ГОДИШНИК НА УНИВЕРСИТЕТА ПО АРХИТЕКТУРА, СТРОИТЕЛСТВО И ГЕОДЕЗИЯ СОФИЯ

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EVALUATION OF NITROUS OXIDE (N_2O) EMISSIONS DURING NITROGEN REMOVAL FROM URBAN WASTEWATER IN SUBMERGED BIOFILM REACTORS

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Keywords: *Nitrous oxide (N_2O), greenhouse gases, wastewater, nitrification, denitrification*

ABSTRACT

Nitrous oxide (N_2O) has a greenhouse effect, which is 273 times higher than that of carbon dioxide according to the latest IPCC estimation. Therefore, even relatively small amounts can result in a significant carbon footprint. N_2O is emitted during the biological nitrogen removal processes of wastewater treatment. This study evaluates direct N_2O emissions during biological nitrification and denitrification in submerged fixed-film reactors using data from the author's pilot plant experiments. The calculations are based on typical parameters and emission factors but an improved approach for their identification, than the widely used, is applied.

1. Introduction

Nitrous oxide (N_2O) plays a significant role in climate change and has environmental impacts. It is not associated with acid rain formation (unlike NO and NO_2). It is present in the atmosphere in small amounts but as greenhouse gas plays significant role in global warming and stratospheric ozone depletion. N_2O has a global warming potential (GWP) 273 times higher than that of carbon dioxide (CO_2) with an average residence time of 100 years according to IPCC's Sixth Assessment Report, published in 2021 [1]. Therefore, even relatively small amounts can result in a significant carbon footprint.

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Global N_2O emissions have significantly increased in the last 4 decades primarily due to a 40 % increase in anthropogenic emissions where agriculture made the largest contribution. Other direct anthropogenic emissions (including those from fossil fuel and industry, biomass burning, waste and wastewater) did not show a significant trend [2]. According to the estimations of the United Nations Framework Convention on Climate Change (UNFCCC), in 2018 N_2O emissions from wastewater treatment and discharge in industrialized countries contributed 2,6 % to the total CO_2 equivalent (CO_2eq) emissions [3].

Biological removal of nitrogen is the most reliable and economical way to treat wastewater of this element [4 – 5]. Microbial processes such as autotrophic nitrification and heterotrophic denitrification have been identified as major sources of N_2O emissions [6]. Nitrification is implemented by different autotrophic bacteria in aerobic conditions with oxidation of ammonia to nitrite and nitrate ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$). Denitrification is implemented by heterotrophic bacteria under anoxic conditions with reduction of nitrate to nitrite followed by its transformation to nitric oxide, nitrous oxide and finally to molecular nitrogen, which is harmless for environment ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$). Under many operation conditions investigated more than 50 % of the converted ammonium was transformed into gaseous nitrogen [7]. Both nitrification and denitrification are able to produce the greenhouse gas N_2O as an intermediate, which is emitted into the atmosphere. This happens under suboptimal conditions regarding pH, temperature, limitation of readily biodegradable organic carbon and nitrogen substrates, presence of dissolved oxygen or hydrogen sulfide in the anoxic denitrification reactor, etc. [6]. Denitrifying wastewater treatment plants tend to have lower N_2O emissions than plants that are designed only for nitrification and/or carbon removal. According to particular investigations [8] the ratio of N_2O production to NO_3 reduction was up to 20 % for the denitrification potential, while the ratio of N_2O emission to NO_3^- production by nitrification was only about 0,2 %. Nevertheless, N_2O emissions to the atmosphere occur predominantly during aerated phases due to the significantly high gas mass transfer from the liquid phase to the air [9].

Wastewater treatment systems using biofilms that grow attached to a support media are an alternative to the widely used suspended growth activated sludge process. They exploit the natural ability of microorganisms to adhere to surfaces and grow. Physiological efficiency has been consistently shown in complex multispecies biofilms. Mixed community of heterotrophic bacteria (that use organic carbon source), autotrophic nitrifying bacteria (that use inorganic carbon source), protozoa, rotifers, nematode, microalgae, fungi and oligochaete worms are used for advanced treatment of wastewater [10 – 11].

Submerged biofilm reactors (SBRs) are equipped with a fixed bed of granular material with a pore size of 0,7 – 8,0 mm. Regular backwashing of the media bed with treated effluent is required for preventing clogging of the filter and removing excess sludge. As these facilities have shown a particular advantage in the attachment of nitrifiers, in the last decades, when nitrogen standards were tightened, biological aerated filters (BAFs) were recognized as a powerful tool for nitrification. BAFs designed for carbon oxidation and suspended solids removal in secondary treatment typically have volumetric BOD_5 loading rates in the range of 1,5 – 6 kg/m^3d. Because of the vulnerability of the autotrophic nitrifiers, combined carbon oxidation and nitrification proceed well when the organic loading at lower temperatures is limited to 2,5 kg BOD_5/m^3d [12]. A wide variety of configurations and media systems have been developed. A downflow BAF with media heavier than water (expanded clay or another mineral media) is illustrated in Fig. 1. The anoxic reactors for denitrification are similar but without process air system.

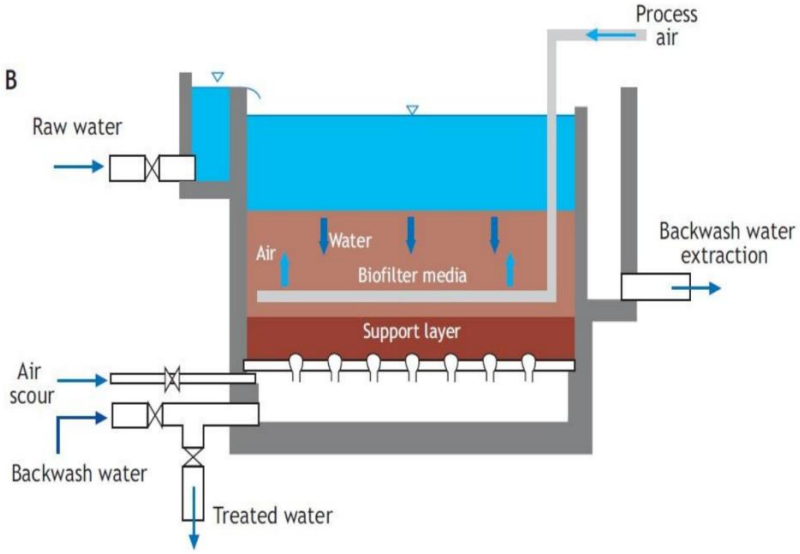

Figure 1. Downflow BAF with media heavier than water [12]

The objective of the present study is to evaluate direct N_2O emissions during nitrification and denitrification in submerged biological reactors (SBRs) using data from author's pilot plant experiments and calculations based on typical parameters and emission factors (EF).

2. Materials and methods

2.1. Pilot plant experiments

For quantification of the N_2O emissions data are used from pilot plant experiments carried out at a municipal WWTP [13]. The experimental system consists of a downflow submerged anoxic biofilm reactor (Column 1) for denitrification followed by a downflow biological aerated filter – BAF (Column 2) to oxidize both organic carbon compounds and ammonium nitrogen (nitrification) as shown in Fig. 2 [14]. Column 1 was supplied with settled wastewater (Q_s = 0,3 dm^3/min = 1 $m^3/m^2/h$) coming from the outlet of the primary clarifiers of the WWTP mixed with nitrified effluent recirculated from the BAF. The experiments started with a recirculation ratio r = 0 to reach r = 3 (3 parts treated effluent to 1 part primary settled influent). The organic matter in the inlet stream serves as a carbon substrate for the heterotrophic bacteria in the anoxic SBR. The experiments were carried out for 2,5 months in autumn under real conditions of day-to-day irregularity of the input wastewater load to the plant. The average water temperature in both reactors varied between 13,9 °C at the beginning of the experiments and 11,1 °C at the end.

2.2. Experimental data used

The operational conditions and process data (average values) are given in Table 1 and Table 2.

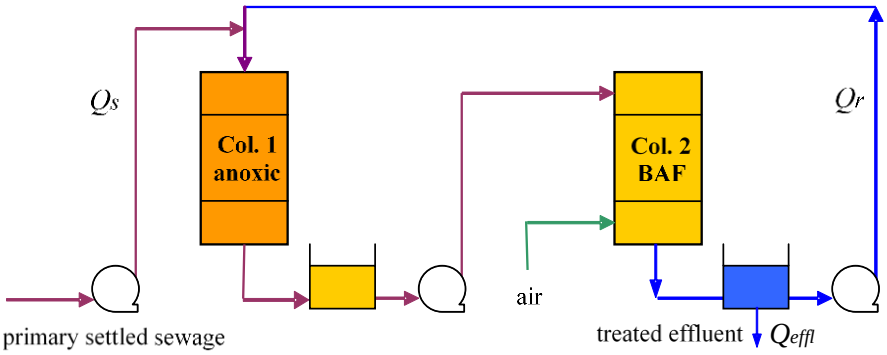

Figure 2. Pilot plant for advanced WW treatment in submerged biological filters
Q_s – primary settled sewage; Q_{effl} – treated effluent; Q_r – recirculated effluent [14]

Table 1. Volumetric loading rates at the inlet of a reactor

			Column 1 (Anoxic)		Column 2 (BAF)	
r	***Q_s***	***Q_d***	**BOD_5**	**NO_x-N**	**BOD_5**	**NH_4-N**
-	dm^3/min	dm^3/d	kg/m^3d	kg/m^3d	kg/m^3d	kg/m^3d
0	0,3	432	2,68	0,01	1,92	0,48
1	0,3	432	2,43	0,18	0,66	0,43
2	0,3	432	2,59	0,29	0,85	0,48
3	0,3	432	3,37	0,28	1,26	0,41

Q_d – daily hydraulic load of the influent (primary settled wastewater);
NO_x-N – total oxidized nitrogen.

Table 2. Total inorganic nitrogen influent and effluent values

				Total inorganic nitrogen		
r	***Q_s***	***Q_d***	***v_f***	**Influent**	**Effluent**	**Removal**
-	dm^3/min	dm^3/d	m/h	g/d	g/d	%
0	0,3	432	1,0	15,72	7,34	53,3
1	0,3	432	2,0	13,48	5,53	59,0
2	0,3	432	3,0	14,64	4,49	69,3
3	0,3	432	4,0	15,47	2,89	81,3

v_f – flow velocity in the filter columns, m/h = hydraulic load, m^3/m^2h.

2.3. N_2O emissions estimation methodology

The quantification of the N_2O emissions from the nitrogen removal pilot plant is based on the IPCC Guidelines for National Greenhouse Gas Inventories [15]. The assessment period is 1 year.

$$N_2O_{emiss} = N_{infl}.EF.44/28, \quad (1)$$

where N_{infl} is the influent total inorganic nitrogen in kg/yr;
EF = 0,0015 kg N_2O-N per kg N_{infl} – calculated emission factor as explained below;
44/28 – the conversion factor from kg N_2O-N to kg N_2O.

To compare the effect of the N_2O gas, its emissions in the wastewater treatment are referenced to CO_2 equivalent (CO_2eq) by multiplication with the N_2O global warming potential GWP = 273.

Most estimates for greenhouse gas inventories usually use fixed emission factors (EF). According to some specialists' views [16], the default values of the N_2O emissions from municipal WWTPs estimated by the IPPC and other international agencies in most cases were much lower than reality. The revised version of the IPCC guidelines [15] increased the default emission factor to 0,016 kg N_2O-N per kg influent total nitrogen (TN_{infl}) – mean value for secondary aerobic treatment domestic WWTP. It is widely used at present by various stakeholders, including national environmental agencies. However, the suggested new approach does not consider the impact of the operating conditions and wastewater composition on N_2O emissions [9].

The present study tries to improve the simplified approach, which uses a very general default EF. Here, the EF is calculated as a mean value of three emission factors given in two sources. Campos et al. [17] gives an example of a conventional activated sludge system with anoxic and aerobic reactors performing the nitrification-denitrification processes to remove both organic matter and nitrogen at internal recycle ratio of 3. There N_2O emissions are equal to 0,5 % of the N treated, which means an emission factor of 0,0032 kg N_2O-N/kg N treated. On the other hand, Table 6A.5 in [15] gives a wide range of EFs from 0,00016 ÷ 0,045 kg N_2O-N/kg N depending on the technology applied. Two values of these emission factors are considered in the present study regarding very similar systems and processes for biological nitrogen removal (BNR) referred there as MLE (Modified Ludzack-Ettinger) (Table 3).

Table 3. N_2O EFs in full-scale domestic WWTPs [15]

Type of treatment process	Categories	References	N_2O emission factor (kg N_2O-N/kg N)
MLE	BNR	Ahn et al. (2010)	0,0007
MLE	BNR	Ahn et al. (2010)	0,0006

Hence, the calculated mean value of 0,0015 kg N_2O-N/kg N_{infl} is used as the EF in formula (1) for estimating the N_2O emissions from the anoxic-aerobic submerged biofilm reactors investigated. This approach is justified for two reasons:

(i) the fact that there are fewer emission studies on biofilm systems and the published N_2O emissions from wastewater treatment are mostly from activated sludge processes;

(ii) according to Gonçalves [18] the microorganisms involved in biological filters are similar to the ones present in activated sludge reactors and the operational conditions required such as pH, temperature and nutrients are of similar relevance.

3. Results and discussion

The results from the calculations of the N_2O emissions from the experimental nitrification-denitrification system are shown in Table 4.

A review on N_2O emissions in biological wastewater treatment [19] finds out that measurements at lab-, pilot- and full-scale WWTP have shown large variations in N_2O emissions during wastewater treatment (0 ÷ 95 % of N-load), in the full-scale WWTPs being 0 ÷ 14,6 % N_2O of N-loaded. The present study uses EF-values from measurements at full-scale WWTPs and the N_2O emissions calculated here are 0,24 % of N loads, which is within the cited range.

Table 4. N_2O emissions from the nitrification-denitrification system

		Influent inorganic nitrogen		EF	Emissions	
r	v_f					
-	m/h	g/d	kg/yr	kg N_2O-N/kgN_{infl}	kg N_2O/yr	kg CO_2eq/yr
0	1,0	15,72	5,738	0,0015	0,014	3,692
1	2,0	13,48	4,920	0,0015	0,012	3,166
2	3,0	14,64	5,344	0,0015	0,013	3,439
3	4,0	15,47	5,647	0,0015	0,013	3,634

The improved approach for the Emission Factor identification using values from similar treatment technologies still has an intrinsic weakness, which is obvious from the Table 4 with the N_2O emissions calculated. It does not take into account the different varieties of the treatment technology as the IPCC formula (1) estimates the nitrous oxide emissions based on the influent nitrogen loads. Hence, no matter what the recirculation ratios and nitrogen removal effects are, the emissions calculated are approximately the same. Nevertheless, this method gives a good idea of their magnitude for the particular wastewater treatment facilities and operating conditions applied.

4. Conclusion

Nitrous oxide (N_2O) is an important greenhouse gas and a major sink for stratospheric ozone. In biological wastewater treatment, microbial processes such as autotrophic nitrification and heterotrophic denitrification have been identified as major sources. The contribution of wastewater management is still controversial as N_2O emissions are poorly measured in wastewater treatment plants and the published N_2O emissions are mostly from activated sludge processes. Therefore, the present study for estimation of the nitrous oxide emissions from submerged biological filters for nitrogen removal gives a good idea of their magnitude for the particular wastewater treatment facilities and operating conditions. The calculations are based on typical parameters and emission factors, but the improved approach applied for the Emission Factor identification, than the widely used, might be a useful tool for quantification of N_2O emissions when direct field measurements of the latter are not available.

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ОЦЕНКА НА ЕМИСИИТЕ НА ДИАЗОТЕН ОКСИД (N_2O) ПРИ ОТСТРАНЯВАНЕ НА АЗОТА ОТ ГРАДСКИ ОТПАДЪЧНИ ВОДИ В ПОТОПЕНИ БИОФИЛМОВИ РЕАКТОРИ

А. Ватралова[1]

Ключови думи: *диазотен оксид (N_2O), парникови газове, отпадъчни води, нитрификация, денитрификация*

РЕЗЮМЕ

Диазотният оксид (N_2O) има парников ефект, който е 273 пъти по-силен от този на въглеродния диоксид съгласно последната оценка на Междуправителствения панел за климатични промени (IPCC). Следователно, дори относително малки количества могат да доведат до значителен въглероден отпечатък. N_2O се отделя по време на процесите на биологично отстраняване на азота при пречистване на отпадъчни води. Това изследване оценява директните емисии на N_2O по време на нитрификация/денитрификация в потопени реактори с фиксирана биомаса с използване на данни от собствени полупромишлени експерименти. Изчисленията са направени въз основа на типични параметри и емисионни фактори, но с приложен подобрен подход за тяхното определяне в сравнение с широко използвания.

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