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Nitrous Oxide Emissions for Early Warning of Biological Nitrification Failure in Activated Sludge

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Abstract

Experiments were carried out to establish whether nitrous oxide (N_2O) could be used as a non-invasive early warning indicator for nitrification failure. Eight experiments were undertaken; duplicate shocks DO depletion, influent ammonia increases, Allylthiourea (ATU) shocks and sodium azide (NaN_3) shocks were conducted on a pilot-scale activated sludge plant which consisted of a 315 L completely mixed aeration tank and 100 L clarifier. The process performed well during pre-shock stable operation: ammonia removals were up to 97.8% and N_2O emissions were of low variability (<0.5ppm). However, toxic shock loads produced a N_2O response of a rise in off-gas concentrations ranging from 16.5 - 186.3 ppm, followed by a lag-time ranging from 3-5 h ((0.43-0.71)*HRT) of increased NH_3-N and/or NO_2^- in the effluent ranging from 3.4 - 41.2 mg.L^{-1}. It is this lag-time that provides the early warning for process failure, thus mitigating action can be taken to avoid nitrogen contamination of receiving waters.

Keywords

Activated sludge; early warning; nitrification; nitrous oxide; toxic shocks

1. Introduction

Nitrogen removal has become an important part of wastewater treatment processes due to the significant impact of nitrogen compounds (NH_4^+-N, NO_3^--N and NO_2^--N) on the aquatic environment and more stringent legislation on wastewater discharges. Discharge limits for nitrogen have been now set between 10 and 15 mg.L^{-1} within the European Community and some developed countries have even more stringent restrictions (Jonsson et al., 2001). To meet this demand, the most commonly used method for nitrogen removal is biological treatment based on aerobic nitrification and anoxic denitrification, both of which may produce nitrous oxide (N_2O) (Colliver and Stephenson, 2002).

In microbial nitrification, N_2O formation can occur in two ways during the oxidation of ammonia (NH_3) to nitrite (NO_2^-) (Prosser, 1989): (i) reduction of NO_2^- catalysed by nitrite reductase (NiR); (ii) chemical decomposition of NO_2^- or intermediates (NH_2OH) of ammonia oxidation (Itokawa et al., 2001). Although the actual mechanism is still largely unknown or debatable, the efficiency of ammonium conversion to N_2O appears to be higher at low oxygen concentrations or low sludge retention times (SRT) (Goreau et al., 1980; Noda et al.,2003; Kampschreur et al., 2008). The biological denitrification process removes the excess nitrogen by reducing NO_2^- and NO_3^- to molecular nitrogen (N_2). It is during this process that N_2O is an obligate intermediate (Wicht, 1996). Several factors, such as low influent COD/total nitrogen (TN,) high dissolved oxygen (DO) and low pH, may stimulate production of N_2O during the denitrification process (Hanaki et al., 1992; Burgess et al., 2002a). Furthermore, N_2O can also be produced by nitrifier denitrification (ND pathway) where the oxidation of NH_4^+ into NO_2^- is followed by the reduction of NO_2^- to N_2O and N_2 (Bock et al., 1995; Itokawa et al., 2001). The sequence of reactions is carried out by only one group of microorganisms, namely autotrophic NH_3-oxidizers, typified by *Nitrosomonas eutropha* (Wrage et al., 2001). It is unsurprising that high N_2O emissions have been observed in a variety of wastewater treatment processes. However, N_2O gas has an adverse impact on the environment (von Schulthess et al., 1994), as it is known to be one of the greenhouse gases under the Kyoto Protocol of 1997 where reduction targets were agreed (Dore et al., 2005).

When toxic upsets occur the system receives a loading shock, resulting in lower treatment efficiency or process failure (Gutierrez et al., 2002). If toxicants do hinder the activity of nitrifying bacteria, it will cause leakage of ammonia into the effluent, often resulting in breaches of discharge consents (Hayes et al., 1998). With the need to stringently monitor toxic shock loads, there has been an increase in new techniques and technologies available for monitoring changes in wastewaters, e.g. on-line NH_3 analysers and respirometers (Vanrolleghem and Lee, 2003). The purpose of these online monitoring instruments is to obtain specific information about changes in wastewater quality (particularly at the inlet) and to ensure treatment efficiency for compliance assessment and control (Bourgeois et al., 2001). There are currently two main types of on-line early warning methods: respirometric methods and microbial methods both of which require analysis of dissolved compounds (Vanrolleghem and Lee, 2003). These technologies allow for early warning but can be costly to maintain, give false negatives (Love and Bott, 2000) and are prone to sensor fouling due to the hostile environment in which the sensors have to be placed (Pedersen and Petersen, 1996). More recently, Burgess et al (2002a) demonstrated a strong relationship between ammonia shock loads and the concentration of N_2O in the off-gas from the aeration tank. This suggests that the changes in N_2O concentration in the exhaust gas from a nitrifying process may be a useful parameter for monitoring such processes (Burgess et al., 2002b; Butler et al., 2005a). As a result, a more efficient early-warning system for the nitrification processes can be established based on N_2O emissions as long as the off-gas N_2O concentration can be monitored on line.

The purpose of this work therefore was to gain a better understanding of the correlation between N_2O accumulation and the increasing of effluent NH_3/NO_2 in wastewater treatment plants (WWTP) under varying shock loads and further to establish whether off-gas N_2O could be used as a non-invasive early warning indicator to predict nitrification failure.

2. Materials and Methods

2.1 Activated sludge pilot plant

A pilot-scale activated sludge plant (Fig. 1) comprising of a control and test lane was used to represent full-scale sewage works as recommended in the literature (Horváth and Schmidtke, 1983). Each lane plant consisted of an aeration tank (315 L) and a clarifier (100 L). An anoxic selector zone with a volume of 10L was used as a dosage mixing area for shock load experiments. For the initial start-up, the aeration basin was filled with half wastewater and half recycled activated sludge (RAS) from a full-scale municipal waste water treatment works (Anglian Water, Cotton Valley, UK).

Fig.1-Schematic diagram of the pilot-scale activated sludge plants

2.2 Plant operation

The influent settled sewage was supplied from Cranfield University Wastewater Treatment Works at a rate of 45 $L.h^{-1}$ giving a hydraulic retention time (HRT) of 7 h. The wasted activated sludge (WAS) and Recycled Activated Sludge (RAS) were delivered by a peristaltic pump (505U, Watson and Marlow, UK). Sludge recirculation was controlled at 100% of the average influent flow. The sludge age was maintained at approximately 15 d after the acclimatization period.

2.3 Experimental design and approach

Prior to the experiments, the pilot plants were operated for at least two sludge ages (30 d) with stable process performance parameters as expected for a full-scale treatment plant. Two lanes were used, a test to measure any response from the shock load and a control to ensure validity of the response. Following each shock load, the test was allowed to return to pre-shock stable-operation for one sludge age before the next shock load. At the start of each shock load (0 h), the mixed liquor dissolved oxygen (MLDO), pH, temperature and mixed liquor suspended solids (MLSS) as well as influent and effluent chemical oxygen demand (COD), NH_3-N, NO_2^--N, NO_3^--N and N_2O were measured in both test and control. The influent and effluent NH_3-N, NO_2^--N, NO_3^--N, N_2O and DO were monitored either every 30 min or every 60 min for the duration of the 9 h experimental period. There was a total of eight shock loads, defined as runs 1-8, with repetition of each experiment (see Table 1).

For Runs 1 and 2, the aim was to reduce the ML DO concentration to <1.0 mg.L^{-1} for 1 h, after which the air was turned back on. This was accomplished by turning the air off at 0 h and then turning it back on at 1 h. Ammonia overload experiments (Runs 3 and 4) were undertaken by adding 2.55 g of NH_3-N (7.5 g of NH_3Cl dissolved in 1 L of distilled H_2O) to the test pilot plant lane with a shock load calculated to exert an instantaneous NH_3-N loading of 2.7mgNH_3-N g $MLSS^{-1}$ (mean value) and an oxygen demand of 3.5 mg.L^{-1} on the 315 L aeration tank. The shock load was added via a peristaltic pump at a rate of 45 L.h^{-1} to the anoxic zone at 0 h.

Allylthiourea (ATU) is an effective inhibitor of nitrification processes, blocking the NH_3-N to NH_2OH step of ammonia oxidation by inhibiting *Nitrosomona*s and not affecting the heterotrophic biodegradation activity (Hall, 1984; Reuschenbach et al., 2003). In this experiment (Runs 5 and 6), a shock load of ATU of 239.4 mg dissolved in 1 L of distilled H_2O was pumped at 45 $L.h^{-1}$ into the anoxic zone at 0 h. Sodium azide (NaN_3) is a strong, selective inhibitor of nitrite oxidation. It inhibits the oxidation of NO_2^- to NO_3^- but does not affect the oxidation of NH_4^+ to NO_2^- (Ginestet *et al.*, 1998). Two NaN_3 shock loads (Runs 7 and 8) were carried out to examine the N_2O response when interrupting the oxidation of nitrite to nitrate. A shock load of 7.245 g of NaN_3 dissolved in 1 L of distilled H_2O was pumped at 45 $L.h^{-1}$ into the anoxic zone at 0 h, a dose calculated to give 75 % inhibition.

2.4 Analytical methods

A gas analyser (7700 IR, Signal, UK), which used a dual-beam non-dispersive infrared (NDIR) method, accurately measured N_2O gas ranging from 0 - 1,200 ppm (± 1 %). The N_2O monitor was calibrated from compressed air and 1,000 ppm N_2O (BOC Group Plc, UK) weekly, with a detection limit of 0.1 ppm. The N_2O concentration was initially read from the front screen panel, but the NaN_3 experiments used a datalogger to store the results (Squirrel 400, Grant, UK). Simultaneously, an N-TOX® N_2O analyser (Water Innovate Ltd, UK) was used in one of the NaN_3 inhibition experiments to quantify off-gas N_2O emissions. The gas analyser remained separate from the activated sludge at all times, drawing off-gas by a small pump housed in the gas analyser from the headspace of a hood on the surface of the aeration tank via Perfluoroalkoxy (PFA) tubing. The non-contact method avoided operational problems normally associated with sensor fouling and corrosion.

Influent and effluent COD, NH_3-N, NO_2^--N, NO_3^--N were detected with Hach vial methods (Camlab and Merck vial method, Vwr International adapted from Standard Methods, APHA, 1998). Mixed liquor suspended solids (MLSS) were measured according to Standard Methods (American Public Health Association, 1998).

3. Results

The pilot-scale activated sludge plant received concentrations of COD and NH_3-N ranging from 136 - 326 and 21.5 - 45.3 $mg.L^{-1}$ respectively (Table 2). Pre-shock stable operation data showed that the pilot plants had COD and NH_3 removals ranging from 64.0 - 91.2 % and 93.5 - 100 % respectively, mimicking that of a full-scale plant (Table 2). During pre-shock operation, N_2O emissions were low and showed little variation ranging from 0 - 0.5 ppm (Table 2). Mixed liquor suspended solids (MLSS) varied from 1508 - 4261 $mg.L^{-1}$ and ML pH ranged from 6.39 - 7.12 in the activated sludge lanes (Table 3). Mixed liquor dissolved oxygen ranged from 1.8 - 4.7 $mg.L^{-1}$ and ML temperature ranged from 16.1 - 21.0℃ (Table 3). During all shock loads, the control-rig was monitored along side the test-rig and no responses in terms of N_2O, ML DO and effluent NH_3; NO_2^- and NO_3^- were observed.

In both the O_2 deprivation runs (Runs 1 and 2), the air was turned off for a period of 1 h and ML DO was seen to drop below 1 $mg.L^{-1}$ (Fig.2). There was no submersible pump to maintain mixing of the MLSS, and so no N_2O was observed in the first hour (Fig. 2). When the air was turned back on, there was an immediate rise in the N_2O concentration and a peak could be seen over the following 2 h at 16.5 and 17.1 ppm for Runs 1 and 2 respectively. In other words, the maximum N_2O emission occurred after 1 h from the start of aeration, which was mainly due to the lower ML DO (below

1 mg.L^{-1}) during the first two hours. After the peak, the N_2O emission rates in two runs were decreased gradually and were stable at relatively low levels after the DO rose to pre-shock concentrations (about 4 h (Run 1) and 5 h (Run 2) after the adjustment).

Fig. 2- Run 1 (a) and Run 2 (b) - Loss of aeration experiment; Headspace N_2O, NH_3-N Effluent, NO_3^--N Effluent and Dissolved Oxygen (secondary y-axis); A vertical line at 7h shows when that the experimental period reached one HRT.

Increases in effluent NH_3 can be seen at 7 h (one HRT) in both runs, although during Run 1 higher increase to 13.1 mg.L^{-1} compared with 3.4 mg.L^{-1} in Run 2 was observed. Nitrite was also monitored in Run 2 and was seen to rise to around 2.5 – 5mg.L^{-1} with effluent NH_3 at the HRT, with a concurrent decrease in effluent NO_3^- concentrations.

In Runs 3 and 4, the ammonia shock experiment, initial influent NH_3 concentration were 32.4 and 41.3 mg.L^{-1} respectively. With ammonia shock loads of 2.82 (Run 3) and 2.61 (Run 4) mgNH_3-N g[MLSS]$^{-1}$, an instantaneous sharp increase was seen in the N_2O emissions (Fig.3), with maximum peaks of 18.3 and 22.3 ppm for Runs 3 and 4 respectively, which then declined to pre-shock concentrations. A sharp increase in effluent NH_3 was also observed after one HRT, with maximum concentrations of 41.2 mg.L^{-1} (Run 3) and 39.1mg.L^{-1} (Run 4) respectively. On the other hand, an increase of effluent NO_2^--N occurred in run 4 (Fig 3b) but on a smaller scale at approximately 1.5 mg.L^{-1} NO_2^--N, which might be explained by the relatively low levels of the ammonia shock load. A simultaneous drop in ML DO, i.e. declining from 2 to 0.3

mg.L^{-1} in Run 3 and 2.8 to 0.8 mg.L^{-1} in Run 4, was seen following the ammonia shock load, recovering 3 h later in both runs. The minimum of the ML DO was accompanied by a peak in N_2O emission 60 min after the start of the ammonia shock loads.

Fig. 3-Run3 (a) and 4(b).Ammonia shock experiment; Headspace N_2O, NH_3-N effluent, NO_3^--N effluent and Dissolved Oxygen (secondary y-axis). A vertical line at 7h shows when that the experimental period reached one HRT.

An initial ATU dose of 23.94 mg, calculated to give a 75 % inhibition to activated sludge (CIWEM, 1997), gave no response. So the dosage was increased to 239.4 mg ATU for runs 5 and 6. After the ATU addition, immediate rises in N_2O off-gas concentrations of 26.7 and 20.1 ppm were observed for Runs 5 and 6 respectively followed by a 4 h recovery period to pre-shock concentrations (Fig. 4). After one HRT, a simultaneous increase in effluent NH_3 and a decrease in effluent NO_3^- were observed in both runs. Maximum observed NH_3-N were at concentrations of 11.4 and 12.5 mg.L^{-1} for Runs 5 and 6, with NO_2^- effluent increasing also at the HRT (Fig 4b). Unlike the two former experiments, ML DO in these two runs increased slightly during first two hours and then reverted to pre-shock concentrations gradually. This indicated that the rise in N_2O off-gas was directly related to toxicity, and not due to the impact of available oxygen.

Fig.4-Run 5 (a) and Run 6 (b). Increased AO inhibition experiment; Headspace N_2O, NH_3-N effluent, NO_3^--N effluent, NO_2^--N effluent and Dissolved Oxygen

(secondary y-axis). A vertical at 7h shows when that the experimental period reached one HRT.

A second N_2O analyser was used for independent verification of the results from the Signal analyser in Run 7. As shown in Fig. 5, an immediate and sharp rise in N_2O emission occurred, peaking at 186.3 and 147.5 ppm for Runs 7 and 8 respectively, but did not recover to pre-shock concentrations. In particular, it should also be mentioned that N_2O emission characteristics or patterns in these two runs were significantly different. A remarkable N_2O peak occurred in Run 7, after which the N_2O profile declined gradually. In contrast, during Run 8, a sharp and continuous rise of N_2O concentration was observed but had not reached a peak until at 7 h (one HRT), followed by a constant level for the prolonged reaction. Concomitantly, there was a drop in effluent NO_3^- at 7h and an increase in effluent NO_2^- to maximum observed concentrations of 9.8 and 8.7 mg.L^{-1} for Runs 7 and 8 respectively. Mixed liquor DO remained at constant levels at approximately 1.5 mg.L^{-1} throughout the test and no ammonia responses were observed.

Fig.5-Run 7(a) and Run 8 (b)– NO inhibition experiment; NH_3-N effluent, NO_3^--N effluent, NO_2^--N effluent, Dissolved Oxygen and Headspace N_2O (secondary y-axis) (*Signal N_2O analyser; **N-TOX N_2O analyser). A vertical line at 7h shows when that the experimental period reached one HRT.

Time sequence analysis for observed N_2O peaks and increases of effluent NH_4/NO_x in these four experiments are summarized in Fig.6. It can be seen that the observed N_2O peak always preceded the appearance of ammonia and nitrite in the effluent by approximately 3~5 h, i.e. 0.43~0.71*HRT.

Fig. 6- Time sequence analysis for observed N_2O peak and effluent NH_4/NO_x increasing during nitrification.

4. Discussion

In both the loss of aeration and ammonia overloading experiments, the transient accumulation of N_2O was observed in the aerobic period, followed by a lag time of approximately 3-5 h before an increase in NH_3-N and NO_2^--N effluent. It is this lag time that provided the early warning. These results confirmed the findings of Burgess et al. (2002b), who proposed that off-gas N_2O from aeration tanks can provide early warning of nitrification failure when effective loss of dissolved oxygen occurs, either due to loss of aeration or a high oxygen demand load. In the oxygen depletion experiments, the N_2O increase was not observed until the air was turned back on. Kimochi et al. (1998) also observed N_2O concentrations in the headspace to be the highest immediately after starting aeration and gradually decreasing with time. Similar results were reported by Zheng et al. (1994) and Burgess et al. (2002b), who both found that a high concentration of N_2O was produced by activated sludge systems during the nitrification process under low DO conditions. Moreover, Noda et al. (2003) revealed that N_2O emission was accelerated under low DO conditions insufficient for nitrification. Previous authors have reported that the mechanism for N_2O release by ammonia oxidisers is a simultaneous reduction of NH_3 and oxidation of NO_2^- (Poth and Focht, 1985; Anderson *et al*., 1993; Bock *et al*., 1995). Research by Poth and Focht (1985) has shown that NO_2^- could act as an electron acceptor during oxygen-limited nitrification. Their findings suggested that ammonia oxidizing bacteria (AOB) such as *Nitrosomonas* possess a nitrite reductase enzyme, which is activated under oxygen-limiting conditions and dominated over the nitrite oxidoreductase enzyme. The decrease in effluent NO_3^- for the experiments when aeration was ceased suggested that the nitrite oxidisers were inhibited due to the lack of oxygen and were unable to oxidise the NO_2^- through to NO_3^-. Also, Laanbroek and Gerads (1993) demonstrated that the ability of ammonia oxidisers to substitute oxygen with nitrite as the terminal electron acceptor at low oxygen concentrations gave them a competitive edge over nitrite oxidisers.

Based on the above discussion, we concluded that the increase in N_2O concentration in DO depleted experiments was a result of the decrease in DO, which caused the bacteria to use nitrite as the terminal electron acceptor (Kuai and Verstraete, 1998). However, in municipal wastewater treatment plants, nitrogen removal is achieved at low oxygenation to reduce cost, i.e. in conditions favorable to N_2O production. So, on-line monitoring ML DO and off-gas N_2O emissions for the biological nitrification processes could be of significance in terms of saving operating costs as well as protecting the environment. Recent simulation studies undertaken by Sivret et al. (2008) indicate that nitrous oxide could be used to provide better control of aeration in nitrifying activated sludge plants.

In both the inhibitor experiments, a N_2O response was followed by an increase in effluent NH_3 and/or effluent NO_2^-. It is again the lag time that provided the early warning for nitrification failure. By the addition of an inhibitor, nitrification did not progress sufficiently, and thus accumulation of ammonia and/or nitrite was observed.

For the ATU inhibitor experiment, since the first step of nitrification was blocked, N_2O emissions were probably produced only through denitrification by heterotrophic denitrifying bacteria. Although the N_2O emission rate from the denitrification pathway is lower under a high oxygen concentration compared to that at low oxygen concentration, N_2O was observed since denitrifying bacteria are able to denitrify in aerobic conditions (Krul and Veemingen, 1977). Likewise, a previous study has also observed that the N_2O concentration increased when an ATU dose of 0.076 $mg.L^{-1}$ was applied to the aeration tank (Burgess et al., 2002b). At full-scale, the off-gases can be captured via a hood before delivery to the N_2O detection system; this has been demonstrated on full-scale industrial and municipal activated sludge plants (Butler et al., 2005b).

Mitigation of nitrification toxicity could be achieved by a range of possible actions; the simplest might be diversion of incoming flow to holding tanks, to be blended into the plant over time. Alteration of process operating conditions that are recognised as favourable to nitrification, e.g. pH adjustment and increasing aeration, is another obvious strategy. If the cause of the toxic event is a known chemical, then a specific mitigation strategy could be used e.g. addition of multivalent cations to prevent nitrification inhibition by ethylenediaminetetraacetic acid (EDTA) (Hu et al., 2003). Bioangmentation with nitrifying bacteria has also been used to improve ammonia removal, however, large amounts would be needed for severe shocks (Abeysinghe et al., 2002). It is also possible that addition of copper could stimulate nitrification (Ensign et al., 1993).

5. Conclusions

All shock loads experiments showed that the observed N_2O peak always preceded the appearance of ammonia/nitrite in the effluent by approximately 3-5 h, i.e. 0.43~0.71*HRT. It is this lag time, before NH_3 and/or NO_2^- appears in the effluent, which provides early warning for nitrification failure. The increase of N_2O emission, therefore, may be a good indicator for monitoring the nitrification process, as they are correlated to both influent wastewater characteristics (e.g. ammonia load, toxic inhibitors) and operational parameters (e.g. DO) for the aeration tank.

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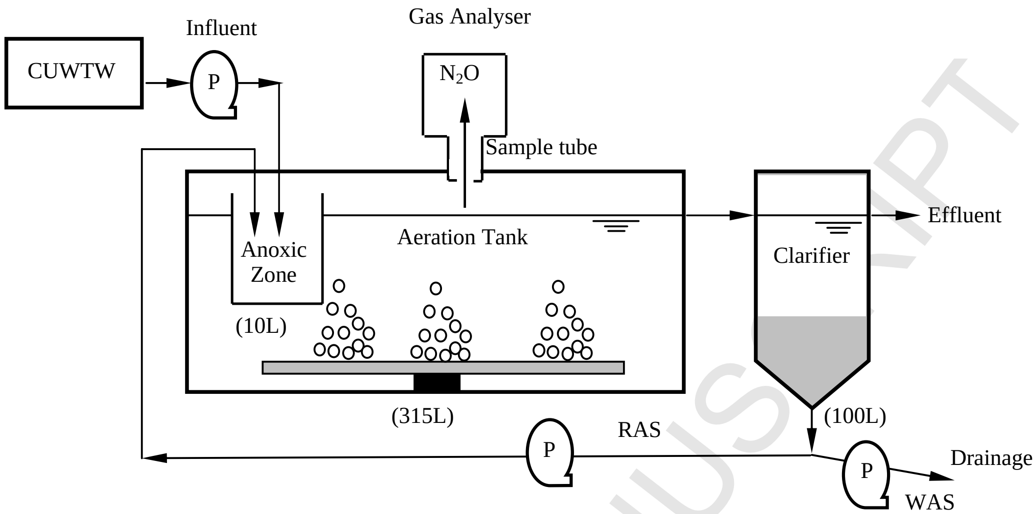
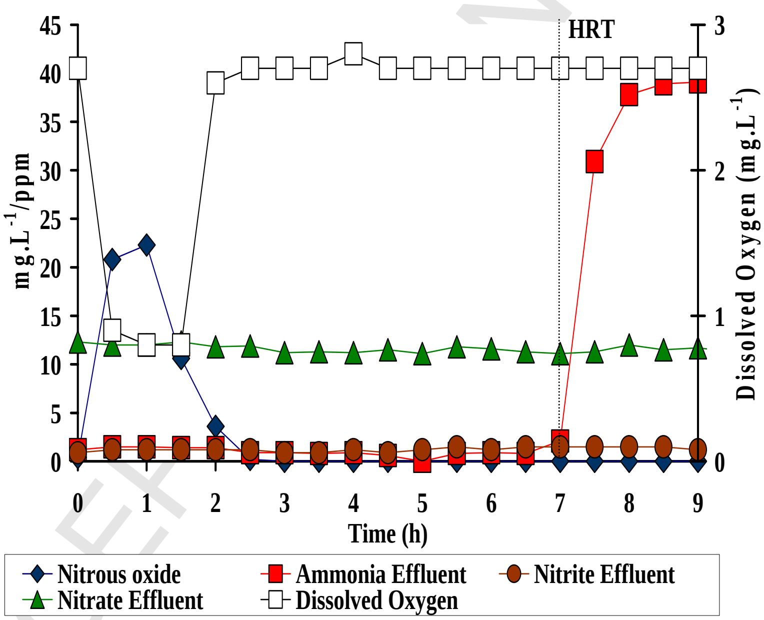


(P-peristaltic pump; RAS-Recycled Activated Sludge; WAS-Wasted Activated Sludge and CUWTW-Cranfield University Wastewater Treatment Works)

b



HRT
mg.L⁻¹/ppm
Dissolved Oxygen (mg.L⁻¹)
Time (h)
0
5
10
15
20
25
30
35
40
45
0
1
2
3
0
1
2
3
4
5
6
7
8
9
Nitrous oxide
Ammonia Effluent
Nitrite Effluent
Nitrate Effluent
Dissolved Oxygen

Shock loads	Experiment	Effect on MLSS(aeration tank)	Source

Table 1-Experimental overview of shock loads and their effects

1	Loss of aeration	DO <1.0 mg.L^{-1} for 1 hour	Burgess *et al*. (2002)
2	Loss of aeration	DO <1.0 mg.L^{-1} 1 for 1 hour	Burgess *et al*. (2002)
3	NH_3 overload	2.82 mgNH_3-N g[MLSS]$^{-1}$ (3.5mg.L^{-1} O_2 demand)	Burgess *et al*. (2002)
4	NH_3 overload	2.61mgNH_3-N g[MLSS]$^{-1}$ (3.5mg.L^{-1} O_2 demand)	Burgess *et al*. (2002)
5	AO[a] inhibition	750 % inhibition (239.4 mg ATU)	CIWEM (1997)
6	AO[a] inhibition	750 % inhibition (239.4 mg ATU)	CIWEM (1997)
7	NO[b] inhibition	75 % inhibition (7.245 g NaN_3)	Tomlinson (1966)
8	NO[b] inhibition	75 % inhibition (7.245 g NaN_3)	Tomlinson (1966)

[a]AO, Ammonia Oxidation
[b]NO,Nitrite Oxidation

Table 2- Influent and effluent COD,NH_3 for pilot plants at pre-shock steady-state condition

Influent (mg.L^{-1})	Effluent (mg.L^{-1})		N_2O(ppm)
	COD	NH_3	

	COD	NH_3		C[a]	T[b]	C[a]	T[b]	C[a]	T[b]
1-O_2	187	26.3	7.11	49	38	0.3	0.4	0.1	0.2
2-O_2	207	24.4	8.48	38	48	0.1	0.0	0.2	0.0
3-NH_3	304	35.4	8.59	65	87	0.2	0.0	0.3	0.0
4-NH_3	326	45.3	7.20	48	40	1.3	1.2	0.1	0.4
5-ATU	136	21.8	6.24	49	34	0.2	0.4	0.0	0.4
6-ATU	163	25.7	6.34	41	58	0.3	1.1	0.4	0.2
7- NaN_3	277	29.4	9.42	40	45	0.0	0.1	0.5	0.0
8- NaN_3	260	21.5	12.09	36	23	0.9	1.4	0.2	0.0

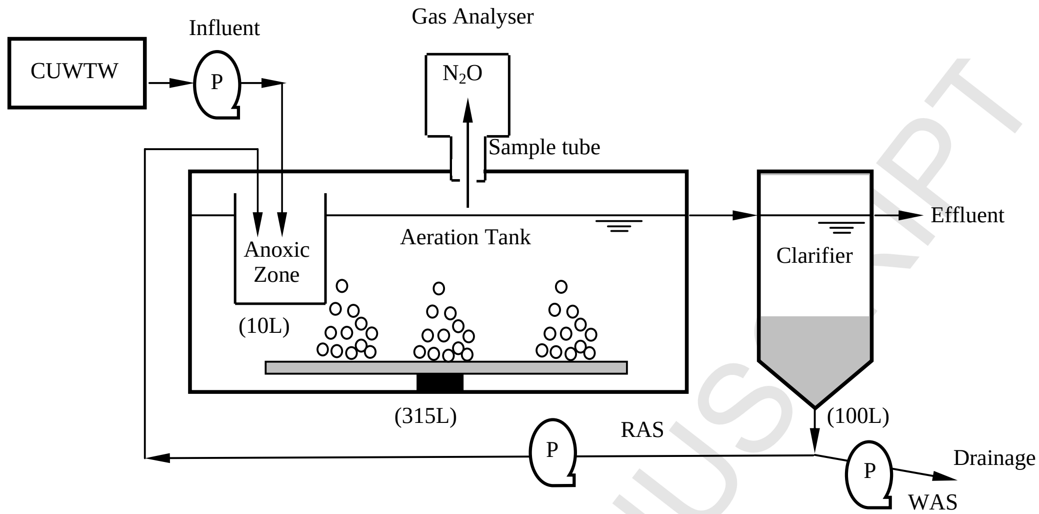
[a]C,Control-rig
[b]T,Test-rig

Table 3-Operational parameters for pilot plants at pre-shock steady-state condition

Shock loads	ML SS ($mg.L^{-1}$)		ML DO ($mg.L^{-1}$)		ML pH		ML Temp. (°C)	
	C[a]	T[b]	C[a]	T[b]	C[a]	T[b]	C[a]	T[b]
1-O_2	2189	1998	2.6	2.8	6.43	6.56	19.6	19.7

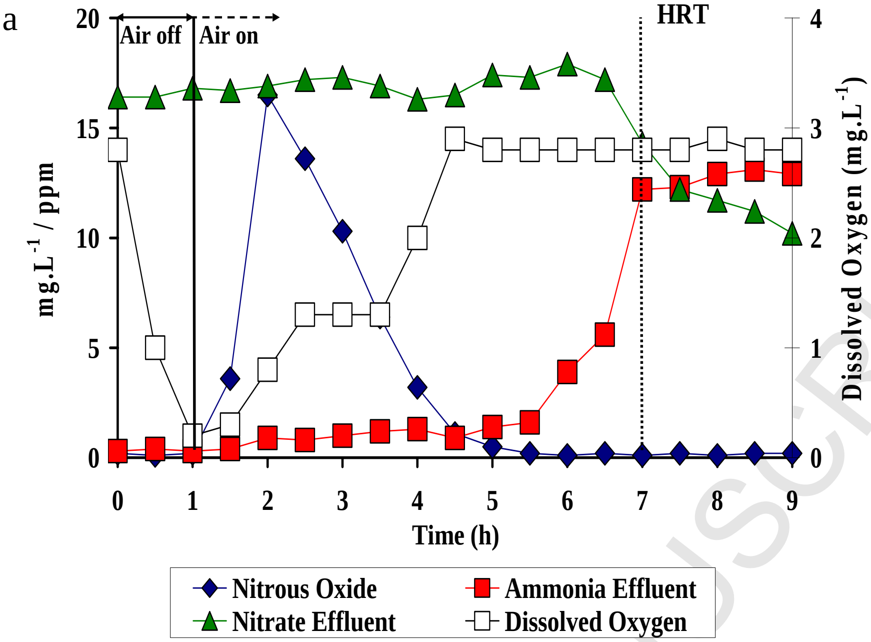
2-O_2	1641	1732	4.3	3.2	6.98	6.82	16.1	16.2
3-NH_3[c]	2321	2256	2.2	2.1	6.58	6.95	19.1	19.2
4-NH_3	2234	2432	2.8	2.7	7.01	6.95	18.4	18.7
5-ATU	1508	2032	4.3	5.2	6.27	6.56	17.7	21.0
6-ATU	1731	2241	2.4	4.7	7.12	6.62	19.9	17.8
7- NaN_3	3918	4261	1.8	2.1	6.62	6.39	18.8	19.4
8- NaN_3	2904	4235	3.7	2.3	6.77	6.73	19.3	19.8

[a]AO, Ammonia Oxidation
[b]NO,Nitrite Oxidation
[c]instantaneous addition



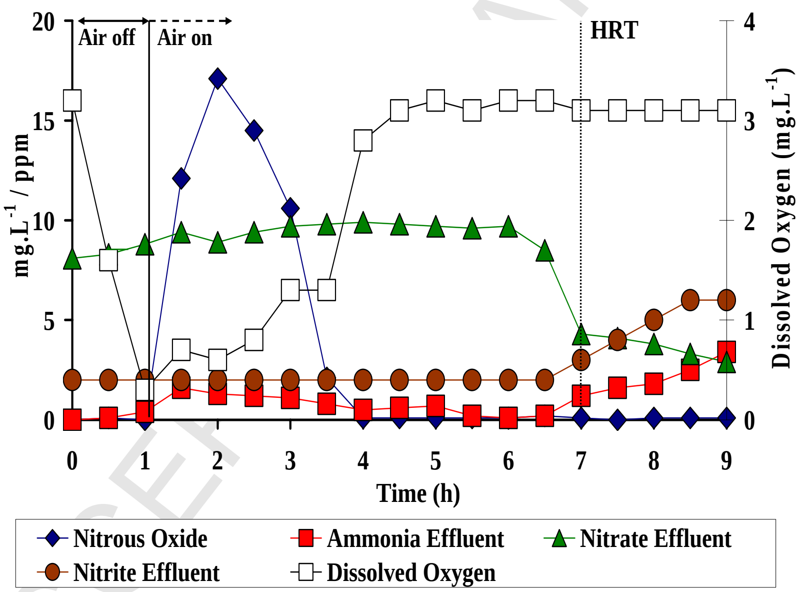
(P-peristaltic pump; RAS-Recycled Activated Sludge; WAS-Wasted Activated Sludge and CUWTW-Cranfield University Wastewater Treatment Works)

a



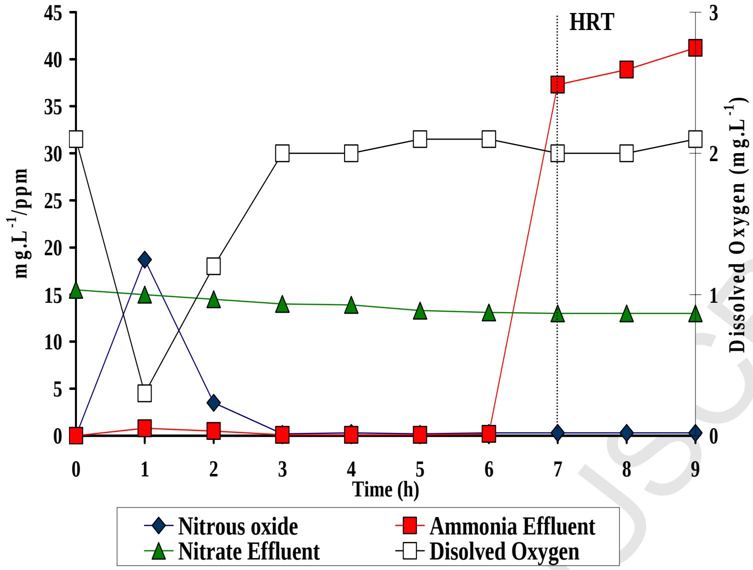
Air off
Air on
HRT
mg.L-1 / ppm
Dissolved Oxygen (mg.L-1)
Time (h)
20
15
10
5
0
4
3
2
1
0
0 1 2 3 4 5 6 7 8 9
Nitrous Oxide
Ammonia Effluent
Nitrate Effluent
Dissolved Oxygen

b



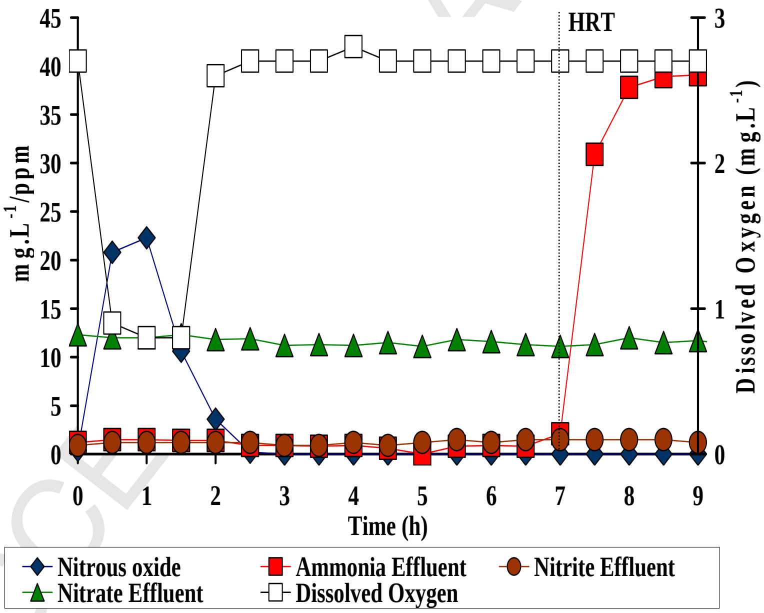
Air off
Air on
HRT
mg.L-1 / ppm
Dissolved Oxygen (mg.L-1)
Time (h)
0
5
10
15
20
0
1
2
3
4
0
1
2
3
4
5
6
7
8
9
Nitrous Oxide
Ammonia Effluent
Nitrate Effluent
Nitrite Effluent
Dissolved Oxygen

a

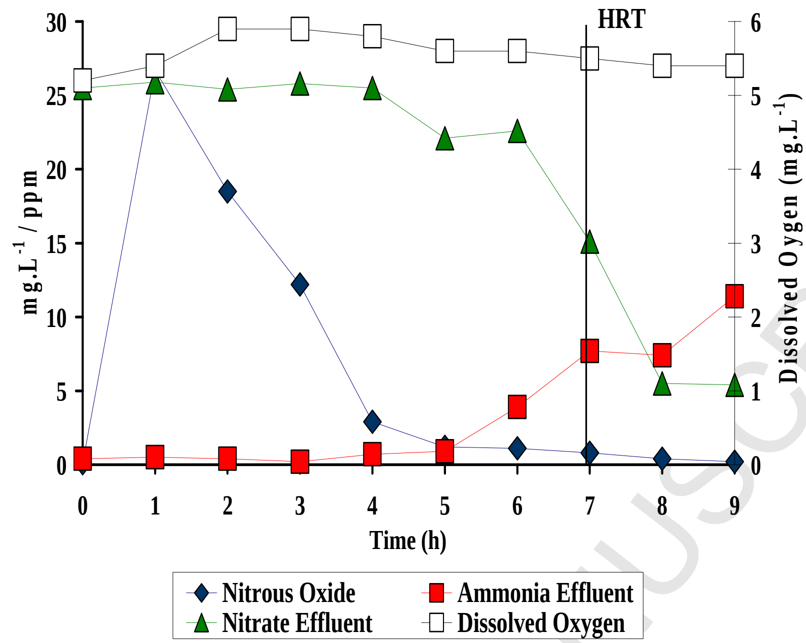


HRT
mg.L-1/ppm
Dissolved Oxygen (mg.L-1)
Time (h)
45
40
35
30
25
20
15
10
5
0
3
2
1
0
0 1 2 3 4 5 6 7 8 9
Nitrous oxide
Ammonia Effluent
Nitrate Effluent
Disolved Oxygen

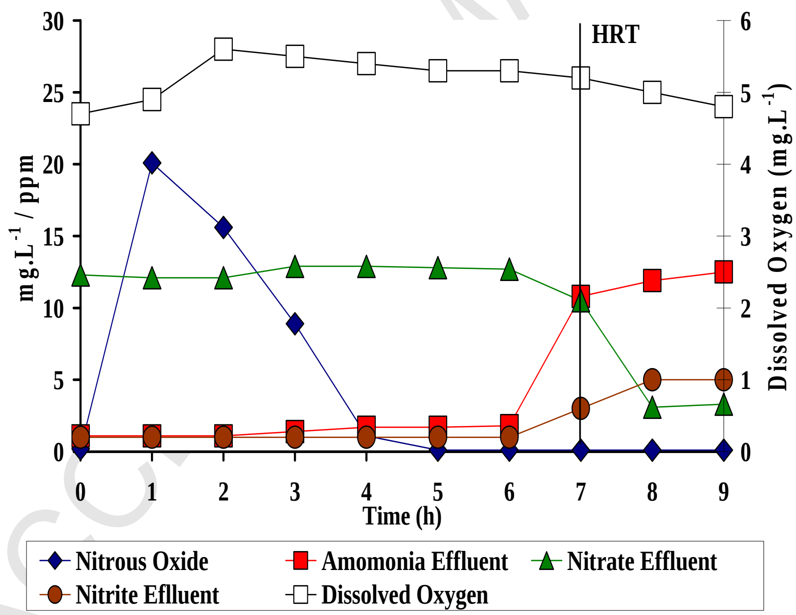
b


45
40
35
30
25
20
15
10
5
0
mg.L -1/ppm
HRT
3
2
1
0
Dissolved Oxygen (mg.L-1)
0 1 2 3 4 5 6 7 8 9
Time (h)
Nitrous oxide
Ammonia Effluent
Nitrite Effluent
Nitrate Effluent
Dissolved Oxygen

a

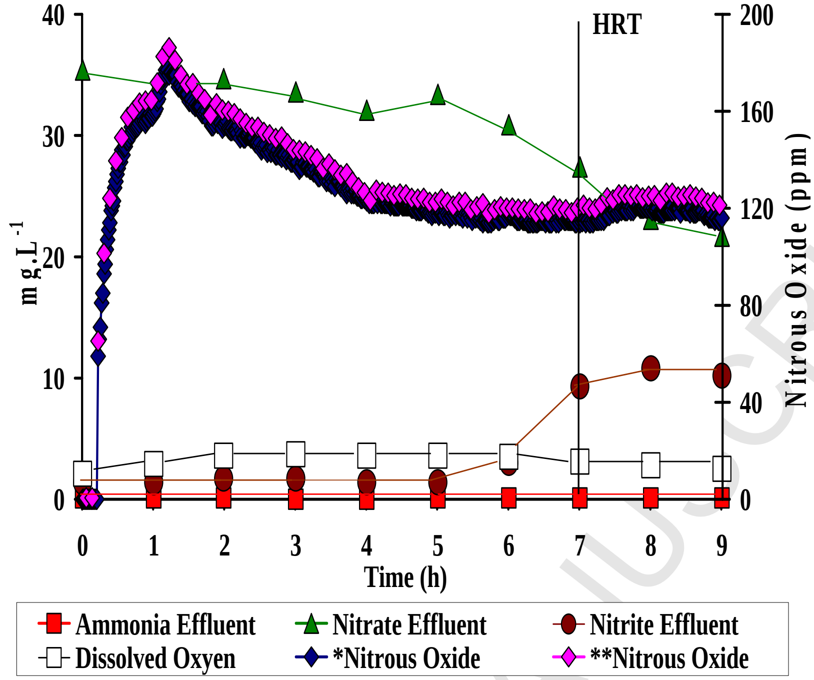

30
25
20
15
10
5
0
mg.L -1 / ppm
6
5
4
3
2
1
0
Dissolved Oygen (mg.L -1)
HRT
0 1 2 3 4 5 6 7 8 9
Time (h)
Nitrous Oxide
Ammonia Effluent
Nitrate Effluent
Dissolved Oxygen

b

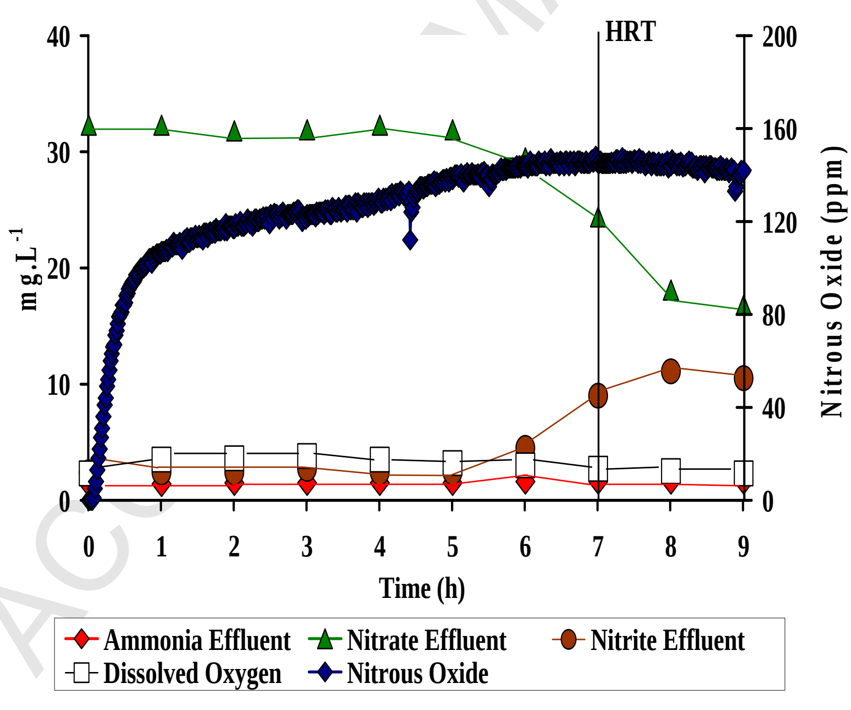


30
25
20
15
10
5
0
6
5
4
3
2
1
0
m g.L -1 / p p m
Dissolved Oxygen (mg.L -1)
HRT
0
1
2
3
4
5
6
7
8
9
Time (h)
Nitrous Oxide
Amomonia Effluent
Nitrate Effluent
Nitrite Effluent
Dissolved Oxygen

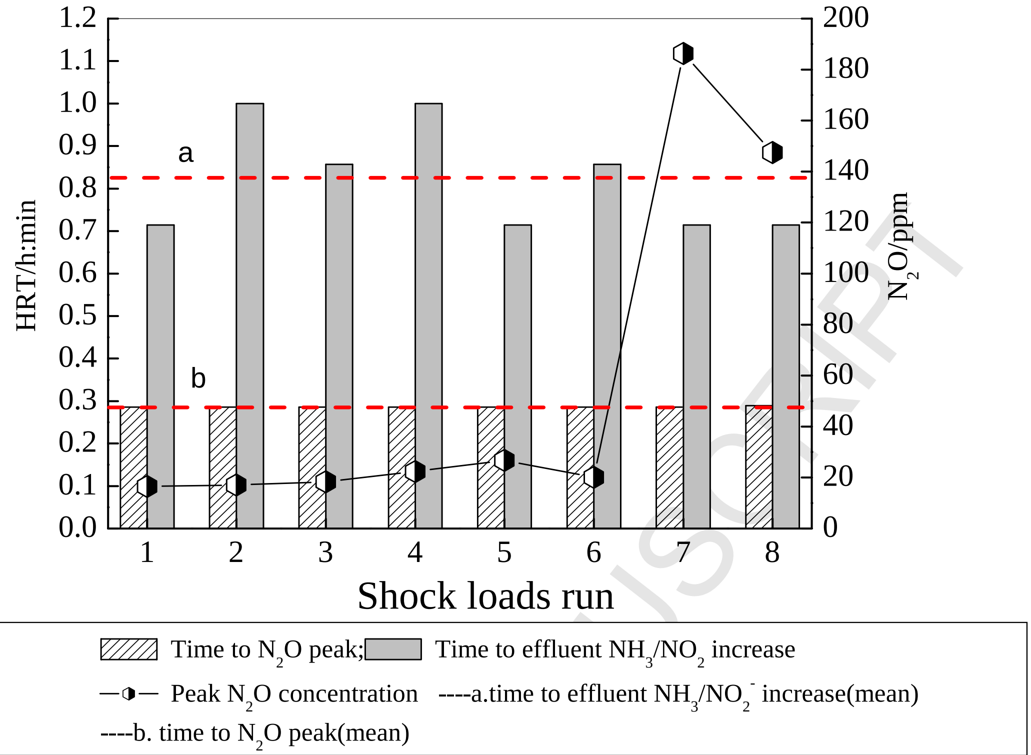
a



40
30
20
10
0
m g.L -1
200
160
120
80
40
0
Nitrous Oxide (ppm)
HRT
0
1
2
3
4
5
6
7
8
9
Time (h)
Ammonia Effluent
Nitrate Effluent
Nitrite Effluent
Dissolved Oxyen
*Nitrous Oxide
**Nitrous Oxide



40
30
20
10
0
mg.L-1
200
160
120
80
40
0
Nitrous Oxide (ppm)
HRT
0
1
2
3
4
5
6
7
8
9
Time (h)
Ammonia Effluent
Nitrate Effluent
Nitrite Effluent
Dissolved Oxygen
Nitrous Oxide


1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
HRT/h:min
200
180
160
140
120
100
80
60
40
20
0
N2O/ppm
a
b
1
2
3
4
5
6
7
8
Shock loads run
Time to N2O peak;
Time to effluent NH3/NO2 increase
Peak N2O concentration
----a.time to effluent NH3/NO2- increase(mean)
----b. time to N2O peak(mean)