Journal of Environmental Management 215 (2018) 358–365

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Wastewater post-treatment for simultaneous ammonium removal and elemental sulfur recovery using a novel horizontal mixed aerobic-anoxic fixed-bed reactor configuration

R.B.S. Guerrero*, M. Zaiat

Biological Process Laboratory, Center for Research, Development and Innovation in Environmental Engineering, São Carlos School of Engineering, University of São Paulo (EESC/USP), Av. João Dagnone, 1100—Santa Angelina, 13.563-120, São Carlos, SP, Brazil

A R T I C L E I N F O

Article history:
Received 25 March 2017
Received in revised form
26 January 2018
Accepted 17 March 2018

Keywords:
Nitrogen removal
Autotrophic denitrification
Biogas desulfurization

A B S T R A C T

A novel horizontal mixed anoxic-aerobic fixed-bed reactor configuration based on nitrification coupled with autotrophic denitrification using hydrogen sulfide as an electron donor was developed. The nitrification removal efficiency (RE) reached values greater than 99% but was slightly affected by the accumulation of dissolved sulfur species in the liquid phase. The denitrification RE reached 99% with a H_2S inlet load of 28.6 g S m^{-3} h^{-1}, although the use of aluminum polychloride (PAC) as a sulfur coagulant in the anoxic zone affected the buffering capacity of the system and resulted in a decrease in the RE. The performance of the reactor was primarily affected by the buffering capacity of the system, and this effect could be controlled with an increase in the $NaHCO_3$ concentration. The recovery of biogenic elemental sulfur was possible using PAC as a coagulant, although the solid collected at the bottom of the settling tank contained only 1.5% S^0.

1. Introduction

The conventional post-treatment of wastewater for biological nitrogen removal involves a combination of autotrophic nitrification and heterotrophic denitrification (Moraes et al., 2013). However, effluents from anaerobic reactors that treat domestic sewage, which is rich in ammonium and poor in organic matter, require a supplemental external carbon source for denitrification (Waki et al., 2008). The use of hydrogen sulfide (H_2S) from biogas as an electron donor for autotrophic denitrification is a suitable alternative that can reduce costs because biogas is produced during the anaerobic process and is often burned in flares (Santos et al., 2016). However, the use of biogas for energy production is limited due to the presence of H_2S, which is highly corrosive. Therefore, when treating wastewater, simultaneous nitrogen removal and biogas biodesulfurization is very attractive.

Certain groups of microorganisms derive energy from the oxidation of inorganic compounds, such as reduced sulfur compounds. Bacteria from the genera *Thiobacillus* and *Thiosphaera* are able to oxidize reduced sulfur compounds (S^{2-}, $S_2O_3^{2-}$, SO_3^{2-} and S^0) using nitrate (NO_3^-) as the final electron acceptor under anoxic/anaerobic conditions (Maslon and Tomaszek, 2009). The stoichiometric reactions involved in aerobic nitrification and autotrophic denitrification under anoxic/anaerobic conditions using sulfide as the electron donor occur according to equations (1)–(5) (Hoffmann et al., 2007; Soreanu et al., 2008).

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (1)$$

$$5H_2S + 8NO_3^- \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O + 2H^+ \quad (2)$$

$$5H_2S + 2NO_3^- \rightarrow 5S^0 + N_2 + 4H_2O + 2OH^- \quad (3)$$

$$H_2S + 4NO_3^- \rightarrow SO_4^{2-} + 4NO_2^- + 2H^+ \quad (4)$$

$$H_2S + NO_3^- \rightarrow S^0 + NO_2^- + H_2O \quad (5)$$

Reactors with different configurations have been studied to determine whether they can perform nitrogen removal using H_2S as the electron donor for autotrophic denitrification. These reactors include aerobic-anoxic fixed-bed reactors (Pantoja Filho et al., 2014), bubble column reactors (Deng et al., 2009), and semi-

---

* Corresponding author.
E-mail addresses: rsolcia@gmail.com, resolcia@yahoo.com.br (R.B.S. Guerrero), zaiat@sc.usp.br (M. Zaiat).

https://doi.org/10.1016/j.jenvman.2018.03.074
0301-4797/

partitioned reactors (Waki et al., 2008). Researchers have examined the use of dissolved sulfide in the liquid phase as an electron donor (Moraes et al., 2011, 2012, 2013; Souza and Foresti, 2013), and the inhibition of nitrification by sulfide has been observed. Reactors in which nitrification and denitrification are conducted in different chambers or zones represent better alternatives for avoiding inhibition. The aerobic-anoxic fixed-bed reactor studied by Pantoja Filho et al. (2014) is a vertical fixed-bed reactor in which nitrification and denitrification are conducted in different zones. In this configuration, biogas is injected at the bottom of the reactor, and the unused biogas and air are discharged together at the top. In contrast, in the semi-partitioned reactor developed by Waki et al. (2008), the nitrification and denitrification processes also occur in a single reactor but without a mixture of unused biogas and air. This feature is important for two reasons: methane contamination with oxygen is prevented, thus permitting post-energy generation, and the mixture of biogas and oxygen can be explosive. This case illustrates the advantages of using horizontal reactors instead of vertical reactors. However, the need to stir and recirculate the sludge as proposed by Waki et al. (2008) could be elliminated by the use of an immobilized cell reactor.

Another advantage associated with the use of H_2S as an electron donor is the possibility of recovering elemental sulfur, which is a product of partial H_2S oxidation. Elemental sulfur is extremely useful, particularly for the manufacture of insecticides and the production of sulfuric acid and fertilizers. However, biogenic sulfur is colloidal, which increases the difficulty of separating solids from liquid (Chen et al., 2016). Using aluminum polychloride (PAC) as a coagulant, Chen et al. (2016) achieved a 97.53% S^0 flocculation rate.

The aim of the present work was to study the technical feasibility of the post-treatment of wastewater for the simultaneous removal of ammonium and recovery of elemental sulfur via a combination of aerobic nitrification and autotrophic denitrification in a novel mixed aerobic-anoxic horizontal fixed-bed reactor (MAAFBR) configuration using H_2S for denitrification. The advantage of this novel reactor configuration is the use of a fixed bed and the increased biomass retention compared with that of suspended-cell reactors. Furthermore, elemental sulfur can be obtained as a product from the process and recovered in a settling tank.

2. Materials and methods

2.1. Experimental setup

The experimental system (Fig. 1) was composed of a horizontal mixed aerobic-anoxic fixed-bed reactor combined with a system for elemental sulfur recovery (slow mixing container and settling tank). In this configuration, aerobic nitrification and H_2S-driven denitrification occurred on opposite sides of the same horizontal reactor due to the different experimental conditions of each side, which favored the development of nitrifying and denitrifying communities in the different zones of the reactor. This biological reactor was coupled with a physical-chemical system that allowed separation of the elemental sulfur produced in the anoxic zone. PAC (16.36% Al_2O_3) was used as a sulfur coagulant.

The horizontal cylindrical acrylic reactor was fabricated with an inner diameter of 96 mm and a length of 890 mm (4.0 L of liquid phase and 1.2 L of headspace). The useful volume for the nitrification and denitrification zones was 2.0 L each. The active length was packed with 14 fixed polyurethane foam strips (23 kg m^{-3}, 95% porosity and average pore size of 543 μm), which constituted 17.91 g of the support material. The reactor had nine sampling ports distributed along the column. A partition divided the headspace of the reactor into two parts to prevent the gases from mixing during discharge. At the bottom of the reactor, two gas stone bubble bars were placed on each side for air and N_2/H_2S dispersion.

Air was supplied to the aerobic zone (2.2–3.5 L min^{-1}) by an aquarium air pump, and synthetic N_2/H_2S was supplied to the anoxic zone (1.0 L min^{-1}). H_2S was chemically produced by the reaction between Na_2S and HCl (Ramírez et al., 2009) and used to feed the bioreactor.

The PAC was supplied in the anoxic zone at 3.0 mL dia^{-1}.

2.2. Inoculum and feed composition

The inoculum was composed of 50% activated sludge obtained from a sanitary wastewater treatment plant (51.8 g total volatile solids (TVS) L^{-1}) and 50% sludge from an up-flow anaerobic sludge blanket (UASB) reactor for the treatment of poultry slaughterhouse wastewater (51.0 g TVS L^{-1}). The granules from the UASB and the aerobic flocs inoculum were fragmented before inoculation.

The composition of the synthetic wastewater (Table 1) simulated the effluents from UASB reactors that treat domestic sewage (adapted from Canto et al. (2008)). Previous reports have shown that the N-NH_4^+ and P-PO_4^{2-} concentration in effluents from UASB

Table 1
Synthetic wastewater composition.

Components	Concentration (mg L^{-1})
NH_4Cl	153.0
KH_2PO_4	65.9
NaCl	50.0
$MgCl_2$ $6H_2O$	1.4
$CaCl_2$ $2H_2O$	0.9
$NaHCO_3$	500.0–1500.0
Acetic Acid	3.7
Isobutyric Acid	1,0
Butyric Acid	0.7
Isovaleric Acid	3.14
Ethanol	11.5

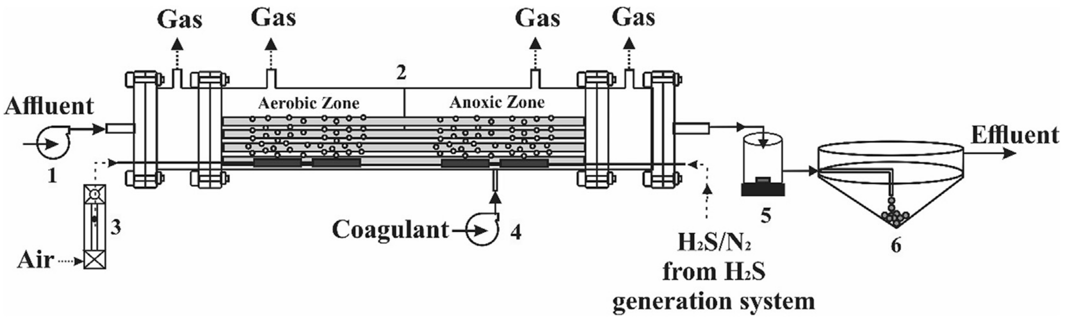

Fig. 1. 1. Synthetic wastewater pump; 2. Horizontal reactor; 3. Air flowmeter; 4. Coagulant pump; 5. Slow mixing container; and 6. Settling tank.