

ELAN[®], an anammox based process, to treat industrial effluents from fish canning industry

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Abstract

The autotrophic nitrogen removal by the ELAN[®] process (partial nitrification and anammox) appears as a good option to remove nitrogen from saline effluents, like those of the seafood industry. A nitrogen loading rate of 0.2 g N/(L·d) was treated with a removal efficiency of 80% when concentrations of 4.3 g NaCl/L were present. The obtained effluent fulfilled the discharge requirements for this industry (outlet total nitrogen concentration has to be lower than 100 mg N/L). However, a punctual salt concentration increase, from 3.8 to 15.9 g NaCl/L, provoked partial inhibition of the ammonia oxidation (40%) and total inhibition of the anammox process. This inhibition was reversible and could be avoided with a progressive adaptation of the biomass to high salts concentrations. The treatment of agro food industrial effluents combining anaerobic digestion for organic matter removal and ELAN[®] for nitrogen removal would minimize the energy demand of the wastewater treatment.

Keywords: Anammox; granular sludge; industrial; partial nitrification; salinity; seafood.

INTRODUCTION

The treatment of saline wastewaters, characteristic of some types of industries (like seafood processing, fish canning, textile dyeing, oil and gas production and tanneries) by biological processes is sometimes difficult. High salinity conditions result in high osmotic pressures which might cause severe inhibition or death of microorganisms (Jin *et al.*, 2012). In this sense, the use of granular biomass could be adequate, because the granulation process increases the concentration of biomass into the reactor and improves the resistance to toxicity (Moussavi *et al.*, 2010). Furthermore, the granule matrix acts as a mass transfer barrier that produces lower local concentrations of toxics on cells than in the bulk liquid (Adav *et al.*, 2008).

The effect of salts concentration has been studied separately in nitrification (Li *et al.*, 2011) and anammox (Dapena-Mora *et al.*, 2010) systems. The adaptation of both types of microorganisms, ammonia oxidizing bacteria (AOB) and anammox, to high salt concentrations was possible. To assess the treatment of saline wastewaters by a combination of both types of microorganisms in one unit is of interest. This potential application will broaden the field of application of the partial nitrification-anammox based systems for the nitrogen removal in saline industrial wastewaters. In this sense Liu *et al.* (2008) tested the effect of NaCl addition in a partial nitrification-anammox single system and observed an enhancement on the total nitrogen removal rate from 425 (without salt) to 637 mg N/L·d (10 g NaCl/L). Although they used a synthetic wastewater, the results obtained showed the possible application to industrial saline wastewaters of the partial nitrification-anammox single unit system. The ELAN[®] process, developed by Aqualia with the know-how of the University of Santiago de Compostela, is a system of this kind performed in a single granular sequencing batch reactor (SBR).

The objective of this work is to test the possible application of the ELAN[®] process to treat an industrial effluent coming from a fish canning industry. This type of industry is very common in the northwest of Spain (Galicia) and the produced effluents are characterized by high fluctuations on

ammonia and salts concentrations.

MATERIALS AND METHODS

A laboratory scale SBR with a useful volume of 1.5 L was operated in cycles of three hours distributed as: 5 min of feeding, 160 min of aeration, 10 min of settling and 5 min of withdrawal. The SBR was fed with the effluent from an anaerobic digester treating a fish canning industrial wastewater (Table 1). The temperature was maintained by a thermostatic bath around 24 ± 1 °C, which is the expected value for the reject water of a mesophilic anaerobic digester. The hydraulic retention time (HRT) varied from 1.0 to 1.5 days along the operation. The nitrogen loading rate (NLR) applied was around 0.20-0.25 g N/(L·d). The dissolved oxygen concentration was maintained between 2-3 mg O₂/L to achieve an adequate balance between the partial nitrification and the anammox processes. The reactor was inoculated with 7.5 g VSS/L of granular biomass from an ELAN[®] pilot plant (200 L) treating the supernatant of a sludge anaerobic digester of a municipal WWTP (Vázquez-Padín *et al.*, 2013). This granular biomass had both, the specific ammonia oxidation and anammox activities, of 0.19 g N/(g VSS·d) at 25°C, while nitrite oxidation activity was not detected.

Table 1. Characteristics of the different batches of industrial wastewater fed to the reactor and operational conditions for the different stages.

Parameter	Stage I	Stage II	Stage III	Stage IV	Stage V
Days of operation	0-30	31-40	41-75	76-130	131-155
pH	7.8±0.1	7.7±0.1	7.8±0.1	7.6±0.1	7.6±0.1
Conductivity (mS)	9.7±0.9	21.2±0.4	9.3±0.2	6.1±0.2	9.8±0.8
NaCl (g/L)	3.8±0.2	15.9±0.8	3.5±0.3	1.9±0.3	4.3±0.4
NH ₄ ⁺ (mg N/L)	280±37	269±38	344±28	206±22	211±19
NO _x ⁻ (mg N/L)	1.4±0.5	3.1±0.4	1.5±0.8	1.1±0.8	1.9±0.7
Inorganic carbon (mg C/L)	339±33	360±25	347±31	284±35	340±29
TOC(mg C/L)	51±6	52±5	53±9	47±10	53±11
Na ⁺ (mg/L)	1575±30	6467±102	1447±128	807±82	1724±194
Cl ⁻ (mg/L)	2182±22	9360±470	2046±80	1029±178	2616±275
PO ₄ ⁻³ (mg/L)	124±16	ND	39±17	96±21	48±12
SO ₄ ⁻² (mg/L)	77±4	165±18	69±49	77±18	156±46
HRT (days)	1.22±0.24	1.47±0.01	1.32±0.15	1.10±0.02	1.10±0.02
NLR (g N/(L·d))	0.24±0.07	0.19±0.03	0.23±0.06	0.19±0.02	0.20±0.01

RESULTS AND DISCUSSION

Nitrogen removal and salinity

During the first 30 days of operation (Stage I) the fed industrial wastewater had a conductivity of 9.7 mS/cm and a salt concentration around 3.8 g NaCl/L (Table 1). The achieved efficiencies of ammonia oxidation and total nitrogen removal were 100 and 85%, respectively; similar to the values obtained in the pilot plant origin of the inoculum. This pilot plant was fed with the effluent of an anaerobic sludge digester with a salt concentration around 0.5 g NaCl/L, although the ammonia concentration was higher (around 1000 mg NH₄⁺-N/L) than in the industrial effluent of this study. This implied that the granular sludge inoculated was already adapted to treat values of conductivity around 8.5 mS/cm, similar to the values used at the beginning of this experiment.

After day 31, the new batch of feeding presented a conductivity of 21.2 mS/cm and a salt concentration of 15.9 g NaCl/L (due to a change from tuna to mussels on the material processed) which caused the failure of the process, with a value of total nitrogen removal of zero. However, even if the ammonia oxidation decreased, it was maintained around 60%, which means that the salt inhibition had a higher effect on anammox bacteria than on AOB. Dapena-Mora *et al.* (2007), working in batch tests, demonstrated that NaCl did not affect anammox activity at concentrations below 8.78 g/L, and they determined that the IC₅₀ was of 13.46 g NaCl/L. The adaptation of

anammox bacteria to high salinity is possible, as it was demonstrated by Yang et al. (2011). These authors treated a NLR of 5.2 g N/(L·d) with 30 g NaCl/L in an anammox system fed with synthetic wastewater and they pointed out as crucial the progressive adaptation to the high salinity after observing two episodes of inhibition due to corresponding sharp increases of salinity. However, no adaptation strategy was used in the present research. That is due to the fact that in the seafood industry it is common to change the raw material from one day to another, which implies also sharp changes on the wastewater composition, mainly in the salt concentrations. In this sense, the salt concentration around 3.8 g NaCl/L (stage I) was related to the manufacture of tuna, while values around 15.9 g NaCl/L (stage II) were related to the manufacture of mussels.

On stage III (day 41), the conductivity of the wastewater fed was of 9.3 mS/cm. The nitrogen removal efficiency was restored to values around 80% (Figure 1.a). This means that the inhibition by salinity in that case was reversible. During the rest of the operation, the nitrogen removal efficiency remained around 80%, while the conductivity and the salt concentrations ranged between 6-10 mS/cm and 1.5-4.7 g NaCl/L, respectively.

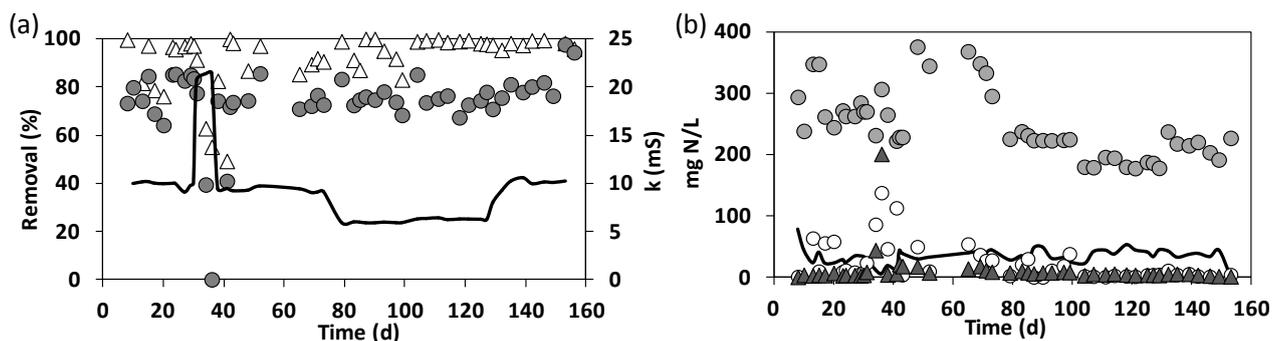


Figure 1. (a) Percentage of NH_4^+ oxidation (Δ) and TN removal (\bullet) and conductivity (\circ); (b) Profile of nitrogen compounds concentrations: NH_4^+ in the influent (\bullet); NH_4^+ (\circ), NO_2^- (\blacktriangle) and NO_3^- (\square) in the effluent.

Effluent quality

The ammonia concentration in the influent varied between 180 and 400 mg NH_4^+ -N/L according to the batches of wastewater collected in the industry. The values of the total nitrogen concentration in the effluent (ammonia, nitrite and nitrate) achieved in the experiment (Figure 1.b) were in a range below 100 mg N/L, which was the limit value for discharge required by the industry. Only between days 35-40, due to the inhibition of the process by high salt concentrations, this limit was exceeded. The nitrate and nitrite concentrations in the effluent were stable during the operational time, with average values of 30 mg NO_3^- -N/L and 5 mg NO_2^- -N/L, respectively. No accumulation of nitrite was observed. Only a punctual value around 200 mg N- NO_2^- /L was measured when the anammox process failed, on days 35-40. Furthermore, the nitrate concentration measured in the effluent coincided with the expected value for the anammox stoichiometry, which indicates a negligible nitrite oxidation activity, since it is reported that the presence of NaCl causes the inhibition of nitrite oxidizing bacteria (Liu *et al.*, 2008).

Granular sludge characteristics

The VSS concentration in the reactor was maintained around 7 g VSS/L. The concentration of solids in the effluent had an average value around 40 mg VSS/L. Values up to 130 mg VSS/L were punctually obtained due to the flotation of some granules caused by the entrapment of the N_2 gas produced in their internal core. The average diameter of granules increased during the experimental time from 2.5 to 3.6 mm, as shown by their size distributions (Figure 2).

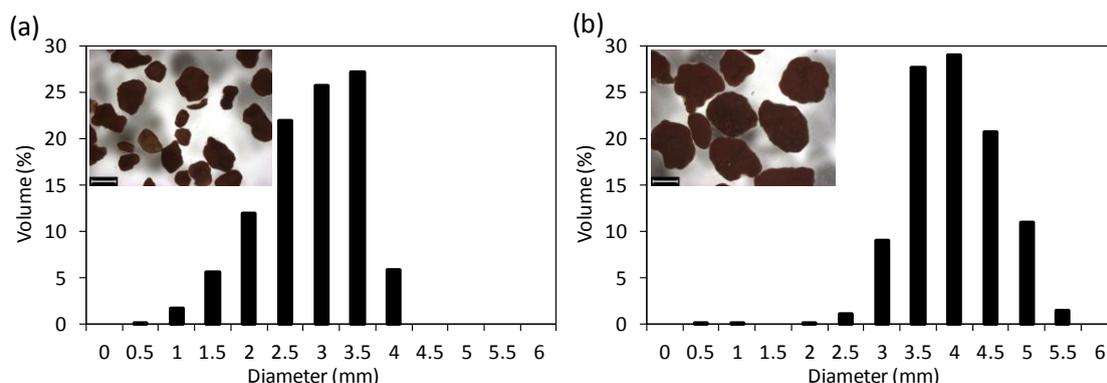


Figure 2. Images and size distributions of granular sludge in percentage of volume respect to the total volume: on day 0 (a) and on day 146 (b). The size bar represents 2 mm.

CONCLUSIONS

Nitrogen removal from effluents produced in the fish canning industry was feasible with the ELAN[®] process (a partial nitrification-anammox process in single unit). The total nitrogen removal achieved was high (80%), but dependent on the salt concentrations. The complete inhibition of anammox bacteria by salt occurred after the sudden increase of its concentration from 3.8 to 15.9 g NaCl/L. This caused one-day break down of the process, although it was reversible. With long-term operation at high salts concentrations a possible alternative should be the adaptation of anammox bacteria but further studies are required. The fact that the ELAN[®] reactor reached the performance required opens the possibility to use this process for nitrogen removal as a post treatment of an anaerobic digester which would be used for organic matter valorisation. This combination is the future of the agro food industry in terms of wastewater treatment since it lowers the energy demand and the sludge production compared to the classic nitrification-denitrification pathway.

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REFERENCES

- Adav, S.S., Lee, D.J., Show, K.Y. and Tay, J.H. (2008). Aerobic granular sludge: Recent advances. *Biotechnology Advances*, **26**(5), 411-423.
- Dapena-Mora, A., Fernandez, I., Campos, J.L., Mosquera-Corral, A., Mendez, R. and Jetten, M.S.M. (2007). Evaluation of activity and inhibition effects on Anammox process by batch tests based on the nitrogen gas production. *Enzyme and Microbial Technology*, **40**(4), 859-865.
- Dapena-Mora, A., Vazquez-Padín, J.R., Campos, J.L., Mosquera-Corral, A., Jetten, M.S.M. and Mendez, R. (2010). Monitoring the stability of an Anammox reactor under high salinity conditions. *Biochemical Engineering Journal*, **51**(3), 167-171.
- Jin, R.-C., Yang, G.-F., Yu, J.-J. and Zheng, P. (2012). The inhibition of the Anammox process: A review. *Chemical Engineering Journal*, **197**(0), 67-79.
- Li, L., Yang, B. and Zhou, P. (2011) Environmental Biotechnology and Materials Engineering, Pts 1-3. Shi, Y.G. and Zuo, J.L. (eds), pp. 522-526.
- Liu, S., Yang, F., Gong, Z. and Su, Z. (2008). Assessment of the positive effect of salinity on the nitrogen removal performance and microbial composition during the start-up of CANON process. *Applied Microbiology and Biotechnology*, **80**(2), 339-348.
- Moussavi, G., Barikbin, B. and Mahmoudi, M. (2010). The removal of high concentrations of phenol from saline wastewater using aerobic granular SBR. *Chemical Engineering Journal*, **158**(3), 498-504.
- Vázquez-Padín, J.R., Morales, N., Gutiérrez, R., Fernández, R., Rogalla, F., Barrio, J.P., Campos, J.L., Mosquera-Corral, A. and Méndez, R. (2013) Implications of full scale implementation of an anammox based process as post-treatment of a municipal anaerobic sludge digester operated with co-digestion, *Water Science and Technology*, in press, doi:10.2166/wst.2013.795.
- Yang, J., Zhang, L., Hira, D., Fukuzaki, Y. and Furukawa, K. (2011). Anammox treatment of high-salinity wastewater at ambient temperature. *Bioresour. Technol.*, **102**(3), 2367-2372.