Clay filter-aid in ultrafiltration (UF) of humic acid solution

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Fouling studies with three different molecular weight cut-off (MWCO) (100 kDa, 30 kDa and 10 kDa) membranes in regenerated cellulose were carried out in the presence of Acros humic acids (HA) at pH 3.0, 6.7 and 9.5. It was shown that the tighter membranes were less fouled compared with the higher MWCO membranes. 100 kDa membrane showed the highest degree of fouling. The role of pH showed that the highest degree of fouling happened at a neutral pH (pH 6.7) and the lowest degree of fouling happened at a basic pH (pH 9.5). Effectiveness of a novel pre-treatment method was applied to the 100 kDa membrane. We added in the HA solution clay particles, homemade synthesized from natural bentonite and denoted Mont-CTAB. We observed a gain in productivity of 25%. 2D-fractal dimension parameter decreased under 1.5, showing a de-organization of the cake due to clay particles in/on the cake and a specific resistance of 4.4×10 11 m/kg was obtained in presence of clays versus 3.6×10 14 m/kg with HA alone. Finally the development of clay assisted ultrafiltration process changes the cake morphology limiting fouling impact and it is hope that for long term experiments, formation of a gel-layer should be limited.

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1. Introduction

Membrane filtration is increasingly used to remove particles, turbidity, and microorganisms from surface and ground water to meet stricter regulations established in drinking water quality. One of the critical issues in the successful application of membrane systems for water treatment is fouling. Several previous studies have demonstrated that natural organic matter (NOM), and in particular humic acids (HA), have a major influence on the flux decline limiting membrane productivity and also membrane lifetime [1–13].

Humic substances are typically characterized by a physical and chemical heterogeneous nature which derives from: (a) the absence of a discrete structural and supramolecular level; (b) the wide variety of sizes and shapes assumed in the solid and colloidal states; (c) the occurrence of complex aggregation and dispersion phenomena in aqueous media and (d) the various degrees of roughness and irregularity of exposed surfaces [14]. These properties have an important role in determining the physical, chemical and biological reactivity of humic substances towards mineral surfaces, metal ions, organic chemicals, plant roots, and micro organisms in soil. Humic and fulvic acids represent the major fraction of dissolved natural organic matter in aquatic environments. They are responsible for natural water color and for initiating photochemical transformations of both organic compounds and trace metals [8,10,15].

In the present study we engaged an original approach integrating macroscopic membrane parameters like percentage of permeate flux decline with time, productivity loss, modified fouling index (MFI), cake resistance (Rc), specific cake resistance (α) with microscopic parameters like 2D-fractal dimension deduced from scanning electronic microscopy (SEM) images of the membrane surfaces. To complete this approach, trans-membrane streaming potential (SP) measurements realized with a homemade apparatus were used to better understand the fouling phenomena in terms of electrostatic interactions.

We have carried out different fouling experiments with varying operating parameters like molecular weight cut-off (MWCO) and pH of the solution to be filtered, under 2 bars of trans-membrane pressure and with and without humic acid concentrations fixed at 5 mg/L. As an extension of previous study, effectiveness of a novel pre-treatment method was studied and applied to the more sensitive fouling membrane 100 kDa. Pre-treatment was done with a naturally occurring clay bentonite from what we extracted the montmorillonite fraction, pillared with Al-polycations, calcinated at 450 °C and chemically modified by a surface active agent (cetyltrimethylammonium bromide, CTAB). In a third part we combined homemade particle clays with UF membranes in order to de-organized cake deposited in presence of humic acids during filtration with the aim to limit membrane fouling.
2. Materials and methods

2.1. Modified fouling index (MFI)

Modified fouling index gives an idea about the fouling potential of the feed. It is based on cake filtration mechanism, as proposed by Boerlage et al. [16]:

\[
\frac{t}{V} = \frac{\mu R_m}{\Delta P S^2} + \frac{\mu I}{2 \Delta P S} V = A + \text{MFI} \cdot V
\]  

(1)

where \( t \) is the filtration time, \( \mu \) is the water viscosity, \( \Delta P \) is the transmembrane pressure, \( S \) is the surface area and \( I \) is the index of fouling which depends upon the specific resistance of the cake and the concentration of the particles which cause fouling.

The filtration is taking place in three stages: (i) the first part is the blocking of the pores, (ii) the second part is the gradual formation of the cake and (iii) the third part is the compression of the cake. When there is formation of an incompressible cake, the relation between \( t/V \) and \( V \) is showed to be linear and the slope of the linear relation will give the fouling indicator MFI which corresponds specifically to fouling power of the feed solution due to cake elaboration on the membrane surface. The results of the test are thus a series of measurements of time and cumulated volumes of the permeate, as reported elsewhere [12,16,17].

2.2. Resistance in series model and cake specific resistance

From filtration theory based on Darcy’s law, considering resistance in a series, one obtains for the liquid flux

\[
J = \frac{Q}{S} = \frac{1}{S} \int \frac{dV}{dt} = \frac{\Delta P}{\mu (R_m + R_c)}
\]  

(2)

with \( J \), the permeate flow \((m^3\cdot s^{-1}\cdot m^{-2})\), \( R_m \), the membrane resistance \((m^{-1})\), \( R_c \), the cake fouling resistance \((m^{-1})\) and total resistance \( S \) is the membrane area and \( \mu \) the dynamic viscosity.

Assumptions usually made are that: (i) the cake resistance is proportional to the solid mass deposited on the membrane surface, and (ii) the cake filtration performance under constant pressure is characterized by an average cake specific resistance \( \alpha \), so that

\[
R_c = \frac{\alpha C_b V}{S}
\]  

(3)

where \( C_b \) is the bulk solids concentration \((\text{in kg/m}^3)\). This equation is used to calculate \( \alpha \) from \( R_c \) where \( \alpha \) is explained in \( \text{m/kg} \), as reported recently by Sioutopoulos et al. [17]

2.3. Determination of fractal dimension (FD) using the box counting method

Well-known box counting method is used to determine the fractal dimension (FD). FD is obtained from the slope of the double-logarithmic graph

\[
\log \text{N} = \text{FD} \log \varepsilon
\]  

(4)

with \( \text{N} \) is the number of full boxes, \( \varepsilon \) the length of one box and \( \text{FD} \) the 2D fractal dimension. A very easy tool to determine 2D-FD is using Image J software, free usable on the web. There are two limits for the 2D-FD parameter: first in the case of a very dense cake the 2D-FD might be equal to 2 and in the presence of some porosities 2D-FD value decreased and is situated between 2 and 1. The second limit concerns the necessity to have homogeneous surfaces.

As illustrated in Fig. 1, the 2D fractal dimension parameter, denoted 2D-FD, is determined for a 100 kDa in regenerated cellulose (Fig. 1a), from scanning electronic microscopy (SEM) images applying the box counting method on the threshold image (Fig. 1b).

2D-FD is 1.88, as reported on the Fig. 1c. The values for the 30 kDa and 10 kDa are respectively 1.91 and 1.95, showing less porous surfaces for the lower MWCO.

Analysis of the filter cake formation mechanism is an effective approach to control membrane fouling. It was found previously that cake layer on the membrane surface presenting microstructure may influence the membrane permeation, [12,18–21]. Numerous studies have been carried out about membrane filtration characteristics or membrane fouling, but most of them focused on cake layer macro-analysis. Microstructure of cake layer including volume fraction of the pores, relative location of the pores, geometrical structure of the pores, has not been explored until now, which is a key factor determining membrane permeate flux, as suggested by Meng et al. [19], and recently related about the development of new in situ tools [22]. The filter cake layer consists of numerous irregular pores of different size spanning several orders of magnitude in length scales. Since the microstructure of cake layer are usually disordered and

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Fig. 1. (a) SEM image showing the regenerated cellulose UF 100 kDa membrane external morphology; (b) threshold image; and (c) double logarithmic plots for the determination of 2D-FD from threshold image.
extremely complicated, it is difficult to investigate the permeability of the cake layer analytically. If the traditional geometry theory cannot give us a good understanding about it, the fractal theory is a usable tool to analyze natural phenomenon, which allows the characterization of objects under microstructure scale.

Senesi et al. [15] reported that humic acid suspensions in aqueous medium are susceptible to exhibit fractal structures. The aggregates formed are having a complicated multi-branched structure. In these cases diffusion of the species toward the surface (or heat away from it) can be the rate limiting process. Meakin [23] reported that diffusion limited deposition on fibers and surfaces also results in open dendrite structures with a “fractal” nature.

All 2D-FD values were found to be in good correlation with that of particle cluster aggregation underlying diffusion-limited aggregation (DLA), as reported by Witten et al. [24] for whom 2D-FD should be situated between 1.50 and 1.75. But the authors also found that the value of FD can also change according to different operating conditions like humic acid solution concentration, pH and ionic strength, [19–21].

2.4. Streaming potential (SP)

According to Helmholtz–Smoluchovsky equation, the streaming potential coefficient, (denoted SP), is given by the following Eq.(5):

\[ \Delta \phi = \frac{\varepsilon \xi}{\mu \chi} \Delta P \]  

(5)

where \( \Delta \phi \) is the transmembrane potential difference, \( \Delta P \) is the transmembrane pressure, \( \varepsilon \) is the permittivity, \( \xi \) is the zeta potential, \( \mu \) is the dynamic viscosity and \( \chi \) is the ionic conductivity of the KCl (0.001 M, pH = 6.5) electrolyte solution and SP the slope of the graph representing the evolution of \( \Delta \phi \) vs \( \Delta P \). From the measurements of variations of potential differences between two Ag/AgCl electrodes vs transmembrane pressure, it is possible to follow the charge evolution of pore walls of the membrane, because the transmembrane potential difference per unit pressure is directly link to the zeta potential of the filtration media (see Eq. (5)). SP measurements can be performed in two different ways: by flow through the membrane pores (trans-membrane SP measurements) or by flow along the top surface of the membrane. If such SP measurements are made along the top surface of the membrane, then the calculation of the zeta potential from the basic experimental data is generally unambiguous, from the Eq. (5). The first method has the advantage of experimental simplicity, however, the calculation requires more care if measurements and interpretation of experimental data may be difficult when measurements are performed with multilayer membranes (support layer(s) + skin layer), with membranes having selective layers, as reported elsewhere [25,26] and also in presence of fouling [12,27,28]. But in the case of low MWCO membranes, i.e. UF or NF membranes, we can hypothesize that the essential of the major part of the trans-membrane pressure occurred in the active layer. Then SP coefficient measured is only informative of the charges brought by the pore walls of the active layer as the support layer contribution is negligible.

2.5. Membrane properties

The membranes used in this study are flat sheet UF membranes in regenerated cellulose (RC) purchased from Millipore, (France) with nominal MWCO of 100 kDa, 30 kDa and 10 kDa. These membranes are having approximate pore sizes of 1.0±0.5 nm, 4±1 nm and 10±3 nm, respectively, as obtained from the manufacturer. The membrane geometrical area is equal to 20 cm². In accordance with membrane supplier instructions, all membranes have been previously chemically washed in three successive steps: 1 h bath with 200 mg/L of sodium hydroxide, 1 h with 50 mg/L of oxalic acid and 4 h with 200 mg/L of chlorine solution. Before each bath, rinsing is carried out using deionized water. All solutions were prepared from deionized water Elga (France) ultra pure (UP) water system (DOC<0.1 mg/L, pH 6.5 and conductivity<1 µS/cm). Cleaning procedure is carried out before each filtration. After fouling, all membranes have been conditioned for SEM analysis.

The filtration cell is a dead-end cell (Model 8200, Amicon®), purchased from Millipore (France). No stirring was employed in any of the experiments. The permeate mass is determined using an electronic balance with an accuracy of 0.1 mg.

2.6. HA solution

Humic acid powder was purchased from Acrôs organics company (France). A concentrated solution was first prepared as follows: dissolving 1 g of humic acid in 62.5 mL of NaOH (2 M) and then supplementing it with up to 1 L of distilled water. This solution was stirred for 24 h and preserved at a temperature of 4 °C in the dark. Solutions of 5 mg/L were prepared by dilution. 2 L of diluted HA solution was used for the experiments at different MWCO and pH and only 1 L for clay assisted filtration study. The pH of the diluted HA solution was determined at 6.5.

Humic acid particle sizes and zeta potentials were determined for the 5 mg/L solution at different pH with Zetasizer 4 apparatus (Malvern Inc., US) (see Fig. 2). We observed that charge and size are changing versus pH of the solution. All experiments were conducted at room temperature (20 °C). The pH was adjusted to 3.0 and 9.5 adding RP HCl and NaOH concentrated solutions.

![Fig2. pH titration graph of Acrôs humic acid in UP water under concentration of 5 mg/L (mean particle size is explained in nm and zeta potential in mV). From K. Kecili thesis, [29].](image)
2.7. Bench scale laboratory unit

The ultrafiltration cell (Model 8200, Amicon®) is connected to manometers for the regulation of transmembrane pressure. The ultrafiltration of HA solutions is carried out in dead-end mode without stirring. The permeate mass is determined using an electronic balance. The pure water flux was determined with milliQ water. The filtration of humic acids was carried out at a constant pressure of 2 bars for 100 min. The flux was measured as a function of time at a constant transmembrane pressure until a quasi steady-state was obtained. At the end of the experiment, the stirred cell was emptied and rinsed with UP water; then the pure water flux is re-evaluated to determine the extent of fouling. All experiments were conducted at room temperature (20 °C) (Fig. 3).

SP apparatus helps to follow membrane charge variations before and after fouling. To this system two Ag/AgCl electrodes are connected which in turn are connected to a milli-voltmeter (PHM250 from Radiometer Analytical, France) presenting a high enter impedance connected via a RS232 to a PC. The software (denoted proFluid 3.) was developed in collaboration with NEOSENS company (Toulouse, France) [12]. For each trans-membrane pressure value a corresponding potential difference was indicated on the milli-voltmeter which is automatically transposed to a PC instantaneously. The same experiment is conducted under different pressures (from 0.5 to 3.0 bars, with 0.5 bar increment). SP and the correlation coefficient R^2 are automatically generated. A mean average value of 1 mV/bar is attached to each SP measurement.

The sign of the SP directly yields the sign of the net charge of the membrane, i.e., the global charge behind the shear plane. We connected the positive potential (E_1) to the feed and the negative to the permeate (E_2), then from the slope we obtained directly the sign of the membrane pore walls, as reported elsewhere [15,18].

2.8. Mont-CTAB synthesis

The bentonite used for the preparation of modified montmorillonite was extracted from the Roussel site in Maghnia (western Algeria). The chemical composition of the bentonite is given in Table 1, from [30].

Clays used in UF operation was elaborated from Maghnia bentonite. We extracted the montmorillonite fraction and did the synthesis of Mont-CTAB in three steps, as illustrated in Fig. 4.

2.8.1. The first step: preparation of Mont-Na

1 mol·L\(^{-1}\) NaCl solution was first added to raw bentonite to replace all exchangeable cations with Na\(^+\) and then rinsed abundantly with deionized water. From this solution all other solid phases were separated by centrifugation and the montmorillonite fraction recovered by settling. The suspension material of lower than 2 \(\mu\)m depth of 10 cm was siphoned off by Anderson pipet. An additional treatment by dialysis was done until a chlorine test with AgNO\(_3\) solution was negative. Finally centrifugation at 3000 rpm during 15 min allows obtaining final montmorillonite denoted Mont-Na.

2.8.2. The second step: pillaring

Pillaring agents, Al-hydroxypolycation, was first prepared. In both cases sodium hydroxide solution was drop wise added with vigorous stirring to AlCl\(_3\) (purchased by Aldrich, France, concentration 1 mmol/L) using a peristaltic pump. The resultant solution was ripened under reflux during respectively 48 h, 10 days and 3 h. The last step was a calcination step at 450 °C to achieve the elaboration of the montmorillonite denoted Mont-Al\(_{13}\).

2.8.3. The third step: CTAB insertion

The adsorbent obtained after intercalation, calcinations and co-adsorption by CTAB was dried at 40 °C for at least 72 h, ground, and protected from light. The use of organic molecules, such as surfactants (CTAB) helps the introduction of an organic molecule into the interlayer along with the pillaring species. For the adsorption of the latter compounds, it is necessary to modify natural clay barriers with organic additives that will transform them into reactive clays for such compounds. The surfactants with a long hydrocarbon chain are of special interest because of their adsorption by clays leads to the formation of organo clays that are highly reactive for retaining hydrophobic compounds that are not retained by natural clays.

<table>
<thead>
<tr>
<th>Chemical composition (wt.%) of Maghnia bentonite.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>Fe(_2)O(_3)</td>
</tr>
<tr>
<td>MgO</td>
<td>Na(_2)O</td>
</tr>
<tr>
<td>CaO</td>
<td>K(_2)O</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td></td>
</tr>
<tr>
<td>69.4%</td>
<td>1.2%</td>
</tr>
<tr>
<td>1.1%</td>
<td>0.5%</td>
</tr>
<tr>
<td>0.3%</td>
<td>0.8%</td>
</tr>
<tr>
<td>0.2%</td>
<td>14.7%</td>
</tr>
<tr>
<td>11%</td>
<td></td>
</tr>
</tbody>
</table>

Loss on ignition at 900 °C in wt.%.
The organic solution of surface active agent (CTAB, cetyl-trimethylammonia bromide, purchased by Aldrich, France) was prepared by mixing 2 g of CTAB powder in 1 L of UP water, and then it was added to the Mont-Al13, and the mixture was stirring for about 3 h to obtain an inorganic–organic matrix, denoted Mont-CTAB. The clay complex so pillared was filtered under vacuum through a dialysis membrane and thoroughly washed with demineralized water repeatedly and then dried at 40 °C. We elaborated for the present study 8 g of Mont-CTAB from 100 g of bentonite. From Zetasizer measurements the isoelectric point of the Mont-CTAB was 3.5, as reported elsewhere [31].

2.9. Scanning electronic microscopy (SEM) analysis

SEM apparatus is employed with a field emission gun (JSM-6301F from JEOL France). Images obtained are from secondary electrons under 3 keV beam energy with magnifications situated between 2000 and 10,000. All samples were desiccated and glued to a carbon support. For the membranes, samples were stored with glutaraldehyde solution (4%), and progressively dehydrated with alcohol solution (10% to 100%) and dried during one night by slow evaporation. All samples were then attached to steel disks with double side-scotch tape. Finally, thin film carbon of 2 nm thickness was deposited under all samples by evaporation under vacuum (BAL-TEC MED 020 Balzers Lichtenstein apparatus). For the Mont-CTAB particles we determined the morphological and size under 3 keV and energy-dispersive detector (EDS) spectra were determined under 20 keV.

3. Results and discussion

3.1. Role of membrane molecular weight cut-off (MWCO) on fouling

We reported in Table 2, the results obtained for each membranes studied, in terms of hydraulic permeability for the virgin membranes (Lp), hydraulic permeability after fouling (Lpf), flux decline, in %, membrane resistance (Rm), cake resistance (Rc), specific cake resistance α and modified fouling index (MFI), parameters. Hydraulic permeability (Lp) coefficients are in a decreasing trend with decreasing MWCO because of the decrease in pore size. YM 100 membrane is having an Lp value 597 L·m⁻²·h⁻¹·bar⁻¹, YM 30 membranes with an Lp of 167 L·m⁻²·h⁻¹·bar⁻¹ and YM 10 membranes an Lp value of 28 L·m⁻²·h⁻¹·bar⁻¹ in the initial state. Furthermore, as a consequence of Darcy’s law (Eq.(2)), the membrane resistance, Rm, was observed increasing with decreasing MWCO.

After filtration with humic acid solution ([HA] = 5 mg/L, pH = 6.7) at a constant pressure of 2 bars, the flux decreased of 22%, 59% and 85% for 10 kDa, 30 kDa and 100 kDa, respectively (see Fig. 5).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>YM 10</th>
<th>YM 30</th>
<th>YM 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lp clean (L·m⁻²·h⁻¹·bar⁻¹)</td>
<td>28±3</td>
<td>167±17</td>
<td>597±50</td>
</tr>
<tr>
<td>Lpf (L·m⁻²·h⁻¹·bar⁻¹)</td>
<td>20±2</td>
<td>83±8</td>
<td>155±16</td>
</tr>
<tr>
<td>Flux decline (%)</td>
<td>22</td>
<td>59</td>
<td>85</td>
</tr>
<tr>
<td>Rm x 10⁻¹² (m⁻¹)</td>
<td>12.9±0.6</td>
<td>2.1±0.1</td>
<td>0.6±0.1</td>
</tr>
<tr>
<td>Rc x 10⁻¹⁴ (m⁻¹)</td>
<td>5.1±0.3</td>
<td>2.2±0.1</td>
<td>1.7±0.1</td>
</tr>
<tr>
<td>α (m⁻¹) (m/kg)</td>
<td>1.0±0.1 - 10⁻¹⁴</td>
<td>4.4±0.1 - 10⁻¹⁴</td>
<td>3.4±0.1 - 10⁻¹⁴</td>
</tr>
<tr>
<td>MFI (s/L²)</td>
<td>4585±460</td>
<td>997±175</td>
<td>1324±135</td>
</tr>
</tbody>
</table>

Fig. 4. Mont-CTAB preparation steps.

Fig. 5. Normalized flux with filtration volume for the filtration of 5 mg/L humic acid solution at pH 6.7, ΔP = 2 bars, T = 20 °C for 100 kDa, 30 kDa and 10 kDa regenerated cellulose membranes.
It was observed, as attempted, that $L_p$ values were decreased drastically due to fouling (Table 2). We can see that, even though YM 100 membrane possessed a greater initial flux, it declined so quickly and severely during the first few minutes (Fig. 6), which can be attributed to initial concentration polarization or pore adsorption of the large aggregates to the pores. Adsorption occurred of course but contributed little to membrane fouling (2% of the total resistance) as reported elsewhere [12]. As the average size of the humic acid particles at the experimental pH of 6.5 was determined as ~250 nm (Fig. 2), there is no possibility for the humic acid particles to enter the pores of all the tested membranes. So the only possible mechanism which can increase total hydraulic resistance is cake formation. Researches on humic acid fouling of microfiltration membranes have suggested that the convective transport and deposition of large aggregates on the membrane surface dominated the fouling by humic substances, [17,32,33].

It was also reported by Aoustin et al. [3] that initial fouling occurred as the result of aggregate deposition, which could catalyze subsequent fouling, even by feed solutions that had been pre-filtered to remove aggregates. They also showed that the role of larger aggregates was shown to be less significant for smaller molecular weight cut-off membranes. So for YM 100 membranes, the initial sharp flux decline can be attributed to the deposition of large aggregates by which complete pore blockage, or pore constriction had occurred, followed by cake formation. With the YM 30 membrane, the initial severe flux decline is less significantly observed comparatively to 100 kDa membrane. Flux decline from the initial value at the end of the filtration experiment was 59%. For the 10 kDa membrane, flux decline at the end of the experiment was only 22% which did not show much flux decline comparing with the other membranes.

Membrane resistance value, $R_m$, was found to be increasing with decreasing MWCO. Total hydraulic resistance was found to increase with decrease in MWCO. For 10 kDa, the $R_m$ value was $12.9 \times 10^{-12}$ m$^{-1}$, for 30 kDa it was found $2.1 \times 10^{-12}$ m$^{-1}$ and for 100 kDa that was $0.6 \times 10^{-12}$ m$^{-1}$. The lower the MWCO, the lower the hydraulic permeability values become, and that is the reason why we found higher membrane resistance values with lower MWCO. For 10 kDa, we determined $R_c$ as $5.1 \times 10^{-12}$ m$^{-1}$, for 30 kDa it was determined as $2.2 \times 10^{-12}$ m$^{-1}$ and for 100 kDa it was $1.7 \times 10^{-12}$ m$^{-1}$. It is interesting to note that cake resistance contributed 29%, 50% and 74% to the total resistance ($R_c + R_m$) for 10 kDa, 30 kDa and 100 kDa membranes, respectively. From these resistance values, it is clear that fouling due to cake layer was more predominant in 100 kDa. In 30 kDa, both of the two resistance components were having equal importance. In 10 kDa, the membrane resistance was the predominant one. Lower flux indeed decreased the amount of fouling by reducing the possibility of pore penetration. As suggested by Aoustin et al. [3], higher flux of 100 kDa membrane could cause severe concentration polarization and membrane solute interaction, resulting in greater amount of fouling.

Concerning the specific resistances calculated from $R_c$, we observed that 30 kDa is higher compared with the others with $4.4 \times 10^{14}$ m/kg, as we obtained $1.0 \times 10^{14}$ and $3.4 \times 10^{14}$ for the 10 kDa and 100 kDa respectively. The same result was observed by other researchers [17] who proposed $\alpha$, for the first time as a new tool to estimate the efficiency of UF seawater pre-treatment before reverse osmosis (RO). The authors reported $\alpha$ values for 100 kDa and 30 kDa in the order of $10^{15}$ m/kg higher than the present results. The difference can be attributed to the absence of salinity in our experiments.

**Table 3**

Experimental results of SP measurements of clean and fouled membranes of YM 100, YM30 and YM 10 membranes KCl $10^{-2}$ M, pH 6.5, T = 20 °C.

<table>
<thead>
<tr>
<th>SP (mV/bar) with KCl $10^{-2}$ M, pH 6.5, T = 20 °C</th>
<th>10 kDa</th>
<th>30 kDa</th>
<th>100 kDa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin membrane</td>
<td>−7.0±0.5</td>
<td>−17±1</td>
<td>−46±5</td>
</tr>
<tr>
<td>Foul ed membrane</td>
<td>−6.4±0.5</td>
<td>−18±1</td>
<td>−18±3</td>
</tr>
</tbody>
</table>

**Fig. 7.** SEM images showing the membrane surfaces of YM 100 membranes fouled by humic acid solutions at (a) pH 6.7, (b) pH 3 and (c) pH 9.5.
Modified fouling index (MFI) values at constant pressure were determined from the slope of the \( t/V \) vs. \( V \) curve. The results show that MFI values increased with MWCO. Boelarge et al. [16] reported that MFI is independent of MWCO. As a contradiction, in our results we found that MFI values depend on molecular weight cut-off of the membrane (Table 2). For 10 kDa, MFI was determined as \( 4585 \pm 460 \) s/L², for 30 kDa as \( 997 \pm 100 \) s/L² and for 100 kDa as \( 1324 \pm 135 \) s/L². MFI value also points towards the low fouling potential of the solution on YM 30 membrane. Reason for the increasing tendency of MFI value on YM 10 can be explained in terms of flux. Flux for the tighter YM 10 membrane was so low that it took more time to permeate the same volume. So the YM 10 membrane was in contact with the solution for a higher amount of time, which in turn can cause a higher adsorption of particles. This could simply increase the cake mass and also the resistance, as described before. That is the reason why MFI value is the highest for 10 kDa membranes.

To further investigate which fouling mechanism is operative, the charge related modifications on the membrane were also taken into account. Results obtained for SP measurements are summarized in Table 3. The results showed that 10 kDa and 30 kDa membranes bring a negative charge at pH 6.4 because of the IEP of the RC membranes which is 2.3, as reported elsewhere [12]. We observed no practical change in their SP values. For 100 kDa, there was a noticeable difference in the SP measurements between the clean and the fouled states.

This further emphasizes the fact that in 100 kDa membrane, fouling happened due to pore penetration of lower molecular weight (smaller than the minimum average particle size) particles of humic acid (estimated in the order of 2000 Da in previous work [34]). In 10 kDa and 30 kDa, because of their smaller pore size, particles are retained, which in a long run, resulted in the formation of a cake to decrease the flux. Furthermore from these data we can conclude that after fouling the charges carried by the YM100 membrane pore walls have been notably reduced. We attributed this modification to the internal fouling by very low molecular weight neutral or positive molecules such as polysaccharides and/or aminosugars.

As observed in the HA zeta potential data vs pH (see Fig. 2) the HA solutions can present negative or positive charges varying between +20 and -40 mV that can explain the partial screening of the negative charge observed. Furthermore we have also checked to eliminate by physical and chemical rinsing/washing this internal fouling but was unsuccessful due to their strong attachment to the pores wall.

We can also consider the role played by the cake which can manage the membrane charges independent of the membrane itself. Further experiments have to be done to give a response to this interrogation.

To analyze the microstructure of the humic acid cake we have done the measurement of 2D fractal dimension (2D-FD) of the surface cake. We have determined the fractal dimension of the fouled membranes of YM 10, YM 30 and YM 100 from SEM images (see Fig. 7) using the bow counting method.

The 2D-FD values were 1.81, 1.62 and 1.57 for YM 10, YM 30 and YM 100 membranes respectively. Those values are in the range of DLA mechanism of deposition. Furthermore, we observed that fouled membranes 2D-FD parameters were in a decreasing trend with increasing MWCO or, in other words, fractal dimension increased with the decrease in permeability, as shown in Fig. 8.

From these fractal dimension values, it can be correlated that a higher value of fractal dimension corresponds to a lower value of permeability. Meng et al. [19] investigated the fouling of membrane bioreactors (MBR) due to cake formation using fractal theory [19,20]. They found that fractal dimension has a linear relationship with cake porosity. According to their observations, permeability increased as FD decreased which is also coherent with our results.

### 3.2. Role of pH on fouling

YM 100 membranes were subjected to humic acid filtration at constant pressures of 2 bars and at different pH solutions: pH 3, pH 6.7 and pH 9.5. The results obtained are summarized in Table 4.

In Table 4 it was shown that all the three initial clean membranes have the same hydraulic permeability value (\( 597 \) L·m⁻²·h⁻¹·bar⁻¹) thus the same membrane resistance value (\( 0.60 \times 10^{12} \) m⁻¹) independent of the pH. Regarding the fouling layer resistance or cake layer resistance, \( R_c \), the highest value is determined for the membrane fouled with humic acid at pH 6.7 and the lowest for the membrane fouléd with humic acid at pH 9.5. In the case of pH 6.7 filtration, \( R_c \) contributed 74% to the total hydraulic resistance, \( (R_c + R_m) \). In acidic pH, (pH 3) \( R_c \) contributed 65% to \( R_t \), which is a considerable amount. In basic pH, (pH 9.5) \( R_c \) contributed only 51% to the total resistance \( (R_c + R_m) \).

Fig. 9 shows the evolution of normalized flux with filtration time and filtered volume during constant pressure filtration of humic acids. Greatest amount of flux decline occurred for humic acid filtration at pH 6.7 (88%) and the lowest for filtration at pH 9.5 (53%). Many authors [1,6,9] described that the highest degree of fouling during humic acid filtration occurred at an acidic pH. Surprisingly, in our case, we found that the greatest flux decline occurred at a neutral pH (pH 6.7) and the lowest amount of fouling at pH 9.5. At an acidic pH, (pH 3) the flux decline was intermediate (68%).

Foulant sizes may strongly affect fouling mechanisms in membrane filtration systems. If foulants have comparable or smaller sizes than the membrane pores, pore blocking may occur. However, if the foulants are generally much larger than the membrane pores, they cannot enter the pores and a cake layer may be formed on the membrane surface, as

![Fig. 8. Evolution of fractal dimension values with fouled membranes 10, 30 and 100 kDa (HA 5 mg/L at pH 6.7, ΔP=2 bars, T=20 °C).](image)
observed before by SP results. The YM 100 membrane is having an approximate pore diameter of 10 nm, and Acrôs humic acid particles are having a minimum average size of 250 nm and a maximum average size of 2500 nm as determined from Zetasizer experiment and reported in Fig. 2. Conventionally, a particle cannot pass through the pores of 100 kDa membrane in the above-mentioned pH ranges. From that an assumption is made that, the only mechanism that can increase the fouling layer resistance is cake layer formation. But to completely understand the fouling mechanisms during humic acid fouling the charge related modifications were also be taken into account one more time.

SP measurements were carried out according to Helmholtz-Smoluchovsky equation (Eq. (5)). Potential difference (mV) values with corresponding $\Delta P$ values were plotted and the slope of the curve gave directly the SP value or charge of the membrane in mV/bar. Clean regenerated cellulose membrane was having a charge of $-46$ mV/bar. The isoelectric point (IEP) of the clean membrane was determined at 2.3. At pH 6.99 and 9.26, the Acrôs HA particles have no apparent physical charge, or they are on their isoelectric point range (see Fig. 2).

For a protein, flux is lowest at the IEP and is highest as the pH is moved away from the IEP. Changes in the pH affect the solubility and conformation of the feed components [10]. In our case, greatest amount of fouling occurred at neutral pH, which can be explained by the fact that, humic acid particles were very close to their isoelectric point and hence the deposition of the humic acid particles on the surface/inside the pores were intensified due to lack of electrostatic repulsion. The charge of the membrane after fouling with humic acid at pH 6.7 became less negative ($-18$ mV/bar) (Fig. 10) which can also be explained by the same phenomenon.

Table 4
YM-100 parameters determined at three pH: pH 3, pH 6.7 and pH 9.5; (Acros [HA] = 5 mg/L, $\Delta P = 2$ bars, $T = 20^\circ$C).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH 3</th>
<th>pH 6.7</th>
<th>pH 9.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_p$ clean</td>
<td>597±100</td>
<td>597±50</td>
<td>597±50</td>
</tr>
<tr>
<td>$L_p$ fouled</td>
<td>210±20</td>
<td>155±25</td>
<td>297±30</td>
</tr>
<tr>
<td>Flux decline (%)</td>
<td>68</td>
<td>88</td>
<td>53</td>
</tr>
<tr>
<td>$R_m \times 10^{12} \text{ m}^{-1}$</td>
<td>0.60±0.03</td>
<td>0.60±0.03</td>
<td>0.60±0.03</td>
</tr>
<tr>
<td>$R_c \times 10^{12} \text{ m}^{-1}$</td>
<td>1.12±0.05</td>
<td>1.72±0.05</td>
<td>0.62±0.03</td>
</tr>
<tr>
<td>$\alpha$ (m/kg)</td>
<td>2.2±0.1 $10^{14}$</td>
<td>3.4±0.1 $10^{14}$</td>
<td>1.2±0.1 $10^{14}$</td>
</tr>
<tr>
<td>MFI (s/L²)</td>
<td>544±55</td>
<td>1358±100</td>
<td>490±50</td>
</tr>
</tbody>
</table>

Even though we assumed that the HA particles could not enter the pores of the membrane due to steric hindrance, from the SP values we can see that lower sized fractions of humic acid particles (which are lower than the minimum average particle size) did enter the pores, as reported elsewhere [34]. Hong and Elimelech [35] reported that the initial permeate flux decline on an NF membrane was due to the pore penetration of Suwannee River humic acid, which was further confirmed by a decrease in TOC rejection at low pH.

MFI values are the highest for pH 6.7 which is in agreement with the percentage of flux decline at the end of filtration. Thus MFI-UF parameter also underlines the fouling capacity of the humic acid solution at pH 6.7.

The shape and conformation of the particles also change according to change in pH. At higher pH, the humic acid macromolecules are having a smaller macromolecular conformation due to the reduced inter chain electrostatic repulsion and thus they can pass easily through the membrane pores [35]. The authors also attributed this to a lower rejection of NOM by the studied NF membrane. This phenomenon can be attributed to the 68% flux decline at the end of the filtration at pH 3 of YM 100 membranes. In our case, with decreasing pH, more carboxylic groups of NOM become protonated, resulting in a reduction in the charge of the humic macromolecules. And as a result, the humic acid particles were increasingly adsorbed to the pores of the membrane and also caused pore plugging, which is obvious from the fouled membrane SP values.

Several studies have focused on identifying which fraction of NOM contributed the most to membrane fouling [34,36]. The general

Fig. 9. Normalized flux with time and normalized flux with volume (for humic acid 5 mg/L solutions at pH 3, pH 6.7 and at pH 9.5, $\Delta P = 2$ bar, $T = 20^\circ$C).

Fig. 10. Streaming potential (SP) values for YM 100 membranes, before filtration with humic acid (clean) and after filtration with humic acid solutions at pH 3, pH 6.7, and pH 9.5 (SP measurements where conducted with [KCl] = 0.001 M at pH 6.5).
census was that the hydrophobic fraction of NOM tends to adsorb favorably on to the membrane surfaces than hydrophilic fraction. Typically, the hydrophobic nature of NOM increases with increasing molecular weight and decreasing acidity. Nilson and Digiano [37] observed increased fouling with increased molecular weight of particles. So, in our study at pH 3, more hydrophobic macromolecules of HA aggregates were readily adsorbed to the hydrophobic cake layer, already formed on the membrane surface, and resulted in a more compact and dense fouling layer. More recently the filtration of 50% HA and sodium alginate (SA) 50% decreases dramatically the UF membrane production due to gel-layer formation [17]. Similar observation was reported in RO for different ratios of HA and SA, in comparison to 100% HA. The authors reported a significant increase of specific fouling resistance \( \alpha \), with increasing SA percentage in a mixture. Furthermore HA particles appeared to be embedded in an alginate matrix [17].

For a clearer and more accurate picture, we were focused towards some microscopic parameters like 2D-fractal dimension (2D-FD) of the surface cake from SEM images.

From SEM images of Fig. 11, 2D-FD values of the humic acid cake formed at different pH were determined. 2D-FD values for membranes fouled by HA at pH 6.7, HA at pH 3 and HA at pH 9.5 were determined as 1.57 ± 0.01, 1.62 ± 0.01 and 1.52 ± 0.01, respectively. As previously observed, 2D-FD stayed in the range of a DLA mechanism of deposition. A highest FD value was reported for membrane fouled by HA at pH 3 and the lowest for the membrane fouled by HA at pH 9.5.

Fractal organization was reported by Pignon et al. for the explanation of cake density assisted by using angular radiation scattering and birefringence techniques [38]. Meng et al. [19–21] used fractal analysis to analyze the cake layer formed in membrane bioreactors (MBR). The authors found that a lower value of fractal dimension corresponds to a lower value of porosity or higher value of permeability which was also coherent with our results. A higher value of fractal dimension indicates a lower value of permeability in the fouled state (or a dense and compact cake layer) and a lower value of FD indicates lower flux decline (or a loose and thin fouling layer). Most recently, a study [39] was conducted on membrane bio-reactor (MBR) fouling and the authors concluded that biological constituents and the morphological properties of activated sludge contributed to the fouling layer resistance. They also concluded that membrane fouling resistance increased exponentially with fractal dimension values of the fouled membrane surface which is also coherent with our results.

![SEM images showing the membrane surfaces of YM 100 membranes fouled by humic acid solutions at (a) pH 6.7, (b) pH 3 and (c) pH 9.5 (magnification×5000).](image)

**Fig. 11.** SEM images showing the membrane surfaces of YM 100 membranes fouled by humic acid solutions at (a) pH 6.7, (b) pH 3 and (c) pH 9.5 (magnification×5000).

<table>
<thead>
<tr>
<th>Chemical conditions</th>
<th>NOM in solution</th>
<th>NOM on membrane surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low pH pH 3</td>
<td>Coiled, compact configuration</td>
<td>Severe flux decline</td>
</tr>
<tr>
<td>High pH pH 9.5</td>
<td>Stretched, linear configuration</td>
<td>Less flux decline</td>
</tr>
</tbody>
</table>

**Fig. 12.** Schematic description of the effect of pH on the conformation of HA macromolecules in solution and on the membrane surface.
As described in Fig. 12, basic pH is favorable to minimize NOM fouling because of the presence of a thin and loosely packed fouling layer. A lower value of fractal dimension was observed for the cake formed at pH 9.5 (1.52) and a higher value of 2D-FD (1.62) was found for cake formed at pH 3 which indicated a more dense cake layer. Thus 2D-FD will be considered in the future as to estimate membrane fouling at a microscopic scale.

3.3. UF-100 intensification using Mont-CTAB filter-aid

Clay assisted UF was previously engaged for the first time in order to decolor wastewaters in the presence of methylene blue [40]. Furthermore, bentonite addition in UF flux enhancement for oil/water emulsion filtration was reported and the presence of clays induced a higher shear stress in crossflow velocity reversing the adsorbed gel layer to the bulk of the liquid phase. It shows that scouring of bentonite caused the erosion of cake deposited [41].

In the present work we focalized on the dramatic consequence of UF-100 kDa membrane fouling by investigating the possibilities of deorganization of the cake by insertion of clay particles in the solution with the aim to help filtration and limit permeate flow dramatic decrease.

3.3.1. Mont-CTAB properties

SEM images and Energy Dispersive X-ray (EDS) spectra of Mont-CTAB clay particles show that grain granular size has different forms with 4–5 different distribution sizes comprised between 4 µm and 100 µm, as illustrated in Fig. 13. Chemical analysis (see Table 1 and Fig. 13) shows that the predominant components are Si, Al and Mg and that Fe, Na, K, Ca, and Cl are less than 5%.

Furthermore the EDS spectra show the presence of Br at 12 keV, proving the insertion of CTAB.

Fig. 14 is the X-ray diffraction (XRD) spectra of the crude bentonite, which exhibits original cristobalite phase mainly besides the montmorillonite phase with a quite important amount of quartz, illite and kaolinite. After sodium modification (Mont-Na), the d-spacing decreases from 14.9 to 11.1 Å, which is consistent with other data found in the literature [29,42].

The replacement of Na⁺ by the aluminum poly-cation (Mont-Al) involved a radical change in the small angle field and the structure appears less crystallized with a larger distribution (20 varying from 4 to 9°). After calcinations, the structure of the Mont-Al showed a more ordered structure (well defined peak) with a d-spacing reaching 19.2 Å, which in accordance with the literature [42].
The modification of the obtained Al-modified Montmorillonite with CTAB did not clearly show the adsorption of the organic cation because of the multiplication of the peaks in the small-angle range when it was expected only a slight change in the structure already calcinated. This point remains to be explained.

Furthermore FTIR spectra obtained for Mont-CTAB (results not reported) showed two major absorption waves (3200–2800 cm\(^{-1}\) and 1600–1700 cm\(^{-1}\)) attributed to valency vibration of OH from the constituting water and from the octahedrical layer of the clay. Peaks located at 3625 and 3440 cm\(^{-1}\) were characteristic of the montmorillonite. The absorption wave of the Si–O bond (900–1200 cm\(^{-1}\)) was clearly visible and centered at 1030 cm\(^{-1}\). The waves located at 520 and 462 cm\(^{-1}\) were attributed to deformation vibrations of Si–O–Al and Si–O–Mg resonators.

The characteristic peaks of OH groups increase for the Mont-Al (inclusion of hydroxy-Al) and decrease for the Mont-CTAB (replacement of H\(_2\)O by CTAB). The evidences of the presence of CTAB are given by the presence of characteristic waves of C–H (3100 cm\(^{-1}\)), CH\(_2\)–N (2926 cm\(^{-1}\)), CH\(_2\)–CH\(_2\) (2700–3150 cm\(^{-1}\)) and CH\(_3\) (1480 cm\(^{-1}\)), confirmed by Br element presence on the SEM-EDS spectra situated at 12 keV (see Fig. 13).

3.3.2. Mont-CTAB assisted UF

Accumulation of HA and HA + Mont-CTAB on the membrane surface shows a gradually developed cake layer with different morphologies comparing the active layer of the RC 100 kDa (Fig. 15a) and after the cake was deposited (Fig. 15b).

A dramatic loss of performances of the UF-100 membrane was also observed as illustrated in Fig. 16a. Then the addition to the HA solution of 2 g/L of Mont-CTAB may help to de-organize the cake deposited.

As illustrated in Fig. 16a it can be seen that the presence of Mont-CTAB has caused less flux decline than HA suspension alone, with a gain of 25%. In the same time the morphology of the UF-100 surface in presence of Mont-CTAB appeared totally different with a non homogeneous cake with the appearance of a crumble morphology (see Fig. 15b).

From this experiment, following the resistance model (Eq. (3)), the resistance of the fouled UF-100 KDa was calculated. R\(_c\) was found to be 1.65 × 10\(^{12}\) m\(^{-1}\) for humic acid cake as in the presence of Mont-CTA R\(_c\) was found to be 0.45 × 10\(^{12}\) m\(^{-1}\). Thus in HA + Mont-CTAB filtration, the total hydraulic resistance was found to be lower than that due to HA alone and R\(_c\) in the presence of Mont-CTAB was found even lower than the R\(_m\) which is 0.67 × 10\(^{12}\) m\(^{-1}\), as reported in Table 4.

In the case of HA alone, cake resistance was the dominant factor of the total resistance, but in the presence of clays, the cake resistance was considerably reduced. This indicated that for HA + Mont-CTAB system, the particulate fouling potential of the feed was lowered. This can be attributed to the lowering of specific cake/fouling resistance which value changes from 3.4 × 10\(^{14}\) m/kg to 4.5 × 10\(^{11}\) m/kg with the Mont-CTAB cake. This decrease was further confirmed by lowering 3 times of R\(_c\) in the presence of Mont-CTAB. The specific cake resistance obtained in the presence of Mont-CTAB, a non deformable particle, would also be a permanent value to be used as reference in future studies, as reported by few authors: Meireles et al. [43] for yeast cakes, Sioutopoulos et al. [17] with HA and sodium alginate fractions in seawater and more recently by Castaing et al. in the presence of microalgae in seawater [44].
Furthermore, modified fouling index (MFI-UF) was determined with HA alone and with HA+Mont-CTAB (Fig. 9b and Table 5). The value of MFI-UF for HA alone was found to be 1358±140 s/L^2 for HA alone. This value is in the same order of magnitude as previously determined [9], as in the presence of Mont-CTAB the MFI was found to be 594±60 s/L^2. Then the consequence of the presence of Mont-CTAB is limiting drastically (3 times) the fouling properties of the HA solution.

Thus, as shown in Fig. 17, in the presence and absence of clays, the 2D-FD parameter helps us to distinguish both surfaces. To resume we obtained a more aerated cake and a lower FD value (1.45) with clays as in the absence of clays and a more dense cake was obtained in comparison with the value of 1.57 determined without Mont-CTAB. With a 2D-FD of 1.45 we are not in the range of DLA mechanism. How to explain this result? So fractals occur in many places in nature and fractal structures appeared naturally in soils and in rock mechanisms. Herrmann et al. [45] reported that it is no surprise to find them also on geological applications. One example is hydraulic fracturing which is used systematically to improve oil recovery and has a considerable importance for the functioning of geothermal wells. An incompressible fluid, in general water, is pushed with pressure deep inside the ground by injecting it into a deep perforation. The fluid penetrates into the soil by opening long cracks that radically go from the injection hole into the material and eventually displace some more viscous fluids that are present in the ground. The authors were interested on the shape of the cracks and on the fluid finger penetrating into the crack [45]. They discussed the opening of brittle via hydraulic fracturing at constant pressure using a square lattice beam model with a disorder. They reported also that while for slow motions the clay behaves like a fluid for high injection pressures, it fractures like a solid and in this fracturing regime the resulting cracks display a ramified structure and seem to obey self-similarity with a fractal dimension of 1.4–1.5.

The consequence of this low 2D-FD in the presence of Mont-CTAB clays is a de-organization of the cake, as attempted, increasing hydraulic permeability (gain of 20%, as reported in the Table 5).

SP results reported in Fig. 18, complete the previous analysis by showing a complete inversion of the membrane pore walls in the presence of Mont-CTAB.

SP value was initially −46 mV/bar, decreased to −18 mV/bar in the presence of HA and after Mont-CTAB filtration it shows a positive value of +1.4 mV/bar. We attributed this modification to an internal fouling by very low molecular weight neutral or positive molecules such as polysaccharides and/or amino-sugars, as reported elsewhere [34]. Another possible reason is that the cake layer, which formed on the active layer of the membrane, itself acted as another membrane; the global charge exerted by the electrical double layer was screened and appeared apparently less negative. In that hypothesis

![HA alone](image1)

![HA + Mont-CTAB particles](image2)

**Table 5**

<table>
<thead>
<tr>
<th>UF membrane MWCO (kDa)</th>
<th>YM100 + HA</th>
<th>YM100 + HA + Mont-CTAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rc (×10^{-12}) (m⁻¹)</td>
<td>1.65</td>
<td>0.45</td>
</tr>
<tr>
<td>MFI-UF (s/L²)</td>
<td>1358±140</td>
<td>594±60</td>
</tr>
<tr>
<td>Permeability loss (%)</td>
<td>71</td>
<td>51</td>
</tr>
<tr>
<td>α (m/kg)</td>
<td>3.4±0.1·10^{14}</td>
<td>4.5±0.1·10^{14}</td>
</tr>
<tr>
<td>2D-FD</td>
<td>1.57</td>
<td>1.45</td>
</tr>
</tbody>
</table>

![2D- Fractal dimension](image3)

Fig. 17. 2D-FD of cake surface imaging in presence of HA with and without Mont-CTAB and morphology of the 100 kDa surface with HA alone (at the top) and in the presence of Mont-CTAB (at the bottom).
the positive charge can be attributed to inorganic groups in bentonite (Al³⁺, Ca²⁺, Mg²⁺) which formed complexes with HA particles and changed the total charge carried by the cake deposited.

We can also hypothesise that the presence of CTAB monomer desorbed in the filtrated solution and penetrating the membrane active layer, as reported elsewhere in presence of DTAB [28].

Further experiments are needed to clarify this point of our work. As a conclusion, less fouling occurred with Mont-CTAB particles and a gain in productivity of 25% was observed. This result opened interesting perspectives to the utilization of UF 100 kDa coupled with clays in order to change the porosity of the cake deposit increasing UF performances, destabilizing HA aggregates and limiting gel-layer formation.

4. Conclusion

Macroscopic parameters like percentage of flux decline with time, modified fouling index (denoted MFI-UF), cake/fouling resistance (Rc) and also specific cake resistance α were applied along with microscopic parameters like 2D-fractal dimension deduced from scanning electronic macroscopic (SEM) analysis for the UF of humic acid (HA) solution. To complete this approach, trans-membrane streaming potential (SP) measurements realized with a homemade apparatus also helped us to better understand the fouling phenomena, due to humic acid cake formation in terms of electrostatic interactions.

Fouling studies with three different MWCOs (100 kDa, 30 kDa and 10 kDa) of RC membranes were carried out in order to understand the role of MWCO in fouling. It was shown that the tighter membranes were less fouled compared with the higher MWCO membranes. Out of the three MWCOs used in our study, the 100 kDa membrane showed the highest degree of fouling and the 10 kDa membrane showed the lowest degree of fouling. Cake/fouling and membrane resistances were equally dominant in the 30 kDa membrane. So applying proper operating conditions like trans-membrane pressure and a careful selection of solution pH and ionic strength, we can predict better performance for the 30 kDa membrane. Fractal dimension showed a correlation with hydraulic permeability as well as with MWCO. It was found that 2D-fractal dimension decreased with decrease in permeability.

The results of different pH experiments conducted under pH 3.0, 6.7 and 9.5 showed that the highest degree of fouling happened at neutral pH (pH 6.7) and the lowest degree of fouling happened at basic pH (pH 9.5). The results were explained in terms of particle size, charge and conformation of the HA particles in different pH solutions. At neutral pH, the humic acid particles were very close to their isoelectric point (IEP) determined at 6.99 and the presence of neurally charged particles in the solution intensified the fouling process because of a lack of electrostatic repulsion. At higher pH, the humic acid macromolecules were having a smaller macromolecular configuration because of the reduced inter chain electrostatic repulsion. Smaller particles can form a more thickly packed cake, which was confirmed from the highest fractal dimension value at acidic pH. The lowest value of fractal dimension was observed at basic pH, which further indicated a thin and loosely packed cake (confirmed from lower 2D-FD values), which was the cause of the lowest fouling at pH 9.5.

As an extension of previous study, effectiveness of a novel pre-treatment method was studied applied to the more sensitive fouling membrane 100 kDa. Pre-treatment was done with a naturally occurring clay namely bentonite from what we extracted the montmorillonite fraction and chemically modified by a surface active agent (cetyltrimethylammonium bromide, CTAB). As a conclusion, less fouling occurred with Mont-CTAB particles added to HA solution with a gain in productivity of 25%. 2D-fractal dimension decreased under 1.5, showing a de-organization of the cake due to clay particles and a specific resistance of 4.4×10⁻³ m/kg was obtained in presence of clays versus 3.6×10⁻³ m/kg with HA alone. Finally the development of clay assisted ultrafiltration process changes the cake morphology limiting fouling impact and limiting gel-layer formation.

The present work opens interesting perspectives to the utilization of clays for the assistance of UF in order to change the porosity of the cake deposit limiting UF fouling.

We have also demonstrated that 2D fractal dimension should be an interesting tool in combination with specific cake resistance α to better control UF fouling. But concerning SEM images and FD parameter, we should in further study compare wet cake with dry cake.

Furthermore as the cake layer surface morphology is different from the cake layer bottom, and as fractal dimension of the cake layer structure may vary as a function of operating conditions, 3D-FD should be determined by new techniques, such as confocal scanning laser microscopy and tomography-XR. Future work will also apply the macroscopic/microscopic methodology of presently work “clay assisted UF” in order to de-organize the too dense cake layer in hollow fibers UF modules by limiting the risk of gel formation, for a sustainable development of low pressure UF as efficient seawater pre-treatments before reverse osmosis or nanofiltration.

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References