Process Biochemistry 48 (2013) 1368–1374

Contents lists available at ScienceDirect

Process Biochemistry

journal homepage: www.elsevier.com/locate/procbio

Post-treatment of fish canning effluents by sequential nitrification and autotrophic denitrification processes

Fajardo Carmen[a,b,*], Mosquera-Corral Anuska[a], Campos José Luis[a], Méndez Ramón[a]

[a] Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, Rúa Lope Gómez de Marzoa, s/n, 15782 Santiago de Compostela, Spain
[b] Department of Biotechnology, Universidad Autónoma Metropolitana, División CBS, San Rafael Atlixco 186, Col. Vicentina, C.P. 09840 México, Mexico

ARTICLE INFO

Article history:
Received 4 August 2011
Received in revised form 30 May 2013
Accepted 2 June 2013
Available online 14 June 2013

Keywords:
Autotrophic denitrification
Fish canning effluent
Nitrification
Nitrogen
Sulphide

ABSTRACT

In this research study a nitrifying/autotrophic denitrifying system was used for the post-treatment of an effluent coming from an anaerobic digester treating the wastewater produced in a fish canning industry. The nitrifying reactor achieved 100% of ammonia oxidation into nitrate. The effluent from this unit was fed to the autotrophic denitrifying reactor which treated a maximum sulphide loading rate (SLR) of 200 mg S^{2-}/L d with removal percentages of 100% and 30% for sulphide and nitrate, respectively. The low nitrate removal efficiency is attributed to sulphide limitations.

The operational costs of this system were estimated as 0.92 €/kg $N_{removed}$, lower than those for conventional nitrification/denitrification processes. For nitrogen removal the SHARON/anammox processes is the cheapest option. However the combination of nitrification and autotrophic denitrification (using elemental sulphur) processes would present a better operational stability compared to the SHARON/anammox system.

1. Introduction

Discharge of effluents produced in the fish-canning industry contributes significantly to the contamination of the environment in the littoral zones of the region of Galicia (Spain) [1]. These effluents have a salinity similar to sea water (up to 41 g Cl^-/L, 12 g Na^+/L and 3.3 g SO_4^{2-}/L), high organic matter content (3–120 g COD/L), and high protein concentrations (0.7–33.8 g/L) (Table 1). Anaerobic digestion of these wastewaters allows COD removal percentages around 70–90%, leading to the formation of high levels of ammonium (up to 5 g N/L) due to protein degradation, producing effluents with a low C/N ratios [9,11,12].

The post-treatment of these effluents by conventional nitrification–denitrification processes is not economically feasible since an additional carbon source is needed. Therefore nitrogen removal by autotrophic processes such as nitrification–autotrophic denitrification or nitrification–anammox is an advisable alternative.

The effluent of an anaerobic digester fed with fish canning wastewater has been successfully treated in a combined SHARON–anammox system [13,14] which allowed the removal of nitrogen loads up to 0.45 g N/L d (calculated taking into account the total volume of the needed system) with an average N removal efficiency of 67%. In order to operate the system under stable conditions, the anammox reactor was fed with an effluent characterized by a NO_2^--N/NH_4^+-N ratio lower than 1 g/g.

High salts concentrations contained in the wastewater from the fish canning industry are known to have negative effects on both organic matter and nitrogen removal processes. Values of IC_{50} (50% of inhibition) have been reported for nitrifying and anammox biomasses of 5.8 and 13.3 g NaCl/L, respectively [15,16]. Nevertheless, results obtained by several authors showed that autotrophic denitrifying biomass was able to operate under salt concentrations up to 33 g NaCl/L without negative effects on its efficiency [17–20].

Fish cannery wastewater also contains high sulphate concentration. Sulphate is reduced into hydrogen sulphide during anaerobic digestion. This compound must be removed from the biogas previously to the use of the biogas for energy generation [21]. Kleerebezem and Méndez [11] proposed to separate H_2S from methane by absorption in a liquid phase and then to use it as electron donor to remove nitrate in a post-denitrification step. Therefore, the combination of nitrification and autotrophic denitrification seems to be a suitable option to remove nitrogen and sulphide compounds from the effluent of an anaerobic digester in operation in a fish cannery.

Autotrophic denitrification was successfully applied to remove both nitrogen and sulphide from industrial wastewater [22]. And,

* Corresponding author at: Department of Biotechnology, Universidad Autónoma Metropolitana, División CBS, San Rafael Atlixco 186, Col. Vicentina, C.P. 09840 México, Mexico. Tel.: +52 55 58044723; fax: +52 55 58044711.
E-mail addresses: carmen.fajardo141@gmail.com, cfaj@xanum.uam.mx (F. Carmen).

1359-5113/$ – see front matter.
http://dx.doi.org/10.1016/j.procbio.2013.06.005

Table 1
Characteristics of the effluents generated by fish canneries.

Parameter (g/L)										Reference
COD_t	COD_s	Oil grease	TKN	NH_4^+-N	Protein	pH	TSS	Cl^-	SO_4^{2-}	
2.90–4.00	1.10–1.30		0.60–0.65	0.38–0.41	0.70–0.84	7.57–7.86	–	–	–	[2]
12.36–5.40	9.71–16.50		–	–	3.34–19.20	–	–	7.8–19.5	0.59–2.70	[3]
–	5.60–6.30		0.48–0.80	–	3.00–5.00	6.00–7.00	11.00–22.00	–	0.98–3.30	[4]
4.80–18.50	4.10–15.80		–	0.60–2.00	–	6.60–7.50	1.30–2.00	7.1–9.1	–	[5]
120.85	96.65		–	6.39	33.82	–	17.93	10.7	–	[6]
50.00–60.00	–		5.00–6.00	2.00–3.00	15.00–18.00	–	–	–	–	[7]
8.00–26.00	7.00–25.00	0.5–1.7	1.20–4.00	0.20–0.70	–	6.50	1.00–2.10	9.3–41.5	–	[8]
6.00			0.54	0.09	–	4.50	6.50	10.8–18.5	2.40	[9]
11.70–25.00			–	0.10–0.20	7.00–12.60	6.00–6.50	0.40–1.10	1.6–7.6	0.20–0.60	[10]

nowadays, its application is gaining interest due to its possible use to treat municipal wastewater containing sulphate [23–26] and its combination with the anammox process to treat industrial wastewater [27] in order to achieve low operational costs.

The objective of this study is to research the operation of a combined system where the nitrification and autotrophic denitrification processes take place sequentially to remove nitrogen from the effluent of an anaerobic digester treating the wastewater from a fish canning industry. Sulphide will be used as electron donor to reduce the nitrate generated during the nitrification step.

2. Materials and methods

2.1. Reactors description

2.1.1. Nitrifying reactor

An activated sludge unit consisting of a mixing basin with a useful volume of 0.5 L coupled to an external settler of 1.0 L was operated during 185 days. The system was operated at a hydraulic retention time (HRT) of 1 day and at room temperature (25.0 ± 0.5 °C). In the aeration basin the pH value ranged from 7.5 to 8.5 and the dissolved oxygen concentration was higher than 2 mg O_2/L. A peristaltic pump was used to feed the reactor and a mammoth pump to recirculate the sludge from the settler to the aeration basin. The system was inoculated with activated sludge (1.52 g VSS/L) collected from the aerobic reactor in operation in a municipal wastewater treatment plant.

The reactor was fed with the effluent from an anaerobic digester treating the wastewater of a fish canning industry (Table 2). As the NH_4^+-N/IC ratio of this effluent was low of 1.09 (g NH_4^+-N/g C), an amount of 1.6 g/L of $NaHCO_3$ were added to avoid alkalinity limitations during nitrification. The ammonia loading rate (ALR) was gradually increased by decreasing the dilution applied to the effluent collected from the anaerobic digester (Table 3).

2.1.2. Denitrifying autotrophic reactor

The autotrophic denitrification was carried out in a sequencing batch reactor (SBR) with a working volume of 1 L. The reactor was inoculated with 1000 mL of sludge (concentration: 3.85 g VSS/L; maximum specific sulphide oxidizing activity: 200 mg S^{2-}/g VSS d) obtained in a batch reactor fed with sulphide and nitrate [28]. The temperature of operation was maintained at 30 ± 1 °C by means of a thermostatic jacket. Complete mixture inside the reactor was achieved with a mechanical stirrer operated at 150 rpm. The pH was maintained at 7.5 by controlled addition of acid or base solutions (HCl 0.5 M, NaOH 0.5 M). The HRT was fixed at 1 day. The head space of the reactor was flushed with a mixture of 95% Ar and 5% CO_2 to maintain anoxic conditions.

The SBR was operated in cycles of 6 h controlled by means of a PLC (CPU224, Siemens). The operational cycle comprised four phases: feeding in stirring conditions (300 min), stirring (30 min), settling (15 min) and effluent withdrawal (15 min). A volumetric exchange ratio of 25% was applied. The reactor was operated during 227 days in four operational stages (Table 4). In Stage I the reactor was fed with a mineral medium consisting in two solutions (A: 1.27 g $Na_2S{\cdot}3H_2O$/L and 3.0 g $NaHCO_3$/L, and B: mineral medium according to Fajardo et al. [28]. Both solutions were fed to the reactor separately at the same flow rate (0.5 L/d). The final nitrate and sulphide concentrations were fixed at 142 mg S^{2-}/L and 453 mg NO_3^--N/L and the S^{2-}/NO_3^- ratio was of 0.13 (mol/mol). From the second stage the solution B was replaced by the effluent of the nitrifying reactor treating the fish canning industry effluent (corresponded to Stage IV of operation of the nitrifying reactor). The inlet nitrogen concentration was gradually increased by the change of A:B flow ratio, registering concentrations of nitrogen from 149 mg NO_3^--N/L to 262 mg NO_3^--N/L. The composition of solution A was kept constant, with exception of the fourth stage when the concentrations were increased to 1.65 g $Na_2S{\cdot}3H_2O$/L and 3.0 g $NaHCO_3$/L respectively. The sulphide concentration ranged from 156 mg S^{2-}/L to 203 mg S^{2-}/L and the S^{2-}/NO_3^- ratio applied varied from 0.28 to 0.45 (mol/mol) in order to simulate those ratios of fish canning industry effluents. The applied sulphide loading rate (SLR) ranged between 140 and 200 mg S^{2-}/L d.

2.2. Nitrifying and autotrophic denitrifying activities

Nitrifying assays were carried out by means of a respirometric method (adapted from [29]). This assay was performed in vials of 15 mL with a liquid volume of 10 mL using a Biological Oxygen Monitor (BOM, YSI 5300) with oxygen selective electrode (YSI 5331) connected to a data acquisition system. The biomass was washed with phosphate buffer (1.43 g/L KH_2PO_4, 7.47 g/L K_2HPO_4). A volume of 10 mL of biomass suspended in the buffer medium was added to each vial. Vials were placed in a thermostatically controlled chamber at 25 °C. Compressed air was used to obtain the oxygen saturation in the liquid medium. The initial nitrogen concentration was fixed in 70 mg N/L. With the measured oxygen consumption rate, the specific activity was calculated as the substrate concentration consumption rate divided by the biomass concentration.