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Effect of dissolved oxygen on nitrate removal using polycaprolactone as an organic carbon source and biofilm carrier in fixed-film denitrifying reactors

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ABSTRACT

Nitrate-nitrogen (NO_3^--N) always accumulates in commercial recirculating aquaculture systems (RASs) with aerobic nitrification units. The ability to reduce NO_3^--N consistently and confidently could help RASs to become more sustainable. The rich dissolved oxygen (DO) content and sensitive organisms stocked in RASs increase the difficulty of denitrifying technology. A denitrifying process using biologically degradable polymers as an organic carbon source and biofilm carrier was proposed because of its space-efficient nature and strong ability to remove NO_3^--N from RASs. The effect of dissolved oxygen (DO) levels on heterotrophic denitrification in fixed-film reactors filled with polycaprolactone (PCL) was explored in the current experiment. DO conditions in the influent of the denitrifying reactors were set up as follows: the anoxic treatment group (Group A, average DO concentration of 0.28 ± 0.05 mg/L), the low-oxygen treatment DO group (Group B, average DO concentration of 2.50 ± 0.24 mg/L) and the aerated treatment group (Group C, average DO concentration of 5.63 ± 0.57 mg/L). Feeding with 200 mg/L of NO_3^--N, the NO_3^--N removal rates were 1.53, 1.60 and 1.42 kg/m^3 PCL/day in Groups A, B and C, respectively. No significant difference in NO_3^--N removal rates was observed among the three treatments. It was concluded that the inhibitory effects of DO concentrations lower than 6 mg/L on heterotrophic denitrification in the fixed-film reactors filled with PCL can be mitigated.

Introduction

Aerobic nitrification is commonly used in recirculating aquaculture systems (RASs) to convert ammonium-nitrogen (NH_4^+-N) to nitrate-nitrogen (NO_3^--N) through nitrite-nitrogen (NO_2^--N) (US EPA, 1996; van Rijn et al., 2006; van Rijn, 2013). Without a nitrate removal unit in an RAS, NO_3^--N can accumulate as high as 400–500 mg/L (van Rijn et al., 2006). Although NO_3^--N is relatively non-toxic to aquatic organisms, in contrast to NH_4^+-N and NO_2^--N, there is increasing evidence that NO_3^--N accumulation can negatively impact aquaculture animals (Hamlin et al., 2008; Davidson et al., 2014). Additionally, NO_3^--N discharged from aquaculture systems is considered to be one of the most important factors related to eutrophication in aquatic environments (Passy et al., 2013). Therefore, increased efforts are now directed toward NO_3^--N control in RASs (Tsukudaa et al., 2015).

Heterotrophic denitrification has been demonstrated as one of the most feasible and cost-effective methods of NO_3^--N

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removal (Chu and Wang, 2011). In the heterotrophic denitrifying process, denitrifying bacteria use organic carbon for growth and as an electron donor. The amount of biodegradable organic carbon in aquaculture water is much lower than that required for denitrifiers, thus organic sources are added intentionally (van Rijn et al., 2006). Several water-soluble carbon sources, such as ethanol, glucose, acetate and methanol, are readily available to heterotrophic bacteria, but require careful dosing and constant supervision to prevent overdosing and starvation periods (Lee et al., 2000), especially with the fluctuations of influent water quality and quantity in RASs (Singer et al., 2008). Recently, a new set of biological degradable polymers (BDPs), including polyhydroxyalkanoate (PHA), poly-3-hydroxybutyric acid (PHB), polycaprolactone (PCL), and polybutylene succinate (PBS), has been developed to serve as both an organic carbon source and a biofilm carrier for denitrification and is referred to as BDP-denitrification (Wu et al., 2012). BDP-denitrification is considered to require less supervision and management for its successful operation than previous methods (Boley et al., 2000).

Most denitrifying bacteria are facultative anaerobes that reduce nitrate in the absence of oxygen (Gómez et al., 2002). Due to the intensive aeration of the grow-out tanks of RASs, high levels of oxygen in the influent process have the potential for inhibiting the denitrifying progress (Singer et al., 2008). Therefore, to create an anaerobic environment, water is pretreated to remove dissolved oxygen (DO) before entering denitrifying reactors. DO can be removed from water by adding sodium thiosulfate (Gómez et al., 2002), or through an ample residence time (Boley et al., 2000). Of course, pretreatment inevitably increases the cost and management needed.

During the BDP-denitrifying process, the biofilm forms on the surface of the polymers, diffusion of oxygen is impeded and large anoxic zones are created above the pores and cracks of the BDPs coupled with carbon storage in the depth of the granules, which should stimulate the heterotrophic denitrifying process (Gutierrez-Wing et al., 2012). Therefore, the negative effect of DO on the BDP-denitrifying process can be expected to be minimized. In our recent study, we observed the effects of DO on heterotrophic denitrification using PBS (Luo et al., 2014) and PCL (under review) as the carbon source and biofilm carrier, contained in beakers. It was determined that the removal of NO_3^--N was highest with DO concentrations up to 6 mg/L achieved by aeration, compared with the anoxic treatment and low DO treatment groups. This finding led us to ask whether DO could also improve BDP-based denitrification in fixed-film denitrifying reactors. If the answer is yes, a convenient method could be supplied to remove NO_3^--N from RASs. The current study was undertaken to investigate the effect of influent DO concentration on heterotrophic denitrification in fixed-bed reactors using polycaprolactone (PCL) as the carbon source and biofilm carrier. Three DO levels in the influent of the reactors, representing common situations encountered in the denitrifying process, were set up. The first group was the anoxic treatment group, in which gaseous nitrogen was added to the water and the water surface was sealed. The second group was the low DO treatment group, in which water was left exposed to air with no aeration and no wax sealing. The third group was the aerated treatment group, in which the water was aerated with a fine-bubble diffuser. The nitrogen removal performance and water quality in the effluent were evaluated to assess the effect of DO in the influent on the PCL-denitrifying reactors.

1. Materials and methods

1.1. PCL

The physical characteristics of polycaprolactone ($[C_4H_6O_2]_n$) (Guanghua Weiye Co. Ltd., Shenzhen, China) are as follows: density, 1.08–1.12 g cm^{-3}; melting point, 60°C. The PCL granules have an ellipsoid shape with dimensions of 2 mm × 3 mm × 4 mm (width × length × height). The granules were cleaned by the ultrasonic technique (0.1 kW, 40 kHz) and subsequently dried at 35°C to a constant mass of ±0.0001 g in a vacuum oven.

1.2. Nitrate nitrogen removal in fixed-bed reactors with PCL as an organic carbon source and film carrier

A continuous experiment was conducted in three fixed-bed reactors (10.5 cm in diameter, 70.00 cm high and 3.5 L working volume; Fig. 1). Each reactor was filled with 50 vol.% fill of PCL granules (1.8 kg). The column surface of the reactor was not covered. The raw synthetic wastewater (SW) was kept in a tank at 22 ± 1°C by a temperature controller, then fed to the denitrifying reactors by a peristaltic pump (BT100-1F, Baoding Longer Precision Pump Co., Ltd., China). The SW was prepared by adding 78 mg K_2HPO_4, 31 mg KH_2PO_4, 95 mg $MgSO_4{\cdot}7H_2O$, 37 mg KCl to 1 L of tap water and 0.2% (V/V) of a trace nutrient solution containing the following compounds: 640 mg EDTA, 550 mg $FeSO_4{\cdot}7H_2O$, 230 mg $ZnSO_4{\cdot}7H_2O$, 340 mg $MnSO_4{\cdot}H_2O$, 75 mg $CuSO_4{\cdot}5H_2O$ and 25 mg $(NH_4)_5Mo_7O_{24}{\cdot}4H_2O$. The hydraulic retention time (HRT) was 5.5 hr according to our previous study.

The three DO groups in the tank that contained SW were the anoxic treatment group (group A), the low DO treatment group (group B), and the aeration treatment group (aerated with air; group C). The water surface of group A was sealed with liquid paraffin to create an anoxic environment in the water and maintain an average DO concentration ranging from 0.12 to 0.55 mg/L. Group B was left open to the air with no aeration and no wax seal, and contained DO in the range of 1.82 to 3.99 mg/L. The DO concentration ranged from 5.29 to 6.56 mg/L in group C and was controlled through an air flow adjuster.

The NO_3^--N concentration in the SW tank was 200 mg/L. NO_3^--N, NO_2^--N, total nitrogen (TN), total ammonium-nitrogen

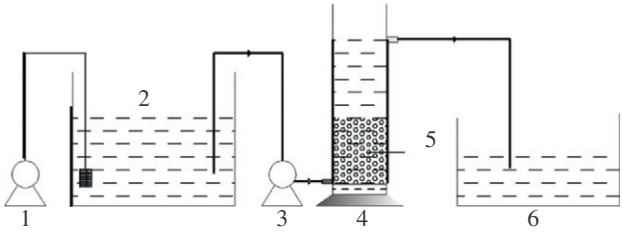

Fig. 1 – System diagram for the continuous experiment: (1) air compressor, (2) influent water reservoir, (3) influent peristaltic pump, (4) reactor column, (5) PCL media, and (6) effluent tank.