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Aerobic granulation with petrochemical wastewater in a sequencing batch reactor under different operating conditions

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ABSTRACT

The aim of this study was to define the best operating conditions for the successful start-up of a granular sludge sequencing batch reactor (GSBR) treating petrochemical wastewater (PW) produced by the integrated gasification combined cycle and characterized by high NH_4^+-N concentration (up to 630 mg/L). Two different start-up strategies were applied during Phases A and B, using different shear forces, inoculum source and pH. The GSBR was fed with a mixture of synthetic medium and real wastewater, and a readily degradable growth substrate (i.e. sodium acetate) was supplied in order to maintain the volumetric organic loading rate at 3 g COD/L d: the share of PW in the influent was gradually increased, depending on the observed reactor performance. In Phase A, aerobic granules irreversibly deteriorated when the share of PW in the influent was increased to 30%. Conversely, a faster and more stable granulation was observed during Phase B, likely due to the higher superficial gas velocity applied (i.e. harsher conditions) and the different sludge used as inoculum (already acclimated to toxic substances): under such conditions, the synthetic medium was completely replaced by the PW. The observed total organic carbon removal efficiencies were similar in Phases A and B (92 ± 6–94 ± 2%, respectively), while NH_4^+-N removal efficiency was higher during Phase B (up to 78% when PW% was 100%). The inoculum with acclimated sludge and the harsher selective pressure (Phase B) were proved to speed up the formation of compact and well settling granules, more resistant to the increase of PW share in the influent.

Keywords: Aerobic granular sludge; GSBR; Petrochemical wastewater; Selective pressure; Superficial air velocity; Inoculum

1. Introduction

Compared to conventional activated sludge systems, distinctive features of the aerobic granular sludge technology are the excellent sludge settleability, the coexistence of heterogeneous biomass able to perform the simultaneous removal of chemical oxygen demand (COD) and nutrients, the lower sludge production due to high biomass retention, the system

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compactness (no need for secondary clarifiers and up to 80% reduction in surface area requirements) and the 60% reduction in energy consumption [1].

For such reasons, the possible application of aerobic granular sludge to the treatment of synthetic [2,3], municipal [1] and industrial [4,5] wastewaters has been widely investigated: in particular, the resilience of aerobic granules to shock loadings and toxins due to the protection provided by a matrix of extracellular polymeric substances and by diffusive processes involved in granule-shaped biomass [6,7] led to promising results when treating different kinds of industrial wastewaters, including high-strength ones containing organics, nitrogen, phosphorus [8–11] and other toxic substances [12], thus encouraging the possible application of this technology to complex substrates [6,13,14].

Among industrial effluents, petrochemical wastewater (PW) is characterized by a highly variable composition [15–17], depending on the processes applied in different facilities worldwide. Due to the presence of toxic substances such as phenols and sulphides, PW is difficult to be effectively treated by conventional technologies based on biological processes [18]. Aerobic granular sludge was successfully applied to the treatment of PW with low ammonium concentration, in presence of an external readily degradable organic substrate for cometabolism, and with gradual biomass acclimation [18]: although the increase of PW share in the influent was gradual, both process performance (in terms of removal efficiency) and granules properties (in terms of settleability) got rapidly worse, and only the addition of a cometabolic substrate (i.e. sodium propionate) allowed the biomass to remain compact and ensure effective COD and nutrients removal.

Besides the effective removal of contaminants under steady-state conditions, the need for a faster and reliable start-up of granular sludge sequencing batch reactors (GSBR) treating complex wastewaters such as PW has become a crucial point, which can be achieved by properly setting the main operating parameters. In particular, during process start-up, some important factors have to be carefully taken into account in order to obtain a good and stable granulation: among the others, the settling time for the selection of fast settling granular aggregates [2], the shear stress for the formation of compact granules [19], the volumetric organic loading rate (vOLR) [4], the source of inoculum, the COD:N ratio [20]. Within this framework, the aim of this study was to investigate the effects of different operating strategies (i.e. the selection of sludge for the inoculum, the applied shear stress, the optimal pH) on the formation of aerobic granules in a GSBR treating PW produced by the integrated gasification combined cycle (IGCC) and characterized by high ammonium concentration (up to 630 mg N/L) and pH (up to 12), as well as by the presence of toxic substances such as cyanides and phenols. The evolution of granules physical and morphological properties, as well as process performance in terms of organic matter and ammonium removal efficiencies were monitored throughout the start-up phase. Moreover, acute toxicity assessments were carried out in order to evaluate the efficacy of the GSBR in reducing the toxicity of the influent. Besides the continuous operation of the GSBR, batch tests were carried out in order to determine the optimal cycle length and pH, which would maximize nitrogen removal. The results achieved in this study would provide useful information for the successful start-up of GSBRs treating similar industrial wastewaters.

2. Materials and methods

2.1. Reactor set-up and operation

A GSBR with a working volume of 3 l, an internal diameter of 11.3 cm and a working height of 30 cm was used to carry out the experiments at controlled temperature (25˚C) and pH. The reactor was operated in 4-h cycles, each cycle consisting of an impulse feeding of 5 min, 222–228.5-min aeration, 8–1.5-min settling and 5-min effluent withdrawal. Settling time was initially set to 8 min (corresponding to a minimal settling velocity of 1.1 m/h), in order to avoid sludge washout, and was gradually decreased to 1.5 min (corresponding to a minimal settling velocity of 6 m/h) as granulation occurred.

A membrane pump was used to provide air, which was introduced via a fine bubble aerator at the bottom of the reactor. Dissolved oxygen (DO) concentration was not controlled throughout the cycle. The volumetric exchange ratio (i.e. effluent volume/total working volume) was 0.5, and the resulting hydraulic retention time was 8 h. Solids retention time was monitored, but not controlled throughout the experimental activity.

Two different start-up strategies were applied and the experimental activity was divided accordingly into Phases A and B (Table 1).

2.2. Seed sludge

The GSBR was inoculated in Phase A with activated sludge taken from the aeration tank of the municipal wastewater treatment plant (WWTP) of Is Arenas, Cagliari, Italy (TSS 2.9 g/L, VSS 2.3 g/L); in

Table 1
Start-up operating conditions during Phases A and B

Operating conditions	Phase A	Phase B
Seed sludge	Domestic WWTP	Petrochemical WWTP
pH control range	7.0 ± 0.2	7.8 ± 0.2
Superficial gas velocity (cm/s)	2	3
Additional supplies	Acetate (COD), P, trace elements	Acetate (COD), P, trace elements[a]

[a] During Phase B, trace elements were progressively reduced as the share of PW in the influent was increased.

Phase B, the activated sludge was taken from the aeration tank of the petrochemical wastewater treatment plant (PWWTP) of Sarroch, Italy (TSS 2.8 g/L, VSS 2.7 g/L), where all the raw or pre-treated liquid streams produced by the different refining processes are collected and treated before final discharge. A proper amount of seed sludge was inoculated into the GSBR at the beginning of Phases A and B, in order to have an initial VSS concentration of 2.0 g/L.

2.3. Wastewater characteristics

The PW tested in this study was provided by SARAS SpA (Sarroch, Italy). It consisted of process water used for the purification of syngas which is produced by the IGCC. Such process water contains, among the others, ammonium, organic acids (e.g. formic), phenols and cyanides. A detailed characterization of PW is provided in Table 2. The PW is treated at full scale by a combination of chemical, physical and biological processes: a preliminary step is aimed at increasing water temperature and pH, and then a steam stripping unit removes the ammonium before the wastewater can enter a trickling filter for the removal of the organic matter. The effluent of the trickling filter is subsequently sent to the main WWTP.

The GSBR was fed with a mixture of synthetic and real PW. Depending on PW composition and share in the influent, proper amounts of sodium acetate (readily biodegradable organic substrate) and K_2HPO_4 were added in order to maintain a vOLR of 3 g COD/L d and an influent COD:P ratio of 100:2, respectively. The amount of real wastewater was increased gradually depending on the observed granulation and overall reactor performance, as summarized in Table 3. Influent COD:N ratio varied according to the real PW composition (which showed a certain variability, especially in terms of NH_4^+-N and COD content).

Table 2
Petrochemical wastewater characteristics

Parameters	Concentration
pH	10–12
NH_4^+-N (mg/L)	240–630
Cyanides (mg/L)	10–15
COD (mg/L)	340–610
TOC (mg/L)	260–490
Phenols (mg/L)	2.5
Formate (mg/L)	1,000-1,500
TSS (mg/L)	300–500

During Phase A, 4.5 mL/L of a stock solution containing trace elements were also added (the composition of the stock solution is reported in Table 4); during Phase B, considering full-scale application perspective, trace elements were progressively reduced as the share of PW in the influent was increased. In order to prevent changes in its physical and chemical characteristics, PW was stored in a refrigerator (4°C).

2.4. Analytical methods

Total suspended solids (TSS), volatile suspended solids (VSS), COD and NH_4^+-N were determined according to Standard Methods [21]. The total organic carbon (TOC) concentration was measured with a TOC analyser (SHIMADZU TOC-V CSN). The concentrations of NO_2^--N and NO_3^--N were determined by ion-chromatography on filtered samples (0.45 μm) using a DIONEX ICS-90 chromatograph equipped with an IonPAC AS14A-5 μm column (DIONEX). Samples were taken from the influent, effluent, at the end of the feeding (t_0) and during the reaction phase at fixed intervals. All samples were properly diluted with de-ionized water before analysis. Image Analysis was performed on representative granules samples taken at the end of the feeding, soon after completely mixed conditions were established: granules were put into a Petri dish on a dark background, and photographs were taken in b/w mode using a high-resolution digital camera placed onto a horizontal holder. ImagePro Plus (v.6) was used to determine granules diameter.

Table 3
Plan of the experimental activity, depending on PW share in the influent

Phase	Day	%PW	Settling time (min)	COD:N
A	1–67	10	8–4	100:11
	68–154	20	4–1.5	100:14–100:10
	155–230	30	1.5	100:12
B	1–10	10	8	100:4
	11–62	20	8–1.5	100:7
	63–97	30	1.5	100:11–100:7.4–100:8
	98–181	50	1.5	100:11–100:14–100:19
	182–203	75	1.5	100:43
	204–257	100	1.5	100:56–100:34–100:40

Table 4
Trace elements in the stock solution

Elements	Concentration (g/L)
EDTA	63.70
$ZnSO_4$·7H2O	22.00
$CaCl_2$	5.54
$MnCl_2 \cdot 4H_2O$	5.06
$FeSO_4 \cdot 7H_2O$	4.99
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1.10
$CuSO_4 \cdot 5H_2O$	1.57
$CoCl_2 \cdot 6H_2O$	1.51

2.5. Acute toxicity tests and nitrification batch experiments

A titrimetric biosensor (ANITA, Ammonium NITrification Analyser) was used to evaluate the acute inhibiting effects of PW on unacclimated sludge, as described in Ficara and Rozzi [22]: nitrification activity of a nitrifying sludge sample is measured in batch conditions by means of pH-stat titration, which exploits the stoichiometric relationship between ammonium oxidation and acidity production. First, the maximum ammonium-oxidizing capacity of nitrifying biomass is assessed in the presence of only ammonium as substrate and taken as reference. Subsequently, increasing volumes of PW are spiked at regular intervals into the sludge sample while its nitrifying activity is continuously monitored. For each dosage of PW, the resulting nitrifying activity is compared with the reference and the corresponding inhibition is calculated. At the end of the experiment, nitrification is fully inhibited by allylthiourea (ATU) to detect the presence of interferences. Table Curve 2D© (Systat Software Inc.) was used to determine and plot the inhibition curves, which were used to calculate the specific inhibitory concentrations (sIC), i.e. the amounts of PW per gram of VSS that causes 10 (sIC10), 50 (sIC50) and 90% (sIC90) acute inhibition on sludge activity. Tests were performed in triplicate using unacclimated sludge drawn from the municipal WWTP of Is Arenas, Cagliari. The same assessments were carried out also using the GSBR effluent, in order to evaluate the residual acute toxicity after the treatment.

As to the nitrification batch experiments, 4- and 6-h tests were performed in PVC reactors with a working volume of 250 mL (internal diameter of 5 cm and working height of 12.7 cm). Tests were run at PW % of 30, 50, 75 and 100. For each test, 125 ml of mixed liquor was taken from the GSBR, and granules were washed with demi-water. Batch reactors were filled with 125 ml of granules suspended in demi-water and 125 ml of PW (properly diluted). Average VSS concentration in the PVC reactors was 0.54 ± 0.05 g/L, vOLR was kept at 0.12 g COD/L d (NaAc was added if needed) and the corresponding specific OLR was 0.22 g COD/g VSS d, the same as in the GSBR. The resulting initial NH_4^+-N concentration varied with the increment in PW%.

3. Results and discussion

3.1. Formation and characteristics of aerobic granules

Since settling time significantly influences the granulation process, favouring granule formation when shortened [2], a settling time of 8 min was initially adopted in this study and gradually decreased to 1.5 min (the corresponding minimum settling velocity was increased from 1.1 to 6 m/h). During Phase A, after achieving granule stabilization, PW share was increased to 20% (day 68): although an increase in granule size was observed (Fig. 1), it was accompanied by filamentous outgrowths on the surface (Fig. 2(a)).

As the settling time was progressively reduced to 1.5 min (day 108), thus increasing the selective pressure, compact aerobic granules started to form and became progressively dominant in the system, replacing most of filamentous aggregates (Fig. 2(b)). The subsequent increase in PW share to 30% on day 155 coincided with the supply of a new stock of wastewater, different from the previous ones in colour (from "transparent" to "black"), COD (370 mg/L) and NH_4^+-N (310 mg/L) concentrations: aerobic granules increased in size, but became loose and fluffy, due to the development of filamentous bacteria which worsened sludge settleability (the observed average SVI_8 was 184 mL/gTSS), as testified by the subsequent washout of granular biomass and the increasing trend of effluent TSS concentration (Fig. 3(a)). Similar negative effects due to the qualitative variation of the industrial wastewater were reported by Inizan et al. [4], who observed the development of filamentous bacteria and a consequent rapid washout of biomass: in that case, the formation of new granules could be only achieved by increasing the amount of phosphorus dosed in the influent (from 1/500 to 1/100 mgP/mg COD), likely due to the formation of phosphorus precipitates which acted as seeding points for aerobic granules formation. In this study, a further increase in phosphorus supply was not contemplated due to the consequent increase in the operating costs; therefore, the granulation process was considered irreversibly inhibited and Phase A was interrupted (day 230).

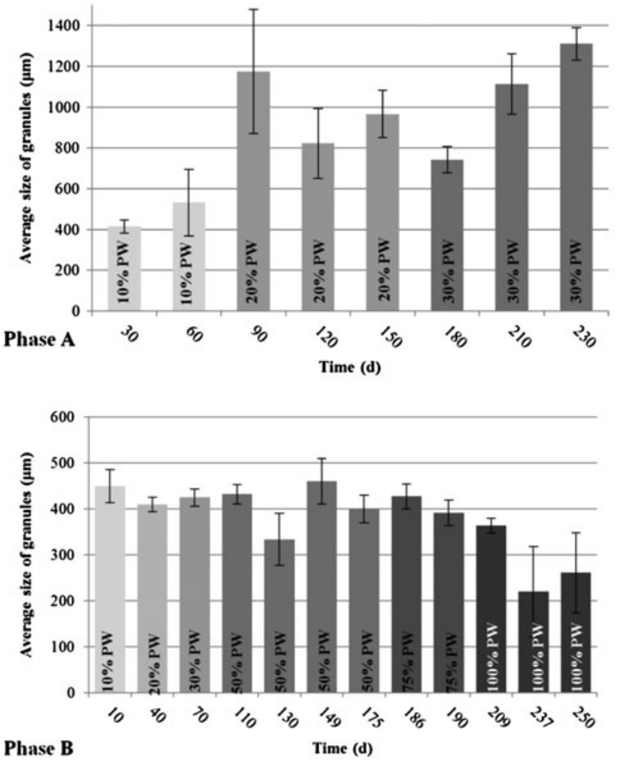

Fig. 1. Average size (diameter) of aerobic granules during Phases A and B.

A new start-up was carried out with different operating conditions during Phase B (Table 1). Compared with Phase A, granule formation was faster during Phase B (first granular aggregates appeared after only 8 d, instead of 20), likely due to the different seed sludge (namely the sludge drawn from the aeration tank of the PWWTP), which was already acclimated to inhibiting substances. In Phase B, the increase in PW% to 20% was possible after only 10 d (68 d were required in Phase A): although a partial loss of granules occurred immediately after the increase in PW%, it was a reversible effect, since small (Fig. 2(c)) and well settling granules became dominant again in the system from day 30 onward. The compactness of such granules was likely due to the higher superficial gas velocity applied (higher selective pressure), compared with Phase A. Granules size did not change significantly until day 204, when the increase of PW% to 100% was followed by the decrease in granules diameter (Figs. 1 and 2(d)): granules were probably hindered to increase in size by the progressive accumulation of NH_4^+-N, which was observed as the PW% was increased to 100%. As previously reported by Yang et al. [20], aerobic granules fed with a synthetic influent with similar NH_4^+-N and COD concentrations (150–1,000 mg/L, respectively) were smaller than those developed at lower NH_4^+-N concentration and higher COD/N ratio (the COD concentration in the influent was kept unchanged). According to the authors, high ammonium concentrations inhibited the formation of aerobic granules, since only conventional sludge flocs were observed. Conversely, in this study, it was possible to obtain very small aerobic granules with initial NH_4^+-N concentration above 200 mg/L.

As shown in Fig. 3(b), the concentration of VSS in the GSBR increased up to 16 g/L in the early stage of Phase B (20% PW), with a corresponding decrease in effluent TSS concentration. A drop of VSS concentration in the GSBR occurred as the PW% was increased to 30% (from day 63) and to 50% (from day 98), together with the increase in effluent TSS concentration. Although the settling ability of aerobic granules gradually worsened, as indicated by the higher effluent TSS concentration, the SVI_8 remained below 70 mL/g TSS, within the range observed in other studies previously reported in literature and concerning the treatment of mixed wastewater rich in toxic organics [12]. The worsening of granules settleability and overall process performance with increasing PW share

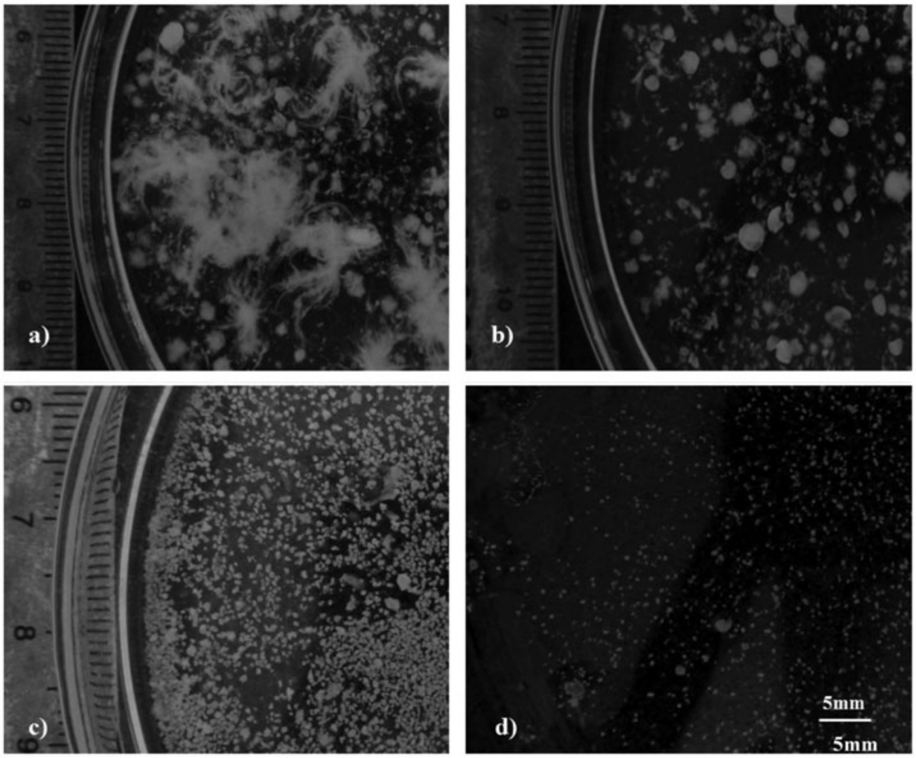

Fig. 2. Aerobic granules collected during Phase A on days 74 (a), 123 (b), during Phase B on days 35 (c) and 236 (d).

in the influent was previously reported in other studies: Zhang et al. [18] observed that the addition of a cometabolic substrate (i.e. sodium propionate) helped in restoring process performance and granules properties. In this study, a readily degradable cometabolic substrate (namely sodium acetate) was already present in the influent during the whole start-up process; therefore, it can be postulated that the PW produced by the IGCC (which contained a much higher amount of NH_4^+-N) had a higher inhibiting effect than the PW used by Zhang et al. [18].

Despite the further increase in PW% to 75 (day 182) and to 100% (day 204), a progressive stabilization of granules size, VSS concentration and SVI_8 was observed, as shown in Figs. 1 and 3(b).

In particular, VSS and effluent TSS concentrations reached average values of 4.9 ± 0.6 g/L and 260 ± 20 mg/L, respectively. Moreover, the average SVI_8 was 30 ± 8 mL/gTSS when PW% was set at 100%, indicating good settling properties.

3.2. TOC and NH_4^+-N removal

Differently from granule physical and morphological properties, process performances during start-up were less fluctuating in terms of TOC and NH_4^+-N removal efficiencies, despite the different operating conditions: in particular, TOC removal efficiencies observed during the whole Phases A and B did not differ significantly from each other and were rather stable (92 ± 6–94 ± 2%, respectively).

In particular, during Phase B, a correlation between NH_4^+-N removal efficiency and changes in PW ammonium content (NH_4^+-N concentration varied significantly with each wastewater supply) was observed (e.g. day 71, Fig. 4(b)); moreover, changes in PW overall composition caused negative effects on granular biomass, which required time for re-acclimation, as confirmed by the temporary decrease of NH_4^+-N removal efficiency observed on days 125–135. NH_4^+-N removal efficiency was stable, but very low, during Phase A: 29 ± 4, 26 ± 7, and 31 ± 9% at PW% of 10, 20, and 30%, respectively (Fig. 4(a)). Considering Phase B (Fig. 4(b)), all NH_4^+-N was removed at 10% of PW, but when PW was increased to 20%, removal efficiency immediately dropped to 68% (day 12) and then to 19% (day 55). Efficiency reached 38% as PW% was increased to 30% (day 63), probably due to the lower NH_4^+-N concentration in the new stock of wastewater (influent concentration varied from 106 to 70 mg/L from day 71 to day 84). After the increase in PW share to 50% (day 98), average NH_4^+-N removal efficiency

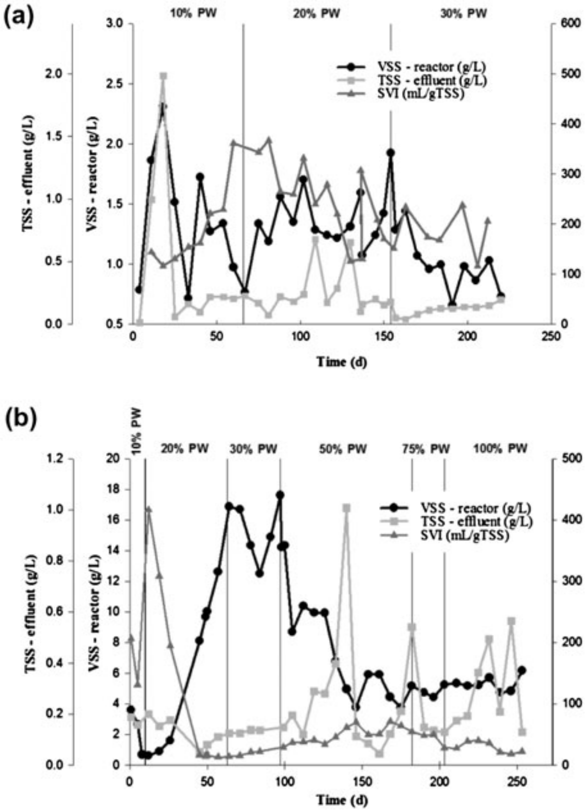

Fig. 3. VSS concentration, SVI_8 and effluent TSS concentration profiles during Phases A (a) and B (b).

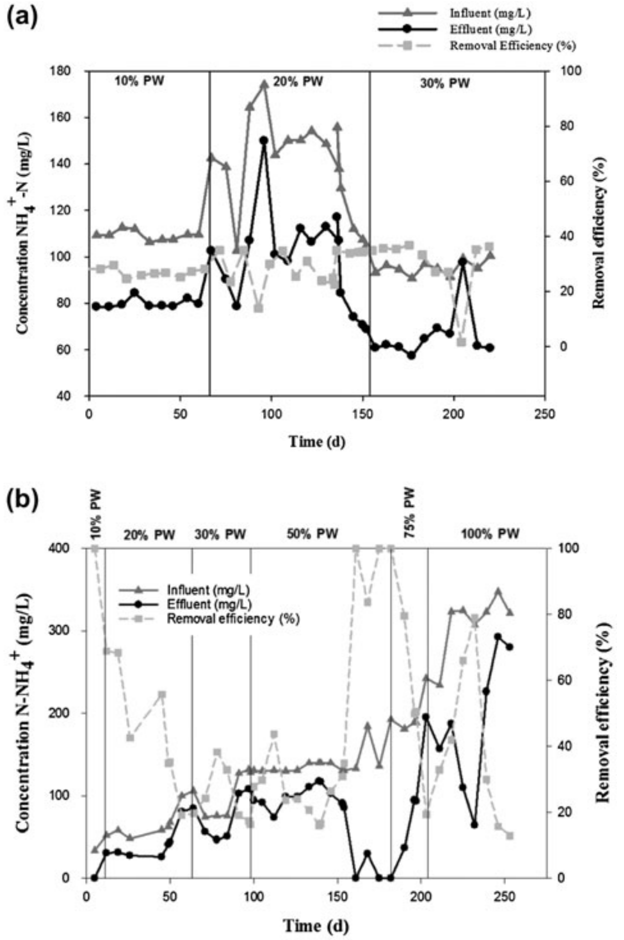

Fig. 4. NH_4^+-N influent and effluent concentrations and NH_4^+-N removal efficiency during Phases A (a) and B (b).

measured until day 154 was 21 ± 5%. Although Zhang et al. [18] reported higher NH_4^+-N removal efficiencies in a granular sludge system treating PW wastewater, it must be considered that influent NH_4^+-N concentration was much higher in this study (240–630 vs. 40 mg/L); therefore, a direct comparison can be misleading; on the other hand, the observed results were in good agreement with those achieved in aerobic granular sludge systems treating other industrial effluents containing complex substrates [12]. Since neither nitrite nor nitrate were detected, nitrogen removal was likely due to microbial synthesis of heterotrophic bacteria [23], rather than nitrification. From day 155, in order to improve NH_4^+-N removal, selected nitrifying bacteria were added once a day into the GSBR for 7 d: this led to an increase in NH_4^+-N removal efficiencies up to 100%, which dropped to approximately 50% immediately after increasing PW% to 75% (day 182), and remained unstable when the PW% was increased to 100% (the average removal efficiency was 37 ± 24%). Differently from the initial stage of Phase B, the formation of both nitrites and, to a small extent, nitrates was observed besides the removal of NH_4^+-N, suggesting that nitrification was occurring after the inoculation of nitrifying biomass, which was effectively retained in the GSBR.

Trends of NH_4^+-N, NO_2^--N and NO_3^--N concentrations during typical GSBR cycles after inoculation of nitrifying biomass are shown in Fig. 5(a) (day 168, PW % of 50%), Fig. 5(b) (day 196, PW% of 75%) and Fig. 5(c) (day 225, PW% of 100%). It is worth observing that the removal of NH_4^+-N corresponds to NO_2^--N production, while NO_3^--N concentrations are negligible in all the considered kinetics: such behaviour may be ascribed to the presence of free ammonia (FA) in the GSBR, which probably hindered the activity of nitrite oxidizing bacteria (NOB). At the given pH (7.8) and temperature (25˚C), the resulting FA concentration in the GSBR was within the range 4.2–7.8 mg N/L, which is far above the threshold concentration range of 0.08–0.82 mg N/L indicated by

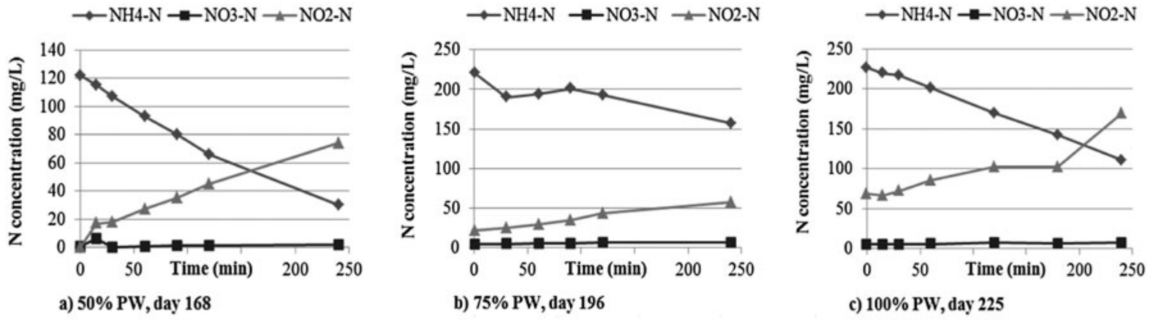

Fig. 5. NH_4^+-N, NO_2^--N, and NO_3^--N profiles during a GSBR cycle on days 168 (a), 196 (b), and 225 (c).

Anthonisen et al. [24] as inhibiting for NOB, and close to the threshold concentration range of 8–120 mg N/L which is inhibiting for ammonium-oxidizing bacteria. At 50% PW, NH_4^+-N removal rate was 0.087 mg NH_4^+-N/mg VSS d (Fig. 5(a)); at 75% PW, NH_4^+-N removal rate decreased to 0.055 mg NH_4^+-N/mg VSS d (Fig. 5(b)). A faster removal was observed when 100% PW was fed (0.094 mg NH_4^+-N/mg VSS d), despite the higher NH_4^+-N initial concentration (Fig. 5(c)).

3.3. pH and cycle time influence on NH_4^+-N removal

Considering the extremely alkaline pH of the PW produced by the IGCC and fed to the GSBR, a preliminary evaluation of the possibility to increase the pH set point from 7.0 ± 0.2 (Phase A) to 7.8 ± 0.2 (Phase B) without compromising NH_4^+-N removal was carried out. In particular, batch experiments were run at different pH (7.2 and 8), with PW% of 30 and 100%: no differences in NH_4^+-N removal rates were observed, as shown in Fig. 6; therefore, the pH control range was set at 7.8 ± 0.2 during Phase B.

Also the possibility to extend cycle length from 4 to 6 h, in order to enhance NH_4^+-N removal, was evaluated: batch experiments were performed with PW% of 50, 75 and 100% at pH 8, and NH_4^+-N concentration profiles were determined. Compared with the 4-h cycle, the removal efficiency at 6 h was only 7.7, 3.8 and 1.8% higher at PW% of 50, 75 and 100%, respectively, suggesting that a longer cycle would not lead to any significant improvement in terms of NH_4^+-N removal.

3.4. Initial and residual PW toxicity

Acute toxicity assessments were carried out on unacclimated activated sludge, in order to evaluate the toxicity of the influent PW (50–100%) before and after treatment by aerobic granular sludge. Fig. 7 shows the inhibition curves obtained: the observed sIC10, sIC50 and sIC90 at PW% of 50–100% were 8.8, 17.2, 33.5 mL/g VSS and 5.2, 9.5, 17.7 mL/g VSS, respectively. When 50% PW was fed to the GSBR (Phase B, days 98–181), the corresponding volume of wastewater per unit of biomass (as VSS) was 88 mL/g VSS, which would lead to 100% inhibition if biomass was not well acclimated, according to acute toxicity assessments: although a progressive decrease

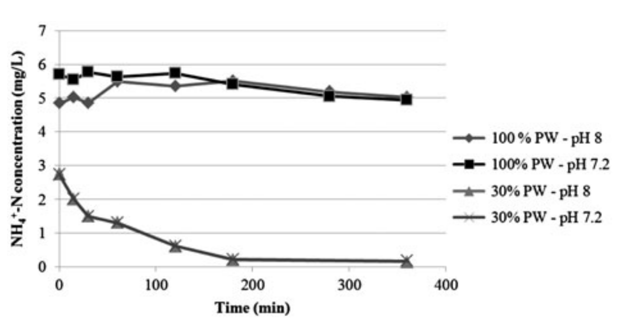

Fig. 6. NH_4^+-N concentration profiles measured in batch reactors fed with 30–100% of PW, under different pH conditions.

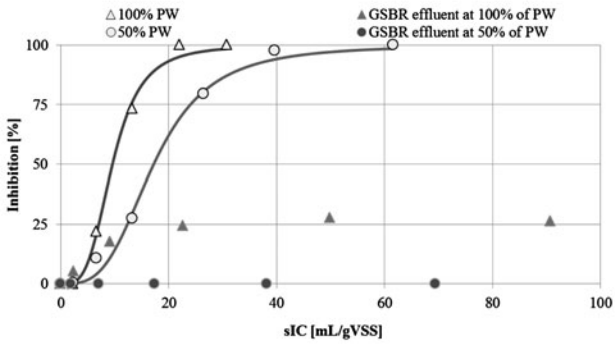

Fig. 7. Inhibition curves determined at PW% of 50–100%, before and after treatment by aerobic granular sludge.

of VSS concentration was observed, biomass activity was not completely inhibited in terms of TOC and NH_4^+-N removal, as reported above, suggesting that biomass acclimation took place in the GSBR and allowed aerobic granules to withstand a high share of PW in the influent.

Moreover, acute toxicity assessments were carried out to evaluate the residual toxicity of the effluent from the GSBR treating 50–100% PW: as shown in Fig. 7, aerobic granules treating 50% PW were able to reduce the initial toxicity significantly and provide a non-toxic effluent (no residual toxicity was observed), while a low residual toxicity (maximum inhibition of 27.8%) was observed in the case of 100% PW.

4. Conclusions

Two start-up strategies for a GSBR-treating PW produced by the IGCC and characterized by high ammonium concentration (up to 630 mg N/L) and pH (up to 12), as well as by the presence of toxic substances such as cyanides and phenols, were evaluated in this study: different seed sludge, pH set point and shear forces were applied and the effects on granule formation and overall process performance were investigated. Main outcomes are the following:

(1) in Phase A, granules appeared from day 20 and became dominant within 68 d. Irreversible breakage and washout of granular aggregates occurred as the PW% was set at 30%. TOC removal efficiency was as high as 92 ± 6%, while NH_4^+-N removal remained stable at 31 ± 9%, despite the worsening of granule physical characteristics;

(2) in Phase B, the use of acclimated sludge as inoculum and harsher environmental conditions (i.e. higher shear stress) allowed the faster formation, development and retention of compact and well settling granules in the GSBR. Again, TOC removal efficiency was high (94 ± 2%);

(3) low NH_4^+-N removal efficiency was achieved during Phase B and related to heterotrophic biosynthesis rather than actual nitrification. The addition of selected nitrifying bacteria led to an improvement in NH_4^+-N removal efficiency up to 100%, although such high process performance got unstable as the share of PW in the influent was further increased;

(4) batch tests showed that neither a higher set point for pH (closer to the pH of PW), nor a prolonged cycle length have any significant effect on NH_4^+-N removal;

(5) aerobic granules were able to reduce the initial toxicity of PW significantly: in particular, no residual toxicity was observed in the effluent when the GSBR was fed with a PW% of 50%. The effluent of the GSBR fed with a PW% of 100% only caused a 27.8% inhibition at 49.9 mL/g VSS, very low if compared with the influent, which caused a 100% inhibition at only 22 mL/g VSS.

The GSBR is currently fed with 100% PW, and further investigation is required in order to maximize process performance and to avoid the supply of the readily degradable organic cometabolic substrate (i.e. sodium acetate), thus reducing the operating costs significantly.

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