Bioresource Technology 187 (2015) 282–287

Contents lists available at ScienceDirect

Bioresource Technology

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

Effects of operation mode on self-alkalization of high-load denitrifying reactor

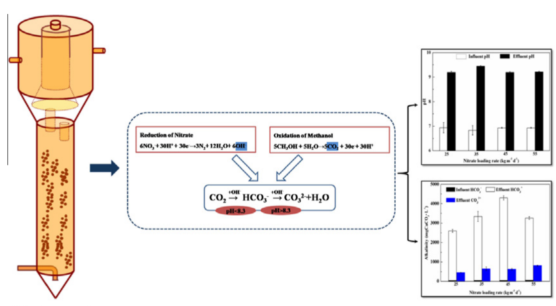
Wei Li, Chenxu Li, Xiaoyu Lin, Yan Liu, Ghulam Abbas, Ping Zheng *

Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, China

HIGHLIGHTS

- Self-alkalization intensity of high-load denitrifying reactors was investigated.
- Mechanism of self-alkalization under different operation modes was revealed.
- Decrease of HRT was optimal operation mode for high-load denitrifying reactor.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 February 2015
Received in revised form 11 March 2015
Accepted 12 March 2015
Available online 19 March 2015

Keywords:
Denitrification
High-load reactor
Operation mode
Self-alkalization

ABSTRACT

To study the alkalization issue and its potential effects on high-load denitrifying system, the effects of operation mode on self-alkalization of high-load denitrifying reactor were investigated. The results showed that both the increase of substrate concentration and decrease of hydraulic retention time (HRT) can induce notable self-alkalization of high-load denitrification reactor (with the nitrogen loading rate (NLR) higher than 25 kg N m^{-3} d^{-1}). The effluent pH surpassed the 9.20 when the influent pH value was 7.0 ± 0.1. The self-alkalization of denitrification process originated from the nitrate reduction, while the methanol oxidation could alleviate the self-alkalization by neutralizing OH^- and setting up a buffering system of HCO_3^-/CO_3^{2-}. At the same NLR, the self-alkalization induced by increase of substrate concentration was remarkably stronger than that induced by decrease of HRT. Keeping the nitrate concentration below inhibition concentration improved the performance of high-load reactor and alleviated the self-alkalization.

1. Introduction

Denitrification, the reduction of nitrate to N_2 under an anoxic condition, is widely applied to the treatment of domestic and industrial wastewaters (Kesserü et al., 2003; Kapoor and Viraraghavan, 1997). Recently, the performance of this technology has been improved greatly, especially for high nitrate-containing (NO_3-N >1000 mg L^{-1}) wastewaters (Li et al., 2013; Adav et al., 2010). The research on high-rate denitrifying reactor has remarkably promoted the development of nitrogen removal technology, saving investment and reducing land requirements (Rabah and Dahab, 2004). However, few studies have been conducted in recent years on this technology (Lew et al., 2012; Franco et al., 2006). The maximum nitrogen loading rate (NLR) was 25 kg N m^{-3} d^{-1} which was reported for the first time in 1987 (Bode et al., 1987).

Denitrifying bacteria are the functional source of denitrifying reactor and the reactor performance largely depends on the bacterial growth and metabolism (Lew et al., 2012; Volcke et al., 2012). The denitrifying bacteria have their pH range for growth and

* Corresponding author. Tel./fax: +86 0571 88982819.
E-mail address: pzheng@zju.edu.cn (P. Zheng).

http://dx.doi.org/10.1016/j.biortech.2015.03.063
0960-8524/

extreme environmental pH inhibits the activity of the denitrifying bacteria. The self-alkalization of high-load denitrification caused pH higher than 9.3, which inhibited the bacterial activity significantly and deteriorated the reactor performance (Glass and Silverstein, 1998; Li et al., 2014a; Jin et al., 2012a). However, few studies have been conducted to investigate the mechanism of self-alkalization and its relationship with the bio-removal of nitrogen and chemical oxygen demand (COD).

In the bio-reactor operation, increasing substrate concentration and shortening hydraulic retention time (HRT) are the two common operation modes to elevate the loading rate (Jin et al., 2012b; Li et al., 2014a). So far, the effect of operation modes on the self-alkalization of high-load (NLR > 25 kg N m^{-3} d^{-1}) denitrification was still in scarce.

Recently, a novel denitrifying automatic circulate (DAC) reactor has been developed successfully, and its nitrogen removal rate (NRR) has reached 55 kg N m^{-3} d^{-1} (Li et al., 2014a). The objective of this study was to investigate the characteristics and mechanism of self-alkalization in high-load denitrifying reactor using two different operation modes.

2. Methods

2.1. Synthetic wastewater

Sodium nitrate ($NaNO_3$) and carbon resource (CH_3OH) were added to get concentrations of 1 g NO_3^--N L^{-1} and 5 g COD L^{-1}, respectively. Other concentrations were prepared with the same reagents as per requirement. The constituents of the mineral medium were (g L^{-1}): 0.05 KH_2PO_3, 0.14 $CaCl_2$, 0.10 $MgSO_4{\cdot}7H_2O$ and 1.0 ml L^{-1} of trace elements solution. The trace elements solution contained (g L^{-1}): 5 EDTA, 5 $MnCl_2{\cdot}4H_2O$, 3 $FeSO_4{\cdot}7H_2O$, 0.05 $CoCl_2{\cdot}6H_2O$, 0.04 $NiCl_2{\cdot}6H_2O$, 0.02 H_3BO_3, 0.02 $(NH_4)_6Mo_7O_2{\cdot}4H_2O$, 0.01 $CuSO_4{\cdot}5H_2O$ and 0.003 $ZnSO_4$. The pH of synthetic medium was in the range of 7.0–7.2.

2.2. Reactor operation

The experiments were carried out in two parallel plexiglass-made DAC reactors (designated as R1 and R2) with inner diameter of 0.06 m, height of 0.45 m and effective volume of 1.25 L (Fig. S1) (Li et al., 2014b). 1.0 L denitrifying granular sludge obtained from another lab-scale DAC reactor with VSS/SS of 0.53 ± 0.07 (Li et al., 2013) was used as tested sludge. Previous study via polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) analysis showed that the parent sludge was dominated by *Hyphomicrobium zavarzinii*, *Thauera* sp. and *Flavobacterium glaciei* (Wang et al., 2014). Both the reactors were started at the NLR of 25 kg N m^{-3} d^{-1} with a fixed effluent recycle ratio (recycling flow to inflow ratio) of 2.0. When the performance of both the reactors was stable, the loading rates of R1 and R2 were elevated progressively by increasing substrate concentration and shortening HRT, respectively. The temperature was in the range of 30.0 ± 1.0 °C. The performances of the reactors were shown in Table S1.

2.3. Analytical methods

The influent and effluent liquid samples were taken with a syringe and filtered with disposable Millipore filter units (0.45 μm pore size) for analyses of pH, alkalinity, calcium, nitrate, nitrite, ammonium and COD. The pH, alkalinity, calcium, nitrate, nitrite, ammonium, COD, suspended solids (SS) and volatile suspended solids (VSS) were determined according to the standard methods (APHA, 2005). The gas samples were taken with a syringe and the contents of N_2, N_2O and CO_2 were determined immediately using a gas chromatography (Agilent 6890, United States) (APHA, 2005).

2.4. Specific nitrate utilization activity assays

The batch assays were performed in serum bottles with a volume of 120 ml. The synthetic wastewaters were prepared with different $NaNO_3$ concentrations. The NO_3^--N/COD ratio was fixed at 5.0. The pH was adjusted as needed (7.0–7.2). The biomass concentration was about 1 gVSS L^{-1}. The temperature was 30 ± 1 °C. Gas and liquid phases were purged with 95% Ar-5% CO_2 for 20 min. The serum bottles were sealed tightly with butyl rubber caps. The NO_3^--N concentration was monitored during the incubation. Specific nitrate utilization activity was estimated from the nitrate removal rate and biomass concentration.

2.5. Calculation

2.5.1. Buffering power (β) calculation

For a steady-state denitrification process, the total buffer concentration remains constant. Therefore, the following mathematical expression (1) for buffering power of a weak acid, acting as a closed buffer, can be applied (Sperelakis, 2012):

$$\beta = \frac{2.303[A]_T K'_a[H^+]}{(K'_a + [H^+])^2} \tag{1}$$

where β is the buffering power, mM·pH^{-1}; K'_a is the apparent dissociation constant, ($10^{-10.30}$, 30 °C); $[H^+]$ is the concentration of H^+, mM; $[A]_T$ is the total acid ($[HCO_3^-] + [CO_3^{2-}]$), mM.

2.5.2. Carbonate system calculation

This study assumed that heterotrophic denitrifying microbes used the organic substrate (methanol) both as fuel and as externally carbon resource. Besides yielding organic molecules for biomass synthesis, CO_2 is the sole oxidized product. All of CO_2 dissolved in the alkaline reaction solution and most of it formed calcium carbonate (Li et al., 2014a), little CO_2 returned to the atmosphere. This was also confirmed by the off-gas with CO_2 concentration below the detection limit. The carbon element conservation was summarized in the following Eq. (2):

$$C_{(CO_3^{2-})} + C_{(HCO_3^-)} = \frac{COD_{in} - COD_{eff}}{1.5 \times 32} - \frac{VSS \times V_R \times 0.53}{SRT \times Q_R \times 12} - \left(C_{(In\ Ca^{2+})} - C_{(Eff\ Ca^{2+})}\right) \tag{2}$$

where $C_{(CO_3^{2-})}$ and $C_{(HCO_3^-)}$ are CO_3^{2-} and HCO_3^- concentration, respectively, mol L^{-1}; COD_{in} and COD_{eff} are influent COD and effluent COD concentration, respectively, mg L^{-1}; 1.5 is for the 1.5 gCOD/ per CH_3OH g; 32 and 12 are relative molar masses of CH_3OH and C, respectively; V_R, Q_R, SRT are efficient reactor volume, L; substrate flow rate, L d^{-1}; sludge retention time, d; respectively. 0.53 is for the content of C element in organic molecule ($C_5H_7NO_2$); $C_{(In\ Ca^{2+})}$ and $C_{(Eff\ Ca^{2+})}$ are influent Ca^{2+} and effluent Ca^{2+} concentration, mol L^{-1}.

2.5.3. Total alkalinity calculation

This study assumed that nitrate or nitrite was converted completely to N_2 besides acting as nitrogen resource for the biosynthesis. This was confirmed by off-gas with N_2O concentration below the detection limit.

$$\Delta C_{(ALK)} = C_{(In\ NO_3-N)} - C_{(Eff\ NO_3-N)} - C_{(Ac\ NO_2-N)} \times 0.6 - \frac{VSS \times V_R \times 0.12}{SRT \times Q_R \times 14} \tag{3}$$