Research on Hydrophilic Nature of Polyvinylpyrrolidone on Polysulfone Membrane Filtration

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Abstract. The membranes used in wastewater filtration are obtained from polymers, this technique is widely applied because of the small installations and low costs as against conventional systems. The polymeric membranes have high mechanical strength and flexibility, but is a challenge to improve in the same time the permeability and retention capacity of the membranes. A process that can improve the membrane properties is the addition of additives to the polymer solution, resulting in noticeable changes in the resulting membrane structure. Polyvinylpyrrolidone (PVP) is a highly hydrophilic polymer, used as a food additive that acts as stabilizer and thickening agent, which brings improvements in membrane properties. This study analyses the effect of polyvinylpyrrolidone (PVP) on the casting solution of the prepared membranes. The polymer solution was prepared from polysulfone (PSf) and N-methyl-2-pyrrolidone (NMP) at different concentrations. The membranes were obtained by phase inversion method. The PSf/PVP/NMP membranes with different concentrations were characterized by contact angle measurements, surface roughness, morphological structure and permeation tests. The results show that the hydrophilic nature of PVP improve the pure water flux, the contact angle and exhibit a higher anti-fouling property.

1. Introduction
Membrane technology is an efficient process in water treatment due to its high removal quality of toxic components and recovery of important elements from industrial effluents. This technique is widely used in food industry, chemical technology and pharmaceutical industry, also for a large area of applications [1].

This domain is of interest for researchers focused to improve the membranes durability, stability in time and high permeation properties. Most of the researches are based on high performance modification in wastewater treatment using hydrophilic membranes, polymers or hydrophilic additives incorporated in membranes [2].

Polysulfone is a thermoplastic polymer often used to prepare polymeric membranes, which contains in the main chain structure the sulfone group (SO₂) and the isopropylidene or ether groups [3-6], defined as aromatic constituents that provide high resistance to oxidation and heat [5, 6]. Polyethersulfone (PES) is another type of polymer used in membrane fabrication due to its thermal, chemical, mechanical resistances and hydraulic stability, applied in ultrafiltration process. Mahendran et al. improved the PES membrane properties by adding polyvinylpyrrolidone (PVP) in polymer casting solution and used as an organic additive [7]. Polyvinylpyrrolidone (PVP) is a hydrophilic...
polymer used in polymer solutions as additive to fabricate membranes by phase inversion technique [8]. PVP has the role of forming pores and water affinity increase of membranes, also [9-10].

The membranes obtained by phase inversion technique is produced by a change in the composition of constituents. A method of this technique is by immersing a polymer/solvent solution in a non-solvent coagulation bath in which a demixing of the solvent from the polymer solution occurs [11].

A disadvantage of membrane technology is the fouling phenomenon which affects retention performance of the membrane and permeation properties [12]. The fouling mechanism consist in blocking the membrane pores with pollutant particles [13]. This particles (foulants) can be organic or inorganic solutes, biological or colloids solids. There are many studies on fouling resistance improvements by changing the membrane fabrication technique or by applying different treatments on membranes already obtained [14]. Another way to avoid the membrane fouling is applied a regularly backwashing and chemical cleaning [15].

Han et al. have studied the effect of PVP addition on 15 wt.% PSf membranes and observed that the additive accelerates the phase separation of the solvent from the film of polymer solution [9]. Saljoughi et al. observed the influence of PVP concentration on pure water flux and on insulin rejection. The study shows that increasing the concentration of PVP to 1.5 wt.%, the water flux increases but the rejection capacity decreases because of macrovoid formation. Further increase in PVP concentration to 9 wt.% produces suppressed macrovoids and water flux decrease [1].

2. Methods and analysis

2.1. Flat-sheet membrane preparation

The membrane samples were obtained from Polysulfone (PSf) and N-methyl-2-pyrrolidone with 2 wt.% addition of Polyvinylpyrrolidone (PVP). Neat PSf membranes with four different concentrations of polymer (23, 25, 27 and 30 wt.%) and modified membranes with PVP additive with 2 wt.% addition in casting solution were of interest in this study, as shown in Table 1. The membranes were prepared by phase inversion method induced by immersing the casted solutions in a non-solvent coagulation bath (distilled water).

| Membrane name | PSf [wt.%] | PVP [wt.%] | NMP [wt.%] |
|---------------|------------|------------|------------|
| 23_PSf/NMP    | 23         | 0          | 77         |
| 25_PSf/NMP    | 25         | 0          | 75         |
| 27_PSf/NMP    | 27         | 0          | 73         |
| 30_PSf/NMP    | 30         | 0          | 70         |
| 23_PSf/PVP/NMP | 23       | 2          | 75         |
| 25_PSf/PVP/NMP | 25       | 2          | 73         |
| 27_PSf/PVP/NMP | 27       | 2          | 71         |
| 30_PSf/PVP/NMP | 30       | 2          | 68         |

2.2. Permeation test

The pure water permeability ($PWP$, L m$^{-2}$ h$^{-1}$ bar$^{-1}$) was determined by using a dead-end cell. The permeation is obtained by measuring the pure water flux at four different pressures ($P$), from 6 to 12 bar, obtaining a linear regression of the pure water flux ($J_w$, L m$^{-2}$ h$^{-1}$). The PWP was calculated by the following equation:

$$PWP = \frac{J_w}{P}$$
2.3. Morphological analysis
The surface membrane images were obtained by Philips FEI, QUANTA 200, a scanning electron microscope (SEM). The samples were dried for 24 hours at 50°C and maintained in dried inert state until the analysis was performed. The membranes were prepared by coating with gold to form a conductive surface.

When analyzing the membrane surface, it can be determined the roughness represented by the average of the peaks and valleys. The surface roughness is an important membrane property because it can be correlated with fouling membrane resistance [16]. The surface roughness average (Ra) was determined by using the top view SEM images in the ImageJ software [ImageJ, http://rsb.info.nih.gov/ij/]. The mechanism to obtain the roughness using ImageJ is based on using the images from SEM analysis that convert the grey contrasts in peaks or valleys, darker grey represents membrane valleys while lighter grey represents membrane peaks. The average of the valleys and peaks it is the roughness average (Ra).

3. Results and discussion
3.1. Permeation tests
Membrane permeability is inversely proportional to the increase of polymer concentration in the casted solution, as seen in Figure 1. Increasing polymer concentration reduces permeability due to decreased solvent ratio (N-methylpyrrolidone), which means that when the membranes are obtained by phase inversion (the transition from the liquid phase to the solid phase), the demixing of the solvent in the water of the coagulation bath is slower and fewer pores are formed in the membrane structure.

![Figure 1. Permeability of PSf/NMP and PSF/PVP/NMP membranes.](image)

The explanation for the permeability increasing when PVP additive is blended in the PSf/NMP cast solution is found in the properties of hydrophilic polyvinylpyrrolidone (increased affinity for water) and in the fact that the additive used is a hydrogen donor.

3.2. Fouling resistance
The relative flux is the ratio between the flux of distilled water and the flux of dye solution, if the value is close to 1 it approaches the ideal state of a membrane where the fouling of the membrane is insignificant.

In Figure 2 it shows that the addition of polyvinylpyrrolidone gives the membrane a low resistance to fouling. On the beginning of the test the flux is higher than at the end, therefore the relative flux is decreasing with the increased dye volume tested and the relative flux values are not close to 1. This phenomenon is explained by the density of the large pores, which means that their size is smaller and the fouling resistance decreases, which was also observed in the morphological analysis (SEM).
Figure 2. Influence of PVP additive in different PSf/NMP membrane concentration on the relative flux.

The highest fouling resistant membranes with PVP additive in casting solution are the membranes with 27 and 30 wt.% PSf due to their similar relative flux with the membranes without PVP addition. More than that, the membranes with 30 wt.% PSf have the same relative flux at the end of the test. The relative flux is lower for the PSf/PVP/NMP membranes because of their small pore size from the membrane surface and the fouling phenomenon appears easier because the particles from the dye solution are blocking easier in membrane pores.

3.3. Morphological analysis

Surface morphology studies were carried out by SEM analysis to evaluate surface membrane changes since the polymer casting solutions were different (Table 1).

Figure 3 shows the pure PSf membranes with the four PSf concentrations and the membranes with 2 wt.% of PVP used as additive. The PVP additive in the membrane composition has led to smaller
pore sizes and is no longer as visible on the surface of the membrane, while the membranes without additive show larger pores. This tendency of pore formation in membranes containing polyvinylpyrrolidone has been well studied by Ochoa et al., 2001; Yoo et al., 2004; Susanto and Ulbricht 2009 [17-19].

This aspect can be explained by the double role of the PVP additive, the main effect being to increase the affinity of the membrane to water and the second is to act as a pore forming agent that can increase the surface of the pores or decrease in pore size depending on its concentration in the casting solution [20].

The surface roughness of the neat membranes is obviously lower than that with PVP additive membranes. It is well established that a membrane with smoother surfaces has a higher resistance to fouling.

| Table 2. Roughness average of membrane surface. |
|-----------------------------------------------|
| PSf [wt %] | PVP [wt %] | Ra    |
|-----------|------------|-------|
| 23        | 0          | 35.2961 |
| 25        | 0          | 31.1571 |
| 27        | 0          | 28.1696 |
| 30        | 0          | 20.1573 |

The membrane surface show a higher roughness due to the addition of PVP, consequently it has a greater number of pores on the membrane surface, explaining the high flux of the PSf/PVP/NMP membranes compared to the flux of the pure membranes. The roughness is also influenced by the concentration of the polymer resulting in a higher roughness. The recorded surface roughness values of pure and composite membranes are shown in Table 3.

Sample morphology was investigated using the Quanta 200 electronic scanning microscope equipped with an EDX elemental composition analyzer at an acceleration voltage of 12.5 kV. The presence of the polyvinylpyrrolidone additive in membranes with different concentrations of PSf was confirmed by the EDX spectra, as shown in EDX mappings from Figure 4 and the concentration values of the elements detected on the surface of the membrane, detailed in Table 3, also.

| Table 3. EDX analysis of PSf/PVP/NMP membranes, [wt.%]. |
|--------------------------------------------------------|
| Element | 23 PSf/PVP/NMP | 25 PSf/PVP/NMP | 27 PSf/PVP/NMP | 30 PSf/PVP/NMP |
|---------|----------------|----------------|----------------|----------------|
| C       | 79.59          | 80.67          | 79.21          | 80.87          |
| O       | 10.75          | 10.59          | 9.55           | 9.46           |
| S       | 6.98           | 7.04           | 7.81           | 9.34           |
| N       | 2.62           | 1.9            | 1.85           | 1.76           |

The EDX analysis was done on the surface of the membranes. For the studied samples the elements of interest are sulfur (S) derived from PSf polymer and nitrogen (N) from PVP additive. The sulfur element is observed at 2.3 keV and the peak for nitrogen (N) is observed at 0.392 keV, respectively.
Figure 4. Spectrum and distribution of elements in EDX membrane analysis.

On the map of nitrogen (N) it can be observed a uniform distribution for all the membranes, that means that the PSf polymer concentration do not have a negative influence on the distribution of PVP additive on membrane structure.

4. Conclusions
The presence of the PVP additive in the membrane composition produces a significant effect on the performance of the polysulfone ultrafiltration membranes.

The main aspect that has been observed is that it improves the permeability of the membrane. Thus, PSf membranes with 2 wt. (%) PVP addition show an increase in flux of approximately 180%, 118%, 195% and 275% for 23 wt.%, 25 wt.%, 27 wt.% and 30 wt.% PSf membranes, respectively.

Due to the ability to form the hydrogen donor complexes it has been observed that the hydrophilic property of the membranes has been improved.

5. References
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