Powdered activated carbon and membrane bioreactors (MBR-PAC) for tannery wastewater treatment: long term effect on biological and filtration process performances

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Abstract

This paper describes the findings of an experimental investigation carried out on a pilot scale membrane bioreactor (MBR) with the addition of powdered activated carbon (PAC) to analyze improvements in effluent quality and in the filtration process. The results refer to a pilot plant monitoring stretched over a period of 594 days: 380 without PAC, 123 with a PAC concentration of 1.5 g/L and 91 with 3 g/L. The sludge residence time and hydraulic retention time were maintained between 30 and 90 days and 50 and 100 hours respectively. Improvements in COD removal were found to be low, but not negligible, and greater than the PAC adsorption effect alone. COD removal stability appeared to increase as PAC concentration increased. No effects were observed on the nitrification processes. The filtration process was evaluated in terms of sludge filterability, fouling rate and fouling reversibility. The fouling rate decreased with an increasing PAC concentration and showed complete reversibility both in presence and in absence of PAC.

Keywords: Tannery wastewater treatment; Membrane bioreactors; Powdered activated carbon; Membrane fouling; Fouling rate

1. Introduction

Powdered activated carbon in suspended activated sludge reactors has been applied both to full scale [1] and pilot scale [2,3] plants for some decades now. The main features of PAC use in conventional activated sludge processes are:

- autotrophic [1] and heterotrophic [4–7] microorganism protection from load peaks of inhibiting compounds;
Due to the high maintenance costs of PAC, successful results achieved in laboratory and pilot scale experiments have found little application on full scale plants.

Membrane bioreactors (MBR) allow operations with higher sludge age and significant reduction in sludge production. In this way, for a given PAC concentration, the decrease of excess sludge removal causes the reduction of PAC maintenance cost. On the other hand, an efficient MBR application development is strictly related to the possibility of running the process with optimal operating conditions: high specific flux, low fouling rate, fouling reversibility and long membrane life-cycle. Previous studies concerning powdered activated carbon dosing in MBR have pointed out an increase in sludge filterability [14, 15] and a decrease in the membrane fouling rate [16–18]. These effects produce lower energy and chemicals consumption for recovery and maintenance membrane cleaning. In this work we study the synergistic effect of MBR and PAC in order to reduce the negative effects of tannery wastewater on membrane application.

The composition of tannery wastewater produces undesirable effects on the viability of MBR application: membrane fouling could be affected by the presence of proteins derived from leather manufacturing [19] and considerable colloid amounts [20]. Moreover, the efficiency of the biological process is negatively affected by the presence of polyphenolic compounds, such as natural and synthetic tannins, commonly recognized as biorefractory [21,22] and inhibiting [23] compounds. Tannins are associated with different inhibition mechanisms by interacting with substrate, intracellular and extracellular enzymes [24]. PAC ability to adsorb tannins and other inhibiting compounds could be effective in protecting biomass from load peaks [4]. It could be beneficial to nitrifiers micro-organisms to grow on a PAC surface [25].

Previous experiments mainly refer to pilot scale experiments on drinkable water [16,18,26], tertiary treatment [27], wastewater reuse [11,28] or low loaded wastewater [17]. PAC-MBR process applications rarely refer to high load industrial wastewater. However, interesting results were obtained on landfill leachate [13,15].

Finally, it must be stressed that no previous papers were found referring to pilot scale investigation on the MBR-PAC process applied to tannery wastewater.

2. Materials and methods

2.1. Pilot plant configuration

Experimental investigations were carried out on a MBR pilot plant with submerged membrane configuration constituted by three tanks (0.26 m³ each one) (Fig. 1):

- T-01 equipped with aeration system;
- T-02 equipped with membrane filtration modules and aeration system for membrane shaking;
- T-03, usually empty, for sludge storage during membrane cleaning.

Process conditions were monitored and controlled by a PLC (Programmable logic controller) connected to:

- feeding, recirculating and permeation pumps;
- oxygen, redox, pH and level sensor;
- blower and air flow sensors.

2.2. Filtration unit

The filtration unit is submerged in tank T-02. It is realized with four horizontal hollow fiber
modules (Mitsubishi); filtering fibers are attached on vertical support serving also as permeate effluent collectors.

Modules have a membrane surface of 1.5 m² each with a nominal cut-off 0.4 µm. Table 1 summarizes the technical features of filtration modules. Membrane fouling was controlled through a cycle alternating filtration and relaxation and by continuous filter shaking with air blowing upwards. Air flow in the filtration tank was maintained at 4 Nm³/h during the whole experimentation. As suggested by the membrane producer, once a given transmembrane pressure value (20 KPa) is achieved, membrane chemical cleaning is required. Periodical cleanings are executed by, first, immerging membrane with ipochlorite (6 g/L) in a basic solution (4% NaOH) and, then, in an acid solution (3.7% HCl) for 15 hours.

Chemical cleaning with ipochlorite should always be executed for oxidizing and removing organic (biotic and abiotic) membrane foulants. Cleaning with acid solution can be avoided where treated wastewater does not contain inorganic foulant compounds. A recirculation flux is maintained between T-01 and T-02. The recirculation

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**Table 1**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Producer</td>
<td>Mitsubishi</td>
</tr>
<tr>
<td>Product name</td>
<td>SUR234</td>
</tr>
<tr>
<td>Membrane type</td>
<td>Hollow fiber</td>
</tr>
<tr>
<td>Modules number</td>
<td>4</td>
</tr>
<tr>
<td>Membrane module surface</td>
<td>m² 1.5</td>
</tr>
<tr>
<td>Total membrane surface</td>
<td>m² 6</td>
</tr>
<tr>
<td>Porosity</td>
<td>µm 0.4</td>
</tr>
<tr>
<td>External fiber diameter</td>
<td>µm 540</td>
</tr>
<tr>
<td>Fiber material</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>Max transmembrane pressure</td>
<td>kPa 80</td>
</tr>
<tr>
<td>Max temperature</td>
<td>°C 40</td>
</tr>
</tbody>
</table>

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factor is defined as the ratio between recirculation and permeate flux.

2.3. Analytical methods and wastewater characteristics

The pilot plant is located in the “Consorzio Cuoiodepur” wastewater treatment plant (S. Miniato, Pisa, Italy). The influent is the tannery industrial wastewater of one of the most important oak leather industrial districts in (Italy and) Europe. The pilot plant’s feed is previously pre-treated in the full scale wastewater treatment plant; the preliminary treatments are: equalization, catalytic sulphide oxidation, primary sedimentation and clariflocculation with polyelectrolyte; the mean values of monitored parameters in the influent are shown in Table 2. Our analyses were made according to Standard Methods [29] procedures.

2.4. Pilot plant monitoring

The pilot plant monitoring scheme is summarized in Table 3; we carried out our analyses twice a week on composite samples of influent, on composite samples of effluent and on grab samples of mixed liquor. The sampling program was interrupted for a 30 day period (between day 260 and day 290) though the pilot plant continued to work regularly.

2.5. Powdered activated carbon characteristics

The activated carbons used are Lambsorb TK/L PAC, produced by Ciba Specialty Chemicals S.p.A. Before starting PAC dosing in the
oxidation tank, adsorption isotherms were evaluated on pilot plant permeate by using concentrations of PAC between 0.8 and 3 g/L. Adsorption tests have been carried out in a laboratory batch reactor (2 L), which was slowly stirred until equilibrium conditions (6 h) were reached. The best fitting was found with the Langmuir isotherm. For example, at 20°C, we found:

\[
x/m = \frac{0.06667 \cdot C_e}{1 - 2.3 \cdot 10^{-4} \cdot C_e} \quad R^2 = 0.96
\]

where \(x/m\) is the amount of COD adsorbed for unit weight of carbon (mg COD/g PAC) and \(C_e\) is the equilibrium COD concentration in solution (mg COD/L).

### 2.6. Operating conditions

WWTP mixed liquor, already adapted to tannery wastewater, was used as inoculum for the pilot plant. During the first 455 days treated flux was maintained at the fixed value of 11.2 L h\(^{-1}\), with a hydraulic retention time (HRT) of 50 hours similar to that of the aerobic tank of the full scale WWTP; during the remaining days (455 to 593) flux was fixed at 5.6 L/h with an HRT of 100 hours. Recirculation factor (recirculation and permeate flux ratio) was fixed at high values (about 15) to reduce the difference between the oxidation/nitrification tank (T-01) and the filtration tank (T-02) sludge concentration. Oxygen concentration was maintained at about 4 mg/L during the whole period in both tanks. Mixed liquor temperature (ranging from 5 to 32°C) was heavily affected by outdoor temperature. After the first 100 days of operation, an antifoaming agent was added to avoid accidental sludge spillage due to foam formation; phosphoric acid was continuously dosed in view of the low phosphor concentration in the feed (0.5–1 mg/L). Excess sludge removal began after 160 days in order to maintain the TSS concentration in the range of 12–18 g/L\(^{-1}\). The excess sludge was removed daily from the aeration tank.

The filtration cycle was divided into a relaxation period of 7 minutes and a working period of 8 minutes; the specific gross flow was fixed at 7 L h\(^{-1}\) m\(^{-2}\) and maintained at the same value during all the experimental period. In this condition, transmembrane pressure can be used as an indicator of the membrane fouling trend.

The four membrane modules in the filtration tank were used two at a time during days 1 to 455, and one at a time from day 455 until the end of experiment. Only when fouling was considered complete for all modules, chemical cleaning took place following the procedure described above.

PAC dosing started on day 380, and two different concentrations were maintained in activated sludge; Table 4 shows pilot plant operating conditions.

### Table 4

Pilot plant operating conditions; PAC concentration in the oxidation tank, sludge residence time (SRT), total suspended solids in the oxidation tank (TSS), hydraulic residence time (HRT), start and end of each period

<table>
<thead>
<tr>
<th>Period</th>
<th>PAC [g L(^{-1})]</th>
<th>SRT [d]</th>
<th>TSS [g/L]</th>
<th>HRT [h]</th>
<th>Start [d]</th>
<th>End [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0</td>
<td>88</td>
<td>15.6</td>
<td>50</td>
<td>1</td>
<td>380</td>
</tr>
<tr>
<td>II</td>
<td>1.5</td>
<td>32</td>
<td>17.2</td>
<td>50</td>
<td>381</td>
<td>455</td>
</tr>
<tr>
<td>III</td>
<td>1.5</td>
<td>74</td>
<td>12.6</td>
<td>100</td>
<td>456</td>
<td>503</td>
</tr>
<tr>
<td>IV</td>
<td>3</td>
<td>95</td>
<td>14</td>
<td>100</td>
<td>504</td>
<td>594</td>
</tr>
</tbody>
</table>

### 3. Results and discussion

Table 5 shows the chemical characteristics of the effluent. On the whole, COD and phenols removal are in a typical range for the treatment (CAS or MBR) of tannery wastewater. On the contrary, nitrification was not always complete probably due to the low temperature achieved in the biological reactors. TSS concentration in the
Table 5
Chemical characteristics of the effluent

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean</th>
<th>Max</th>
<th>Min</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>832</td>
<td>1290</td>
<td>424</td>
<td>176</td>
</tr>
<tr>
<td>TN (mgN/L)</td>
<td>222</td>
<td>373</td>
<td>78</td>
<td>74</td>
</tr>
<tr>
<td>N-NH₄⁺ (mgN/L)</td>
<td>82</td>
<td>272</td>
<td>5</td>
<td>85</td>
</tr>
<tr>
<td>Phenols (mg/L)</td>
<td>32</td>
<td>67</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>&lt;5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>pH</td>
<td>7.1</td>
<td>8.1</td>
<td>6.4</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 6
Mean temperature, COD removal, COD removal standard deviation; percentage are referred to mean COD in the inlet during each period. *Statistical significance of difference between mean removal percentage of each period and period I (estimated with Student’s t-test)

<table>
<thead>
<tr>
<th>Experimental periods</th>
<th>Mean T, [°C]</th>
<th>Mean COD removal [%]</th>
<th>Statistical significance of difference * [%]</th>
<th>COD removal standard deviation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period I</td>
<td>20</td>
<td>774</td>
<td>—</td>
<td>442</td>
</tr>
<tr>
<td>Period II</td>
<td>12</td>
<td>816</td>
<td>99</td>
<td>37</td>
</tr>
<tr>
<td>Period III</td>
<td>145</td>
<td>81</td>
<td>99</td>
<td>27</td>
</tr>
<tr>
<td>Period IV</td>
<td>24</td>
<td>795</td>
<td>98</td>
<td>278</td>
</tr>
</tbody>
</table>

permeate was below 5 mg/L as expected for a microfiltration effluent.

The following figures (Figs. 2–4) show the results of process monitoring in terms of COD, nitrogen, suspended solids and temperature.

3.1. Improvement of COD removal

Table 6 shows mean COD removal referring to the four different operating periods. On the basis of the results shown in Table 6, there is evidence of an improvement in COD removal percentage in presence of PAC; on the basis of COD concentration in the influent (Table 2 and Fig. 3), such improvement ranges from 80 to 160 mg/L of COD, during the periods under consideration. As shown in Table 6, the difference in mean COD removal during each period in presence of PAC displays a high statistical significance when compared with mean COD removal in absence of PAC (Student’s t-test was applied). It is also important to note that the results obtained in presence of PAC during period II and III are not related to an increase in biological kinetics due to higher temperature (Table 6).

By considering the influent COD concentration (Fig. 3) during the periods with PAC (II, III and IV), the overall COD removal improvement was 4.95 kg COD, corresponding to 5.33 kg of total PAC dose. The obtained ratio of 0.92 kg COD removed/kg PAC dosed, is significantly higher than the value obtained by considering the experimentally estimated Langmuir isotherms. In fact, even considering the maximum value of permeate COD ($C_e = 1290$ mg/L) with the estimated Langmuir isotherm, it is possible to estimate a ratio of 0.12 g COD adsorbed per g of
Fig. 2. Total and volatile suspended solids in the oxidation tank.

Fig. 3. CODin: COD in the influent. CODout: COD in the effluent. CODfilt: COD measured on filtered sludge samples (through Whatman 41 filter paper). %CODremoval: percentage of COD removal in the MBR pilot plant.

Fig. 4. Nitrification process: Total Kjeldahl Nitrogen in the influent (TKN_in), ammonium and nitrate concentration in the effluent (N-NH4_+ out, N-NO3_− out) and temperature.
PAC dosed. By considering the Langmuir isotherm, with an equilibrium COD concentration $C_e$ equal to the mean COD concentration of permeate and the total amount of PAC dosed, it is possible to estimate the COD removal due to the adsorption process during each period; such amount, corresponding to 4–6 mg/L, is negligible if compared with the inflow COD. Therefore, the observed COD removal improvement of 80–160 mg/L can be justified only by taking into account a synergistic effect between the PAC and the activate sludge. According to the literature, this effect [10] could be related to an improvement in biodegradation efficiency on adsorbed substrates, even if an improvement on PAC adsorption capacity is possible [11]. During period IV, the improvement in COD removal was lower despite a higher PAC concentration (3 g/L), but the evaluation of results has to take into account the fact that qualitative changes occur in the influent wastewater throughout the year. The investigation with 3 g/L of PAC has been carried out from April to July (2004) when tannery wastewater is characterized by the highest organic load of the year; as a matter of fact, by considering the same period of the year in absence of PAC, the mean COD removal in the MBR pilot plant from April to July (2003) was lower if compared with the mean value of the year (76.4% vs 77.4%).

3.2. COD removal stability

Even if an increase in COD removal is not clearly related to PAC concentration, PAC presence was clearly related to a stabilization of COD removal percentage: standard deviation calculated on COD removal during MBR - PAC process decreased up to about 60% of initial value. Fig. 5 shows relative frequencies of COD removal percentage associated to the three different PAC concentrations. The adsorbing capacity of PAC in presence of peak loads and subsequent desorbing are probably the reason for this behavior. It is not possible to exclude, however, that such results could be related to the protection offered by PAC to microorganisms from inhibiting compounds. Contact between biomass and inhibiting compounds could be limited both because of PAC adsorption of inhibiting compounds and because of protection offered to the microorganisms by the bio-film on the PAC surface.

![Fig. 5. Stabilization of COD removal. Relative frequencies of COD removal percentage associated to the three different PAC concentrations.](image)
For full scale application, a limitation in variability of effluent COD could be useful especially for wastewater treatment plants with a tertiary treatment, usually present in tannery wastewater treatment plants (Fenton, clarificoculation, etc).

3.3. Nitrification efficiency in the presence of PAC

The expected improvements in the nitrification process in presence of PAC were not observed. In the treated tannery wastewater, nitrification is highly inhibited on both full scale and pilot scale plants and high SRT are required to meet a complete oxidation of nitrogen compounds.

Combined titrimetric and respirometric essays were carried out, with ammonium additions, in order to estimate ammonium oxidizing bacteria (AOB) maximum growth rate; respirometric essay (with nitrite additions) were carried out in order to estimate nitrite oxidizing bacteria (NOB) [31–33].

The estimated kinetic parameters of AOB and NOB are largely lower (mean values of $\mu_{\text{max}} = 0.18$ and $0.16 \text{ d}^{-1}$ (20°C and pH 7.8) respectively for AOB and NOB) if compared with data referring to domestic wastewater treatment.

In order to compare the effects of PAC addition on the nitrification process, two periods with similar temperature and SRT were selected (Table 7).

Table 7
Comparison of nitrification efficiency with and without PAC

<table>
<thead>
<tr>
<th></th>
<th>May–July 2004, no PAC</th>
<th>May–July 2005, PAC = 3 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean temp., [°C]</td>
<td>23</td>
<td>24.2</td>
</tr>
<tr>
<td>Nitrification efficiency [%]</td>
<td>97.4</td>
<td>95.8</td>
</tr>
<tr>
<td>SRT [d]</td>
<td>88</td>
<td>95</td>
</tr>
</tbody>
</table>

3.4. Fouling rate and reversibility

In order to evaluate the PAC effect on the fouling rate, we selected a period (from day 250 to 450) with almost constant TSS concentration (mean value 17.7 g/L). The inverse of cumulative volume filtered per unit area of membrane between two cleaning cycles was used to represent the fouling rate. In this way, low values indicate a lower tendency to fouling. As shown in Fig. 6, since addition of PAC in the oxidation tank began, the filtration process became more stable by comparison to the previous period.

PAC dosing determines a positive effect on the fouling rate, probably due to the fact that organic membrane foulants are partly adsorbed [30]. On full scale applications, a reduction in the fouling rate is associated not only to a lower consumption of chemicals but also to a reduction of chemical cleaning frequency, strictly related with the membrane module life, and to energy saving.

In order to evaluate fouling reversibility, filtration tests were carried out after each cleaning. The applied procedure consisted in monitoring the TMP of each module at different tap water flow rates. The test results, reported as example in Table 8, referred to the flow of 25 L/hm$^2$ and 20°C, indicate that in presence of PAC the cleaning with basic solution alone is sufficient; on the contrary, in the absence of PAC the same results could be obtained only with both basic and acid chemical cleaning. Such effect appears to be stronger in the presence of 3 g/L of PAC.

Fig. 6. Fouling rate with and without PAC.
Table 8
Modules TMP after basic and acid cleanings at 25 L/h flow

<table>
<thead>
<tr>
<th>PAC concentration [g/L]</th>
<th>Mean TMP after cleaning with basic solution [KPa]</th>
<th>Mean TMP after cleaning with acid solution [KPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.5</td>
<td>10</td>
</tr>
<tr>
<td>1.5</td>
<td>10</td>
<td>9.5</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>

3.5. PAC effect on operational TMP

Specific permeate flow (L/hm²) and air flow in the filtration tank were maintained at a fixed value during the experimental period. Assuming a total filtration capacity recovery after each chemical cleaning, a hypothesis supported by the data shown above, it is possible to compare TMP during all periods between two cleanings to evaluate if PAC presence causes an increase or decrease in sludge filterability. Two other factors affecting TMP values are important in comparing TMP: sludge temperature and TSS concentration.

Dynamic viscosity of sludge was assumed to be related to temperature like dynamic viscosity of water: under such hypothesis it was possible to estimate TMP at 20°C through the following equation:

$$TMP_{20} = \frac{\mu_{20°C}}{\mu_T} \cdot TMP_T$$

where $TMP_{20°C}$ is the transmembrane pressure at 20°C, [KPa]; $TMP_T$ the transmembrane pressure at temperature $T$, [KPa]; $\mu_{20°C}$ the water dynamic viscosity at 20°C, [N·sec/m²]; and $\mu_T$ is the water dynamic viscosity at temperature $T$ [N·sec/m²].

The obtained TMP values were related to TSS concentration during the periods with and without PAC. As expected, during the treatment without PAC, TMP mean values showed a corresponding increase when TSS (Fig. 7) concentration increased; nevertheless, TMP values were not significantly affected by the presence of PAC in the TSS range between 9 and 18 g/L.

Fig. 7. Mean TMP at different TSS concentration in the oxidation tank with and without PAC.

4. Conclusions

MBR application appears to be an interesting solution for tannery wastewater treatment, although it has not been studied thoroughly until today. Wastewater characteristics and variability need adequate treatment strategies and process solutions. In this paper we have discussed the possible benefits of using MBR + PAC. This technological solution appears to be a novel one as far as tannery wastewater treatment is concerned. The most interesting results are observed in the context of process stabilization, with a significant decrease in effluent quality variability, on the one hand, and with regard to the filtration process on the other. Finally, PAC dosing enhances typical MBR system stability in terms of effluent quality, allowing a better control of the operational criticisms related to the fouling rate, fouling reversibility and membrane life cycle.

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References


