

Membrane filtration of surface water for the removal of humic substances

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In this study the removal of humic substances from synthetic water through ultrafiltration (10, 100 kDa) and microfiltration membranes (0.2 μm) has been investigated. Two membrane configurations (flat sheet and tubular) have been used, and their performances compared. Permeate and retentate samples were analyzed by UV254 nm absorbance to evaluate humic acid removal while permeability and flux decay test were performed to estimate biofouling caused by organic material. Filtration tests with a model solution have shown that the studied UF membranes are effective, with a removal efficiency of UF membrane of 85-90% at humic acid concentration over 7.5 mg/L, while MF membrane are very efficient only if used in tubular configuration, reaching organic matter removal of 90%.

1. Introduction

Membrane processes have increased rapidly over the past decade in potable water production offering several advantages over conventional treatment such as compact module, lower energy consumption, environmental friendliness and high quality product independently on fluctuations in feed quality. MF and UF processes have been increasingly used in drinking water treatment as an alternative technology to conventional filtration and clarification, in order to remove particles, turbidity, microorganisms and natural organic matter (NOM). The latter can be considered a mixture of organic compounds whose major fraction is the one relative to the humic substances (Yuan and Zyney, 1999). Humic substances are complex, acidic organic molecules formed by the decomposition of plants, animals and microbial material. They first came to prominence in agriculture, because of their positive influence on the structure, water retention properties, and nutrient status of soils but they pose problems to the water supply industry. Removal of NOM is extremely important and it has become a challenging research in current development of water purification technologies, not only because it affects the odour, colour and taste of water but mainly because it is considered as a precursor of disinfection by-products (DBPs). The most dangerous DBPs, recently recognised to be human carcinogens are halogenated organic compound such as trihalomethanes (THMs) and haloacetic acids (HAAs), derived from reaction of organic material with free chlorine used as a disinfectant in conventional treatment. DBPs control can be done by minimizing natural organic matter (precursors) in the raw water, by reducing disinfectant doses, by removing DBPs after they form or by using alternative disinfectants. Katsoufidou et al. (2005) studied humic acid rejection on polyethersulfone hollow fiber membrane (whose Molecular Weight Cut-Off –

MWCO – was 150 kDa) obtaining rejections close to 20% in the absence of calcium and up to 75% with 2 mM Ca^{2+} . Mozia and Tomaszewska (2004) studied a hybrid process (powdered activated carbon PAC/UF) with membranes prepared from polyacrylonitrile (MWCO 110 kDa); filtration test on natural waters showed that a PAC dosage of 100 mg/L enhanced organics removal from 44% to 64% and reduced membrane fouling by preventing organics from adsorption onto the membrane surface. Other researchers (Lin et al., 1999) found that the use of PAC either as a pretreatment agent or as an additive in the integrated PAC-UF system exhibits an increased membrane fouling. Aoustin et al. (2001) studied the influence of calcium concentration on humic acid rejection through membrane of MWCO 10 and 100 kDa. They obtained rejections of 84-92% at CaCl_2 concentration in the range of 0.5-4 mM. Domany et al. (2002) tested four polyether-sulfon membrane of MWCO 5, 6, 15, 100 kDa obtaining a satisfactory removal efficiency of 85-90% for model solution and 62-69% for natural well-water.

In this study the removal of humic substances from model-solution through ultrafiltration (10, 100 kDa – flat sheet configuration) and microfiltration membranes (0.2 μm - flat sheet and tubular configuration) has been investigated. Permeate and retentate samples were analyzed by UV254nm absorbance to evaluate humic acid removal while permeability and flux decay test were performed to estimate biofouling caused by organic material.

2. Materials and Methods

2.1 Experimental apparatus

Experimental studies have been carried out in a tangential flow laboratory pilot plant Minitan S, (Millipore) equipped with a single flat sheet polyvinylfluoride membrane and a tangential flow laboratory pilot plant Membralox® XLAB 3 (EXEKIA, Bazet-France) with a single tube ceramic ultrafiltration membrane Membralox® TI-70. Figure 1 shows the two pilot plants used for the present study. Temperature is controlled by the tank jacket, which is connected to a thermostat CRIOTERM 10-80. Three flat sheet membranes were tested with a MWCO of 10, 100 kDa and 0.2 μm , while the tubular membrane used has a MWCO of 0.2 μm .

2.2 Feed water characteristics

A model solution was created to supply constant quality of water sample by simulating real surface water: it contained CaCl_2 as a representative of naturally occurring multivalent cations, NaHCO_3 as a natural buffer system, kaolinite and α -alumina as natural turbidity and humic acid as natural organic matter. A commercial humic acid (Aldrich) was employed in the present experiments. Humic acid stock solution was prepared by dissolving 100 mg Aldrich Humic Acid (AHA) in 1 L distilled water, the pH of the solution was set to 10 by using NaOH to assure complete dissolving of humic acid since the latter is insoluble at low pH; solution was then filtered through 0.2 μm membrane filter. Background solution was prepared by dissolving 2.5 mg/l α -alumina and 2.5 mg/l kaolinite in deionized water (Milli-Q) in ultrasound bath for 20 min. Solution was then supplemented with NaHCO_3 and CaCl_2 and the desired humic acid concentration was adjusted using humic acid stock solution (100 mg/L AHA). After all the components were added, the solution was mixed rapidly for an hour with magnetic stirrer.

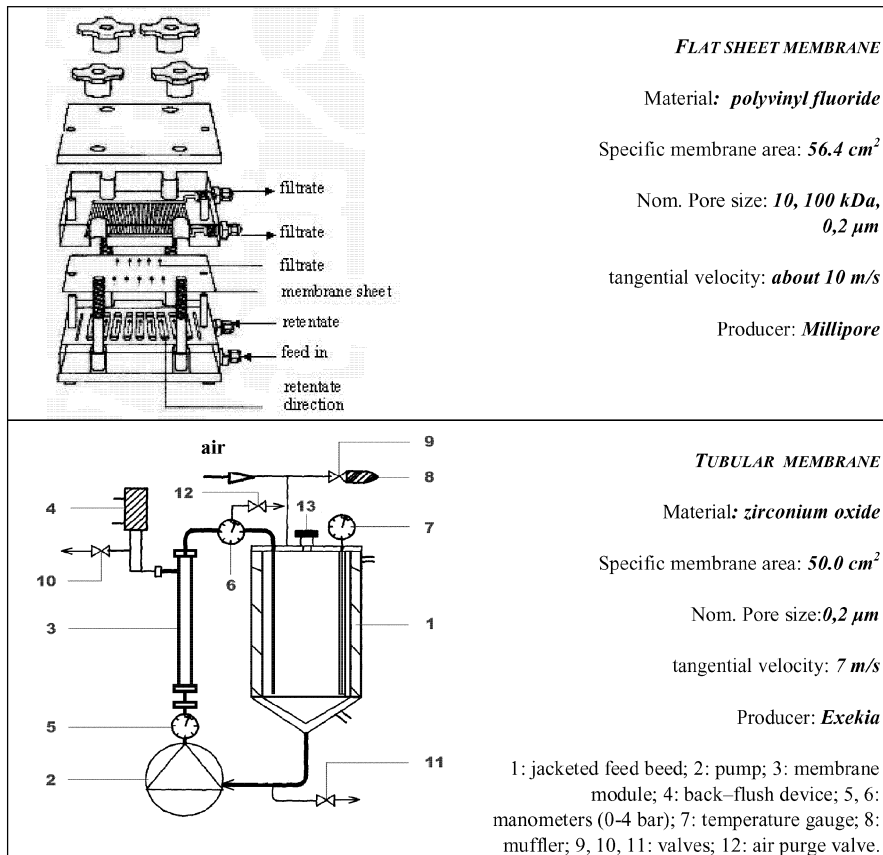


Figure 1. Experimental apparatus employed for ultrafiltration.

The average characteristics of synthetic water are presented in Table 1.

Table 1. Synthetic water characteristics.

<u>NOM</u>	
(Aldrich Humic Acid)	2.5-5.0-7.5-10 mg/L
<u>Inorganic particles</u>	
Kaolinite	2.5 mg/L
α -Alumina	2.5 mg/L
<u>Salts</u>	
NaHCO_3	0.5 mM
CaCl_2	0.5 mM

2.3 Testing procedure

The effect of membrane cut-off and AHA concentration on membrane performance was studied. Permeability, flux decay and concentration tests were executed for different AHA concentrations for each membrane. During the flux decay tests, the transmembrane pressure (TMP) was adjusted to 1 bar and temperature was controlled by the water jacket and kept constant to the value $T = 20^\circ\text{C}$. Permeate flux was measured for 3 h manually and the samples were collected from retentate and permeate and analyzed for the parameters such as humic acid concentration, pH, turbidity.

AHA concentrations were determined by UV absorbance measurements in a spectrophotometer (Lambda 2S PerkinElmer) at the wavelength 254 nm; AHA concentration was correlated linearly with UV 254nm ($R^2 = 0.9994$). After each test, the equipment and membrane were washed with an alkaline solution (NaOH) and rinsed with distilled water until pH returned to the value of about 7.

2. Results

In this study UF an MF filtration test with three flat sheet membranes and a tubular membrane were carried out to evaluate the effects of membrane cut-off (10, 100 kDa and 0.2 μm), membrane configuration (flat sheet and tubular) and feed composition on membrane performance regarding AHA rejections and fouling.

3.1 Permeability and flux decay tests

Permeability tests were performed to evaluate membrane resistance to mass transfer at different AHA concentration; they were carried out by measuring the permeate flowrates with varying transmembrane pressure. In each run the operating parameters (temperature, cross flow velocity and feed concentrations) were constant (steady-state conditions). Figures 2 and 3 show the influence of TMP on permeate flowrates at different AHA concentrations, for flat sheet membranes of 10 and 100 kDa MWCO, respectively. Figure 4 and 5 show instead the effect of TMP for MF membranes (0.2 μm), for flat sheet (Fig. 4) and tubular (Fig. 5) configurations.

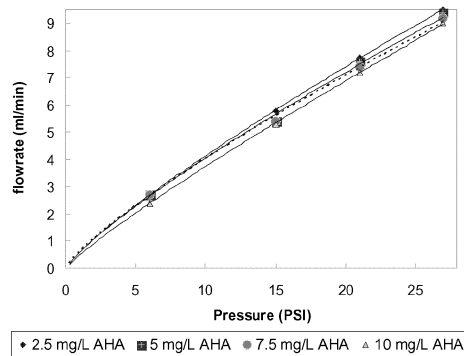


Figure 2. Influence of TMP and AHA on permeate flow rates for 10 kDa membrane.

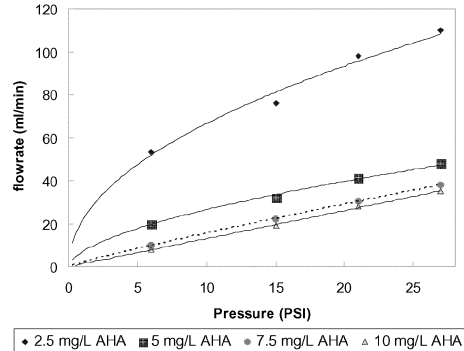


Figure 4. Influence of TMP and AHA on permeate flow rates for 0.2 μm flat sheet membrane.

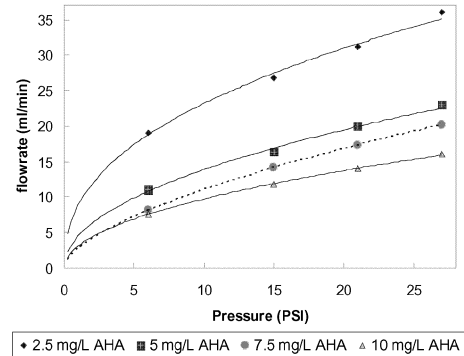


Figure 3. Influence of TMP and AHA on permeate flow rates for 100 kDa membrane.

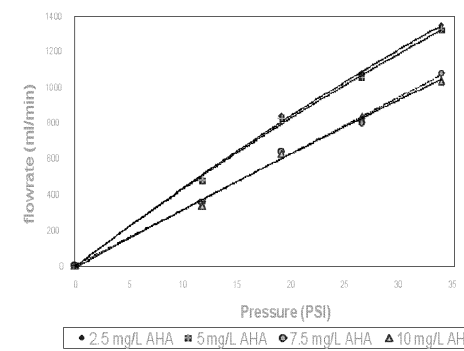


Figure 5. Influence of TMP and AHA on permeate flow rates for 0.2 μm tubular membrane.

The analysis of Figs 2-5 shows that permeate flowrates increase at higher transmembrane pressures and at higher AHA concentrations for both UF and MF membranes. As can be seen, all tested membranes present no significant flux decline over the running time; this has been addressed to a minimal concentration polarisation.

3.1 Rejection tests

Figure 6 shows the results of rejection experiments towards three parameters, *i.e.* AHA, turbidity and conductivity, representative of organic material, dissolved solids and dissolved salts present in surface water, respectively. As for AHA retention, the examined UF membranes (10, 100 kDa) are both suitable for the humic acid removal; rejections of AHA is higher than 90% at 7.5 mg/L AHA for both MWCO. As a consequence of the higher pore size, flat sheet MF membrane (0.2 μm), with respect to UF membranes, shows very lower rejections ranging from 15-20%, thus confirming a previous experimentation (Salladini et al., 2007), in which the removal efficiency of MF flat sheet membranes was improved by adding divalent cations (CaCl_2) enhancing AHA removal. On the contrary, tubular membrane having the same cut-off (0.2 μm) exhibits average rejections of more than 90%, even higher than those of UF membranes. This excellent behaviour has been attributed to the different configuration used (tubular instead than flat) but can be also due to the different membrane material (ceramic instead than polymeric); as a matter of fact, it is recognized that ceramic membranes are rarely used in the treatment of water due to their low mechanical resistance. As for turbidity and conductivity, 10 kDa UF membrane is still effective, reaching rejection of about 60% and 50%, respectively, while 100 kDa UF membrane is less effective with rejections ranging from 10 to 25%; on the contrary, both MF membranes are effective towards turbidity, reaching very high rejection coefficients independently from their configuration, while both of them are low efficient towards conductivity; as a matter of fact a reduction of conductivity can be reached by using membranes with lower cut-off, able to retain also dissolved salts in solution (nanofiltration and reverse osmosis). Figs 7-8 show AHA rejections as a function of TMP for MF membranes, showing that the above reported rejections are quite independent on the applied pressure. Only flat sheet MF membrane shows a higher rejection coefficient for high AHA levels (7.5 – 10 mg/L) at low TMP (6 PSI), but it seems of low significance.

4. Conclusions

Filtration test with a model solution have shown that the studied UF flat sheet membranes are effective in the removal of humic acid. Permeate flow rates and AHA rejections were found to be quite stable during filtration time, suggesting that no cake development on the membrane surface occurred. Removal efficiency of UF membrane is high enough (85-90%) at AHA concentration over 7.5 mg/L.

As a consequence of larger pore diameter, flat sheet MF membrane resulted ineffective in AHA removal with rejection ranging from 15-20%, while tubular MF membrane showed removal efficiency of 90%, attributed to the different membrane configuration. Further studies may clarify if this effect should be attributed to the different membrane material (ceramic instead than polymeric), by using MF tubular polymeric membrane.

5. Acknowledgements

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6. References

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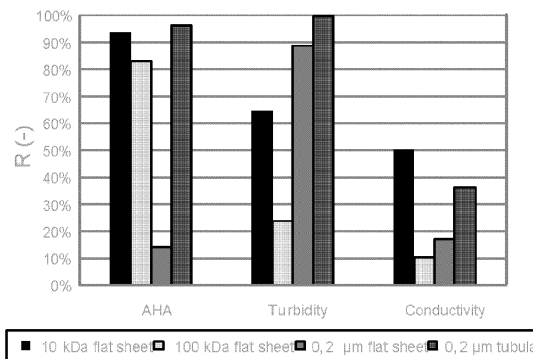


Figure 6. Rejection coefficient during filtration through 10 kDa, 100 kDa, 0.2 μm flat sheet membrane and 0.2 μm tubular membrane at pH=7, TMP=18.9 PSI, T=20°C, AHA 7.5 mg/L.

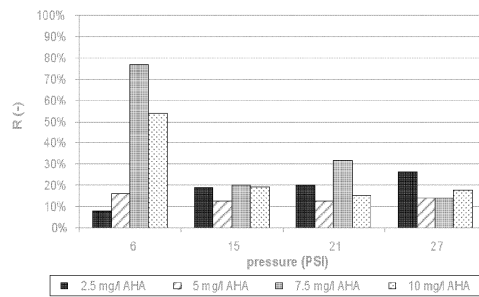


Figure 7. Influence of TMP on AHA rejection for 0.2 μm flat sheet membrane.

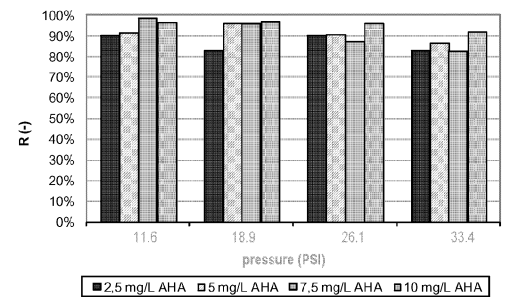


Figure 8. Influence of TMP on AHA rejection for 0.2 μm tubular membrane.