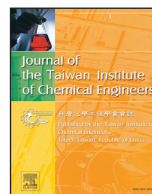




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Applying an activated carbon/silver catalyst to the decomposition of the aqueous solutions of tetramethyl ammonium hydroxide

Li-Wei Lu, Yen-Ping Peng*, Cheng-Nan Chang

Department of Environmental Science and Engineering, Tunghai University, Taichung 40704, Taiwan

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ABSTRACT

This study applied catalytic (AC/Ag) ozonation combined with hydrogen peroxide (H₂O₂) to investigate the feasibility of tetramethyl ammonium hydroxide (TMAH) decomposition. The synthesized catalysts were characterized using X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy. The pH of the isoelectric point of AC/Ag was 10.8. Subsequently, the removal efficiency of the system was examined using operational parameters such as pH condition (3, 5, 7, 9, 11, and 12), AC/Ag dosage (0.5, 1, 1.5, and 2 g/L), and H₂O₂ (4.4, 8.8, 17.6, and 26.4 mM). The results revealed that the optimal mineralization rate of TMAH was 72% when using the 1.5 g/L AC/Ag catalyst combined with 8.8 mM H₂O₂ at pH 11. The removal rate of 500 mg/L-TMAH was 81%, and the end products in nitrate and ammonium were 167 mg/L and 102 mg/L, respectively, for a 60 min reaction time. Tert-butyl alcohol (TBA) was used as an •OH scavenger to assess the contributions of direct and indirect ozonation. The results indicated that indirect ozonation dominated in TMAH mineralization. The calculated krad value of the AC/Ag/H₂O₂ ozonation method was $1.91 \times 10^{-2} \text{ min}^{-1}$, which was higher than that in the AC/Ag ozonation ($1.21 \times 10^{-2} \text{ min}^{-1}$) and sole ozonation ($1.70 \times 10^{-3} \text{ min}^{-1}$) methods.

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1. Introduction

In recent years, because of the rapid development of thin-film transistor liquid crystal displays (TFT-LCDs) and semiconductor industries, anisotropic chemical wet etching has become widely used to fabricate microstructures on single-crystal silicon wafers. The main components of wastewater from the TFT-LCD manufacturing processes are strippers, such as dimethyl sulfoxide (DMSO or (CH₃)₂SO) and monoethanolamine (MEA or C₂H₅ONH₂), developers, such as tetramethyl ammonium hydroxide (TMAH or (CH₃)₄NOH), and chelating agents [1]. Therefore, wastewater treatment methods have been extensively studied. Among wastewater chemicals, TMAH is a major component of the photoresist developer used in the lithography step of the LCD manufacturing process [2]. It is also used as an alkaline etchant and cleaning solution in semiconductor manufacturing [3].

In addition, TMAH dissociates into tetramethyl ammonium ions and hydroxyl ions in aqueous solution [4]. TMAH, with four methyl groups, is a chemically stable compound that cannot be treated effectively by the conventional activated sludge process. Biological degradation is inhibited when the concentration of TMAH exceeds 150 mg/L [5]. Dermal exposure to TMAH not only

causes alkaline chemical burns but also respiratory deterioration and abrupt fatality [6].

Ozone is a powerful oxidant that can be identified through direct and indirect reaction pathways. In direct reactions, ozone reacts with the dissolved substance. Indirect reactions comprise three steps: initiation, chain propagation, and termination [7]. In indirect reactions, hydroxyl radicals are the main and non selected oxidants, and are more potent than ozone [8]. Catalytic ozonation is a new, favorable development in advanced oxidation processes (AOPs). Because of its potentially higher effectiveness, it degrades or mineralizes the refractory organic pollutants [9].

Catalytic ozonation can be divided into two types: homogeneous and heterogeneous reactions [10]. The technologies employed include H₂O₂/ozone, ultraviolet (UV)/ozone, photocatalysis, transit element ions, and catalyst-dosed ozonation [11–13]. Using activated carbon (AC) was discussed for increasing the mineralization of the organic compounds in ozonation reactions [14].

Currently, TMAH can be treated with anaerobic biodegradation [15,16], catalytic oxidation [17], photocatalytic degradation [18], or ion exchange technologies [19]. Kim and Choi applied TiO₂ to photocatalytically degrade TMAH, indicating that •OH could initiate the degradation of TMAH by either abstracting H-atoms or adding to unsaturated carbon atoms in hydrocarbon molecules. The •OH behaviors and the product distribution were closely related and that the reaction with OH radicals took place not only

* Corresponding author.

E-mail address: yppeng@thu.edu.tw (Y.-P. Peng).

on the TiO₂ surface but also in the solution bulk [18]. So, AOP offers the possibility of removing TMAH more effectively than through conventional water treatment methods. AOP technology is continually being developed for intractable target pollutants, particularly organic ones. Catalysts used in ozonation include carbon materials (AC, graphene, and carbon nanotubes), metal oxides, and doped metal oxides on supports such as AC and silicon dioxide (SiO₂) [10]. Noble metals, such as Pd or Pt, or metal oxides, such as Mn, Co, Ni, and Ag, have been used as catalysts for catalytic ozonation [20]. The high versatility of Ag catalysts is commonly attributed to the presence of various Ag–O interactions. Ag nanoparticles loaded on AC exhibit high activity suitable for environmental applications [21]. However, the dominant role of oxidation in catalytic ozonation may vary by situation.

The hydrogen peroxide process with ozone has been widely used to enhance the oxidation of organic compounds [22,23]. Hey et al. proposed that additions of H₂O₂ prior to ozone treatment could improve the removal of pharmaceuticals from wastewater effluents and reduce the reaction time [24]. The peroxone ozonation process (H₂O₂/O₃) is based on the fact that the conjugate base of H₂O₂ can form •OH radicals with ozone [25]. In peroxone ozonation, H₂O₂ overdose can act as a scavenger which results in a reaction with •OH instead of ozone in acidic or alkaline conditions. Thus, adjusting the optimum ratio of H₂O₂/O₃ is vital. In addition, researchers have reported that combining H₂O₂ with various ozonation systems, such as H₂O₂/UV/O₃, H₂O₂/Fe₃O₄/SiO₂/O₃, and Fe²⁺/H₂O₂/O₃, can enhance the degradation of organic matter [26,27].

In this study, AC/Ag was employed as a catalyst for ozonation, and adding H₂O₂ to enhance TMAH degradation. Comparative experiments were conducted to investigate its catalytic ability, the catalytic mechanism, and intermediates formed during ozonation of TMAH.

2. Materials and methods

2.1. Materials

All chemicals, including silver nitrate (AgNO₃), hydrogen peroxide (H₂O₂, 35 wt.%), ammonium hydroxide (NH₄OH), sodium hydroxide (NaOH), hydrogen chloride (HCl) (Merck, Germany), were of analytical grade. Milli-Q ultrapure water (specific resistance ≥ 18 M Ω cm) was used in all experiments. TMAH (25% w/w, Merck, USA) was dissolved in water and diluted to 500 mg/L. The pH was adjusted using 1 N HCl and 1 N NaOH solutions.

AC samples (G306, AC Ind. Ltd., China) were selected as the catalyst carriers. Silver was deposited on the carbon surfaces by using the Tollens method [28]. Briefly, silver nitrate was added to a concentrated ammonium hydroxide solution, followed by drop-by-drop addition of 50 mL of 1.84 M NaOH_(aq) and stirring until the brown precipitate was dissolved. A fixed amount of AC was added to the aforementioned solution and stirred for 24 h. The solution was filtered through 0.45 μ m fiberglass paper. The catalyst obtained was dried overnight at 120 °C.

2.2. Analytical methods

The structural features and crystallinity of the samples were studied through X-ray diffraction (XRD, Philips X' Pert PRO, The Netherlands) using CuK α radiation and scanning at 2 θ from 10° to 90°. Scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS, Hitachi SU8000) were used to investigate the morphology of and elements on the surfaces of the materials. The pH of the point-of-zero charge (pH_{pzc}) of the catalyst was measured using a powder addition method. The isoelectric point was determined using a zeta potential analyzer (ZETCOM ZC-3000,

Table 1
The EDS analysis of catalyst.

	Element	Weight%	Atomic%
AC	C	95.96	98.45
	S	4.04	1.55
	Total	100	
AC/Ag	C	13.78	58.95
	Ag	86.22	41.05
	Total	100	
AC/Ag _(reuse 1)	C	28.55	68.53
	Ag	63.38	16.94
	O	8.07	14.53
	Total	100	

Japan). The concentration and mineralization of TMAH were analyzed using ionic chromatography (Metrohm, 883, USA) and total organic carbon analysis (TOC) (Systematic, 1010, USA), respectively. The TOC analysis was performed in accordance with the standard wet-oxidation method (5310D) [29].

2.3. Catalytic ozonation procedure

The catalytic ozonation of the TMAH solutions (500 mg/L) was conducted in a 3 L vessel. Ozone was produced from pure oxygen in the generator (C-L010DTI, Germany) and was continuously bubbled into the reactor. A stirrer was used to improve the mixing of the TMAH solution with the catalyst. The reaction was conducted for 60 min. Subsequently, 10 mL samples were withdrawn using a syringe equipped with a filter at fixed intervals. The role of the •OH scavenger was tested using TBA to determine the kinetic rate constant of various ozonation systems. Furthermore, catalytic ozonation enhancement was investigated by adding H₂O₂.

3. Results and discussions

The SEM images of the catalysts (AC, AC/Ag and, AC/Ag (reuse1)) are presented in Fig. 1(a), (b), and (c). Silver was immobilized on the activated carbon and was dispersed on the uneven surface. The catalyst had an irregular surface, as shown in Fig. 1(b) and (c). Furthermore, the catalyst reused after TMAH degradation retained the same conformation, as shown in Fig. 1(c).

As shown in Table 1, the EDS results of the AC sample indicate that the atomic percentages were 98.45% carbon and 1.55% sulfur. By contrast, the percentages of carbon and silver in the AC/Ag sample were 58.95% and 41.05%, respectively. This result illustrates that silver was successfully deposited onto the surface of AC. The elemental contents of the used catalyst (AC/Ag (reuse1)) after ozonation treatment were analyzed to investigate the ability to reuse the material. The atomic percentages of silver and carbon on the surface of AC/Ag (reuse1) were 16.49% and 63.42%, respectively. This result indicates that the AC/Ag catalyst facilitated ozonation treatment. However, further studies on the stability of Ag/AC are warranted.

The XRD patterns of the AC and AC/Ag catalysts are shown in Fig. 2. The silver reflection peaks were observed at 2 θ of 38.02°, 44.22°, 64.47°, and 64.32°. Deschatre et al. [30] reported that the silver peaks appeared at 2 θ of 38.00°, 44.23°, 64.50°, and 77.30°, which was similar to our results. In addition, Yan et al. [31] reported that the carbon reflection peaks appeared at 2 θ of 26.5°, which is inconsistent with our study. Notably, the XRD spectra exhibited no significant changes after the catalysts had been reused once or twice, indicating that AC/Ag catalysts are sufficiently durable for wastewater treatment.

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