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SHARON process as preliminary treatment of refinery wastewater with high organic carbon-to-nitrogen ratio

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ABSTRACT

In this study, a partial nitrification reactor (SHARON, Single reactor for High activity Ammonium Removal Over Nitrite) was used to treat ammonium-rich (up to 620 mg N/L) petrochemical wastewater produced by the integrated gasification combined cycle (IGCC) and characterized also by a high organic carbon-to-nitrogen ratio (C/N, up to 1.1 g_C/g_N). The reactor was initially fed with a synthetic influent containing only NH₄-N as substrate, then a preliminary acute toxicity test was used to assess the potential inhibiting effect of IGCC wastewater on SHARON biomass: the observed IC₁₀, IC₅₀, and IC₉₀ (14.9, 54.5, and 200 mL/L, respectively) suggested a prudential operating strategy based on the gradual replacement of the synthetic medium with the IGCC wastewater. As the synthetic influent was replaced by the IGCC wastewater, the resulting influent alkalinity-to-NH₄-N ratio (expressed as inorganic carbon-to-nitrogen molar ratio, C_{inorg}/N) influenced process performance in terms of NH₄-N removal efficiency. Despite the high influent C/N ratio, when the reactor was fed only with the IGCC wastewater, the ammonium removal efficiency was as high as 53 ± 10%, the corresponding effluent NO₂-N/NH₄-N ratio was 1.14 ± 0.42 and nitrate production was low. The presence of the organic substrate allowed the development of heterotrophic bacteria, as indicated by the high dissolved organic carbon removal efficiency (80 ± 8%) and the low effluent C/N ratio (0.20 ± 0.04). Such reactor performance made the effluent suitable for its subsequent treatment by anammox (ANAerobic AMMonium OXidation), providing useful information about the applicability of the SHARON process for the preliminary treatment of IGCC wastewater and similar ammonium-rich industrial wastewaters with high C/N ratio.

Keywords: Ammonia; Autotrophic nitrogen removal; Refinery wastewater; SHARON; Toxic compounds

1. Introduction

Compared to conventional biological processes based on nitrification and denitrification, the applica-

tion of partial nitrification (SHARON, Single reactor for High activity Ammonium Removal Over Nitrite) coupled with autotrophic anammox (ANAerobic AMMonium OXidation) represents a technical and cost-effective alternative technology [1] for the treatment of nitrogen-rich streams. This combined process

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was shown to be extremely efficient for the treatment of wastewaters characterized by high ammonium concentration and low content of readily degradable organic carbon (i.e. low C/N ratio) like sludge digester supernatant and landfill leachate [2–4], as long as the influent alkalinity-to-NH₄-N molar ratio (expressed as inorganic carbon-to-nitrogen molar ratio, C_{inorg}/N) was equal to 1.

In previous studies, the possibility to integrate a steam stripping unit with the SHARON-anammox or the SHARON-denitrification processes for the treatment of sour water containing toxic substances and characterized by high ammonium content (up to 2,000 mg N/L) and low organic carbon-to-nitrogen ratio (C/N, up to 0.15 g_C/g_N) was successfully investigated [5,6].

If the industrial wastewater containing toxic substances and high concentrations of ammonium is characterized also by a high content of readily degradable organic matter (i.e. a high C/N ratio), the SHARON-anammox process may lack in terms of nitrogen removal, since the activity of ammonium oxidizing bacteria (AOB) can be hindered in the first step of the process (SHARON) [7,8], and denitrification may take place in the second step rather than anaerobic ammonium oxidation (according to previous studies, anammox bacteria are not able to compete for nitrite with denitrifying bacteria in the presence of sufficiently high amounts of readily degradable organic carbon [9–12]).

However, the growth of heterotrophic denitrifiers is limited by the availability of readily degradable organic carbon sources; therefore, if most of the easily biodegradable organic carbon is oxidized in the previous partial nitrification step, the amount of organic matter actually available for denitrification will be low enough to avoid any competition between heterotrophic denitrifiers and autotrophic anammox bacteria: the coexistence of both microbial populations would lead to a low total nitrogen concentration in the effluent since part of the nitrate produced by the anammox process can be consumed by heterotrophic denitrification [13].

Within this framework, the possibility to apply the SHARON process for the treatment of refinery wastewater produced by the integrated gasification combined cycle (IGCC) and characterized by a high content of formate and ammonium, a high C/N ratio (up to 1.1), as well as by the presence of toxic substances like cyanides and phenols, was investigated in this study: in particular, a preliminary evaluation of the possibility to completely replace the steam stripping unit and trickling filter currently applied at full-scale with the SHARON-anammox process was carried out, in order to implement an advanced biological treatment with low environmental impact.

Since formate can be easily degraded under aerobic conditions and can be used as the electron donor for nitrate and nitrite reduction under anoxic conditions [14], its presence in the IGCC wastewater at high concentration may hinder both the partial nitrification and the anammox steps. Therefore, the efficacy of the SHARON process in reducing the content of the organic matter without compromising ammonium removal was investigated, in view of its coupling with anammox. Acute toxicity assessments were used as a predictive tool to determine the potential inhibiting effect of IGCC wastewater toward unacclimated biomass taken from the SHARON reactor, and results were used to choose the best operating strategy for reactor start-up. Process performance was monitored in terms of, among the others, ammonium and organic matter removal efficiency, nitrite production, and nitrate build-up. The results achieved in this study would provide useful preliminary information for the efficient pretreatment of similar industrial wastewaters by the SHARON process.

2. Materials and methods

2.1. Reactor setup

A continuous flow stirred tank reactor with a working volume of 2 L was operated as a chemostat (no biomass recirculation) at controlled temperature ($35 \pm 0.5^\circ\text{C}$), as described in Milia et al. [6]. The pH control range was set at 7.0 ± 0.2 . The hydraulic retention time (HRT) and the solids retention time (SRT) were kept at 1.25 d. The reactor was inoculated with activated sludge drawn from the municipal wastewater treatment plant of Cagliari, Italy (TSS, 3.9 g/L; VSS, 3 g/L).

2.2. Influent composition

In order to promote biomass acclimation to high N concentration, the reactor was initially fed with a synthetic medium, whose composition was NH₄-N 350 mg/L (as NH₄HCO₃), KH₂PO₄ 1,000 mg/L, MgSO₄ 100 mg/L, and trace elements solution 10 mL/L [5].

The IGCC wastewater (i.e. the process water used for the purification of syngas which is produced by the IGCC) was supplied by SARAS SpA refinery located in Sarroch (Italy): the IGCC uses a gasification system to convert fuel (i.e. heavy refining liquid residues) into a synthesis gas (syngas) and produce steam. The syngas contains, among the others, CO, H₂, CO₂, H₂S, CH₄, NH₃, organic acids (e.g. formic), ammonium formate, and cyanides, therefore it must

be purified before it can fuel a combustion turbine generator. The IGCC wastewater is currently treated at full scale by a combination of chemical, physical, and biological processes: in particular, a preliminary step is aimed at increasing water temperature and pH, then a steam stripping unit removes the ammonium before the wastewater can enter a trickling filter (where the organic matter is removed). The main characteristics of the IGCC wastewater are summarized in Table 1.

The IGCC wastewater was gradually added to the synthetic medium. For the whole study, the influent flow-rate was kept at 1.1 mL/min, with a corresponding volumetric nitrogen loading rate up to 0.5 g_N/L d. Depending on the amount of real IGCC wastewater dosed in the influent, the experimental activity can be divided as reported in Table 2, where SHARON influent characteristics are also indicated.

2.3. Analytical methods

Ammonium (as NH₄-N), COD, cyanides, phenols, and alkalinity were determined according to Standard Methods [15]; formate, nitrite (as NO₂-N), and nitrate (as NO₃-N) were determined by ion chromatography using a DIONEX ICS-90 chromatograph equipped with an AS14A Ion-PAC 5- μ m column; total organic carbon (TOC) and dissolved organic carbon (DOC) were measured using a TOC analyzer (SHIMADZU TOC-V CSN). Analyses were performed in triplicate. Free ammonia (FA) and free nitrous acid (FNA) concentrations were calculated as described in Anthonisen et al. [16].

A titrimetric biosensor (ANITA, Ammonium NITrification Analyzer) was used as described in Milia et al. [5] for the evaluation of the potential acute inhibiting effects of IGCC wastewater on AOB, by monitoring the amount of base added to neutralize

the acidity produced during the nitrification process in batch conditions. The pH-stat titration unit consisted of a 1 L thermostated (35°C) and stirred vessel, an aeration system, and an automatic titration system, including a pH meter, a dosing system to maintain the fluctuation of nitrifying sludge pH within ± 0.03 , and a data logging system. Tests were performed in triplicate on biomass drawn from the lab-scale SHARON reactor at the end of Phase I (the biomass used for the experiments was already acclimated to high ammonium concentrations, but not to the toxic substances contained in the IGCC wastewater): predetermined volumes of IGCC wastewater were progressively added to the mixed liquor, and the nitrification activity measured after each dosage was compared with the activity initially measured in the presence of only ammonium as substrate, which was taken as reference to calculate the inhibition (ammonium was provided by adding 25 mL of a stock solution containing 1 g/L NH₄Cl into the thermostated vessel). At the end of the experiment, nitrification was fully inhibited by allylthiourea (ATU) to detect the presence of interferences. To avoid any disturbance due to different alkalinity, the pH of both the IGCC wastewater and the stock solution was brought close to that of the nitrifying sample. The reduction of AOB activity (i.e. the inhibition) was plotted vs. the cumulated volume of IGCC dosed during the toxicity test per liter of mixed liquor (X , expressed as mL/L): the experimental data were interpolated using TableCurve 2D[®] (Systat Software Inc.) and the parameters of the inhibition curve (m , k) were determined. The volumes of IGCC wastewater per liter of mixed liquor that cause 10% (Inhibitory Concentration, IC10), 50% (IC50), and 90% (IC90) inhibition on AOB activity were calculated using the interpolating curve.

3. Results and discussion

In order to achieve biomass acclimation to high nitrogen concentration, the reactor was initially fed with a synthetic influent containing only NH₄-N (350 mg/L) as substrate and characterized by a C_{inorg}/N molar ratio of 1 (Phase I): NH₄-N removal efficiency rapidly increased up to 56% (day 16), as shown in Fig. 1, and the corresponding effluent NO₂-N/NH₄-N ratio was 1.27.

The successful selection of AOB was confirmed by the negligible NO₃-N build-up (the highest NO₃-N concentration in the effluent was 10 mg/L) and it was related, as expected, to the combined effects of the high process temperature (35°C) and the low applied HRT (1.25 d), as previously reported in literature

Table 1
Main characteristics of IGCC wastewater

Parameter (u.m.)	Value
NH ₄ -N (mg/L)	up to 620
pH (-)	10.8 \pm 0.3
Alkalinity (mg _{CaCO3} /L)	4,111 \pm 113
Formate (mg/L)	1,498 \pm 100
Cyanides (mg/L)	10.4 \pm 1
Phenols (mg/L)	1.2 \pm 0.8
TOC (mg/L)	444 \pm 99
DOC (mg/L)	424 \pm 94
DOC/TOC (-)	0.96 \pm 0.02
COD (mg/L)	584 \pm 129
TOC/COD	0.76 \pm 0.01

Table 2

Plan of the experimental activity, depending on the amount of real IGCC wastewater (w.w.) dosed in the influent

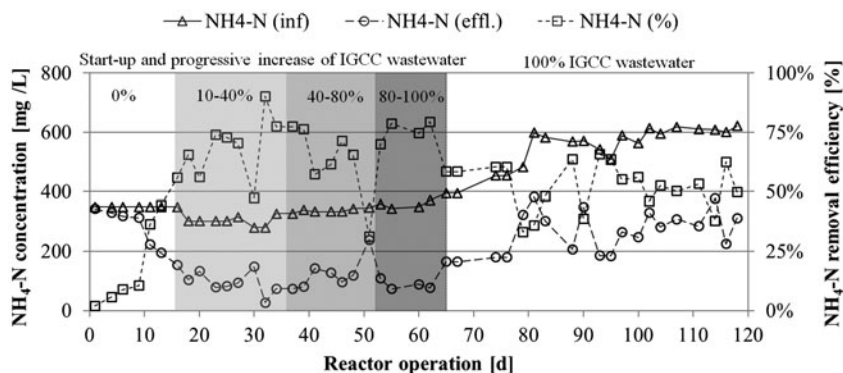
Phase (d)	IGCC w.w. (%)	NH ₄ -N conc. (mg/L)	NH ₄ -N load (g _N /L d)	DOC (mg/L)	Alkalinity (mg _{CaCO3} /L)	C _{inorg} /N (mol _C /mol _N)
I (0–16)	0	350	0.28	0	2,500	1.0 ± 0.01
II (17–36)	10–40	302 ± 16	0.24 ± 0.02	58 ± 7	2,607 ± 269	1.2 ± 0.08
III (37–52)	40–80	337 ± 7	0.27 ± 0.01	190 ± 42	3,512 ± 341	1.4 ± 0.09
IV (53–64)	80–100	351 ± 8	0.28 ± 0.01	323 ± 35	3,992 ± 224	1.5 ± 0.05
V (65–118)	100	0.43 ± 0.06	487 ± 71	4,150 ± 20	1.1 ± 0.17	

[8,17]. Also the high NH₄-N concentration played a role in the selection of AOB: depending on pH (7.0 ± 0.2) and temperature (35°C), the resulting FA concentration in the SHARON reactor was within the range 1.4–3.4 mg N/L, which is above the threshold concentration range of 0.08–0.82 mg N/L indicated by Anthonisen et al. [16] as inhibiting for nitrite oxidizing bacteria (NOB); since the resulting FNA concentration was within the range 0.02–0.04 mg N/L (below the threshold concentration range of 0.06–0.83 mg N/L which is considered inhibiting for NOB), FA rather than FNA contributed to AOB selection, although Hawkins et al. [18] proved that the actual role of FA in the selection of AOB is of less importance compared with other process parameters.

At the end of Phase I (day 16), an acute toxicity assessment was carried out in order to determine the proper operating strategy (i.e. how to replace the synthetic influent with the IGCC wastewater): in particular, it was used as a predictive tool to determine the potential inhibiting effect of IGCC wastewater toward biomass taken from the SHARON reactor (the reactor was fed with synthetic wastewater only, therefore biomass was already acclimated to high NH₄-N concentration, but not to the toxic compounds contained in the IGCC wastewater). As shown in Fig. 2, biomass was clearly inhibited by IGCC wastewater

(IC10, IC50, and IC90 were 14.9, 54.5, and 200 mL/L, corresponding to a share of IGCC wastewater in the daily influent of approximately 2, 7, and 25%, respectively); hence, the information gathered by toxicity assessment suggested a prudential operating strategy based on the gradual replacement of the synthetic influent with the IGCC wastewater, which was carried out in the subsequent Phases II, III, and IV.

A similar operating strategy was already proved to be successful for the treatment of ammonium-rich sour water characterized by a higher toxicity (the IC10, IC50, and IC90 were 3.6, 8.7, and 21.1 mL/L, respectively), as reported by Milia et al. [6]; in that study, toxicity tests were used also to assess the acclimation of biomass to the toxic substances contained in the wastewater. Although the toxicity of IGCC wastewater used in the present study was lower and the acclimation of biomass was taken for granted, the overall system response to the progressive replacement of the synthetic influent with the IGCC wastewater was investigated: as shown in Fig. 1, no significant detrimental effect was observed in terms of ammonium removal efficiency, which progressively increased from day 16 till day 64 (an average NH₄-N removal of 69 ± 13%, 68 ± 8%, and 76 ± 4% was achieved in Phases II, III, and IV, respectively), indicating that biomass could successfully withstand the increasing

Fig. 1. Trend of NH₄-N removal efficiency, influent and effluent NH₄-N concentration.

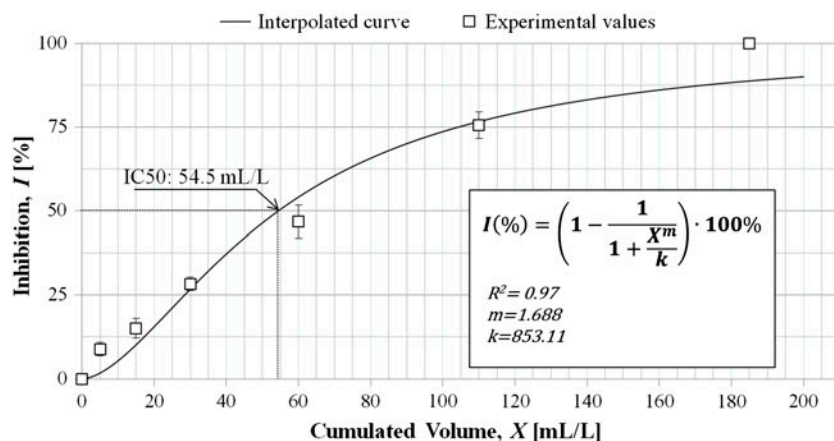


Fig. 2. Inhibition curve determined via acute toxicity assessment carried out on biomass drawn from the SHARON reactor on day 16 (m , k = curve parameters).

concentrations of toxic substances contained in the IGCC wastewater.

The increase of $\text{NH}_4\text{-N}$ removal efficiency was accompanied by a corresponding increase of effluent $\text{NO}_2\text{-N}$ concentration and $\text{NO}_2\text{-N}/\text{NH}_4\text{-N}$ ratio (mean values were 208 ± 40 mg/L and 2.40 ± 0.97 , 212 ± 51 mg/L and 2.06 ± 0.88 , 259 ± 19 mg/L and 2.85 ± 1.05 in Phases II, III, and IV, respectively), as shown in Fig. 3. Again, $\text{NO}_3\text{-N}$ build-up was low (the highest $\text{NO}_3\text{-N}$ concentration in the effluent was 20 mg/L), confirming that AOB overcame NOB successfully.

The effluent $\text{NO}_2\text{-N}/\text{NH}_4\text{-N}$ ratio in Phases II, III, and IV was higher than the optimal value required for the anammox process (i.e. 1.32). Such a high $\text{NH}_4\text{-N}$ conversion into $\text{NO}_2\text{-N}$ was related to the simultaneous presence in the influent of NH_4HCO_3 and the additional alkalinity provided by the IGCC wastewater, which resulted in a $C_{\text{inorg}}/\text{N}$ molar ratio higher than 1. According to nitrification stoichiometry, 2 mol of inorganic carbon are required for the conversion of

1 mol of ammonium into nitrite; therefore, if the influent $C_{\text{inorg}}/\text{N}$ molar ratio is equal to 1, half of influent ammonium is expected to be converted into nitrite. The role played by the $C_{\text{inorg}}/\text{N}$ molar ratio in regulating the $\text{NH}_4\text{-N}$ conversion into $\text{NO}_2\text{-N}$ is confirmed by the results shown in Fig. 4: the observed $\text{NH}_4\text{-N}$ removal efficiency was close to the expected value, changing coherently with the influent $C_{\text{inorg}}/\text{N}$ molar ratio.

Starting from day 30 (Phase II), the performance of the SHARON reactor was assessed also in terms of organic matter (DOC) removal. As shown in Fig. 5, DOC removal efficiency increased from day 30 (Phase II, 20%) to day 64 (end of Phase IV, 70%), as the amount of real IGCC wastewater (i.e. the organic load) in the semi-synthetic medium progressively increased.

When only the IGCC wastewater was fed to the SHARON reactor (from day 65, Phase V), a slight decrease of the observed $\text{NH}_4\text{-N}$ removal efficiency occurred ($52.5 \pm 9.9\%$), as shown in Fig. 1: as

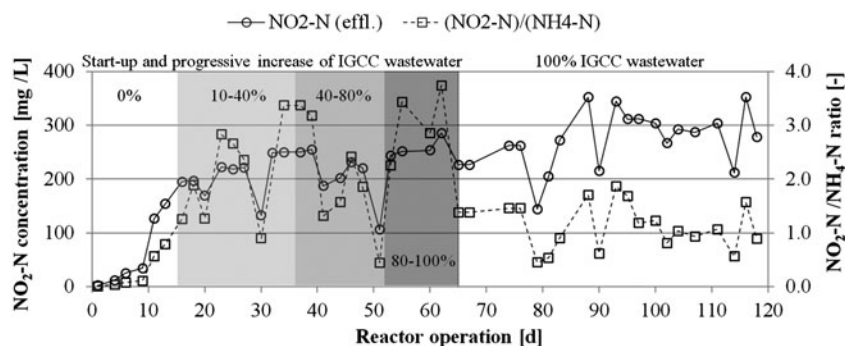


Fig. 3. Trend of effluent $\text{NO}_2\text{-N}$ concentration and $\text{NO}_2\text{-N}/\text{NH}_4\text{-N}$ ratio.

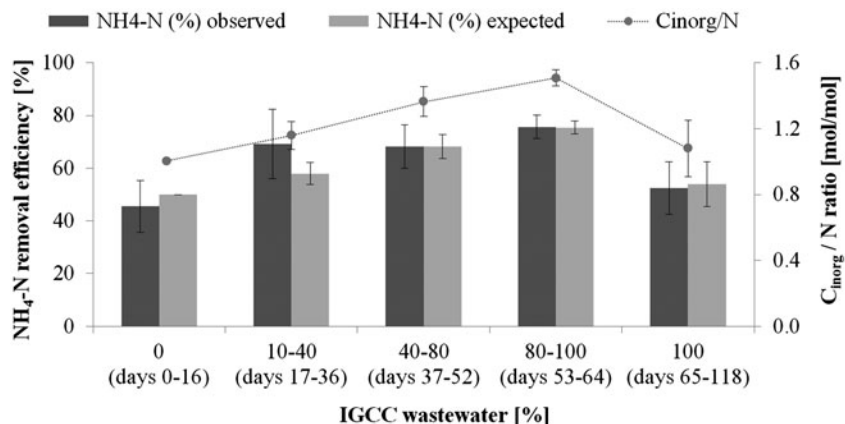


Fig. 4. Observed and expected NH₄-N removal efficiency related to the C_{inorg}/N molar ratio, resulting from the influent composition.

previously discussed for Phases II, III, and IV, the observed NH₄-N removal efficiency was again close to the expected value (Fig. 4), indicating that such behavior was due to the reduced C_{inorg}/N molar ratio rather than biomass inhibition. From the same day onward, the effluent NO₂-N/NH₄-N ratio correspondingly decreased to 1.14 ± 0.42 , close to the optimal value required for the anammox process (Fig. 3). As in the previous research Phases (days 0–64), nitrate build-up was found to be low (the highest NO₃-N concentration in the effluent was 30 mg/L) compared to nitrite, as shown in Fig. 6. Such process performance did not differ significantly in terms of ammonium conversion into nitrite from those previously reported in literature and concerning the treatment of reject water (i.e. the typical application of the SHARON process), despite the presence of toxic substances and the high influent C/N ratio: Fux et al. [19] obtained 60% NH₄-N removal and an effluent NO₂-N/NH₄-N ratio of 1.4 at 30°C with similar HRT (1.05 d), NH₄-N concentration

(619 ± 21 mg/L), NH₄-N loading rate (0.56 g_N/L d), and influent C_{inorg}/N molar ratio (1.2 ± 0.04); Van Dongen et al. [20] achieved 53% NH₄-N removal and an effluent NO₂-N/NH₄-N ratio of 1.09 in a SHARON reactor operated at higher NH₄-N concentration ($1,180 \pm 140$ mg/L) and loading rate (1.2 g_N/L d).

In the present study, the DOC removal efficiency observed during Phase V was high ($80 \pm 8\%$) and got stabilized from day 97 till the end of the experimental activity (steady state conditions, $89 \pm 1\%$, Fig. 5). In a previous study, a DOC removal efficiency of $65.2 \pm 1.0\%$ was achieved in a SHARON reactor treating sour water at high NH₄-N concentration (2,000 mg/L) and relatively low content of organic matter (DOC, 240 ± 92 mg/L) [5]: such lower DOC removal efficiency may depend also on the different characteristics of the organic matter, since readily degradable formate was not present in the sour water and concentration of toxic phenols was higher (up to 31 mg/L).

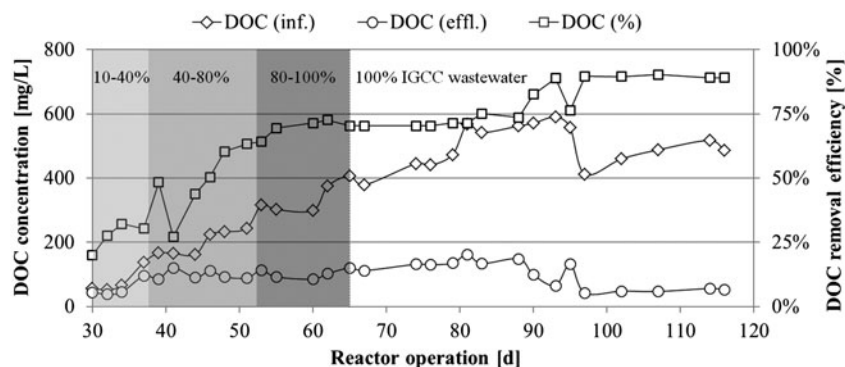


Fig. 5. Trend of DOC removal efficiency, influent and effluent DOC concentration.

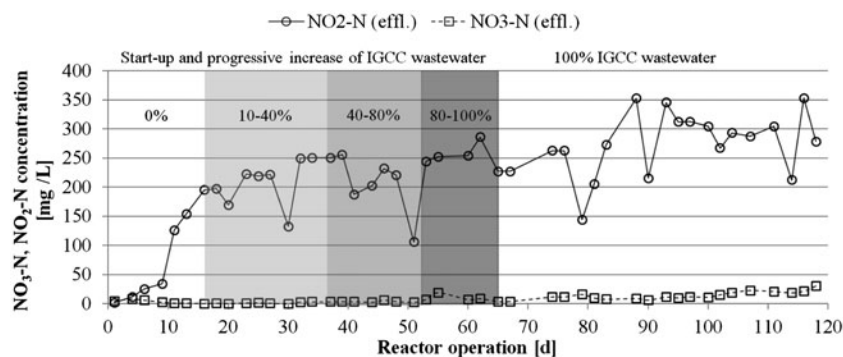


Fig. 6. Nitrate build-up and effluent nitrite concentration profile observed during the experimental activity.

In the present study, the high DOC removal efficiency suggested the development of heterotrophic bacteria in the SHARON reactor. The development of biomass in the system was indicated by the increase of VSS concentration (Table 3): since both influent DOC and $\text{NH}_4\text{-N}$ concentrations increased (especially in Phase V, Table 2), such higher VSS concentration should be ascribed to the combined development of both heterotrophic and autotrophic bacteria.

Despite the high C/N molar ratio and the high observed DOC removal efficiency due to heterotrophic biomass activity, process performance was not compromised in terms of ammonium removal. As previously reported in literature, an influent C/N ratio of 0.15 $\text{g}_\text{C}/\text{g}_\text{N}$ did not cause any negative effect on AOB activity [6]. On the other hand, influent C/N ratios above 0.3 $\text{g}_\text{C}/\text{g}_\text{N}$ caused a 10% loss of AOB activity in a sequencing batch reactor with a dissolved oxygen concentration above 2 mg/L [7]. Hanaki et al. [21] reported that the inhibitory effect due to the heterotrophic activity on nitrifiers was strengthened by low DO concentration (0.5 mg/L), since the transport of ammonia from the bulk water phase to the cells of the ammonia oxidizers could be hindered by the presence of the crowded cells of heterotrophs which assimilate the ammonia and consume the oxygen before it reaches the nitrifiers [8]. In this study, the dissolved oxygen concentration was always around 4 mg/L

(i.e. not limiting): this may be one of the reasons why an influent C/N ratio up to 1.1 did not cause any detrimental effect on partial nitrification process.

The effluent from the SHARON reactor was suitable for the subsequent treatment by the anammox process in terms of nitrogen load and, since the average C/N ratio measured from day 97 was $0.2 \pm 0.04 \text{ g}_\text{C}/\text{g}_\text{N}$, also in terms of organic load [8,22]: in particular, formate (which accounted for more than 80% of TOC) was almost completely removed (98%) during Phase V, hence most of the readily degradable organic matter was degraded in the partial nitrification step. Ruscalleda et al. [13] reported that the low degradability of the residual organic matter would limit the development of heterotrophic denitrifiers and the consequent competition with anammox bacteria. The combination of both processes (heterotrophic denitrification and anaerobic ammonium oxidation) would lead to a lower nitrogen concentration in the final effluent, since part of the nitrate produced by the anammox process will be consumed by heterotrophic denitrification: thus, the coexistence of these two processes becomes advantageous in terms of nitrogen discharge, with lower nitrate concentration in the effluent.

As for the toxic substances, cyanides were almost completely removed (99%) and phenols were not detected in the effluent, thus reducing the risk of inhibition in the subsequent anammox treatment step significantly.

Table 3
VSS concentration in the SHARON reactor

Phase	(%) IGCC wastewater	VSS (mg/L)
I	0	164 ± 34
II	10–40	155 ± 27
III	40–80	140 ± 13
IV	80–100	211 ± 39
V	100	284 ± 37

4. Conclusions

In this study, a SHARON reactor was used to treat ammonium-rich IGCC wastewater with high C/N ratio, in view of its coupling with the anammox process:

- (1) the preliminary evaluation of IGCC wastewater acute toxicity suggested to implement a

- prudential operating strategy based on the gradual replacement of the synthetic influent with the IGCC wastewater;
- (2) as the synthetic influent was gradually replaced by the IGCC wastewater, the resulting influent C_{inorg}/N molar ratio influenced process performance in terms of NH_4-N removal efficiency;
 - (3) based on the observed NH_4-N removal efficiency, no significant detrimental effect of the high organic carbon-to-nitrogen ratio (C/N) on process performance was observed;
 - (4) despite the high C/N ratio and the presence of toxic substances like cyanides and phenols, the SHARON reactor produced an effluent suitable for the subsequent treatment by anammox in terms of both nitrogen and organic load;
 - (5) these results are encouraging and provide useful preliminary information about the possibility to apply the SHARON process for the preliminary treatment of IGCC wastewater or other industrial wastewaters with similar characteristics;
 - (6) the possible application of the anammox process for the treatment of the effluent from the SHARON reactor is worthy of being investigated, since the combined SHARON-anammox process would represent an interesting alternative to chemical-physical-biological treatments, with potential considerable cost savings.

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