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Laboratory investigation of using and fouling and cleaning of polyethersulfone membranes employed in the removal of carboxymethylcellulose and poly(vinyl alcohol) from aqueous solutions

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ABSTRACT

One of the most significant environmental difficulties arising in textile industry is that of the rejection of water with great chemical load in important quantities, and one of the steps that generate pollution by increasing the COD of the textile industry effluent is the desizing step. Thus, the use of methods, which need weak chemical addition, such as ultrafiltration combined to a targeted selection of the sizing agents enables to reduce significantly the environmental impact of the desizing step of textile treatment engineering. Moreover, the wastewater rejected after the stage of desizing contains of valuable materials such as the carboxymethylcellulose and the poly(vinyl alcohol), which do not undergo notable changes in their physical properties nor their chemical properties during the processes of sizing and desizing. In fact, these two water-soluble polymers are more and more massively used in textile industry to replace the starch, which remains the most used natural sizing agent. The main objective of this paper is to expose experimental results obtained for several ultrafiltration polyethersulfone membranes employed in the removal of poly(vinyl alcohol) and carboxymethylcellulose from aqueous solutions, and to discuss the efficiency of enzymatic degradation of carboxymethylcellulose applied to treat the obtained ultrafiltrate and as well to clean the fouled membranes.

Keywords: Ultrafiltration; Membrane; Carboxymethylcellulose; Poly(vinyl alcohol); Enzymatic cleaning; Textile industry

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1. Introduction

Ultrafiltration is a pressure driven membrane process with the ability to separate molecules in solution on the basis of size. An ultrafiltration membrane retains species with molecular weight higher than the membrane cut off, while freely passing small molecules as solvents and microsolutes [1–4].

One of the most significant environmental difficulties, arising in textile industry, is that of the rejection of important quantities of water containing large amounts of chemical species. Besides, the step that is extremely largest contributor to waste and pollution, in the textile industry effluent, is the desizing step [5]. Desizing is usually the first wet finishing operation performed on woven fabric. It is the process used for removing the size material from the warp yarns. Indeed, before weaving, the warp yarns are covered with a layer of polymer to

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withstand the mechanical stress during weaving. These polymer coatings are so-called sizes and the application procedure is called sizing. Desizing generates substantial quantities of wastewater and it contributes largely to the increase of the chemical oxygen demand (COD) of the effluent because of the rejection of non-biodegradable macromolecular organic species. Thus, the use of methods, which need weak chemical addition, and which are able to remove macromolecular species, such as ultrafiltration, combined to a targeted selection of the sizing agents enables to reduce significantly the negative environmental impact of the desizing step in textile industry [6–10]. Besides, the recycling of the selected sizing agents combined to an enzymatic treatment of the effluent before its rejection allows significant reduction in wastewater pollution [11–13].

The limitation of ultrafiltration is essentially the membrane fouling which is still unsolved and constitute one of the most important hurdles for the implementation of the process in the textile industry, since textile wastewaters provide variety of fouling problems [14–16].

Carboxymethylcellulose (CMC) and poly(vinyl alcohol) (PVA) are water-soluble polymers largely used in the textile industry as sizing agents.

Carboxymethylcellulose is the only water-soluble derivate of cellulose that is used as a sizing agent. It is furthermore one of the principal additives used to increase the adhesion of the starch-based sizing agents on cotton. Nevertheless, carboxymethylcellulose is known to be very difficult to degrade. Therefore, its recovery and its re-use in the sizing step, or its degradation before rejection as waste could be useful, economically and ecologically, at best, and ecologically, at least.

Poly(vinyl alcohol), for its part, does not have any serious toxicity for the microorganisms and does not block nitrification. However, its recovery has a true importance in the control of pollution and its re-use would have, obviously, a significant economical impact.

The main objective of this paper is to expose experimental results obtained after investigation study, carried out at laboratory scale, for several ultrafiltration polyethersulfone membranes, employed in the removal of carboxymethylcellulose and poly(vinyl alcohol) from aqueous solutions, and to discuss the efficiency of enzymatic degradation of carboxymethylcellulose applied to treat the obtained ultrafiltrate and as well to clean the fouled membranes.

2. Experimental

2.1. Chemicals

Carboxymethylcellulose (CMC) (MW: 90,000; DS = 0.7) and poly(vinyl alcohol) (PVA) (MW: 72,000) are used to prepare the macromolecular metal complex solutions.

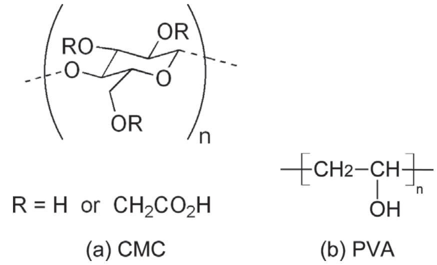

Fig. 1. Chemical structure of CMC and PVA.

Fig. 1 gives the structure of the employed polymers. The ionic strength of the solutions is maintained at 0.1 M using potassium chloride. Cellulase Aspergillus Niger is used to prepare the enzymatic cleaning solutions employed in this study. According to the supplier indications, its molecular weight is 34.000 and its activity equals 0.26 U/mg (1 Unit corresponding to the quantity of enzyme which release 1 μmol/min of equivalent glucose when cellulose is used as substrate). Carboxymethylcellulose is purchased from Aldrich. All other chemicals are purchased from Fluka AG and chemicals employed in this study are all used without further purification.

2.2. Membrane, apparatus and experimental procedures

The ultrafilters used are PBQK and PBTK polyethersulfone membranes supplied by Millipore. They are asymmetric membranes of hydrophobic nature and their molecular weight cut-off are respectively 50,000 and 30,000. They are employed in a Millipore magnetic stirred cell and the device is operated in a batch mode. The effective membrane area is 45.3 cm^2, the feed volume is 300 ml and the rotational speed is set to be 500 rpm during all the trial runs. The ultrafiltration cell is pressurized with nitrogen and pressure is controlled by a manometer placed at the top of the cell (Fig. 2).

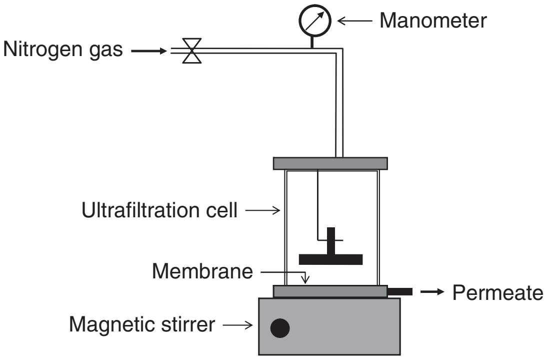

Fig. 2. Schematic of the stirred cell used in the experiments.

Before use, the membranes are compacted by filtration of pure distilled water at 1.5 bar for 1 h to avoid the changes of compaction during experimental runs. With the employed cell, flux measurements are possible immediately on applying the pressure. However, the first 10 cm^3 of permeate are discarded, in all trial runs, and then solute rejections are obtained by analysing the next set of 10 cm^3 of permeate. The rejection rate R, which measures the membrane's separating capabilities is defined as: $R\,(\%) = \left(1 - \frac{c_P}{c_0}\right) \times 100$. Where c_0 is the concentration of solute upstream of the membrane and c_p is the concentration of solute downstream from the membrane. A Carl Zeiss ABBE refractometer is used to measure the ultrafiltrate concentrations of polymer solutions. Besides, the permeate flux is defined as the volume of permeate flowing through the membrane per unit time per unit membrane area. It is expressed, in the present study, in l/hm^2, and its values are calculated by measuring permeate volume at regular intervals of time.

2.3. Membrane cleaning

Cleaning of the membranes is made according to two methods. The first method concerns only the membranes employed in the concentration of CMC. It consists of an enzymatic cleaning and it is performed by washing the membranes with water. Next, immersing them in a cellulase solution of 1 g/l at 40°C for 10 min, then filtering the 1 g/l of cellulase solution through the membranes, either, at 40°C for 1 h under a pressure of 2 bar and finally, storing the membranes in distilled water for several days.

The second cleaning method, used for cleaning the membranes employed in the treatment of both CMC and PVA is performed by alternating filtration of pure distilled water and chlorine at 1.5 bar, for 20 and 10 min, respectively, until the flux of pure distilled water is enhanced.

3. Results and discussion

3.1. Ultrafiltration of CMC through the PBTK and the PBQK membranes

Figs. 3 and 4 illustrate the variation of the permeate flux with the applied pressure for pure distilled water and CMC aqueous solutions of several concentrations, ultrafiltered through the PBTK and the PBQK membranes. A linear evolution of flux, of pure solvent, with pressure, for the PBTK and the PBQK membranes, is observed. These results are in accord with the Darcy law, which describes the flux of solvent through a porous medium. Concerning the macromolecular solutions, the discrepancy from linear proportionality of flux to applied pressure reveals the establishment of polarisation layer near the membranes. It is important to accentuate on the fact that during ultrafiltration of the macromolecular solutions, it is observed that the fall of solvent flux is more important for the 50,000 cut-off membrane (PBQK) than the 30,000 cut-off membrane (PBTK). This phenomenon can be explained by the fact that membranes with smaller pores have higher resistance, thus the pressure gradient increase due to concentration polarization build-up have smaller influence on

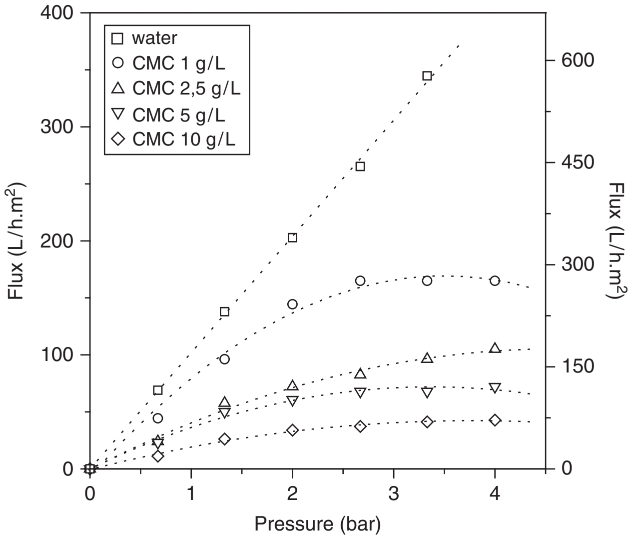

Fig. 3. Ultrafiltration of aqueous solutions of CMC 90,000 at several concentrations through the PBTK membrane. (The axis at right concerns pure water flux, while the left one concerns ultrafiltration of polymer solutions).

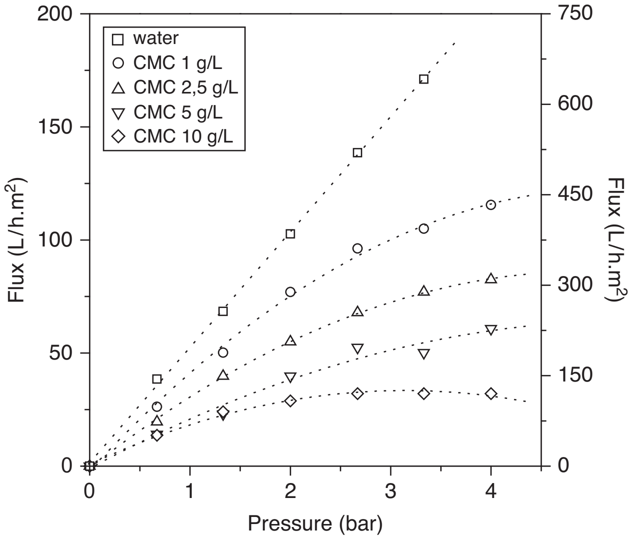

Fig. 4. Ultrafiltration of aqueous solutions of CMC 90,000 at several concentrations through the PBQK membrane. (The axis at right concerns pure water flux, while the left one concerns ultrafiltration of polymer solutions).

membrane flux. Besides, it is reported in the literature that a relatively high-molecular-weight cut-off membrane, even though it may have a higher flux, is more susceptible to internal fouling than a membrane with a lower molecular weight cut-off which have lower pure water flux, but often provides a more sustained flux because less internal fouling occurs [4].

The rejection of CMC is, without surprise, close to 100% for all the treated aqueous macromolecular solutions. Indeed, the polymer molecular weight has been chosen so that to be greater than the cut-off of the membranes.

3.2. Effect of ultrafiltration of CMC on solvent flux

The flux of pure distilled water diminishes sharply for the used membranes comparatively to the new membranes (Figs. 5 and 6). This phenomenon is observed for the two membranes and it is marked, more intensely, for the PBQK membrane. We can thus conclude that membrane surface is modified. In fact, the membrane surface is modified as soon as it is put in contact with the first ultrafiltered CMC aqueous solution. This behaviour can be explained by the macromolecular adsorption that occurs rapidly and uniformly on all solid surfaces in contact with aqueous solutions of hydrophilic polymers [17,18]. This leads to conclude that the initial permeability to solvent to be taken into account is not that of the new membrane, but that of the membrane that has been in contact with the polymeric solution and we note whereas this permeability can be enhanced after cleaning (Figs. 7 and 8).

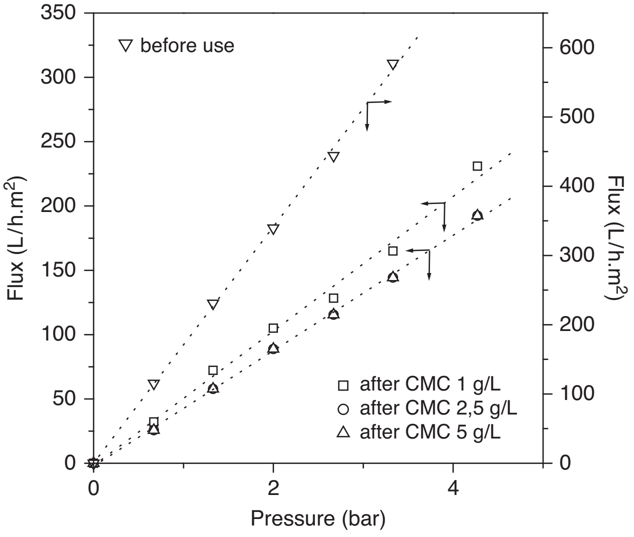

Fig. 5. Modification of the permeability of the PBTK membrane to pure distilled water after ultrafiltration of the CMC solutions.

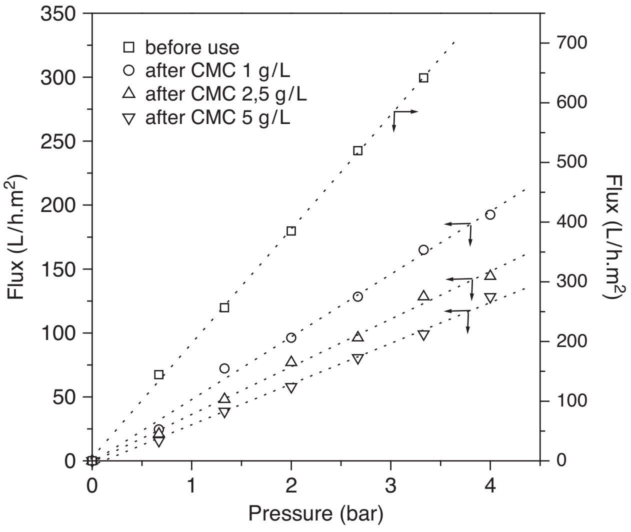

Fig. 6. Modification of the permeability of the PBQK membrane to pure distilled water after ultrafiltration of the CMC solutions.

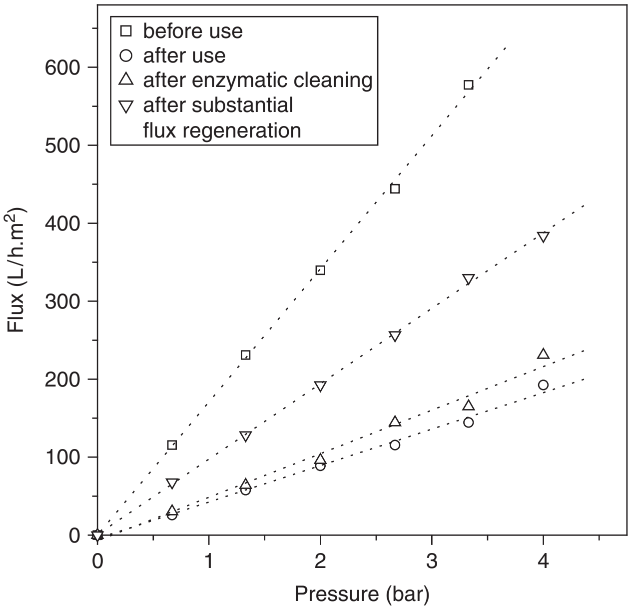

Fig. 7. Effect of the cleaning on the flux of pure distilled water for the PBTK membrane.

3.3. Enzymatic cleaning of the membranes

Figs. 7 and 8 show, for the membranes PBTK and PBQK, the enhancement of the flux after enzymatic cleaning, done as described in the experimental section. Worthy of note that, even if amelioration is observed, it is not significant, mainly for the PBTK membrane for which a particularly good quality flux sample has however been used. Thus, in order to have more flux augmentation, the membrane samples have been stored,

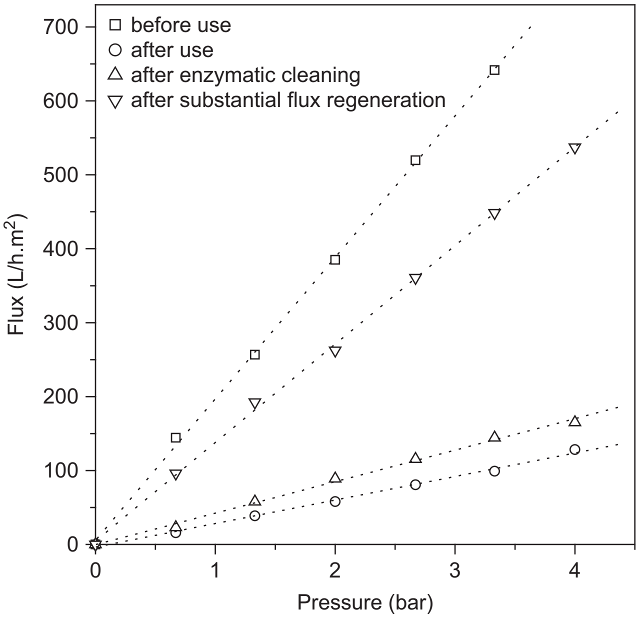

Fig. 8. Effect of the cleaning on the flux of pure distilled water for the PBQK membrane.

after enzymatic cleaning, in pure distilled water, for several days. After this treatment, we have observed, for the PBQK and the PBTK membranes a significant amelioration of the flux that can be considered as a partial regeneration of flux as shown in Figs. 7 and 8. Thus, the cleaning procedure employed in this study enables to improve the membrane performance until the obtaining of regenerated membrane. Nevertheless, the mechanism of this promising modification needs more investigations before any categorical conclusion.

3.4. Ultrafiltration of PVA through the PBTK and the PBQK membranes

The Figs. 9 and 10 show, for PVA, as previously for CMC (Fig. 4 and 5), a discrepancy from linear proportionality of flux to applied pressure when macromolecular aqueous solutions are ultrafiltered through the employed membranes, except for the 1 g/l solution ultrafiltered through the PBQK membrane. That reveals the establishment of polarisation layer near the skin of the membranes during the ultrafiltration of most of the macromolecular solutions.

The Figs. 11 and 12 show that the solvent permeability diminishes in a drastic way after the ultrafiltration of the PVA solutions but the evolution of solvent flux with pressure remains linear for the employed membranes. Elsewhere, Fig. 12 shows that the chlorine cleaning does not give significant modification in flux. The results gathered in these figures (Figs. 9–12) lead to the conclusion that fouling occurs in a more severe mode during ultrafiltration of PVA, comparatively to CMC. Thus, cleaning procedure must be reinvestigated so as to find a relevant method to enhance flux for the used membranes, particularly when concentrated macromolecular solutions of PVA are treated.

Note that, as for the CMC solutions, the rejection is close to 100% for all the treated aqueous macromolecular solutions of PVA.

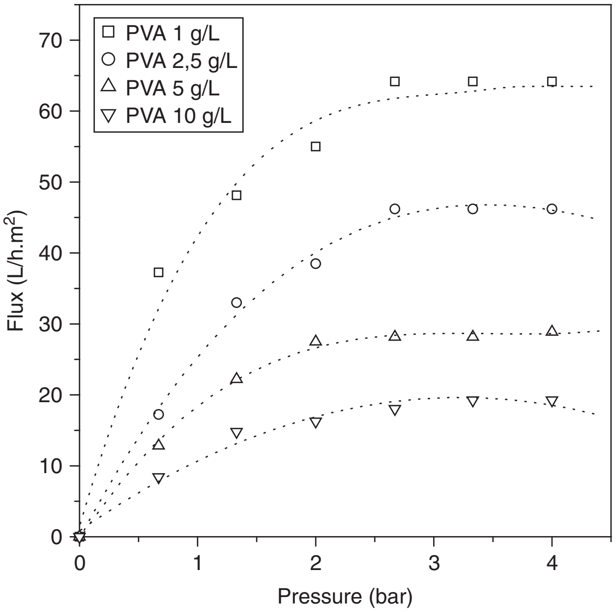

Fig. 9. Ultrafiltration of aqueous solutions of PVA 72,000 at several concentrations through the PBTK membrane.

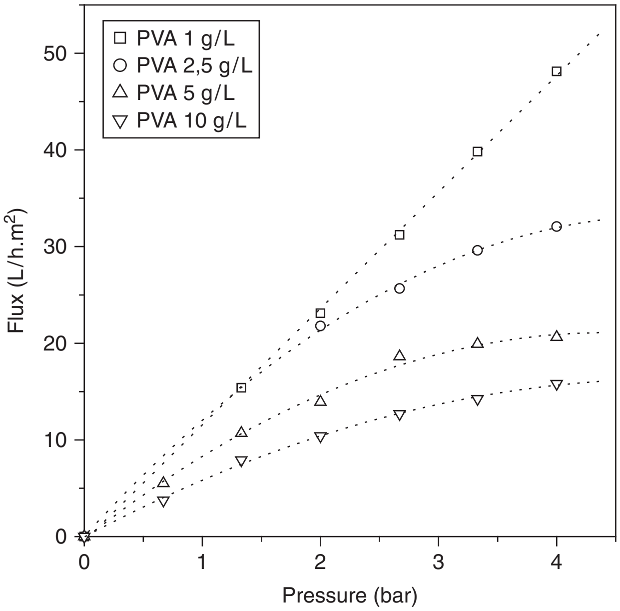

Fig. 10. Ultrafiltration of aqueous solutions of PVA 72,000 at several concentrations through the PBQK membrane.

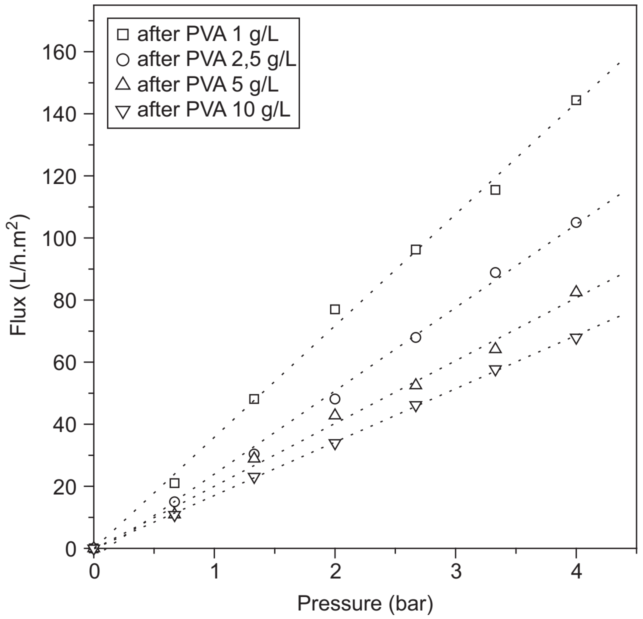

Fig. 11. Modification of the permeability of the PBTK membrane to pure distilled water after ultrafiltration of the PVA solutions.

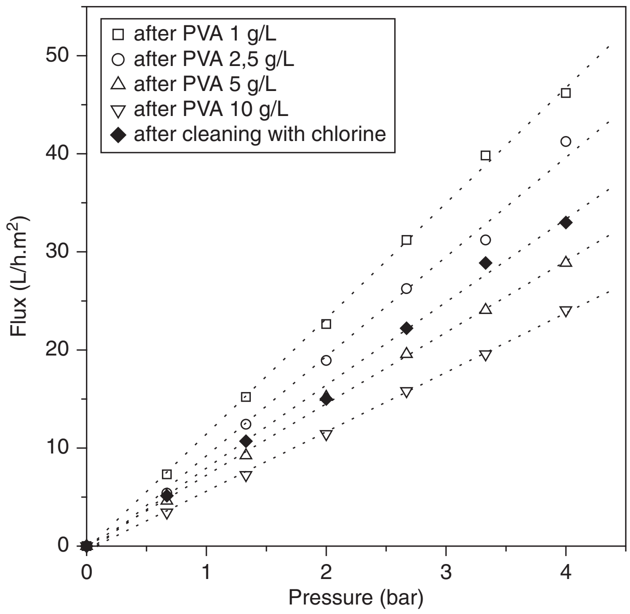

Fig. 12. Modification of the permeability of the PBQK membrane to pure distilled water after ultrafiltration of the PVA solutions.

3.5. Determination of gel concentration

To complete the study of membrane fouling and to quantify it, Fig. 13 can be used, it illustrates the graphic determination of gel concentration for both of the two studied membranes according to the model of the film [19–26]. The obtained gel concentrations are respectively 28 g/l for CMC and 25.6 g/l for PVA ultrafiltered through the PBTK and PBQK membranes. These results are in good agreement with the viscosity behaviour of the two polymers.

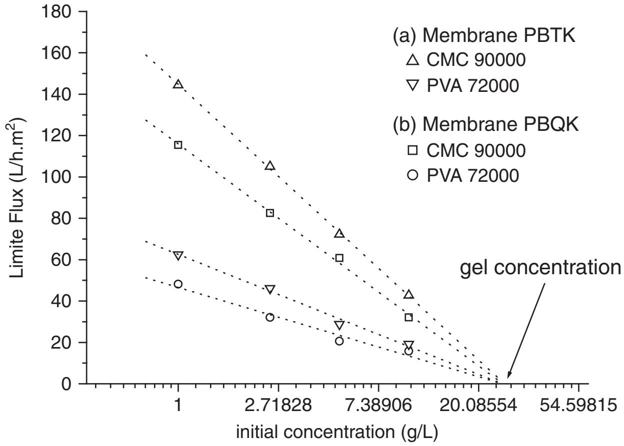

Fig. 13. Determination of gel concentration.

3.6. CMC degradation

Fig. 14 illustrates the effectiveness of the enzymatic degradation of CMC with cellulase. The results are those of the initial solutions and the obtained ultrafiltrates through the PBQK membrane. The detection of glucose in both of the feed solutions and the ultrafiltrates indicates the occurrence of the CMC degradation by the employed cellulase and the effectiveness of the process.

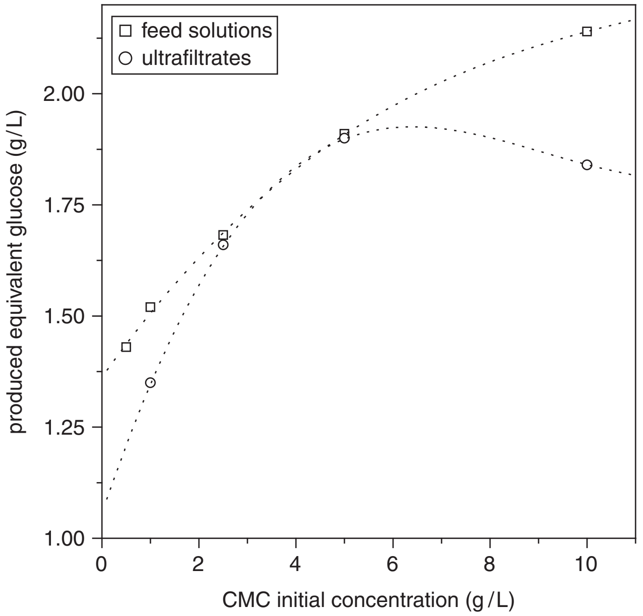

Fig. 14. CMC degradation by cellulase.

4. Conclusion

This study illustrates the efficiency of ultrafiltration in the treatment of aqueous solutions of PVA and CMC. Solvent flux measurements made it possible to observe the effect of the ultrafiltration of the macromolecular solutions on the permeability of the studied membranes. The discrepancy from linear proportionality of flux to applied pressure during the ultrafiltration of the macromolecular solutions reveals the establishment of polarisation layer near the membrane and the film model has been used to determine the gel concentration of the employed membranes. Two modes of cleaning have been investigated and the enzymatic cleaning followed by storage of the membranes in pure distilled water seems to be effective to regenerate partially the membrane solvent flux for the membranes fouled after ultrafiltration of CMC aqueous solutions. Furthermore, the enzymatic degradation of CMC has been investigated and the choice of Cellulase Aspergillus Niger for this purpose is apparently a good option. However, further investigations are necessary to conclude categorically, this is the aim of an underway study.

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