

Polysulfone Based Membranes for Removal of Polysaccharides from Aqueous Solutions by Means of Ultrafiltration Process

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This study concerns the ultrafiltration of aqueous solutions of water-soluble polysaccharides. The process is used to remove carboxymethylcellulose and soluble starch from aqueous solutions. These biopolymers are widely used in the textile industry as sizing agents and their recovery is of great importance relating to evident economic and environmental benefits, since both the size agents and the clean water are reusable inside mill processes and since the rejected liquid wastes must be as clean as possible.

Polysulfone and poly(sodium 4-styrene sulfonate) were blended so as to obtain materials of various compositions and the blends were used to prepare ultrafiltration membranes by phase-inversion method. Then, the polysulfone based membranes, employed in a magnetic stirred cell, operating in a batch mode, were used to remove the polysaccharides from aqueous solutions. To investigate the performance of the membranes in removing the macromolecular species, the Dubois spectroscopic method was used.

The objective of this paper is to present and describe the Dubois colorimetric method and to discuss the use of this method in the analysis of the permeates resulting from ultrafiltration of polysaccharides aqueous solutions. It will focus on the accuracy of the method and its suitability for this application.

1. Introduction

The textile industry ranks among the most water-consuming industries (Karmakar, 1999). Besides, textile processing mills discharge great quantities of wastewater, both hot and contaminated. The literature is richly documented about the nature of these contaminants (Patel, 2015), their negative effects on the environment (Muthu, 2020), and the evident necessity to enforce rigorous effluent remediation methods since the problem isn't resolved to date (Yusuf, 2018).

The treatment of the effluents that the textile industry produces must be done to prevent outdoor pollution. This treatment, which concerns the effluents leaving the mills, remains necessary whatever the environmental good practices applied indoors the mills. However, encouraging good practices, such as water saving and water reuse as well as recycling valuable materials instead of rejecting them as wastes, can have great benefits through decreased costs of purchased water and reduced costs of wastewater treatment (Bhatia, 2017). One of the ways to prospect is to focus on the cleaning of wastewater streams originating from individual textile processes, instead of collecting all the wastewater streams together and, after eventual pH adjustment, sent to communal wastewater treatment plants, as it is usually done (Petricin et al., 2015). Even if the realization of this process is generally difficult in practice, it is possible to some extent for a few steps of textile processing (Manivasakam, 2013). For this purpose, it is important to speak about the wastewater generated from the desizing step which contains significant quantities of organics in the form of sizing materials. The danger of this hot wastewater stream lies in the fact that it can account for half or more of a finishing mill's organic pollutant load (Bergenthal, 1984), and its importance lies in the fact that it can be one of the most valuable rejects, both in term of energy and water saving and in term of materials recovery and reuse.

Among the sizing materials which are reusable, starch, and other water-soluble polysaccharides like carboxymethylcellulose (CMC), seem to be the most important. Indeed, natural starch and its derivatives still constitute the most used of sizing agents in the textile industry throughout the world (Goswami et al., 2004). This paper gives a laboratory-scale study of the ultrafiltration of aqueous solutions of water-soluble polysaccharides acting as sizing materials through polysulfone-based membranes. The target macromolecules are namely CMC and soluble starch. The preparation and characterization of the membranes were given in previous papers (Belazzougui et al., 2019, 2022). This study highlights the relevance of the Dubois phenol-sulfuric acid colorimetric method (Dubois et al., 1951, 1956) for the analysis of the permeates resulting from ultrafiltration of the polysaccharides aqueous solutions. The paper reports the background of the method and its suitability to apprehend and control the selectivity of ultrafiltration membranes against water-soluble polysaccharides thanks to the examination of experiment results.

2. Concise background about the Dubois phenol-sulfuric acid colorimetric method

The phenol-sulfuric acid method is an easy, sensitive, rapid, and reliable colorimetric method widely used to measure the total carbohydrate present in aqueous solutions (Jain et al., 2017). The method detects almost all carbohydrates, namely mono-, di-, oligo-, and polysaccharides (Nielsen, 2010). The method was established by Dubois et al. (1951, 1956) in the middle of the above century. In that period, several methods for the determination of microquantities of sugars were developed within a few years, especially in connection with paper partition chromatography, but direct photometric procedures, as Dubois one, disregarded them (Timell et al., 1956) and established themselves as the best, to the point of being still widely used today. Indeed, while chromatographic methods have now largely replaced many of them, Dubois method continues to be commonly used for research and quality assurance, and it is still taught in numerous academic programs (BeMiller, 2017).

2.1 Principle of the method

The method consists in subjecting a sample of an aqueous solution containing one or a mixture of carbohydrates to the combined effect of an aqueous solution of phenol and concentrated sulfuric acid.

The role of concentrated sulfuric acid is to break down the polysaccharides, oligosaccharides, and disaccharides into monosaccharides. Under the effect of the hot acidic medium, pentoses are dehydrated to furfural, and hexoses to hydroxymethylfurfural which react with phenol to produce a characteristic yellow-orange color compound measurable by UV-Visible spectroscopy, at 490 nm for hexoses, and 480 nm for pentoses. Figure 1 gives the furfural and hydroxymethylfurfural structures.

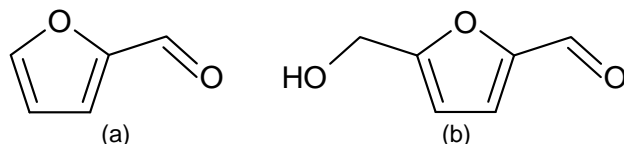


Figure 1: Structure of (a) furfural, and (b) hydroxymethylfurfural

2.2 Application of the method for the analysis of the permeates of polysaccharides treated by means of the ultrafiltration process

The use of the phenol-sulfuric acid method for the analysis of the permeates of polysaccharides acting as textile sizing agents, treated by means of the ultrafiltration process, gathers several advantages summarised below:

- The no selectivity of the method is an asset for such an application. Indeed, the method can be used, as illustrated in this paper, regardless CMC or soluble starch solution is treated.
- The method is suitable for the control of the membrane selectivity against the target polysaccharides, and also for the characterization of the membrane since intrinsic characteristics such as the cut-off can be determined using the ultrafiltration process itself employed to ultrafiltrate sets of mass-calibrated water-soluble polymers. And a well-known polysaccharide, namely Dextran, is one of the most widely used for this purpose. In the results section, the determination of the membrane cut-off gives a practical illustration of this application.
- The method is sensitive to extremely diluted aqueous solutions of carbohydrates. This quality makes it suitable for the analysis of low-concentrated ultrafiltrates.
- The simplicity of the method allows it to be a control protocol easy to implement in any textile processing mill provided that it has a quality control laboratory.

3. Materials and Methods

3.1 Chemicals

Polymers and solvent for membranes preparation were polysulfone (PS) (Aldrich; MW: 35 000), and poly(sodium 4-styrenesulfonate) (PSSNa) (Aldrich; MW: 70 000), N-methylpyrrolidone (NMP) (Merck; GC 99%). Membrane cut-off determination was done using Dextran (Fluka AG; MW: 1 500; 4 000; 7 000; 10 000; 50 000; 110 000). Synthetical sizing solutions used were carboxymethylcellulose (CMC) (Aldrich; MW: 90 000; DS = 0.7) and starch soluble (Fluka AG). Enzymatic cleaning of the membranes was done using aqueous solutions of Cellulase *Aspergillus Niger* (Sigma Aldrich; MW: 34 000). The enzymatic cleaning method was described in previous papers (Belazzougui et al., 2011). All chemicals were used without further purification. Figures 2 and 3 give respectively the structure of the polymers employed as membrane materials, and the structure of the CMC and starch. Dubois method: sulfuric acid (Fluka; AG 96%) and phenol (Fluka; Reag. Ph. Eur., 99%); Phenol, 80%, wt/wt in H₂O.

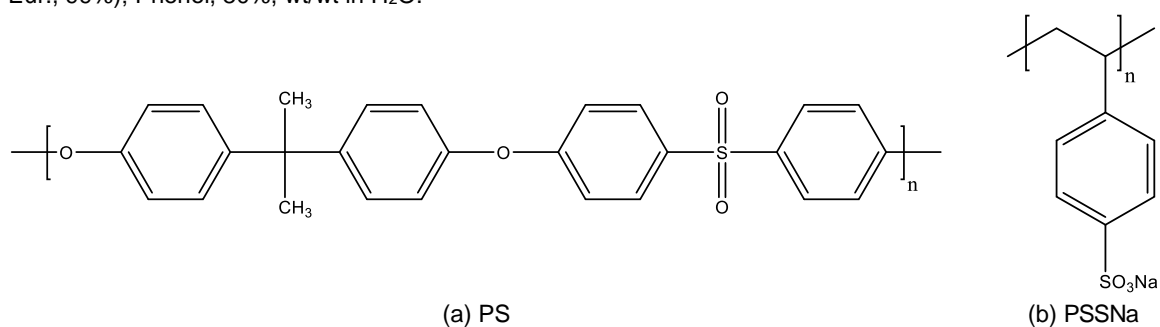


Figure 2: Structure and acronyms of (a) polysulfone, and (b) poly(sodium 4-styrenesulfonate)

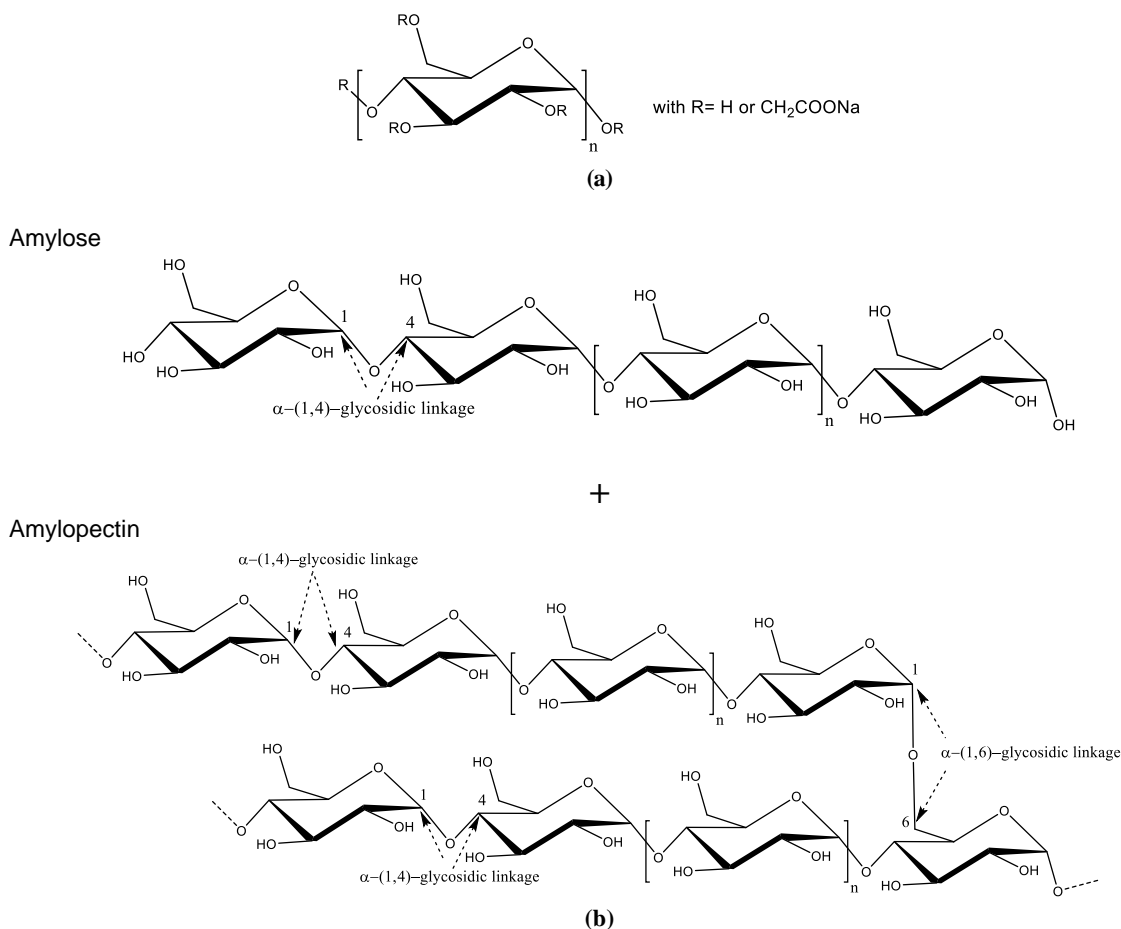


Figure 3: Structure and acronyms of (a) polysulfone, and (b) poly(sodium 4-styrenesulfonate)

3.2 Membrane preparation, ultrafiltration apparatus, and ultrafiltrates characterization

The ultrafilters were obtained by the classical Loeb and Sourirajan phase-inversion method (Loeb and Sourirajan, 1962). The polymer solutions were cast on a glass plate using a Film Applicator (Bird 284, Erichsen) that allowed to obtain casted films of 200 μm thickness. The cast polymer solutions were, then, immersed in a 45 $^{\circ}\text{C}$ water bath to ensure the coagulation of the cast films. Table 1 summarizes the composition of the polysulfone-based membranes labeled PS-S1 and PS-S2 according to the relative amount of PSSNa in the polymer blend, i.e. 1 wt % and 3 wt % respectively. The role of PSSNa is to improve the hydrophilicity of the blend because the polysulfone is a typical hydrophobic material and because hydrophilicity permits the diminishment of the fouling tendency of ultrafiltration membranes.

Table 1: Composition of the membranes

Membrane	PS (g)	PSSNa (g)	NMP (g)
PS-S1	1,98	0,02	8
PS-S3	1,94	0,06	8

The membranes were employed in a Millipore magnetic stirred cell (Cat. No. XFUF 076 01) and the device was operated in a batch mode. The ultrafiltration cell was pressurized with nitrogen and pressure was controlled by a manometer placed at the top of the cell.

The fluxes were calculated from the flow rates and were expressed by volume flux per unit time and unit area (L/h.m^2). The extent of membrane fouling was expressed in terms of relative water flux reduction, RFR given in the expression (1), which was calculated from the water fluxes at the same pressure before and after the use of the membranes for ultrafiltration of polysaccharides solutions.

$$\text{RFR (\%)} = \left(1 - \frac{J_t}{J_0}\right) \times 100 \quad (1)$$

where:

J_0 : pure water flux before use

J_t : pure water flux after use

Rejection rate R (%) was calculated using the expression (2) below:

$$\text{R(\%)} = \left(1 - \frac{c_p}{c_0}\right) \times 100 \quad (2)$$

where:

c_0 : the concentration of solute upstream of the membrane

c_p : the concentration of solute downstream from the membrane

4. Results and discussion

4.1 Colorimetric characterization of CMC and starch by phenol-sulfuric acid method

The UV-visible spectra of CMC and soluble starch aqueous solutions of several concentrations were obtained thanks to the Dubois spectroscopic method. Spectra, given in Figure 4 revealed characteristic maximum absorption peak at 486 nm for CMC and 488 nm for starch.

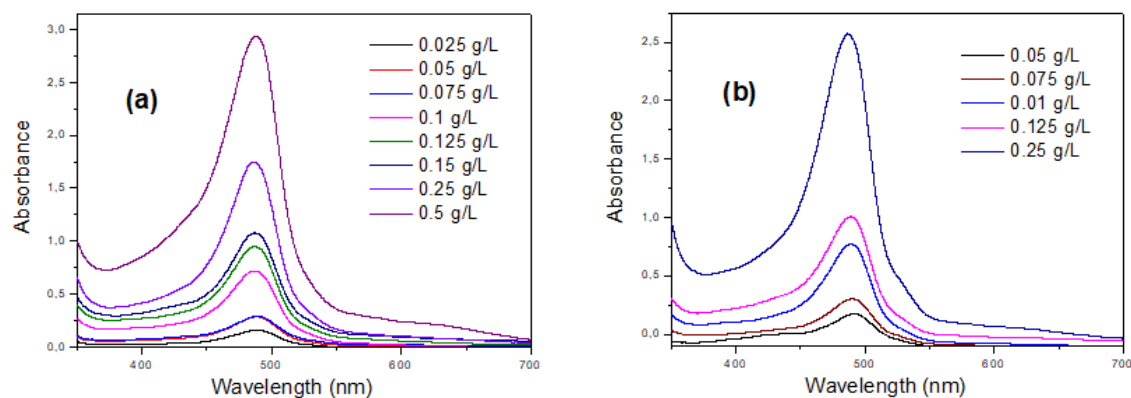


Figure 4: UV-visible absorption spectra for CMC (a) and Starch (b) aqueous solutions

The clear appearance of absorption maxima pics in the spectra, even for low concentrations, shows the adaptation of the method for the estimation of the polysaccharides quantities contained in solutions of unknown low concentrations. The method can therefore be used for the analysis of the ultrafiltrates obtained when CMC or starch aqueous solutions are ultrafiltered through the studied polysulfone-based membranes.

4.2 Determination of the PS-S1 membrane cut-off

The membrane cut-off is, by definition, the molecular weight for which rejection is greater than 90%. Figure 5 shows that the PS-S1 membrane exhibits a large rejection area and the cut-off can be estimated at 50 kDa. This result is in good agreement with the results given below concerning the rejection of CMC 90 000 aqueous solutions ultrafiltered through the membrane. Besides, the correct shape of the cut off graph confirmed the suitability of the Dubois method for the analysis of dextran aqueous solutions whatever its molecule weight.

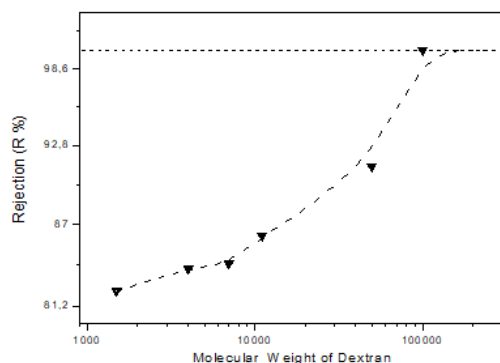


Figure 5: Molecular cut-off curve of PS-S1 membrane

4.3 Ultrafiltration of CMC and starch through PS-S1 and PS-S3 membranes

The RFR calculation highlighted the fouling resistance of the PS-S1 and PS-S3 membranes after the treatment of 1 g/L CMC aqueous solutions. Indeed, Figure 6a reveals a relative water flux reduction of less than 25%. The compartment after starch ultrafiltration was different with an RFR close to 65%. This negative result can be attributed to the particularly high viscosity of starch aqueous solutions. However, it was possible to regenerate partially the solvent flux after enzymatic cleaning, and an acceptable RFR of 35% was obtained after cleaning.

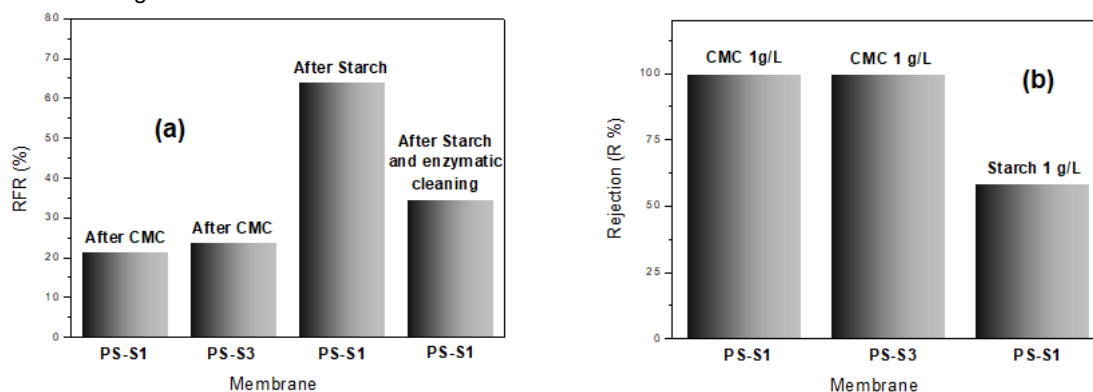


Figure 6: Ultrafiltration of CMC and starch. (a) RFR and (b) Rejection rate of the membranes PS-S1 and PS-S3

Concerning the selectivity of the membranes, as expected, CMC was totally rejected by both PS-S1 and PS-S3 membranes. Indeed, the membrane cut-off was largely higher than the CMC molecular weight allowing the complete rejection of CMC 90 000 by the two membranes. Contrary, starch is very weakly rejected by the PS-S1 membrane, with a rejection rate close to 60%. This low rejection could be explained by the nature of the two polymers constituting starch. Indeed, the combination of linear conformation, short dimensions, and the uncharged nature of amylose fraction could allow it to pass through the microporous membrane without resistance. The Dubois spectrometric method used for the ultrafiltrate analysis is, in addition, very sensitive and permits to detect all polysaccharides that cross the membrane. Figure 6b gives the results commented above.

5. Conclusions

Polysulfone-based membranes were used to ultrafiltrate aqueous solutions of CMC and starch. Before and after ultrafiltration of the macromolecular solutions, solvent flux measurements made it possible to observe an important solvent flux regeneration for PS-S1 and PS-S3 membranes after CMC ultrafiltration without any special cleaning, as well as after starch ultrafiltration after enzymatic cleaning. The partial recovery of initial solvent flux revealed good anti-fouling capabilities for the PS-S1 and PS-S3 membranes allowing to say that the introduction of PSSNa in the blend materials was efficient to improve the resistance to fouling of the membranes. The Dubois spectrometric method used for the analysis of the ultrafiltrates was relevant both in the determination of the cut-off of the PS-S1 membrane, which was found to be close to 50 kDa, and for the estimation of the selectivity of PS-S1 and PS-S3 membranes against CMC and starch, which was found to be complete for CMC and close to 60 % for starch.

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