Short Communication

The effect of ozone on tannery wastewater biological treatment at demonstrative scale

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Article info

Article history:
Received 11 March 2009
Received in revised form 25 May 2009
Accepted 6 June 2009
Available online 4 July 2009

Keywords:
Tannery wastewater treatment
Sludge production
SBBGR technology
Ozonation

Abstract

This paper reports the results obtained during an investigation aimed at transferring to the demonstrative scale an aerobic granular biomass system (SBBGR – Sequencing Batch Biofilter Granular Reactor) integrated with ozonation for the efficient treatment of tannery wastewater. The results show that the integrated process was able to achieve high removal efficiencies for COD, TSS, TKN, surfactants and colour with residual concentrations much lower than the current discharge limits. Furthermore, the process was characterised by a very low sludge production (i.e., 0.1 kg dry sludge/m³ of treated wastewater) with interesting repercussions on treatment costs (about 1 € per m³ of wastewater).

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1. Introduction

The world’s industries regularly produce new compounds that are resistant to biological degradation and/or can inhibit the activity of the biomass occurring in treatment plants. To remove these pollutants, a sharp increase in sludge production is expected, since after conventional biological treatment at least a physical–chemical polishing step is necessary (Bidga, 1995; Gogate and Pandit, 2004). In Europe, not only is sludge production continuously increasing, but disposal costs are also rising (Ginestet, 2007; Laturnu et al., 2007), which explains why great effort is presently being made worldwide to find innovative replacement technologies, aimed at a greater compactness and lower sludge production than conventional ones can offer. In such a contest, the Water Research Institute of the Italian National Research Council, has been involved during recent years in developing a new technology, whose acronym is SBBGR (Sequencing Batch Biofilter Granular Reactor), characterised by high effectiveness and minimum sludge production. SBBGR is a periodic biofilter in which the biomass grows mainly as granules; these granules are entrapped in the pores produced by packing the reactor with a filling material which allows greater biomass retention in the reactor to be obtained (up to 40 kg/m³) with reduction of excess sludge production (Di Iaconi et al., 2005a,b). This technology is effective also for treating industrial recalcitrant wastewater since it allows biological degradation to be integrated with chemical oxidation, by equipping the biological system with an ozonation unit, used with the aim of making recalcitrant compounds biodegradable.

Considering the interesting results obtained by using this integrated process at laboratory scale (Di Iaconi et al., 2003, 2006), in 2005, the European Commission financed, within the framework of the LIFE-Environment Programme, its transfer to the demonstrative scale (Perbiof project; www.perbiof-europe.com) for treating tannery wastewater chosen as representative of recalcitrant wastewater (Reemtsma and Jekel, 1997).

The present paper reports the main results obtained during this experimental campaign.

2. Methods

2.1. Demonstrative plant and operation

Fig. 1 shows the sketch of demonstrative plant used during the experimental campaign, which consisted of a SBBGR system equipped with an ozonation unit. The SBBGR consisted of a cylindrical reactor (internal diameter: 0.9 m; working volume 1 m³) partly filled (fixed bed volume: 0.38 m³) with biomass support material (wheel shaped plastic elements; features: 7 mm high, 8 mm diameter specific area 650 m²/m³, 0.95 density, and bed porosity 0.74) packed between two surfaces of slabs, two pumps (Pc and PR in Fig. 1) for filling and recirculation operations, a blower for air supply, a motorised valve (Vm in Fig. 1) for drawing operations and a programmable logic controller (PLC) for controlling and monitoring the system. A pressure meter set at the bottom of the reactor measured on-line biofilter headlosses due to biomass
growth and retained suspended solids occurring in the wastewater while the reactor was in operation. When a fixed value of headloss was reached, a washing step was carried out by means of compressed air until the headloss decreased to a predefined value. The washing water was entirely collected and measured (as TSS) in order to calculate the specific sludge production. The ozonation unit consisted of a pump (P₀ in Fig. 1), which extracted the biologically treated wastewater from the SBBGR (at a flow rate of 2 m³/h) and drove it through an ozone reactor (volume: 0.25 m³) supplied with a residual ozone destroyer. The pump was equipped with a Venturi type injector for dosing ozone produced by means of an ozone generator. Finally, the ozonated wastewater came back to the SBBGR for the final biological degradation.

Considering that the aim of the ozonation was to enhance the biodegradability of recalcitrant compounds, the plant carried out a treatment cycle organized in four consecutive phases: a filling, a biological degradation, a chemical + biological oxidation and a drawing phase. During the filling phase, a fixed volume of wastewater to be treated was pumped into the SBBGR at a flow rate of 0.5 m³/h. In the biological degradation phase, during which the ozonation unit was deactivated in order to permit the removal of biodegradable pollutants, the filled wastewater was continuously aerated and recycled at a flow rate of 2 m³/h (by means of pump Pᵦ in Fig. 1) through the biomass supporting material until a complete removal of biodegradable pollutants was obtained. In the successive phase, the ozonation unit was activated allowing the chemical partial oxidation of recalcitrant compounds to take place in the ozone reactor, thus generating biodegradable compounds that were recycled by means of pump Pᵦ through the SBBGR’s biomass. Finally, the treated wastewater was withdrawn by gravity from the reactor (by means of motorised valve Vₘ in Fig. 1) and the plant was ready to start a new treatment cycle.

In order to evaluate the effect of ozone on plant performances, in the first period of experimentation (i.e., period I), the ozonation unit was not used, so that the wastewater was treated only biologically, whereas in the successive period (i.e., period II) the biological treatment was integrated with ozonation. The plant operative conditions during both periods are summarized in Table 1.

The plant was fed with the primary effluent of one of the largest tannery wastewater treatment plants of the Avellino area (located in Campania, a southern Italian region).

### 2.2. Analytical methods

DOC (dissolved organic carbon), COD (chemical oxygen demand), BOD₅ (biochemical oxygen demand), TKN (total Kjeldahl nitrogen), TSS (total suspended solids) and surfactants were determined according to the standard methods [APHA, 1998]. The colour was measured by absorption at 660 nm. DO (dissolved oxygen) and pH were measured on-line by using selective probes whereas NOₓ–N (oxidised nitrogen) was measured by a UV 400 Tethys on-line analyzer. Ozone was measured in the gas flow at the entry and exit of the ozone reactor by means of a UV analyzer, to allow the consumption to be calculated. The specific sludge production (as kg TSS/kg CODremoved) was calculated dividing TSS discharged with the effluent + TSS removed

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Period I</th>
<th>Period II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration (d)</td>
<td>240</td>
<td>90</td>
</tr>
<tr>
<td>Applied volumetric load (kg COD/(m³ bed d))</td>
<td>1–4</td>
<td>4</td>
</tr>
<tr>
<td>Hydraulic retention time (d)</td>
<td>8–2</td>
<td>2</td>
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<tr>
<td>Cycle time (min)</td>
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<td>480</td>
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<tr>
<td>Phase:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filling</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Biological degradation</td>
<td>420</td>
<td>360</td>
</tr>
<tr>
<td>Chemical + biological oxidation</td>
<td>–</td>
<td>60</td>
</tr>
<tr>
<td>Drawing</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Applied ozone dose (g O₃/m³ of treated wastewater)</td>
<td>–</td>
<td>150</td>
</tr>
<tr>
<td>Headloss set point for washing operation (m)</td>
<td>3.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Fig. 1. Sketch of the demonstrative plant.
by the BOD5 values. As for total suspended solids (TSS) and nitro-organic compounds recalcitrant to biological treatment as proved
high COD removal efficiencies (higher than 90%), the discharge

3. Results and discussion

The plant performances recorded at maximum investigated applied organic load (i.e., 4 kg COD/m³bed d) during both periods are summarized in Table 2.

As for period I (i.e., when the wastewater was treated only by SBBGR), the data in Table 2 show high removal efficiencies for COD, TSS, surfactants and colour with residual concentrations much lower than the discharge limits. Fig. 2 shows COD, DOC and colour, respectively. A sludge production of 0.04 kg of TSS/kg CODremoved was obtained with a washing operation frequency of around 7 days. Such a low value of sludge production (one magnitude order lower than that commonly reported for conventional biological systems; Barjenbruch, 2007; Canler and Perret, 1994; Le Tallec et al., 1999; Pujol et al., 1992) can be explained by considering the high sludge age value (i.e., ≈ 150 d). In such circumstances, the microorganisms spend more time than in conventional systems in the endogenous metabolism phase, where the biomass decay rate is high, and thus the net biomass production rate is low.

As for period II (i.e., when the biological degradation was integrated with ozonation), the data in Table 2 show high removal efficiencies for COD, TSS, surfactants and colour with residual concentrations much lower than the discharge limits. Fig. 2 shows COD, DOC, TKN and NOx-N profiles recorded during a typical treatment cycle of period II. Looking at the COD and DOC profiles, it is possible to distinguish four consecutive trends: the first and second of which are typical of readily, and slowly, biodegradable pollutant removal, respectively; the third trend shows that the biological treatment is complete whereas the fourth, which coincides with the ozonation phase, highlights the benefits produced by using ozone. The COD balance of the “chemical + biological oxidation” phase demonstrates that the COD removal was due mostly to biological degradation of the biodegradable organic products formed by ozonation. In fact, from the COD profile, it is possible to observe that during this phase about 80 mg/L of COD were removed (i.e., the difference between 145 and 65 mg/L). Taking into account the ozone consumed (i.e., 20 mg/L; see Table 2), a biological removal of 60 mg/L results. This result confirms that ozonation was used with the specific aim to render biodegradable the recalcitrant compounds.

As for oxidised nitrogen, Fig. 2 shows that its concentration is low throughout the cycle indicating that simultaneous denitrification takes place at a constant rate during the whole cycle (the nitrogen consumption for biomass growth can be neglected because of very low excess biomass production as reported below). This can be ascribed to both high biomass concentration (i.e., 35 kg VSS/m³) and transient conditions (typical of sequential reactors), since in such conditions oxygen cannot penetrate inside the deeper layers of the biomass, while denitrifying bacteria can find carbon sources coming from storage or hydrolysis products of particulate organic matter present in the feed.
The process was characterised by a very low sludge production also during period II (around 0.1 kg of TSS/m³ of treated wastewater) with interesting repercussions on treatment costs (about 1 € per m³ of wastewater). This result is of great interest, since the biological and polishing (based on Fenton reactive) steps usually carried out at conventional tannery wastewater treatment plants not only produce a huge quantity of sludge (about 3 kg dry sludge/m³) but also greatly effect the treatment cost (about 4–5 € per m³ of wastewater) (Bidga, 1995; Collivignarelli et al., 2000).

4. Conclusions

The introduction of an ozonation step in the treatment cycle of a periodic biofilter for treating tannery wastewater at demonstrative scale improves the biological treatment effectiveness allowing the COD and surfactants discharge limits to be met. Moreover, in comparison with the conventional tannery wastewater treatment, the integrated process reduces the sludge production and operative costs by 30 and 4 times, respectively.

References


