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Perspective for Emission and Control of Nitrous Gas in Biological Wastewater Treatment

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ABSTRACT. Being the third most significant anthropogenic greenhouse gas, nitrous gas (N_2O) has 300-fold stronger effect than carbon dioxide (CO_2) and 4 ~ 30-fold stronger effect than methane (CH_4). In this study, the main sources and mechanisms of N_2O emission from biological wastewater treatment were reviewed, and the possible mitigation strategies were discussed. Parameters including dissolved oxygen, temperature, pH, organic carbon, and nitrite concentration have influences on the emission of N_2O. The possible mitigation strategies were put forward by controlling these parameters in biological wastewater treatment and inducing modified technologies such as simultaneous nitrification-denitrification, denitrifying phosphorus removal, and aerobic granular sludge. In order to obtain a near-zero N_2O emission, applying typical catalysts in the nitrification or denitrification tank to decompose N_2O into harmless gas is recommended. Moreover, a method of developing photochemical processes to transform N_2O could also be suggested.

Keywords: Nitrous gas, biological wastewater treatment, N_2O emission mitigation

1. Introduction

Greenhouse gas (GHG) emission has received great attention over the past decades (Liu et al., 2018). Typical GHG includes nitrous gas (N_2O), carbon dioxide (CO_2), and methane (CH_4). Among them, N_2O has 300-fold stronger effect than CO_2 and 4 ~ 30-fold stronger effect than CH_4 (Muthuraman et al., 2019). N_2O featured in colorless, nonflammable, sweet-smelling is stable in the atmosphere for prolonged periods (Government of Canada, 2017). It has been identified as a significant constituent in several aspects of atmospheric chemistry (Miyahara et al., 2010). Being the third most significant anthropogenic greenhouse gas, N_2O has been categorized as the greatest contributor to stratospheric ozone depletion (Portmann et al., 2012). The estimated growth of N_2O emission is expected up to 14.49 Mt/y by 2020 (Muthuraman et al., 2019).

The industrial sector is regarded as the most significant emission source after agriculture (Liu et al., 2018; Yu et al. 2019), where wastewater treatment is an important resource for N_2O emission. According to data from Ednhofer et al. (2014), the emission of N_2O from wastewater treatment accounted for 3.56% of the total emission load, increasing 20% compared with the past twenty years. Khalil and Rasmussen (1992) also estimated the global N_2O emission, putting forward that the annual N_2O emission rate from sewage was 0.3×10^{12} ~ 3.0×10^{12} kg/y, contributing to 3% ~ 30% of total N_2O emission. Therefore, the emission of N_2O during wastewater treatment cannot be ignored, and it converts water pollution to air pollution problems, which is opposite to the initial biological design intention to remove nitrogen from wastewater.

Online and continuous monitoring of N_2O has been employed in recent years for accurate quantification of N_2O emissions from biological wastewater treatment systems (Sabba et al., 2018). In a biological wastewater treatment plant, N_2O discharged from an activated sludge pool is usually collected using a closed floating chamber. This technology was originally designed based on a solid surface emission test. During the aeration phase, dissolved N_2O is stripped from the liquid phase; during the non-aeration phase, fresh air can be added from the bottom of the vessel and the sampled N_2O can be extracted from the top of the vessel. After the sample of exhausted gas is extracted, the sample can be analyzed by gas chromatograph (Law et al., 2012; Chen et al., 2018).

Studies showed that substantial amount of N_2O was produced during nitrogen removal process in biological nutrient removal (BNR) plants (Osada et al., 1995). It is reported that about 0.05% ~ 25% of nitrogen is converted to N_2O in the process of BNR (Vasilaki et al., 2019). There are two biological processes aiming at nitrogen removal: nitrification and denitrification. The main formation of nitrous in wastewater is ammonium, which is converted into nitrite or nitrate during nitrification process. While nitrite is reduced to dinitrogen gas during denitrification process. These two nitrous removal proc-

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esses both lead to the emissions of N_2O. N_2O is an intermediate in the heterotrophic denitrification process and is often generated by ammonia-oxidizing bacteria (AOB). In order to complete nitrogen conversion in a limited time, relatively high nitrification and denitrification rates are required, contributing to the emission of N_2O. In addition, bacteria communities change due to the changes of process conditions, which will also affect N_2O production. The N_2O emission is also associated with processes of biological wastewater treatment, during which the emission load is various depending on operation parameters (Kampschreur et al., 2009). Therefore, in this study, the main sources and mechanisms of N_2O emission from biological wastewater treatment were reviewed, and the possible mitigation strategies were discussed.

2. The Mechanism of N_2O Emission during Biological Wastewater Treatment

The BNR processes in biological wastewater treatment produce a large number of GHG such as CO_2, CH_4, and N_2O. In this section, the mechanisms of N_2O production, including nitrification and denitrification are discussed.

2.1. Nitrification

In general, during the nitrification process, NH_4^+ or NH_3^- is oxidized to NO_3^- via NO_2^-. Most of the microorganisms involved in the nitration reaction are obligate autotrophic microorganisms. Nitrification process can be divided into two phases. In the first phase, ammonia-oxidizing bacteria convert NH_4^+ into NO_2^-; there are two enzymes that participate in the reaction: ammonia monooxygenase (AMO) and hydroxylamine oxidoreductase (HAO) (Scala and Kerkhof, 1998). In the second phase, NO_2^- is converted to NO_3^- by nitrite oxidizing bacteria; the catalytic enzyme is nitrite oxidoreductase (NOR). N_2O is neither intermediate nor final product throughout the reaction; therefore, N_2O is a by-product. The complete path is described in Figure 1. The process of biological nitrification is a series of enzymatic reactions. According to Law et al. (2012), the autotrophic AOB usually lack the nitrous oxide reductase gene, which is the root cause of N_2O production. The enzyme participates in the reaction, but its total amount before and after the reaction does not change. The activity of the enzyme is related to the temperature and the pH of the environment.

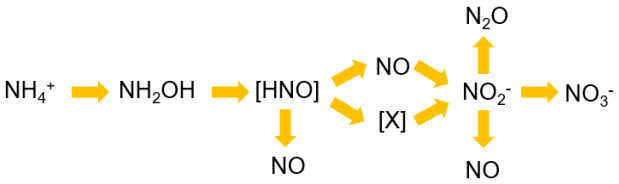

Figure 1. Pathway of nitrification.

2.2. Denitrification

Denitrification is a process in which NO_3^- or NO_2^- is reduced to N_2O and N_2 by heterotrophic facultative anaerobic microorganisms under anaerobic or hypoxic conditions. Enzymes play a key role in denitrification process, and there are four enzymes involved: nitrate reductase (Nar), nitrite reductase (Nir), nitricoxide reductase (Nor), and nitrous oxidereductase (Nos) (Yu et al., 2010). The complete path is shown in Figure 2. Two modes of nitrate removal can occur in biological processes, including assimilatory and dissimilatory nitrate reduction. Dissimilatory denitrification is responsible for biological denitrification for enhanced nitrogen removal and bacterial cell respiratory electron transport chain for the oxidation of a variety of organic and inorganic substrates.

Compared with the nitrification process, N_2O is an intermediate substance that is produced during the denitrifycation process. At present, there are two main explanations for the production of N_2O in the denitrification process. The first one is losing of Nos activity in the denitrifying bacteria. N_2O generated in the third stage was unable to escape, resulting in N_2O accumulation from the water (Parton et al., 1996). The second is that part of the denitrifying bacteria does not have a Nos system, and its final product is only N_2O. The amount of N_2O produced is directly related to the activity of Nar (Parton et al., 1996). Similar with the nitrification process, the activity of the enzyme in denitrification process is determined by factors such as dissolved oxygen, organic carbon sources, and nitrites (Song et al., 2018; Zhang et al., 2019).

Figure 2: Pathway of denitrification.

3. Factors Influencing the Emission of N_2O in Biological Wastewater Treatment

The main form of nitrogen in wastewater is ammonia, which can be converted into nitrite or nitrate during nitrification process and thus dinitrogen gas is reduced in denitrification stage. Both nitrification and denitrification processes can lead to the emission of nitrogen oxides (Kampschreur et al., 2009). Figure 3 summarizes the important factors which have significant effects on N_2O emission. The concentrations of dissolved oxygen (DO) and nitrite play important roles in both nitrification and denitrification processes, and the ratio of chemical oxygen demand/nitrogen (COD/N) affects denitrification process. In this section, the key factors influencing N_2O emission are reviewed and discussed.

Table 1 illustrates eleven different types of plants including full scale, lab scale, and synthetic biological wastewater treatment plants. The characteristics of wastewater varies among different plants. The full-scale plants are the field plants handling real wastewater such as municipal wastewater treatment plant, factorial wastewater treatment plant, soil stretch wastewater treatment plant and etc. While lab scale and synthetic wastewater treatment plants are designed to obtain some objectives with designed size and operating parameters. In order to investigate major influence factors, the summary of operating parameters is showed in Table 1.

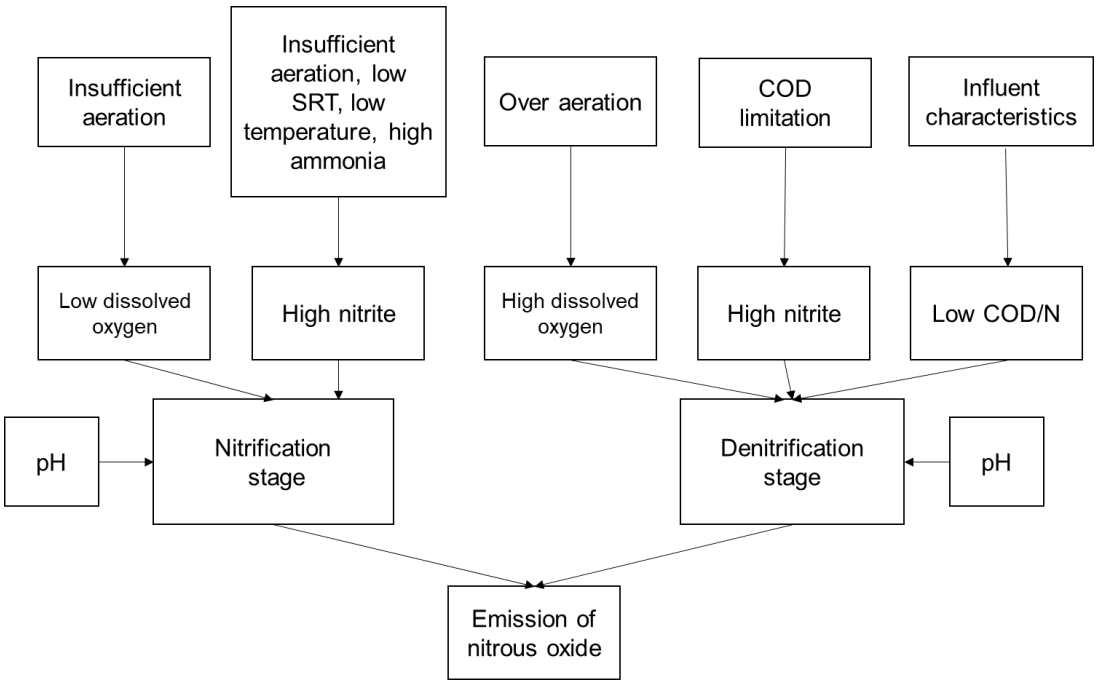

Figure 3. Important factors leading to the N_2O emission.

3.1. Dissolved Oxygen

The N_2O emission is affected by the concentration of dissolved oxygen in both nitrification and denitrification processes (Kampschreur et al., 2009). During the nitrification process, the ammonia is converted into nitrite by oxidation, in which process N_2O is produced, followed by the oxidation from nitrite to nitrate. Under the condition of low oxygen, the oxidation rate of nitrite to nitrate is lower than that of ammonia to nitrite. The emission of N_2O increases with low dissolved oxygen concentration resulting from insufficient aeration (Zeng et al., 2003). The reason for this is that in oxygen-limiting conditions, autotrophic ammonia oxidizers use nitrite as the terminal electron acceptor to save oxygen for the oxygenation reaction of ammonia to hydroxylamine (Kampschreur et al., 2009). As a result, more nitrite is consumed by AOB and ammonium-oxidizing archaea (AOA), leading to the rising of N_2O emission.

On the other hand, The N_2O emission is also enhanced in the denitrification process if overload oxygen is provided. The concentration of dissolved oxygen can influence activities of many kinds of dominant enzymes (Tallec et al., 2006). During denitrification, dissolved oxygen can induce N_2O production by affecting the function of the denitrifying enzyme system, among which the nitrous oxide reductase is more sensitive to dissolved oxygen compared to others. As a result, even a small amount of dissolved oxygen presented will cause the decline of nitrous oxide reductase, leading to the emission of N_2O.

Garrido et al. (1997) did a research and worked out a model to investigate the influence of dissolved oxygen concentration on nitrite accumulation and N_2O emission in a suspension reactor. The results showed that with the increase of dissolved oxygen concentration, the nitrite concentration increased, reaching a peak at about 1.5 mg/L, and then climbed down. There was almost no nitrite when the dissolved oxygen concentration was over 2.5 mg/L. The similar trend was also observed in the nitrite simulation curve. The concentration of nitrate witnessed an upward trend as dissolved oxygen inclined, with a similar trend of simulation data, staying almost stable after 2.5 mg/L oxygen concentration. In contrast, ammonia decreased as dissolved oxygen rose up. The conclusion was described as that in the low oxygen concentration, nitrite concentration was higher, which resulted in the higher emission of N_2O.

3.2. Nitrite Concentration

It is acknowledged that nitrite concentration has a big influence on both nitrification and denitrification processes. Shen et al. (2014) put forward that the emission of N_2O increased with high nitrite concentration. Peng et al. (2015) did a research and found that AOB was very sensitive to nitrite. The denitrification of AOB, which was accelerated with increasing concentration of nitrite, caused accumulation of nitrous gas. The reason for this was that the AOB denitrification process was promoted by nitrite reductase Gene nirK and nitric oxide reductase Gene norB mRNA under the condition of high nitrite concentration (Yu and Chandran, 2010).

3.3. Ammonia Concentration

The emission of N_2O increased as increasing ammonia concentration (Ahn et al., 2010). Shen et al. (2014) indicated that one possible reason was that a high nitrifying activity occurred under high ammonium conditions, which might induce high N_2O emission. According to the results from Shen et

Table 1. Different Types of Wastewater Treatment Plants and Their Influencing Factors

Reference	Type of plant	Main character of wastewater	Main effect factors
Czepiel et al. 1995	Full-scale municipal wastewater treatment plant	Influent BOD_5 at 20 °C of approximately 250 mg/L with an estimated suspended solids concentration of 220 mg/L	Aerated and non-aerated phases
Kampschreur et al. 2008	Full scale commercial wastewater treatment plant	Reject water with TKN = 1265 ± 41 mg/L	Dissolved oxygen, nitrite, aeration rate, pH
Teiter and Mander, 2005	Municipal wastewater treated by wetlands	BOD_7 = 96 g/m^2; total N = 34 g/m^2; total P = 4.7 g/m^2	Operation factors of wetland
Kong et al. 2002	Soil-trench wastewater treatment	Influent of wastewater in Japan: BOD = 252 mg/L, TN = 192 mg/L, TP = 26 mg/L; in China: BOD = 266 mg/L, TN = 87 mg/L	Structure of the treatment system
Tallec et al. 2006	Lab scale urban wastewater treatment plants	1.9 mg/L TNK, 0.1 mg/L of $N\text{-}NO_2$, 21 mg/L of $N\text{-}NO_3$, 25.9 mg O_2/L of COD, 2.8 mg O_2/L of BOD	Various conditions of oxygenation, a gradient of methanol addition
Sun et al. 2013	Full-scale SBR wastewater treatment plant	The whole year: COD = 390 ~ 570 mg/L; TN = 60 ~ 90 mg/L	DO concentration, water temperature, influent COD/N
Quan et al. 2012	Laboratory-scale	Three aeration rates (0.2, 0.6, and 1.0 L air/min) and three COD/N ratios (1:0.22, 1:0.15, and 1:0.11)	Aeration rate and the COD/N ratio
Shen et al. 2014	Lab scale municipal wastewater treatment plants	510 mg/L sodium acetate, 10 mg/L yeast extract, 153 mg/L NH_4Cl, 46 mg/L Na_2HPO_4, 90 mg/L $MgSO_4•7H_2O$, 14 mg/L $CaCl_2•2H_2O$	Different initial ammonium concentrations; different initial nitrite concentrations
Shiskowski and Mavinic, 2006	Lab scale synthetic wastewater	Concentration of TOC = 200 mg C/L; COD = 520 mg/L; organic N = 12 mg N/L	Oxygen, nitrite concentration, pH manipulation
Adouani et al. 2015	Denitrification step in lab scale wastewater treatment	Concentration of $NH_4\text{-}N$ = 6 mg/L	Temperature
Lemaire et al. 2006	Lab scale artificial wastewater treatment	DO = 0.35 ~ 0.5 mg/L; pH = 7.0 ~ 7.5; 230 mg/L COD as acetate; 23 mg/L NH_4-N; 18 mg/L PO_4-P	Carbon source

al. (2014), it could be observed that the nitrite production rate was increased from 3.30 to 4.78 mg/g/h with increasing initial ammonium concentrations from 7.7 to 52.4 mg/L, indicating that nitrite-oxidizing bacteria (NOB) activities might be lowered with increasing ammonium concentrations. The activity of NOB decreased as the concentration of nitrate showing a decreasing trend from 5.65 to 4.5 mg/g/h. This meant that with increasing of the initial ammonium concentration, the activity of AOB did not change, while that of NOB decreased, which could be due to a higher competition ability of AOB than NOB for oxygen. As a result, N_2O emission changed from 0.01 to 0.09 mg/g/h, showing that high N_2O emission rate occurred with increasing ammonium concentration.

3.4. Temperature

The emission of N_2O is high under the condition of low water temperature (Sun et al., 2013). According to Adouani et al. (2015), the N_2O emission rate and percentage of N_2O rose up due to the decrease of temperature. The reason for this was that low temperature slowed down all denitrification enzyme activities and especially N_2O reductase activities, inducing important emissions of N_2O. In addition, N_2O reductase could be inhibited by the accumulation of N_2O in the biological reactor, which explained the accumulation and emission of N_2O, causing a significant pollution transfer to the atmosphere.

3.5. COD/N Ratio

During denitrification process, limited organic carbon was observed to increase the emission of N_2O (Vonschulthess et al., 1995). Quan et al. (2012) investigated the impact of various COD/N ratio in synthetic wastewater mixed with pig manure digestate liquid. The studies showed the proportions of N_2O emission to the influent nitrogen loading rate at the aeration rates at 0.2, 0.6, and 1.0 L air/min were 8.2, 6.1, and 3.8% at a COD: N ratio of 1:0.22; 7.0, 5.1, and 3.5% at a COD: N ratio of 1:0.15; and 4.4, 2.9, and 2.2% at a COD: N ratio of 1:0.11, respectively. It could be seen that at the same aeration rate, with the decreasing of COD: N ratio, the proportions of N_2O emission rose up.

In addition, organic carbon source also plays an important role in the generation of N_2O. The type of microorganisms could be influenced by various carbon sources, resulting in different emission load of N_2O. Studies showed that high N_2O emission was caused by the low diversity of population due to single carbon source (Lemaire et al., 2006). Addition of an external organic carbon source, methanol, led to an appreciable reduction of the N_2O emission from 4.5 to 0.2% of the nitrogen load (Park et al., 2006). The reason for this might be due to the activity of different bacteria which digested carbon source and emitted N_2O. N_2O accumulated as soon as organic carbon became limiting and bacteria started to consume internal sto-

rage compounds (poly-b-hydroxybutyrate) (Kampschreur et al., 2008).

3.6. Solution pH Level

The emission of N_2O is also affected by the pH level of wastewater. The level of pH was shown to have a major impact on the N_2O production rate. Under the condition of investigated pH range of 6.0 ~ 8.5, the specific N_2O production was observed to be the lowest between pH 6.0 and 7.0 at a rate of 0.15 ± 0.01 mg N_2O-N/h/g volatile suspended solids (VSS). Nevertheless, N_2O emission rate increased with pH, reaching a maximum rate of 0.53 ± 0.04 mg N_2O-N/h/g VSS at pH = 8.0. (Law et al., 2011). This result indicated that the tested pH caused an increase in the N_2O production rate by promoting the activity of the AOB. Pan et al. (2012) did a similar study and concluded that the maximum N_2O reduction rate was much more sensitive to pH variation than nitrate and nitrite reduction rates. The optimal range of pH was 7.5 to 8.0. It could be summarized that in pH range of 6.0 ~ 9.0, the maximum N_2O reduction rate was strongly influenced by pH, with its value gradually increasing from pH = 6.0, reaching its highest level at about 350 mg N/(gVSS × hour) at pH = 8.0, followed by a decrease to about 200 mg N/(gVSS × hour) at pH = 9.0. A similar trend with respect to pH changing was witnessed in nitrate and nitrite reduction rates. However, the nitrite and nitrate reduction rates were lower than N_2O emission rate at the same pH level. These results suggested that the electrons competition among different nitrogen oxides reductase likely played a role in N_2O accumulation at low pH conditions. The affinity of N_2O reductase with respect to N_2O decreased as pH increasing (Pan et al., 2012).

4. Possible Mitigation Strategies

N_2O is a powerful greenhouse gas with a very long lifetime of 150 years and a 320-fold stronger effect than CO_2 (Adouani et al., 2015). It is, therefore, necessary to investigate and control the anthropogenic emissions of N_2O. Anthropogenic N_2O emissions come mainly from energy processes, chemical industries and agriculture and waste treatments. Wastewater treatment is responsible for 3.2% ~ 10% of the total N_2O emissions (Daelman et al., 2015). Therefore, mitigating the emission of N_2O in wastewater treatment process is of great need.

4.1. Control of Operating Parameters

Dissolved oxygen: As for the concentration of dissolved oxygen, low dissolved oxygen in nitrification process and high dissolved oxygen in denitrification process contribute to increased emission of N_2O. This means that during the nitrification process the supply of oxygen should be sufficient in order to minimize N_2O emission. Therefore, high aeration can be applied in nitrification process to support sufficient oxygen, inhibiting N_2O emission (Kampschreur et al., 2008). Some of the biological wastewater treatment plants tend not to apply high aeration due to taking energy consumption into consideration. The emitters might consider that increased energy consumption will lead to rising level of carbon dioxide, which is also a dominant greenhouse gas. However, during nitrification process, obtaining enough oxygen is necessary because N_2O is much more harmful and difficult to handle than CO_2.

However, in some cases involving denitrification process such as biofilm-granular sludge systems, high aeration could be practically difficult because increased oxygen concentrations resulted in inhibition of denitrification (Kampschreur et al., 2008). Law et al. (2012) pointed out that the process characteristics of wastewater treatment plants designed and operated for near-complete denitrification contributed to lower and more stable N_2O generation than the plants with partial denitrification. Therefore, in order to obtain lower N_2O generation, features concerning in denitrification process employed in wastewater treatment plants should be designed to achieve near-complete denitrification. The balance between influent flow and load, low dissolved oxygen concentration, high recycle rate, large bioreactor volume, long solid retention time, and external carbon source dosing are the design features which need to be considered.

Nitrite concentration: Taking nitrite concentration into consideration, high nitrite concentration in both nitrification and denitrification processes will lead to the emissions of N_2O. The factors influencing high nitrite accumulation in nitrification process include insufficient aeration, low solid retention time, low temperature and high ammonia concentration. To control such factors, in full-scale wastewater treatment plants, designing features should be taken into consideration. In detail, loadings are buffered and the risk of transient oxygen depletion is reduced due to the systems equipped with large bioreactor volumes and influent flow-balancing (Law et al., 2012). Similarly, Desloover et al. (2012) also concluded some strategies to reduce accumulation of NH_2OH and NO_2^-. The strategies included sufficiently high and constant dissolved oxygen, adapted aeration regime, low free nitrous acid. An end-of-pipe treatment was put forward, which could be supported by the implementation of a newly proposed GHG crediting system. The end of pipe treatment was employed to ensure sufficient copper availability, supporting N_2O reductase synthesis.

Ratio of COD/N: When it refers to the COD/N, low N_2O emission could be resulted from high COD/N and extra carbon resources. To achieve sufficiently high COD/N, external COD needs to be provided in the pre-settling stage, and lower COD is able to be removed from sewage. In addition, choosing a proper carbon source is necessary (Desloover et al., 2012). Park et al. (2006) found that the amount of N_2O produced during wastewater treatment decreased from 4.5% to 0.2% of the total N, by introducing methanol as additional carbon source. Shen et al. (2014) used acetate as the initial carbon source, drawing conclusions that with the initial acetate concentration at 250, 500, and 1000 mg/L, the concentration of N_2O emitted at 90 min was 0.75, 0.05, and 0.035 mg/L, respectively. It can be concluded that increasing variety of carbon sources, as well as increasing concentration of carbon sources, is able to achieve low N_2O emission.

4.2. Modified Biological Wastewater Treatment Technology

Simultaneous nitrification-denitrification technology: Simultaneous nitrification-denitrification (SND) is a modified biological wastewater treatment technology which was developed in recent years (Iannacone et al., 2019). Microbial simultaneous nitrification-denitrification process is the conversion of the ammonium ion to nitrogen gas in a single bioreactor. The process is dependent on flow characteristics, reaction kinetics, mass loading of readily biodegradable chemical oxygen demand (rbCOD) and DO concentration (Liu et al., 2019). It is a new technology for denitrification of wastewater that carries out nitrification and denitrification processes under the same operating conditions in a same reactor. In the SND process, the AOB denitrification, nitrification bacteria nitrification, heterotrophic denitrification, and other processes in the same reactor are performed at the same time. Since N_2O release may occur in each reaction process, the release characteristics of N_2O during the SND process are more complicated.

The N_2O emission in the SND process under hypoxic conditions is an essential product of microbial metabolism. Both heterotrophic denitrifying bacteria and AOB can produce N_2O, and the denitrification of AOB is the main reason for N_2O production (Zhang et al., 2019). Furthermore, denitrification using intracellular polyhydroxyalkanoates (PHAs) as a carbon source increases the amount of generated N_2O (Yin et al., 2018). However, under high-loading phosphorus conditions, microorganisms can synthesize more PHAs to reduce the denitrifycation enzyme electrons, thereby reducing the amount of N_2O during heterotrophic denitrification process. In addition, in the SND system, the optimal control of the particle size of the sludge aggregates can achieve N_2O reduction control (Di Bella and Torregrossa, 2013). By controlling the particle size of the sludge aggregates at 0.45 to 0.9 mm, high nitrification and denitrification activities can be achieved at the same time, thereby reducing N_2O emissions.

Denitrifying ohosphorus removal: Denitrifying phosphorrus removal means that denitrifying phosphate-accumulating bacteria use NO_3^- or NO_2^- as electron acceptors under anoxic conditions, and uses internal carbon source PHAs to achieve excess phosphorus absorption in water (Zhou et al., 2010). N_2O is the main denitrification by-product in this process. The conversion of PHAs plays an important role in the accumulation of N_2O. The reduction of N_2O is relatively low when using PHAs as a carbon source. In addition, during this process, NO_2 or free nitrous acid can inhibit the activity of denitrification enzyme and the absorption of phosphorus, resulting in denitrification efficiency and a large number of N_2O production.

The production of N_2O in denitrifying phosphorus removal process mainly occurs in the process of anoxic phosphorus denitrifying and aeration nitrification (Mandel et al., 2019). In the anoxic denitrification stage, continuous water intake and aeration stage can be adopted to reduce N_2O production by adjusting aeration to prevent nitrification bacteria from denitrifying to avoid N_2O accumulation. Research found that when continuously adding NO_2 and using propionic acid as a carbon source in the denitrifying phosphorus removal process, the electronic competition between denitrifying enzymes can be reduced and NO_2^- accumulation can be reduced (Jiang et al., 2019). Choosing the right carbon source is beneficial to the reduction of N_2O in the system. Wang et al. (2014) found that increasing the concentration of influent phosphorus can reduce the formation of N_2O. When the concentration of phosphorus increased from 5 to 50 mg/L, the total N_2O production decreased from 1.64% of total nitrogen to 0.16%.

Aerobic granular sludge: The aerobic granular sludge process has good application prospects in wastewater treatment due to its good sedimentation performance and high microbial concentration (Mandel et al., 2019). However, its spatial structure will lead to incomplete denitrification and cause N_2O production, because the denitrifying and nitrifying bacteria in the particles are difficult to have pure anoxic and aerobic conditions. Temperature can affect N_2O production by affecting the metabolic activities of functional microbes. Studies from Bao et al. (2018) found that as the temperature increased from 10 to 30 °C, the average N_2O emission factor decreased in the range of 0.15% ~ 0.70% N_2O-N/NH_4^+-N oxidized in the first aeration phase and 0.14% ~ 0.15% N_2O-N/NH_4^+-N-oxidized in the second aeration phase. With the increase of temperature, an aerobic environment is more likely to form within the granular sludge. The accumulation of NO_2^- in the system decreases, contributing to the decrease of N_2O production.

Other novel methods: Besides controlling operational parameters, some other novel strategies have been developed by researchers. From previous studies, it was learned that microorganisms played an important role in transferring nitrite. Richardson et al. (2009) did a research on enzyme regulation relating to bacteria in denitrification stage. The denitrifying bacteria converted endogenous cytotoxic NO to N_2O in order to protect themselves. They could exist in several forms possessing very different enzymatic activities towards N_2O reduction, which might be caused by changes at the catalytic site [Cu_4S]. In order to reduce the generation of N_2O, the genetic expression of the enzyme could be changed on some catalytic sites. Miyahara et al. (2010) studied a new branch of denitrifying bacteria called Pseudomonas stutzeri TR2. It was observed that the strain TR2 produced low levels of N_2O even under aerobic conditions. After all conditions tested, the strain TR2 was proved to release little levels of N_2O through exhibiting strong denitrification process. Particularly, when exposed to both N_2O and nitrite, the strain TR2 bacteria had an affinity of N_2O as substrate. Consequently, this kind of newly found microorganism has a potential to reduce N_2O emissions when applied to sewage disposal fields.

5. Recommendations for Near-Zero Emissions of N_2O from Biological Wastewater Treatment

In this study, the parameters influencing N_2O emission from biological wastewater treatment and the possible mitigation strategies were comprehensively reviewed. During nitrogen removal process, N_2O was produced due to the nitrifycation and denitrification. Dissolved oxygen, temperature, pH, organic carbon, and other factors affect the release of N_2O. The

emission of N_2O can be reduced by controlling influencing parameters in biological wastewater treatment and inducing modified technologies. However, no matter how to adjust the operating parameters and water quality conditions, N_2O will always be released more or less. Up to now, N_2O removal technologies in biological wastewater treatment plants were not widely proposed and developed. The reason might be the little contribution to the anthropogenic N_2O emission budget and the consideration of economic or legislative incentives.

Although the technologies of N_2O removal in biological wastewater treatment plant are relatively few, some methods concerning N_2O removal from industrial gases were investigated. The catalytic reduction of N_2O by CO molecule over the surface of Si-embedded MoS_2 was investigated by Esrafili (2019). The results indicated that the adsorbed N_2O can be easily decomposed to N_2 without activation energy. Fe-ZSM-5 catalysts were used to remove N_2O from gas by Richards et al. (2018). Comparison of catalysts with relatively high and low Fe loadings achieved comparable levels of N_2O decomposition when propane is present. The characteristics of catalytic were influenced by Fe loading and Si:Al ratio. In addition, a photochemical process was put forward as an efficient method to remove N_2O, which could be obtained under the condition of atmospheric pressure and room temperature without any catalysts. N_2O was diluted and decomposed into N_2, O_2, and NO using a 193 nm ArF excimer laser (Tsuji et al., 2004).

Consequently, a recommendation that applying typical catalysts in the nitrification or denitrification tank to decompose N_2O into harmless gas is reasonable. Moreover, methods of developing photochemical processes to transform N_2O can also be considered. Nevertheless, these technologies require a relevantly high cost but the emission of N_2O accounts for only a little part. Therefore, in the future work, research on N_2O removal from gas emissions in biological wastewater treatment plant has great potential to mitigate GHG emission.

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