Glycerine as a carbon source in nitrite removal and sludge production

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HIGHLIGHTS

- Denitritation in wastewater with high nitrite concentration.
- Glycerine may be successfully used as sole carbon source for denitritation.
- COD/N ratio affects denitritation rate, final gaseous products and sludge production.

ARTICLE INFO

ABSTRACT

The study examined how the COD/N ratio (2.0, 2.5, 3.0, 3.5, 4.0) and cycle length (24 h and 12 h), influence the effectiveness and the rate of nitrite reduction, and the final gaseous products of denitritation, when glycerine was a carbon source. In addition, daily sludge production (ΔX) was both estimated by calculating heterotrophic sludge yield (Y_{HD}) (ΔX_{YHD}), and determined by making daily measurements of biomass concentration (ΔX_{exp}). The results indicated that there were discrepancies between ΔX_{exp} and ΔX_{YHD}, which shows that estimating daily biomass production by calculating heterotrophic sludge yield gives estimates which are not particularly accurate. Therefore, to find the optimal COD/N ratio, ΔX_{exp} was taken into consideration.

The study showed that at a COD/N ratio of 2.0, complete nitrite elimination was not observed (nitrite effectiveness removal 68%); at COD/N ratios of 2.5–4.0, denitritation effectiveness was around 100%. However, at a COD/N ratio of 2.5, N_2O concentration was 2 times higher than at the higher COD/N ratios (3.0–4.0). With a 12 h cycle length, the denitritation rate was highest (18.85 mg $N-NO_2$/g VSS h) at a COD/N ratio of 3.5, whereas the rate was 1.61-times lower (9.0 mg $N-NO_2$/g VSS h) at a ratio of 3.0. Although the denitritation rates differed at these COD/N ratios, nitrites were completely reduced in the first 2 h of the cycle. However, ΔX_{exp} was 0.66 g VSS/d at a COD/N ratio of 3.5, which was 30% higher than at a ratio of 3.0. This means that, taking into consideration the effectiveness and the rate of denitritation, its final gaseous products and sludge production, the most optimal COD/N ratio was 3.0 when glycerine was a carbon source.

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1. Introduction

Elimination of nitrogen is one of the main problems in wastewater treatment. Although effective technologies have been developed to remove nitrogen from municipal wastewater (nitrification followed by denitrification) nitrogen removal from wastewater with a low COD/N ratio (landfill leachate, reject water) is still problematic, due to the lack of available carbon for denitrification. Therefore, during treatment of wastewater with a low COD/N ratio, external carbon sources have to be supplied. So far, commercially available carbon sources like low molecular weigh alcohols (e.g. methanol and ethanol) and volatile fatty acids (e.g. acetic acid) have been used most often. This is because these carbon sources are easily biodegraded and enable high denitrification rates. However, all these commercial carbon sources generate additional treatment costs which cause that carbon source and sludge management costs account for more than 50% of the total cost of treating wastewater. So, in order to lower costs connected with the addition of carbon, two different approaches can be used: (i) technological solutions involving processes based on short-cut denitrification (denitritation) [1,2], which allows complete reduction of nitrite at lower organics concentration, and (ii) the use of waste products as a carbon source [3,4]. One of these waste products that shows great potential is glycerine. Glycerine is a by-product of biodiesel production, and its supply exceeds demand. In many

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countries nowadays, diesel is supplemented with biodiesel, so its production is still increasing [5].

However, in addition to costs, the selection of an external carbon source should take into account other factors: COD demand, the denitrification effectiveness and rate, the final gaseous products of denitrification/denitritation (N_2 is preferable to N_2O) and sludge production [6,7].

Previous studies have focused on the choice of technological parameters that allow complete nitrogen elimination at the lowest possible COD/N ratio because of the high cost of commercially available carbon sources. However, focusing exclusively on a low COD/N ratio can lead to other problems. Some studies have indicated that improper COD/N ratios can lead to N_2O accumulation during denitrification [8,9]. Not all studies agree on this point, however. According to some researchers, lowering the COD/N ratio too far favors N_2O formation [8,10]. In contrast, Wu et al. [11] reported that N_2O emissions in wetlands were lowest at a COD/N ratio of 5.0. In this study, increasing the COD/N ratio to 20 led to N_2O emissions that were 10 times larger than at COD/N ratios of 10 and 5. Therefore, in order to avoid the formation of N_2O, the optimal COD/N ratio should be experimentally determined for a particular combination of substrate and reactor.

Because N_2O is an intermediate in the denitrification process, it is always formed in nitrite/nitrate reduction. It is emitted by denitrifying bacteria, most nitrifying bacteria and denitrifying fungi [12–14]. However, it is important to minimize N_2O emissions by promoting complete denitrification through the use of appropriate operational and technological conditions, such as COD/N ratio. Although N_2O only accounts for 0.03% of total greenhouse gas emissions [15,16], it is more than 300 times more potent than CO_2 as a greenhouse gas.

Another aspect that should be considered in biological wastewater treatment is the production of excess biomass. Sludge treatment has become more challenging and more costly due to increased restrictions on sludge reuse and disposal. To lower costs, it is better to reduce the production of excess sludge during wastewater treatment rather than to post-treat the sludge, and one of the most important parameters lowering of biomass production is type of organic carbon source [17].

Taking into account the desirability of reducing costs, N_2O emissions, excess sludge production, this study investigated how COD/N ratio affects the effectiveness and rate of denitritation when glycerine is used as a carbon source. This was done with the aim of finding a COD/N ratio that would promote high effectiveness and rate of denitritation to N_2 and with the lowest production of excess sludge.

2. Materials and methods

2.1. Process configuration

The activated sludge was obtained from the denitrifying tank of the municipal wastewater treatment plant (60,000 m^3/d) Olsztyn, Poland. The experiment was carried out in three SBRs, operated in parallel with a working volume of 5 L each. The reactors were equipped with stirrers rotating at 50 rpm and an air supply system. Air was supplied by porous diffusers placed at the bottom of the tank. The pH in the reactors was at 8–8.5. The volumetric exchange rate was 0.5 d^{-1}. The system was operated at room temperature (20–22 °C).

The SBRs were operated with 24 h or 12 h working cycles. Each cycle consisted of the following phases: filling (5 min), mixing (22 h of the 24 h working cycle or 10 h of the 12 h working cycle), aeration (1 h) (in order to re-oxygenation of wastewater), and

settling and decantation (1 h). In the aeration phase, DO concentration was maintained at 2.0 ± 0.2 mg O_2/L.

2.2. Experiment organization

There were two stages, in which the COD/N ratio and the length of the SBR cycle differed. In the notation that will be used here, the subscript indicates the COD/N ratio and the number of hours in the operational cycle, e.g. $SBR_{2.0\_24}$ means the reactor with a COD/N ratio of 2.0 and a cycle length of 24 h. Thus, in stage I, were $SBR_{2.0\_24}$, $SBR_{3.0\_24}$, $SBR_{4.0\_24}$. In stage 2, were $SBR_{2.5\_12}$, $SBR_{3.0\_12}$, $SBR_{3.5\_12}$.

2.3. Characteristics of the influent

Reactors, inoculated with the denitrifying activated sludge from the municipal wastewater treatment plant, were fed by synthetic, high nitrite wastewater, with the addition of glycerine as an external carbon source. The synthetic wastewater used in this study contained: NaCl, 1.01 mg/l; $N_2HPO_4 \cdot 12H_2O$, 184.8 mg/l; $MgSO_4 \cdot 7H_2O$, 1.67 mg/l; $CaCl_2 \cdot 2H_2O$, 0.35 mg/l; $MnCl_2 \cdot 4H_2O$, 0.117 mg/l; $FeCl_3 \cdot 6H_2O$, 0.2 mg/l, $NaHCO_3$, 60.8 mg/l, $ZnSO_4$, 0.4 mg/l. Sodium nitrite ($NaNO_2$) was a source of nitrite. Nitrite concentration at the beginning of the SBR cycle was 100 mg $N-NO_2$/L. The chemical composition of glycerine was as follows: glycerol 80–85%, ash (NaCl) <7%, M.O.N.G. (matter organic non glycerol) <2%, methanol <0.5%, with the remaining portion consisting of water (product specification from Biodiesel Manufacturing Plant, Poland). The solution of glycerine was prepared in the following way: 113 g of glycerine were dissolved in 1 L of distilled water which resulted in 100 mg COD/ml. To obtain the required COD/N ratios in stage I and II, the proper volumes of glycerine solution were added to the synthetic wastewater.

2.4. Chemical analyses

Daily measurements of pollutant concentration in the effluent from the reactors included: chemical oxygen demand (COD), nitrites and nitrates. The activated sludge was analyzed for mixed liquor suspended solids (MLSS) and volatile suspended solids (VSS). In steady-state conditions, the measurements of COD, nitrites and nitrates during the SBR cycle were done. The analyses were performed according to APHA [18]. The N_2O concentration was determined using gas chromatography (Agilent 5890) with an electron capture detector (ECD) and a Poropak Q column (2 m × 2.1 mm, 100–120 mesh). The N_2 concentration was determined using gas chromatography (Agilent 6890) with a thermal conductivity detector (TCD) and a 2 m × 2.1 mm column (60–80 mesh). In both cases, 10 mL/min high-purity helium was used as the carrier gas. The VFAs were analyzed using a gas chromatograph (GC, Varian 3800, Australia) equipped with a capillary column (Factor-Four VF-1 ms, 30 m, 0.25 mm i.d., 1.0 μm film; Varian) and flame ionization detector. Helium was used as a carrier gas with a flow rate of 1.0 mL/min. The samples were analyzed according to Gilroyed et al. [19]. The total concentration of VFAs was the sum of the concentrations of individual analyzed VFAs.

3. Results and discussion

3.1. The effectiveness of denitritation

One of the main factors influencing the effectiveness of nitrate/nitrite reduction is the COD/N ratio in the system influent. For conventional denitrification of municipal wastewater, it has been determined that the proportion of organic compounds to nitrogen