Integration between chemical oxidation and membrane thermophilic biological process

G. Bertanza, M. C. Collivignarelli, B. M. Crotti and R. Pedrazzani

ABSTRACT

Full scale applications of activated sludge thermophilic aerobic process for treatment of liquid wastes are rare. This experimental work was carried out at a facility, where a thermophilic reactor (1,000 m³ volume) is operated. In order to improve the global performance of the plant, it was decided to upgrade it, by means of two membrane filtration units (ultrafiltration –UF-, in place of the final sedimentation, and nanofiltration –NF-). Subsequently, the integration with chemical oxidation (O₃ and H₂O₂/UV processes) was taken into consideration. Studied solutions dealt with oxidation of both the NF effluents (permeate and concentrate). Based on experimental results and economic evaluation, an algorithm was proposed for defining limits of convenience of this process.

Key words | economic evaluation, H₂O₂/UV, liquid waste, ozone, termophilic process

INTRODUCTION

Thermophilic aerobic process is a biological treatment operating at high temperatures (T ≥ 45°C); examples of application of this process at full-scale are rare, despite recognised advantages in comparison with the mesophilic one: higher degradation rate of organic substrate, lower sludge production and rapid inactivation of pathogens (LaPara & Alleman 1999; Rozich & Bordacs 2002; Suvilampi & Rintala 2002; Rozich et al. 2004; Visvanathan et al. 2007). On the contrary, termophilic conditions cause the increase of suspended solids concentration in the effluent, because of poor settling properties of suspended biomass; in addition, a remarkable content of residual organic matter, which is biodegradable under mesophilic conditions, can be still present in the effluent. The identification of economically and technically sustainable solutions to these relevant drawbacks is a challenge for a wider application of thermophilic process.

This research was carried out at a real scale facility, where a thermophilic reactor (1,000 m³ volume) is operated. After several years of working in a conventional configuration (suspended growth biomass reactor with final sedimentation and sludge recycle line), the plant was upgraded by substituting final sedimentation with an ultrafiltration (UF) unit. Later, the adoption of a further filtration step downstream (nanofiltration, NF) was required, in order to improve effluent characteristics.

Once this final lay-out of the biological-membrane filtration process was completed and started, the integration with chemical oxidation was taken into consideration. The aim of chemical oxidation depends on the stream where it could be applied: for instance, UF/NF permeate (COD removal improvement) or NF concentrate (improvement of organic matter biodegradability before recirculation into biological reactor). On the other hand, field experience (Rozich et al. 2004) has also shown that chemical oxidation could control foaming and enhance flux rates of UF.

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Oxidation processes studied in this work (ozonation and UV/H₂O₂) were chosen due to the fact that the Company already owns specific equipments; this research, in fact, was aimed at evaluating existing facilities efficiency rather than at identifying optimum chemical oxidation process.

Both effluents of NF (permeate and concentrate) were submitted to chemical oxidation (pilot plants) and, based on experimental results and economic evaluation, an algorithm was proposed for assessing limits of convenience of this process. Results of full scale biological and membrane-biological plant monitoring (along a 6 years period) are also reported, in order to highlight benefits of adoption of the double membrane filtration step.

**MATERIALS AND METHODS**

**Full scale facility**

Industrial waste treatment facility Idroclean Spa (located in Northern Italy), where this research was carried out, has several treatment lines covering an area of 14,000 m²; the plant has license to treat hazardous (exception for carcinogenic and mutagenic) and non-hazardous industrial wastes (liquid, slurry and solid) for an yearly amount up to 90,000 t.

Liquid wastes are subjected to a chemical-physical treatment, aimed at metal control, upstream the biological process. In Table 1, main characteristics of the mixture fed to the thermophilic unit are summarised. The biological concrete reactor (1,000 m³) is covered in order to ensure odour and temperature control and to enhance oxygen transfer efficiency (pure oxygen is supplied by a micro bubble aeration—OXY DEP—system). The plant has worked in the standard configuration (i.e. with a gravity settling unit) from 2002 to October 2005, before being equipped with filtration units. On November 2005, an ultrafiltration (UF) unit (2 parallel lines) was installed in place of gravity settling step. Each line is provided with two modules, equipped with 99 tubular multichannel ceramic membranes, covered by titanium and zirconium dioxide. Membrane cut-off is 300 kDa and minimum and maximum working pressures are 3 and 5 bars, respectively. Concentrate is then recirculated back into the biological unit. Nanofiltration (NF) unit (four parallel lines) has worked since January 2007; every line consists of two modules, equipped with four polyamide spiral membranes. Membrane cut-off is 300 Da and minimum and maximum working pressures are 20 and 30 bars, respectively. Concentrate (about 20 m³/d) is recirculated back into the chemical-physical pre-treatment, upstream the biological unit. A final activated carbon filtration unit is in operation, before discharge into the municipal sewage.

**Chemical oxidation pilot plants**

Three pilot plants (Figure 1) were used for testing ozonation (plant “A”) and UV/H₂O₂ process (plants “B” and “C”), respectively. Ozonation pilot plant “A” is equipped with a Wedeco ozone generator (series SWO/GSO). Ozone is produced from pure oxygen. The stainless steel batch reactor (480 L) is equipped with an ozone destroying system for exhaust gas treatment and a recycle pump (5 m³/h). Ozone is injected by a Venturi type static mixer. The UV pilot plant “B” consists of a 10 L storage tank (equipped with an electrical heating system), a 2 L stainless steel reactor containing one low-pressure mercury vapour lamp (80 W), a recycle pump (100–2,000 L/h). The glass batch reactor (2 L volume) of pilot plant “C” is equipped with two 125 W medium pressure mercury vapour lamps, a mechanical stirrer and a water cooling system.

**Table 1 | Characteristics of waste stream fed to the thermophilic biological unit (obtained from 6 years monitoring period); < d.l. = below instrument detection limit**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>M.U.</th>
<th>Average</th>
<th>Min</th>
<th>Max</th>
<th>Parameter</th>
<th>Value</th>
<th>M.U.</th>
<th>Average</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow [m³/d]</td>
<td>249</td>
<td></td>
<td>150</td>
<td>516</td>
<td></td>
<td>Cu [mg/L]</td>
<td>0.03</td>
<td></td>
<td>&lt; d.l.</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>COD [mg/L]</td>
<td>24,000</td>
<td></td>
<td>15,723</td>
<td>39,300</td>
<td></td>
<td>Cr [mg/L]</td>
<td>0.007</td>
<td></td>
<td>&lt; d.l.</td>
<td>0.070</td>
<td></td>
</tr>
<tr>
<td>N-NH₄⁺ [mg/L]</td>
<td>250</td>
<td></td>
<td>126</td>
<td>450</td>
<td></td>
<td>Ni [mg/L]</td>
<td>3.8</td>
<td></td>
<td>2.0</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>N-NO₂⁻ [mg/L]</td>
<td>1,190</td>
<td></td>
<td>620</td>
<td>1,560</td>
<td></td>
<td>Zn [mg/L]</td>
<td>0.73</td>
<td></td>
<td>0.30</td>
<td>1.40</td>
<td></td>
</tr>
</tbody>
</table>
Experimental procedure

Assessment of thermophilic biological plant efficiency was carried out based on COD and nitrogen daily monitoring (24 h average samples) of influent and effluent streams; temperature, biomass amount in the biological reactor (TSS and VSS) and excess sludge flow were also measured with the same frequency. Monitoring activity was carried out from January 2002 to December 2008.

Chemical oxidation tests were carried out on the following streams:

- NF permeate, in order to reduce COD concentration (using H₂O₂/UV process and ozonation);
- NF concentrate, in order to increase the biodegradability (partial oxidation using H₂O₂/UV process) with the aim of recycling this flow directly into the biological unit.

Tested treatment conditions were as follows:

- plant “A”: O₃ dosage = 100–400 mg/L; reaction time = 120–240 min; wastewater COD = 2,500 mg/L;
- pilot plant “B”: H₂O₂/COD w/w ratio = 50–200%, reaction time = 15–400 min; wastewater COD = 2,200–25,000 mg/L (tests with diluted wastewater were also carried out);
- pilot plant “C”: H₂O₂/COD w/w ratio = 86–300%, reaction time = 24–60 min; wastewater COD = 8,000 mg/L (tests with diluted wastewater were also carried out).

In order to assess the effect of chemical oxidation on biological treatability under thermophilic conditions, standard respirometric tests were modified: in particular, OUR (Oxygen Uptake Rate) tests were carried out at 45°C temperature and using thermophilic biomass as inoculum.

A simplified mathematical model of thermophilic biological process was developed, so as to better understand plant performance. Mass balance of organic matter on the reactor can be written as follows (assumed complete mixing configuration was experimentally assessed: Gallati et al. 2007):

\[
V \frac{dC}{dt} = Q (C_i - C) - \frac{\mu}{\frac{Y}{K_s + C}} C \cdot x \quad V
\]

where:

- \(C_i\) inlet COD concentration (mg/L);
- \(C\) outlet COD concentration (mg/L);
- \(V\) reactor volume (L);
- \(Q\) influent flow rate (L/h);
- \(\mu\) heterotrophic biomass growth rate (1/h);
- \(\frac{Y}{K_s + C}\) COD degradation rate (mgCOD/L/h);
- \(Y\) yield coefficient (mgSS/mgCOD);
- \(K_s\) substrate semi-saturation constant (mgCOD/L);
- \(x\) biomass concentration (mg/L).

Economic assessment

For evaluating economic feasibility of chemical oxidation, the following statements were assumed.
Oxidation of NF permeate

Oxidation cost must be compared with cost of activated carbon treatment (i.e. the last treatment, downstream membrane filtration, before discharge) for the removal of the same amount of COD. Costs were estimated as follows:

- Electric energy for UV lamps (€/d):
  \[ W_{UV} \times HRT_{UV} \times C_{kWh} \times Q_p \]

- Electric energy for ozone production (€/d):
  \[ E_{ozone} \times D_{ozone} \times C_{kWh} \times Q_p \]

where:
- \( W_{UV} \) lamp power per reactor unit volume (kW/m³);
- \( HRT_{UV} \) treatment contact time (h);
- \( C_{kWh} \) energy specific cost (assumed = 0.1 €/kWh);
- \( Q_p \) permeate flow (m³/d);
- \( E_{ozone} \) specific energy for ozone production (assumed = 10 kWh/kgO₃);
- \( D_{ozone} \) ozone dosage (kgO₃/m³).

Hydrogen peroxide (€/d): \( D_{H_2O_2} \times C_{H_2O_2} \times Q_p \)

Ozone (€/d): \( D_{ozone} \times C_{oxygen} \times Q_p / \eta_{prodO_3} \)

where:
- \( D_{H_2O_2} \) hydrogen peroxide dosage (kgH₂O₂/m³);
- \( C_{H_2O_2} \) hydrogen peroxide cost (€/kgH₂O₂);
- \( C_{oxygen} \) oxygen cost (€/kgO₂);
- \( \eta_{prodO_3} \) oxygen to ozone conversion efficiency (kgO₃/kgO₂).

Besides:

\[ \text{COD}_{rem} = Q_p \times \text{COD}_p \times \eta \]

where:
- \( \text{COD}_{rem} \) removed COD (kgCOD/d);
- \( \text{COD}_p \) COD concentration in the permeate (kgCOD/m³);
- \( \eta \) COD removal efficiency achieved by chemical oxidation.

Dosages of hydrogen peroxide and ozone, respectively, leading to oxidation cost equal to carbon adsorption cost can be calculated as:

\[ D_{H_2O_2} = (\text{COD}_p \times \eta \times C_{A.C} - W_{UV} \times HRT_{UV} \times C_{kWh})/C_{H_2O_2} \]

\[ D_{ozone} = \text{COD}_p \times \eta \times C_{A.C}/(E_{ozone} \times C_{kWh} + C_{oxygen}/\eta_{prodO_3}) \]

where \( C_{A.C} \) = activated carbon treatment specific cost (= 5 €/kgCOD₉rem, from plant operation data).

These equations indicate the minimum COD removal efficiency to be achieved by means of chemical oxidation (under certain dosage conditions) so that chemical oxidation is more convenient than activated carbon adsorption.

Oxidation of NF concentrate

Chemical oxidation yields direct removal of organic matter and contributes to an additional (biological) removal, due to the increased biodegradability of concentrate (which is recirculated back to the biological reactor). Overall COD removal (CODrem) is hence obtained by the sum of oxidized COD (CODox) and biodegraded COD (CODbiod), as follows:

\[ \text{COD}_{rem} = \text{COD}_{ox} + \text{COD}_{biod} \]

\[ = (\text{COD}_c \times Q_c \times \eta + (\text{COD}_c \times Q_c \times (1 - \eta)) \times (\text{BOD/COD})_{ox})/\text{kgCOD/d} \]

where:
- \( \text{COD}_c \) COD concentration of concentrate (kgCOD/m³);
- \( Q_c \) concentrate flow (m³/d);
- \( (\text{BOD/COD})_{ox} \) BOD/COD ratio after chemical oxidation.

Calculation of chemical oxidation cost is the same as previously described if \( Q_p \) is changed in \( Q_c \) and \( \text{COD}_p \) in \( \text{COD}_c \). Moreover, cost of additional biological degradation has to be taken into account, as follows:

Biological treatment (€/d): \( C_{bio} \times \text{COD}_{biod} \)

where \( C_{bio} \) = biological treatment specific cost ( = 0.5 Euro/kgCOD₉biod, from plant operation data).

The equivalence between costs of chemical oxidation (plus biological treatment) and activated carbon adsorption for the removal of the same amount of COD, in this case,
gives, for UV/H₂O₂ and ozone systems, respectively:

\[
(BOD/COD)_{\text{ox}} = \left( \frac{W_{\text{UV}} \times \text{HRT}_{\text{UV}} \times C_{\text{kWh}} + D_{\text{H₂O₂}} \times C_{\text{H₂O₂}}}{\eta \times C_{\text{A,C}} \times C_{\text{COD}}_{\text{c}} / (C_{\text{A,C}} - C_{\text{bio}})} \times (1 - \eta) \times C_{\text{COD}}_{\text{c}} \right)
\]

\[
(BOD/COD)_{\text{ox}} = \left( E_{\text{ozone}} \times C_{\text{kWh}} \times D_{\text{ozone}} + D_{\text{ozone}} \times C_{\text{oxygen}} / \eta_{\text{prodO₃}} - \eta \times C_{\text{A,C}} \times C_{\text{COD}}_{\text{c}} / (C_{\text{A,C}} - C_{\text{bio}}) \times (1 - \eta) \times C_{\text{COD}}_{\text{c}} \right)
\]

These equations indicate minimum performances (in terms of COD removal and BOD/COD ratio modification) to be achieved by means of chemical oxidation, so as to get economic suitability with respect to activated carbon adsorption.

**RESULTS AND DISCUSSION**

**Performance of combined membrane-biological process**

A six years monitoring period was considered. The introduction of UF notably increased the biomass amount in the reactor: from 50 kgTSS/m³ to 130 kgTSS/m³. Consequently, the VSS/TSS ratio was lowered (down to 26%), due to the mean cell-residence time increase. Sludge load decreased from 0.055 to 0.015 kgCOD/kgTSS/d.

In order to highlight difference in biomass efficiency due to the presence of UF, OUR tests were conducted using biomass taken from an activated sludge sample by means of either UF or sedimentation. In the former case, OUR values (mgO₂/gVSS/h) were threefold higher (data not shown): this means that biomass retained by membranes (within biological reactor) plays a major role in organic matter removal.

Therefore, increased COD removal capacity and effluent characteristic stability achieved after installation of UF step (Figure 2) were explained considering the double effect of membranes: 1) physical retention of organics for longer time within the system and 2) possibility of retaining dispersed bacteria which otherwise would be lost with the effluent (Malpei & Azzellino 2000).

Better removal was also obtained after installing a heat exchanger that maintained biological reactor temperature closely around 50°C (data not shown).

Monthly COD removal efficiency was calculated all along the monitoring period (data not shown): it passed...
from about 70% (conventional lay-out) to 81% (UF stage adoption) and to 88% (NF stage adoption).

Monitoring data analysis, together with the application of mathematical model, evidenced the presence of a consistent fraction (around 5,000 mg/L) of refractory COD. Also for this reason, chemical oxidation was considered as an interesting solution.

Chemical oxidation tests

Ozonation

Ten tests were carried out with plant “A” on NF permeate. COD removal efficiency ranged from 7 to 16%, passing from the lower reaction time (120 min) and ozone dosage (100 mg/L) to the strongest tested conditions (240 min reaction time; 400 mg/L dosage).

H$_2$O$_2$ + UV process: effect of wastewater characteristics

A first series of tests was conducted with pilot plant “B” using NF concentrate and permeate, characterized by high COD concentrations (around 25,000 and 2,200 mg/L, respectively). It yielded that, although under the best conditions removal efficiency was as high as 70% (Figure 3) and sometimes a better biodegradability was achieved, performance was affected by residual colour of wastewater. In fact, highest efficiency was achieved for a dilution factor (with water) of 1:5, while higher dilution (1:10) led to a decrease; in this case, probably, the reaction rate reduction due to lower initial COD concentration prevailed on rate increase due to lower colour interference. Actually, a second set of tests was performed with less concentrated wastewater (around 8,000 mg/L); in this case, also a modest dilution (1:2) led to lower COD removal efficiency. These results show that oxidation efficiency is strongly affected by wastewater characteristics and these can vary remarkably depending on fed wastes and performances of upstream treatments.

H$_2$O$_2$ + UV process: effect of temperature

The effect of temperature was also investigated, since effluents from the biological process are warm (45°C). Actually, a temperature increase from 25 to 45°C yielded a slightly higher COD reduction (from 21 to 28%) under the same hydrogen peroxide dosage (90% with respect to initial COD) and reaction time (60 min).

H$_2$O$_2$ + UV process: effect of hydrogen peroxide dosage

Effect of hydrogen peroxide dosage and contact time is clearly shown by results reported in Figure 3. Actually, during the second series of tests which was carried out with low COD wastewater, changing hydrogen peroxide dosage from 90% to 150% (with respect to initial COD) did not yield a remarkable improvement of COD abatement (which passed from 28% to 36%).

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**Figure 3** | Treatment of NF permeate (A) and concentrate (B) during the first series of tests (H$_2$O$_2$/UV process): effect of dilution factor on COD removal efficiency. Dos = H$_2$O$_2$ dosage; tc = reaction time.
The comparison of results obtained with plants “B” and “C”, respectively, allowed an evaluation of influence of lamp type (low or medium mercury vapour pressure). Under same treatment conditions (reaction time, hydrogen peroxide dosage, temperature), except power input (40 W/L reactor and 125 W/L reactor for plant “B” and “C”, respectively), similar results were obtained (data not shown).

In summary, chemical oxidation performance seemed to be strongly affected by wastewater characteristics; in fact, while appreciable COD removal was achieved during the first series of tests with \( \text{H}_2\text{O}_2/\text{UV} \) process, worst results were in general obtained with ozonation and with the second kind of wastewater submitted to \( \text{H}_2\text{O}_2/\text{UV} \) process. In this case, COD removal did not exceed 36%; actually, a slight increase of NF-concentrate biodegradability was observed: \( \text{BOD}_5/\text{COD} \) ratio passed from 5% to 15%; this is also confirmed by OUR measurements carried out before (measured values in the range 0.7–1.6 mgO\(_2\)/gVSS/h) and after (measured values in the range 1.9–2.9 mgO\(_2\)/gVSS/h) chemical oxidation with plant “B” (second series of tests).

**Figure 4** | Chemical oxidation of NF concentrate (A: \( \text{H}_2\text{O}_2/\text{UV} \) process; B: ozonation): minimum performance to be reached in order to achieve economic sustainability.

**Figure 5** | Chemical oxidation of NF permeate (A: \( \text{H}_2\text{O}_2/\text{UV} \) process; B: ozonation): minimum performance to be reached in order to achieve economic sustainability.
ECONOMIC CONSIDERATIONS

While in some cases good results (in terms of COD removal) were obtained by the application of chemical oxidation, sometimes treatment of wastewater yielded unpredictable and not satisfactory performance.

Since the Company already owns equipments for possible installation of chemical oxidation (which might be run up with a minimum investment effort), an economic evaluation of operating costs was required in order to evaluate if chemical treatment can be in any case considered an interesting solution for the studied facility. Economic calculations illustrated in “materials and methods” section allowed plotting graphs reported in Figures 4 and 5: curves represent the economic equivalence conditions between chemical oxidation and activated carbon adsorption (which is currently installed). Obtained results satisfy convenience criteria only in some cases: hence, in practical application, once the oxidation plant was installed, this algorithm could be a useful tool in order to decide, day by day, if chemical oxidation might be convenient and which flow (permeate or concentrate) should be treated.

CONCLUSIONS

The real case of a waste treatment facility was studied in this work. Possible application of chemical oxidation (ozonation and H₂O₂/UV process) in order to improve the performance of membrane-thermophilic biological process was investigated. Several experiments were carried out for testing chemical oxidation efficiency under different operating conditions; both the effluents of NF step (concentrate and permeate) were submitted to chemical oxidation. While in some cases good results (in terms of COD removal) were obtained, in other cases, treatment of wastewater yielded unpredictable and not satisfactory performance. Actually, chemical oxidation efficiency appeared to be strongly affected by wastewater characteristics and these can vary remarkably depending on fed wastes and performances of upstream treatments. Nevertheless, an economic evaluation of operating costs showed that chemical oxidation can be a suitable solution although high performances can not be continuously achieved. A graphical representation of minimum efficiency to be reached so as to ensure economic feasibility was developed in order to allow plant manager to evaluate, day by day, the convenience of applying chemical oxidation.

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REFERENCES