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## MEMBRANE PERFORMANCE IN THE TREATMENT OF THE EFFLUENT FROM A ZIRCONIUM SILICATE PRODUCTION INDUSTRY

Zirconium silicate sands are produced by different branches of industry for several applications in the ceramic industry. This production can be made by different milling processes: dry milling and wet milling. The wet milling yields a smaller particle size. This is a great yield process which implies more stages: addition and removal of water, sedimentation, and addition of alumina ( $Al_2O_3$ ), NaOH and a coagulant, generally a polyelectrolyte, which are used to control the process and the quality of the wastewater. Polyelectrolyte allows formation of flocs for the separation of zirconium silicate solids from the water. This experimental study was made with two main purposes: 1) to reuse the polyelectrolyte in the process of coagulation and 2) to reuse the water in the milling process, therefore reducing the amount of wastewater. As a result, some environmental benefits will be obtained: reuse of the water and better quality of the wastewater; and also economical benefits: saving of polyelectrolyte and water, and greater yield in the production process. Membrane technologies are suitable for the removal of suspended solids and organic compounds, like a polyelectrolyte, from water. Some experimental tests were carried out in a pilot-plant scale in order to assess the viability of different membrane processes in the treatment of the effluent from a zirconium silicate production industry. This work presents the results of membrane performance obtained in these experiments.

Keywords: *polyelectrolyte, membrane, suspended solids, water treatment, zirconium silicate*

### 1. INTRODUCTION

In the Valencian Community (Spain), there are different branches of industry that produce zirconium silicates for the ceramic industry. These silicates production can be made in two different milling processes: dry milling and wet milling. The wet milling is a more complex process, since it requires the addition of water and

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some reagents like alumina ( $\text{Al}_2\text{O}_3$ ), calcium carbonate ( $\text{CaCO}_3$ ) and sodium hydroxide ( $\text{NaOH}$ ) to control the process.

The product of the wet milling is a liquid that contains the suspension of zirconium silicate solids in water. The zirconium solids have to be separated from the water to obtain the final product for the ceramic industry. This separation is generally made by sedimentation using a polyelectrolyte as a coagulant [1], [2]. After sedimentation the settled zircon solids are dried to become a final product. The wastewater from the decanter contains a certain amount of suspended solids and polyelectrolyte [3]. This wastewater can be directly discharged or it can require further treatment depending on its characteristics.

The treatment of this effluent in order to remove solid and polyelectrolyte will result in water reusing in the production process, and polyelectrolyte reusing in the coagulation process. This will yield significant environmental and economical benefits for the company.

Membrane technology is considered a suitable way for treating the wastewater and removing zircon solids and the polyelectrolyte. The method proposed for the treatment of the zirconium silicate effluent is shown in figure 1. It consists in a pre-treatment that allows removal of suspended solids, which can be made by conventional filtration or microfiltration (MF) through membranes [4], [5], [6], and a further membrane treatment to concentrate the polyelectrolyte. Ultrafiltration (UF) and nanofiltration (NF) are the most suitable membrane processes to remove the polyelectrolyte, depending on the molecular weight and chemical characteristics of this compound.

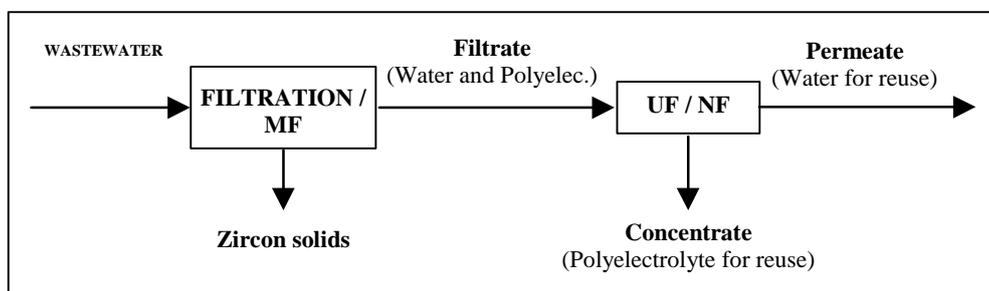


Fig. 1. Treatment proposed for the effluent from a zirconium silicate production

The permeate from the membrane treatment will be the water for reuse in the production process, and the concentrate stream should have a polyelectrolyte concentration suitable for its reusing in the coagulation process after the wet milling.

Several experimental tests have been carried out to assess the viability of polyelectrolyte concentration by UF and NF. This work presents the results of membrane performance in these experiments.

## 2. MATERIALS AND METHODS

### 2.1. FEED WATER

The feed water used in the experimental tests consisted of model solutions prepared with the commercial polyelectrolyte AP 273. It is an anionic polyelectrolyte, soluble in water and difficult to biodegrade. Model solutions were prepared with 5 ppm of polyelectrolyte, which is the typical concentration of polyelectrolyte in the wastewater. The feed water was pretreated with 0.45 micron filters before being treated in the membrane pilot plant.

### 2.2. UF AND NF MEMBRANES

Table 1 summarizes the main characteristics of the membranes tested in the pilot plant. Five ultrafiltration membranes from Orelis company were tested, with the following cut-off values: 10, 30, 40, 50 and 100 kDa. Most of the membranes were made of polyethersulphone (PES), except the ones with a 40 kDa cut-off, which were made of polyvinilidene fluoride (PVDF), and the ones with a 50 kDa cut-off, which were made of acrylonitrile copolymers (A).

Nanofiltration experiments were performed with the membrane DS-5 from Osmonics (General Electric), which has an approximate cut-off of 150–300 Da.

Table 1

Characteristics of the membranes tested

Membrane process	Company	Membrane
Ultrafiltration	Orelis	100 kDa (PES)
		50 kDa (A)
		40 kDa (PVDF)
		30 kDa (PES)
		10 kDa (PES)
Nanofiltration	Osmonics	DS-5

### 2.3. PILOT PLANT DESCRIPTION AND TEST CONDITIONS

The membrane pilot plant used in the experiments is shown in figure 2. It is equipped with a plate and frame module with the capacity for four membranes, each of 30 cm<sup>2</sup> area. In all the experiments, the feed was a 5 ppm polyelectrolyte solution that was filtered before entering the membrane module, and the concentrate was recirculated to the feed tank in order to concentrate it as much as possible.

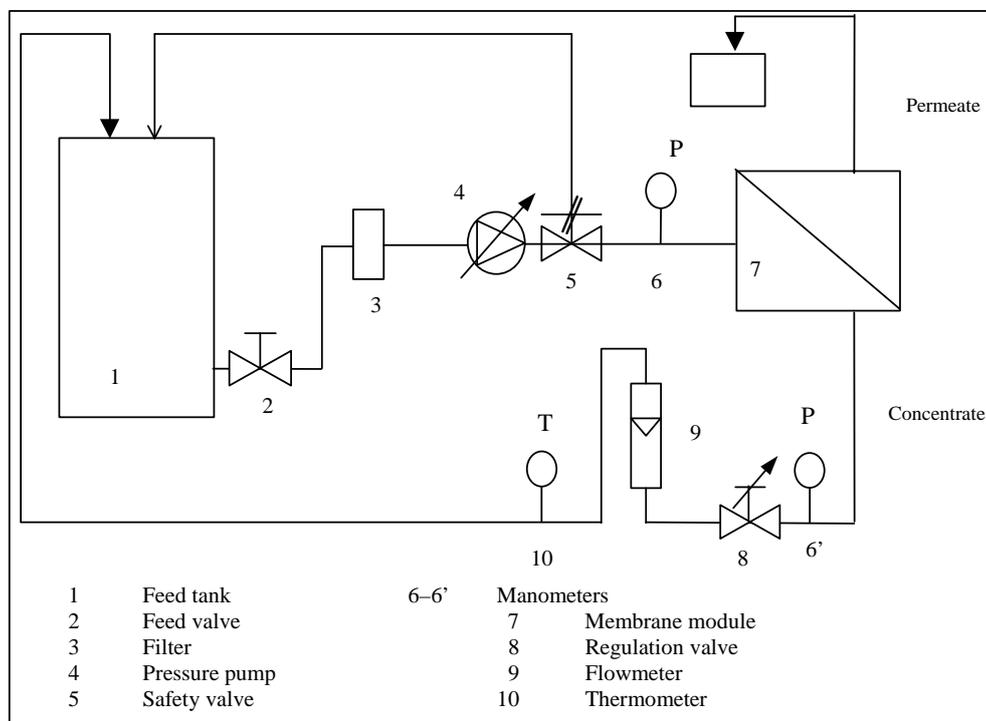


Fig. 2. Diagram of the membrane pilot plant used in the experiments

Table 2

Main conditions of the experimental tests

Experiment	Process	Pressure (bar)	Time (hours)	Membrane tested
1	UF	4	35	100 kDa (PES)
				50 kDa (A)
				30 kDa (PES)
				10 kDa (PES)
2	UF	4	30	50 kDa (A)
3	UF	4	27	40 kDa (PVDF)
4	UF	4	26	30 kDa (PES)
5	NF	8	67	DS-5

Table 2 summarizes the main conditions of five experiments. In the first experiment, four UF membranes of different cut-off values (10, 30, 50 and 100 kDa) were tested simultaneously. In the second, third and fourth experiments, the membranes of 50, 40 and 30 kDa, respectively, were tested. Finally, a NF experiment was performed with four membranes of the same characteristics. In the UF tests and in the NF test, the working pressures were 4 bar and 8 bar, respectively.

The volume of feed water was the same in all the tests (50 dm<sup>3</sup>). All the experiments lasted until the liquid in the feed tank was concentrated as much as possible (about 2 dm<sup>3</sup>), so the time of each one was different depending on the permeate flow through of the membranes.

During the experiments permeate flow was periodically measured in order to calculate the membrane flux ( $J_v$ ) based on the following expression:

$$J_v = \frac{F_p}{A_{\text{memb}}}, \quad (1)$$

where  $F_p$  is the permeate flow and  $A_{\text{memb}}$  is the effective area of the membrane.

Furthermore, the samples of feed and permeate were periodically taken to measure the polyelectrolyte concentration in each stream. This concentration was determined by viscosity measurement using Canon–Fenske viscosimeters, since this parameter is directly proportional to the concentration of the polymer [7].

### 3. RESULTS AND DISCUSSION

#### 3.1. RESULTS OF THE UF EXPERIMENTS

Figure 3 shows the membrane permeability in the first experiment, in which four membranes of different cut-offs were tested. As can be seen in this figure, the permeate flux of the 50 kDa membrane is significantly higher than the permeate flux of the other three membranes, which have similar values of flux. This can be due to the different material and characteristics of the membranes, since the 50 kDa membrane is made of acrylonitrile copolymers, while the other three membranes are made of polyethersulphone.

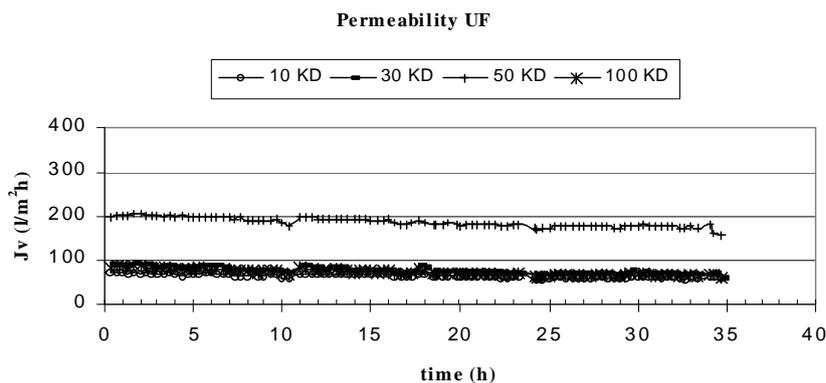


Fig. 3. Membrane permeability in the first experiment

As regards the membrane selectivity, figure 4 shows the evolution of polyelectrolyte concentration in this first experiment. According to our previous experience got from membrane processes and the theory about membrane technology, it was expected that polyelectrolyte concentration increased progressively as feed was being concentrated, as a result of polyelectrolyte rejection by the membrane. However, figure 4 shows that concentration values of the feed kept quite constant, instead of increasing significantly with time. This could be caused by poor polyelectrolyte rejection by the membrane, but permeate concentration values show that there is not polyelectrolyte. Anyway, since viscosimetry is not a precise method for measuring polyelectrolyte concentrations when values of concentration are closer to zero [3], it cannot be assured that permeate concentration values are really close to zero as figure 4 shows. So, it was possible that some of the membranes tested (the highest ones) did not reject the polyelectrolyte causing that feed water was not concentrated during the experiment.

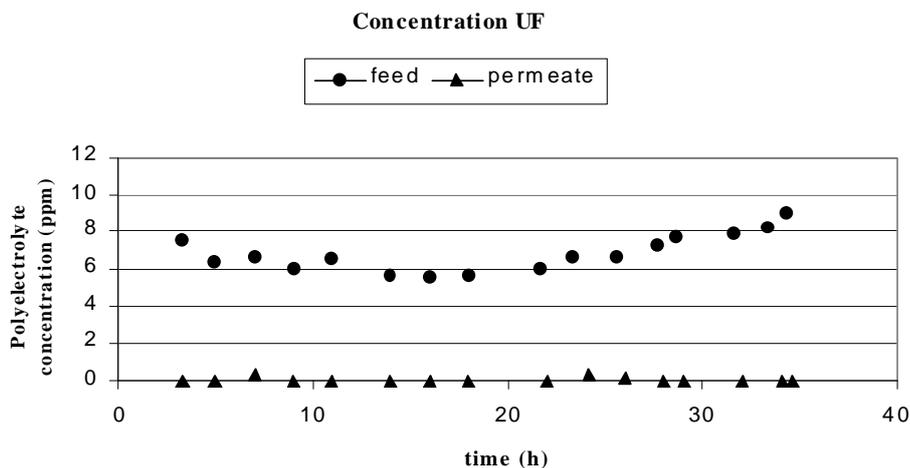


Fig. 4. Evolution of polyelectrolyte concentration in the first experiment

As a consequence of this result, it was decided to test only the membranes with the same cut-off at the same time in order to determine which membrane rejects the polyelectrolyte in greater proportion. With this purpose, in the experiments 2, 3 and 4, membranes of 50, 40 and 30 kDa were tested, respectively. Figure 5 shows the average permeate flux obtained in each of these experiments. This average permeate flux becomes stable at the value approaching  $100 \text{ dm}^3/\text{m}^2\text{h}$ , and it keeps quite constant during most of the experiment showing that there is not fouling or blocking of the membranes due to polyelectrolyte concentration.

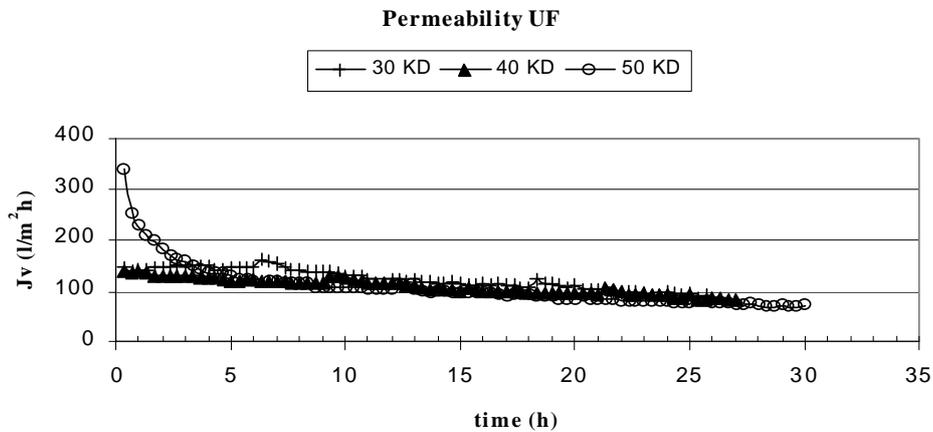


Fig. 5. Average permeate flux in experiments 2, 3 and 4

On the other hand, figures 6, 7 and 8 show the evolution of polyelectrolyte concentration in experiments 2, 3 and 4, respectively. As can be observed, the results are very similar to those obtained in the first experiment: instead of increasing with time, the values of polyelectrolyte concentration in the feed tank remain quite constant during all the experiments, and permeate values indicate that there is not polyelectrolyte.

A higher increase in the concentration values was measured in the experiment with 30 kDa membranes: from 5 ppm of the original feed water to 10 ppm of the final concentrate in the tank. However, this increase did not correspond to the one expected if the polyelectrolyte rejection by the membrane approached 100% (as permeate values indicate), which would have been a value around 150 ppm.

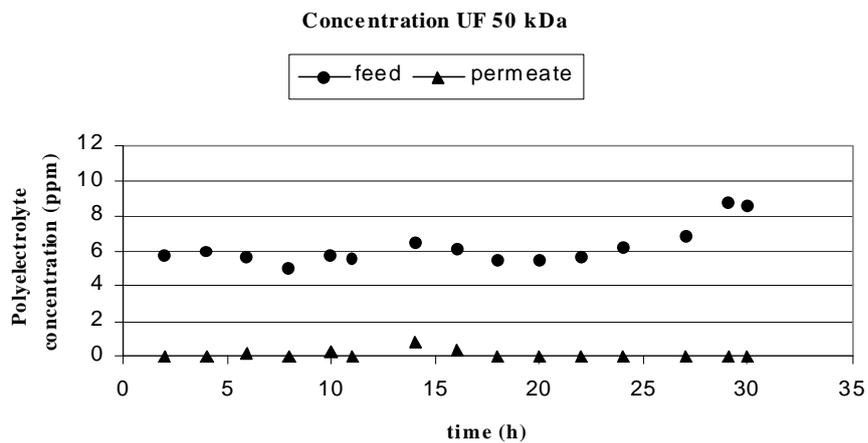


Fig. 6. Evolution of polyelectrolyte concentration in the experiment with 50 kDa membranes

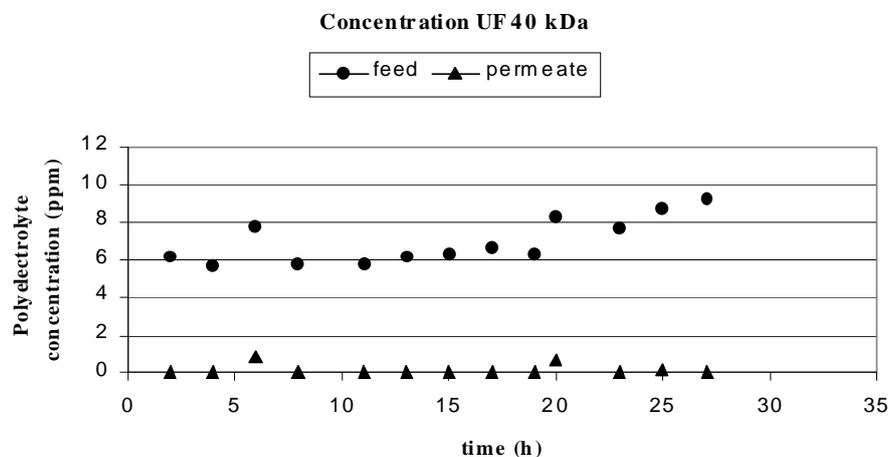


Fig. 7. Evolution of polyelectrolyte concentration in the experiment with 40 kDa membranes

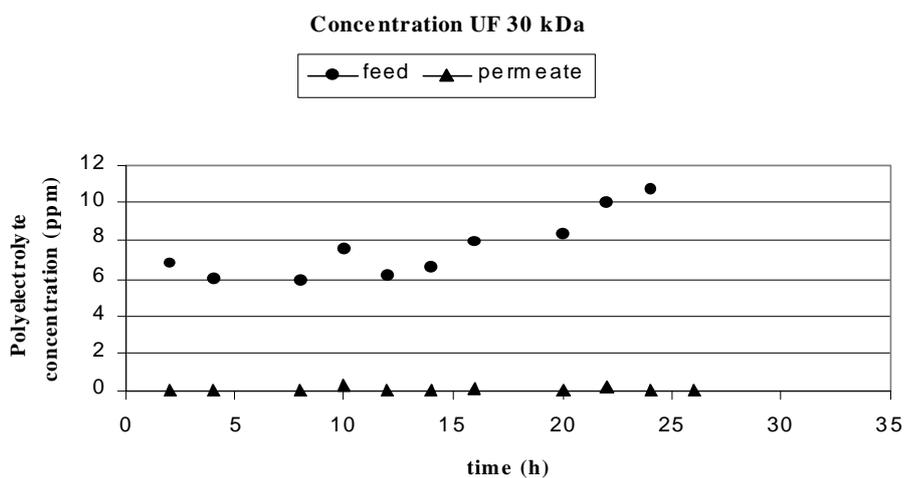


Fig. 8. Evolution of polyelectrolyte concentration in the experiment with 30 kDa membranes

As a consequence of these results, it was decided to test nanofiltration membranes, since they have a smaller pore size that should yield a more significant increase in feed concentration.

### 3.2. RESULTS OF THE NF EXPERIMENTS

The permeability of all the membranes tested remained quite constant (figure 9), which indicated that there was no fouling or blocking caused by polyelectrolyte.

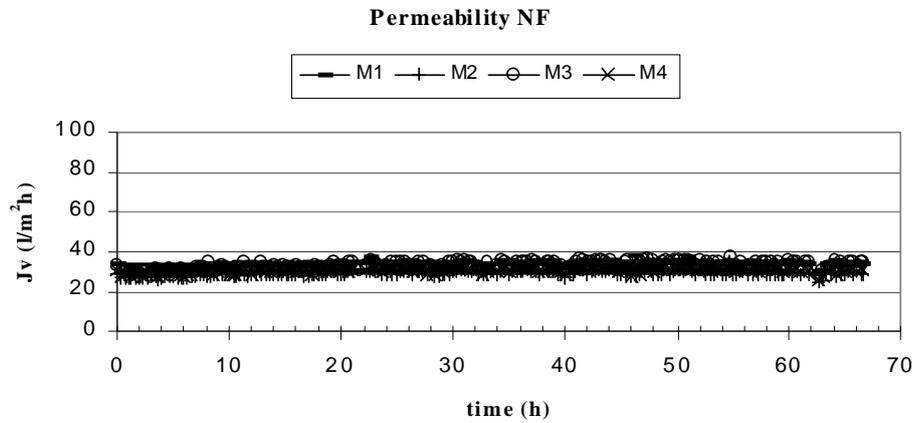


Fig. 9. Evolution of permeate flux in the experiment with NF membranes

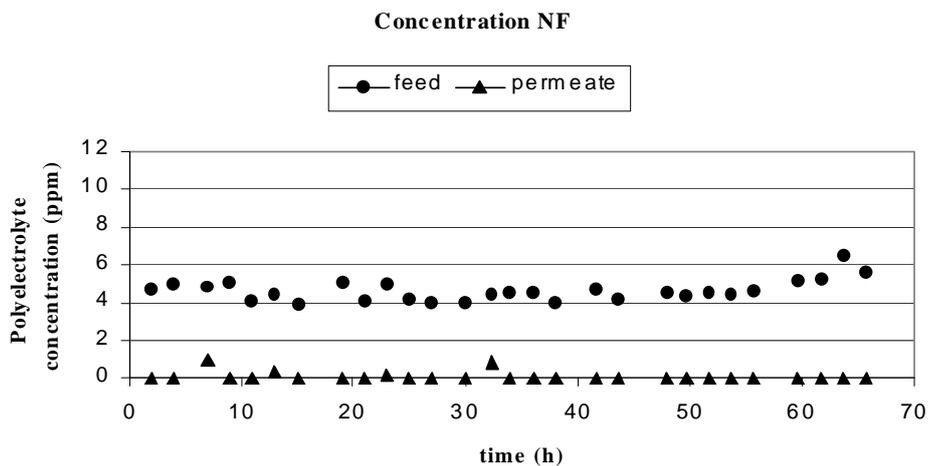


Fig. 10. Evolution of polyelectrolyte concentration in the experiment with NF membranes

Figure 10 shows the results of polyelectrolyte concentration evolution in the experiment with NF membranes. These results were identical to those obtained previously in the UF experiments: there was no increase in polyelectrolyte concentration in the feed, and the permeate concentration was close to zero. Since polyelectrolyte particles are larger than the pores in the NF membrane tested, the concentration of the feed should have increased significantly instead of being constant. This result can only be explained by polyelectrolyte degradation during the experiments. Since the concentrate is recirculated to the feed tank, it is possible that polymer chains break due to their friction with mechanical parts of the pilot plant (pressure pump), so viscosity does not increase and, consequently, value of polyelectrolyte does not increase.

#### 4. CONCLUSIONS

According to the results obtained in the experiments with UF and NF membranes, the following conclusions can be drawn:

- There is a significant difference in the permeability of the UF membranes tested. The 50 kDa membrane shows quite high permeate flux values, which can be associated with the difference in the material and membrane structure.
- Permeate flux remained quite constant in all the experiments, which proves that there was not any kind of fouling or membrane blocking due to the polyelectrolyte.
- Viscosity measurements show that polyelectrolyte concentration in all the experiments was very close to zero, so the polyelectrolyte rejection by the membrane is very high, approaching 100%.
- Polyelectrolyte concentration in the feed tank did not increase as expected. This can be explained by the degradation of the polyelectrolyte during the experiment due to mechanical friction as feed is being recirculated.

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