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Study on the degradation of tetramethyl ammonium hydroxide using ultrasonic and ozone procedures

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ABSTRACT

Tetramethyl ammonium hydroxide (TMAH) is a corrosive and toxic chemical with a stable structure. Therefore, it is important to check whether surface water or wastewater contains TMAH. In addition to using ultrasound and ozone procedures to degrade TMAH in wastewater, in this study, the effects of TMAH degradation were explored by combining the two procedures while varying the reaction conditions. According to the experimental results, the degradation efficiency of TMAH by the single ultrasonic process was un-satisfactory, and the highest degradation ratio was only 8.4% after for 60 min, while the highest total organic carbon (TOC) mineralization ratio was only 7.1%. Ozonation is more effective for the degradation of TMAH, where the highest TMAH removal rate and mineralization rate can reach 58.4% and 21.8%, respectively. As the ultrasound is combined with the ozone procedure (named as sonozone) at the optimal condition, the TMAH removal ratio reaches 89.5% following by mineralization ratio of 77.5%. The toxicity test performed using the cell survival rate showed that ozonation and sonozone have better effects for improving the cell viability and reducing the toxicity of the water sample, and the sonozone process proves that the combination of two procedures indeed has synergistic oxidation efficiency.

Keywords: Ultrasound; Ozonation; Sonozone; TMAH; Degradation; Mineralization

1. Introduction

With the rapid development of science and technology, the integrated circuit industries and the semiconductor industries require a wide range of raw materials and chemicals, and the properties of wastewater produced during the development process are relatively complex. The properties of those chemicals and their toxicities have an unknown impact on the environment, when they are directly discharged in the wastewater even if their concentration is extremely low. Therefore, environmental protection issues derived from various types of industrial wastewater or high-tech industrial wastewater have gradually drawn increasing attention every year.

In recent years, tetramethyl ammonium hydroxide (TMAH), which is a nitrogen-containing organic compound with the chemical formula $C_4H_{13}NO$, has been widely used for developing processes and etching processes in the semiconductor industries and photovoltaic industries. Except for its high alkalinity, TMAH also results in high concentration of ammonia nitrogen in wastewater. Due to the restriction of ammonia-nitrogen release standard for high-tech industries in Taiwan, how to effectively degrade, recycle or handle this solvent is a key-point for various types of researches. Wastewater containing high strength TMAH may not be rapidly degraded through traditional biological treatment methods. If it is excessively discharged into waters, it will cause damage to the water ecological environment, including the negative effects such as water eutrophication, water odor, and consumption of dissolved oxygen in water.

According to the report on domestic TMAH occupational disasters in recent years, most of the causes of the disaster are that the human body is exposed to high concentrations of TMAH, causing fatal risks of skin corrosion, muscle paralysis, and breathing difficulties. There were

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many accidents due to skin exposure to TMAH in Taiwan and caused three reported acute poisoning deaths [1–4]. The Hsinchu Science Park regulates TMAH emissions in two phases. The first phase was implemented in 2014 with a limit of 60 mg/L. The second phase was implemented in 2015 with a limit of 30 mg/L.

There are already various literatures on TMAH treatment methods, including biological treatment, photocatalytic procedures, ion exchange procedures and activated carbon adsorption procedures. Although the biological program, ionic exchange resin or activated carbon process can effectively reduce the TMAH concentration, it takes longer treatment duration [5–8]. In addition, the removal of TMAH still takes place through physical adsorption, either through activated carbon or ion exchange resin, and it does not degrade TMAH or reduce its toxicity.

Advanced oxidation processes (AOPs) refer to the direct mineralization of pollutants in water into CO_2 and H_2O and other inorganic substances through physical or chemical methods or a reaction procedure that will convert pollutants into substances with low toxicity and easy biodegradation substances [9]. AOPs are thought to use hydroxyl radicals (·OH) generated during the process to attack organic matters in water and has been proven to be an effective treatment process for hazardous wastewater. Den et al. [10] and Kim and Choi [11] both degrades TMAH with a photolysis procedures, and the results shown in their observations indicated that the removal ratio of TMAH were ranging from 29% to 95.8%, after 360 min of reaction. Among them, TMAH degradation started with demethylation, and the reaction rate of this procedure was slow, and the follow-up was that TMAH reacts rapidly with ·OH to form alcohols and is continuously demethylated after the dehydrogenation reaction, and the final products are NO_2^- and NO_3^-. Chiou et al. [12] combined UV, O_3, and H_2O_2 to degrade TMAH and found that the UV/O_3 process is the best operation mode to show that UV-produced energy stimulates ozone to produce oxygen and hydroxyl radicals in water, which is the main mechanism for the degradation of TMAH. However, the addition of H_2O_2 results in a competition effect that causes the degradation of TMAH to increase instead of decrease.

In addition to the above-mentioned AOPs, ultrasonic and ozone procedures are often used in wastewater treatment. Ultrasonic waves generate cavitation bubbles in water through vibrations and pressures in the frequency range from 20 to 1,000 kHz (the temperature is up to about 5,000 K in air bubbles and the pressures is about 200–500 atm), so the ultrasonic process can be used to oxidize the pollutants in water using ·OH generated through thermal cracking reaction and the reaction of water molecules [9,13]. Ozone has a high oxidizing power, with a reduction potential of 2.07 V, second only to fluorine (2.87 V) and ·OH (2.33 V) [14], therefore, it can effectively destroy organic substances in wastewater. Ozone is characterized by a catalytic reaction and chain reactions to produce ·OH, which reacts with oxidants and organic pollutants to achieve the purpose of decomposing and mineralizing organic pollutants. In recent years, ultrasonic processes have often been combined with other AOPs to generate more ·OH to decompose organic pollutants in wastewater, reducing experimental costs and reaction time [13,15]. Ma [9] degraded ethylenediamine using the sono-Fenton process and found that the combination of ultrasound and Fenton processes was helpful to improve the degradation efficiency of ethylenediamine, but excessive addition of Fe^{2+} or H_2O_2 caused an inhibitory effect and was not conducive to the reaction. Wang et al. [16] used the US/Fe_3O_4/O_3process to degrade tetracycline antibiotics. The experimental results showed that the combination of ultrasound and ozone could increase the removal ratio of tetracycline, and the removal ratio increases with the increase of ozone flow. Wang et al. [17] used US, O_3, and US/O_3 procedures to degrade acephate. The authors found that the removal ratio using the US process alone was only 22.9%, and the removal ratio using the O_3 process was 60.6%; when the US/O_3 processes were carried out, the removal ratio increased to 87.6%. Because the main mechanism of degradation of AOPs is oxidation reaction by ·OH when the ultrasonic wave reacts with O_3, the formed OH is dispersed in liquid, which is beneficial to increase the amount of OH generated, thus effectively increasing the degradation efficiency of organic pollutants [18].

Therefore, this study tried to use the ultrasound, ozone and their combination, sonozone, to decompose TMAH in water. In addition to analyzing the concentration change of TMAH during oxidation, the decomposition effects of TMAH are investigated based on different reaction factors to obtain the optimal operating conditions. At the same time, TMAH degradation and mineralization could be effectively performed, and changes in water toxicity before and after the reaction could be clarified through changes in cell viability.

2. Materials and methods

2.1. Standards and reagents

The chemical reagents used in this study were TMAH ($C_4H_{13}NO$, ACROS ORGANICS, Belgium), sodium hydroxide (NaOH, OSAKA, Japan), and an aqueous solution of sulfuric acid (H_2SO_4, PANREAC, Spain). During the analytical processes, potassium nitrate (KNO_3), ammonium chloride (NH_4Cl), sodium nitrite (Na_2NO_2) and hydrogenophtalate potassium ($C_8H_5KO_4$) were used in determining NO_3^-, NO_2^-, NH_4^+, and total organic carbon (TOC) concentration. These chemicals were the purest grade commercially available (from Merck, Germany) and were used without further purification.

2.2. Experimental apparatus and treatment designs

The experimental equipment diagram is shown in Fig. 1. The ultrasonic equipment is an ultrasonic generator (S&M-VCX750, 20 kHz, maximum power 750 W, USA). When the ultrasonic generator is operated, it is powered by a 110 V power supply and the energy output can be controlled. An ozone generator (TRIOGEN/LAB2B/UK) in high voltage discharge produces ozone, and the flow control device (Bronkhortst/EL-FLOW select F-201 CV/F-211 CV, Taiwan) is used to fix the aeration flow. The reaction tank is a Pyrex glass cylinder (1 L), and the pH meter (Eutech/CyberScan pH 510, Taiwan) and the oxidation-reduction potential meter (Eutech/CyberScan pH 510, Taiwan) are placed in

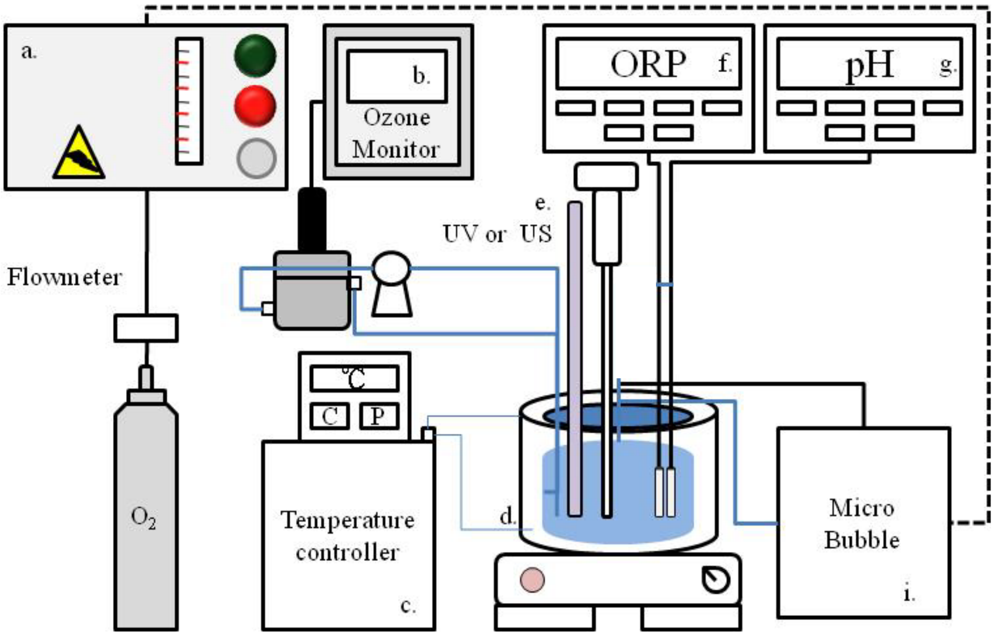

Fig. 1. Schematic of the experimental apparatus designed for TMAH decomposition.

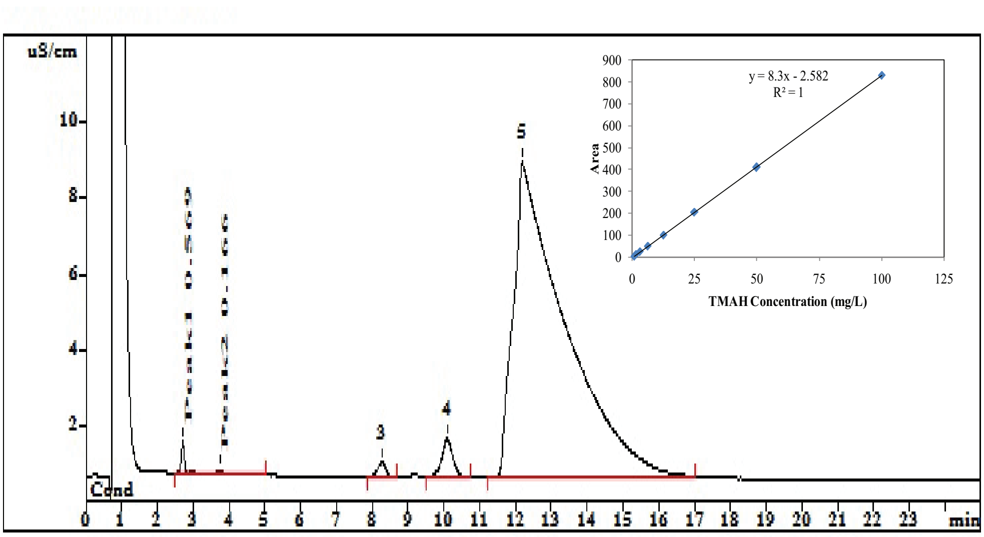

Fig. 2. Ion chromatography spectrum of TMAH determination in IC analysis.

the reaction cylinder. The ozone concentration in the water can be obtained by pumping the aqueous solution into the water ozone concentration monitor (Zezawa, OZ-301, Taiwan). The reaction temperature was controlled by a constant temperature water bath, and the temperature in the tank is controlled through the interlayer of the reactor. The ozone micro-bubble process was operated by ozone process, as described previously; microbubbles use a micro-bubble generating device (Fluid Metering, Inc/MODEL/USA) to form microbubbles between water and ozone by applying a pressure difference.

The initial concentration of TMAH in this study was based on the studies of relevant scholars and set at 50–500 mg/L [11,19], and the volume of the water sample for the experiment was 1,000 mL. The reaction parameters discussed included pH, ultrasonic power, ozone flow, reaction temperature, etc.

2.3. Analysis

In this study, TMAH was analyzed using an ion chromatograph (IC Metrohm 790 Personal); cation is analyzed using a tubular column Metrosep C4 with the analytical eluant of 2.5 mM nitric acid at the flow rate of 1 mL/min. The residence time is 12.1 min. Fig. 2 shows the analysis chromatography of TMAH and its calibration curve, and the R-square vale of the calibration curve is 1. The analysis of ammonium ions was the same as that of TMAH and the residence time was 3.07 min. Nitrate ions were analyzed using an IC equipped with a tubular column MetrosepA Supp 5-100/4.0; the eluant is 3.2 mL sodium carbonate +1.0 mM sodium bicarbonate and the flow rate of eluant is 0.7 mL/min where and the residence time is 7.02 min. The analysis of nitrite in water is based on the spectrophotometric method (NIEA W418.52C) released by the Environmental Protection Agency, Taiwan. The determination of the mineralization efficiency in the TMAH treatment is based on the change in the TOC concentration in the water sample, which is performed using a TOC analyzer. The analysis of ozone concentration in water is performed with an ozone concentration analyzer, and the detection range of ozone concentration is 0–10 mg/L.

Analytical steps of solution toxicity followed our earlier study [20] and are shown below. The toxicities of the tetracycline samples before and after treatment were determined based on the rate of liver cell viability, where viability was confirmed by cell counting. In all experiments, cells were treated with tetracycline water samples for 24 h before and after oxidation. Cell viability was determined using a blue formazan assay in which colorless 3-(4,5-dimethyl-thiazol-2-yl)-2,5-diphenyl tetrazolium bromideis metabolized to a blue-colored product by mitochondrial dehydrogenases. Absorbance was recorded at 540 nm using a SpectraMAX 340 reader. The data were expressed as the mean percentages of viable cells compared to the control.

3. Results and discussion

3.1. Degradation of TMAH by ultrasound

This study remove the TMAH by ultrasound first and investigates the effects of different ultrasonic watt, pH, and temperature. It can be seen from Table 1 that if the original TMAH solution with un-adjusted pH value is directly subjected to the reaction, after 120 min of ultrasonic oxidation process, the degradation ratio of TMAH is below 1.8%. In addition, the TOC variation is lower than the instrument detection limit (0.224 mg/L) and can't be used to calculate the mineralization ratio. This result is also verified by the ORP change monitored during the experiment. The initial ORP value was approximately 45–52 mV (data not shown) and was reduced to 22–26 mV after 120 min of reaction, indicating that this reaction does not have sufficient oxidative efficiency; therefore, it cannot effectively degrade TMAH. However, we can know that a higher ultrasonic watt will have a positive effect on the decomposition of organic matter. In addition, as can be seen from Table 1, if the pH of the solution is adjusted to 3, 5, 7, 9, and 11, respectively, and the reaction time is shortened to 60 min with ultrasonic watt of 100 W, the removal ratio of TMAH is between 0.8% and 3.9%. Meanwhile, the results obtained at pH 7 are slightly higher than other pH values; however, the gaps between them are insignificant. This phenomenon may be due to a simple ultrasound process that reacts with organic matter through the generation of cavitation bubbles and the generation of ·OH by reacting with H_2O. However, the generated ·OH cannot effectively decompose TMAH. At the same time, due to the poor volatility of TMAH, it is not easy to enter cavitation bubbles and conduct a pyrolysis reaction. Therefore, after 60 min of reaction, the degradation ratio is below 3.9%, and the mineralization rate is also below 2.5%. The effects of different reaction temperatures are also discussed in Table 1. From the table, it can be seen that the removal ratio of TMAH increases from 15°C to 55°C, the removal rate of TMAH also increases from 2.1% to 8.4%, and the mineralization rate reaches up to 5.7%. It showed that the increase of reaction temperature contributed to the degradation of TMAH, and the ORP change during the reaction had the same trend. The initial ORP value was about 150 mV, and it increased to 190–268 mV after the reaction. The higher the reaction temperature, the higher the ORP value. However, since the ultrasound process itself is exothermic, the effect is insignificant as the temperature increases, indicating that a single ultrasound process provide insufficient oxidizing power. Under these conditions, the highest degradation rate and mineralization rate are all below 10%.

Table 1
Degradation and mineralization of TMAH by ultrasound at different reaction conditions

Ultrasonic watt (W)	pH	Temperature (°C)	Degradation efficiency of TMAH (%)	Mineralization efficiency of TMAH (%)
50	11	25	1.6[b]	–[a]
75	11	25	1.7[b]	–[a]
100	11	25	1.8[b]	–[a]
100	3	25	0.8	–[a]
100	5	25	1.2	–[a]
100	7	25	3.9	2.5
100	9	25	2	1.1
100	11	25	1.0	–[a]
100	7	15	2.1	1.3
100	7	35	5.1	3.1
100	7	45	6.3	4.1
100	7	55	8.4	5.7

[a] Under the detection limit of TOC (0.224 mg/L)
[b] Reaction time was 120 min

3.2. Degradation of TMAH by ozonation

Since the single ultrasound process cannot effectively degrade TMAH, we adopted removing TMAH with ozone and discussed the effects of different ozone flow rates, pH values and TMAH concentrations on the ozonation of TMAH. Fig. 3 shows the change in ORP values of TMAH using an ozone process at different ozone flow rates. In this reaction, the pH was not pre-adjusted (~pH 7), and the reaction time was extended to 120 min in order to be able to have a complete understanding of the changes in the various factors during the reaction process. It can be clearly seen from the figure that the ORP increased to 800–900 mV after 10 min of reaction, and the higher the O_3 flow rate, the higher the ORP rise, and it remained constant at 900–1,000 mV after 120 min. However, the data show that when the ozone flow rate increased to 500 mL/min and 1,000 mL/min, the ORP value slightly decreased, and the ORP value was about 950 mV after 120 min. This result is because more than 500 mL/min of O_3 introduced into the reaction vessel may result in

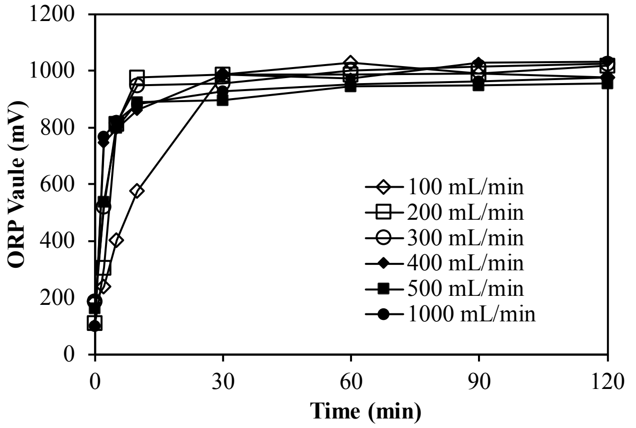

Fig. 3. Profiles of ORP values in TMAH degradation by ozonation with different ozone gas flows.

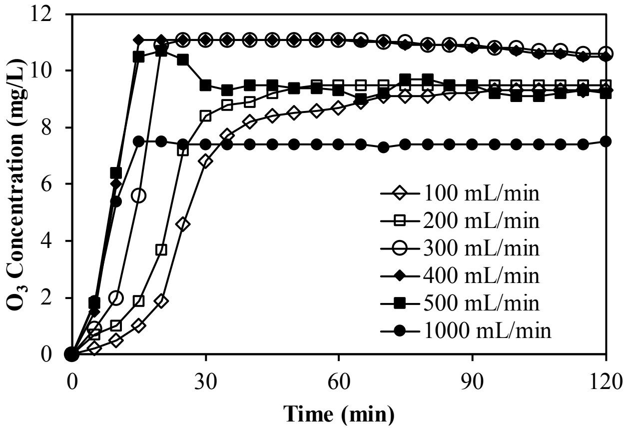

Fig. 4. Profiles of DO_3 concentrations in TMAH degradation by ozonation with different ozone gas flows.

a state of turbulent flow in the reaction due to the introduction of excessive O_3. Ozone bubbles cannot be effectively dissolved in water, and the residence time in water may be shortened. The increase in ORP also slows down, as you can see from Fig. 4; the dissolved ozone concentration in the water sample rises rapidly with the introduction of ozone. After 15–30 min of reaction, the dissolved ozone concentration in the water sample remains more stable. After 120 min of reaction, the ozone concentration is between 7.5 and 10.6 mg/L, and the highest value occurs when the ozone introduction flow is 400 mL/min. When the ozone introduction flow rate increased to 500 mL/min, the O_3 concentration shows a decrease after 20 min of reaction, and the highest dissolved ozone concentration measured at 1000 mL/min is also the lowest, which can verify the aforementioned ORP phenomenon. Fig. 5 shows the trend of the removal ratio of TMAH after degradation and mineralization with different ozone flow. It is found in this figure that when the ozone flow rate is 100, 200, 300, 400, 500, and 1,000 mL/min, after a 120 min reaction, the removal rate of TMAH is 15.5%, 23.4%, 33.3%, 37.8%, 26.3%, and 21.4% respectively, and removal rate is best under the condition of the ozone flow of 400 mL/min, where the result is consistent with the ORP. Excessive O_3 introduction does not improve the removal efficiency of organic matter. Mineralization ratio also has a similar trend; after 120 min reaction, TMAH mineralization ratios were 6.2%, 6.3%, 8.7%, 17.4%, 4.7%, and 3.1%, respectively. When the removal ratio is best at the ozone flow is 400 mL/min, the mineralization rate reached 17.4%.

Table 2 summarizes the experimental results of TMAH treatment with ozone process at different pH, temperature, and initial temperature of TMAH, where in subsequent experiments, the ozone flow rate is fixed at 400 mL/min. It is found in Table 2 that it is more efficient for TMAH to be degraded by ozone in alkaline conditions than in acidic conditions. The highest removal efficiency of TMAH reaches 70.9% following by 47.6% of mineralization. In addition, the highest dissolved ozone concentration obtained from continuous monitoring during the reaction process is 6.8, 6.9, 7.9, 9.4, and 10.3 mg L^{-1}, respectively, at pH 3 to pH 11. It is known that the ozone has a chance to generate more ·OH due to higher dissolved ozone concentration under alkaline conditions, and the degradation efficiency of TMAH is improved by the production of this free radical [21–23]. Table 2 also shows the results of TMAH degradation using ozone at different reaction temperatures. It can be seen that higher reaction temperatures reduce the degradation efficiency of ozone for TMAH, although when the temperature increases from 25°C to 55°C, the degradation ratio of TMAH is only reduced by 14.6%. It is understood that the increase of temperature shortened the residence time of ozone molecules in water, and therefore it cannot be effectively applied to the degradation and mineralization of organic pollutants.

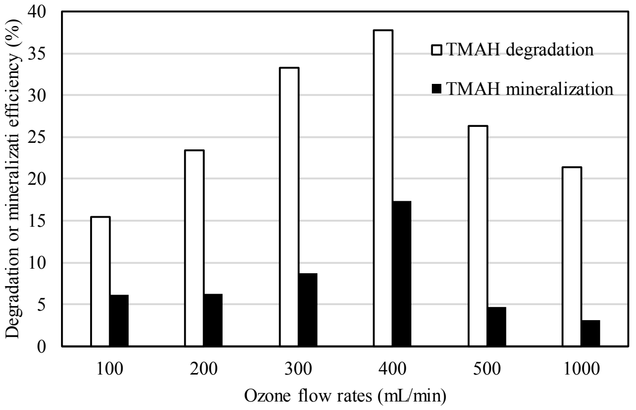

Fig. 5. Degradation and mineralization of TMAH by ozonation with different ozone gas flows.

From Table 2, it can also be found that under the condition of high initial TMAH concentration, the degradation efficiency of TMAH by ozone oxidation gradually decreases, because higher concentrations of organic substances exist in the water sample and react with the same amount of ozone molecules. The occurrence of competition phenomena reduces the percentage of organic matter that is decomposed. This phenomenon can also be verified by the profiles of dissolved ozone concentration presented in Fig. 6. When the initial TMAH concentration is low, the dissolved ozone concentration in the water will reach an equilibrium very fast, indicating that the ozone introduced into the system by the ozone generator does not require

Table 2
Degradation and mineralization of TMAH by ozonation at different reaction conditions

Item	Condition	Degradation efficiency of TMAH (%)	Mineralization efficiency of TMAH (%)
pH			
	3	10.1	3.0
	5	23.7	9.2
	7	37.8	17.4
	9	52.8	21.8
	11	70.9	47.6
Temp. (°C)			
	25	70.9	47.6
	35	66.1	45.3
	45	64.1	33.0
	55	56.3	30.6
TMAH conc. (mg/L)			
	50	70.9	47.6
	100	57.1	41.7
	200	37.9	21.7
	300	32.6	19.9
	400	24.3	16.5
	500	21.4	14.4

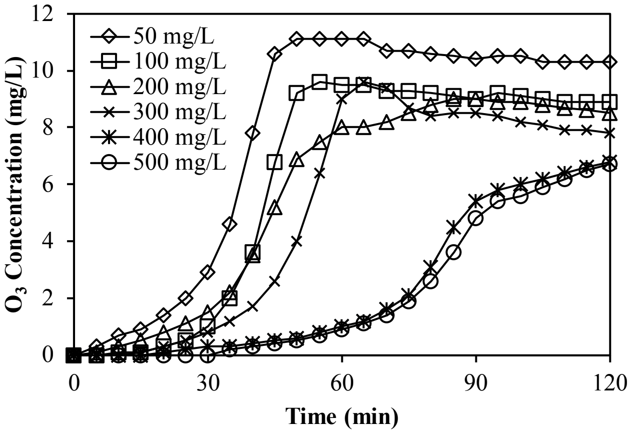

Fig. 6. Profiles of DO_3 concentrations in TMAH degradation by ozonation with different initial TMAH concentrations.

continuous oxidation reaction. But when the concentration of TMAH is higher than 400 mg/L, it can be seen from the figure that the concentration of ozone dissolved in aqueous solution is always low, and rapid accumulation does not begin until about 75 min. However, even when the reaction reaches 120 min, the concentration of dissolved ozone still gradually increased, showing that under this condition, although the oxidation of organics has slowed down. Comparing with the experimental results of lower TMAH concentration found that the ozone introduced into the system would continue to be consumed during the reaction with higher TMAH concentration and be used for the degradation of TMAH. This phenomenon can also be observed by the ORP trend of degradation of TMAH by the ozone process (data were not shown). As the concentration of TMAH increases, the maximum ORP value after 120 min of reaction decreases from 1,119 mV to 900 mV, showing that the oxidation capacity has been consumed because of the existence of a large number of organic matter.

Kim and Choi [11] and Wang and Liang [19] both discussed the final product formed by TMAH degradation and found that if TMAH can be effectively degraded or even mineralized, nitrogen contained in organic matter may be converted to NH_4^+ or NO_3^-. In this study, it is found that the highest mineralization rate can reach 47.8% by ozonation under optimal experimental parameters, indicating that 47.8% of TMAH are attacked by ·OH and release nitrogen after it is completely oxidized. Fig. 7 shows the changes of concentrations of NH_4^+-N, NO_2^--N, and NO_3^--N during the degradation of TMAH by the ozone process. It can be seen from the figure that TMAH begins to decrease after 10 min of reaction, and the concentration after 120 min is only 4.5 mg N/L, and the concentration of NH_4^+-N was 0.32 mg N/L after 10 min of reaction. After 120 min, the concentration of NH_4^+-N increased to 0.45 mg/L and showed a slow tendency to decrease. It was almost impossible to measure NO_2^--N in the first 10 min of reaction. Although there was occasional detection of NO_2^- in the process, the concentration was much lower than 0.01 mg N/L; the trend of NO_3^--N concentration was opposite to TMAH. After 10 min of reaction, the concentration was 0.08 mg/L, the concentration reached 3.14 mg/L after 120 min, and the concentration showed a significant increase. It can be seen that after the reaction, the main by-product of TMAH is NH_4^+ and NO_3^- in the initial stage. After a long time of oxidation, NO_3^- is the main product. This result is because that the ·OH reacts with TMAH continuously; the nitrogen component of the amino is partially released into the aqueous solution and is continuously oxidized to NO_3^--N.

3.3. Degradation of TMAH by sonozone

As mentioned earlier, the ozone process can remove 70.9% of TMAH in sufficient reaction time with proper pH and flow adjustment, and the mineralization rate can reach 47.6%. However, according to the researches [17,18], when the ·OH formed by the reaction of ultrasound and O_3 is dispersed in the liquid, it is beneficial to increase the production of ·OH and enhance the degradation ratio of organic pollutants. Therefore, this study also uses the sonozone process for the degradation of TMAH and explores the effect of different wattages and temperatures on the degradation of TMAH by the sonozone. Due to the higher performance of ozone in the overall reaction than that of ultrasound, the experimental setting of the sonozone process is based on the ozone reaction with pH and ozone flow set at 11 and 400 mL/min. From Table 3, it can be found that when the ultrasonic power is 25 W, 50 W, 75 W, 100 W, and 200 W, the TMAH removal rates after 120 min of reaction are 71.8%, 74.0%, 78.2%, 89.5%, and 81.9%, respectively. When the ultrasonic power is 100 W, the efficiency obtained by combining with the ozone process is higher than the power of other ultrasonic waves; however, when the power of ultrasonic waves was increased to 200 W, the removal rate

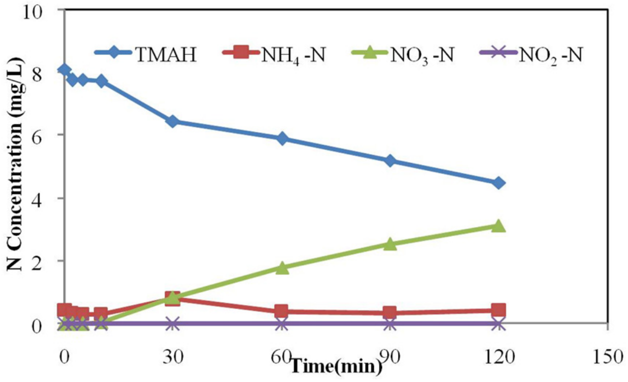

Fig. 7. Profiles of TMAH-N, NH_4^+-N, NO_2^--N and NO_3^--N concentrations in TMAH degradation by ozonation.

Table 3
Degradation and mineralization of TMAH by sonozone at different reaction conditions

Item	Condition	Degradation efficiency of TMAH (%)	Mineralization efficiency of TMAH (%)
Ultrasonic watts (W)[a]			
	25	71.8	47.4
	50	74.0	49.1
	75	78.5	58.5
	100	89.5	67.5
	200	81.9	52.8
Temp. (°C)[b]			
	25	89.5	67.5
	35	76.1	55.9
	45	67.1	47.2
	55	61.4	33.6

[a] pH 11, O_3 flow rate 400 mL/min, temp. 25°C, TMAH 50 mg/L
[b] pH 11, O_3 flow rate 400 mL/min, ultrasonic watt 100 W, TMAH 50 mg/L

decreased slightly, and the mineralization rate of TMAH showed a similar phenomenon. The mineralization rates were 47.4%, 49.1%, 58.5%, 67.5%, and 52.8%. This result is due to the fact that ultrasonic waves can effectively improve the ability of the ozone process to degrade pollutants, and in particular, increase the efficiency of the main reaction mechanism of bond-breaking during the oxidation of pollutants [24]. When the ultrasonic wave reacts with the ozone reaction, at least the following reaction mechanisms may occur: (I) Organic contaminants to be treated are directly pyrolyzed in ultrasonically generated eddy bubbles [Eq. (1), where []))] denotes the ultrasound]; (II) After the generation of ·OH by applying ultrasonic to water molecules, ·OH will degrade the organic contaminants to be treated [Eq. (2)]; (III) The ozone molecules react directly with the organic contaminants to be treated. In addition to degrading the contaminants, H_2O_2 may also be produced. [Eq. (3)]; and (IV) ·OH generated by ozone reaction degrades organic matter [Eq. (4)].

However, a synergistic effect may also occur in the combination of these two procedures (reaction mechanism V) [25,26]. Oxygen atoms are generated when ozone molecule undergoes a thermal cracking reaction in an ultrasonically generated cavitation bubble [Eq. (5)] [27]. Oxygen atoms react with water molecules to produce twice the amount of ·OH [Eq. (6)]. Enough ·OH may combine and generate H_2O_2 [Eq. (7)] or degrade organic contaminants to be treated [Eq. (8)]. Therefore, sonozone not only has separate mechanisms for the decomposition of organic matter by individual ultrasound and ozone, but also has a stronger oxidizing energy because of the synergistic effect. As a result, sonozone should have better processing performance.

In addition to the ultrasonic power, the increase in temperature found in Table 1 is beneficial to the degradation of TMAH in the ultrasonic process, but the increase in temperature in Table 3 is detrimental to the oxidation process of the ozone process. Therefore, in Table 3, we discussed the degradation of TMAH by the sonozone process at different reaction temperatures. It was found that when the temperature was 25, 35, 45, and 55°C, the removal rate reached 26.5%, 20.5%, 21.2%, and 14.3% after 10 min of reaction, respectively. After 120 min of reaction, the removal rate increased to 89.5%, 76.1%, 67.1%, and 61.4% (ultrasonic power is 100 W). It is understood from the removal ratio that when the reaction temperature increases, the removal effect has a clear tendency to decrease, indicating that when ultrasound and ozone are combined, increase in the temperature is beneficial to the ultrasound process. However, because the adverse effect on ozone is greater than the positive effect on the ultrasound process, as a whole, the increase in temperature does not contribute to the sonozone process. The mineralization ratio of TMAH had similar trend at different temperatures. After 120 min of reaction, the mineralization rates were 67.5%, 55.9%, 47.2%, and 33.6%, respectively.

Reaction mechanism I

$$))) + X \rightarrow \text{products} \quad (1)$$

Reaction mechanism II

$$))) + H_2O \rightarrow \cdot OH\ (+ X) \rightarrow \text{products} \quad 2)$$

Reaction mechanism III

$$O_3 + X \rightarrow \text{products} + H_2O_2 \quad (3)$$

Reaction mechanism IV

$$O_3 + H_2O \text{ or } HO_2^- \text{ or } H_2O_2 \rightarrow \cdot OH\ (+ X) \rightarrow \text{products} \quad (4)$$

Reaction mechanism V

$$O_3 +))) \rightarrow O_2 + O(^3P) \quad (5)$$

$$O(^3P) + H_2O \rightarrow 2\cdot OH \quad (6)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad (7)$$

$$\cdot OH + X \rightarrow \text{products} \quad (8)$$

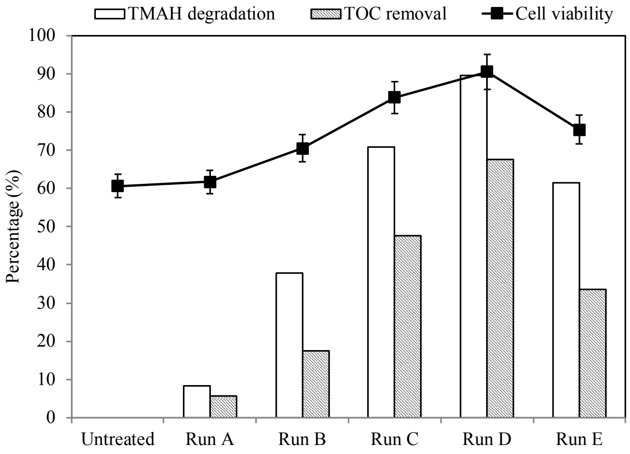

Fig. 8. Profiles of TMAH degradation, TOC removal and cell viability by different treatment processes. Run A: ultrasonic watt = 100 W; Run B: pH 7, O_3 flow rate 400 ml/min; Run C: pH 11, O_3 flow rate 400 ml/min; Run D: pH 11, O_3 flow rate 400 ml/min, ultrasonic watt = 100 W, temp. 25°C, and Run E: pH 11, O_3 flow rate 400 ml/min, ultrasonic watt = 100 W, temp. 55°C.

3.4. Change of toxicity of TMAH solution via cell viability

In order to understand whether the toxicity of TMAH during its degradation is synchronous with the change of organic matter concentration, this study used the liver cell viability of rats as an indicator. The water samples before and after treatment were incubated with liver cells to calculate the survival ratio to determine if there is a decrease in the toxicity of the water sample. Fig. 8 summarizes the results of TMAH degradation rate, mineralization rate, and cell viability under different conditions. It can be seen from the figure that the survival rate of cells in untreated TMAH water sample is about 60.5%. If ultrasound was conducted, (Run A, ultrasonic watt = 100 W), due to the poor treatment efficiency, cell viability increased slightly to 61.7%. When reacted with ozone (Run B: pH 7, O_3 flow rate 400 mL/min, Run C: pH 11, O_3 flow rate 400 mL/min), cell viability was increased to 70.5% and 83.8% due to the increase of TMAH removal rate. Run D (pH 11, O_3 flow rate 400 mL/min, ultrasonic watt = 100W, temp. 25°C), and Run E (pH 11, O_3 flow rate 400 mL/min, ultrasonic watt = 100 W, temp. 55°C) treat TMAH under different conditions with the sonozone process, with the highest cell survival ratio appearing in Run D. This result is due to the fact that the organic matter removal ratio and mineralization ratio are the highest under this condition; therefore, the toxicity of the water sample also reduced significantly. This trend is similar to the phenomena recorded in the previous researches [28,29]. Even the sonozone leads the effectively degradation of TMAH, the maximum TOC removal was 67.5%, which indicating that about 32.5% of the degraded TMAH was not mineralized by sonozone. Hence, the changes in toxicity based on the cell viability measurements need to be evaluated in addition to the degradation efficiencies. Eleven experimental runs were carried out (including the data shown in Figs. 5 and 8) to determine the relationships between TMAH mineralization with cell viability (Fig. 9).

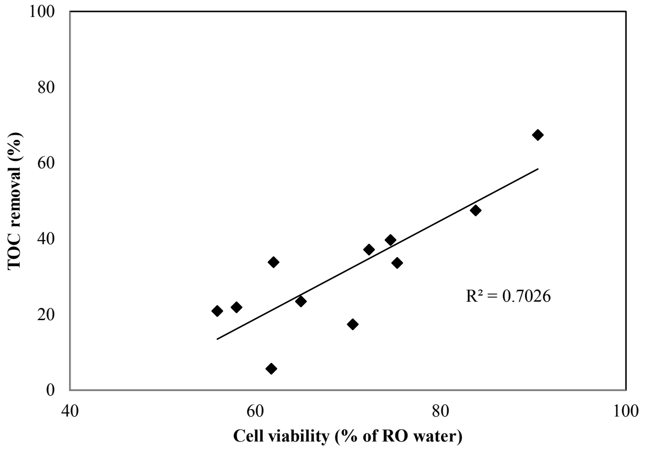

Fig. 9. Relationship between TOC removal and cell viability in TMAH degradation.

For the treatment of TMAH by sonozone and ozonation, a good relationship was found between TOC removal and cell viability ($R^2 = 0.70$), indicating that the mineralization of TMAH increased the cell viability, or decreased the toxicity of TMAH sample. This also demonstrates that the TOC removal during TMAH degradation was the critical factor in the toxicity reduction. Furthermore, the results shown in other references [5–8,19] indicated that five hours to several days are necessary to effectively degrade the TMAH by aerobic, anaerobic, physical and chemical processes. In this study, less than two hours are necessary to degrade and detoxify the TMAH water sample at an appropriate experimental condition. Therefore, as the toxicity of TMAH is reduced by the sonozone process, the wastewater could be further easily treated with other traditional biological methods.

4. Conclusions

The main purpose of this study was to use the ultrasonic procedures, ozone procedures, and a combination of these two procedures to treat TMAH wastewater that was configured in the laboratory to explore the effects of different reaction factors and to discuss the changes in degradation, mineralization, and toxicity of TMAH. Ultrasound has a better removal effect at neutral pH, and TMAH degradation increases with reaction temperature and ultrasonic power. However, ultrasound alone cannot effectively degrade and mineralize TMAH. Ozonation process helps to increase the TMAH degradation efficiency at higher pH and lower reaction temperature, but when the TMAH concentration reaches 200 mg/L or above, the degradation efficiency is significantly reduced, indicating that initial lower concentration helps the ozonation process degrade TMAH. The sonozone process shows that the synergistic effect of the combination of ultrasound and ozone procedures has contributed to the degradation and mineralization of TMAH and the reduction in toxicity. The primary key to the reduction in toxicity of organic matter is the ability to effectively mineralize organic matter into CO_2.

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