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Synthesis and Characterization of Thin Film Composite Membranes of Chitosan, Crosslinked with Gluteraldehyde, and Polysulfone --Manuscript Draft--

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Abstract:	A breakthrough in membrane synthesis is the development of thin film composite membranes. Various studies have been conducted to evaluate the effect of a thin and dense layer of hydrophilic polymers on a porous support, generally an ultrafiltration (UF) membrane in order to obtain a fouling resistant membrane. Although polysulfone is a slightly hydrophobic polymer, it has excellent mechanical stability, chemical and thermal resistance and good resistance to chlorine. Chitosan (CHI) membranes have high hydrophilicity, being less prone to fouling, but have a lower mechanical and chemical resistance. For understanding the influence of CHI on composite membrane performance, thin film CHI/PSf membranes crosslinked with glutaraldehyde (GLU) were synthesised and characterized through Scanning Electron Microscopy, contact angle measurements, and pure water permeability assays.

Synthesis and Characterization of Thin Film Composite Membranes of Chitosan, Crosslinked with Gluteraldehyde, and Polysulfone

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Keywords: Thin Film Composite Membranes; Polysulfone, Chitosan; Gluteraldehyde,

I Abstract

An important obstacle to be overcome in order to have greater use of membrane technology for liquids purification is the phenomenon of "fouling", which is a result of specific interactions between membrane and feed components.^[1] A breakthrough in membrane synthesis is the development of thin film composite membranes, making possible to optimize each layer independently, in order to improve membrane performance as a whole. Various studies have been conducted to evaluate the effect of a thin and dense layer of hydrophilic polymers on a porous support, generally an ultrafiltration (UF) membrane in order to obtain a fouling resistant membrane. Although PSf is a slightly hydrophobic polymer, it has excellent mechanical stability, chemical and thermal resistance and good resistance to chlorine. Chitosan (CHI) membranes have high hydrophilicity, being less prone to fouling, but have a lower mechanical and chemical resistance. For understanding the influence of CHI on composite membrane performance, thin film CHI/PSf membranes crosslinked with glutaraldehyde (GLU) were synthesised and characterized through Scanning Electron Microscopy, contact angle measurements, and pure water permeability assays.

II Experimental

PSf UF membranes were produced by phase inversion with a solution of PSf / Solvent 15% by weight, at 25°C, cast over a nonwoven polyester support CU424 (Crane Nonwovens) with a 100 µm thickness

CHI was dissolved in an aqueous solution of acetic acid 1M for a final concentration of 0.5% by weight. GLU, was added to the solution during its preparation, to work as a crosslink agent. Concentrations of 1%, 3% and 5% of GLU by weight, relative to CHI concentration, were used. A 100 µm layer of CHI/GLU solution was spread over the PSf membranes. The membranes were heated up to 40°C for 1h. Finally, they were inserted into a coagulation bath containing 75% ethanol and 25% water for 3h at 25°C. The membranes were washed with demineralized water.

The influence of GLU in the membranes permeation rate, hydrophilicity, selectivity, chemical stability, and toxicity were investigated.

III Results and Discussion

Permeability tests results for all synthesized membranes are presented in Figure I. By increasing GLU concentration in the casting solution reduced membrane permeability. This reduction was attributed to a compaction of the membrane structure, which leads to a decrease in the polymer chains mobility and in the membrane void volume.

Student's t- test (95% confidence) showed that there was a reduction in the membrane contact angle (Table I) with the introduction of 5% GLU, from 76.9 ± 5.4 to 67.8 ± 6.7 , making it more hydrophilic.^[2,3] For CHI membranes with different GLU concentration no significant change in contact angle had been observed.

Membranes atomic force microscopy (MFA) images suggest that higher GLU concentrations result in less rough membranes. The effect of surface roughness seems to be important only before the gel layer formation, when the particles still interact with the membrane surface. The increase in the membrane roughness accelerates the particles deposition on the membrane surface, leading to a decrease in flux.^[4] Contrary results were reported by Hirose *et al.*^[5], who observed an increase in flux with an increase in membrane surface roughness, and attributed this phenomenon to the increase of the area available for membrane transport.

Membrane separation capacity was evaluated using MgSO_4 (1,000 mg/L), and NaCl (2,000 mg/L) solutions. Rejection of bivalent and monovalent ions did not exceed 25% and 12%, respectively. The low selectivity found appears to be closely linked to the coagulation bath with ethanol.

Even though the use of water as a second non-solvent reduced membranes permeability it did not significantly improve its selectivity. Similarly, the introduction of GLU as a crosslinking agent has not led to a significant improvement in membrane selectivity.

SEM images showed that immersion of PSf/CHI membrane into HCl solution (pH = 2, 3h), have increased its pores sizes, indicating that CHI layer was dissolved. The introduction of GLU chemically stabilized the membrane, making less susceptible to acid attack. Membrane surface crosslinked with 3% GLU apparently was not affected by the HCl solution. However, the membranes crosslinked with 1% and 5% GLU showed an increasing in their pore size after immersion, compared to the untreated membranes, suggesting an increased susceptibility to acid attack.

The potential for GLU membrane releasing was evaluated through acute and chronic toxicity assays using *Daphnia similis* and *Ceriodaphnia dubia*, respectively. PSf/CHI membranes, with and without crosslinking of the CHI layer, were immersed for 24h in natural water. None of tested membranes induced acute or chronic toxicity to the water at which they remained in contact, under tested conditions.

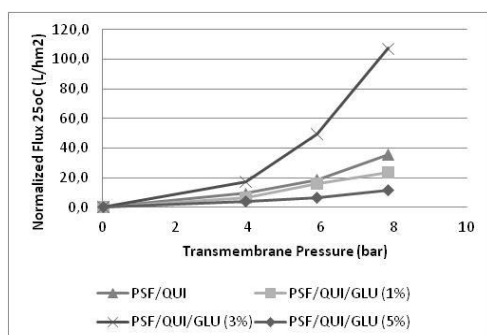


Figure 1 - Effect of crosslinking with GLU in the membrane permeability PSf/CHI.

Table I – Membranes Contact Angles

	Mean	Stand. Dev.	Var.	Fc (2,5%)
PSf/QUI	76,9	5,4	24,72	-
PSf/QUI/GLU (1%)	67,8	8,5	61,91	5,82
PSf/QUI/GLU (3%)	73,5	8,8	67,20	5,82
PSf/QUI/GLU (5%)	67,8	6,7	38,88	5,7
PSf	74,0	8,4	56,50	5,7

IV Conclusions

Introduction of a second non-solvent in the QUI coagulation bath led to less porous membranes as compared to the ones obtained with 100% ethanol. However, it did not significantly improve its selectivity. The introduction of GLU as a CHI crosslinking agent reduced membrane roughness and permeability, and increased hydrophilicity, but did not improve membrane's selectivity. Membranes crosslinked with 3% of GLU were resistant to hydrochloric acid attack.

There was no acute or chronic toxicity in relation to the test organisms *Daphnia similis* and *Ceriodaphnia dubia*, respectively, in samples of water that remained in contact with the membranes with and without crosslinking of the CHI layer, indicating that no GLU was released from the membrane.

V References

- (1) GEISE, G.M.; LEE, H.S.; MILLER, D.J.; FREEMAN, B.D.; MCGRATH, J.E.; PAUL, D.R.. *Journal of Polymer Science*. **2010**, 48, 168.
- (2) MULDER, M. "Basic principles of membrane technology." *Kluwer Academic Publishers*, United States, second edition, **1996**.
- (3) CHERYAN, M. "Ultrafiltration and Microfiltration Handbook". *Technomic Publishing CO, Inc*, United States, **1998**
- (4) RANA, D.; MATSUURA, T. *American Chemical Society*. **2010**, 110, 2448.
- (5) HIROSE, M.; ITO, H.; KAMIYAMA Y. *Journal of membrane Science* **1996**, 188, 115.

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Abstract

Thin film composite chitosan, cross-linked with glutaraldehyde, and polysulfone membranes were synthesized and the influence of chitosan and glutaraldehyde on membrane performance was evaluated. Polysulfone ultrafiltration membranes, used as porous support for the chitosan layer, were produced by phase inversion via immersion precipitation. The influence of glutaraldehyde as a chitosan crosslinking agent on membrane hydrophilicity, permeability, selectivity, chemical stability in acidic medium, and toxicity were investigated. Increasing glutaraldehyde concentrations turned the membrane less rough, more hydrophilic and less permeable, which was attributed to a compaction of the membrane structure. Membranes separation capacity was evaluated using two different ionic solutions, magnesium sulphate (MgSO_4 – 1,000 mg/L), and sodium chloride (NaCl – 2,000 mg/L). Rejection of bivalent and monovalent ions did not exceed 25% and 12%, respectively. Scanning electron microscopy images showed that the membrane surface cross-linked with 3% glutaraldehyde apparently was not affected by immersion into HCl solution, pH 2. However, the membranes cross-linked with 1% and 5% glutaraldehyde showed an increase in pore size after immersion, compared to the untreated membrane, suggesting an increased susceptibility to acid attack. The potential for glutaraldehyde releasing was evaluated through acute and chronic toxicity assays using *Daphnia similis* and *Ceriodaphnia dubia*, respectively. None of tested membranes induced acute or chronic toxicity to the water they remained in contact with, under tested conditions.

Keywords: Thin Film Composite Membranes; Polysulfone, Chitosan; Glutaraldehyde

I Introduction

Over the last decades, membrane processes emerged as the leading separation technology for water and wastewater treatment.^[1] Despite many advantages presented by membrane processes for these applications, there are still important issues that should be addressed, for instance a better control of fouling, which arises from specific interactions between membrane and feed components.^[1,2] The separation process by the membrane is a surface phenomenon, as a consequence the interaction of many contaminants and the membrane occurs, resulting in permeate flow declining, and for this reason significant effort is directed for overcoming this problem, including membrane surface modification, focusing on fouling reduction.^[3] A breakthrough in membrane synthesis is the development of thin film composite membranes, which consist of an ultra thin selective layer atop a porous support backing, generally an ultrafiltration (UF) membrane. The development of this kind of membrane made it possible to optimize each layer independently, improving membrane performance as whole. Various studies are being conducted to evaluate the effect of a thin and dense layer of hydrophilic polymers on a porous support, in order to obtain fouling resistant membranes. In these studies, the thin film is generally applied to the UF membrane in order to make its surface

smoother, more hydrophilic, and negatively charged, which are desired characteristics for fouling prevention.^[2,4]

Polysulfone (PSf) is an important polymer in commercial membrane fabrication, especially as an UF membrane and as a support for composite membranes. Most of the thin film composite membranes produced are cast using PSf membranes as its porous support because of its intrinsic mechanical stability and chemical and thermal resistance, and good resistance to chlorine, although it is slightly hydrophobic.^[2]

Chitosan (CHI), a natural polymer obtained through chitin deacetylation, has been extensively studied in composite membrane development since it is non-toxic, and hydrophilic, with good film forming properties. CHI membranes, although less prone to fouling, have low mechanical and chemical resistance, restricting their extensive use in water and wastewater treatment. CHI is a weak base, insoluble in water and organic solvents, but soluble in dilute aqueous acidic solutions ($\text{pH} < 6.5$), due to protonation of free amine groups. However, these free amine groups can be easily modified to improve membrane's mechanical and chemical stability.^[3,4,5,6]

Cross-linking is one of the most promising procedure for CHI structure modification, generating insoluble cross-linked networks and improving its mechanical strength and physicochemical properties.^[4] Cross-linking often occurs via chemical reactions, the chains being connected by covalent bonding. Glutaraldehyde (GLU), although very toxic, is the most commonly used crosslinking agent for CHI. CHI crosslinking with GLU occurs through a Schiff's base reaction between aldehyde ends of the crosslinking agent and amine moieties of CHI to form imine functions.^[4,5,6]

For understanding the influence of CHI on composite membrane performance, thin film CHI/PSf membranes, cross-linked with glutaraldehyde (GLU), were synthesized and characterized through scanning electron microscopy (SEM), atomic force microscopy (MFA), contact angle measurements, pure water permeability and selectivity assays. Membranes acute and chronic toxicity, due to GLU release, were also evaluated.

II Experimental

II.1 Materials

Polysulfone UDEL 3500 was obtained from Solvay Advanced Polymers and N-methylpyrrolidone (NMP) from BASF Corporation. The polyester support CU424 was kindly donated by Crane Nonwovens.

Chitosan, with a deacetylation degree higher than 75%, was purchased from Sigma Aldrich. Ethanol and acetic acid were supplied from Labsynth.

II.2 Thin film composite membranes preparation

PSf UF membranes were produced by phase inversion with a 15% by weight solution of PSf/NMP, at 25°C, cast over the polyester support CU424, with a 100 μm thickness.

CHI was dissolved in an aqueous solution of acetic acid 1M for a final concentration of 0.5% by weight. GLU was added to the solution during its preparation, to work as a crosslink agent, at concentrations of 1%, 3% and 5% by weight, relative to CHI concentration. The composite membranes were prepared by coating the PSf membranes with a 100 μm layer of CHI/GLU solution. The membranes were heated up to 40°C, for 1h, and then inserted into a coagulation bath containing 75% ethanol and 25% water for 3h at 25°C. The membranes were washed with copious amount of demineralized water and put to dry at room temperature.

II.3 Membrane Characterization

II.3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to study the surface characteristics and to probe the cross-sections views of the PSf and PSf/CHI membranes. SEM studies were carried out using a FEI Quanta 600 FEG scanning electron microscope at accelerating voltage of 20 kV. Membrane samples were prepared by soaking in isopropanol for 3h, then in hexane for 3h, and finally dried in air for 24h. Cryogenic membrane breaking was done after samples immersion in liquid nitrogen.

II.3.2 Atomic Force Microscopy (AMF)

The roughness of the membranes was determined by AFM using a MFP 3D Asylum Research microscope in the tapping mode.

II.3.3 Contact Angle

The contact angles of water on the membranes were measured by the Sessile Drop method using a Krüss contact angle goniometer. The average contact angle was obtained by measuring the same sample contact angle at three or more different spots.

II.3.4 Pure Water Flux Measurements

Rectangular cast membrane samples with dimensions of approximately 105 x 145 mm, and fully rinsed to remove residual solvent were used in the permeation experiments. Assays were carried out using demineralized water, electrical conductivity lower than 1 μ S/cm. Demineralized water was pumped from the reservoir by a positive displacement diaphragm pump. The system was operated with full streams recirculation (concentrate and permeate streams returning to the feed tank) and operation pressure was set through a needle valve installed in the concentrate line. After steady state was reached, the following parameters were recorded: permeate flow; feed, permeate and concentrate pressures; and feed and permeate temperatures. Permeation tests with pressures of 4, 6 and 8 bar were carried out.

Pure water flux was normalized for a reference temperature according to the Equation 1:^[7]

$$J_s = J_m \times (1.03)^{(T_s - T_m)} \quad (1)$$

Where:

J_s - permeate flux at standard temperature (25°C)

J_m - permeate flux at the temperature measured during the tests

T_s - standard temperature (25°C)

T_m - temperature reading during the tests

II.3.5 Membrane Selectivity

Selectivity tests of the thin film composite membranes, with and without addition of glutaraldehyde, were used to evaluate the rejection of mono and divalent ions. The assays were performed with two different solutions: 2.0 g/L of NaCl and 1.0 g/L MgSO_4 .

The ions concentrations were determined indirectly, through the electrical conductivity measurement. Calibration curves relating the electrical conductivity with the ions concentrations were obtained by dilution of the previously prepared solutions.

The experiments followed the same procedure described in II.3.4. The cell test was first fed with the NaCl solution and subsequently with the MgSO_4 solution. During the tests, the following operating pressures were used: 4, 6, and 8 bar. For each of the pressures, the permeate flow, as well as its conductivity, were measured.

Using the calibration curves, the permeate concentrations of Na^+/Cl^- or $\text{Mg}^{2+}/\text{SO}_4^{2-}$ ions were determined. For each pressure, the membrane rejection (R) was calculated using the Equation 2.

$$R = (\text{Cf} - \text{Cp})/\text{Cf} \quad (2)$$

Where:

Cp - concentration of Na^+/Cl^- ($\text{Mg}^{2+}/\text{SO}_4^{2-}$) in the permeate

Cf - concentration of Na^+/Cl^- ($\text{Mg}^{2+}/\text{SO}_4^{2-}$) in the feed stream

II.3.6 Degradability in acidic medium

Since CHI membranes are stable at alkaline pH, only the degradability in acid medium was evaluated. The conditions used in the acidic chemical cleaning were simulated: pH and immersion time in the acid solution of HCl. Degradability of PSf/CHI membranes, with and without GLU addition, was evaluated. Membrane samples were dried at room temperature for 24 hours and then weighed on semi-analytical scale. Subsequently, they were immersed in aqueous hydrochloric acid at pH 2.0 for 3 hours. After this period, samples were thoroughly washed with copious amount of demineralized water and put to dry at room temperature for 24 hours. The final weight of the membrane was observed for loss of mass determination.

Samples of the membranes were analyzed with SEM to check possible surface damage.

II.3.7 Membranes acute and chronic toxicity

Toxicity tests performed with the thin film composite membranes were conducted to assess whether these membranes would release any toxic compound to the water, specifically GLU, after they come into contact with. Acute and chronic toxicity tests were performed using *Daphnia similis* and *Ceriodaphnia dubia*, respectively, and natural water, with hardness adjusted to 44 ± 2 ppm by addition of CaCO_3 . Membranes were immersed in water samples for 24 hours and after this period, water samples were taken to be used in the toxicity tests.

Static 48 h acute toxicity tests were carried out with the cladoceran *D. similis* to evaluate its survival after exposure to the water samples that remained in contact with the membranes. Young organisms were exposed to the water samples according to a standard procedure [8]. Water samples were considered to have acute toxicity if the number of immobile organisms at the end of the test was higher than 10%.

The chronic effects search for water samples that remained in contact with the composite membranes were performed on *Ceriodaphnia dubia*, according to NBR 13373:2005 [9]. One neonate was exposed to water samples (10 replicates) for eight days and their growth and reproduction were registered and compared to the control samples (natural water with hardness adjusted to 44 ± 2 ppm). The assays were validated when at least 15 neonates were obtained at the control samples during the test period. The influence of the water in the organisms' reproduction was evaluated through statistical analyses (F test and the Student's T test at the level of 95% confidence).

III Results and Discussion

Figure I (a) shows a SEM image of the PSf membrane surface. Membrane average pore size and its pore size distribution (Figure II) were evaluated with the software ImageJ. The membrane average pore size was estimated at $6.3 \pm 3.2\text{nm}$. Approximately 88% of the membrane pores have sizes $\leq 10\text{ nm}$.

AFM 3D image of the PSf membrane top layer is presented in Figure I (b). The membrane surface roughness, evaluated by scanning the same sample in three different areas of $2 \times 2\mu\text{m}$, was estimated at $5.2 \pm 0.6\text{ nm}$.

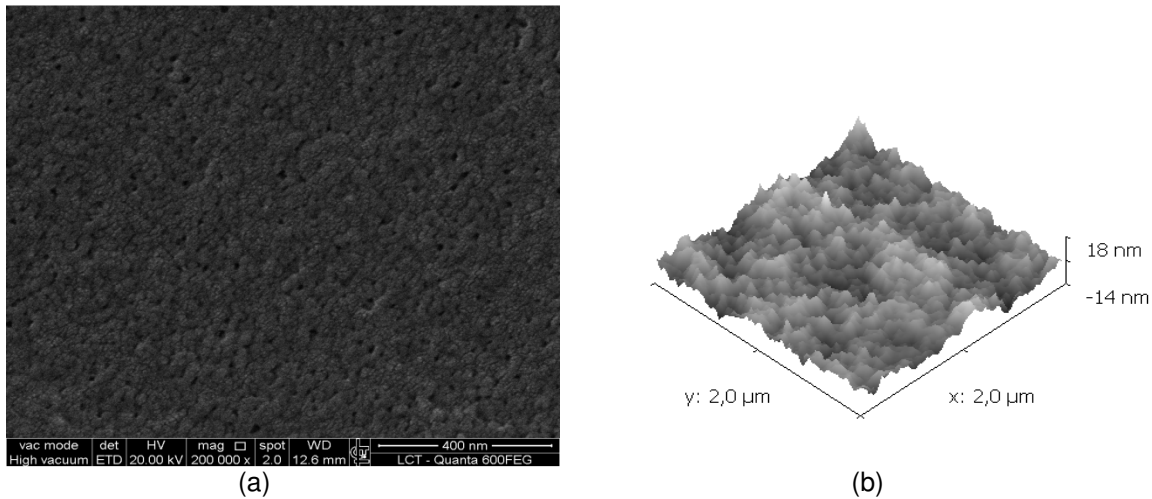


Figure I – Polysulfone membrane selective layer – (a) SEM and (b) AFM images. SEM – scale 400 nm; AFM: 2.0 x 2.0 μm samples

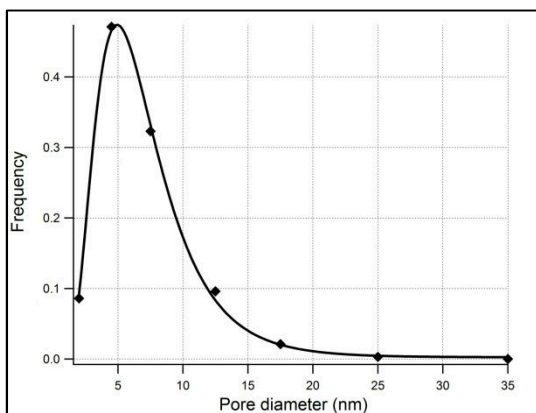


Figure II – PSF membrane pore size normal distribution

Figure III shows details of CHI layer deposited on the PSf membrane. It is possible to see the PSf granules and the presence of a thin and dense top layer, of approximately 11 μm. The presence of a second layer, just beneath the CHI top layer, where the polymer appears between the PSf granules, can also be observed.

Permeability tests results for all synthesized membranes are presented in Figure IV, in which it could be observed that increasing GLU concentration in the casting solution results in a reduction in membrane permeability. This reduction was attributed to a compaction of the membrane structure, which leads to a decrease in the polymer chains mobility and in the membrane void volume. The high permeability presented by the PSf/CHI/GLU (3%) was attributed to a higher permeability of the PSf membrane.

Student's t- test (95% confidence) showed that there was a reduction in the membrane contact angle (Table I) with the introduction of 5% GLU, from 76.9 ± 5.4 to 67.8 ± 6.7 , making it more hydrophilic.^[2,10,11] For CHI membranes with different GLU concentration no significant change in contact angle was observed.

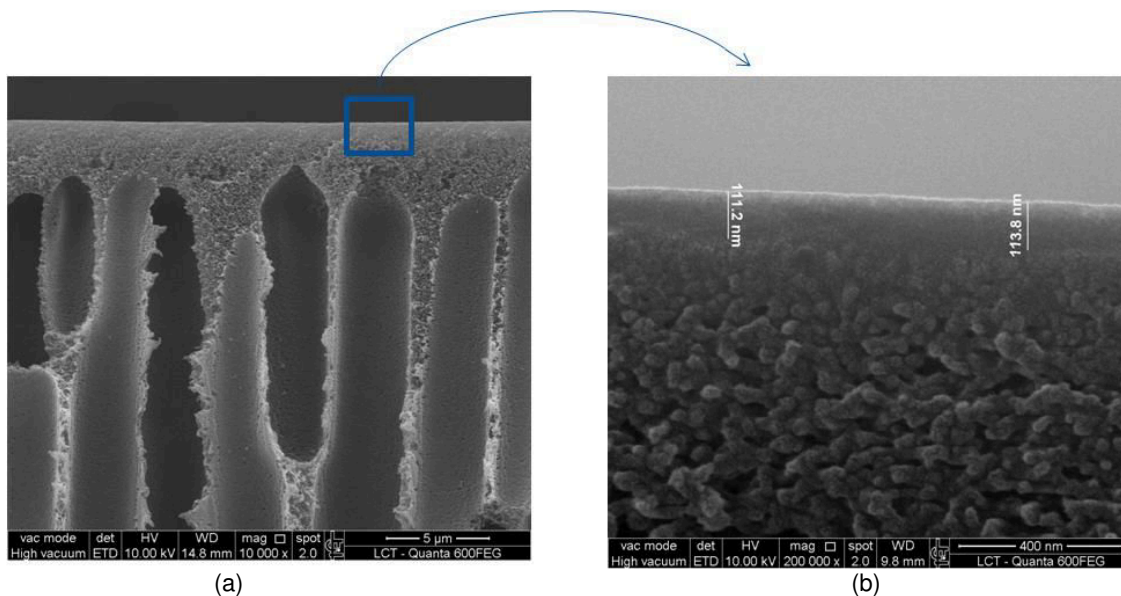


Figure III – SEM images of the PSf/CHI composite membranes. (a) scale: 5mm; (b) scale: 400nm.

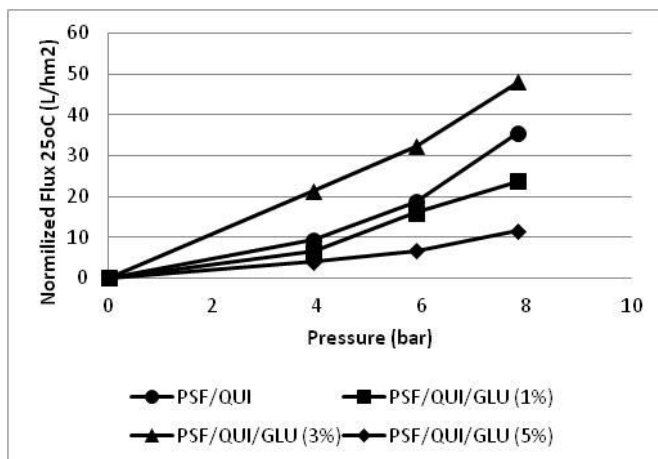


Figure IV - Effect of crosslinking with GLU in the membrane permeability PSf/CHI.

Table I – Membranes Contact Angles

	Mean	Standard Deviation	Variance	Fc (2.5%)
PSf/QUI	76.9	5.4	24.72	-
PSf/QUI/GLU (1%)	67.8	8.5	61.91	5.82
PSf/QUI/GLU (3%)	73.5	8.8	67.20	5.82
PSf/QUI/GLU (5%)	67.8	6.7	38.88	5.70
PSf	74.0	8.4	56.50	5.70

AFM analyses suggested that higher GLU concentrations resulted in less rough membranes. Composite membranes with 1, 3 and 5% GLU addition, showed surface roughness of 22.6 nm, 8.8 nm, and 5.5 nm, respectively. Based on these results, a greater membrane surface roughness was expected for the PSf/CHI membrane than for those membranes where

CHI was cross-linked with GLU. However, AFM analysis showed a surface a roughness of 4.4 nm for the CHI/PSf membrane. This inconsistency was related to the fact that, for those membranes, roughness measurement was obtained from a single scan area of 2x2µm. These are preliminary results and a more detailed analysis, including making roughness measurements in more than one area and scanning larger areas.

Observing SEM images of the composite membrane surface (Figure V) it is possible to see part of the PSf/CHI pores. However, for membranes were CHI was cross-linked with GLU, it was not possible to distinguish the surface pores, suggesting that GLU introduction led to a decrease in pore size. The effect of surface roughness seems to be important only before the gel layer formation, when the particles still interact with the membrane surface. However, the increase in the membrane roughness accelerates the particles deposition on the membrane surface, leading to faster a decrease in flux.^[12] Contrary results were reported by Hirose *et al.*^[13], who observed an increase in flux with an increase in membrane surface roughness, and attributed this phenomenon to the increase of the area available for membrane transport.

Membrane separation capacity was evaluated using MgSO₄ (1,000 mg/L), and NaCl (2,000 mg/L) solutions (Figure V). Rejection of bivalent and monovalent ions did not exceed 25% and 12%, respectively. The low selectivity found appears to be closely linked to the coagulation bath with ethanol. Even though the use of water as a second non-solvent reduced membranes permeability it did not significantly improve its selectivity.^[14] Similarly, the introduction of GLU as a crosslinking agent has not led to a significant improvement in membrane selectivity.

SEM images of composite membranes after immersion into HCl solution, pH 2 for 3 hours, are shown in Figure VI. PSf/CHI membrane seems to have had its pores sizes increased, indicating the occurrence of CHI dissolution. The introduction of GLU chemically apparently stabilized the membrane, making less susceptible to acid attack. Membrane surface cross-linked with 3% GLU seems not to have been affected by the HCl solution. However, the SEM images suggest that the membranes cross-linked with 1% and 5% GLU have had an increasing in their pore size after immersion, compared to the untreated membranes, indicating an increased susceptibility to acid attack. Although the visual analyses of SEM images suggest the occurrence of membranes degradation after immersion in acidic medium, these results could not be confirmed since no mass lost was detected using the semi-analytical balance. SEM images of the membranes cross-sections are needed to establish whether the CHI dissolution really occurred.

None of tested membranes induced acute or chronic toxicity to the water at which they remained in contact, under tested conditions. Immobility rates were below 10% for all of the water samples tested in acute toxicity assays (with and without GLU addition). It was also observed that the introduction/increase in GLU concentration did not increase water samples acute toxicity. Student's T test with 95% confidence revealed that water samples that remained in contact with the membranes evaluated (with and without GLU addition) did not presented chronic toxicity with respect to *Ceriodaphnia dubia*.

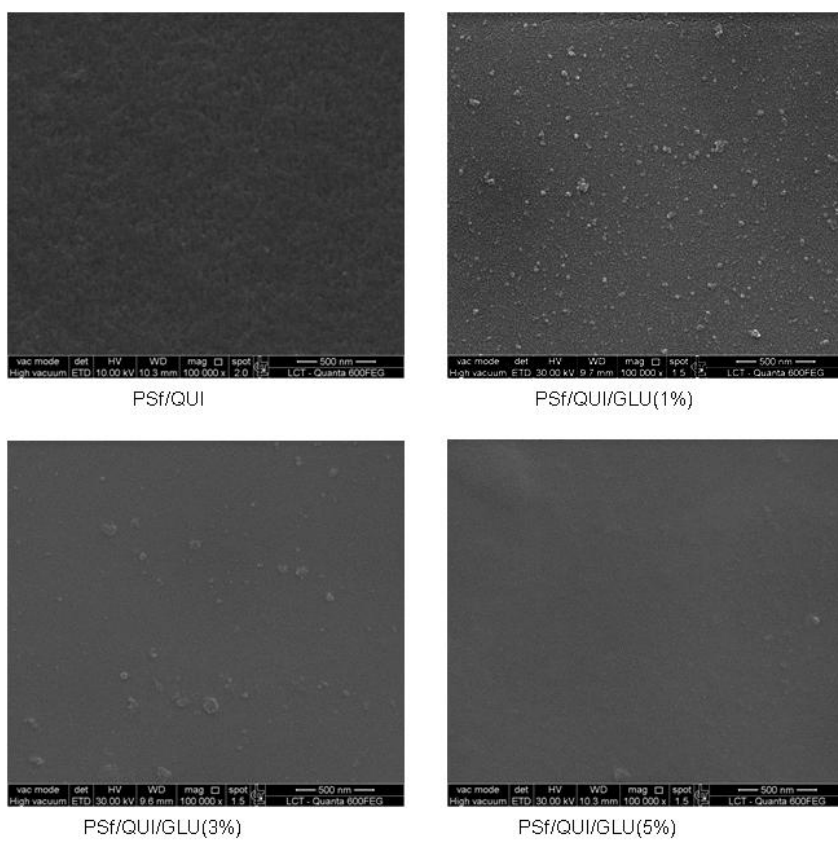


Figure IV – SEM images of composite membranes surface: effect of GLU addition. Scale: 500 nm

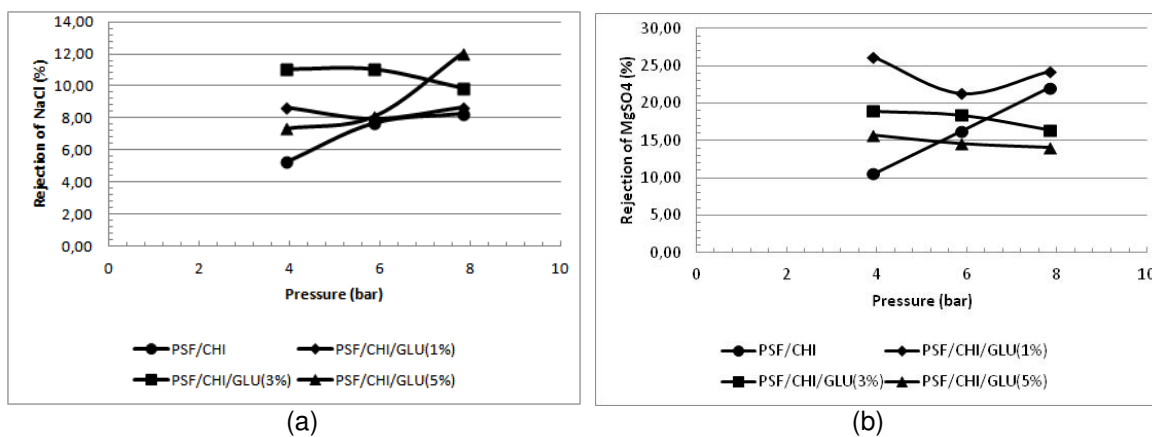


Figure V – Influence of glutaraldehyde in membranes selectivity: (a) NaCl rejection; (b) MgSO₄ rejection

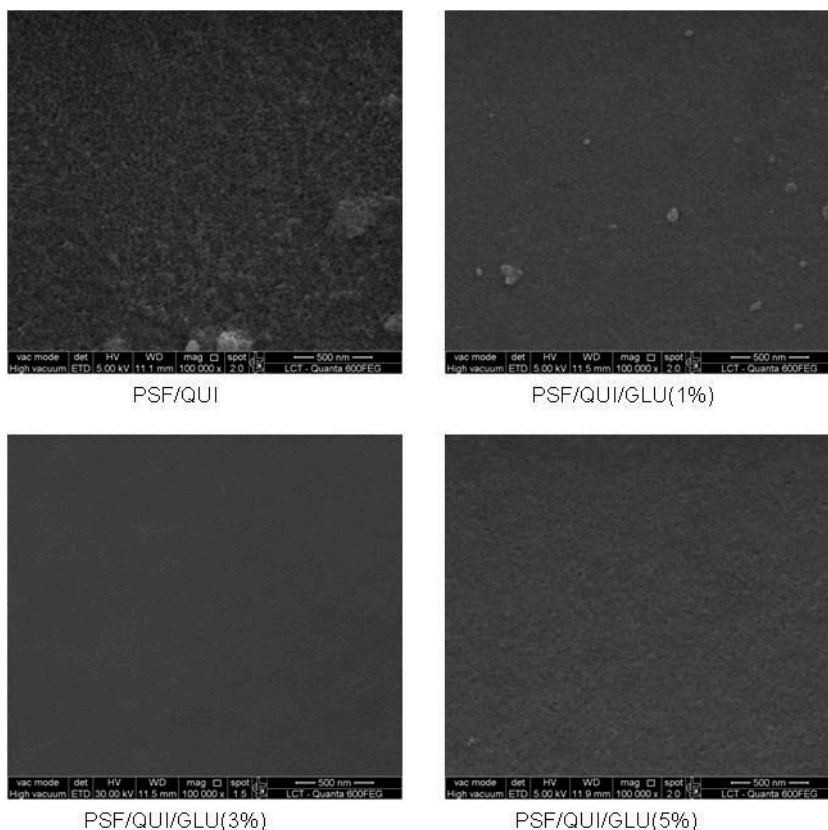


Figure V – SEM images of the membranes surface after their immersion in HCl aqueous solution (pH=2, 3 hours).

Conclusions

Introduction of a second non-solvent in the QUI coagulation bath led to less porous membranes as compared to the ones obtained with 100% ethanol. However, it did not significantly improve its selectivity. The introduction of GLU as a CHI crosslinking agent reduced membrane roughness and permeability, and increased its hydrophilicity. However, it did not improve membrane's selectivity. Membranes cross-linked with 3% of GLU were resistant to hydrochloric acid attack.

There was no acute or chronic toxicity in relation to the test organisms *Daphnia similis* and *Ceriodaphnia dubia*, respectively, in samples of water that remained in contact with the membranes with and without crosslinking of the CHI layer, indicating that no GLU was released from the membrane.

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References

- (1) GEISE, G.M.; LEE, H.S.; MILLER, D.J.; FREEMAN, B.D.; MCGRATH, J.E.; PAUL, D.R.. *Journal of Polymer Science*. **2010**, 48, 168.

- (2) RANA, D.; MATSUURA, T.. *Chem. Rev.*, **2010**, 110, 2448-2471.
- (3) TSAI, H.S.; WANG, Y.Z.. *Polymer Bulletin*, **2008**, 60, 103-113.
- (4) TAN, S.H.; AHMAD, A.L.; MOHD NAWAWI, M.G.; HASSAN, H.. *AJSTD*, **2002**, 19, 69-83.
- (5) HUANG-SHIAN, T.; WANG, Y.Z.. *Polymer Bulletin*, **2008**, 60, 103-113.
- (6) URAGAMI, T.; MATSUDA, T.; OKUNO, H.; MIYATA, T.. *Journal of Membrane Science*, **1994**, 88, 243-251.
- (7) PUCCA, P.T.. "Produção e caracterização de membranas de microfiltração e ultrafiltração pelo método de inversão de fases, utilizando polissulfona como matéria-prima", *Universidade de São Paulo*, **2010**.
- (8) ABNT NBR 12713. Aquatic ecotoxicology-acute toxicity – assay method for *Daphnia* spp (*Cladocera crustacea*). **2004**.
- (9) ABNT NBR 13373. Ecotoxicologia Aquática – Toxicidade Crônica - Método de Ensaio com *Ceriodaphnia* spp (CLADOCERA, CRUSTACEA). **2005**.
- (10) MULDER, M. "Basic principles of membrane technology." *Kluwer Academic Publishers*, United States, second edition, **1996**.
- (11) CHERYAN, M.. "Ultrafiltration and Microfiltration Handbook". *Technomic Publishing CO, Inc*, United States, **1998**.
- (12) RANA, D.; MATSUURA, T.. *American Chemical Society*, **2010**, 110, 2448.
- (13) HIROSE, M.; ITO, H.; KAMIYAMA Y.. *Journal of Membrane Science*, **1996**, 188, 115.
- (14) KOLLS, W.F.C.. "Membrane formation by phase inversion in multicomponent polymer systems. Mechanisms and morphologies". PhD thesis. Hoogstraten, Belgium, **1998**.

