Chemical Engineering Journal 254 (2014) 472–478

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Oxidative degradation of TMAH solution with UV persulfate activation

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HIGHLIGHTS

- The UV/$S_2O_8{}^{2-}$ is an effective method for degrading TMAH at acidic condition.
- The TMAH degradation is affected by pH, $S_2O_8{}^{2-}$ dose, UV intensity, and temperature.
- The demethylation mechanism is the main TMAH degradation pathway.
- TMAH degradation byproducts are identified and transformed to nitrate and ammonium.

ARTICLE INFO

Article history:
Received 20 March 2014
Received in revised form 26 May 2014
Accepted 27 May 2014
Available online 4 June 2014

Keywords:
TMAH
Sodium persulfate
Remediation
Wastewater treatment
Sulfate radical
Advanced oxidation process

ABSTRACT

Tetramethylammonium hydroxide (TMAH) is an alkaline, neuronal toxic, and chemically stable compound; furthermore, it is widely used in the high-tech industry as a developing agent. Disposal of TMAH wastewater from an industrial plant is a difficult and costly problem. Ultraviolet light (UV) activated persulfate ($S_2O_8^{2-}$) is an advanced oxidation process proven to be effective in destroying a variety of organic pollutants. This bench-scale study investigated the feasibility of using the UV/$S_2O_8^{2-}$ process to treat TMAH. The effects of various operational parameters, including pH conditions, dosages of persulfate, UV intensities, and system temperatures were evaluated. The results revealed that pH 2 exhibited higher decay rate of TMAH ($k_{obs} = 0.0331 \pm 0.0031$ min^{-1}) than other pH conditions (pH 7 and 11) at 20 °C. In general, the TMAH decay increased with increasing persulfate dosage; however, the highest TMAH degradation rate was observed with a persulfate concentration of 50 mM. Also, higher reaction temperature and stronger UV irradiation can increase the degradation of TMAH. TMAH degradation byproducts were identified and finally transformed to nitrate and ammonium, which suggested that the demethylation mechanism was the main degradation pathway.

1. Introduction

In recent years, due to increasing demand for electronic products, the semiconductor and thin-film-transistor liquid-crystal display (TFT-LCD) industries are rapidly growing. Their manufacturing processes involve a variety of highly complex and delicate units, such as photolithography, stripping, etching, and cleaning, etc., and various organic solvents are used for cleaning the wafers and panels. Hence, a large amount of organic solvent containing wastewater is generated [1]. Tetramethylammonium hydroxide (TMAH, $(CH_3)_4NOH$) is typically one of several ingredients in commercial etching/stripping mixtures or alkali washing liquid [1,2]. TMAH is a high alkaline, neuronal toxic, and chemically stable compound [3,4]. Shibata et al. [5] reported about 2500 tons of TMAH per year being discharged from a factory in Japan. Moreover, Chang et al. [1] also indicated that up to about 30,000 cubic meters of TMAH-containing wastewater can be discharged each day from a six-generation TFT-LCD factory in Taiwan. TMAH concentrations in raw wastewater can be high as about 1000 mg/L, which is suspected of being harmful to aquatic life, and is much greater than the reported median lethal concentration value of 55.6 mg/L/48 h (based on Daphnia magna (water flea) bioassays) [6].

TMAH-containing wastewater can be treated with aerobic biodegradation [7], anaerobic biodegradation [1,4], catalytic oxidation [8], photocatalytic degradation [3], or ion exchange [5] technologies. Among them, biodegradation is the most common process applied for treating TMAH-containing wastewater in the semiconductor and TFT-LCD industries. Anthony [7] and Urakami et al. [9] reported that TMAH could be degraded by some aerobic microbes, such as *Methylotroph* and *Paracoccus*, etc. Aerobic TMAH degradation occurs mainly via the demethylation pathway (i.e., resulting in the removal of a methyl group (-CH_3) from a molecule). TMAH is initially decomposed to trimethylamine (TMA, $(CH_3)_3N$), and

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http://dx.doi.org/10.1016/j.cej.2014.05.116
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then progressively degraded to dimethylamine (DMA, $(CH_3)_2NH$), methylamine (MoMA, CH_3NH_2) and ammonia (NH_3) [3,7,9]. Additionally, Chang et al. [1] and Hu et al. [2] reported that TMAH-containing wastewater can be successfully treated by the up-flow anaerobic sludge blanket technique. However, their results indicated that high concentrations of TMAH (>4500 mg/L) [2] or the presence of inhibitory chemicals (e.g., surfactants and sulfate) in wastewater would constrain the microbial growth and restrict biological TMAH degradation. TMAH-containing wastewater alternatively could also be treated by catalytic oxidation technology [8]. This process involves the reaction mechanism of pyrolyzing TMAH to TMA and further decomposing TMA to N_2, H_2O, and CO_2 through a base metal series or Pt series oxidation catalyst. Although 1% TMAH-containing wastewater could be completely decomposed during the process, it seems too expensive to be applied to industrial scale wastewater treatment. It is noteworthy that, ion exchange is also a potential technology [5], which recovers TMAH from the wastewater by three steps, i.e. cation exchange, elution and conversion. However, if the chemical composition of the wastewater is complicated, the functionality of ion exchange resin would be rapidly depleted. Due to TMAH recalcitrant characteristics, TMAH might not be effectively removed by conventional wastewater treatment processes; therefore, a TMAH wastewater treatment alternative is needed.

Persulfate anion ($S_2O_8^{2-}$) is a strong oxidant (e.g., in the salt form of sodium persulfate, SPS) with a redox potential of 2.01 V (Eq. (1)) [10], which is recognized as effective in degrading a variety of organic contaminants present in soil and groundwater [11,12]. Persulfate reaction mechanism is based on the generation of the strong sulfate radical ($SO_4^{-\bullet}$) and/or hydroxyl radical ($HO^\bullet$) through various persulfate activations for degrading organic contaminants [13]. Common persulfate activations include heating [11,14–16], transitional metals induced electron transfer [17–19], and alkaline pH adjustment [20–22]. Additionally, UV irradiation as an effective method of water disinfection can be considered as a form of energy for persulfate activation. It has been reported that one mole of persulfate can be activated to generate two mole of sulfate radical under UV irradiation in accordance with Eq. (2) [23–26] for degrading organic contaminants in wastewater. The research group of Dionysiou has reported the promising degradation of the selected emerging organic contaminants (e.g., cyanobaterial toxin cylindrospermopsin, endosulfan, and microcystin-LR) by UV photolysis and advanced oxidation processes (AOPs) (such as UV/TiO_2, UV/H_2O_2, UV/$S_2O_8^{2-}$, and UV/HSO_5^-) [27–29]. More specifically, among UV/peroxide systems evaluated, UV/$S_2O_8^{2-}$ usually shows the most effective process for the removal of contaminants at either the same molar or mass concentrations of peroxide oxidants. Results of these studies suggest that UV based AOPs exhibits a feasible approach to remove recalcitrant organic contaminants from water resources. Lin et al. [26] found that the UV/$S_2O_8^{2-}$ process achieved complete degradation of phenol (0.5 mM) within 20 min with a UV wavelength of 254 nm irradiating a 84 mM $S_2O_8^{2-}$ solution. Moreover, Fang and Shang [24] discovered that 100% of the bromine atoms in dibromoacetamide can be converted to bromate by the UV/$S_2O_8^{2-}$ process, and Gao et al. [30] demonstrated that the UV/$S_2O_8^{2-}$ process at pH 3, 6.5, and 11 can effectively decompose the sulfamethazine in aqueous phase within 45 min with a UV wavelength of 254 nm and a $S_2O_8^{2-}$ concentration of 0.2 mM.

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \qquad E^o = 2.01\ \mathrm{V} \tag{1}$$

$$S_2O_8^{2-} \xrightarrow{UV} 2SO_4^{-\bullet} \tag{2}$$

Based on the oxidative potential of the UV/$S_2O_8^{2-}$ process, the objective of this study was to evaluate utilization of UV irradiation to activate $S_2O_8^{2-}$ to degrade TMAH in water. Therefore, the effects of solution pHs, dosages of $S_2O_8^{2-}$, UV intensities, and temperatures on the TMAH degradation were explored in this study. Additionally, the reaction intermediates were identified, and the oxidation pathways were proposed.

2. Materials and methods

2.1. Chemicals

The water was purified by a Millipore reverse osmosis (RO) purification system. Dimethylamine 2 M in tetrahydrofuran solution ($(CH_3)_2NH$) was purchased from Acros; sodium persulfate ($Na_2S_2O_8$, >99.0%) was purchased from Merck; tetramethylammonium hydroxide 25% w/w aq. solution ($(CH_3)_4NOH$, >99.9%), methylamine hydrochloride ($CH_3NH_2{\cdot}HCl$, 99% min), and trimethylamine hydrochloride ($(CH_3)_3N{\cdot}HCl$, 98% min) were purchased from Alfa Aesar; sulfuric acid (H_2SO_4, 95% min), potassium hydrogen phthalate ($KHC_8H_4O_4$, 99.5% min), and 2,6-pyridinedicarboxylic acid ($C_7H_5NO_4$, 99%) were purchased from Aldrich; acetone (CH_3COCH_3, 99.5% min), sodium nitrite ($NaNO_2$, 99.7% min), phosphoric acid (H_3PO_4, 86.5% min), and acetic acid (CH_3COOH, >80%) were purchased from J.T. Baker; starch ($(C_6H_{10}O_5)_n$), sodium carbonate (Na_2CO_3, 99.5% min), sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$, 99.5% min), sodium bicarbonate ($NaHCO_3$, 99.7% min), potassium dichromate ($K_2Cr_2O_7$, >99.8%), and sodium hydroxide (NaOH, >99%) were purchased from Riedel-dehaën; ammonium chloride (NH_4Cl, 98.5% min), sodium nitrate ($NaNO_3$, 99% min), potassium iodide (KI, 99.5% min) were purchased from Union Chemical Works.

2.2. Experimental procedure

Experiments were performed in a 3 L reaction flask. The reaction solution (2.5 L) was mixed by a magnetic stirrer to ensure homogeneity during the reaction. A mercury lamp emitting 254 nm monochromatic UV light (8 or 15 W UV irradiance to be 1.3 or 4.5 mW/cm^2, respectively, Sparkie GLQ-D287 supplied by Biddy Photronic Co., Taiwan) with quartz tube protection was placed in the center of the reaction flask.

In the first phase of experiments, the feasibility of an UV/$S_2O_8^{2-}$ process (i.e., 15 W UV/100 mM SPS) in degrading the 1.1 mM TMAH at various pH conditions (i.e., 2, 7, and 11) was investigated. Solution pH was adjusted by a pH controller (pH/ORP controller PC-310, Suntex Instruments), which pumped either 1 N H_2SO_4 or NaOH solutions; in addition, the solution pH was maintained within a pH unit ±0.2 of the target pH during the course of reaction. At each designated sampling time, 10 mL of aqueous sample was collected using a glass pipette from a sampling port on the flask cover for analyzing TMAH, associated byproducts, SPS, and total organic carbon (TOC).

When the optimum pH was determined, which resulted in the highest TMAH degradation rate in the first phase of experiments, further experiments were conducted to investigate the influence of SPS doses (i.e., 10, 50 and 100 mM), UV intensities (i.e., 8 and 15 W), and temperatures (i.e. 10, 20, and 30 °C) on the TMAH degradation rate. The procedure in these experiments was similar to that described earlier. Control tests were conducted in parallel. All tests were performed in duplicate and averaged data were reported.

2.3. Analysis

Analysis of TMAH and its ionic intermediates were performed using an ion chromatograph (IC, Metrohm 790 Personal), which was equipped a conductivity detector and separation was done