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## Ultrafiltration of aqueous solutions containing dextran

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### Abstract

The use of membrane technologies for water recycling has increased over the last decades, however, its use is limited due to the fouling of the membranes. This study investigates some different parameters thought to be responsible for membrane fouling. Two different ultrafiltration membranes have been used in this investigation in order to carry out filtrations of feed solutions containing dextran with a molecular weight between 36,000 and 44,000 Da. The influence of some operating conditions such as applied pressure, concentration of dextran, content of calcium and pH of the feed solution on the performance of the filtration has been studied.

*Keywords:* Ultrafiltration; Dextran; Water treatment

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### 1. Introduction

According to United Nations estimations, by 2025 two-thirds of the world population will not have enough drinking water. Today, industry and agriculture use 90% of the world's fresh water supply while just 10% is consumed as drinking water [1]. For this reason industries need to focus on reducing the amount of process water used and

at the same time recycling as much water as possible.

Worldwide there are a number of studies that have been conducted to treat various types of wastewater using membrane technology for the purpose of recovery and recycling of water. These studies included microfiltration (MF) and ultrafiltration (UF) of wastewater from fishmeal production, nanofiltration (NF) and reverse osmosis (RO) of food industry wastewaters, and biological treat-

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ment in combination with UF, NF and RO for the treatment of municipal wastewater [2].

Ultrafiltration (UF) is a relatively low-pressure membrane process whose use in water treatment has increased rapidly in the last decade due to stricter regulations for finished water quality, decreased cost, improved membrane materials and modules, simplicity of installation and improved reliability when compared with conventional treatment processes such as sedimentation and rapid filtration [3]. The applications of UF can be analyzed from two different points of view. In some cases, the aim of the process is to recover or concentrate some valuable substances from a solution — this is common practice in the chemical and pharmaceutical industries [4]. Another application related to this is the concentration of a wastewater stream for further treatment where a higher concentration is required, seen in some advanced oxidation processes. The second main application consists of removing undesirable products such as particles, colloids, high molecular weight materials, bacteria and viruses [3,5] from an effluent stream in order to obtain more purified water. One example of this consists of membrane systems for potable water treatment, which are already in use in several countries [6].

Even though UF presents a wide range of advantages for its industrial application, its use is limited due to deterioration of the membrane performance over time and fouling. Fouling causes a reduction in permeate flux due to the accumulation of material on the membrane or blocking of the pores. For this reason, before starting an ultrafiltration process design it is important to study all the factors affecting its performance. These can be divided into the factors related to the membrane itself and the factors related to the filtration process conditions. As reported by Cuperus and Smolders [7], membrane parameters can be classified into two categories: physical-chemical parameters and functional parameters. The former include the pore size and shape, porosity, skin thickness, surface roughness and charge, zeta potential and contact

angle. Functional parameters include aspects such as membrane permeability, solute sieving and mechanical strength. From a practical perspective, the functional parameters determine the suitability of a membrane for a particular application [8].

The main filtration parameters are the initial concentration and the molecular weight of the substances contained in the feed solution and the pressure applied, all of which affect the permeability and the retention of the process. In addition, the pH and the ionic strength of the solution appear to play an important role in the process [5,9]. In this sense, calcium and phosphates have been directly implicated with membrane fouling due to the formation of insoluble calcium salts, and as possible catalysts or bridging agents between membrane and solutes [10]. On the other hand, the pH can affect the structure of the molecules contained in the aqueous solution as well as the surface membrane charge. Ghosh and Schnitzer [11] pointed out that at high pH and low ionic strength, humic acids have a large, flexible and linear shape, while at low pH and high ionic strength they turn into a small, rigid and spherical shape. With regards to the influence of pH on the membrane, if a membrane contains amine groups, at low pH it will become positively charged, while a membrane containing carboxylic acids will be negatively charged at mid to high pH [12].

## 2. Materials and methods

### 2.1. Test cell

The test cell is a low pressure filtration cell GN 10-400 supplied by Berghof (Germany). It consists of a PTFE support disk where two cylinders are placed. The inner cylinder is made of glass and it contains the feed solution, and the external cylinder is made of Plexiglas and serves as burst shield. The Plexiglas cylinder has a security valve to ensure an immediate pressure reduction in case of overpressure. On the surface of the PTFE support disk, a Tyvec paper should be laid in order to protect the membrane (76 mm).

The test cell is capable of working with a feed solution volume of 400 mL, a maximum pressure of 10 bar and a maximum temperature of 100°C. Experiments were carried out at room temperature and the cell was pressurized by air. In order to reduce the fouling of the membrane, the test cell is also equipped with a stirrer, which was used at a stirring rate of 300 rpm. Fig. 1 illustrates the experimental equipment.



Fig. 1. Test cell.

## 2.2. Chemicals

The feed solution of the tests consisted of stock solutions containing dextran FP40- research grade supplied by Serva (Heidelberg, Germany) with a molecular weight range between 36,000 and 44,000 Da. Fig. 2 shows a scheme of a dextran molecule.

The rest of the chemicals used were supplied by Merck (Darmstadt, Germany):  $\text{KH}_2\text{PO}_4$  (crystalline, extra pure),  $\text{Na}_2\text{HPO}_4$  (for analysis),  $\text{Na}_2\text{CO}_3$  (for analysis),  $\text{NaHCO}_3$  (extra pure) and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (crystalline grade for analysis).

## 2.3. Membranes

The two membranes used for this study were supplied by Microdyn-Nadir (Wuppertal, Germany). The first one was a C030FM membrane with a molecular weight cut off (MWCO) of 30 kDa and made of cellulose. It can be used in a pH range from 1 to 12 and until a maximum temperature of 55°C. The second membrane was a P020F membrane with a MWCO of 20 kDa and made of polyethersulfone. It can be used in all pHs and until a maximum temperature of 95°C.

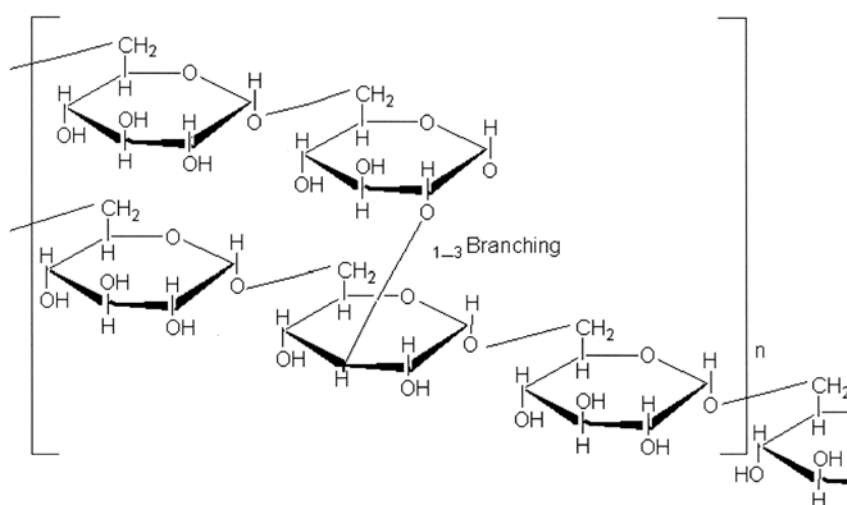


Fig. 2. Chemical structure of dextran [13].

#### 2.4. Experimental procedure

The first step of the experimental procedure was the preparation of the membranes. The day before the experiment, the membrane was washed for a couple of minutes with tap water. It was then kept submerged in distilled water for the whole night. Once the membrane was placed in the test cell, 400 mL of distilled water were introduced into the cell. Then the pressure was adjusted (from 1 to 3 bar depending on the experiment) and the permeate was collected. These experiments with water were carried out in order to be able to compare the performance of the membrane with water and with the solution containing dextran.

During each experiment the time to collect a certain volume of permeate was measured in order to know the evolution of the flux and the permeability throughout the filtration. After collecting 100 mL of permeate the experiment was considered as being finished. After the test with water, the same procedure was done with the solution containing dextran. A final sample named retentate was withdrawn from the test cell after the experiment.

The following samples were analyzed for COD content: feed, 20 mL, 40 mL, 60 mL, 80 mL, 100 mL and retentate. In some experiments the pH and the conductivity of these samples were also measured.

COD was measured spectrophotometrically and Cuvette Tests LCK 114 supplied by Dr. Bruno Lange GMBH & Co. (Düsseldorf, Germany) were used for the preparation of the samples. The pH was measured by means of a pHmeter 761 Calimatic from Knick (Dülmen, Germany) and a Conductivitymeter 703 supplied by Knick (Dülmen, Germany) was used to measure the conductivity of the samples.

### 3. Experimental results and discussion

The experimental part of this project can be divided into four different sections. The first part studies the influence of the initial concentration

of dextran by carrying out experiments with different concentrated solutions. The second part investigates the influence of the pressure applied by ultrafiltrating the same feed but at different pressures. The third part analyses the pH influence by ultrafiltrating feed solutions with different pH, while part four examines the influence of the Ca content in the feed solution.

From the data measured in each experiment the evolution of the flux, the permeability, and the retention were calculated as follows:

$$\text{Flux (L/m}^2\text{h)} = \frac{\text{Volume of permeate}}{\text{Time} \times \text{Membrane area}} \quad (1)$$

$$\text{Permeability (L/m}^2\text{h)} = \frac{\text{Flux}}{\Delta p} \quad (2)$$

$$\text{Retention} = 1 - \frac{\text{COD}_{\text{permeate}}}{\text{COD}_{\text{feed}}} \quad (3)$$

#### 3.1. Influence of the concentration of dextran in the feed solution

To study the influence of the initial concentration, solutions containing 1, 3, 5, 8 and 10 mg/mL of dextran were prepared and ultrafiltrated with 2 different membranes 30 and 20 kDa. The pressure applied in this set of experiments was 1 bar. The results for the permeability vs. the volume of the permeate collected are shown in Figs. 3 and 4. From these pictures it can be concluded that the flux is higher when working with the 30 kDa membranes since the pores offer a lower resistance than the 20 kDa membrane pores. However, the results of the experiments at the highest concentration, i.e. 10 mg/mL, appear to be of special interest since the flux (or permeability) follows a similar tendency when working with both membranes. This suggests that an increase in the concentration reduces the differences between the two membranes, mainly due to the formation of a fouling layer which controls the filtration.

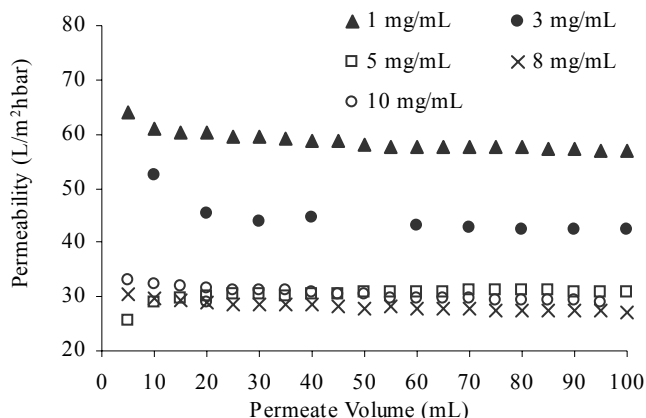


Fig. 3. Permeability vs. volume of permeate. 20 kDa membrane.

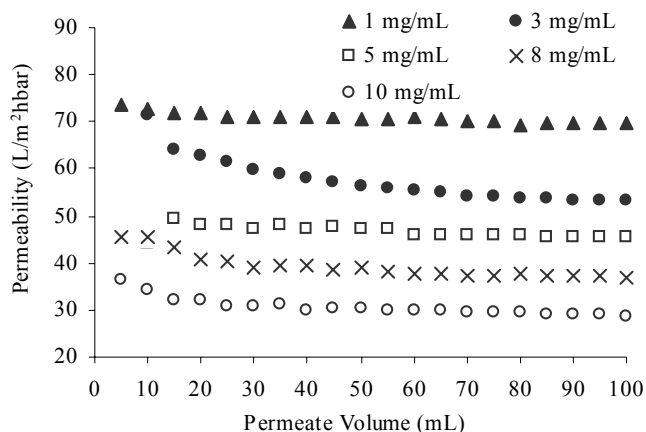


Fig. 4. Permeability vs. volume of permeate. 30 kDa membrane.

The results also show an inverse relationship between concentration and flux — as the concentration increases the flux decreases. This is because the higher the concentration, the higher the amount of particles in the solution and therefore, the greater chance that a deposition layer on the surface of the membrane will form. It was also noticed that the flux in the 20 kDa membrane decreased when increasing the concentration from 1 to 3 mg/mL, however, when increasing the concentration from 5 to 10 mg/mL no significant differences were observed. This is because when a solution containing 5 mg/mL is ultrafiltered the 20 kDa membrane is already fouled due to a cake layer formed on the surface. On the other hand,

the 30 kDa membrane did not illustrate this behaviour due to the larger membrane pores.

From these experiments the retention was calculated according to Eq. (3). The values of the retention vs. the concentration of dextran used in each experiment are depicted in Fig. 5. From these results the different tendencies of the 30 kDa and 20 kDa membrane can be seen. The retention of the 30 kDa membrane increased when increasing the concentration of the feed solution, while the retention of the 20 kDa membrane decreased when increasing the initial concentration. The increase in the retention when increasing the initial concentration (as occurs with the 30 kDa membrane) can be explained taking into account that some

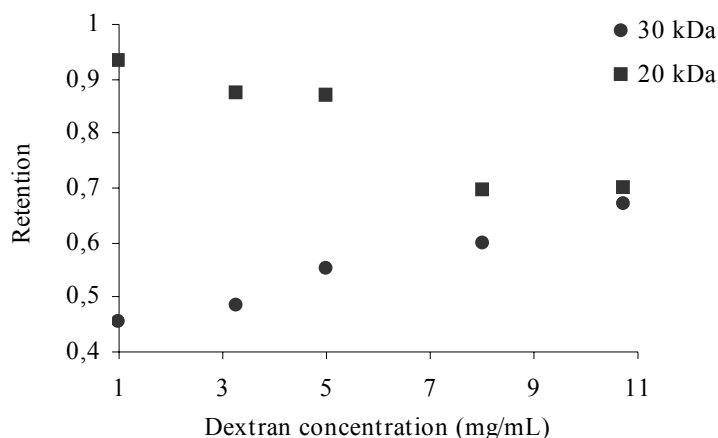


Fig. 5. Retention vs. dextran concentration.

particles that are able to pass through the pores can get stuck there, provoking a decrease in the pore diameter and thus, making the membrane more selective. The decrease in the retention when increasing the concentration, as seen with the 20 kDa membrane, can be explained by assuming that when the initial concentration increases, a cake layer formation is more likely to happen. When this cake layer forms not only do the particles have difficulties to cross but also the water. This implies that the amount of water in the permeate phase decreases and thus the percentage of particles increases, i.e. the retention decreases.

### 3.2. Influence of the transmembrane pressure

To study the influence of the pressure, experiments maintaining the initial concentration of dextran fixed (3 mg/mL) and using the 30 kDa membrane were carried out varying the pressure applied. The studied pressures were 1, 1.5, 2, 2.5 and 3 bar. As expected, the flux tended to be higher the higher the applied pressure was since the drive force was bigger. However, the permeabilities decreased when increasing the applied pressure. Fig. 6 shows the permeability of these experiments vs. the volume of permeate.

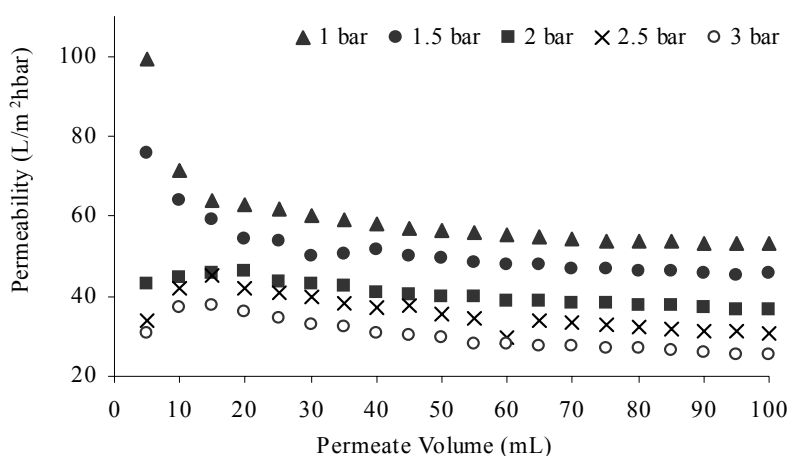


Fig. 6. Permeability vs. volume of permeate.

Fig. 7 shows the influence of the applied pressure on the retention achieved at the end of each experiment. The highest retention is achieved when working at the lowest pressure. This is due to the fact that an increase in the pressure applied implies an increase of the flux, which at the same time favours the concentration polarization on the surface of the membrane. As a result of the concentration polarization, more particles cross the membrane because the difference in the concentration between both sides of the membrane increases.

### 3.3. Influence of the pH of the feed solution

To study the influence of the pH, ultrafiltrations were carried out of solutions containing 3 mg/mL of dextran at 4 different pHs, maintaining the

applied pressure at 1 bar and with 30 and 20 kDa membranes. The operating conditions of the experiments included in this section are described in Table 1.

Figs. 8 and 9 represent the values of the permeability vs. the volume of permeate of the experiments with the 30 and 20 kDa membrane. From these figures it can be concluded that pH does not greatly influence the permeability of the membrane. This may be a consequence of the non-dissociating nature of the dextran since variations in the behaviour of these membranes depending on the pH have been reported in the literature when using polyelectrolyte feed solutions such as humic acids [4,10]

From the values of the COD measured from the last permeate collected and the original sample, the retention can be calculated as shown

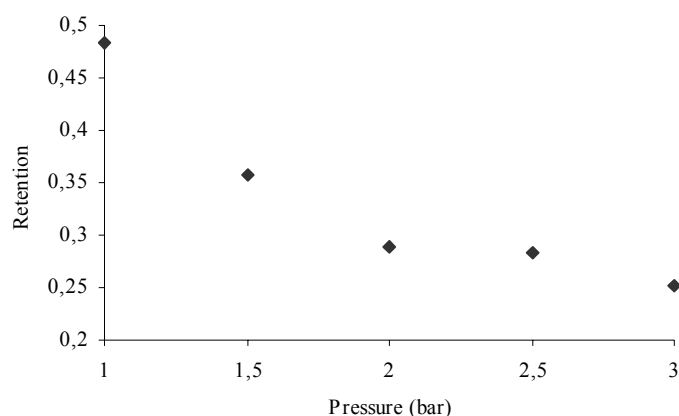


Fig. 7. Retention vs. applied pressure.

Table 1  
Operating conditions

Membrane (kDa)	Initial dextran concentration (mg/mL)	Pressure (bar)	pH	Buffer solution
20	3	1	4.85	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$
20	3	1	5.96	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$
20	3	1	8.01	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$
20	3	1	9.87	$\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$
30	3	1	4.7	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$
30	3	1	5.81	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$
30	3	1	8.23	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$
30	3	1	10.22	$\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$

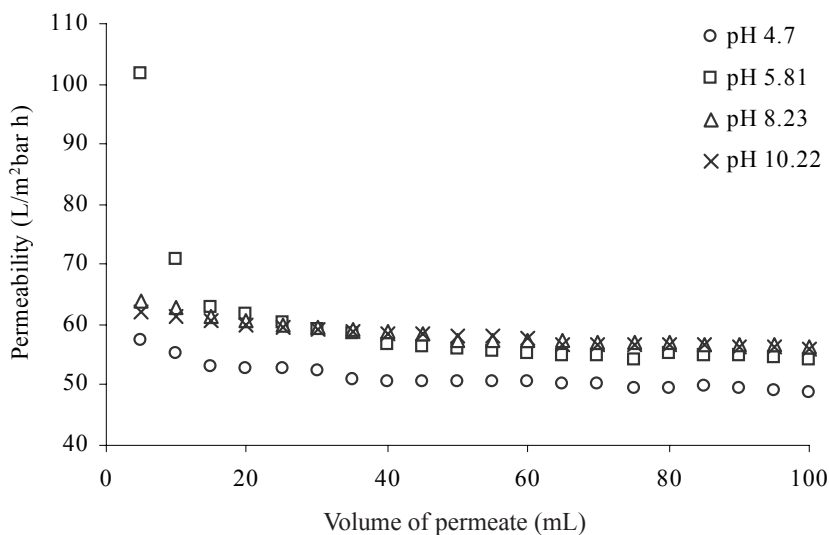


Fig. 8. Permeability vs. volume of permeate. 30 kDa membrane.

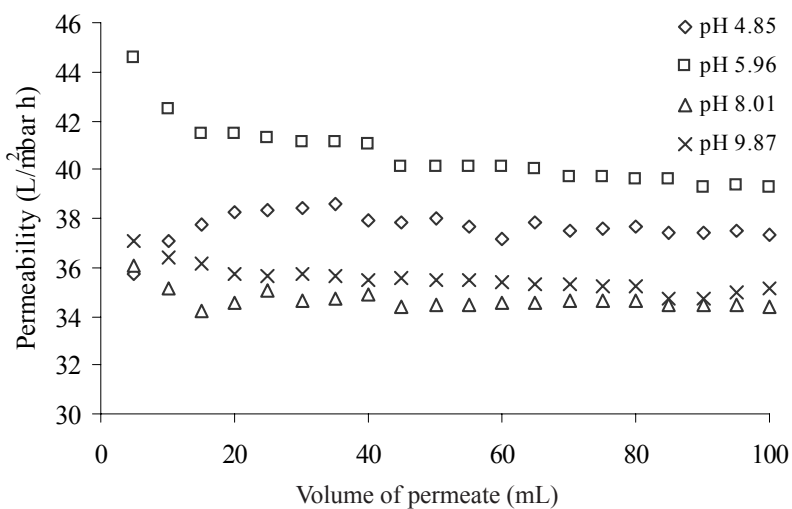


Fig. 9. Permeability vs. volume of permeate. 20 kDa membrane.

in Eq. (3). The values of the retention of each one of the experiments mentioned above are depicted versus the pH of the initial solution in Fig. 10. In this figure it can be observed that the variations of the retention in both membranes slightly depend on the pH of the solution.

According to these results it can be concluded that under the operating conditions studied, the pH is not a determining factor for the retention achieved at the end of the filtration nor for the variations in the permeability of the membrane.

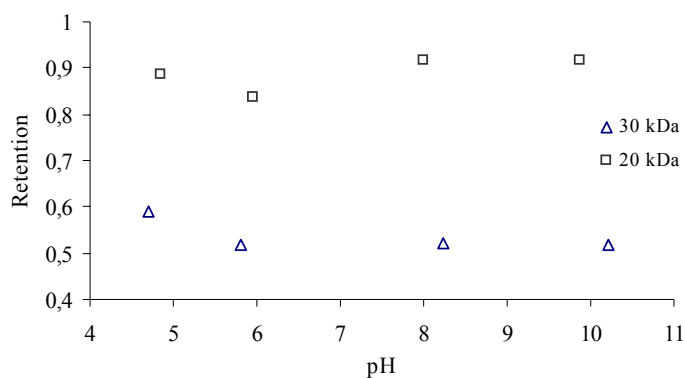


Fig. 10. Retention vs. pH of the initial solution.

### 3.4. Influence of the calcium contained in the initial solution

The influence of the calcium contained in the feed solution was studied by carrying out experiments at pH 5 and varying the amount of Ca added to the feed. The operating conditions of these experiments are shown in Table 2.

In Figs. 11 and 12 the permeability of these experiments is depicted vs. the volume of the permeate collected. From these figures it can be observed that the higher the amount of calcium added to the feed solution the lower the permeability of the 30 kDa cellulose membrane. This may be due to the formation of insoluble calcium salts or colloids with the solute, or due to the characteristics of the calcium to act as a bridge between the solutes and the membrane. The influence of the amount of  $\text{Ca}^{2+}$  when using the polyethersulfone 20 kDa membrane was found to be nonconclusive.

The different behaviour of both membranes may be a consequence of the different characteristics of the membranes — the 20 kDa membrane is hydrophobic and the 30 kDa membrane is hydrophilic. The calcium could be attached more easily to the hydrophilic than to the hydrophobic membrane and thus, the fouling of the membrane would more likely occur in the hydrophilic membrane. This would explain the fact that with a higher concentration of calcium the flux is lower in the hydrophilic membrane but not in the hydrophobic one.

Fig. 13 represents the retention achieved at the end of each experiment versus the amount of calcium added to the feed solution. The retention slightly decreases with the increase of calcium.

## 4. Conclusions

The results suggest that as the concentration of dextran in the feed is increased, that the total

Table 2  
Operating conditions

Membrane (kDa)	Initial dextran concentration (mg/mL)	Pressure (bar)	pH	Buffer solution	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (mg/L)
20	3	1	4.78	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$	18.3
20	3	1	4.79	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$	218.2
20	3	1	4.8	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$	765
30	3	1	5	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$	18.3
30	3	1	4.75	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$	218.2
30	3	1	4.77	$\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$	765

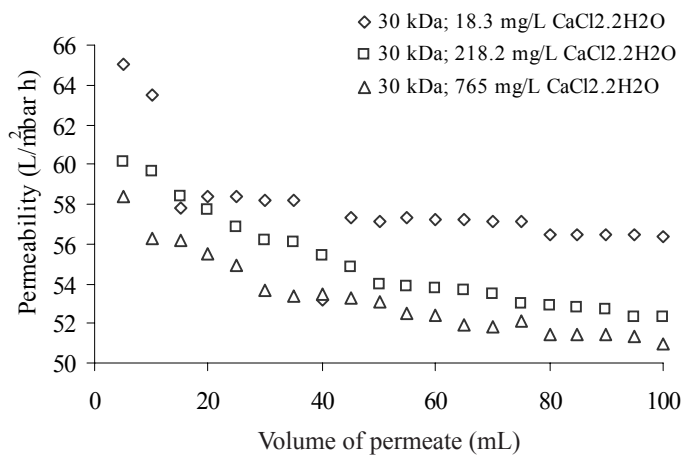


Fig. 11. Permeability vs. volume of permeate. 30 kDa membranes. Initial solutions containing 3 mg/mL of dextran and different amounts of CaCl<sub>2</sub>·2H<sub>2</sub>O.

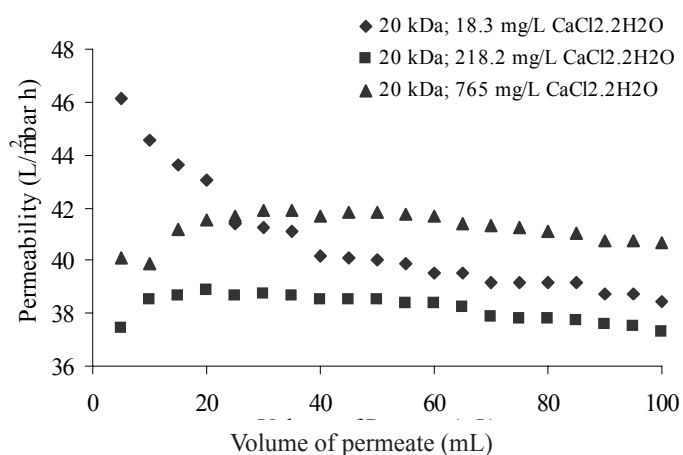


Fig. 12. Permeability vs. volume of permeate. 20 kDa membranes. Initial solutions containing 3 mg/mL of dextran and different amounts of CaCl<sub>2</sub>·2H<sub>2</sub>O.

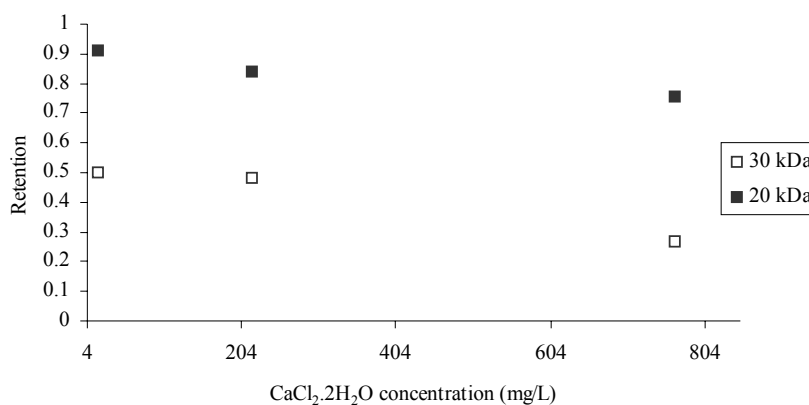


Fig. 13. Retention vs. concentration of calcium.

flux through the membrane decreases. It was also observed that when working with a feed containing 10 mg/mL of dextran, both membranes (20 kDa and 30 kDa) had the same permeability due to the formation of a fouling layer which controls the filtration.

It can be concluded that increasing transmembrane pressure is related to an increase in the flux and a decrease in the permeability. Moreover, as a result of increasing the pressure, a phenomenon known as concentration polarization occurs and thus, the retention decreases.

Under the operating conditions studied the pH of the feed solution appeared to be a non-determining factor for the retention and the flux. On the other hand, the calcium content of the feed was found to be dependent on the surface characteristics of the membranes.

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