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Nitrite pathway in A^2/O WWTPs: Modelling organic matter reduction, operational cost and N_2O emissions

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ABSTRACT

Deciding whether the implementation of the nitrite pathway is useful for the treatment of a given wastewater depends on several criteria such as organic matter availability, N and P removal, N_2O emissions and operational costs. This work is a simulation-based study with a conventional Anaerobic/Anoxic/Oxic (A^2/O) WWTP where the nitrite pathway can be implemented. The outcomes are general correlations to calculate the minimum COD requirements for a certain influent and a practical decision tree on the opportunities of nitrite pathway in A^2/O WWTPs as a function of the influent wastewater composition (for P and N concentrations in the ranges 3–11 mgPO_4^{-3}-P·L^{-1} and 20–60 mg NH_4^+-N·L^{-1}). This study shows that the implementation of the nitrite pathway reduces the COD requirements (depending on the influent, between 9 and 68%). It also can lead to a reduction in aeration costs. For an equivalent COD in the influent, the implementation of the nitrite pathway compared to the nitrate pathway results in a reduction of 41-47% in aeration costs and similar sludge production, leading to a reduction in the operational cost index of 10-16%. However, it is essential to note that this strategy can also lead to increased N_2O emissions, with an emission factor for the nitrite pathway in the range of 2.5–17 times that of the nitrate pathway.

1. Introduction

Nutrient removal (N and P) is mandatory for many WWTPs. Conventional biological nitrogen removal (BNR) involves two main processes called nitrification and denitrification. Nitrification is the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-), while denitrification is the reduction of nitrate to nitrogen gas. The commonly used biological process for removing P is the well-established enhanced biological phosphorus removal (EBPR), which is based on the enrichment of activated sludge in phosphorus accumulating organisms (PAO) (Oehmen et al., 2007). The simplest WWTP configuration combining the processes required to achieve simultaneous biological C/N/P removal is the widely used anaerobic-anoxic-aerobic (A^2/O) continuous plant (Tchobanoglous et al., 2014). Various operational strategies have been studied under the A^2/O configuration with the aim of improving the quality of treated effluents and significantly reducing its energetic and economic burden. Aeration requirements and excess sludge treatment represent the highest operating costs of a WWTP (Changqing et al., 2011). Many strategies have been put forward to reduce the aeration needs and, among them, the nitrite pathway or shortcut biological N removal has attracted much attention, particularly for wastewaters with a low chemical oxygen demand (COD) to N ratio.

Nitrite pathway, i.e. autotrophic ammonium oxidation to nitrite (nitritation) and posterior heterotrophic nitrite denitrification (denitritation), results in 40% lower COD requirements for denitrification, savings in aeration costs and lower sludge production (Turk and Mavinic, 1986) when compared to the conventional nitrification/denitrification processes based on the complete oxidation of ammonium to nitrate and nitrate denitrification (nitrate pathway). It is therefore not surprising that numerous studies are looking for the best strategies to implement it (Duan et al., 2022; Liu et al., 2020; Regmi et al., 2014; Xu et al., 2021). Thus, a configuration involving nitrite-reducing denitrifying PAO (DPAO) and N removal via nitrite appears to be a good alternative to treat wastewaters with a low COD/N influent ratio with lower aeration needs and less sludge production.

Two major issues arise against the nitrite shortcut process: the potential nitrite inhibition on biological processes (Zhou et al., 2011) and the potential nitrous oxide (N_2O) production and emissions (Kirim et al.,

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2022). Regarding the first issue, although inhibition of DPAO by nitrite has been reported (Zhou et al., 2010), the possibility of long-term stable maintenance of simultaneous denitritation and P-removal has also been demonstrated experimentally (Guisasola et al., 2009; Tayà et al., 2013; Vargas et al., 2011). With respect to N_2O emissions, different production pathways have been described in parallel to the nitrification and denitrification processes (Massara et al., 2017; Spérandio et al., 2016), which gives some ability to predict its emissions for different scenarios.

Since an electron donor is required for both denitrification and EBPR, low loaded influents may result in a failure of one of these processes depending on the plant configuration, the influent C/N/P and the control strategies applied (Guerrero et al., 2014). This challenge can be overcome by adding external carbon or metal salts for chemical P precipitation, but with a resulting increase in operational costs.

There are also several operational strategies that can minimise the adverse effect of low COD, but designing and/or retrofitting existing WWTPs is not a straightforward issue due to the complex interactions between the different operational variables. For example, the choice of an internal recycle is a trade-off decision: a high internal ratio can decrease the effluent nitrate/nitrite at expenses of a higher operational cost. Besides that, an excessive ratio increases the oxygen load to the anoxic reactor and reduces the available carbon source for denitrification. Then, the value of the optimal internal recycling ratio should be carefully selected to optimise a WWTP performance (Baeza et al., 2004).

Considering this complex scenario, it is not surprising that mathematical modelling has become a very useful tool for the prediction of WWTP performance under different operational conditions and when different control strategies are applied (Henze et al., 2008; Jeppsson et al., 2013). The activated sludge models (ASM) developed by the International Water Association (IWA) (Henze et al., 2000) describe the biological and chemical transformations occurring in activated sludge systems. Besides the default models (ASM1, ASM2 and ASM3), several extended ASM-based models have been put forward to predict the WWTP performance under different scenarios. For instance, the ASM2d-N_2O model (Massara et al., 2018; Solís et al., 2022a) has recently been proposed to account for N_2O emissions in WWTPs with C/N/P removal and has proven to be a good prediction tool for full-scale WWTP conditions (Solís et al., 2022c).

The main objective of this work is to provide, for the first time, easy manageable tools/correlations for A^2/O WWTPs to estimate the organic matter requirements to meet legal discharge limits (TN < 10 mgN·L^{-1} and P < 1 mgP·L^{-1}) when treating different wastewaters and using nitrite or nitrate pathway for N-removal. The obtained correlations could be used as a preliminary rule of thumb to decide the most suitable pathway for each wastewater. For this purpose, an A^2/O WWTP is simulated in numerous scenarios, determining the COD requirements for different N and P influent content, both for nitrite and nitrate pathways. The competitive advantages and drawbacks of nitrite pathway implementation regarding COD requirements to meet N and P discharge limits, N_2O emissions, economic cost and type of carbon source are also discussed.

2. Materials and methods

2.1. Description of WWTP configuration and influent data

This work studies a conventional A^2/O WWTP, designed for the biological removal of N, P and organic matter (Fig. 1). Table 1 summarizes the volumes of the reactors and the operational parameters chosen for the study. The volumes were initially based on general design parameters (Tchobanoglous et al., 2014) but the reactors were increased in size to ensure good plant performance for the full range of influent values tested. Two different dissolved oxygen (DO) set points in the aerobic reactor were used to achieve ammonium oxidation to nitrate (DO = 3.0 mg/L) or nitrite (DO = 0.8 mg/L).

The influent characteristics are summarized in Table 2. The COD was fractionated into soluble inert organics (S_I), particulate inert organics (X_I), biomass (X_H, X_{PAO}, X_{AOB} and X_{NOB}), soluble fermentable substrate (S_F), volatile fatty acids (S_A) and slowly biodegradable substrate (X_S), using different values depending on the scenario. The concentrations of PO_4^{3-} studied were for 3, 5, 7, 9, 11 mg P·L^{-1} and the influent NH_4^+ concentration ranged from 20 to 60 mg N·L^{-1}.

2.2. Model description

The kinetic model used was the novel ASM2d-N_2O developed by Massara et al. (2018). The ASM2d-N_2O model can predict COD, P and N removal and N_2O production in full-scale WWTPs (Solís et al., 2022c). The ASM2d-N_2O model structure is based on the ASM2d model (Henze et al., 2000) and can account for the three known N_2O production biological pathways. On the one hand, it was extended with the 2-pathway model for N_2O emissions by AOB, developed by Pocquet et al. (2016). Moreover, it includes the denitrification processes described in the

Table 1
Operational conditions.

Parameter	Description	Value
V1	Anaerobic reactor volume	2800 m^3
V2	Anoxic reactor volume	2800 m^3
V3	Aerobic reactor volume	9000 m^3
Q_{IN}	Influent flowrate	20000 m^3 d^{-1}
RI	Ratio of internal recycle to influent flowrate	5
RE	Ratio of external recycle to influent flowrate	1/3
Q_W	Purge flowrate	300 m^3 d^{-1}
DO_{NO3P}	DO setpoint aerobic reactor (nitrate pathway)	3.0 mg L^{-1}
DO_{NO2P}	DO setpoint aerobic reactor (nitrite pathway)	0.8 mg L^{-1}

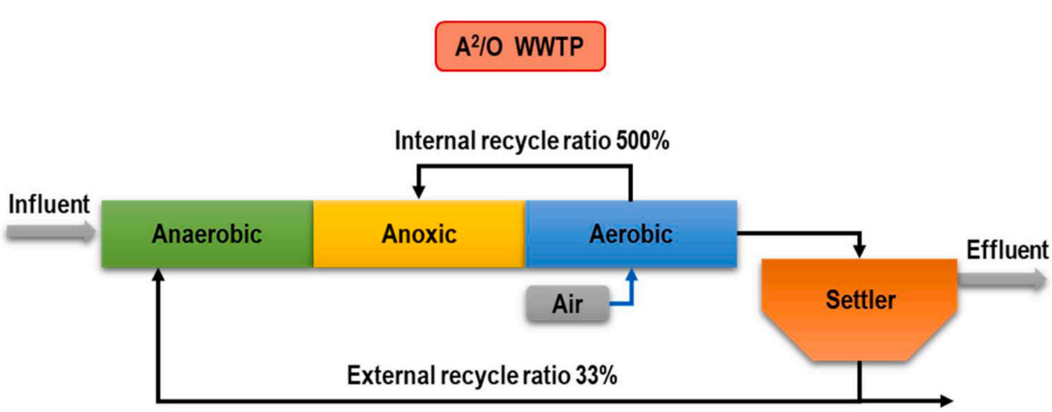

Fig. 1. Schematics of the A^2/O WWTP configuration.

Table 2
Influent characteristics.

Composition	Concentration ($mg \cdot L^{-1}$)
PO_4^{3-}-P	3–11
NH_4^+-N	20–60
NO_3^--N	2.6
TSS	58
X_I	45.6
S_I	30

Activated Sludge Model for Nitrogen (ASMN), developed by Hiatt and Grady (2008). ASMN describes the N_2O production by OHO and PAO as an obligate intermediate of the denitrification process. The complete description of the model can be found in the supplementary information, including model components (Table S1), stoichiometry (Tables S2 and S3), kinetic equations (Table S4), kinetic parameters (Table S5) and stoichiometric parameters (Table S6).

To evaluate the plant performance, each scenario was simulated with constant flow and wastewater composition until achieving steady state conditions. Simulations of 200 days were required to ensure steady state for nitrate pathway and 300 days for nitrite pathway.

2.3. Selection of influent variables and effluent discharge variables

Both cases (nitrite pathway and nitrate pathway) were simulated for different wastewater compositions in the range reported in Table 2. The minimum amount of organic matter that was necessary to meet the discharge limits for N and P, considering only soluble nitrogen (S_{NH4}, S_{NO3}, S_{NO2}) and phosphate (S_{PO4}) was obtained for each pair of N and P concentrations in the wastewater under two different scenarios. In the first scenario, all organic matter was considered to be like volatile fatty acids (S_A) to simulate the most favourable organic matter composition for PAO, whereas in the second scenario only slowly biodegradable organic matter (X_S) was used to have a less favourable organic matter fractionation. For the latter case, the stoichiometric parameters i_{NXS} and i_{PXS} were assumed to be zero, to avoid an unrealistic increase of P and N load when increasing X_S concentration.

The P and N content of the particulate compounds in the effluent was not considered, because a change in the amount of biomass in the effluent could interfere with the results provided by the model, resulting in too high and unrealistic organic matter requirements. Then, the biomass concentration in the effluent was considered to be negligible, e. g. by installing a sand filter removing the non-settled biomass in the sedimentation tank.

2.4. Methodology for determining organic matter requirements

The effluent legal discharge limits considered were $PO_4^{3-} < 1$ mg $P \cdot L^{-1}$, TN < 10 mgN$\cdot L^{-1}$ and COD <125 mg $O_2 \cdot L^{-1}$ (EEC Council, 1991). Effluent organic matter never exceeded the discharge limits because the model was run with the minimum amount of organic matter in the influent. The minimum required concentrations of S_A and X_S were estimated using the MATLAB optimisation function *fminbnd* and minimising independently equation (1) for N and (22) for P.

$$fobjN = abs(S_{NH4} + S_{NO2} + S_{NO3} - 10) \quad (1)$$

$$fobjP = abs(S_{PO4} - 1) \quad (2)$$

Where S_{NH4}, S_{NO2}, S_{NO3} and S_{PO4} are the effluent steady state nitrogen concentrations of ammonium, nitrite, nitrate and phosphorus concentration of orthophosphate obtained for a given influent composition. Then, the optimisation of equation (1) by modifying S_A in the influent led to the obtention of S_A-N, i.e. the minimum amount of S_A for satisfying N discharge limits, while the optimisation of equation (2) by modifying S_A in the influent gave S_A-P, i.e. the minimum amount of S_A to get P discharge limits. The same procedure was applied to determine X_S-N and X_S-P but modifying X_S in the influent.

2.5. Evaluation criteria

Various criteria have been used to assess the performance of a WWTP (Gernaey et al., 2014; Stare et al., 2007). In this study, the operation cost index (OCI [$kWh \cdot d^{-1}$]) that combines costs for sludge disposal, aeration and pumping was calculated with equation (3).

$$OCI = AE + PE + f_{SP} \cdot SP \quad (3)$$

Where, AE is aeration energy, PE is pumping energy, and SP is sludge production for disposal. The weight f_{SP} has a value of 5 to account for the sludge production processing being carried out in that system and the expected sludge disposal cost savings as a result.

Average aeration energy (AE [$kWh \cdot d^{-1}$]) was based on equation (4).

$$AE = \frac{24}{t_{obs}} \int_{t_{start}}^{t_{end}} \left(3.0248 \cdot 10^{-4} \cdot V \cdot K_L a(t)^2 + 0.5882 \cdot 10^{-2} \cdot V \cdot K_L a(t)\right) dt \quad (4)$$

Where, $K_L a$, is the oxygen transfer rate value expressed in h^{-1}, V is the volume of the aerobic reactor (m^3) and t_{obs} represents the total length of the evaluation period in days, i.e., $t_{end} - t_{start}$. $K_L a(t)$ values were obtained from the model simulation of a proportional integral control loop implemented to maintain the DO setpoint in the aerobic reactor.

Pumping energy (PE [$kWh \cdot d^{-1}$]) was calculated as a weighted average sum of the various pumped flows in the system under study, using equation (5).

$$PE = \frac{1}{t_{obs}} \int_{t_{start}}^{t_{end}} \left(f_{PE\_Q_{int}} \cdot Q_{int} + f_{PE\_Q_r} \cdot Q_r + f_{PE\_Q_w} \cdot Q_w + f_{PE\_Q_{pu}} \cdot Q_{pu}\right) \cdot dt \quad (5)$$

Where, Q_{int} is the internal recycle flow, Q_r is the external recycle flow, Q_w purge flow and Q_{pu} is the underflow from secondary clarifier, all flows expressed in $m^3 \cdot d^{-1}$. Table 3 shows the values used for the PE factors.

Sludge production for disposal (SP [$kg \cdot d^{-1}$]) was calculated as the mass of solids accumulated in the plant or removed from the process with the equation (6):

$$SP = \frac{1}{t_{obs} \cdot 1000} \cdot \left(M_{TSS}(t_{end}) - M_{TSS}(t_{start}) + \int_{t_{start}}^{t_{end}} TSS_x(t) \cdot Q_x(t) \cdot dt\right) \quad (6)$$

Where, $Q_x(t)$ ($m^3 \cdot d^{-1}$) is the sludge flow and TSS_x is the total solids concentration in the sludge flow stream. M_{TSS} is defined as the sum of the total suspended solids mass (in kg) present in the plant, including reactors and secondary settler (equation (7)).

$$M_{TSS}(t) = M_{TSS,an}(t) + M_{TSS,anox}(t) + M_{TSS,aer}(t) + M_{TSS,s}(t) \quad (7)$$

With,

$$M_{TSS,x}(t) = TSS_{,x}(t) \cdot V_x \quad (8)$$

Subscripts 'an', 'anox, 'aer' and 's' refer to the reactors and the secondary settler. V_x is the volume of each unit process in m^3.

Table 3
Pumping energy factors.

Factor	Value	Units
$f_{PE\_Q_{int}}$	0.004	$kWh \cdot m^{-3}$
$f_{PE\_Q_r}$	0.008	$kWh \cdot m^{-3}$
$f_{PE\_Q_w}$	0.050	$kWh \cdot m^{-3}$
$f_{PE\_Q_{pu}}$	0.075	$kWh \cdot m^{-3}$

3. Results and discussion

3.1. Selection of internal recycle ratio and DO setpoint

The first step of this work was to set a suitable internal recycle ratio (R_I) for all the simulations, since it was detected (in a preliminary set of simulations) that the results of minimum amount of readily biodegradable organic matter (S_A) required to meet the nutrient discharge limits depended on the recycle ratio. Fig. S1 displays the S_A requirements for different R_I (i.e. 2, 4, 5, 6, 8) for an influent ammonium range of 10–60 mgN·L^{-1} and an influent P of = 7 mgP·L^{-1}. For R_I = 2, the S_A requirements rose severely for influent ammonium values higher than 35 mgN·L^{-1}. A similar effect was observed at R_I = 4 for influent ammonium values higher than 50 mgN·L^{-1}. This sudden increase is caused by nitrate/nitrite limitations due to insufficient internal recycle. Therefore, it was decided to use an R_I of 5 in all subsequent simulations, as it is the minimum R_I value that did not show any limitation in the range of influent ammonium values used.

Another required preliminary step was the choice of two proper DO setpoints in the aerobic reactor that would allow either nitrate or nitrite pathway. The nitrite pathway is achieved by creating conditions under which nitrite-oxidizing bacteria (NOB) are eliminated from the system while ammonia-oxidizing bacteria (AOB) are retained. Mathematically, equation (9) should be satisfied to eliminate NOB while retaining AOB:

$$\mu_{NOB} - b_{NOB} < 1/SRT < \mu_{AOB} - b_{AOB} \quad (9)$$

where μ_{NOB} and μ_{AOB} are the apparent growth rates of NOB and AOB, respectively, b_{NOB} and b_{AOB} the apparent decay rates of these populations, and SRT the sludge retention time.

The aim was to select a DO setpoint of the aerobic reactor that satisfied equation (9), also considering that DO affects the apparent growth rate values. Then, a simulation study under different DO setpoints was performed to find proper setpoints for nitrite pathway and nitrate pathway. Fig. S2 shows the steady-state AOB and NOB concentrations obtained for each DO setpoint. Nitrite pathway obtainment was considered successful when the ratio AOB/NOB was higher than 4.5 and ammonium oxidation was complete (NH_4^+ < 1 mgN·L^{-1}). This ratio prevented nitrate formation and enabled nitrogen removal mainly via nitrite. As can be observed in Fig. S2, the range where AOB are retained while NOB are washed out is very narrow. Considering these results, the DO setpoint selected to reach nitrite pathway was 0.8 mg L^{-1} while a DO set-point of 3 mg L^{-1} was chosen for nitrate pathway in all subsequent simulations. Stable biological nitrogen removal was obtained with both strategies.

3.2. Minimum SA requirements under different scenarios

The minimum amount of S_A required to meet legal discharge limits (TN < 10 mgN·L^{-1} and P < 1 mgP·L^{-1}) was evaluated for influent NH_4^+ concentrations in a range of 20–60 mgN·L^{-1} and phosphate concentrations in the range of 3–11 mgP·L^{-1}, using R_I = 5, and under two different DO setpoints (0.8 mg·L^{-1}and 3 mg L^{-1}) to achieve both nitrite and nitrate pathway. Fig. 2 shows the S_A requirements for nitrogen (solid lines) and phosphorus removal (dashed lines). Fig. 2-left (and Fig. S3) summarizes the results for nitrate pathway and Fig. 2-right (and Fig. S4) for nitrite pathway. S_A requirements increase proportionally to the increase of ammonium in the influent. Tables S7 and S8 report the AOB/NOB ratios obtained for each specific scenario to verify that NOB washout was really accomplished in the nitrite pathway scenario.

Regarding the results for nitrate pathway, the S_A requirements for N removal (S_A-N, solid lines) start at around 140 mgCOD·L^{-1} at the lowest influent N load (20 mgN·L^{-1}) and increase up to 570 mgCOD·L^{-1} for an influent with 60 mgN·L^{-1} and 11 mgP·L^{-1}. The S_A-N is also affected by the influent P (i.e., the slope of S_A-N vs influent ammonium increases with influent P) showing an additive effect of increasing both N and P

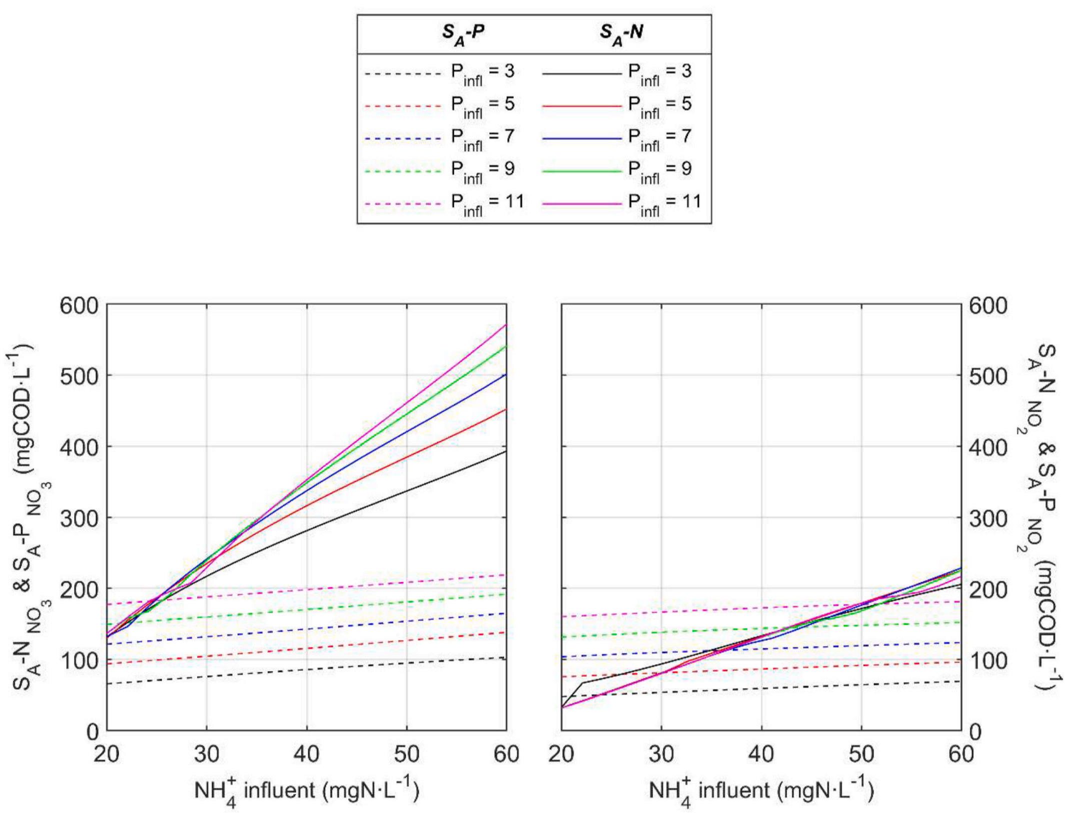

Fig. 2. Minimum S_A requirements to meet the legal P and TN effluent limits (PO_4^{3-} < 1 mgP·L^{-1} and TN < 10 mg N·L^{-1}) when operating under nitrate pathway (left) and nitrite pathway (right) conditions.

concentrations. The rationale is that the influent COD is preferably consumed by PAO in the anaerobic reactor and, thus, higher EBPR activity results in higher COD requirements. Besides, the electrons for nitrate reduction in the anoxic reactor are both provided by the organic matter not degraded under anaerobic conditions and by the stored PHA involved in the DPAO metabolism.

The S_A requirements for P removal (S_A-P, dashed lines) increase almost linearly with the influent P in the range tested (3–11 mgP·L^{-1}) for a given ammonium concentration. Moreover, S_A-P increases when N in the influent increases and parallel S_A-P lines are observed for different influent P values. Considering both S_A-N and S_A-P, the limiting step under nitrate pathway conditions is usually related to N removal (except for influent ammonium values lower than 25 mg N·L^{-1}). That means that, in most cases, S_A limitations would result in an effluent that does not meet TN requirements.

Concerning the results for the nitrite pathway (Fig. 2-right), the S_A-N requirements also increase when the influent ammonium concentration increases, but the observed values are less than 50% of those of the nitrate pathway. Moreover, S_A-N requirements are not significantly affected by the increased P concentration and therefore the lines obtained for different P levels in the influent mostly overlap. On the other hand, the S_A-P lines have the same trend as in the nitrite pathway, but the absolute values are slightly lower. In this case, both N or P removal can be the limiting step depending on the specific case, and only for influent ammonium concentrations above 50 mgN·L^{-1} N, S_A-N becomes the only limiting factor.

Comparing both scenarios, the S_A requirements are always lower when using nitrite pathway either for meeting P or TN discharge limits. Depending on the specific influent, reductions in the overall need for S_A between 9% and 68% can be achieved (see Supplementary Information 3). For instance, for an influent of 9 mgP·L^{-1} and 40 mgN·L^{-1}, S_A-P and S_A-N under nitrate pathway conditions are 171 mg COD L^{-1} and 359 mg COD·L^{-1}, respectively. When the nitrite pathway is implemented, both requirements are reduced to 145 and 136 mg COD·L^{-1}, respectively, which would represent a reduction of 60% in the overall S_A needs. Reduction of organic matter requirements is, obviously, one of the major advantages of using the nitrite pathway.

Table 4
Correlations of S_A and X_S requirements for nitrate and nitrite pathway.

Scenario	Correlation	
S_A requirements		
Nitrate pathway	S_A-P = 2.51 + 14.03 P + 1.046 N	(10)
	S_A-N = 66.51–14.67 P + 4.72 N + 0.600 P N	(11)
Nitrite pathway	S_A-P = −4.51 + 14.12 P + 0.517 N	(12)
	S_A-N = −32.92 – 3.169 P + 4.144 N + 0.066 P N	(13)
X_S requirements		
Nitrate pathway	X_S-P = −7.21 + 31.45 P + 3.22 N	(14)
	X_S-N = −18.73 – 7.67 P + 8.80 N + 0.305 P N	(15)
Nitrite pathway	X_S-P = −29.52 + 27.67 P + 1.68 N	(16)
	X_S-N = −78.00 – 0.367 P + 5.69 N + 0.008 P N	(17)

3.3. *Development of general correlations (S_A)*

To improve the usability of the modelling results described in the previous section, different correlations were proposed, their parameters were fitted by least squares and their performance was evaluated. The best correlations in terms of ability to correctly describe the above data while maintaining low complexity are shown in Table 4. These correlations can be useful for a simple and reliable estimation of the S_A requirements for WWTPs with A^2/O configuration treating wastewater with influent nutrient concentrations in the ranges of 3–11 mgP·L^{-1} and 20–60 mgN·L^{-1}.

Thus, equations (10) to (13) can describe S_A requirements based only on the influent N and P. Correlations (10) and (12) for S_A-P were expressed as linear equations ($y = b_0+b_1·P + b_2·N$), while correlations (11) and (13) for predicting S_A-N were extended with a non-linear summand ($y = b_0+b_1·P + b_2·N + b_3·P·N$) for a better description of the observed N-P dependence. These equations correlated well with the original model data, obtaining R^2 values of 0.9993, 0.9923, 0.9997 and

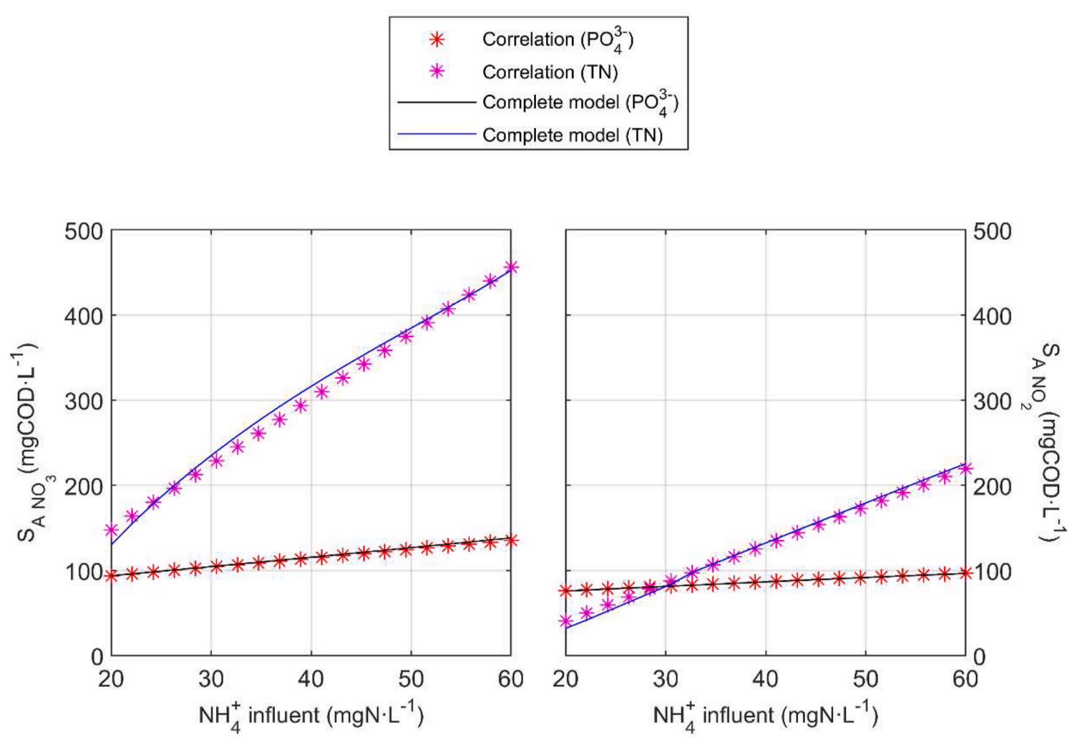

Fig. 3. Comparison of the predicted S_A requirements using the proposed correlations and the model runs for an influent of 5 mg P·L^{-1} under (left) nitrate pathway and (right) nitrite pathway conditions.

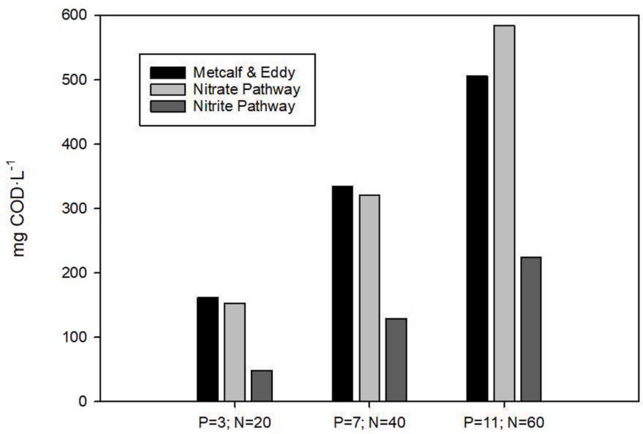

Fig. 4. Comparison of the S_A predictions with equations (10-13) versus Metcalf and Eddy's recommendations on readily biodegradable COD requirements. Three different influent compositions (low, medium and high) are evaluated.

0.9925 for equations (10) to (13). For example, Fig. 3 compares the results of the model run under different conditions for a given influent with 5 mg P·L^{-1} with the values predicted by equations (10-13), showing the goodness of the fit. The equations in Table 4 are implemented in an Excel file that can be found in supplementary information 2.

The maximum S_A value obtained with equations (10) and (11) for a given influent determines the minimum S_A required to meet the discharge limits when the nitrate pathway is applied. Equations (12) and (13) allow the same determination but for the nitrite pathway scenario. Metcalf and Eddy (Tchobanoglous et al., 2014), a widely used book for WWTP design, also recommends certain threshold ratios for the design of WWTP configurations aiming at simultaneous C, N and P removal (A^2/O and UCT): a readily biodegradable COD (rbCOD) content of 6.6 g rbCOD·g^{-1}NO_3^--N and 10 g rbCOD·g^{-1}P for nitrate pathway. Fig. 4 compares the correlations obtained in this work to those in Metcalf and Eddy (Tchobanoglous et al., 2014) in three different case studies, Case 1: 3 mgP·L^{-1} and 20 mgN·L^{-1}, Case 2: 7 mgP·L^{-1} and 40 mgN·L^{-1}, Case 3: 11 mgP·L^{-1} and 60 mgN·L^{-1}. The correlations obtained in this study predict approximately the same S_A requirements under the nitrate pathway. The S_A requirements for nitrite pathway (not provided in the reference book) result 50%–72% lower.

Finally, Fig. 5 shows a useful decision tree based on correlations (10) to (13) to select the best operational conditions for the proper treatment of a given wastewater under an A^2/O configuration. If the S_A content is not enough to meet the desired effluent concentrations, alternatives should be considered: the addition of an external carbon source, the addition of chemicals for phosphate precipitation, or the implementation of the nitrite short-cut pathway. For example, given an influent water with 350 mgCOD·L^{-1} as S_A, 5 mgP·L^{-1}, and 30 mgN·L^{-1}, the S_A-P and S_A-N are 104 and 225 mgCOD·L^{-1} respectively. Hence, S_A-N is

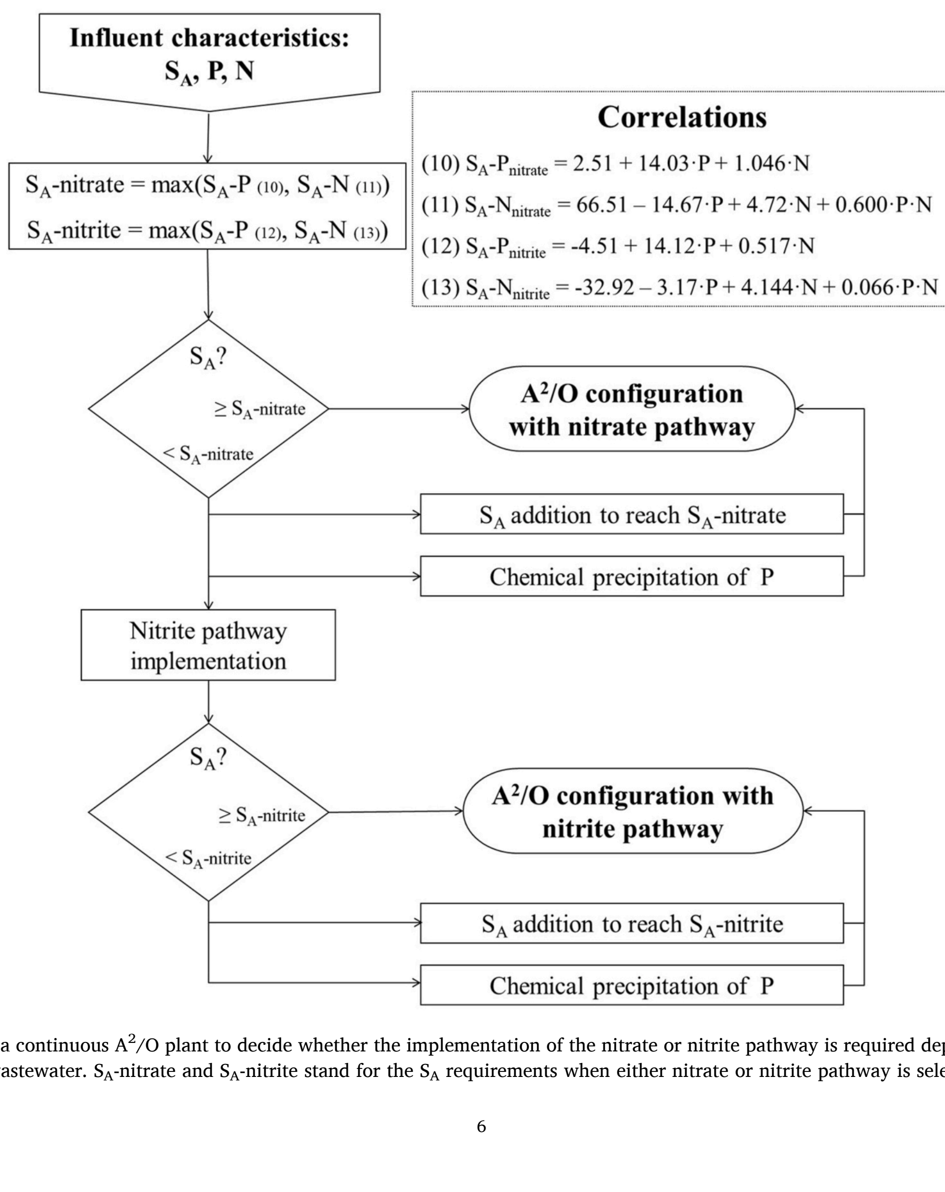

Fig. 5. Decision tree for a continuous A^2/O plant to decide whether the implementation of the nitrate or nitrite pathway is required depending on the S_A, P and N content of the influent wastewater. S_A-nitrate and S_A-nitrite stand for the S_A requirements when either nitrate or nitrite pathway is selected.

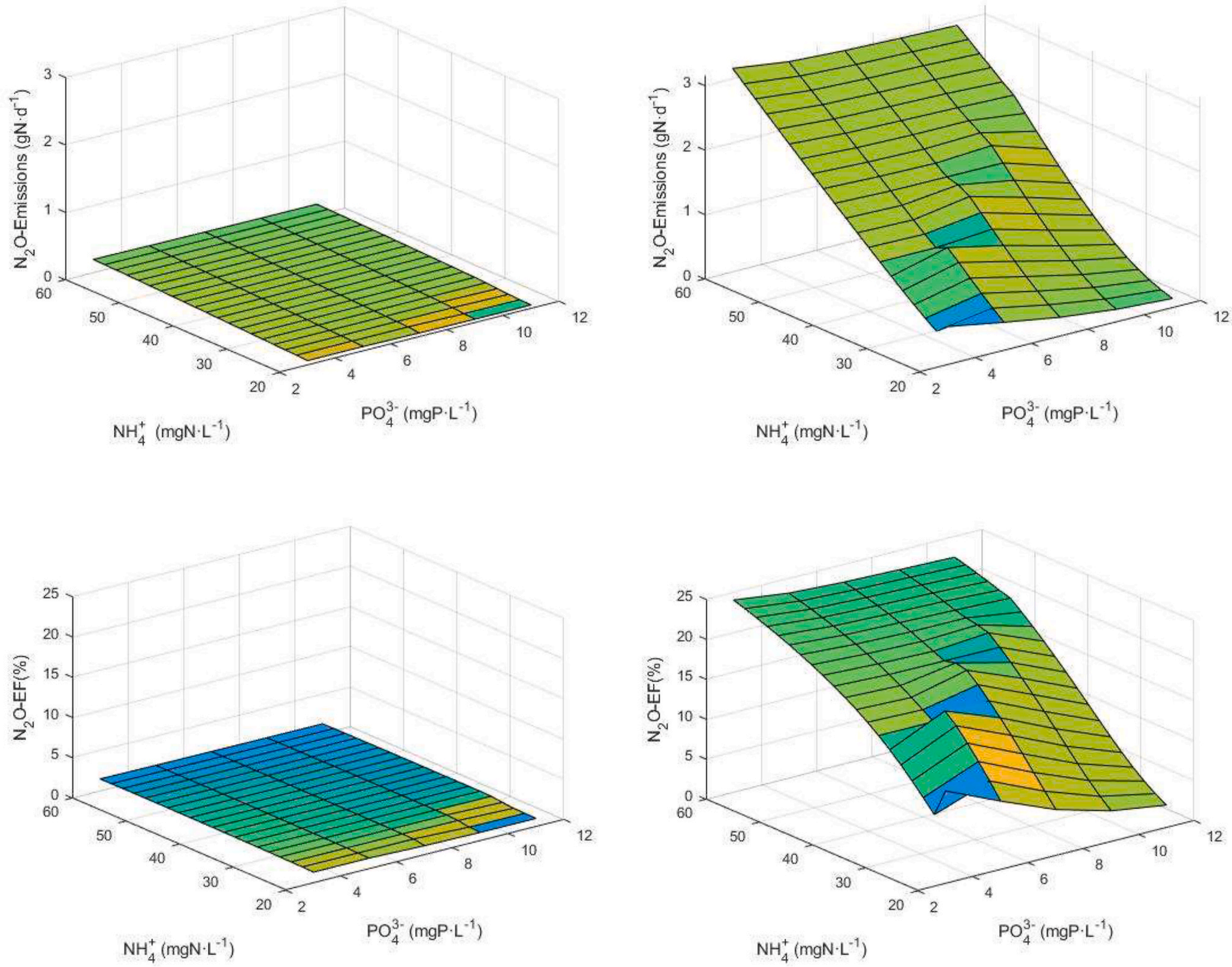

Fig. 6. N_2O emissions (top) and N_2O-EF (bottom) for different runs under nitrate (left) and nitrite (right) pathway.

Table 5
Influent conditions, OCI results and N_2O emissions under nitrate and nitrite pathway for different scenarios.

Scenario	Low	Medium	High
Influent concentrations			
PO_4^{3-} ($mgP{\cdot}L^{-1}$)	3	7	11
NH_4^+ ($mgN{\cdot}L^{-1}$)	20	40	60
S_A ($mg{\cdot}L^{-1}$)	155	347	590
Nitrate Pathway			
k_La (d^{-1})	68.0	130.0	202.5
AE ($kWh{\cdot}d^{-1}$)	4123	8800	15371
PE ($kWh{\cdot}d^{-1}$)	7968	7968	7968
SP ($kg{\cdot}d^{-1}$)	1884	3295	5021
OCI	17742	26653	38401
N_2O-EF (%)	1.35	1.37	1.25
Nitrite Pathway			
k_La (d^{-1})	38.9	81.8	133.2
AE ($kWh{\cdot}d^{-1}$)	2200	5087	9062
PE ($kWh{\cdot}d^{-1}$)	7968	7968	7968
SP ($kg{\cdot}d^{-1}$)	1916	3322	5034
OCI	15915	23021	32132
N_2O-EF (%)	3.38	6.40	7.81

limiting but the value is lower than the actual S_A content in the influent and thus, nutrient removal through the nitrate pathway is possible. On the other hand, for a wastewater with 350 $mgCOD{\cdot}L^{-1}$ as S_A, 9 $mgP{\cdot}L^{-1}$, and 60 $mgN{\cdot}L^{-1}$, S_A-P and S_A-N are 192 and 542 $mgCOD{\cdot}L^{-1}$, respectively. Thus, the organic matter necessary for these conditions is higher than that available in the wastewater and N and P removal could not meet legal discharge limits. In this case, the S_A-P and S_A-N under the nitrite pathway are 154 and 223 $mgCOD{\cdot}L^{-1}$, respectively. Since the required S_A is lower than that in the wastewater (350 $mgCOD{\cdot}L^{-1}$), nutrient removal thorough the nitrite pathway is possible.

3.4. Evaluating the effect of nitrite pathway on N_2O emissions and WWTP economy

Textbook knowledge and the previous sections show that the organic matter requirements are much lower using the nitrite pathway. However, the nitrite pathway can also entail other detrimental aspects that should also be considered for a comprehensive evaluation of both processes. For example, it has been extensively reported that nitrite accumulation triggers off N_2O production and, thus, N_2O emissions: high nitrite and low DO promote the NirK and Nor enzymes activity and, thus, the N_2O production through the ND pathway (Massara et al., 2017; Pocquet et al., 2016). Hence, a plant operating under nitrite shortcut conditions may lead to higher GHG emissions which may not compensate the carbon savings from avoiding the full nitrate pathway. Fig. 6 shows the N_2O emissions and N_2O emission factor (N_2O-EF), i.e., the percentage of N that is emitted as N_2O compared to the influent nitrogen ammonium load, for different runs under a wide range of influent ammonium and P under nitrate and nitrite pathway and using the minimum S_A required to remove N and P.

The results show that the N_2O-EF predicted via nitrate were in the range 1.0–1.5, considerably lower than the range 2.8–24.0 obtained via nitrite. Analysing the ratio between both emissions for each simulation, it was found that via nitrite represents between 2.8 and 17 times the emission via nitrate. The highest N_2O emissions were obtained at the highest influent N, because of the high nitrite accumulation. It was also observed that with an increase in influent P, the emission factor decreased. Higher S_A requirements are needed to remove high influent P concentrations and, therefore, N_2O denitrification is promoted.

Although the current values in a full-scale WWTP are likely to differ from the emissions predicted by the model, these results demonstrated a clear trend of increasing N_2O emissions when using the nitrite pathway. Therefore, there is a trade-off between the operational costs and the overall sustainability of the WWTP. In particular, the results showed that aiming at the reduction of costs related to aeration costs and external carbon dosage with the implementation of the nitrite pathway could lead to a considerable increase in N_2O emissions and consequently a higher carbon footprint. In any case, operation strategies based on phase alternation (Zou et al., 2022) and intermittent aeration (Solís et al., 2022b) could also be applied to reduce these emissions.

Besides N_2O emissions, the implementation of nitrite pathway also influences the WWTP economy since it reduces aeration needs. Table 5 summarizes the results of the evaluation criteria described in Section 2.4, obtained under the nitrate and nitrite pathway in different scenarios with enough S_A to perform either pathway. The OCI values for nitrite pathway were reduced in the range 10-16% compared to those for nitrate pathway. The main difference appeared in the aeration costs (AE was reduced in the range 41-47%), while similar sludge production was observed (SP increased 0.3-2% for nitrite pathway). For example, the aeration energy requirements were 8800 $kWh{\cdot}d^{-1}$ in the case of an influent with 7 $mgP{\cdot}L^{-1}$ and 40 $mgN{\cdot}L^{-1}$ under the nitrate pathway configuration, while the energy requirements were 5087 $kWh{\cdot}d^{-1}$ for the nitrite pathway scenario. Although the most important factor in the OCI reduction are the aeration costs, this is not the result of reduced oxygen requirements compared to full nitrification. Stoichiometrically, the oxidation of ammonium to nitrite represents 25% less oxygen than the oxidation of ammonium to nitrate, but considered globally, the nitrate produced can be reused as an electron acceptor during the denitrification process, recovering the excess oxygen used for the oxidation of nitrite to nitrate. Then, the main reason for the decrease in aeration costs is the lower DO setpoint required to decrease NOB activity for the nitrite pathway, which increases the driving force of oxygen transfer (DO saturation – DO setpoint) and hence reduces the required k_La (Table 5). Full-scale studies have already demonstrated the significant savings of power demand when implementing a moderate decrease in DO setpoint while ensuring a good effluent quality (Pasini et al., 2021).

N_2O emissions were also simulated for these three scenarios. The emissions for the nitrite pathway were lower than those shown in Fig. 6. For all three cases, the emission via nitrite is between 2.5 and 6.2 times that of the nitrate pathway. These results can be understood because the simulations via nitrite are run with the amount of organic matter needed for the nitrate pathway, which represents a higher amount than strictly necessary. The high values obtained in Fig. 6 can be related to the fact that these are all scenarios in which the minimum amount of organic matter necessary to meet the discharge limits is used. In fact, one of the proposed strategies to decrease emissions is using denitrification as an N_2O sink (Chen et al., 2020), which would be clearly favoured by an excess of organic matter.

3.5. Analysis of X_S requirements: development of general correlations

All the previous simulations have been conducted assuming that the influent organic matter was readily biodegradable organic matter or fermentation products, *i.e*, VFA. However, the COD fractionation in real wastewaters is much more complex and the degree of COD biodegradability is another interesting factor to consider in the previous simulations (Vollertsen and Hvitved-Jacobsen, 2002). PAO can only use short-chain VFAs and, thus, a preliminary anaerobic hydrolysis process would be required to favour PAO growth in the case of an influent with complex COD. Thus, the presence of slowly biodegradable organic matter would benefit the denitrification process and would alter the organic matter requirements for complete nutrient removal (Daigger and Littleton, 2014). For instance, an influent may contain a sufficient amount of COD in terms of slowly biodegradable COD but the hydrolysis could be limiting step and P removal not achieved. This issue was studied with an additional set of simulations where the influent carbon source was set as particulate or slowly biodegradable carbon source (X_S), *i.e.*, organic matter that is hydrolysed to easily biodegradable fermentable organic matter (S_F) which then ferments to produce S_A.

Fig. 7 shows the amount of X_S required to meet the TN and P legal discharge limits (X_S-N and X_S-P, respectively) for the same N and P ranges and scenarios used in section 3.2. For these simulations, X_S was free of N and P (model parameters $i_{NXS} = i_{PXS} = 0$), to avoid increasing the N and P load with increasing X_S, which could mislead the interpretation of the results. The values of Figs. 7 and 2 are very different, reflecting the importance of the wastewater COD fractionation in these simulations. For the case of nitrate pathway, X_S-P becomes the limiting step for a much wider range of concentrations than that for S_A-P. The increase in X_S-P with respect to S_A-P is very important, up to 290% (11 $mgP{\cdot}L^{-1}$, 60 $mgN{\cdot}L^{-1}$), indicating that the processes of X_S hydrolysis to S_F or S_F fermentation to S_A are competing with denitrification processes and reduce the available S_A for PAO. However, if both X_S-P and X_S-N are considered, total X_S requirements do not differ much from S_A requirements for some high N scenarios. Supplementary information 3 includes a comparison of X_S and S_A requirements for a wide range of influent concentrations. The use of X_S for the nitrate pathway can increase the COD requirements from 0 to 127%, while for the nitrite pathway the increase ranges from 14 to 103%. In any case, these results are obtained with the default parameters used in the ASM2d model for hydrolysis and fermentation processes and specific parameter calibration might be needed for each particular WWTP.

Regarding the results for nitrite pathway, X_S-P and X_S-N also increase with respect those of S_A, in this case up to 208% (11 $mgP{\cdot}L^{-1}$, 60 $mgN{\cdot}L^{-1}$). X_S-N does not become a limiting factor in most of the wastewater composition scenarios. Comparing the overall X_S needs in both pathways, the nitrite pathway also systematically requires less COD as in the case of S_A. The reduction in X_S requirements ranges from 23 to 58% depending on the specific influent.

General correlations and a decision tree can be obtained for X_S requirements likewise the case of S_A. These results would ease the decision of A^2/O configuration needed when treating wastewater with nutrient concentrations in the ranges 3–11 $mgP{\cdot}L^{-1}$ and 20–60 $mgN{\cdot}L^{-1}$ and slowly biodegradable organic matter. Table 4 also shows the correlations for estimating X_S requirements: equations (14) and (16) for X_S-P and (15) and (17) for X_S-N, following the same type of equations used for S_A estimations. These equations also highly correlate with the original model data, giving R^2 values of 0.9877, 0.9966, 0.9969 and 0.9993 for equations (14) to (17). Fig. 8 shows the goodness of fit of the correlations for a given influent with 5 mg $P{\cdot}L^{-1}$.

Fig. 9 shows a decision tree based on equations (14) to (17) that can be used to select the best operational conditions for the proper treatment of a given wastewater under an A^2/O configuration with slowly biodegradable organic matter. The same individual cases as in section 3.2 are discussed to ease the comparison. For a wastewater of 350 $mgCOD{\cdot}L^{-1}$ as X_S, 5 $mgP{\cdot}L^{-1}$ and 30 $mgN{\cdot}L^{-1}$, the X_S-P and X_S-N were 247 and 253 $mgCOD{\cdot}L^{-1}$. These values were lower than those in the wastewater (350 $mgCOD{\cdot}L^{-1}$) and nutrient removal via the nitrate pathways was possible. On the other hand, for a wastewater with 350 $mgCOD{\cdot}L^{-1}$ as X_S, 9 $mgP{\cdot}L^{-1}$, and 60 $mgN{\cdot}L^{-1}$, the X_S-P and X_S-N were 469 and 605 $mgCOD{\cdot}L^{-1}$, respectively. As observed, the organic matter necessary was higher than that available in the wastewater and nitrite pathway implementation would be needed for nutrient removal. The X_S-P and X_S-N requirements using nitrite pathway were 320 and 264 $mgCOD{\cdot}L^{-1}$.

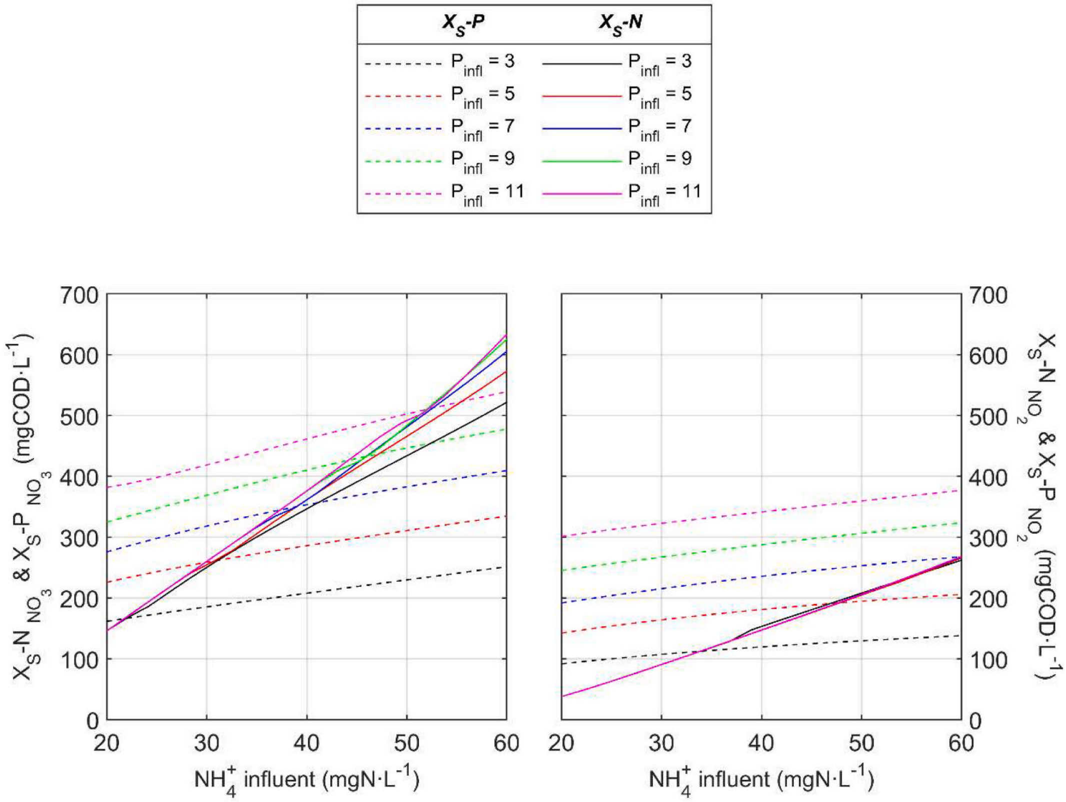

Fig. 7. Minimum X_S requirements to meet the legal P and TN discharge limits ($PO_4^{3-} < 1$ mgP·L^{-1} and TN < 10 mg N·L^{-1}) operating under nitrate pathway (left) and nitrite pathway (right) conditions.

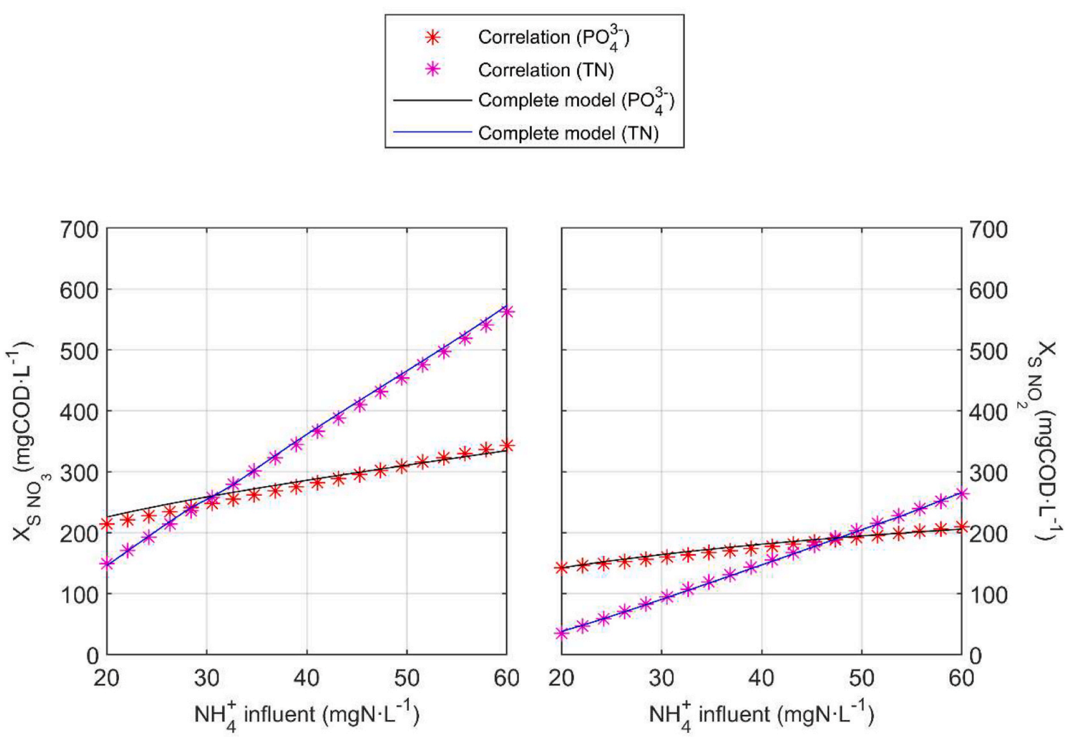

Fig. 8. Comparison of the predicted X_S requirements using the proposed correlations and the model runs for an influent of 5 mg P·L^{-1} under (left) nitrate pathway and (right) nitrite pathway conditions.

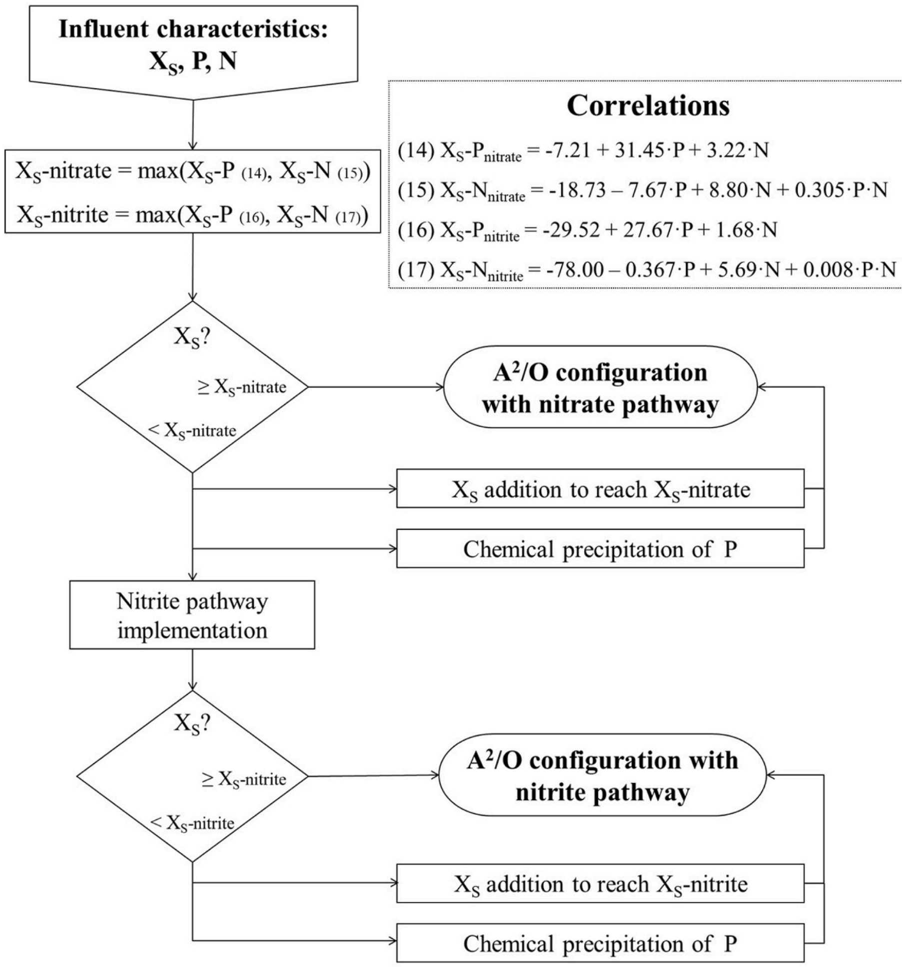

Fig. 9. Decision tree for a continuous A^2/O plant to decide whether the implementation of the nitrate or nitrite pathway is required depending on the X_S, P and N content of the influent wastewater. X_S-nitrate and X_S-nitrite stand for the X_S requirements when either nitrate or nitrite pathway is selected.

These values are lower than that in the wastewater (350 mgCOD·L^{-1}) and nutrient removal through the nitrite pathway was possible.

3.6. Practical implications

The main objective of this study was to obtain general correlations describing the amount of organic matter (S_A or X_S) that would be required, both via nitrate and via nitrite, to remove N and P down to the European default discharge limits. The plant was oversized to avoid kinetic limitations and its operational parameters were selected to be the same over the whole range of influent values evaluated, thus avoiding noise due to additional changes. For example, the internal recirculation ratio was selected at 500% because no additional COD increase at higher RI values was observed for high ammonium concentrations. Also, the oxygen concentration via nitrate or via nitrite remained the same for all simulations. Thus, the results should be considered as the minimum COD requirements for each scenario, i.e. the lower limit if the plant is well dimensioned and operating correctly. A higher COD concentration might be necessary if, for example, a lower recycle ratio or a higher DO concentration is used.

The findings are specific to the studied configuration (A^2/O system), and hence extrapolation to other systems such as sequenced batch reactors, University of Cape Town (UCT), reverse A^2/O or other configurations should be done carefully and would preferably require additional simulations with these configurations. Nevertheless, the nitrite pathway requires consistently less organic matter than the nitrate pathway, which can help to achieve P or TN discharge limits.

The operational mode leading to NOB washout was based on DO reduction. The model predicts that NOB washout can be stably maintained by setting a DO value, although in practice the inherent variability of operational conditions, as well as the existence of different NOB microorganisms (with different kinetic characteristics), would make it more difficult. However, there are alternative methods to achieve NOB washout, such as sludge treatment by free nitrous acid (FNA) and free ammonia (FA) (Duan et al., 2019a, 2019b, 2022). In this case, given that the conditions in the aerobic reactor may be with a higher oxygen concentration, organic matter requirements can also be reduced in the case via nitrite, but the economic results may be less favourable, since, as we have seen, the main saving of the nitrite pathway is due to the reduction in aeration requirements.

Finally, the implementation of the nitrite pathway reduces operational costs compared to the traditional nitrate pathway, but on the downside N_2O emissions, which contribute to global warming, can also be higher. The model consistently predicts higher N_2O emissions for the nitrite pathway and, currently, research efforts are set to develop operational modes and control strategies to decrease this undesirable effect (Bellandi et al., 2020; Chen et al., 2020; Santín et al., 2017; Solís et al., 2022a, 2022b). For example, implementing mitigation strategies such as optimizing the DO concentration in the aeration tank to reduce N_2O production and using anoxic periods to enhance N_2O denitrification can decrease N_2O emissions. Another solution is to integrate an appropriate N_2O abatement technology for off-gas treatment, such as chemical scrubbing or biological N_2O reduction. Therefore, it is necessary to develop and implement comprehensive strategies that consider both the cost savings and environmental impact of the nitrite pathway to ensure sustainable and efficient wastewater treatment.

4. Conclusions

The decrease of COD requirements when implementing nitrite pathway (nitritation/denitritation) for N removal was quantified for a conventional A^2/O WWTP aiming at simultaneous C/N/P removal. The organic matter requirements were clearly reduced (depending on the influent, between 9 and 68% less S_A and between 23 and 58% less X_S). It was shown that a higher amount of organic matter as X_S was required when compared to S_A since the limiting step may be hydrolysis of X_S or fermentation of S_F, which limits PAO activity. General correlations were developed to help estimate S_A and X_S requirements in nitrite or nitrate pathway scenarios for the design of future WWTPs.

Nitrite pathway route has several advantages compared to the nitrate pathway (conventional nitrification-denitrification), such as less aeration needs (41-47%), less COD demand, and lower costs (10-16%). Therefore, the implementation of the nitrite pathway reduces energy requirements and external COD needs, allowing the removal of N in wastewaters with low COD/N ratio.

On the downside, the model predicts a considerable increase of N_2O emissions with nitrite pathway, 2.8–17 times the emission via nitrate for the scenarios using the minimum COD required and 2.5–6.2 times in scenarios with excess of COD. However, several N_2O mitigation strategies can be proposed to improve this scenario, which can help reduce emissions while maintaining the cost savings achieved through the nitrite pathway. Then, it is essential to design WWTPs that consider both the environmental impact and cost savings associated with the use of the nitrite pathway.

CRediT authorship contribution statement

Àlex Gaona: Methodology, Software, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Borja Solís:** Methodology, Software, Data curation, Visualization. **Javier Guerrero:** Methodology, Software, Formal analysis, Investigation. **Albert Guisasola:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Data curation, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Juan A. Baeza:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2023.137453.

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