Biochemical Engineering Journal 131 (2018) 24–30

Contents lists available at ScienceDirect

Biochemical Engineering Journal

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

Regular article

Effect of influent pH on biological denitrification using biodegradable PHBV/PLA blends as electron donor

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ARTICLE INFO

Article history:
Received 2 August 2017
Received in revised form 4 November 2017
Accepted 11 December 2017
Available online 15 December 2017

Keywords:
Denitrification
Influent pH
Biodegradable polymer
PHBV/PLA
DNRA

ABSTRACT

Poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/poly (lactic acid) (PHBV/PLA), a biodegradable polymer blend, was used as both carbon source and biofilm carrier in a packed-bed bioreactor. The effect of influent pH on denitrification performance in PHBV/PLA supported denitrification system was further investigated. Results showed that the nitrate removal efficiency kept high level under an alkaline influent while largely decreased under an acidic influent. When the influent pH was 5.68, nitrate removal efficiency was about 34% of that on neutral or alkaline conditions. Meanwhile, dissimilatory nitrate reduction to ammonia process (DNRA) was enhanced on acidic condition. Furthermore, ΔpH (the difference between influent and effluent pH) and effluent TOC both increased on alkaline condition, and they sharply rose to 2.75 and 23.37 mg L^{-1} with an influent pH of 10.38. It was found that there were obvious positive correlations among influent pH, ΔpH and TOC. Moreover, based on the characteristics of microbial hydrolysis and denitrification processes, the effect mechanism of influent pH on nitrate removal was deeply explored. A better knowledge of the effect of influent pH on nitrate removal will be significant for the solid-phase denitrification in practice.

1. Introduction

Nitrate pollution in the surface waters mainly including some lakes and rivers has become a serious issue worldwide [1]. The wastewater with high nitrate concentration will increase the potential risks of eutrophication and toxic algal blooms in these receiving waters [2]. Recently, the government of China has paid attention to the water eutrophication, and issued a series of regulations and rules including “water pollution control action plan”[3] and “urban black odor water remediation work guide”[4]. In response to these policies' requirements, it is urgent to reduce or remove nitrate from wastewater to cope the problems.

Solid-phase denitrification process as an emerging technology has received increasing attention in recent years. It is a new type of heterotrophic biological denitrification in which insoluble biodegradable substances are used as carbon source and biofilm carrier simultaneously [5]. A vast of biopolymers, including poly(ε-caprolactone) (PCL) [6–9], poly(butylene succinate) (PBS) [10,11]; polyhydroxyalkanoates (PHAs) [12–15], poly (L-lactic acid) (PLLA) [16,17], polyvinyl alcohol (PVA) [18], PHBV/PLA[19], starch/PCL [20] and starch/PVA [21], have been widely investigated for nitrate removal due to their good biodegradability. Previous studies have explored the effects of operation parameters (mainly including nitrate loading rate (NLR), temperature, dissolved oxygen (DO) and salinity) on denitrification performance in these solid-phase denitrification systems. It was found that the denitrification rates increased when the NLRs increased properly, while over-loading of nitrate could not improve the denitrification performance [22]. Meanwhile, some studies indicated that the denitrification rate sharply declined when temperature is below optimal. The nitrate removal efficiency at 15 °C was only 55.06% of that at 25 °C in starch/PCL supported denitrification system [23]. Moreover, no significant difference on NO_3^--N removal rates was observed in PCL supported denitrification system when the influent DO ranged from 0.28 to 5.63 mg L^{-1} [24]. Furthermore, it was found that the existence of salinity could improve the nitrate removal efficiency and stability of PBS supported denitrification system for real recirculating aquaculture system effluent treatment [10]. However, there was limited information about the effect of influent pH on denitrification performance in solid phase denitrification systems.

In general, the optimal pH range reported for denitrification process is 7–9, values outside this range can retard the denitrification process [25]. It was reported denitrification was achieved at higher pH of 7.5-9.0, while it was significantly inhibited at pH

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https://doi.org/10.1016/j.bej.2017.12.008
1369-703X/

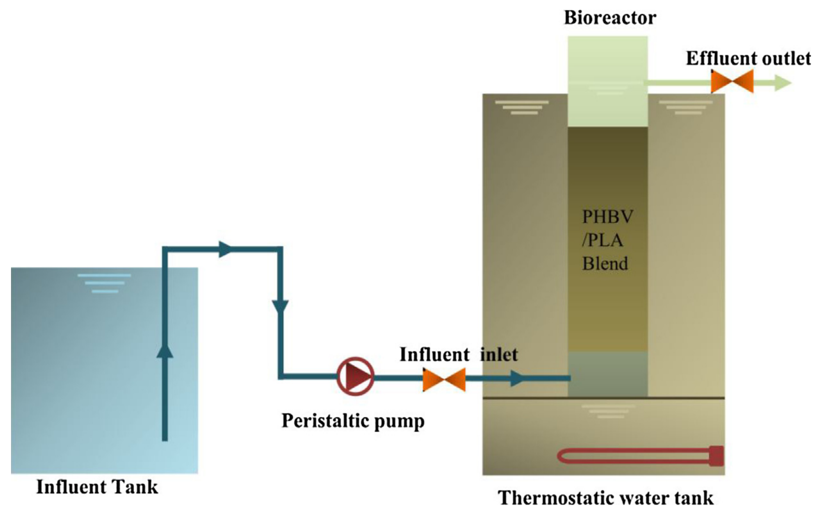

Fig. 1. Scheme of the experimental setup.

values of 6.5 and 7.0 in a SBR denitrification system [26]. However, the effect of pH on denitrification performance is more complicated and comprehensive in a polymer supported denitrification system. Influent pH affected not only denitrification process but also the amount of available carbon source from the polymers' hydrolysis process [11,23]. In this study, PHBV/PLA polymer blends were used as carbon source as well as biofilm carriers for nitrate removal in a packed-bed bioreactor. The objectives of the present study were as follows: (1) to investigate the effect of influent pH on denitrification performance; (2) to develop the equations about the relationships between influent pH and effluent characteristics; (3) to get more insights about the effect mechanism of influent pH on nitrate removal.

2. Materials and methods

2.1. Materials

The biodegradable PHBV/PLA granules (60%/40%, w/w) used in this experiment were identical with our previous study [27]. The physical characteristics of PHBV/PLA granules were as follows: diameter, 3 mm; height, 3 mm; dry weight, 0.0460–0.0512 g/granule; surface area, 8.28–9.22 $cm^2\ g^{-1}$.

Synthetic wastewater was prepared by $NaNO_3$ and KH_2PO_4 in tap water, containing about 15 $mg\ L^{-1}$ NO_3^--N and 5 $mg\ L^{-1}$– PO_4^{3+}-P. There was no any measure to control the DO level in synthetic water, and the influent DO concentration was about 9.10–9.80 $mg\ L^{-1}$.

2.2. Experimental setup

Continuous experiment was performed in a laboratory-scale packed-bed setup using a 60 mm inner diameter and 400 mm long cylindrical Plexiglas, which was placed in a thermostatic tank to keep the temperature as $30 \pm 2\,^{\circ}C$ (Fig. 1). A Plexiglas mesh disc (58 mm diameter, 2 mm pore size) was placed at the lower end of the column (a height of 50 mm) to support the PHBV/PLA granules. The PHBV/PLA granules served as both carbon source and biofilm carrier, packing the column up to a height of 250 mm. Water height in the reactor was 300 mm, which would avoid the attachment between air and granules.

2.3. Experimental procedure

The operation of the reactor started by inoculating the activated sludge taken form Quyang municipal wastewater treatment plant, Shanghai (with a final concentration of 800 $mg\ L^{-1}$ MLSS). After the inoculation for 3 days, the synthetic wastewater was pumped into the reactors at a flow rate of 5.89 ml/min (HRT = 2 h) from the bottom of the column. To explore the effect of influent pH on denitrification performance, a set of experiments was devised. After a stable denitrification performance (start-up period), then the average influent pH value was controlled to 5.68–10.38 corresponding to different phases. The influent pH in phases III–VII (except phase II) were controlled by adding HCl or NaOH [23] into the synthetic wastewater. The influent pH in phase II was controlled by adding $NaHCO_3$ into the influent, thus, the effluent TOC was not shown because that residual $NaHCO_3$ in the effluent affected the analysis of TOC. And the influent characteristics and operation parameters were shown in Table 1.

2.4. Analytical methods

The influent and effluent samples were collected and analyzed daily. Water samples were filtered through 0.45 μm membrane (Denmark, Germany) before analysis. The concentrations of NO_3^--

Table 1
Experimental operation parameters and the influent characteristics.

Date(d)	Phase	HRT(h)	T(°C)	pH	NO_3^--N(mg/L)	NLR(kg/(m³ d))
1–25	Start-up	2	30 ± 2	7.42 ± 0.09	15.47 ± 0.82	0.186
26–39	I	2	30 ± 2	7.51 ± 0.05	15.22 ± 0.57	0.183
40–46	II	2	30 ± 2	8.81 ± 0.10	14.25 ± 0.38	0.170
47–54	III	2	30 ± 2	9.57 ± 0.09	14.58 ± 0.19	0.175
55–61	VI	2	30 ± 2	10.38 ± 0.08	15.35 ± 0.42	0.184
62–68	V	2	30 ± 2	8.27 ± 0.04	15.29 ± 0.37	0.183
69–75	VI	2	30 ± 2	6.69 ± 0.02	15.33 ± 0.35	0.184
76–82	VII	2	30 ± 2	5.68 ± 0.07	15.05 ± 0.44	0.181