

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

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ABSTRACT

Introduction. 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) characterized by high TOC and NH_4^+ -N concentrations (up to 490 and 630 mg/L, respectively).

Methods. A GSBR was used to carry out the experiments: two different start-up strategies (Phases A and B) were applied by varying shear forces, inoculum source and pH. The GSBR was fed with a mixture of synthetic and real PW, which was gradually increased depending on the observed reactor performance.

Results. In phase A, aerobic granules irreversibly deteriorated when the percentage of PW in the influent was raised to 30%. A faster and more stable granulation was observed during phase B, likely due to the higher superficial gas velocity applied (harsher conditions) and to the different sludge used as inoculum (already acclimated to toxic substances). The observed TOC removal efficiencies were similar in phases A and B (92 and 95%, respectively), while NH_4 -N removal efficiency was higher during phase B (28 vs 32%). Phase B is still in progress (the rate of PW in the influent is currently set to 50%).

Conclusion. The inoculum with acclimated sludge and the harsher selective pressure (phase B) were proved to speed-up the formation of small, dense and well settling granules, more resistant to the increase of PW rate in the influent. Further investigation is required in order to achieve stable granules treating 100% real PW, with high NH_4^+ -N and TOC removal.

Keywords: aerobic granular sludge; GSBR; petrochemical wastewater; selective pressure; superficial air velocity; inoculum.

1. INTRODUCTION

The development of aerobic granular sludge has been widely studied for the treatment of synthetic [1], municipal [2] or industrial wastewater [3][4]. Results about granulation and process performance when treating different kinds of industrial wastewaters, including high-strength ones containing organics, nitrogen and phosphorus [5] and other toxic substances [6], are promising and encourage the possible application of this technology to complex substrates [7].

Currently, improving the removal of contaminants in granular sludge sequencing batch reactors (GSBR) has become a crucial point, which can be achieved by properly changing the main operating parameters in order to select biomass and enhance treatment processes [8].

Due to the peculiar structure of aerobic granules, also petrochemical wastewater (PW) can be treated in GSBR by cometabolism, if proper biomass acclimation occurs [9].

Nevertheless, during a start-up there are some operational factors to take into account: among the others, the settling time to select fast settling particles [1], the shear stress [10], the COD:N ratio [11], the organic loading rate (OLR) [3]. Furthermore the presence of toxic and inhibitory compounds in petrochemical wastewater can affect granulation and the overall efficiency of the system. Within this framework, the aim of this study was to investigate the feasibility of developing aerobic granules to treat petrochemical

wastewater characterised by high pH (up to 12), rich in organic matter (TOC, 260-490 mg/L) and ammonia (240-630 mg/L) and containing toxic substances like cyanides and phenols: different operating configurations (i.e. sludge inoculum, shear stress, pH) were tested and the effects on granule formation and process performance were investigated in terms of, among the others, granule physical and morphological properties, TOC and NH_4^+ -N removal efficiencies. Batch tests were run to study and improve nitrogen removal efficiencies considering different cycle lengths and pH; moreover, acute toxicity assessments were carried out in order to evaluate the efficacy of the system in reducing also the toxicity of the influent.

2. MATERIALS AND METHODS

2.1 Reactor set-up and operation

The experimental work was performed using a GSBP with a working volume of 3 litres, an internal diameter of 10 cm and a working height of 30 cm. The reactor was operated at room temperature (25°C) in 4-h cycles, each cycle consisting of an impulse feeding of 5 min, 221-229 min aeration, 8-1.5 min settling and 5-10 min effluent withdrawal. Settling time was initially set to 8 min, in order to avoid sludge washout, and was gradually decreased to 1.5 min 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) was not controlled throughout the cycle. Volumetric exchange ratio (effluent volume/total working volume) was 0.5 and the resulting Hydraulic Retention Time (HRT) was 8 hours.

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

Table 1 Start-up operating conditions during phase 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	2.8
Additional supplies	Acetate (COD), P, trace elements	Acetate (COD), P

2.2 Seed sludge

The GSBP 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 phase B the activated sludge was taken from the aeration tank of the petrochemical wastewater treatment plant (PWTP) of Sarroch, Italy (TSS 2.8 g/L, VSS 2.7 g/L).

2.3 Wastewater characteristics

The GSBP was fed with a mixture of synthetic and real PW, adding acetate as readily biodegradable organic substrate in order to maintain a volumetric organic loading rate (vOLR) of 3 $\text{g}_{\text{COD}}/\text{L}\cdot\text{d}$. During phase A, nutrients and trace elements were also added to avoid limiting conditions. PW was stored in a refrigerator (4°C) to prevent changes in physical and chemical characteristics.

Raw petrochemical wastewater was obtained from the Integrated Gasification Combined Cycle (IGCC), part of the SARAS SpA facilities operating in Sarroch, Italy, where heavy oils are combusted under oxygen deficiency conditions to produce synthesis gas (syngas), used to produce energy after being purified. Detailed composition of petrochemical wastewater is given in Table 2. Real wastewater is currently treated at full scale by a combination of chemical-physical (i.e. steam stripping) and biological treatments (i.e. trickling filter). The amount of real wastewater was increased gradually depending on the observed granulation and reactor performance (Table 3). Influent COD:N ratio varied according to the real PW composition (a certain variability was observed, especially in NH_4^+ -N and COD content).

2.4 Analytical Methods

Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), NH_4^+ -N and PO_4^- -P were determined according to Standard Methods [12]. The TOC concentration was measured with a TOC analyser (SHIMADZU TOC-V CSN). 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 filtered (0.45 μm) and properly diluted with de-ionized water before analysis. Granule density was determined by dextran-blue method, according

to [1]. Image Analysis was performed on representative granule 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 camera placed onto a horizontal holder. ImagePro Plus (v.6) was used to calculate granule diameter.

Table 2 Petrochemical wastewater characteristics

Parameters	Concentration
Alkalinity (ppmCaCO ₃)	4100
pH	10-12
NH ₄ ⁺ -N (mg/L)	240-630
Cyanide (mg/L)	10-15
COD (mg/L)	340-610
TOC (mg/L)	260-490
Phenol (mg/L)	2.5
Formate (mg/L)	1000-1500
TSS (mg/L)	300-500

Table 3 Fractions of PW and influent characteristics during Phases A and B

Phases	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
	155-220	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
	98-133	50	2	100:11 - 100:14

2.5 Acute toxicity tests and batch experiments

A titrimetric biosensor (ANITA, Ammonium NITrification Analyser) was used in order to evaluate the acute inhibiting effects of PW on unacclimated sludge, as described in Ficara and Rozzi [13]. Tests were performed in triplicate using unacclimated sludge drawn from the municipal WWTP of Cagliari. Experimental data were interpolated in order to determine and plot the inhibition curves, which were used to calculate the inhibitory concentrations (IC), i.e. the amounts of real wastewater per gram of VSS that causes 10 (IC10), 50 (IC50) and 90% (IC90) acute inhibition on sludge activity. The same assessments were carried out also using the GSBREffluent, in order to evaluate the residual acute toxicity after the treatment.

As to the batch experiments, 4- and 6-hour tests were performed in PVC reactors with a working volume of 250 mL (internal diameter of 5cm and working height of 12.5 cm). Tests were run at 30, 50, 75, 100% of PW. For each test, 125 ml of mixed liquor were taken from the GSBREffluent, 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 batch 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 GSBREffluent. The resulting NH₄⁺-N concentration varied with the increment of PW%.

3. RESULTS AND DISCUSSION

3.1 Formation and characteristics of aerobic granules

In this study, a settling time of 8 min was initially adopted and was gradually decreased to 1.5 min (settling time significantly influences granulation process, favouring granule formation when shortened, as reported by Beun et al. [1]). During phase A, the increase of PW rate to 20% was possible after 68 days: although an increase of granule size was observed (Figure 1), it was accompanied by filamentous outgrowths on the surface (Figure 2a), with a corresponding worsening of sludge settleability (SVI₈ increased up to 300 mL/g, Figure 3a). On day 108, most of filamentous aggregates had been replaced by more compact aerobic granules (average diameter was 1mm) with VSS concentration inside the GSBREffluent of 1.4±0.3 g/L. Increase of PW load to 30% coincided with applying a new stock of wastewater, different

from the previous stocks in odour, colour, COD (370 mg/L) and $\text{NH}_4^+\text{-N}$ (310 mg/L) concentrations; aerobic granules increased in size, but became loose and fluffy, developing filamentous outgrowths which worsened sludge settleability. The change of sludge morphology led to an irreversible wash-out. Similar negative effects due to the variation of the applied industrial wastewater were reported by Inizan et al. [3], who observed filamentous outgrowth and a consequent rapid washout of the biomass. Despite the decrease of OLR from 5 to 2-3 kg COD/m³d, the cited authors did not observe granule formation for 60 days, until the dosage of external phosphorus was increased (from 1mg/500mgCOD to 1mg/100mgCOD), likely due to the formation of phosphorus precipitates, which might provide as seeding points for aerobic granules formation [3].

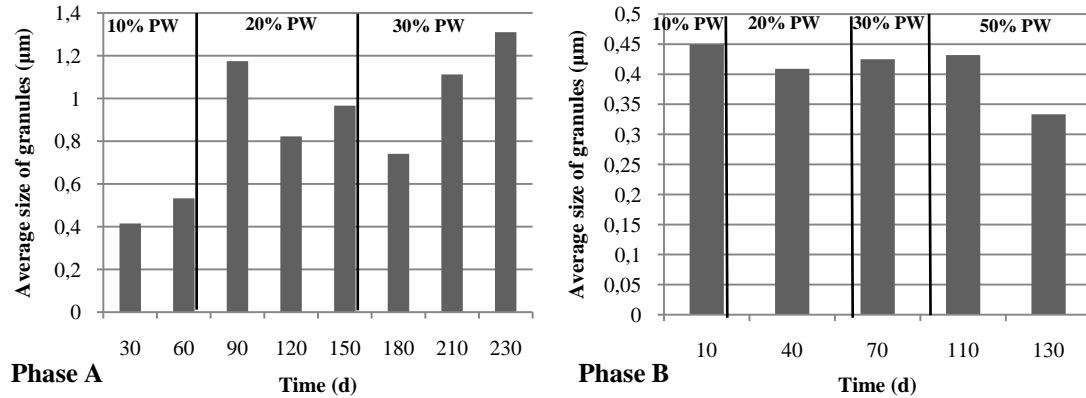


Figure 1. Average size of aerobic granules during phases A and B.

Compared with phase A, a faster granulation was observed during phase B (first granular aggregates appeared after 20 and 8 days, respectively), likely due to the different seed sludge which was already acclimated to inhibiting substances. In phase B, the increase of PW% to 20% was possible after 10 days: although a partial loss of granules occurred, it was a reversible effect and very small (average diameter of 0.4 mm), but dense (48 gTSS/Lgran) and well settling (SVI_8 , 10 mL/gTSS) granules became dominant again in the system from day 30 (Figure 2b). As shown in Figure 1, granule size did not change significantly throughout phase B (average value of 0.4 ± 0.05 mm). The compactness and density of such granules were likely due to the higher superficial gas velocity applied (higher selective pressure). Moreover, also the higher $\text{NH}_4^+\text{-N}$ concentration probably hindered granules to increase in size: as previously reported by Yang et al. [11], aerobic granules fed with a synthetic influent with similar $\text{NH}_4^+\text{-N}$ and COD concentrations (150 and 1000 mg/L, respectively) were smaller than those developed at lower $\text{NH}_4^+\text{-N}$ concentration (the COD concentration in the influent was kept unchanged).

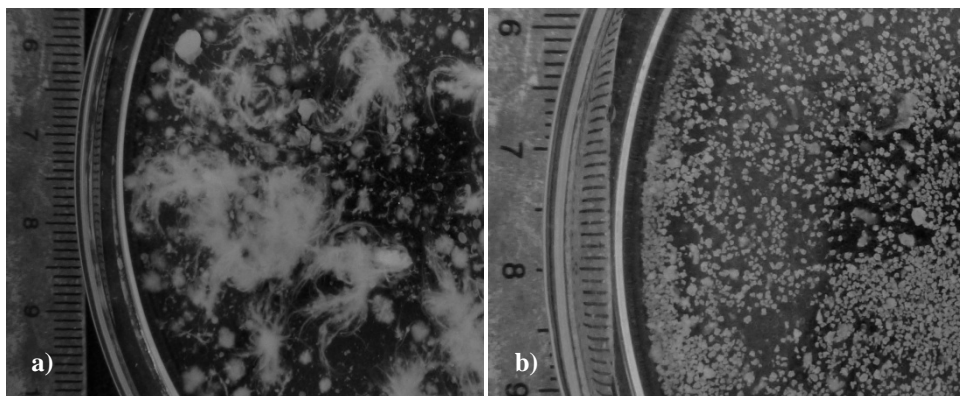


Figure 2. Details of aerobic granules drawn in phase A at day 74 (a) and B at day 35 (b).

In accordance with the high sludge density and settleability, the concentration of VSS in the GSBP increased up to 16 g/L in phase B with a corresponding decrease of effluent TSS concentration below 80 mg/L (the threshold level according to Italian regulations) and the increase of SRT to 86 d (20% of PW), as shown in Figure 3b. A slight, reversible drop of VSS concentration in the GSBP occurred as the PW%

was increased to 30%. When the PW% was further increased to 50%, a decrease of granules average diameter from 0.4 to 0.3 mm was observed and it was accompanied by a drop of VSS concentration to 5 g/L (effluent TSS concentration increased correspondingly from 135 to 390 mg/L, with the consequent decrease of SRT to 7d). Settling ability of the granules gradually worsened, but SVI remained under 70 mL/gTSS, within the range observed by other authors when treating mixed wastewater rich in toxic organics [6]. The worsening of granules settleability and removal of pollutants with increasing PW% was previously reported in literature: process performance could be restored by the addition of a co-metabolic substrate [9].

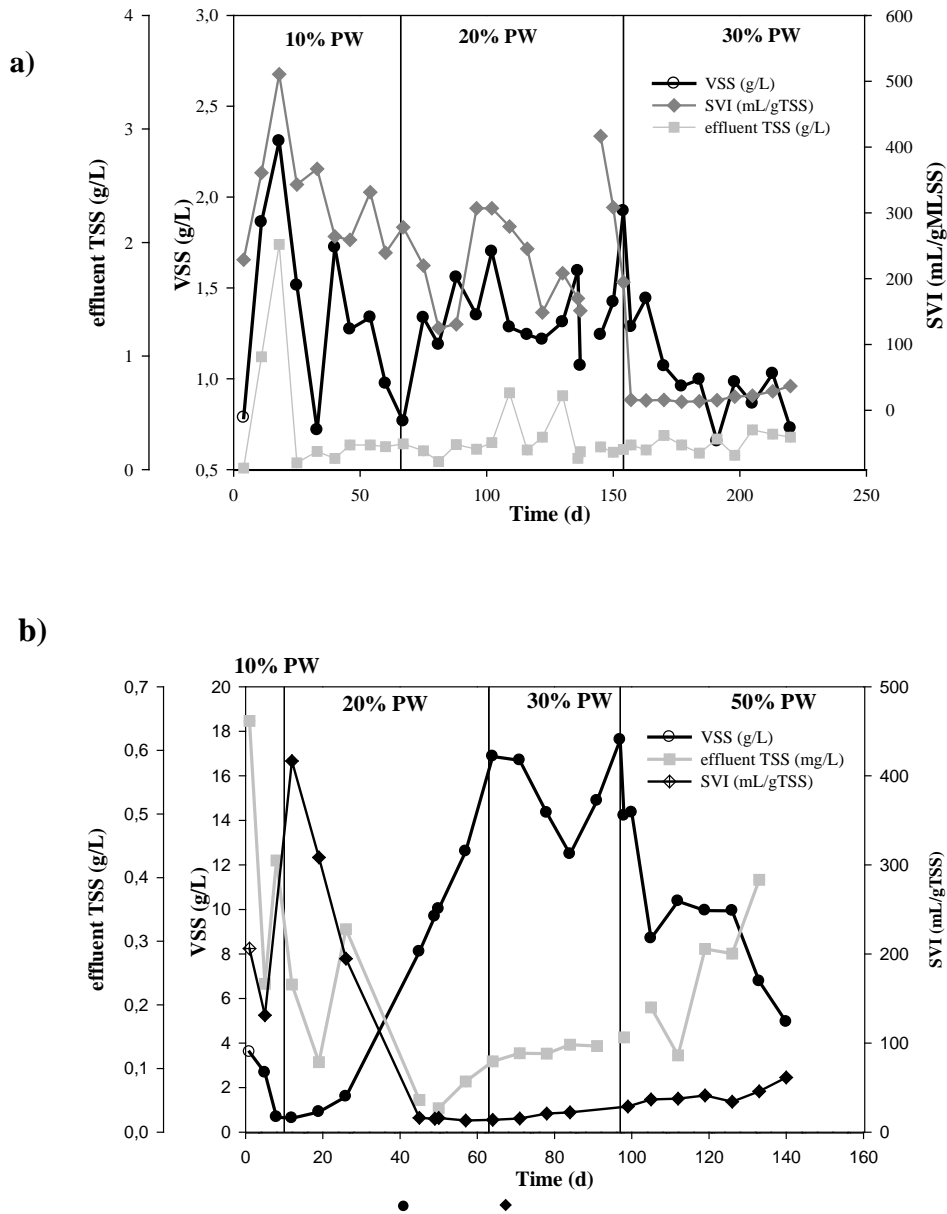


Figure 3. VSS, SVI and effluent TSS concentration profiles during phases A (a) and B (b).

3.2 TOC and NH_4^+ -N removal

Differently from granule physical and morphological properties, process performances during start-up were less affected in terms of TOC and NH_4^+ -N removal efficiencies, despite the different operating conditions: in particular, TOC removal efficiencies observed during phases A and B were rather stable and similar (average values of $92\pm 6\%$ and $93\pm 2\%$, respectively).

$\text{NH}_4^+\text{-N}$ removal efficiency was extremely influenced by the PW, since the $\text{NH}_4^+\text{-N}$ concentration varied with each wastewater supply. In particular, it was noticed that biomass needed to acclimate every time a new stock of PW was used, as suggested by temporary decrease of VSS concentration and $\text{NH}_4^+\text{-N}$ removal efficiency, especially during phase B. $\text{NH}_4^+\text{-N}$ removal efficiency was stable during phase A: $29\pm 4\%$, $26\pm 7\%$ and $31\pm 9\%$ respectively at 10, 20 and 30% of PW, as shown in Figure 4a. Considering phase B (Figure 4b), all $\text{NH}_4^+\text{-N}$ was removed at 10% of PW, but when PW was increased to 20%, removal efficiency decreased from 68 to 19%. Efficiency improved when 30% of PW was fed, probably due to the lower $\text{NH}_4^+\text{-N}$ concentration in the new stock of wastewater (from day 71 to day 84). After the increase of PW rate to 50%, average value was $21\pm 5\%$. Measured $\text{NH}_4^+\text{-N}$ removal efficiencies were lower if compared to the average value of 94% previously reported in literature and concerning a GSBRT treating petrochemical wastewater with different characteristics [9]: in particular, $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$ and COD concentrations were much lower (42.9, 36 and 282 mg/L, respectively) than those measured in the PW used in the present work. Nevertheless, the results are in good agreement with those observed with aerobic granular sludge treating other industrial effluents containing complex substrates [6]. Since neither nitrite nor nitrate were detected, removed nitrogen was simply due to microbial requirement for the biosynthesis of heterotrophic bacteria [14] rather than for nitrification.

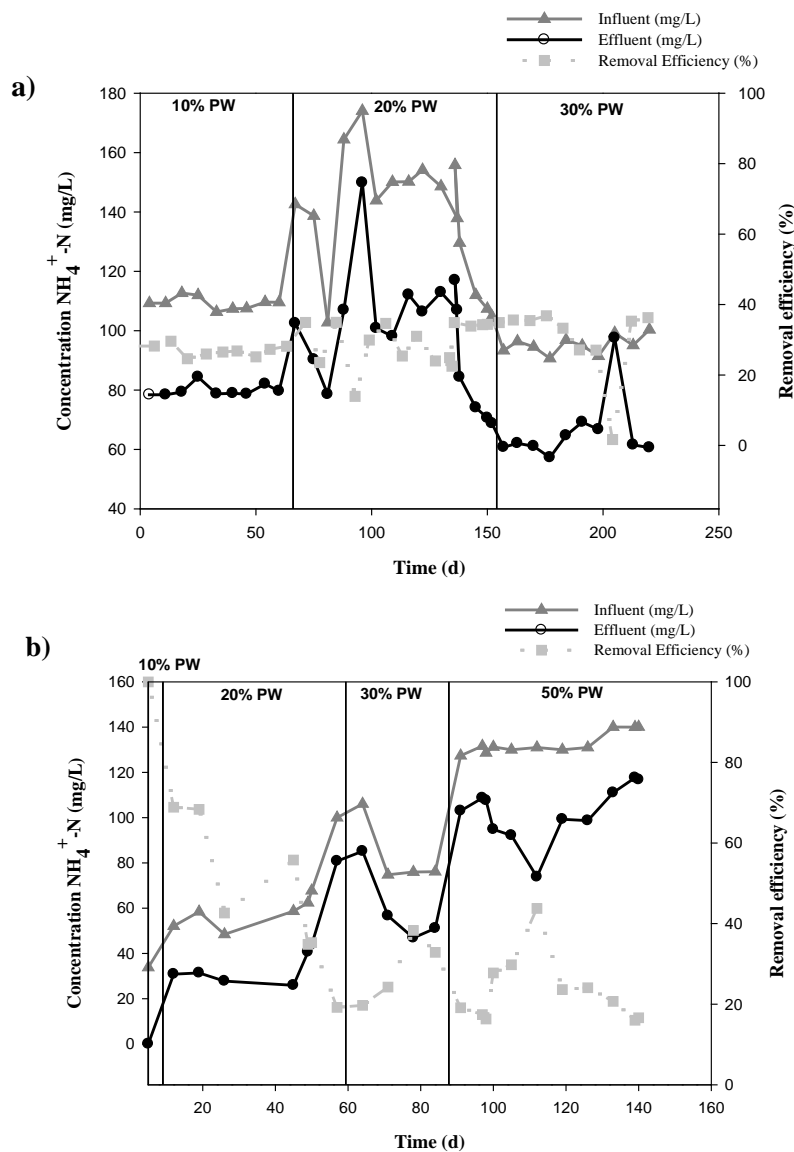


Figure 4. $\text{NH}_4^+\text{-N}$ influent and effluent concentrations and $\text{NH}_4^+\text{-N}$ removal efficiency during phases A (a) and B (b).

3.2.1 pH and cycle time influence on $\text{NH}_4^+\text{-N}$ removal

Considering the extremely alkaline pH of the PW fed to the GSB, also the pH control range was changed in phase B. In order to determine if the change of pH set-point could affect $\text{NH}_4^+\text{-N}$ removal, batch experiments were carried out at different pH (7.2 and 8) (Figure 5). Furthermore, to enhance $\text{NH}_4^+\text{-N}$ removal, it was considered to extend cycle time to 6h and batch experiments were performed at this regard at 50, 75 and 100% of PW at pH 8 (Figure 6). Compared with the 4-hour cycle, the removal efficiency was 7.7, 3.8 and 1.8% higher at 50, 75 and 100% of PW%, respectively, suggesting that a longer cycle time would not lead to a significant improvement in terms of $\text{NH}_4^+\text{-N}$ removal.

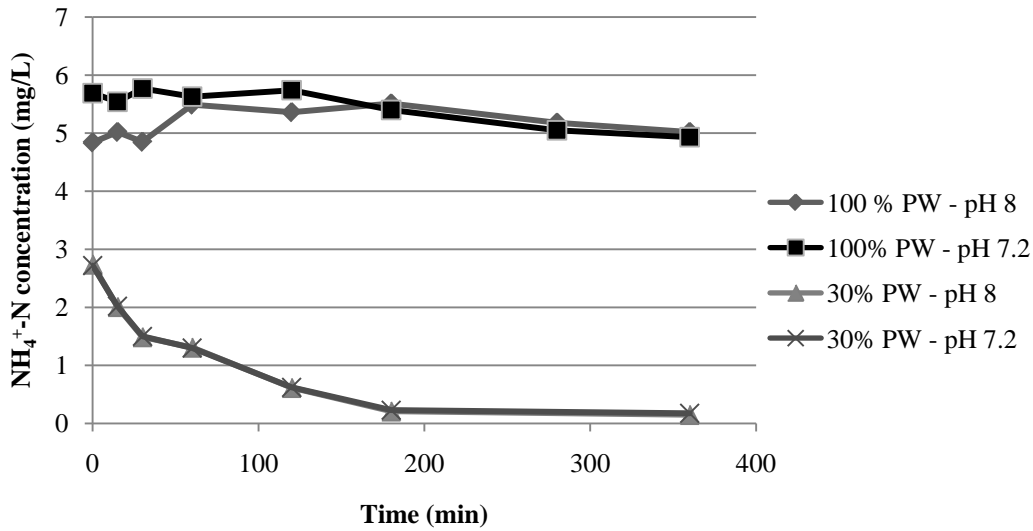


Figure 5. $\text{NH}_4^+\text{-N}$ concentrations profiles measured in batch reactors fed with 30 and 100% of PW, during a 4h-cycle under different pH conditions.

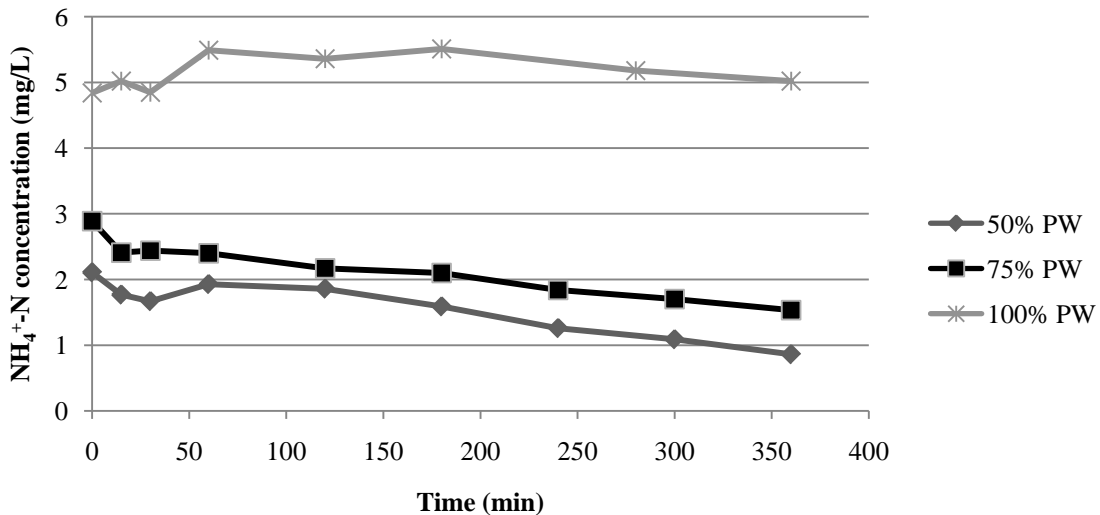


Figure 6. $\text{NH}_4^+\text{-N}$ concentration profiles measured in batch reactors fed with 50, 75 and 100% of PW, during a 6h-cycle.

3.3 PW and GSB effluent toxicity on activated sludge from municipal WWTP

Acute toxicity assessments were carried out on unacclimated sludge, using 100% PW and 50% PW. Figure 7 shows the corresponding inhibition curves: the observed IC10, IC50 and IC90 for 100% and 50% were 5.2, 9.5, 17.7 mL/gVSS and 8.8, 17.2, 33.5 mL/gVSS, respectively. When 50% PW was fed to the GSB (period B, days 98-133), the corresponding volume of wastewater per unit of biomass (as VSS) was 88 mL/gVSS, which would lead to 100% inhibition if biomass was not well acclimated, according to

toxicity assessments: although a progressive decrease of VSS concentration was observed, biomass activity was not completely inhibited in terms of TOC and $\text{NH}_4^+\text{-N}$ removal, as reported above, suggesting that biomass acclimation took place in the GSB and allowed aerobic granules to withstand high loads of PW.

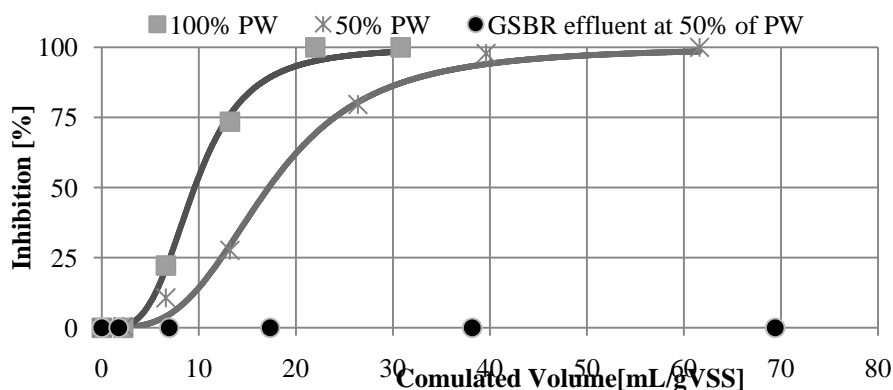


Figure 7. Inhibition curves at 50 and 100% of PW.

Moreover, an acute toxicity assessment was carried out to evaluate the residual toxicity of the effluent drawn from the GSB treating 50% PW: as shown in Figure 7, aerobic granules were able to reduce the initial toxicity significantly and provide a non-toxic effluent (no residual toxicity was observed).

4. CONCLUSIONS

Two start-up strategies for a GSB treating petrochemical wastewater produced by the IGCC process and containing high TOC and $\text{NH}_4^+\text{-N}$ concentrations were evaluated in this study (phases A and B): different seed sludge, pH set-point and shear forces were applied and the effects on granule formation and overall process performance were investigated.

In phase A granules appeared from day 20 and became dominant within 60 days. Irreversible breakage and wash-out of granular aggregates occurred as the PW% was set at 30%. TOC removal efficiency was as high as $93\pm 1.5\%$, while $\text{NH}_4^+\text{-N}$ removal remained stable at $29\pm 2\%$ as the worsening of granule physical characteristics occurred. In phase B, the use of acclimated sludge as inoculum and harsher environmental conditions (i.e., higher shear stress) allowed the formation, development and retention of compact, dense and well settling granules in the GSB. Again, TOC removal efficiency was high ($93\pm 2\%$), while low $\text{NH}_4^+\text{-N}$ removal was observed and related to heterotrophic biosynthesis rather than actual nitrification. In particular, batch tests showed that a higher set-point for pH (closer to the pH of petrochemical wastewater) has no significant effect on $\text{NH}_4^+\text{-N}$ removal. Moreover, the GSB fed with 50% PW was able to provide an effluent with negligible residual toxicity. The GSB is currently fed with 50% PW, and further investigation is required in order to improve process performance (in terms of $\text{NH}_4^+\text{-N}$ removal efficiency), so that PW% in the influent can be increased to 75% and 100%.

References

- [1] Beun, J.J., Hendriks, A., Van Loosdrecht, M.C.M., Morgenroth, E., Wilderer, P.A., Heijnen, J.J.: Aerobic granulation in a sequencing batch airlift reactor. *Water Research* **36**: 702-712 (2002)
- [2] Liu, X., Dong, C.: Simultaneous COD and nitrogen removal in a micro-aerobic granular sludge reactor for domestic wastewater treatment. 2011 International Conference on Risk and Engineering Management (REM), *Systems Engineering Procedia* **1**: 99-105 (2011)
- [3] Inizan, M., Freval, A., Cigana, J., Meinhold, J.: Aerobic granulation in a sequencing batch reactor (SBR) for industrial wastewater treatment. *Water Science & Technology* **52** (10-11): 335-343 (2005)
- [4] Mosquera-Corral, A., Garrido, J.M., Méndez, R.: Aerobic granulation with industrial wastewater in sequencing batch reactors. *Water Research* **38**: 3389-2299 (2004)

- [5] Kishida, N., Tsuneda, S., Kim, J.H., Sudo, R.: Simultaneous nitrogen and phosphorus removal from high-strength industrial wastewater using aerobic granular sludge. *J Environmental Engineering* **35**: 153-158 (2009)
- [6] Liu, L., Sheng, G., Li, W., Tong, Z., Zeng, R., Liu, J., Xie, J., Peng, S., Yu, H.: Cultivation of aerobic granular sludge with a mixed wastewater rich in toxic organics. *Biochemical Engineering Journal* **57**: 7-12 (2011)
- [7] Val del Rio, A., Figueroa, M., Arrojo, B., Mosquera-Corral, A., Campos, J.L., Garcia-Torriello, G., Méndez, R.: Aerobic granular SBR systems applied to the treatment of industrial effluents. *Journal of Environmental Management* **95**: S88-S92 (2012)
- [8] Wei, D., Shi, L., Yan, T., Zhang, G., Wang, Y., Du, B.: Aerobic granules formation and simultaneous nitrogen and phosphorus removal treating high strength ammonia wastewater in sequencing batch reactor. *Bioresource Technology* **171**: 211–216 (2014)
- [9] Zhang, H., He, Y., Jiang, T., Yang F.: Research on characteristics of aerobic granules treating petrochemical wastewater by acclimation and co-metabolism methods. *Desalination* **279**: 69-74 (2011)
- [10] Lochmatter, S., Holliger, C.: Optimization of operation conditions for the startup of aerobic granular sludge reactors biologically removing carbon, nitrogen, and phosphorous. *Water research* **59** :58-70 (2014)
- [11] Yang, S., Tay, J., Liu, Y.: Inhibition of free ammonia to the formation of aerobic granules. *Biochemical Engineering Journal* **17**: 41–48 (2004)
- [12] APHA: Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, DC (2005)
- [13] Ficara, E. and Rozzi, A.: pH-stat titration to assess nitrification inhibition, *J. Environ. Eng.* **127** pp. 698-704 (2001)
- [14] Jungles, M.K., Figueroa, M., Morales, N., Val del Rio, A., Ribeiro da Costa R. H., Campos J.L., Mosquera-Corral, A., Méndez, R.: Start up of a pilot scale aerobic granular reactor for organic matter and nitrose removal. *J Chem Technol Biotechnol* **86**: 763-768 (2011)