Research Article

Application of Ozone Related Processes to Mineralize Tetramethyl Ammonium Hydroxide in Aqueous Solution

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Tetramethyl ammonium hydroxide (TMAH) is an anisotropic etchant used in the wet etching process of the semiconductor industry and is hard to degrade by biotreatments when it exists in wastewater. This study evaluated the performance of a system combined with ultraviolet, magnetic catalyst ($\text{SiO}_2/\text{Fe}_3\text{O}_4$) and O_3 , denoted as UV/ O_3 , to TMAH in an aqueous solution. The mineralization efficiency of TMAH under various conditions follows the sequence: UV/ O_3 > UV/ H_2O_2 / O_3 > $\text{H}_2\text{O}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{O}_3$ > $\text{H}_2\text{O}_2/\text{O}_3$ > $\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{O}_3$ > O_3 > UV/ H_2O_2 . The results suggest that UV/ O_3 process provides the best condition for the mineralization of TMAH (40 mg/L), resulting in 87.6% mineralization, at 60 min reaction time. Furthermore, the mineralization efficiency of $\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2/\text{O}_3$ was significantly higher than that of O_3 , $\text{H}_2\text{O}_2/\text{O}_3$, and UV/ H_2O_2 . More than 90% of the magnetic catalyst was recovered and easily redispersed in a solution for reuse.

1. Introduction

The semiconductor industry is an important component of the electronics industry, whose global market yield has already exceeded that of the automobile industry. Anisotropic chemical wet etching is widely used in the semiconductor industry to fabricate microstructures on single crystal silicon wafers [1]. Of all the anisotropic etchants, the inorganic KOH (potassium hydroxide) and organic TMAH (tetramethyl ammonium hydroxide) solutions are the most commonly used [1, 2]. Moreover, TMAH solution has also attracted attention because it is clean room compatible, nontoxic, and easy to handle. It also exhibits excellent selectivity to silicon oxide and silicon nitride masks [3, 4]. It has been estimated that, for an 8 in wafer manufacturing facility with a monthly production of 20,000 wafer units, TMAH is by far the most concentrated chemical in wastewater [5]. Biological processes are the most widely accepted treatment for organic wastewater of both domestic and industrial origins; however,

available information on the biodegradability of TMAH is scarce. Chemical oxidation involving various forms of advanced oxidation processes (AOPs) can be employed as preliminary treatment to convert the potentially biorefractory compounds into intermediate products that are more amenable to biodegradation [6].

Ozone (O_3) is a chemical agent widely used for the mineralization (i.e., transformation into CO_2 and inorganic ions) of herbicides and related biorecalcitrant organic contaminants in water [7]. Disadvantages of ozonation alone (O_3 system) for water treatment are the high energy cost required for its generation and very limited mineralization of refractory COD in industrial effluents. Indeed, hydroxyl radical is a less selective and more powerful oxidant than molecular ozone. A common objective of AOPs is to produce a large amount of radicals (especially $\cdot\text{OH}$) to oxidize the organic matter. Alternative procedures involving ozonation catalyzed with H_2O_2 [5], UV light [6], catalysts [1], and Fe^{2+} [8, 9] allow a quicker removal of organic pollutants, because such catalysts

FIGURE 1: Experimental sketch of UV/H₂O₂/O₃ system.

improve the oxidizing power of O₃ yielding a significant reduction of its economic cost.

The present study assessed the function of UV light, magnetic catalyst (SiO₂/Fe₃O₄), and H₂O₂ on the enhancing O₃ to mineralize TMAH. A concentration of total organic carbon (TOC) was chosen as a mineralization index of decomposition of TMAH. The effects of pH value of aqueous solution and ionic strength, Cl⁻, on the mineralization of TMAH were examined in this study.

2. Material and Methods

The batch experiments of mineralization reaction were conducted in a 2.3 L glass flask reactor as illustrated in Figure 1. The UV irradiation source was two 8 W lamps encased in a quartz tube with wavelengths of 254 nm. A UVX Radiometer (UVP Inc., USA) was employed for the determination of UV light intensity. The UV intensity of one 8 W UV lamp at 254 nm is 18.6 mW/cm². The ozone generator is from Triogen with the capacity of 10 g/hr. The flow rate of ozone air stream was 4 L/min directed into the photoreactor, and the inlet ozone concentration was 26 mg/L. The concentration of ozone was analyzed online by an ozone analyzer (Anseros, Ozamat GM-6000-PRO). H₂O₂ was added into the reactor by a syringe pump at constant dosage rate. The pH value of the solution was controlled by the addition of 0.01 N H₂SO₄/NaOH during the whole reaction time. The effects of pH values, ionic strength, and the initial concentration of Cl⁻ on mineralization efficiency of the UV/O₃ process were examined by varying one factor while keeping the other parameters fixed.

2.1. Catalysts Preparation. Magnetite (Fe₃O₄) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without any further purification. A total of 1.08 L of aqueous solution containing 20 g of Fe₃O₄ particles was held in a 2 L beaker

at 90°C; the pH was maintained at 9.5 with 0.1 N NaOH, while being stirred by a mechanic stirrer. An appropriate amount of 20 g Na₂O · nSiO₂ was dissolved in 100 mL of deionized water; the aqueous solution was then mixed with the aqueous solution containing magnetite (Fe₃O₄) with a mechanic stirrer for 30 min. At last, the magnetic catalysts (i.e., SiO₂/Fe₃O₄) were dried at 105°C, after the pH value of the slurry solution was maintained at 8 with 5 N H₂SO₄.

2.2. Instrumental Analysis. Tetramethyl ammonium hydroxide, TMAH (C₄H₁₀NO, MW = 98), supplied by Aldrich (USA) was used as the target compound in this study. Hydrogen peroxide (H₂O₂) of 35 wt.% supplied by Shimadzu Co. (Japan) was injected into the reactor at a constant feed rate by syringe pump. All chemicals from several suppliers were reagent grade. The mineralization efficiency of TMAH by this advanced oxidation process was determined by the analytical results of a TOC analyzer (Tekmar, Dohrmann Phoenix 8000). Na₂SO₃ solution (1.0 g/L) and Spectroquant Picco colorimeter test kit (Merck, Germany) was used to quench and measure residual dissolved ozone in samples for TOC analysis, respectively. This instrument utilizes the UV-persulfate technique to convert organic carbon into carbon dioxide (CO₂), analyzed by an infrared CO₂ analyzer and calibrated with potassium hydrogen phthalate. The magnetic properties and the isoelectric point (IEP) of the catalysts were determined by a vibrating sample magnetometer (Lake Shore, 7407) and a Zetasizer (Nano ZS ZEN 3600), respectively.

3. Results and Discussion

3.1. Surface Characteristics of Magnetic Photocatalyst. Figure 2 showed the surface zeta potential versus pH for the magnetic catalyst SiO₂/Fe₃O₄, and this same process was repeated two times. The pH of the isoelectric point (IEP) for the magnetic catalyst SiO₂/Fe₃O₄ was 2.8. The IEP for SiO₂

FIGURE 2: Zeta potential of magnetic catalysts ($\text{SiO}_2/\text{Fe}_3\text{O}_4$).

particles and Fe_3O_4 particles was previously determined by other procedures and ranged from 2 to 3 and from 6.5 to 6.8, respectively [10]. Therefore, the results observed that Fe_3O_4 (core) was almost covered by SiO_2 (shell) because the IEP of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ was close to SiO_2 particles.

The magnetic properties of the $\text{SiO}_2/\text{Fe}_3\text{O}_4$ and Fe_3O_4 core were measured with a vibrating sample magnetometer (VSM), as shown in Figure 3. The M-H plots showed the change in M_s of the particles, after the incorporation of a SiO_2 shell. The saturation magnetization (M_s) was 39.2 emu g^{-1} and was observed in $\text{SiO}_2/\text{Fe}_3\text{O}_4$. The results indicated that the prepared samples exhibited paramagnetic behaviors at room temperature [11].

3.2. Mineralization Efficiency of TMAH under Various Conditions. To confirm the roles of O_3 , UV, and H_2O_2 in the mineralization reaction of TMAH, five sets of experiments were performed to compare the mineralization efficiency of TMAH under various conditions as a function of time, which is given as $\eta_{\text{TOC,TMAH}} = (\text{TOC}_0 - \text{TOC})/\text{TOC}_0$, and the results are shown in Figure 4. Condition (a) denotes a reaction system with UV 254 nm, power density of 37.2 mW/cm^2 , and $dC_{\text{H}_2\text{O}_2}/dt$ of $2.5 \times 10^{-4} \text{ mol/min}$ (called UV/ H_2O_2). The obtained $\eta_{\text{TOC,TMAH}}$ was 38.5% after 60 min of reaction time. We also attempted to mineralize TMAH by H_2O_2 alone, and the result indicated that H_2O_2 does not possess the ability to mineralize TMAH. As is the case with UV, with H_2O_2 , theoretically, the photolysis of one mole H_2O_2 leads to two moles $\cdot\text{OH}$ according to (1), and the resulting $\cdot\text{OH}$ with higher oxidation potential could mineralize TMAH (38.5%) as follows:

Condition (b) represents a reaction system with only O_3 , and the resulting percentage of $\eta_{\text{TOC,TMAH}}$ was approximately 49.2% after 60 min of reaction time. There are two mechanisms through which O_3 can degrade organic pollutants,

namely, (i) direct attack and (ii) indirect attack through the formation of hydroxyl radicals [12]. The observed $\eta_{\text{TOC,TMAH}}$ is better than that for UV/ H_2O_2 . Under condition (c), using H_2O_2 and O_3 (denoted here as $\text{H}_2\text{O}_2/\text{O}_3$), a better $\eta_{\text{TOC,TMAH}}$ (approximately 58.1% at $t = 90 \text{ min}$) was achieved as compared to the values under conditions (a) and (b), thereby confirming the strong oxidation ability of $\text{H}_2\text{O}_2/\text{O}_3$. The oxidation potential of $\text{H}_2\text{O}_2/\text{O}_3$ is based on the fact that the conjugate base of H_2O_2 can catalyze ozone into the formation of $\cdot\text{OH}$ (Gottschalk et al., 2000). An optimum dose ratio of $\text{H}_2\text{O}_2/\text{O}_3$ has often been shown to be in the molar range of 0.5–1 depending on the presence of promoters and scavengers. H_2O_2 itself can act as a scavenger as well as an initiator, and therefore determining the optimum dose ratio of $\text{H}_2\text{O}_2/\text{O}_3$ is important [7]. With the stoichiometric molar ratio of $\text{H}_2\text{O}_2/\text{O}_3$ being 0.5, the overall reaction of H_2O_2 catalyzes O_3 to produce $\cdot\text{OH}$ as shown in (2). In this study, the dosage rates of O_3 and H_2O_2 are $5.0 \times 10^{-4} \text{ mol/min}$ and $2.5 \times 10^{-4} \text{ mol/min}$, respectively; consider the following

Condition (d), in which UV and O_3 (denoted as UV/ O_3) were employed, yielded a value of approximately 87.6% for $\eta_{\text{TOC,TMAH}}$ after 60 min of reaction time, which is far better than conditions (a), (b), and (c). Due to the strong photolysis of ozone in combination with UV radiation ($\epsilon_{254 \text{ nm}} = 3300 \text{ M}^{-1} \text{ cm}^{-1}$ for O_3), the decay rate of ozone for decay resulting from the UV is higher than that resulting from H_2O_2 by a factor of approximately 1000 [7]; this results in the production of more hydroxyl radicals according to (3) and (4), which in turn results in higher mineralization efficiency, as follows:

Condition (e), involving UV, O_3 , and H_2O_2 (denoted as UV/ $\text{H}_2\text{O}_2/\text{O}_3$), resulted in a poor efficiency ($\eta_{\text{TOC,TMAH}} = 72.3\%$ at $t = 60 \text{ min}$) as compared to condition (d). In the UV/ O_3 process, the amount of residual O_3 in the aqueous solution was small due to the high decay rate of O_3 by UV irradiation, and subsequently H_2O_2 , when added, will react with $\cdot\text{OH}$ instead of with O_3 as indicated in (5). Under this condition, H_2O_2 behaves as a scavenger of $\cdot\text{OH}$ and a small value of $\eta_{\text{TOC,TMAH}}$ results. In this study, we also evaluated the effect of the addition of H_2O_2 on the mineralization efficiency of UV/ O_3 , and the experimental results (data not shown) indicated that even the relatively low H_2O_2 dosage of $dC_{\text{H}_2\text{O}_2}/dt = 5.0 \times 10^{-5} \text{ mol/min}$ causes the molar ratio of $\text{H}_2\text{O}_2/\text{O}_3$ to have a value considerably below 0.5. The mineralization efficiency of UV/ O_3 with the addition of H_2O_2 is poorer than that without the addition of H_2O_2 . This result led to the conclusion that adding H_2O_2 into the UV/ O_3 process will result in a negative effect on $\eta_{\text{TOC,TMAH}}$ as follows:

FIGURE 3: Magnetization versus applied magnetic field for magnetic catalysts ($\text{SiO}_2/\text{Fe}_3\text{O}_4$).

Condition (f), involving $\text{SiO}_2/\text{Fe}_3\text{O}_4$, O_3 , and H_2O_2 (denoted as $\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2/\text{O}_3$), resulted in a high efficiency ($\eta_{\text{TOC, TMAH}} = 69.0\%$ at $t = 60$ min) as compared to condition (a). To evaluate the ability of catalyst adsorption, the adsorption experiment at $\text{SiO}_2/\text{Fe}_3\text{O}_4 = 0.2$ g and initial concentration of TMAH = 40 mg/L revealed that the adsorption of TMAH was less than 10% within 60 minutes. The mineralization efficiency of $\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2/\text{O}_3$ was significantly higher than that of pure O_3 , possibly because $\text{SiO}_2/\text{Fe}_3\text{O}_4$ and H_2O_2 could react with the dissolved O_3 molecules to generate reactive oxidative species (O_2^- , $\text{HO}_2^\cdot$, $^\cdot\text{OH}$, and O_3^-) via free-radical chain reactions. The initiator (H_2O_2) could induce the formation of superoxide ions (O_2^-) from O_3 molecules, and $^\cdot\text{OH}$ formed in the chain reaction was used for the mineralization of organic compounds [13]. Furthermore, the paramagnetic behaviors of the prepared $\text{SiO}_2/\text{Fe}_3\text{O}_4$ gave rise to the magnetic catalyst $\text{SiO}_2/\text{Fe}_3\text{O}_4$, which could be separated more easily through the application of a magnetic field. According to the experimental results, >90% of the magnetic catalyst was recovered and easily redispersed in a solution for reuse.

Condition (h), involving $\text{SiO}_2/\text{Fe}_3\text{O}_4$ and O_3 (denoted as $\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{O}_3$), resulted in a high efficiency ($\eta_{\text{TOC, TMAH}} = 60.1\%$ at $t = 60$ min) as compared to condition (a). The mineralization efficiency of $\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{O}_3$ was significantly higher than that of pure O_3 possibly because of the enhancement of reactive oxidative species with the chain reaction of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ and the dissolved O_3 .

As a result, the mineralization efficiency of TMAH under various conditions follows the sequence: $\text{UV}/\text{O}_3 > \text{UV}/\text{H}_2\text{O}_2/\text{O}_3 > \text{H}_2\text{O}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{O}_3 > \text{H}_2\text{O}_2/\text{O}_3 > \text{SiO}_2/\text{Fe}_3\text{O}_4/\text{O}_3 > \text{O}_3 > \text{UV}/\text{H}_2\text{O}_2$. Figure 4 presents the

FIGURE 4: Dependence of mineralization of TMAH on time at various conditions. Experimental conditions: case (a): UV ($\lambda_{254} = 37.2 \text{ mWcm}^{-2}$, dosing rate of H_2O_2 ($dC_{\text{H}_2\text{O}_2}/dt$) = $2.5 \times 10^{-4} \text{ mol/min}$; case (b): dosing rate of O_3 (dC_{O_3}/dt) = $5.0 \times 10^{-4} \text{ mol/min}$; case (c): $dC_{\text{H}_2\text{O}_2}/dt = 2.5 \times 10^{-4} \text{ mol/min}$, $dC_{\text{O}_3}/dt = 5.0 \times 10^{-4} \text{ mol/min}$; case (d): UV ($\lambda_{254} = 37.2 \text{ mWcm}^{-2}$, $dC_{\text{O}_3}/dt = 5.0 \times 10^{-4} \text{ mol/min}$; case (e): UV ($\lambda_{254} = 37.2 \text{ mWcm}^{-2}$, $dC_{\text{O}_3}/dt = 5.0 \times 10^{-4} \text{ mol/min}$, $dC_{\text{H}_2\text{O}_2}/dt = 2.5 \times 10^{-4} \text{ mol/min}$. The initial concentration of TMAH ($C_{\text{TMAH},0}$) for all cases was 40 mg/L; case (f): $\text{SiO}_2/\text{Fe}_3\text{O}_4 = 0.2 \text{ g}$, $dC_{\text{O}_3}/dt = 5.0 \times 10^{-4} \text{ mol/min}$, $dC_{\text{H}_2\text{O}_2}/dt = 2.5 \times 10^{-4} \text{ mol/min}$. The initial concentration of TMAH ($C_{\text{TMAH},0}$) for all cases was 40 mg/L.

variations of TOC and pH of the TMAH solution under the UV/O_3 process as a function of time. As shown in Figure 4, the removal of TOC is close to 87.6% at $t = 60$ min, indicating that the UV/O_3 process could mineralize TMAH efficiently. Furthermore, the pH value of the reaction solution without a buffer system decreased considerably from 10 to 4.5 during the entire reaction time, thereby revealing that acid intermediates are formed before TMAH is converted into CO_2 .

3.3. Effect of pH on the Mineralization Efficiency of UV/O_3 .

The direct attack on organic pollutants by molecular ozone (commonly known as ozonolysis) occurs under acidic or neutral conditions. At a high pH value, ozone decomposes to nonselective hydroxyl radicals according to (6), which in turn oxidizes the organic pollutants. Many researches [6, 12] found that an increasing pH accelerates ozone decomposition to generate hydroxyl radicals, which destroy organic

TABLE 1: The pseudo-first-order rate constant k_{obs} , half-life $t_{1/2}$, and correlation coefficients for degradation of TMAH by UV/O₃ at different pH values. (Experimental conditions: pH values were adjusted by H₂SO₄ and NaOH and fixed at a constant value during the whole reaction time; the other conditions were the same as in Figure 4(d).)

pH	k_{obs} (1/min)	R^2
3.0	0.0315	0.942
5.0	0.0313	0.917
7.5	0.0312	0.973
10.0	0.0318	0.907

compounds more effectively than ozone. Therefore, the pH of aqueous solution is an important factor that determines the efficiency of ozonation since it can alter the degradation pathways as well as kinetics. One has

For the combined oxidation process, UV/O₃, the effect of pH on the mineralization efficiency is more complex. The study [14] found that neither low pH values nor high pH values of the UV/O₃ could provide a degradation rate better than that obtained by the simultaneous application of UV/O₃ with neutral pH values.

The pH values of the aqueous solution were controlled to stay between 3 and 10 to evaluate the pH effect on the mineralization efficiency of TMAH by the UV/O₃ process, as shown in Figure 5. As the pseudo-first-order kinetic hypothesized, Table 1 reveals that the influence of the pH value on the reaction rate is negligible at pH values in the range from 3 to 10. It is clear from (6) that more hydroxyl radicals were produced at high pH values, thus enhancing the mineralization rate of TMAH. However, the production of hydroxyl radicals by the UV/O₃ process also proceeds according to (3) and (4), and it was not influenced by the pH value of the aqueous solution. Furthermore, the high OH[−] ion content of the system may trap the mineralization generated CO₂ in the solution and, as a result, bicarbonates and carbonates are formed in the alkaline system. Both bicarbonates and carbonates are efficient scavengers of hydroxyl radicals due to their very high reaction rate constants with the hydroxyl radicals ($k = 8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for bicarbonates and $k = 3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for carbonates). Thus, due to the influence of the increase in hydroxyl radicals and the formation of scavengers, the comprised results causing the pH effect on the mineralization of TMAH by UV/O₃ are negligible for pH values of the solution in the range from 3 to 10. Note that a buffer system was not introduced in the later experiments, except for the experiment relating to the pH effect.

3.4. Effect of Chloride Ion and Ionic Strength on the Mineralization Efficiency of UV/O₃. The effect of chloride ions, which are frequently present in industrial wastewater, on the mineralization efficiency of TMAH with UV/O₃ was evaluated, as shown in Table 2. The mineralization rate of the TMAH solution containing chloride ion by the UV/O₃ process could not be expressed by the pseudo-first-order

TABLE 2: The mineralization efficiency of TMAH by UV/O₃ at different chloride concentrations. (Experimental conditions are as shown in Figure 4(d).)

Cl [−] (mg/L)	$\eta_{\text{TOC, TMAH}}$ (%)
0	87.56
100	80.08
200	78.58
300	76.05
500	74.73

FIGURE 5: Time variation of TOC and pH using UV/O₃ process to mineralize TMAH. Experimental conditions were the same as those of case (d) in Figure 4.

kinetic. So, the mineralization efficiency shown in Table 2 was illustrated by $\eta_{\text{TOC, TMAH}}$ at the reaction time of 60 min. The experimental results indicate that $\eta_{\text{TOC, TMAH}}$ decreased with an increase in the chloride ion concentration. Chloride ions are likely to retard the efficiency of the mineralization of TMAH by competing for the oxidizing hydroxyl radicals and ozone molecules. Chloride ions can be oxidized by ozone as per (7) and (8) [15], and they can be converted into ClO[−] and Cl₂. Thus, the effective concentration of ozone was decreased by chloride ions, and the oxidation potential of the resulting products, HOCl and Cl₂, was lower than that of ozone. Furthermore, chloride ions may also act as scavenger with regard to the hydroxyl radical as per (9) [15]. One has

Ionic strength may affect the effective concentration of a compound in a solution and this becomes more significant in the presence of polar compounds [16]. As noted, TMAH is a

FIGURE 6: Reuse performance of magnetic catalyst.

TABLE 3: The pseudo-first-order rate constant k_{obs} , half-life $t_{1/2}$, and correlation coefficients for degradation of TMAH by UV/O₃ at different concentrations of K₂SO₄. (The other experimental conditions were the same as in Figure 4(d).)

K ₂ SO ₄ (mg/L)	k_{obs} (1/min)	R^2
0	0.0320	0.977
100	0.0309	0.948
300	0.0313	0.969
500	0.0307	0.981

quaternary ammonium compound. Its ammonium ions are surrounded by anions in solutions, resulting in shielding off oxidizing agents such as O₃ and hydroxyl radicals. Presumably, it decreases the mineralization efficiency of TMAH by the UV/O₃ process. The experimental study [16] examined the effect of ionic strength on the solubility of O₃ for various types of inorganic solutions. These researchers concluded that there is no significant effect on the solubility of O₃ in sulfate solutions. Additionally, sulfates are not oxidized by ozone molecules and hydroxyl radicals. In the present study, attempts have been made to evaluate the effect of ionic strength on the mineralization of TMAH in sulfate solutions by the UV/O₃ process, and the results are shown in Table 3. As can be seen in the table, the variation of the ionic strength neither facilitates nor suppresses the mineralization of TMAH. This indicates that, in the UV/O₃ process, the inhibition of the mineralization of polar organic compounds in an aqueous solution is not significant at high ionic strengths.

The reuse experiments were carried out by evaluating the stability of catalyst activity. In this experiment, 0.2 g L⁻¹ of magnetic catalyst (SiO₂/Fe₃O₄) was used at an initial concentration of 40 mg/L of TMAH. After the ozonation process, the magnetic catalyst (SiO₂/Fe₃O₄) was collected by magnetic force. The clear solution was used for analytical determination, and the magnetic catalyst was used directly in the subsequent catalytic ozonation process. This same process was repeated four times and the removal of TMAH in the reuse experiment is shown in Figure 6. The catalytic activity of SiO₂/Fe₃O₄ remained constant and no obvious deactivation (<15%) was observed after being used four times. From the results of the reuse and recovery experiments, the magnetic catalyst SiO₂/Fe₃O₄ is considered to show considerable promise in water treatment use.

4. Conclusions

The major results of applying the advanced oxidation process to mineralize TMAH can be summarized as follows.

(1) The rank of treatment conditions based on the mineralization efficiency of TMAH has the sequence: UV/O₃ > UV/H₂O₂/O₃ > H₂O₂/SiO₂/Fe₃O₄/O₃ > H₂O₂/O₃ > SiO₂/Fe₃O₄/O₃ > O₃ > UV/H₂O₂.

(2) The experimental results of this study suggest that UV irradiation 37.2 mWcm⁻² UV (254 nm) and O₃ flow rate of 0.5 × 10⁻⁴ mol/min provide the best condition for the mineralization of TMAH (20 mg/L), resulting in 95% mineralization, at 60 min reaction time. Adding H₂O₂ into the UV/O₃ process will suppress the mineralization efficiency.

(3) The mineralization efficiency of SiO₂/Fe₃O₄/H₂O₂/O₃ was significantly higher than that of O₃, H₂O₂/O₃UV/H₂O₂. More than 90% of the magnetic catalyst was recovered and easily redispersed in a solution for reuse.

The addition of chloride ions in reaction solution will suppress the mineralization efficiency of the UV/O₃ process. Ionic strength and variable pH values (from 3 to 10) in reaction solution show no effect on the mineralization efficiency of the UV/O₃ process.

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References

- [1] H. W. Chen, Y. Ku, and Y. L. Kuo, "Photodegradation of o-Cresol with Ag deposited on TiO₂ under visible and UV light irradiation," *Chemical Engineering and Technology*, vol. 30, no. 9, pp. 1242–1247, 2007.
- [2] M.-L. Wang and B.-L. Liu, "Kinetics of two-phase reaction of o-phenylene diamine and carbon disulfide catalyzed by tetrabutylammonium hydroxide in the presence of potassium hydroxide," *Journal of the Chinese Institute of Engineers*, vol. 30, no. 3, pp. 423–430, 2007.
- [3] P. M. Sarro, D. Brida, W. V. D. Vlist, and S. Brida, "Effect of surfactant on surface quality of silicon microstructures etched

- in saturated TMAHW solutions,” *Sensors and Actuators A*, vol. 85, no. 1, pp. 340–345, 2000.
- [4] I. Zubel and M. Kramkowska, “The effect of isopropyl alcohol on etching rate and roughness of (100) Si surface etched in KOH and TMAH solutions,” *Sensors and Actuators A*, vol. 93, no. 2, pp. 138–147, 2001.
- [5] W. Den, F.-H. Ko, and T.-Y. Huang, “Treatment of organic wastewater discharged from semiconductor manufacturing process by ultraviolet/hydrogen peroxide and biodegradation,” *IEEE Transactions on Semiconductor Manufacturing*, vol. 15, no. 4, pp. 540–551, 2002.
- [6] S.-P. Tong, D.-M. Xie, H. Wei, and W.-P. Liu, “Degradation of sulfosalicylic acid by O_3 /UV O_3 /TiO₂/UV, and O_3 /V-O/TiO₂: a comparative study,” *Ozone: Science and Engineering*, vol. 27, no. 3, pp. 233–238, 2005.
- [7] C. Gottschalk, J. A. Libra, and A. Saupe, *Ozonation of Water and Waste Water*, Wiley-VCH, New York, NY, USA, 2000.
- [8] T. K. Chen, C. H. Ni, and J. N. Chen, “Nitrification-denitrification of opto-electronic industrial wastewater by anoxic/aerobic process,” *Journal of Environmental Science and Health A*, vol. 38, no. 10, pp. 2157–2167, 2003.
- [9] P. Cañizares, R. Paz, C. Sáez, and M. A. Rodrigo, “Costs of the electrochemical oxidation of wastewaters: a comparison with ozonation and Fenton oxidation processes,” *Journal of Environmental Management*, vol. 90, no. 1, pp. 410–420, 2009.
- [10] D. E. Keller, D. C. Koningsberger, and B. M. Weckhuysen, “Elucidation of the molecular structure of hydrated vanadium oxide species by X-ray absorption spectroscopy: correlation between the V...V coordination number and distance and the point of zero charge of the support oxide,” *Physical Chemistry Chemical Physics*, vol. 8, no. 41, pp. 4814–4824, 2006.
- [11] J. Xu, Y. Ao, D. Fu, and C. Yuan, “Low-temperature preparation of anatase titania-coated magnetite,” *Journal of Physics and Chemistry of Solids*, vol. 69, no. 8, pp. 1980–1984, 2008.
- [12] J. Hoigne and H. Bader, “The role of hydroxyl radical reactions in ozonation processes in aqueous solutions,” *Water Research*, vol. 10, no. 5, pp. 377–386, 1976.
- [13] B. Kasprzyk-Hordern, M. Ziólek, and J. Nawrocki, “Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment,” *Applied Catalysis B*, vol. 46, no. 4, pp. 639–669, 2003.
- [14] T. S. Müller, Z. Sun, M. P. Gireesh Kumar, K. Itoh, and M. Murabayashi, “The combination of photocatalysis and ozonolysis as a new approach for cleaning 2,4-dichlorophenoxyacetic acid polluted water,” *Chemosphere*, vol. 36, no. 9, pp. 2043–2055, 1998.
- [15] J. de Laat and T. G. Le, “Effects of chloride ions on the iron(III)-catalyzed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process,” *Applied Catalysis B*, vol. 66, no. 1–2, pp. 137–146, 2006.
- [16] D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, *Analytical Chemistry*, Thomson Learning, Singapore, 2000.