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Odour Control Strategies in Wastewater Treatment Plants: Activated Sludge Recycling and Oxidized Nitrogen Recycling

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One of the main concerns associated with wastewater management is the emission of unpleasant odours. The odorous impact derived from wastewater treatment plants (WWTPs) is a source of public environmental complaints in residential areas near these facilities, since odour pollution can cause significant negative effects on the quality of life and the environment. This odorous contamination typically derives from the presence of volatile sulphur compounds (VSCs) and volatile organic compounds (VOCs), some of which have very low odour threshold values, as is the case of H_2S. For this reason, odour prevention strategies in wastewater treatment facilities need further research to find effective and low-cost technologies for the control of malodorous emissions. The purpose of this study was the reduction of the emission of malodorous compounds in WWTPs based on the optimization of the use of by-products derived from wastewater treatment such as the oxidized nitrogen (N-NO_X) from residual streams rich in nitrate (N-NO_3^-) or nitrite (N-NO_2^-) and activated sludge (AS) from the mixed liquor of the nitrification tank or secondary settler. In the experimental tests, gas-tight 2.1 L glass bottles with synthetic septic wastewater were used to evaluate the potential of N-NO_x and AS at different concentrations to biodegrade H_2S, acetic acid and α-pinene as model odorants. Among the most remarkable results, odorant adsorption losses were observed during preliminary abiotic tests (4 h) with concentration losses of 25 % for H_2S and α-pinene, and 7 % for acetic acid. The experiments carried out at different concentrations of AS (0, 10, 25, 50, 100 mg VSS/L) and oxidized nitrogen concentrations (1.5, 5, 7.5 and 10 mg N-NO_x/L) showed an efficient H_2S removal at 7.5–10 mg N-NO_x/L and 50–100 mg VSS/L. However, NO_3^- supported a more effective H_2S abatement than NO_2^-. The concentration of acetic acid showed a slight decrease due to its degradation by microorganisms (from 27 to 23 ppm_v in 4.5 h), concomitantly with the complete biological oxidation of H_2S. Conversely, α-pinene concentrations experienced a similar gradual decrease than in the abiotic tests, with a low influence of NO_3^-, NO_2^- and AS concentrations. Finally, a marked reduction of NO_2^- was observed when increasing AS concentration, suggesting that higher concentrations of NO_2^- compared to NO_3^- are required for complete biological oxidation of odorants during wastewater treatment.

1. Introduction

One of the main concerns associated with Wastewater Treatment Plants (WWTPs) is the emissions of malodours (Lewkowska et al., 2016). Volatile sulphur compounds (VSCs) and volatile organic compounds (VOCs) rank among the most typical compounds that contribute to the wastewater management odour footprint (Hu and Liu, 2018; Lebrero et al., 2011). In particular, hydrogen sulphide (H_2S) and volatile fatty acids (VFAs) emissions are the main responsible of odour nuisance in WWTPs (Beghi et al., 2012; Dinçer et al., 2020). Physical-chemical treatment have been previously tested in literature to mitigate the emission of odorants from wastewater treatment. However, these conventional solutions present important disadvantages such as the use of chemicals and energy consumption. For this reason, biological odour prevention methods have emerged as an economically and environmentally sustainable alternative for the minimization of odour pollution in WWTPs. In this context, the recirculation to the headworks of nitrates derived from centrate oxidation and activated sludge (AS) from the secondary settler could foster the adsorption and further oxidation of VSCs and VOCs in the raw wastewater. More specifically, activated sludge recycling (ASR) is based on the recirculation of waste activated sludge from the secondary settler or mixed liquor of the nitrification tank to the WWTP headworks.

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These AS streams can adsorb and biologically oxidize most biogenic dissolved odorous compounds (e.g., sulphide, volatile fatty acids) in the influent (Kiesewetter et al., 2014). Similarly, oxidized ammonium recycling (OAR) consists of the recycling of residual streams rich in nitrate ($N\text{-}NO_3^-$) or nitrite ($N\text{-}NO_2^-$) to the WWTP headworks. The addition of nitrate or nitrite as electron acceptors to the influent wastewater promotes an *in-situ* anoxic odorant oxidation (Estrada et al., 2015). The present work evaluates the influence of the concentrations of fresh activated sludge, nitrate and nitrite on the removal of H_2S, acetic acid and α-pinene, here selected as model odorants.

2. Materials and methods

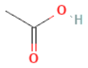
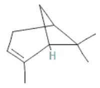
2.1 Synthetic wastewater

In order to mimic the physico-chemical characteristics and composition of a model urban wastewater, a modified synthetic wastewater (SW) was prepared according to Bajaj et al. (2008) as follows (mg/L in tap water): 250 of glucose, 110 of meat extract, 160 of casein peptone, 30 of NH_2COH_2, 7 of NaCl, 4 of $CaCl_2 \cdot 2H_2O$, 2 of $MgSO_4 \cdot 7H_2O$, 112 of $K_2HPO_4 \cdot 3H_2O$, 0.5 of $CuCl_2 \cdot 2H_2O$, and 1100 of $NaHCO_3$.

2.2 Chemical odorants

In this study, hydrogen sulphide (H_2S), acetic acid ($C_2H_4O_2$) and α-pinene ($C_{10}H_{16}$) were used as model odorous compounds. Table 1 shows the chemical formula, odour perception, Henry solubility (H^{cc}), molecular weight and structure of each volatile compound.

Table 1: Main characteristics of the model odorous compounds evaluated.

Compound	**Chemical formula**	**Odour perception**	**Odour threshold value (ppm, v/v)** (Nagata, 2003)	H^{cc}	**Molecular weight (g/mole)**	**Molecular structure**
Hydrogen sulphide	H_2S	Rotten egg	0.00041	0.00091 (Rinker and Sandall, 2000)	34.10	
Acetic Acid	$C_2H_4O_2$	Vinegar	0.0060	14 (Hartungen et al., 2004)	60.05	
α-pinene	$C_{10}H_{16}$	Pine, tupentine	0.018	0.00029 (Leng et al., 2013)	136.23	

2.3 Experimental set-up

Aliquots of 300 mL of SW supplemented with different concentrations of nitrate or nitrite (Table 2) by stock solutions of $NaNO_3$ or $NaNO_2$ (2 g/L) were added into glass bottles of 2.1 L, which were then closed with butyl septa and aluminium caps. The headspace was subsequently flushed with helium in order to provide anaerobic conditions. In order to mimic a septic wastewater, the target odorous compounds were injected into the bottle headspace through the butyl septum with a total mass of 2.10, 0.42 and 0.07 mg of acetic acid, α-pinene and H_2S, respectively (corresponding to 2 µL of liquid acetic acid, 0.5 µL of liquid α-pinene and 250 µL of gaseous H_2S at 22 %). After injection, each bottle was pressurized with helium at 500 mbar in order to fulfil the technical requirements of the mass spectrometer used to quantify the odorants in the headspace. Subsequently, each bottle was vigorously shaken for 2 min to facilitate gas-liquid equilibrium and the initial concentrations of each target compound was analysed in the headspace by mass spectrometry (MS). Finally, different concentrations of fresh activated sludge were injected into the aqueous phase (Table 2) and the monitoring of odorant concentration was carried out at 30, 60, 180 and 270 min. The glass bottles were gently incubated in a horizontal rotary incubator at 7 rpm and at ambient temperature (21 ºC). It is important to highlight that control experiments (i.e., without the supplementation of oxidized nitrogen and activated sludge) were also performed following the procedure previously described.It is important to highlight that ammonia concentration in the centrates from anaerobic digestion is ranged between 900 - 1500 mg/L, which could be transformed into $N\text{-}NO_3$ or $N\text{-}NO_2$, considering the centrate flowrate (Q_C) and the influent raw wastewater flowrate (Q_O), with maximum $N\text{-}NO_3$ or $N\text{-}NO_2$ concentrations of 6 - 10 mg N/L. Likewise, the volatile suspended solids (VSS) of waste activated sludge from secondary settlers is ranged between 4000 - 12000 mg VSS/L, from which a maximum AS concentration of 100 mg VSS/L could be recirculated if the waste activated sludge flowrate (Q_W) and the influent raw wastewater flowrate (Q_O) are considered (Toledo and Muñoz, 2022).

Table 2: Experimental design of the OAR and ASR assays

Bottle identification	AS concentration (mg VSS/L)	N-NO_3 and N-NO_2 concentration (mg/L)	Number of experiments
B1	0	1.5	8
		5	
		7.5	
		10	
B2	10	1.5	8
		5	
		7.5	
		10	
B3	25	1.5	8
		5	
		7.5	
		10	
B4	50	1.5	8
		5	
		7.5	
		10	
B5	100	1.5	8
		5	
		7.5	
		10	

3. Results and discussion

3.1 Evaluation of odorant fate under abiotic conditions

The initial headspace concentrations of acetic acid, α-pinene and H_2S under abiotic conditions accounted for 26, 16 and 11 ppm_v, respectively (Figure 1). The concentration of acetic acid, α-pinene and H_2S showed a slight decrease after 270 min of experiment, which represented a ≈ 25 % loss for α-pinene and H_2S and > 7 % for acetic acid. Taking into account that the gas-liquid equilibrium was reached at time 0, abiotic losses were associated to odorant adsorption onto the glass surface or butyl septum. Adsorption phenomena of odorants in glass is related to an elicit ionic adsorption of molecules to the silanol groups (positive ion exchange mode) and a hydrophobic adsorption mediated by the siloxane groups (Costa et al., 2020).

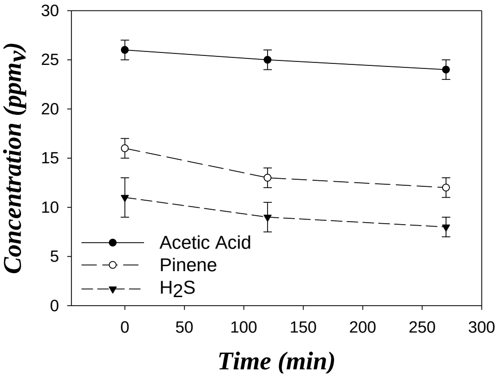


Figure 1: Time course of acetic acid, α-pinene and H_2S headspace concentrations under abiotic conditions

3.2 Influence of N-NO_x and activated sludge concentration on odorant fate

In this study, the biological oxidation of H_2S under anoxic conditions was confirmed (Figure 2). The headspace concentration of H_2S progressively decreased as the concentration of NO_3^-, NO_2^- and AS increased. More specifically, a sharp decrease in H_2S headspace concentration was recorded for the first 60 min of assay, followed by a gradual decrease in H_2S fate along with the occurrence of lower gas-liquid concentrations gradients. The fastest depletion of H_2S was observed at 10 mg NO_x/L and 100 mg VSS/L. In this context, the supplementation of septic wastewater with 100 mg VSS/L reduced H_2S concentration to 0 ppm_v in 4.5 h even at the lowest NO_3^- and NO_2^- concentrations tested. The addition of NO_3^- or NO_2^- to the influent wastewater promotes anoxic conditions, where oxidized nitrogen is used as an electron acceptor by microorganisms (e.g., chemolithotrophic bacterial species or Sulphur Oxidizing Bacteria “SOB”) which are capable of oxidizing dissolved sulphide and other biodegradable odorants, thus preventing their further release as malodorous emissions (Kiesewetter et al., 2014). Overall, NO_3^- (Figure 2a) was more effective than NO_2^- (Figure 2b) to biodegrade H_2S regardless of the AS and N-NO_x concentrations. The anoxic oxidation of H_2S by OAR and ASR can be described by Eq (1) and Eq (2) (Yang et al., 2005):

$$3H_2S + 2NO_2^- + 2H^+ \xrightarrow{SOB} 3S^0 + N_2 + 4H_2O \tag{1}$$

$$5H_2S + 2NO_3^- + 2H^+ \xrightarrow{SOB} 5S^0 + N_2 + 6H_2O \tag{2}$$

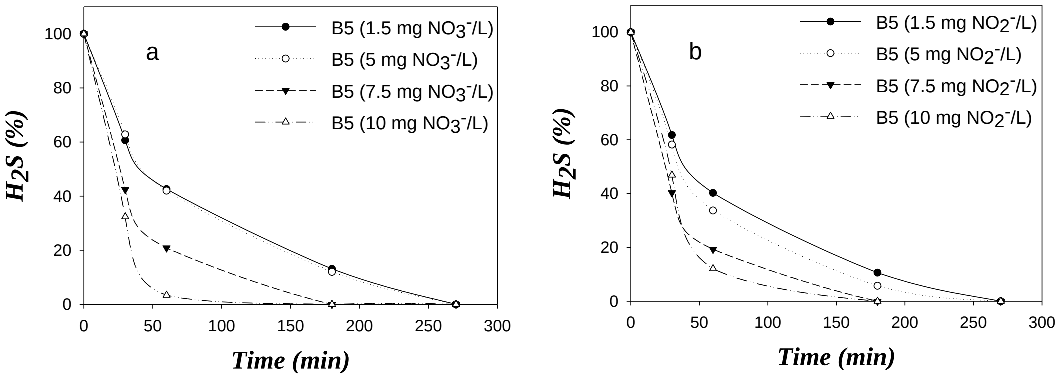


Figure 2: Time course of H_2S headspace concentration under different concentrations of N-NO_3^- (a), N-NO_2^- (b) and activated sludge (100 mg VSS/L)

However, the addition of NO_3^- under sulphur limiting conditions could lead to a potential reduction of NO_3^- to NO_2^- during biological H_2S oxidation according to Eq (3). This fact could cause toxicity problems in the environment or river ecosystems, in particular at low pH values (Alleman, 1985).

$$H_2S + NO_3^- + 2H^+ \xrightarrow{SOB} S^0 + NO_2^- + H_2O \tag{3}$$

In the case of acetic acid (Figure 3a), the experiments conducted at 0, 10 and 25 mg VSS/L showed a slight increase in acetic acid concentration regardless to the concentration of NO_3^-, NO_2^- and AS supplemented, reaching a maximum value of 30 - 31 ppm$_v$. In the assays carried out at 50 and 100 mg VSS/L, acetic acid concentration remained almost constant for the first 180 min and a gradual decrease in concentration was observed from 27 ± 1 to 23 ± 1 ppm$_v$ due to the anoxic biodegradation of this odorant. In fact, most microorganisms present in AS can use the electron acceptor capacity of NO_3^- or NO_2^- to metabolize readily biodegradable compounds such as VFAs, which are key substrates in the biological removal of phosphate and nitrogen in AS processes (Janssen et al., 2002). On the other hand, the initial concentration of α-pinene of 13 ± 2 ppm$_v$ gradually decreased to a final concentration of 8 ± 1.5 ppm$_v$, which accounted for a removal of 20 - 25 % of this odorant compound. Based on the low aqueous solubility of α-pinene (Table 1) and the low influence of NO_3^-, NO_2^- and AS concentrations on α-pinene fate (Figure 3b), the observed decrease in concentration could be attributed to adsorption phenomena on solid surfaces (Hale et al., 2015).

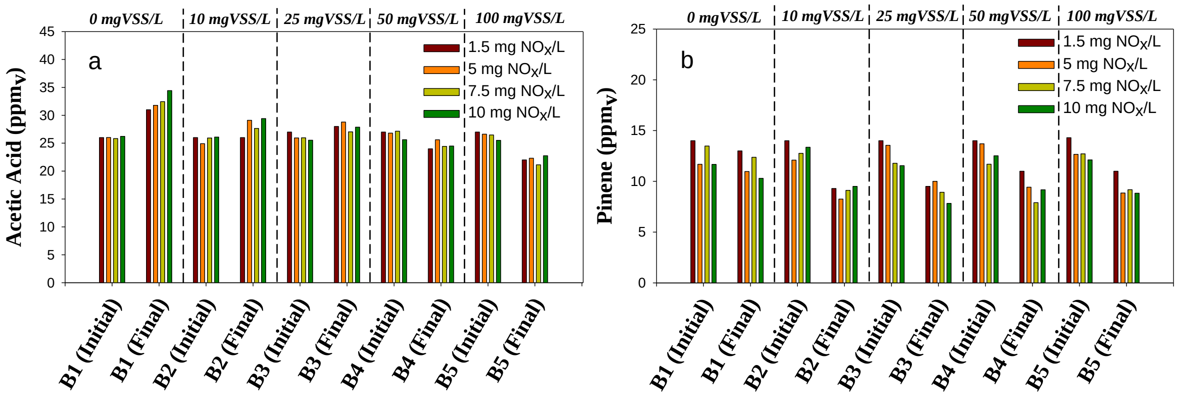


Figure 3: Initial and final concentrations of acetic acid (a) and α-pinene (b) at the different activated sludge and N-NO_x (NO_3^- or NO_2^-) concentrations

3.3 Evaluation of N-NO$_x$ fate during odorant oxidation

Test carried out at 1.5 and 5 mg NO_3^-/L supported a complete NO_3^- depletion at AS concentrations higher than 25 mg VSS/L (Figure 4a), which was likely responsible for the incomplete biological oxidation of H_2S. However, the reduction of NO_2^- was considerably more pronounced than that of NO_3^- regardless of the concentration of AS (Figure 4b). This fact explains the lower effectiveness of NO_2^- during odorant oxidation (see section 3.1) and suggests that higher concentrations of NO_2^- are required to carry out the complete biological oxidation of H_2S.

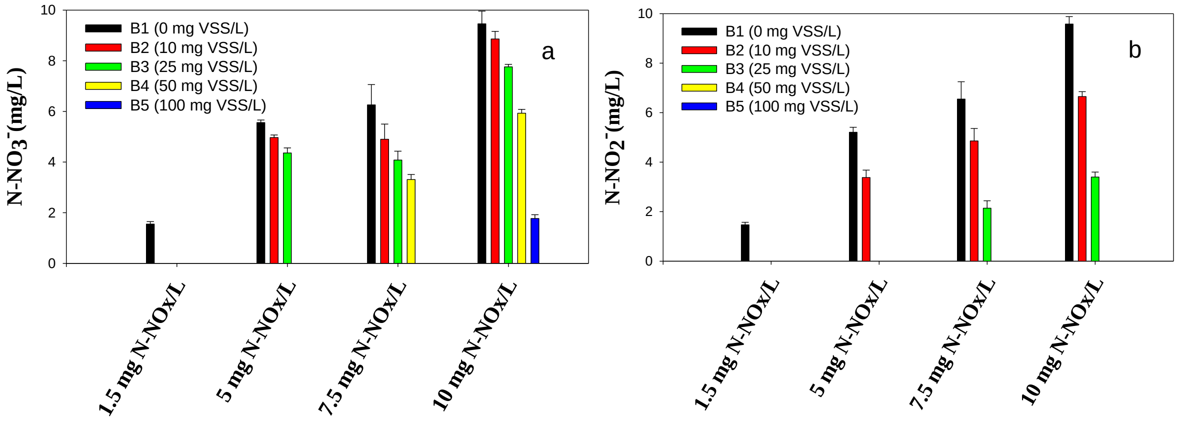


Figure 3: Final concentration of N-NO_3^- (a) and N-NO_2^- (b) as a function of the initial N-NO_x (N-NO_3^- or N-NO_2^-) supplemented at different concentration of activated sludge

In addition, the reduction of NO_3^- to NO_2^- during OAR and ASR simulations was also evaluated (Table 2). The tests carried out at concentrations ≥ 5 mg NO_3^-/L and 25 mg VSS/L experienced a partial reduction of NO_3^- to NO_2^-. Indeed, final values of 2.40, 2.86 and 4.44 mg NO_2^-/L were recorded in the tests conducted with initial concentrations of nitrate of 5, 7.5 and 10 mg NO_3^-/L, respectively, when 100 mg VSS/L were supplemented.

Table 2: Reduction of NO_3^- to NO_2^- during OAR and ASR simulations

AS concentration (mg VSS/L)	Initial NO_3^- concentration (mg N/L)	Final NO_3^- concentration (mg N/L)	Final NO_2^- concentration (mg N/L)
0	1.5	1.55	-
10		-	-
25		-	-
50		-	-
100		-	-
0	5	5.56	-
10		4.97	-
25		4.36	-
50		-	2.40
100		-	2.40
0	7.5	6.26	-
10		5.58	-
25		4.90	1.77
50		3.31	2.96
100		-	2.86
0	10	9.46	-
10		8.86	-
25		7.76	1.98
50		5.93	4.14
100		1.77	4.44

4. Conclusions

ASR and OAR were confirmed as an effective and low-cost odour control strategy. According to the results obtained, the most effective and rapid H_2S abatement was found at oxidized nitrogen (N-NO_3^- or N-NO_2^-) activated sludge concentrations of 7.5 - 10 mg/L and 50 - 100 mg VSS/L, respectively. Acetic acid was partially metabolized by microorganisms (from 27 to 23 ppm_v in 4.5 h) when complete biological oxidation of H_2S was reached and a slight decrease in α-pinene concentration was observed (from 13 to 8 ppm_v in 4.5 h) by adsorption phenomena. Moreover, NO_3^- supported a more effective odorant abatement than NO_2^-. Finally, a marked reduction of NO_2^- was observed when increasing AS concentration, suggesting that higher concentrations of NO_2^- compared to NO_3^- are required to carry out the complete biological oxidation of odorants during wastewater treatment.

Acknowledgments

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