

Optimization of activated sludge recycling and oxidized ammonium recycling as odour control strategies in wastewater treatment plants

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ABSTRACT

New odour prevention strategies in wastewater treatment facilities need to be investigated to find effective and low-cost technologies for the control of malodorous emissions. In this study, the potential of activated sludge (AS) and oxidized nitrogen (N-NO_x) recycling as an environmentally-friendly and cost-effective strategy for the prevention and minimization of odour nuisance during wastewater treatment was evaluated and optimized using H₂S, acetic acid and α-pinene as model odorants in 2.1 L gas tight bottles. This approach uses by-products from wastewater treatment to mitigate odour annoyance. Preliminary abiotic tests showed headspace concentration losses of 25% for H₂S and α-pinene, and 7% for acetic acid due to odorant adsorption in 4 h. The experiments carried out at different concentrations of AS (0, 10, 25, 50, 100 mg VSS/L) and oxidized nitrogen (1.5, 5, 7.5 and 10 mg N-NO_x/L) revealed an effective H₂S removal at 7.5–10 mg N-NO_x/L and 50–100 mg VSS/L. Interestingly, NO₃⁻ was more effective than NO₂⁻ as electron acceptor during the biodegradation of H₂S regardless of the AS concentration and N-NO_x concentrations. In the presence of dissolved H₂S and AS concentrations of 50–100 mg VSS/L, acetic acid was partially metabolized by microorganisms at the end of experiment (from 27 to 23 ppm_v in 4.5 h), while α-pinene concentrations experienced a similar gradual decrease than in the abiotic tests. Finally, the assays carried out at concentrations ≥5 mg NO₃⁻/L and 25 mg VSS/L showed a reduction of NO₃⁻ to NO₂⁻ correlated with the biological oxidation of H₂S, which suggested the need to control NO₃⁻ supply under sulphur limiting conditions to prevent toxicity problems during wastewater treatment.

1. Introduction

Nowadays, the emissions of malodours represent one of the main concerns associated with Wastewater Treatment Plants (WWTPs), and the main cause of public environmental complaints in Courts [1]. In the last two decades, the increase in the number of complaints from residents in adjacent areas to WWTPs has resulted in the systematic evaluation of the odour impact derived from such facilities. In this context, the EU member states are enforcing WWTP operators to find cost-effective strategies for the prevention and minimization of malodours during wastewater management [2–4].

Volatile sulphur compounds (VSCs) and volatile organic compounds

(VOCs) rank among the most typical compounds that contribute to the wastewater management odour footprint [5]. In particular, hydrogen sulphide (H₂S) and volatile fatty acids (VFAs) emissions are the main responsible of odour nuisance in WWTPs [6,7]. H₂S is a toxic compound generated from the biological reduction of sulphate (SO₄) or thiosulfate under anaerobic conditions by Sulphate Reducing Bacteria (SRB). Environmental parameters such as the concentration of sulphate, dissolved oxygen, biological oxygen demand, pH, temperature and retention time impact on H₂S formation [8]. On the other hand, VFAs are intermediate products from the anaerobic fermentation of easily biodegradable organic matter [9].

A wide number of physical-chemical methods have been previously

Abbreviations: AS, activated sludge; ASR, activated sludge recycling; BOD, biological oxygen demand; C_w, aqueous-phase concentration; C_g, gas-phase concentration; GC, gas chromatography; GC-TCD, gas chromatography with thermal conductivity detector; H^{cc}, Henry solubility; MS, mass spectrometry; N-NO_x, oxidized nitrogen; OAR, oxidized ammonium recycling; PAO, phosphate accumulating organisms; Q_c, centrate flow; Q_o, influent waterflow; Q_w, waste or rejected activated sludge flow; QIC, quartz inlet heated capillary; SEM, secondary electron multiplier; SOB, sulphate oxidizing bacteria; SRB, sulphate reducing bacteria; SW, synthetic wastewater; VFAs, volatile fatty acids; VOCs, volatile organic compounds; VSCs, volatile sulphur compounds; VSS, volatile suspended solids; WWTP, wastewater treatment plant.

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Table 1
Main characteristics of the model odorous compounds evaluated.

Compound	Chemical formula	Odour perception	Odour threshold value (ppm, v/v) [20]	H^{cc}	Molecular weight (g/mol)	Molecular structure
Hydrogen sulphide	H ₂ S	Rotten egg	0.00041	4.43E-01 [21]	34.10	
Acetic acid	C ₂ H ₄ O ₂	Vinegar	0.0060	2.88E-05 [22]	60.05	
α -Pinene	C ₁₀ H ₁₆	Pine, turpentine	0.018	1.39E+00 [23]	136.23	

tested and reported in literature to minimize the emission of VSCs and VOCs during wastewater treatment, which include photocatalysis [10], the dosing of oxidizing agents [11] or chemical precipitation [12]. However, the high demand of energy and chemicals are important drawbacks of these conventional solutions. In this context, biological odour prevention methods have emerged as an economically and environmentally sustainable alternative for the minimization of odour pollution in WWTPs. The use of by-products derived from wastewater treatment, such as the recirculation to the headworks of nitrates derived from centrate oxidation and activated sludge (AS) from the secondary settler, can foster the adsorption and further oxidation of VSCs and VOCs in the raw wastewater.

More specifically, activated sludge recycling (ASR) consists of the recirculation of a fraction of waste activated sludge from the secondary clarification or mixed liquor of the nitrification tank to the WWTP headworks. These activated sludge streams, which contain a concentration of dissolved oxygen and volatile suspended solids of 2–3 mg O₂/L and 4000–12,000 mg VSS/L, respectively, and a high microbial diversity, can adsorb and biologically oxidize most biogenic dissolved odorous compounds (e.g., sulphide, volatile fatty acids) in raw wastewater [13]. Similarly, oxidized ammonium recycling (OAR) consists of the recycling of residual streams rich in nitrate (N-NO₃⁻) or nitrite (N-NO₂⁻) to the WWTP headworks or upstream in the sewer system. The addition of nitrate or nitrite as electron acceptors to the influent wastewater promotes an in-situ anoxic odorant oxidation [14,15]. As N-NO₃⁻ and N-NO₂⁻ are typically not present in significant concentrations in raw domestic wastewater, effluents with high NH₄⁺ concentration such as centrates from anaerobic digestion of mixed sludge could be nitrified and recycled to the plant headworks [16]. Despite the potential of these low-cost odour prevention strategies has been successfully validated at pilot and full scale, the fundamentals of these technologies remain largely unexplored.

This work aimed at evaluating the influence of the concentrations of fresh activated sludge, nitrate and nitrite on the removal of H₂S, acetic acid and pinene, here selected as model odorants. This will set the fundamentals of ASR and OAR, and help optimizing its use in WWTPs.

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 [17] as follows (mg/L in tap water): 250 of glucose, 110 of meat extract, 160 of casein peptone, 30 of NH₂COH₂, 7 of NaCl, 4 of CaCl₂·2H₂O, 2 of MgSO₄·7H₂O, 112 of K₂HPO₄·3H₂O, 0.5 of CuCl₂·2H₂O, and 1100 of NaHCO₃. The physico-chemical characterization of the SW was carried out according to Standard Methods for the Examination of Water and Wastewater [18,19]. The initial pH was 8.1 ± 0.1.

2.2. Chemical odorants

The model odorous compounds used in this study were hydrogen sulphide (H₂S), acetic acid (C₂H₄O₂) and α -pinene (C₁₀H₁₆). H₂S was

supplied in a gas cylinder manufactured by Linde (Spain) at 22% in N₂. Acetic acid with a level of purity over 99.9% was purchased from Pan-Reac AppliChem (Spain) and α -pinene was acquired with a purity level of 98% from Sigma-Aldrich Co. (U.S.A.). Table 1 shows the main characteristics of each volatile compound according to its chemical formula, odour perception, Henry solubility (H^{cc}), molecular weight and structure.

2.3. Experimental set-up

Gas-tight 2.1 L glass bottles were used to carry out the OAR and ASR experiments. Aliquots of 300 mL of SW supplemented with different concentrations of nitrate or nitrite (see Section 2.4) were added to the glass bottles, which were then closed with butyl septa and aluminium caps. The air atmosphere in the headspace was subsequently displaced with helium at a final pressure of 0.5 bar for 10 min in order to provide anaerobic conditions. The O₂ headspace composition was quantified by gas chromatography (GC) using a Varian GC-TCD to ensure an oxygen content lower than 1% in all experiments. The target odorous compounds (H₂S, acetic acid and α -pinene) were injected into the bottle headspace in order to mimic a septic wastewater. Thus, a total mass of 0.07, 2.10 and 0.42 mg of H₂S, acetic acid and α -pinene, respectively, was injected through the butyl septum (corresponding to 250 μ L of gaseous H₂S at 22%, 2 μ L of liquid acetic acid and 0.5 μ L of liquid α -pinene). A low concentration of α -pinene was selected due to the lower contribution of this odorant in odour emissions derived from WWTPs [24]. The mass of each odorant was injected considering the thermodynamic equilibrium between the concentrations in the gas phase and in the aqueous phase under dilute solutions at a constant temperature [25]. Thus, the Henry's law constants, known as air-water partitioning coefficients, were used to estimate the total mass of the target compounds to be injected, which can be expressed as:

$$H^{cc} = \frac{C_a}{C_g}$$

where H^{cc} is the dimensionless partitioning coefficient of the odorant, C_a is the odorant aqueous-phase concentration (mg/L) and C_g is the odorant gas-phase concentration (mg/L). Table 1 shows the dimensionless partitioning coefficient for each target odorant.

After injection of the target odorants, each bottle was pressurized with helium at 500 mbar using a pressure gauge 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 (see Section 2.5) 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 (WSBPR8080-C, Wheaton Science) at 7 rpm and at ambient temperature (21 °C). The nitrate and nitrite concentrations were measured at time 0 and 270 min.

Table 2

Experimental design of the OAR and ASR assays.

Bottle identification	AS concentration (mg VSS/L)	N-NO _x 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	

N-NO_x corresponds to the concentration of N-NO₃ or N-NO₂.

2.4. Odorant fate under abiotic conditions

Control experiments without N-NO_x and activated sludge were performed following the procedure described in Section 2.3 (i.e., with the same odorant concentrations in the headspace). Briefly, 300 mL of tap water were added into the glass bottles of 2.1 L, which were then closed with butyl septa and aluminium caps. The air in the headspace was displaced with helium at a final pressure of 0.5 bar for 10 min and the oxygen content in the headspace was analysed by GC-TCD. Aliquots of 250 μL of gaseous H₂S at 22%, 2 μL of liquid acetic acid and 0.5 μL of liquid α-pinene were then injected through the butyl septum and each bottle was pressurized with helium at 500 mbar. Subsequently, each bottle was vigorously shaken for 2 min and the concentration of each odorant was analysed in the headspace by MS at 0, 120 and 270 min in order to evaluate its behaviour under abiotic conditions.

2.5. Influence of nitrate and nitrite concentration on odorant fate

The residual stream of oxidized nitrogen (N-NO_x) obtained from the nitrification of centrate was substituted in the laboratory by 2 g/L stock solutions of NaNO₃ or NaNO₂. In this context, a typical ammonia concentration of 900–1500 mg/L in the centrates could be transformed into N-NO₃ or N-NO₂, which would entail maximum N-NO_x concentrations of 6–10 mg N/L in the influent raw wastewater assuming a typical centrate to influent raw wastewater ratio (Q_C/Q_O) of 0.004–0.12 [16,26], where Q_C stands for the centrate flowrate and Q_O is the influent raw wastewater flowrate. The influence of N-NO₃ and N-NO₂ concentrations (0, 1.5, 5, 7.5, 10 mg N-NO_x/L) on odorant removal was herein investigated (Table 2).

2.6. Influence of activated sludge concentration on odorant fate

Fresh activated sludge was collected from the AS external recirculation line of the denitrification/nitrification WWTP of Valladolid (Spain). The volatile suspended solids (VSS) concentration of the AS ranged between 6000 and 7000 mg VSS/L [15]. VSS concentrations typically present in secondary settlers average 4,000–12,000 mg VSS/L, which would entail maximum AS concentrations of 100 mg VSS/L in the influent raw wastewater assuming a conventional Q_W/Q_O ratio of 0.002–0.13 [27], where Q_W stands for the waste activated sludge flowrate. Thus, the influence of biomass concentrations (0, 10, 25, 50,

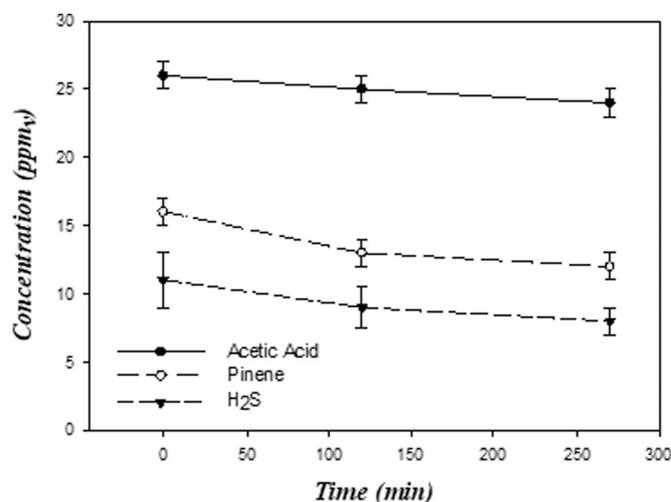


Fig. 1. Time course of acetic acid, α-pinene and H₂S headspace concentrations under abiotic conditions.

100 mg VSS/L) on odorant removal was herein investigated (Table 2).

2.7. Analytical procedures

The activated sludge VSS concentration was analysed following the methodology proposed by APHA, AWWA & WEF [18]. Nitrate and nitrite concentrations were measured by HPLC-IC according to García [28]. The concentration of O₂ in the headspace was measured by GC-TCD as described by Posadas [29]. A Hiden QGA mass spectrometer, manufactured by Hiden Analytical (United Kingdom), was used to quantify the odorant concentrations in the headspace. This spectrometer consists of a simple quadrupole with an APSI ionization source, an internal dual secondary electron multiplier (SEM) and Faraday detector and a precision quartz inlet heated capillary (QIC) sampling interface. The QIC capillary inlet can operate at pressures from 100 mbar to 2 bar and high temperatures (200 °C), providing fast response times of less than 300 ms for most common gases and vapours, including water and organic vapours. The injection of the headspace of the bottles was conducted at a sweep rate of 50 mL/min. QGA boasts a standard mass range of 1–200 atomic mass units (amu) and with detection over an extremely high dynamic range up to 100%, detecting concentration above 0.1 ppm_v. The Faraday and SEM detectors were previously calibrated using the MASsoft Professional software and atmospheric air. Moreover, the QGA mass spectrometer was also calibrated from a pressurized bottle with helium containing H₂S, acetic acid and α-pinene in the gas phase at 440, 436 and 411 ppm_v, respectively. For this purpose, 6 mL of gas H₂S (22%), 3 μL of acetic acid and 8 μL of α-pinene were injected into an empty glass bottle of 2.1 L and allowed to volatilize. Then, the bottle was pressurized with helium at 500 mbar prior to analysis.

3. Results and discussion

3.1. Evaluation of odorant fate under abiotic conditions

A control experiment in the absence of N-NO_x and activated sludge was carried out in order to evaluate the fate of odorants under abiotic conditions (Fig. 1). The initial headspace concentrations of acetic acid, α-pinene and H₂S accounted for 26, 16 and 11 ppm_v. A slight decrease in the concentration of α-pinene and H₂S down to 12 and 8 ppm_v, respectively, was recorded after 270 min of experiment, which represented a ≈25% loss for each odorant. The fact that the gas-liquid equilibrium was reached at time 0 suggests that abiotic losses were associated to odorant adsorption onto the glass surface or butyl septum.

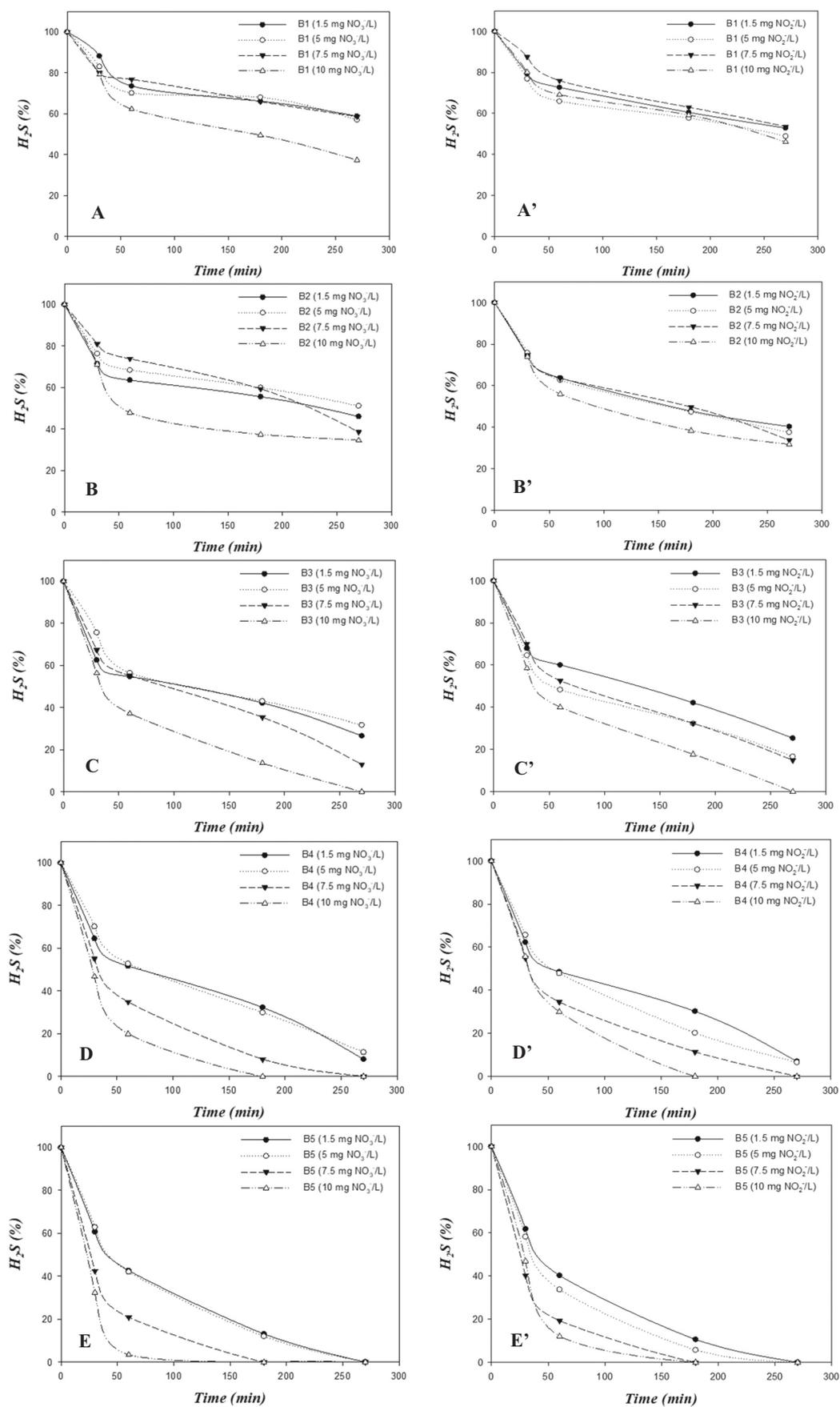


Fig. 2. Time course of H_2S headspace concentration under different concentrations of $N-NO_3^-$ (A, B, C, D, E), $N-NO_2^-$ (A', B', C', D', E') and activated sludge (A-A': 0 mg VSS/L; B-B': 10 mg VSS/L; C-C': 25 mg VSS/L; D-D': 50 mg VSS/L; E-E': 100 mg VSS/L).

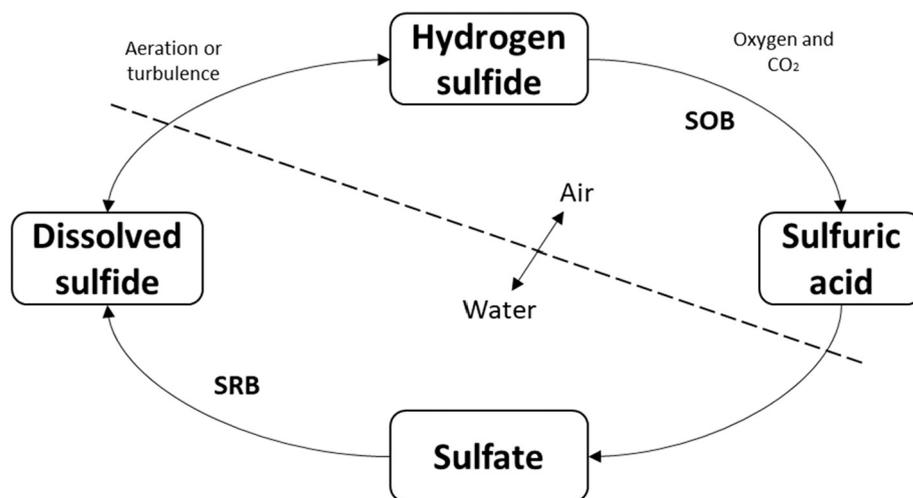


Fig. 3. Sulphide cycle in the headspace and aqueous phases.

Adsorption phenomena of odorants in glass is related to an elicited ionic adsorption of molecules to the silanol groups (positive ion exchange mode) and a hydrophobic adsorption mediated by the siloxane groups [30]. In the particular case of acetic acid, adsorption losses averaged >7%.

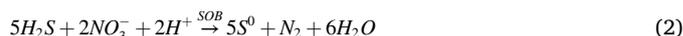
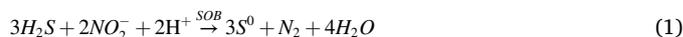
3.2. Influence of N-NO_x and activated sludge concentration on odorant fate

Odorant fate in the gas phase was monitored for a total experimental period of 270 min (4.5 h), which corresponded with the maximum elapsed time between the reception of the raw wastewater in the WWTP headworks and its secondary treatment.

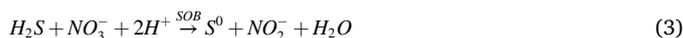
The biological oxidation of H₂S under anoxic conditions was confirmed in the present study (Fig. 2). A more rapid decrease in the headspace concentration of H₂S was observed at increasing concentrations of NO₃⁻, NO₂⁻ and AS. More specifically, a sharp decrease in H₂S headspace concentration was recorded for the first 60 min of assay, followed by a gradual decrease in H₂S fate along with the occurrence of lower gas-liquid concentrations gradients. The fastest depletion of H₂S was observed at 10 mg NO_x/L and 100 mg VSS/L (Fig. 2E and E'). In this context, the supplementation of septic wastewater with 100 mg VSS/L reduced H₂S concentration to 0 ppm_v in 4.5 h even at the lowest NO₃⁻ and NO₂⁻ concentrations tested (Figs. S1 and S2). However, when nitrate or nitrite concentrations lower than 5 mg NO_x/L were supplemented, the complete biological oxidation of H₂S was not reached at AS concentrations lower than 100 mg VSS/L. The anoxic H₂S oxidation was incomplete in the tests conducted with 1.5–5 mg NO_x/L and 10–25 mg VSS/L (Figs. S1 and S2). Overall, NO₃⁻ was more effective than NO₂⁻ as electron acceptor to biodegrade H₂S regardless of the AS and N-NO_x concentrations. However, the use of NO₂⁻ for odour mitigation in WWTPs would lead to a lower energy consumption during the oxidation of the ammoniacal nitrogen present in the centrate resulting from the dehydration of anaerobic digestion sludge.

This study showed that the combination of OAR and ASR was effective to oxidize biologically H₂S. Specifically, the addition of nitrate or nitrite to the influent wastewater promotes anoxic conditions, where oxidized nitrogen is used as an electron acceptor by microorganisms (e. g., chemolithotrophic bacterial species) in order to oxidize dissolved sulphides and any readily biodegradable odorants, thus preventing their further release as malodorous emissions [13,31]. The creation of anoxic conditions via addition of N-NO_x and the microbiological oxidation of H₂S by nitrate/nitrite reducing bacteria have been hypothesized as the main mechanisms governing H₂S fate during OAR and ASR. The anoxic oxidation of H₂S by Sulphur Oxidizing Bacteria (SOB) can be described

by Eqs. (1) and (2) [32]:



However, when NO₃⁻ is added under sulphur limiting conditions, a potential reduction of NO₃⁻ to NO₂⁻ could occur during biological H₂S oxidation according to Eq. (3). This process could cause toxicity problems in the environment or river ecosystems, in particular at low pH values [33].



In addition, H₂S can be used by SOB (i.e., *Thiobacillus* sp.), which proliferates especially in hot and humid environments, to generate sulfuric acid (H₂SO₄) (Fig. 3). H₂SO₄ is a well known corrosive agent for steel, copper and even concrete structures responsible for large economic losses in WWTPs [34].

Fig. 4 displays the evolution of the headspace concentration of acetic acid during the experimental period at different concentrations of NO₃⁻ and NO₂⁻ (1.5, 5, 7.5 and 10 mg/L) and activated sludge (0, 10, 25, 50 and 100 mg VSS/L, respectively). The assays carried out at 0, 10 and 25 mg VSS/L revealed a slight increase in acetic acid concentration regardless of the concentration of NO₃⁻, NO₂⁻ and AS supplemented, reaching a maximum value of 30–31 ppm_v (100%) by 270 min in the absence of biomass (4A - 4A') and by 180 min at 10 and 25 mg VSS/L (4B - 4B' and 4C - 4C', respectively). Based on the high aqueous solubility of acetic acid (Table 1), this increase in acetic acid concentration could be due to the fact that the liquid-gas equilibrium was not reached at time zero despite the vigorous shaking of the bottles for 2 min. In the tests conducted at 50 and 100 mg VSS/L (4D - 4D' and 4E - 4E', respectively), 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 (Figs. S1 and S2). In fact, most microorganisms present in activated sludge can use the electron acceptor capacity of NO₃⁻ or NO₂⁻ to metabolize readily biodegradable compounds such as VFAs. In this context, acetic acid is a key substrate in the biological removal of phosphate and nitrogen in AS processes, feeding the biochemical routes of phosphorous accumulation and denitrification and supporting enhanced elimination rates of these nutrients [35,36].

Indeed, a certain concentration of VFAs is required in the influent raw wastewater to trigger the phosphorus release mechanism by Phosphate Accumulating Organisms (PAO) in WWTPs [37]. Therefore, the recycling of N-NO_x might inhibit biological phosphorus removal by PAO

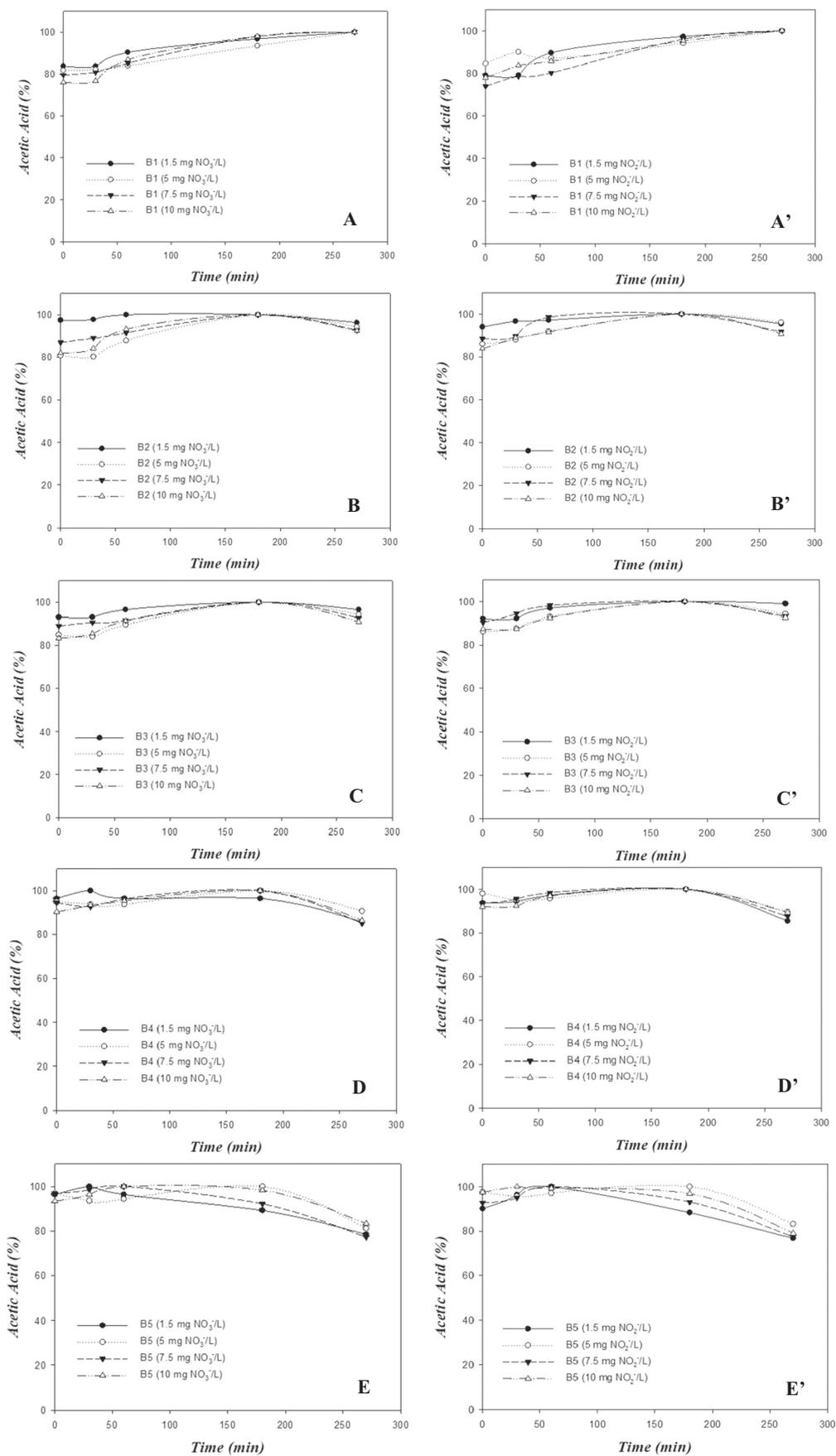


Fig. 4. Time course of acetic acid concentration under different concentrations of N-NO_3^- (A, B, C, D, E), N-NO_2^- (A', B', C', D', E') and activated sludge (A-A': 0 mg VSS/L; B-B': 10 mg VSS/L; C-C': 25 mg VSS/L; D-D': 50 mg VSS/L; E-E': 100 mg VSS/L).

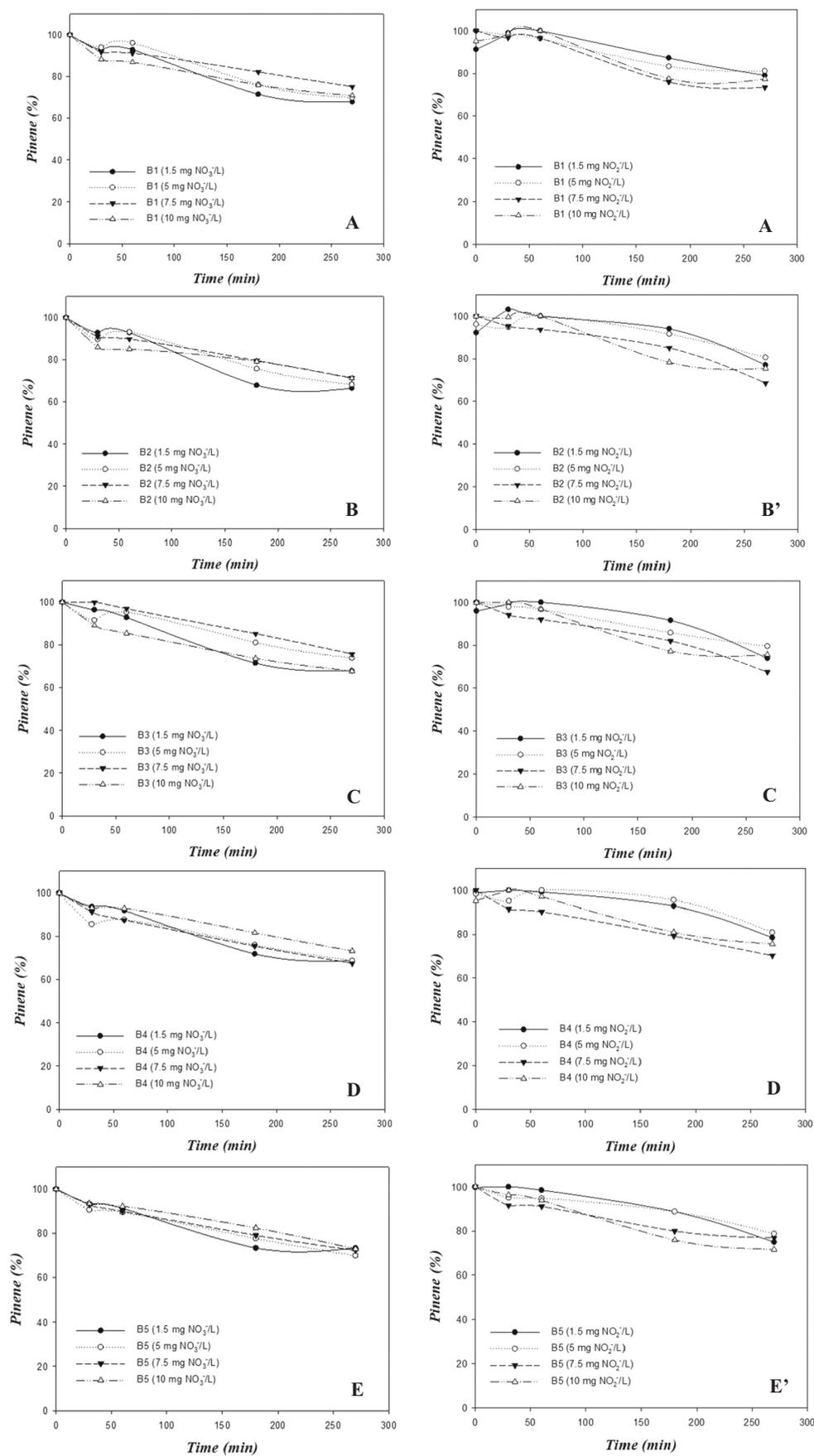


Fig. 5. Time course of α -pinene concentration under different concentrations of $N-NO_3^-$ (A, B, C, D, E), $N-NO_2^-$ (A', B', C', D', E') and activated sludge (A-A': 0 mg VSS/L; B-B': 10 mg VSS/L; C-C': 25 mg VSS/L; D-D': 50 mg VSS/L; E-E': 100 mg VSS/L).

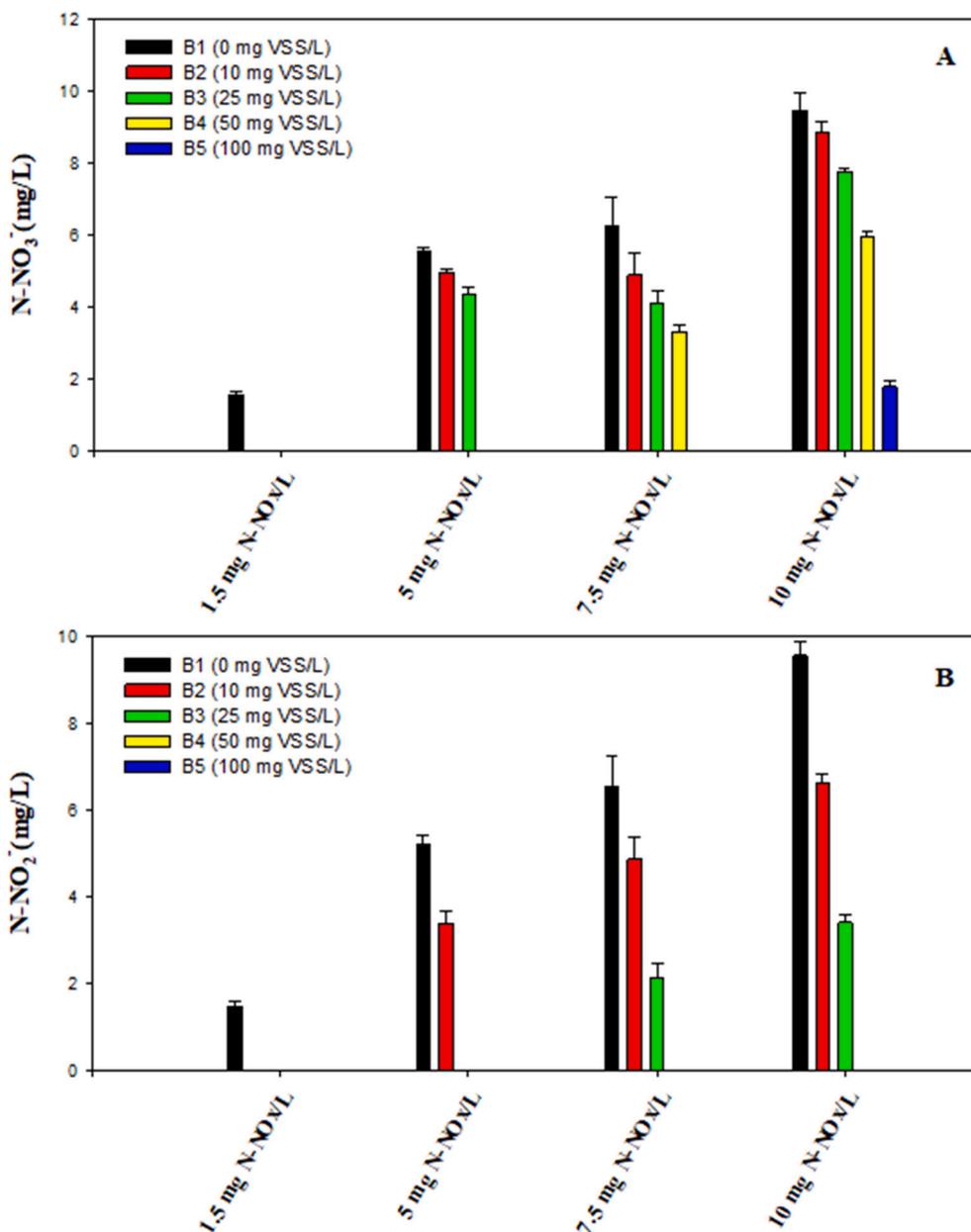


Fig. 6. Final concentration of N-NO_3^- (A) and N-NO_2^- (B) as a function of the initial N-NO_x supplemented at different concentration of activated sludge.

under carbon (BOD) limiting conditions [7]. However, in the presence of dissolved H_2S , OAR and ASR did not significantly consume acetic acid even at the highest N-NO_x and AS concentrations (Figs. S1 and S2), which would prevent a pernicious impact on biological phosphorous removal.

On the other hand, the initial concentration of α -pinene of 13 ± 2 ppm_v (100%) gradually decreased to a final concentration of 8 ± 1.5 ppm_v, which accounted for a removal of 20–25% of this odorant compound (Figs. S1 and S2). 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 (Fig. 5), the observed decrease in concentration could be attributed to adsorption phenomena. Previous studies have highlighted the high tendency of α -pinene to be adsorbed to solid surfaces [38].

3.3. Evaluation of N-NO_x fate during odorant oxidation

N-NO_x concentration was determined at the end of each assay in order to confirm that heterotrophic denitrification was the main

mechanism responsible of odorant degradation during OAR and ASR. A gradual reduction in the final NO_3^- and NO_2^- concentration was recorded when increasing the activated sludge concentration (Fig. 6). 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 (Fig. 6A), 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 (Fig. 6B). This fact explains the lower effectiveness of NO_2^- during odorant oxidation (see Section 3.2) and suggests that higher concentrations of NO_2^- are required to carry out the complete biological oxidation of H_2S . Finally, the reduction of NO_3^- to NO_2^- during OAR and ASR was also evaluated (Table 3). The tests carried out at concentrations ≥ 5 mg NO_3^-/L and 25 mg VSS/L experience 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. These environmental conditions supported a

Table 3

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		1.55	–
10		–	–
25	1.5	–	–
50		–	–
100		–	–
0		5.56	–
10		4.97	–
25	5	4.36	–
50		–	2.40
100		–	2.40
0		6.26	–
10		5.58	–
25	7.5	4.90	1.77
50		3.31	2.96
100		–	2.86
0		9.46	–
10		8.86	–
25	10	7.76	1.98
50		5.93	4.14
100		1.77	4.44

complete biological oxidation of H_2S (Fig. 3E and E'). In this context, Dutra [39] observed that concentrations above 1 mg NO_2^-/L exerted a high level of toxicity in aquatic ecosystem and were likely to occur in poorly oxygenated environments such as that prevailing in the ASR and AOR assays here conducted.

Finally, nitrogen compounds in wastewater play a key role in eutrophication and toxicity problems in receiving water bodies, causing problems in aquatic ecosystem (i.e., lack of oxygen and poor water quality). Previous studies developed alternative treatments for the biological removal of nutrients from wastewater to reach acceptable levels such as anaerobic ammonium oxidation process or denitrifying phosphate removal, with nitrate and nitrite as electron acceptors supporting anoxic phosphate uptake [40–42]. In this case, the nitrification of centrate from anaerobic digestion of sewage sludge in a separate aeration unit to transform ammonia into nitrate and nitrite would provide an economic benefit since OAR entails a reduction in the nitrogen load to the WWTP, as well as a cost-effective strategy for the prevention and minimization of odours that would potentially be emitted into the atmosphere [16,26].

4. Conclusions

ASR and OAR were here confirmed as an effective and low-cost odour control strategy, which can be integrated into wastewater treatment facilities with significant environmental and economic benefits. The combination of OAR and ASR at concentrations of 7.5–10 mg NO_x/L and 50–100 mg VSS/L, respectively, supported the most effective and rapid H_2S abatement. NO_3^- supported a more effective odorant abatement than NO_2^- under sulphur controlling conditions. However, the use of NO_2^- would allow lower energy consumption during nitrification of the centrate with the subsequent economic benefit. On the other hand, acetic acid was partially metabolized by microorganisms when complete biological oxidation of H_2S was reached, which might inhibit biological phosphorous removal. In addition, the slight decrease in α -pinene concentration matched the decrease observed by adsorption during the abiotic tests and 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 to carry out the complete biological oxidation of odorants during wastewater treatment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2022.102655>.

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