

## Treatment of winery wastewaters in a membrane submerged bioreactor

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**Abstract** Wine production is seasonal, and thus the wastewater flow and its chemical oxygen demand (COD) concentrations greatly vary during the vintage and non-vintage periods, as well as being dependant on the winemaking technologies used, e.g. red, white or special wines production. Due to this seasonal high variability in terms of organic matter load, the use of membrane biological reactors (MBR) could be suitable for the treatment of such wastewaters. MBR offers several benefits, such as rapid start up, good effluent quality, low footprint area, absence of voluminous secondary settler and its operation is not affected by the settling properties of the sludge. A pilot scale hollow fibre MBR system of 220 L was fed by adequately diluting white wine with tap water, simulating wastewaters generated in wineries. The COD in the influent ranged between 1,000 and 4,000 mg/L. In less than 10 days after the start up, the system showed a good COD removal efficiency. The COD elimination percentage was always higher than 97% regardless of the organic loading rate (OLR) applied (0.5–2.2 kg COD/m<sup>3</sup> d), with COD concentrations in the effluent ranging between 20 and 100 mg/L. Although the biomass concentration in the reactor increased from 0.5 to 8.6 g VSS/L, the suspended solids concentration in the effluent was negligible. Apparent biomass yield was estimated in 0.14 g VSS/g COD.

**Keywords** Membrane bioreactor; water reuse; winery wastewaters

### Introduction

Wine production is seasonal, and thus the characteristics of the wastewater generated in wineries varied with time in terms of flow and chemical oxygen demand (COD) concentrations. The wine production process is divided into two main periods: the vintage and non-vintage. During the vintage period, grapes are harvested, pressed and the juice is fermented into wine. This period lasts for a few weeks a year and most of the organic matter load and wastewater flow generated in wineries is produced during this period. In contrast, the non-vintage period is characterised by other cellar activities, such as stabilisation, filtration, maturation, blending and bottling (van Schoor, 2000). During the non-vintage period, both the wastewaters flow and the COD concentrations are relatively low. These variations in flow and COD content of the wastewater produced in wineries should be taken into account when designing their treatment.

The treatment and disposal of winery wastewaters represent a complex issue because of their particular characteristics. Firstly, the ratio between the readily biodegradable COD and the total COD varies from 0.3 during the non-vintage period up to 0.9 during the vintage period (Brucculeri *et al.*, 2005). Secondly, wastewater flow is not constant. In medium and large wineries, 50% of the total flow (more than 1.5 million litres per year) is generated during the vintage period, whereas for small wineries, this percentage is higher, around 80% (Chapman *et al.*, 2001). COD concentrations in winery wastewaters often range from 800 to 12,800 mg/L, with maximum values of 25,000 mg/L, depending on the harvest and processing activities (Petruccioli *et al.*, 2002). Total COD

concentrations and average flow rates of  $7.1 \pm 3.5$  g/L and  $4.6$  m<sup>3</sup>/d (with peaks up to  $24$  m<sup>3</sup>/d), respectively, during harvest period and  $6.8 \pm 4.9$  g/L and  $1.4$  m<sup>3</sup>/d, respectively, in the non-vintage period were described by Andreottola *et al.* (2005). These high fluctuations in the organic matter load significantly affect the operation of the biological systems used for their treatment.

Owing to the low nutrient content present in these wastewaters, the addition of nitrogen and phosphate sources is recommended for their biological treatment (Kalyuzhnyi *et al.*, 2001). Urea ( $0.11$  g urea/g COD) and orthophosphoric acid ( $0.018$  g H<sub>3</sub>PO<sub>4</sub>/g COD) were added to a sequencing batch biofilm reactor in order to guarantee the process of cellular systems (Andreottola *et al.*, 2002).

Several biological systems have been used for winery wastewater treatment, either anaerobic or aerobic. Anaerobic processes do not require oxygen and therefore the energy requirements and sludge production is much less than in aerobic treatment, making the process simpler and cheaper (Rajeshwari *et al.*, 2000). However, anaerobic systems are less efficient than aerobic processes in terms of COD removal and they could be affected by variations in the organic loading rate (OLR). Implementation of conventional anaerobic treatment (especially in countries with cold climate) is often hindered by the necessity of maintaining an operational temperature higher than ambient temperature (Kalyuzhnyi *et al.*, 2001). The treatment of winery wastewaters in anaerobic systems was accomplished in upflow anaerobic sludge blanket systems (UASB; Bal and Dhagat, 2001) or in anaerobic filters (AF; Oliva *et al.*, 1995).

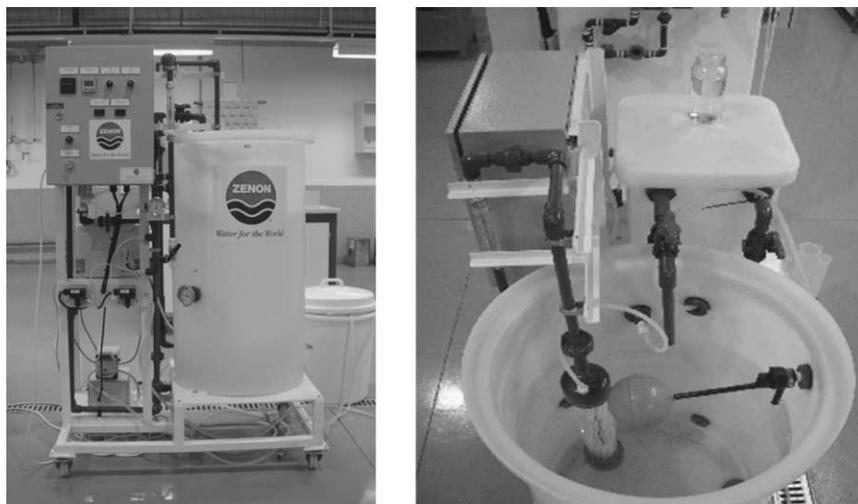
The use of conventional activated sludge systems is sometimes problematic due to the bad settling properties of the sludge. These conditions are caused by the development of filamentous bacteria or the formation of dispersed flocs, resulting in an effluent with a high solids concentration and turbidity. An alternative to these systems could be the application of sequencing batch reactor (SBR; Ruiz *et al.*, 2002). Biofilm systems, such as trickling filters, rotating biological contactors or fixed-bed reactors are also used for winery wastewater treatment (Andreottola *et al.*, 2002).

Membrane bioreactor (MBR) technology is a modification of conventional activated sludge systems, in which the secondary settler is replaced by membrane filtration units (van der Roest *et al.*, 2002). This makes feasible a good control of solids retention time (SRT) and hydraulic retention time (HRT) in the system. MBRs are not affected by the settling properties of the sludge and the use of filtration membranes makes the concentration of suspended solids in the effluent negligible. Moreover, the operation of MBR at high OLR does not affect the quality of the effluent (Rozzi and Malpei, 2003; Artiga *et al.*, 2005). Therefore, taking into account these properties of MBR systems and the variations of flow and COD concentrations in winery wastewaters, the treatment of these wastewaters in a MBR is interesting. The main objective of this research was to study the performance of a pilot scale MBR treating winery wastewater.

## Materials and methods

### Experimental setup

A pilot scale Zenon ZW-10 submerged MBR system was used during the experiments (Figure 1). In this system, a ZW-10 hollow fibre ultrafiltration membrane module was submerged in the aeration tank (220L). The membrane module had a nominal surface area of  $0.9$  m<sup>2</sup>. Aeration was provided by using a blower and the air flow rate was measured with a rotameter. Dissolved oxygen (DO) concentration in the mixed liquor was always maintained in the range of  $3$ – $4$  mg/L. The membrane module was operated in cycles of  $15$  minutes of permeation and  $45$  seconds of backwashing with permeate. A Bourdon type manometer was used to monitor the transmembrane pressure



**Figure 1** Pictures of the MBR used during the experiments

(TMP), which was always kept below 50 kPa (maximum value recommended by the manufacturer).

The reactor was inoculated with approximately 0.5 g VSS/L from an activated sludge plant and fed with a mixture of white wine and tap water. Wine with a COD of 160 g/L was diluted with tap water to achieve a soluble COD concentration of 1–4 g/L. This solution was used to create an influent with similar characteristics to the wastewaters generated in wineries (purges and washing waters). Nitrogen and phosphate sources were added as  $\text{NH}_4\text{Cl}$  and  $\text{KH}_2\text{PO}_4$ , respectively, to maintain a COD/N/P ratio of 100/5/1. The reactor was operated continuously for 50 days.

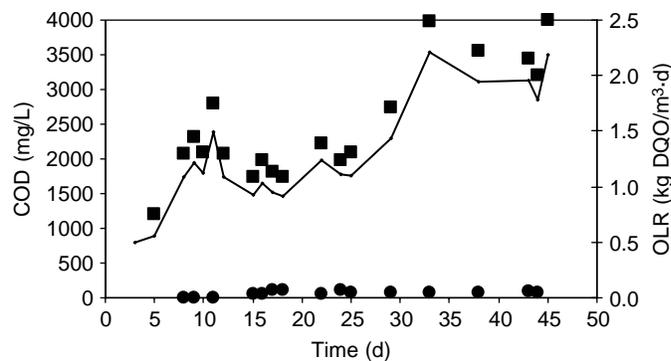
#### Analytical methods

Chemical oxygen demand (COD) was measured using an adaptation of the standard method 5,220 C (Standard Methods, 1989) proposed by Soto *et al.* (1989). Soluble COD analyses were done with filtered samples through 0.45  $\mu\text{m}$  filters. pH and DO were determined by using specific electrodes. The biomass concentrations were measured in terms of volatile suspended solid (VSS) according to the procedure described in the standard method 2,540 E (Standard Methods, 1989).

#### Results and discussion

High COD removal efficiencies were achieved in the MBR system, even a few days after the start up. MBR operated at OLR varying from 0.5 to 2.2 kg COD/m<sup>3</sup> d and the COD removal efficiency was always higher than 97%, with an average COD concentration in the effluent ranging between 20 and 100 mg/L (Figure 2). This indicates that the system was reliable with regard to OLR variations. Similar results were found by Rozzi and Malpei (2003) who indicated that organic matter removal percentage in a membrane bioreactor was not affected by the variation of OLR applied to the system or the COD concentration in the influent. Permeate flow was fixed at 5 L/h, approximately, which results in a HRT of 1.8 days.

The permeability of the membrane was tested prior to starting up the reactor by using tap water, and a value of 207 L/(m<sup>2</sup> h bar) was obtained. The membrane permeability gradually diminished during the operation of the reactor with winery wastewaters (Figure 3) due to fouling. In order to limit membrane fouling, two strategies recommended



**Figure 2** Total COD concentrations in the influent (■) and effluent (●) and OLR (–) applied to the system

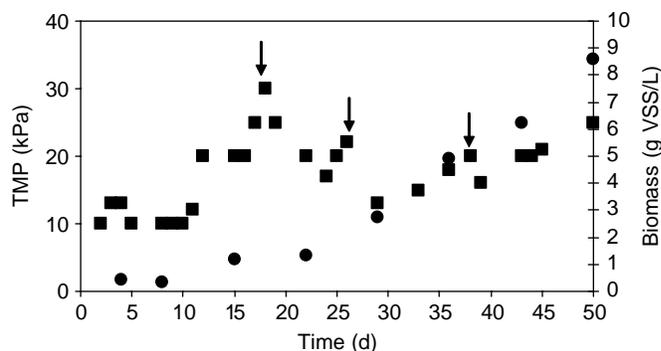
by the membrane manufacturer were employed: (1) continuous physical cleaning by using low pressure air to maintain a turbulent flow pattern along the vertical membrane fibres combined with the membranes backwashing with permeate; and (2) maintenance chemical cleaning with NaClO solution (200 mg/L). This chemical cleaning was applied for 15 minutes every 10–12 days depending on operational conditions when the TMP reached values of 20–30 kPa, and it caused a decrease of 5–10 units in the TMP (Figure 3).

Biomass concentrations in the reactor gradually increased from 0.5 to 9 g VSS/L during the 50 operating days (Figure 3). However, a permeate free of suspended solids was obtained. Biomass was not purged during the whole experimental period and its production was lower than that observed in other systems, with an apparent biomass yield of 0.03–0.08 g VSS/g COD. The maintenance of high biomass concentrations in the reactor negatively affected both the membrane permeability and the oxygen transfer capacity in the system, especially when VSS content is higher than 8 g VSS/L.

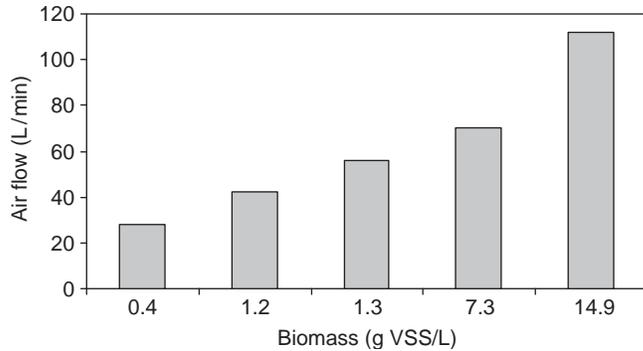
Figure 4 shows that higher air flow rates were required to maintain the dissolved oxygen concentration in the MBR around 4–6 mg/L when the biomass concentration increased until values of  $8 \pm 4$  g VSS/L.

For that reason, maintenance chemical cleaning was done more frequently during the last experimental period when the biomass concentration in the reactor increased. The same effect was found by other authors (van der Roest *et al.*, 2002; Cornel and Krause, 2003), who suggested that operation of these systems should be accomplished with biomass concentrations around 10–15 g VSS/L.

At the end of the experiment, the biomass was removed from the reactor and the membrane module was submerged in clean water. Afterwards, the membrane was subjected to



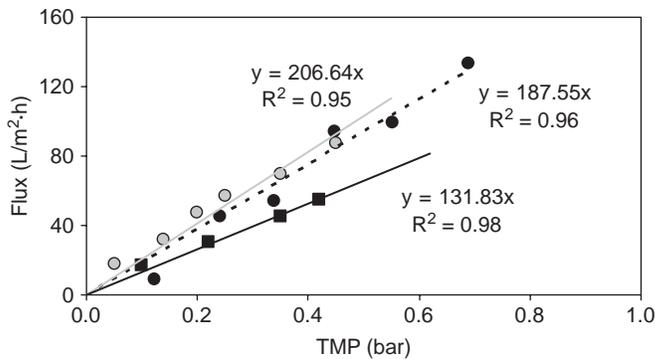
**Figure 3** TMP (■) and biomass concentrations in the reactor (●). The arrows indicate chemical cleaning with NaClO solution (200 mg/L) for 15 minutes



**Figure 4** Air flow rate versus biomass concentrations in the MBR

an intensive chemical cleaning with NaClO solution (200 mg/L) for 8 hours. The permeability was determined after cleaning with tap water and after chemical cleaning and compared with the value obtained before starting up the MBR (Figure 5). It can be observed that the permeability of the membrane module was recovered by 91% after the intensive chemical cleaning of the membrane, which indicates that the membrane was not affected by irreversible fouling. Wrong strategies of fouling control could affect the operation of the membrane module and decrease its lifetime.

A cost estimation analysis was done for the MBR on the basis of wastewater generation of 1,000 m<sup>3</sup>/d and a payback of 5 years for the capital investment (Table 1). The total annualised cost is €0.36/m<sup>3</sup> treated water, which is similar to €0.38/m<sup>3</sup> that obtained by Lubello *et al.* (2003) operating with similar MBR. This cost is very competitive when considering the treated water for some potential reuse application.



**Figure 5** Permeability of the membrane module during the experiment. Initial permeability (○), permeability of the membrane at the end of the operation after cleaning with water tap (■) and after chemical cleaning with NaClO (●)

**Table 1** Summary of general cost analysis

Investment	Description	Cost (€/d)
Capital	Civil works + reactor (550 m <sup>3</sup> )	308
	Membrane module	13
	Pumps (2 units)	2
Operational	Chemical	10
	Energy	34
Total		367

## Conclusions

The MBR showed a stable response in a short operation time. Permeate COD concentrations were lower than 100 mg/L during the whole experimental period, which leads to COD removal efficiencies higher than 97%. The increases of OLR did not affect either the operation of the MBR or the quality of the effluent. However, a more frequent maintenance clean was required when the MBR was operated at higher biomass concentrations (> 8 g VSS/L) since they cause a drop of the oxygen capacity of the reactor.

These results demonstrated the high capacity, efficiency and reliability of the MBR treating winery wastewaters. Furthermore, due to their flexibility and stability, these systems are of interest when high seasonal organic loads are applied and a high quality effluent is required, e.g. water reuse. Future cost reductions in the membrane modules, evolution of the water price (taking into account the high quality effluent obtained, it could be reused for equipment washing, landscape or agricultural irrigation) or more restrictive legal requirements will make membrane bioreactors a good alternative for wastewater treatment. However, the membrane modules lifetime and maintenance are still the problematic aspects of this technology.

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## References

- Andreottola, G., Foladori, P., Nardelli, P. and Denicolo, A. (2005). Treatment of winery wastewater in a full-scale fixed bed biofilm reactor. *Water Sci. Technol.*, **51**(1), 71–79.
- Andreottola, G., Foladori, P., Ragazzi, M. and Villa, R. (2002). Treatment of winery wastewater in a sequencing batch biofilm reactor. *Water Sci. Technol.*, **45**(12), 347–354.
- Artiga, P., Oyanedel, V., Garrido, J.M. and Méndez, R. (2005). An innovative biofilm-suspended biomass hybrid membrane bioreactor for wastewater treatment. *Desalination*, **179**, 171–179.
- Bal, A.S. and Dhagat, N.N. (2001). Upflow anaerobic sludge blanket reactor. A review. *Indian J. Environ. Health*, **43**(2), 1–82.
- Brucculeri, M., Bolzonell, D., Battistoni, P. and Cecchi, F. (2005). Treatment of mixed municipal and winery wastewaters in a conventional activated sludge process: a case study. *Water Sci. Technol.*, **51**(1), 889–898.
- Chapman, J.A., Baker, P. and Wills, S. (2001). *Winery Wastewater Handbook: Production, Impacts and Management*, Winetitles, Adelaide, Australia.
- Cornel, P. and Krause, S. (2003). State of the art on MBRs in Europe. *International Conference. Application and Perspectives of MBRs in Wastewater Treatment and Reuse*, Cremona, Italy.
- Kalyuzhnyi, S., Gladchenko, M., Sklyar, V., Kizimenko, Y. and Shcherbakov, S. (2001). One and two stage upflow anaerobic sludge bed reactor pre-treatment of winery wastewater. *Appl. Biochem. Biotechnol.*, **90**, 107–123.
- Lubello, C., Gri, R., de Bernardinis, A.M. and Simonelli, G. (2003). Ultrafiltration as tertiary treatment for industrial reuse. Water science and technology. *Water Supply*, **3**(4), 161–168.
- Oliva, L.C.H., Zait, M. and Foresti, E. (1995). Anaerobic reactor for food processing wastewater treatment established technology and new development. *Water Sci. Technol.*, **32**(12), 157–163.
- Petruccioli, M., Cardoso, J., Eusebio, A. and Federici, F. (2002). Aerobic treatment of winery wastewater using a jet-loop activated sludge reactor. *Process Biochem.*, **37**, 821–829.
- Rajeshwari, K.V., Balakrishnan, M., Kansal, A., Lata, K. and Kishores, V.V.N. (2000). State of the art of anaerobic digestion technology for industrial wastewater treatment. *Renew. Sust. Energ. Rev.*, **4**(2), 135–156.
- Rozzi, A. and Malpei, F. (2003). Perspectives of MBR use for agroindustrial wastewater treatment and reuse. *International Conference. Application and Perspectives of MBRs in Wastewater Treatment and Reuse*, Cremona, Italy.

- Ruiz, C., Torrijos, M., Sousbie, P., Lebrato, J.M., Moletta, R. and Delgenes, J.P. (2002). Treatment of winery wastewater by an anaerobic sequencing batch reactor. *Water Sci. Technol.*, **45**(10), 219–224.
- Standard Methods for the Examination of Water and Wastewater* (1989). 17th edn, American Public Health Association. American Water Works Association. Water Environment Federation, Washington DC, USA.
- Soto, M., Veiga, M.C., Méndez, R. and Lema, J.M. (1989). Semimicro COD determination method for high-salinity wastewater. *Environ. Technol. Lett.*, **10**, 541–548.
- van der Roest, H.F., Lawrence, D.P. and van Bentem, A. (2002). *Membrane bioreactors for municipal wastewater treatment*, STOWA, IWA Publishing, London, UK.
- van Schoor, L.H. (2000). Management options to minimise negative environmental impacts at wine cellars. *Wineland*, July, 97–100.