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Continuous Flow Experimental Study on Ozonation of Ibuprofen Catalyzed by Silicate-Based Microfiltration Membrane

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Abstract: In the treatment of drinking water, the ibuprofen (IBP) disinfection by-products, toxicity, and its impact on drinking water safety have caused widespread attention in domestic and overseas research areas. We studied the removal efficiency of IBP under the following conditions: combination of good catalytic activity of a silicate-based microfiltration membrane with the strong oxidizing ability of ozone in the continuous flow experiment mode and various influencing factors. This research revealed that with the increase of pH and hydraulic retention time, the removal efficiency of IBP exhibited an increasing trend; with the increase of alkalinity and humic acid concentration in water, the removal efficiency of IBP was obviously inhibited. Free radical inhibitors and electron spin resonance (ESR) analysis demonstrated that hydroxyl radical (·OH) is an important active species during the reaction of ozone-catalyzed IBP with the silicate-based microfiltration membrane.

Keywords: silicate-based microfiltration membrane; catalytic ozonation; ibuprofen; continuous flow experiment; influencing factors

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1. Introduction

Ibuprofen (IBP), chemically known as 2-methyl-4-(2-methyl-propyl) phenylacetic acid, is a typical nonsteroidal anti-inflammatory drug (NSAID) with anti-inflammatory and antipyretic effects and has a good effect on muscle pain and rheumatic diseases [1]. Compared with other anti-inflammatory and pyrolytic drugs, such as aspirin and acetaminophen, IBP shows superior performance with low toxicity, high efficacy, and minimal side effects [2]. As a result, IBP is widely used around the world. Because of the formation of the false persistent phenomenon, the wide application of IBP has caused great harm to the aquatic ecosystem of plants and animals. IBP, as an important PPCPs pollutant, may cause digestive tract infections and weaken the immune ability of the human body after long-term drinking of water contaminated by IBP and long-term exposure to such drugs [3,4]. IBP has been detected in the Pearl River, Haihe River, and Yellow River in China [5,6]—it is present in surface water in the amount of up to 0.4 μg L^{-1} and in drinking water up to 1.3 μg L^{-1} [7,8]. Studies have shown that the conventional biological treatment process has a good removal effect on IBP with a removal efficiency of 70%, but the products of the conventional biological treatment process have biological toxicity similar to IBP [9]. However, it is important to note that complete removal may not always be possible, and efforts to reduce the amount and concentration of these compounds can still be effective in reducing harm to the environment and public health.

IBP presence in water sources can have negative effects on aquatic organisms, as well as on human health through contaminated water supplies. Therefore, it is important

to increase efforts to remove these compounds from natural waters and wastewater to minimize their negative effects. He et al. [10] synthesized the MnO_2 nanocrystals catalytic ozonation for ibuprofen. They found that the active species in this oxidation system playing conspicuous roles in IBP degradation were ·OH, $\cdot O^{2-}$, and $^1O_2$. However, the catalyst MnO_2 is difficult to be separated from the solution after the reaction. Quero et al. [11] used 12 g/L O_3 to degrade IBP. In the experiment, when pH was 9 and hydraulic retention time was 20 min, 1 mg/L IBP could basically be all removed, but IBP did not achieve good mineralization. Moreover, through the detection of oxidation products after the reaction, it was found that intermediate compounds with greater toxicity were generated. Méndez-Arriaga et al. [12] used ultrasound to degrade IBP. Ultrasound increased the degradation of IBP from 30 to 98% within 30 min. Although ultrasound could efficiently remove IBP and convert it into biodegradable intermediates degraded in a subsequent biological step, it required high power consumption and generated noise. Liu et al. [13] discovered that 93% of IBP photodegradation can be achieved by prepared photocatalyst with a degradation rate constant at 0.011 min^{-1} with ·OH being the dominant active species in the photodegradation of IBP by g-C_3N_4/Bi_2WO_6/rGO under visible light. However, due to the high cost of these catalysts or the cumbersome catalytic process, it is necessary to develop an economical, inexpensive, and easily separable catalyst to use in the advanced oxidation techniques for catalyzing ozone by removing IBP in water.

Silicate cement is a cost-effective and widely utilized construction material. Silicate-based materials' strength and durability come from both cement's workability and its hydration reaction with water [14,15]. Silicate cement has the potential to react with water at ambient temperature, resulting in sufficient strength and enhanced durability. This not only makes it more eco-friendly but also prolongs its life span. Our team mixed silicate cement and quartz particles evenly with deionized water in a certain proportion and synthesized a silicate-based microfiltration membrane by the extrusion method [16]. Because there are metal oxides and alkaline substances in silicate cement, the silicate-based microfiltration membrane has the potential to catalyze the ozonation of organic matter.

In this study, IBP was removed by using the advanced oxidation technology of ozone oxidation catalyzed by the flat-plate and low-cost silicate-based microfiltration membrane. This research was focused on the parameters of the heterogeneous catalytic ozonation of IBP in order to address the need for higher catalytic efficiency with the low-cost membrane. In particular, key factors affecting the catalytic process, such as pH, alkalinity, natural organic matter (NOM), hydraulic residence time, and reactive species, were analyzed. Finally, the active species of ozone catalyzed by the membrane were investigated.

2. Materials and Methods

2.1. Materials

IBP (analytically pure) was purchased from Sahn Chemical Technology (Shanghai, China) Co., LTD. Analytical grade reagents of humic acid and sodium bicarbonate were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All solutions were prepared with Milli-Q ultrapure water. The synthesized process of silicate-based microfiltration membrane is in the Supplementary Materials. The appearance and micromorphology of silicate-based microfiltration membranes are shown in Figure 1. The technical parameters of the silicate-based microfiltration membrane are listed in Table 1.

Table 1. The technical parameters of silicate-based microfiltration membrane.

Project	Technical Parameters
Diameter (mm)	50
Thickness (mm)	3
Mean pore size (μm)	2.2
Porosity (%)	31
Effective contact area (cm^2)	7.0

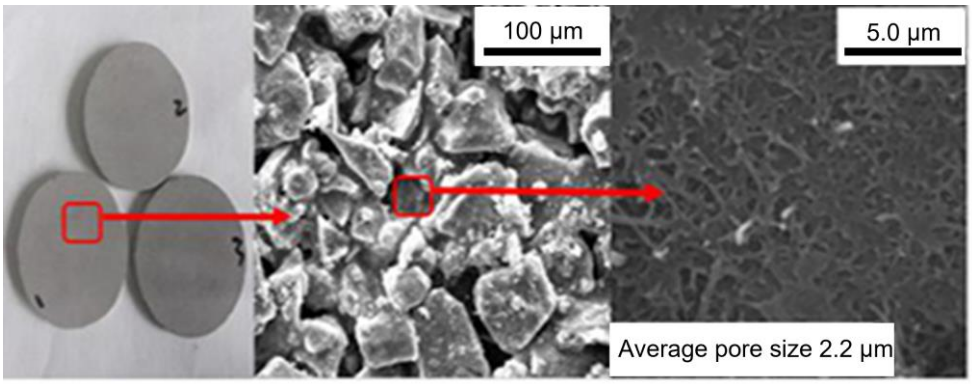

Figure 1. The appearance and micromorphology of silicate-based microfiltration membrane.

2.2. Experimental Equipment

The experimental device is a self-designed organic glass reactor. The continuous flow test process is as follows: After the ozone generator (CF-G-3-010g, Qingdao Guolin Equipment Co., LTD, Qingdao, China) is turned on and stabilized for a period of time, the mixture of ozone and oxygen is continuously injected into the reactor. At the same time, deionized water is injected using the peristaltic pump (YZ1515X, Lange constant-current Pump Co., LTD, Baoding, China) into the reaction tower at a certain velocity. The effluent is no longer returned to the reaction tower for direct discharge. By controlling the gas flow and the working current of the ozone generator, the desired initial ozone concentration is achieved after stabilization. After the system is stable for 1 h, the deionized water is switched to an IBP solution containing a certain concentration for water distribution, and then samples are taken at certain intervals to measure the concentration of residual ozone in the water and the concentration of residual IBP after oxidation. The reaction device is shown in Figure 2.

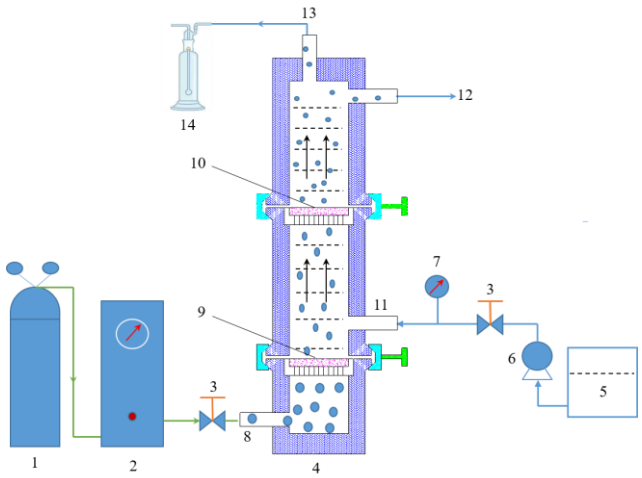

Figure 2. The schematic of experimental equipment: 1—oxygen cylinder, 2—ozone generator, 3—valve, 4—reactor, 5—distribution tank, 6—peristaltic pump, 7—pressure gauge, 8—air inlet, 9—quartz plate, 10—silicate-based microfiltration membrane, 11—water inlet, 12—water outlet (and sampling outlet), 13—air outlet, and 14—exhaust absorption bottle.

In the experiment of catalytic ozonation, a G3-type quartz plate (average pore size 2.2 μm) is used at the bottom of the reactor for aeration, and a silicate microfiltration membrane is used at the top for the catalytic reaction. In the process of sole ozonation experiment, a quartz plate of the same size in G3 type is used to replace the silicate-based microfiltration membrane in the reactor.

2.3. Analysis

The concentration of IBP was detected by 1200LC high-performance liquid chromatograph (HPLC) from Agilent. The determination was performed on Agilent C18 column (Zorbax Eclipse XDB-C18, 4.6 × 150 mm, 5 μm) with mobile phase consisting of acetonitrile, 0.3% formic acid solution = 70:30 (V:V), at a flow rate of 0.8 mL/min. The sample size was 100 μL. The UV detector was used for detection, and the detection wavelength was 222 nm. The concentration of dissolved ozone in the solution was detected by the indigo method [17]. The inlet ozone concentration ($[O_3]_0$) was the dissolved ozone concentration after the steady operation of the device with deionized water used as the medium with a mixture of oxygen and ozone injected. The total organic carbon (TOC) was tested by the total organic carbon tester (TOC-VCPH, Shimazu Company, Kyoto, Japan).

In the process of sole ozonation and catalytic ozonation of IBP, the obtained samples were filtered by 0.45 μm hydrophilic filtration membrane before HPLC and tested within 1 day after the end of the experiment to ensure the validity and accuracy of the experimental data.

3. Results and Discussions

3.1. Influence of Ibuprofen Concentration

The initial concentration of IBP varied from 2 mg/L to 20 mg/L, and the removal efficiencies of IBP, TOC, and residual ozone concentration were selected as the investigation indexes. The experimental results are shown in Figure 3. When the initial concentration of IBP increases from 2 mg/L to 20 mg/L, the removal efficiency of IBP in the single ozone process decreases from 77.4% to 50.1%. In the ozone-membrane process, the removal efficiency of IBP decreases from 97.0% to 81.1%. Compared with the single ozone process, the combined process can improve the removal of the target by more than 20 percentage points. In the combined process, when dissolved ozone passes through a silicate inorganic membrane, alkaline substances and some metal oxides in the pore of the silicate microfiltration membrane promote the decomposition of ozone into free radicals with the strong oxidizing ability and react with the target, thus improving the removal efficiency of IBP.

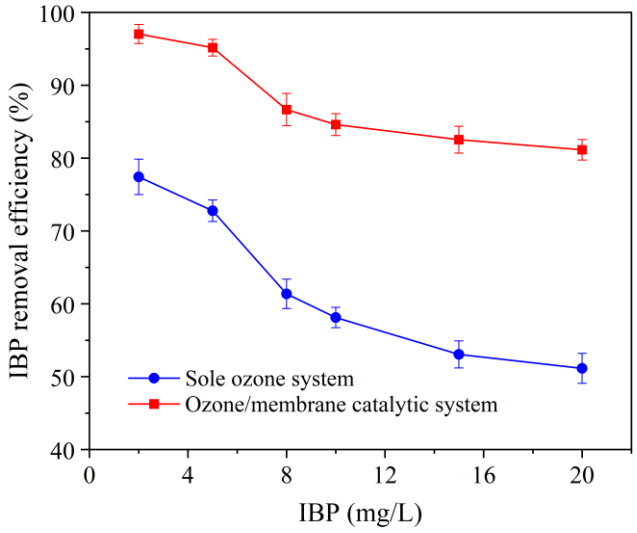

Figure 3. The removal efficiency of IBP under the following conditions: $[O_3]_0$ = 2.5 mg/L, gas flow 0.2 L/min, liquid flow 25 mL/min, and HRT 10 min, pH 6.5.

As can be seen from Figure 4, the TOC removal efficiency decreases with the increase of the initial concentration of IBP in the sole ozone process and the combined process. Compared with ozone oxidation alone, TOC removal efficiency could be increased by 20 percentage points. The TOC removal efficiency of IBP is also significantly increased in the ozone/membrane combined process.

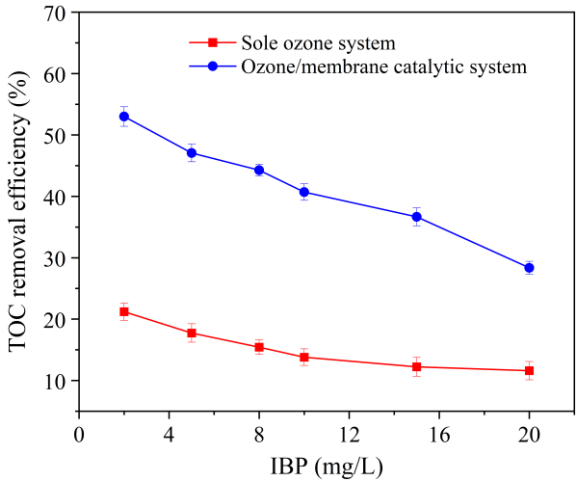

Figure 4. The TOC removal efficiency at different concentrations of IBP.

To further confirm the performance of the ozone/membrane system for removing IBP, those reported various catalysts under similar reaction conditions are compared and summarized in Table 2. The degradation efficiency and TOC removal efficiency of IBP are in the high-performance category in previously reported literature, suggesting that the ozone/membrane system exhibits efficient catalytic performance and a significant degree of mineralization toward IBP.

Table 2. Comparisons of degradation of IBP by various catalysts with ozone.

Catalysts	IBP (mg/L)	Ozone	Degradation Efficiency	TOC Removal	References
α-MnO_2	10.0	0.5 mg/min	99.5%	32.3%	[10]
Fe/Mn co-doped biochar	50.0	4.93 mg/min	95.4%	80.5%	[18]
Ferrosilicon	10.0	9.0 mg/L	75.0%	68.0%	[19]
Fe/CNT	20.0	50.0 mg/L	100%	50.0%	[20]
Membrane	10.0	2.5 mg/L	87.6%	43.6%	This study

3.2. Influence of Ozone Concentration

It can be seen from Figure 5 that the removal efficiency of IBP by a single ozone process and combined ozone-membrane process increases with the increase of ozone concentration in the reaction tower. When the concentration of ozone in the reaction tower was 2.0 mg/L, the IBP removal efficiency was 61.8% by ozone-alone process and 89.7% by the ozone-membrane combined process. When the concentration of ozone in the reactor was increased to 2.5 mg/L, the removal efficiency of IBP by ozone-alone process was 72.4%, while that by the ozone-membrane combined process was 95.2%. When the ozone concentration of the reaction tower was increased to 3 mg/L, the IBP removal efficiency of the ozone-alone process was 85.3%, while that of the ozone-membrane process was 97.8%. In view of the above studies, the removal efficiency of IBP was higher when the ozone concentration is above 2.5 mg/L in the ozone-membrane process. The IBP removal efficiency at 3 mg/L ozone concentration was not significantly higher than that at 2.5 mg /L ozone concentration. Therefore, 2.5 mg/L ozone concentration was selected during the experiment.

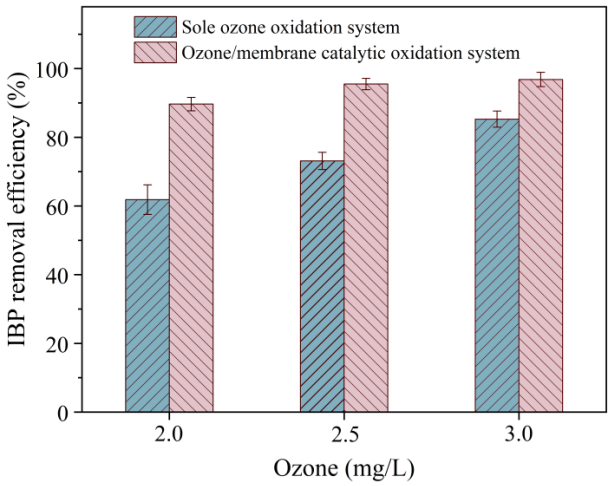

Figure 5. The effect of ozone concentration ($[O_3]_0$) on IBP removal efficiency under the following conditions: $[IBP]_0$= 5 mg/L, gas flow 0.2 L/min, liquid flow 25 mL/min, and HRT 10 min, pH 6.5.

3.3. Influence of Solution pH

In the study of ozone removal efficiency of organic matter, solution pH is a decisive factor. The OH^- in the solution can react with ozone, promote the decomposition of ozone, increase the decomposition rate of ozone, and increase the formation rate of ·OH. Therefore, the dissolution of ozone dissolved in water leads to the enhancement of decomposition and the generation of more hydroxyl radicals with the increase of the concentration of OH^- ions in the reacting water.

As can be seen from Figure 6, with the increase of solution pH, the removal efficiency of IBP in the ozone-membrane process gradually increased. When the pH of the solution was 3.5, the removal efficiency of IBP was only 83.2%. When the pH of the solution was 8.5, the removal efficiency of IBP increased to 97.7%. The concentration of residual ozone tended to be stable when the pH of the solution was acidic. When the pH of the solution was basic, the concentration of residual ozone dropped sharply. When the pH of the solution was 8.5, the IBP removal efficiency reached 97.7%, and the residual O_3 concentration reached the lowest value of 1.2mg/L. When the pH of the solution was 6.5, the IBP removal efficiency was 95.2%, which is a high removal efficiency. When the pH value of the solution was 6.5, the removal efficiency of IBP did not increase significantly with the increase in pH. Considering all factors comprehensively, the pH of the solution was selected as 6.5 in the continuous flow test.

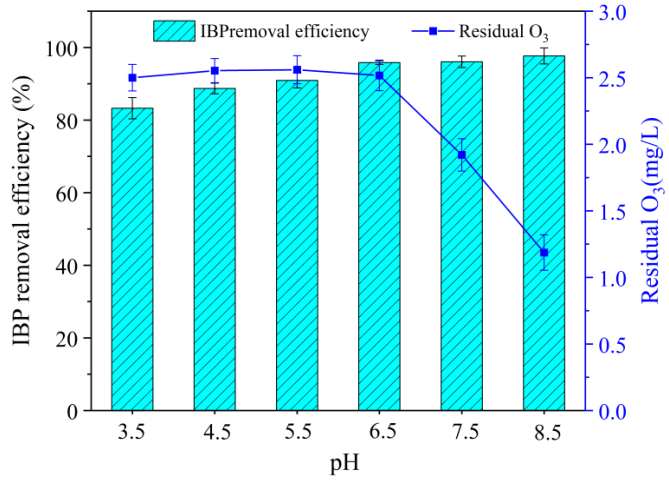

Figure 6. The effect of pH on ibuprofen removal efficiency under the following conditions: $[IBP]_0$= 5 mg/L, $[O_3]_0$ = 2.5 mg/L, gas flow 0.2 L/min, liquid flow 25 mL/min, and HRT 10 min.

3.4. Influence of Alkalinity

The alkalinity content of natural water is very high, and the reaction rate of HCO_3^- with ·OH is very fast. The reaction of HCO_3^- with hydroxyl radical generates carbonate radicals which inhibit the decomposition of ozone and the generation of free radicals. The reaction rate is constant at 8.5×10^6 $L \cdot M^{-1} \cdot s^{-1}$ [21]. The concentration in surface water and underground water is about 50–200 mg/L [21]. Therefore, the effect of bicarbonate alkalinity on IBP removal should be considered.

It can be seen from Figure 7 that bicarbonate alkalinity has a certain inhibitory effect on the removal of IBP. When the bicarbonate alkalinity increased from 0 to 500 mg/L, the removal efficiency of IBP decreased from 95.2% to 58.1%. On the contrary, the concentration of residual ozone increased from 1.2 mg/L to 2.3 mg/L, and the change in residual ozone concentration showed an upward trend. The strong effect of a high concentration of bicarbonate ions on the removal efficiency of IBP can be explained by the formation of calcium carbonate on the membrane pore surface. Studies have shown that [16] there are a large number of alkaline substances in the form of polymeric calcium silicate hydrate, calcium hydroxide, and ettringite on the pore wall of silicate-based microfiltration membrane. When ionic water containing bicarbonate passes through the pore wall of the membrane, calcium carbonate precipitates will be formed on the surface of the pore wall, which can be attached to the pore surface, thus preventing water from contacting with ozone on the pore wall and slowing down the decomposition rate of ozone. As a result, the residual ozone concentration reflected in the effluent increases.

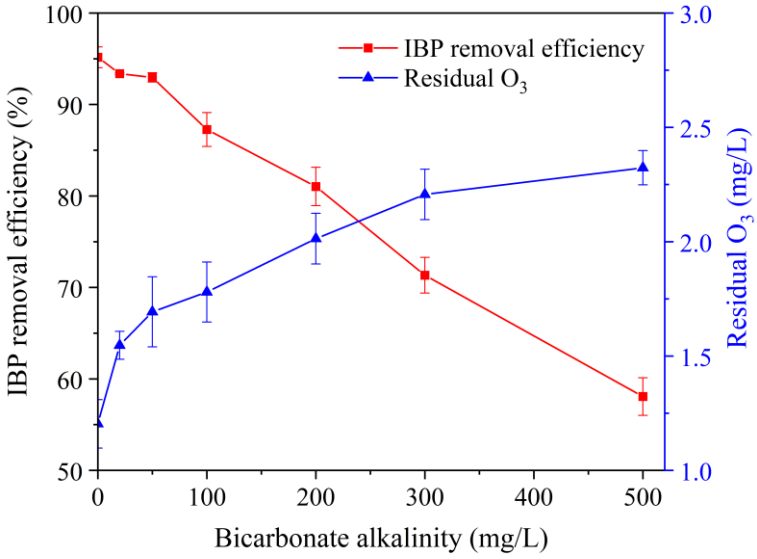

Figure 7. The effect of alkalinity on ibuprofen removal efficiency under the following conditions: $[IBP]_0$ = 5 mg/L, $[O_3]_0$ = 2.5 mg/L, gas flow 0.2 L/min, liquid flow 25 mL/min, and HRT 10 min.

3.5. Influence of Humic Acid Concentration

The humic acid content in natural water ranges from 0 to 100 mg/L. Humic acid can induce, promote, and inhibit the formation of free radicals. In order to better investigate the application of ozonation technology catalyzed by silicate-based microfiltration membrane in water, humic acid of a certain concentration was added to tap water to study the effect of silicate-based microfiltration membrane catalyzing ozone removal of IBP. The experimental results are shown in Figure 8.

It can be seen from Figure 8 that humic acid concentration has a very complex effect on the removal of IBP in the continuous flow reaction system of ozonation of IBP catalyzed by silicate microfiltration membrane. When the humic acid concentration was 2.0 mg/L, the removal efficiency of ibuprofen after system stabilization decreased by 3 percentage points to 92.46% compared with that without humic acid, which was 95.16%. When humic

acid concentration increased from 4.0 mg/L to 20.0 mg/L, IBP removal efficiency did not decrease significantly. When the humic acid concentration increased from 20.0 mg/L to 40.0 mg/L, the IBP removal efficiency showed an obvious downward trend. When the humic acid concentration increased to 40.0 mg/L, the IBP removal efficiency decreased to 78.14%, which was 17 percentage points lower than that without humic acid. This phenomenon is likely due to the active groups on the surface of the humic acid, such as phenolic hydroxyl, competing with IBP, resulting in a lower removal efficiency of ibuprofen. Figure 8 also shows that with the increase of humic acid concentration, the concentration of residual ozone in effluent decreases gradually. It may be that the active groups on the surface of humic acid [22] promote the decomposition of ozone and reduce the concentration of residual O_3 in effluent while competitively reacting with IBP.

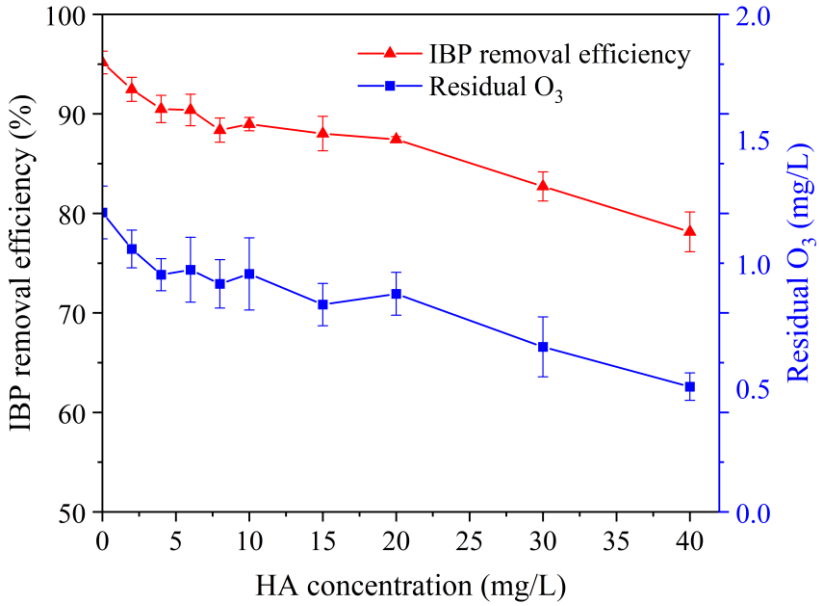

Figure 8. The effect of humic acid concentration on ibuprofen removal efficiency under the following conditions: $[IBP]_0$ = 5 mg/L, $[O_3]_0$ = 2.5 mg/L, gas flow 0.2 L/min, liquid flow 25 mL/min, HRT 10 min, and pH 6.5.

3.6. Influence of Hydraulic Residence Time

Under continuous flow reaction conditions, different hydraulic retention times can be changed by adjusting the water yield. The hydraulic retention time of the reaction tower was adjusted to 5 min, 10 min, 15 min, 20 min, and 25 min, respectively, and the removal efficiency of IBP and TOC catalyzed by the silicate microfiltration membrane was explored using different hydraulic retention times. The experimental results are shown in Figure 9.

Figure 9 shows that with the increase of hydraulic retention time pairs, the removal efficiency of IBP and TOC in the reaction system gradually increases. It may be that the longer the hydraulic retention time is and the longer the contact time between ibuprofen and hydroxyl radical and ozone is, the higher the removal efficiency of ibuprofen will be if the effective collision probability is increased. There is a difference of 5 percentage points between the removal efficiency of IBP when the hydraulic retention time is 10 min and that when the hydraulic retention time is 15 min. Therefore, the hydraulic retention time selected in this experiment is 10 min.

3.7. Formation of ·OH in the Reaction System

According to the degree of inhibition of bicarbonate alkalinity on IBP removal by ozonation catalyzed by silicate-based microfiltration membrane, the removal of IBP by ozonation catalyzed by silicate-based microfiltration membrane may be mainly due to the oxidation of ·OH. In order to further verify that the removal of IBP in a catalytic ozone

oxidation system is mainly based on the oxidation of ·OH, electron spin resonance (ESR) technology was used to characterize the active species in the oxidation system of sole ozone process and membrane-ozone combined process. In this study, DMPO was used as a free radical catcher to capture ·OH generated in two oxidation systems.

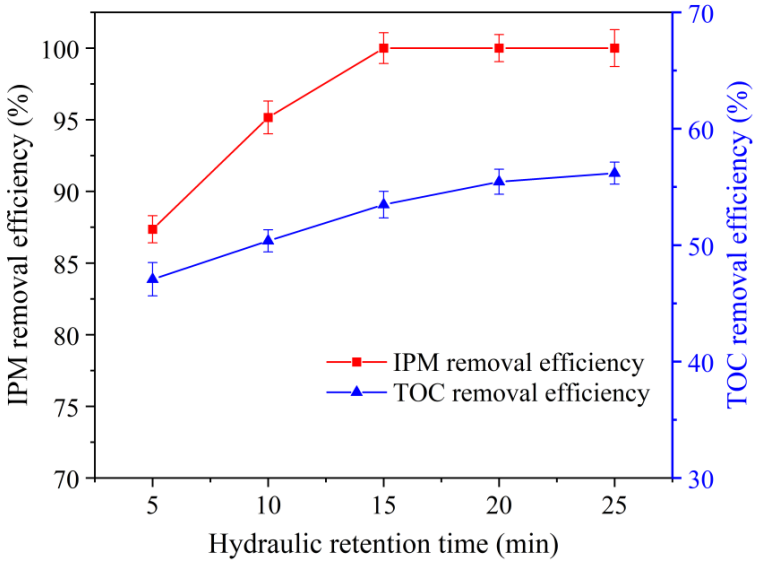

Figure 9. The effect of hydraulic retention time on ibuprofen removal efficiency under the following conditions: $[IBP]_0$ = 5 mg/L, $[O_3]_0$ = 2.5 mg/L, gas flow 0.2 L/min, and pH 6.5.

As can be seen from Figure 10, a group of free radical spectral lines with a peak height ratio of 1:2:2:1 appeared in the ESR spectra of sole ozonation and catalyzed ozonation systems with the addition of DMPO capture agent, and its hyfine structural parameters were α_N = 1.49 mT, α_H = 1.49 mT. This is the same as the parameter of the radical spectral line of the DMPO-OH adduct [23]. It can be seen that ·OH is formed in both oxidation reaction systems. In addition, the figure also shows that the DMPO-OH signal intensity obtained by the membrane-ozone combined process is significantly higher than that obtained by the sole ozonation process. It further shows that the existence of a silicate-based microfiltration membrane is conducive to the formation of ·OH from ozonolysis.

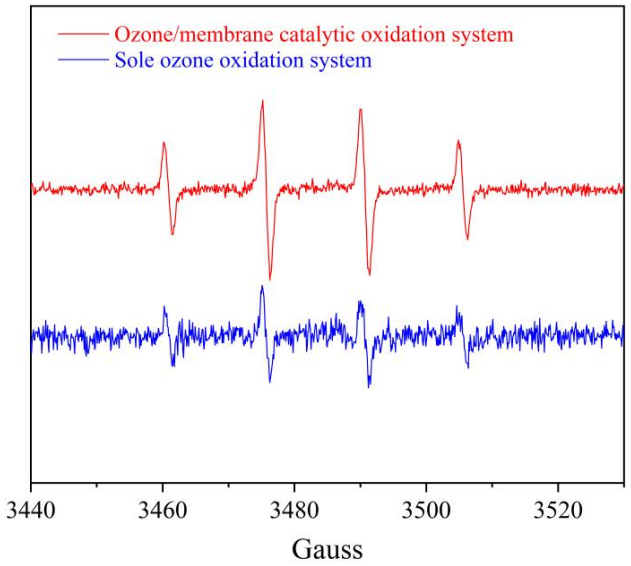

Figure 10. The spectrum of ESR in both ozonation and catalytic ozonation with silicate-based microfiltration membrane.

4. Conclusions

Through the continuous flow experimental study of ozonated ibuprofen catalyzed by the silicate-based microfiltration membrane, the following conclusions have been obtained:

The removal efficiency of IBP by ozone-membrane catalysis system is more than 81.1%, which is 20 percentage points higher than that of sole ozone oxidation. Compared with ozone oxidation, TOC removal efficiency can also be increased by 20 percentage points. With the increase of pH, ozone concentration and hydraulic retention time, the removal efficiency of IBP shows an increasing trend; with the increase of alkalinity and humic acid concentration in water, the removal efficiency of IBP is significantly inhibited. Through radical inhibitor and electron spin resonance (ESR) analysis, it is proved that hydroxyl radical (·OH) is an important active species in the ozonation of IBP catalyzed by the silicate-based microfiltration membrane.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15122184/s1, Text S1: the production process of silicate-based microfiltration membrane.

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Data Availability Statement: Data will be made available on request.

Conflicts of Interest: The authors declare no conflict of interest.

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