

## Oxidation of methyl methacrylate from semiconductor wastewater by O<sub>3</sub> and O<sub>3</sub>/UV processes

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### Abstract

This study investigated the oxidation of methyl methacrylate (MMA) by sole ozonation and ozone/UV treatments. The semi-batch ozonation experiments were proceeded under different reaction conditions to study the effects of ozone dosage and UV radiation on the oxidation of MMA. The experimental results indicated that both the oxidation of MMA by the sole ozonation and O<sub>3</sub>/UV processes can completely decompose MMA to form the following intermediates within 30 min reaction time. To increase the applied ozone dosage can significantly raise the removal efficiency of MMA. However, the mineralization of MMA via the direct oxidation reaction of molecular ozone was slow, while introducing the UV radiation can promote the mineralization rate of MMA. In addition, the pH value of the oxidized solution in the O<sub>3</sub>/UV treatment decreased lower than that in the sole ozonation treatment of about 1 unit. The possible scheme of the decomposition pathway of MMA under the ozonation process is proposed in this study. Formic acid and acetic acid were found to be the main ozonated intermediates.

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### 1. Introduction

The semiconductor related manufactures were very popular industries in Taiwan for the past several decades. The semiconductor manufacturing involves with many complex and delicate processes, including silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, and cleaning, etc. [1]. More than two hundreds of organic and inorganic compounds were used in the manufacturing processes. Therefore, the wastewater from the semiconductor industry commonly contains various organic solvents, acids, bases, salts, and other inorganic chemicals. Especially, the organic compounds which are considered high toxic and bioresistant are difficult to be treated in the general wastewater treatment processes. Methyl methacrylate (MMA) being one of these compounds is chosen as the target compound in this study. MMA is the monomer compound of poly methyl

methacrylate (PMMA). PMMA is widely used as the resist in the photo-lithography processes of the semiconductor manufactures. MMA is also applied in the manufacture of many resin and plastic products. Another significant use of MMA is employed for the polymer productions of various methacrylate esters [2].

MMA has the solubility of 16 g/L in water, vapor pressure of 4.2 kPa, and log  $P_{ow}$  value (octanol–water partition) of 1.83 at 20 °C. Hydrolysis of MMA is found insignificant at neutral and acidic pH environments, and becomes remarkable in the condition of higher pH value. In addition, MMA would be rapidly absorbed in the oral or inhalatory administration of human beings. MMA is also reported irritating to the eyes and mucous membranes. The aquatic toxicity of MMA is obvious and the risk of bioaccumulation is limited since the low log  $P_{ow}$  value is indication of high mobility within the aquatic system [2,3]. MMA has *in vitro* the potential for induction of mutagenic effects, especially clastogenicity. However, there is no relevant concern on carcinogenicity of MMA in humans and animals [2].

Ozonation is an effective way to reduce the chemical oxidation demand (COD) and total organic carbons (TOCs) by

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oxidizing the stream solutions with ozone [4]. Ozone may attack on the pollutants via two different reaction pathways: (1) the direct ozonation by the ozone molecule, and (2) the radical ozonation by the highly oxidative free radicals such as hydroxyl free radicals, which are formed by the decomposition of ozone in the aqueous solution [5,6]. The radical ozonation is non-selective and vigorous. The ozonation process in the acid condition mainly takes place through the direct oxidation reaction, which is selective [7,8]. Ozonation combined with ultraviolet (UV) radiation is deemed as a more effective process to remove organics comparing to the sole ozonation. UV radiation is commonly employed to enhance the ozone decomposition yielding more free radicals resulting in a higher ozonation rate [9]. The degradation of less reactive compounds may be accelerated with the presence of free radicals [10]. In addition, the related studies have examined the feasibility of using ozone or other oxidants (so-called advanced oxidation processes, AOPs) to treat the toxic and refractory organic compounds in order to increase their biodegradability for the subsequent biological treatment [11–13].

Note that a few studies in the related oxidation of MMA have been found. The study investigated the oxidation of MMA by ozonation and  $O_3/UV$  in the aqueous or methanol-containing solutions. Methanol was as the solvent added into the aqueous solution for simulating the wastewater of semiconductor manufacture processes. The semi-batch ozonation experiments of the MMA solutions are proceeded under different reaction conditions. The concentrations of MMA, ozonated intermediates, pH, and COD are analyzed at specified time intervals to study the decomposition of MMA. COD is chosen as a mineralization index of the ozonation of MMA, while the value of pH is measured continuously in the course of the experiments. One may note that TOC is not considered as the appropriate index of the mineralization for the ozonation of MMA. It is because that MMA would be volatilized from the sampling solution during the procedure of TOC analysis, which consists the nitrogen gas purge step in the acidifying process for the elimination of inorganic carbon. All these results can provide useful information about the decomposition of MMA by ozonation with UV radiation.

## 2. Materials and methods

The concentration of MMA was chosen at about 500 mg/L according to the formula of semiconductor processes. The chemical formula of MMA was  $C_5H_8O_2$  (MW = 100.12), which was purchased from Aldrich (reagent grade) and used without any further purification. Two different prescriptions of the solutions were prepared with the deionized water without other buffer solutions and the methanol-containing solution, respectively. The methanol-containing solution with the concentration of methanol as 19.4 g/L was used to simulate the background of wastewater released from manufacture plants in this study.

Fig. 1 shows a schematic diagram of the ozonation apparatus as a semi-batch type. The reactor was made from Pyrex glass with an effective volume of 5.5 L and 17.2 cm inside diame-

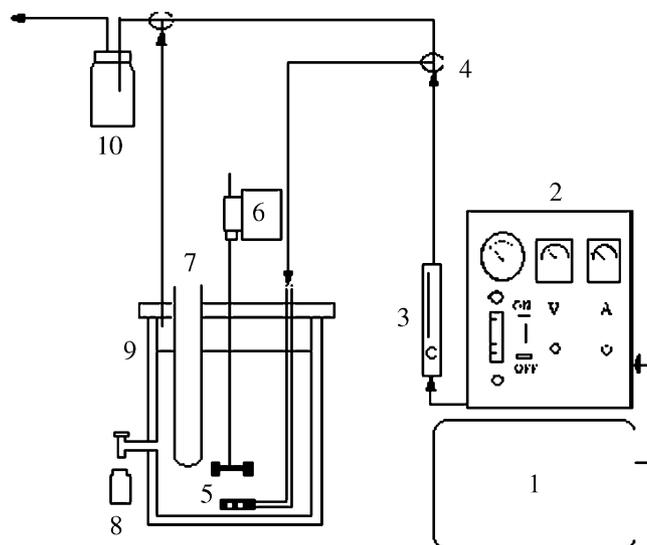


Fig. 1. Schematic apparatus of ozonation system: (1) oxygen tank, (2) ozone generator, (3) flow meter, (4) three-way valve, (5) gas diffuser, (6) stirrer, (7) ultra-violet lamps, (8) sampling port, (9) reactor, and (10) KI solution.

ter. The reactor was equipped with water jacket to maintain a constant solution temperature at 25 °C in all experiments. The reactor design is based on the criteria of the shape factors of a standard six-blade turbine [14]. The gas diffuser in the cylindrical shape with the pore size of 10  $\mu\text{m}$  was located at the bottom of reactor. Two quartz tubes of 3.8 cm outside diameter symmetrically installed inside the reactor were used to house the UV lamps. The low-pressure mercury lamps (Osram, HNS-20W) emitted principally at 254 nm. The radiation intensity was measured by a digital radiometer (ultra-violet products, Upland CA, USA) with a model UVP-25 radiation sensor. Light intensity ( $I_{UV}$ ) of 35.96  $\text{W}/\text{m}^2$  is employed to test the effect of UV radiation on the ozonation. About 3.7 L solution is used in each experiment, while the total sampling volume is within 5% of solution. The stirring speed was set as high as 800 rpm to ensure the complete mixing of gas and liquid phases according to previous tests [10].

The ozone generator was manufactured by JEU TU CO., Japan (series no., SG-01A-PSA4). The ozone concentration in the fed-gas was maintained at 10 or 20 mg/L, and the gas flow was 1.78 L/min in all experiments with constant gas pressure (1 kg f/cm<sup>2</sup>). The concentration of ozone in the feed-gas was measured by the potassium iodide technique according to the standard methods [15]. The concentration of MMA was analyzed by an HPLC (Bio-Rad 1350) equipped with a UV/vis spectrophotometer (Bio-Rad 1706) at a wavelength of 254 nm and a C18 reverse-phase column (Hypersil BDS C18, 5  $\mu\text{m}$ ). The mobile phase was prepared with acetonitrile, water, and acetic acid with the volume ratio of 700:300:4.5. The concentrations of the acetic and formic acids were also analyzed by the HPLC system using another column (YMC-Pack ODS-AQ) with a detection wavelength of 220 nm and the mobile phase of 20 mM  $H_3PO_4$ - $NaH_2PO_4$  (pH 2.8) aqueous solution. The analytical method for measuring the COD value follows the standard methods [15]. The pH value during the

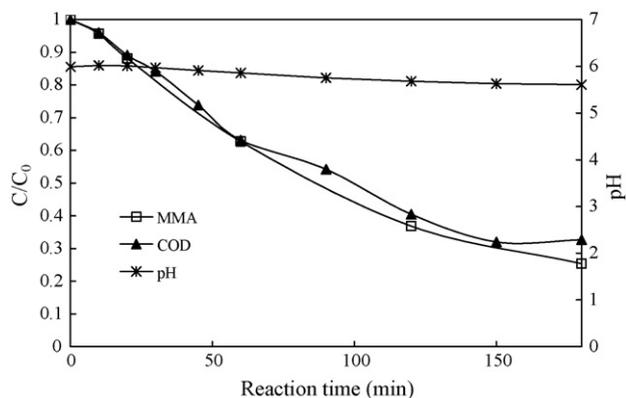


Fig. 2. Variations of MMA concentration, COD and pH with reaction time in aeration process.  $[MMA]_0 = 505.3$  mg/L,  $[COD]_0 = 906.7$  mg/L,  $[q] = 1.78$  L/min, and  $[O_3] = 0$  mg/L.

experiments was measured by a pH meter (SUNTEX, model PC-310).

### 3. Results and discussion

#### 3.1. Oxidation of MMA by $O_3$ and $O_3/UV$ in aqueous solution

Before the ozonation processes, a gas stripping test was performed to measure the volatility of MMA in the aqueous solution. Fig. 2 shows that the decay of MMA and COD almost displays the same trend. It reveals that MMA was apt to volatilize from the aqueous solution into the gas phase during the experiments, which elucidated that the decreases of MMA and COD were caused by the volatile mechanism. As a result, 12 and 75% of MMA were volatilized into the air phase in 30 and 180 min during the aeration process, respectively. On the contrast, the pH value does not change significantly during the aeration period with the values of 5.99 and 5.61 at initial time and 180 min, respectively. The slight decrease of the pH value may be resulted from some carbon dioxide dissolved into the solution.

The oxidation of MMA in the aqueous solution by sole ozonation was shown in Fig. 3. The MMA concentration, COD, and

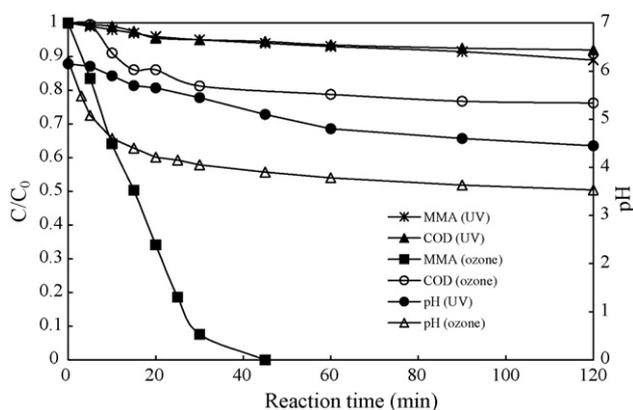


Fig. 3. Variations of MMA concentration, COD and pH with reaction time in sole ozonation and UV process.  $[MMA]_0 = 505.3$  mg/L,  $[COD]_0 = 906.7$  mg/L,  $[q] = 1.78$  L/min,  $[O_3] = 10$  mg/L, and  $[I_{UV}] = 35.96$  W/m<sup>2</sup>.

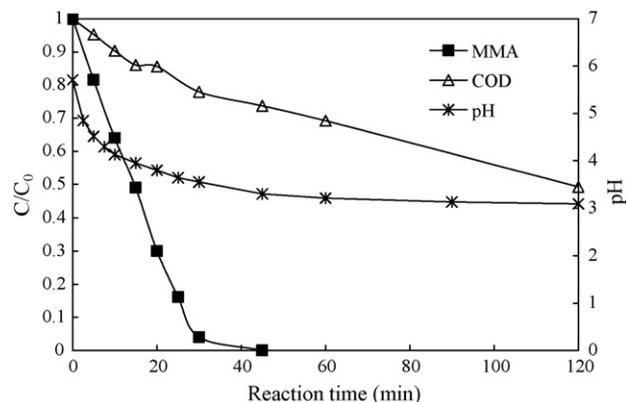


Fig. 4. Variations of MMA concentration, COD and pH with reaction time in  $O_3/UV$  process.  $[MMA]_0 = 505.3$  mg/L,  $[COD]_0 = 906.7$  mg/L,  $[q] = 1.78$  L/min,  $[O_3] = 10$  mg/L, and  $[I_{UV}] = 35.96$  W/m<sup>2</sup>.

pH changed apparently within the ozonation time of 30 min. The removal of MMA and COD were 93 and 19% in 30 min, respectively. The decrease of COD became remarkably slower after the ozonation time of 30 min. In addition, the pH value decreased rapidly from the weakly acidic solution (pH 6.21) to the acidic condition (pH about 4.0), which implied the oxidation of MMA mainly via the direct ozonation reaction with molecular ozone. The reason for the inconsistent decrease of COD with the decrease of MMA concentration unlike Fig. 2 is due to the generation of the hydrophilic intermediates by the chemical reaction of MMA and ozone. Apparently, the removal rate of MMA via the ozonation reaction would be faster compared with the volatilization. The pH value of the solution decreases rapidly in the early period and then gradually approaches to a constant. However, the mineralization of MMA ozonation was resistant to the direct oxidation reaction of molecular ozone due to the small COD removal of 24% in 120 min. The variations of MMA and COD via the direct photolysis were also shown in Fig. 3. It is found that the direct photolysis of MMA with the removal efficiency of 11% in 120 min is relatively slower than the ozonation process.

Fig. 4 shows the oxidation results of MMA in the aqueous solution by the  $O_3/UV$  treatment. At the reaction time of 30 min, the removal of MMA and COD were 96 and 22%, respectively. The degradation of COD could further increase to 51% in 120 min. It showed that the removal efficiency of MMA by the ozone/UV process was higher than that by the ozonation alone. It is due to that the presence of the UV radiation would decompose the dissolved ozone concentration and accompany the generation of OH radicals simultaneously. As a result, the overall decomposition rate of MMA is only slightly accelerated by the presence of the UV radiation. The mineralization rate in the  $O_3/UV$  process is greater than that in the sole ozonation process due to the generation of OH radicals. The OH radicals have greater reactivity toward the organic compounds to enhance the mineralization. Moreover, the pH value of the ozonated solution in the  $O_3/UV$  process was 0.5 units lower than that in the sole ozonation process, indicating the different ozonation mechanisms.

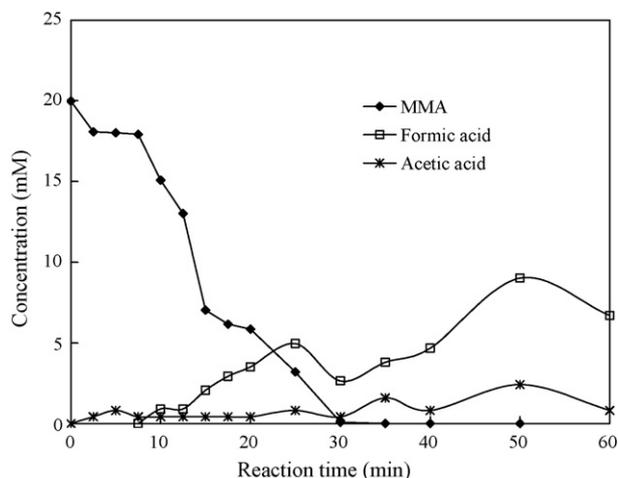


Fig. 5. Variations of MMA, formic acid and acetic acid with reaction time in sole ozonation process.  $[MMA]_0 = 19.98$  mM (2000 mg/L),  $[q] = 1.78$  L/min, and  $[O_3] = 40$  mg/L.

### 3.2. The ozonation pathway of MMA

According to the analysis of HPLC, the formic and acetic acids were detected during the decomposition of MMA in the conditions of  $O_3$  and  $O_3/UV$  treatments. The concentration variations of formic and acetic acids in the sole ozonation and  $O_3/UV$  processes of MMA were shown in Figs. 5 and 6, respectively. Formic acid was considered as the ozonation product of acetic acid. In generally, the formation of these low-weight organic acids might decrease the mineralization rate. The concentrations of the formic and acetic acids started to appear in the later stages of the ozonation processes. In addition, the concentration of the formic acid was greater than that of the acetic acid. The difference between the  $O_3$  and  $O_3/UV$  treatments regarding the observed intermediates from the decomposition of MMA was not significant. However, the condition of  $O_3/UV$  gives the greater ability for the subsequent oxidation of the organic acids. Therefore, the combination of ozone with UV radiation is recommended for treating the MMA solution as far as the COD reduction is concerned, although the sole ozonation process may be sufficient for the removal of MMA.

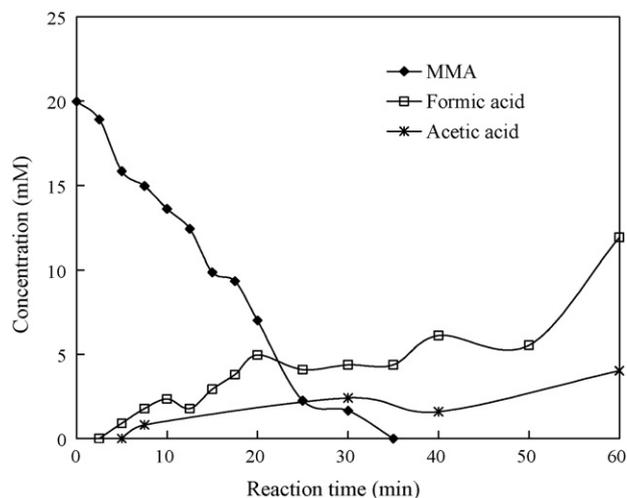


Fig. 6. Variations of MMA, formic acid and acetic acid with reaction time in  $O_3/UV$  process.  $[MMA]_0 = 19.98$  mM (2000 mg/L),  $[q] = 1.78$  L/min, and  $[O_3] = 40$  mg/L.

According to the molecular structure of MMA, the first attack of molecular ozone or OH radicals on MMA is mainly toward the position of carbon double bonds (C=C), which has the activating effect by denoting the electron density. Methyl formate and formaldehyde were expected to be formed and then oxidized to become formic and acetic acids. However, methyl formate and formaldehyde were not found in the HPLC analysis. It revealed that decomposition of methyl formate and formaldehyde were very fast to generate the acetic and formic acids. Accordingly, the possible scheme of the decomposition pathway of MMA to become carbon dioxide and water under the ozonation processes is proposed in Fig. 7.

### 3.3. Oxidation of MMA by UV radiation, $O_3$ , and $O_3/UV$ in methanol-containing solution

The variations of MMA concentration, and pH in the methanol-containing solution during the air stripping, sole ozonation, UV radiation and  $O_3/UV$  processes were shown in Figs. 8 and 9, respectively. The oxidation of MMA by the UV radiation alone was weak with the MMA removal of mere 11% in 120 min (Fig. 8). On the other hand, the degradation of MMA

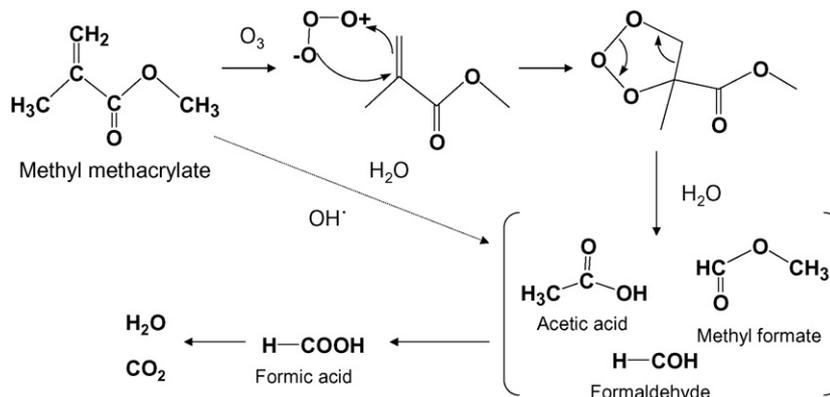


Fig. 7. Possible scheme of the decomposition pathway of MMA under ozonation.

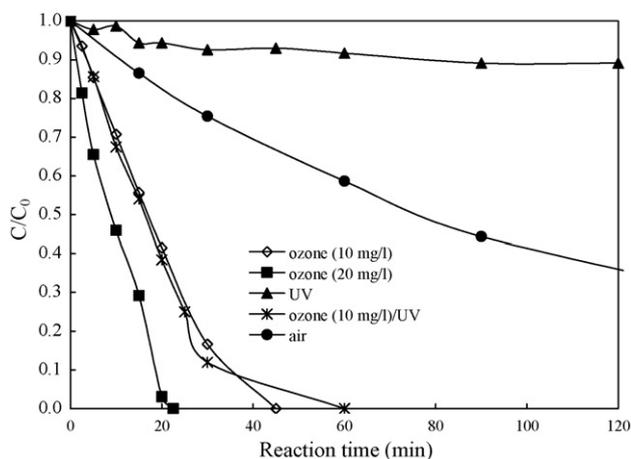


Fig. 8. Variations of MMA concentration with reaction time in methanol-containing solution via various processes.  $[MMA]_0 = 505.3$  mg/L,  $[q] = 1.78$  L/min,  $[O_3] = 10$  or  $20$  mg/L, and  $[I_{UV}] = 35.96$  W/m<sup>2</sup>.

via the sole ozonation and O<sub>3</sub>/UV processes with the same ozone dosage ( $[O_3] = 10$  mg/L) was close with the MMA removal of 83 and 88% in 30 min, respectively. The situation was similar to that in the aqueous solution. Furthermore, the presence of methanol slightly affected the ozonation of MMA as illustrated in Figs. 3, 4 and 8. The phenomena is consistent with the observation of Alborzfar et al. [16], which indicated that the oxidation rate of 3,4-dichlorobut-1-ene is independent of the addition of methanol due to the slow reaction rate between ozone and methanol. To increase the ozone dosage as  $[O_3] = 20$  mg/L can significantly raise the removal rate efficiency of MMA, while the MMA would be completely decomposed in 22 min. The time for the complete decomposition of MMA with  $[O_3] = 20$  mg/L was about half of those with  $[O_3] = 10$  mg/L. Note that the analysis of COD was not performed for the ozonation process of PMMA in the methanol-containing solution due to that the methanol contributes the great interference in the COD measurement.

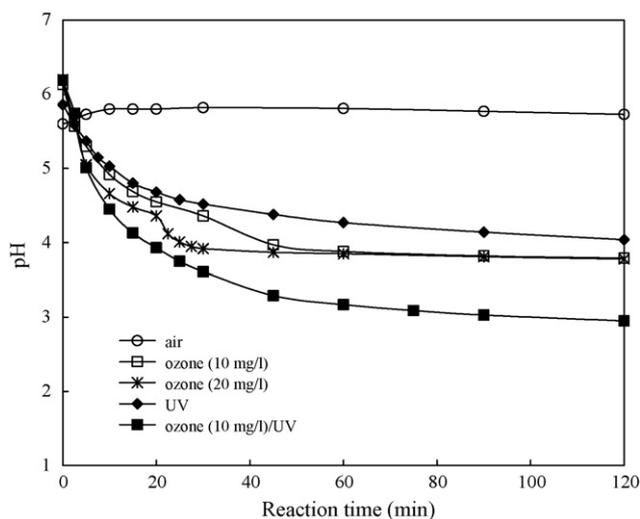


Fig. 9. Variations of pH with reaction time in methanol-containing solution via the various processes.  $[MMA]_0 = 505.3$  mg/L,  $[q] = 1.78$  L/min,  $[O_3] = 10$  or  $20$  mg/L, and  $[I_{UV}] = 35.96$  W/m<sup>2</sup>.

As indicated in Fig. 9, the cases of the sole ozonation process with different ozone dosages have the similar trend of pH variation of the final value about 4. The pH value of the oxidized solution in the O<sub>3</sub>/UV process was about 1 unit lower than those in the sole ozonation process in the methanol-containing solution. On the other hand, the variations of pH in the methanol-containing solution were similar to those in the aqueous solution under the same condition.

#### 4. Conclusions

Methyl methacrylate (MMA) is one of the chemicals in semiconductor manufacturing processes and exists in its wastewater. In this study, ozonation combined with UV radiation is employed as an effective way for the removal of MMA in the aqueous and methanol-containing solutions. The decomposition of MMA accompanies with the removal of chemical oxidation demand (COD) and the generation of organic acids. The following conclusions may be drawn:

1. The decomposition rate of MMA increases with the ozone concentration of feed gas, while is not significantly enhanced by the presence of UV radiation. The MMA in the aqueous or methanol-containing solutions can be decomposed completely to form the intermediates by the sole ozonation or O<sub>3</sub>/UV processes within 30 min reaction time. On the other hand, increasing the ozone dosage significantly raises the degradation efficiency of MMA. According to the structure of MMA, the carbon double bonds (C=C) may be the first attack position by the molecular ozone or hydroxyl free radicals. The formic acid and acetic acid are the main ozonation intermediates of MMA.
2. The mineralization rate of MMA through the direct oxidation reaction of molecular ozone is slow. However, the O<sub>3</sub>/UV system gives the higher mineralization rate than the sole ozonation system. The pH value of the oxidized aqueous or water/methanol solutions in the O<sub>3</sub>/UV process would decrease lower than that in the sole ozonation one.

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#### References

- [1] H.L. Sheng, R.Y. Chung, Chemical and physical treatments of chemical mechanical polishing wastewater from semiconductor fabrication, *J. Hazard. Mater. B* 108 (2004) 103–109.
- [2] U.S. Environmental Protection Agency, Toxicological review of methyl methacrylate (CAS no. 80-62-6). In Support of Summary Information on the Integrated Risk Information System (IRIS), Washington, DC, 1998.
- [3] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, *Environmental Organic Chemistry*, John Wiley and Sons, New York, NY, USA, 1993.
- [4] C.G. Hewes, R.R. Davison, Kinetics of ozone decomposition and reaction with organics in water, *AIChE J.* 17 (1971) 141–147.
- [5] M.D. Gurol, P.C. Singer, Kinetics of ozone decomposition: a dynamic approach, *Environ. Sci. Technol.* 16 (1982) 377–383.

- [6] J.L. Sotelo, F.J. Beltrán, F.J. Benítez, J. Beltrán-Heredia, Ozone decomposition in water: kinetic study, *Ind. Eng. Chem. Res.* 26 (1987) 39–43.
- [7] F.J. Beltrán, P. Alvarez, Rate constant determination of ozone-organic fast reactions in water using an agitated cell, *J. Environ. Sci. Health A* 31 (1996) 1159–1178.
- [8] M. Hautaniemi, J. Kallas, R. Munter, M. Trapido, Modeling of chlorophenol treatment in aqueous solutions. 1. Ozonation and ozonation combined with UV radiation under acidic conditions, *Ozone Sci. Eng.* 20 (1998) 259–282.
- [9] H.W. Prengle, Experimental rate constants and reactor considerations for the destruction of micropollutants and trihalomethane precursors by ozone with ultraviolet radiation, *Environ. Sci. Technol.* 17 (1983) 743–747.
- [10] C.Y. Chang, Y.H. Chen, H. Li, C.Y. Chiu, Y.H. Yu, P.C. Chiang, Y. Ku, J.N. Chen, Kinetics of decomposition of polyethylene glycol in electroplating solution by ozonation with UV radiation, *J. Environ. Eng.* 127 (2001) 908–915.
- [11] L. Li, W. Zhu, P. Zhang, Q. Zhang, Z. Zhang, TiO<sub>2</sub>/UV/O<sub>3</sub>-BAC processes for removing refractory and hazardous pollutants in raw water, *J. Hazard. Mater. B* 128 (2006) 145–149.
- [12] M. Daniele, A. Bila, Filipe Montalvão, C.S. Alessandra, M'arcia Dezotti, Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement, *J. Hazard. Mater. B* 117 (2005) 235–242.
- [13] N.C. Shang, Y.H. Yu, H.W. Ma, C.H. Chang, M.L. Liou, Toxicity measurements in aqueous solution during ozonation of mono-chlorophenols, *J. Environ. Manag.* 78 (2006) 216–222.
- [14] W.L. McCabe, J.C. Smith, P. Harriott, *Unit Operations of Chemical Engineering*, McGraw-Hill, New York, NY, USA, 1993.
- [15] APHA (American Public Health Association), *Standard Methods for Examination of Water and Wastewater*, 18th ed., APHA, Washington, DC, 1992.
- [16] M. Alborzfar, K. Escande, S.J. Allen, Removal of 3, 4-dichlorobut-1-ene using ozone oxidation, *Water Res.* 34 (2000) 2963–2970.