Anoxic biodesulphurisation of WWTP biogas using previously nitrified digestate centrate

Feliu Sempere*,[1], Camino Sánchez[1], Ángela Baeza-Serrano[1], Tatiana Montoya[1], Vicente Fajardo[1], Gloria Fayos[2]

[1]Global Omnium Medioambiente S.L., fesena@globalomnium.com
[2]Empresa General Valenciana del Agua S.A.

INTRODUCTION

Anaerobic digestion has taken on a very important role in the technical and economic management of wastewater treatment plants (WWTPs), because in addition to removing pathogens and stabilising biosolids, it also enables the valorisation of volatile solids into biogas and co-digestion with other organic wastes to increase biogas yield.

In WWTPs biogas is normally used in boilers for drying sewage sludge, and in combined heat and power (CHP) engines to produce electricity and useful thermal energy, decreasing the dependence of the installations on external energy and promoting renewable energy sources. In this context, an essential requirement is that the biogas that is produced be of high quality to decrease technical maintenance of the boilers and CHP units, so biogas impurities such as hydrogen sulphide (H_2S) and siloxane compounds, among others such as ammonia and volatile organic compounds, must be removed.

The H_2S generated in anaerobic digesters is usually controlled by dosing ferric salts, and using activated carbon filters to further remove H_2S, siloxane and volatile organic compounds. Both strategies have an economic impact and increase WWTP operating costs, being biological desulphurization and specifically under anoxic conditions a potential technical and economical alternative. In this sense, nitrification of centrate from anaerobic sewage sludge digestion presents a major opportunity as an electron acceptor in anoxic biogas biodesulphurisation, avoiding to purchase chemical nitrate and reducing total nitrogen recirculated to WWTP headworks.

The objective of the work presented here was to demonstrate the effectiveness of biodesulphurisation of biogas using biogenic nitrate from centrate nitrification in anoxic suspended biomass bioreactors (SBBs), aiming to avoid the reported operational problems normally found in biotrickling filters due to elemental sulphur (S^0) bed clogging.

MATERIALS AND METHODS

Centrate and biogas streams treated came from a WWTP treating 152402 population equivalent.

CENTRATE NITRIFICATION

- Laboratory scale: experiments carried out in two 1.5 L batch reactors (hydraulic residence time (HRT) of 1.0-7.0 days, ammonium inlet loads (ILs) of 3.7-30.8 gN m^{-3} h^{-1}) to obtain design criteria to scale-up the process:
  - R1: under O_2 saturation and lower centrate loads.
  - R2: O_2 < 1-2 mg L^{-1}.
- Pilot scale: 4 m^3 aerobic reactor, under semicontinuous centrate feeding (HRT 1.6-19.3 days, ILs of 0.0-18.0 gN m^{-3} h^{-1}).

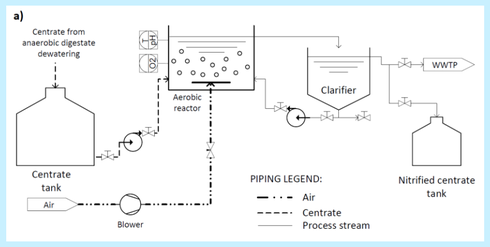

Fig. 1 – Centrate nitrification pilot plant set-up.

BIOGAS DESULPHURISATION

- Two SBBs operated in parallel, at 2.8-14.8 min gas residence time (GRT).
- Start-up using WWTP activated sludge.
- Clarifiers installed to avoid biomass-wash-out.
- $NaHCO_3$ supplied every 7-10 days as alkalinity source.

Fig. 2 – Biodesulphurisation pilot plant.

RESULTS

CENTRATE NITRIFICATION – Laboratory scale

- Lower centrate loads in R1 than R2 decreased NH_3 equilibrium concentrations, avoiding inhibition of ammonia oxidising bacteria (AOB) and nitrite oxidising bacteria (AOB). ⇨ HRTs shorter in R1.
- At higher centrate loads nitrite was detected due to inhibition of NOB, regardless of O_2 concentration. ⇨ NOB depleted in both reactors. Enrichment in AOB to 50 - 53% abundance.

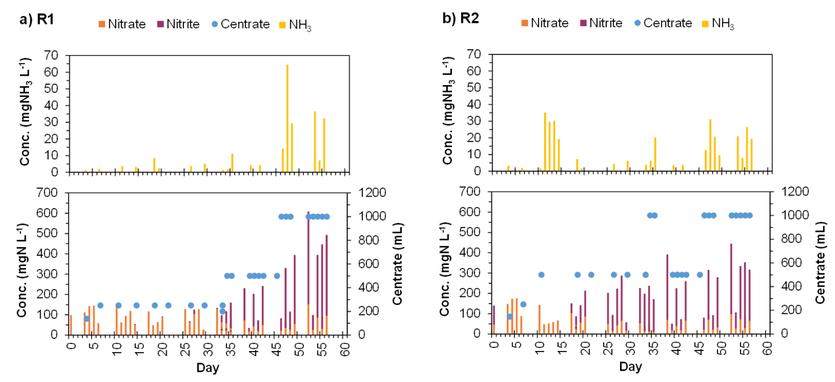

Fig. 3 – Evolution of nitrate, nitrite, free ammonia and centrate in: a) R1, and b) R2..

CENTRATE NITRIFICATION – Pilot scale

- Semicontinuous centrate feeding avoided AOB and NOB inhibition.
- Nitrite was only measured sporadically, and also corresponded to alkalinity accumulation.

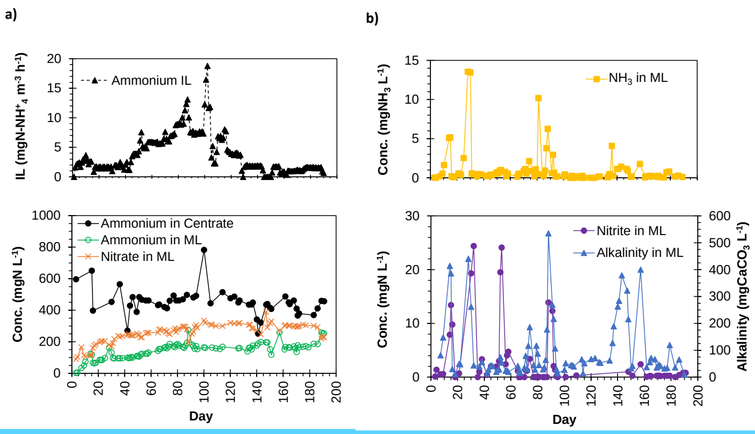

Fig. 4 – Evolution in the pilot scale nitrification reactor of the concentration of: a) ammonium in centrate, ammonium IL, ammonium and nitrate in mixed liquor (ML), and, b) nitrite, alkalinity and free ammonia in ML.

BIOGAS DESULPHURISATION

- Short start-up, only 21 days.
- Both nitrate and alkalinity in the liquid medium had a critical effect on H_2S removal efficiency (RE) (Fig. 5).
- At nitrate >10 mgN L^{-1} and alkalinity >100 mg$CaCO_3$ L^{-1} high H_2S RE values were obtained, regardless of H_2S concentration treated (Fig. 6) and operational temperature (even down to 10 °C).

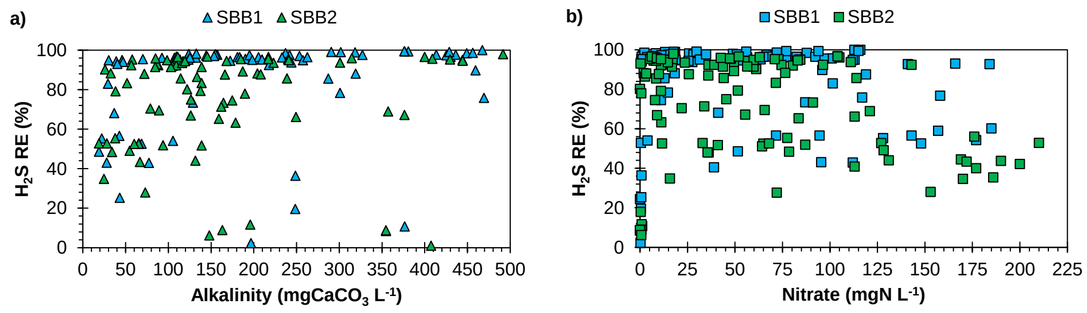

Fig 5 – H_2S RE versus: a) alkalinity in the liquid medium, b) nitrate in the liquid medium.

- At GRT of 5.9 min average RE of 90-95% were achieved, decreasing RE in SBB2 at 3.8 min despite lower average H_2S concentrations were treated, but still CHP H_2S concentration limits were met (Table 1).
- Due to H_2S partial oxidation to S^0 pH ranged 5.5-6.8 without automatic control ⇨ Decrease operational costs.
- Savings per kg H_2S day^{-1} treated of 14 € day^{-1} (activated carbon), and 25 € day^{-1} (ferric chloride) are estimated.

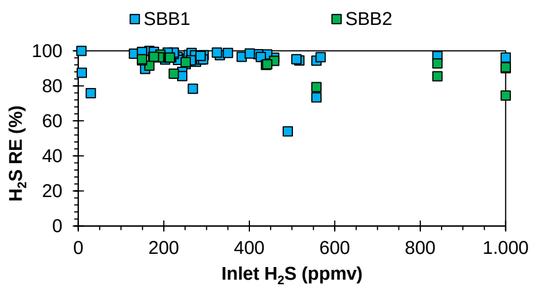

Fig 6 – H_2S RE versus H_2S inlet concentration in both SBBs at 5.9 min GRT with nitrate and alkalinity in the liquid medium above 10 mgNL^{-1} and 100 mgCaCO$_3$ L^{-1}.

	GRT (min)	Inlet H_2S (ppmv)	Outlet H_2S (ppmv)	H_2S (RE)
SBB1	5.87 ± 1.83	321 ± 205	16 ± 24	95%
SBB2	5.90 ± 1.98	457 ± 270	46 ± 39	90%
SBB2	3.81 ± 0.95	247 ±122	33 ± 34	86%

Table 1 – SBBs performance at different GRT with nitrate and alkalinity in the liquid medium above 10 mgNL^{-1} and 100 mgCaCO$_3$ L^{-1}.

CONCLUSIONS

- Semi-continuous feeding of digestate centrate allowed NOB adaptation to achieve full nitrification, 60-83% up to ammonium ILs of 19 gN m^{-3} h^{-1}. The resulting nitrate-rich stream was shown to be an adequate source of nitrate as electron acceptor for successful long-term anoxic biogas biodesulphurisation.
- H_2S concentrations in the outlet stream below the requirements of CHP engines (<100 ppmv) were obtained.
- This work demonstrates the feasibility of the combined process for H_2S treatment, potential valorisation of precipitated elemental sulphur and a reduction in the reagents currently used to control H_2S (ferric chloride and activated carbon). Centrate feeding should be automatised based on liquid medium probes and/or H_2S concentrations in the outlet stream.

+ INFO: Sempere et al. (2022). Journal of Hazardous Materials, 439: 129641. https://doi.org/10.1016/j.jhazmat.2022.129641.

Fondo Europeo de Desarrollo Regional
Una manera de hacer Europa
UNIÓN EUROPEA
"Proyecto cofinanciado por los fondos FEDER, dentro del Programa Operativo FEDER de la Comunitat Valenciana 2014-2020"
GENERALITAT VALENCIANA
IVACE INSTITUT VALENCIÀ DE COMPETITIVITAT EMPRESARIAL

AKNOWLEDGEMENTS
This work was supported by State Research Agency of the Spanish Ministry of Science and Innovation (grant agreement PTQ2019-010456/AEI/10.13039/501100011033) and by the Valencian Institute of Business Competitiveness (IVACE) through the European Regional Development Fund (ERDF) of the European Union (grant agreement IMIDCA/2020/13). The authors thank laboratory and maintenance staff for their continuous support, and to the Public Entity of Wastewater Sanitation (EPSAR) of the Valencian Community (Spain), attached to the Department of Agriculture, Rural Development, Climate and Ecological Transition, owner of the WWTP where the work has been carried out.

Programa Torres Quevedo
AYUDAS A LA CONTRATACIÓN DE PERSONAL INVESTIGADOR
GOBIERNO DE ESPAÑA MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES