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Desalination 221 (2008) 518–525

DESALINATION

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Use of a hybrid membrane bioreactor for the treatment of saline wastewater from a fish canning factory

P. Artiga[a], G. García-Toriello[a], R. Méndez[b], J.M. Garrido[b]*

[a]*Espina & Delfín, Vía Edison 9, E-15890, Santiago de Compostela, Spain*
[b]*Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, Campus Sur, E-15782, Santiago de Compostela, Spain*
email: equenlla@usc.es

Received 17 January 2007; accepted 30 January 2007

Abstract

A new pilot scale hybrid biofilm-suspended biomass membrane bioreactor was used to treat two wastewater streams generated in a fish canning factory. During a first stage, wastewater generated during tuna cooking with brine was treated. COD and N content were between 7.8–11.8 g COD/L and 1.2–1.8 g N/L, respectively. Salt concentration was up to 84 g/L. COD removal efficiency was affected by salinity, but after 73 operating days adaptation of the sludge to the hypersaline conditions took place. COD efficiency of 92% was obtained after adaptation of the sludge to the salinity.

During a second stage, wastewaters generated during tuna cooking by steam injection were treated. HRT was fixed at 5 d. Organic loading rate was up to 4 kg COD/m^3 d. COD concentration in the permeate was lower than 100 mg/L throughout this period. Salt concentration below 15 g/L did not affect nitrification. NLR was gradually increased up to 0.7 kg N/m^3 d. Total nitrogen concentration in the permeate was lower than 100 mg N/L, and nitrate was below 65 mg N/L during the whole experimental period. Moreover, very low nitrate concentrations of less than 1 mg N/L were observed during the period in which a NLR up to 0.55 kg N/m^3 d was applied.

Keywords: Biofilm; Suspended biomass; Hybrid MBR; Saline wastewater

1. Introduction

Fish canning factories in Europe are mostly concentrated in Spain. The Spanish fish canning factories manufacture a high variety of raw materials. Tuna accounted for more than a half of the total production in this sector of industry. The main processes in tuna fish canning factories are defrosting, cooking, canning and cleaning. These processes generate different liquid streams with very different pollutant concentrations that may be segregated and treated separately, before being discharged. Among all wastewaters, tuna cooking effluents have the highest protein content.

*Corresponding author.

Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

doi:10.1016/j.desal.0000.00.000

Cooking in these factories is usually carried out either by steam injection or by immersion in brine tanks. These effluents can account to 1% of the overall flow of the factory and around 10% of the total organic load discharged [1].

Wastewater treatment of most streams generated in a fish canning factory located in Galicia (NW Spain) is done efficiently by using a dissolved air flotation system. However, COD concentration of the discharge sometimes did not fulfill the legal requirements, as result of the discharge of the cooking stream. Due to this reason, it was decided to study the application of a biological process for treating this high polluted stream. However, this factory as most of the tuna processing factories in Spain, is located beside the shore, and has very low land availability for building up a conventional biological reactor, even for treating only the cooking streams. For these reasons, a membrane bioreactor (MBR) could be used for treating such stream, due to the lower footprint requirement of MBR with regard to conventional systems.

The hybrid MBR system is characterized by the presence both of suspended biomass and biomass growing in biofilms. This system was developed by the University of Santiago de Compostela for treating wastewaters at high nitrogen and organic loading rate, and showed high removal efficiency. The high capacity of this system was obtained because the fast-growing heterotrophs grow in suspension and the slow-growing nitrifiers grow in the biofilm. Heterotrophs growing in suspension has competitive advantage over fixed biomass for COD, due to the diffusion limitations of substrates in the biofilms. Therefore biofilm growth is at a disadvantage with respect to substrate availability for heterotrophs. For this reason nitrifiers are not outcompeted in the biofilms by heterotrophs. Thus, biofilms with high nitrifying activity can be obtained, even operating simultaneously at high OLR of up to 6.5 kg COD/m^3 d and NLR of 0.8 kg N/m^3 d [2–4]. The objective of this study was to evaluate the use of the hybrid biofilm-suspended biomass MBR system for treating streams, generated during tuna cooking using either brine or steam injection processes.

2. Materials and methods

2.1. Reactor

A 0.5 m^3 hybrid MBR pilot plant was used during the study (European patent EP 1484287 B1). It was composed by three chambers: an anoxic chamber of 0.2 m^3 volume; an aerobic chamber 0.2 m^3 and a filtration chamber 0.1 m^3 connected in series (Fig. 1). The influent was fed from a 1 m^3 storage tank to the anoxic chamber of the hybrid MBR. In the aerobic chamber, biomass was maintained growing both in suspension and in biofilms. The biofilms grew on small Kaldness K-3 (Anox-Kaldness, Norway) plastic support particles that move freely in the chamber by aeration. These support particles are made of polyethylene with a density of 950 kg m^{-3}. The filling fraction of the support particles in the aerobic chamber was 20%. Three different membrane modules were tested during different periods of time:

(i) A Zenon ZW-10 ultrafiltration hollow fiber membrane module (Zenon Environmental, Canada). The ZW-10 filtration surface was

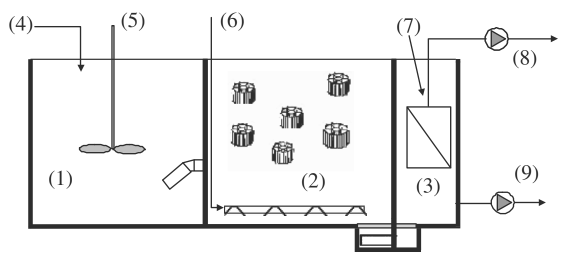

Fig. 1. Schematic of the hybrid MBR used: (1) anoxic chamber, (2) aerobic chamber with the plastic support particles, (3) membrane filtration chamber, (4) influent, (6) air spargers, (7) membrane filtration module, (8) permeate pump, (9) sludge purge pump.

a 0.04 µm pore size and had a total surface of 0.9 m^2.

(ii) An ultrafiltration hollow fiber module manufactured by Porous Fibers, Bask Country, Spain. The Porous Fibers filtration surface was a 0.4 µm pore size and had a total surface of 0.9 m^2.

(iii) An external tubular ultrafiltration X-Flow module, model 11 PE (X-Flow B.V., Enschede, The Netherlands). The X-Flow was a 0.03 µm pore size and had a total surface of 0.150 m^2 and 8.0 mm tubes.

2.2. Strategy of operation

The pilot plant was operated during around 325 days in a fish canning factory located in Galicia (NW Spain). Tuna cooking in this factory is usually carried out either by steam injection or by immersion in brine tanks. Due to this reason, the research was divided into two different stages; Stage 1, in which wastewater generated during tuna cooking in brine tanks was fed (from day 0 till day 98); and Stage 2, from day 100 till day 225, in which wastewater produced during tuna cooking with steam injection was fed. Saline concentration of the brine wastewater was higher, between 73 and 83 g/L dissolved salts, than the values observed for the steam wastewater, between 2 and 15 g/L salts (Table 1). During the first experimental stage, raw brine wastewater was fed to the system by increasing gradually the influent flow rate.

The Zenon ZW-10 membrane module was used during the first stage (till operating day 98). During the second experimental stage the three membrane modules were tested. Between days 100 and 112 the Zenon ZW-10 was tested. After day 112 this module was replaced by the porous fibers module that was used till the end of this research (day 225). The external membrane module was operated during two different periods, between days 117 and 176 and between day 218 till day 225.

Table 1
Characterisation of the two raw wastewaters employed during the study

Parameters	Brine wastewater first stage	Steam wastewater second stage
pH	6.5	
Conductivity (mS/cm)	27–89	20
Total COD (g/L)	8–12	17–26
Soluble COD (g/L)	7–11	16–25
Fats concentration (g/L)	0.5–0.7	0.7–1.7
TSS (g/L)	1.1–2.1	1–1.2
VSS (g/L)	0.7–0.9	0.9–1
Total nitrogen (g/L)	1.2–1.8	2.5–4
NH_4^+ -N (g/L)	0.4–0.7	0.2

The raw steam injection wastewater stream was diluted with a mixture of tap water and seawater, maintaining the salinity of the feeding in values similar to those observed for the raw wastewater. The percentage of the industrial influent was progressively increased during this period until day 318, when only industrial wastewater was fed to the systems. Hydraulic retention time (HRT) was maintained in 5 days, during most of the second period. This strategy was done in order to avoid nitrification inhibition by high free ammonia concentration and to study the effects of the dilution degree in the membrane permeability and fouling. The two tuna cooking streams presented high COD and N concentrations, the salinity being much higher in the brine wastewater.

2.3. Analytical methods

Samples were taken at the influent, mixed liquor and permeate of the reactor. Chemical oxygen demand (COD) was measured using an adaptation the standard method 5220 C proposed by Soto et al. [5]. Soluble COD analysis in the reactor was done with filtered samples through a 0.45 µm filter. Total nitrogen (TN) in the liquid phase was measured using a total organic nitrogen analyzer (Dohrmann DN-1900). Ammonia concentration was measured by using the phenol-hypochlorite method [6]. Nitrite and nitrate ions were determined by using spectrophotometric methods. Total suspended solids (TSS) and fats concentration was analyzed following the standard methods [7]. Turbidity was measured by using a turbidity meter (HANNA, model LP-2000). pH and dissolved oxygen (DO) were determined by using specific electrodes.

3. Results and discussion

3.1. First stage (days 0–98)

During the first stage, wastewater produced during tuna cooking with brine was fed to the system. COD concentration of the influent ranged between 7.8 and 11.8 g COD/L. One of the main characteristics of this wastewater is the high saline content, which was between 73 and 83 g/L, measured either in terms of total dissolved solids or by using a conductivity meter. The unit was inoculated with sludge from a conventional activated sludge plant diluted in tap water. HRT of the unit was gradually decreased from 20 to 5 days during this stage. The biomass in the reactor was exposed to increasing salt concentrations that rose from 1 until 43 g/L during the first 30 operating days. From day 45 on, the salinity in the reactor was between 60 and 83 g/L dissolved salts. Dissolved oxygen concentration in the reactor was controlled between 2 and 6 mg/L. Temperature of the reactor during the experiments varied between 6 and 15°C (winter season) and pH between 7.1 and 7.8.

Evolution of both COD concentration in the permeate and of the OLR applied are shown in Fig. 2. During the first 73 operating days, COD concentration in the permeate was affected by the observed increase of salinity. COD gradually increased from 500 mg/L up to 2400 mg/L in the permeate and COD removal efficiency of the unit decreased from 95 to 65%. Organic

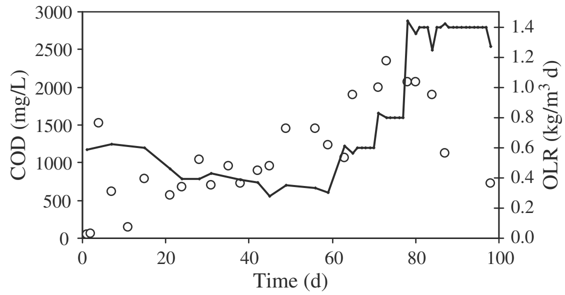

Fig. 2. Evolution of the applied OLR (¾) and COD concentration in the permeate (○) of the hybrid MBR unit.

loading rate (OLR) was maintained between 0.6 and 0.3 kg COD/m^3 d during the first 60 operating days. From day 60 on, OLR was gradually increased from 0.3 up to 1.4 kg COD/m^3 d. From day 73 on, COD in the permeate gradually diminished with time. The COD efficiency increased gradually from day 80 on, from 77 to 92%. This was obtained with the reactor operating at the highest OLR of 1.4 kg COD/m^3 d and saline concentration of 83 g/L. This indicated a possible acclimation of the sludge to the hypersaline conditions in the reactor, as was referred Lefebvre and Moletta [8] for the biological treatment of saline wastewaters. The hybrid MBR was not inoculated with halophilic microorganism cultures in order to increase efficiency of biological reactors with salt concentration above 5%, as recommended by some authors [8].

Total nitrogen (TN) in the influent was between 1.2 and 1.8 g N/L. Most of the TN was hydrolyzed to ammonia in the reactor. However, nitrification was not observed throughout the first stage. This was a result of the very high saline concentration of the wastewater, up to 83 g/L salts. Moussa et al. [9] found 36 and 95% inhibition of ammonia oxidation at NaCl concentrations of 16.5 and 65.9 g/L, respectively. Campos et al. [10] found full inhibition of nitrification around 250 mM salts for non adapted sludge during batch assays, and inhibition of nitrification above 41.9 g/L salts in a continuous system acclimated to salinity. Turbidity of the permeate, in terms of NTU, ranged between 2 and 7. Suspended solids concentration in the permeate was negligible. The suspended biomass fraction grew as dispersed biomass that did not settle. Despite that biomass in the hybrid MBR was not purged throughout this period, suspended biomass concentration in the reactor attained low values, up to 4.0 g TSS/L. A very low apparent biomass yield of only 0.03 g-VSS/g-COD was measured during this period.

The permeability of hollow fibber module used in this stage (Zenon ZW-10) sharply decreased after operating day 5, from 200 L/h m^2 bar to 50 L/h m^2 bar. It was observed that the permeability was between 50 and 20 L/h m^2 bar, from day 7 on. Permeability values observed in the first 5 experimental days were similar to those obtained with tap water. Moreover, fouling of the hollow fibers caused by inorganic scaling was observed. Precipitation of calcium phosphate was observed on the membrane surface. Moreover some small crystals of undissolved NaCl were isolated and identified on the membrane surface. NaCl crystals were also found in the suspended biomass. Fouling control was done once per week. Maintenance chemical cleaning took place approximately every week, by using 200 mg/L sodium hypochlorite (first operating days), and later by applying in different steps sodium hypochlorite and citric acid.

Membrane bioreactors could provide an adequate solution to solve the sedimentation problems encountered by other authors in either CAS or SBR systems at high salt concentrations [8]. The MBR system showed a good COD efficiency after an acclimation period of 73 days. Nevertheless, fouling cause operational problems of operation in this system, and probably a longer experimental period might be necessary in order to estimate the effects of the salts on the membrane life.

3.2. Second stage: steam injection wastewater (days 100–225)

From day 100 on, the unit was fed with the wastewater stream generated during tuna cooking by steam injection. During the first operating weeks, the raw wastewater was diluted with both seawater and tap water, maintaining the salt concentration of the influent. HRT was fixed in 5 d. This strategy had two different objectives: to avoid inhibition of nitrification by high free ammonia concentrations, and to maintain the volumetric flow treated in the hybrid MBR constant. Thus COD and TN concentration of the influent were gradually increased throughout this stage. Temperature varied between 15 and 26°C and pH between 6.8 and 7.8. Dissolved oxygen concentration in the aerobic chamber was maintained between 2 and 6 mg/L.

COD concentration in the influent and OLR were gradually increased during this stage by increasing the fraction of raw wastewater in the feeding medium (Fig. 3). COD up to 16,000 mg/L and OLR up to 4 kg COD/m^3 d were applied to the unit. COD of the permeates obtained either in the hollow fiber membrane or in the external membrane was similar. COD in the permeate was almost constant and below 150 mg/L, and was not affected by increases of both COD and OLR in the influent. Turbidity of the permeate

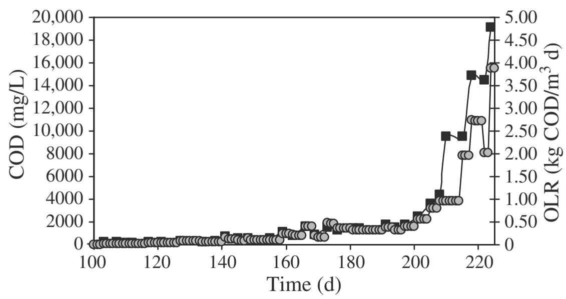

Fig. 3. Evolution of COD concentration in the influent (■) and OLR applied to the unit (●) during the second experimental stage.

was usually below 2 NTU. Analysis of treatment efficiencies showed that the permeate quality is consistently high, between 50 and 99% with COD removals that increased at increasing OLR (Fig. 4).

In the hybrid MBR, the biomass grew both in suspension and on carriers that move freely in the water volume by aeration. Between operating days 100 and 200, TSS gradually increased from 0.5 up to 2.4 g TSS/L. From day 200 till day 225, period in which the OLR was increased from 0.5 up to 4 kg COD/m^3 d, biomass concentration gradually increased up to 8.4 g TSS/L. Apparent biomass yield was around 0.12 g-VSS/g-COD throughout this stage, independently of the applied organic loading rate.

From day 100 till day 187 the anoxic chamber was aerated, in order to promote nitrification in the reactor. During this period N concentration in the influent was increased gradually from 100 to 400 mg N/L, in order to avoid nitrification inhibition by free ammonia. Salt concentration in the wastewater, below 15 g/L, did not inhibited nitrification of the wastewater. The nitrogen loading rate, NLR, was increased up to 0.08 kg N/m^3 d. Both, nitrogen ammonia or nitrogen nitrate concentration in the permeate was between 4 and 40 mg N/L. Only traces of nitrite were detected in the permeate, when the nitrification process started in the hybrid MBR.

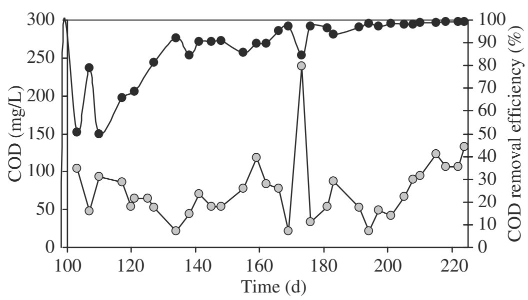

Fig. 4. Evolution of COD removal efficiency (●) and COD in the permeate (●) of the hollow fibre membrane module.

From operating day 188 on, aeration of the anoxic chamber was interrupted. This was done in order to promote denitrification of nitrogen ions formed. Between operating days 188 and 225 NLR increased gradually from 0.08 up to 0.7 kg N/m^3 d. N concentration in the influent was gradually increased from 400 up to 3400 mg N/L. The increase of NLR did not affect to the efficiency of the unit. Total nitrogen concentration in the permeate was lower than 100 mg N/L and nitrogen nitrate was below 65 mg N/L during the whole experimental period. Very low nitrate concentrations of less than 1 mg N/L were observed during the operating days 210 and 224. During this short period of time the highest NLR were applied to the unit. It is important to stress that nitrate recycled to the anoxic chamber did not account for the very high efficiency observed in the unit. The recirculation ratio was 3, and only a small amount of nitrate was recycled to the anoxic chamber as result of the very low nitrate concentration observed. This indicated that a large fraction of nitrate formed was nitrified and denitrified in the aerobic or in the membrane filtration chambers. Probably inside the biofilms denitification occurs, irrespective of aerobic conditions in both chambers.

Hybrid MBR systems may be useful to avoid the negative effects of competition between nitrifiers and heterotrophs on the efficiency and capacity of the systems. In a previous work with a Hybrid MBR, Oyanedel et al. [3] found that heterotrophs grew mainly in suspension as suspended heterotrophs has competitive advantage over fixed heterotrophs over COD. This favoured the development of biofilm with high nitrifying activity. Moreover, specific ammonia oxidation activity of the biofilm, was maintained around 0.8 g N/g-protein d (around 0.4 g N/g-VSS·d) and was not affected by the applied OLR. During the present research, determination of biomass specific heterotrophic or activities was not carried out. Nevertheless, the maximum OLR and Nitrogen removal rate attained, 4 kg COD/m^3 d and

0.55 kg N/m^3 d, were comparable to those of 3.8 kg COD/m^3 d and 0.75 kg N/m^3 d, obtained by a previous research done at laboratory scale [2]. Removal rate in terms of COD the hybrid MBR was in the range of values of 2–8 kg COD/m^3 d referred in a new biofilm MBR system, in which a biofilm reactor is combined with a MBR [11]. However, one important feature of the hybrid MBR is the high nitrogen removal capacity and efficiency.

During this stage, three different filtration membrane modules were tested. The hollow fiber ultrafiltration module was used until operating day 112, in which permeability diminished to 10 L/h m^2 bar (Fig. 5). At the operating day 113 this module was replaced by the porous fibers microfiltration module. Between days 113 and 125 permeability was between 55 and 106 L/h m^2 bar, but then gradually diminished till 10 L/h m^2 bar. The tubular external membrane was operated during two different periods: between days 117 and 176 and later during days 218–225. Till day 134, permeability was above 200 L/h m^2 bar and later decreased gradually till 100–145 L/h m^2 bar (Fig. 5). At the day 176, breakdown of the recirculation pump of the external membrane forced the stop of the module. Lower values of permeability were obtained after day 218, in which permeability of the external module decreased from 70 to only 25 L/h m^2 bar.

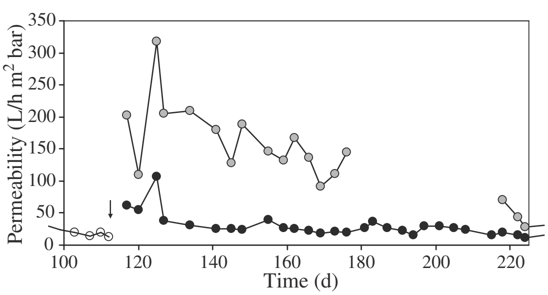

Fig. 5. Permeability of the three membrane modules employed during the second stage. Zenon ZW-10 (○), porous fibers (●) and X-Flow (●) modules. The arrow in the figure indicated the replacement of the ZW-10 by the porous fibers membrane at the operating day 113.

4. Conclusions

A new pilot scale hybrid biofilm-suspended biomass membrane bioreactor was used to treat two wastewater streams, generated in a fish canning factory. During a first stage, wastewater generated during tuna cooking with brine was treated. COD and N content were between 7.8–11.8 g COD/L and 1.2–1.8 g N/L, respectively. Salt concentration was up to 84 g/L. COD removal efficiency was affected by salinity, but after 73 operating days adaptation of the sludge to the hypersaline conditions took place. COD efficiency of 92% was obtained after adaptation of the sludge to the salinity. OLR up to 1.4 kg COD/m^3 d was applied. Total nitrogen (TN) in the influent was between 1.2 and 1.8 g/L. Most of the TN was hydrolyzed to ammonia in the reactor. However, nitrification was not observed throughout the first stage. This was a result of the very high saline concentration of the wastewater. Fouling cause operational problems of operation in this system, and probably a longer experimental period might be necessary in order to estimate the effects of the salts on the membrane life. Biomass yield of only 0.03 g-VSS/g-COD was estimated.

During a second stage, the wastewater generated during tuna cooking by steam injection was treated. HRT was fixed at 5 d. One of the main characteristics of the hybrid MBR is the high capacity and efficiency that were obtained, even considering that biomass concentration was below 2–4 g TSS/L throughout most of the period. Organic loading rate was up to 4 kg COD/m^3 d. COD concentration in the permeate was lower than 100 mg/L. Salt concentration below 15 g/L did not affect nitrification. NLR was gradually increased up to 0.7 kg N/m^3 d. Total nitrogen concentration in the permeate was lower than 100 mg N/L, and nitrate was below 65 mg N/L during the whole experimental period. Moreover, very low nitrate concentrations of less than 1 mg N/L were observed during the period in which a NLR up to 0.55 kg N/m^3 d was applied. Biomass yield during this period was around 0.12 g-VSS/g-COD.

Acknowledgements

To the "Consellería de Innovación, Industria e Comercio, Xunta de Galicia" that funded this research through the project PGIDIT05TAM013E and especially to Jacobo Bouzada and Sonia Barros, personnel of the consulting company of engineering "3R Ingeniería Ambiental" for the technical assistance that made feasible this project.

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