Treatment of high strength aqueous wastes in a thermophilic aerobic membrane reactor (TAMR): performance and resilience

Maria Cristina Collivignarelli, Alessandro Abbà, Giorgio Bertanza and Giacomo Barbieri

ABSTRACT

In the present work, the thermophilic aerobic membrane reactor technology was studied for the treatment of high strength aqueous wastes mainly containing dyes, surfactants and solvents. The thermophilic biomass resilience and the process stability under critical conditions (such as rapid rise of the mixed liquor pH, oxygen supply interruption, etc.) were also evaluated. The experimental work was carried out with the use of a pilot plant at semi-industrial scale, which was managed throughout for 14 months; the operation temperature was 49 °C and the organic loading rate was increased from 3 to 12 kgCOD m⁻³ d⁻¹. Critical conditions, especially the interruption of oxygen supply, affected the pilot plant performance but did not cause a complete system break down. After the temporary reduction of process performance, also proven by the decrease in the oxygen consumption, the normal working conditions were restored. Moreover, the longer non-aerated phase involved a significant reduction (40%) of volatile suspended solids concentration in the biological reactor and the increase of 30% in foaming power; nevertheless, once the oxygen supply was reactivated, optimal conditions were rapidly restored. Therefore, the study showed the high resilience of the thermophilic biomass, which was able to recover full functionality after critical events.

INTRODUCTION

Generally, aqueous wastes contain specific substances that can not be treated with conventional (biological) wastewater processes due to toxicity effects, and, therefore, chemical and physical processes shall be preferred (Ahmed et al. 2017). In this study, three different kinds of high strength aqueous wastes with remarkable concentration of dyes, surfactants and solvents were treated. The main issues related to the treatment of colored waste concern biological resistance of strong dyes and toxicity of organic compounds (Joshi et al. 2004). The removal of surfactants with conventional biological process is difficult due to their toxic effects and foam formation at high concentrations (Dhouib et al. 2005). Also chlorinated organic solvents and aromatic solvents are known to involve several problems in biological systems (Ma et al. 2016). For treating such aqueous wastes, the most commonly applied systems are physical processes (activated carbon, membrane filtration), conventional and advanced chemical oxidation (Fenton, photo-Fenton) and electrochemical processes (Rodríguez et al. 2005; Tian et al. 2012; Hayat et al. 2015; Ahmed et al. 2017; Collivignarelli et al. 2017c; Moreira et al. 2017). However, the main disadvantages of chemical treatments rely on their high operating costs compared to biological processes (Zangeneh et al. 2015). Therefore, several biological technologies have been developed in recent years for aqueous waste treatment (Mutamim et al. 2013; Pajoumshariati et al. 2017). Among these, the thermophilic aerobic membrane reactor (TAMR) is able to treat organic and inorganic compounds (Visvanathan et al. 2007; Collivignarelli et al. 2015a). In previous studies, the authors demonstrated the potential of this technology for the treatment of high strength wastewater (Collivignarelli et al. 2014) and municipal sewage sludge.
(Collivignarelli et al. 2015b, 2017a, 2017b), also in combination with chemical oxidation (Bertanza et al. 2010).

In addition to investigating the treatability of the target aqueous wastes, the present experimentation assessed the resilience of the thermophilic biomass to external perturbations (i.e. pH increase, oxygenation interruption, trouble to the electro-mechanical equipment of the pilot plant) and its capacity of adaptation to different conditions (organic loading rate – OLR – increase).

Based on the experimental results, a TAMR plant at full-scale (similar to the one described in Collivignarelli et al. 2015c) is being realized, in order to improve the aqueous wastes pretreatment section in an industrial wastewater treatment plant (WWTP) in Northern Italy.

**METHODS**

The experimental research was divided into four phases and several aqueous wastes were treated, including light and high strength wastes containing dyes, surfactants and solvents.

During the whole experimentation, the operative conditions adopted for the semi-industrial scale plant were the same as the TAMR design at full-scale.

**The industrial WWTP**

The full-scale treatment plant where the research was conducted is located in northern Italy. It consists of three main units (Figure 1). The first one (Unit I) is devoted to the aqueous waste pretreatment and includes storage-equalization tanks, microscreening and grit removal (only for septic tank wastewater) and two parallel chemical-physical treatment lines (coagulation, flocculation and sedimentation). The second unit (Unit II) consists of an activated sludge plant (predenitrification scheme) for the joined treatment of pretreated aqueous wastes and urban wastewater. The third unit (Unit III) includes the treatment of chemical and biological sludge derived from the two previous units.

Unit I is being upgraded by adding a TAMR plant, in order to make it possible to feed high strength aqueous wastes which treatment at present is not authorized.

**Figure 1** | Flow scheme of the industrial WWTP.
Pilot plant description and settings

The pilot plant (Figure 2) was placed in the facility described in the previous paragraph and consists of a biological reactor (1 m³ volume), which is thermally insulated to keep a constant temperature (49 °C), and an ultrafiltration unit (vessel), consisting of seven tubular ceramic membranes (300 kDa molecular cut-off, 10 nm nominal pore size). The plant includes a mixed liquor recirculation line, equipped with temperature control and oxygen supply devices, two storage tanks for the inlet wastewater and the effluent permeate, two filters (nominal pore size 1.5 mm) placed on the mixed liquor recirculation line and the ultrafiltration line, a control panel and a display that instantly shows the dissolved oxygen (DO) concentration and the temperature. During the whole experimentation, the extraction of thermophilic sludge was not carried out. The DO concentration is measured by a probe placed in the biological reactor, the operative conditions were set based on the design parameters of the full-scale facility under construction: the DO concentration between 2 and 6 mg L⁻¹, hydraulic retention time (HRT) = 5 d. The plant configuration and the geometrical characteristics of TAMR are described in Collivignarelli et al. (2017b).

The aqueous wastes

Table 1 shows the chemical-physical characteristics of the aqueous wastes (A.W.) that were mixed and fed to the TAMR plant. For each category, different aqueous wastes were analysed. Light strength wastes (landfill leachate and aqueous wastes deriving from chemical factories) can be characterized by gross parameters such as chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP). High strength colored wastes were derived from both the chemical-pharmaceutical and dyeing-producing sectors, while the two remaining wastes, characterized by high surfactant (non-ionic TAS, tetrakis active substances, anionic methylene blue active substances, MBAS, and total surfactants) or solvent concentrations, were produced by chemical factories. The different kinds of aqueous wastes were mixed together in such an amount that the chosen OLR value could be obtained and diluted with urban wastewater if necessary.

Experimental program

The experimentation was carried out over a 14 months period. During the first phase, only light strength wastes were fed in order to investigate their thermophilic biological
treatability and to assess the biomass response to sudden pH variations of the mixed liquor (this was the first type of perturbation that we wanted to evaluate). During this phase, actions to be carried out for restoring normal working conditions were identified. Colored wastes were fed during the second phase, which was focused on assessing the behavior of the system after the switching-off of oxygen supply (for 7 consecutive days): this is the second type of critical situation studied. During the third phase, surfactant wastes were treated and power suspension was the investigated critical situation. For 3 days, oxygen supply, mixed liquor recirculation and temperature control were interrupted. Solvent wastes were treated during the last phase, where the second type of trouble was simulated for 14 days. In this case, the biomass resilience under most adverse condition was verified.

During each period, the OLR was progressively increased from $3 \text{ kgCOD m}^{-3} \text{ d}^{-1}$ (this is the lower limit to ensure the autothermal conditions) up to $12 \text{ kgCOD m}^{-3} \text{ d}^{-1}$ in order to assess the response of the biomass to the joined effect of the occurrence of a critical condition and the influent load increase. The OLR growth was obtained by means of the gradual increase of COD concentration in the inlet substrate (due to the increase of aqueous waste amount in the feeding tanks).

We want to underline that the critical conditions for investigation were selected together with the operation staff and the manager of a real scale facility where a similar technology is used (Collivignarelli et al. 2015c). These conditions are considered to be representative of typical troubles having a significant probability to occur during the normal operation of such plants. The experimental program is summarized in Table 2.

### Table 1 | Characteristic of industrial aqueous wastes fed

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Light strength wastes</th>
<th>Colored wastes</th>
<th>Surfactant wastes</th>
<th>Solvent wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5</td>
<td>5.9</td>
<td>11</td>
<td>3.6</td>
</tr>
<tr>
<td>Electrical cond. [mS cm$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>110</td>
</tr>
<tr>
<td>COD [mg L$^{-1}$]</td>
<td>64,800</td>
<td>52,800</td>
<td>89,250</td>
<td>280,600</td>
</tr>
<tr>
<td>TN [mg L$^{-1}$]</td>
<td>4,280</td>
<td>70</td>
<td>60</td>
<td>2,591</td>
</tr>
<tr>
<td>N-NH$_4^+$ [mg L$^{-1}$]</td>
<td>329</td>
<td>n.a.</td>
<td>n.a.</td>
<td>584</td>
</tr>
<tr>
<td>N-NO$_3^-$ [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>29</td>
</tr>
<tr>
<td>N-NO$_2^-$ [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.5</td>
</tr>
<tr>
<td>TP [mg L$^{-1}$]</td>
<td>142</td>
<td>250</td>
<td>314</td>
<td>92</td>
</tr>
<tr>
<td>Total surfactants [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>TAS [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>MBAS [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Methylene chloride [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Chloroform [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Acetone [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ethyl acetate [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Isopropanol [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>t-Metilpropanol [mg L$^{-1}$]</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

n.a., not available; A.W., aqueous waste.

We want to underline that the critical conditions for investigation were selected together with the operation staff and the manager of a real scale facility where a similar technology is used (Collivignarelli et al. 2015c). These conditions are considered to be representative of typical troubles having a significant probability to occur during the normal operation of such plants. The experimental program is summarized in Table 2.

### Monitoring plan and analytical methods

During the experimentation, temperature, DO and ultrafiltration unit pressure gauges were monitored. The first two parameters were continuously measured by means of a probe (Endress + Hauser Oxymax W COS31), whereas the pressure was measured daily and the transmembrane pressure (TMP) was calculated (as the difference between the average pressure of feeding side and the permeate side) in order to keep ultrafiltration fouling under control. The sampling points were inlet (IN), mixed liquor and permeate (OUT). COD, N-NH$_4^+$, N-NO$_3^-$, N-NO$_2^-$, TN, total surfactants, non-ionic surfactants (TAS), anionic surfactants (MBAS) and electrical conductivity were measured, according to Italian standard methods APAT & IRSA-CNR (2003).
TP was analyzed by an inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer Optima 8300) and pH with a WTW Sentix 940-3 probe. Solvent concentration was analyzed by a gas chromatograph (GC PerkinElmer Autosystem XL GC) with headspace injector. All these parameters were monitored in the mixed liquor and in the permeate (OUT) three times a week. The inlet substrate was analyzed every feeding step (equal to 5 days).

Furthermore, the monitoring of DO concentrations in the biological reactor (automatically recorded) was carried out with the aim to evaluate the biomass activity. This measurement allows comparison of the OUR (oxygen uptake rate) of thermophilic biomass in the optimal working conditions and in the critical events. Other respirometric tests were performed for the measurement of the readily biodegradable COD fraction (RBCOD) on the inlet and outlet samples, using both thermophilic and mesophilic biomass (the last coming from the biological reactor of the full-scale WWTP). These tests were performed weekly, following the methodology proposed by Ziglio et al. (2001).

In order to estimate the effects of critical conditions on biomass characteristics, the foaming power (FP) was determined according to Nakajima & Mishima (2005). This test was performed to evaluate any foam problem related to critical events (this parameter was monitored before and after malfunction conditions).

### RESULTS AND DISCUSSION

#### Overall organic matter removal efficiency

The average COD input and output concentrations were equal to 29,300 mg L\(^{-1}\) and 7,300 mg L\(^{-1}\) respectively, throughout the experimentation. The permeate COD was affected by both the OLR and the simulated troubles occurrence (critical events), whose influence is described in the following sections. The correlation between the OLR and the organic removal rate (ORR) is shown in Figure 3 for the different waste categories. As for the light wastes, high COD removal yields were achieved for an OLR as high as 5 kg COD m\(^{-3}\) d\(^{-1}\). For the colored wastes the removal efficiency was around 72% notwithstanding the increase of OLR value up to 6.5 kg COD m\(^{-3}\) d\(^{-1}\), thus showing a great process stability. Very good performances were also measured for both surfactant and solvent wastes: even at very high OLR (up to 12 kg COD m\(^{-3}\) d\(^{-1}\)) the COD removal yield did not decrease below 68%. It is worth noting that the OLR was much greater compared to the typical values adopted for the mesophilic membrane biological reactor (MBR) process (0.4–1.3 kg COD m\(^{-3}\) d\(^{-1}\); Domínguez et al. 2012). As a general outcome, high process and effluent quality stability were observed all along the experimentation.

#### Light wastes

As reported earlier the pilot plant was effective in treating this kind of waste up to a given OLR. These wastes were actually already pretreated in the chemical-physical line (Unit I) at the industrial WWTP. The results will be used for deciding, case by case, the optimal treatment chain to be adopted (either chemical-physical or TAMR) in the full-scale plant, depending on the economic aspects (which were out of the scope of the present work).

#### Colored wastes

In this case, we wanted to verify the waste treatability using the TAMR process because it is well known that dyes may cause toxic effects on conventional aerobic biomass as well as produce harmful reaction byproducts (aromatic amines) (Aravind et al. 2010). Indeed, despite a good COD removal rate (see earlier), only a poor color removal, mainly due to ultrafiltration, was achieved (data not shown). Possible membrane fouling did not occur. However, the tested conditions were much more drastic than expected in the future full-scale application. In the latter, aqueous waste will be fed to the TAMR unit only after chemical-physical pretreatment in the existing facility (Unit I).
Surfactant wastes

Table 3 shows non-ionic surfactants (TAS) and anionic surfactants (MBAS) influent and permeate average concentrations, removal yields and relative standard deviations (std. dev.).

The average removal yields of MBAS and TAS were 92% and 36%, respectively, so that the effluent concentration was always below 90 mg L$^{-1}$ (except one case).

In particular, the TAMR process showed a good performance even with high OLR: 89% and 43% removal yield for MBAS and TAS, respectively, with OLR = 12 kg$_{\text{COD}}$ m$^{-3}$ d$^{-1}$.

Solvent wastes

Table 4 shows the minimum and maximum concentration of solvents in the influent and permeate and the average
removal yields (with std. dev.). All solvents were removed with high efficiency, especially methylene chloride (92%), isopropanol (87%) and 1-metilpropanol (91%). Indeed, it was supposed that stripping contributed to solvents removal due to the high temperature and turbulence (induced by oxygen supply) rather than biodegradation (Collivignarelli et al. 2014; Priya & Philip 2015). For example, methylene chloride has a boiling point 39 °C and the water solubility decreases at high temperature. However, this has not to be considered as a negative aspect because the TAMR process at the full-scale will be closed and the exhaust gas conveyed to a proper treatment unit for organics (thermos-catalytic) destruction.

**Process resilience to critical events**

During the whole experiment, stress conditions were created in order to study the thermophilic biomass resilience. In addition, the ultrafiltration unit was not damaged due to the malfunction conditions and it showed TMP (between 0.2 and 0.5 bar) always lower than critical value (corresponding to a fouling grade that could compromise the optimal membrane operation) equal to 1 bar. In Figure 4, the input and output COD concentration patterns are reported, together with the mixed liquor pH. Critical events are also evidenced. The following can be observed:

- First critical event: a rapid rise of the mixed liquor pH (up to 9.5) was caused by injecting a basic reagent (sodium hydroxide) into the mixture feed. The OLR was also increased, resulting in a reduction of the process performance, which led to permeate COD increase and oxygen utilization reduction. After pH adjustment to 7 (with nitric acid) and the temporary suspension of waste feeding (for 7 days), normal working conditions were restored. The reduction of process performance is also

<table>
<thead>
<tr>
<th>Solvents</th>
<th>IN Average concentration [mg L⁻¹]</th>
<th>OUT Average concentration [mg L⁻¹]</th>
<th>Removal yield [%]</th>
<th>Std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene chloride</td>
<td>40 – 194</td>
<td>1.5 – 20</td>
<td>92</td>
<td>0.16</td>
</tr>
<tr>
<td>Chloroform</td>
<td>284 – 1,893</td>
<td>5 – 503</td>
<td>75</td>
<td>0.21</td>
</tr>
<tr>
<td>Acetone</td>
<td>189 – 993</td>
<td>107 – 260</td>
<td>65</td>
<td>0.16</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>162 – 2,129</td>
<td>68 – 617</td>
<td>64</td>
<td>0.09</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>800 – 1,576</td>
<td>38 – 171</td>
<td>87</td>
<td>0.06</td>
</tr>
<tr>
<td>1-Metilpropanol</td>
<td>1,029 – 3,512</td>
<td>70 – 363</td>
<td>91</td>
<td>0.03</td>
</tr>
</tbody>
</table>
proven by the trend of DO concentration. The results are reported in Figure 5, which show the oxygen consumption rate before the critical event (a), during malfunction condition (b) and after restore operation (c). In particular, an increase in pH led to a reduction of 70% in OUR values, compared to the average (2.5 mgDO gVSS\(^{-1}\) L\(^{-1}\) in optimal working conditions). Moreover, no foaming problem was found.

- Second critical event: the same trouble (interruption of oxygen supply) was recreated over a short and a long period. In both cases, the negative effect was clear: variation of the mixed liquor pH and increase of the COD concentration of the permeate. During the longer non-aerated phase, the reduction of 40% in volatile suspended solids (VSS) concentration in the biological reactor and the increase of 30% in FP (with respect to the value measured in the optimal working conditions equal to 500 mL L\(^{-1}\) air), identify a hydrolytic effect of biomass, according to Collivignarelli et al. (2017b); nevertheless, once the oxygen supply was switched on again, optimal conditions were rapidly restored.

- Third critical event: the power suspension did not cause any reduction in process performance or modification of biomass characteristics in either respirometric activity or foaming issue. Supplementary operations were therefore not necessary and the most important operating parameters (pH and temperature) were not significantly modified.

In short, we could verify that when restoring normal operating conditions after the occurrence of a critical
event the thermophilic biomass was able to rapidly reactivate its optimal performance, thus showing its high resilience.

**Experimental insights**

Two additional crucial aspects were investigated in this work: the excess sludge production and the modifications of wastewater biodegradability after TAMR treatment.

As for the first point, specific sludge production was calculated both in the whole experimental period and in the different phases, based on VSS accumulation (measured in the biological reactor) in relation to the amount of COD removed. A low specific sludge production was observed compared to other biological treatments (Table 5), and this is recognized as a very important advantage (Simstich et al. 2012; Collivignarelli et al. 2015a). During the first two phases the lowest sludge production of the whole experimentation was observed: 0.03 kgVSS produced kg⁻¹COD removed. The average of the overall period was 0.04 kgVSS produced kg⁻¹COD removed, which is four times lower than the typical specific production of mesophilic MBR.

Finally, Table 6 shows the measured RBCOD in the inlet substrate and the permeate. These tests were carried out either with the thermophilic biomass of the TAMR pilot plant or the mesophilic biomass taken from the full-scale industrial WWTP. The average thermophilic RBCOD of the raw waste mixture was greater than the mesophilic RBCOD: this confirms that thermophilic treatment is preferable for this kind of aqueous wastes. On the contrary, the permeate RBCOD value obtained under mesophilic conditions proves the good biological treatability of the TAMR permeate in a subsequent mesophilic process (which is the situation that is being adopted in the full-scale facility).

**CONCLUSIONS**

The main outcomes of this research are the following:

- The average COD removal yield was 75%, with an OLR ranging between 3 and 12 kgCOD m⁻³ d⁻¹.
- The colored wastes did not cause inhibition of the thermophilic biomass; surfactants and solvents were removed up to efficiencies as high as 85% and 81%, respectively, even at the highest OLR values (12 kgCOD m⁻³ d⁻¹).
- The rapid increase of pH and the interruption of oxygen supply caused a worsening of the process performance and biomass quality (decrease on DO utilization rate, thus possible inhibition, and increase of foam formation). Once the optimal conditions were re-established, a rapid recovery of the typical performance was observed; instead, the temporary block of electro-mechanical devices did not represent a criticality.
- A very low specific sludge production was observed (0.04 kgVSS produced kg⁻¹COD removed) in comparison to mesophilic biological membrane reactors.

In summary, the experimentation shows the relevance of applied research in order to optimize and improve the performance of wastewater treatment facilities. The study of the TAMR process at the pilot scale and the analysis of process behavior during critical events revealed the importance for the technology scale up at the full-scale.

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REFERENCES


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