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Treatment of a submerged anaerobic membrane bioreactor (SAnMBR) effluent by an activated sludge system: the role of sulphide and thiosulphate in the process.

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Abstract

This work studies the use of a well-known and spread activated sludge system (UCT configuration) to treat the effluent of a submerged anaerobic membrane bioreactor (SAnMBR) treating domestic wastewater. Ammonia, phosphate, dissolved methane and sulphide concentrations in the SAnMBR effluent were around 55 mg NH_4-N·L^{-1}, 7 mg PO_4-P·L^{-1}, 30 mg non-methane biodegradable COD·L^{-1}, and 105 mg S^{2-}·L^{-1} respectively. The results showed a nitrification inhibition caused by the presence of sulphur compounds at any of the solids retention time (SRT) studied (15, 20 and 25 days). This inhibition could be overcome increasing the hydraulic retention time (HRT) from 13 to 26 h. Among the sulphur compounds, sulphide was identified as the substance which caused the nitrification inhibition. When the nitrification was well established, removal rates of nitrogen and phosphorus of 56% and 45% were reached respectively. The sulphide present in the influent was completely oxidised to sulphate, contributing this oxidation to the denitrification process. Moreover, the presence of methanotrophic bacteria, detected by FISH technique, could also contribute to the

denitrification.

Keywords

Activated sludge; inhibition; submerged anaerobic membrane bioreactor; sulphide; thiosulphate

1 Introduction

Anaerobic treatments of domestic wastewater involve various advantages compared to conventional treatments. These advantages include the production of biogas, which allows energy recovery from the wastewater, and reduction in sludge generation. However, the effluent of anaerobic treatments (i.e., submerged anaerobic membrane bioreactors (SAnMBR) and upflow anaerobic sludge blanket (UASB) reactors) contains nitrogen and phosphorus concentrations similar to that found in the influent wastewater; low concentrations of biodegradable organic matter; and significant concentrations of sulphide and dissolved methane (Giménez et al., 2011; Khan et al., 2011; Foresti et al., 2006). Therefore, it is necessary a further treatment aiming at nutrient and dissolved gases removal.

The characteristics of these effluents make it suitable to be treated by an activated sludge system with biological nutrient removal. Nitrogen can be removed by nitrification and denitrification processes. In this latter process, the required electron donor can be a carbon source (volatile fatty acids, methane) or the sulphide present in the effluents of the anaerobic treatments (Fajardo et al., 2012). However, the sulphide concentration in the effluent of the anaerobic processes depends on the wastewater sulphate concentration which can notably vary considering the geographical location. Moreover, some studies (Sears et al., 2004; Erguder et al., 2008; Moraes et al., 2013)

mention the possible nitrifying bacteria inhibition in the presence of sulphide. Other studies (Takasaki et al., 2007; Juliette et al., 1993; Beristain-Cardoso et al., 2010) also mention that this inhibition may be caused by reduced sulphur components such as thiosulphate.

The phosphorus in the effluent can be removed by a biological process (EBPR) or by chemical precipitation. The EBPR is widely accepted as one of the most economical and sustainable processes. However, the low concentrations of biodegradable organic matter in the effluent of an anaerobic treatment could prevent high phosphorus removal efficiencies.

The dissolved methane is a very inexpensive carbon source and an effective greenhouse gas, being necessary their removal. Important dissolved methane concentrations can be found in the effluent of UASB and SAnMBR reactors, ranging from 20 to 40% of the methane in the biogas (Arceivala and Asalkar, 2007). According to the literature, it is possible to use methane as carbon source for denitrification in anoxic conditions (Islas-Lima et al., 2004) by methanotrophic bacteria.

This paper presents a study for the treatment of a SAnMBR effluent in order to eliminate nitrogen, phosphorus, sulphide and dissolved methane using a conventional activated sludge system with nutrient removal. Moreover, the paper presents the results obtained in off-line tests carried out to assess the nitrification inhibition in the presence of sulphur compounds (sulphide and thiosulphate).

2 Materials and methods

2.1 Pilot plant description

An activated sludge pilot plant located at the Carraixet WWTP (Valencia, Spain) has

been operated for two years. The results from a five months period are presented in this work. The activated sludge pilot plant consists of 800 L reactor (anaerobic 84 L, anoxic 332 L, and aerobic 384 L) and an 80 L secondary clarifier (Fig. 1). The pilot plant was operated under UCT configuration, treating the effluent of a SAnMBR which received domestic wastewater (Giménez et al., 2011). The anaerobic and the anoxic reactors were covered to minimize the superficial aeration and the loss of dissolved gases. On-line sensors and items of automatic equipment were installed in order to automate and control the pilot plant operations and gather on-line data about the state of the process. The on-line sensors consisted of: pH-Temperature, ORP, dissolved oxygen, suspended solids, ammonium and nitrate. The data acquisition and the pilot plant control were performed by a SCADA.

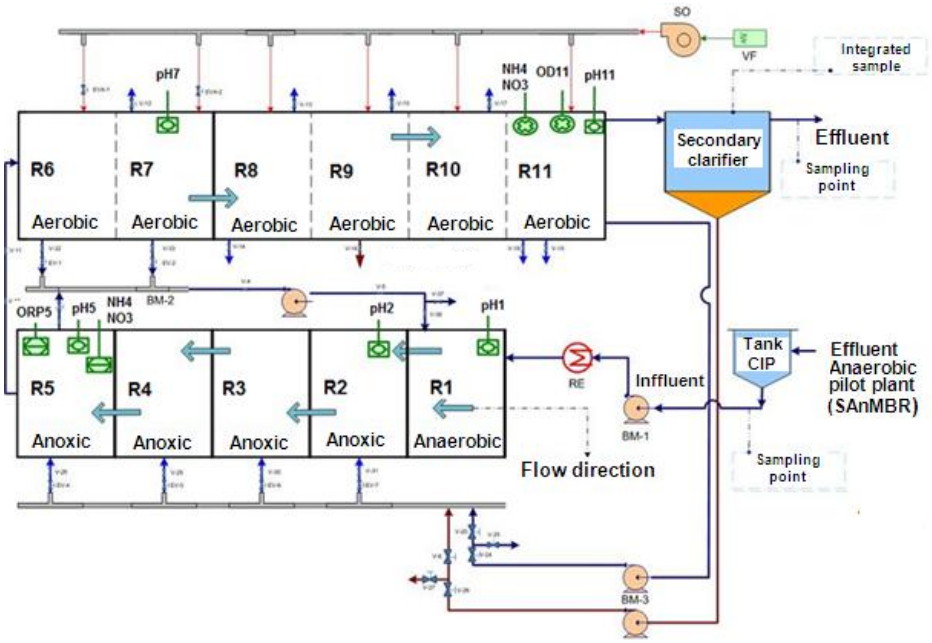

Fig. 1. Activated sludge pilot plant.

2.2 Off-line experiments

In order to assess the nitrification process during the experimental period, off-line batch experiments were carried out. The tests were developed using an automatic respirometry equipment BIOCALIBRA (Ribes et al., 2012). BIOCALIBRA device operation is based

on the application of respirometric techniques using continuous recording of dissolved oxygen concentration in a system. This registration of the dissolved oxygen in time allows to calculate the OUR (oxygen uptake rate). In function of the substrate availability, it is possible to calculate the endogenous OUR or the exogenous OUR. The exogenous OUR is obtained during the degradation of an external substrate (organic matter, ammonia nitrogen, inhibitor, etc.), allowing to obtain the activated sludge response after the addition of a certain amount of the substrate. The endogenous OUR is obtained during the absence of any kind of external substrate.

The impact of sulphide and thiosulphate on nitrifying bacteria was evaluated in a 7 L batch jacketed reactor using biomass from the pilot plant. After and endogenous period, around 36 mg NH_4-N·L^{-1} of ammonium were added to the reactor maintaining sulphide or thiosulphate concentrations about 3-5 mg S·L^{-1} and 10-12 mg S·L^{-1}, respectively. The addition of sulphide and thiosulphate to the reactor was performed with a stock solution of sodium sulphide ($Na_2S·9H_20$) and sodium thiosulphate ($Na_2S_2O_3·5H_20$), respectively. Both stock solutions were prepared at a concentration of 10 g·L^{-1}. The dissolved oxygen concentration was maintained between 1 and 2.5 mg·L^{-1}, and the temperature was controlled in 20ºC. In each experiment sulphide or thiosulphate was continuously added during 3 h under aerobic conditions to maintain the required concentrations. During the addition, the pH was adjusted between 7 at 8 with HCl in order to avoid any inhibition related to this parameter. Then, the sulphide or thiosulphate addition was stopped and the experiment was maintained until the initial ammonium concentration was depleted. During all the experiment, the concentration of ammonium, nitrite, nitrate, sulphide or thiosulphate and the OUR were measured.

2.3 Analytical methods

Influent, effluent, anaerobic, anoxic and aerobic reactor samples were analysed 3 times a week in order to evaluate the performance of the biological process. The parameters analysed were: total suspended solids, volatile suspended solids, volatile fatty acids, alkalinity, ammonium, phosphate, sulphide, thiosulphate and sulphate. Moreover, total and soluble chemical oxygen demand (COD), total nitrogen and dissolved methane were also determined once a week. Solids, COD, ammonium, phosphate and sulphide were determined according to Standard Methods (APHA, 2005). Sulphate and thiosulphate were measured by ion chromatography (761-Compact IC, Metrohm). Alkalinity and VFA concentrations were determined by titration according to the method proposed by Moosbruger et al., 1992. The dissolved methane in the influent stream was determined with the Henry law equation, measuring the methane concentration in the biogas produced in the SAnMBR using a gas analyser (X-Stream X2, Emerson). In addition, a sludge sample from the reactor was analysed once a week using the FISH technique to identify the different microorganism involved in the process (Amann et al., 1990). The same methods were used for the off-line experiments.

3 Results and discussion

The results reported in this paper were divided into two experimental periods, which mainly differ in the solids retention time (SRT) and the hydraulic retention time (HRT) used: Period A (SRT=25 d and HRT=13h) and period B (SRT=25, 20, 15 d and HRT=26h). The influent stream entering the activated sludge pilot plant showed a low

non-methane biodegradable COD (30 ± 8 mg $COD \cdot L^{-1}$), a high concentration of nutrients (55 ± 9 mg NH_4-$N \cdot L^{-1}$, 7 ± 2 mg PO_4-$P \cdot L^{-1}$), and sulphide (105 ± 10 mg $S^{-2} \cdot L^{-1}$) and a dissolved methane concentration around 43 ± 10 mg $COD \cdot L^{-1}$. After the start-up, the SRT and the HRT were set at 25 d and 13 h, respectively (Period A). In this period, the dissolved oxygen concentration in the aerobic zone was maintained at 1 mg $O_2 \cdot L^{-1}$ and the temperature varied between 18 and 21ºC. Under these operational conditions, a high level of nitrification should have been obtained. However, as Fig. 2 shows, during this period the nitrification process was poor (<37%), obtaining nitrogen and phosphorus removal efficiencies about 25% and 64%, respectively.

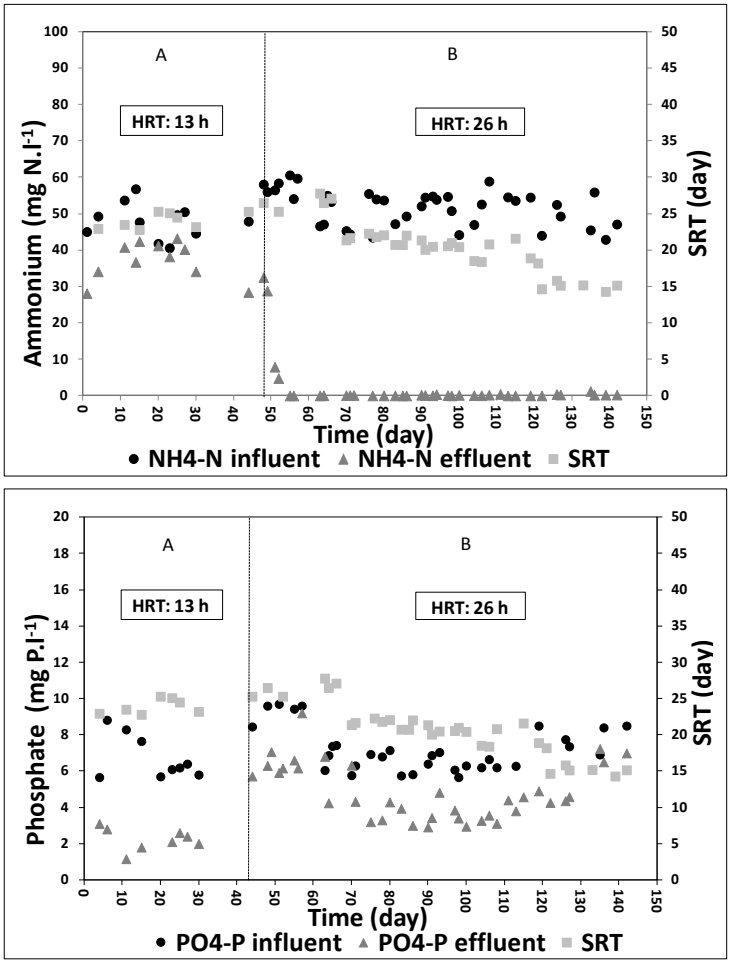

Fig. 2. Evolution of ammonium, phosphate and SRT in the activated sludge system (periods A and B).

3.1 Nitrification assessment

In order to assess the low nitrification observed in period A, two off-line respirometric batch experiments (Fig. 3 and Fig. 4) were carried out with the activated sludge of the pilot plant.

3.1.1 Experiment 1

Fig. 3 shows the evolution of the ~~oxygen uptake rate (~~OUR~~)~~ of the activated sludge grabbed from the aerobic reactor of the pilot plant, containing ca. 30 mg NH_4-N·L^{-1}. As can be seen, in stage I, the OUR increased reaching a maximum value after 0.32 d. From this point, the OUR decreased steeply until the ammonium was almost depleted (stage II). At the beginning of stage III, 30 mg NH_4-N·L^{-1} were added to determine anew the response of the nitrifying biomass. The system quickly reached a maximum OUR value (0.024 d) decreasing later meanwhile the ammonium was being consumed. The rate of ammonium consumption in stage I and III was 1.61 and 3.29 mg N·L^{-1} h^{-1} respectively, indicating that during stage I the ammonium oxidation was inhibited.

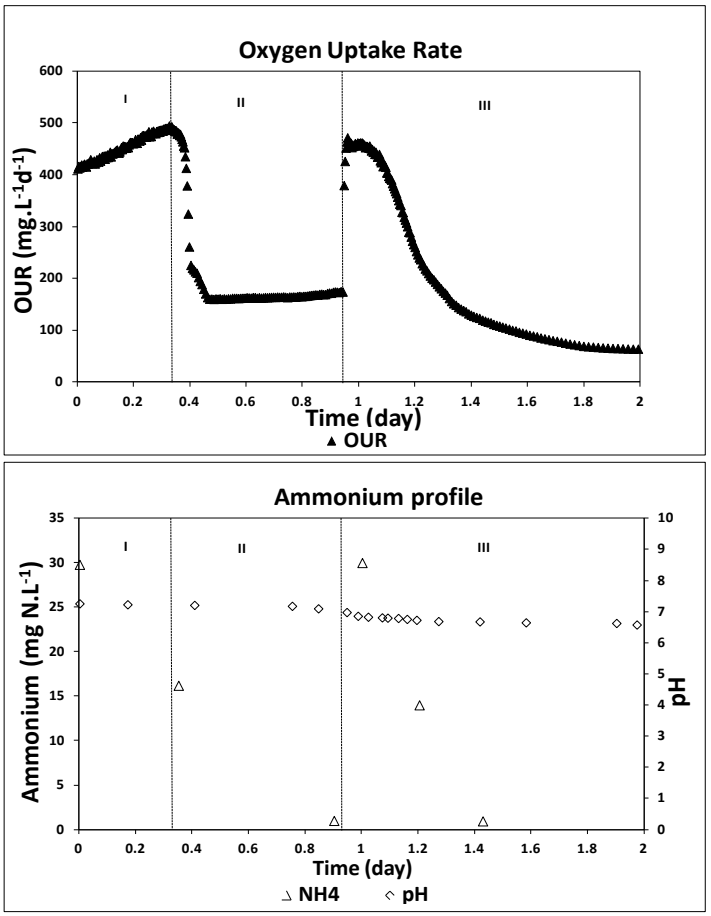

Fig. 3. Evolution of OUR and ammonium in the experiment 1.

3.1.2 Experiment 2

In order to validate experiment 1 and to obtain more detailed information about stages I and II, a second off-line respirometric batch experiment was performed with activated sludge grabbed from the aerobic reactor of the pilot plant, containing in this case ca. 40 mg NH_4-N·L^{-1} (Fig. 4). As in the first experiment, the sludge was maintained under aerobic conditions observing, as in experiment 1, a steep decrease in the OUR value when the ammonium was completely depleted (end of stage I, Fig. 4). In this second experiment the ammonium consumption rate in the stage I was 1.83 mg N·L^{-1} h^{-1}, a similar value to the one obtained in the first experiment. Fig. 4 shows that ammonium was oxidized to nitrite and nitrate in stage I. Then, in stage II, when ammonium had

been depleted, nitrite was oxidized to nitrate.

The results obtained in both experiments (1 and 2) point out that the inhibition of the nitrification observed in the pilot plant was maintained during the first hours of the experiment (stage I). Under the prolonged aerobic conditions kept in the batch reactor, the inhibition completely disappeared obtaining a complete nitrification (stage II). This inhibition can be attributed to the presence of sulphide or thiosulphate in the pilot plant which inhibits the nitrifying activity (Sears et al., 2004; Bejarano et al., 2012). Although during period A the influent sulphide was completely oxidised to sulphate throughout the pilot plant, sulphide concentrations around 7.6 mg $S \cdot L^{-1}$ were observed in the anaerobic reactor and thiosulphate concentrations around 5.8 and 2.5 mg $S \cdot L^{-1}$ were found in the anaerobic and in the anoxic reactor, respectively.

Moreover, the results show that nitrite-oxidizing bacteria are very sensitive to the presence of sulphur compounds causing nitrite accumulation. Nevertheless, this accumulation is not permanent since, once all the ammonium is consumed, nitrite is oxidized to nitrate (Fig. 4, stage II).

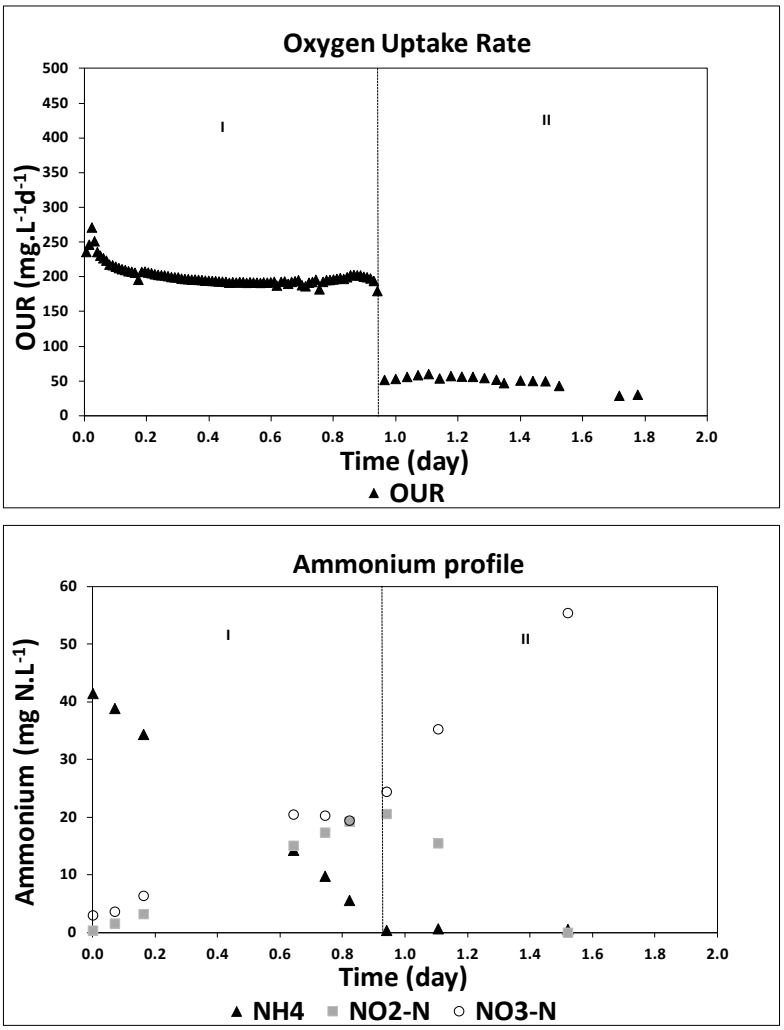

Fig.4. Evolution of OUR and ammonium in the experiment 2.

The batch experiments revealed that the HRT in the aerobic zone of the pilot plant seemed to be not enough to overcome the inhibition associated with the sulphur compounds. Once these sulphur compounds were completely oxidized to sulphate in the batch reactor, nitrification process was totally recovered. In order to enhance the nitrification process in the pilot plant, the HRT in the pilot plant was increased to 26 h during period B (Fig. 2). The SRT during this period was varied between 25 and 15 d, in order to observe the influence of this parameter on the process. The dissolved oxygen concentration was kept at 1 mg $O_2 \cdot L^{-1}$ and the temperature ranged from 18 to 21ºC. As can be observed in Fig. 2, during period B, the recovery of nitrification was observed

reaching a complete nitrification, at any of the SRT tested, (ammonium consumption rates around 5.61 mg $N \cdot L^{-1}$ h^{-1}) and an average nitrogen and phosphorus removal of 56% and 45%, respectively. Sulphide and thiosulphate were not observed in the anaerobic and anoxic reactors, in period B. During this second period, the influent biodegradable organic matter only covered about 30% of the COD required for the denitrification observed. Therefore, other pathways such as sulphide oxidation and methanotrophic denitrification should be considered when evaluating the denitrification process.

3.2 Effect of sulphide and thiosulphate on nitrification

In order to confirm if the nitrification inhibition observed was caused by the presence of sulphide and/or thiosulphate, two batch experiments were carried out using sludge from the aerobic zone of the pilot plant. Experiment 3 was carried out during period A when the nitrification was inhibited in the pilot plant and the ammonium concentration in the sludge was about 44 $mg \cdot L^{-1}$. Experiment 4 was carried out during period B when full nitrification was obtained in the pilot plant. As previously stated, the influent sulphide concentration was the same in both periods.

3.2.1 Experiment 3. Effect of sulphide on nitrification

In this experiment (Fig. 5), once the initial ammonium concentration was depleted and after an endogenous period, sulphide and ammonium were added to the reactor as detailed in chapter 2.2. In stage II (Fig. 5), ammonium depletion was not observed while sulphide was present. Once the sulphide addition was stopped, the ammonium depletion was observed (stage III). Although in this experiment the sulphide provoked a drastic inhibition of nitrification, this inhibition was reversible. The rate of ammonium

consumption in stage I and III was 2.72 mg $N \cdot L^{-1}$ h^{-1} and 1.35 mg $N \cdot L^{-1}$ h^{-1} respectively. The difference between both rate values indicates that, although the inhibition is reversible, the prolonged sulphide addition considerably affects the rate of ammonium consumption of the nitrifying organisms.

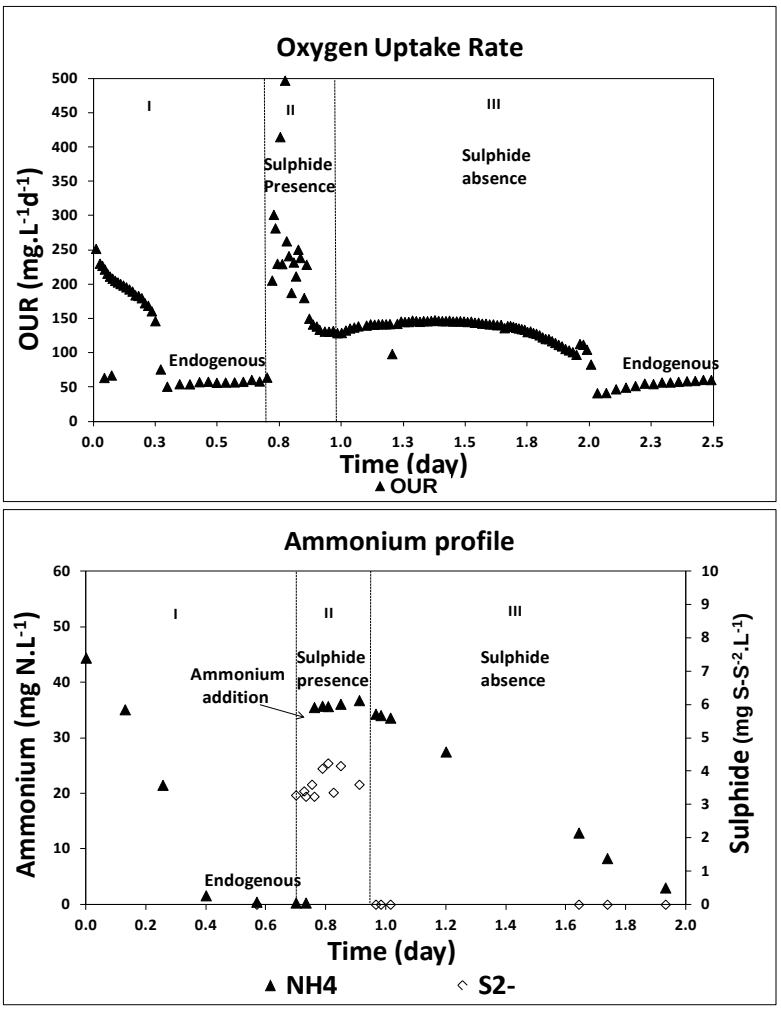

Fig. 5. Evolution of OUR and ammonium in the experiment 3 (sulphide addition).

3.2.2 Experiment 4. Effect of thiosulphate on nitrification

In this experiment, after a first endogenous period, ammonium was added to the reactor (Fig. 6, stage II) in order to observe the activity of the nitrifying biomass. Then, after a second endogenous period, thiosulphate and ammonium were added (Fig. 6, stage III) to the reactor as detailed in chapter 2.2. During stage III, the ammonium depletion was

observed immediately when the thiosulphate addition was performed (Fig. 6, stage III). The rate of ammonium consumption in stage II and III was 5.84 mg $N \cdot L^{-1}$ h^{-1} and 6.19 mg $N \cdot L^{-1}$ h^{-1} respectively, indicating that the inhibition is not observed when thiosulphate is added. The OUR behaviour was the same before and after the thiosulphate addition (stage II-III). These experiments demonstrated that the thiosulphate did not provoke a nitrification inhibition.

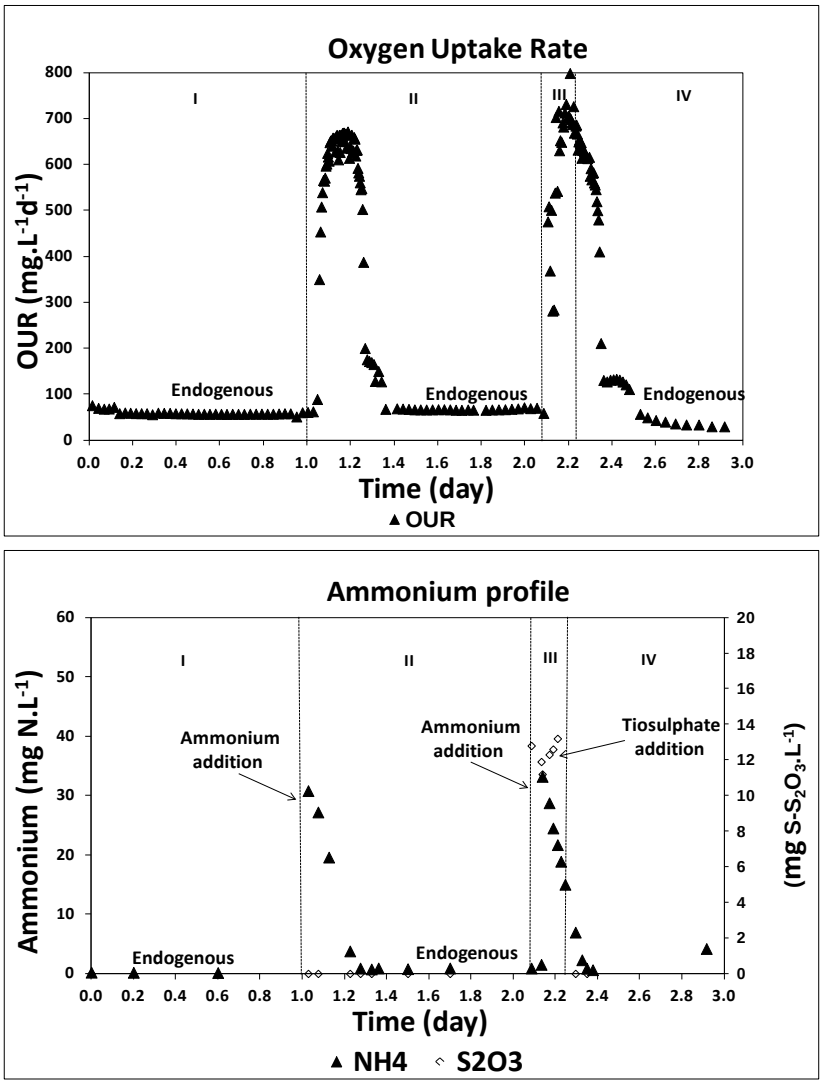

Fig. 6. Evolution of OUR and ammonium in the experiment 4 (thiosulphate addition).

3.3 Microbiological analysis

The abundance of the different groups of microorganisms taking part in the process was determined by the FISH technique. The microbiological study carried out during period A showed the presence of ammonia-oxidizing *Betaproteobacterial* (AOB) (8 ± 1 %), nitrite-oxidizing bacteria *Nitrospirae* (NOB) (6 ± 2 %), denitrificans bacteria *Azoarcus-Thauera-Castellaniella* (3 ± 1 %), polyphosphate accumulating organisms *Accumulibacter phosphatis* (PAOs) (5 ± 2 %) and *type I* and *type II* methanotrophic organisms (11 ± 3 % and 4 ± 3 %, respectively). During period B, an increase in AOB, NOB and, to a lesser extent, in methanotrophic bacteria was observed: *AOB* (16 ± 2 %), NOB (12 ± 1%) and methanotrophic (13 ± 2 %, *type I* and 4 ± 1 % *type II*). Moreover, denitrificans bacteria (4 ± 1 %) and PAOs (3 ± 1 %) were observed.

The FISH analysis corroborates the results observed in both periods. The enhancement of the nitrification process in Period B was confirmed with the increase in the AOB and NOB, which duplicated their abundance. The decay in the phosphorus removal in Period B is in accordance with the decrease in the PAOs abundance. Moreover, methanotrophic bacteria, mainly Type I, were found in both periods, indicating that the influent methane was being biodegraded.

4 Conclusions

The treatment of SAnMBR effluent with a high sulphide concentration by means of an activated sludge system showed an inhibition of the nitrification process when the HRT was 13 h. The low nitrification observed at this HRT was attributed to the inhibition of the nitrifying biomass in the presence of sulphur compounds. This inhibition disappeared when the HRT was increased up to 26 h. The results indicated that full

nitrification and nitrogen and phosphorus removal efficiencies of 56 % and 45%, respectively, were obtained at this high HRT. Thus, the HRT in the activated sludge system has a high influence on the nitrification process when the concentration of sulphur compounds in the influent stream is high. Furthermore, the results pointed out that sulphide oxidation and methanotrophic denitrification take part in the nitrogen removal because of the low COD available in the SAnMBR effluent.

The nitrification inhibition process observed in the pilot plant was evaluated in batch experiments which showed that sulphide is the substance which causes the nitrifying biomass activity decay. Moreover, it was observed that the presence of thiosulphate did not provoke nitrification failure.

Based on the obtained results, it can be concluded that it is possible to use an activated sludge system (UCT configuration) to treat domestic effluents from anaerobic reactors (SAnMBR or UASB systems).

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