Development of an Organic-Inorganic PVDF/Nanoclay Ultrafiltration Composite Membrane

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Abstract

Ultrafiltration (UF) and microfiltration (MF) membrane synthesis using poly(vinylidene fluorine) (PVDF) has become usual in the recent years because of PVDF low prices, chemical and thermal stability, mechanical proprieties, radiation resistance and low superficial energy and dielectric constant. However, PVDF membranes has some limitations in water, sewage and aqueous mixtures treatment, due to its hydrophobicity (LIU, et al., 2007; ZHAO, et al., 2008).

Based on the principle that hydrophilicity is an antifouling performance prerequisite, various membrane modification methods have been explored in order to incorporate hydrophilic proprieties in the conventional hydrophobic membrane (ZHAO, et al., 2008; LIU, et al., 2011b).

The incorporation of inorganic nanoparticles in polymeric solutions has been extensively studied because of its simplicity. This blending modification intends to improve porous membrane performance, reducing its hydrophobicity, and others morphological properties (YAN, et al., 2006; LIU, et al., 2011b).

The main objective of this study is to perform a comparison between the composite (PVDF/Clay) UF membrane and simple (PVDF) UF membrane. Both membranes were synthesized by phase inversion process and permeation tests were conducted to evaluate the membrane performance.

The experimental results indicate that the composite (PVDF/Clay) UF membrane presents better pure water flux compared to simple PVDF membranes. Additional work has been developed to understand the hole of clay nanoparticles on the improvement of membrane performance.

Keywords: clay nanoparticles, phase inversion, poly(vinylidene fluoride), ultrafiltration

INTRODUCTION

Poly(vinylidene fluorine) (PVDF) is a semicrystalline polymer. The $-C-C-$ bond of main macromolecular straight chain is surrounded by fluorine and hydrogen atoms ($-CH_2-CF_2-$), resulting in: excellent mechanical stability due to spatial arrangement of CH_2 e CF_2 groups along the polymeric chain, influencing its crystalline structure (LIU, et al., 2011b); thermal stability, due to fluorine atoms high electronegative and the C–F high bound dissociation energy (LOVINGER and REED, 1980); and chemical stability for a wide range of chemical products such as halogens, oxidants, inorganic acids, and aromatic, aliphatic and chlorinated solvents (HASHIM, et al., 2011).

These properties and its low prices, radiation resistance and low superficial energy and dielectric constant, make the PVDF one of the most popular polymer for microfiltration (MF) and ultrafiltration (UF) membranes (LIU, et al., 2007; ZHAO, et al., 2008).

Despite the previously presented advantages, some problems with PVDF membranes still exist, which constrain new developments and applications of this kind of membrane, especially for drinking water production and wastewater treatment.

Due to the strong hydrophobic nature of the PVDF membrane, there are no hydrogen bond interactions in the boundary layer between the membrane interface and water, resulting in low membrane wettability and reduced permeated flow. Moreover, hydrophobic membranes are more fouling susceptible during the treatment of aqueous solutions containing natural organic matter (NOM) (LIU, et al., 2011b), because the repulsion by hydrophobic surface of the water molecules is a spontaneous process, with an increasing entropy, and, thus, NOM molecules have a tendency to adsorb on membrane surface (BRANT and CHILDRESS, 2004; DU, et al., 2009).

Based on the principle that hydrophilicity is an antifouling performance prerequisite, various membrane modification methods have been explored in order to incorporate hydrophilic proprieties in the conventional hydrophobic membrane (ZHAO, et al., 2008).

The blending modification is ordinarily used to obtain desired functional properties together with the membrane synthesis. Thus, the synthesis and modification processes can be performed in only one step (ZHAO, et al., 2008). Until now, three main types of additives were introduced to modify the porous PVDF membrane: hydrophilic polymers or pore forming additives, amphiphilic copolymers, and inorganic particles (LIU, et al., 2009).

In the past years, the addition of inorganic particles in polymer solutions has become an attractive method for the polymeric membranes synthesis. Research has focused on the preparation of composite or organic-inorganic hybrid membranes by the incorporation of inorganic particles, in order to modify membranes properties for various purposes. Inorganic nanoparticles incorporation has improved the performance of the membranes and their properties, like hydrophobicity, fouling resistance, mechanical properties, and permeability. This occurs, because nanoparticles have unique properties (electronic, magnetic, optical, thermal and mechanical stability) and due to their small size, high activity and high surface area (YAN, et al., 2006).

MONTICELLI et al. (2007) study demonstrates that modified polysulfone (PSU)-clay had better permeate flux and higher contaminants rejection performance when compared to the pure PSU membranes. The modified membrane showed a lower contact angle, because the clay increases membrane wettability, and also mechanical properties improvements were observed.

The main objectives of this study are the ultrafiltration membranes synthesis using the poly (vinylidene fluoride) (PVDF) and inorganic nanoparticles clay (bentonite hydrophilic), by phases inversion process and to perform a comparison between the composite (PVDF/Clay) UF membrane and simple (PVDF) UF membrane.

EXPERIMENTAL
Materials
Commercial poly(vinylidene fluorine) (PVDF) polymer (Kynar Flex® 2821 copolymer (poly(vinylidene fluorine) and hexafluoropropylene)) and N-methyl-2-pyrrolidone (NMP) solvent,

99.1 g mol^{-1} molecular weight, were used in the polymeric solution. The polyvinylpyrrolidone (PVP), 10,000 g mol^{-1} average molecular weight, was used as pore former. The clay (hydrophilic bentonite) nanoparticles, with ≤ 25 micron average particle size and 180.1 g mol^{-1} molecular weight, were used as additive. All this chemicals were used as they were received. Demineralized water was prepared in the laboratory by double step reverse osmosis was used for membrane casting and membrane performance evaluation.

The PVDF (Kynar Flex 2821) was kindly donated from Arkema Química Ltda (Arkema France Brazilian filial). The NMP was provided from Cosmoquímica Indústria e Comércio Ltda and fabricated by Basf Coporation. The PVP and clay nanoparticles were both acquired from Sigma Aldrich.

Casting solution preparation and membrane casting procedure
The base solution was prepared with a PVDF fixed concentration (18% weight) dissolved in N-methyl-2-pyrrolidone (NMP) solvent, at 50ºC and stirred for 24 hours or until the generation of a homogenous polymeric solution had been obtained. For solutions containing PVP, the final complex solution was obtained by the addition of the 1% PVP (based on PVDF mass) together with PVDF. For solutions containing clay nanoparticles, 4% of clay nanoparticles (based on PVDF mass) were direct added and dispersed in the solution previously prepared. This mixture was stirred for 24 hours at 50ºC until the total dispersion of the clay nanoparticles and the final complex solution was obtained. Table 1 show the composition of each mixture.

Table 1. Different composite PVDF membranes

Membrane No.	PVDF (wt%)	NMP (wt%)	PVP (wt%)[1]	Clay nanoparticles (wt%)[1]
M1	18	82	0	0
M2	18	82	1	0
M3	18	82	0	4
M4	18	82	1	4

[1] wt% is based on PVDF mass

Phase inversion by immersion precipitation method (Figure 1), was used for membrane casting. The polymeric solution was spread onto a glass plate to produce a flat sheet membrane, and obtained film was immediately immersed in coagulation bath. After coagulation bath, cast membranes were immersed in water bath (demineralized water at ambient temperature), for at least 24 hours for removing any residual solvent. Table 2 shows membrane casting parameters.
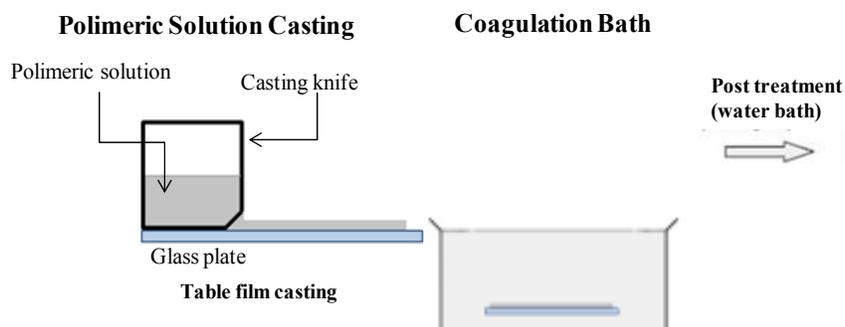

Figure 1. Phase inversion by immersion precipitation process steps

Table 2. Casting parameters for flat sheet membranes

Casting Temperature	ambient
Casting knife	100μm
Casting Speed	0.04 m/s
Coagulation Bath	demineralized water
Coagulation Bath Temperature	25ºC
Coagulation Bath Time	2 minutes

Membrane performance evaluation

For synthesized membrane performance evaluation, demineralized water flow tests were conducted using a cross flow test cell (Figure 2). For these tests wet membranes were used and at least three different rectangular samples (0.13 meters x 0.09 meters) were cut for three different membranes. The system was pressurized to 0.07 MPa. Each test was run for one hour and permeate flow samples were determined using a graduated cylinder and a stop watch, with measures taken each five minutes.
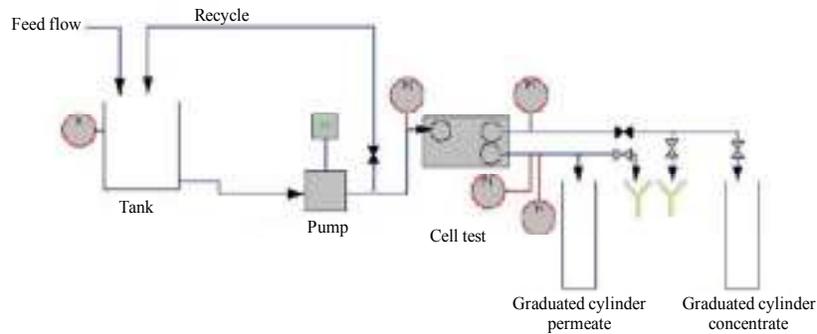
Reference: (PUCCA, 2010) adapted

Figure 2. Performance evaluation test system

Based on the series resistance model, the permeate flux (J; [$m^3/m^2.h$]) was calculated using the equation 1 and the clean membrane hydraulic resistance (R_M [m^{-1}]) was calculated using equation 2.

$$J = \frac{V}{A.t} \qquad (1)$$

where, V = permeate water volume by membrane (m^3); A = membrane effective surface area (m^2); t = permeation time (h)

$$R_M = \frac{\Delta P}{\mu.J} \qquad (2)$$

where, J = flux ($m^3/m^2.s$); ΔP = transmembrane pressure (Pa); μ = cinematic water viscosity (Pa.s)

RESULTS AND DISCUTION

Demineralized water flow test is a preliminary evaluation of the effect of PVP and clay nanoparticles addition on the PVDF membrane performance.

Table 3 and Figure 3 present results regarding pure water permeate flow of different membranes. It can be noted that PVP additive and clay nanoparticles affects membranes permeability. The highest

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permeate flux was presented by M2 membrane with 0.1672 $m^3.m^{-2}.h^{-1}.MPa^{-1}$ and M4 showed the second highest permeate flux with 0.0569 $m^3.m^{-2}.h^{-1}.MPa^{-1}$.

Table 3. Additives effect on PVDF membrane permeability

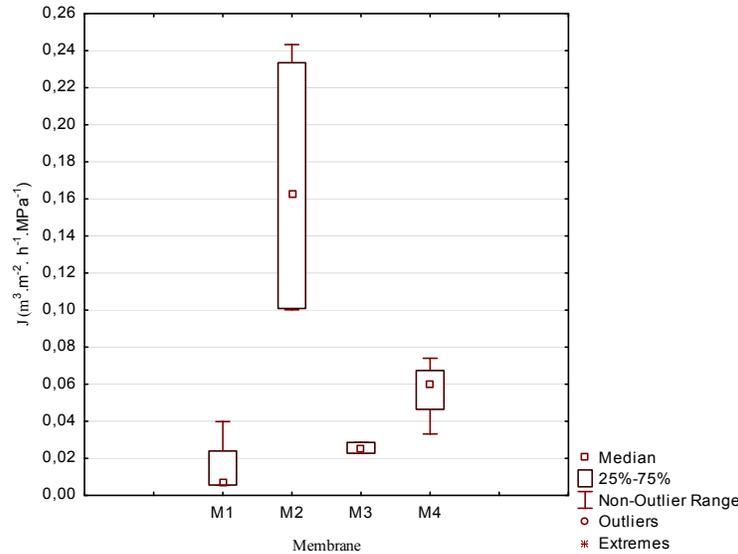| Membrane No.	Average permeate flow ($m^3.h^{-1}$)	Average permeate flux (($m^3.m^{-2}.h^{-1}.MPa^{-1}$))
M1	0.0008	0.0148
M2	0.0091	0.1672
M3	0.0014	0.0257
M4	0.0031	0.0569

Figure 3. Additives effect on PVDF membrane permeability

The membrane performance evaluation tests suggest that M3 has increased 75% of pure water permeate flux comparing with M1, control, membrane. Moreover, the M4 membrane further improved around 120% pure water permeate flux comparing with M3 and around 285% comparing with M1.

It can be noted that the clay nanoparticles addition improved membrane (M3 and M4) permeability, comparing with simple PVDF membrane (M1). These results were expected since improvement of pure water flux with the clay nanoparticle (GHAEMI, et al., 2011) and Al_2O_3 nanoparticle (YAN, et al., 2006) addition were observed.

In the study of GHAEMI et. al. (2001) it is argued that clay nanoparticles addition increases membrane hydrophilicity and induces changes in membrane surface and morphology. According to their results, no matter of the clay nanoparticles concentration added in the polyethersulfone polymer solution, higher membrane hydrophilicity, porosity and thinner skin layer are formed, increasing its permeability.

According to the results presented on Table 3 and Figure 3, membrane produced with the combination of clay nanoparticles and PVP (M4) presents a much better permeability compared with the membrane in which only clay nanoparticles had been used (M3), what can possible be associated to membrane pores plugging by clay nanoparticles, so the use of a pore former, like PVP,

can help to avoid this effect. This hypothesis is in agreement with previous reports, that discuss the hypothesis that nanoparticles agglomeration can plug PVDF membrane pores (LIU, et al., 2011a), however it is necessary to analyze membrane internal structure in order to confirm it.

Figure 4, Figure 5, Figure 6 and Figure 7, are plots of membranes pure water flux with time. It can be seen in Figure 5 and Figure 7 that for membranes with PVP (M2 and M4) the permeate flux dropped fast in the first 20 minutes and then became relatively stable. Figure 4 and Figure 6 show that for membranes without PVP (M1 and M3) permeate flux is relatively stable all the time. This behavior can possible be associated with the membrane internal pore structure.
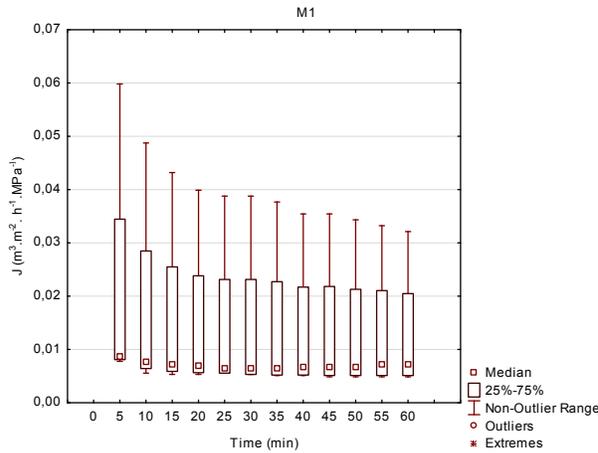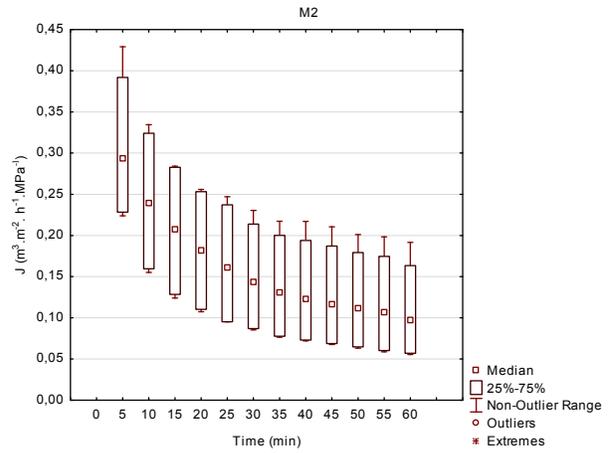

Figure 4. M1 permeability effect in time

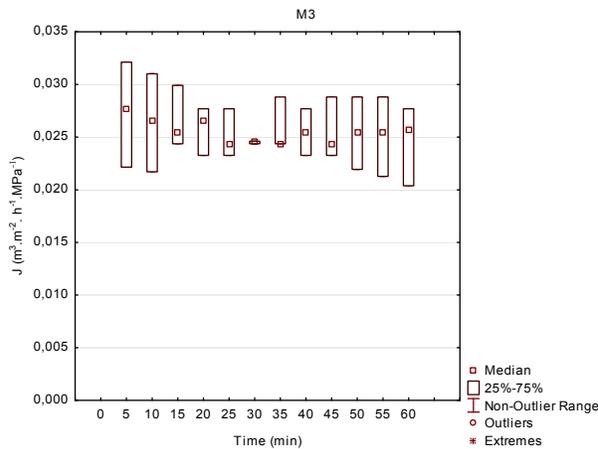

Figure 5. M2 permeability effect in time

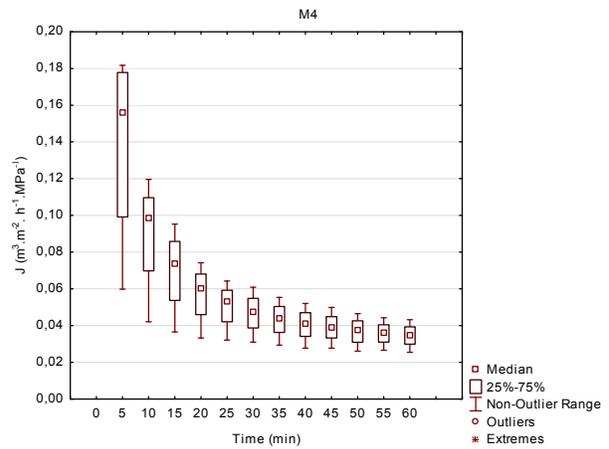**Figure 6.** M3 permeability effect in time

Figure 7. M4 permeability effect in time

Table 4 presents the results of membrane hydraulic resistances. Clay nanoparticles addition in the M3 membrane resulted in a hydraulic resistance about 4 times lower the one for control membrane (M1). Combination of clay nanoparticles and PVP as membrane additives contributed for an additional reduction in the resistance, membrane (M4). However both membranes presented a higher hydraulic resistance, compared to membrane (M2).

It is important to note that presented results are preliminary and that additional studies should be carried out in order it could be possible to have a better understanding about the effect of clay nanoparticles on membrane morphological and chemical properties, and how it can affect membrane performance.

Table 4. Effect of additives on PVDF membrane clean membrane hydraulic resistances

Membrane No.	Average hydraulic resistance (m^{-1})
M1	20×10^{12}
M2	1×10^{12}
M3	5×10^{12}
M4	3×10^{12}

CONCLUSIONS

In this preliminary study, the influence of clay nanoparticles and PVP on the performance of PVDF membrane has been evaluated. A comparison between the composite UF membrane and simple UF membrane has been analyzed. The membranes have been prepared from a complex solution with PVDF, clay nanoparticles and/or PVP, synthesized by the phase inversion method. The results of membrane performance evaluation test suggest that composite membrane (PVDF/Clay nanoparticles) can improve pure water permeate flux (74%) compared with simple PVDF membrane. Moreover, the additions of pore former (PVP) further improved pure water permeate flux (121%) compared with PVDF/Clay nanoparticles membrane. Additional studies should be carried out to obtain a better understanding about the influence of clay nanoparticles on membrane morphology and performance.

REFERENCES

BRANT, J. A. and CHILDRESS, A. E., 2004. Colloidal adhesion to hydrophilic membrane surfaces. *Journal of membrane Science,* October, **241**(2), pp. 235-248.

DU, J. R., PELDSZUS, S., HUCK, P. M. and FENG, X., 2009. Modification of poly(vinylidene fluoride) ultrafiltration membranes with poly(vinyl alcohol) for fouling control in drinking water treatment. *Water Research,* October, **43**(18), pp. 4559-4568.

GHAEMI, N. et al., 2011. Preparation, characterization and performance of polyethersulfone/organically modified montmorillonite nanocomposite membranes in removal of pesticides. *Journal of Membrane Science,* October, **382**(1-2), p. 135– 147.

HASHIM, N. A., LIU, Y. and LI, K., 2011. Stability of PVDF hollow fibre membranes in sodium hydroxide aqueous solution. *Chemical Engineering Science,* April, **66**(8), pp. 1565-1575.

LIU, F., ABEDB, M. M. and LI, K., 2011a. Preparation and characterization of poly(vinylidene fluoride) (PVDF) based ultrafiltration membranes using nano g-Al2O3. *Journal of Membrane Science,* January, **366**(1-2), p. 97–103.

LIU, F., DU, C.-H., ZHU, B.-K. and XU, Y.-Y., 2007. Surface immobilization of polymer brushes onto porous poly(vinylidenefluoride) membrane by electron beam to improve the hydrophilicity and fouling resistance. *Polymer,* May , **48**(10), pp. 2910-2918.

LIU, F. et al., 2011b. Progress in the production and modification of PVDF membranes. *Journal of Membrane Science,* June , **375**(1-2), pp. 1-27.

LIU, F. et al., 2009. Preparation of hydrophilic and fouling resistant poly(vinylidene fluoride) hollow fiber membranes. *Journal of Membrane Science,* December, **345**(1-2), pp. 331-339.

LOVINGER, A. J. and REED, D. J., 1980. Inhomogeneous thermal degradation of poly(vinylidenefluoride) crystallized from the melt. *Macromolecules,* July, **13**(4), pp. 989-994.

PUCCA, P. T. P., 2010. *Produção e aracterização de membranas de microfiltração pelo método de*

inversão de fases, utilizando polisulfona como matéria prima. Masters Dissertation*,* São Paulo: s.n.

YAN, L., LI, Y. S., XIANG, C. B. and XIANDA, S., 2006. Effect of nano-sized Al2O3-particle addition on PVDF ultrafiltration membrane performance. *Journal of Membrane Science,* Volume **276**, p. 162–167.

ZHAO, Y.-H., QIAN, Y.-L., ZHU, B.-K. and XU, Y.-Y., 2008. Modification of porous poly(vinylidene fluoride) membrane using amphiphilic polymers with different structures in phase inversion process. *Journal of Membrane Science,* March , **310**(1-2), p. 567–576.