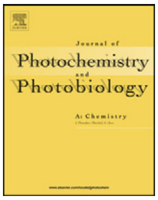
Journal of Photochemistry and Photobiology A: Chemistry 216 (2010) 221–227

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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



On the photocatalytic degradation of phenol and dichloroacetate by $BiVO_4$: The need of a sacrificial electron acceptor

Nikola C. Castillo[a,b,*], Laura Ding[a], Andre Heel[b,1], Thomas Graule[b], Cesar Pulgarin[a,**]

[a] École polytechnique fédérale de Lausanne (EPFL), Faculté des Sciences de Base, Institut des Sciences et Ingénierie Chimiques, Groupe de Génie Électrochimique, CH-1015 Lausanne, Switzerland
[b] Laboratory for High Performance Ceramics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland

ARTICLE INFO

Article history:
Available online 16 September 2010

Keywords:
Bismuth vanadate
Visible light photocatalysis
Hydrogen peroxide, Electron scavenger

ABSTRACT

The photodegradation of phenol and dichloroacetic acid (DCAA) by $BiVO_4$ was studied in the absence as well as presence of selected electron scavengers. The experiments were performed under the visible (vis) irradiation of aqueous solutions over a wide pH range (1–13). Phenol was photocatalytically degraded by $BiVO_4$ into *p*-benzoquinone below pH 3 and into an open-ring structure at pH 13. Methylene blue (MB) accelerated the reaction below the isoelectric point of $BiVO_4$ and did not undergo significant degradation. In presence of H_2O_2, phenol was rapidly degraded up to pH 9. The degradation rates are two orders of magnitude higher than in absence of electron scavenger. The degradation of dichloroacetic acid was only possible in presence of H_2O_2. High initial concentrations of H_2O_2 inhibit the reaction and its consumption is very fast. Sequential additions of this sacrificial electron acceptor (SEA) enables the total degradation of a 1 mM DCAA solution.

1. Introduction

Since the discovery of the Honda–Fujishima effect in 1972 [1], semiconductor photochemistry has evolved – among others – into twin disciplines solar energy conversion water photoelectrolysis [2,3] and photocatalytic oxidation of pollutants [4,5]. TiO_2 has proved the best material for application eversince but researchers are still looking for better performing ones. Thus $BiVO_4$ was presented in 1998 as a promising candidate for oxygen evolution in the half reaction of water decomposition due to its electronic band structure allowing the absorption of visible light up to 540 nm and an unusually high valence-band edge for a metal oxide [6,7]. As a side effect, Kohtani et al. reported the photocatalytic degradation of endocrine disruptor 4-*n*-nonylphenol at pH 13 to favor the phenolate form of the compound. The alkylphenolates yielded an open-ring structure with one acid and one aldehyde group (direct hole transfer), or a catechol ($^\bullet$OH attack) after 80% degradation of the initial compound. However no smaller products nor CO_2 could be detected. This was ascribed to the weaker oxidative power of $BiVO_4$ photoholes than of TiO_2 ones [8,9].

Other pollutants such as rhodamine B [10], methyl orange [11] and methylene blue [12] were also reportedly degraded by pure monoclinic $BiVO_4$ although the experimental conditions were not always optimal (e.g. possible photosensitization by the dye not mentioned, reductive bleaching not excluded, minor oxidation of easily degraded functional groups; see Table 1). Recombination is a matter of concern for $BiVO_4$ [13], so a number of metals have been loaded as electron traps on the surface of the semiconductor such as Ag [14] and Cu [15]. Alternatively, Long et al. suggested to use composite semiconducting particles by loading Co_3O_4 onto $BiVO_4$ for phenol degradation. Those should also suppress recombination because charge separation is favored by an electric field created within each nanoparticle [16]. Finally, the use of $AgNO_3$ as sacrificial electron acceptor to test O_2 evolution activity may have inspired Xie et al. to reduce Cr(VI) as they oxidized phenol [17].

Apart from the work by Kohtani et al. at pH 13 [9,14,18], $BiVO_4$ has not yet been reported as a reliable photocatalyst for the degradation of recalcitrant organic pollutants more than 10 years after the discovery of its photoactivity [6]. Several reasons could explain this: (a) photocatalytic activity has mainly been tested by the simple-to-measure decolorization of dyestuff beside oxygen evolution and has not risen much interest among the community specialized in the degradation of recalcitrant organic pollutants; (b) $BiVO_4$ is not that good a photocatalyst, and results showing its inability to degrade typical model pollutants well known to be degraded by UV-driven TiO_2 photocatalysis remained unpublished.

---

[*] Corresponding author at: École polytechnique fédérale de Lausanne (EPFL), Faculté des Sciences de Base, Institut des Sciences et Ingénierie Chimiques, Groupe de Génie Électrochimique, CH-1015 Lausanne, Switzerland.

[**] Corresponding author.

E-mail addresses: nikola.castillo@epfl.ch (N.C. Castillo), cesar.pulgarin@epfl.ch (C. Pulgarin).

[1] Present address: Marketing, Knowledge and Technology Transfer, Empa - Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland.

1010-6030/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2010.08.021

Nomenclature

BQ	*p*-benzoquinone, $C_6H_4O_2$
DCA	dichloroacetate anion, $CHCl_2COO^-$
DCAA	dichloroacetic acid, $CHCl_2COOH$
e^-_{cb}	conduction-band electron
h^+_{vb}	valence-band hole
$HOO^\bullet$	hydroperoxyl radical
HQ	hydroquinone, $C_6H_4(OH)_2$
IEP	isoelectric point
LMB	*leuco* methylene blue, $C_{16}H_{20}N_3SCl$
MB	methylene blue, $C_{16}H_{18}N_3SCl$
$^\bullet MB^-$	semi-reduced methylene blue
$^\bullet O_2{}^-$	superoxide anion
$^\bullet OH$	free hydroxyl radical
$^\bullet OH_s$	surface-bound hydroxyl radical
PhOH	phenol, C_6H_5OH

Some of us have been studying the degradation of model as well as real organic pollutants by a number of advanced oxidation processes (AOP) [22,23]. In particular, phenol and dichloroacetic acid (DCAA) are degraded over TiO_2 under UV irradiation by the two major possible pathways, *i.e.* electrophilic attack of the aromatic ring by surface hydroxyl radical, and direct hole transfer, respectively [24]. In order to reach total mineralization of an organic pollutant, small aliphatic acid intermediates will eventually undergo a photo-Kolbe oxidation. Such reaction is therefore of major importance and can be well assessed by the degradation of DCAA because the presence of the two Cl atoms make decarboxylation the most dominant initial degradation pathway [25,26]. In this contribution, we discuss the conditions required to degrade such pollutants by visible-light driven photocatalysis over flame-made $BiVO_4$ nanoparticles and the use of a number of electron scavengers to improve the reaction.

2. Experimental

Phenol (Reag. ACS, Riedel-de Haën, Germany), dichloroacetic acid (99%, Fluka, Germany), hydrogen peroxide solution 35% by weight (puriss., stabilized Sigma–Aldrich, Germany), methylene blue (pure USP, AppliChem GmbH, Germany), $Cu(ClO_4)_2{\cdot}6H_2O$ (pure, Riedel-de Haën, Germany) and $K_2S_2O_8$ ($\geq$99%, for analysis ACS, Acros Organics, Belgium), were all used as received. MilliQ water was used throughout the experiments.

Table 2
Physico-chemical properties of $BiVO_4$ nanoparticles.

Crystal phase	E_g (eV)	*SSA* ($m^2 g^{-1}$)	*IEP*
Monoclinic	2.50	24.4	2.3

2.1. $BiVO_4$ nanopowders

$BiVO_4$ nanoparticles were made by flame spray synthesis with *in situ* crystallization as reported in a previous work [21]. Crystal phase, bandgap energy (E_g), BET specific surface area (*SSA*) and surface isoelectric point (*IEP*) are summarized in Table 2.

2.2. Photocatalytic degradations

Photocatalytic activity was evaluated in cylindrical 60 mL Pyrex glass reactors with a top septum lid for sampling. Aqueous solutions were aerated under magnetic stirring (500 rpm) and exposed to the irradiation of five 18 W Philips TLD blue SLV fluorescent tubes (emission maximum at $\lambda = 445$ nm; no overlap with any of the chemicals' absorption but $BiVO_4$; global radiation flux at reactor distance = $58\,W\,m^{-2}$). Two ventilation fans ensured a stable temperature of 25 °C inside the reactors throughout the experiments [21].

$BiVO_4$ powder was dispersed ultrasonically in the reactors filled with MilliQ water, and then a phenol or DCAA solution was added to the reactor. The pH was adjusted with $HClO_4$ and NaOH. The suspensions were then stirred in the dark to reach adsorption equilibrium. Concentration of the photocatalyst was set to $0.5\,g\,L^{-1}$ in all phenol degradations and to $1.0\,g\,L^{-1}$ in all DCAA degradations. Initial phenol and DCAA concentrations were 53.1 μM (5 ppm) and 1.06 mM (137 ppm), respectively. The pH of DCAA solutions was naturally 4.5 so the acid ($pK_a = 1.35$ [27]) is dissociated into dichloroacetate (DCA). 0.7 mL aliquots were collected with a syringe at pre-established reaction times and subsequently filtered (0.22 μm millipore membranes) prior to HPLC analysis. High Performance Liquid Chromatography with a Diode Array Detector (Agilent 1100 series) and a reverse phase Spherisorb silica col-

Table 1
Chronological list of pollutants degraded by $BiVO_4$-based photocatalysts.

Year	Photocatalyst	Pollutant	Comment	Ref.
2003	$BiVO_4$	4-*n*-Alkylphenols	pH 13, solar simulator. Ring opening into aldehyde-acid/catechols but no smaller aliphatic acids	[9]
2005	Ag–$BiVO_4$	4-*n*-Alkylphenols	pH 13, solar simulator. Degradation rates increased by Ag loading on long-chain alkylphenols but mineralization still negligible; no effect on PhOH	[14]
2005	Ag–$BiVO_4$	PAHs[a]	In acetonitrile, solar simulator	[18]
2006	Co_3O_4–$BiVO_4$	Phenol	0.8% Co_3O_4 loaded as co-catalyst. Efficient mineralization and recycling of photocatalyst	[16]
2006	$BiVO_4$	Phenol	PhOH degradation at pH 1.5. Enhancement of degradation and mineralization by simultaneous reduction of Cr(VI) below *IEP*	[17]
2006	$BiVO_4$	Rhodamine B	Natural sunlight, dye sensitization not excluded. Dealkylation of the R–N(Et)$_2$ dye	[10]
2006	$BiVO_4$	Methyl orange	High-pressure Hg lamp, dye sensitization not excluded. Decolorization of the azo dye	[11]
2007	$BiVO_4$	Methylene blue	W halogen lamp, dye sensitization not excluded	[12]
2008	Cu–$BiVO_4$	Methylene blue	Hg lamp. Dealkylation of the R–N(Me)$_2$ dye	[15]
2009	$BiVO_4$	Methylene blue	Solar simulator, dye sensitization not excluded. Dye degradation by amorphous $BiVO_4$	[19]
2010	$BiVO_4$	Methylene blue	UV, blue, and white light sources. Surface poisoning upon recycling	[20]
2010	$BiVO_4$	Methylene blue	Blue light, dye sensitization and reductive photobleaching excluded. Dealkylation of the R–N(Me)$_2$ dye by amorphous $BiVO_4$	[21]

[a] Polycyclic aromatic hydrocarbons.

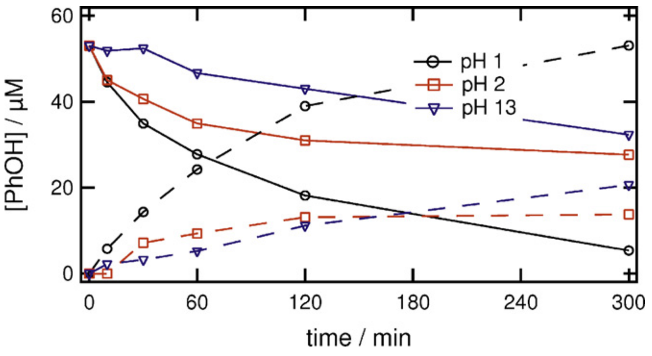


Fig. 1. Degradation of a 53.1 μM phenol solution (–) in a 0.5 g L^{-1} $BiVO_4$ suspension at pH 1, 2 and 13. The build-up of intermediates in arbitrary units (- - -) are ascribed to BQ for pH 1 and 2 and to an unidentified compound at pH 13.

umn C-18 (Macherey-Nagel) was used to detect PhOH, H_2O_2 and *p*-benzoquinone (BQ) by UV absorption at 220, 220 and 244 nm, respectively. The mobile phase consisted of an acetonitrile:water gradient. $[H_2O_2]$ was confirmed by Merckoquant Peroxide Test strips at levels between 0.5 and 25 mg L^{-1}.

DCAA was isolated with a Supelcogel H column and its concentration was measured with a refraction index detector. The mobile phase was a 5 mM H_2SO_4 solution.

3. Results and discussion

3.1. Phenol degradation

Phenol was degraded down to 10% of its initial concentration after a 300-min long irradiation of a $BiVO_4$ suspension at initial pH 1 (Fig. 1). At pH 2, phenol was degraded to a lower extent, the activity was even more reduced at pH 3 and became null for the range 4 < pH < 13 (Fig. 2). These results are in agreement with the experiments by Xie et al. at pH 1.5 [17]. It is worth to note that the dramatic drop in activity occurs across the isoelectric point of $BiVO_4$ (*IEP* = 2.3). Phenol is uncharged in acidic and neutral media ($pK_a = 9.99$ [27]) and weakly adsorbs onto hydrophilic oxides surface so it cannot react with valence-band holes, h_{vb}^{+}. It rather reacts with surface-bound hydroxyl radicals, $^{\bullet}OH_s$ [24]:

$$^{\bullet}OH_s + PhOH \rightarrow {}^{\bullet}Ph(OH)_2 \qquad (1)$$

The sole activity of $BiVO_4$ below its *IEP* must thus be related to the formation of reactive oxygen species (ROS) on the surface of positively charged $BiVO_4$. It is not clear whether such species can form on negatively charged $BiVO_4$ and if so, why they cannot oxidize phenol. One possibility is that the oxidation of adsorbed water is not favored on negatively charged $BiVO_4$. At pH 13, a significant amount of phenol was degraded in a more linear fashion suggesting zero order kinetics (Fig. 1).

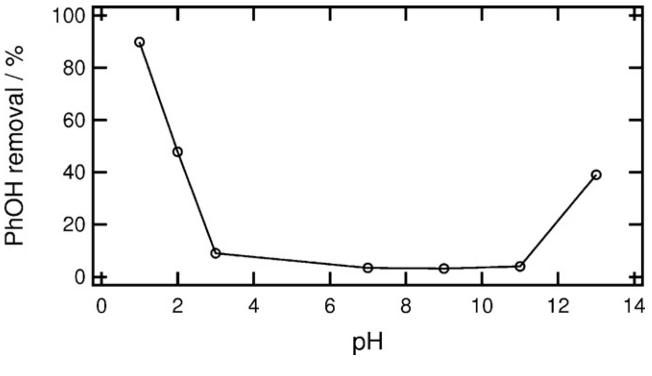


Fig. 2. Phenol removal as a function of pH from a 53.1 μM solution after 300 min of irradiation with 0.5 g L^{-1} $BiVO_4$.

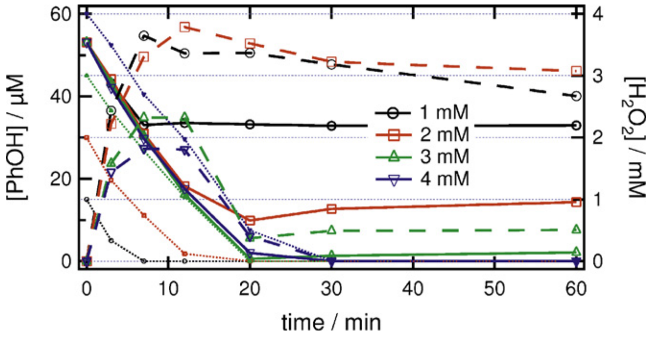


Fig. 3. Degradation of a 53.1 μM phenol solution in a 0.5 g L^{-1} $BiVO_4$ suspension with different initial $[H_2O_2]$ at pH 7. Concentration of PhOH (–), H_2O_2 (···) and BQ in a.u. (- - -) are plotted.

The fact that two different reaction rate laws apply at opposite pH values suggests two different reaction pathways. On the one hand, phenol is degraded following pseudo-first order kinetics below the *IEP* of the photocatalyst. The build-up of *p*-benzoquinone, BQ, as main intermediate, symmetric to phenol disappearance (Fig. 1), is in good agreement with the widely accepted electrophilic hydroxylation of phenol (reaction (1)) [28]. On the other hand, the zero order found at pH 13 is reminiscent of the rate laws found for the degradation of long-chained alkylphenols with $BiVO_4$ [9]. The deprotonated state of phenol at such high pH ($pK_a = 9.99$) may favor a different pathway. Indeed, Kohtani et al. suggested a 6-carbon open-ring structure with a carboxylic group on C1 and an aldehyde one on C6[2] as their main degradation product from direct hole transfer [9]. The linear and very symmetric build-up of the HPLC peak of a fairly high polar compound in the current work may well correspond to such type of muconic acid-like compound (Fig. 1). As a matter of fact, the absence of absorption band at $\lambda > 230$ nm is characteristic of a molecule that has lost its aromaticity by ring cleavage. The oxidation through direct hole transfer to adsorbed phenolate is consistent with the suggestion made above: the oxidation of adsorbed water is unfavored above the *IEP* of $BiVO_4$. Moreover, Kohtani et al. observed a negligible production of free $^{\bullet}OH$ at pH 12 [29], which is consistent with the lack of phenol hydroxylation products (BQ) at pH 13.

3.2. Phenol degradation in the presence of electron scavengers

3.2.1. H_2O_2

Addition of 3 mM H_2O_2 into the photocatalytic reactor prior to irradiation lead to the total degradation of phenol at pH 7 within 20 min (Fig. 3). However, for lower H_2O_2 initial concentrations, the reaction is immediately quenched after the entire consumption of H_2O_2. The evolution of $[H_2O_2]$ from several initial concentrations shows that the decomposition is linear, with a consumption rate of 3×10^{-6} M s^{-1}. The degradation of PhOH occurs in the presence of H_2O_2: up to $t = 7$ min for $[H_2O_2]_0 = 1$ mM; up to $t = 20$ min for $[H_2O_2]_0 = 2$ mM (Fig. 3). BQ is concomitantly formed upon PhOH removal. BQ reaches its maximum concentration, $[BQ]_{max}$, at 7 min for $[H_2O_2]_0 = 1$ mM, *i.e.* when $[H_2O_2]$ reaches zero. $[BQ]_{max}$ is shifted to 12 min when $[H_2O_2]_0$ is doubled; H_2O_2 obviously lasts longer in the reactor. It is worth to note that [BQ] starts to decrease after the total consumption of H_2O_2 in these two runs. This slow decrement may not reflect photocatalytic degradation but rather redox

---

[2] The aldehydic acid was wrongly named *cis,cis*-4-alkyl-6-oxo-2,6-hexadienoic acid. The correct nomenclature should be *cis,cis*-4-alkyl-6-oxo-2,4-hexadienoic acid since the second double bond lies between C4 and C5.

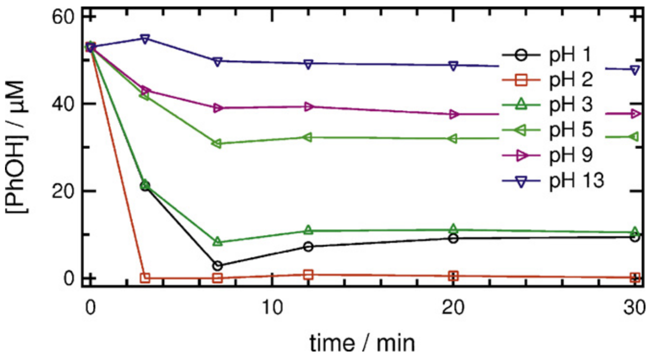


Fig. 4. Degradation of a 53.1 µM phenol solution in a 0.5 g L^{-1} $BiVO_4$ suspension at several initial pH with 1 mM H_2O_2.

equilibrium reactions with hydroquinone, HQ:

$$BQ + 2e^- + 2H^+ \rightleftharpoons HQ \quad E^\circ = +0.6992\,V \qquad (2)$$

The shift towards the right is consistent with the pH drop observed at the end of the run: $4.5 < pH_{final} < 5.0$. At higher $[H_2O_2]_0$, [BQ] rapidly starts to decrease before $[H_2O_2]$ reaches zero. The H_2O_2/PhOH molar ratio for the complete degradation of phenol at pH 7 is about 55. If complete degradation of BQ is sought too, the ratio becomes 75.

The H_2O_2/PhOH ratio and the reaction kinetics are pH dependent. Higher rates are observed at low pH and thus lower H_2O_2/PhOH ratios are required (Fig. 4). The ratio for full degradation is ≤20 at pH 2, while it rises to about 55 at pH 7. The accumulation of BQ in all runs with significant PhOH degradation shows that 1 mM H_2O_2 is not sufficient to completely degrade both PhOH and BQ even at pH 2 (data not shown). The use of H_2O_2 as electron scavenger for TiO_2 photocatalysis, along with its decomposition kinetics was studied in the early 1990s [30,31] and later reviewed by Ilisz et al. [32]. The photocatalytic decomposition of H_2O_2 on TiO_2 surface can proceed either by reduction

$$H_2O_2 + e^-_{cb} + H^+ \rightarrow {}^\bullet OH_s + H_2O \qquad (3)$$

$${}^\bullet OH_s + e^-_{cb} + H^+ \rightarrow H_2O \qquad (4)$$

or by oxidation

$$H_2O_2 + h^+_{vb} \rightarrow HOO^\bullet + H^+ \qquad (5)$$

$$HOO^\bullet + h^+_{vb} \rightarrow O_2 + H^+ \qquad (6)$$

in two-electron transfer processes. The combination of Eqs. (3)–(6) yields:

$$2H_2O_2 \xrightarrow{2h\nu,\,TiO_2} 2H_2O + O_2 \qquad (7)$$

which is nothing else than a photocatalyzed disproportionation of H_2O_2 [33]. The amount of H_2O_2 can thus affect both the formation of $HOO^\bullet/{}^\bullet O_2{}^-$ and ${}^\bullet OH$ [34], which are usually formed through reactions summarized by:

$$e^-_{cb} + O_2 + H^+ \rightarrow HOO^\bullet \qquad (8)$$

$$h^+_{vb} + H_2O \rightarrow {}^\bullet OH_s + H^+ \qquad (9)$$

Note that the radicals produced in reactions (8) and (9) are identical to those from (5) and (3), respectively. However, reactions (3) and (8) are reductions while (5) and (9) are oxidations, *i.e.* opposite types of electron transfer are expected to yield the same species. If we assume that reactions (8) and (9) occur upon irradiation of $BiVO_4$ under certain pH conditions (Figs. 1 and 2), it is difficult to establish whether ${}^\bullet OH_s$ comes from hole (9) or electron (3) transfer when H_2O_2 has been added.

As reviewed by Dionysiou et al. high concentrations of H_2O_2 can also be detrimental because it may compete with trace pollutants for ${}^\bullet OH$ in a chain reaction both on the surface and in the solution bulk [35]:

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HOO^\bullet \qquad (10)$$

$$HOO^\bullet + {}^\bullet OH \rightarrow H_2O + O_2 \qquad (11)$$

Note that one H_2O_2 molecule scavenges two ${}^\bullet OH$. Not only is H_2O_2 consumed in this scheme but ${}^\bullet OH$ are lost to yield the same reaction products as in reaction (7). One last option is the reaction of H_2O_2 with $HOO^\bullet$, which can produce both surface-adsorbed and free hydroxyl radicals [5]:

$$H_2O_2 + HOO^\bullet \rightarrow {}^\bullet OH + H_2O + O_2 \qquad (12)$$

From the above considerations, the fate of ${}^\bullet OH_s$ from the one-electron reduction of H_2O_2 (reaction (3)) is either: (a) further reduction to H_2O (reaction (4)), (b) decomposition of H_2O_2 (reactions (10) and (11)), or (c) the electrophilic attack of a pollutant (e.g. reaction (1)). A competition between these four reactions is thus expected. Similarly, the fate of $HOO^\bullet$ from the one-electron oxidation of H_2O_2 (reaction (5)) is either further oxidation to O_2 (reaction (6)) or other deactivation pathways (e.g.: reaction (11)).

The competition between those reactions will depend on the availability of the pollutants, their nature, pH, and on the surface properties of the photocatalyst such as degree of hydroxylation and the nature of the active sites. The high values of the H_2O_2/PhOH ratio and its different values under different pH conditions are ascribed to the complexity of the system. Assuming pseudo-first order kinetics for phenol degradation, the reaction rates with H_2O_2 are around two orders of magnitude higher than in absence of electron acceptor at pH < *IEP*. The decomposition of H_2O_2 is faster for pH values closer to the *IEP* with a maximum decomposition rate at pH 2 which could not be measured because H_2O_2 was entirely decomposed within 3 min (Fig. 4).

H_2O_2 can considerably speed up the degradation of phenol, which was achieved by only $BiVO_4$ at pH < *IEP*. Above the *IEP*, the function of H_2O_2 is to activate $BiVO_4$ and extend its activity to more neutral pH values by working as sacrificial electron acceptor.

3.2.2. *Methylene blue*

The decolorization of methylene blue (MB) is widely used to test the activity of novel photocatalysts, including our flame-made $BiVO_4$ [21] (Table 1). MB is stable in acidic media, where both its oxidation and reduction are reversible. The presence of MB (5.7 µM) accelerates the degradation of a 53.1 µM phenol solution at pH 2. The rate is not as fast as with H_2O_2 but MB is not consumed since it is regenerated within µs [36]. The proposed reaction mechanism between the conduction-band electron and MB is as follows:

$$2e^-_{cb} + 2MB \rightarrow 2{}^\bullet MB^- \qquad (13)$$

$$2{}^\bullet MB^- + 2H^+ \rightarrow MB + LMB \qquad (14)$$

$$LMB + O_2 \rightarrow MB + H_2O \qquad (15)$$

The combination of Eqs. (13)–(15) yields:

$$2e^- + 2H^+ + O_2 \xrightarrow{2h\nu,\,MB,\,BiVO_4} H_2O \qquad (16)$$

MB is neither consumed nor produced in this reaction, as opposed to H_2O_2 in reaction (7). Therefore it should not be regarded as a sacrificial electron acceptor (SEA) and is better described as a redox mediator or as a co-catalyst. Unlike H_2O_2, MB does not enable the degradation of phenol at pH > *IEP* of $BiVO_4$. This issue is addressed elsewhere in detail [36].

3.3. *Dichloroacetic acid degradation*

Dichloroacetate anion (DCA) could not be degraded at pH 4.5 in absence of electron acceptor (Fig. 5). The kinetics of the complete

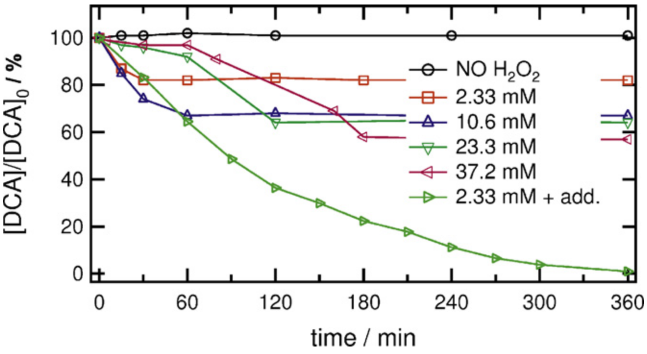


Fig. 5. Degradation of a 1.06 mM DCA solution in a 1.0 g L^{-1} BiVO$_4$ suspension with varying initial [H$_2$O$_2$] at pH 4.5. The run with stepwise additions included 10 loads of H$_2$O$_2$ at 30 min intervals.

mechanism of DCA degradation by TiO$_2$ photocatalysis was studied by Zalazar et al. [37]. Only one hole is sufficient to mineralize one DCA molecule by direct hole transfer, although adsorption on the photocatalyst surface is a prerequisite [38]:

$$\mathrm{TiO_2 + CHCl_2COO^- \rightleftharpoons CHCl_2COO^-_{ads}} \tag{17}$$

$$\mathrm{CHCl_2COO^-_{ads} + h^+_{vb} \rightarrow CHCl_2COO^\bullet} \tag{18}$$

$$\mathrm{CHCl_2COO^\bullet \rightarrow HCl_2C^\bullet + CO_2} \tag{19}$$

$$\mathrm{O_{2ads} + HCl_2C^\bullet \rightarrow CHCl_2O_2{}^\bullet} \tag{20}$$

$$\mathrm{2CHCl_2O_2{}^\bullet \rightarrow 2COCl_2 + H_2O_2} \tag{21}$$

$$\mathrm{COCl_2 + H_2O \rightarrow CO_2 + 2HCl} \tag{22}$$

Note that reaction (21) is a bimolecular step that requires the vicinity of two CHCl$_2$O$_2{}^\bullet$ radicals to yield two short-lived phosgene molecules and one H$_2$O$_2$. In the present work, it seems that photogenerated holes from BiVO$_4$, h^+_{vb}, were not powerful enough to oxidize DCA (reaction (18)) or that DCA did not adsorb on BiVO$_4$ (Eq. (17)). The latter is a realistic scenario from an electrostatic point of view because both DCA and BiVO$_4$ surface are negatively charged at pH 4.5.

Based on the results found for phenol, DCA degradation was attempted with the best electron acceptor, *i.e.* sacrificial H$_2$O$_2$ (see Subsection 3.2). With an initial H$_2$O$_2$ concentration of 2.33 mM, DCA was degraded to 82% of its initial concentration within 30 min (Fig. 5). Accordingly, with [H$_2$O$_2$]$_0$ = 10.6 mM, DCA was degraded to 67% of its initial concentration within 60 min, until H$_2$O$_2$ was totally consumed, as it was the case for PhOH. The role of H$_2$O$_2$ can be manifold. Reaction (3) can prevent charge recombination and extend the lifetime of holes, and favor reaction (18). In the mean time, H$_2$O$_2$ can contribute to the formation of $^\bullet$OH$_s$ through reaction (3) and/or reaction (9). DCA is known to be oxidized by free $^\bullet$OH in a homogeneous H$_2$O$_2$-UV system [39], but surface-bound hydroxyl radicals are reportedly unreactive towards DCA [38]. It is concluded that DCA is either oxidized by valence-band holes, whose lifetime is extended by the addition of H$_2$O$_2$, or by free $^\bullet$OH resulting from the acid-catalyzed hydrolysis of surface μ-peroxo species, as suggested by Nakamura & Nakato [40]:

$$\mathrm{[Ti-O-O-Ti]_s + H_2O \rightarrow [Ti-O-OH\,HO-Ti]_s} \tag{23}$$

When the O–O bond in TiO–OH breaks, a free hydroxyl radical is released [5]:

$$\mathrm{[Ti-O-OH\,HO-Ti]_s \rightarrow [Ti-O^\bullet\,HO-Ti]_s + {}^\bullet OH} \tag{24}$$

This issue is still under debate but it is becoming clear that the generation of free $^\bullet$OH from metal oxide surfaces requires the presence of surface peroxo groups. The geometry of these groups seems critical for the process [40,41].

With [H$_2$O$_2$]$_0$ = 23.3 and 37.2 mM, an induction period was observed before the degradation started (Fig. 5). Besides, final [DCA] was around 60% of [DCA]$_0$, *i.e.* very close to the run with [H$_2$O$_2$]$_0$ = 10.6 mM. This indicates that high concentrations of H$_2$O$_2$ inhibit the degradation of DCA. It can be argued that surface sites are not available to DCA adsorption until a large fraction of H$_2$O$_2$ is decomposed [35] by reaction (7), but also mainly by reactions (10) and (11) – which are favored by excess H$_2$O$_2$ – combined to $^\bullet$OH$_s$ generation through reactions (3), (9) and/or (12). Indeed, the induction time reaches 60 min for [H$_2$O$_2$]$_0$ = 37.2 mM. This transient poisoning of the photocatalyst is in agreement with the claims of Bahnemann et al., who found that DCA adsorption on colloidal TiO$_2$ (Eq. (17)) is a prerequisite for its oxidation [38]. Hirakawa & Nosaka also found that high amounts of adsorbed H$_2$O$_2$ would inhibit reaction (8) on adsorbed O$_2$ [34].

The continuous availability of a reactant in low amounts can be provided by a fed-batch or by dropwise addition. Fig. 5 shows the effect of several additions of concentrated H$_2$O$_2$ to renew [H$_2$O$_2$] = 2.33 mM after each addition and try to supply the reactor with fresh H$_2$O$_2$ as soon as it is totally consumed. Total degradation of a 1 mM DCAA solution is thus achieved after 6 h of irradiation. It is worth to note that the total amount of added H$_2$O$_2$ is equivalent to the run with [H$_2$O$_2$]$_0$ = 23.3 mM, which was largely inefficient, with <40% of the initial concentration of DCA being degraded. This is an important observation. It shows that most H$_2$O$_2$ is wasted if not added at a proper time and in an adequate amount. [H$_2$O$_2$] should hence be carefully controlled and kept at a constant level either by continuous addition or *in situ* generation. The formation of H$_2$O$_2$ as a byproduct in reaction (21) may even lower the demand of added H$_2$O$_2$. Dionysiou et al. found that the optimal H$_2$O$_2$ to contaminant molar ratio for the degradation of 4-chlorobenzoic acid (C$_7$H$_5$ClO$_2$) in a continuous-mode configuration was equal to 5.33, above which inhibitory effects were observed [35]. In the present work, total degradation was achieved with a 21.7 molar ratio by repeated H$_2$O$_2$ additions. This value is much higher and DCA is mineralized after one single hole transfer [37] while 4-chlorobenzoic acid is a larger molecule. This observation emphasizes the ease of decomposition of H$_2$O$_2$ and the potential improvements to be made by adjusting some reaction engineering parameters.

3.4. *Choice of the electron acceptor on the basis of band edges*

In an ideal photocatalytic system, only the photocatalyst needs to be supplied. All other agents are expected to be “naturally” present: sunlight, water/organic pollutants as hole scavenger, and dissolved atmospheric oxygen as electron scavenger. The alternative electron acceptors studied in this work present different features: hydrogen peroxide is consumed in reaction (3) but it is efficient and “green” (reaction products are only H$_2$O and O$_2$, reaction (7)). One problem related to larger scale application is the liquid state and facile thermal decomposition of H$_2$O$_2$, which require special handling. Methylene blue is a cheap organic dye, readily available as an easy-to-handle powder. Its role as electron acceptor is not sacrificial because it is regenerated to its initial state (reactions (13)–(15)), so it can be used in catalytic amounts: MB/PhOH molar ratio is 0.1 in the present study. Once the target pollutant is totally degraded, the degradation of the dye itself could become an issue, as in dye-sensitized solar cells (DSSC) [42]. Aqueous Cu^{2+} had no effect on the degradation reaction under any of our experimental conditions (1 μM ≤ c_0(Cu^{2+}) ≤ 1 mM, pH 7; data not shown). Its redox potential is not pH dependent, although oxides and/or hydroxides may precipitate in basic conditions. Its reduction is expected to yield metallic copper that might deposit on the photocatalyst unless some parallel Fenton-like redox process allows its regeneration [30,43]. Peroxydisulfate anion can be used for pollutant oxidation but its actual role is not clear. This compound is

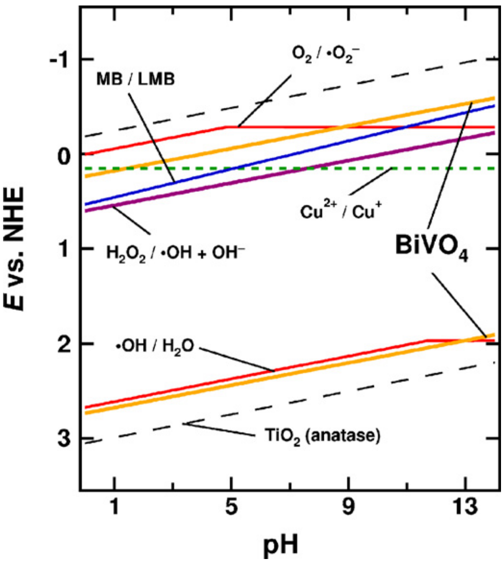


Fig. 6. Redox potential – pH diagram of selected couples used as electron scavenger. Band edge energies of TiO_2 and $BiVO_4$ are also displayed. The one-electron reduction potential of $S_2O_8{}^{2-}$ – is equal to that of H_2O_2. Data from [5,27,47,48]. Values for the conduction band of $BiVO_4$ are calculated from the onset potential of dark reduction performed on a thin film electrode at pH 4 and extrapolated by the Nernst equation ($E(\mathrm{pH}) = E_{\mathrm{pH}4} - 0.059(\mathrm{pH} - 4)$; unpublished data). The potential of the valence-band edge is 2.50 V more positive than the potential of the conduction-band edge as measured by DRS [21].

known to oxidize phenol into hydroquinone (HQ) in aqueous solution through the so-called Elbs persulfate oxidation [44], it was formerly used as a precursor in the synthesis of H_2O_2 under very acidic conditions [45], and its slow thermal homolysis leads to $^•$OH radicals [46]. Its redox potential is pH independent and the reaction product is sulfate. In this study, DCA was partially degraded in a peroxydisulfate solution with and without photocatalyst and hence no further investigations were carried out (data not shown).

The redox potentials of all these electron scavengers are plotted *vs.* the solution pH in Fig. 6 along with the band edges of $BiVO_4$. The valence-band edge is practically at the same level as free hydroxyl radical formation up to pH 12, where $^•$OH generation becomes thermodynamically unfavored. On the other hand O_2 reduction seems viable down to pH 8. The work of Kohtani et al. on the detection of free $^•$OH and $^•O_2{}^-$ carried out at pH 12 with the same method as Hirakawa et al. [34] fits well this picture: evidence for $^•O_2{}^-$ generation but not for $^•$OH [29]. The reduction potentials of the acceptors used in this work are all more positive than $E_{O_2/^•O_2^-}$ and than the potential of conduction-band electrons. This means that the electron transfer reaction should be thermodynamically favored. All energies and potentials, with the exception of Cu^{2+}/Cu, vary linearly between pH 0 and 4.5. Therefore, the energy picture cannot explain the differences in activities found over this range across the *IEP* of the photocatalyst. Indeed, other parameters such as adsorption energies, steric hindrance and electrostatic interactions do also play a role. The authors believe that reactivity more strongly depends on surface interactions because phenol degradation in absence of an electron scavenger and in presence of MB is only observed below the *IEP*. On the other hand the photocatalytic activity in presence of H_2O_2 is determined by its consumption rate, which is a kinetic parameter rather than a thermodynamic one.

$BiVO_4$ turns out to be an efficient photocatalyst under visible irradiation (λ_{max} = 450 nm) for the degradation of model pollutants phenol and DCAA at natural pH provided that H_2O_2 is available on the photocatalyst surface. Due to the high decomposition rate and the price of H_2O_2, the use of this SEA is only viable by continuous addition. A steady state formation of H_2O_2 inside the reactor would best solve this problem and allow the extended use of $BiVO_4$ as a powerful, non-selective, visible-light photocatalyst for the complete mineralization of recalcitrant organic pollutants. $BiVO_4$ shows best activity close by the isoelectric point of 2.3 and below. The use of MB as a regenerating electron acceptor is promising and deserves further investigation. Simultaneous reduction of Cu^{2+} was not successful at natural pH.

4. Conclusion

Aqueous phenol was degraded by $BiVO_4$ photocatalysis under visible light below the isoelectric point of $BiVO_4$ (pH 2.3). The degradation rate was enhanced by the addition of MB as a regenerating redox mediator. A more effective and even highly efficient degradation was achieved in the presence of sacrificial H_2O_2 up to pH 9. But degradation is then limited by the kinetics of H_2O_2 consumption. Dichloroacetate was also degraded in presence of low H_2O_2 concentrations. Competitive adsorption seems to inhibit DCA degradation when high H_2O_2 concentrations are used, so the system is more efficient with controlled and consecutive addition of low H_2O_2 amounts. The need of hydrogen peroxide as a sacrificial electron acceptor has been identified as a critical issue for the photocatalytic degradation of phenol and dichloroacetic acid by pure $BiVO_4$. H_2O_2 is required if this material is to be used in realistic advanced oxidation processes and not limited to applications under extreme pH conditions.

Acknowledgments

The authors thank the Secrétariat d'État Suisse à l'éducation et à la recherche (SER) for its support to the project SER C06.0074 in the framework of the Cost Action 540 "PHONASUM" from the European community; N. Leresche for the degradation experiments with MB. Dr J.A. Rengifo-Herrera contributed to fruitful discussions and experimental setups.

References

[1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (5358) (1972) 37–38.

[2] A. Kudo, Y. Miseki, Heterogeneous photocatalyst materials for water splitting, Chem. Soc. Rev. 38 (1) (2009) 253–278.

[3] J. Tang, J.R. Durrant, D.R. Klug, Mechanism of photocatalytic water splitting in TiO_2. Reaction of water with photoholes, importance of charge carrier dynamics, and evidence for four-hole chemistry, J. Am. Chem. Soc. 130 (42) (2008) 13885–13891.

[4] A.G. Agrios, P. Pichat, State of the art and perspectives on materials and applications of photocatalysis over TiO_2, J. Appl. Electrochem. 35 (7–8) (2005) 655–663.

[5] A. Fujishima, X. Zhang, D.A. Tryk, TiO_2 photocatalysis and related surface phenomena, Surf. Sci. Rep. 63 (12) (2008) 515–582.

[6] A. Kudo, K. Ueda, H. Kato, I. Mikami, Photocatalytic O_2 evolution under visible light irradiation on $BiVO_4$ in aqueous $AgNO_3$ solution, Catal. Lett. 53 (3–4) (1998) 229–230.

[7] A. Kudo, K. Omori, H. Kato, A novel aqueous process for preparation of crystal form-controlled and highly crystalline $BiVO_4$ powder from layered vanadates at room temperature and its photocatalytic and photophysical properties, J. Am. Chem. Soc. 121 (49) (1999) 11459–11467.

[8] S. Kohtani, S. Makino, A. Kudo, K. Tokumura, Y. Ishigaki, T. Matsunaga, O. Nikaido, K. Hayakawa, R. Nakagaki, Photocatalytic degradation of 4-*n*-nonylphenol under irradiation from solar simulator: comparison between $BiVO_4$ and TiO_2 photocatalysts, Chem. Lett. 31 (7) (2002) 660–661.

[9] S. Kohtani, M. Koshiko, A. Kudo, K. Tokumura, Y. Ishigaki, A. Toriba, K. Hayakawa, R. Nakagaki, Photodegradation of 4-alkylphenols using $BiVO_4$ photocatalyst under irradiation with visible light from a solar simulator, Appl. Catal. B 46 (3) (2003) 573–586.

[10] L. Zhang, D. Chen, X. Jiao, Monoclinic structured $BiVO_4$ nanosheets: hydrothermal preparation, formation mechanism, and coloristic and photocatalytic properties, J. Phys. Chem. B 110 (6) (2006) 2668–2673.

[11] L. Zhou, W. Wang, S. Liu, L. Zhang, H. Xu, W. Zhu, A sonochemical route to visible-light-driven high-activity $BiVO_4$ photocatalyst, J. Mol. Catal. A: Chem. 252 (1–2) (2006) 120–124.

[12] X. Zhang, Z. Ai, F. Jia, L. Zhang, X. Fan, Z. Zou, Selective synthesis and visible-light photocatalytic activities of $BiVO_4$ with different crystalline phases, Mater. Chem. Phys. 103 (1) (2007) 162–167.

[13] M. Long, W. Cai, H. Kisch, Visible light induced photoelectrochemical properties of n-$BiVO_4$ and n-$BiVO_4$/p-Co_3O_4, J. Phys. Chem. C 112 (2) (2008) 548–554.

[14] S. Kohtani, J. Hiro, N. Yamamoto, A. Kudo, K. Tokumura, R. Nakagaki, Adsorptive and photocatalytic properties of Ag-loaded $BiVO_4$ on the degradation of 4-*n*-alkylphenols under visible light irradiation, Catal. Commun. 6 (3) (2005) 185–189.

[15] H. Xu, H. Li, C. Wu, J. Chu, Y. Yan, H. Shu, Z. Gu, Preparation, characterization and photocatalytic properties of Cu-loaded $BiVO_4$, J. Hazard. Mater. 153 (1–2) (2008) 877–884.

[16] M. Long, W. Cai, J. Cai, B. Zhou, X. Chai, Y. Wu, Efficient photocatalytic degradation of phenol over $Co_3O_4/BiVO_4$ composite under visible light irradiation, J. Phys. Chem. B 110 (41) (2006) 20211–20216.

[17] B. Xie, H. Zhang, P. Cai, R. Qiu, Y. Xiong, Simultaneous photocatalytic reduction of Cr(VI) and oxidation of phenol over monoclinic $BiVO_4$ under visible light irradiation, Chemosphere 63 (6) (2006) 956–963.

[18] S. Kohtani, M. Tomohiro, K. Tokumura, R. Nakagaki, Photooxidation reactions of polycyclic aromatic hydrocarbons over pure and Ag-loaded $BiVO_4$ photocatalysts, Appl. Catal. B 58 (3–4) (2005) 265–272.

[19] J. Yu, Y. Zhang, A. Kudo, Synthesis and photocatalytic performances of $BiVO_4$ by ammonia co-precipitation process, J. Solid State Chem. 182 (2) (2009) 223–228.

[20] Y. Zhou, K. Vuille, A. Heel, B. Probst, R. Kontic, G.R. Patzke, An inorganic hydrothermal route to photocatalytically active bismuth vanadate, Appl. Catal. A 375 (2010) 140–148.

[21] N.C. Castillo, A. Heel, T. Graule, C. Pulgarin, Flame-assisted synthesis of nanoscale, amorphous and crystalline, spherical $BiVO_4$ with visible-light photocatalytic activity, Appl. Catal. B 96 (3–4) (2010) 335–347.

[22] D. Gumy, S.A. Giraldo, J. Rengifo, C. Pulgarin, Effect of suspended TiO_2 physicochemical characteristics on benzene derivatives photocatalytic degradation, Appl. Catal. B 78 (1–2) (2008) 19–29.

[23] M. Lapertot, C. Pulgarín, P. Fernández-Ibáñez, M.I. Maldonado, L. Pérez-Estrada, I. Oller, W. Gernjak, S. Malato, Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton, Water Res. 40 (5) (2006) 1086–1094.

[24] R. Enríquez, A.G. Agrios, P. Pichat, Probing multiple effects of TiO_2 sintering temperature on photocatalytic activity in water by use of a series of organic pollutant molecules, Catal. Today 120 (2) (2007) 196–202.

[25] D.W. Bahnemann, S.N. Kholuiskaya, R. Dillert, A.I. Kulak, A.I. Kokorin, Photodestruction of dichloroacetic acid catalyzed by nano-sized TiO_2 particles, Appl. Catal. B 36 (2) (2002) 161–169.

[26] R. Enriquez, B. Beaugiraud, P. Pichat, Mechanistic implications of the effect of TiO_2 accessibility in TiO_2–SiO_2 coatings upon chlorinated organics photocatalytic removal in water, Water Sci. Technol. 49 (4) (2004) 147–152.

[27] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 90th ed., CRC Press, Boca Raton, 2009.

[28] K.-i. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, A. Itaya, Heterogeneous photocatalytic decomposition of phenol over TiO_2 powder, Bull. Chem. Soc. Jpn. 58 (7) (1985) 2015–2022.

[29] S. Kohtani, K. Yoshida, T. Maekawa, A. Iwase, A. Kudo, H. Miyabe, R. Nakagaki, Loading effects of silver oxides upon generation of reactive oxygen species in semiconductor photocatalysis, Phys. Chem. Chem. Phys. 10 (2008) 2986–2992.

[30] T.Y. Wei, Y.Y. Wang, C.C. Wan, Photocatalytic oxidation of phenol in the presence of hydrogen peroxide and titanium dioxide powders, J. Photochem. Photobiol. A 55 (1990) 115–126.

[31] V. Auguliaro, E. Davi, L. Palmisano, M. Schiavello, A. Sclafani, Influence of hydrogen peroxide on the kinetics of phenol photodegradation in aqueous titanium dioxide dispersion, Appl. Catal. 65 (1) (1990) 101–116.

[32] I. Ilisz, K. Föglein, A. Dombi, The photochemical behavior of hydrogen peroxide in near UV-irradiated aqueous TiO_2 suspensions, J. Mol. Catal. A: Chem. 135 (1) (1998) 55–61.

[33] B. Jenny, P. Pichat, Determination of the actual photocatalytic rate of hydrogen peroxide decomposition over suspended titania. fitting to the Langmuir–Hinshelwood form, Langmuir 7 (5) (1991) 947–954.

[34] T. Hirakawa, Y. Nosaka, Properties of O_2^- and OH formed in TiO_2 aqueous suspensions by photocatalytic reaction and the influence of H_2O_2 and some ions, Langmuir 18 (8) (2002) 3247–3254.

[35] D.D. Dionysiou, M.T. Suidan, I. Baudin, J.-M. Laîné, Effect of hydrogen peroxide on the destruction of organic contaminants-synergism and inhibition in a continuous-mode photocatalytic reactor, Appl. Catal. B 50 (4) (2004) 259–269.

[36] N.C. Castillo, N. Leresche, J. Teuscher, J.-E. Moser, A. Heel, T. Graule, C. Pulgarín, Adsorbed methylene blue on $BiVO_4$ nanoparticles catalyzes the photocatalytic degradation of aqueous phenol, Langmuir, in press.

[37] C.S. Zalazar, C.A. Martin, A.E. Cassano, Photocatalytic intrinsic reaction kinetics. II: Effects of oxygen concentration on the kinetics of the photocatalytic degradation of dichloroacetic acid, Chem. Eng. Sci. 60 (15) (2005) 4311–4322.

[38] D.W. Bahnemann, M. Hilgendorff, R. Memming, Charge carrier dynamics at TiO_2 particles: reactivity of free and trapped holes, J. Phys. Chem. B 101 (21) (1997) 4265–4275.

[39] C.S. Zalazar, M.D. Labas, R.J. Brandi, A.E. Cassano, Dichloroacetic acid degradation employing hydrogen peroxide and UV radiation, Chemosphere 66 (5) (2007) 808–815.

[40] R. Nakamura, Y. Nakato, Primary intermediates of oxygen photoevolution reaction on TiO_2 (rutile) particles, revealed by in situ FTIR absorption and photoluminescence measurements, J. Am. Chem. Soc. 126 (4) (2004) 1290–1298.

[41] T. Hirakawa, K. Yawata, Y. Nosaka, Photocatalytic reactivity for $O_2^{\bullet-}$ and $OH^{\bullet}$ radical formation in anatase and rutile TiO_2 suspension as the effect of H_2O_2 addition, Appl. Catal. A 325 (2007) 105–111.

[42] A. Nozik, R. Memming, Physical chemistry of semiconductor–liquid interfaces, J. Phys. Chem. 100 (31) (1996) 13061–13078.

[43] R. Cai, Y. Kubota, A. Fujishima, Effect of copper ions on the formation of hydrogen peroxide from photocatalytic titanium dioxide particles, J. Catal. 219 (1) (2003) 214–218.

[44] S.M. Sethna, The Elbs persulfate oxidation, Chem. Rev. 49 (1) (1951) 91–101.

[45] G. Goor, J. Glenneberg, S. Jacobi, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2007 (Ch. Hydrogen peroxide, pp. 18–20).

[46] R.L. Johnson, P.G. Tratnyek, R.O. Johnson, Persulfate persistence under thermal activation conditions, Environ. Sci. Technol. 42 (24) (2008) 9350–9356.

[47] R. Memming, Mechanism of the electrochemical reduction of persulfates and hydrogen peroxide, J. Electrochem. Soc. 116 (6) (1969) 785–790.

[48] A. Mills, J. Wang, Photobleaching of methylene blue sensitised by TiO_2: an ambiguous system? J. Photochem. Photobiol. A 127 (1–3) (1999) 123–134.