THE ANAMMOX PROCESS AS THE SECOND STEP FOR THE TREATMENT OF AMMONIUM RICH REFINERY WASTEWATER WITH HIGH C_{org}/N RATIO

MILIA S.[1], PERRA M.[2], TOCCO G.[2] and CARUCCI A.[2,1]

[1] IGAG-CNR, via Marengo 2, 09123 Cagliari, Italy
[2] University of Cagliari (DICAAR), via Marengo 2, 09123 Cagliari, Italy
E-mail: smilia@unica.it

ABSTRACT

The combination of partial nitritation and anammox (anaerobic ammonium oxidation) has been mainly applied to the treatment of wastewaters with high ammonium concentration and low content of biodegradable organic carbon. So far, only few studies have focused on the application of partial nitritation-anammox process to the treatment of ammonium-rich wastewaters characterized also by a high organic carbon to nitrogen ratio (C_{org}/N), as well as by the presence of toxic substances: in this study, an anammox reactor was started-up and fed with the effluent from a partial nitritation reactor treating IGCC (Integrated Gasification Combined Cycle) wastewater, in order to evaluate its feasibility as an alternative to the currently applied chemical-physical-biological treatment.

A sequencing batch reactor was inoculated with granular anammox biomass and run at controlled temperature (35±0.5 °C) and pH (7.7±0.3). The synthetic influent containing NH_4-N (up to 250 mg/L) and NO_2-N (up to 330 mg/L) was progressively replaced by the IGCC wastewater, which had been pre-treated in the lab-scale partial nitritation reactor. When the reactor was fed with the synthetic medium at the target nitrogen loading rate (NLR, 0.350 $g_N/L \cdot d$), the observed NH_4-N removal efficiency was 93±5%, and no nitrite was detected in the effluent. Good overall process performance was maintained as increasing amounts (up to 65%) of the effluent from the partial nitritation system were fed to the anammox reactor: NH_4-N and NO_2-N removal efficiencies were 98.9±1.0% and 96.6±2.1%, respectively, and nitrite specific removal rate peaked at 0.28 $g_{NO2\text{-}N}/g_{VSS} \cdot d$. On day 154, a nitrogen shock load was applied to evaluate anammox stability during start-up: despite system sensitivity to the sudden increase of nitrogen load, process performance was recovered and the percentage of IGCC wastewater in the influent could be raised to 100% with fairly good NH_4-N and NO_2-N removal efficiencies (85.7±5.8% and 88.2±2.3%, respectively). Anammox granules were compact (diameter, 636±20 μm) and dense (86.5±3.4 g_{TSS}/L_{gran}), with good settling properties. The total organic carbon (TOC) removal efficiency was low: since most of TOC (around 80±8%) had been removed in the preliminary partial nitritation step (results not shown), it can be assumed that the residual TOC entering the anammox reactor was slowly biodegradable, therefore heterotrophic denitrifiers did not compete with anammox biomass for nitrite.

The results indicate that anammox start-up can be successfully achieved and the process can be applied in combination with a preliminary partial nitritation step for the treatment of ammonium-rich IGCC wastewater, thus providing useful information also for the treatment of similar wastewaters with high C_{org}/N ratio and containing toxic substances.

Keywords: ammonium, anammox, autotrophic nitrogen removal, industrial wastewater, organic carbon.

1. Introduction

The combination of a partial nitritation step (SHARON, Single reactor for High activity Ammonium Removal Over Nitrite) followed by anaerobic ammonium oxidation (anammox) represents a reliable, cost-effective and energetically efficient alternative for the treatment of ammonium-rich wastewaters with a low organic carbon to nitrogen ratio (C_{org}/N) (Jenni *et al.*, 2014). On the other hand, if the ammonium-rich wastewater is characterized also by a high C_{org}/N ratio, the SHARON-anammox process may lack in terms of nitrogen and organic matter removal: Mosquera-Corral *et al.* (2005) observed a 10% inhibition of ammonia oxidizing bacteria (AOB) activity when 0.3 g_C/g_N was fed to a partial nitritation reactor, likely due to a decreasing affinity of AOB for ammonia. As for the subsequent treatment step (anammox), the presence of significant amounts of readily degradable organic substrate fosters the development of heterotrophic denitrifiers, since anammox bacteria are not able to compete for nitrite due to their lower growth rate (Van Hulle *et al.*, 2010).

So far, only few studies have focused on the application of the partial nitritation-anammox process to the treatment of ammonium-rich wastewaters characterized also by a high readily organic carbon to nitrogen ratio and by the presence of toxic substances: Milia *et al.* (2014) investigated the feasibility of the SHARON process as the preliminary treatment of refinery wastewater produced by the Integrated Gasification Combined Cycle (IGCC) and characterized by a C_{org}/N ratio up to 1.1 (due to the presence of readily degradable formates), as well as by the presence of cyanides and phenols. Based on those results, a granular anammox reactor was started-up in this study and fed with the effluent from the SHARON reactor treating IGCC wastewater, in order to evaluate its feasibility as the final treatment step in the double stage SHARON-anammox process: reactor performance was investigated in terms of nitrogen removal rate (NRR, i.e. the amount of NH_4-N and NO_2-N removed per litre of reactor per day), nitrite discharge rate (NitDR, i.e. the amount of NO_2-N discharged per litre of reactor per day), total organic carbon (TOC) removal efficiency, granules physical and morphological properties, overall effluent quality. A comprehensive set of information was gathered, which can be also useful for the treatment of similar wastewaters characterized by a high C_{org}/N ratio, as well as by the presence of toxic substances.

2. Materials and methods

2.1. Reactor set-up and operation

A sequencing batch reactor (working volume, 2 litres) was inoculated with anammox granular biomass drawn from Dockhaven (NL) wastewater treatment plant, and run at controlled temperature (35±0.5 °C) and pH (7.7±0.3). The 8-hour cycle configuration consisted of 200-400 min mixed feeding, 70-270 min mixing, 5 min settling and 5 min effluent withdrawal. Mechanical mixing during both feeding and reaction phase was provided by a marine impeller (110±5 rpm). The final volumetric exchange ratio (i.e., the ratio between the influent volume and the total working volume) was 0.2, and the corresponding hydraulic retention time (HRT) was 40 hours.

2.2. Influent composition

A synthetic influent containing NH_4-N (up to 250 mg/L) and NO_2-N (up to 330 mg/L) was initially fed to the anammox reactor, in order to promote biomass acclimation in strictly controlled conditions. To simulate physiological variations of the real influent, the NO_2-N/NH_4-N molar ratio was allowed to fluctuate in the range 1.07-1.67 (optimal value for anammox is 1.32). The effluent of the lab-scale SHARON reactor treating real IGCC wastewater was progressively added to the synthetic medium, following an exponential law. IGCC wastewater and SHARON effluent characteristics are summarized in Table 1.

Table 1: Main characteristics of IGCC wastewater and SHARON effluent.

Type	NH_4-N mg/L	TOC mg/L	C_{org}/N	Formates mg/L	Cyanides mg/L	Phenols mg/L
IGCC	526±85	487±71	up to 1.1	1498±100	10.4±1	1.2±0.8
SHARON effl.	272±70	101±40	0.18±0.05	< 10	< 0.1	n.d.

n.d.: not detected

2.3. Analytical methods

Ammonium (as NH_4-N), NO_2-N, NO_3-N and TOC concentrations in reactor influent and effluent were determined as previously described in Milia *et al.* (2014), and analyses were performed in triplicate. Total suspended solids (TSS), Cyanides, phenols and alkalinity were determined according to Standard Methods (2005), while formates were determined using a DIONEX ICS-90 chromatograph equipped with an AS14A Ion-PAC 5μm column. Liquid samples were taken at fixed intervals during the mixed reaction phase and specific removal rates for NO_2-N were calculated as the ratio between the removal rates (determined from the slope of each concentration profile) and biomass concentration in the reactor. Granule density was determined by dextran blue method. Image Analysis (IA) was performed on representative granules samples: each sample (60 mL) was put into a Petri dish on a light background, and pictures were taken in b/w mode via a high resolution digital camera placed onto a horizontal holder. Image-Pro Plus v.6 was used to determine granule size (*mean diameter*, calculated as the average length of diameters measured at 2 degree intervals and passing through granule centroid).

3. Results and discussion

3.1 Nitrogen and organic matter removal

As the nitrogen loading rate (NLR) in the synthetic medium was progressively increased from 0.13 to 0.35 $g_N/L \cdot d$ (days 0-55), process performance was good in terms of nitrogen removal: as shown in Figure 1a, the NRR got progressively closer to the applied NLR, and the NitDR was always negligible. The same trend was observed when the synthetic medium was replaced by increasing amounts of real effluent from the SHARON reactor (from day 56), indicating stable process performance and good biomass acclimation.

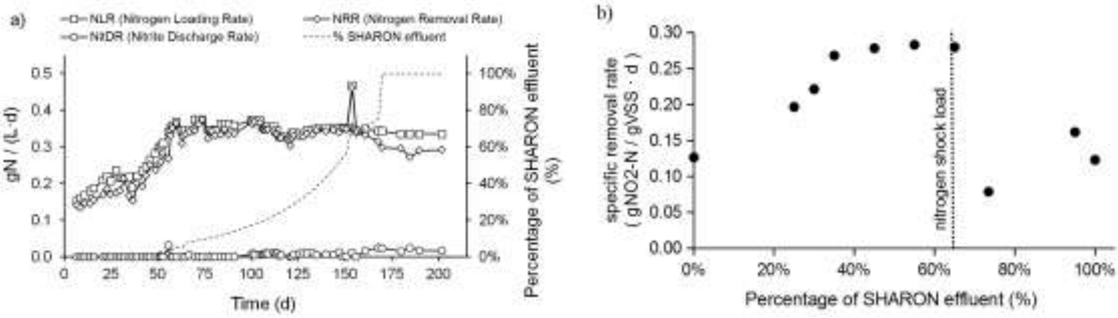

Figure 1: (a) profiles of NLR, NRR and NitDR; (b) NO_2-N specific removal rates.

On day 154, a nitrogen shock load was applied in order to evaluate anammox stability: although no negative effects on process performance were observed immediately after the sudden increase of the applied NLR (from 0.35 to 0.47 $g_N/L \cdot d$), a slight decrease of the NRR was observed from day 160, together with a corresponding increase of the NitDR (Figure 1a). Such behaviour clearly indicated a delayed response of anammox biomass to external stressful events: in particular, process performance could be restored only partially, since NRR and NitDR stabilized from day 170 till the end of the experimental activity, but they did not get back to the values observed before the nitrogen shock load. Correspondingly, the NH_4-N and NO_2-N removal efficiencies observed before and after the nitrogen shock load changed from 98.9±1.0% and 96.6±2.1% to 85.7±5.8% and 88.2±2.3%, respectively. If also nitrate is considered for calculations, the nitrogen removal efficiency (NRE) before and after the nitrogen shock load was 86±4% and 72±3%, respectively: both values are comparable with those determined by Dapena-Mora *et al.* (2004a,b) in a SBR treating synthetic wastewater (78% and 82% at NLR of 0.1-0.7 and 1.4 $g_N/L \cdot d$, respectively). Also the maximum nitrite specific removal rate was affected by the sudden increase of NLR: before the shock load, it was stable at 0.28 $g_{NO2\text{-}N}/g_{VSS} \cdot d$, and dropped to 0.12 $g_{NO2\text{-}N}/g_{VSS} \cdot d$ in the following weeks (Figure 1b). The maximum nitrite removal rates were comparable with those determined by Puyol *et al.* (2013) using biomass drawn from an expanded bed reactor (0.30 $g_{NO2\text{-}N}/g_{VSS} \cdot d$) and a membrane bioreactor (0.29 $g_{NO2\text{-}N}/g_{VSS}\cdot d$) fed with synthetic wastewater at NLR of 3.36 and 0.35 $g_N/L\cdot d$, respectively. If total nitrogen is considered, the removal rates observed in this study (0.49 $g_{Ntot}/g_{VSS}\cdot d$) were comparable with those obtained by Dapena-Mora *et al.* (2004a), i.e. 0.5 $g_{Ntot}/g_{VSS}\cdot d$. Nitrate production due to anammox activity stabilized at 0.22±0.05 $g_{NO3\text{-}N}/g_{NH4\text{-}N}$, in agreement with the stoichiometric values of 0.26 and 0.16 $g_{NO3\text{-}N}/g_{NH4\text{-}N}$ proposed by Strous *et al.* (1998) and Lotti *et al.* (2014), respectively.

As the amount of real pre-treated wastewater in the influent was increased, no significant heterotrophic denitrification could be observed (TOC removal was always lower than 4%), so no competition between anammox bacteria and heterotrophic denitrifiers occurred: Ruscalleda *et al.* (2008) reported that anammox activity is not hindered by denitrifiers when wastewater contains slowly biodegradable organic substrate. In the present study, the organic matter actually available for denitrification was probably low due to the high efficacy of the preliminary treatment step (SHARON), which removed most of the readily degradable formates (> 95%) and 80±8% of initial TOC (Milia *et al.*, 2014a). As for the removal of toxic substances, cyanides and phenols were not detected in the effluent.

3.2. Granules properties and overall effluent quality

Granules *mean diameter* did not change significantly throughout the experimental activity (636±20 μm). At a closer look, as the amount of real pre-treated wastewater in the influent was increased, the percentage of granules with a *mean diameter* ≤ 200 μm increased from 4.2% to 11.9%, the percentage of those in the range 300≤d≤600 μm consequently decreased from 49.9% to 39.8%, while the percentage of granules with a *mean diameter* > 600 μm did not change significantly (Figure 2).

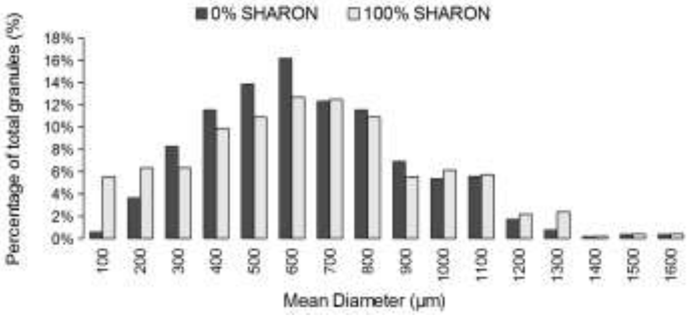

Figure 2: Granule size distribution on days 36 (0% SHARON) and 195 (100% SHARON).

The increasing amount of pre-treated wastewater in the influent had no significant effects on granule density, which was always high (86.5±3.4 g_{TSS}/L_{gran}). Due to such high density, anammox granules were easily retained in the reactor and TSS concentration in the effluent was always low (< 20 mg/L).

4. Conclusions

The feasibility of the anammox process as the final step for the treatment of ammonium-rich IGCC wastewater with high C_{org}/N ratio was assessed in this study. Results showed that reactor start-up can be successfully achieved by gradually increasing the amount of real wastewater in the influent. Even though the system was shown to be sensitive to nitrogen shock loads, process performance remained fairly good and comparable with other results reported in literature in terms of NRR, NitDR and NRE. In order to avoid any competition between anammox bacteria and heterotrophic denitrifiers, the preliminary partial nitritation step must guarantee a high removal of the organic matter, so that only slowly or not biodegradable carbon sources are left in the influent to the anammox reactor. The information achieved in this study for the treatment of IGCC wastewater is useful and can be extended also to the treatment of similar wastewaters characterized by a high C_{org}/N ratio and containing toxic substances. Further investigation of process performance in the long-term operation is needed.

ACKNOWLEDGMENTS

The Authors wish to thank Dr. Giulia Puggioni for her valuable help in reactor maintenance and laboratory activities.

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