OH ions in the solution leads to the formation of cadmium hydroxide complexes, which causes an increase in cadmium retention. In all cases NF-25 membrane shown the best rejection results (up to 90% for CdSO₄).

4. Conclusions

In this study, CA-NF membranes were successfully prepared via NIPS. The SEM pictures elucidated the asymmetric structure of CA-NF membranes made of a dense top-layer supported on porous sub-layer. Membrane characterization evidenced the hydrophilic character of the membrane and the decreasing of the porosity of the membrane by increasing the CA concentration in the polymeric dope solution employed for membrane preparation. The reduction of the porosity caused a decreasing of water

permeability through the membrane, but increased the salt retention. The mechanism of transport through the membrane is dominated by the size exclusion mechanism. On the basis of the hydration energies and hydrated radii of the ions the sequence of rejection is: $R(\text{Na}_2\text{SO}_4) > R(\text{CaCl}_2) > R(\text{NaCl})$. CA NF membranes were successfully applied for cadmium removal, with a rejection up to 98%. Results evidenced that the Cd^{2+} associated with the divalent anion is rejected more than the cadmium associated with monovalent anions, in relation to the steric hindrance and hydration energy. Moreover, the retention decreases when the salts concentration increases, from 10^{-4} to 10^{-2} mol.L $^{-1}$. The obtained results demonstrated that the viability of the employment of the developed CA-NF membranes for removal of cadmium from contaminated water.

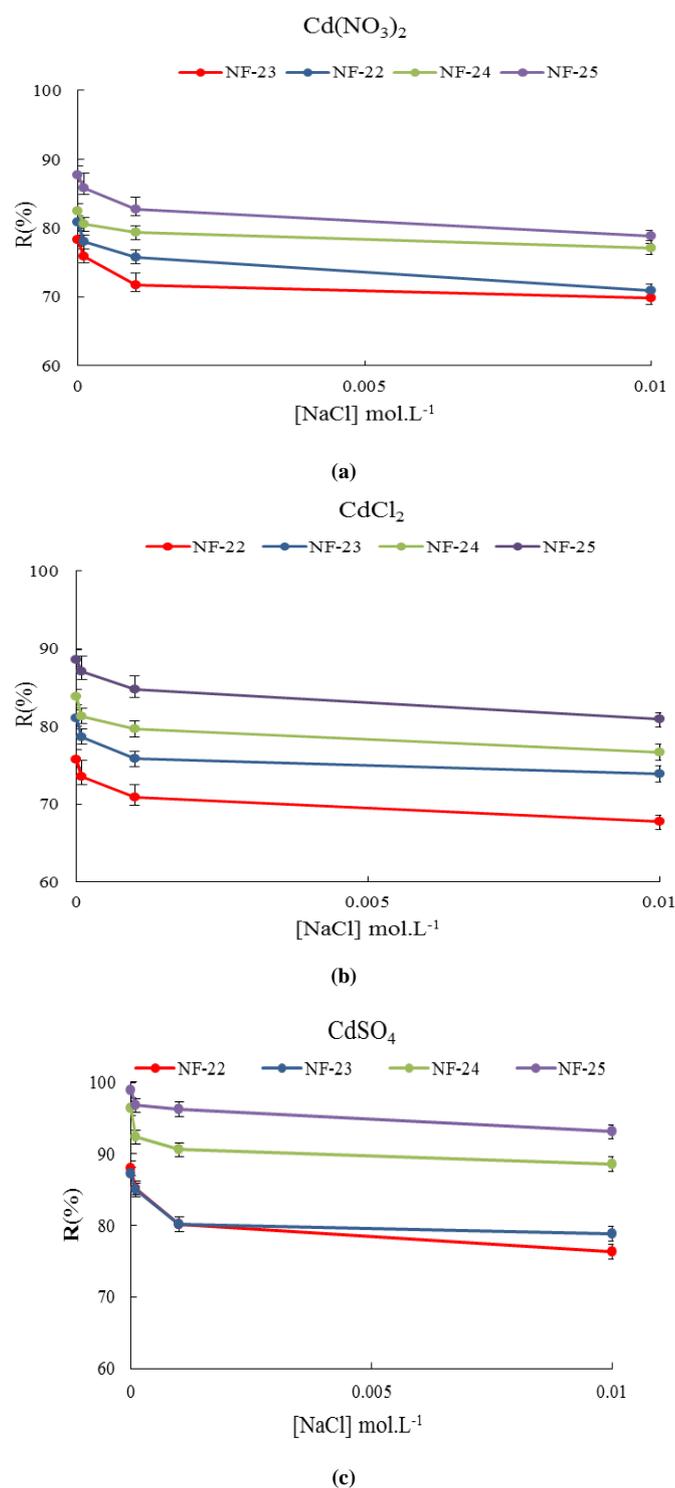


Fig. 6. Cadmium salts retention a) $\text{Cd}(\text{NO}_3)_2$; b) CdCl_2 ; c) CdSO_4 ; as a function of ionic strength, $T = 25^\circ\text{C}$, at $\text{pH}=6,8$ and $[\text{Cd}^{2+}]=10^{-3}$ mol.L $^{-1}$.

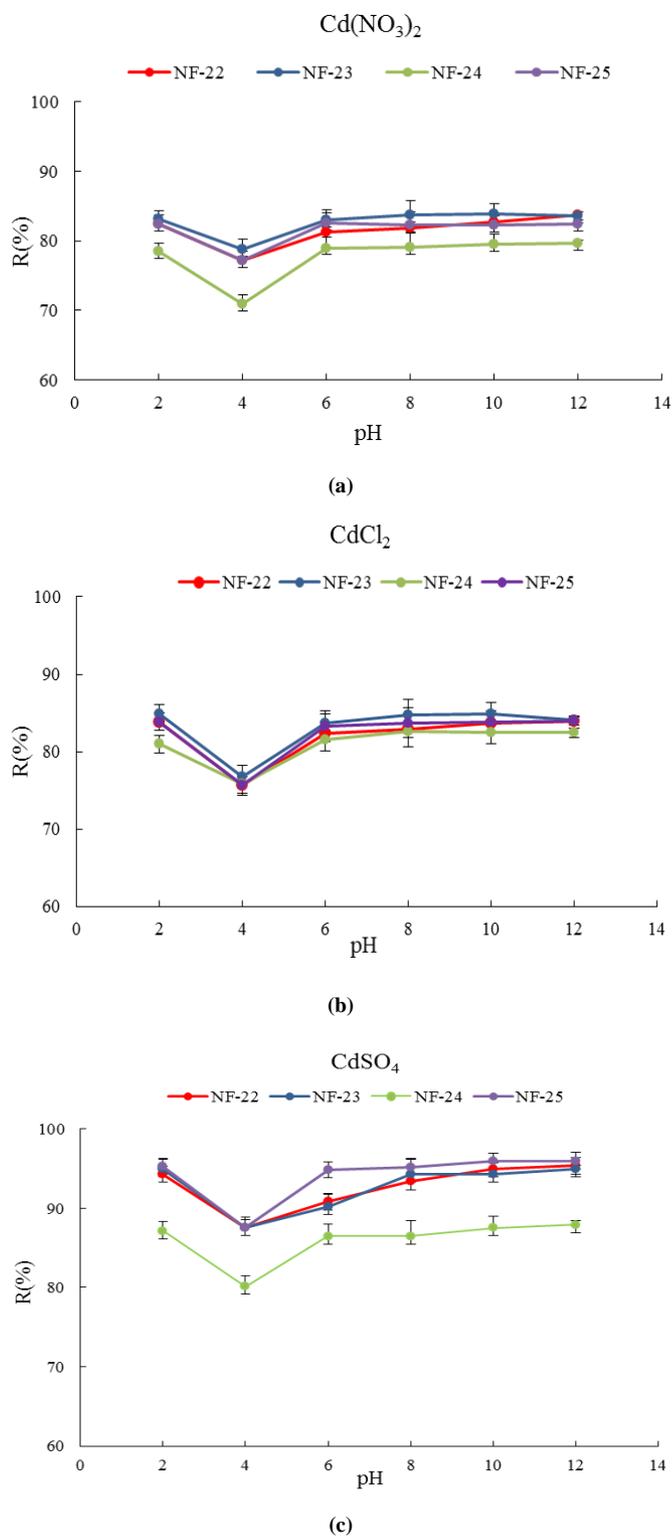


Fig. 7. Cadmium salts retention a) $\text{Cd}(\text{NO}_3)_2$; b) CdCl_2 ; c) CdSO_4 ; as a function of pH, at $C=10^{-33}$ mol.L $^{-1}$ and $T = 25^\circ\text{C}$.

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