Desalination and Water Treatment
www.deswater.com

35 (2011) 131–137
November

doi: 10/5004/dwt.2011.3132

Cycling batch vs continuous enrichment of endogenous nitrifiers in membrane bioreactors treating petrochemical wastewater

Silvia Di Fabio[a,*], Cristina Cavinato[b], David Bolzonella[a], Giuseppe Vecchiato[c], Francesco Fatone[a]

[a]*Department of Biotechnology, University of Verona, Strada Le grazie 15, I-37134 Verona – Italy*
Tel. /Fax: +39 (045) 8027965; email: silvia.difabio@univr.it
[b]*Department of Environmental Sciences, University of Venice, Calle Large Santa Marta, Venice – Italy*
[c]*Simagest srl, Via della Chimica 5, Porto Marghera, Venice-Italy*

Received 28 November 2010; Accepted 06 June 2011

ABSTRACT

Petrochemical wastewater treatment is a new sector for the possible widespread application of membrane bioreactor technology. In this field, hard to degrade compounds such as amines and nitrogen residuals were generally the major issues. In addition, over the last years the irregular operation of the manufacturing plants involved drastic variability of the wastewater's loadings and characteristics, so as to call for more flexible schemes of the treatment plants. This paper compares two different schemes of a continuously fed membrane bioreactor to adequate the nitrification potential to the influent loadings. These are: a) controlled and continuous external ammonia dosage; b) sequencing batch nitrifier enrichment. On the basis of lab and pilot-scale treatment of real petrochemical wastewater, the cyclic batch enrichment process proved to be reliable, cost-effective, and easy to control, being more flexible with respect to changeable influent loadings.

Keywords: Membrane bioreactor; Petrochemical wastewater; Nitrification; Batch and continuous

1. Introduction

Oil refinery sector is using large amount of water in different processes (i.e., desalting, distillation cracking) and in cooling systems. Mineral oils and hydrocarbons are the main pollutants found in wastewater generated by refineries, while other major pollutants are hydrogen sulphide, ammonia, phenols, benzene, cyanides and suspended solids containing metals and inorganic compounds (e.g., halides, sulphates, phosphates, sulphides) [1]. Where refineries are associated with chemical manufacturing complexes a wide and variable range of chemical components can be present in addition to the compounds arising from oil processing [2]. In particular, spent caustic and other hazardous wastes may be generated in significant quantities.

Currently wastewater from petrochemical industries is usually treated by conventional activated sludge processes with specific pretreatments dedicated to oil/water separation and, frequently, clari-flocculation for metals removal [3]. Although biological systems are capable of removing many of the dissolved organic carbons, some recalcitrant components are not adequately eliminated (i.e., amines and nitrogen residuals) in conventional processes. Moreover petrochemical wastewater can contain many substances toxic for the biological processes: in particular nitrification may be, directly or indirectly, inhibited by a compounds as phenols, benzene, heavy metals [4]. In addition, problems of biological foaming may arise [5]. At this regard membrane bioreactor

*Corresponding author.

(MBR) was recently proposed as a technology adequate to treat wastewaters from refineries and petrochemical industries. Tightening effluent regulations and increasing need for reuse of treated water have generated interest in the treatment of petrochemical wastewater with the advanced MBR process [3]: this fact is demonstrated by the growing number of MBRs in petrochemical sites [6,7]. Hence research into using this technology in these industrial sectors is at the forefront of the state-of-the-art in this area [6].

MBRs offer several advantages when compared to conventional activated sludge processes, e.g., smaller footprint (i.e., more compact installations unlike secondary clarifiers), high sludge ages (i.e., up to 300 d), and less sludge production [8,9]. Since the membrane in MBR replaces the clarifier of a conventional activated sludge process (CASP) with an ultimate barrier for biomass control and solids separation is achieved by means of filtration rather than gravity settling, the quality of the effluent is not dependent on mixed liquor suspended solids (MLSS) concentration and characteristics (i.e., settleability), and it is not affected during events that can upset the biological process. A MBR system is a highly effective treatment process and is especially recommended for wastewater treatment in areas requiring a high quality effluent (i.e., discharge to bathing waters or for water reuse) [10–14] or when dealing with high strength liquors that require effective nitrification [15].

Up to the 80s the petrochemical productions were mostly located in the USA and Europe; but in recent years the major industries were located in the Middle East and Asia. Consequently, large petrochemical wastewater treatment plants in Europe and USA initially designed to treat regular continuous loadings, stable in terms of quality and quantity, are now receiving wastewaters with very variable loadings and characteristics, both due to seasonal and irregular industrial production.

This present scenario calls the researchers to deal with the set-up and validation of flexible schemes and operations of the wastewater treatment plants.

This paper compares two possible MBR's schemes that can cope with such a variable petrochemical inlet and set up to increase the nitrification potential of the reactor. In particular, the external ammonia dosage in a conventional multizone anoxic-aerobic continuously MBR was analyzed and compared to a cyclic batch enrichment of endogenous nitrifiers, thus hybridizing the bioreactor.

The first part of the paper deals with the main chemical-physical characteristics of the industrial wastewater and the long term impact on all the configurations being tested. The second part deals with a direct comparison between the two different aforementioned plant's schemes. Finally, the technical feasibility of these two approaches is discussed on the basis of both lab-scale batch tests and pilot studies.

2. Materials and methods

2.1. The pilot-scale membrane bioreactor

The pilot plant had a total reactor volume of 4.7 m^3 divided into four compartments, the first one of which is available for the cyclic batch growth of endogenous nitrifiers while the next two are fed in a continuous predenitrification-nitrification scheme. The last compartment contains the membrane filtration unit itself (Figs. 1a and 1b). The ultra filtration (UF) system was equipped with a ZeeWeed 230 hollow fibre submerged membrane module with filtration area of 21.7 m^2. It was operated continuously using an automatic control system under a combined filtration cycle that included forward permeation/relaxation steps followed by forward permeation/backwashing steps run on a three-to-one sequence of repetitions.

On start up the pilot MBR was seeded with activated sludge from a full scale MBR plant that treated a petrochemical wastewater. The pilot was then operated continuously for two years using real petrochemical wastewater in order to investigate the best possible strategies to use when trying to improve the nitrifying performance of this plant.

Two different approaches were investigated to allow increases in the nitrification potential of the MBR activated sludge. In the first approach, external ammonia was dosed into the continuously fed influent line (Fig. 1a) while in the second approach, the further enrichment of nitrifiers was obtained by running periodic cyclic batches: endogenous nitrifiers were periodically grown in a separate batch reactor and cyclically fed to the MBR reactor (Fig. 1b).

2.2. Continuously-fed strategy

The aim of the first experiment was to investigate any increase in the nitrification potential following gradual stable increases of influent flow rate and specific loadings during continuous operation. At this regard three runs were carried out.

During the first run of the pilot MBR plant, it was continuously operated according to the same specific loadings of the parallel full scale MBR. Under the subsequent Runs 2 and 3, the influent flow rate was increased in order to allow an almost doubling of the specific NLRs (Table 1).

Daily composite samples of influent wastewater and permeate were taken and analyzed using standard methods such as ion chromatography (e.g., Dionex AG14 and AS14 columns) in order to ascertain the concentration of the major biochemical parameters (i.e. pH, alkalinity, COD, sCOD, rbCOD, TKN, $N–NH_4$, $N–NO_2$, $N–NO_3$, TSS, TP, $P–PO_4$). The activated sludge was analyzed for MLSS, mixed liquor volatile suspended (MLVSS) and the specific nitrification rates (SNRs).

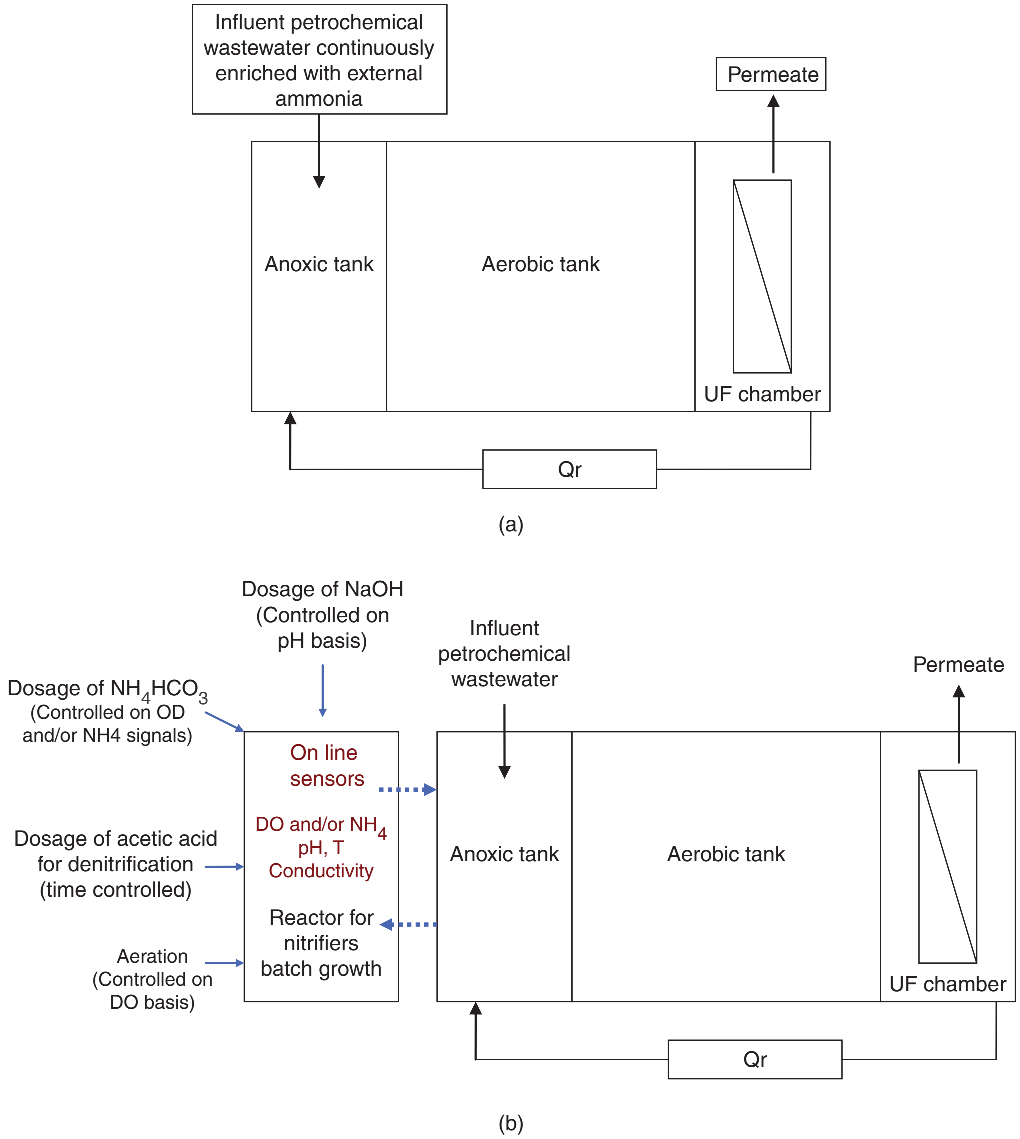

Fig. 1. (a) MBR continuously-fed scenario; (b) MBR with cyclic batch enrichment of nitrifiers scenario.

2.3. Cyclically fed strategy

2.3.1. Batch growth of endogenous nitrifiers

The optimal conditions to growth the endogenous nitrifiers were investigated in terms of pH and substrate source.

Laboratory batch tests were carried out to find out the optimal pH to grow the endogenous nitrifiers. Anthonisen et al. reported that unionized ammonia (NH_3, free ammonia, FA) inhibited nitrification reaction: inhibition of nitrite oxidation began at 0.1–1.0 mg/l of FA, while that of ammonia oxidation was observed at

Table 1
Main operating conditions of the continuously fed MBR

	Qin (m^3/d)	HRT (h)	SRT (d)	Temperature (°C)	MLSS (g/l)	MLVSS (g/l)	F/M (KgCOD/kgVSS/d)	NLR (kgN-NH_4/m^3/d)
Run 1	4.7	17.9	60	32.2	3.9	3.1	0.03	0.008
Run 2	7.1	11.8	55	31.7	4.4	3.5	0.03	0.010
Run 3	9.4	8.9	45	31.5	5.2	4.2	0.03	0.014

10–150 mg/l [16]. The batch reactors were regularly sampled to allow measurement of the specific nitrification rate (SNR), and ammonium bicarbonate was periodically added according to the measured nitrification potential [17].

The fraction of free ammonia in the activated sludge bulk was calculated according to the following equations [18]:

$$\text{Free ammonia as } NH_3 = \frac{17}{14} \times \frac{N(\text{mg / l}) \times 10^{pH}}{K_b / K_w + 10^{pH}}$$

where

$$K_b / K_w = e^{\frac{6344}{273+T(°C)}}$$

Total ammonia as where K_b is the ionization constant of the ammonia equilibrium equation and K_w is the ionization constant of water.

The influence of different substrates, ammonium chloride and ammonium bicarbonate, was tested at pilot scale.

The growth of nitrifiers at the pilot scale level was carried out in a 1.2 m^3 reactor that was initially seeded with activated sludge taken from the full scale MBR plant. This bioreactor which encouraged nitrifiers growth was controlled on the basis of pH and ammonia levels using in-situ Hach-Lange digital probes. pH was maintained in the range 6.9 to 7.2 and ammonia in the range of 15 to 25 mg/l by automatic controlled external dosing of sodium hydroxide and ammonium chloride (or ammonium bicarbonate) respectively. In this way no free ammonia was present in the medium during growth. Dissolved oxygen (DO) concentration was always maintained at a level over 5 mgO_2/l. All the on-line measured parameters were logged using an Endress Hauser Memograph RSG 10 data logger and periodically downloaded for further processing.

The SNRs were calculated using data collected from the on-line sensors whose reliability was periodically checked ex-situ using respirometry lab-scale batch tests [17].

2.3.2. The cycling enrichment of endogenous nitrifiers in pilot MBR

Two consecutive runs were carried out in the continuously fed pilot MBR, before and after the cyclic batch dosage. Both runs lasted about 60 d with the nitrogen loading rate (NLR) being 0.08 kgN/m^3 per day for the first run. The NLR was increased during the second run by external dosing with ammonium bicarbonate proportionally with the expected SNRs, while the SRT was maintained unvaried at 60 d.

Also in this case daily composite samples of influent wastewater and permeate were collected and analyzed.

3. Results and discussion

Petrochemical wastewater may contain a number of inhibitors and/or toxic compounds that affect biological nitrification (i.e., heavy metals, phenols, cyanides, chlorides, etc), as shown in Table 2 together with the concentrations of conventional pollutants, pH and alkalinity.

It must be noted that as a consequence of the reduced operation of the petrochemical manufacturing plants, the wastewater stream was unvaried for volumetric flowrate, while changed a lot for chemical-physical characteristics. This meant that the MBR reactor volume was effectively oversized by a factor of about 500 l of reactor per person equivalent (PE), calculated on a COD loading basis. As a consequence, the normal loading conditions were as low as: Food to Microorganisms ratio of 0.04 $gBOD_5$/gMLVSS, NLR of 40 g TKN per m^3 of oxidation tank volume per day.

3.1. Long-term enhancement of the nitrification potential whilst maintaining a stable increase in influent loading in the continuously fed bioreactor

Results from the continuous enrichment showed that a gradual increases of nitrogen loading rate and specific

Table 2
Chemical-physical characteristics of the petrochemical wastewater

		Average	Variation coefficient (%)
COD	mgO_2/l	89.6	42
sCOD	mgO_2/l	82.3	32
TKN	mgN/l	13.6	72
$N\text{-}NH_4$	mgN/l	5.3	76
P-tot	mgP/l	0.7	71
Chlorides	mgCl/l	1257	31
Pb	mg/l	3.9	59
Ni	mg/l	5.1	29
Cd	mg/l	0.6	33
Cu	mg/l	6.3	67
Total hydrocarbons	mg/l	2.5	400
Total PAHs	Mg/l	23.9	53
Total cyanides	Mg/l	16.1	75
Alkalinity	$mgCaCO_3$/l	432	25
pH		8.9	6

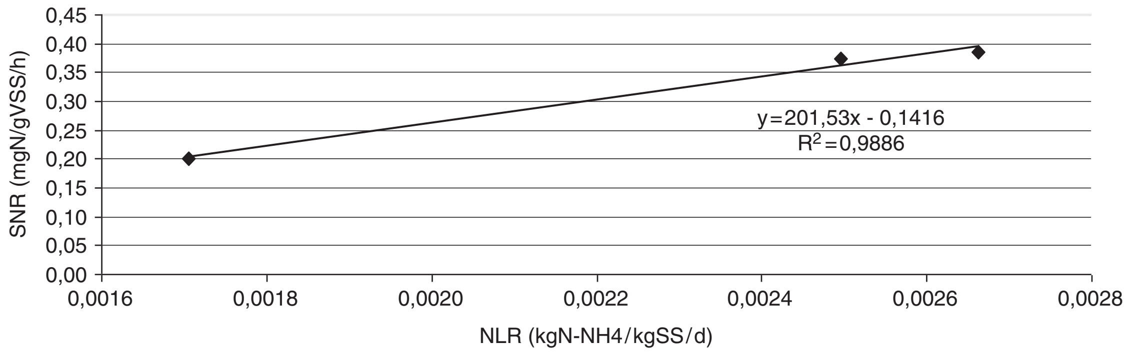

Fig. 2. Linear increase of SNR with NLRs in the conventional continuously-fed MBR.

nitrogen load in the reactor during continuous operation over Runs 2 and 3 led to a linearly proportional increase in the nitrification rates as depicted in Fig. 2. This behaviour demonstrated that the nitrification biological kinetics proved substrate-limited at the applied NLRs, and that the effect of the inhibitors in the influent wastewater did not compromise the ammonia oxidation process.

However due to the unforeseen variations in the quality and quantity of the influent wastewater stream generated in the industrial manufacturing area, which often proved sudden and drastic (as shown in Table 1), it was found that the nitrification process in the continuously fed MBR was greatly compromised.

3.2. *Enhancement of the nitrification potential by cycling batch enrichment*

The lab-scale batch tests were specifically carried to see how any variation in FA level affected the growth rate of the nitrifying biomass. It was found that when operating with a pH of 8 and ammonia concentration between 15–25 mg/l at 20°C a corresponding level of FA between 1.0 and 0.6 was present in the mixed liquor. In agreement to literature, at these concentrations the nitrite oxidizing biomass was inhibited as demonstrated by nitrite accumulation occurring inside the bioreactor as shown in Fig. 4. Conversely at a pH of 7 and same operating conditions of temperature and ammonia, a level of 0.1 mg/l of FA was developed. However this concentration was not causing inhibition to NOB and an optimal growth of nitrifiers was achieved with a complete conversion to nitrate. This led to a decoupling from the SNR after 11 d as shown in Fig. 3.

As far as influence of substrates is concerned, the ammonium chloride and ammonium bicarbonate were taken into consideration to investigate the effect of salinity on the autotrophic biomass. Since the petrochemical wastewater contained about 1.3 gCl/l (see Table 2), the endogenous nitrifiers were assumed to be acclimatized to this salinity. However the inoculum activated sludge fed with ammonium chloride showed that concentrations higher than 1.5 to 1.7 gCl/l caused a drastic reduction in the nitrification rates (Fig. 5). This reduction was not in agreement with the other research studies carried out in this same area such as Chen et al. who found the maximum tolerance level of chloride was 6.5 g/l in a fresh culture grown without chloride [19]. On the other hand, Yu et al. reported that daily and seasonal varia-

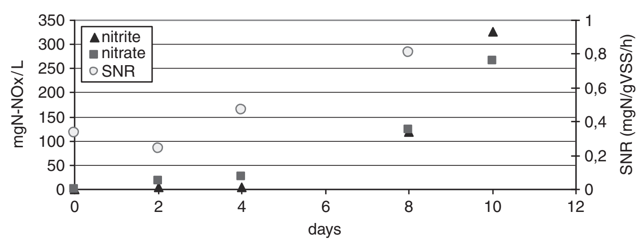

Fig. 4. Lab-scale batch growth nitrifer species at pH 8.

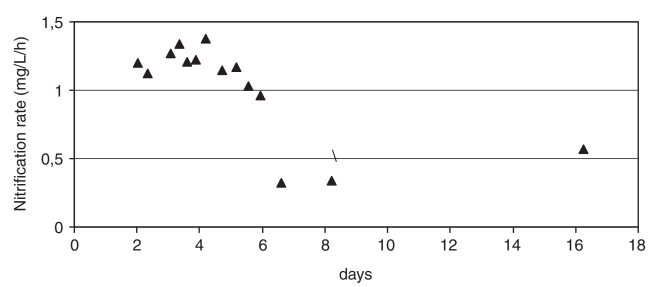

Fig. 5. Pilot scale batch growth of nitrifiers on a substrate of ammonia chloride.

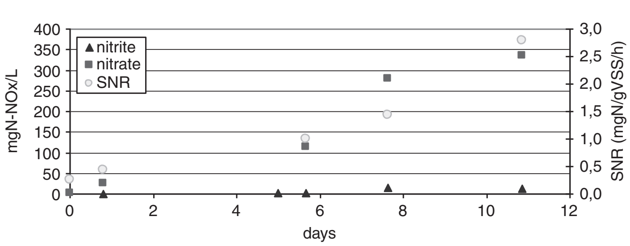

Fig. 3. Lab-scale batch growth of nitrifer species at pH 7.

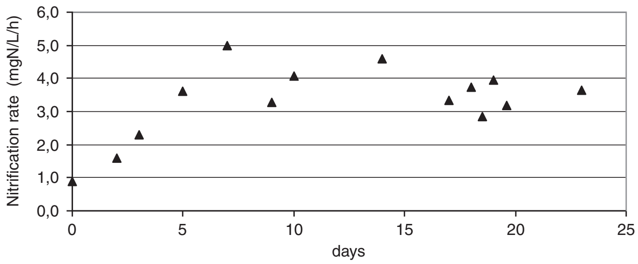

Fig. 6. Pilot scale batch growth of nitrifiers on a substrate of ammonia bicarbonate.

tion of influent chloride concentration from 3.5 to 6.0 g/l might cause incomplete nitrification in the two largest biological treatment plants based in Hong Kong [20].

A more successful test was carried out using ammonium bicarbonate dosing. The result of this test shown in Fig. 6 concludes that 8 to 10 d are sufficient to allow maximal SNR, which itself increases from 1 to 4 mgN/l/h.

In this test, the nitrification rate increases in the first 8 d, while it remains almost unchanged in subsequent days (Fig. 6).

Therefore the growth with ammonia bicarbonate proved that after 8 to 10 d the sludge enriched with nitrifiers could be moved to the continuously fed MBR part of the plant configuration. Hence for the next 50 d the plant was fed according to this regime with a NLR of 0.022 kgN/m^{3}d, which increased proportionally with the addition of the batch nitrifiers. As in the previous run in which no sludge enrichment took place, complete ammonia nitrification was always observed in the permeate, thus demonstrating the stable increase in the overall nitrification potential.

3.3. Comparison of the two proposed approaches and practical considerations

When comparing the continuous dosage of nitrogen versus a cyclic enrichment process as discussed in this paper, it is important to consider the difference in the nitrogen, alkalinity, oxygen levels needed and the process time requirements. Hence, in Table 3, the results from the pilot MBR's are scaled up to an equivalent reactor volume of 7,680 m^3. These are then compared with the former plant configuration that was tested taking into account a standard increase of the SNR of 0.1 gN/kgVSS.h.

The cyclic enrichment allowed for a more rapidly way to achieve an increase in nitrification potential and a more flexible way to operate the overall MBR reactor. Energy requirements and costs for chemicals also showed to be lower in the case of a batch growth. All these parameters suggested that this approach should be considered a more feasible way to operate a bioreactor subjected to sudden changes in the influent nitrogen loads and characteristics.

Table 3
Oxygen and chemical demands to increase the nitrification potential: continuously fed vs cycling batch

CONTINUOUSLY FED				
Time demand	60	d		
Oxygen demand	8729	kgO_2	1746	kWh
Nitrogen demand	2016	kgN	5670	€
NaOH demand	–	kgNaOH	0	€
CYCLIC BATCH				
Time demand	10	d		
Oxygen demand	2188	kgO_2	438	kWh
Nitrogen demand	505	kgN	1420	€
NaOH demand	1430	kgNaOH	3337	€

Oxygen supply by air microbubble diffusers (OTR_{field} 5 kgO_2/kWh); specific cost of NaOH 0.7 €/kg (solution 30%); specific cost of ammonia 0.7 €/kg (solution 32%).

4. Conclusions

The paper compares two different plant configurations that could be used to increase the nitrification potential in MBRs that treat petrochemical wastewaters, which are themselves characterized by rapid changes of quality and quantity.

The main conclusions of the study are summarized as follows:

- The best conditions to develop a nitrifying biomass should be investigated by laboratory and pilot trials taking into consideration different environmental conditions.
- The in-situ cycling batch enrichment of nitrifiers proved a flexible and feasible process configuration to be used to improve MBR nitrification rates. The time required to achieve an increase of 0.1 gN/kgVSS.h was approximately 10 d and considered sufficiently long enough to deal with any sudden variation of nitrogen loadings in the petrochemical wastewater influent stream.
- The batch growth of endogenous nitrifiers caused a stable increase of the nitrification potential as the

bacterial populations were already acclimatized to the environmental conditions of the continuously fed membrane bioreactors.
- This growth process can be controlled by cheap and widespread on-line sensors (e.g. pH, DO, conductivity, and NH_4 probes). On the other hand, the optimization of the ammonia dosing used in the continuously fed MBR proved much more difficult.
- The costs of both the chemicals and the energy consumed for air delivery proved lower in the case of the plant configuration that utilized the cycling batch enrichment of nitrifiers.

References

[1] W. Humphreyand E. Witt, Biological treatment of high strength petrochemical wastewater, U.S. Environmental Protection Agency, Washington, D.C., EPA/600/2–79/172.

[2] CWW BREF [6, EC 2003] European Commission, Integrated Pollution Prevention and Control (IPPC) Draft Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries Draft 1–July 2010 European Commission Directorate –general JRC Joint Research Centre, Institute for Prospective Technological Studies (Seville).

[3] J.J. Qin, M.H. Oo, G. Tao and K.A. Kekre, Feasibility study on petrochemical wastewater treatment and reuse using submerged MBR, J. Membr. Sci., 293 (2007) 161–166.

[4] W. Gujer, Nitrification and me - a subjective review, Water Res., 44(1) (2010) 1–9.

[5] R. Poffe, J. Vanderleyden and H. Verachtert, Characterisation of a Leucothrix-type bacterium causing sludge bulking during petrochemical wastewater treatment, Eur. J. appl. microbiol. Biotechnol., 8 (1979) 229–235.

[6] B. Lesjean, V. Ferre, E. Vonghia and H. Moeslang, Market and Design Considerations of the 37 larger MBR Plants in Europe, Desalin. Water Treat., 6 (2009) 227–233.

[7] S. Cattaneo, F. Marciano, L. Masotti, G. Vecchiato, P. Verlicchi and C. Zaffaroni, Improvement in the removal of micropollutants at Porto Marghera industrial wastewaters treatment plant by MBR technology, Water Sci. Technol., 58(9) (2008) 1789–96.

[8] S. Churchouse, Membrane bioreactors for wastewater treatment — operating experiences with the Kubota submerged membrane activated sludge process, Membr. Technol., 83 (1997) 5–9.

[9] M. Takht Ravanchia, K. Tahereh and A. Kargarib, Application of membrane separation processes in petrochemical industry: a review, Desalination, 235 (2009) 199–244.

[10] F. Fatone, P. Battistoni, D. Bolzonella, P. Pavan and F. Cecchi, Long-term experience with an automatic process control for nitrogen removal in membrane bioreactors, Desalination, 227(1–3) (2008) 72–84.

[11] F. Fatone, A. L. Eusebi, P. Pavan and P. Battistoni, Exploring the potential of membrane bioreactors to enhance metals removal from wastewater: pilot experiences, Water Sci. Technol., 57 (2008) 505–511.

[12] F. Fatone, S. Di Fabio, D. Bolzonella and F. Cecchi, Fate of aromatic hydrocarbons in Italian municipal wastewater systems: An overview of wastewater treatment using conventional activated-sludge processes (CASP) and membrane bioreactors (MBRs), Water Res., 45 (2011) 93–104.

[13] D. Bolzonella, F. Fatone, S. Di Fabio and F. Cecchi, Application of membrane bioreactor technology for wastewater treatment and reuse in the Mediterranean region: Focusing on removal efficiency of non-conventional pollutants, J. Environ. Manage., 91(12) (2010) 2424–31.

[14] D. Bolzonella, F. Fatone, P. Pavan and F. Cecchi, Poly-chlorinated dibenzo-p-dioxins, dibenzo-furans and dioxin-like poly-chlorinated biphenyls occurrence and removal in conventional and membrane activated sludge processes, Biores. Technol., 101(24) (2010) 9445–54.

[15] M. Gander, B. Jefferson and S. Judd, Aerobic MBRs for domestic wastewater treatment: a review with cost considerations, Sep. Purif. Technol., 18(2) (2000) 119–130.

[16] A.C. Anthonisen, R.C. Loehr, T.B.S. Prakasam and E.G. Srinath, Inhibition of nitrification by ammonia and nitrous acid, J. Water Pollut. Control Fed., 48 (1976) 835–852.

[17] H.G. Kristensen, P.E. Jørgensen and M. Henze, Characterization of functional microorganism groups and substrate in activated sludge and wastewater by AUR, NUR and OUR, Wat. Sci. Technol., 25(6) (1992) 43–57.

[18] W. Bae, S. Baek, J. Chung and Y. Lee, Optimal operational factors for nitrite accumulation in batch reactors, Biodegradation, 12 (2002) 359–366.

[19] G.H. Chen, M.T. Wong, S. Okabeb and Y. Watanabeb, Dynamic response of nitrifying activated sludge batch culture to increased chloride concentration, Water Res., 37 (2003) 3125–3135.

[20] S.M. Yu, W.L. Leung, K.M. Ho, P.F. Greenfield and W.W. Eckenfelder, The impact of sea water flushing on biological nitrification–denitrification activated sludge sewage treatment process, Proceedings of the first IWA Asia–Pacific regional conference (Asian Waterqual 2001) (Part I), Fukuoka, September 12–15, 2001. p. 987–1000.