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Calculation of N_2O Emission in the Wastewater Treatment Process of Paper Mill

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***Abstract*—Aiming at the quantification of the N_2O production from wastewater treatment plants (WWTPs) of papermaking industry, we provided a practical mathematical model. Primarily, the TNs (influent and effluent) were off-line measured with the ultraviolet spectrophotometry, and the flowrate of wastewater was the field data from on-line monitoring system. Subsequently, combining with the two variables, the determinate emission rate factor of N_2O was applied to the estimation of the N_2O emission. The results showed that the averaged 15.234 mg/m^3 of N_2O was emitted during the biological nitrogen removal process in a paper mill. In addition, we analyzed some influencing factors during the operation in this article, including the dissolved oxygen (DO), pH, nitrite concentration and COD/N ratios. And the nitrite concentration in the wastewater directly increased the N_2O generation, except that other parameters have the modest influence. Compared with the researches on N_2O emissions, the proposed model is simplified to be dedicated to the wastewater treatment of papermaking industry.**

Keywords*—GHG emissions; wastewater treatment; nitrous oxide; total nitrogen

I. INTRODUCTION

Greenhouse gases (GHGs) are those gases in the atmosphere that absorb and reflect radiation in a specific wave length range, such as water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3). They have been identified as the trigger of the "greenhouse effect", which resembles that the gases trap solar radiation leading climate warming in the earth. Since the industrial activities increased, the anthropogenic GHG emissions have multiplied with the growing industrial development. There is an assumption that the GHG emissions following the present rate can lead to that earth's surface temperature in 2047 that would go beyond the historical limit [1]. In the recent years, the scientists also predicted that, continuing the current rate of GHG production, it could surpass the prescriptive global warming threshold of 2 °C by 2036, considered as the upper limit to the global warming from the IPCC [2].

Particularly, according to IPCC, the most dangerous gas with a much higher global warming potential (GWP) in a 100 year-period than CO_2, N_2O can exist in a stationary atmosphere for almost a century and damage the ozone layer of the earth sustainably on account of the reaction to the O_3 [3-5].

Origin from both the natural and human activities, N_2O production becomes one of the concerned topic. It's estimated that N_2O from human-related sources accounted for 38% of the total N_2O emissions [6]. The wastewater treatment plants (WWTPs) have been reported as one of the main industrial sources of GHG emission, which originate from two distinct sources, on-site and off-site emission. On-site GHG emission occurring inside the specific sections used for the biological processes that the contaminants are removed to produce CO_2, CH_4 and N_2O. Apart from the specific sections, the indirect GHG generation from energy production, material consumption as well as the transportation of fuel is identified as off-site emission [7].

The pulp and paper industry is the third largest producer of wastewater in the industrial circle. Diverse approaches are examined for the wastewater treatment in paper mills, which involve the technologies of biology and physiochemistry contributing to GHG generation. The N_2O emissions from the pulp and paper industry in the wastewater treatment of WWTPs mainly occur from the on-site system. In the biological treatment of wastewater, N_2O is emitted along with several GHGs. Although compared to other GHGs, N_2O is relatively less in quantitative terms, it is more dangerous for the environment owing to its high GWP.

There are various processes for producing N_2O in WWTP: denitrification, nitrification and chemical reactions [8]. Accordingly, in this study, the quantification of N_2O emissions from wastewater treatment in paper mill was implemented.

II. MATERIALS AND METHODS

A. Calculation of Emission of N_2O in the Biological Treatment of Wastewater

It's generally recognized that N_2O is an obligatory intermediate in the heterotrophic pathway and also a by-product during the autotrophic nitrification. Meanwhile, N_2O is identified as a type of harmful gas with its high global warming potential (GWP=298). In this study, it is ascertained that 0.5% of total nitrogen is reduced to N_2O [9] during denitrification and released to the atmosphere, the N_2O emission rate was affirmed as follows:

$$R_{N_2O,\ generation} = 0.005$$

Therefore, in the denitrification process N_2O emissions are detected [10]. It is calculated by the following formula:

$$N_2O_{emission} = Q_{influent} \times (TN_{in} - TN_{out}) \times R_{N_2O,\ generation} \quad (1)$$

where, $N_2O_{emission}$ is the N_2O emission [kg N_2O /day]; $Q_{influent}$ is the average influent flow rate per day [m^3/day]; TN_{in} is the total nitrogen from the influent [kg/m^3]; TN_{out} is the total nitrogen from the effluent [kg/m^3]; $R_{N2O,\ generation}$ is the emission rate of N_2O in kg N_2O/kg N.

B. Determination of Total Nitrogen (TN) of Wastewater in the Paper Mill

From 16th to 21st April and from 4th to 20th July of 2018, the wastewater samples were collected from the SBR system of the wastewater treatment plant in Guangzhou Paper Mill. The TN of wastewater in each sample was measured off-line. At 120-124 °C, under the certain condition of alkaline potassium persulfate (NaOH-$K_2S_2O_8$), the nitrogenous compounds can be completely converted into the nitrate [11]. Thus, via the measurement of nitrate, the determination of TN was achieved indirectly. Owing to the characteristic absorption peak of nitrate in the wavelengths of 220 nm and 275 nm, the TN concentration in wastewater were measured by ultraviolet spectrophotometry at the wavelengths of 220 nm and 275 nm.

III. RESULTS AND DISCUSSIONS

A. Emissions of N_2O in WWTP from a Paper Mill

Primarily, as shown in Figure 1, the flow rate of wastewater in the SBR process of the paper mill was the field data from the on-line monitoring. Meanwhile, the wastewater samples were collected and indirectly measured by the above method, including the requisite total nitrogen of influent (TN_{in}) and the total nitrogen of effluent (TN_{out}) (see Figure 2).

As shown in Figure 3, the nitrogen oxide (N_2O) emission in wastewater treatment plants is showed, which fluctuates strongly. The results showed that the N_2O emission from the SBR process of wastewater treatment plant in the paper mill was 15.234 mg/m^3 on average. Although it was relatively small compared to the CO_2 emission in the WWTP, N_2O has a global warming potential which is 298 times higher than that of CO_2 in a 100-year period.

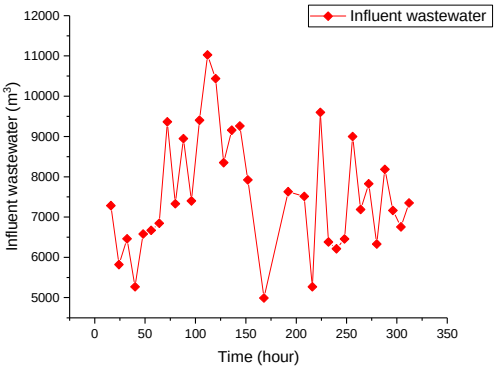

FIGURE I. FLOWRATE OF THE INFLUENT IN THE SBR PROCESS OF WASTEWATER TREATMENT PLANT OF THE PAPER MILL.

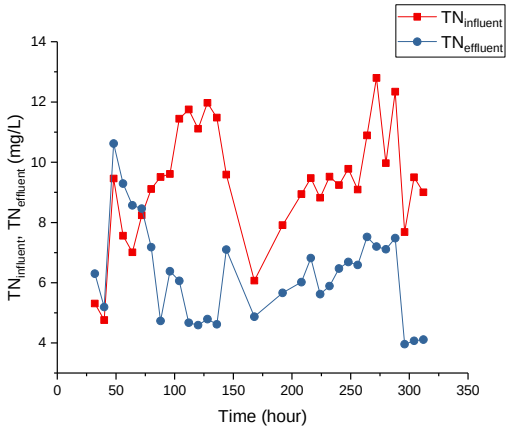

FIGURE II. TOTAL NITROGEN CONTENTS OF THE INFLUENT AND EFFLUENT IN THE SBR PROCESS OF WASTEWATER TREATMENT PLANT OF THE PAPER MILL.

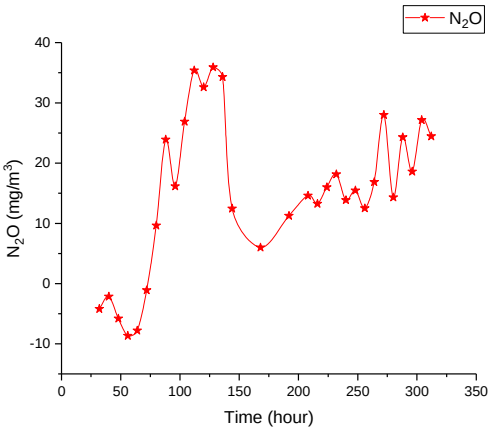

FIGURE III. CALCULATED N2O EMISSIONS IN THE SBR PROCESS OF WASTEWATER TREATMENT PLANT OF THE PAPER MILL

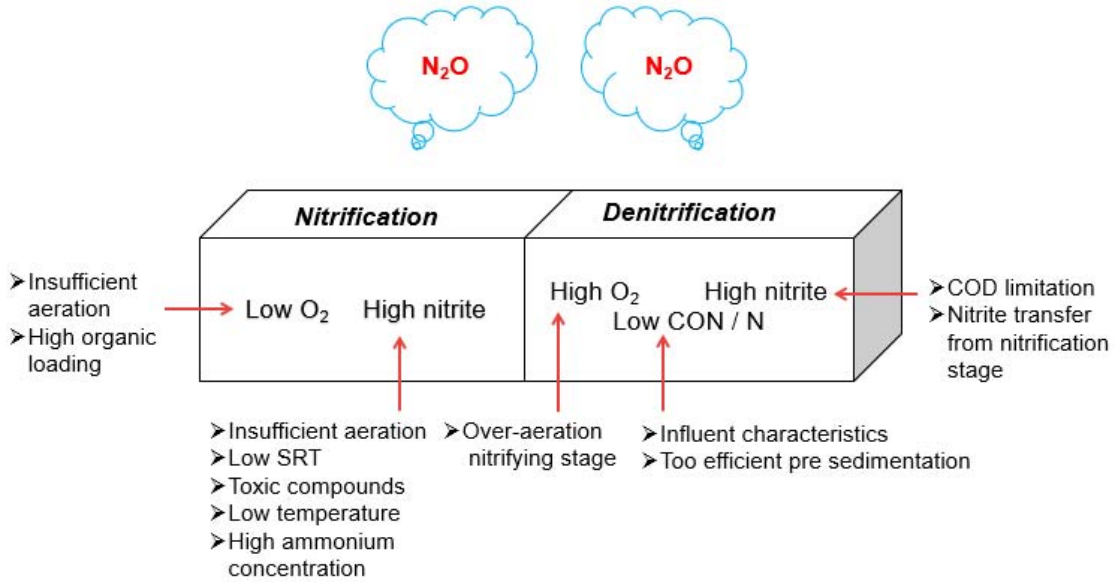

FIGURE IV. INFLUENCING FACTORS OF N_2O EMISSIONS IN THE SBR PROCESS OF WASTEWATER TREATMENT PLANT

B. Parameters Affecting the N_2O Emission

During the wastewater treatment, some dominate parameters in the running of the process are considered as the factors of N_2O generation, such as dissolved oxygen (DO), nitrite, chemical oxygen demand for nitrogen (COD/N) and partial pH (shown in Figure 4).

1) Dissolved oxygen

The DO concentration is generally recognized as a critical factor for controlling N_2O emission reduction during biological nitrous removal. It has been generally accepted that, while the DO concentration in the bio-reactor is lower than 0.5 mg/L, the N_2O accumulation are increasing. As an inhibitor, the rising DO concentration would decline activity of denitrification enzymes. As a consequence, N_2O wouldn't be reduced and release to the atmosphere. Moreover, in the full-nitrification processes, there existed some synergistic effects of DO and pH on the N_2O accumulation.

2) Nitrite

It's commonly recognized that the concentration of nitrite has crucial effects on N_2O emissions in the biological treatment of wastewater. Batch experiments were carried out to investigate the effect of nitrite on N_2O generation and emission during denitrifying phosphorus removal. Compared to NO_3-N, N_2O emission was much higher when NO_2-N was used as the electron acceptor [12]. Numerous studies have reported that nitrite accumulation (10-50 mg/L) inhibited the growth of denitrifying bacteria. An inhibition of N_2O reductases by the toxicity of NO_2-N was observed [13].

3) COD/N ratio

Noted that the ratio of COD/N can affect the involution of biological nitrogen removal. The classical COD/N ratio gradients (1.5, 2.5, 3.5 and 4.5) was examined by [14] and the result indicated that, during the treatment of the ratio of 1.5, as high as 10% nitrogen was converted to gaseous N_2O and emitted it. Figure 5 shows the COD in wastewater from wastewater treatment plants in the paper mill. However, the accurate mechanism theory hasn't been revealed and the control of COD/N was supposed to be limited, which might not be the direct factor for the N_2O emissions.

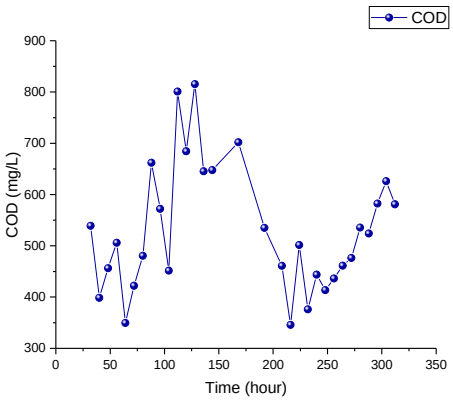

FIGURE V. VARIATION OF COD IN THE SBR PROCESS OF WASTEWATER TREATMENT PLANT OF THE PAPER MILL.

The present works on the COD/N ratio for the N_2O reduction, was that under the COD/N ratios higher than 10, the denitrifying microorganisms would be enriched leading to the N_2O emission increasing tempestuously.

4) pH

It's commonly reported that in a fully aerated culture, the N_2O production by the nitrosomonas relies on the pH in the wastewater. Currently, between the pH of 6 and 8.5, N_2O emission is linear growth with the pH increasing. Similar to the

observations by [15], during denitrification, the amount of N_2O generation was rising following the pH decreased from 8.5 to 6.5. On the contrary, in a denitrification basin, pH below 6.8 was detected during the N_2O formation. As shown in Figure 6, the pH in wastewater treatment plant from the paper mill is generally between 7 and 8 and quite stable, which indicated that, in this system, the effect of pH on the N_2O emission was slight.

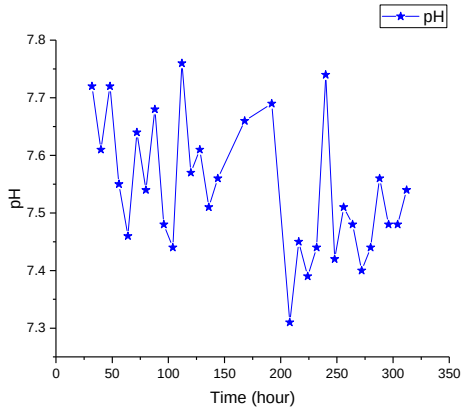

FIGURE VI. VARIATION OF THE PH IN THE SBR PROCESS OF WASTEWATER TREATMENT PLANT OF THE PAPER MILL.

IV. CONCLUSION

In this article, the N_2O emissions from the SBR process of wastewater treatment plant (WWTP) in a paper mill were calculated, and the factors that affected the production of N_2O were also analyzed in detail. Primarily, the TN of wastewater was indirectly measured by the UV spectrophotometry. Subsequently, combining with the TNs (influent and effluent) and the flowrate of wastewater, the determinate emission rate of N_2O was applied to the estimation of the N_2O emissions. The results showed that the N_2O emission from the SBR process of wastewater treatment plant in the paper mill was 15.234 mg/m^3 on average.

Several key operational parameters had effects on the N_2O emission. The DO and pH of wastewater had synergistic effects on the N_2O accumulation; the pH of wastewater changing in a narrow range (7-8) had slight effects on the N_2O emission; the nitrite concentration in the wastewater directly increased the N_2O generation in the biological nitrogen removal processes; the COD/N ratio was the indirect-acting factor on the N_2O emissions.

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