

Effect of ionic strength and pH over the removal of natural organic matter. Cationic- Anionic PAN membranes

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SUMMARY

1. INTRODUCTION

Natural organic matter in aquatic environments can form carcinogenic organochlorine compounds when is chlorinated [1]. On the other hand, the lack of water in the southeast of Spain is the main reason to study new alternatives of purification techniques and their optimisation. As a consequence, it will improve the use of natural waters.

The objective of this work is to study the removal of humic acids by means of an ultrafiltration system using cationic and anionic membranes of polyacrylonitrile (50 kDa MWCO), and analyze effects of pressure, conductivity and pH.

In the current paper three different waters were tested, humic acid (HA) solutions from Aldrich Chemical Co., water of Amadorio swamp and water of Pedrera swamp. These superficial water are situated in southeast of Spain, in the province of Alicante.

2. EXPERIMENTAL

2.1 Feed solution

Commercial humic acid (sodium salt, Aldrich) was used as the feed water. A stock solution was prepared by dissolving 0.5 g humic acid in 1-L deionised water and filtering through 0.45 µm membrane filter. Humic acid solutions were prepared by diluting this stock solution in DI water until a concentration of 10 mg/L. The pH was adjusted by addition of buffer solution (pH 4-8 phosphate buffer 0.2 M; pH 2.5 H₃PO₄ 0.2 M buffer) until a concentration of 25 mM. In order to adjust conductivity between 500-6000 µS/cm, a 0.1M KCl solution was added.

Each natural water was pre-filtered using a 0.45 µm membrane filter to remove particulate materials. With the aim of increasing water concentration of Pedrera swamp, reverse osmosis membrane (Hidrowater, model RO 0206-19) was used. In each surface water, conductivity was adjusted to 500-6000 µS/cm by addition of KCl (0.1M).

The characteristics of water mencionated above are shown in table 1.

Table 1. Summary of feed water characteristics

Type of water	pH at 20°C	UVA _{254nm} (1/cm)	DOC (mg/L)	SUVA (L/m.mgC)
Pedreira	8.5	0.045	3.2	1.4
Amadorio	8.6	0.034	2.0	1.7
HA Aldrich	7.0	0.8	10.0	8.0

To characterize the molecular size of NOM (MWCO) it was used a membrane fractionation technique proposed by Aiken [2]. Differences in the fraction of NOM passing successive membranes yield a discrete size distribution. For this fractionation a wide range of molecular weight cutoffs (MWCOs) was employed 30, 10, 5, 1 and 0.5 kDa of Cellulose regenerated and acetate cellulose membranes from Millipore. Measures of rejection coefficients for every UF membrane are shown in figure 1.

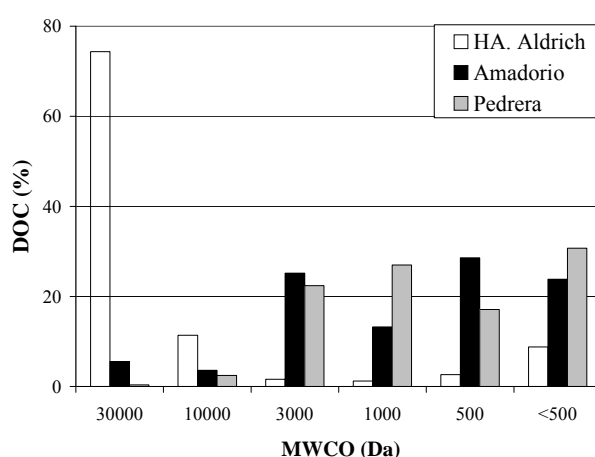


Figure 1. Overall NOM rejection during 180 mL filtration, with various MWCO membranes.

2.2. Analytical methods

Dissolved Organic Carbon (DOC) was measured using a Shimadzu 5000 total organic carbon analyser.

UV absorbance was measured in a UV/VIS spectrophotometers (Shimadzu UV-1601) at 254 nm wavelength and the pH was previously adjusted at 7 adding NaOH or HCl to samples. Specific absorbance (SUVA) was calculated as the ratio of UVA to DOC.

Conductivity and pH were measured using a Mettler-Toledo apparatus.

2.3 Membranes

Ultrafiltration disc membranes made of polyacrilonitrile (PAN) anionic and cationic with a MWCO of 50kDa (obtained from Rhodia Orelis, mod. IRIS 3050 and IRIS 3042), were used. All disc membranes had a 63.5 mm of diameter, effective area of 2780.5 mm². The max pressure of work was 4 atm.

Membrane characteristics are shown in table 2.

Table 2. Characteristics of membranes used in the study.

Membrane	Material	MWCO Dalton	Pressure max. atm	Code	Model	Make
ANIONIC	polyacrilonitrile anionic	50000	4	RAY 100 3042	Rayflow	Rhodia
CATIONIC	polyacrilonitrile cationic	50000	4	RAY 100 3050	Rayflow	Rhodia

2.4 UF process

Ultrafiltration experiments were carried out in a dead-end stirred cell filtration system (figure 2). The system consisted in a filtration cell (Model 8200, Millipore, corp.) with a total internal volume of 200 mL and active surface area of 2780.5 mm². The liquid feed pressure was maintained by extra-dry grade nitrogen.

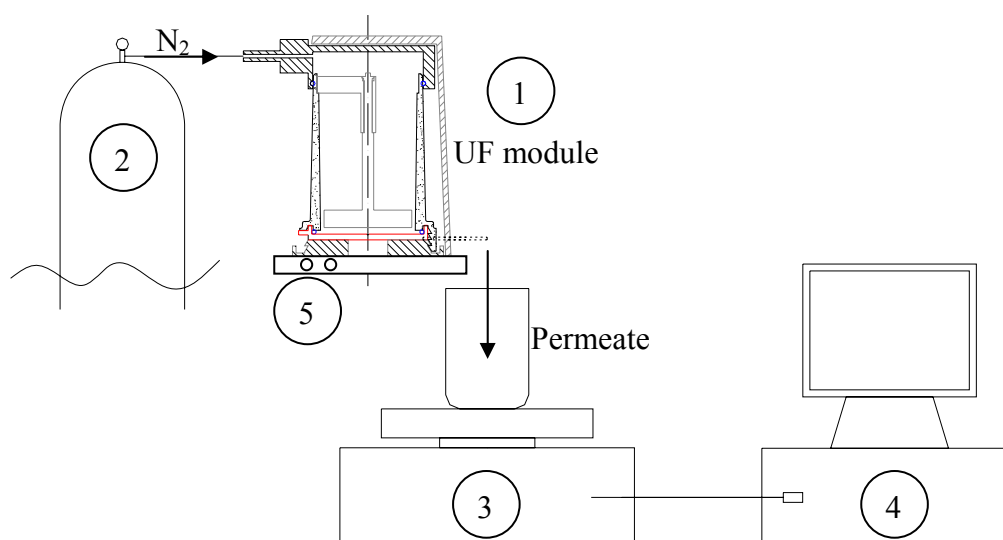


Figure 2. Schematic diagram of the experimental apparatus. 1-ultrafiltration module (Amicon 8200), 2-gas cylinder (Nitrogen), 3-Analytical balance, 4-computer registration, 5-electronic stirrer.

2.4.1 Filtration protocol

Membranes were first compacted permeating pure water at 400 kPa during 8 hours. Ultrafiltration experiments were carried out in a stirred cell apparatus (Model 8200 Amicon Millipore).

The stirred cell was initially filled with DI water and in every experiment pH, conductivity and pressure were adjusted. The water flux was measured as a function of time at a constant pressure until steady flux was achieved. Then, the stirred cell was emptied and refilled with a humic acid solution and the system was repressurized. The filtrate flow rate was measured with the filtrate mass using an analytical balance. Permeate samples were collected periodically for subsequent concentration analysis. At the end of the filtration experiment, the stirred cell was emptied and refilled with DI water at the same pH, conductivity and pressure, as initial experiment. In all experiments the stirring speed was

fixed to 200 rpm using a Micromix electronic stirrer. All experiments were carried out using the compacted membrane at 20 °C of temperature. Conductivity, pH and pressure were adjusted to following ranges, respectively: 500-6000 $\mu\text{S}/\text{cm}$, 2.7-9 and 100-400 kPa.

3. RESULTS AND DISCUSSION

3.1 Membrane characterization

Hydraulic Resistance

The hydraulic resistance (R) of each membrane was analysed by measuring pure water permeability of the membrane. That value reflects the water capacity to pass through the membrane normalized by transmembrane pressure. The figure 3a shows the fluxes of pure water as a function of transmembrane pressure for cationic and anionic membranes. The flux increases linearly with pressure rising at low pressure and it tends to an asymptotic value at high pressure. The membrane permeability was determined by linear regression of the filtrate flux versus pressure data.

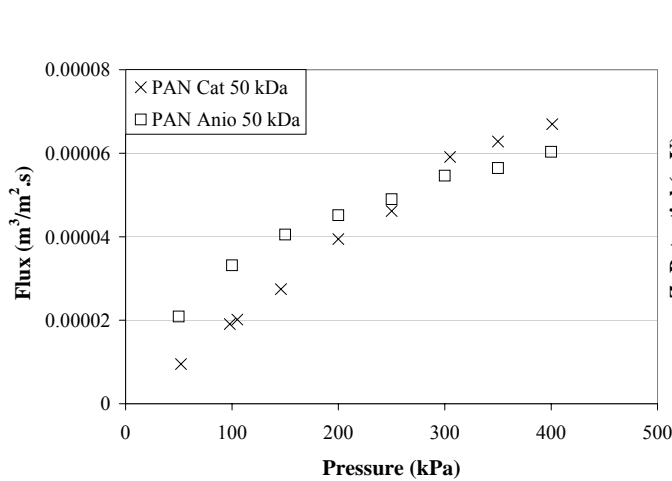


Figure 3a. Flux versus pressure.

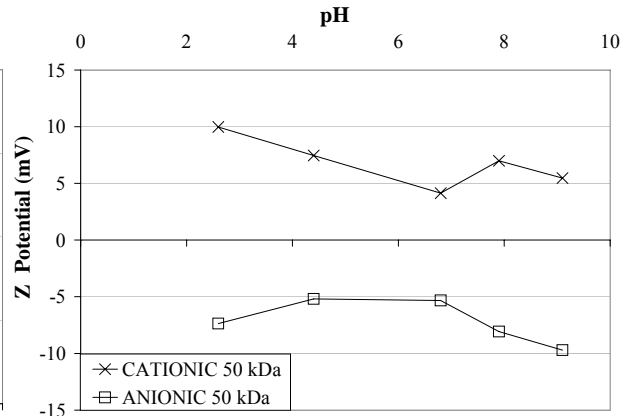


Figure 3b. Z potential versus pH.

The hydraulic resistance has been estimated using Darcy equation:

$$J = \frac{\Delta P}{\mu R m} \quad (\text{Eq.1})$$

J = Flux ($\text{m}^3/\text{m}^2.\text{s}$)

ΔP = Pressure (Pa)

R_m = Hydraulic resistance (m^2/m^3)

μ = Viscosity (Pa.s)

The values of hydraulic resistance of anionic and cationic membranes used in the study can be observed in table 3.

Z potential

The most common technique for evaluating the membrane surface charge is to determine the streaming potential as a function of the applied pressure [6]. Experimental data for the apparent zeta potential of the two polyacrylonitrile membranes are shown in figure 3b. The

studies were performed using 10 mM KCl solutions buffered with 1 mM phthalate (for pH 2.5-6), 1 mM phosphate (pH 6-8.5). Cationic membranes have a positive zeta potential for all pH values, with a slightly decrease with the increase of pH. The anionic membranes have a negative zeta potential for all values of pH. Table 3 shows Zeta potential values.

Table 3. Properties of membranes used in the study

Membrane	Water flux (P = 100 kPa, m ³ /m ² .s)	Zeta potential pH 7 (mV)	Hydraulic resistance (m ⁻¹)
ANIONIC	3.31.10 ⁻⁵	-5.5	3.35.10 ¹²
CATIONIC	2.02.10 ⁻⁵	+4.9	5.34.10 ¹²

Polyacrilonitrile cationic membrane has a hydraulic resistance value bigger than anionic membrane being 38 % approximately, the difference between those values. As a result, the latter one has more flux in the same proportion (40%).

3.2 Removal organic matter from synthetic water

3.2.1 Effect of pressure

The study carried out to determine the effect of the pressure in the humic acid ultrafiltration, has been realized for a range of pressures between 100 and 400 kPa.

All experiments had an initial concentration of humic acid of 10 mg/L, pH 7 and 1000 µS/cm.

Figures 4 and 5 show the results obtained of each studied membrane at different pressures. For each membrane it has been represented, the flux reductions of permeate versus time of ultrafiltration and DOC removal versus concentration factor (Vo/V).

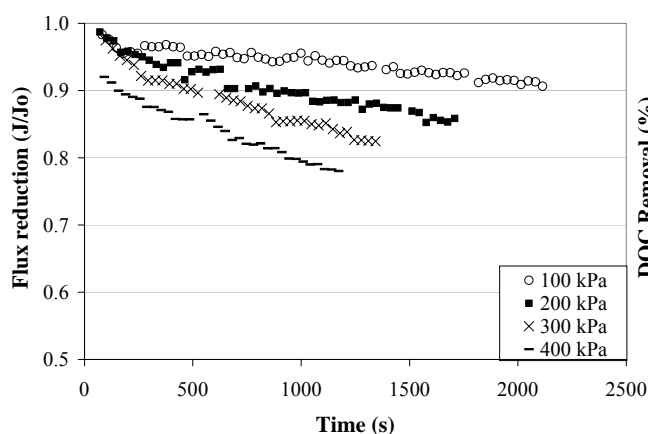


Figure 4a. Flux reduction versus time

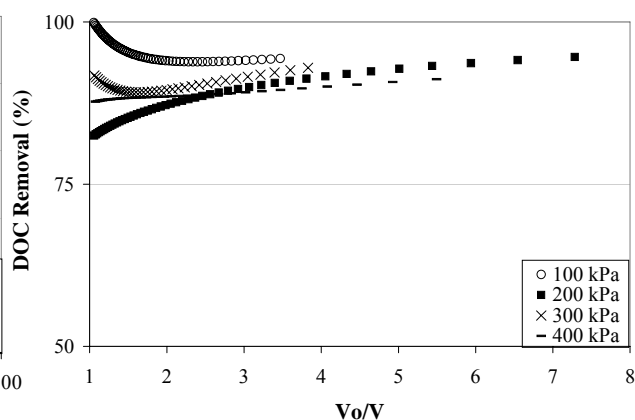


Figure 4a. DOC removal versus concentration factor

Figure 4. Cationic PAN membrane.

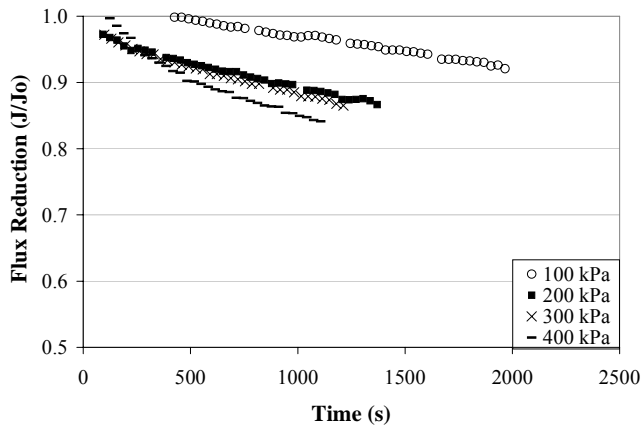


Figure 5a. Flux reduction versus time

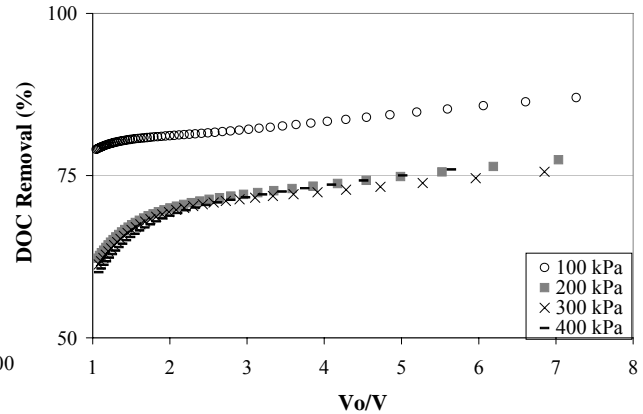


Figure 5a. DOC removal versus concentration factor

Figure 5. Anionic PAN membrane.

Figures 4a and 5a illustrate that the permeate flux declines, at different pressure values, for both membranes, in ultrafiltration experiments, using a 10 mg/L of humic acid solution.

Related to anionic and cationic membrane

- The flux of permeate decreases when rises the ultrafiltration time.
- The flux of permeate declines further as the pressure increases. It can be observed in data presented in Table 4. At the end of ultrafiltration experiment and using the cationic membrane, flux reduction is 22 %, at 400 kPa of pressure. However, working at 100 kPa of pressure, the flux reduction is 9 %. In anionic membrane the flux reduction is 7.5% at 100 kPa and this value is nearly twice (16%) at 400kPa.
- Irreversible fouling is greater at high pressures.

Table 4. Flux reduction at the end of ultrafiltration experiment and irreversible fouling after a posterior cleanliness with distiller water.

P (kPa)	CATIONIC		ANIONIC	
	Flux reduction (%)	Irreversible fouling (%)	Flux reduction (%)	Irreversible fouling (%)
100	8.9	5.7	7.5	2.0
200	14.3	8.7	12.8	6.0
300	17.4	7.6	13.3	5.9
400	21.6	13.0	15.8	9.1

Figures 4b and 5b show, the DOC removal decreases with the pressure increase for cationic and anionic membranes. In addition, DOC removal increases with the concentration factor (Vo/V) rise.

In anionic membranes, rejection coefficients increase as ultrafiltration process is carried out, attaining a value greater than 75% at the end of experiment. At the beginning of experiment, using cationic membranes, there is a slightly decrease of DOC removal for all pressures although, for values greater than Vo/V=2, that trend changed. At the end of ultrafiltration experiment the values of DOC removal are greater than 87%.

3.2.2 Effect of conductivity

The study carried out to determine the effect of conductivity in the humic acid ultrafiltration, has been realized in a conductivity range of 1000 and 6000 $\mu\text{S}/\text{cm}$.

Potassium chloride (KCl) was used to control ionic strength of solutions.

All experiments had a 10 mg/L initial concentration of humic acid and pH 7.

All experiments carried out at 100 kPa pf pressure.

In figures 6 and 7 are represent the results obtained for each studied membrane at different conductivities. For each membrane it has been represented the flux reductions of permeate versus time of ultrafiltration, and DOC removal versus concentration factor (Vo/V).

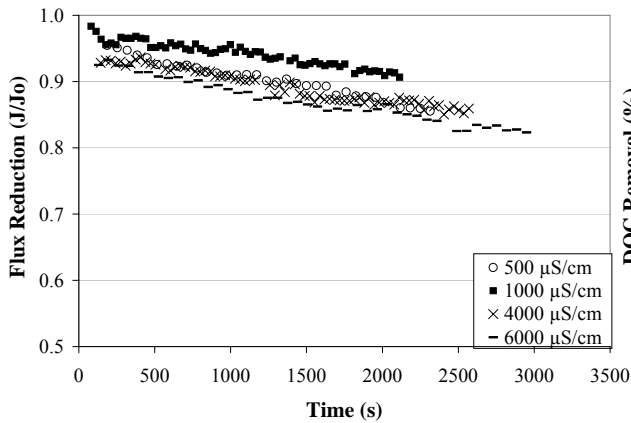


Figure 7a. Flux reduction versus time

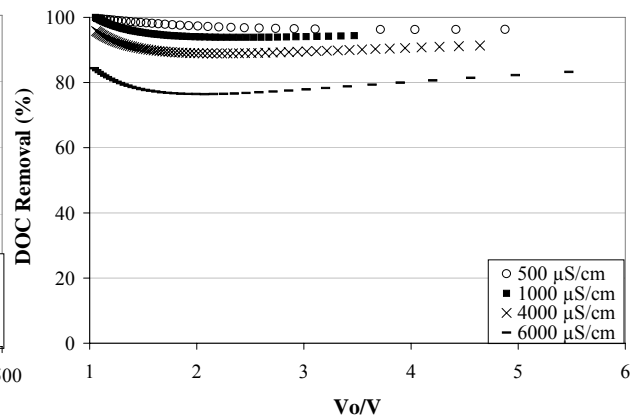


Figure 7b. DOC removal versus concentration factor

Figure 7. Cationic PAN membrane.

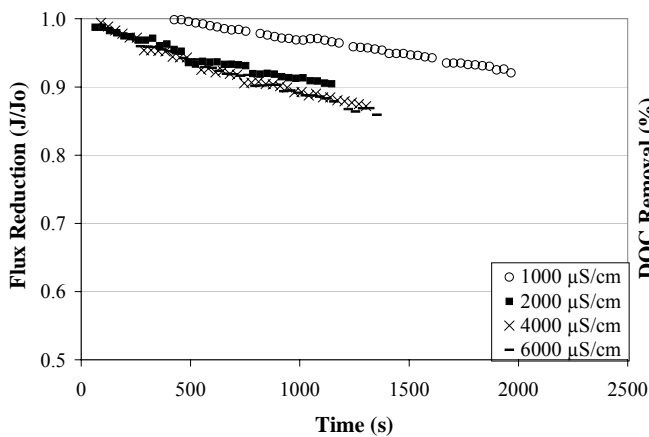


Figure 8a. Flux reduction versus time

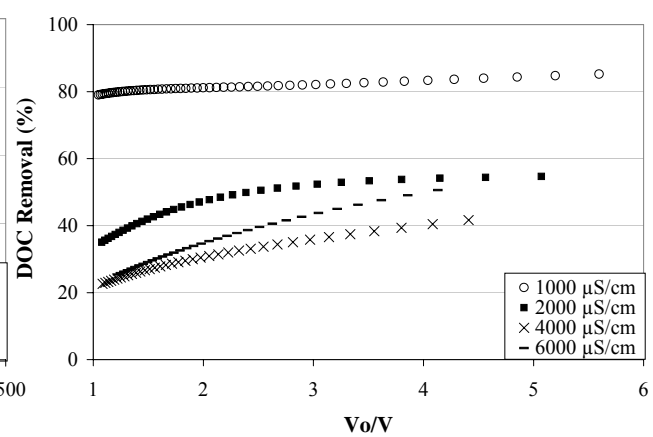


Figure 8b. DOC removal versus concentration factor

Figure 8. Anionic PAN membrane.

The experiments show an increase in humic acid adsorption as the ionic strength increases for both membranes. Therefore, it causes an increase of flux reduction at high conductivity of the humic acid solution.

The values of flux reduction calculated for each solution condition at the end of each ultrafiltration experiment are shown in table 5. For cationic membrane, flux reduction increases 8% if the conductivity increase from 2000 to 6000 $\mu\text{S}/\text{cm}$. For anionic membranes, flux reduction increases approximately 6% when the conductivity of the solution increases from 1000 to 6000 $\mu\text{S}/\text{cm}$.

Table 5. Flux reduction at the end of ultrafiltration experiment and irreversible fouling after a posterior cleanliness with distiller water.

Conductivity ($\mu\text{S}/\text{cm}$)	CATIONIC		ANIONIC	
	Flux reduction (%)	Irreversible fouling (%)	Flux reduction (%)	Irreversible fouling (%)
500/1000	14.1	8.6	7.4	2.0
2000	8.9	5.7	9.4	2.9
4000	14.2	7.4	12.5	4.7
6000	17.2	11.5	13.4	5.2

At high conductivity solution, DOC removal decreases for both membranes. Table 6 shows that 96 and 82 % of the DOC was removed ultrafiltrating at low conductivity solutions (500-1000 $\mu\text{S}/\text{cm}$) for cationic and anionic membrane respectively. Additionally, 77-43 % of DOC removal was reached working at a high conductivity.

The increased ionic strength reduces the electrostatic repulsion among humic acid molecules resulting in an increase in adsorption [8]. At high conductivity humic acid molecules have a more compacted geometry and this fact give rise to the pass of the molecules through the membrane. This effect is greater in anionic membranes, because the negative charge of this membrane repulse easily humic acids with negative charge.

Table 6. Efficiency of DOC removal at the end of ultrafiltration experiment.

Conductivity ($\mu\text{S}/\text{cm}$)	DOC removal (%)	
	Cationic	Anionic
500/1000	96	82
2000	94	52
4000	90	37
6000	77	43

3.2.3 Effect of pH

The study carried out to determine the effect of pH in the humic acid ultrafiltration, has been realized in a pH range of 2.7 to 9.

The pH was adjusted by addition of buffer solution (pH 4-8 phosphate buffer 0.2 M; pH 2.5 H_3PO_4 0.2 M buffer) until a concentration of 25 mM. All experiments had an initial concentration of humic acid of 10 mg/L and 1000-1500 $\mu\text{S}/\text{cm}$ of conductivity.

All experiments were carried out at 100 kPa of pressure.

In Figures 9 and 10 are represented the results obtained for each studied membranes at different pH. For each membrane it has been represented the flux reductions of permeate versus time of ultrafiltration, and DOC removal versus concentration factor (V_0/V).

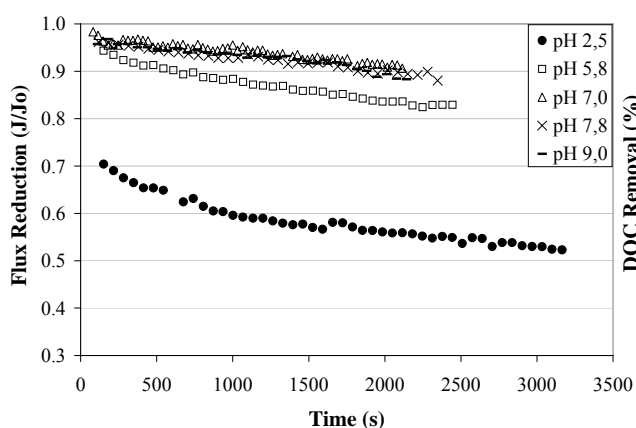


Figure 9a. Flux reduction versus time

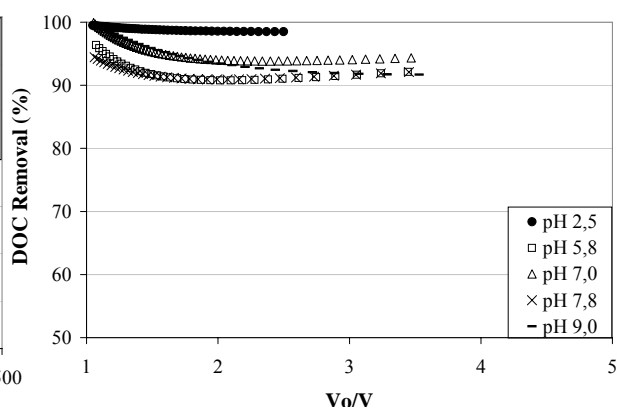


Figure 9b. DOC removal versus concentration factor

Figure 9. Cationic PAN membrane.

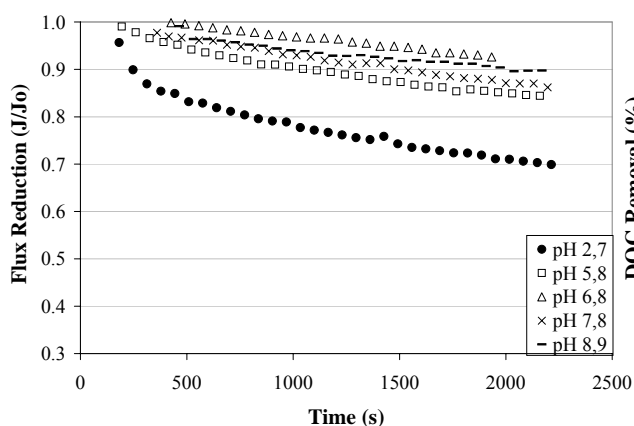


Figure 10a. Flux reduction versus time

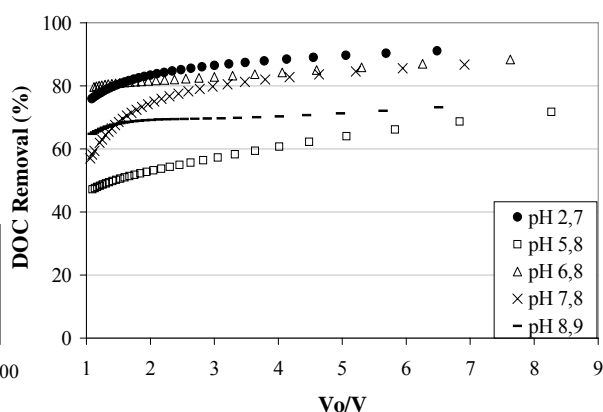


Figure 10b. DOC removal versus concentration factor

Figure 10. Anionic PAN membrane.

Figures 9a and 10a show data for the normalized filtrate flux during ultrafiltration of 10 mg/L humic acid solutions at different pH using cationic and anionic PAN membranes.

The decrease of flux was the faster one at pH 2.5-2.7, with $J/J_0=0.53$ (cationic PAN membrane) and 0.58 (anionic PAN membrane) at the end of experiment, compared with $J/J_0=0.9-0.8$ at pH 7-9 after the same filtration time. The rapid flux decline in these ultrafiltration experiments was caused by the humic acid adsorption. The results of flux reduction are

summarized in table 7. In this table it can be observed that irreversible fouling is bigger at acid pH.

The data in figures 9a and 10a also suggest that the flux in both membranes, at acid pH, quickly falls from the beginning of experiment. At long time, the flux reduction has a similar tendency that the rest of experiments at neutral or basic pH.

Table 7. Flux reduction at the end of ultrafiltration experiment and irreversible fouling after a posterior cleanliness with distiller water.

pH	CATIONIC		ANIONIC	
	Flux reduction (%)	Irreversible fouling (%)	Flux reduction (%)	Irreversible fouling (%)
2.5	47.2	29.7	42.3	24.8
5.8	17.2	15.3	12.8	12.2
7.0	8.9	13.2	5.7	6.8
7.8	10.8	7.0	4.4	1.9
9.0	11.3	10.3	4.1	5.9

The Z potential, previously studied (figure 3b) indicates membrane surface charge. Cationic PAN membranes have a positive zeta potential for all studied pH.

Anionic PAN membranes have a negative Zeta potential for all studied pH. Moreover, with pH increasing the absolute value of Zeta potential, also increases.

At low pH, membranes have a more positively charge than those ones at neutral or basic pH. However, humic acids have negative charge. This opposite charge, not only provokes an increase of adsorption of humic acids (with negative charge) on membrane surface, but also, into membrane pores. It has lead with the fact, that exists more attraction (with more positively charge at low pH), causing an increasing of flux reduction [5].

The DOC removal was slightly greater at low pH in cationic and anionic membranes (table 8).

Taking into account the cationic membrane, at the end of experiment, DOC removal reach a 98 %, at pH 2.5, even though, at pH 7, it was 94 %. On the other hand, for anionic PAN membrane, at low pH the reduction is 85% for pH 2.7 and 83% for pH 7.

Table 8. Efficiency of DOC removal at the end of ultrafiltration experiment.

pH	DOC removal (%)	
	Cationic	Anionic
2.5	98	85
5.8	92	57
7.0	94	83
7.8	92	80
9.0	92	70

3.2.4 Comparison of anionic-cationic PAN membrane

Figure 11 represents the variation of permeate flux and flux reduction versus time for the experiments realized with cationic and anionic membranes. Figure 12 represents DOC removal versus concentration factor (V_0/V).

In the all experiments the solutions haven an initial concentration of humic acid of 10 mg/L, pH 7, and 1000 $\mu\text{S}/\text{cm}$.

All experiments were carried out at 100 kPa of pressure.

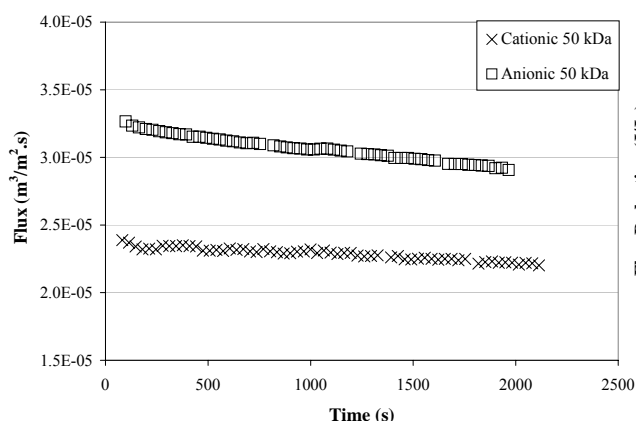


Figure 11a. Permeate Flux versus time

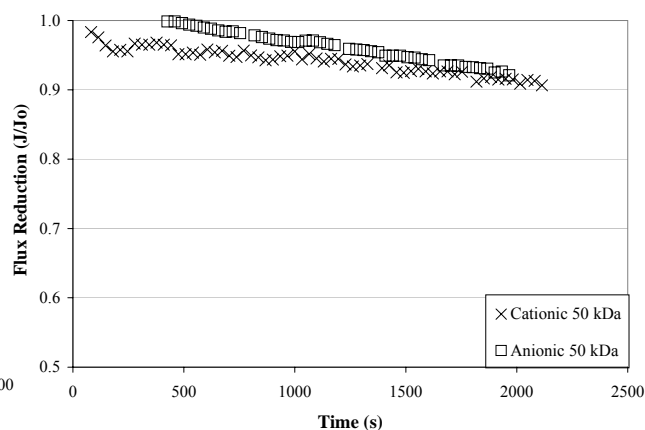


Figure 11b. Flux reduction versus time

Figure 11. Cationic/Anionic PAN membranes.

- Despite of the fact that cationic and anionic PAN membranes have the same molecular cut off (50000 Da), hydraulic resistance of the first one is bigger than that showed by the second one
- The permeate flux reduction in cationic membrane takes place in the first moments of AH adsorption onto and into the membrane. In table 9 it can be observed that the value of flux reduction is slightly higher in cationic membrane than in anionic one but this difference is more evident if irreversible fouling is compared.

Table 9. Flux reduction at the end of ultrafiltration experiment and irreversible fouling after a posterior cleanliness with distiller water

Membrane	Flux reduction (%)	Irreversible fouling (%)
Cationic 50 kDa	8.9	5.7
Anionic 50 kDa	7.5	2.5

- Cationic membrane has positive charge and humic acid has negative charge, this opposite charge provokes a humic acid adsorption in the surface of the membrane, and humic acid molecules are strongly retained. For that reason, the cleaning of the membrane is more difficult.

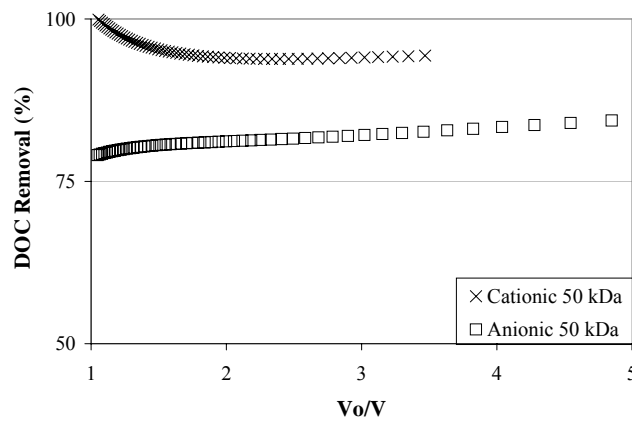
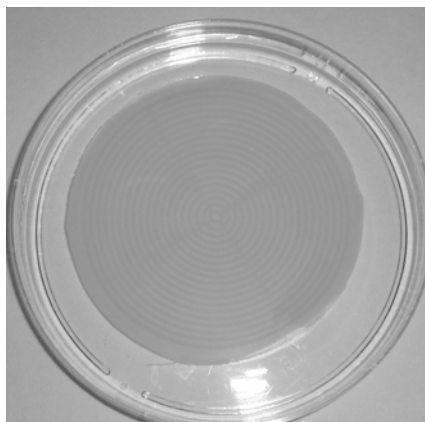
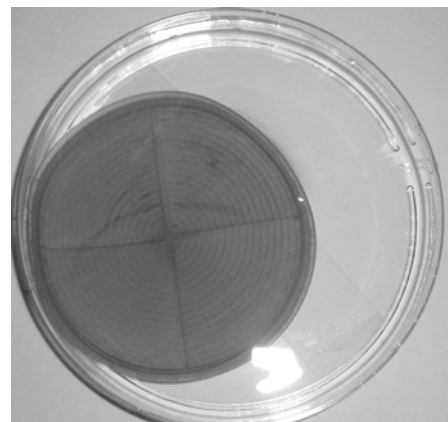


Figure 12. Cationic/Anionic PAN membranes. DOC removal versus factor concentration.

- DOC removal is greater in cationic membranes (94%) than in anionic membranes (82%) at the end of experiment. The positive charge of the cationic membrane retains strongly small molecules. Due to the charge of the membrane surface, in anionic membrane, the molecules introduced in pores are repelled because the charge of the surface of the membrane is the same of the humic acids.
- In ultrafiltration experiment with cationic membrane, when the value of V_o/V increases, DOC removal decreases. This tendency could be explained, because at the initial period of ultrafiltration experiment there is a big adsorption of humic acid molecules in free hollows and on the surface of cationic membrane. When the active centres are occupied, the molecules of humic acid previously adsorbed repel to molecules with the same positive charge and causing a decrease of DOC removal with the increasing of V_o/V .
- The anionic membrane tends to repel humics acids, and humic acid molecules have more difficulty in keeping adsorbed on the membrane and therefore, they cross pores easier.
- In photography 1 it is possible to observed the anionic and cationic membrane after the ultrafiltration experiment using 10 mg/L of humic acid solution. Cationic membrane acquires a brown intense colour, due to the greater adsorption of humic acids on this one. Anionic membrane has a slight yellowish coloration



Anionic 50 kDa



Cationic 50 kDa

Photography 1. Cationic/Anionic PAN membranes after the humic acid ultrafiltration experiment. $[HA]_o = 10$ ppm. $1000 \mu S/cm$. pH 2.5. $P = 100$ kPa.

3.2 Removal of organic matter from natural water

Figure 13 shows the flux reduction versus time for ultrafiltration experiments realized with cationic and anionic PAN membranes to treat water Amadorio's and Pedreras's swamp. DOC removal versus concentration factor (V_o/V) is represented in figure 14.

All experiments were carried out at 100 kPa of pressure.

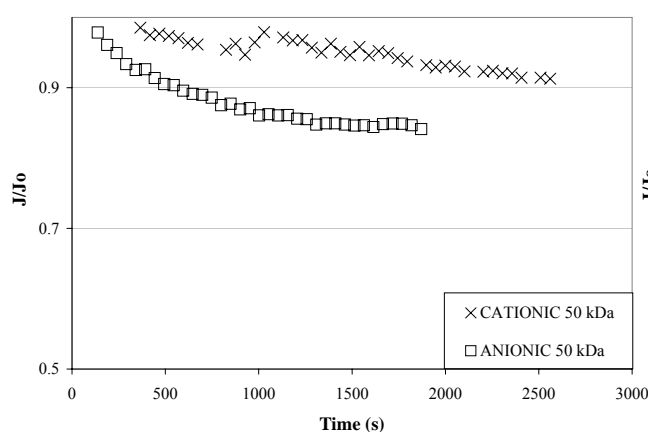


Figure 13a. Amadorio swamp

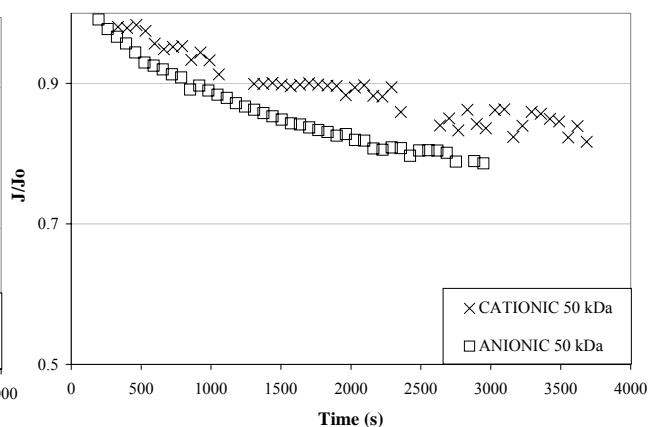


Figure 13b. Pedrera swamp

Figure 13. Cationic/Anionic PAN membrane. Flux reduction during ultrafiltration experiment.

The decrease of flux reduction is major when natural waters of swamp are treated comparing with synthetic waters (Aldrich), though the concentration was higher in last ones. The differences can be explained by the different composition of the organic matter (Figure 1). Natural organic matter has molecules with low distribution of molecular weight, and humic acid of Aldrich has a higher distribution of MWCO.

Permeate flux reduction is higher in anionic membrane than in cationic membrane, probably because of differences of matter composition [7] (hydrophobic and hydrophilic character). Irreversible fouling is higher in anionic PAN membrane (table 10).

Table 10. Flux reduction at the end of ultrafiltration experiment and irreversible fouling after a posterior cleanliness with distiller water

Membrane	Flux reduction (%)			Irreversible fouling (%)		
	Amadorio	Pedrera	HA Aldrich	Amadorio	Pedrera	HA Aldrich
Cationic 50 kDa	9.6	13.9	8.9	1.6	2.0	5.7
Anionic 50 kDa	15.5	21.2	7.4	5.7	11.0	2.5

DOC removal is smaller in natural waters than in synthetic waters (table 11). At the end of ultrafiltration experiment, DOC removal values are 69% for cationic membrane and 53% for anionic membrane in Amadorio swamp. However, for Pedrera swamp, those values were 41 and 33% approximately, whereas in synthetic waters they were 93-81% respectively.

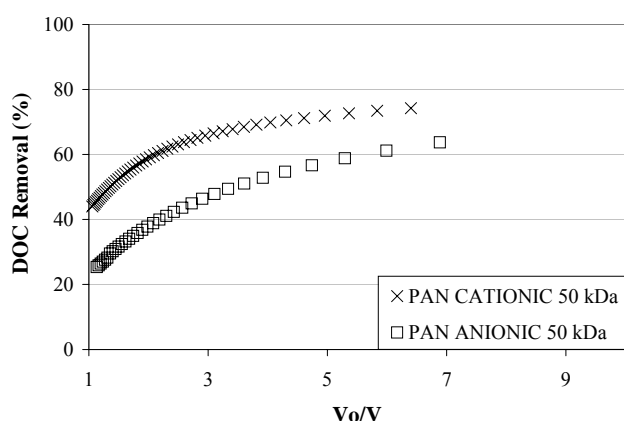


Figure 14a. Amadorio swamp

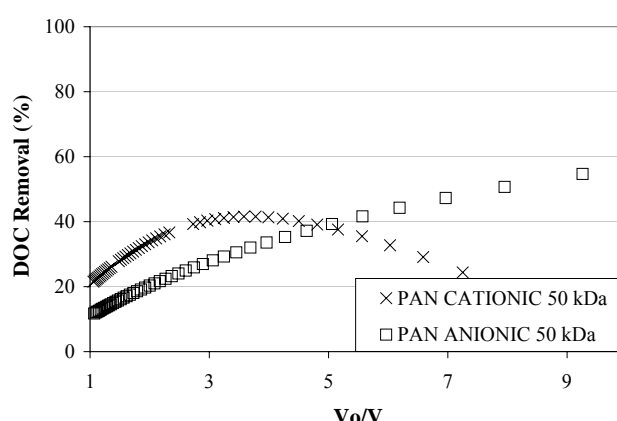


Figure 14b. Pedrera swamp

Figure 14. Cationic/Anionic PAN membrane. DOC Removal versus concentration factor.

Table 11. Efficiency of DOC removal at the end of ultrafiltration experiment.

Membrane	DOC Removal (%)		
	Amadorio	Pedrera	HA Aldrich
Cationic 50 kDa	69	41	93
Anionic 50 kDa	53	33	81

4. CONCLUSION

This study shows that the best remove of NOM occurs using PAN cationic membranes than PAN anionic membranes. The behaviour of fouling is similar in both membranes, although it is slightly higher using cationic PAN membranes in the ultrafiltration of synthetic waters.

Table12: Efficiency of DOC removal and flux reduction $P=100\text{kPa}$, $1000\ \mu\text{S/cm}$, pH 6,8.

Membrane	DOC removal ($V_o/V=2$)	Flux reduction ($t=1200\text{s}$)
PAN cationic 50kDa	93 %	6%
PAN anionic 50kDa	79%	4%

The DOC removal decreases and the fouling increases with pressure increase in PAN membranes.

High ionic strength produces an important decrease of DOC removal in anionic membranes. Similar effects can be observed in cationic membrane but less pronounced.

Table13: Efficiency of DOC removal and flux reduction $P=100\ \text{kPa}$ and pH 6,8.

Membrane	DOC removal ($V_o/V=2$)		Flux reduction ($t=1200\text{s}$)	
	$1000\ \mu\text{S/cm}$	$6000\ \mu\text{S/cm}$	$1000\ \mu\text{S/cm}$	$6000\ \mu\text{S/cm}$
PAN cationic 50kDa	93 %	80%	6%	12%
PAN anionic 50kDa	79%	35%	4%	13%

The flux slightly declines as the conductivity increases for cationic and anionic membranes.

The humic acid solution at pH 2.7 shows the worst flux decline for PAN cationic membranes. This effect is similar in anionic membranes however, is less marked. Low pH causes an increase of DOC removal for both membranes.

Table14: Flux reduction. P=100 kPa, 1000 μ S/cm. T= 1200s

Membrane	Flux reduction (pH 6,8)	Flux reduction (pH 2.7)
PAN cationic 50kDa	6 %	42%
PAN anionic 50kDa	4%	25%

This study shows that the best remove of DOM takes place using PAN cationic membranes. High ionic strength produces a decrease of DOC removal in cationic and anionic PAN membranes. Low pH provokes an important fouling rise of membranes. Results are in accordance with those published by other authors [3][4].

In order to remove a major percentage of organic matter in natural waters it would suit to use membranes with a smaller pore size.

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