The role of copper(II) ions in the photocatalytic oxidation of 1,4-dioxane

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Abstract

The effect of Cu^{2+} on the photocatalytic oxidation of 1,4-dioxane was evaluated. The addition of Cu^{2+} led to an enhancing effect in the photocatalytic degradation and mineralisation of 1,4-dioxane for both pH 3 and 5. This positive role of Cu^{2+} was attributed to its involvement in the ligand-to-metal charge transfer (LMCT) process, where Cu^{2+} formed complexes with 1,4-dioxane and/or its intermediate products, providing an alternative routes for the oxidation reaction via photoredox mechanism. The supporting evidence to the complexes formation has been confirmed using an electron spin resonance (ESR) spectroscopy and the semi-empirical PM3 calculation.
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1. Introduction

1,4-Dioxane is primarily used as a solvent stabiliser in manufacturing sectors such as processes degreasing, electronics, metal finishing, fabric cleaning, pharmaceuticals, pesticides, antifreeze, membranes, paper manufacturing, etc. It has a propensity to enter the environment due to its high volatility and its solubility in water. It has been found as a pollutant in ground and surface waters. Information on the long-term exposure of humans to 1,4-dioxane has yet to be established. However, it has been classified by the United States Environmental Protection Agency (U.S. EPA), the International Agency for Research on Cancer (IARC) and the Agency for Toxic Substances and Disease Registry (ATSDR) as a probable human carcinogen [1].

1,4-Dioxane does not respond to phase transfer processes (e.g. carbon adsorption and air stripping) [2] or chemical treatments using chlorine or permanganate [3–6]. It is also highly resistant to biodegradation [7]. Efficient removal of 1,4-dioxane in water has been reported with advanced oxidation processes (AOPs), including photochemical degradation

(H_2O_2/UV, O_3/UV), photocatalysis (TiO_2/UV, H_2O_2/Fe^{3+}/UV) and chemical oxidation processes (O_3, O_3/H_2O_2, H_2O_2/Fe^{2+}) [3–6,8–13]. Among them, heterogeneous photocatalysis with TiO_2 has been observed as the most attractive process. Not only that it does not require the use of expensive oxidants such as O_3 and H_2O_2, the process is effective for a wide range of pH values. Nonetheless, there is a limitation that the photogenerated electron–hole pairs can recombine within nanoseconds, giving low quantum efficiency [14,15]. Attempts have been made to improve the performance of TiO_2 using transition metal ions including Cu^{2+}, Fe^{3+} or Mn^{2+} to trap the photogenerated electron via $M^{n+} + e_{cb}^{-} \rightarrow M^{(n-1)+}$ [16–21]. Despite that, the impact of transition metal ions on the photocatalytic reactions has not always been positive [20,21]. While there is scope for further investigation into the role played by Cu^{2+} in a photocatalytic reaction, such studies are also useful since transition metal ions can co-exist with organic pollutants in natural and wastewaters. With their ability to form multiple oxidation states, they have been responsible for many oxidative–reductive processes [22].

To date no studies have addressed the effect of Cu^{2+} on the photocatalytic oxidation of 1,4-dioxane. Mehrvar et al. [12] examined the photocatalytic degradation of 1,4-dioxane using two different commercial TiO_2 powders and found that UV100 TiO_2 performed twice better than Degussa P25 at the optimum

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loadings. Nakajima et al. [23] evaluated the effect of combining sonolysis and photocatalysis for destruction of 1,4-dioxane and observed a synergistic effect. Maurino et al. [3], Hill et al. [10] and Mehrvar [11] investigated the distribution of degradation products from the photocatalytic degradation of 1,4-dioxane and detected ethylene glycol diformate (EGDF) as the main intermediate products of 1,4-dioxane. In this work, we study the role of Cu^{2+} in the photocatalytic oxidation of 1,4-dioxane and EGDF. The interactions of Cu^{2+} with 1,4-dioxane and EGDF are to be established using electron spin resonance (ESR) spectroscopy and semi-empirical PM3 calculations.

2. Experiment

2.1. Chemicals

Degussa P25 TiO_2 (80% anatase, 20% rutile) (Degussa Corporation) was used as the photocatalyst. 1,4-Dioxane, ethylene glycol diformate (EGDF), perchloric acid, copper(II) nitrate and acetonitrile were of analytical grade and used without purification. All solutions were prepared using water from a Millipore Milli-Q water purification system.

2.2. Photoactivity studies

The photoactivity studies were performed in a slurry-type, spiral reactor; where the detailed of the design can be found in Matthew et al. [24]. A 20 W BLB fluorescent lamp (NEC, wavelength range of 300–400 nm with maximum emission at 360 nm) was used as the light source. Fifty milliliters of TiO_2 suspension (1 g/L) was dispersed in an ultrasonic bath for 30 min before being added to the reactor. The suspension was illuminated for 30 min in order to remove any residual organic matters in the system. Subsequently, the light was turned off and 1,4-dioxane was added to give an initial 1,4-dioxane concentration of 0.25 mM. The slurry was mixed for 5 min in the dark followed by 1 h of photoreaction. Two pH conditions, pH 3.0 and 5.0, were investigated.

Samples were collected intermittently and filtered prior to total organic carbon (TOC, Shimadzu TOC-V$_{CSH}$) and high performance liquid chromatography (HPLC, Waters 2695) analyses. A reverse phase C18 Atlantis column (4.6 mm × 250 mm) was used to perform the separation. The mobile phase consisted of water and acetonitrile (95/5 v/v) with flowrate of the mobile phase was maintained at 1 mL/min. The concentrations of 1,4-dioxane and its intermediate product (i.e. EGDF) were measured at their maximum absorbance wavelength by a photodiode array detector. Zeta potential measurements were also carried out using Brookhaven ZetaPALS in order to monitor the removal kinetics of adsorbed intermediate products during the photocatalytic reactions. The samples were collected and subjected to analysis immediately.

To investigate the effect of copper(II) ions on the photocatalytic oxidation of 1,4-dioxane, copper(II) nitrate was added into the system. For all experiments, the concentration of copper(II) ions was fixed at 0.1 mM. Inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin-Elmer) was used

to monitor the change in dissolved Cu concentration during the photocatalytic reaction. The sample was filtered through 0.45 μm PTFE filter prior to the analysis. Control experiments were conducted to assess the significance of homogeneous photolysis reactions both in the absence and in the presence of Cu^{2+}.

In a separate series of experiments, the photocatalytic activity of the EGDF (the main intermediate product from the photocatalytic degradation of 1,4-dioxane) was also evaluated. The concentration of EGDF was fixed at the same molar concentration (i.e. $\sim 0.25 \pm 0.03$ mM) as that used in the photocatalytic studies of 1,4-dioxane with all other operating parameters remained unchanged.

2.3. Dark adsorption studies

The adsorption of 1,4-dioxane and EGDF onto TiO_2, with and without Cu^{2+}, was studied. The experiments were performed in a 100 mL glass bottle. All operating parameters were maintained at the same condition as those used in the photocatalytic studies. The suspension was allowed to mix for 30 min at constant stirring rate before samples were collected. The samples were filtered through 0.45 μm PTFE filter prior to HPLC and TOC analysis.

2.4. Complexation studies

Electron spin resonance (ESR) was used to study the interaction of aqueous Cu^{2+} with 1,4-dioxane and EGDF. Solutions of $Cu(NO_3)_2$ were added to 1,4-dioxane (or EGDF) to yield a molar ratio of Cu^{2+} (1 mM)/1,4-dioxane (3 mM) (or EGDF) = 1:3 with pH adjusted to 3 and 5. ESR spectra were recorded at 150 K using a Bruker Elexsys 500 spectrometer with a SuperX Bruker ER049X Microwave Bridge. The microwave frequency was 9.76 GHz and microwave power 6.346 mW. Spectra were collected and analysed using WinEPR software (Bruker).

3. Results and discussion

3.1. The effect of UV, TiO$_2$ and Cu^{2+} on the photo(catalytic) oxidation of 1,4-dioxane

Upon mixing of 1,4-dioxane with TiO_2 in the dark, the concentration of 1,4-dioxane in solution remained unchanged for both pH 3 and 5 (results not shown), indicating insignificant adsorption of 1,4-dioxane onto TiO_2. Under UV radiation alone, a substantial amount of 1,4-dioxane was degraded, however its conversion into CO_2 was insignificant. When Cu^{2+} was added into the system, an increase in the photodegradation and mineralisation rates of 1,4-dioxane was observed. Further enhancement was seen under TiO_2 photocatalytic oxidation. With UV, Cu^{2+} and TiO_2, the photocatalytic degradation and mineralisation of 1,4-dioxane continued to improve considerably, giving the best performance among all the systems studied. These effects of UV, TiO_2 and Cu^{2+} on the photo(catalytic) oxidation of 1,4-dioxane are clearly illustrated in Fig. 1.

As also shown in Fig. 1, the conversion of 1,4-dioxane into CO_2 (i.e. the mineralisation) was mildly affected by the change
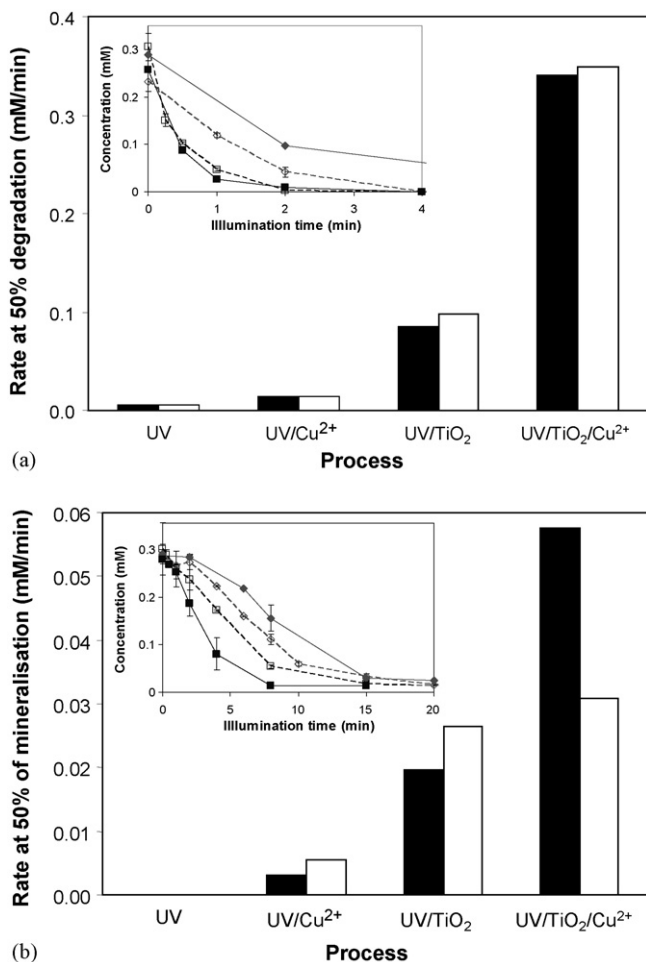
Fig. 1. Comparison of (a) degradation and (b) mineralisation of 1,4-dioxane at pH 3 (■) and pH 5 (□) UV/TiO$_2$/Cu^{2+}. Condition: [TiO$_2$] = 1 g/L, [1,4-dioxane] = 0.25 mM), [Cu^{2+}] = 0.1 mM at: (a) pH$_0$ = 3 ± 0.5 and (b) pH$_0$ = 5 ± 0.5 Fig. 1 inset. Comparison of concentration–time plot of: (a) degradation and (b) mineralisation of 1,4-dioxane, UV/TiO$_2$ (pH 3 (♦)/pH 5 (◊)) and UV/TiO$_2$/Cu^{2+} (pH 3 (■)/pH 5 (□)).

in pH, for both UV and UV/Cu^{2+} systems. For UV/TiO$_2$, the photocatalytic mineralisation of 1,4-dioxane at pH 5 was slightly faster compared to that at pH 3. Typically, these pH dependence rates are associated with the changes of the surface charge of photocatalyst, net charge of the organic compound, changes in its adsorption mode, and the distribution of hydroxyl radicals [25]. Since the dark adsorption study showed that 1,4-dioxane interacted poorly with the TiO$_2$ surfaces for both pH values, the enhancement in the 1,4-dioxane degradation at pH 5 is most probably due to the a higher amount of the hydroxyl radicals produced.

For UV/TiO$_2$/Cu^{2+}, the trend was reverted, the mineralisation of 1,4-dioxane into CO$_2$ at pH 3 was better than that at pH 5. These phenomena are closely related to the interaction of Cu^{2+} with the intermediate products of 1,4-dioxane, where the details will be discussed later.

To understand the effect of pH on the photocatalytic oxidation of 1,4-dioxane, the distribution of the intermediate products was investigated. By means of HPLC/PDA, EGDF was detected to be the major intermediate product from the degradation of

1,4-dioxane, agreed with previous works by Minero et al. [27], Maurino et al. [3] and Hill et al. [10]. Stefan and Bolton [28] and Maurer et al. [29] proposed that upon attack of OH radicals, 1,4-dioxane is transformed into 1,4-dioxanyl radical via H-abstraction. The radical then reacts with oxygen and generates the peroxyl radical which reacts further to produce α-oxyl radical. By the cleavage of C–C bond, the α-oxyl radical is then converted into EGDF.

Fig. 2 shows the variation in concentration of 1,4-dioxane, EGDF and total organic carbon (TOC) with illumination time at pH 3 and 5 for the various systems studied. As illustrated in Fig. 2(a, b, e and f), in the absence of Cu^{2+}, high conversion of 1,4-dioxane into EGDF was recorded (∼71%). This agreed well with the finding by Maurino et al. [3], for which a high conversion of 1,4-dioxane into EGDF has also been documented. Hill et al. [10] reported that 1,4-dioxane was mineralised via an accumulation and slower degradation of EGDF. At pH 3, the estimated amount of the total intermediate products (which was calculated from the difference between the total organic carbon concentration and the concentration of 1,4-dioxane) was in close approximation to the amount of EGDF produced (see Fig. 2(e)). This indicates that 1,4-dioxane is degraded via a two-step reaction (i.e. 1,4-dioxane $\xrightarrow{k1}$ EGDF $\xrightarrow{k2}$ CO$_2$), where the mineralisation rate is governed by the viability of EGDF to undergo oxidation. With the addition of Cu^{2+}, further enhancement was seen in the photocatalytic mineralisation of 1,4-dioxane, and the net production of EGDF decreased appreciably (see Fig. 2(g)). This denotes that the positive effect of Cu^{2+} at pH 3 is attributed to its role in facilitating EGDF oxidation.

In contrast to pH 3, the photocatalytic oxidation of 1,4-dioxane by UV/TiO$_2$ at pH 5 could have involved more than a simple two-step mechanism. As displayed in Fig. 2(f), the estimated generation of the total intermediate products deviated significantly from the net production of EGDF. Moreover, a "steady" EGDF concentration ("plateau") was observed between 2 and 6 min (see Fig. 2(f)). It should also be noted that other intermediate products were present significantly, and those intermediates could have competed for OH radicals with EGDF for the oxidative mechanism. When Cu^{2+} was added into the system, the plateau disappeared and the EGDF concentration was closer to the concentration of total intermediate products compared to that of the UV/TiO$_2$ system. This reflects that the presence of Cu^{2+} accelerates not only the conversion of 1,4-dioxane into EGDF but also the subsequent oxidation of EGDF.

3.2. The effect of UV, Cu^{2+} and TiO$_2$ on the photo(catalytic) oxidation of ethylene glycol diformate

Since the role of Cu^{2+} in the photocatalytic oxidation of 1,4-dioxane has been demonstrated to be related to its interaction with EGDF, a separate investigation was carried out to evaluate the influence of Cu^{2+} on the oxidation of EGDF. Fig. 3 shows the photocatalytic performance of EGDF at pH 3 and 5.

Under UV illumination alone, some degradation of EGDF was observed while it transformed inefficiently into CO$_2$ (Fig. 3
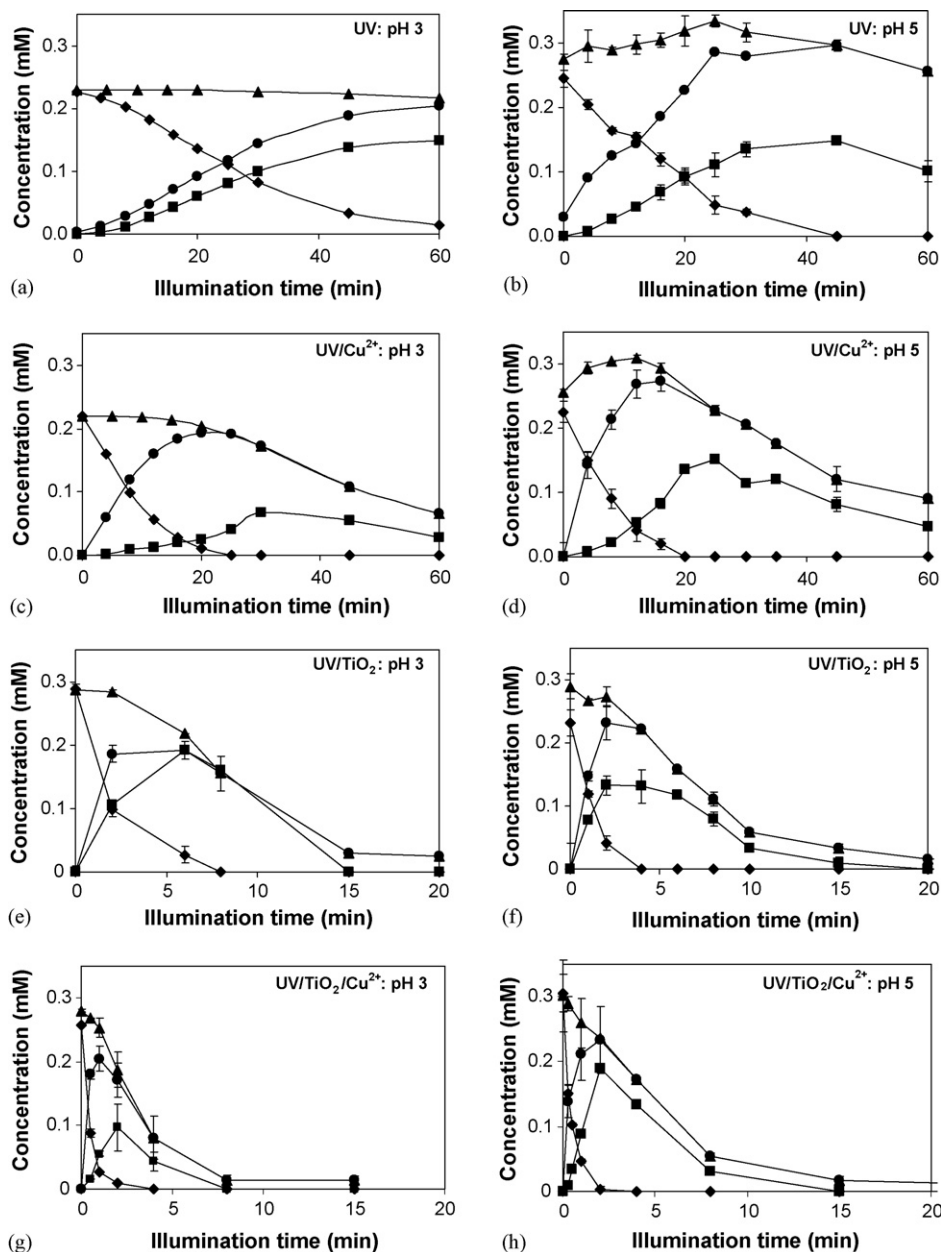
Fig. 2. Comparison of photocatalytic oxidation profile of 1,4-dioxane and its intermediate products under various conditions—UV: (a) pH 3 and (b) pH 5; UV/Cu^{2+}: (c) pH 3 and (d) pH 5; UV/TiO$_2$: (e) pH 3 and (f) pH 5; UV/TiO$_2$/Cu^{2+}: (g) pH 3 and (h) pH 5. Condition: [TiO$_2$] = 1 g/L, [1,4-dioxane] = 0.25 mM, [Cu^{2+}] = 0.1 mM; (▲) TOC, (♦) 1,4-dioxane, (■) EGDF and (●) Total intermediates.

inset). The addition of Cu^{2+} improved both the degradation and mineralisation of EGDF. Compared to pH 5, the enhancing effect was more pronounced at pH 3.

When EGDF was mixed with TiO$_2$ in the dark, it interacted poorly with the TiO$_2$ surface for both pH 3 and 5 (results not shown). For the UV/TiO$_2$, the photocatalytic reaction was improved dramatically. As shown in Fig. 3, the EGDF mineralisation proceeded as fast as its degradation, suggesting thereby the absence of accumulation of degradation products of EGDF. Moreover, it also highlights that the oxidation of the intermediate products of EGDF cannot be the rate-limiting step in the photocatalytic oxidation of 1,4-dioxane.

With UV, TiO$_2$ and Cu^{2+}, the photocatalytic oxidation of EGDF was further enhanced. Compared to UV/TiO$_2$, both the photocatalytic degradation and mineralisation of EGDF was enhanced by a factor of 2 and 1.4 at pH 3 and 5, respectively. The more prominent enhancing effect observed at pH 3 compared to that at pH 5 corresponded well with the observation in Fig. 2(e and g) and (f and h), where we also observed a greater effect of Cu^{2+} on the net formation of EGDF in the photocatalytic oxidation of 1,4-dioxane at pH 3.

Fig. 4(a and b) shows the concentration–time plots of EGDF oxidation, with and without the addition of Cu^{2+}. As displayed in Fig. 4, the photocatalytic degradation and mineralisation of
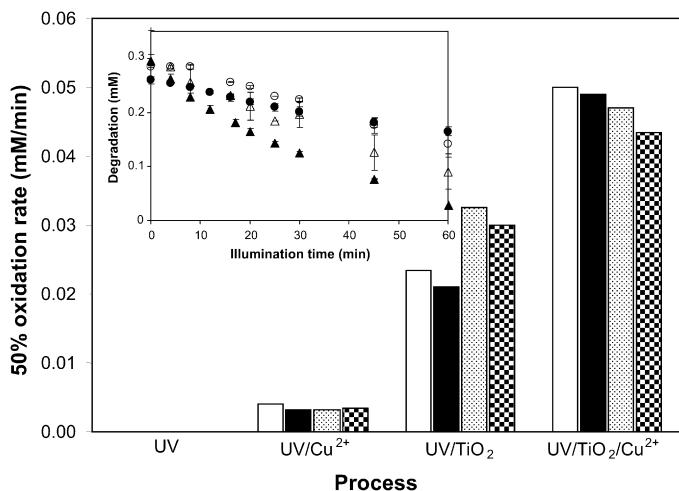
Fig. 3. Comparison of photocatalytic performance of EGDF at pH 3 (($\square$) degradation/($\blacksquare$) mineralisation) and pH 5 (($\boxdot$) degradation/($\boxtimes$) mineralisation). Condition: $[TiO_2] = 1$ g/L, $[EGDF] = 0.28$ mM, $[Cu^{2+}] = 0.1$ mM. Fig. 3 inset. Concentration–time plot of 1,4-dioxane degradation, UV (pH 3 ($\bullet$)/pH 5 ($\circ$)) and UV/Cu^{2+} (pH 3 ($\blacktriangle$)/pH 5 ($\triangle$)).
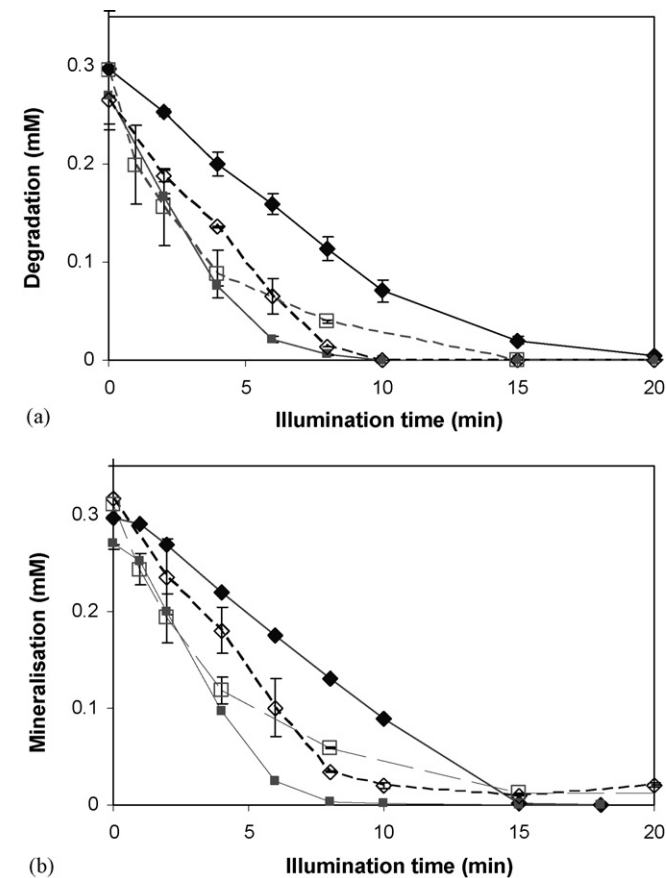
Fig. 4. Comparison of photocatalytic: (a) degradation and (b) mineralisation of EGDF under different pH conditions: ($\blacklozenge$)/($\lozenge$) UV/TiO_2 (pH 3/pH 5), (($\blacksquare$)/($\square$)) UV/TiO_2/Cu^{2+} (pH 3/pH 5). Condition: $[TiO_2] = 1$ g/L, $[EGDF] = 0.28$ mM, $[Cu^{2+}] = 0.1$ mM.
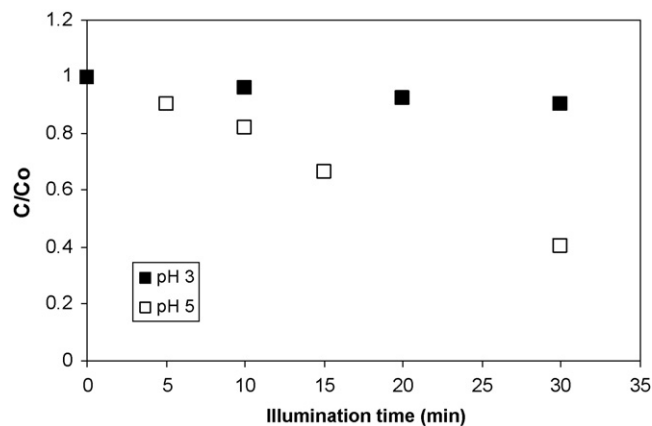

Fig. 5. Comparison of the change in total dissolved copper concentration during the photocatalytic oxidation of EGDF. Condition: $[TiO_2] = 1$ g/L, $[EGDF] = 0.28$ mM, $[Cu^{2+}] = 0.1$ mM.

EGDF by UV/TiO_2 was found to be more superior at pH 5 than that at pH 3. With UV/TiO_2/Cu^{2+}, the initial photocatalytic degradation and mineralisation rates at pH 5 were comparable to that at pH 3. However, as the reactions proceeded, both the photocatalytic degradation and mineralisation at pH 5 were slower than those at pH 3. This less enhancement of Cu^{2+} in the photocatalytic degradation and mineralisation of EGDF at pH 5 rationalises the phenomenon in Fig. 1, which shows a slower rate of 1,4-dioxane conversion into CO_2 at pH 5 in the UV/TiO_2/Cu^{2+} system.

Apart from EGDF, several short chain organic acids and/or aldehydes have been reported to form during the photocatalytic degradation of 1,4-dioxane. Maurino et al. [3] observed the formation of glycolic acid, formic acid, formaldehyde and oxalic acid at pH 5.5. Mehrvar et al. [11] detected acetic acid, formic acid, β-hydroxybutyric acid and glycolic acid as the intermediate products of 1,4-dioxane using GC/MS and IC. Some of these intermediates have been reported to interact very strongly with TiO_2 surfaces [31–33]. These intermediates, however, were undetectable by our current HPLC/PDA method.

The electrophoretic analysis was also used to study the fate of these adsorbed intermediates, as well as their influence on the overall kinetics [34]. For both pH values, the zeta potential of TiO_2 remained unchanged throughout the photocatalytic oxidation of 1,4-dioxane and/or EGDF (results not shown). In the presence of Cu^{2+}, the zeta potential values of the photocatalyst remained unchanged during the photocatalytic reactions. This indicates that the removal of adsorbed intermediate products was not the rate-controlling step. The formation of an intermediary poison, as reported by Bideau et al. [30], due to the interaction between Cu^{2+} and acetic acid forming an adsorbed diacetate complex species, could be ruled out.

In the present study, we monitored the change in Cu concentration during the photocatalytic reaction using ICP-OES. At pH 3, Cu remained as dissolved species whereas, the total dissolved Cu concentration dropped drastically at pH 5 (Fig. 5). This draws to the attention that the retardation in the photocatalytic oxidation of EGDF at pH 5 observed at the later stage of the photocatalytic reaction, as shown in Figs. 3 and 4, may be due

to formation of insoluble Cu species. Presence of the insoluble Cu species affects light penetration as well as reduces the availability of dissolved Cu^{2+} to interact with EGDF (as discussed in the next section—to be the main role of Cu^{2+}).

3.3. The role of copper(II) ions

To date, various postulations have been proposed to explain the role of Cu^{2+} in the photocatalytic oxidation of organic pollutants [18,16,21,22,35–41]. Sykora [35] reported that Cu^{2+} may play a role as an electron scavenger at the surface of TiO_2, since its redox potential (+0.34 V) is more positive than the flat potential of conduction band (−0.3 V) [35]. However, Butler and Davis [18] commented that the electron trapping mechanism by Cu^{2+} would not be viable if the metal ions adsorbed poorly onto TiO_2 surface. Previously, we [16] have shown that the electron scavenging mechanism may have an effect if the metal ions possessed a tendency to form complexes with the adsorbed intermediate products. The complexes formed between Cu^{2+} and the highly adsorbed intermediates improved the interaction between the metal ions and the surface of the photocatalyst. In this study, due the unchanged zeta potential values of the photocatalyst during the photocatalytic oxidation, it could be deduced that the adsorbed intermediates degraded rapidly upon contact with UV and TiO_2. Hence, the ability of Cu^{2+} to complex with the adsorbed intermediates of 1,4-dioxane and subsequently to trigger the electron scavenging mechanism would be unlikely.

Some authors postulated [22,37] that the enhancing effect of Cu^{2+} could be ascribed to the ability of metal ions to accelerate the mediation of electrons to O_2, thereby quenching the electron–hole pair's recombination. In this work, it is suggested that this mechanism may not be the main reason leading to the positive effect of Cu^{2+}, as there is no direct evidence to indicate the presence of surface interaction between Cu^{2+} and TiO_2.

A few researchers [22,35–37] have proposed that the beneficial effect of Cu^{2+} could be due to its role as promoters for free radical reactions. Litter [37] reported that Cu^{2+} could enhance the dissociation of H_2O_2 to give $^\bullet OH$ via a mechanism known as photo-Fenton type reaction. Although the production of H_2O_2 from the reduction of oxygen on the illuminated TiO_2 has been shown to be thermodynamically feasible in several review papers [25,26,37], no data has yet to be published to indicate that the amount of H_2O_2 produced is sufficient to drive the photo-Fenton type reaction. Cai et al. [38] reported an enhanced production of H_2O_2 in TiO_2 photocatalysis when Cu^{2+} was added as electron acceptor; however this positive effect of Cu^{2+} was only evidenced under saturated oxygen environment. In this study, as the experiment was conducted under ambient condition, it is anticipated that the photo-Fenton type reaction may not be the driving mechanism for the enhancing effect.

From Fig. 2(c and d) and Fig. 3, it can be seen that the oxidation of 1,4-dioxane and EGDF can be induced by the combination of UV and Cu^{2+} (i.e. in the absence of TiO_2). This marks the likelihood of Cu^{2+} to catalyse the oxidation mechanism via the ligand-to-metal charge transfer process. To confirm this, an ESR analysis was conducted to detect the complex formation between Cu^{2+} with 1,4-dioxane and EGDF. Fig. 6(a and

b) compares the ESR spectra of the organo-metal complex at pH 3 and 5, respectively.

At pH 3, the ESR spectrum of Cu^{2+} showed a similar spectrum to those reported by Sato et al. [42], suggesting the $Cu(H_2O)_6{}^{2+}$ complex is in the tetragonally distorted octahedral environment. At pH 5, the ESR spectrum of Cu^{2+} was shifted slightly. One possible explanation to this could be due to the co-existence of two (or more) copper species at pH 5.

Upon mixing of Cu^{2+} with 1,4-dioxane, no change in the $g_\perp$ value was observed at pH 3 (see Fig. 6(a)), whereas the $g_\perp$ value shifted from 2.09 to 2.15 at pH 5 (see Fig. 6(b)). The interaction of EGDF into Cu^{2+} at pH 3 led to a shift in the $g_\perp$ value from 2.09 to 2.17 and the $g_\perp$ value shifted from 2.09 to 2.2 at pH 5 (see Fig. 6(b)). The shift confirms the existence of strong interaction between Cu^{2+} and EGDF at both pH 3 and 5, while the distortion in the ESR spectra of the complex with EGDF from the tetragonal symmetry (or D4h symmetry characteristic) indicates a different coordination mode and geometry around the metal center.

Borel and Leclaire [43] studied the structure of $Cu(CH_3CH_2COO)_2 \cdot 0.5C_4H_8O_2$ and showed that dioxane was bind to Cu^{2+} through oxygen molecule. Building from this, a semi-empirical parameter model 3 (PM3) simulation package was used in this study to model the interaction of Cu^{2+} with 1,4-dioxane and EGDF. In water, Cu^{2+} complexes
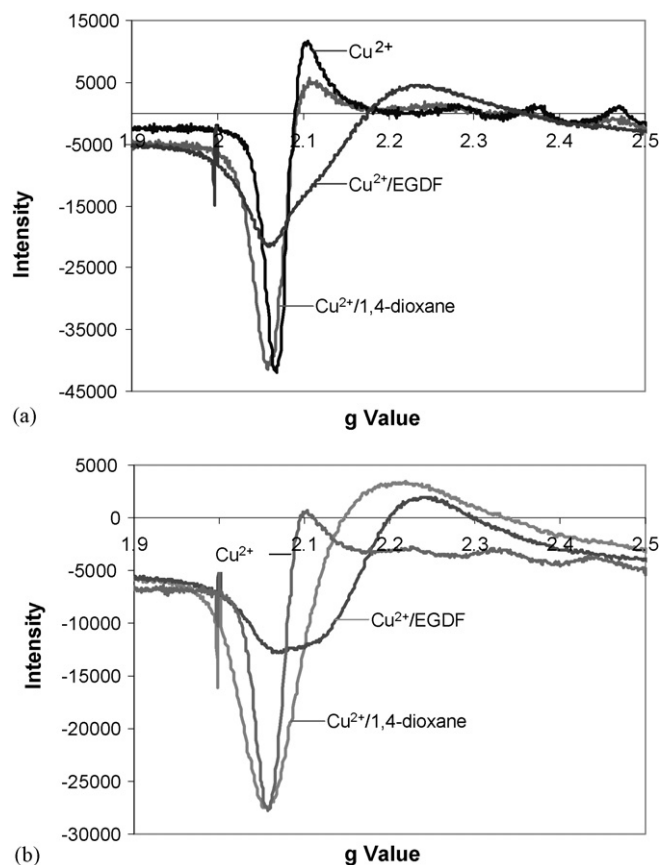

Fig. 6. ESR spectra of Cu(II)complexes in aqueous solution recorded at: (a) pH 3 and (b) pH 5. Condition: $[Cu(NO_3)_2]$ = 1 mM, [1,4-dioxane] = 2.5 mM and [EGDF] = 2.8 mM.
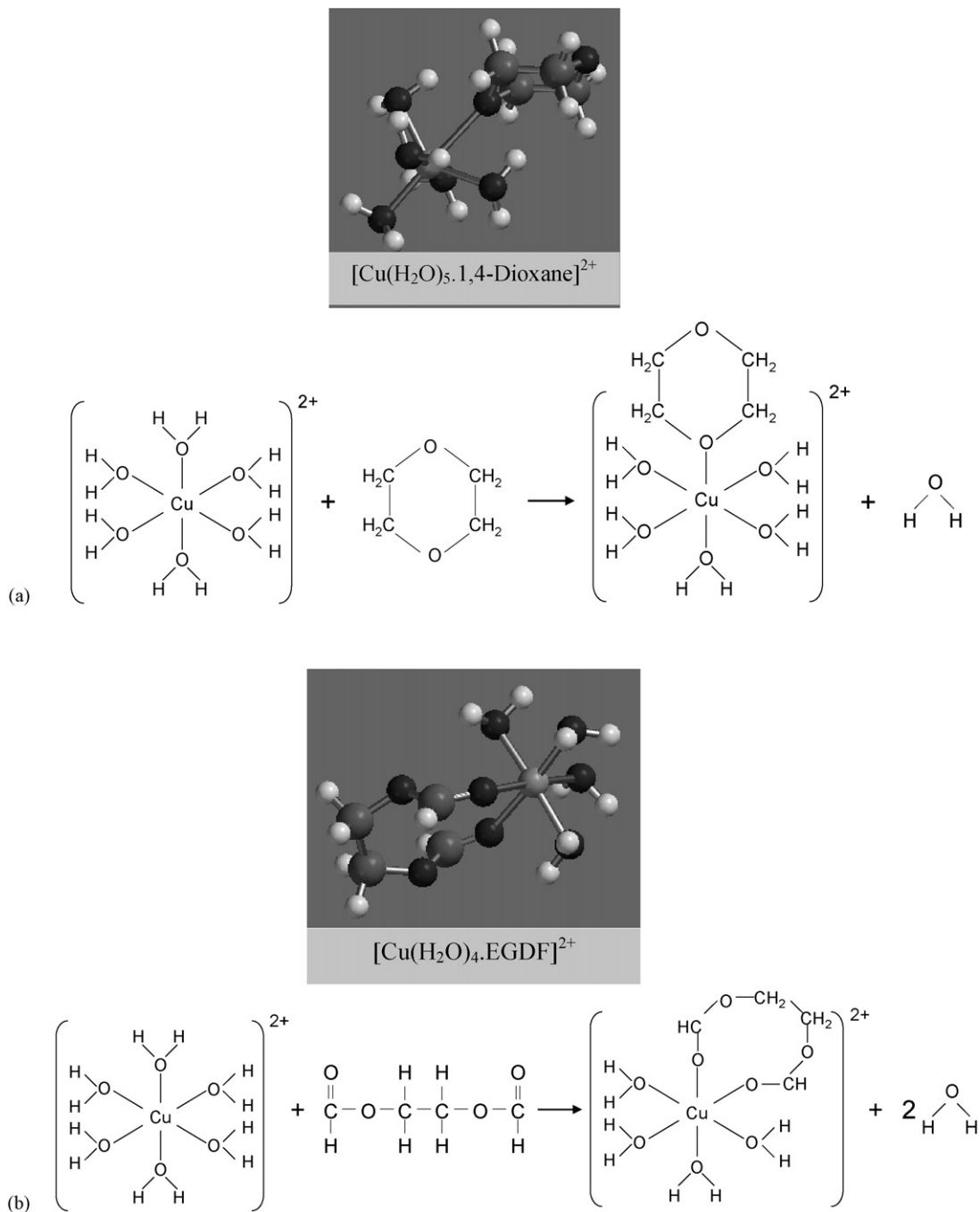
Fig. 7. Ion structures of Cu^{2+} interacted with: (a) 1,4-dioxane and (b) EGDF obtained from the semi-empirical PM3 calculation.

readily with water molecules to form hexaaquacopper(II) ions, $[Cu(H_2O)_6]^{2+}$. As soon as 1,4-dioxane interacts with Cu^{2+}, the monodentate water ligand is displaced by the oxygen atom on 1,4-dioxane molecule and $[Cu(H_2O)_5 \cdot C_4H_4O_2]^{2+}$ ion is formed (Fig. 7(a)). On the other hand, when EGDF interacts with Cu^{2+}, two monodentate water ligands are displaced by the oxygen atom on EGDF molecule, giving a $[Cu(H_2O)_4 \cdot C_4H_6O_4]^{2+}$ ion (Fig. 7(b)). This indicates that 1,4-dioxane has acted as a unidentate ligand whereas, EGDF as a bidentate ligand. Sato et al. [42] and Oess et al. [44] reported that as the hydroxyl moieties group was displaced, it led to a lower symmetry of

the ligands around copper ion and thus a broadening effect. As such, the distortion in the ESR spectra of complex with EGDF from tetragonal symmetry and the broadening effect can be explained by change in the complexation from monodentate to bidentate. Due to the fact that the ESR spectra of the complex with EGDF were so broad, the hyperfine structures in the $g_{\parallel}$ region became unobservable.

The interaction between Cu^{2+} with 1,4-dioxane and EGDF, obtained from the ESR studies and the semi-empirical PM3 calculations, clearly showed that the positive role of Cu^{2+} was due to its involvement in the metal-to-ligand charge transfer

process. As Cu can form multiple oxidation states [22], the partially filled electron allows Cu^{2+} to coordinate with 1,4-dioxane and/or EGDF. Upon irradiation, the metal-to-ligand charge transfer is triggered, where Cu^{2+} will undergo a reduction and the organic ligands partake in the oxidation process, thus creating a photoredox reaction. Many persistent organics such as phenol [35,45,46], glycine [47], iminodiacetic [48] have also been reported to be degraded efficiently via this reaction.

4. Conclusions

It was observed that 1,4-dioxane can be degraded effectively by TiO_2 photocatalysis. At pH 3, the photocatalytic oxidation of 1,4-dioxane involved a two-step reaction with the overall performance controlled by the degradation of EGDF. At pH 5, as the photocatalytic oxidation of 1,4-dioxane involved a more complex process, the reaction kinetic was also influenced by the proficiency of EGDF to undergo oxidation.

The addition of Cu^{2+} further promoted the photocatalytic reaction, which was, attributed to the interaction of Cu^{2+} with 1,4-dioxane and/or its intermediates products, in particular EGDF. As shown from the ESR studies and the semi-empirical PM3 calculation, Cu^{2+} formed complexes with 1,4-dioxane and EGDF, which subsequently catalysed the photocatalytic reaction of these organic compounds via a ligand-to-metal charge transfer mechanism. In the presence of Cu^{2+}, the photocatalytic oxidation of EGDF at pH 5 was slower than that at pH 3. This was attributed to the insoluble Cu species formed during the photocatalytic oxidation of 1,4-dioxane and EGDF at pH 5.

Acknowledgements

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