Model based evaluation of partial nitritation in a SHARON reactor

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ABSTRACT
SHARON-Anammox is a more sustainable alternative for biological nitrogen removal from high concentrated ammonium streams than a conventional treatment based on nitrification-denitrification. This paper focuses on the evaluation, by means of numerical simulation, of the partial oxidation of ammonium to nitrite in the first stage of this totally autotrophic process. Operational and wastewater compositional parameters such as nitrogen loading rate, inorganic carbon, biodegradable organic carbon and pH were evaluated considering a continuously aerated SHARON reactor at both, steady and transient states. These tested parameters influenced on the reaction pH since no control was considered and, consequently, chemical equilibrium reactions, biomass substrate availability, and inhibition levels inside the reactor. The low hydraulic residence time, in combination with the reactor performance without solids retention, made the system susceptible to biomass wash out. The use of simulation allowed the prediction of the response of a SHARON reactor for partial nitritation purposes under different situations and, therefore, to improve the design of its operational strategy.

INTRODUCTION
Ammonium removal from urban wastewaters and other pollutant streams is often achieved biologically by means of classical nitrification-denitrification. Nitrification is an aerobic autotrophic process that consists on the oxidation of ammonium to nitrite (nitrification), and the further oxidation of nitrite to nitrate (nitratation). Thereafter, the nitrate generated during nitrification is reduced to molecular nitrogen in presence of organic carbon and absence of oxygen by heterotrophic denitrification. When the amount of biodegradable organic carbon available in the wastewater is not high enough for the complete denitrification, the supply of an external organic carbon source becomes necessary, which implies an increase of the treatment cost.

The incipient, totally autotrophic, combined process SHARON-Anammox represents a more sustainable alternative for nitrogen removal than the conventional nitrification-denitrification (van Dongen et al., 2001; Alin, 2006) and, consequently, it has gained a lot of interest in the recent years. This technology allows the integration of energetic valorisation via anaerobic digestion and nitrogen removal without the restriction of the availability of readily biodegradable organic carbon for denitrification. No external organic carbon requirements exist, either. Other advantages of the SHARON-Anammox process are the energy savings linked to aeration requirements, the low sludge production and the possibility to work at high nitrogen loads (Mulder, 2003).
In the SHARON process -Single reactor High activity Ammonia Removal Over Nitrite- (Hellinga et al., 1998), ammonium is partially converted to nitrite by ammonium oxidizing bacteria (AOB, X_{AO}) in a perfectly mixed reactor without sludge retention, under aerobic conditions and at relatively high temperature (−35°C). Hence, in a SHARON reactor there is no difference between hydraulic residence time (HRT) and solids retention time (SRT) since it operates as a chemostat. Nitrite oxidizing bacteria (NOB, X_{NO}) do not interfere when the process is well controlled due to the short HRT and high temperature. Under these conditions NOB grow more slowly than AOB. The stoichiometry of the complete nitritation, neglecting biomass growth, can be written as indicates equation (i):

\[ \text{NH}_4^+ + 2\text{HCO}_3^- + 1.5\text{O}_2 \rightarrow \text{NO}_2^- + 2\text{CO}_2 + 3\text{H}_2\text{O} \]  

(i)

Anammox is the acronym of ANaerobic AMMonium OXidation (Mulder et al., 1995), a biological autotrophic conversion process in which almost equimolar amounts of ammonium and nitrite are combined to form molecular nitrogen in absence of oxygen. Thus, when treating concentrated ammonium streams, the Anammox process needs to be applied in combination with a partial nitritation. Neglecting biomass growth, Anammox reaction can be expressed as shown in equation (ii), with a stoichiometric nitrite/ammonium ratio equal to 1. When biomass is accounted this ratio increases up to 1.32 (Strous et al., 1998).

\[ \text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \]  

(ii)

As previously mentioned, the integrated SHARON-Anammox system usually is configured as two different reactors, although other approaches linking partial nitritation and anaerobic ammonium oxidation in just one reactor are also being studied (Third et al., 2001). Additionally, other potential uses of the SHARON technology include nitrogen removal by nitrification-denitrification via nitrite (Fux et al., 2003; Gali et al., 2007).

Fluctuations in the wastewater composition and/or operational performance are expected to occur when treating raw or previously digested industrial streams (van Kempen et al., 2001). This fact may affect the SHARON effluent quality and, consequently its suitability for a subsequent Anammox process, where the desired NO_2^-/N/H_2-N ratio is approximately one. The aim of this work was to evaluate by numerical simulation the role of different critical parameters which affect the achievement of a properly partial nitritation in the first stage of a SHARON-Anammox system.

**MATERIALS AND METHODS**

**The SHARON model**

All simulations carried out during this study were executed using the mathematical model for the SHARON process proposed by Magri et al. (2007). The treatment of ammonium rich wastewaters, which also contained readily and slowly biodegradable organic substrates (S_S and X_S, respectively) and phosphates (S_{PO4}), is considered to be exclusively under aerobic conditions. Three different microbial populations were included in the model: heterotrophic biomass (X_B) responsible of the oxidation of biodegradable organic substrates that might be present in the wastewater; and nitrifying organisms both ammonia and nitrite oxidizing bacteria (X_{AO} and X_{NO}). For AOB and NOB, free ammonia (FA, NH_3) and free nitrous acid (FNA, HNO_2) are considered to be, respectively, the real substrate although both populations can be inhibited by this chemical species at sufficiently high concentrations. Due to the significant influence of the pH on the process performance (affecting chemical equilibrium reactions, substrates availability for biomass growth, and inhibition levels...
inside the reactor) it was considered as a state variable and, therefore, it was dynamically calculated. The direct influence of the pH on microbial growth kinetics was also considered. Aeration was assumed to be controlled through the establishment of a dissolved oxygen set-point in the liquid bulk. No additional controls were regarded. Stripping of carbon dioxide (CO₂) and ammonia were also included as a function of the oxygen liquid-gas transfer. Kinetic parameter values were taken into account according to Magri et al. (2007). Fortran was used as the programming language in the computational implementation of the model and the numerical solution was approximated by the Runge-Kutta-Fehlberg adaptive step-size integration method.

**Boundary conditions**

Simulations of the behaviour of a SHARON reactor at the steady state (after 100 days of continuous simulation) were carried out considering an inflow with total ammonium (S_{NH₄}) and phosphate concentrations equal to 2000 mg N L⁻¹ and 100 mg P L⁻¹ respectively, and a pH value of 8.00 (except when specified otherwise). The S_{RC}/S_{NH₄} (inorganic carbon/total ammonium) molar ratio of the inlet was fixed to one unless when its influence was studied. HRT was set to a prudent value of 2 days by default. Temperature of the reactor was considered constant at 35°C and dissolved oxygen was fixed at 3 mg O₂ L⁻¹. Table 1 summarizes the simulations executed in this work. Presence of biodegradable organic matter in the wastewater was only taken into account when its effects were explicitly evaluated.

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The process efficiency in terms of effluent nitrite to ammonium molar ratio (S_{NO₂}/S_{NH₄}) was also analyzed under transient conditions, assuming initial steady state. The process sensitivity to a given step perturbation was evaluated after waiting for one day since it was introduced.

**SIMULATION RESULTS**

**Effects of the inlet inorganic carbon to ammonium molar ratio (S_{RC}/S_{NH₄})**

Inorganic carbon, mainly bicarbonate (HCO₃⁻), is expected to be the main buffer agent in the wastewater. The speciation fractions of the carbonate system (CO₂-HCO₃⁻-CO₃²⁻) will depend on the pH, temperature and ionic strength of the medium likewise the others chemical equilibrium reactions involved. This component is also the carbon source used by autotrophic biomass for cellular synthesis.

According to equation (i), the nitritation process is highly influenced by the ammonium to bicarbonate ratio present in the wastewater. This dependence at the steady state is outlined in Figure 1, where the predicted nitrogenous components concentrations and pH, the active biomasses growth, the total respiration rate, and the effluent S_{NO₂}/S_{NH₄} ratio are depicted as a function of the inlet S_{RC}/S_{NH₄} ratio. The desired outlet quality was predicted when approximately analogous molar amounts of S_{RC} and S_{NH₄} were fed into the reactor. An increase on S_{RC}/S_{NH₄} implied a rise in the amount of S_{NH₄} (NH₄⁻-NH₃) oxidized, similarly as previously described by Volcke et al. (2002). Ammonium oxidizing biomass content inside the reactor was proportional to the S_{RC}/S_{NH₄} ratio of the wastewater, as well as the biological activity in terms of OUR-Oxygen Uptake Rate-. Nitrite oxidizers growth was not predicted by simulation in the tested conditions.
When evaluating the dynamic response of a SHARON reactor to a step perturbation on the inlet $S_{IC}/S_{NH4}$ ratio ($S_{NH4}$ was kept constant), the main changes on the effluent $S_{NO3}/S_{NH4}$ ratio were predicted in the case that $S_{IC}/S_{NH4}$ increased (Figure 2). In this situation, a pH rise inside the reactor was expected due to a longer presence of positive ions ($S_{Z}$) in the wastewater. The linearity between the inorganic carbon fed and the CO$_2$ stripped disappeared and the concentration of free ammonia inside the reactor increased, working not only as substrate but also as inhibitor for ammonium oxidizing bacteria. Furthermore, a high pH value might inhibit nitrification by itself. For modelling purposes it is necessary to accurately characterize these inhibitory phenomena specifically in the system considered because they can vary widely, particularly in the case of FA (Figure 3). Although these inhibitions are reversible, the low HTR of the reactor (operated as a chemostat) makes wash out of ammonium oxidizers very likely to happen. According to the transient conditions here established, this fact would occur if $\Delta S_{IC}/S_{NH4} > 15\%$ (the $S_{IC}/S_{NH4}$ ratio is supposed to recover its initial value after one day perturbation). This risk might be reduced if the partial nitrification was operated in a reactor with biomass retention (Ganigué et al., 2006). $X_{NO}$ growth should be then prevented by a different mechanism than the wash out -i.e.: free ammonia inhibition, since $X_{NO}$ are more sensible to this phenomenon than $X_{AO}$ (Anthonisen et al., 1976).
Effects of the nitrogen loading rate (NLR)

NLR of the reactor is determined by two different kinds of parameters, one operational (HRT) and the other compositional (SNH). The process efficiency calculated at the steady state for a given NLR (500-1500 mg N 1\(^{-1}\) d\(^{-1}\)) might differ depending on which of these parameters was modified with respect to its default value (Figure 4). When varying SNH (1000-3000 mg N 1\(^{-1}\)), the modelled effluent SNO/SNH ratio experienced a sudden drop at sufficiently high NLR (≥ 1225 mg N 1\(^{-1}\) d\(^{-1}\)) due to the inhibitory FA levels inside the reactor. On the other hand, when HRT was modified (4.0-1.3 d), besides the harmful effects of high NLR (there was a slight difference on the threshold value with respect to the previous case), low values (≤ 550 mg N 1\(^{-1}\) d\(^{-1}\)) also acted in detriment of the process because they allowed growth of nitrite oxidizing bacteria and nitrate accumulation inside the reactor. Higher NLR than those established here have been reported as feasible in the literature when operating a continuously aerated SHARON reactor with pH control (Van Hulle et al., 2005). When evaluating the effect of a perturbation on the HRT, more immediate destabilization was predicted at high NLR.

Effects of the inlet readily biodegradable organic carbon to ammonium molar ratio (S\(_B\)/SNH)

The influence of biodegradable organic carbon was evaluated considering acetic acid as the exclusive BOD (Biological Oxygen Demand) source, so that in this case S\(_B\) = BOD. Although
interesting, the effect of factors such as the presence of (hydrolysable) slowly biodegradable organic substrates ($X_5$) or the composition of $S_5$ has not been analyzed.

The presence of an organic substrate in the inlet favoured nitrite production and ammonium assimilation due to heterotrophic growth. Thus, an increase of the effluent $\text{S}_{\text{NO}_2}/\text{S}_{\text{NH}_4}$ ratio was predicted (Figure 5), which is in agreement with experimental observations (Mosquera-Corral et al., 2005). At sufficiently high values of $S_5$, the nitration process was expected to destabilize and ammonium to by-pass the treatment without being oxidized or air-stripped due to the high pH reached inside the reactor. This behaviour was not related to a lack of oxygen in the medium (dissolved oxygen was kept at set-point and diffusion phenomena inside biological flocks were not considered). However, non accumulation of $S_5$ in the effluent was predicted.

The response of the system to a perturbation on the BOD content of the wastewater was similar to that predicted when evaluating the effects of inorganic carbon. The effluent $\text{S}_{\text{NO}_2}/\text{S}_{\text{NH}_4}$ ratio increased proportionally to the organic content of the inlet until a threshold ($S_5/\text{S}_{\text{NH}_4} = 0.35$ on molar basis) was reached, in which the pH value rose enough to destabilize the process.

![Figure 5. Influence of the inlet $S_5/\text{S}_{\text{NH}_4}$ on the SHARON process performance at steady state.](image)

**Effects of the inlet pH**

The pH of the wastewater also influenced the $\text{S}_{\text{NO}_2}/\text{S}_{\text{NH}_4}$ ratio in the SHARON effluent (Figure 6), existing a direct relation between both parameters in the range of pH 6.50-8.50. When the pH of the wastewater was identical to that of an ideal solution of $S_5$ and $\text{S}_{\text{NH}_4}$ ($\text{pH} = 7.59$ at 35°C; $\text{S}_{\text{NH}_4} = 2000$ mg N l$^{-1}$; $S_5/\text{S}_{\text{NH}_4} = 1$ (molar); $I_{\text{C}_{\text{S}}_2} = I_{\text{C}_{\text{S}}_{\text{PO}_4}}$; $I_{\text{C}}$: ionic charge) then the value of $\text{S}_{\text{NO}_2}/\text{S}_{\text{NH}_4}$ was equal to one. Otherwise, predicted $\text{S}_{\text{NO}_2}/\text{S}_{\text{NH}_4}$ ratio depended on the charge balance inside the reactor, which affected the pH, the inorganic carbon equilibrium and, therefore, the CO$_2$ stripped due to the liquid-gas transfer associated with aeration.

In order to improve the operation of a SHARON reactor when treating wastewaters with a fluctuant composition, it should be interesting to consider some additional control besides dissolved oxygen set-point. Control strategies based on the adjustment of the air flow rate for aeration meantime CO$_2$ stripping and/or the pH reaction by means of acid/base addition have been evaluated in the literature.
using simulation (Volcke et al., 2005; 2006). The purpose of these studies was to identify the control strategy which better assisted the guidance of the SHARON process, disengaging the ratios $S_{NO}/S_{NH4}$ fed and $S_{NO2}/S_{NH4}$ produced.

![Figure 6. Influence of the inlet pH on the SHARON process performance at steady state.](image)

**CONCLUSIONS**

Partial nitritation process in a continuous and perfectly mixed reactor without sludge retention was evaluated by means of numerical simulation. For this purpose, default values were initially assigned to each parameter subjected to evaluation and subsequently modified assuming both, steady and transient states.

Ammonium oxidation to nitrite was proportional to the concentration of inorganic carbon in the wastewater. Nitrogen loading rate may influence differently the process depending on the considered variable. Thus, varying the hydraulic residence time the process became unstable at high NLR values due to free ammonia inhibition of ammonium oxidizing bacteria and, at low values because of the accumulation of nitrate as result of nitrite oxidizers growth. When modifying $S_{NH4}$, harmful effects were predicted only at high NLR. Besides, the usual low HRT linked to the reactor performance as a chemostat could easily result in the wash out of the active biomass if the process operation was not well managed. Low concentrations of biodegradable organic carbon interfered with nitritation, resulting in an increase of the nitrite to ammonium ratio on the effluent. Moreover, at sufficiently high concentrations of organic matter, a destabilization of the process, not related with a lack of dissolved oxygen, was predicted. Variations on the pH of the wastewater might also influence on the quality of the SHARON effluent. The reacting pH was affected by the tested parameters since no control for this variable was implemented.

In order to improve the SHARON reactor performance when treating wastewaters with a fluctuant composition, it should be necessary to consider some effective control strategy. The establishment of a dissolved oxygen set-point for aeration control has been shown as not sufficient. Simulation is a useful tool to predict the response of a SHARON reactor for partial nitritation purposes under different situations and, therefore, to improve the design of its operational strategy.
REFERENCES