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Effect of hydrophilic / hydrophobic fractions of Natural Organic Matter on irreversible fouling of membranes

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Abstract:

Natural organic matter (NOM) has been identified as a major factor affecting membrane processes performances, but its impact is difficult to quantify from global parameters such as organic carbon content. The extent of fouling due to the different fractions of NOM from surface water has been examined in dead-end ultrafiltration using criteria such as flux decline and irreversibility in regard with organic matter rejection. The most important flux decline was observed during the filtration of the hydrophilic acids fraction whereas fulvic acids led to the most irreversible fouling. Furthermore, the hydrophilic fraction lost its fouling character when mixed with other fractions underlining that interactions between numerous components are possibly more important than the composition itself.

Keywords: ultrafiltration, natural organic matter, irreversible fouling, water treatment, membrane

1. Introduction

The last fifteen years have seen the expansion of membrane processes in water treatment applications. Although the efficiency of membrane processes has been widely reported (Arnal *et al.*, 2004; Bodzek and Konieczny, 1998; Di Zio *et al.*, 2005; Madaeni, 1999), limitations still exist due to the accumulation of material at the surface of the filter known as fouling.

Fouling is most commonly experienced as an increase in transmembrane pressure over time at constant flux requiring either backwashing or chemical cleaning to remove accumulated material.

Since the arrival of membrane processes, many studies have been conducted in order to improve the knowledge about phenomena responsible for fouling with different and complementary ambitions:

- to anticipate and control it by adjusting the process parameters (Crozes *et al.*, 1997; Espinasse *et al.*, 2002)
- to be able to predict filtration performances (Boerlage *et al.*, 2003; Ghidossi *et al.*, 2006; Park *et al.*, 2006; Peng *et al.*, 2004)
- to identify “critical fractions” of water in order to ensure their removal before the membrane filtration by a suitable pre-treatment (Koh *et al.*, 2006; Lin *et al.*, 2001; Mosqueda-Jimenez and Huck, 2006).

Natural organic matter (NOM), which is omnipresent in surface water, is of interest in most of the studies due to its complexity increasing the multiplicity of mechanisms involved during surface water treatment. Although decline of flux is systematically observed in water treatment, the origin and mechanisms of fouling are still difficult to identify and quantify. Fouling by NOM depends, besides hydrodynamic conditions, on characteristics of feed water as well as of membrane surface. Thus some studies evaluated the influence of the hydrophilic character of NOM on fouling: in a general way, humic substances generate a more important fouling than fulvic acids (Aoustin *et al.*, 2001; Jucker and Clark, 1994; Schafer, 1999; Schafer *et al.*, 2000) explained by their low solubility and their hydrophobic character. Lin *et al.* (2000) identified a more important decline of flux when filtering the hydrophilic fraction on

polysulfone ultrafiltration membrane, despite little rejection. On the other hand the hydrophilic fraction has some times been identified as less limiting (Cho *et al.*, 2000).

Furthermore, it is also important to know the impact of fouling on the process and to evaluate the reversibility of fouling layers. The increasing degree of irreversibility will lead to a rise in operating costs and environment impacts which are important to anticipate: reversible fouling can be removed by rinsing steps (Bessiere, 2005), low irreversible fouling implied the necessity to process backwashes whereas high irreversible matter accumulation can only be removed by chemical cleanings.

The aim of this paper is to further investigate the impact of the different NOM fractions on flux decline and on the appearance of irreversible fouling during dead-end ultrafiltration. To do that, water is fractionated using resins and the effect of each fraction is discussed with regard to their impact during dead-end filtration.

2. Materials and methods

2.1. Fractionation

The raw water investigated in the current study was sampled from Albert Water Treatment Works (AWTW), a moorland water works in the north of England, situated in Halifax. The water source is typical of a NOM rich water which is characterised as having low turbidity (2.0-7.0 NTU), low alkalinity (20 mg.L⁻¹ CaCO₃), high colour (44-160 Hazens) and high dissolved organic carbon (DOC) (6.6-13.3 mg.L⁻¹).

The separation process and the hydrophilic / hydrophobic balance determination are undertaken using resins Amberlite XAD-7HP and XAD-4 successively (Rohm and Haas, Germany).

This method (Fig. 1) leads to separation of dissolved organic matter into four different fractions (Malcolm and MacCarthy, 1992):

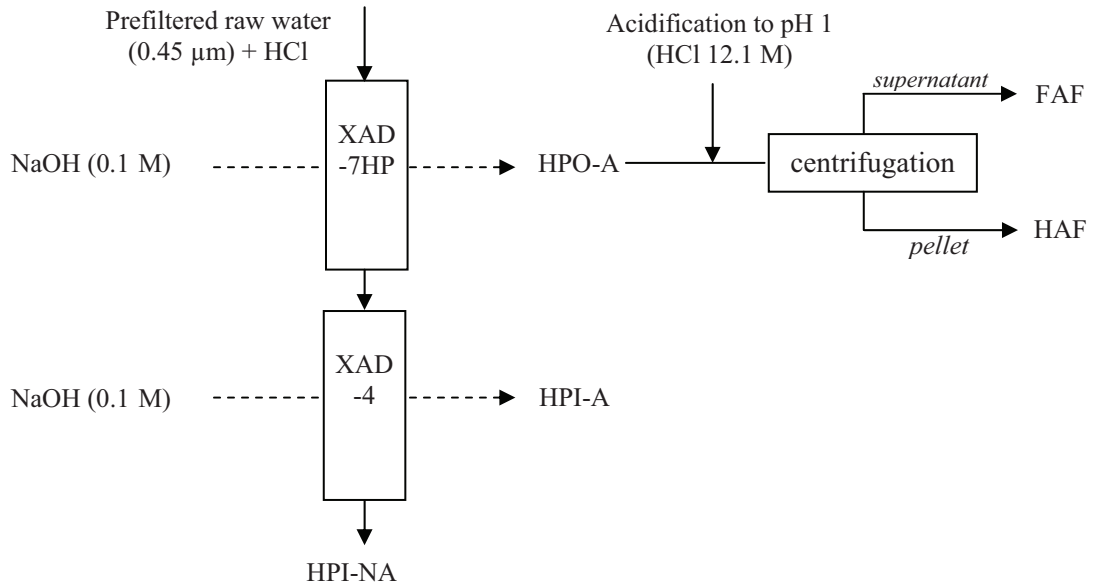


Fig. 1: Schematic of the procedure of fractionation

- Hydrophobic acid (HPO-A) adsorbed on resin XAD-7HP at pH 2 (and desorbed with NaOH 0.1M). This fraction consists of humic substances themselves made of fulvic acids (FAF) and humic acids (HAF) separated by centrifugation after acidification.
- Hydrophilic acid substances (HPI-A) adsorbed on resin XAD-4 at pH 2 (and desorbed by NaOH)
- Non-adsorbed hydrophilic substances (HPI-NA) which are recovered in the permeate of XAD-4.

The proportion of each fraction in the raw water is determined by analysis of Dissolved Organic Carbon (DOC) on Shimadzu TOC Analyser 5000A (Milton Keynes, UK) - defined as

the organic carbon that pass through a 0.45µm filter - with respect to the DOC of the raw water (RW):

$$\%fraction = 100 \cdot \frac{DOC_{fraction} \cdot V_{fraction}}{DOC_{RW_{0.45\mu m}} \cdot V_{RW_{0.45\mu m}}}$$

2.2. High-performance size-exclusion chromatography (HPSEC)

The HPSEC analysis were carried using an HPLC (Shimadzu VP series, Shimadzu, Milton Keynes, UK) with a UV detection set to 254 nm. The column was a TSK – gel G3000SW 7.5 mm (ID) *30 cm and the guard column was a TSK gel 7.5 mm (ID) * 7.5 cm (Tosh Biosep GmbH, Stuttgart, Germany). The mobile phase was 0.01 M sodium acetate at a flow rate of 1 ml min⁻¹. With HPSEC, large molecules are eluted from the column first and smaller molecules after.

2.3. Filtration device

The filtration experiments were carried out with a bench scale unit (fig. 2) with ultrafiltration membranes made of polysulfone having a low molecular weight cut off (100 kDa). This device is made up of a 200 mL filtration cell (KST47, Advantec MFS, Dublin, USA) receiving a flat sheet membrane of 47 mm in diameter corresponding then to a filtration surface of 12.5 cm².

The pressure was kept constant by the way of a 50 L buffer tank supplied by pressurised air. The permeate was collected in a vessel located on an electronic balance and the cumulated mass was recorded with a 5 s frequency via the software Regkey.

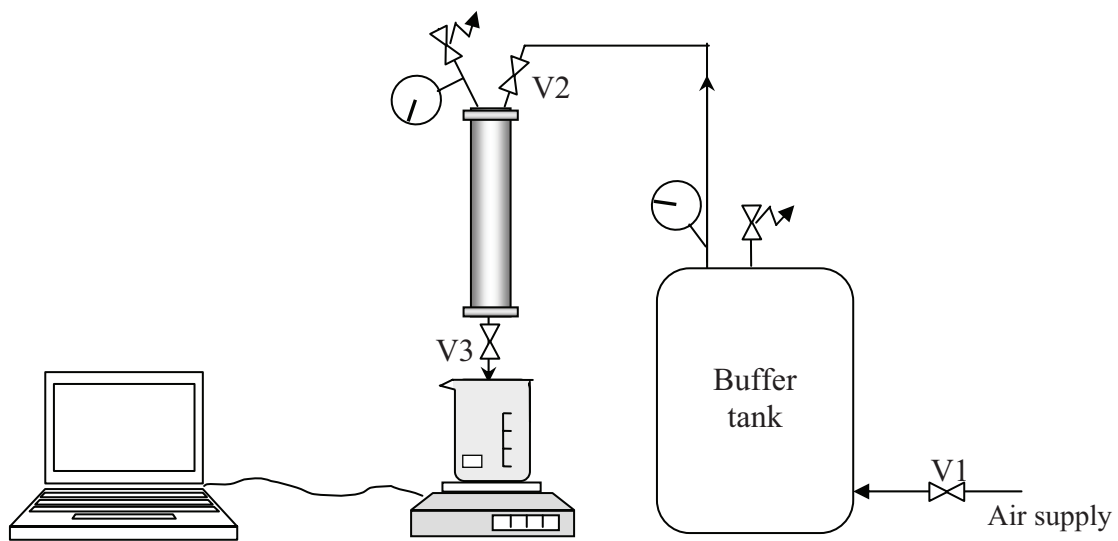


Fig. 2: Schematic of the filtration bench scale unit

2.3. Processing

The fouling was evaluated by considering its extent during filtration with regard to its irreversibility as this point is considered as the key parameter to allow a suitable way to run water production (by adjusting hydraulic actions frequencies to take off fouling layers). So the experiment was sequenced in two main parts:

- A filtration step: the cell is filled with the raw water or the fraction being considered, the required pressure (here 1 bar) is adjusted via the valve V1 and the filtration started while opening the valve V3. The filtration was run until 190 mL of permeate was collected.
- A rinsing phase: the remaining suspension was removed and the cell carefully rinsed three successive times with ultrapure water in order to remove all the matter not irreversibly accumulated at the membrane surface (or in the pores). This step allows determination of the instantaneous irreversibility of fouling. This step has also been

done after a 24 h soaking in ultrapure water at 4°C in order to evaluate the long term irreversible fouling.

The permeate flux is linked to the transmembrane pressure (ΔP) and the additional resistance due to fouling (R_f) through Darcy's law (Darcy, 1856):

$$J = \frac{\Delta P}{\mu \cdot (R_m + R_f)}$$

where μ is the viscosity at the experiment temperature and R_m is the clean membrane hydraulic resistance (here $7.5 \times 10^{11} \text{ m}^{-1}$ as mean value).

3. Results

3.1. Water characterisation

The distribution of natural organic matter in terms of DOC is reported in figure 3: humic substances (HAF and FAF), *i.e.* hydrophobic compounds, account for 72% of NOM, with a predominance of fulvic acids (58%). The two hydrophilic fractions (HPI-A and HPI-NA) are in equivalent quantities (13% and 15% respectively).

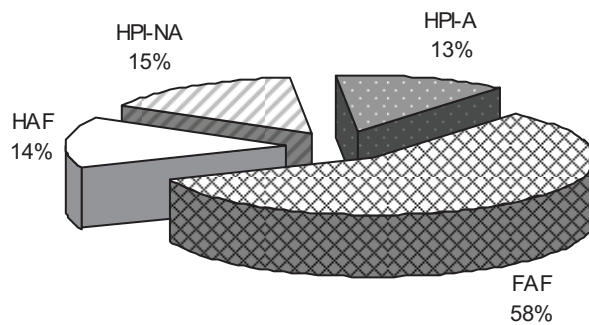


Fig. 3: Natural organic matter distribution

The observed distribution between hydrophilic and hydrophobic compounds is noticeably different of values reported in the literature which often presents equivalent quantities for surface waters (Aouabed *et al.*, 2001; Martin-Mousset *et al.*, 1997).

During filtration experiments, size of compounds is expected to play an important part in mechanisms involved and so on fouling (Fan *et al.*, 2001; Lin *et al.*, 1999). The raw water

HPSEC (High-performance size-exclusion chromatography) analysis, presented in figure 4, revealed six size peaks where the most abundant peak is > 5 kDa. The size band attributed to each peak was determined using a method described by (Matilainen, 2007).

The relative size of fractions has also been estimated (fig. 5). Those results underline that the HPI-A fraction is made of the smallest compounds whereas HAF presents the upper molecular size.

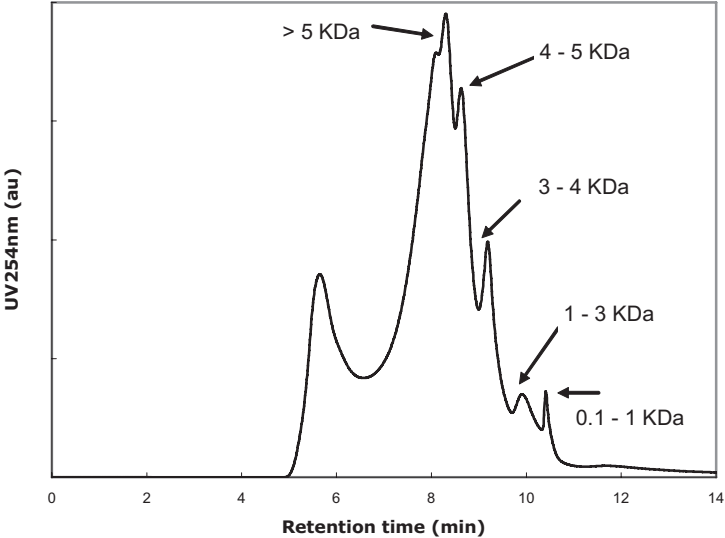


Fig. 4: HPSEC chromatogram of raw water

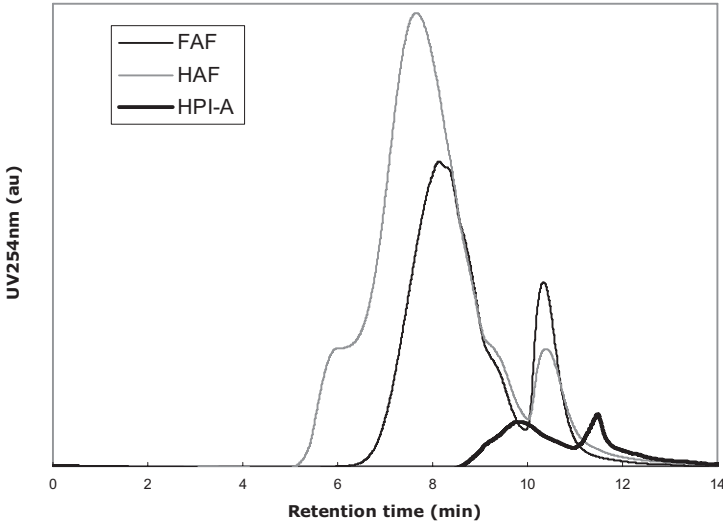


Fig. 5: HPSEC chromatogram of fractions

complete blocking here appears after a filtration time of 33 minutes corresponding to a filtered volume of 80 L.m⁻². Humic acids generate more fouling than raw water whereas fulvic acids lead to the lowest decline of flux.

The impact of fouling generated by HPI-NA fraction, underlined in the past (Fan *et al.*, 2001; Lee *et al.*, 2004), is here difficult to evaluate ($R_f < 5 \times 10^{10} \text{ m}^{-1}$) as its concentration in organic carbon resulting from the fractionation procedure is low.

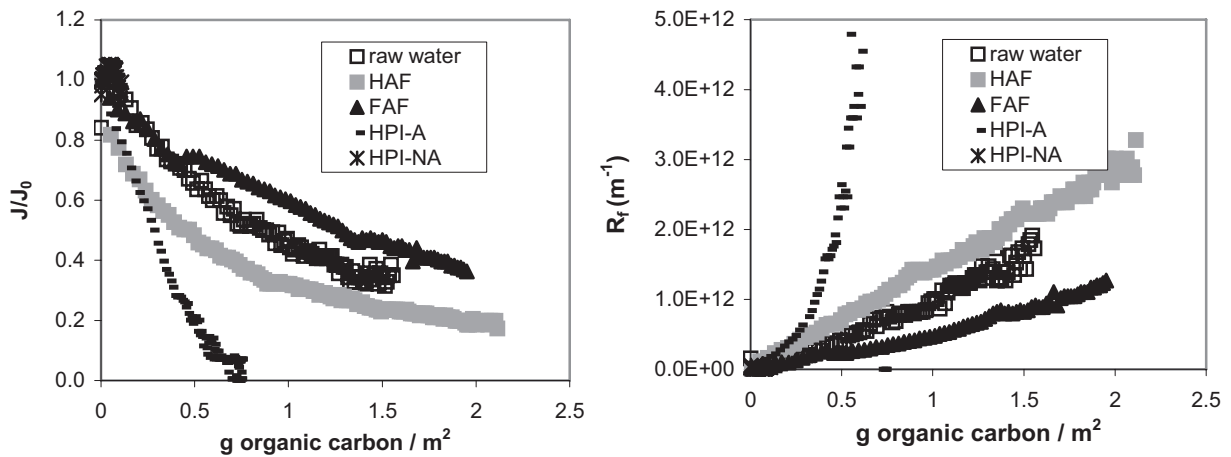


Fig. 6: Specific flux versus accumulated mass for the different fractions

For the same quantity of organic carbon reaching the membrane surface, the fouling resistance can be very different (Table 2) according to the NOM fraction considered: a difference of a factor of 10 is observed between the FA and HPI-A fractions for example.

Table 2: Fouling resistance (R_f) after filtration of 0.5 g organic carbon .m⁻²

Fraction	$R_f (\text{m}^{-1})$
Raw water	4.1×10^{11}
HAF	7.5×10^{11}
FAF	2.3×10^{11}
HPI-A	2.6×10^{12}

A surprising observation is that a part of the natural organic matter of the raw water can exhibit propensity to fouling well above that obtained for raw water. To check such a trend was remaining in presence of other fractions, water has been restored by mixing all the fractions within the proportions shown in figure 3.

Fouling resulting from the filtration of this restored water is compared to the one induced by the raw water and the prefiltered raw water (fractionation procedure is made on 0.45 μm filtered water as shown in figure 1). The evolution of relative flux and fouling resistance for those three suspensions are reported in figure 7.

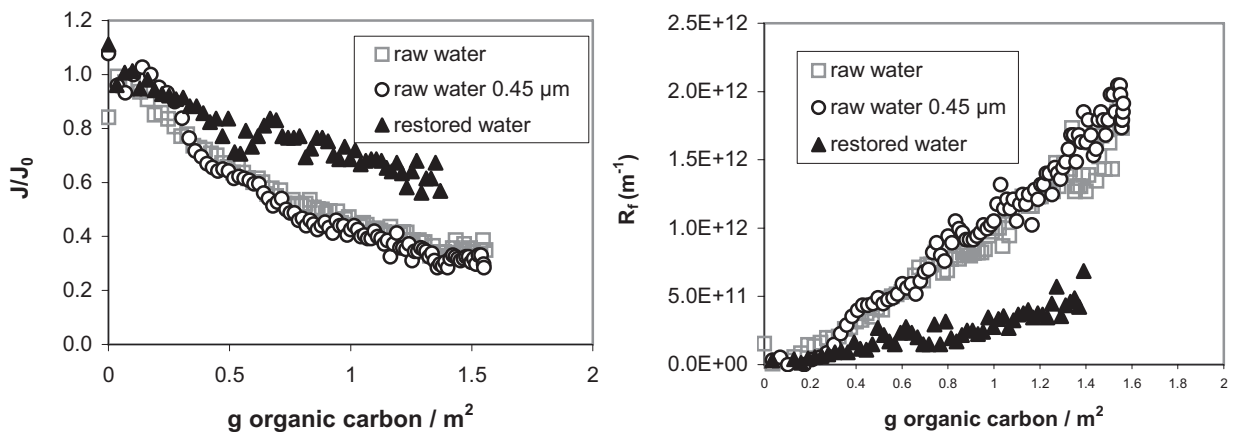


Fig. 7: Comparison of fouling by raw water, prefiltered raw water and restored water

Firstly, raw water and prefiltered raw water present the same decline of flux (up to 70%) – at least for the duration of our experiments – which confirms the impact of dissolved and colloidal material on membrane fouling.

Then, the restored water appeared to be less limiting than the initial raw water. This point can be explained by two aspects possibly simultaneous: the restored water presents some differences in overall characteristics: turbidity is 1.1 NTU, DOC 8.56 $\text{mg}\cdot\text{L}^{-1}$ and absorption at 254 nm, 36 m^{-1} underlining that some of the material is possibly lost during the fractionation procedure. The second hypothesis concerns the likely modifications of structure because of the change in pH during the fractionation.

Similar fouling experiments performed in previous studies (Jarusutthirak *et al.*, 2002) have shown flux reduction around 20 % and 30 % (i.e. relative flux between 70 % and 80 %) after filtration of around 3 g of organic carbon per membrane square meter. These results were obtained during filtration of effluent organic water fractions on a 8 kDa cut-off membrane. Results presented in figure 6 in the current paper show more important flux decline and also more significant differences between water fractions for a similar quantity of organic carbon filtered. These differences could be attributed to membrane material (Polyamide in Jarusutthirak *et al.*, 2002 versus Polysulfone in this work), to the membrane cutoff or the origin of the raw water.

3.3. Irreversibility

As shown in the introduction, irreversibility is a key parameter as it will influence the process through the necessity to make hydraulic or chemical actions having an impact as well on the production costs as well as on the environment.

The reversibility study has been done by evaluating the flux using ultra pure water after a rinsing step and after a 24h soaking in order to estimate reversible polarisation concentration (by comparison with the permeability at the end of the filtration experiment) and possible desorption and/or relaxation of cake respectively.

The ratios of the permeability at the end of each step (L_p) by the one of the new membrane (L_{p_0}) are reported in figure 8.

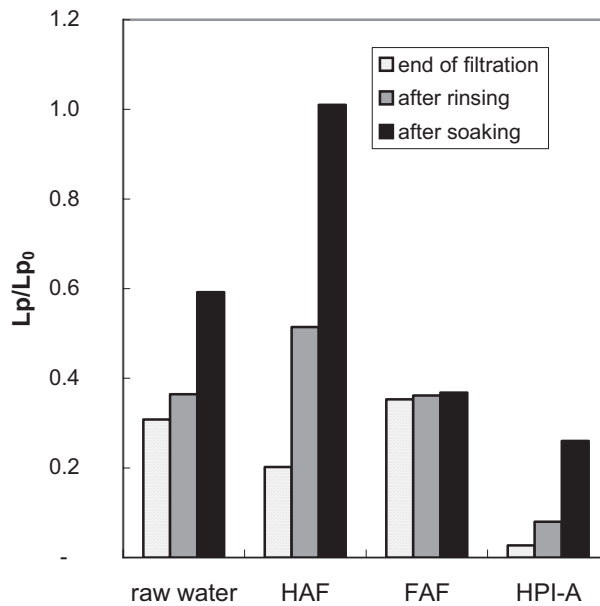


Fig. 8: Reversibility after rinsing and soaking step

Although fulvic acids present less fouling during the filtration, they are more limiting when considering the overall process: in fact, rinsing steps as well as soaking are here inefficient to remove the accumulated matter. At the opposite end, fouling induced by humic acids fraction is totally reversible after a soaking step indicating that solute – membrane interactions are here not so strong. Similarly to the raw water, the HPI-A, which exhibits more pronounced fouling, is slightly reversible with a rinsing just after filtration but shows a more important reversibility after soaking: time can lead to relaxation of an important part of mass accumulation.

3.4. NOM removal

Fouling results can be correlated with NOM removal as the rejected solutes are expected to contribute to fouling phenomena.

NOM removal, presented in figure 9, has been estimated by measuring UV absorption and DOC in the feed water and in the permeate.

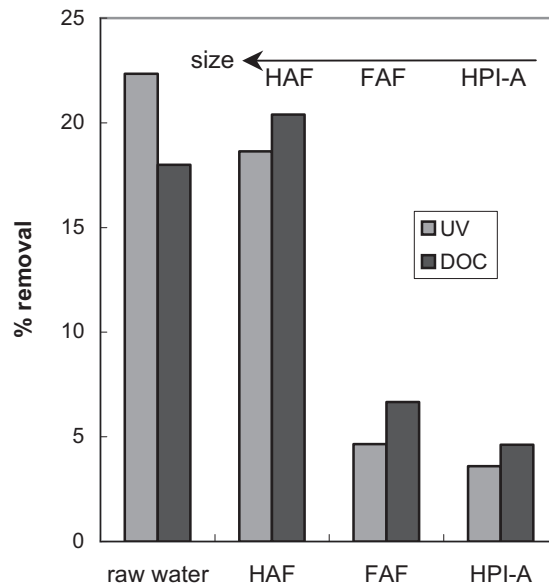


Fig. 9: Estimation of removal of natural organic matter by UV and DOC

Similarities between organic removal and relative size of each fraction (figure 5) exist showing the preponderance of size mechanisms (when considering that adsorption phenomenon on the membrane has reached a stationary state).

Looking at the removal in terms of molecular size (fig. 10) it clearly appears that big compounds are better removed, confirming size mechanisms for the retention.

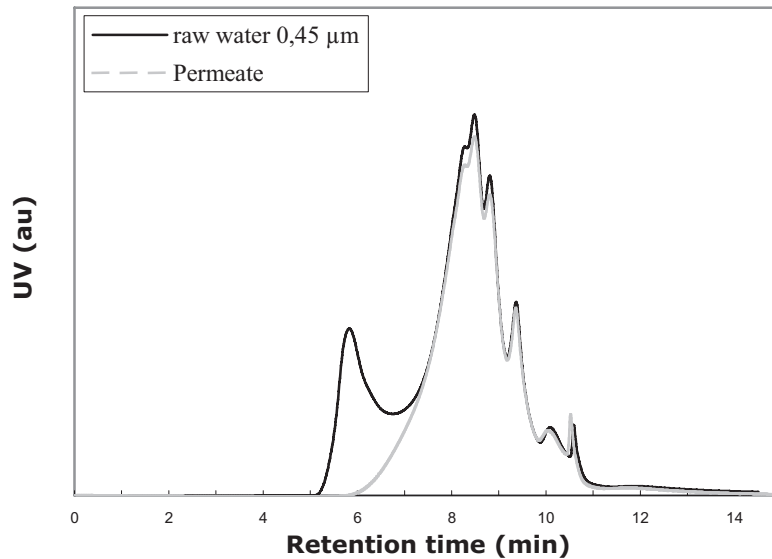


Fig. 10: Estimation of removal of natural organic matter by HPSEC

Furthermore, this size of compounds correspond in majority to humic acids, which is in good agreement with important removal observed in terms of UV and DOC (19% and 20% respectively).

4. Discussion

A deeper results analysis can be done by coupling removal with filtration experiments (summarized in table 3): removal of fulvic acids is low which is in good agreement with fouling as it was the fraction leading to the lower flux decline. For the hydrophilic fraction, many questions remain: the removal is low in spite of a great extent of fouling. Several hypotheses can be made:

- this fraction could contain inorganic compounds – non detected by UV or DOC measurements – able to obstruct membrane's pore by precipitating.

- A fraction in small quantity can lead to important fouling as underlined by Howe and Clark (2002) who showed that 5 % of the organic matter is responsible for fouling phenomenon as proposed in the past.

The analysis of molecular size (fig. 4 and 5) combined with filtration experiments (fig. 6) allows identification the fraction leading to the most important fouling as the one made of smallest compounds (HPI-A). This observation supposes that fouling phenomena are more attributed to internal blocking or adsorption than size effects.

Table 3: Qualitative observations on each fraction

Fractions	% in raw water	Flux decline	Irreversibility	Retention
RW	100	++	+++	++
HAF	14	+++	++	++
FAF	58	+	++++++	-
HPI-A	13	++++++	+++	--

When considering the HPI-A fraction, it appears that the fouling induced with this fraction is very pronounced: this fraction seems critical with regard to fouling. It could be interesting to investigate if a correlation can be highlighted between fouling potential of a water and its HPI-A concentration. However, this fraction seems to lose its fouling character when it is mixed with other fractions to recreate the original water: such a trend underlines that interactions between the different fractions can inhibit some of the specificities of isolated fractions. If such a trend is confirmed, we can prejudge that interactions between the multiples components of the water are as important as the composition itself.

Furthermore, it appears that fulvic acid fraction – which does not present significant propensity to fouling – is highly irreversible as well after rinsing and after soaking. As in water production the filtration process is made of successive filtration and backwashes

periods, after a while fulvic acids fraction could be expected to constitute an important part of fouling layer.

5. Conclusion

Different conclusions can be drawn from these results:

- The HPI-A fraction leads to significant fouling (with complete membrane blocking after filtration of 80 L.m⁻²) of the polysulfone membrane whereas the organic matter removal observed is low (less than 5%).
- This propensity to fouling of HPI-A is less pronounced when this fraction is reintroduced with the others to restore the raw water: it is postulated that interactions between different fractions inhibit the HPI-A fouling character.
- The fulvic acids fraction (FAF) does not exhibit important fouling during the filtration (result correlated with a low retention of about 6%) but can be partly responsible for long term fouling in an industrial plant as this fouling is totally irreversible (after rinsing).

Those results show that the composition of the raw water (in terms of hydrophobic and hydrophilic balance) has important consequences on fouling but can not be directly linked to the fouling propensity during filtration. Those difficulties could come from the chemical composition, although necessary to understand water behaviours, which is not sufficient to describe fouling because of interactions between water components that modify the specificities of isolated fractions. In future, studies on the importance of fouling with different mixtures of fraction could help to improve the prediction of fouling from chemical composition of water.

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