Remediation of Wastewater From Paper Mill Industry by Ultrafiltration and Aerated Lagoon

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Abstract: Paper mill industries produce large quantities of wastewater containing large amounts of organic matter. This study has allowed characterizing ultrafiltration by the organic matter in the effluent at each level of the production line and treatment with aerated lagoons to measure its effectiveness and consider the advantages of treatment with membrane reactor for environmental protection receiver. Chemical oxygen demand (COD), dissolved organic carbon (DOC), specifuer absorbance(SUVA index), absorbance, ratio absorbance 465/Absorbance 665 (E4/E6) were used for this purpose. It was shown that COD load ranges between 925 (D1) to 3355 mgO2/L (EOP). The low biodegradability of waste paper was pointed out by th values of the ratio COD/DBO5 which were 8.2, 7.9 and 3.8, respectively for exit launder samples DO, EOP, D1. From the SUVA index and the ratio E4/E6, it was noted the aromatic and humic character of organic compounds in the effluent. While applying the ultrafiltration, the removal rate of organic matter increased when the membrane pore diameter decreased. Between 0.45 mm and 30 Kda, the removal rate was relatively low except for DO and Primary treatment entence (ED) samples. Between 1 and 30 Kda, a High elimination was observed since it reached almost 95% at 1 kDa for ED and DO samples.

Key words: paper mill wastewater, ultrafiltration, diafiltration, dissolved organic mater; aerated lagoon treatment.

INTRODUCTION

Dissolved organic matter is a heterogeneous mixture of organic macromolecules whose main components are the humic substances. It plays a great role in the carbon cycle and in many physical, chemical or biological reactions and in the transport and transformation of contaminants. This organic matter is present in all compartments of the environment and poses enormous treatment problems. Several authors have shown that paper mill effluents are very rich in organic matter, particularly lignin[1]. Methods for fractioning of organic matter are based mostly on the difference of molecular weight of organic compounds. This operation can be done either by ultrafiltration[2] or by gel permeation on Sephadex G-type[3]. The separation of compounds may be performed by HPLC[4] or by adsorption on macroporous resin Amberlite XAD-4[5] and by a cascade of DAX-8 and XAD-4.[8,9]. The organic solvent extraction is often used as a complementary method to ultrafiltration or gel permeation[10]. Ultrafiltration allows separation according to the sizes of the various components and provides a size distribution of dissolved organic molecules using membranes with different cut-off. The sizes refer to apparent molecular weight[10]. The ultrafiltration use can be done according to two modes: concentration and diafiltration. The dissolved organic matter of secondary effluent includes non-biodegradable substances, deriving from the raw wastewater, as well as compounds released during the treatment process. The macromolecular fraction is mainly composed of extracellular polymeric substances (EPS), i.e., biopolymers of microbial origin. These are especially polysaccharides, which are excreted for the adhesion of bacteria onto surfaces (biofilm formation) or the cohesion of other bacteria (formation of microbial aggregates), and proteins, which maybe act as exo-enzymes, but also nucleic acids and lipids[11]. While the formation of a filter cake due to the deposition of
particulate matter is controllable by appropriate hydrodynamic conditions and backwashing, the character and size of fouling-causing substances being smaller than 0.45 mm are not yet completely identified. Literature\cite{10} indicates the significance of colloids of the size fraction between 0.45 and 0.1 mm in secondary effluent, whereas it is suggested the relevance of organic macromolecules with sizes between 0.1 and 0.01 mm regarding the fouling of low-pressure membranes\cite{11}. Further studies pointed out the particular impact of dissolved organic macromolecules on the loss of filtration performance in micro- and ultrafiltration\cite{12}.

Ultrafiltration was used to fractionate the organic matter of surface waters\cite{13,14}, water swamps\cite{15}, drinking water and wastewater\cite{16}, lake water\cite{17}. It is also used to study the organic matter in landfill leachates\cite{18,19}.

Ultrafiltration is interesting compared to other methods of fractionation because it is not destructive and is reagentless\cite{20}. Problems of interaction between the membrane and the dissolved compounds may also occur. This technique has however the disadvantage of not differentiating between organic and minerals compounds. In addition, the organic fractions obtained do not belong to a well-defined group of molecules. Interactions between the membrane and the dissolved compounds may also exist\cite{21,22}.

In this study the water samples from different levels of a chain of paper production were fractionated by ultrafiltration, followed by aerated lagoon treatment to evaluate its effectiveness.

**MATERIALS AND METHODS**

Samples were collected from the production lines of the pate: exit Laundering (DO, D1 and EOP), primary treatment entrance (ED), aerated lagoon entrance (SD) and aerated lagoon exit (SL). The pattern of the whole chain is illustrated by Figure 1. Analyses of raw samples and after filtration were carried out for characterization. The COD analyses were carried out according to the AFNOR standards (NFT 90-101). Measurements of dissolved organic carbon DOC were carried out by a carbon analyzer (OI Analytical model 1010). After the sample acidification by phosphoric acid, mineral carbon (CO\textsubscript{2}) is removed by nitrogen bubbling. The sodium persulfate is then introduced into the sample. This oxidant reacts with the organic carbon in the sample at 100 °C to form CO\textsubscript{2}. This is again purged from the solution and detected by IR analyse. The amount of CO\textsubscript{2} is proportional to the mass of carbon in the sample. The detection limit is estimated at 0.2 mg CL\textsuperscript{-1}. Measurements of UV absorbance were performed using a UV visible spectrophotometer SAFAS MC2. The accuracy is 0005 optic density unit between 220 and 700 nm.

Ultrafiltration tests were made in frontal ultrafiltration stirred magnetic Millipore cells (capacity 600 mL) by diafiltration in order to reduce the phenomena of concentration polarization on the surface of the membrane\cite{23,24}. This test is performed after filtration of samples from membrane diameter of 0.45 μm and 0.2 μm in a Millipore cell volume of 600 mL. The cell can withstand a pressure of 3 bars, but a pressure of 1.5 bars was used here. This value was optimized in previous work in the laboratory. Millipore membranes used for fractionation are respective cut-off: 30, 10, 1 K Da. The membranes are made of regenerated cellulose and are considered non-ionic. This type of membranes has already been used in many works\cite{25,26,27} and were chosen in order to compare the results with those of the literature. Beforehand, it was verified that oxygen had no influence on filtration. Indeed, one can expect an oxidation of organic compounds and consequently to a change in the distribution of apparent molecular weight in organic matter from the effluent, which was not the case. The experimental setup was depicted by fig. 1.

100 mL of the filtered effluent (on membrane cellulose nitrate porosity 0.45 μm and 0.2 μm) are introduced into the cell. The effluents studied have all been diluted so as to obtain samples where the percentage of DOC is around 150 mg C/L, in order to limit the phenomenon of concentration polarization. The determination of the ionic strength is possible through the empirical equation 1\cite{28}. This equation is valid for ionic strengths below 0.3 mol/L and requires measurement of the conductivity of the solution.

\[
\log I = 1.159 + 1.009 \log \chi
\]

(1)

\( I \) (mmol/L) the ionic strength \( \chi \) (dS/m) the solution conductivity

\[
I = \frac{1}{2} \left[ \sum C_i Z_i^2 \right]
\]

(2)

\( C_i \) and \( Z_i \) respectively the specie i concentration and charge.

**RESULTS AND DISCUSSION**

Table 1 shows the characteristics of the water at each stage of the chain. It can be noted that samples from the production lines of dough (DO, EOP, D1) have a high conductivity, which may reflect the presence of dissolved ionic species. These species are higher in the DO sample than in the others. Loss on ignition
showed that suspended solids are almost all volatile. There is a high nitrogen content compared to the phosphorus one. Turbidity observed here is related to the color of various effluents and organic pollution. This turbidity is low at the output D1 laundering and out of lagoon. These results might be related to the ventilation of the system or a possible presence of algae which take nitrogen released during the denitrification. Out of lagoon, it can be note an increase of nitrogen and phosphorus. Indeed the two

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**Fig. 1: Experimental setup**

**Table 1: Characteristic of crude effluent**

<table>
<thead>
<tr>
<th>Sampler</th>
<th>pH</th>
<th>pH (ms.m⁻¹)</th>
<th>COD (mgO₂L⁻¹)</th>
<th>BOD₅ (mgO₂L⁻¹)</th>
<th>SM (mg.L⁻¹)</th>
<th>NTk (mg.L⁻¹)</th>
<th>Pₗ (10⁷mg.L⁻¹)</th>
<th>Turb (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO</td>
<td>2.1</td>
<td>7.8</td>
<td>2950</td>
<td>360</td>
<td>10</td>
<td>6.90</td>
<td>36</td>
<td>22</td>
</tr>
<tr>
<td>EOP</td>
<td>10.1</td>
<td>4.5</td>
<td>3355</td>
<td>420</td>
<td>50</td>
<td>10.6</td>
<td>9</td>
<td>29</td>
</tr>
<tr>
<td>D1</td>
<td>2.2</td>
<td>4.7</td>
<td>925</td>
<td>240</td>
<td>18</td>
<td>10.9</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>ED</td>
<td>7.5</td>
<td>3.3</td>
<td>900</td>
<td>186</td>
<td>106</td>
<td>10.1</td>
<td>24</td>
<td>100</td>
</tr>
<tr>
<td>SD</td>
<td>6.7</td>
<td>2.3</td>
<td>865</td>
<td>190</td>
<td>74</td>
<td>3.17</td>
<td>9</td>
<td>53</td>
</tr>
<tr>
<td>SL</td>
<td>7.6</td>
<td>2.4</td>
<td>510</td>
<td>105</td>
<td>30</td>
<td>12</td>
<td>16</td>
<td>3</td>
</tr>
</tbody>
</table>

**Table 2: Effluent characteristic after filtration on membrane 0.45µm**

<table>
<thead>
<tr>
<th>Sampler</th>
<th>COD(mgO₂/L)</th>
<th>DOC(mgC/L)</th>
<th>Absorbance (dilution / 5)*</th>
<th>E4/E6</th>
<th>SUVA(254nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>254nm</td>
<td>280nm</td>
<td>465nm</td>
</tr>
<tr>
<td>DO</td>
<td>2720</td>
<td>1920</td>
<td>8.0000</td>
<td>2.6750</td>
<td>0.0668</td>
</tr>
<tr>
<td>EOP</td>
<td>3290</td>
<td>2368</td>
<td>19.0000</td>
<td>8.0000</td>
<td>0.1526</td>
</tr>
<tr>
<td>D1</td>
<td>854</td>
<td>555</td>
<td>3.5054</td>
<td>0.2813</td>
<td>0.0021</td>
</tr>
<tr>
<td>ED</td>
<td>728</td>
<td>502</td>
<td>3.3269</td>
<td>1.0623</td>
<td>0.0641</td>
</tr>
<tr>
<td>SD</td>
<td>824</td>
<td>574</td>
<td>2.3262</td>
<td>1.0493</td>
<td>0.0534</td>
</tr>
<tr>
<td>SL</td>
<td>494</td>
<td>389</td>
<td>3.0359</td>
<td>0.8260</td>
<td>0.0748</td>
</tr>
</tbody>
</table>
Fig. 2: Removal rate as a function of membrane

Fig. 3: Species repartition in different PMA fractions

The nitrate ions can induce a change in the storage of polyphosphates (In the presence of nitrate ions these polyphosphates are stored in the form of long chains).

The nitrate ions during the release phase is unfavorable for the phosphate removal\(^{20}\)

\[\text{elements are linked because the presence of nitrate ions}\]

\[\text{during the release phase is unfavorable for the}\]

\[\text{phosphate removal}^{20}\]
It is well-known that a nitrate ion concentration exceeding 20 mg/L inhibits the elimination of phosphorus. Regarding the conductivity, it decreases from 7 ms.m\(^{-1}\) to 2.4 ms.m\(^{-1}\). The COD decreases strongly from 2950 to 510 mgO\(_2\)/L, while the concentration of nitrogen increases from 6.90 to 12 mg/L.

Crude Samples DO, EOP, and D1 are highly polluted. The COD load ranges between 925 (D1) to 3355 mgO2/L (EOP) and the ratio values COD/DBO5 of 8.19 (OD), 7.9 (EOP) and 3.8 (D1), reflect the low biodegradability of waste paper. However, this non-biodegradability decreases sharply at the exit of laundering D1 (COD/DBO5 = 3.8). It remains around 4 despite the processing chain in place. This trend is clear in the measurements of DOC and absorbance (Table 2) showing the aromatic and humic character of organic compounds in the effluent (2 < Index SUVA\(_{254nm}\) <4) and the humic compounds (high E4/E6).

While analysing Fig. 2, the removal rate of organic matter increases when the membrane pore diameter decreases. Between 0.45 mm and 30 Kda, the removal rate is relatively low except for DO and ED samples. Between 1 and 30 Kda, a strong elimination is observed

The elimination of organic matter in ED and DO samples reached almost 95% at 1 kDa while for samples SD, SL, EOP and D1, it is necessary to be below 1 KDa to achieve this rate of elimination. The distribution of organic matter samples DO, D1 and SL (fig. 3) according to the PMA indicates that the fractions of high molecular weight (> 30 Kda) have a high proportion of DCO. However, fractions of PMA low (<1 kDa) represent only a small percentage. These effluents are composed of molecules of high molecular weight that can be eliminated by ultrafiltration on membranes of 30 KDa. In the case of EOP and ED samples, the distribution is almost uniform, the high proportion was observed for LDCs between 1 and 10 Kda. In the case of SD a strong elimination, require membrane less than 1 KDa.

**Conclusion:** This study evaluated the effectiveness of wastewater from paper mill industry treatment by ultrafiltration and aerated lagoon. Several cut-offs were used according to the size distribution of molecules. From the results it was shown the possibility to eliminate up to 60% of the organic material with apparent molecularweight going from 0.2 mm to 30 kDa. The removal rate can reach 100% with the combination of several membranes.

**REFERENCES**


