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Treatment of Organics Contaminated Wastewater by Ozone Micro-Nano-Bubbles

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Abstract: The efficiency of ozone for the treatment of organics contaminated wastewater is limited by its slow dissolution rate and rapid decomposition in the aqueous phase. Micro-nano-bubbles (MNBs) are a novel method to prolong the reactivity of the ozone in the aqueous phase, thereby accelerating the treatment of the contaminant. In this study, the effects of pH and salinity on the treatment efficiency of ozone MNBs were examined. The highest efficiency was observed in weak acidic conditions and an increase in salinity enhanced the treatment efficiency significantly. Furthermore, the treatment of highly saline industrial wastewater as well as multi-contaminant groundwater containing persistent organics were also investigated. Treatment using ozone MNBs had a considerable effect on wastewaters that are otherwise difficult to treat using other methods; hence, it is a promising technology for wastewater treatment.

Keywords: micro-nano-bubbles; ozone; organics contaminated wastewater

1. Introduction

Organics contamination has long been a serious environmental issue and has drawn much attention [1,2]. Organic contaminants such as dyes, petrochemicals and agrochemicals are major pollutants in wastewater [3], and can be extremely harmful to the environment and the human body. Numerous technologies have been developed to degrade such contaminants, including physical adsorption, biological processes, and chemical oxidation [4]. However, the efficiency of physical adsorption is very limited for wastewater containing complex components [5]. Biological methods are inefficient for relatively persistent contaminants and usually take more time compared to chemical methods [6]. Also, microbial activities in the biological methods are significantly influenced by the surrounding conditions, and are unsuitable for certain cases such as the treatment of wastewater with high salinity [7].

Chemical oxidation is a commonly used method for the treatment of organics contaminated wastewater [8–10]. It is more efficient than biological methods, and can be used for the treatment of some persistent contaminants [6]. The oxidants can efficiently break down organic contaminants into smaller compounds or even convert them into carbon dioxide and water [11]. Ozone is a very good agent for wastewater treatment because of its strong oxidation ability [12,13]. It is widely used in the treatment of pharmaceuticals in water [14], and can be applied as a pre-treatment to convert persistent contaminants into more biodegradable compounds [15]. However, the treatment efficiency of wastewater by ozone is very limited due to the low concentration of dissolved ozone. Hence, methods that can enhance the dissolution efficiency of ozone and increase the concentration of aqueous phase ozone are of great importance.

Micro-nano-bubbles (MNBs) are bubbles with a diameter between tens of nanometers and several tens of micrometers [16,17]. MNBs have significantly lower rising velocity than normal bubbles, and their negatively charged surface prevent them from coalescence, therefore, they persist in water for a longer period [18,19]. Bubbles with radii of 150 nm to 200 nm can even persist for two weeks [20]. Moreover, MNBs possess high internal pressure and large specific surface area, which can significantly improve mass transfer rate from bubbles into the aqueous phase and result in higher dissolved gas concentration in the aqueous phase [18,21,22]. MNBs can potentially be combined with ozone for application in wastewater treatment. MNBs can prolong the reactivity and also increase the concentration of dissolved ozone [18], thereby increasing the treatment efficiency of ozone.

The purpose of this study is to investigate the feasibility and efficiency of applying ozone MNBs to wastewater treatment. Firstly, methyl orange was chosen as the representative contaminant to experimentally study the effect of pH and salinity conditions on the treatment efficiency of ozone MNBs. Furthermore, treatment of industrial wastewater with a high salinity concentration, and contaminated groundwater containing complex organic components were conducted to study the treatment ability of ozone MNBs on wastewater that was not suitable for biological treatment.

2. Materials and Methods

2.1. Experimental Facilities

2.1.1. Micro-Nano-Bubble Generator

A spiral liquid flow-type micro-nano-bubble generator (ASUPU ASK3, Asupu Co., Ltd., Suntogun, Shizuoka, Japan) was used to generate MNBs in this research and detailed information about the generator is published in previous work by the authors [21]. Water was pumped into the generator, and the liquid flow was rotated at high-speed to form a maelstrom-like cavity. Ozone was injected into the generator, and ozone MNBs were generated through the centrifugation effect. In this research, the flow rate of water was 10 L/min, and the injection rate of ozone was 1 L/min.

2.1.2. Ozone Generator

Ozone used in this research was produced by an ozone generator (3S-OW-100, Tonglin Ltd., Beijing, China) based on the corona discharge method. The supplied ozone concentration was approximately 80 mg/L.

2.1.3. Size Distribution Analyzer

The quantity and size distribution of the generated ozone MNBs were measured by a nanoparticle tracking analyzer (NanoSight LM-10, Malvern Instruments, Malvern, Worcestershire, UK). MNBs were generated in water and the water containing the MNBs was analyzed. Bubbles were lit up by laser illumination, and an ultra-microscope fitted with a camera was used to track the movement of the bubbles. The measurements ranged from 10 nm to 1000 nm and the size distribution of the bubbles was calculated based on the Stokes-Einstein equation.

2.1.4. UV Spectrophotometer

The concentration of methyl orange was measured by a UV spectrophotometer (DR6000, Hach, Loveland, CO, USA). The intensity of light absorbed by the methyl orange solution was measured and the concentration of methyl orange was determined based on Beer-Lambert law.

2.1.5. Gas Chromatograph

The concentration of benzene, chlorobenzene, nitrobenzene, and p(o)-nitrochlorobenzene was measured by a gas chromatograph (GC-310C, SRI Instruments, Torrance, CA, USA). Each of the samples was measured twice, and the deviation was less than 0.005 mg/L.

2.1.6. Chemical Oxygen Demand (COD) Measurement Devices

The COD was measured following the EPA method 410.3. The wastewater was diluted 10 times and mercuric sulfate was used to remove interference of chlorides. The samples were heated by a digester (DRB-200, Hach, Loveland, CO, USA) and the COD value was measured using a UV spectrophotometer.

2.1.7. Reaction Tank

All the experiments were conducted in an acrylic tank with internal dimensions of 0.8 m (length) × 0.2 m (height) × 0.2 m (width). The volume of wastewater was 20 L, and all the treatments were conducted at 20 °C. The schematic for the wastewater treatment using ozone MNBs is shown in Figure 1.

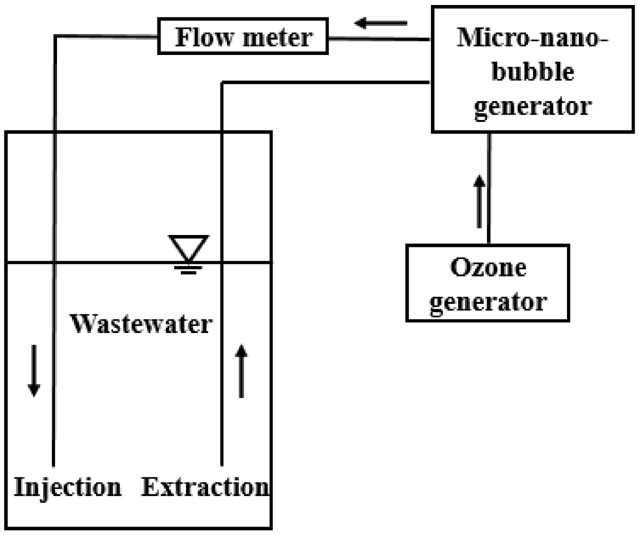

Figure 1. The schematic for wastewater treatment by ozone MNBs.

2.2. Experimental Setup

2.2.1. Effects of pH and Salinity

The effects of pH and salinity on the treatment efficiency of ozone MNBs were studied. Methyl orange, which can be easily degraded by ozone, was used as the target contaminant. 20 L methyl orange solution at a concentration of 50 mg/L was used as the initial wastewater.

In the tests at different pH, the pH of the initial solution was 7, and hydrochloric acid or sodium hydroxide were used to adjust the solution to pH 3, 5, 9, and 11. In the tests at different salinity concentrations, sodium chloride was used to adjust the salinity of methyl orange solution to 0.01 M, 0.1 M, and 1 M.

In each test, ozone MNBs were generated in the 20 L methyl orange solution for 50 min and samples were taken every 10 min to determine the concentration of methyl orange during the treatment. Each test was conducted twice to ensure the repeatability of the data. In the treatment of methyl orange at various initial pH conditions, the solution pH after treatment was also measured. All the tests were conducted at 20 °C.

2.2.2. Treatment of Industrial Wastewater with High Salinity

Industrial wastewater containing large amount of sodium ions, chloride ions, sulfate radicals, and nitrate radicals was taken from a wastewater treatment company in Guangzhou, China. The salinity was over 200 g/L and the initial pH was 9.9, which would make it difficult for most microorganisms to survive. The concentrations of the major ions in the wastewater are shown in Table 1. Multiple organic contaminants including dyes and esters were present in the wastewater, and the chemical oxygen demand (COD) was used to describe the concentration of contaminants. 20 L of wastewater was stored in the reaction tank, and ozone MNBs were generated inside the wastewater for 14 h to conduct the treatment. The solution temperature was controlled at 20 °C and samples were taken and analyzed using the COD measurement devices.

Table 1. Major ionic concentrations in the wastewater.

Ion	K^+	Na^+	Cl^-	SO_4^{2-}	NO_3^-
Concentration (mg/L)	1710 ± 0.02	114000 ± 0.02	123000 ± 0.02	58500 ± 0.09	23300 ± 0.08

2.2.3. Treatment of Contaminated Groundwater with Complex Organic Components

To investigate the treatment efficiency of contaminated groundwater with complex organic components by ozone MNBs, contaminated groundwater was extracted from a contaminated site in Nanjing, China, which used to serve as a chemical factory. The main contaminants in the groundwater were benzene, chlorobenzene, nitrobenzene, and p(o)-nitrochlorobenzene, and their initial concentrations are shown in Table 2. 20 L wastewater, with an initial pH = 6.7, was stored in the reaction tank and treated by ozone MNBs for 30 min at 20 °C. The concentrations of the contaminants after the treatment were measured using gas chromatography.

Table 2. The initial concentration of the main contaminants in groundwater.

Contaminant	Benzene	Chlorobenzene	Nitrobenzene	p(o)-nitrochlorobenzene
Initial concentration (mg/L)	30.5 ± 5.1	14.8 ± 2.5	502.8 ± 57.5	9.5 ± 0.6

3. Results and Discussion

The quantity and size of the MNBs affect their mass transfer efficiency. Larger amounts of the MNBs result in larger total surface area and increases the mass transfer flux from bubbles to solution, and smaller bubble size results in higher internal pressure and larger specific area. The size distribution of the ozone MNBs was measured twice and the derivation was within 20%. 2.3×10^8 ozone MNBs were observed per mL and the size distribution is shown in Figure 2. The diameters of the ozone MNBs mainly ranged from 40 nm to 370 nm, and the Sauter mean diameter was 265 nm.

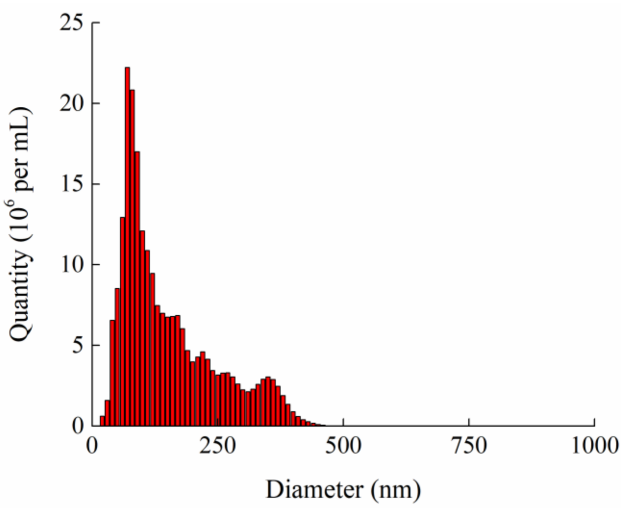

Figure 2. Size distribution of the ozone MNBs.

The pH affects the stability of ozone and the degradation pathway of organic contaminants; therefore, the treatment efficiency by ozone MNBs at various pH was investigated. In this study, the initial pH was adjusted to 3, 5, 7, 9, and 11, and the concentration of methyl orange during the treatment using ozone MNBs is shown in Figure 3. The tests were conducted twice, and the deviation was less than 0.9 mg/L.

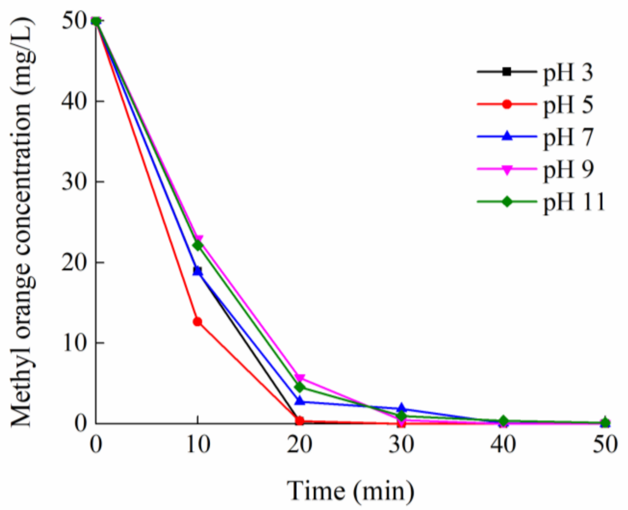

Figure 3. Effects of pH on the treatment of methyl orange by ozone MNBs.

At various pH conditions, i.e., the pH = 3 to 11, the ozone MNBs showed significant treatment efficiency on methyl orange. The removal rate of contaminants after 20 min was over 80%, and over 90% after 30 min. Compared with results reported by Chen [23], at pH 9 the treatment efficiency by ozone MNBs was over two times higher than ozone, which proved that MNBs can greatly improve the treatment efficiency by ozone. According to our previous research, under the same conditions, the treatment efficiency by ozone MNBs was 40 times higher than ozone millimeter bubbles [18,24].

The highest treatment efficiency was observed at pH 5 and the removal rate of methyl orange at 10 min was 14% higher than that at pH 7. The lowest treatment efficiency was observed at pH 9 and pH 11. The treatment of methyl orange at various pH conditions followed pseudo-first-order kinetics, which is in agreement with other works where azo dyes were degraded by ozone [25–27]. The pseudo-first-order rate constant at pH 5 was twice that at pH 11.

According to the mechanism proposed by Staehelin and Hoigne, OH^- ions react with dissolved ozone to produce $\cdot O_2^-$ free radicals, and H^+ ions promote $\cdot O_2^-$ free radicals to turn into $HO_3\cdot$ free radicals, which are further decomposed to $\cdot OH$ free radicals [28]. Both H^+ and OH^- ions are needed for the formation of $\cdot OH$ free radicals. Moreover, the dissociation constant p*K*a for methyl orange is 3.46 [29] and therefore, methyl orange will be in a molecular state or an ionic state when the pH condition is lower or higher than this value. The ionic form of methyl orange is more hydrophilic in solution and can be degraded by $\cdot OH$ free radicals and dissolved ozone [30]. Thus, in the current study, pH 5 was found to be the optimal condition for treatment of methyl orange. On the other hand, alkaline condition or strong acidic condition would result in a decline in the treatment efficiency.

As methyl orange can also be oxidized by ozone directly, ozone MNBs showed efficient treatment in various pH conditions. Similar results were also reported by Sevimli and Sarikaya [25], in which the solution pH showed a slight effect on ozone utilization.

The pH of the solution after being treated by ozone MNBs is shown in Table 3. In all the experiments, the solution pH showed a slight decrease after the treatment. Similar results were reported by Chen [23], Gül [31], and Constapel [32], and the formation of aldehyde and organic acids is speculated as the main reason.

Biological methods may be inhibited by high salinity concentration and the salt has to be removed before biological treatment [7]. Treatment using ozone MNBs is expected to be a more efficient method.

The treatment efficiency by ozone MNBs at various salinity conditions is shown in Figure 4. The tests were conducted twice and the deviation was less than 1.0 mg/L.

Table 3. Solution pH before and after treatment by ozone MNBs.

Initial pH	3.0 ± 0.1	5.0 ± 0.1	7.0 ± 0.1	9.0 ± 0.1	11.0 ± 0.1
Final pH	2.5 ± 0.1	3.9 ± 0.1	6.8 ± 0.1	8.2 ± 0.1	9.0 ± 0.1

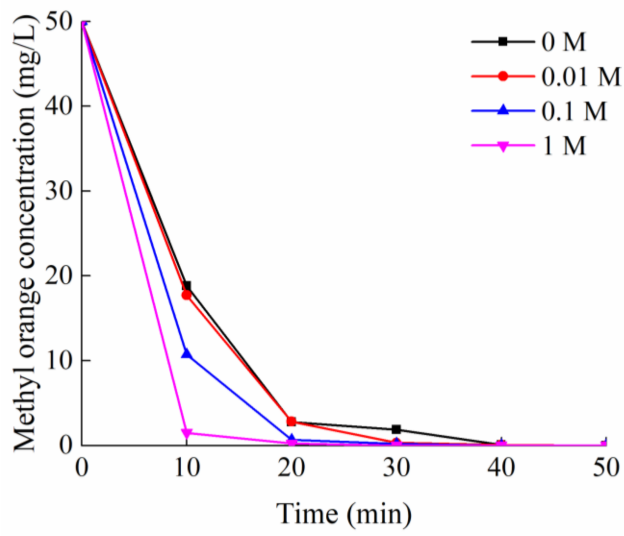

Figure 4. Effects of salinity on the treatment of methyl orange by ozone MNBs.

The treatment efficiency of ozone MNBs increased with the salinity concentration. At 10 min, 62% methyl orange was degraded in the 0 M test, whereas 78% methyl orange was degraded in the 0.1 M test and over 96% methyl orange was degraded in the 1 M test. In all tests, methyl orange was totally removed after 50 min of the treatment. The treatment of methyl orange at various salinity conditions also followed pseudo-first-order kinetics and the pseudo-first-order rate constant at 1 M was 32% higher than that at 0 M. Similar results were reported by Yuan et al. [33] and Wang et al. [34] who stated that, in the treatment of azo dye by peroxydisulfate, the dye degradation is enhanced at high chloride concentrations. Chloride was speculated to accelerate the oxidation of methyl orange by ozone, and therefore, high treatment efficiency was observed at high salinity. Moreover, the addition of sodium chloride increased the surface tension [35] and resulted in higher internal pressure of the MNBs. The higher internal pressure further resulted in higher mass transfer efficiency of ozone from the MNBs to the solution [36] and enhanced the treatment of contaminants.

The internal pressure of the MNBs can be described by Young-Laplace Equation,

$$P_{\text{in}} - P_{\text{out}} = \frac{2\sigma}{R}, \quad (1)$$

where P_{in} is the inner pressure of the MNB, P_{out} is the ambient pressure, σ is the surface tension, and R is the radius of the MNB.

Furthermore, industrial wastewater which contained high salinity concentration was chosen as the target contaminant and the treatment efficiency by ozone MNBs was studied. The COD of the wastewater during the treatment by ozone MNBs is shown in Figure 5.

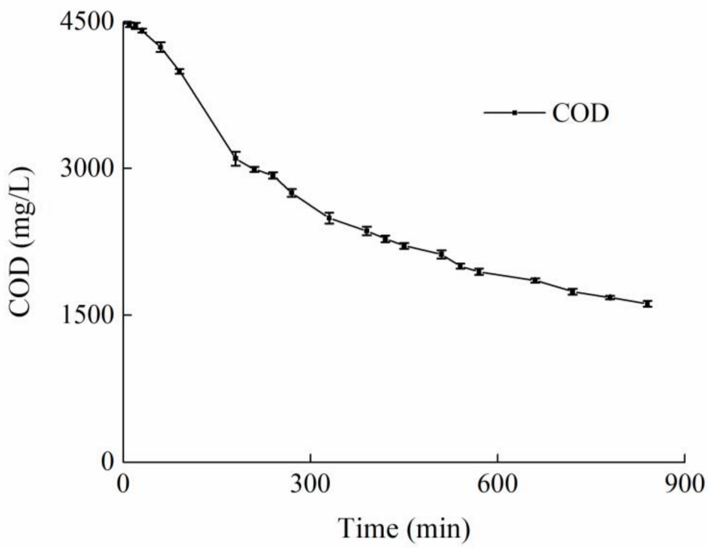

Figure 5. Treatment of wastewater with high salinity by ozone MNBs.

Similar to the results of methyl orange treatment, ozone MNBs showed significant treatment effect on wastewater with high salinity, with the COD decreasing 63% after the 14 h treatment. The COD removal rate gradually slowed down due to the formation of stable by-products. More efficient removal of the contaminants can be achieved by combining hydrogen peroxide with ozone MNBs [37].

Contaminated groundwater containing complex organic components was treated to further study the treatment feasibility and efficiency of persistent contaminants using ozone MNBs. The removal rate after treatment is shown in Figure 6.

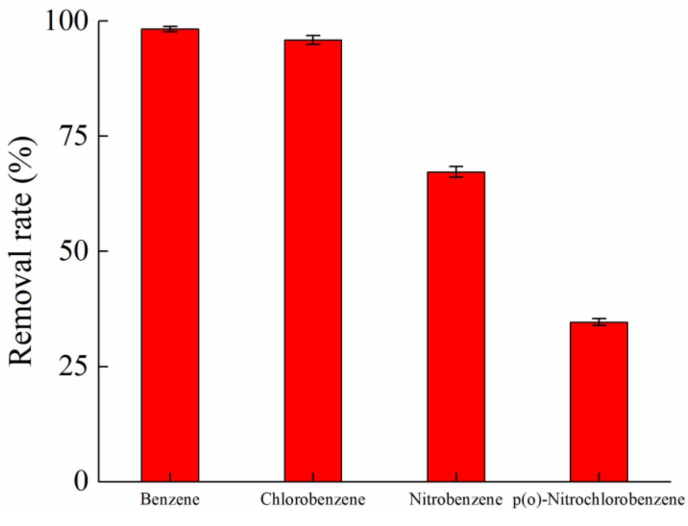

Figure 6. Treatment of groundwater with complex organic components by ozone MNBs.

Ozone MNBs showed efficient attenuation of benzene and chlorobenzene and their removal rate was over 95% after 30 min of treatment. The initial concentration of nitrobenzene was over 500 mg/L and 67% was removed after 30 min of treatment. P(o)-nitrochlorobenzene is considered to be relatively persistent due to the electron withdrawing effect of the nitro and chlorine groups [38]; around 35% removal efficiency was achieved after treatment. The ozone MNBs showed strong oxidation ability and significant treatment efficiency and proved to be feasible for the treatment of water containing relatively persistent contaminants. Additionally, hydrogen peroxide [37,39] or granulated activated carbon [31] can be used to accelerate the formation of active hydroxyl radicals, which can further enhance the cleavage of aromatic rings and result in more efficient degradation of persistent contaminants.

The treatment by ozone MNBs included direct oxidation by ozone molecules and oxidation by hydroxyl radicals which were formed through ozone decomposition. The oxidation mechanism involves hydroxyl substitution on the benzene rings and opening of the aromatic rings [40]. During oxidation, the degradation of methyl orange proceeds through the cleavage of the azo group that connected the two aromatic rings [41], and by-products such as toluene, *p*-xylene, 2,3,5-trimethyl hexane, and 4-aminoazobenzene are subsequently produced [23,42]. The by-products can be further oxidized to small molecules such as carbon dioxide, water, and sulfates. With the addition of chloride, chlorinated aromatic compounds as well as chlorinated organic products would be generated during the treatment of methyl orange by ozone MNBs [34]. Some of these compounds showed bioaccumulation tendencies and presented high toxicological risk [33]. Further attempts to identify the by-products and explore the underlying mechanisms are needed for the application of ozone MNBs in wastewater treatment.

4. Conclusions

In this study, the feasibility and efficiency of applying ozone MNBs to wastewater treatment were studied.

Methyl orange was chosen as the representative contaminant for the initial laboratory tests to study the effects of pH and salinity on the treatment efficiency of ozone MNBs. The treatment efficiency of methyl orange at various pH and salinity conditions follows pseudo-first-order kinetics. Alkaline or strong acidic conditions limit the treatment and the highest efficiency is observed at pH 5. Although salt accelerates the treatment of methyl orange by ozone MNBs, the potential formation of chlorinated aromatic compounds should be checked.

Furthermore, the treatment of industrial wastewater with high salinity was conducted. The COD removal rate for wastewater with high salinity was over 63% after the 14 h treatment, and ozone MNBs showed a significant effect on the removal of organic contaminants from wastewater with high salinity.

Also, the treatment of contaminated groundwater with complex persistent organic components was conducted. Ozone showed a remarkable effect on the removal of persistent organic contaminants, and most of the benzene and chlorobenzene were removed after the 30 min treatment.

Overall, ozone MNBs were proved to be a promising technology for organics contaminated wastewater treatment.

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