Post-irradiation effect and reductive dechlorination of chlorophenols at oxygen-free TiO$_2$/water interfaces in the presence of prominent hole scavengers

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Abstract

Heterogeneous photocatalysis with TiO$_2$ nanoparticles for the detoxification of waste-waters and other media is typically achieved by oxidative pathways involving ultimately photogenerated surface-trapped holes (i.e. surface-bound $^\bullet$OH radicals). However, reductive pathways may coexist. The degradation of 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) was examined in irradiated O$_2$-free aqueous media in the presence of prominent hole scavengers such as polyethyleneimine (PEI), triethylamine (TEA), 2-propanol (IPA) and ethylenediaminetetraacetic acid (in the EDTA^{4-} state) to assess the role of photogenerated electrons. The presence of these scavengers imparts a blue-violet color to the nanoparticles corresponding to a broad absorption band in the 400–850 nm region. A post-irradiation effect was observed when irradiation was terminated, which we ascribe to an electron transfer from radical species formed by hole scavenging to the TiO$_2$ particles (reminiscent of the doubling current phenomena in semiconductor electrodes). The two chlorophenols degraded in oxygen-free media, a process inhibited by PEI, TEA and IPA. In the presence of EDTA, degradation of 2,4-dichrophenol occurred by dechlorination only after a 120-min induction period, a process attributed to the accumulated electrons on the particle surface. HPLC analyses revealed that the intermediate products were not those expected from typical oxidative pathways in aerated aqueous media. The degradative process is inferred to take place first by electron attachment to the halophenol to yield phenoxy related radicals and then by secondary reactions with water and/or with each other. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: 2,4-Dichlorophenol; Pentachlorophenol; TiO$_2$ particles; Photolysis
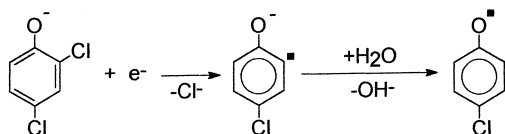
1. Introduction

Chlorinated hydrocarbons are widely used in plastics, pesticides and wood preservatives. Of particular interest, small quantities of the herbicide 2,4-dichlorophenol (2,4-DCP) and the fungicide pentachlorophenol (PCP) [1] are typically found in drinking and ground waters. They are highly stable chemically in these media and their greater solubility in fatty materials compared to water can lead to significant risks of bioaccumulation in animals and humans [2]. Photomineralization of these two pollutants by direct photolysis in natural sunlight in estuarine waters (25 µg l^{-1}) can take weeks to months (half-lives ca. 6–14 days) [3]. Thus, the active interest in the last two decades in developing faster degradative processes that could easily be applied to the treatment of waste-waters (see, for example [4]).
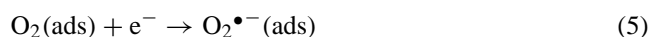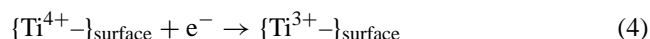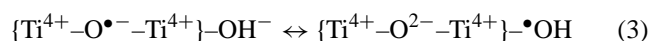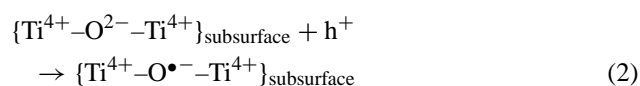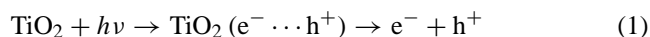
The principles of heterogeneous photocatalysis involving titanium dioxide as the photocatalyst have been discussed in several recent reviews [5–11]. Suffice to note that absorption of photons whose energy is >3.2 eV (for anatase) leads to formation (Eq. (1)) of conduction band electrons (e$^-$) and valence band holes (h$^+$) which subsequently diffuse to the particle surface, in competition with bulk recombination, to be trapped by surface defect sites, surface states or by surface-adsorbed oxidizing or reducing agents. Trapped electrons reduce pre-adsorbed acceptors and trapped holes oxidize pre-adsorbed electron donors; subsequently, these are followed by other secondary steps. Acceptors and donors need to be pre-adsorbed at the photocatalyst particle surface to allow the slower chemistry to effectively compete with the ultrafast electron/hole recombination at the surface [12]. In
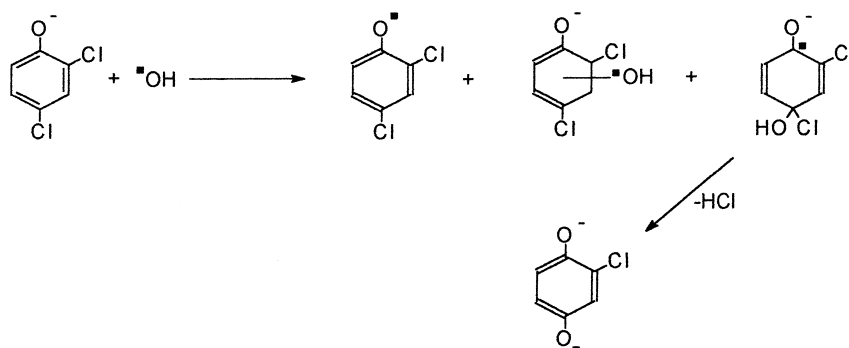
Scheme 1. Electron attachment onto the 2,4-DCP anion and production of the 4-chlorophenoxy radical.

a TiO$_2$ dispersion, the donor is typically OH$^-$ and/or H$_2$O, and the acceptor is the ubiquitous O$_2$ molecule to produce •OH(ads) radicals (Eq. (3)) and the superoxide radical anion (Eq. (5)), respectively.

$$TiO_2 + h\nu \rightarrow TiO_2 \, (e^- \cdots h^+) \rightarrow e^- + h^+ \tag{1}$$

$$\{Ti^{4+}\text{–}O^{2-}\text{–}Ti^{4+}\}_{subsurface} + h^+$$
$$\rightarrow \{Ti^{4+}\text{–}O^{\bullet-}\text{–}Ti^{4+}\}_{subsurface} \tag{2}$$

$$\{Ti^{4+}\text{–}O^{\bullet-}\text{–}Ti^{4+}\}\text{–}OH^- \leftrightarrow \{Ti^{4+}\text{–}O^{2-}\text{–}Ti^{4+}\}\text{–}^{\bullet}OH \tag{3}$$

$$\{Ti^{4+}\text{–}\}_{surface} + e^- \rightarrow \{Ti^{3+}\text{–}\}_{surface} \tag{4}$$

$$O_2(ads) + e^- \rightarrow O_2^{\bullet-}(ads) \tag{5}$$

$$O_2^{\bullet-}(ads) + H^+ \rightarrow HO_2^{\bullet}(ads), \quad pK_a = 4.85 \tag{6}$$

On protonation, O$_2^{\bullet-}$(ads) yields the hydroperoxy radical HO$_2^{\bullet}$(ads) (Eq. (6)). The electron can also be trapped at Ti^{4+} sites to produce surface Ti^{3+} sites (Eq. (4)) which impart a blue-violet coloration to the TiO$_2$ particles in the presence of hole scavengers (e.g. polyvinyl alcohol (PVA) [13]) in oxygen-free dispersions analogous to that observed when TiO$_2$ is UV-irradiated in an oxygen-free atmosphere [14].

The photodegradation of 2,4-DCP and PCP at titania/water interfaces in aerated aqueous TiO$_2$ dispersions has been examined extensively under oxidative conditions [15–20]. Mineralization to CO$_2$ and Cl$^-$ ions typically follows formation of several hydroxylayed intermediate products expected from surface-bound •OH radical attack on the substrates. Pulse radiolytic studies [21–23,24] suggest another degradation pathway that involves direct reduction of the chlorophenols by photogenerated electrons [25]. Using 2,4-DCP as the model substrate, Schemes 1 and 2 illustrate the fate of this substrate under reductive and oxidative conditions, respectively, albeit in homogeneous media by analogy with PCP [25]. Nonetheless, they may provide a clue as to what may also transpire in a heterogeneous medium.

An important clue from these two schemes is that both the reductive and oxidative pathways generate phenoxyl radicals, albeit different ones (p-chlorophenoxyl radical in Scheme 1, and the dichlorophenoxyl, dichlorodihydroxycyclohexadienyl and chloro-p-semiquinone radicals in Scheme 2), following which further secondary reactions may lead to different intermediate products.

To examine their effects in a photocatalytic process, electrons have to be produced in sufficient quantity at the semiconductor/solution interface where chemistry takes place. To suppress scavenging of electrons by molecular oxygen, we examined the reactions under an argon atmosphere and in the presence of such hole scavengers as ethylenediaminetetraacetic acid (EDTA), polyethyleneimine (PEI), triethylamine (TEA) and 2-propanol (IPA) to diminish the rate of electron/hole recombination and to shut-off oxidative reactions of more diluted 2,4-DCP and PCP. Particular emphasis is placed on the degradation of the dichlorophenol.

2. Experimental

PCP and 2,4-DCP (>98%) were Aldrich products as were other phenols (e.g. catechol, hydroquinone, p-benzoquinone, chloro-p-benzoquinone, chlorohydroquinone, 4,6-dichlororesorcinol, 2-chlorophenol and 4-chlorophenol) and used as received to aid in the HPLC identification of intermediate species that might likely form from the photocatalytic processes. Ethylenediaminetetraacetic acid (H$_4$EDTA), TEA, and IPA were Fisher reagents; PEI (ca. 1220 monomers per molecule) was obtained from Sigma. The concentrations of these hole scavengers were: 1×10^{-3} mol l^{-1} for H$_4$EDTA, 2 g l^{-1} for PEI, 2% v/v for both TEA and IPA to give the effective concentrations of the scavenging sites for each as listed in Table 1. Titanium dioxide (P-25) and aluminium oxide C were kindly provided by Degussa Canada Ltd. and were used as received. Silicon dioxide was from Fluka; it

Scheme 2. Reaction between the hydroxyl radical and the 2,4-DCP anion yielding ultimately the 2-chloro-p-semiquinone radical anion.

Table 1
Concentrations of hole scavengers used and effective concentrations of the hole scavenging sites

Hole scavengers	EDTA^{4-} [a]	PEI	TEA	IPA
Concentration (mol l^{-1})	1.00×10^{-3}	4.02×10^{-5}	0.144	0.261
Number of scavenging sites per molecule (or polymeric unit)	4	1220[b]	1	1
Effective concentration of scavenging sites (mol l^{-1})	0.004	0.049	0.144	0.261

[a] Preponderant form of H$_4$EDTA at pH 3; pK_as are 0.0, 1.5, 2.0 and 2.66 for the carboxylic functions and 6.16 and 10.24 for the ammonium functions (see [42]).

[b] Average number of monomers in a polymeric unit.

was ground, sonicated in 100 ml of water, filtered and dried in air for 15 h and subsequently ground again before use. Acetonitrile (BDH, Omnisolv grade) and doubly distilled water were used as HPLC solvents. The pH (Corning glass electrode) was adjusted either with H$_2$SO$_4$ or NaOH, as required.

Unless noted otherwise, 50 ml of a solution at a given pH was stirred with 0.10 g of TiO$_2$ (or SiO$_2$ or Al$_2$O$_3$) giving a 2 g l^{-1} loading in a pyrex reactor for ca. 30 min prior to irradiation to allow the particles and the substrates to equilibrate. For reactions carried out after a "long dark time", the dispersion was stirred in the dark for ca. 150 min before irradiation. The reactor was left open to air for reactions performed under air-equilibrated conditions. For reactions carried out in an argon atmosphere, the pyrex reactor was sealed with a rubber septum followed by purging with "high purity grade" argon gas at 50 ml s^{-1} throughout the entire reaction period. All experiments were carried out at pH ca.3.

The irradiation source was a 1000 W Hg/Xe lamp operated at 825 W with a power density of 170–190 mW cm^{-2} at the reactor (coherent radiation 210 power meter). A water jacket was used to filter out IR radiation. 2 ml samples were collected periodically, and filtered through a MSI 25 mm nylon membrane (pore size 0.22 μm) prior to liquid chromatographic, Cl$^-$ ion and UV spectral analyses. Dispersions were continually stirred during irradiation.

HPLC analyses of products from the reaction with 2,4-DCP were done on a Waters chromatograph (501 HPLC pump, 441 absorbance detector, and a HP-3396A integrator). A Whatman Partisil ODS 3, C-18 reverse phase column was employed at ambient temperature; the detection wavelength was 214 nm. The mobile phase consisted of CH$_3$CN/H$_2$O/H$_3$PO$_4$ at a ratio of 40:60:0.1 v/v. The flow rate was 2.3 ml min^{-1} and the pressure was 1×10^3 lb/in.^{2}. Chloride ion analyses were done using a Canadawide specific chloride ion electrode; the calibration was done using solutions of Fisher Certified NaCl. UV absorption measurements were carried out on a Shimadzu UV-265 spectrophotometer also equipped with an integrating sphere assembly to record reflectance spectra of samples deposited on Whatman filters (BaSO$_4$ was the reference standard).

In this study, the term "hole" signifies either the photo-generated charge carrier in the valence band of the semiconductor or the surface trapped hole (h$_t^+$; i.e. the $^\bullet$OH radical).

3. Results and discussion

3.1. Spectra and post-irradiation effect

An aqueous dispersion containing titania is typically white when irradiated with light at wavelengths below the bandgap energy (3.2 eV; λ = 385 nm) whether the system is aerated or argon-purged. However, when the irradiated titania dispersion also contains a hole scavenger (Table 1) the color changes dramatically to blue-violet, the intensity of which depends on the period of irradiation and on the nature of the hole scavenger (see Table 2). The hole scavengers appear to range in the order PEI > EDTA > TEA ∼ IPA. The appearance of this color correlates with the reflectance

Table 2
Intensities of the color change from white to violet on irradiation of an oxygen-free TiO$_2$ dispersion in the presence of a hole scavenger[a]

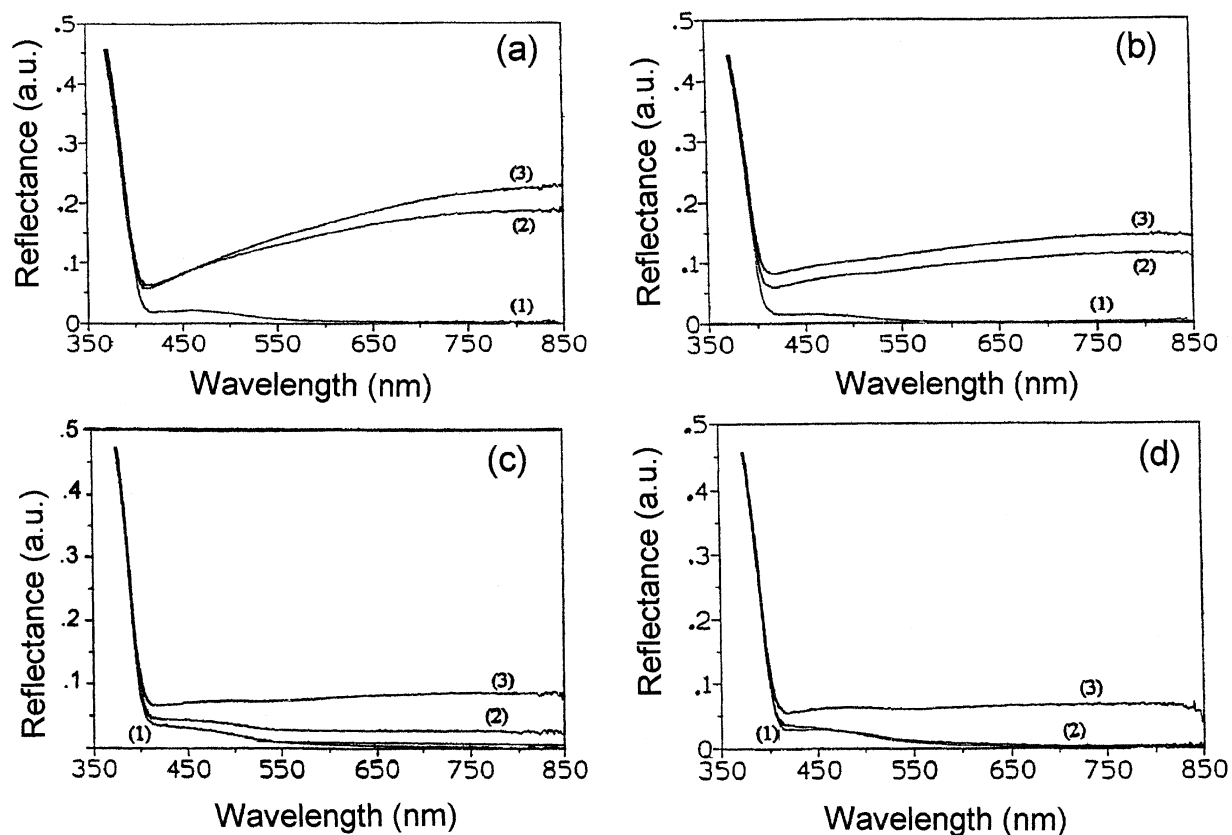| Irradiation time (min)	TiO$_2$ alone	TiO$_2$ + EDTA	TiO$_2$ + PEI	TiO$_2$ + TEA	TiO$_2$ + IPA
0	0	0	0	0	0
5	0	m	s	0	0
10	0	s	vs	0	0
180	0	s	vs	m	m

[a] m: medium; s: strong; vs: very strong.

Fig. 1. Reflectance spectra of TiO$_2$ aqueous dispersions in the presence of a hole scavenger under an argon atmosphere. Spectra (1) taken before irradiation; spectra (2) taken after 15 min of irradiation; and spectra (3) recorded after 180 min of illumination. Conditions: TiO$_2$ loading = 2 g l^{-1}, pH 3; (a) [PEI] = 2 g l^{-1}; (b) [EDTA] = 1 × 10^{-3} M; (c) [TEA] = 2% v/v; (d) [IPA] = 2% v/v.

spectra of the titania particulates which displayed a monotonic increase in absorption with increasing wavelength from ca. 400–850 nm (the limit of our spectrophotometer). The relevant spectral results for the TiO$_2$/PEI, TiO$_2$/EDTA, TiO$_2$/TEA and TiO$_2$/IPA systems are presented in Fig. 1a, b, c, and d, respectively, for periods of 0, 15 and 180 min of irradiation. The significant rise in absorption below 400 nm is due to the usual intrinsic bandgap absorption of titania. The spectral intensities above 400 nm correlate with the qualitative observations reported in Table 2; we found no correlation between the concentration of the hole scavenging sites and the absorption intensity at 800 nm.

Irradiated titania dispersions containing PCP and 2,4-DCP under an argon atmosphere remained white throughout. However, when a hole scavenger was also added, the dispersion turned rapidly blue-violet. The color persisted during the entire irradiation period and its intensity was similar to those described in Table 2. This was born out by reflectance spectral results illustrated in Fig. 2a for dispersions containing EDTA (spectrum **a**), EDTA and 2,4-DCP (spectrum **b**), and EDTA and PCP (spectrum **c**) after 15 min of irradiation. The increased absorption from spectrum **a** to spectrum **b** is likely due to the formation of some highly absorbing intermediate species in the 500–700 nm region adsorbed onto the TiO$_2$ particles. This increased absorption is even more

pronounced in spectrum **c**, which may be due to the presence of tetrachlorobenzoquinone derived from the degradation of PCP. This intermediate has a broad band centered around 550 nm (Fig. 3); for comparison, the spectra of PCP and another possible intermediate product tetrachlorocatechol are also reported. Fig. 4 illustrates the absorption spectrum of 2,4-DCP and two potential intermediate products (chlorohydroquinone and chloro-*p*-benzoquinone) that might result from the degradation of the dichlorophenol.

Fig. 2b shows the reflectance spectral changes that occurred when an argon-purged aqueous TiO$_2$ dispersion containing the hole scavenger EDTA and the PCP substrate is irradiated for periods of 0–180 min (spectra **b–d**). After 15 min, spectrum **b** shows the band at 575 nm for the tetrachlorobenzoquinone intermediate which degrades on further illumination to 75 min (spectrum **c**). Continued irradiation under argon leads to a further increase in absorption again with a band at 550–575 nm (spectrum **d**) superposed on the very broad band from ca. 400 to 850 nm. We attribute the former to a lesser chlorinated benzoquinone species.

Under the conditions used for the spectra of Fig. 1b–d, removal of the septum from the reactor so as to expose the dispersion to air led to an immediate bleaching of the colored dispersion. However, the dispersion containing the PEI hole scavenger necessitated 10–15 min exposure to air to
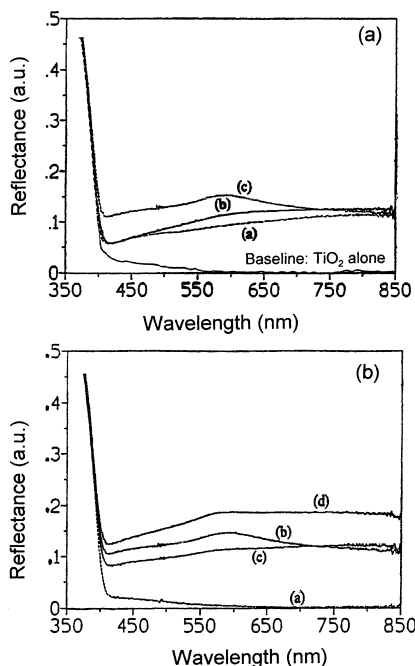
Fig. 2. (a) Reflectance spectra after 15 min of illumination under an argon atmosphere of TiO$_2$ particles in an aqueous dispersion containing (**a**) EDTA, (**b**) EDTA and 2,4-DCP, and (**c**) EDTA and PCP. Conditions: TiO$_2$ loading $= 2\,g\,l^{-1}$; [EDTA] $= 1 \times 10^{-3}\,M$; [2, 4-DCP]$_o$ $= 96\,\mu M$; [PCP]$_o$ $= 55\,\mu M$; pH 3. (b) Reflectance spectra of irradiated TiO$_2$ particles (loading $= 2\,g\,l^{-1}$) under an argon atmosphere in solution with EDTA ($1 \times 10^{-3}\,M$) and PCP ($55\,\mu M$); pH 3: (**a**) before irradiation; (**b**) after 15 min irradiation; (**c**) after 75 min illumination; and (**d**) after 180 min of irradiation.

cause a similar bleaching of the coloration. The nature of the broad absorption and blue-violet coloration in such a dispersion was examined further at PEI concentrations and TiO$_2$ loading of $10\,g\,l^{-1}$. The inset to Fig. 5a summarizes the first-order temporal growth of the coloration at 800 nm ($k_{rise} = 0.15 \pm 0.02\,min^{-1}$) which reaches maximal intensity after 30 min of irradiation, subsequent to which irradiation was stopped. Interestingly, growth of the band continued in the dark. After 45 min, the contents of the reactor were
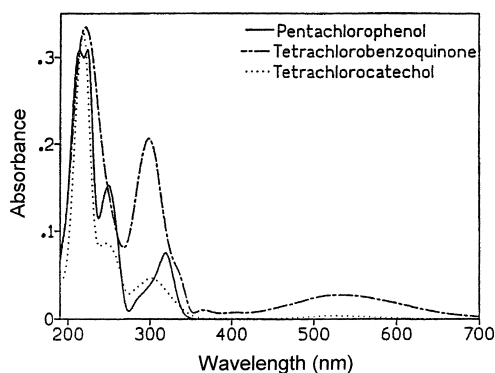

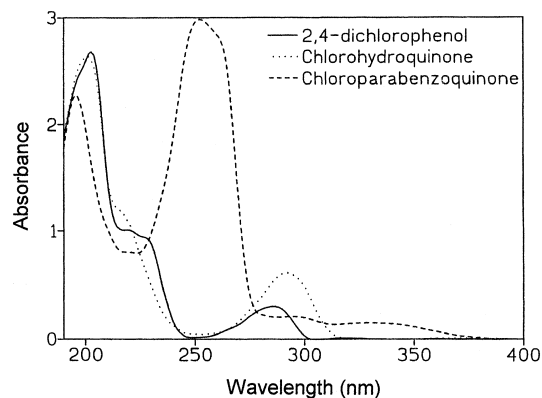Fig. 3. UV–VIS spectra of PCP and expected intermediates: tetrachlorobenzoquinone and tetrachlorocatechol.

Fig. 4. UV–VIS spectra of 2,4-DCP and expected intermediate products: chlorohydroquinone and chloro-*p*-benzoquinone.

exposed to air and irradiation was restarted. This led to a biphasic decay of the 400–850 nm broad band (refer to Fig. 1a). A similar behavior was observed when the colored TiO$_2$ particulates were placed on a Whatman filter and exposed to air in the dark (Fig. 5b). Again the color (as evidenced by the decay of the band monitored at 800 nm)
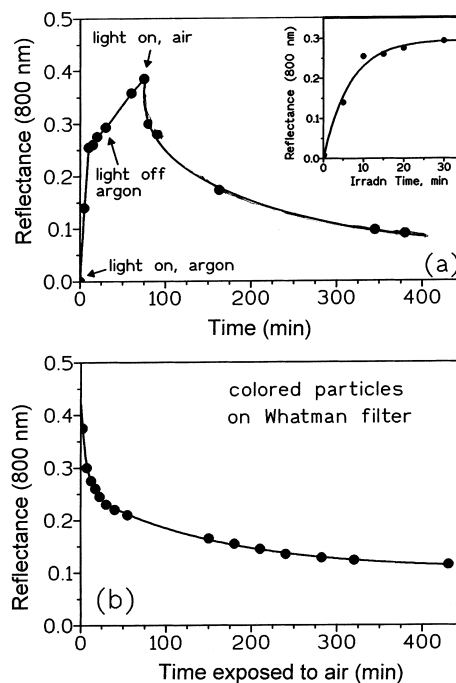

Fig. 5. (a) Biphasic decay of the reflectance at 800 nm under air for an irradiated argon-purged aqueous dispersion at pH 3 containing TiO$_2$ (loading $= 10\,g\,l^{-1}$) and the PEI hole scavenger ($10\,g\,l^{-1}$). Inset depicts the growth of the reflectance at 800 nm vs. irradiation time (min). Solid circles represent specimens kept in the dark but under air; nearly identical results were obtained from specimens taken from irradiated dispersions and placed under air. (b) Evolution of the reflectance at 800 nm for the argon-purged aqueous TiO$_2$ (loading $= 10\,g\,l^{-1}$) dispersion at pH 3 containing PEI ($10\,g\,l^{-1}$). All data points were obtained with the TiO$_2$ particulates from the dispersion and analyzed 2.5 min after the 2-ml samples were collected (time needed to sample, filter and set-up the specimen for spectra collection with the integrating sphere assembly).
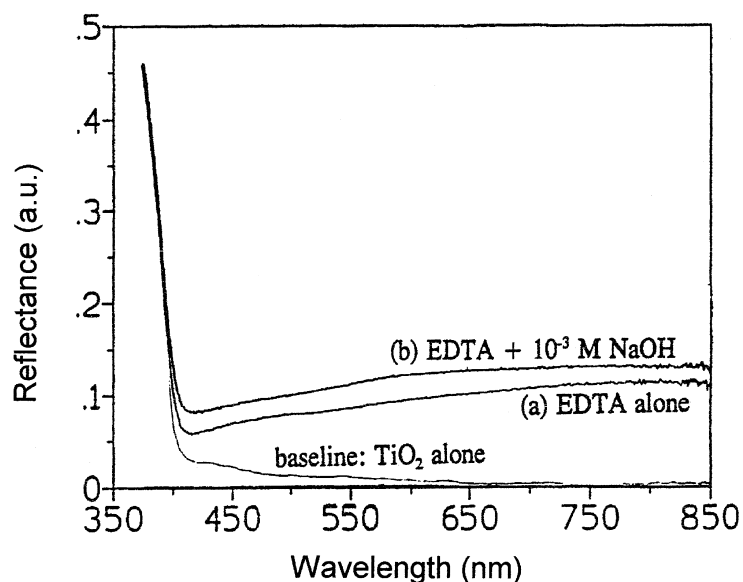
Fig. 6. pH effect on the reflectance spectra of irradiated TiO$_2$ particulates (loading in the titania dispersion, $2\,g\,l^{-1}$) in the presence of EDTA (1×10^{-3} M) and under an argon atmosphere: (**a**) TiO$_2$ + EDTA; (**b**) TiO$_2$ + EDTA + 1 mM NaOH.

disappeared via fast and slow decay kinetics with an even slower decay at very long times (several more hours): $k_{fast} = 0.15 \pm 0.01\,min^{-1}$ ($t_{1/2} = 5\,min$) and $k_{slow} = 6.4 \pm 0.7 \times 10^{-3}\,min^{-1}$ ($t_{1/2} = 109\,min$)[1]. Note that the strong intense blue-violet coloration was attenuated significantly after ca. 15–20 min of exposing the aqueous dispersion to air (i.e. half-lives 3–4), whereas longer times were needed to achieve a similar attenuation for the particles on the Whatman filter.

The blue-violet color of such titania dispersions which display the broad band in the spectra of Figs. 1 and 2, and again repeated in Fig. 6 for alkaline dispersions (1 mM NaOH; spectrum **b**), is reminiscent of the coloration and spectra of (i) irradiated TiO$_2$ colloidal sols in oxygen-free environments [14] and in the presence of PVA capable of hole scavenging [13,26], and (ii) of nanostructured TiO$_2$ electrodes under weak and strong accumulation of electrons produced electrochemically [27]. Irradiated TiO$_2$ sols displayed a broad band at ca. 700 nm at pH 3 shifting to 800 nm in alkaline media (pH 10) [13]. Such spectral changes may be caused either by free electrons in conduction band states of the semiconductor or by trapped electrons at titanium(IV) sites in TiO$_2$ particles [13,28–31] with the charge being compensated by surface adsorption of H$^+$ ions in the Helmholtz layer [32]. The monotonic absorbance increase in the TiO$_2$ electrodes originated with intra- and inter-band transitions of electron accumulated in conduction band states [27], and the

pH dependence of the band with electrons localized in surface states [33]. Interestingly, the onset potentials for charge accumulation and coloration efficiency were independent of electrolyte composition [27]. Curiously, however, these authors found no spectral evidence for electron trapping in nanostructured TiO$_2$ electrodes under weak accumulation conditions because of the low content of surface Ti^{IV} states [34] that could act as electron traps (ca. 4%) with the remainder lying in the particle bulk as conduction band states.

In the present instance, the lack of any pH-dependent spectral shifts infers that the number of reductive species (free or trapped electrons) at the TiO$_2$/solution interface may not be significant. Rather, they are more likely trapped in sub-surface sites [13]. In their low-temperature EPR studies, Howe and Gratzel [30] identified no less than four different species arising from trapped electrons, in line with earlier EPR results obtained under different conditions [31]: (i) interstitial Ti^{3+} in the particle bulk and (ii) three different Ti^{3+} sites located on the particle surface that can impart an intense blue coloration to TiO$_2$ particles. The several decays seen in Fig. 5b would be consistent with the above in that the faster decay may arise from scavenging of electrons by air oxygen diffusing onto the particle surface in spite of the barrier posed by the hole scavenger PEI. The slower decays may involve the sub-surface electrons requiring O$_2$ to diffuse into the crystalline bulk and react with electrons in sub-surface sites/traps deeper in energy than the O$_2$/O$_2^{\bullet-}$ redox couple (see Scheme 3).
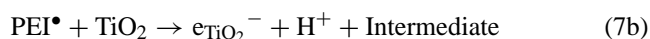
Most important about the data of Fig. 5a is the absorption growth in the dark. Photochemically this represents a post-irradiation effect by which termination of irradiating the dispersion leads to additional absorption. We attribute this absorption increase to transfer of additional electrons

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[1] For these experiments, 2-ml samples were collected at various time intervals and filtered onto a Whatman filter followed by recording the reflectance spectrum. The time for the handling was ca. 2.5 min. For the results displayed in Fig. 5a, the reactor contents were sampled several times with new TiO$_2$ particulates examined with or without irradiation. By contrast, the data reported in Fig. 5b refer to the behavior of one sample on a Whatman filter left in the dark exposed to air and for which the reflectance spectrum was monitored at various time intervals.
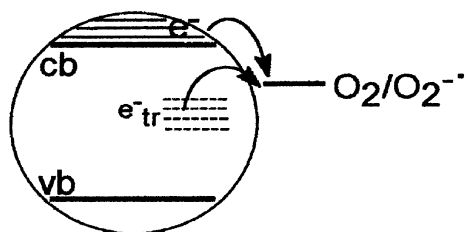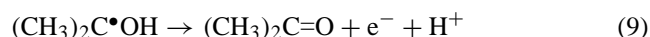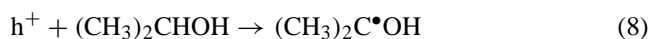
Scheme 3. Cartoon illustrating the scavenging of conduction band electrons and trapped electrons to yield the superoxide radical anion.

onto TiO_2 particles from a $PEI^\bullet$ radical formed by hole scavenging (Eq. (7)).

$$PEI^{\bullet+} \rightarrow H^+ + PEI^\bullet \tag{7a}$$

$$PEI^\bullet + TiO_2 \rightarrow e_{TiO_2}{}^- + H^+ + \text{Intermediate} \tag{7b}$$

This process is analogous to the "doubling current phenomena" reported for ZnO [35] and TiO_2 [36] semiconductor electrodes, whereby the measured anodic current is twice that expected when a hole scavenger (e.g. IPA) is present and the system is oxygen-free (see, for example Eqs. (1), (8) and (9)).

$$h^+ + (CH_3)_2CHOH \rightarrow (CH_3)_2C^\bullet OH \tag{8}$$

$$(CH_3)_2C^\bullet OH \rightarrow (CH_3)_2C{=}O + e^- + H^+ \tag{9}$$

3.2. Degradation of 2,4-DCP

3.2.1. Direct photolysis of 2,4-DCP

Fig. 7 illustrates the temporal course of the direct photolysis of 2,4-DCP under different conditions: (i) substrate alone in air-equilibrated media ($k = 0.16 \pm 0.01\,\mu M\,min^{-1}$; $k_{Cl} = 0.10 \pm 0.01\,\mu M\,min^{-1}$), (ii) substrate in argon-purged

aqueous media ($k = 0.28 \pm 0.01\,\mu M\,min^{-1}$), and (iii) the substrate in the presence of EDTA in argon-purged media ($k = 0.017 \pm 0.004\,min^{-1}$; $k_{Cl} = 0.17 \pm 0.03\,\mu M\,min^{-1}$). No dechlorination occurred in the argon-purged solutions (ii). In air-equilibrated media, the extent of degradation is consistent with the extent of dechlorination (ca. 44%, loss of one Cl function). As well, oxygen slows down the degradation nearly two-fold. The results infer there exist different degradative pathways in the direct photolysis of this dichlorophenol. In this regard, Boule and coworkers [1,37] identified products arising by the photocontraction of the ring and to loss of one chlorine function. By contrast, Plimmer and Klingebiel [38] reported tetrachlorophenoxyphenols and tetrachlorodihydroxybiphenyls as intermediate products (no dechlorination) from the Riboflavin photosensitized oxidation of 2,4-DCP. In the present work, HPLC analyses revealed three intermediates, none of which could be identified with expected aromatic functions. The presence of EDTA during photolysis led to the same intermediates but at longer irradiation times.

3.2.2. Degradation of 2,4-DCP in various UV-irradiated metal-oxide dispersions

3.2.2.1. Air-equilibrated TiO_2 dispersions.
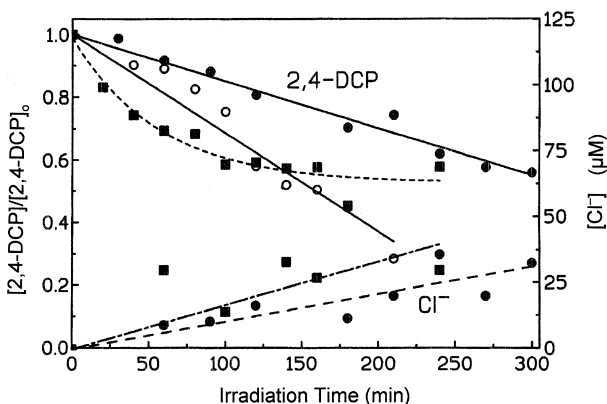The temporal course of the degradative process is depicted in Fig. 8a

Fig. 7. Degradation of 2,4-DCP under direct UV photolysis and various other conditions (no photocatalyst used): data denoted by solid circles are from air-equilibrated solutions in the absence of EDTA; empty circles represent data for argon-purged solutions in the absence of EDTA; and the solid squares denote data points obtained for an argon-purged solution in the presence of EDTA. The graph also summarizes formation of chloride ions for the corresponding solutions. Note that no chloride was formed or detected for the argon-purged solution without EDTA.
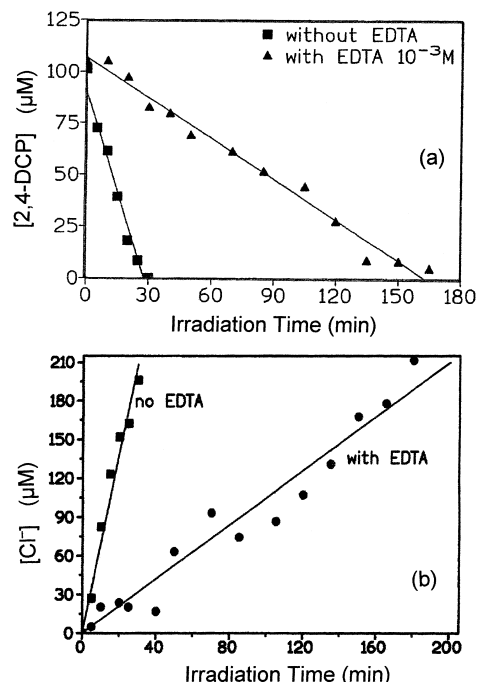

Fig. 8. (a) Zero-order degradation of 2,4-DCP on TiO_2 particles in the absence (solid squares) and presence of EDTA (1×10^{-3} M; solid triangles) under air-equilibrated conditions; [2, 4-DCP]$_0$ = 105 μM (solid triangles) and 96 μM (solid squares); TiO_2 loading = 2 g l^{-1}; pH 3. (b) Zero-order evolution of chloride ions as a function of irradiation time from the dispersions noted above in the presence of 1 mM EDTA (solid circles) and without EDTA (solid squares).
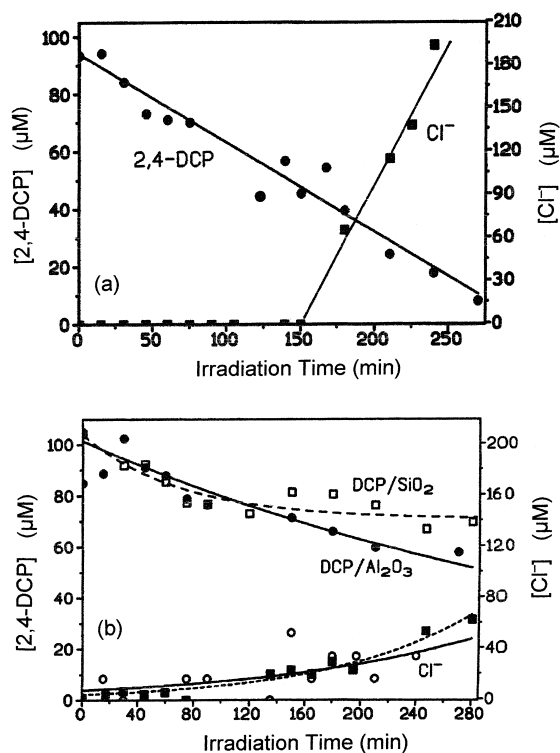
Fig. 9. Degradation of 2,4-DCP and chloride ion generation in various argon-purged aqueous metal-oxide (loading $= 2\,g\,l^{-1}$) dispersions at pH 3. (a) $[2,4\text{-DCP}]_o = 96\,\mu M$; (b) data points depicted by squares are for the SiO$_2$ dispersions; circles depict data for the Al$_2$O$_3$ dispersions; $[2,4\text{-DCP}]_o = 105\,\mu M$.

and the temporal evolution of chloride ions is illustrated in Fig. 8b for dispersions with and without EDTA, respectively. Both degradation and chloride formation take place by apparent zero-order kinetics: in the absence of EDTA, $k = 3.4 \pm 0.2\,\mu M\,min^{-1}$ and $k_{Cl} = 6.9 \pm 0.03\,\mu M\,min^{-1}$, whereas with EDTA, $k = 0.66 \pm 0.02\,\mu M\,min^{-1}$ and $k_{Cl} = 1.05 \pm 0.04\,\mu M\,min^{-1}$. Clearly, EDTA has a five-fold retardation effect on the degradation. Similar inhibitions have been reported, e.g. phenol with respect to nitrobenzene [39]. Whatever the nature of the intermediates, dechlorination is nearly complete.

3.2.2.2. Argon-purged TiO$_2$ dispersions.

Fig. 9a presents the loss of the dichlorophenol ($k = 0.31 \pm 0.02\,\mu M\,min^{-1}$), about 90% after 270 min of irradiation, and evolution of the same extent of dechlorination ($k_{Cl} = 2.01 \pm 0.07\,\mu M\,min^{-1}$) albeit preceded by an induction period of ca. 150 min. The absence of molecular oxygen in the dispersion causes a 10-fold retardation of the degradation (see Section 3.2.2.1) and chloride formation is three times slower. Also, worth noting is the loss of 2,4-DCP at the same rate as for direct photolysis ($k = 0.28 \pm 0.01\,\mu M\,min^{-1}$) which perhaps fortuitous may infer that direct photolysis in titania dispersions cannot be precluded entirely. Consequently, we examined this possibility by investi-

gating the degradation in non-photosensitive metal-oxide dispersions.

3.2.2.3. Argon-purged SiO$_2$ and Al$_2$O$_3$ dispersions.

Degradation under these conditions appears to be inhibited considerably with respect to the TiO$_2$ system, under otherwise identical conditions, and the loss kinetics are apparent first-order. For SiO$_2$ dispersions, $k = 0.014 \pm 0.004\,min^{-1}$ and $k_{Cl} = 0.0098 \pm 0.0009\,min^{-1}$, whereas for Al$_2O_3$ systems, $k = 0.0024 \pm 0.0003\,min^{-1}$ and $k_{Cl} = 0.006 \pm 0.003\,min^{-1}$. Consequently, we deduce that direct photolysis may in fact have little importance in the degradation of the dichlorophenol in argon-purged titania suspensions, even though in all four cases (direct photolysis and Sections 3.2.2.1–3.2.2.3) HPLC analyses showed intermediates formed with identical retention times at 2.2, 3.25 and 5.0 min. The TiO$_2$ system also showed an additional intermediate at a retention time of 1.75 min. We were unable to positively identify the nature of these products. None were the expected hydroquinones, catechols or benzoquinones. Related to this, a radiolytic study of the degradation of 4-chlorophenol by •OH radicals reported only non-aromatic products and a small quantity of polymerized phenols identified by gas chromatography–mass spectrometry (GC–MS) techniques [22].

3.2.3. Influence of hole scavengers on the degradation of 2,4-DCP in UV-irradiated TiO$_2$ dispersions

3.2.3.1. Dispersions equilibrated for ca. 30 min in the dark.
The temporal changes in the concentration of 2,4-DCP in the absence and presence of three of the hole scavengers (PEI, TEA and IPA) used are summarized in Fig. 10. No degradation of 2,4-DCP occurred within 270 min of irradiation of the argon-purged dispersions compared to a dispersion with no
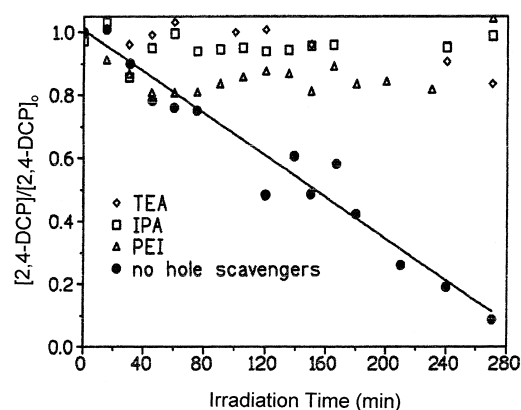

Fig. 10. Graph illustrating the influence of the hole scavengers on the degradation of 2,4-DCP in irradiated argon-purged TiO$_2$ dispersions (loading $= 2\,g\,l^{-1}$; pH 3) — solid circles: no hole scavengers present; empty triangles: PEI and $[2,4\text{-DCP}]_o = 96\,\mu M$; empty squares: IPA and $[2,4\text{-DCP}]_o = 105\,\mu M$; empty diamonds: TEA and $[2,4\text{-DCP}]_o = 105\,\mu M$.
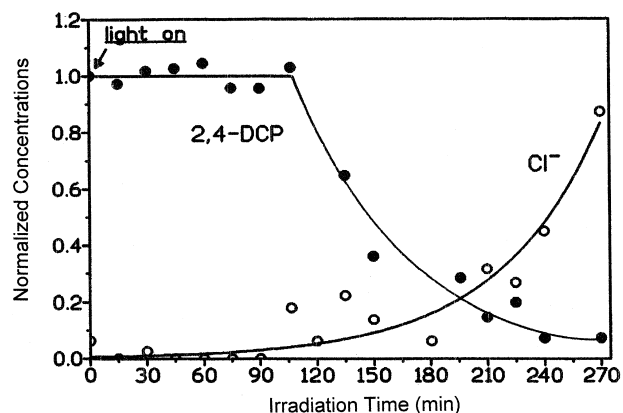
Fig. 11. Time evolution of the degradation of 2,4-DCP and chloride ion formation in irradiated argon-purged aqueous titania (loading $= 2\,g\,l^{-1}$) dispersions in the presence of 1 mM EDTA; pH 3 and $[2, 4\text{-DCP}]_o = 96\,\mu M$.

hole scavenger present; for the latter, degradation was nearly 90% complete within this time ($k = 0.31 \pm 0.02\,\mu M\,min^{-1}$). Under otherwise identical conditions, in the presence of EDTA (Fig. 11), however, after a 120-min induction period, about 95% degradation of the dichlorophenol ($k = 0.017 \pm 0.002\,min^{-1}$) and evolution of chloride ($k_{Cl} = 0.036 \pm 0.002\,min^{-1}$) take place via first-order kinetics. During the induction period, no changes occurred under irradiation.

The inhibition of the degradation of dichlorophenol by the PEI, TEA and IPA hole scavengers, and to some extent EDTA, infers that degradation of 2,4-DCP in argon-purged TiO$_2$ dispersions may involve ultimately oxidation by the photogenerated surface-bound $^\bullet$OH radicals. Three points must be considered to account for the results. (1) Competition between the hole scavengers and the 2,4-DCP for adsorption to the TiO$_2$ surface sites. A strongly bound hole scavenger may diminish or even suppress completely adsorption of 2,4-DCP. (2) Competition for the photogenerated holes between 2,4-DCP and the scavenger. (3) The existence and accumulation of photogenerated electrons on the TiO$_2$ particle surface (Fig. 1) when hole scavengers are present in the argon-purged aqueous dispersions.

PEI is a viscous liquid and is strongly adsorbed on TiO$_2$ particles. In its presence, the concentration of accumulated electrons is significant and 2,4-DCP has little chance to adsorb onto TiO$_2$ and react with photogenerated charge carriers. For TEA and IPA scavengers, less efficient in the extent of accumulated electrons (Fig. 1), the [e$^-$] may be too low for any significant reaction with these reductive species.

EDTA presents a rather peculiar case. Degradation of 2,4-DCP begins only after 120 min of irradiation. The oxidative species (i.e. $^\bullet$OH radicals) which degraded the 2,4-DCP in a TiO$_2$/2,4-DCP argon-purged dispersion cannot be at the origin of the degradation of the phenol after the induction period. First, it is unlikely that EDTA would stop scavenging these $^\bullet$OH radicals after 120 min of irradiation inasmuch as the concentration of this hole scavenger was ten times greater than that of 2,4-DCP (1 mM versus ca. 0.100 mM,

respectively). Second, the degradation kinetics are zero-order in the absence of EDTA but first-order in its presence, for experiments carried out under otherwise identical conditions. It took about 300 min of irradiation to achieve ca. 90% degradation in the absence of EDTA, whereas it required only ca. 150 min after the induction period to achieve the same level of degradation of 2,4-DCP in the presence of EDTA. Third, when EDTA is present in the dispersion, dechlorination occurs concomitantly with degradation of 2,4-DCP, whereas in the absence of this scavenger, dechlorination started only after ca. 150 min from the beginning of the degradation of the phenol (see Fig. 9a). Fourth, the intermediate products formed during the 2,4-DCP degradation in the presence of EDTA are different (as attested by HPLC retention times) from those produced in the absence of EDTA.

From Scheme 1, it is possible to tentatively deduce what intermediates may be formed in dispersions in the absence of EDTA (and other hole scavengers). This is shown in Eq. (10).

$$\tag{10}$$
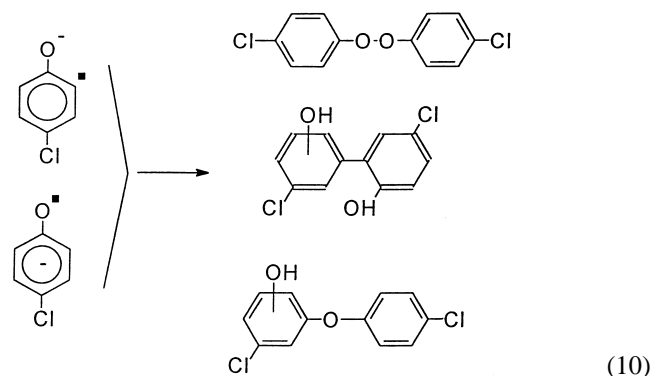
In the presence of EDTA, both radicals in Eq. (10) may also react with EDTA$^{\bullet+}$ to produce other species.

The rate of degradation of 2,4-DCP in an air-equilibrated titania dispersion in the presence of EDTA is two to three times slower ($k = 0.66 \pm 0.02\,\mu M\,min^{-1}$) than in argon-purged dispersions ($k \sim 1.6\,\mu M\,min^{-1}$), under otherwise identical conditions. This suggests that EDTA and 2,4-DCP compete for the photogenerated oxidative species more effectively in air-equilibrated media than in argon-purged media, and there is also significant competition between O$_2$ and 2,4-DCP for the photogenerated electrons; the latter competition is obviously suppressed in argon-purged dispersions [2].

3.2.3.2. Dispersions equilibrated for longer times in the dark (EDTA present).
As noted earlier, the 120-min induction period prior to the initiation of the degradation of 2,4-DCP was rather unusual. We, therefore, examined this aspect and sought to further understand the influence that the

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[2] We cannot entirely preclude reaction between 2,4-DCP and any radical species formed from hole scavenging by EDTA; in this latter case, the 120-min induction period may then be needed to produce a significant concentration of EDTA$^{\bullet+}$ species.

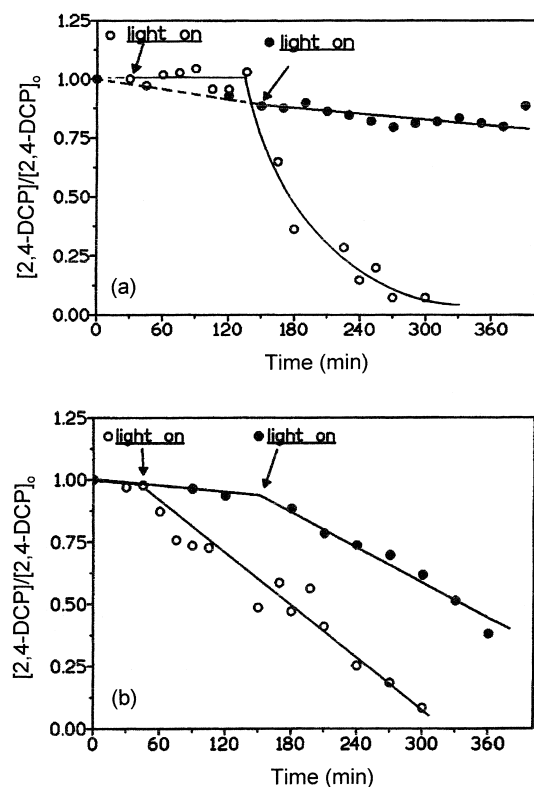Fig. 12. (a) Influence of the dark stirring time prior to irradiation on the degradation of 2,4-DCP (96 μM) on TiO$_2$ particles (loading = 2 g l^{-1}) in the presence of EDTA (1 × 10^{-3} M) in argon-purged dispersions (pH 3). Empty circles refer to a dispersion stirred for 30 min before irradiation; full circles depict a dispersion stirred for 150 min before irradiation. (b) Influence of the dark stirring time prior to irradiation on the degradation of 2,4-DCP on TiO$_2$ particles (loading = 2 g l^{-1}) in the absence of EDTA in argon-purged dispersions at pH 3. Empty circles denote the dispersion was stirred for 45 min in the dark before irradiation and [2, 4-DCP]$_o$ = 96 μM; full circles describe a dispersion stirred in the dark for 150 min prior to illumination and [2, 4-DCP]$_o$ = 105 μM.

time needed for prior equilibration of the dispersion components might have on the subsequent course of the degradation.

Fig. 12b illustrates the outcome of stirring an argon-purged TiO$_2$/2,4-DCP dispersion containing no EDTA. The zero-order kinetics of degradation of 2,4-DCP were very similar (k = 0.31 ± 0.02 μM min^{-1} versus k = 0.24 ± 0.02 μM min^{-1}) whether the dispersion was pre-equilibrated in the dark for 45 or 150 min, respectively. By contrast, for identical dispersions but with 1 mM EDTA present, the different equilibration times in the dark led to significantly different behavior as illustrated in Fig. 12a. When the dispersion was pre-equilibrated for only ca. 30 min prior to irradiation, there ensued a 120-min induction period prior to the first-order degradation of 2,4-DCP. However, when the dispersion was equilibrated for 150 min prior to irradiation, degradation was very slow and followed zero-order kinetics (k = 0.035 ± 0.007 μM min^{-1}). We presume that this longer equilibration period allowed the hole scavenger EDTA to completely block nearly all the titania

particle surface sites, thereby excluding 2,4-DCP from the relevant surface sites and rendering any interaction with the reductive species less efficient.

4. Conclusions

We have revisited the interaction of two chlorinated phenols (2,4-DCP and PCP) with titania aqueous dispersions under a variety of conditions to examine whether the photogenerated electrons play a role during the photocatalytic degradation of this type of aromatic pollutants. Photo-electrons generated during irradiation of argon-purged titania dispersions in the presence of suitable hole scavengers (PEI, EDTA, TEA and IPA) accumulate on the particle surface in sufficient quantities as evidenced by a medium to very strong blue-violet coloration of the particulates and by reflectance spectral measurements. The efficiency of such accumulation appears to be EI > EDTA > TEA ~ IPA. Most importantly, a post-irradiation effect was discovered when a titania dispersion containing the PEI hole scavenger was irradiated for ca. 45 min and then irradiation terminated, reminiscent of the doubling current phenomena for semiconductor electrodes. The coloration lasted several hours (reflectance spectra), probably owing to poor diffusion of oxygen through the PEI coating of the surface. For the other hole scavengers, discoloration of the blue-violet particles was almost immediate.

In the presence of PEI, TEA and IPA hole scavengers, no degradation of 2,4-DCP occurred within 4.5 h of irradiation; however, for EDTA the 2,4-DCP removal began only after 2 h in argon-purged titania dispersions. Photogenerated electrons may also play a role in the photocatalytic degradation of chlorinated phenols, hereto reported only for aliphatic chlorinated substrates (see, for example [11,40]) and a hexachlorocyclohexane isomer (lindane) [41]. Under the conditions used, none of the products evidenced by HPLC retention times are those typically found (hydroquinones, catechols and benzoquinones) in photocatalyzed processes carried out in aerated aqueous media. Considering the species illustrated in Scheme 2, it is not unlikely that the nature of some of the intermediate products might be hydroxybiphenyls, diphenyl ethers, and peroxides.

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