Journal of Hazardous Materials 165 (2009) 306–316

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Identification of the degradation pathways of alkanolamines with TiO_2 photocatalysis

Chung-Shin Lu[a,*], Chiing-Chang Chen[b], Fu-Der Mai[c], Hua-Kuang Li[a]

[a] Department of General Education, National Taichung Nursing College, Taichung 403, Taiwan, ROC
[b] Department of Science Application and Dissemination, National Taichung University, Taichung 403, Taiwan, ROC
[c] Department of Biochemistry, School of Medicine, Taipei Medical University, Taipei 110, Taiwan, ROC

ARTICLE INFO

Article history:
Received 15 June 2008
Received in revised form
28 September 2008
Accepted 29 September 2008
Available online 15 October 2008

Keywords:
Alkanolamine
DMAMP
DMAE
TiO_2
Photocatalytic

ABSTRACT

The present study deals with the photocatalytic degradation of the alkanolamine, 2-dimethylamino-2-methyl-1-propanol (DMAMP), in the presence of TiO_2 particles and UV-A ($\lambda = 365$ nm) radiation. The obtained results show complete oxidation of DMAMP after 20 h, and a little over 90% of DMAMP was mineralization after 64-h of treatment. The effects of the solution pH, catalyst loading, and anions on the photocatalytic degradation of DMAMP were investigated, as well as the reaction intermediates that were formed during treatment. To the best of our knowledge, this is the first time that reports the degradation pathways of DMAMP. A number of intermediates were identified by GC/MS techniques during the treatment of DMAMP, following three tentative degradation routes. The first one is based on the oxidation of the primary alcohol group leading to the formation of corresponding aldehyde and carboxylic acid. The second route is based on the rupture of the N–C bond to form 2-methylpropanal and acetone. The last degradation route is based on the cyclization of the β-amino alcohol group to form the oxazolidine derivatives.

1. Introduction

Alkanolamines are organic compounds that possess the chemical properties of both amines and alcohols. These versatile chemicals are used extensively by chemical and pharmaceutical industries as lubricants, corrosion protection, emulsifying agents, and as ingredients of various pharmaceutical preparations. Furthermore, they are often utilized for metal surface finishing, natural gas purification, and as additives and dyes in cleaning solutions [1]. In 1993, approximately 20 million kg of alkanolamines were used for natural gas purification in the United States [2]. Because alkanolamines are used in many ways, and since they have been identified as pollutants in certain wastewater effluents [1,3], the development of a simple and effective removal method is necessary.

Conventional water treatment methods based on adsorption or reverse osmosis principles can be used, but these methods involve only phase transfer of pollutants without degradation. Accordingly, a subsequent waste treatment has to follow [4]. Biological wastewater treatments combining nitrification and denitrification processes often leave one or more nitrogen species in the effluent stream [5]. Moreover, the use of these biological processes to remove organic pollutants from wastewater is limited to low concentration. Diluting wastewater to a suitable concentration for the microorganisms leads to economically unfeasible volumes. Furthermore, selected contaminants can harm the bacteria populations used, resulting in a decrease of their biological activity. The slow reaction rates and need to dispose of activated sludge are large drawbacks of biological treatment methods [6,7].

Titanium dioxide (TiO_2)-based photocatalytic oxidation is a promising technology in water and wastewater treatment because TiO_2 is a cheap, stable, and nontoxic catalyst [8]. It has been shown that solar radiation can be used in photocatalysis, which would make it economically competitive for water and wastewater treatment [9]. The TiO_2-mediated photocatalysis process has been successfully used to degrade pollutants during the past few years [10–13]. The initial step in TiO_2-mediated photocatalysis degradation is proposed to involve the generation of an (e^-/h^+) pair, leading mainly to the formation of hydroxyl radicals ($^{\bullet}OH$), as well as superoxide radical anions ($O_2^{\bullet -}$), and hydroperoxyl radicals ($^{\bullet}OOH$), and these radicals are the oxidizing species in the photocatalytic oxidation processes [14–16]. Among them hydroxyl radicals are the most powerful oxidizing species that TiO_2 photocatalysis produces and can attack organic contaminants present at or near the surface of TiO_2 [17].

2-Dimethylamino-2-methyl-1-propanol (DMAMP) was selected as the model compound for photocatalytic studies

---

[*] Corresponding author. Tel.: +886 4 2219 6999; fax: +886 4 2219 4990.
E-mail address: cslu6@ntcnc.edu.tw (C.-S. Lu).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.09.127

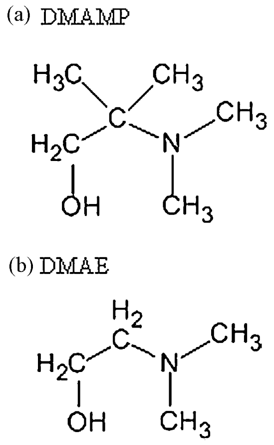

Fig. 1. Chemical structures of DMAMP (a) and DMAE (b).

since it is extensively used as an emulsifying agent, corrosion inhibitor, resin solubilizer, and catalyst for the production of foams, a stabilizer for finishes, and raw material for chemical synthesis [18]. In our study, we investigated various parameters that may affect the photodegradation of DMAMP in the presence of TiO_2 suspensions, in order to obtain a better understanding on TiO_2 photocatalysis. To the best of our knowledge, this is the first study that reports the degradation pathways of DMAMP. This study focused on the identification of the reaction intermediates and understanding of the photodegradation pathways of DMAMP in the TiO_2/UV light process. To obtain a better understanding on the mechanistic details of this TiO_2-assisted photodegradation of alkanolamine with UV irradiation, the photocatalytic degradation of structurally similar 2-dimethylaminoethanol (DMAE) was also examined and compared with that of DMAMP.

2. Experimental

2.1. Materials and reagents

2-Dimethylamino-2-methyl-1-propanol and 2-dimethylaminoethanol were obtained from Sigma–Aldrich and Acros, respectively. The chemical structures of both alkanolamines are shown in Fig. 1. Other chemicals used were of reagent grade and used as received without further purification. The TiO_2 nanoparticles (P25, ca. 80% anatase, 20% rutile; particle size, ca. 20–30 nm; BET area, ca. 55 $m^2 g^{-1}$) were supplied by Degussa. De-ionized water was used throughout this study. The water was purified with a Milli-Q water ion-exchange system (Millipore Co.) to give a conductivity of 1.8×10^7 Ω-cm.

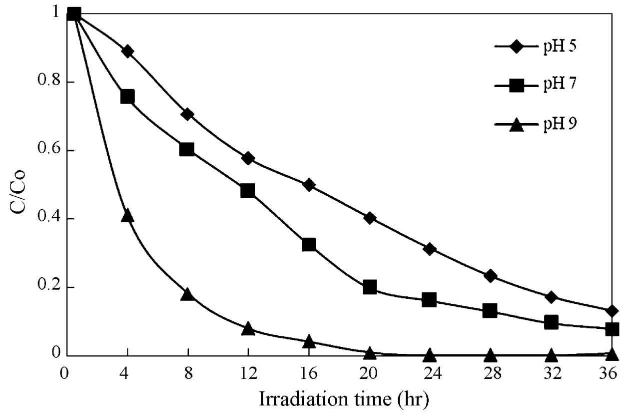

Fig. 2. pH effect on the photocatalytic degradation rate of DMAMP. Experimental conditions: DMAMP concentration 8.5×10^{-4} M; TiO_2 concentration 0.5 g L^{-1}.

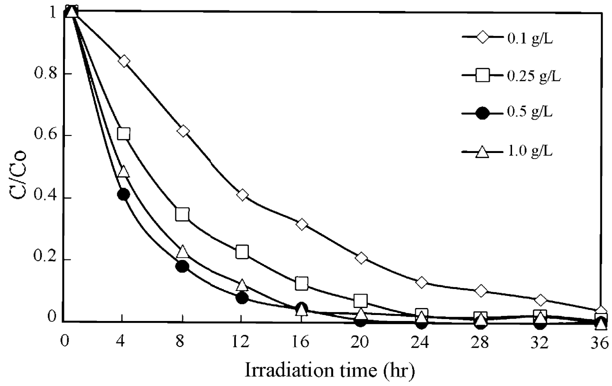

Fig. 3. Effect of TiO_2 dosage on the photocatalytic degradation rate of DMAMP. Experimental conditions: DMAMP concentration 8.5×10^{-4} M; pH 9.

2.2. Apparatus and instruments

The apparatus for studying the photocatalytic degradation of DMAMP has been described elsewhere [19]. The C-75 Chromato-Vue cabinet of UVP provides a wide area of illumination from the 15-W UV-365 nm tubes positioned on two sides of the cabinet interior. Solid-phase microextraction (SPME) was utilized for the analysis of DMAMP and intermediates resulting from the photocatalytic degradation process. SPME holder and fiber-coating divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS 50/30 μm) were supplied from Supelco (Bellefonte, PA). GC/MS analyses were conducted with a PerkinElmer AutoSystem-XL gas chromatographer interfaced to a TurboMass selective mass detector. The mineralization of DMAMP was monitored by measuring the total organic carbon (TOC) content with a Dohrmann Phoenix 8000 Carbon Analyzer, which employs a u.v./persulfate oxidation method by directly injecting into the aqueous solution.

2.3. Procedures and analysis

DMAMP solution (8.5×10^{-4} M) with the appropriate amount of photocatalyst was mixed and used in photocatalytic experiments. For reactions in different pH media, the initial pH of the suspensions was adjusted by the addition of either NaOH or $HClO_4$ solutions. Prior to irradiation, the suspensions were magnetically

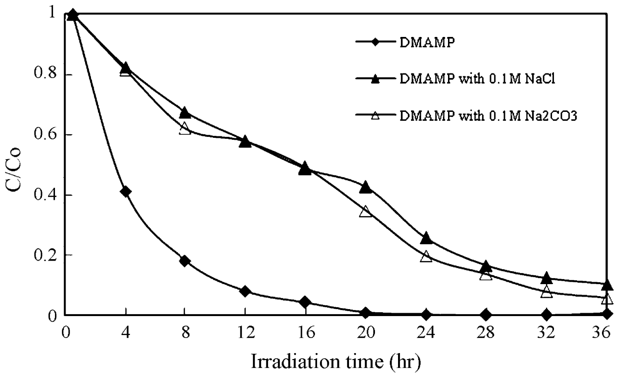

Fig. 4. Effect of anions on the photocatalytic degradation rate of DMAMP. Experimental conditions: DMAMP concentration 8.5×10^{-4} M; TiO_2 concentration 0.5 g L^{-1}; pH 9.