Coagulation/flocculation/ultrafiltration for natural organic matter removal in drinking water production

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Abstract Membrane fouling by natural organic matter (NOM), namely by humic substances (HS), is a major problem in water treatment for drinking water production using membrane processes. Membrane fouling is dependent on membrane morphology like pore size and on water characteristics namely NOM nature. This work addresses the evaluation of the efficiency of ultrafiltration (UF) and Coagulation/Flocculation/UF performance in terms of permeation fluxes and HS removal, of the water from Tagus River (Valada). The operation of coagulation with chitosan was evaluated as a pretreatment for minimization of membrane fouling. UF experiments were carried out in flat cells of 13.2 \times 10^{-4} \text{m}^2 of membrane surface area and at transmembrane pressures from 1 to 4 bar. Five cellulose acetate membranes were laboratory made to cover a wide range of molecular weight cut-off (MWCO): 2,300, 11,000, 28,000, 60,000 and 75,000 Da. Severe fouling is observed for the membranes with the highest cut-off. In the permeation experiments of raw water, coagulation prior to membrane filtration led to a significant improvement of the permeation performance of the membranes with the highest MWCO due to the particles and colloidal matter removal.

Keywords Coagulation; humic substances; ultrafiltration; water treatment

Introduction
Membrane processes, namely ultrafiltration (UF) and nanofiltration (NF) play an important role in surface water treatment for drinking water production due to the capability of natural organic matter (NOM) removal. NOM is the precursor of the formation of disinfection by-products that are health hazards and therefore their content in water is regulated. Several authors (Combe et al., 1999; Gwon et al., 2003) described NOM as one of the major fouling agents during filtration of surface waters by microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). Krasner et al. (1996) verified that NOM is composed by a variety of organics like humic substances, hydrophilic acids, carbohydrates, aminoacids and proteins and Hong et al. (1997) referred that a large fraction of NOM is constituted by humic substances (HS) that contain aromatic and aliphatic components with carboxylic and phenolic functional groups. The HS are important constituents of the organic colloidal phase and can also be adsorbed by inorganic colloids. There are studies (Laïné et al., 1989; Hong et al., 1997; Combe et al., 1999; Fan et al., 2001) that found that membrane fouling by NOM is dependent on membrane characteristics, like pore size and charge, on water properties such as pH, salt concentration and hardness, on the operating conditions of the membrane filtration and on the organic matter characteristics. The diversity of NOM characteristics like molecular weight (MW), charge and hydrophobic/hydrophilic character is crucial to the definition of membrane/solute physico-chemical interactions that play an important role on membrane fouling. Chelam et al. (1997) verified that in NF membranes, fouling was more influenced by colloidal materials than by organic matter dissolved. Jarusutthirak et al. (2002) defined colloidal NOM as the molecules with MW > 3,500 Da and found that these colloids caused the greatest flux decline in the UF membranes. Fan et al. (2001) verified that the
fouling mechanism of MF membranes involved a combination of adsorption and colloidal fouling by organics with MW > 30,000 Da in the internal pore structure of the membrane. Howe et al. (2002) found that small organic and inorganic colloids are important membrane foulants but the organic fraction is always the major fouling material. Schäfer et al. (2000) found that the membrane fouling was dependent on membrane pore size and its interactions with large colloids in MF, small colloids and organic aggregates in UF and calcium-organic precipitates in NF. These authors also concluded that the formation of a foulant layer modifies the membrane rejection of the membranes.

In order to reduce membrane fouling by NOM, coagulation/flocculation with aluminum and iron based coagulants has been used as a pre-treatment in water treatment processes involving membranes. Lahoussine-Turcaud et al. (1990) studied the effect of coagulation prior to ultrafiltration of Seine River water and found that this pre-treatment marginally improved the membrane permeate flux. Nonetheless, these authors referred that significant benefits from coagulation prior to membrane filtration can be achieved for waters containing colloidal and macromolecular materials. Although, metal ions like Al$^{3+}$ and Fe$^{3+}$ were traditionally used in coagulation/flocculation of natural waters, their use poses the problem of the formation of sludge that requires additional treatment. An alternative coagulant that does not pose this problem is the chitosan, a cationic biodegradable biopolymer that leads to the formation of biodegradable sludge and simplifies the sludge treatment and disposal. The application of chitosan as a coagulant in drinking water production was described by Eikebrook (2001) that found that this biopolymer may be used for water’s color removal with good results.

Based on the literature review, membranes with different morphologies can be fouled by NOM fractions with different characteristics showing that fouling is highly dependent on NOM and on membrane properties. The aim of this work is to investigate the permeation characteristics of water from Tagus river (Valada) for a wide range of UF membranes with different MWCO in order to find the UF membrane that leads to the best performance in terms of productivity and NOM removal. Prior to the UF operations a coagulation/flocculation treatment with chitosan will be investigated.

### Methods

**Valada surface water**

Water samples were collected in Tagus River – Valada – a Portuguese drinking water source. The samples were kept refrigerated at 4°C for 10 days, the time required to perform all the experiments.

The characterization of water in terms of pH, conductivity, UV absorbance at 254 nm ($\text{UVA}_{254\text{ nm}}$) is presented in Table 1. The contributions to UV absorbance of raw water are due to the particles and large colloids that scattered light and to the organics, namely HS present on water. The filtration of raw water by a 0.45 μm membrane leads to the particles and large colloids removal and therefore the $\text{UVA}_{254\text{ nm}}$ of the filtered water is related only with $\text{UV}_{254\text{ nm}}$ adsorbing organics, namely the HS.

### Table 1: Tagus River water characteristics (Valada)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH$_{25\text{ C}}$</td>
<td>7.7</td>
</tr>
<tr>
<td>Conductivity$_{25\text{ C}}$ ($\mu$S/cm)</td>
<td>260</td>
</tr>
<tr>
<td>$\text{UVA}_{254\text{ nm}}$ (cm$^{-1}$) no filtered water</td>
<td>0.101</td>
</tr>
<tr>
<td>$\text{UVA}_{254\text{ nm}}$ (cm$^{-1}$) filtered water</td>
<td>0.606</td>
</tr>
</tbody>
</table>
Coagulation/flocculation experiments

The coagulation/flocculation experiments were carried out in a jar-test equipment at room temperature with chitosan (86.5% deacetylated) supplied by Primex, Norway. Chitosan was added under rapid mixing at 200 rpm for 1 min. The flocculation step was performed at 30 rpm for 20 min and was followed by a 60 min settling period. The removal \( R \) of particles plus UV254 nm adsorbing organics (HS) is calculated by
\[
R = \frac{UV_{Arw} \times UV_{Ac}}{UV_{Ac}}
\]
where \( UV_{Ac} \) and \( UV_{Arw} \) are the absorbance in the clarified water and in the raw water, respectively. The removal of HS is calculated in the same manner, but clarified and raw waters were filtered before UVA254 nm measurements.

Membrane preparation

A series of five cellulose acetate asymmetric membranes were prepared in the laboratory according to the phase inversion method described by Kunst et al. (1974). The cellulose acetate (38.9% acetyl content) was supplied by Eastman–Kodak. Table 2 displays the casting solution compositions and the film casting conditions of CA1, CA2, CA3, CA4 and CA5 membranes.

Membrane characterization

The membranes were characterized in terms of pure water hydraulic permeability \( (L_p) \) and molecular weight cut-off (MWCO). The membrane hydraulic permeability was determined by the slope of the variation of the pure water flux versus the transmembrane pressure. In order to determine the MWCO, permeation experiments of neutral reference solutes were performed. These solutes are polyethyleneglycols (PEG) of 600, 1,000, 3,000, 6,000 and 10,000 Da (supplied by Merck) and Dextrans of 10,000, 40,000, 70,000 and 110,000 Da (supplied by Pharmacia).

The feed solute concentration was 1 g/L. The solute rejection \( (f) \) is defined as
\[
f = \frac{C_f - C_p}{C_f}
\]
with \( C_f \) and \( C_p \) the feed and the permeate concentration, respectively. The solute rejection is calculated in terms of Total Organic Carbon (TOC) content. Table 3 shows the hydraulic permeability \( (L_p) \) and the molecular weight cut-off (MWCO) of the five membranes.

**Table 2** Casting solutions compositions and film casting conditions

<table>
<thead>
<tr>
<th>Membrane</th>
<th>CA1</th>
<th>CA2</th>
<th>CA3</th>
<th>CA4</th>
<th>CA5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casting solution composition (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>17</td>
<td>17</td>
<td>17</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Acetone</td>
<td>63</td>
<td>56</td>
<td>53</td>
<td>48</td>
<td>43</td>
</tr>
<tr>
<td>Formamide</td>
<td>20</td>
<td>27</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>Casting conditions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature of solution (°C)</td>
<td>22</td>
<td>22</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Evaporation time (min)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Gelation medium (1–2 h)</td>
<td>water 0–3°C in all the cases</td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>

**Table 3** Membrane characterization

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( L_p ) (kg/h/m²/bar)</th>
<th>MWCO (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA1</td>
<td>3.4</td>
<td>2,300</td>
</tr>
<tr>
<td>CA2</td>
<td>50.5</td>
<td>11,000</td>
</tr>
<tr>
<td>CA3</td>
<td>65.2</td>
<td>28,000</td>
</tr>
<tr>
<td>CA4</td>
<td>100.0</td>
<td>60,000</td>
</tr>
<tr>
<td>CA5</td>
<td>164.9</td>
<td>75,000</td>
</tr>
</tbody>
</table>
membranes. The MWCO of each membrane is the intersection of the curve $\log \left( \frac{f}{1-f} \right)$ versus solute molecular weight and the 95% rejection line.

**Permeation experiments**

A flat-cell unit described by Afonso et al. (1990) was used in the permeation experiments. The membrane surface area was $13.2 \times 10^{-4}$ m$^2$. The experimental set-up is presented in Figure 1.

All membranes were compacted through permeation experiments with deionized water at a pressure of 5 bar and for a period of 3 hours. This avoids pressure effects on membrane structure in subsequent experiments. The permeation experiments of the solutions of the reference solutes for the membrane characterization purpose were performed at a trans-membrane pressure of 1 bar and at a feed recirculation flow rate of 200 L/h. The permeation experiments of Tagus River water were performed at a feed recirculation rate of 200 L/h and at pressures ranging from 1 to 4 bar. In all the permeation experiments the feed temperature was kept at 25°C and the stabilization time for each experimental run was 45 minutes. Between the runs the membranes were washed with deionized water until permeate flux recovers at least 90% of the original value.

The feed and the permeates were analyzed in terms of UVA$_{254}$ nm. The UF rejection coefficients to particles plus adsorbing organics (humic substances) were defined as $f=\frac{\text{UVA}_f - \text{UVA}_p}{\text{UVA}_f}$ where UVA$_f$ and UVA$_p$ are the feed and the permeate absorbance, respectively. The feed concentration was an average of the values relative to feed samples taken at the beginning and at the end of each experimental run. The rejection coefficients of HS were calculated in the same manner but the feed was filtered before UVA$_{254}$ nm measurements. The overall removal of particles plus HS in the sequence of coagulation/flocculation/UF was calculated by $R=\frac{\text{UVA}_{rw} - \text{UVA}_p}{\text{UVA}_{rw}}$ where UVA$_{rw}$ and UVA$_p$ are raw water and the permeate absorbance, respectively.

**Analytical methods**

The pH was measured in a Crison micropH 2002 at 25°C. The conductivity was measured using a 525 Crison conductimeter at 25°C. The TOC measurements for the reference solutions of PEG and Dextran were performed in a Dohrmann Carbon Analyzer DC-85A. The UVA$_{254}$ nm was determined with an UV-VIS scanning spectrophotometer Jasco V-530 using cells with 1 cm length.

**Results and discussion**

Figure 2 shows the performance of coagulation for the removal of HS and for the removal of particles plus HS using two different doses of chitosan, 5 and 10 mg/L. It can be observed that...
The removal of particles plus HS increases from 25% to 31% when the coagulant dose increases. Lower removals of 12% and 22% were obtained for HS for the coagulant doses of 5 and 10 mg/L, respectively. This means that the HS were removed in a small extension. Figure 3 presents the variation of the removals of HS and of particles plus HS in coagulation experiments performed with a coagulant dose of 5 mg/L at different values of pH. This figure shows that particles plus HS removals are practically the same at pH 6.6 and at pH 7.7 but they strongly decrease for pH 8.2. These results show that at pH 6.6 and 7.7, coagulation destabilizes the particles and the HS and causes their aggregation in a greater extent than at the basic pH of 8.2. These results differ somehow from the ones obtained by Eikebrokk (1999) that verified that the fraction of natural organic matter removed, decreased drastically when the water pH was higher than 7.0. In the subsequent experiments of coagulation/flocculation/UF, a chitosan dose of 5 mg/L was used.

Figures 4, 5, 6, 7 and 8 present the variation of the permeate fluxes as a function of transmembrane pressure for the membranes CA1, CA2, CA3, CA4 and CA5 respectively, in the UF of raw water and pretreated water. The pretreatment of raw water was an operation of coagulation/flocculation with 5 mg/L of chitosan. From Figures 4 and 5 one can notice that for the membranes with the lowest cut-off (CA1 and CA2), permeate fluxes of raw water and pretreated water are identical and present a linear behavior with the variation of transmembrane pressure. This linear behavior is also presented by CA3 and CA4 membranes in the UF experiments of pretreated water (Figures 6 and 7). However, in UF of raw water, these membranes present a non-linear behavior of the permeation fluxes with transmembrane pressure. The same non-linear behavior is observed in Figure 8 in the UF experiments performed with the membrane with the highest cut-off, CA5, for raw and pretreated waters. This non-linear behavior is very pronounced in UF of raw water and a limiting flux of 202 kg/h/m² is reached at a pressure of 2 bar meaning that the CA5 membrane presents concentration polarization and severe fouling. The UF results obtained for the more
permeable membranes, CA4 and CA5, show that there is an increase of permeation fluxes when water is pretreated by coagulation/flocculation and that this pretreatment leads to the removal of the major membrane fouling agents and to the enhancement of UF productivity.

Figure 9 represents the UF rejection coefficients of particles plus HS as a function of pressure for raw water and all the CA membranes studied. Figure 9 shows that the CA1 membrane, with the lowest MWCO presents the rejection coefficients for particles plus HS close to 85% and these are practically independent of pressure. These rejection coefficients for the CA2 and CA3 membranes slightly decrease with transmembrane pressure and vary from 63 to 58% and from 59 to 54%, respectively. The membranes with the highest MWCO, CA4 and CA5 present rejection coefficients of 44% that are independent of pressure. This behavior is due to the fact that for these membranes the fouling is very pronounced and leads to the formation of a fouling layer at the membrane surface.

Figure 10 presents the UF rejection coefficients of HS for raw water and for all the membranes and shows that the rejections coefficients are lower than the ones obtained for the particles plus HS.

Figures 11 and 12 show the UF rejection coefficients of HS and of particles plus HS as a function of pressure for the CA membrane series for pretreated water. Regarding Figure 11 one can notice that rejections coefficients to particles plus HS decrease for pretreated water comparatively to raw water. This shows that coagulation/flocculation removes essentially particles and colloidal matter present on water that are too large to pass through membrane pores and that are also important fouling agents which removal leads to the increase of CA3, CA4 and CA5 permeation fluxes. This is in accordance with Taniguchi et al. that found in their UF experiments that cake formation by aggregates present in unfiltered feed water was the dominant mode of membrane fouling. Although, UF rejection coefficients of HS and of
particles plus HS decrease in UF of pretreated water for all the membranes, Figures 13 and 14 show that the overall removals of these substances in UF combined with coagulation/flocculation pretreatment are higher than the UF rejection coefficients of HS and of particles plus HS obtained in the UF permeation experiments with raw water.

Conclusions
The results of this work show that membrane pore size plays a fundamental role on UF performance, both in terms of productivity (fluxes) and water quality (rejection coefficients). A linear pattern of permeation fluxes as a function of the transmembrane pressure is obtained for the membranes with the lowest MWCO, CA1 and CA2, in all the permeation experiments. This pattern is different for CA3 and CA4 membranes in the permeation experiments performed with raw water and for the membrane with the highest MWCO, CA5, in the UF of raw and pretreated water. The coagulation/flocculation pretreatment removes particles and colloidal matter leading to the improvement of UF productivity mainly to the CA4 and CA5 membranes and to the enhancement of HS removal. The membrane with the lowest MWCO when processes raw water or pretreated water presents a good performance in terms of productivity and high HS removal.

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References


