Insights into the removal of gaseous oxytetracycline by combined ozone and membrane biofilm reactor

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ABSTRACT

Gaseous emerging organic compounds (GEOCs) may harm human health and ecological environment. High temperature composting of livestock manure may produce oxytetracycline (OTC) waste gas. Here, we investigated treatment OTC in waste gas by combined ozone and membrane biofilm reactor (MBfR) with desulphurizing bacteria. The performance, the microbial community, gene function and the mechanism for OTC removal in the ozone-MBfR were evaluated. The ozone-MBfR system could achieve more degradation of OTC completely than MBfR. *Desulfovibrio*, *Lentimicrobium*, *Aminivibrio*, *Thioalkalispira*, *Erysipelothrix*, *Mangroviiflexus*, *Azoarcus*, *Thauera*, *Geobacter*, *Paracoccus*, and *Dethiosulfatibacter* were the dominant genera. *Pseudomonas*, *Escherichia*, *Bacteroides*, *Salmonella*, *Paracoccus*, *Stappia* were contribution to OTC degradation. With the addition of ozone, the community diversity increased; some genera, such as *Tenericutes-uncultured*, and *Desulfovibrio*, increased in abundance, whereas others, such as *Thauera*, and *Petrimonas*, decreased. Ozone destroyed the enol structure in OTC molecular structure and produces biodegradable products, ozone oxidation was combined with biodegradation, to achieve thoroughly degrade OTC in waste gas. The novel hybrid ozone-MBfR is a cost-effective and robust alternative to GEOCs treatment.

Keywords: Bacterial community, Degradation mechanism, Gaseous emerging organic contaminants, OTC in waste gas, Ozone and biological process

1. Introduction

Ecological and environmental protection has become a global concern, carbon dioxide emission from conventional fossil fuels contribute to global warming [1], while emerging organic pollutants (EOPs) are serious environmental concerns known for their prominent adverse and hazardous ecological effects, and persistence in nature [2]. Antibiotics, as emerging pharmaceutical pollutants, are widely used as veterinary drugs in livestock breeding. However, these antibiotics cannot be fully absorbed in the animal intestine, and as much as 30–90% of the maternal compounds will be excreted through feces or urine [3]. The widespread use of tetracycline antibiotics results in the detection of mg/kg or even hundreds of mg/kg tetracycline residues in animal feces [4]. Antibiotics in animal feces were degraded by high temperature composting (70°C) [5]. During the process of manure composting at high temperature, the high temperature and heap turning made the aerosol containing OTC diffuse into the atmosphere, producing OTC waste gas. Oxytetracycline amendment resulted in a dose-dependent and spe-

cies-specific effect on the gut microbiomes and resistomes of two mite species [6]. Antibiotic resistance genes (ARGs) would reduce the efficacy of antibiotic treatment [7]. Gaseous emerging organic compounds (GEOCs) may harm human health and ecological environment because of their toxicity and health risks. Antibiotic resistance gene pollutants were detected in the air of livestock farms, and the stacking of livestock manure would produce sulfur nitrogen odor and emerging organic pollutants [8]. Gaseous emerging pollutants such as brominated flame retardants, phthalates, pharmaceuticals, oxytetracycline (OTC), and personal care products have been detected in indoor air, dust, and pharmacy industry [9]. Phthalate is found in many cosmetics, toys and food packaging, which can interfere with endocrine, reduce sperm number, and seriously lead to testicular cancer. The degradation products of oxytetracycline after composting were still macromolecular substances EOTC ($M/Z = 461$), α -APO-OTC ($M/Z = 443$) and β -APO-OTC ($M/Z = 443$) [10]. The combination of antibiotics, antibiotic resistance genes (ARGs) and bacteria in compost were released into the atmospheric environment, long-term human ex-

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posure to this environment would lead to risks of infectious diseases, toxic effects, allergies and cancers [11].

Extensive research and application have been undertaken using advanced oxidation, absorption, electrochemical or biological processes to reduce oxytetracycline emission [12]. The degraded polylactic acid showed around a two times higher OTC adsorption quantity than virgin polylactic acid via biofilm-related alteration of physiochemical properties [13]. Biotechnology is a promising technology for emerging organic contaminants removal using membrane bioreactor, biological filter, biofilm reactor [14]. Membrane bioreactor with nitrifying bacteria degraded OTC [15]. Native bacteria degraded OTC in estuarine sediments [16]. Terminal electron-accepting conditions may influence on the soil microbial community such as nitrate reducing bacteria, sulfate reducing bacteria and degradation of organic contaminants of emerging concern [17]. *Trametes versicolor*, *Ganoderma lucidum*, *Chlorella sorokiniana* could degrade pharmaceuticals of emerging concern in aquatic systems by metabolic biodegradation or in conjunction with other compounds [18]. The succession of the dominated genus from *Ca. Kuenenia* to *Ca. Anammoxoglobus* and the positively relationship of parts of ARGs with the dominant bacterium were fulfilled by succession of the potential resistant species induced by ARGs after Cu^{2+} inhibition [19]. *Methanosarcina* was contribution to transformation of oxytetracycline, the FeOn(OH)m modified oyster shell powders and enrichment culture could accelerate the transformation of oxytetracycline [20].

Ozone oxidation is also a promising technology for waste gas OTC treatment [21, 22], ozone could react with harmful organic compounds quickly and decompose them, and degrade organic compounds into simpler products [23]. Ozone could fast removal of the antibiotic flumequine from aqueous solution, convert it to low molecular weight carboxylic acids [24]. Effluent organic matter had effect on the removal of emerging contaminants by ozonation [25]. The addition of MnO_2 , H_2O_2 promoted the transformation of ozone into hydroxyl radical, thus improving the oxidation efficiency of emerging pollutants [26]. But, ozone oxidation may cause

secondary pollution during the OTC degradation, bioreactor, its disadvantages, include large volume of bioreactor and slow adaptation to biotoxic TOC in waste gas [27]. Therefore, the combined process of ozone-bioreactor could thoroughly and effectively degrade emerging contaminants of livestock composting waste gas [28]. The combination of ozonation and biological activated carbon filtration could achieve removals of 50% for dissolved organic carbon and more than 90% for a wide range of trace organic chemicals [29], almost all drugs and personal care products from treated wastewater could be degraded by biofilter after pre-ozonation [30]. OTC treatment has been widely studied in soil and water, but has received little attention in waste gas. This suggests that coupling of ozonation and membrane biofilm reactor (MBfR) with desulphurizing bacteria for degradation of OTC in waste gas, desulphurizing bacteria may be mutated into OTC degrading bacteria after the supply of gaseous OTC, to realize degrade OTC in waste gas thoroughly.

The objective of this work is to study the degradation of oxytetracycline in waste gas by the integrating reactor of an ozone reactor and a membrane biofilm reactor (MBfR) with desulphurizing bacteria, to reduce biotoxicity, eliminate secondary pollution from ozone oxidation and run stability. The study analysis bacterial community structure and functional genes in MBfR were assessed by 16S rDNA sequencing and metagenome sequencing. The intermediate products of oxytetracycline degradation in ozone-MBfR were identified by LC-TOF-MS/MS. The mechanistic for ozone-biological degradation of oxytetracycline were elicited, which is believed to promote the application of the ozone-MBfR.

2. Materials and Methods

2.1. Experimental Procedure

The experimental setup of the ozone-MBfR integrated reactor for oxytetracycline removal in waste gas was shown in Fig. 1. The integrated reactor included an ozone reactor, a polysulfone hollow

Fig. 1. Schematic diagram of an integrated with an ozone and a membrane biofilm reactor unit for the treatment of waste gases containing oxytetracycline (OTC).

fiber membrane biofilm reactor, a waste gas mixture (OTC and air) generation system, and a nutrient supply system. The activated sludge from municipal wastewater treatment plant was used to isolate desulphurizing bacteria, which could degrade OTC with the addition of OTC. The microbial nutrient solution containing desulphurizing bacteria was sprayed onto the membrane surface to form biofilm using a subaqueous pump. The recirculating medium was replaced with freshly medium every one week. Ozone with lower concentration is used as the pretreatment to reduce the threat of ozone to the biofilm on the hollow fiber membrane. Therefore, the ozone concentration was selected as 10, 20, 30, 40 and 50 ppm, and the ozone inlet flow rate was $0.15\text{--}0.3\text{ L}\cdot\text{min}^{-1}$.

Batch tests on MBfR or ozone-MBfR, the OTC supplied from the gas cylinders, was first diluted with the compressed air, passed through an air mixture bottle, ozone supplied from the ozone generator; simulated OTC waste gas was flowed upwards through the MBfR, or simulated OTC waste gas first flowed through the ozone reactor and then flowed upwards the bottom of the MBfR. MBfR was operated during 91 d under the conditions of OTC inlet concentration of $0.05\text{--}1.5\text{ mg}\cdot\text{m}^{-3}$, gas residence time (GRT) of 14.5 s, dissolved oxygen (DO), $0.2\text{--}1.5\text{ mg L}^{-1}$; pH of recirculating medium, 7.6–7.8; spray rate of $30\text{ mL}\cdot\text{min}^{-1}$ at room temperature. The influence of OTC inlet concentration was investigated from days 1 to 91, OTC inlet concentration, $0\text{--}0.5\text{ mg}\cdot\text{m}^{-3}$ (Phase I, 0–35 d), $0.6\text{--}1.0\text{ mg}\cdot\text{m}^{-3}$ (Phase II, 36–63 d), $1.1\text{--}1.5\text{ mg}\cdot\text{m}^{-3}$ (Phase III, 64–91 d). The O_3 -MBfR integrated reactor was operated during 50 days under the conditions of OTC inlet concentration of $0\text{--}1.0\text{ mg}\cdot\text{m}^{-3}$, gas residence time (GRT) of 14.5 s, dissolved oxygen (DO), $0.2\text{--}1.5\text{ mg L}^{-1}$; pH of recirculating medium, 7.6–7.8; spray rate of $30\text{ mL}\cdot\text{min}^{-1}$ at room temperature.

2.2. 16S rDNA Sequencing and Metagenomic Sequencing

Biofilm samples from MBfR were collected to identify and better understand bacterial population compositions and bacterial species which were effective on OTC degradation. The biofilms attached to the membrane surface of MBfR were sampled, assessed by 16s rRNA and Metagenomics sequencing, and identify the predominant microorganisms by the procedures of DNA extraction, quantification, purification, polymerase chain reaction (PCR) amplification, cloning and sequencing, gene library construction, Illumina high-throughput sequencing and sequencing data analysis. The metagenome sequencing raw data have been deposited in the NCBI Sequence Read Archive database with the accession number SAMN20079337.

2.3. Identification of the Intermediate Products of OTC Degradation

The intermediate products from OTC ozonation, OTC degradation in circulating fluid of MBfR and ozone-MBfR were identified by LC-TOF-MS/MS (Ultimate3000-timsTOF) with Hypersil GOLD C18 column ($1.9\text{ }\mu\text{m}$, $2.1 \times 100\text{ mm}$) after liquid extraction. The LC-TOF-MS/MS conditions were as follows: mobile phases were 0.1% formic acid (A) and acetonitrile (B). For gradient elution, initial 5% B was increased to 60% within 2 min and then increased to 100% in a further 6 min and keep this condition for 2 min. Finally, the gradient was returned to the initial conditions of 5%

B for 2 min. The injection volume was $3\text{ }\mu\text{L}$ and flow rate was $0.3\text{ mL}\cdot\text{min}^{-1}$ at the column temperature of 40°C .

2.4. Analytical Methods

The OTC concentration was determined by HPLC (Agilent 1260) with a poroshell 120 ES-C18 column ($4.6 \times 150\text{ mm}$ 2.7-Micron) after filtration through a $0.22\text{ }\mu\text{m}$ membrane (Syringe) filter. The mobile phase was composed of a mixture of acetonitrile and 0.825% phosphoric acid water (8.25 mL phosphoric acid / 1 L water), the initial composition was acetonitrile/phosphoric acid water (5/95, v/v), and the gradient was changed to acetonitrile/phosphoric acid water = 40:60(v/v) over 6min. Flowrate and injection volume were maintained at $1\text{ mL}\cdot\text{min}^{-1}$ and $100\text{ }\mu\text{L}$, respectively. OTC was detected at 268 nm by a diode array detector. The retention time for OTC was found to be 3.92 min.

Ozone concentration was measured by an electro-chemical gas analyzer (AIC-800-03, Shenzhen aopul Co. Ltd). Gas flow rates were measured using Model LZB-1 flow meters with units of $0.1\text{ m}^3\cdot\text{h}^{-1}$. The pH values were measured by a Model pHB-3 pH Tester (Sanxin Instrument Company, Shanghai, China). Dissolved oxygen was determined by DO analyzer (YSI Pro20i, Yellow Springs Instrument Inc., USA).

3. Results and Discussion

3.1. Performance of OTC Removal in Waste Gas

Gaseous oxytetracycline removal performance of the MBfR and ozone-MBfR were shown in Fig. 2. Fig. 2(a) showed the performance of the MBfR with desulphurizing bacteria for OTC removal with the supply of gaseous OTC concentration from 0.05 to $1.5\text{ mg}\cdot\text{m}^{-3}$ during the 91-d continuous running test. With OTC inlet concentration maintained at $0.09 \pm 0.04\text{ mg}\cdot\text{m}^{-3}$ in Phase I from days 1 to 35, OTC removal efficiency increased from 45.5 to 94.1%, 2 g sodium lactate was added every two days to replenish the carbon source, the microorganisms on the membrane gradually adapted to the oxytetracycline exhaust gas, oxytetracycline removal efficiency gradually increased. In phase II, when OTC concentration was increased to $0.60 \pm 0.08\text{ mg}\cdot\text{m}^{-3}$ at 36 d, OTC removal efficiency fell to 92.1% at 36th d, and then was stabilise at $95.3 \pm 3.2\%$ from days 37 to 63. In phase III, when OTC concentration was further increased to $1.33 \pm 0.12\text{ mg}\cdot\text{m}^{-3}$ at 64 d, OTC removal efficiency decreased temporarily but gradually recovered to the steady state at $97.2 \pm 1.6\%$ from days 64 to 91. The results indicated that microbes have been developed increasingly strong tetracycline resistance to overcome OTC bactericidal toxicity in long-term exposure of OTC, the domesticated desulphurizing bacteria in MBfR showed high tolerance to the OTC during the long-term operation.

Fig. 2(b) showed the performance of the integrated ozone-MBfR reactor for oxytetracycline removal during the 50-d continuous running test. OTC removal efficiency sharply fell, but gradually recovered to almost completely remove from days 3 to 10 after the supply of ozone concentration of 10 ppm. When ozone concentration was increased to 10 ppm at 11 d, OTC removal efficiency experienced an obvious fluctuation and could ascend to almost 100% at 20th d. Maintained the OTC inlet concentration at a low

Fig. 2. Oxytetracycline removal performance of (a) MBfR and (b) ozone-MBfR.

concentration range of 0–0.2 $\text{mg}\cdot\text{m}^{-3}$ from days 21 to 50, when the ozone intake concentration was increased to 30 ppm, the OTC removal efficiency complete removal. When ozone inlet concentration was increased to 40 ppm, OTC was still completely removal. Until the ozone concentration rised to 50 ppm at 43 d, the OTC removal efficiency began to decline and become less stable. This illustrated that ozone-MBfR had good OTC degradation performance under the conditions of ozone inlet concentration of 30–40 ppm, microorganisms in MBfR could efficiently adapt to the ozone, play a stable and efficient removal of OTC.

Pre-oxidation of ozone resulted in the formation of non-toxic degradation products, to improve the biodegradability and reduce OTC biotoxicity, microorganisms could more thoroughly degrade OTC and their primary products, eventually turn OTC into nitrates, CO_2 and H_2O [31]. Appropriate of ozone oxidation could also reduce OTC biotoxicity [32]. Thus, a bench scale system integrated with an ozone reactor and a membrane biofilm reactor unit should eliminate secondary pollution from decomposition of OTC by ozone process and more thoroughly degraded.

3.2. Bacterial Community under OTC Stress

As shown in Fig. 3(a), at the phylum level, *Proteobacteria* (47.7–86.9%), *Bacteroidetes* (9.7–39.0%), and *Firmicutes* (1.4–8.8%) were dominant phylum in Phase I–III. Within the stress of OTC, *Proteobacteria* was the most abundant bacteria, which demonstrated that *Proteobacteria* was adapted to OTC stress and used OTC as carbon and energy sources, *Firmicutes* was of relatively high percentage of peptidoglycan of cytoderm, which was beneficial to generate resistance of OTC [33]. Some phyla, such as *Firmicutes* and *Synergistetes*, increased in abundance, whereas others, such as *Proteobacteria*, decreased.

At the genus level, OTUs in Phase I–III could be taxonomically classified into 375, 375 and 317, respectively. As shown in Fig. 3(b), the bacterial community was divided into three function groups, sulfur reducing bacteria (SRB), sulfur oxidizing bacteria (SOB), and fermentative bacteria (FB), their relative abundances were 19.5–36.2%, 19.3–38.4% and 22.0–29.6%, respectively. With OTC concentration increasing from phase I to phase II, the abundan-

Fig. 3. Microbial community of MBfR at (a) phylum level, (b) at genus level under OTC stress.

Fig. 5. Bacterial community in the MBfR and ozone -MBfR (a) at phylum, (b) at genus.

matic modification protein (*tetX*). The resistance proteins encoded by tetracycline resistance genes were categorized into four groups based on their function. Ribosomal protection protein protects ribosome from the translation inhibition of OTC [37]. Tetracycline efflux pump could reduce OTC concentration by using membrane transporter OTC to peripheral cytoplasm [38]. Enzymatic modification protein could inhibit OTC combination with tetracycline target via modifying tetracycline target and then inactivate OTC [39]. *tetX* was identified as an NADH-dependent flavoprotein that performed OTC with hydroxylation dependent on oxygen. The enzyme encoded by *tetX* was able to transform both natural and semi-synthetic tetracyclines [40]. Tetracycline resistance proteins (K06962) may form polysaccharides on the cytomembrane to reduce the antibiotic into the cell [33].

Pseudomonas with *tetG* and *tetR* occupied highest ratio (38.45%)

Fig. 6. Metagenome functional genes assigned to tetracycline resistance and functional contribution of bacterial genera.

in OTC resistant bacteria followed by *Escherichia* (36.57%). The antibiotics resistant bacteria (ARB) were mainly represented by taxa with genes *tetG*, *tetG*, such as *Pseudomonas*, *Escherichia*, *Bacteroides*, *Paracoccus*, *Stappia* and etc. *Pseudomonas* could effectively degrade OTC [36]. *Bacteroides* could degrade macromolecules effectively [40] and could transform tetracycline [41]. Therefore, these bacteria were responsible for OTC metabolism.

3.5. OTC Degradation Products

In MBfR without ozone, the intermediate products from OTC biodegradation such as $C_{22}H_{20}N_2O_8$ ($m/z = 443$), $C_{20}H_{18}N_2O_8$ ($m/z = 415$), $C_{20}H_{15}NO_3$ ($m/z = 318$), $C_{18}H_{16}O_5$ ($m/z = 313$), $C_{20}H_{15}NO_2$ ($m/z = 302$), $C_{11}H_{13}NO_2$ ($m/z = 192$) and $C_{10}H_{12}O$ ($m/z = 149$) were detected by LC-TOF-MS/MS. The intermediate products from OTC ozone oxidation such as $C_{22}H_{24}N_2O_{10}$ ($m/z = 477$), $C_{22}H_{24}N_2O_9$ ($m/z = 461$), $C_{22}H_{20}NO_8$ ($m/z = 426$) and $C_{21}H_{18}NO_8$ ($m/z = 412$) were detected in the sample after ozone reaction. In the ozone-MBfR, the intermediate products from OTC degradation such as $m/z = 274$, $m/z = 246$, $m/z = 218$, $m/z = 192$, $m/z = 179$, $m/z = 149$, $m/z = 113$ and $m/z = 81$ were detected in the sample after ozone-biodegradation. The minimum intermediate molecular weight product detected in MBfR only was $C_{10}H_{12}O$ ($m/z = 149$) with two ring structures. The smallest product detected in ozone-MBfR was C_6H_8 ($m/z = 81$) with a chain-like structure. By comparing the intermediate products detected in MBfR and ozone-MBfR, it could be seen that ozone-biodegradation could degrade OTC more thoroughly.

3.6. Mechanistic Insights of Zone-Biodegradation of OTC

Proposed OTC degradation pathways for ozone-MBfR integrated reactor were shown in Fig. 7. Ozone could degrade OTC into intermediate products, these intermediate products and OTC were oxidized to nitrate, carbon dioxide, water by biological degradation. In the OTC ozone oxidation process, the C11a-C12 double bond of OTC underwent 1, 3-dipole ring addition reaction by ozone, adding oxygen to generate $C_{22}H_{24}N_2O_{10}$ ($m/z = 477$) [42]; dehydration

Fig. 7. Proposed degradation pathways of oxytetracycline in the ozone-MBfR.

of C6, deamination of C2, and secondary alcohol oxidation of C5 of OTC produced $C_{22}H_{20}NO_8$ ($m/z = 426$), to further get $C_{21}H_{18}NO_8$ ($m/z = 412$) after demethylation of C4 of OTC. In the OTC biodegradation process, the intermediate products from OTC ozone oxidation and OTC were further degraded by microorganisms. OTC was demethylated to produce $C_{20}H_{20}N_2O_9$ ($m/z = 433$) [43], to get $C_{20}H_{15}NO_3$ ($m/z = 318$) after deamination and dehydration. When C and D rings of OTC were cleaved, and after decarbonization and deoxidation, the product $M/Z = 274$ was generated. The C ring of OTC was decomposed gradually, to produce $C_{15}H_{19}NO_2$ ($m/z = 246$), $C_{13}H_{15}NO_2$ ($m/z = 218$) and $C_{11}H_{13}NO_2$ ($m/z = 192$) successively. The amide group of $C_{11}H_{13}NO_2$ ($m/z = 192$) was cleaved, resulting in the products ($m/z = 179$) and $C_{10}H_{12}O$ ($m/z = 149$). These products were further metabolized into sorbic acid ($m/z = 113$) [44]. Sorbic acid was stripped of its hydroxyl radical and oxygen atoms to chain-like structure C_6H_8 ($m/z = 81$), which

was eventually degraded to CO_2 and H_2O . Thus, ozone oxidation could degrade OTC into readily biodegradable substances with low biotoxicity, the products and OTC were biodegraded to nitrate, carbon dioxide, and water. Ozone was combined with MBfR biodegradation could achieve completely removal of OTC in waste gas.

3.7. Environmental Implication and Engineering Application

Resource recovery of solid waste refers to the comprehensive utilization of solid waste to make it available as secondary resources, such as biomass resources into hydrogen production, biodiesel [45, 46], Kaolin-clay into Kaolin-jute fibers filters [47], sludge disposal [48], agricultural solid waste composting into organic fertilizer to diminish the challenges to the global environment. The recycling process of compost will produce odor waste gas. Biological processes have become the mainstream technology for malodorous waste

gases treatment.

Compared with the intermediate products of OTC degradation by ozone oxidation and biodegradation, ozone oxidation had insufficient degradation on OTC, and microorganism could not degrade OTC more thoroughly and produce intermediates. Therefore, the combination of ozone oxidation and MBfR achieved complete removal of OTC in exhaust gas. This provides a new way of GEOCs treatment using the novel hybrid ozone and membrane biofilm reactor, serves the purpose to build emerging organic pollutant emission control strategy based on ozone-MBfR, has scientific basis for potential application value.

4. Conclusions

The paper revealed that the integrated with ozone and membrane biofilm reactor could thoroughly degrade OTC in waste gas. The dominant genera include *Desulfovibrio*, *Lentimicrobium*, *Aminivibrio*, *Thioalkalispira*, *Erysipelothrix*, *Mangroviiflexus*, *Azoarcus*, *Thauera*, *Geobacter*, *Paracoccus*, and *Dethiosulfatibacter*. Eleven tetracycline resistance genes, including *tet32*, *tet36*, *tetO*, *tetW*, and *tetQ*, *tetA*, *tetC*, *tetG*, *tetX*, *tetR*; dimethylamine and amidogroup metabolic genes *dmd*, *qhpA*, *fdhA* and *formamidase* existed in a membrane bioreactor. With the addition of ozone, some genera, such as *Tenericutes-uncultured*, and *Desulfovibrio*, increased in abundance, whereas others, such as *Thauera*, and *Petrimonas*, decreased. The OTC degradation mechanism of ozone-MBfR was that pre-oxidation of ozone could destroy the enol structure and produce easily biodegradable products, those products were further biodegradation to inorganic matter. Pre-oxidation of ozone help to degrade gaseous OTC more thoroughly.

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Author Contributions

X.L.C. (M.S. student) takes charge of investigation, scientific experiments, data curation, formal analysis and writing; Z.S.W. (Professor) provided supervision, theoretical foundation, and experimental guidance; Z.S.H. (Ph.D. student) takes charge of manuscript reviewing & editing; H.Y.J. (M.S. student) assisted in conducting experiments and computational analysis; X.L.X. (Ph.D. student) is responsible for in literature researches.

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