

Photocatalytic degradation of bis(2-chloroethoxy)methane by a visible light-driven BiVO₄ photocatalyst



Yi-Ching Lu^a, Chiing-Chang Chen^b, Chung-Shin Lu^{c,*}

^a Department of Chemistry, National Changhua University of Education, Changhua 500, Taiwan, ROC

^b Department of Science Application and Dissemination, National Taichung University of Education, Taichung 403, Taiwan, ROC

^c Department of General Education, National Taichung University of Science and Technology, Taichung 404, Taiwan, ROC

ARTICLE INFO

Article history:

Received 5 April 2013

Received in revised form 29 July 2013

Accepted 4 August 2013

Available online 5 September 2013

Keywords:

Photocatalysis

BiVO₄

Visible light

Haloether

Pathway

ABSTRACT

Haloethers are widely used in industrial applications, and the release of these toxic and carcinogenic species into the environment is a cause for great concern. In this study, BiVO₄ powder is prepared and used as a visible-light catalyst for the photocatalytic degradation of bis(2-chloroethoxy)methane (BCEXM). The as-prepared BiVO₄ photocatalyst is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectra (DRS) and BET surface area analysis. The proposed vis/BiVO₄/H₂O₂ system is found to successfully degrade BCEXM up to 96.8% in 20 h under optimal operating parameters. The photodegradation of BCEXM follows the first-order kinetics and parameters, such as system pH, catalyst dosage, substrate concentration, and the presence of anions are found to influence the degradation rate. To scrutinize the mechanistic details of BCEXM photodegradation, the intermediates of the process are separated, identified, and characterized by solid-phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS). The probable photodegradation pathways are proposed and discussed.

© 2013 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Bis(2-chloroethoxy)methane (BCEXM) is classified as a haloether. It is used primarily as the starting compound in the production of polysulfide elastomers. These polysulfides are used extensively in a variety of sealant applications because of their tolerance of high temperatures and resistance to degradation by many solvents [1]. Annual production of BCEXM is between 25 and 50 million pounds, and the US Environmental Protection Agency lists it as a high production volume chemical [2,3]. The release of this substance into the environment is of great concern because of its toxicity and carcinogenicity. It has been detected in river water and drinking water in the United States and abroad [4,5]. BCEXM is stable in aqueous media and non-biodegradable in river water; exposure to the general population thus likely occurs through the consumption of contaminated drinking water, and finding a method for treating BCEXM-containing wastewater is a crucial and pressing challenge.

A number of methods have been investigated to remove organic compounds from wastewater, including adsorption through

various materials [6,7], chemical oxidation [8], microbial action (biodegradation) [9,10] and photocatalysis [11,12]. However, each method has its respective limitations and disadvantages. Adsorption involves only the phase transfer of pollutants without degradation; chemical oxidation cannot mineralize all organic substances; and biological treatments are characterized by slow reaction rates and requires the disposal of activated sludge [13,14]. Photocatalytic degradation is a promising approach due to its high degradation and mineralization efficiency. TiO₂ is the most widely studied material for photocatalysis and has been successfully used for degrading haloethers [15]. Although TiO₂ is highly oxidative, chemically stable, inexpensive and nontoxic, it works only under UV light irradiation. It is therefore desirable to develop new photocatalysts which effectively use visible light sources (e.g., the sun or conventional fluorescent lamps) [16].

A series of studies has shown that composite oxides formed with bismuth and other transition metals (such as W [17] and V [18]) have photocatalytic activity, which can split water into H₂ and O₂ or cause various organic compounds to oxidatively degrade under visible-light irradiation. In recent years, BiVO₄ has been shown to be a good visible-light-driven photocatalyst [19]. It possesses a bandgap of 2.3–2.4 eV, which is smaller than that of the TiO₂ photocatalyst (3.2 eV) and shows good absorption results for visible light [20]. BiVO₄ mainly possesses three crystal structures, namely tetragonal zircon, monoclinic scheelite and tetragonal

* Corresponding author at: 129, Sec. 3, San-min Road, Taichung 40401, Taiwan, ROC. Tel.: +886 4 2219 6999; fax: +886 4 2219 5451.

E-mail address: cslu6@nutc.edu.tw (C.-S. Lu).

scheelite. Some organic pollutants have been reported to degrade in a monoclinic BiVO_4 suspension under visible-light irradiation [21–23].

No prior study has investigated the degradation of haloethers by visible-light-driven photocatalysts, and very little is known about the use of BiVO_4 in the treatment of haloethers in aqueous solutions. This paper presents the first report of the photocatalytic degradation of BCEXM using BiVO_4 as a catalyst. Various parameters that may affect the photodegradation of BCEXM in the presence of BiVO_4 suspensions are investigated to obtain a better understanding of BiVO_4 photocatalysis. This study also focuses on the identification of the reaction intermediates and the understanding of mechanistic details of the photodegradation of BCEXM in the BiVO_4 /visible light process.

2. Experimental

2.1. Material

Bis(2-chloroethoxy)methane was obtained from ChemService (99.5%) and used without further purification. Stock solution containing 10 mg/L of BCEXM in water was prepared, protected from light, and stored at 4 °C. Bismuth nitrate (Aldrich, 98%) and ammonium metavanadate (Panreac, 99%) were used as the precursors of bismuth vanadate (BiVO_4). Other chemicals were of reagent grade and used as such without further purification. De-ionized water was used throughout this study. The water was purified with a Milli-Q water ion-exchange system (Millipore Co.) for a resistivity of $1.8 \times 10^7 \Omega\text{-cm}$.

2.2. Preparation and characterization of BiVO_4

BiVO_4 powder was synthesized in an aqueous medium as reported previously [24]. Forty mmole of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 40 mmol of NH_4VO_3 were dissolved separately into 500 mL of 2.0 mol/L nitric acid solution. After mixing the solution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 , 7.5 g of urea was added. The mixed solution was then stirred for 24 h at 90 °C. The urea hydrolysis led to an increase in the pH of the solution, resulting in the crystallization of BiVO_4 [25]. The vivid yellow precipitate was washed several times with distilled water and absolute alcohol and then dried at 60 °C for 10 h. Finally, the dried powder was calcined at 450 °C for 15 min.

The phase and composition of the as-prepared BiVO_4 powder were measured by X-ray diffraction (XRD) using an X-ray diffractometer (PHILIPS X'PERT Pro MPD). The morphology of the BiVO_4 powder was analyzed using a field-emission scanning electron microscope (FE-SEM, HITACHI S-4800). The binding energy of Bi, V, and O was measured using an X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 250). The peak position of each element was corrected by C1s (284.6 eV). The UV–vis diffuse reflectance spectrum of the BiVO_4 powder was measured using a UV–vis spectrophotometer equipped with an integration sphere (Perkin Elmer Lambda 35). The Brunauer–Emmett–Teller (BET) surface area of the photocatalyst was determined using a Micromeritics ASAP 2010 nitrogen adsorption apparatus.

2.3. Apparatus and instruments

The apparatus used to study the photocatalytic degradation of BCEXM is described elsewhere [26]. The C-75 Chromato-Vue cabinet of UVP provided a wide area of illumination from the 15-W visible-light tubes positioned on two sides of the cabinet interior. Solid-phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS) were used to analyze the BCEXM and intermediates resulting from the photocatalytic degradation

process. A SPME holder and fiber-coating divinylbenzene-carboxen-polydimethylsiloxane (DVB-CAR-PDMS 50/30 μm) were sourced from Supelco (Bellefonte, PA). GC/MS analyses were run on a Perkin-Elmer AutoSystem-XL gas chromatograph interfaced with a TurboMass selective mass detector. The mineralization of BCEXM was monitored by measuring the total organic carbon (TOC) content with a Dohrmann Phoenix 8000 Carbon Analyzer using a UV/persulfate oxidation method by directly injecting the aqueous solution into the instrument.

2.4. Procedures and analysis

BCEXM solution (10 mg/L) with the appropriate amount of photocatalyst was mixed and used in photocatalytic experiments. For reactions in different pH media, the initial pH of the suspension was adjusted by adding either NaOH or HNO_3 solution. Prior to irradiation, the suspension was magnetically stirred in the dark for ca. 30 min to ensure the establishment of an adsorption/desorption equilibrium. The appropriate amount of hydrogen peroxide was then added. Irradiation was carried out using two visible lamps (15 W). After each irradiation cycle, the amount of the BCEXM residual was determined by SPME-GC/MS. The aqueous BiVO_4 dispersion was sampled (5 mL) and centrifuged to separate the BiVO_4 particles. The clear solution was then transferred into a 4-mL sample vial. The SPME fiber was directly immersed into the sample solution to extract BCEXM and its intermediates for 30 min at room temperature, with magnetic stirring at 550 ± 10 rpm on a Corning stirrer/plate (Corning, USA). Finally, the compounds were thermally desorbed from the fiber to the GC injector for 24 min. Separation was carried out in a DB-5 capillary column (5% diphenyl/95% dimethylsiloxane), 60 m, 0.25-mm i.d., and 1.0- μm thick film. A split-splitless injector was used with an injector temperature of 250 °C and a split flow of 10 mL/min. The helium carrier gas flow was 1.5 mL/min. The oven temperature was programmed at 60 °C for 1.0 min and then increased at 8 °C/min until it reached 240 °C. It was kept at this temperature for 0.5 min, and the total run time was 24 min.

Mass spectrometric detection was performed in full-scan conditions for both electron impact (EI) and chemical ionization (CI) using isobutane as the reagent gas. The ion source and inlet line temperatures were respectively set at 220 and 250 °C. Electron impact mass spectra were obtained at 70 eV of electron energy and monitored from 20 to 350 m/z . The mass spectrometer was tuned regularly with perfluorotributylamine using the fragment ions at m/z 69, 131, 219 and 502. EI mass spectra were identified using the NIST 2008 Library, and the analytes were automatically identified using NIST MS-Search 2.0 software. Chemical ionization mass spectrometry was used in the positive ionization mode, and isobutane was used as the reagent gas at an apparent pressure of 4.4×10^{-4} Torr in the ionization source. The full scan mode with a mass range of m/z 40–350 was used to confirm the analytes. Autotuning software was used to adjust the reagent gas flow and the lens and electronic tuning.

2.5. Analysis of hydroxyl radicals

The formation of hydroxyl radicals ($\cdot\text{OH}$) in the vis/ $\text{BiVO}_4/\text{H}_2\text{O}_2$ system was detected by the fluorescence technique using coumarin as a probe molecule. The experimental procedures were similar to those used in the measurement of photocatalytic activity except that the aqueous solution of BCEXM was replaced by an aqueous solution of 1×10^{-3} M coumarin. The visible light irradiation was continuous and sampling was performed every 2 h for analysis. The solution was analyzed after filtration on a Shimadzu RF-5301PC fluorescence spectrophotometer. The product of the coumarin hydroxylation, 7-hydroxycoumarin, gave a peak at a wavelength of about 456 nm by excitation with a wavelength of 332 nm.

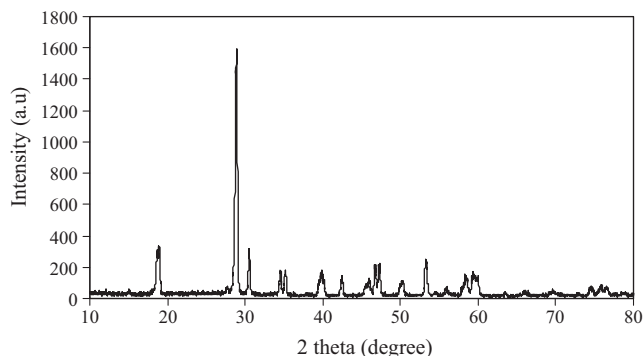


Fig. 1. XRD pattern of the as-prepared BiVO_4 photocatalyst.

3. Results and discussion

3.1. Characterization of BiVO_4

The crystal structure of the as-prepared BiVO_4 photocatalyst was investigated using XRD measurement. The diffraction pattern shown in Fig. 1 identifies the crystal form of BiVO_4 as being monoclinic scheelite, according to JCPDS card no. 14-0688 (lattice constants of $a = 5.195 \text{ \AA}$, $b = 11.701 \text{ \AA}$, $c = 5.092 \text{ \AA}$).

Fig. 2 shows the morphology of the synthesized BiVO_4 powder under a field-emission SEM microscope. The SEM analysis indicated that the microparticles of the BiVO_4 sample were mainly polyhedral in morphology (6–8 μm in edge length), but a small amount of irregular particles was also formed in BiVO_4 . The BET measurement showed that the specific surface area of the as-prepared BiVO_4 photocatalyst was $0.37 \pm 0.04 \text{ m}^2/\text{g}$. EDS analysis revealed percent content of the elements (wt%) as Bi, 61.65%; V, 15.05%; O, 18.24%, indicating that the elemental composition of the

as-prepared product consisted of bismuth, vanadium, and oxygen with a molar ratio of $\text{Bi}:\text{V}:\text{O} = 13.71:13.73:52.99$, which was very close to the $\text{Bi}:\text{V}$ molar ratio (1:1) in monoclinic BiVO_4 .

The optical absorption property of a semiconductor is relevant to its electronic structure feature, and is recognized as the key factor in determining its photocatalytic activity [27]. Fig. 3 shows the UV–vis diffuse reflectance spectra of the as-prepared BiVO_4 . The observed results of the BiVO_4 diffuse reflection spectra showed obvious absorption in the visible light region up to about 550 nm. The band gap (E_g) of BiVO_4 was estimated to be 2.35 eV, indicating that the BiVO_4 sample had a band gap suitable for photocatalytic degradation of organic contaminants under visible-light irradiation [28].

Fig. 4a displays two strong symmetrical characteristic peaks for the spin-orbit split of Bi 4f peaks located at ca. 158.9 and 164.2 eV, which is consistent with the Bi 4f_{7/2} and Bi 4f_{5/2} signals induced by Bi^{3+} ions [29]. The V 2p orbit shows the peak at 516.8 eV (Fig. 4b), which was attributed to V^{5+} of BiVO_4 particles [30]. The asymmetric XPS of O1s indicated that different oxygen species were present in the near-surface region. They were the lattice oxygen (529.8 eV) in crystalline BiVO_4 and the chemisorbed OH^- (531.6 eV) on the surface [31].

3.2. Photocatalytic reaction

3.2.1. Effect of H_2O_2 dosage

Fig. 5 shows the photodegradation efficiencies of BCEXM as a function of irradiation time with the as-prepared BiVO_4 and different amounts of H_2O_2 under visible-light irradiation. The results indicated that if only the BiVO_4 powder was added in the solution under visible-light irradiation, BCEXM did not show photodegradation. However, the degradation rate increased significantly when a small amount of H_2O_2 was added. The highest degradation efficiency was observed with 1.05 g/L H_2O_2 , which degraded 96.8% of the BCEXM in 20 h. The “ H_2O_2 -only”

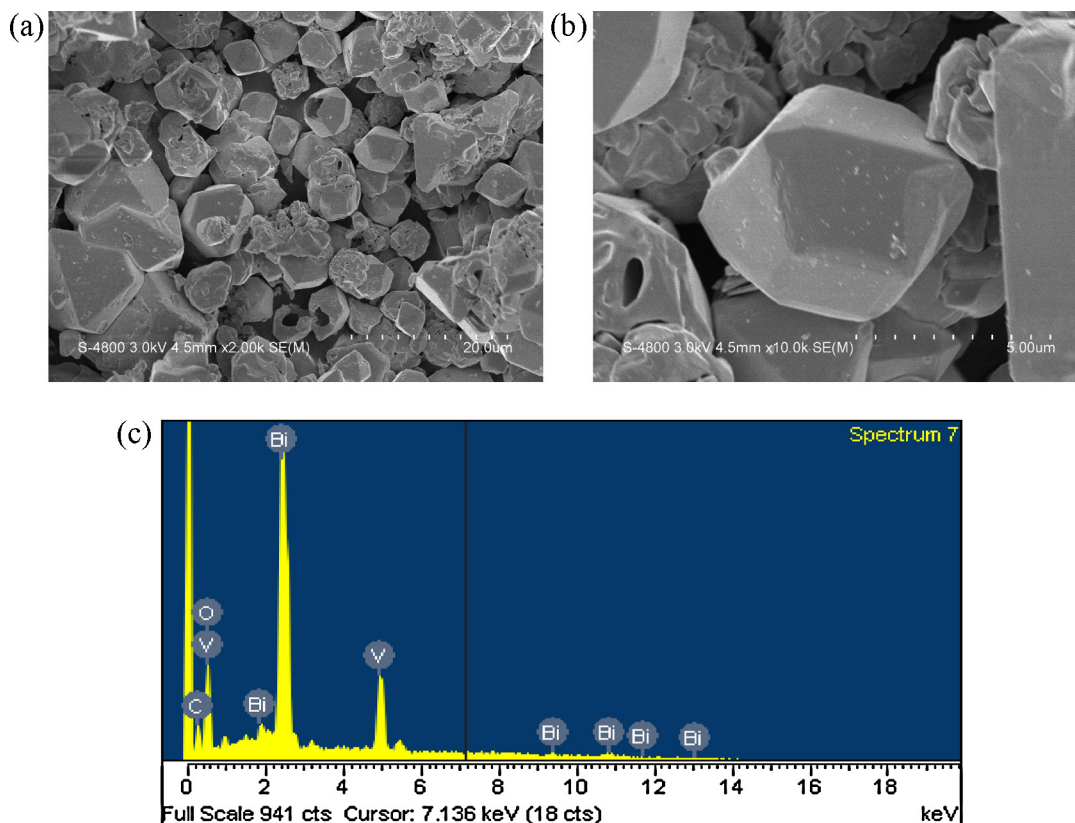


Fig. 2. SEM image and EDS spectrum of the as-prepared BiVO_4 photocatalyst.

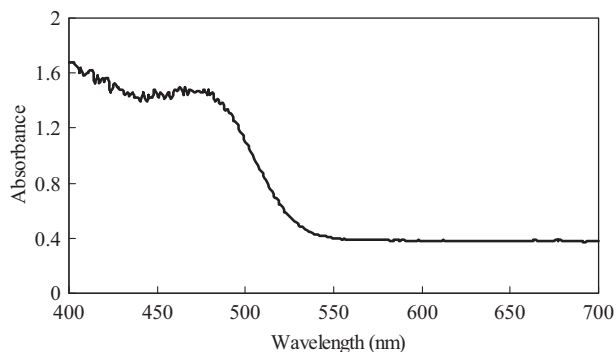


Fig. 3. UV-vis diffuse reflectance spectrum of the as-prepared BiVO₄ photocatalyst.

experiment conducted in the presence of visible-light irradiation, but in the absence of photocatalyst, did not result in any measurable degradation of BCEXM. In addition, BCEXM could not be decomposed without visible-light irradiation, indicating visible light, H₂O₂ and BiVO₄ are indispensable for the efficient degradation of BCEXM. The possible photocatalytic mechanism in the vis/BiVO₄/H₂O₂ system is described as follows [28]:

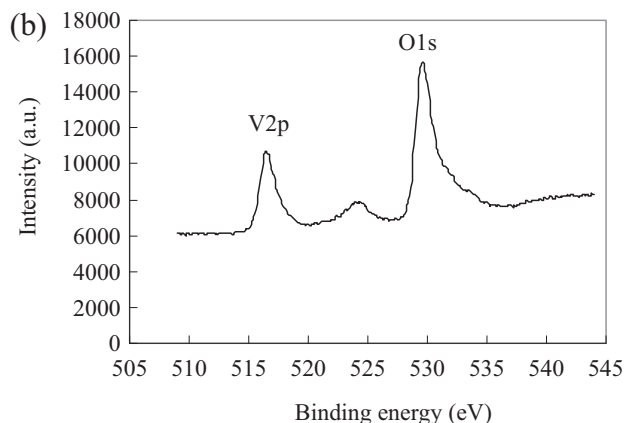
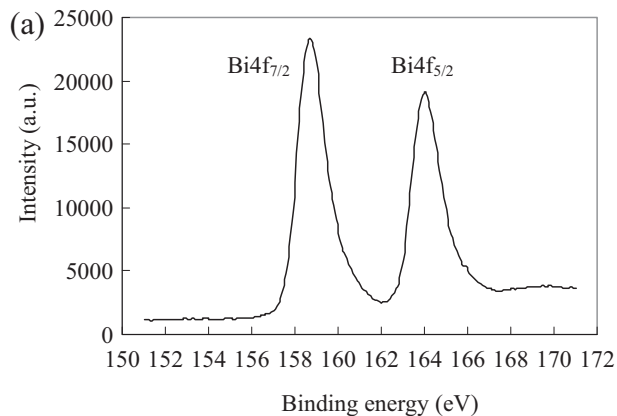
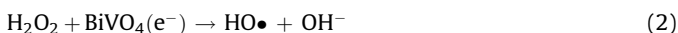
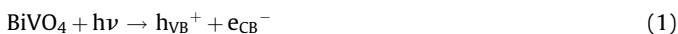


Fig. 4. XPS spectra of the as-prepared BiVO₄ photocatalyst: (a) Bi4f; (b) V2p and O1s.

The generation of photogenerated electron and hole occurred when the BiVO₄ suspension was irradiated under visible light (Eq. (1)). Hydrogen peroxide was one of the most effective electron-trapping agents, and HO[•] was generated when H₂O₂ trapped the photogenerated electron (Eq. (2)). The HO[•] generated from the above reaction exhibited a strong oxidizing capacity and was available to oxidize BCEXM. Therefore, the appropriate amount of additive H₂O₂ could enhance the photocatalytic degradation efficiency. However, as shown in Fig. 5, insufficient amounts of H₂O₂ resulted in insufficient generation of HO[•] to act as the oxidizer, resulting in weaker photocatalytic activity. On the other hand, when H₂O₂ was overdosed, the photocatalytic activity also decreased because of the presence of excess H₂O₂. The excess H₂O₂ molecules scavenged the HO[•] to generate a much weaker hydroxyl radical, HO₂[•], which could further react with the remaining strong HO[•] to form ineffective oxygen and water, as shown in Eqs. (3) and (4). In addition, the photocatalytic oxidation could be inhibited when the excess H₂O₂ reacted with oxidative h⁺ on the catalyst surface (Eq. (5)), with the overall oxidation capabilities of the system being significantly reduced through the generation of oxygen [32].

3.2.2. Effect of catalyst dosage

In the photocatalytic processes, the amount of photocatalyst is an important parameter affecting the degradation rate of organic compounds. Hence, the effect of BiVO₄ dosage on the degradation of BCEXM was investigated using BiVO₄ at different concentrations, keeping all other parameters constant. The results clearly showed that negligibly small BCEXM degradation under visible-light irradiation without catalysts for 20 h, compared with the results obtained in the presence of BiVO₄ photocatalysts with different dosages (Fig. 6). The photocatalytic degradation rate was

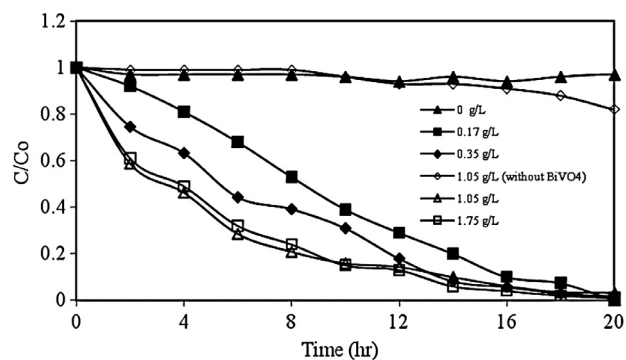


Fig. 5. Effect of H₂O₂ dosage on the photocatalytic degradation rate of BCEXM. Experimental conditions: BCEXM concentration 10 mg/L; BiVO₄ concentration 1 g/L; pH 5.

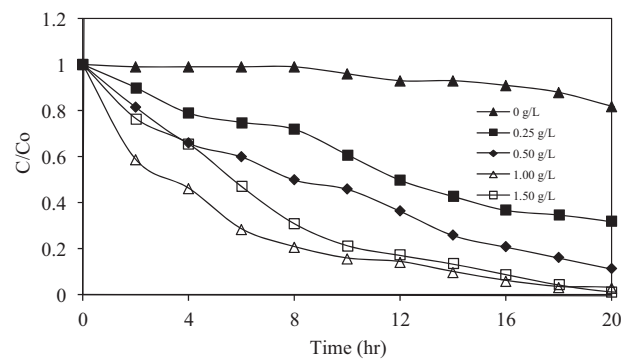


Fig. 6. Effect of BiVO₄ dosage on the photocatalytic degradation rate of BCEXM. Experimental conditions: BCEXM concentration 10 mg/L; H₂O₂ concentration 1.05 g/L; pH 5.

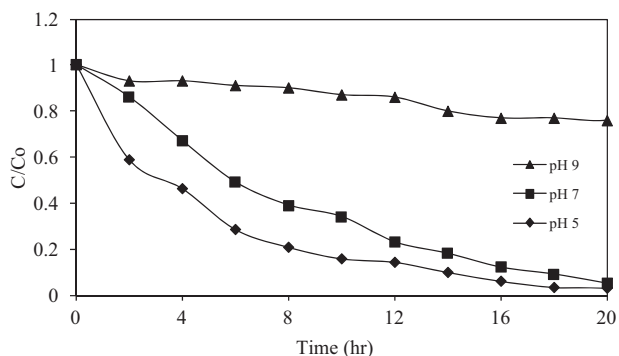


Fig. 7. pH effect on the photocatalytic degradation rate of BCEXM. Experimental conditions: BCEXM concentration 10 mg/L; BiVO₄ concentration 1 g/L; H₂O₂ concentration 1.05 g/L.

found to increase with BiVO₄ dosage, but higher dosages corresponded with slower reaction rates. The positive correlation between degradation rate and catalyst dosage could be attributed to the increase in catalyst surface area, leading to increased light absorption and consequently creating a higher number of active species. However, when BiVO₄ was overdosed, the intensity of incident visible light was attenuated because BiVO₄ particles shielded visible light and increased the suspension's turbidity, thus reducing light transmission. Furthermore, the increase of light scattering which counteracted the positive effect came from the dosage increment and therefore reduced the overall performance [33].

3.2.3. Effect of initial pH value

According to previous studies, pH value is a key factor in determining the degradation rate of some organic compounds in the photocatalytic process [34,35]. Fig. 7 shows the influence of the initial pH value on the photodegradation rate of BCEXM in the vis/BiVO₄/H₂O₂ system. The dosages of BiVO₄ and H₂O₂ were fixed at 1.0 g/L and 1.05 g/L, respectively. The results indicated that the degradation rate decreased as pH increased, and proceeded much faster under an acidic pH. At higher pH levels, the reduced photocatalytic performance of BiVO₄/H₂O₂ under visible light irradiation was likely due to a special property of H₂O₂ [36] in that, in an alkaline medium, H₂O₂ becomes highly unstable resulting in self-decomposition of H₂O₂, and this phenomenon is strongly dependent on pH [37]. This self-decomposition rapidly breaks down the H₂O₂ molecules into water and oxygen (see Eq. (6)) causing the molecule to lose its oxidant capability and renders it inert as a source of hydroxyl radicals.



The degradation rate of BCEXM in the vis/BiVO₄/H₂O₂ process was therefore reduced significantly at higher pH values.

3.2.4. Effect of substrate concentration

It is important both from the mechanistic and the application point-of-view to study the dependence of the photocatalytic reaction on the substrate concentration. Degradation efficiency was found to be inversely correlated to initial BCEXM concentrations from 10 to 50 mg/L at constant BiVO₄ and H₂O₂ dosages (Fig. 8). This negative effect could be explained by the high concentration of organic molecules competing with the electron acceptors (oxygen or H₂O₂) for adsorption onto active sites, thus partially inhibiting electron trapping. In addition, a high initial concentration of pollutants also resulted in the formation of significant amounts of intermediates which, in turn, could compete in the adsorption process and radical trapping. Thus, as

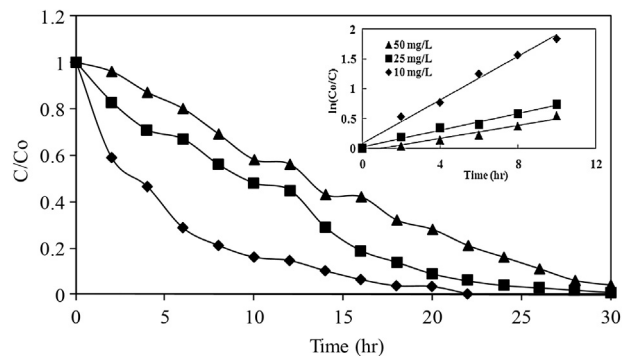


Fig. 8. Effect of initial substrate concentration on the photocatalytic degradation rate of BCEXM. Experimental conditions: BiVO₄ concentration 1 g/L; H₂O₂ concentration 1.05 g/L; pH 5.

the concentration of parent compounds was increased, the ratio of oxidizing radicals to parent compounds decreased and, as a consequence, their removal rate also decreased [38].

Previous investigations have found that the influence of the initial concentration of the organic compound on the photodegradation efficiency could be described by first-order kinetics [39]. The inset of Fig. 8 shows the results of regression analysis based on the first-order reaction kinetics for the degradation of BCEXM in the photocatalytic process. Degradation rate constants (k_{app}) were determined from the slope of $\ln [\text{BCEXM}]_0/[\text{BCEXM}] = k_{app}t$ plots. Table 1 lists the calculated values of k_{app} and the linear regression coefficients for the first-order kinetics of the photodegradation of the studied compound. It appears that the degradation of BCEXM follows first-order kinetics. As shown in Table 1, the degradation rate constants increased as initial concentrations decreased, indicating a faster reaction rate at lower initial concentrations.

3.2.5. Effects of anions

The study on the effects of anions on the photocatalytic degradation of BCEXM is important because anions are common in natural water and industrial wastewater. The effects of the presence of various anions such as chloride, nitrate, bicarbonate, carbonate and sulfate were studied using 0.05 M solutions of their sodium salts and an initial concentration of 10 mg/L of BCEXM in the vis/BiVO₄/H₂O₂ system. The results showed that all these anions significantly inhibited the degradation (see Fig. 9). To investigate the effect of variation of the concentration of anion on the degradation rate of BCEXM, sulfate was also added at a different concentration (0.1 M) in the initial solution. It can be seen that the photodegradation efficiency of BCEXM decreases further with increasing the concentration of anion. The inhibition effects of anions could be explained as the reaction of positive holes (h^+) and hydroxyl radicals (HO^\bullet) with anions that behaved as h^+ and HO^\bullet scavengers resulting in prolonged BCEXM removal [40]. A major drawback resulting from the high reactivity and non-selectivity of HO^\bullet was that it also reacted with non-target compounds present in the background water matrix, *i.e.* inorganic anions present in water. This results in a higher HO^\bullet demanded to accomplish the desired degree of degradation [41].

Table 1
Kinetic parameters (rate constants and linear regression coefficients R^2) for photocatalytic degradation of bis(2-chloroethoxy)methane at various initial concentrations.

Initial concentration (mg/L)	k_{app} (h^{-1})	R^2
10	0.1826	0.9888
25	0.0701	0.9869
50	0.0543	0.9572

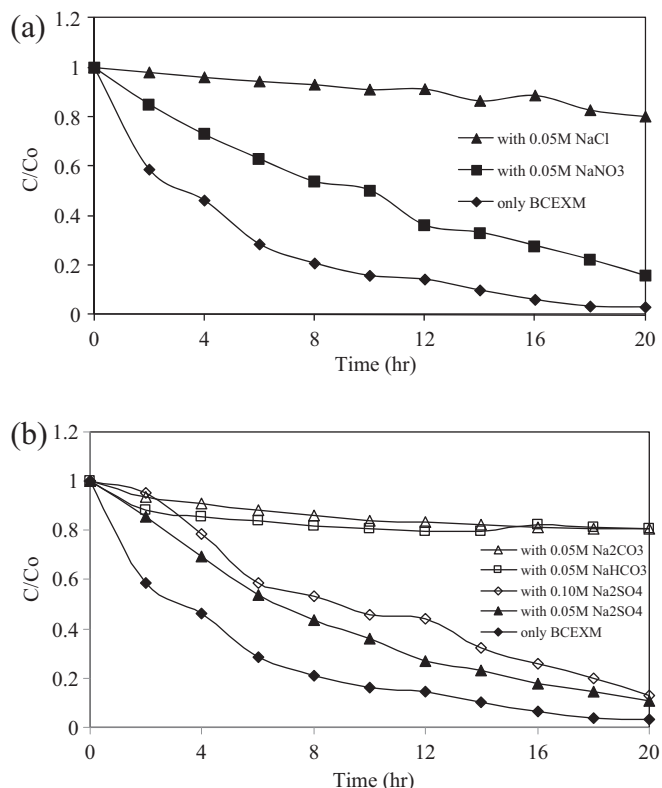


Fig. 9. (a) Effect of chloride and nitrate ions on the photocatalytic degradation rate of BCEXM. (b) Effect of bicarbonate, carbonate and sulfate ions on the photocatalytic degradation rate of BCEXM. Experimental conditions: BCEXM concentration 10 mg/L; BiVO₄ concentration 1 g/L; H₂O₂ concentration 1.05 g/L; pH 5.

3.2.6. Evolution of TOC

The complete degradation of an organic molecule by photocatalysis normally leads to the conversion of all its carbon atoms to gaseous CO₂ and of the heteroatoms into inorganic anions that remain in solution. To study the total mineralization of BCEXM, the total organic carbon (TOC) was determined as a function of irradiation time. Fig. 10 shows the decrease in the TOC percentage of BCEXM during the photocatalytic degradation. The complete removal of 10 mg/L of BCEXM was achieved after 20 h of treatment, and the corresponding carbon mineralization was 45%. The treatment was prolonged to 78 h to test whether the mineralization could be completed as well. Approximate 85% of BCEXM was mineralized within 78 h of photocatalytic reaction time. Complete mineralization of BCEXM was not achieved after 78 h of oxidation although BCEXM disappeared after 20 h. This significant difference between degradation efficiency and mineralization efficiency

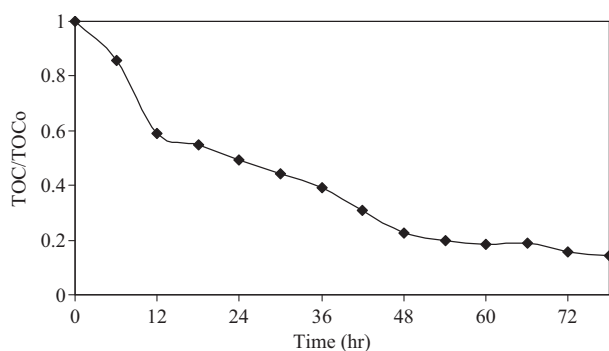


Fig. 10. Depletion of TOC measured as a function of irradiation time for an aqueous solution of BCEXM (10 mg/L) in the vis/BiVO₄/H₂O₂ system.

implies that the products of BCEXM oxidation mostly stayed at the intermediate product stage under the present experimental conditions.

3.3. Separation and identification of the intermediates

In considering a new treatment process, both the removal of the target compound and the formation of degradation products are of great importance. The following general approach was adopted to identify each degradation product. The molecular mass of each unknown compound was determined using positive ion chemical ionization (CI) mass spectrometry through the abundant protonated molecule, and the structural data were then obtained from the electron impact (EI) fragmentation patterns and library searching. The presence and number of chlorine atoms in the suspected intermediates could be easily obtained by taking into account both the relative intensity of the ³⁵Cl/³⁷Cl signals and the differences between the two masses.

Fig. 11 shows the EI and CI mass spectra of the identified intermediates. Compound **A** was identified as bis(2-chloroethyl)-carbonate by a library search with a fit value of 97%. The molecular mass was determined from the CI mass spectrum as $m/z = 186$ by the observation of an $[M+H]^+$ ion of 187. The triple signals of protonated molecular ion 187/189/191 appeared to be in a ratio of 9:6:1, and the double signals of basic peak 63/65 were in a ratio of 3:1 due to the natural ratio of the chlorine isotope. Based on this, the intermediate product could be confirmed to contain two chlorine atoms.

The molecular mass of compound **B** was determined from the CI mass spectrum as $m/z = 108$ by the observation of an $[M+H]^+$ ion of 109. The mass spectrum showed the characteristic ion at $m/z = 63$ corresponding to the group $[CH_2CH_2Cl]^+$. The fragment ion 63/65 appeared to be in a ratio of 3:1 due to the natural ratio of the chlorine isotope. It could be deduced that a chlorine atom was present in the molecular ion of this intermediate. According to mass spectrometric analyses, compound **B** was tentatively identified as (2-chloroethoxy)methanal. As the pure compound **B** was not commercially available, a more conclusive identification was difficult.

Compound **C** was identified as 2-chloroethanol with a fit value of 86% found by searching the mass spectra library. The molecular mass was determined from the CI mass spectrum being $m/z = 80$ by the observation of an $[M+H]^+$ ion of 81. This compound was further identified by matching its retention time and mass spectra with that of an authentic standard. They exhibited the exact retention times and similar mass spectra.

3.4. Degradation pathways of BCEXM

To understand the active species involved in the photocatalytic process, hydroxyl radicals ($\cdot OH$) were detected in the vis/BiVO₄/H₂O₂ system by the fluorescence technique using coumarin as a probe molecule. Coumarin readily reacts with $\cdot OH$ to produce a highly fluorescent product, 7-hydroxycoumarin [42–44]. Fig. 12 shows the changes of fluorescence spectra from 10⁻³ M coumarin solution under visible-light irradiation with irradiation time in the presence of BiVO₄/H₂O₂. It could be seen that a gradual increase in the fluorescence intensity at about 456 nm was observed with increasing irradiation time. The generated fluorescence spectrum had the identical shape and maximum wavelength with that of standard 7-hydroxycoumarin. This suggested that fluorescent product 7-hydroxycoumarin was formed during BiVO₄ photocatalysis due to the specific reaction between $\cdot OH$ and coumarin. Therefore, hydroxyl radicals were shown to be the active species during BiVO₄ photocatalytic reaction.

Scheme 1 presents the molecular structure of the degradation intermediates and the tentative photocatalytic degradation pathway of BCEXM. Any carbon atom possessing two functional

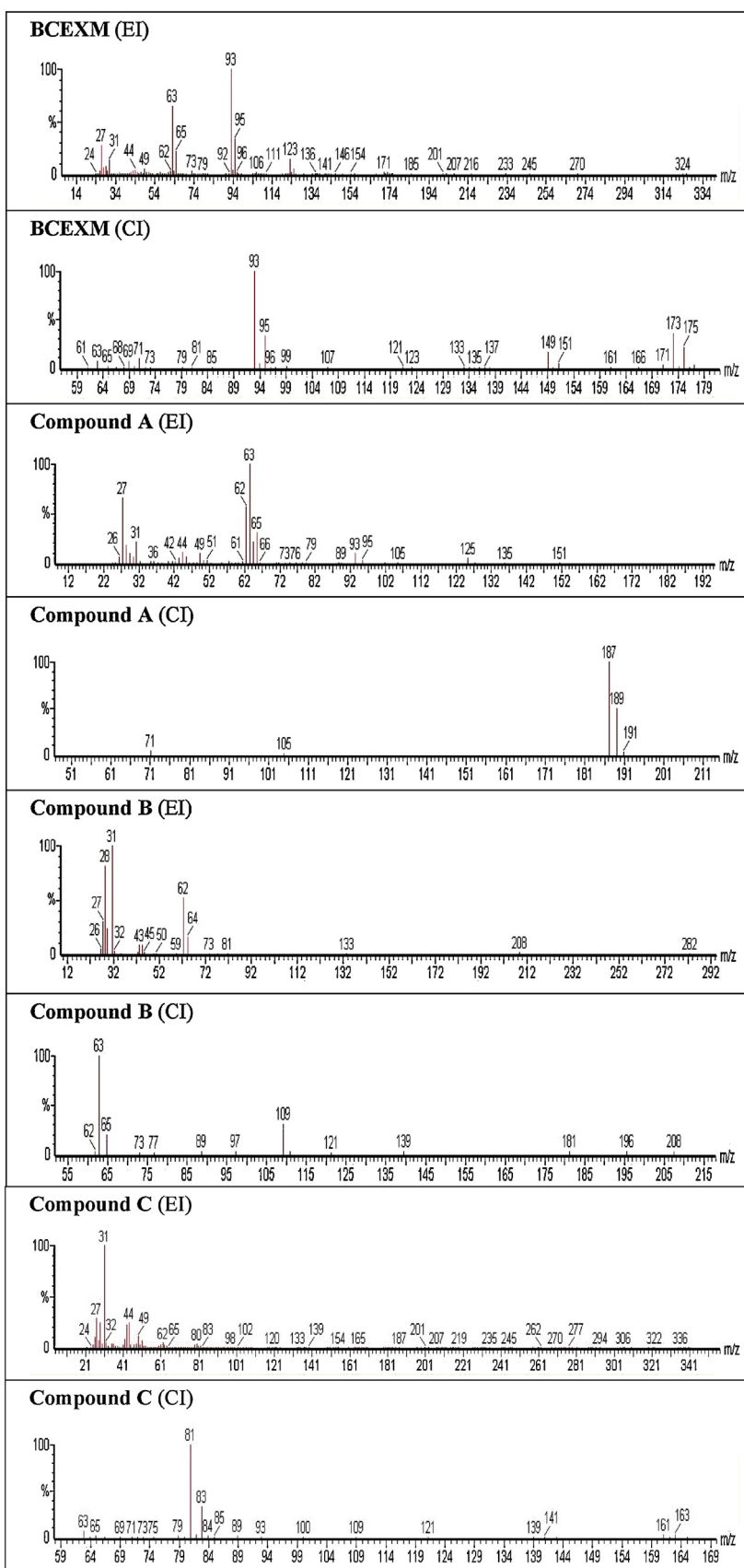
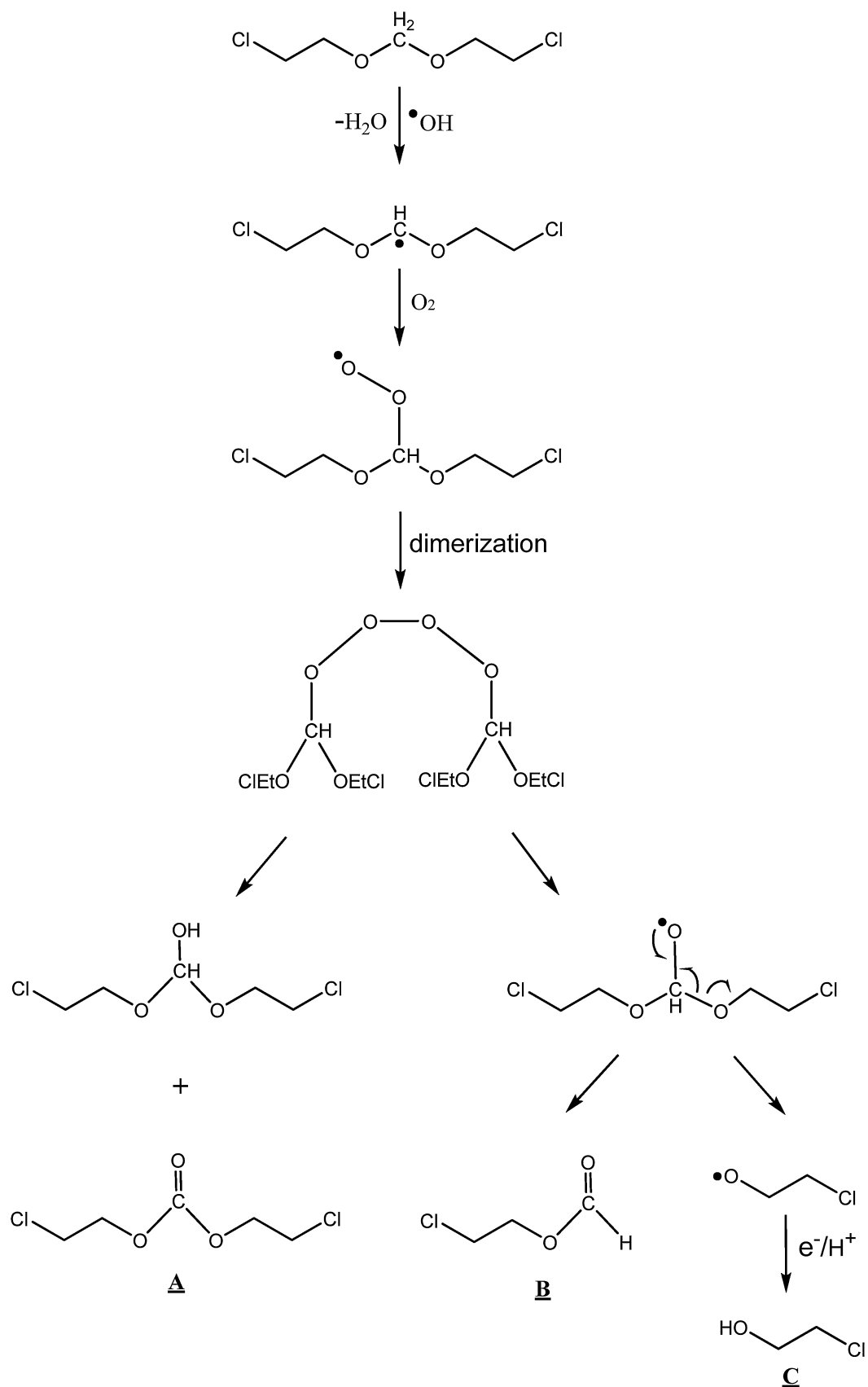


Fig. 11. EI and CI mass spectra of intermediates formed during the photodegradation of BCEXM after being separated by the GC/MS method.

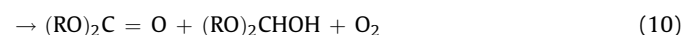


Scheme 1. Proposed photodegradation pathway of bis(2-chloroethoxy)methane in the vis/BiVO₄/H₂O₂ system.

groups is known to be unstable [45]. Therefore, it is particularly noteworthy that a single carbon atom situated between two heteroatoms (e.g., oxygen in the case of BCEXM) might be a reactive center susceptible to attack. In addition, it is well known that the HO• radical is an electrophile and that C–H bonds adjacent to oxygen are responsible for a pronounced stereoelectronic effect that produces high rates of H-atom abstraction [46]. Therefore, the H atoms attached to the carbon atom situated between two oxygen atoms in BCEXM were the most prone to radical attack.

Initial attack by HO• radicals on BCEXM might involve hydrogen atom abstraction from the carbon atom situated between two oxygen atoms and result in the formation of a carbon-centered radical. The carbon-centered radical reacted at a diffusion-controlled rate with oxygen, forming a peroxy radical [47]

(Eqs. (7) and (8)). Dimerization of peroxy radicals yielded the corresponding tetroxide, which could follow a number of competing reaction pathways leading to different intermediates [48] as shown schematically in Eqs. (9)–(12).



where RO is the 2-chloroethoxy group.

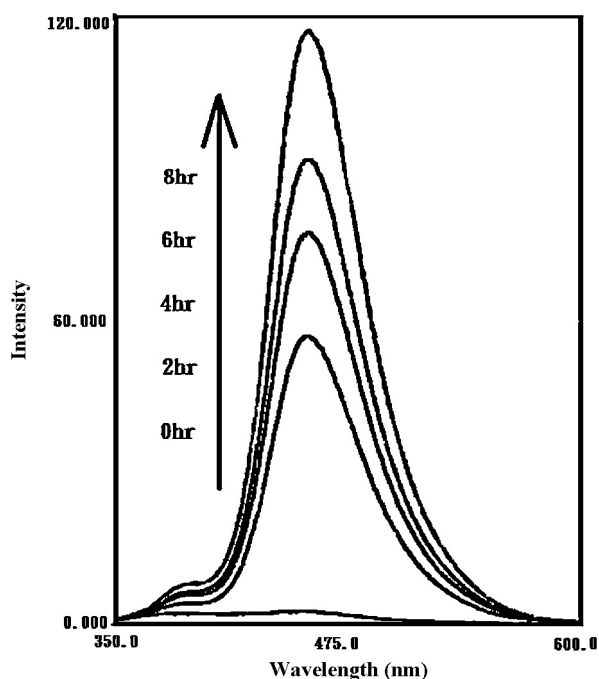
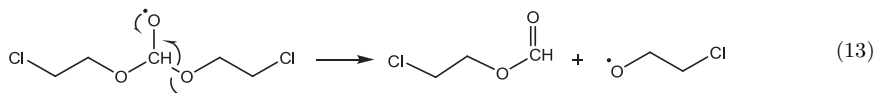


Fig. 12. Fluorescence spectral changes observed during illumination of BiVO₄/H₂O₂ in a 1 × 10^{−3} M aqueous solution of coumarin (excitation at 332 nm). Each fluorescence spectrum was recorded every 2 h of visible-light irradiation.

Eq. (10), the so-called Russell mechanism [49], leads to the production of bis(2-chloroethyl)carbonate (compound A) and bis(2-chloroethoxy)methanol. Eq. (11) results in the direct formation of hydrogen peroxide and two equivalents of bis(2-chloroethyl)carbonate. Eq. (12) leads to the formation of two alkoxy radicals and a molecule of oxygen. The alkoxy radical produced by this sequence might react further by β-bond fragmentation (Eq. (13)) leading to (2-chloroethoxy)methanal (compound B) and a ClCH₂CH₂O• radical as the precursor of 2-chloroethanol (compound C). The H atom necessary for O–H bond formation was proposed to originate from the proton reduction by photogenerated electron H⁺ + e[−] → H• as already observed in the degradation of the insecticide fenitrothion by Kerzhentsev et al. [50].



Once the intermediates were formed, they could be further degraded by hydroxy radical attack until the final products of carbon dioxide and water were formed. Pace et al. [51] indicated that the photo-oxidation of 2-chloroethanol yielded intermediates such as acetic, glycolic, and formic acids and acetaldehyde. It was shown previously that these organic acids and acetaldehyde could be photocatalytically degraded into CO₂ and water [52].

4. Conclusion

As-prepared BiVO₄ powder exhibits the typical pattern for a monoclinic scheelite structure and shows a high degree of photocatalytic activity under visible light irradiation. In the presence of an appropriate amount of H₂O₂, BiVO₄ is an effective photocatalyst for eliminating BCEXM. Photocatalytic reactions conducted for 20 h resulted in a 96.8% decrease in BCEXM concentrations, and the photodegradation rate is found to increase with BiVO₄ dosage, but the reaction slows at high dosages. The photodegradation is much more efficient under acidic conditions and decreases with increasing pH. In addition, the presence of inorganic anions such as chloride, nitrate, bicarbonate, carbonate and sulfate, which are often present in natural water and industrial wastewater, decreases the photocatalytic degradation rate of BCEXM. Three kinds of intermediate products derived from the BCEXM degradation are identified as bis(2-chloroethyl)carbonate, (2-chloroethoxy)methanal, and 2-chloroethanol. The possible degradation route is based on hydrogen abstraction by the hydroxyl radical to form a carbon-centered radical which then reacts with oxygen to form a peroxy radical. Peroxy radicals react with one another to produce an alkoxy radical. The β-bond fragmentation of the alkoxy radical produces different intermediates. This study not only provides useful information for research on haloether decomposition, but also facilitates the development of new application of BiVO₄.

Acknowledgment

This research was supported by the National Science Council of the Republic of China (NSC 101-2113-M-025-001).

References

- [1] Ellerstein SM, Bertozzi ER. Polysulfides Kirk–Othmer Encyclopedia of Chemical Technology. third ed. New York: John Wiley and Sons; 1982.
- [2] Black SR, Decosta KS, Patel PR, Mathews JM. [¹⁴C]bis(2-chloroethoxy)methane: comparative absorption, distribution, metabolism and excretion in rats and mice. *Xenobiotica* 2007;37:427–40.

- [3] USEPA Office of Pollution. Prevention and Toxics (OPPT), High Production Volume Chemicals. <http://www.epa.gov/oppt/iur/tools/data/2002-vol.htm> [06.03.07].
- [4] Sittig M. Handbook of Toxic and Hazardous Chemicals and Carcinogens, third ed. NJ: Noyes Public; 1991.
- [5] Fawell JK, Hunt S. Environmental Toxicology: Organic Pollutants. New York: Wiley; 1988.
- [6] Lin SH, Juang RS. Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review. *J Environ Manage* 2009;90:1336–49.
- [7] Wang S, Peng Y. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem Eng J* 2010;156:11–24.
- [8] Crimi M, Ko S. Control of manganese dioxide particles resulting from in situ chemical oxidation using permanganate. *Chemosphere* 2009;74:847–53.
- [9] Schaefer CE, Yang X, Pelz O, Tsao DT, Streger SH, Steffan RJ. Aerobic biodegradation of iso-butanol and ethanol and their relative effects on BTEX biodegradation in aquifer materials. *Chemosphere* 2010;81:1104–10.
- [10] Haritash AK, Kaushik CP. Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. *J Hazard Mater* 2009;169:1–15.
- [11] Qi L, Yu J, Jaroniec M. Enhanced and suppressed effects of ionic liquid on the photocatalytic activity of TiO_2 . *Adsorption* 2013;19:557–61.
- [12] Yu J, Li Q, Liu S, Jaroniec M. Ionic-liquid-assisted synthesis of uniform fluorinated B/C-codoped TiO_2 nanocrystals and their enhanced visible-light photocatalytic activity. *Chem Eur J* 2013;19:2433–41.
- [13] Pelizzetti E, Maurino V, Minero C, Carlin V, Pramauro E, Zerbinati O, et al. Photocatalytic degradation of atrazine and other s-triazine herbicides. *Environ Sci Technol* 1990;24:1559–65.
- [14] Wang KH, Hsieh YH, Chou MY, Chang CY. Photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide suspensions in aqueous solution. *Appl Catal B Environ* 1999;21:1–8.
- [15] Chen CC, Wu RJ, Yao IC, Lu CS. Bis(2-chloroethoxy)methane degradation by TiO_2 photocatalysis: parameter and reaction pathway investigations. *J Hazard Mater* 2009;172:1021–32.
- [16] Kohtani S, Tomohiro M, Tokumura K, Nakagaki R. Photooxidation reactions of polycyclic aromatic hydrocarbons over pure and Ag-loaded BiVO_4 photocatalysts. *Appl Catal B Environ* 2005;58:265–72.
- [17] Qin Z-Z, Liu Z-L, Liu Y-B, Yang K-D. Synthesis of BiVO_3 for degradation of organic compounds under visible-light irradiation. *Catal Commun* 2009;10:1604–8.
- [18] Shen F-R, Lai M-H, Yang C-K, Fu I-P, Liang N-Y, Chen W-T. Photocatalytic production of hydrogen by vanadium oxides under visible light irradiation. *J Taiwan Inst Chem Eng* 2012;43:95–101.
- [19] Cruz AM, Perez UMG. Photocatalytic properties of BiVO_4 prepared by the coprecipitation method: degradation of rhodamine B and possible reaction mechanisms under visible irradiation. *Mater Res Bull* 2010;45:135–41.
- [20] Xie B, Zhang H, Cai P, Qiu R, Xiong Y. Simultaneous photocatalytic reduction of Cr(VI) and oxidation of phenol over monoclinic BiVO_4 under visible light irradiation. *Chemosphere* 2006;63:956–63.
- [21] Shang M, Wang W, Sun S, Ren J, Zhou L, Zhang L. Efficient visible light-induced photocatalytic degradation of contaminant by spindle-like PANI/BiVO_4 . *J Phys Chem C* 2009;113:20228–33.
- [22] Castillo NC, Ding L, Heel A, Graule T, Pulgarin C. On the photocatalytic degradation of phenol and dichloroacetate by BiVO_4 : the need of a sacrificial electron acceptor. *J Photochem Photobiol A Chem* 2010;216:221–7.
- [23] Sun S, Wang W, Zhou L, Xu H. Efficient methylene blue removal over hydrothermally synthesized starlike BiVO_4 . *Ind Eng Chem Res* 2009;48:1735–9.
- [24] Kohtani S, Makino S, Kudo A, Tokumura K, Ishigaki Y, Matsunaga T, et al. Photocatalytic degradation of 4-n-nonylphenol under irradiation from solar simulator: comparison between BiVO_4 and TiO_2 photocatalysts. *Chem Lett* 2002;31:660–1.
- [25] Yu J, Kudo A. Effects of structural variation on the photocatalytic performance of hydrothermally synthesized BiVO_4 . *Adv Funct Mater* 2006;16:2163–9.
- [26] Chen CC, Lu CS, Mai FD, Weng CS. Photooxidative N-de-ethylation of anionic triarylmethane dye (sulfan blue) in titanium dioxide dispersions under UV irradiation. *J Hazard Mater B* 2006;137:1600–7.
- [27] Tang J, Zou Z, Ye J. Efficient photocatalytic decomposition of organic contaminants over CaBi_2O_4 under visible-light irradiation. *Angew Chem Int Ed* 2004;43:4463–6.
- [28] Zhang Z, Wang W, Shang M, Yin W. Photocatalytic degradation of rhodamine B and phenol by solution combustion synthesized BiVO_4 photocatalyst. *Catal Commun* 2010;11:982–6.
- [29] Jiang HQ, Nagai M, Kobayashi K. Enhanced photocatalytic activity for degradation of methylene blue over $\text{V}_2\text{O}_5/\text{BiVO}_4$ composite. *J Alloys Compd* 2009;479:821–7.
- [30] Madhusudan P, Ran J, Zhang J, Yu J, Liu G. Novel urea assisted hydrothermal synthesis of hierarchical $\text{BiVO}_4/\text{Bi}_2\text{O}_3\text{CO}_3$ nanocomposites with enhanced visible-light photocatalytic activity. *Appl Catal B Environ* 2011;110:286–95.
- [31] Long M, Cai W, Cai J, Zhou B, Chai X, Wu Y. Efficient photocatalytic degradation of phenol over $\text{Co}_3\text{O}_4/\text{BiVO}_4$ composite under visible light irradiation. *J Phys Chem B* 2006;110:20211–16.
- [32] Xiao Q, Zhang J, Xiao C, Tan XK. Photocatalytic degradation of methylene blue over $\text{Co}_3\text{O}_4/\text{Bi}_2\text{WO}_6$ composite under visible light irradiation. *Catal Commun* 2008;9:1247–53.
- [33] Yu J, Zhang L, Cheng B, Su Y. Hydrothermal preparation and photocatalytic activity of hierarchically sponge-like macro-/mesoporous titania. *J Phys Chem C* 2007;111:10582–89.
- [34] Wang KH, Hsieh YH, Wu CH, Chang CY. The pH and anion effects on the heterogeneous photocatalytic degradation of o-methylbenzoic acid in TiO_2 aqueous suspension. *Chemosphere* 2000;40:389–94.
- [35] Leng W, Liu H, Cheng S, Zhang J, Cao C. Kinetics of photocatalytic degradation of aniline in water over TiO_2 supported on porous nickel. *J Photochem Photobiol A Chem* 2000;131:125–32.
- [36] Chu W, Choy WK, So TY. The effect of solution pH and peroxide in the TiO_2 -induced photocatalysis of chlorinated aniline. *J Hazard Mater* 2007;141:86–91.
- [37] Chan CY, Tao S, Dawson R, Wong PK. Treatment of atrazine by integrating photocatalytic and biological processes. *Environ Pollut* 2004;131:45–54.
- [38] Gimeno O, Carbajo M, Lopez MJ, Melero JA, Beltran F, Rivas FJ. Photocatalytic promoted oxidation of phenolic mixtures: an insight into the operating and mechanistic aspects. *Water Res* 2007;41:4672–84.
- [39] Dai K, Peng T, Chen H, Zhang R, Zhang Y. Photocatalytic degradation and mineralization of commercial methamidophos in aqueous titania suspension. *Environ Sci Technol* 2008;42:1505–10.
- [40] Mahmoodi NM, Arami M, Limaee NY, Gharanjig K. Photocatalytic degradation of agricultural N-heterocyclic organic pollutants using immobilized nanoparticles of titania. *J Hazard Mater* 2007;145:65–71.
- [41] Konstantinou IK, Albanis TA. TiO_2 -assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations, a review. *Appl Catal B Environ* 2004;49:1–14.
- [42] Xiang Q, Yu J, Wong PK. Quantitative characterization of hydroxyl radicals produced by various photocatalysts. *J Colloid Interface Sci* 2011;357:163–7.
- [43] Ishibashi K, Fujishima A, Watanabe T, Hashimoto K. Detection of active oxidative species in TiO_2 photocatalysis using the fluorescence technique. *Electrochem Commun* 2000;2:207–10.
- [44] Yu X, Yu J, Cheng B, Huang B. One-pot template-free synthesis of monodisperse zinc sulfide hollow spheres and their photocatalytic properties. *Chem Eur J* 2009;15:6731–9.
- [45] Gan Q, Jans U. Nucleophilic reactions of phorate and terbufos with reduced sulfur species under anoxic conditions. *J Agric Food Chem* 2007;55:3546–54.
- [46] Xu XR, Zhao ZY, Li XY, Gu JD. Chemical oxidative degradation of methyl tert-butyl ether in aqueous solution by Fenton's reagent. *Chemosphere* 2004;55:73–9.
- [47] Stemmler K, Gunten U. OH radical-initiated oxidation of organic compounds in atmospheric water phases: part 1. Reactions of peroxy radicals derived from 2-butoxyethanol in water. *Atmos Environ* 2000;34:4241–52.
- [48] Wu T, Cruz V, Mezyk S, Cooper WJ, O'Shea KE. Gamma radiolysis of methyl t-butyl ether: a study of hydroxyl radical mediated reaction pathways. *Radiat Phys Chem* 2002;65:335–41.
- [49] Russell GA. Deuterium isotope effects in the autooxidation of alkyl hydrocarbons. Mechanism of the interaction of peroxy radicals. *J Am Chem Soc* 1957;79:3871–7.
- [50] Kerzhentsev M, Guillard C, Herrmann JM, Pichat P. Photocatalytic pollutant removal in water at room temperature: case study of the total degradation of the insecticide fenitrothion (phosphorothioic acid O,O-dimethyl-O-(3-methyl-4-nitro-phenyl) ester). *Catal Today* 1996;27:215–20.
- [51] Pace G, Berton A, Calligaro L, Mantovani A, Uguagliati P. Elucidation of the degradation mechanism of 2-chloroethanol by hydrogen peroxide under ultraviolet irradiation. *J Chromatogr A* 1995;706:345–51.
- [52] Herrmann JM, Tahiri H, Guillard C, Pichat P. Photocatalytic degradation of aqueous hydroxy-butandioic acid (malic acid) in contact with powdered and supported titania in water. *Catal Today* 1999;54:131–41.