Treatment of winery wastewater in a full-scale fixed bed biofilm reactor

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Abstract The treatment of winery wastewater was performed at full-scale applying a two-stage fixed bed biofilm reactor (FBBR) system for the discharge in the sewerage. The results of the first year of operation at the full-scale plant are presented. Values of removed organic loads and effluent concentrations were interpreted on the basis of the COD fractionation of influent wastewater assessed through respirometric tests. The average removal efficiency of total COD was 91%. It was not possible to reach an higher efficiency because of the unbiodegradable soluble fraction of COD (about 10% of total COD on average during the whole year), that cannot be removed by biological process or settling. Due to the high empty space offered by the plastic carriers, FBBRs did not require backwashing during the seasonal operationing period of the plant (September–March). In comparison with other treatment systems the FBBR configuration allows one to ensure a simple management, to obtain high efficiency also in the case of higher fluctuations of flow and loads and to guarantee a good settleability of the sludge, without bulking problems.

Keywords COD fractionation; COD removal; fixed bed biofilm reactor; respirometry; winery wastewater

Introduction Several treatment alternatives for winery wastewater have been proposed by many authors through experiments both on pilot scale and on full scale with the aim to find efficient technologies characterized by a low cost and an easy management. Conventional systems are activated sludge reactors, SBR systems and aerobic biofilm systems such as RBC (Mueller et al., 1994). More recently, some advanced treatments have been applied, operating under both aerobic conditions such as moving bed biofilm reactors (Andreottola et al., 2002) or anaerobic conditions such as UASB reactors (Andreottola et al., 1997). Biofilm systems offer an interesting advantage for the treatment of wastewater with high concentration of readily biodegradable COD, thanks to their ability at oxidizing with high rate soluble compounds diffusible into the biofilm. Among the biofilm systems, fixed bed biofilm reactors (FBBR) are an alternative for the treatment of wastewater characterized by high organic loads and seasonal production. FBBR systems, where the biomass grows on plastic carriers with an high void ratio, offer some advantages such as: (1) a decrease of the required volume with respect to the conventional activated sludge systems; (2) the reduction of bulking problems, because the concentration of solids reaching the final settler is reduced, being made up only of biomass detached from the plastic elements; (3) the absence of return flow and backwashing due to the high void ratio of the filling media; (4) an easier management with respect to the conventional activated sludge plants.

In this research a full-scale FBBR system was applied for the aerobic treatment of winery wastewater. Wastewater was produced by a small winery located in the province of Trento (Italy), processing about 350 t of grapes per year (30% red and 70% white wine). The treatment plant was built in 2001 on the basis of experimentation at pilot scale, carried out in
order to evaluate the treatment capacity of the FBBR system for the discharge into sewerage and to assess the design parameters. The results of the pilot-plant monitoring have been published previously (Gatti and Nardelli, 1994). Here the results of the first year of operation at the full-scale plant (2001–2002) are presented. Values of removed organic loads and effluent concentrations were evaluated on the basis of the COD fractionation of influent wastewater assessed through respirometric tests.

**Methods**

**The full-scale treatment plant**

The full-scale plant is covered and made up of: [1] screen with mesh of 3 mm; [2] homogenization/equalization tank ($V = 20 \text{ m}^3$) equipped with on-line pH probe, pH neutralization and air supply using membrane plates; [3] 1st stage FBBR made up of two reactors (each with $V = 12.5 \text{ m}^3$) operating in parallel followed by a 3 m$^3$ settler (design rate in the settler equal to 1 m h$^{-1}$); [4] 2nd stage FBBR ($V = 12.5 \text{ m}^3$) followed by a 8 m$^3$ final settler (design maximum rate in the settler equal to 0.4 m h$^{-1}$); [5] discharge. Sludge collected from the bottom of the settlers was sent to a static thickener ($V = 9 \text{ m}^3$) and finally transferred to another plant for dewatering. The scheme of the full-scale plant is shown in Figure 1.

Neutralization of acidic pH was provided in the equalization tank by adding wastewater produced by washing processes in the winery previously stored in another tank ($V = 3.5 \text{ m}^3$) and characterized by a pH over 9.0.

The 1st stage, divided in two parallel reactors, offers a flexibility in the period with high flow rate (grape harvest time) and in the other period of the year characterized by lower flow rate. In the 1st stage FBBR the organic matter was removed with high rate, thanks to the high applied surface loads. The 2nd stage was built to improve quality of effluent wastewater before discharge. The most important parameter for the plant design is the maximum volumetric applied load for COD, assumed equal to 4 kgCOD m$^{-3}$ d$^{-1}$ for the 1st FBBR stage (value obtained from the pilot-plant monitoring), able to guarantee a COD removal efficiency higher than 70%.

The FBBR reactors are made up of steel and are transportable (reactors are installed on rails). This solution offers the possibility to start up the reactors before the grape harvesting period, by colonizing the fixed bed in another plant (in our case in a MWWTP with a capacity of 100,000 PE). The fixed bed in the biological reactors was made up of plastic carriers with the following properties: (1) made of polypropylene (density of 1.05 g cm$^{-3}$); (2) characterised by a spherical shape and dimension of about 11 cm; (3) having a specific surface of 140 m$^2$ m$^{-3}$; (4) void ratio equal to 95%. The plastic material filled almost the total volume of the reactor. All FBBR reactors were aerated adopting a fine bubble aeration system (Messner plates). Influent wastewater was filled at the bottom of the reactors.

![Figure 1 Scheme of the full-scale plant for the winery wastewater treatment](image-url)
Grab samples of influent wastewater were collected after the sieve and after homogenisation, while average 24-hour samples of treated effluents were collected at the outlet of the 1st and the 2nd FBBR reactors. Lab analyses of total COD, 0.45-μm-filtered COD, total suspended solids (TSS), volatile suspended solids (VSS), organic N, NH4-N and PO4-P concentrations in the influent and effluent wastewater were carried out according to Standard Methods (1995). The soluble COD was measured according to the method referred to by Mamais et al. (1992), that proposes to measure soluble and flocculated COD (sfCOD) in wastewater after the addition of zinc sulphate, pH equal to 10.5 and filtration on 0.45-μm membrane. In this way sfCOD is made up only of soluble compounds, while colloidal solids are not taken into account. Analyses of influent and effluent wastewater were carried out weekly. Respirometric tests were carried out about every month using the equipment described previously in Ziglio et al. (2001).

### Characterization of the influent wastewater

The wastewater flow rate was 4.6 m$^3$ d$^{-1}$ on average during the harvesting period (during September and October) with peaks up to 24 m$^3$ d$^{-1}$, and equal to 1.4 m$^3$ d$^{-1}$ on average in the period from November to March (Table 1). During the subsequent period of decanting, many days are characterized by flow rate equal to zero, but sometimes flow rate peaks reached 21.8 m$^3$ d$^{-1}$.

### Chemical parameters

The main statistical data about the influent wastewater characterization, summarised in Table 1, confirm the typical composition of winery wastewater. COD loads applied to the biological reactor were affected significantly by the high fluctuations of the influent concentrations (6,957±4,300 mgCOD L$^{-1}$ as annual average) and flow rate correlated to the winery production cycle. SfCOD is the most part of total COD, equal to 86.2% on average during the whole year. In order to guarantee the heterotrophic synthesis additional nitrogen and phosphorus was provided. Temperature ranged from 4°C to 18°C. At the plant pH in the influent wastewater was measured continuously in order to provide neutralization. For about 80% of the data collected from September to March (222 days) the pH was lower than 7.0.

### Respirometric tests on influent wastewater

Biodegradability of influent wastewater was evaluated on the basis of respirometric tests. By carrying out two respirometric tests in parallel (the first with raw wastewater and the

### Table 1 Statistical data of influent wastewater during the harvest (September–October) and during the period November–March. Average value and standard deviation are indicated

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>September–October</th>
<th>November–March</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Number of samples</td>
<td>Value</td>
</tr>
<tr>
<td>Influent flow rate</td>
<td>m$^3$ d$^{-1}$</td>
<td>4.6±5.9 measured every day</td>
<td>1.44±4.3 measured every day</td>
</tr>
<tr>
<td>Total COD</td>
<td>mg L$^{-1}$</td>
<td>7130±3533 16</td>
<td>6802±4982 18</td>
</tr>
<tr>
<td>sfCOD</td>
<td>mg L$^{-1}$</td>
<td>5805±2906 16</td>
<td>5652±4560 18</td>
</tr>
<tr>
<td>TSS</td>
<td>mg L$^{-1}$</td>
<td>692±815 15</td>
<td>722±740 17</td>
</tr>
<tr>
<td>NH4-N</td>
<td>mg L$^{-1}$</td>
<td>21.2±24.8 13</td>
<td>18.2±27.2 17</td>
</tr>
<tr>
<td>Organic N</td>
<td>mg L$^{-1}$</td>
<td>25.1±28.8 13</td>
<td>29.2±22.7 13</td>
</tr>
<tr>
<td>PO4-P</td>
<td>mg L$^{-1}$</td>
<td>6.4±7.2 13</td>
<td>6.7±7.4 15</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>5.7 (range 3.9–8.2) 62</td>
<td>5.6 (range 4.0–11.4) 160</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>17±0.9 14</td>
<td>9.2±3.0 51</td>
</tr>
</tbody>
</table>
second with 0.2 μm-filtered wastewater) the same respirogram was obtained, indicating that the oxygen uptake rate (OUR) depends mainly on colloidal and soluble compounds. A typical respirogram obtained for 0.1 L of raw wastewater (collected in the period after the harvest) added to 1 L of sludge collected from the settler is shown in Figure 2A. With the addition of ethanol only, the obtained respirogram is shown in Figure 2B.

After the addition of wastewater different OUR dynamics can be observed in the respirogram of Figure 2A:

1. The rapid increase of OUR due to the oxidation of fermentation products (indicated as RBCOD1 in Figure 2A);
2. A slow increase of OUR related to the utilization of fermentable compounds (rapidly available for biodegradation by heterotrophic microorganisms and indicated as RBCOD2 in Figure 2A) and the simultaneous storage of COD;
3. The slow decrease of OUR due to the utilization of previously stored compounds and of SBCOD;
4. The endogenous respiration rate.

The storage effect was interpreted as suggested by Karahan-Gül et al. (2002) by calculating the OUR of storage with a straight line (line 5 in Figure 2). The exogenous OUR for the utilization of fermentable compounds, calculated by subtracting the endogenous respiration and the contribution of storage from the measured OUR values, was equal to 37.2 mgO₂ L⁻¹ h⁻¹. This latter value is very similar to the one found for the removal of ethanol only (Figure 2B), equal to 32.3 mgO₂ L⁻¹ h⁻¹. Ethanol represents about 90% of influent COD in the period after the grape harvest as measured by Bories et al. (1998) for different kind of French winery wastewater.

**COD fractionation**

On the basis of the respirogram the fractionation of the influent total COD was evaluated, on the basis of the subdivision proposed in the Activated Sludge Model No. 2 developed by IWA (Henze et al., 1999). The results of COD fractionation are indicated in Figure 3, where the values for two different periods (harvesting and decanting periods) are compared. The value of the yield coefficient \( Y_H \) during storage was measured in the respirogram of Figure 2B, obtained using a known amount of ethanol. A value of \( Y_H \) equal to 0.75 was found.

According to Henze et al. (1999) the readily biodegradable COD (RBCOD) can be considered as the sum of two contributions produced by two different processes: (1) utilization of the products of fermentation, dominated by the presence of acetate; (2) utilization of fermentable compounds. These two term are indicated in Figure 3 as RBCOD1 and RBCOD2 respectively. RBCOD1 represents about 8% of the sfCOD concentration as annual

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**Figure 2** Example of a respirogram obtained after the addition of (A) raw wastewater and (B) 420 mgCOD L⁻¹ ethanol to the sludge. Contributions (1)–(5) are described in the text.
The value of RBCOD2 was equal to 80% of the sfCOD. RBCOD is the most part of total COD, equal to 75.4% as annual average. This value was also confirmed using the rapid respirometric test proposed by Ziglio et al. (2001), that takes about 30 minutes to be carried out and is based on the assumption that the biomass can utilise the readily biodegradable substrate in wastewater in the same way as acetate (CH$_3$COO$^-$. In the respirometric test suggested by Ziglio et al. (2001) a calibration curve using sodium acetate has to be defined; in this case the measured value of $Y_H$ was 0.75, equal to the value obtained from the respirogram of ethanol shown in Figure 2B.

The percentages of RBCOD1 and RBCOD2 increased in the period after the grape harvest as a consequence of fermentation processes. The slowly biodegradable COD (SBCOD) concentration was low, equal to 3.0% of total COD on average, and remained quite constant during the year. Unbiodegradable soluble fraction of COD was equal to 12.4% during the period September–October and equal to 7.2% during the period November–March. This fraction is discharged in the effluent wastewater without any change, while part of the unbiodegradable particulate COD can be removed by settling.

The fraction of COD made up of active biomass is quite negligible, being less than 0.24% of total COD, as measured from the exponential growth with high S/X ratio (COD/SSV > 300) at 20°C and after addition of ATU, according to the method referred to by Kappeler and Gujer (1992). From the respirometric test the net growth rate, $\mu_{r-m_H}$, was in the range 6.3–8.8 d$^{-1}$ and the amount of active biomass was in the range between 9 and 19 mgCOD L$^{-1}$. With regards to this latter respirometric method, we considered that the test can be useful for the assessment of aerobic active biomass in wastewater, thanks to its easiness, while the use of direct methods based on the use of fluorescent probes it is most adequate for the detection of active bacteria in the sludge (inter alia Ziglio et al., 2002). The low concentration of bacteria in wastewater suggested potential difficulties for the colonization of plastic media at the beginning of the operating period. Therefore the start-up of the FBBR tanks before the harvesting period was planned, as indicated above.

**Figure 3** Fractionation of total COD in influent wastewater during (A) the period September–October (average of 3 samples) and (B) the period November–March (average of 4 samples). n.m. = value not measured.

The choice of a biofilm system for the treatment of the winery wastewater was justified by the high RBCOD fraction. The biodegradable percentage was in fact equal to 71.4% and 80.7% during harvesting and decanting period respectively, while the percentage of slowly hydrolysable COD was negligible. On the basis of the high fluctuations of the influent flow rate, the HRT in the 1st and 2nd stages varied widely. Therefore the influent and
Effluent concentrations have been correlated by taking into account the HRT calculated on the basis of the daily flow rate. Removal efficiencies were calculated considering filtered COD in the effluent and shown in Table 2, where the values of the FBBR specific loads are also synthesized.

### Total COD removal

The volumetric total COD loads applied to the 1st FBBR stage during the whole period of experimentation (September–March) reached 8.0 kgCOD m$^{-3}$ d$^{-1}$ (2.4 kgCOD m$^{-3}$ d$^{-1}$ on average). The average removed load was 2.0 kgCOD m$^{-3}$ d$^{-1}$, giving an average removal efficiency during the year equal to 80% (range 67–97%), demonstrating the almost complete removal of RBCOD in the 1st FBBR stage. The specific total COD loads applied to the 2nd FBBR stage ranged from 0.2 to 4.5 kgCOD m$^{-3}$ d$^{-1}$ (1.3 kgCOD m$^{-3}$ d$^{-1}$ on average), while the average removed load was 0.8 kgCOD m$^{-3}$ d$^{-1}$, giving an efficiency of 51% on average.

By considering both the FBBR stages, the removal efficiency of total COD was 91% on average (Figure 4). It was not possible to reach a higher efficiency because of the nonbiodegradable fraction of soluble COD (about 10% of total COD on average during the whole year), that cannot be removed by biological process or settling. In the whole plant the average applied and removed COD loads were equal to 1.57 and 1.43 kgCOD m$^{-3}$ d$^{-1}$ respectively. The 1st stage contributes for the most part to the oxidation of biodegradable COD, while the 2nd stage was built only for the refining of 1st stage effluent in the case of presence of slowly biodegradable COD or in the case of flow rate peaks. The maximum COD load applied in the 1st FBBR stage, equal to 8.0 kgCOD m$^{-3}$ d$^{-1}$, is two times higher than the value of 4 kgCOD m$^{-3}$ d$^{-1}$ assumed for the design and obtained from the pilot-plant monitoring.

### Soluble COD removal

In Figure 5 the applied and removed sfCOD loads in the 1st and the 2nd FBBR stage are shown, expressed as daily load per unit of surface and volume for the whole period of experimentation (September–March). With regards to the 1st FBBR stage the applied sfCOD loads were between 0.1 and 7.4 kg sfCOD m$^{-3}$ d$^{-1}$ (1.9 kg sfCOD m$^{-3}$ d$^{-1}$ on average). The average removed load was 1.7 kg sfCOD m$^{-3}$ d$^{-1}$, giving a removal efficiency of 84% on average. This latter result is in agreement with the expected values on the basis of the RBCOD available in the influent wastewater. In fact the rapidly utilizable COD is about 88% of the sfCOD concentration, as indicated above, confirming the quite complete depletion of these fractions in the 1st FBBR stage. As a consequence of the low sfCOD concentration effluent from the 1st stage, the loads applied to the 2nd stage were equal to 0.6 kg sfCOD m$^{-3}$ d$^{-1}$ (range 0.04–1.5 kg sfCOD m$^{-3}$ d$^{-1}$) with a removal efficiency of about 60% (removed load equal to 0.4 kg sfCOD m$^{-3}$ d$^{-1}$ on average).
long HRT in the 2nd stage it was not possible to obtain a higher removal efficiency, as a consequence of the nonbiodegradable soluble fraction of the influent COD. In the whole plant the applied sfCOD loads were between 0.09 and 2.6 kg sfCOD m$^{-3}$ d$^{-1}$.

The sfCOD concentration effluent from the 1st FBBR stage was in the range 36–1450 mg sfCOD L$^{-1}$ (615 mg L$^{-1}$ on average); effluent concentration from the 2nd stage ranged between 36 and 685 mg sfCOD L$^{-1}$ (212 mg L$^{-1}$ on average). The peak in the effluent wastewater equal to 685 mg sfCOD L$^{-1}$ is a consequence of a high peak of COD load in the influent (produced by a high flow rate equal to 23 m$^3$ d$^{-1}$), that also caused a sfCOD peak effluent from the 2nd stage.

TSS removal efficiency in the two-stage FBBR was equal to 78% as an annual average. With regards to nutrients, the removal of the most part of nitrogen and phosphorous...
concentration from the influent wastewater was due principally to heterotrophic bacteria synthesis.

**Management aspects**

**Effluent concentrations.** As mentioned above the nonbiodegradable soluble COD is discharged in the effluent wastewater without any change, due to the fact that it is made up of compounds not biodegradable in biological reactors and not able to be removed in the final settler. From respirometric tests the nonbiodegradable and soluble fraction of COD was equal to 9.8% on average during the whole period. In confirmation, during the experimentation the average removal efficiency of total COD was 91%.

**On-line monitoring.** Dissolved oxygen in the 1st stage FBBR was monitored on-line and controlled around 2 mgO2 L\(^{-1}\) at the outlet of the 1st FBBR stage. The control of the aeration supply was implemented in order to minimise energy costs.

**Sludge management.** Thanks to the very high empty space offered by the plastic carriers (95%), the FBBRs did not require backwashing during the operating period of the plant (September–March). The detached biomass showed good settleability characteristics. The sludge extracted from the settlers was thickened and then transported to a municipal wastewater treatment plant for dewatering.

**Comparison with other treatment systems.** In comparison with the conventional activated sludge scheme the FBBR configuration allows (1) to reduce slightly the volume of the reactors, (2) to give a simpler management, (3) to overcome problems related to higher fluctuations of flow and loads and (4) to guarantee a good settleability of the sludge, without bulking problems during the whole period of monitoring (3 years up to March 2004). On the other hand the rapid start-up of the FBBR system requires the availability of a good biofilm development, that needs a previous colonization of the filling media.

**Conclusions**

The two-stage FBBR applied to the treatment of winery wastewater allows us to obtain a high removal efficiency of total COD equal to 91% on average, reaching an effluent COD concentration equal to 212 mgCOD L\(^{-1}\) on average for most of the operational period. The difficulty in reaching lower COD concentration in the effluent wastewater is due to the nonbiodegradable soluble fraction of COD (equal to 9.8% on average), as demonstrated from the results of respirometric tests. The application of a respirometric approach allows us to understand the fate of the different COD fractions through the treatment plant. Furthermore the characterisation of influent wastewater regarding the biodegradability allows us to go more in depth in the interpretation of the removed loads in the biological process.

In the light of the positive aspects obtained during the experimentation, the FBBR system looks like an interesting alternative for treatment of winery wastewater to be discharged into a sewer system.

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**References**


