Tertiary nitrification in pure oxygen moving bed biofilm reactors

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Abstract Two bench-scale reactors, fed with the secondary effluent of a municipal wastewater treatment plant (WWTP), were used in order to study tertiary nitrification in pure oxygen moving bed biofilm reactors (PO-MBBRs) with patented KMT® media as biofilm carriers. The process allowed to measure very high nitrification rates, both in ammonia limiting conditions (up to 7 gN m^{-2} d^{-1}; oxygen-to-ammonia nitrogen ratio higher than 3–4 mgO_2 $(mgN)^{-1}$) and in oxygen limiting conditions (up to 8 gN m^{-2} d^{-1}; oxygen-to-ammonia nitrogen ratio lower than 1–2 mgO_2 $(mgN)^{-1}$). Since the process proved flexible and reliable, it is suitable for full-scale application to municipal WWTPs. Typical application could regard, but is not limited to, tertiary nitrification of secondary effluent from existing high-purity oxygen activated sludge systems designed to achieve only organic carbon removal.

Keywords Ammonia limiting conditions; oxygen limiting conditions; pure oxygen moving bed biofilm reactor (PO-MBBR); tertiary nitrification

Water Science and Technology **vol 41 No 4–5 pp 361–368** © IWA Publishing 2000

Introduction

Biological processes based upon suspended biomass (i.e., activated sludge processes) are effective for tertiary nitrification (i.e., after a conventional secondary treatment for organic carbon oxidation) in municipal wastewater treatment plants (WWTPs), but they need a tertiary settling tank and biomass recycling.

Biofilm processes have proved to be very reliable for tertiary nitrification, because of the higher volumetric loading rates that can be applied and the low solids build-up in the reactor. This allows the use of smaller reactors usually with no need of tertiary settling tanks.

Moving-bed biofilm reactors (MBBRs) were chosen as tertiary nitrification reactors because, compared to the available fixed-bed biofilm reactors (biofilters), they are characterised by low head losses, no filter bed channeling (that is, a complete use of the bioreactor volume), no need of periodic backwashing.

Low-density polyethylene (density slightly less than 1.0 g cm^{-3}) KMT® biofilm carriers were used. They consist in small cylindrical elements (diameter 10 mm; height 8 mm) with an internal cross and small longitudinal fins on the outside surface. The filling ratio (volumetric filling in empty reactor) can be increased up to 70%, corresponding to a theoretical specific surface area of 500 m^2 m^{-3} and a void fraction of 95%. Since the biofilm growth mainly occurs in the protected internal faces of the carriers, an actual specific surface area of about 350 m^2 m^{-3} can be assumed.

KMT® biofilm carriers have been already successfully used for nitrification (Ødegaard and Rusten, 1993; Hem *et al.*, 1994; Rusten *et al.*, 1994, 1995; Pastorelli *et al.*, 1996, 1997a, 1997b). Previous studies on tertiary nitrification have shown that nitrification rate is first order (Hem *et al.*, 1994) or nearly first order (Pastorelli *et al.*, 1997a, 1997b) with respect to dissolved oxygen when oxygen limiting conditions are established (i.e., oxygen-to-ammonia nitrogen ratio lower than 2 mgO_2 $(mgN)^{-1}$). This may imply that liquid film diffusion could play an important role as the limiting step of the process (Harremoës, 1978).

Although a linear link between nitrification rates and dissolved oxygen can mean high energetic consumption, still dissolved oxygen concentration may be used to control the nitrification process at high ammonia loading rate or at low temperature.

Pure oxygen (PO) rather than air was used as oxygen supply in MBBRs because it allows higher dissolved oxygen concentration and higher oxygen transfer efficiency, therefore higher nitrification rate and better process control with lower energetic consumption.

Materials and methods

Description of the experimental equipment

Tertiary nitrification was studied in two bench-scale pure oxygen moving bed biofilm reactors (PO-MBBRs). A simplified flow-sheet of the bench-scale plant is shown in Figure 1. Technical data of the plant are reported in Table 1. Further details can be found in Quinto (1998) and Rinaldi (1998).

Secondary settled wastewater was fed to the two bench-scale PO-MBBRs (R1 and R2) through a first mixed, non-aerated feed tank (FT) by means of two variable-rate, peristaltic pumps. The FT tank was operated on a fill-and-draw basis, as an equalisation tank.

The two PO-MBBRs were mechanically mixed. Pure oxygen was supplied by means of porous diffusers. Pure oxygen flow rates could be adjusted adequately by means of manual control valves. Wastewater temperature was controlled and maintained around 18±2ºC by means of a thermostat.

No final settling tank was provided, because of the low biomass growth in tertiary nitrification systems.

Wastewater characteristics

The bench-scale reactors were fed with the secondary effluent of Bergamo WWTP, near Milan (design capacity 220,000 p.e., actual dry weather flow rate 72,000 $m^3 d^{-1}$).

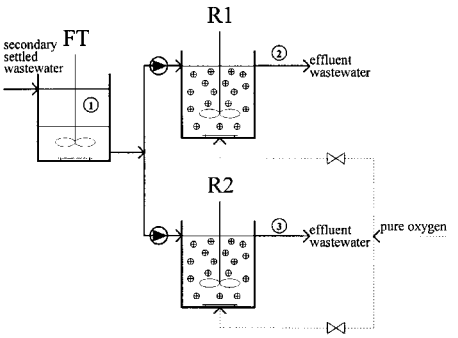

Figure 1 Simplified flow-sheet of the bench-scale plant with sampling points

Table 1 Technical data of the bench-scale plant

Technical data		FT tank	R1 reactor	R2 reactor
Height	[m]	0.40	0.13	0.13
Diameter	[m]	0.36	0.10	0.10
Volume	[l]	40.7	1.0	1.0
Biofilm surface	[dm^2]	–	12→8	12→6
Daily flow rate	[$l\ d^{-1}$]	–	4–16	4–16

Table 2 Characteristics of the secondary settled wastewater used to feed the bench-scale reactors (as supplied from Bergamo WWTP)

Parameter		N.	Minimum	Maximum	Average	Standard deviation	Coefficient of variation
TSS	[mgTSS l^{-1}]	22	2	25	7.9	5.7	0.73
BOD	[mgBOD l^{-1}]	14	6	28	13.1	5.3	0.41
COD	[mgCOD l^{-1}]	22	10	125	41.5	25.8	0.62
NH_4^+–N	[mgN l^{-1}]	22	1.5	27.1	16.0	7.4	0.46
Total N	[mgN l^{-1}]	22	7.1	35	20.7	6.7	0.32

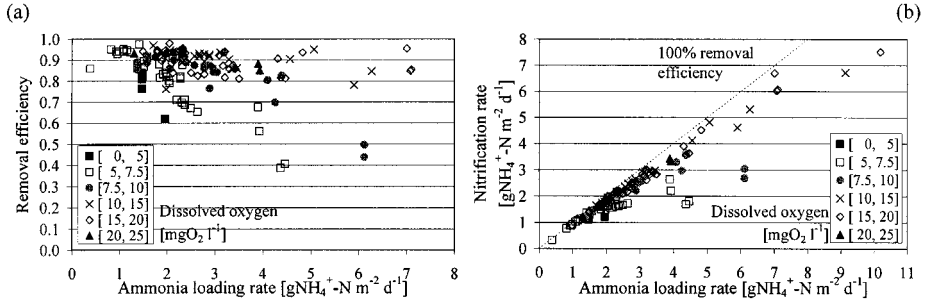

Figure 2 Removal efficiency (a) and nitrification rate (b) versus ammonia loading rate

More than 200 l of secondary effluent were supplied every 7–14 days to the laboratory where the bench-scale tests were carrying out. The wastewater was then stored in a refrigerator room (4ºC) and, when needed, rested some hours at ambient temperature before filling the FT tank.

Characteristics of the secondary settled wastewater used to feed the bench-scale reactors (as supplied from Bergamo WWTP) are summarised in Table 2.

Table 2 clearly shows that secondary treatment at Bergamo WWTP (pure oxygen-activated sludge system in covered tank) allows good BOD and COD removal but no or poor nitrification, due to the very short sludge retention time (about three days).

When ammonia nitrogen concentration in the effluent of Bergamo WWTP was low due to occasional nitrification (mainly during summer months), a suitable solution of ammonium chloride has been dosed in order to correct ammonia nitrogen concentration up to about 30 mgN l^{-1}.

Monitoring, sampling and analyses

Monitoring. Temperature, dissolved oxygen and pH were measured in each reactor every workday, immediately before sampling. Pure oxygen flow rates were monitored using flow meters.

Sampling. Samples of the influent, equalised wastewater (sampling point 1 in Figure 1) and of the effluent of the two PO-MBBRs (sampling points 2 and 3 in Figure 1) were taken three to five days a week. The samples were analysed immediately after sampling for ammonia and nitrate.

Analytical methods. Total suspended solids (TSS), BOD, COD, total nitrogen (TN), ammonia (NH_4^+–N) and nitrate (NO_3^-–N) were measured according to the Standard Methods (1995). 0.45-μm filters were used for filtration of samples.

Biomass attached on the carriers was measured as the difference of the dry weight (105∞C) of an adequate number of biofilm carriers before and after accurate 7-day cleaning in diluted (5%) hydrogen chloride solution.

Results and discussion

Experimental programme

The first PO-MBBR was operated for 574 days, the second PO-MBBR was started-up after 193 days and therefore was operated for the last 381 days.

In the following discussion results from both reactors R1 and R2 are taken together, without further distinction.

The experimental programme aimed to study nitrification kinetic of PO-MBBRs using (1) ammonia loading rate and (2) dissolved oxygen as control parameter.

The reactors were always operated in order to achieve either the maximum removal efficiencies or the maximum nitrification rates. Therefore, with the aim of maximising the removal rates, after reaching stable nitrification rates, a progressive reduction of the available biofilm surface area from 0.12 m^2 to 0.08 and 0.06 m^2 for reactors R1 and R2 respectively (obtained progressively removing biofilm carriers from the reactors) was carried out. So, for each reactor it was possible to define two different operating conditions: the so-called "low-loading" conditions (up to about 3 gN m^{-2} d^{-1}) and "high-loading" conditions (more than 3, up to about 10 gN m^{-2} d^{-1}). Dissolved oxygen was increased independently up to 30 mgO_2 l^{-1}.

As a result of these wide operating conditions, ammonia nitrogen concentration in the reactor has ranged between less than 1 and 17 mgN l^{-1}. Therefore, it was possible to explore both "ammonia limiting" conditions (mostly representing maximum removal efficiencies) and "oxygen limiting" conditions (mostly representing maximum nitrification rates).

Removal efficiencies and nitrification rates

Removal efficiencies vs. ammonia loading rates are shown in Figure 2a, while nitrification rates vs. ammonia loading rates are shown in Figure 2b.

Apart from 5 events (of more than 140 experimental data), nitrification efficiency was always higher than 60%, even if high nitrification efficiency was not a mandatory aim of the research, in order to study oxygen limiting conditions. Of course, maximum nitrification efficiencies correspond to lower ammonia loading rates, even if nitrification efficiencies higher than 90% has been achieved at ammonia loading rate higher than 4 gN m^{-2} d^{-1}, provided that dissolved oxygen was higher than 10–15 mgO_2 l^{-1}. This represent a significant consequence of the use of pure oxygen.

At constant dissolved oxygen concentration, a maximum ammonia loading rate exists that maximises the nitrification rate. Higher ammonia loading rates cause reduced nitrification efficiency. This effect is more evident with regard to dissolved oxygen concentration lower than 10 mgO_2 l^{-1}.

In order to obtain the same effect at higher dissolved oxygen concentration, higher ammonia loading rates than those applied have had to be required. For dissolved oxygen concentration higher than 10 mgO_2 l^{-1}, nitrification rates higher than 4 gN m-2 d-1 can be reasonably maintained with removal efficiencies higher than 80%.

Oxygen-to-ammonia nitrogen ratio

Removal efficiencies versus oxygen-to-ammonia nitrogen ratio (O/N) and ammonia nitrogen-to-oxygen ratio (N/O) are shown in Figures 3a and 3b respectively.

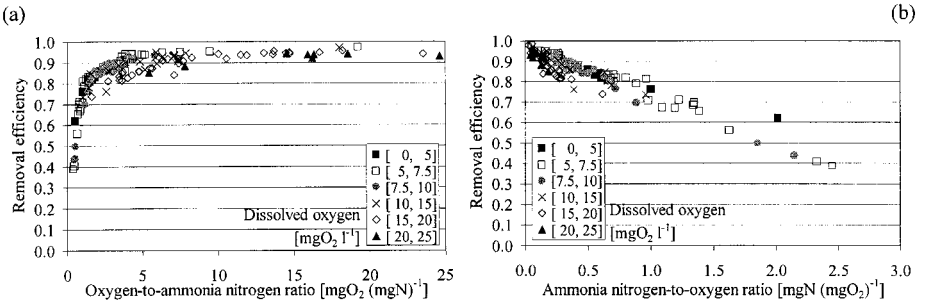

Figure 3 Removal efficiency versus O/N (a) and N/O (b) ratios

Experimental data show that ammonia limiting conditions are characterised by oxygen-to-ammonia nitrogen ratio higher than 3–4 mgO_2 $(mgN)^{-1}$, while oxygen limiting conditions are characterised by oxygen-to-ammonia nitrogen (O/N) ratio lower than 1–2 mgO_2 $(mgN)^{-1}$. Transition range (oxygen-to-ammonia nitrogen ratio between 1–2 and 3–4 mgO_2 $(mgN)^{-1}$) represent optimum operating conditions where both nitrification efficiencies and nitrification rates are maximised. In this situation the use of both the substrates is optimised.

Nitrification kinetic

Operating conditions and results at different ammonia nitrogen and dissolved oxygen concentrations are summarised in Tables 3 and 4 respectively. In Tables 3 and 4, only data corresponding to ammonia limiting and oxygen limiting conditions respectively have been considered.

Nitrification rates versus dissolved oxygen concentration at low-loading and high-loading conditions are shown in Figures 4a and 4b respectively. In Figures 4a and 4b, all the data collected have been considered.

Representations of nitrification rate vs. dissolved oxygen concentration (and also of nitrification rate vs. ammonia nitrogen concentration, not reported in the paper) generally show scattered data. This can be explained taking into account the wide range of ammonia loading rates and the effect of the operating conditions on biofilm thickness and population dynamics, that is biomass specialisation.

In fact, a three-month progressive increase of ammonia loading rate from 2.5–3.0 gN m^{-2} d^{-1} (low-loading conditions) to 7.0–8.0 gN m^{-2} d^{-1} (high-loading conditions) has caused a corresponding progressive increase of nitrification rate from 2.5–3.0 to 6.0–7.0 gN m^{-2} d^{-1} and only a small increase of biofilm surface density from 3.2–3.6 to 4.4–4.7 gTSS m^{-2}. Therefore, the specific nitrification rate (calculated as the ratio between nitrification rate and biofilm surface density) increased from about 0.80 gN $(gTSS)^{-1}$ d^{-1} to about 1.40 gN $(gTSS)^{-1}$ d^{-1}, showing a strong increase of biofilm activity.

Data on Tables 3 and 4 and on Figures 4a and 4b show that the use of pure oxygen can increase nitrification rates, but this effect is maximised at oxygen limiting conditions.

Theoretical approach

Bonomo *et al.* (1999), in a companion paper, has presented a comparison of one-dimensional biofilm reactor models that use simplified (fixed-order, i.e. zero- and first-order) and Monod kinetics, assuming biofilms as homogeneous layers containing uniformly distributed bacterial cells.

Table 3 Operating conditions and results at different ammonia nitrogen concentration (105 data corresponding to ammonia limiting conditions: oxygen-to-ammonia ratio higher than 2 mgO_2 $(mgN)^{-1}$)

Ammonia nitrogen concentration range [mgN l^{-1}]							
Parameter		**[0.0–1.0]**	**[1.0–1.5]**	**[1.5–2.0]**	**[2.0–3.0]**	**[3.0–5.0]**	**[5.0–10]**
N. of data	[–]	11	21	20	28	20	5
DO	[mgO_2 l^{-1}]	16.81±8.48	17.56±6.84	10.20±4.05	12.07±4.82	12.50±4.30	18.50±1.77
NH_4^+–N	[mgN l^{-1}]	0.74±0.22	1.28±0.16	1.83±0.14	2.52±0.33	3.86±0.63	5.44±0.25
O/N ratio	[–]	22.95±10.13	13.96±6.24	5.60±2.31	4.86±2.01	3.23±0.99	3.41±0.41
Loading rate	[gN m^{-2} d^{-1}]	1.45±0.33	2.23±1.34	2.13±1.08	2.39±0.89	3.17±1.03	4.53±1.53
Removal rate	[gN m^{-2} d^{-1}]	1.38±0.33	2.10±1.28	1.98±1.02	2.13±0.82	2.72±1.09	3.74±1.35
Efficiency	[–]	0.95±0.02	0.94±0.01	0.93±0.02	0.89±0.02	0.85±0.03	0.82±0.02

Table 4 Operating conditions and results at different dissolved oxygen concentration (77 data corresponding to oxygen limiting conditions: oxygen-to-ammonia ratio lower than 4 mgO_2 $(mgN)^{-1}$)

Parameter		Dissolved oxygen concentration range [mgO_2 l^{-1}]				
		[0.0–5.0]	[5.0–7.5]	[7.5–10]	[10–15]	[15–20]
N. of data	[–]	7	31	23	8	8
DO	[mgO_2 l^{-1}]	4.26±0.37	6.75±0.71	8.39±0.75	11.25±1.00	18.26±1.75
NH_4^+–N	[mgN l^{-1}]	3.50±1.99	5.61±4.07	4.83±3.73	5.60±3.03	6.09±2.42
O/N ratio	[–]	1.45±0.53	1.86±1.20	2.29±0.87	2.44±1.00	3.23±0.73
Loading rate	[gN m^{-2} d^{-1}]	1.53±0.19	2.21±0.90	2.92±1.34	4.46±2.44	5.34±2.56
Removal rate	[gN m^{-2} d^{-1}]	1.20±0.04	1.62±0.40	2.26±0.70	3.63±1.77	4.32±1.94
Efficiency	[–]	0.79±0.08	0.78±0.14	0.82±0.12	0.83±0.06	0.82±0.04

Two different situations have been compared: one rate-limiting substrate with or without liquid film diffusion. The results obtained have shown that, neglecting liquid film diffusion, the use of a simplified kinetic approach compared to the Monod kinetic approach determines an unjustified overestimate of the removal rate, especially for thin biofilm (i.e., biofilm characterised by biofilm constant α lower than about 4).

The above mentioned data have been used to validate the model because (1) tertiary nitrification is one of the biochemical process that does not require the use of multi-substrate, multi-species biofilm models due to the lack of competition between autotrophs and heterotrophs for oxygen and (2) the use of pure oxygen can increase nitrification rate in thin biofilm, without the need to increase biofilm thickness.

In fact, since biofilm density averages between 30 and 50 mgTSS cm^{-3}, biofilm thickness can be estimated around 85 μm at low-loading conditions and around 110 μm at high-loading conditions. In this situation, values of the biofilm constant α between 1 and 3 can be calculated, using the following equation:

$$\alpha = \sqrt{r_{a,0} L_f / (D_f K_S)}$$

where:

α =biofilm constant (dimensionless)

$r_{a,0}$=zero-order (maximum) reaction rate per unit biofilm area [$M L^{-2} T^{-1}$]

L_f =biofilm thickness [L]

D_f =molecular diffusion coefficient into the biofilm [L^2 T^{-1}] (for ammonia: 1.2–1.3 cm^2 d^{-1})

K_S =saturation constant [$M L^{-3}$] (for ammonia: 0.3–0.7 mgN l^{-1})

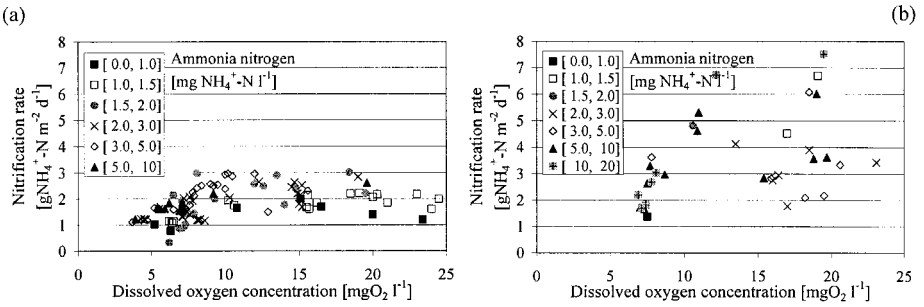

Figure 4 Nitrification rate versus dissolved oxygen concentration at low-loading (a) and high-loading (b) conditions

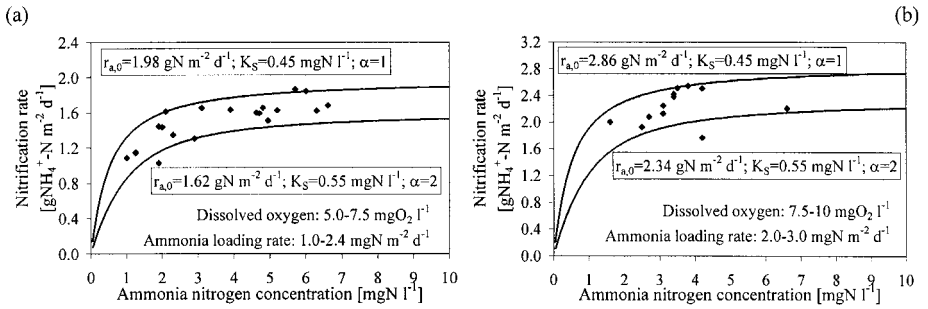

Figure 5 Nitrification rate versus ammonia nitrogen concentration at different dissolved oxygen concentration: experimental data and calculated kinetics

Figures 5a and 5b show that calculated kinetics (maximum and minimum approximation, considering ±10% variation around average values for $r_{a,0}$ and K_S) fit well the experimental data.

Conclusions

Two bench-scale reactors, fed with the secondary effluent of a municipal wastewater treatment plant, were used in order to study tertiary nitrification in PO-MBBRs with patented KMT®media as biofilm carriers.

The process was studied in view of its application to full-scale WWTPs. It proved flexible, reliable and easy-to-operate and allowed to measure very high nitrification rates, both in ammonia limiting conditions (up to 7 gN m^{-2} d^{-1}; oxygen-to-ammonia nitrogen ratio higher than 3–4 mgO_2 $(mgN)^{-1}$) and in oxygen limiting conditions (up to 8 gN m^{-2} d^{-1}; oxygen-to-ammonia nitrogen ratio lower than 1–2 mgO_2 $(mgN)^{-1}$).

Typical application could regard, but is not limited to, tertiary nitrification of secondary effluent from existing high-purity oxygen activated sludge systems designed to achieve only organic carbon removal. In fact, combined carbonaceous and nitrogenous material oxidation, particularly if performed in covered reactors (i.e., enclosed systems), is difficult to obtain due to the build-up of carbon dioxide (mainly released by biological conversion of organic matter), together with nitrification activity, that can cause a pH depression that could inhibit nitrification itself. In this kind of WWTP, PO-MBBR technology seems suitable because (1) pure oxygen supply should not pose particular problems, (2) PO-MBBRs typically are uncovered reactors and (3) tertiary nitrification (i.e., segregated from organic carbon oxidation) should not suffer from carbon dioxide build-up and pH depression, provided that sufficient alkalinity is available.

Bench-scale tests suggest that better tertiary nitrification efficiencies with regard to both volume required and energetic consumption could be achieved with two PO-MBBRs in series: the former with very high ammonia loading rate and dissolved oxygen concentration high enough to continue to guarantee oxygen limiting conditions, the latter with lower ammonia loading rate and only residual dissolved oxygen concentration (that is, no need of aeration/oxygenation) because low ammonia nitrogen concentration in the effluent implies ammonia limiting conditions and these conditions take no advantage of high dissolved oxygen concentration.

A full-scale opportunity to verify the experimental results summarised above is offered by Bergamo WWTP, where BAS-Bergamo Ambiente e Servizi (public company that provides environmental services - water supply, wastewater collection and treatment and solid waste management - for the town of Bergamo, Northern Italy) and SIAD (private company

specialised in industrial gas manufacturing and distribution) have recently started-up a 1.400-m^3 PO-MBBR filled with 670 m^3 of KMT® carriers (ammonia nitrogen concentration up to 25 mgN l^{-1}; flowrate up to 42,000 m^3 d^{-1}) using an old, disused, uncovered aerobic digestion tank easily convertible to the PO-MBBR technology.

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