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Simultaneous removal of SO_2 and NO in a rotating drum biofilter coupled with complexing absorption by Fe^{II}(EDTA)

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ABSTRACT

A promising process of microbial desulfurization and denitrification integrated with complexing absorption is under the development for simultaneous removal of SO_2 and NO in a rotating drum biofilter (RDB). The process employs Fe^{II}(EDTA) to improve the NO mass transfer, the denitrifiers bacteria (NR) for the denitrification, and the sulfate reducing bacteria (SRB) for the desulfurization. Experimental results demonstrated that NO removal efficiency was significantly improved from 57.1% to 93.0% in the presence of 10 mM Fe^{II}(EDTA) in the 60-day operation. Meanwhile, the SO_2 removal efficiency reached around 90%. Parametric tests showed the maximal removal efficiency of SO_2 and NO could be achieved at 98.5% and 93%, respectively, in the conditions of 2000 mg/m^3 SO_2, 800 mg/m^3 NO, 1.8 min of empty bed residence time (EBRT), and 2 vol% oxygen. The microbial community analysis with the high-throughput sequencing indicated that the dominant denitrification bacteria with a maximal abundance of 35.7% were *Pseudomonas* which was mainly distributed in the external sphere of RDB and the dominant SRB was *Desulfovibrio,* which was mainly distributed in nutrient solution with a maximal abundance of 6.1%.

1. Introduction

The rapid industrial development in the recent years increases the emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) which are the principal cause of the acid rain. In addition, NO_x contribute to the photochemical smog, the depletion of the ozone layer, as well as global warming [1,2]. With the stringent emission standards of NO_x and SO_2 imposed by Gothenburg and Kyoto Protocols, the development of new technology and/or improvement of currently used methods are essential. Presently, chemical and physical technologies [3–6] such as oxidation absorption reduction [7], NO × SO process [8,9] and wet flue gas desulfurization coupled with selective catalytic reduction [10] are popular for the simultaneous NO_x and SO_2 removal. Although those conventional technologies play an important role in the NO_x and SO_2 removal, they are costly and generate secondary pollutants.

Biotechnologies e.g., biofiltration have been regarded as a potential cost-effective alternative to conventional air pollution control technologies due to its low cost, easy operation and management, and low risk in secondary pollutant generation [11]. In the past decades, some research on the simultaneous biological removal of SO_2 and NO_x has been reported [12,13]. Han et al. [14] has proved that under the anaerobic condition, the co-cultured bacteria had a better performance than the solely denitrifying microorganisms in the combined NO/SO_2 biodegradation process. The research also showed that the simultaneous removal of NO and SO_2 from flue gas by liquid-phase catalytic oxidation-biological purification performed well under certain conditions. Most of the above work presented a low NO_x removal efficiency due to the limitation of the NO mass transfer, which retarded the industrial application of simultaneous removal of NO and SO_2 by a biotrickling filters [15,16].

It has been confirmed that Fe^{II}(EDTA) can significantly enhance the NO mass transfer rate [17–21]. Fe^{II}(EDTA) can chelate NO into the solution to form Fe^{II}(EDTA)-NO (Eq.(1)). On the other hand, SO_2 can dissolve in the solution and produces SO_3^{2-} and SO_4^{2-}. These compounds can be reduced to sulfide (S^{2-}) by sulfate reducing bacteria (SRB) in the anaerobic bioreactor (Eq.(2)) [22]. The produced sulfide can be used as electron donor by the autotrophic denitrifying bacteria to reduce Fe^{II}(EDTA)-NO, thus regenerating the absorbent Fe^{II}(EDTA) to sustain the continuous NO removal (Eqs.(3) and (4)) [23]. Wang et al. [24] has established a simultaneous absorption of NO and SO_2 by Fe^{II}(EDTA) combined with Na_2SO_3 solution without biofilter on the purpose of investigation

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on the reaction products and mechanism, the majority consumed SO_2 were converted into SO_4^{2-} and the NO was reduced to N_2O. Chen et al. [25] have found that based on NO and SO_2 absorption into Fe^{II}(EDTA) solution in a scrubber combined with biological reduction, more than 87% Fe^{III}(EDTA) and 98% Fe^{II}(EDTA)-NO could be reduced.

$$NO(aq) + Fe^{II}(EDTA) \leftrightarrow Fe^{II}(EDTA) - NO \quad (1)$$

$$SO_2 \overset{water}{\rightarrow} SO_4^{2-}/SO_3^{2-} \overset{SRB}{\rightarrow} S^{2-} \quad (2)$$

$$4Fe^{II}(EDTA) - NO + HS^- \rightarrow 4Fe^{II}(EDTA) + 2N_2 + SO_4^{2-} + H^+ \quad (3)$$

$$Fe^{II}(EDTA) - NO + HS^- \rightarrow Fe^{II}(EDTA) + \frac{1}{2}N_2 + S^0 + OH^- \quad (4)$$

This work aimed at demonstrating the feasibility of the simultaneous removal of SO_2 and NO with Fe^{II}(EDTA) as a solvent in a rotating drum biofilter (RDB). The parametric tests including the inlet SO_2 and NO concentration, empty bed residence time (EBRT), and O_2 concentration was also investigated to their impacts on the bioreactor performance. Additionally, the microbial community in the RDB was analyzed to figure out the dominant bacteria pertained to the biological denitrification and desulfurization.

2. Materials and methods

2.1. Chemicals

NO (5% in N_2, v/v), N_2 (99.999%), O_2 (99.999%), and SO_2 (0.5% in N_2, v/v) were obtained from Zhejiang Jingong Co, China. Disodium ethylenediaminetetraacetate (Na_2EDTA, Titriplex) $FeCl_2{\cdot}4H_2O$ (99.5%), $FeCl_3{\cdot}6H_2O$ (99.5%), d-glucose (99.5%) were obtained from Shanghai Chemical Reagent Co. (Shanghai, China). All other chemicals were analytical-grade reagents, commercially available and used without further purification.

The Fe^{II}(EDTA) solution was prepared with equal concentration (40 mM) of Na_2EDTA and $FeCl_2$. The solution pH was adjusted with 0.1 mM phosphate buffer (pH 7.0). The Fe^{II}(EDTA)-NO complex solution was prepared by bubbling NO through the ferrous EDTA solution until full breakthrough of NO was observed (The inlet and outlet concentration of NO was measured to be equal with a NO_x analyzer) in the effluent. The prepared solution was kept in glass serum vials under N_2 positive pressure in order to avoid the oxidation of the ferrous EDTA in the solution. The Fe^{II}(EDTA)-NO saturated solution exhibited negligible break down over a period of one week under a blanket of inert gas.

2.2. Source of biomass and media composition

A concentrated active sludge was collected from a secondary sedimentation tank in the Hangzhou Qige Wastewater Treatment Plant, China. After 2-week culture in 8 L liquid medium (containing 500 mg/L Na_2SO_4, 500 mg/L KNO_3, and 3500 mg/L $C_3H_5O_3Na$), the enriched sludge was inoculated to the RDB. 500 mL of nutrient medium was replaced manually once a day from the lumen of the rotating drum. The pH value of medium was maintained at 7.0 and temperature was 30 ± 5 °C.

The culture media includes 3500 mg/L $C_3H_5O_3N_a$, 500 mg/L NaCl, 2000 mg/L K_2HPO_4, 600 mg/L $MgSO_4{\cdot}7H_2O$, 500 mg/L $NaHCO_3$ and 1 mL/L of trace elements solution ($CuSO_4$, 1.0 g/L; $FeSO_4$, 1.0 g/L; $MnSO_4$, 5.0 g/L; Na_2MoO_4, 1.0 g/L; and $ZnCl_2$, 2.0 g/L).

2.3. Start-up of the RDB

As shown in Fig. 1, the RDB treatment system was composed of gas supply section, an inspection section, and the main unit of the RDB. The start-up of the RDB was initiated with 2 L enriched sludge and 8 L culture media with 100–1000 mg/L sulfate and 100–1000 mg/L nitrate. The nutrient liquids promoted the growth of autotrophic bacteria and the rotating drum provided a sufficient contact between the packing layer and the nutrient liquids for the bacteria attachment. The effect of pH on the removal efficiency of NO and SO_2 was investigated as show in Fig. S1, and the optimal pH was neutral or slightly alkaline for the growth of bacteria and enzyme activity. Hence, the pH value was adjusted to around 7.0, and the sample was taken to monitor the removal efficiency of SO_4^{2-} and NO_3^-. A certain concentration of SO_2 (~389 mg/m^3) and NO (~417 mg/m^3) balanced by the N_2 was supplied to the RDB instead of the SO_4^{2-} and NO_3^-. The NO and SO_2 were absorbed by the solvent and the absorbed NO and SO_2 were biologically reduced by the bacteria in the biofilm. During the RDB operation, the nutrient was cautiously added at a certain rate to provide the adequate nutrition for the growth of bacteria.

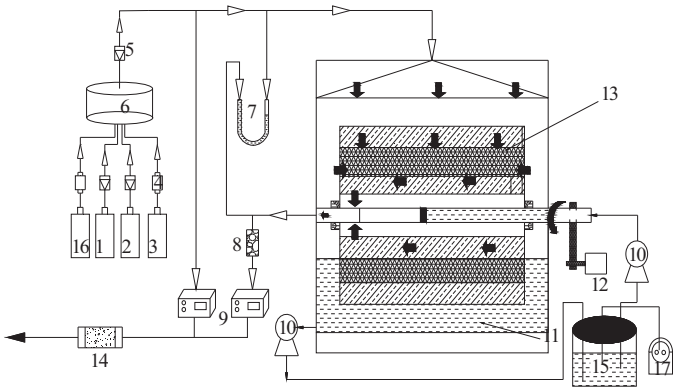

Fig. 1. Schematic representation of the laboratory-scale system. (1) N_2 cylinder, (2) O_2 cylinder, (3) NO cylinder, (4) digital mass flowmeter, (5) rotatmeter, (6) gas mixed container, (7) pressure meter, (8) dryer, (9) flue gas analyzer, (10) metering pump, (11) nutrient solution, (12) motor, (13) packing material, (14) tail gasabsorber, (15) nutrients reservoir, (16) SO_2cylinder, (17) pH control system.

2.4. Experimental procedures

After the start-up period, the performance of the simultaneous removal of SO_2 and NO in the RDB was evaluated. In a typical test, the pH value was maintained at 7.0 and temperature was 30 ± 5 °C. The inlet concentration of SO_2 and NO was kept at around 2000 mg/m^3 and 800 mg/m^3, respectively. In addition, the effects of SO_2 concentration (~2500 mg/m^3), NO concentration (180–1200 mg/m^3), EBRT (0.5–7 min), and O_2 concentration (~8 vol%) on the performance of the RDB were also investigated. Three samples named as S1, S2, and S3 were collected from the bottom of nutrient solution to investigate the evolution of microbial community after the start-up period, the SO_2 inlet concentration investigation, and the completion of all the parametric tests, respectively. On top of that, after the completion of all the parametric tests, another three samples were collected along the radius of layers (external radius, median radius and inner radius named as R1, R2 and R3) to investigate the distribution of microbial community along the packing.

2.5. DNA extraction, amplification, and high-throughput sequencing

Genomic DNA was extracted from the cells according to the instruction of the DNA isolation kit obtained from Shanghai Biotechnology Co., Ltd. Purified DNA was used as a template for PCR amplification with high-fidelity DNA polymerase. The 16 S rRNA genes were amplified using the universal primers 341F:

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