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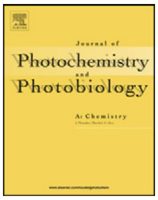

Molecular dynamics simulations of adsorption of hydrophobic 1,2,4-trichlorobenzene (TCB) on hydrophilic TiO_2 in surfactant emulsions and experimental process efficiencies of photo-degradation and -dechlorination

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ABSTRACT

Molecular dynamics simulations have been carried out to assess event details in the adsorption of the hydrophobic substrate 1,2,4-trichlorobenzene (TCB) on the hydrophilic TiO_2 particle surface in the presence of the biosurfactant 4-O-(4′,6′-di-O-acetyl-2′,3′-di-O-alkanoyl-β-D-mannopyranosyl)-D-erythritol (MEL) and the SDS (sodium dodecylsulfate) surfactant in aqueous media at ambient temperature with interaction forces between organic molecules and TiO_2 calculated from Lennard–Jones and Coulomb potential models. The surfactant and the TCB substrate were arranged in the vicinity of TiO_2 using 768 water molecules in the simulations. Results indicate that the MEL molecules adsorb on the TiO_2 surface in ca. 5 ps ($k = 2 \times 10^{11}\ s^{-1}$) through the oxygen atoms of the hydrophilic functions. Contact distance between the MEL and the TiO_2 surface shortened further after 10 ps with adsorption controlled mostly by van der Waals' forces. The TCB molecules are trapped within the alkyl chains of the MEL system, which subsumes TCB to a greater extent by the repulsion of water, thereby facilitating the TCB molecules to approach the highly hydrophilic and positively charged TiO_2 particle surface. Along with the simulations, also examined was the photodegradation of this hydrophobic TCB substrate that takes place at the TiO_2/water interface in the presence of the MEL biosurfactant. For comparison, the advantages of the MEL in this task and of the commonly used SDS surfactant were determined under otherwise identical experimental conditions (200 mg L^{-1} of surfactants) by examining the dynamics of the photo-induced degradation and dechlorination of TCB. The photodegradation of TCB was nearly quantitative in MEL/TiO_2 in contrast to only ca. 22% complete in SDS/TiO_2 dispersions. It is deduced that wastewater treatments with the highly hydrophilic TiO_2 are seriously limited in their photodegradation of hydrophobic pollutants, an issue easily resolvable by the presence of biodegradable surfactants.

1. Introduction

The photodegradation of chlorinated aromatic compounds with metal oxide semiconductors, such as titanium dioxide, occurring through oxidative/reductive processes has been investigated actively for nearly three decades [1,2]. Recent years have witnessed much effort being directed at the detoxification of chloride-containing pesticides in TiO_2 dispersions using solar pilot-scale plants [3]. Most of the reported studies, however, have focused typically on the photodegradation of water-soluble chlorinated pollutants such as 4-chlorophenol and 2,4-dichlorophenoxyacetic acid, among others [4]. Processes were most efficient when the organic pollutants were in direct intimate contact with the TiO_2 surface. Thus, the water solubility of organic pollutants appears to be an important factor underlying process kinetics. Accordingly, the photodegradation of hydrophobic pollutants on a highly hydrophilic TiO_2 surface is expected to present some challenges. In this regard, some studies have described means to circumvent the hydrophobic/hydrophilic issue. For instance, Minero et al. [5] reported that oxygen atoms at or in the vicinity of the TiO_2 surface could be replaced by fluorine atoms in fluorinated acid media, which led to the reforming of the TiO_2 surface and to the

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greatly changed tendency of the surface to adsorb hydrophobic substrates. The study by Yin et al. [6] demonstrated the successful photoreductive dehalogenation of chlorinated benzenes on ZnS nanocrystallite particles in N,N-dimethylformamide (DMF) media under UV irradiation. By contrast, Fabbri et al. [7] circumvented the hydrophobic/hydrophilic issue, so as to have a hydrophobic pollutant (e.g. chlorophenols) approach the hydrophilic TiO_2 surface, by the addition of a surfactant such as sodium dodecylsulfate (SDS). In this regard, TiO_2-mediated photoreactions can lead to mineralization (i.e. to carbon dioxide) of different types of surfactants [8] in competition with targeted pollutants for surface active sites of TiO_2 particles. Dynamics of the degradation of aromatic substrates in media containing alkylated surfactants (e.g. SDS) tend to be relatively slow [9,10]. For instance, the presence of SDS in the photodegradation of 2,4,5-trichlorophenol inhibited both the reaction dynamics and the formation of major aromatic intermediates [7]. Nonetheless, adsorption of surfactants onto the metal oxide surface in the photodegradation of pollutants has some advantages [11]. The use of particular surfactants that can resist oxidation by ${}^{\bullet}OH$ radicals has been proposed by Hidaka et al. [12]. Recent studies from this group examined the photodegradation of a series of cationic and anionic surfactants alone and as mixed surfactant complexes [13–16].

The 1,2,4-trichlorobenzene substrate (hereafter denoted TCB) is a well-known aquatic contaminant often found in potable waters and known to accumulate in soils and underground waters of industrial contaminated sites [17]. It is used industrially as a carrier to apply dyes to polyester materials, as a heat transfer medium, as a degreaser and as a lubricant. It is also used as a termite pesticide and as an aquatic herbicide. About 93% of TCB enters the environment through industrial discharges, albeit it evaporates eventually into the atmosphere, with about 2.6% and 2.4% left in terrestrial soil and aquatic sediments, respectively, and the rest ending up in water [18]. Biodegradation of TCB under aerobic conditions with half-lives of 28–180 days produces succinate and chloroacetate as byproducts, whereas under anaerobic conditions the byproducts are 1,4-dichlorobenzene and chlorobenzene (half-lives, 112–722 days) [19].

Removal of slightly water-soluble TCB-type substrates from aquatic ecosystems by an abiotic methodology presents a rather challenging task unless surfactants such as the anionic SDS and sodium dodecylbenzenesulfonate (SDBS) surfactants are added to the aquatic system at critical micellar concentrations (cmc) to emulsify the hydrophobic pollutants and permit their extraction from soils and underground waters [20]. Accordingly, addition of surfactants can enhance the contact between the TiO_2 surface and the hydrophobic pollutants. However, such surfactants tend to remain in high concentrations after the photodegradation process has ceased, and thus may cause further environmental pollution [21]. To circumvent the latter problem and permit hydrophobic substrates to interact with hydrophilic TiO_2 we examined the possible role of a biosurfactant, such as the glycolipid 4-O-(4′,6′-di-O-acetyl-2′,3′-di-O-alkanoyl-β-D-manno-pyranosyl)-D-erythritol (MEL) surfactant, to achieve such task with the biosurfactant being highly adsorbed on the hydrophilic TiO_2 surface and being easily biodegraded by microorganisms [22].

This article reports first on molecular dynamics simulations carried out with the aim of probing how the MEL biosurfactant might best bring the hydrophobic substrate to, or otherwise close to the hydrophilic metal-oxide surface in comparison with the straight alkyl chain SDS surfactant, and then examines the usage of a saturated aqueous mixture of TCB, a representative member of hydrophobic chlorinated aromatic pollutants, and the biodegradable MEL glycolipid biosurfactant [22,23] with regard to the oxidative/reductive photo-degradation and -dechlorination of TCB in comparison with processes when in the presence of the more commonly used SDS surfactant.

2. Experimental

2.1. Materials and reagents

The glycolipid 4-O-(4′,6′-di-O-acetyl-2′,3′-di-O-alkanoyl-β-D-mannopyranosyl)-D-erythritol was synthesized in aqueous media using a *Pseudozyma antarctica* seed culture and soybean oil by an otherwise synthesis approach reported earlier [22]. Gas chromatographic–mass spectrometric (GC–MS) techniques and matrix-assisted laser desorption/ionization time-of-flight mass spectrometric analyses (MALDI-TOF/MS) revealed a structure of the MEL biosurfactant composed of C8 (38%), C10 (51%) and C12 (11%) fragments, all of which accounted for more than 99% MEL. Reagent grade sodium dodecylsulfate (SDS: $[C_{12}H_{25}OSO_3]^-Na^+$) and 1,2,4-trichlorobenzene were obtained from Tokyo Kasei Kogyo Co. Titanium dioxide was Degussa P-25 with particle size of 20–30 nm (transmission electron microscopy; TEM) of composition 87% anatase and 13% rutile (X-ray diffraction), and with a BET surface area of 53 $m^2\,g^{-1}$ (Brunauer–Emmett–Teller measurements).

2.2. Molecular dynamics simulations

The initial adsorption behaviors of the hydrophobic 1,2,4-TCB substrate and the surfactants on the TiO_2 surface in aqueous media were simulated by a molecular dynamics method. The interaction forces between organic molecules and TiO_2 were calculated using the Lennard–Jones and Coulomb potential models using the reference parameters reported elsewhere [24–29]. The point charges of each atom in the organic molecules were calculated by the MOPAC-2000 software. The point charges for surface oxygen atoms on TiO_2 were 1.267, whereas the charges of other oxygens and titanium atoms were −1.267 and +2.534, respectively [28]. The adsorption behaviors of organic molecules on the TiO_2 surface in aqueous media at ambient temperature were estimated using Leapfrog and RATTLE algorithms [30].

2.3. Photochemical procedures

To a 50-mL aqueous surfactant dispersion in a 124-mL Pyrex glass reactor also containing either 200 $mg\,L^{-1}$ of the MEL biosurfactant (CAC, 0.0040 mM [22]) or 200 $mg\,L^{-1}$ of the SDS surfactant (cmc, 8 mM [31], others report a cmc of 20–30 mM [32]) were added a 100 $mg\,L^{-1}$ saturated aqueous mixture of 1,2,4-trichlorobenzene (water solubility: 38 $mg\,L^{-1}$ [33], 49 $mg\,L^{-1}$ [34,35]; toxicity, oral/rat, LD_{50} 756 mg/kg [35]) and 50 mg TiO_2 particles (1.0 $g\,L^{-1}$). The dispersion was sonicated for ca. 1 min and then purged with oxygen gas for 15 min, following which the solution was exposed to UVA radiation using a 75-W Hg light source (Toshiba SHL l00 UVQ; incident irradiance on reactor, 1.4 $mW\,cm^{-2}$; effective irradiance on dispersions, 0.99 $mW\,cm^{-2}$; wavelength range, 310–400 nm; maximal emission, 360 nm) while being stirred continually by magnetic agitation. Subsequently, unreacted TCB was extracted from the UV-irradiated sample using hexane (50 mL) after being shaken for 15 h in a Taitec Co. BR-23FP bioshaker BR-23FP (speed, 200 rpm). Exploratory control experiments ascertained that the TCB could be extracted quantitatively from the aqueous TiO_2 dispersion by this extraction method. The degradation dynamics of the chlorinated aromatic substrate were monitored both by a Hitachi U-3310 UV–visible spectrophotometer at 226 nm after extraction with hexane and by a gas chromatographic (GC) technique using a Shimadzu Model 2014 chromatograph equipped with an aquatic column and a FID detector. Formation of chloride ions (i.e. dechlorination) from

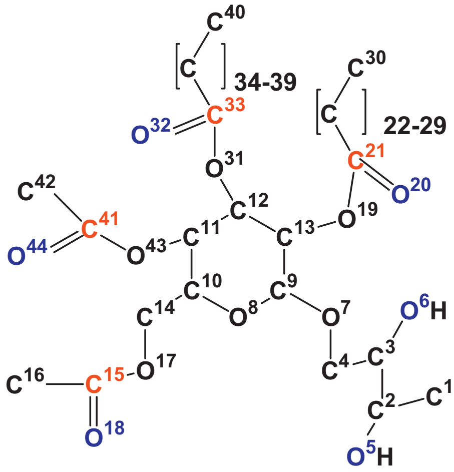

Fig. 1. Structure of the MEL surfactant and the numbering scheme used in the Molecular Orbital calculations of point charges and frontier orbital electron densities. Atoms colored blue are those with the greatest negative charge, whereas those colored red are the atoms with the greatest frontier orbital electron densities. Copyright 2009 by Elsevier B.V. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)
Adapted from Ref. [22].

the degradation of TCB was monitored with a JASCO liquid chromatograph (HPLC) equipped with a CD-5 conductivity detector and the I-524 anion column.

3. Results and discussion

3.1. Adsorption behavior of 1,2,4-TCB on the TiO_2 surface in the presence of surfactants

The initial pH of the dispersions was 6.0, against an iso-electric point (i.e.p.) of ca. 6.5 for P-25 TiO_2 determined by the zeta potential method. Molecular orbital calculations earlier showed that the oxygen atoms in the MEL biosurfactant structure bore the most negative charge [22]. Averaged partial point charges of all the oxygen atoms in the MEL were 6-fold greater (negatively) than the charges on the carbon atoms (Fig. 1). Accordingly, the oxygen atoms in the MEL structure are the positions of closest approach of the biosurfactant to the TiO_2 positive surface.

The initial adsorption behaviors of the surfactant (MEL and SDS) molecules and the TCB molecule, as they approach the TiO_2 surface in aqueous media, are depicted in the cartoons of Fig. 2. The surfactant and the TCB were arranged in the vicinity of the TiO_2 surface in the simulation with 768 water molecules displayed in the initial models of Fig. 2. To facilitate visualization as to how the TCB and the surfactant approach the particle surface, the water molecules were excluded from the rest of Fig. 2. The MEL molecule adsorbs on the TiO_2 surface in approximately 5 ps ($k = 2 \times 10^{11}\ s^{-1}$) through the oxygen atoms of the hydrophilic functions; contact distance between the MEL and the TiO_2 surface is shortened further after 10 ps with adsorption controlled by van der Waals' forces. The TCB molecules get trapped within the long alkyl chains of the MEL system, which subsumes TCB to a greater extent by the repulsion of water. The oxygen atoms of the hydrophilic functions of the MEL structure are not easily desorbed from the TiO_2 surface because of the large array of such functions about the pyrano ring (see Fig. 1).

Contrary to the MEL biosurfactant, the sulfate function ($-OSO_3^-$) of the SDS surfactant adsorbs onto the positive TiO_2 surface (pH of dispersion, 6.0; pzc of TiO_2, 6.5), while also interacting with the water molecules. The TCB molecule is adsorbed to the long alkyl chain of SDS through hydrophobic interactions. Unfortunately, the adsorbed sulfate function is detached from the alkyl chain of the SDS molecule by the events (desulfonation) on the metal-oxide surface occurring faster than seems to be the reductive and/or oxidative degradation of the TCB substrate, as evidenced by the experimental data.

We established above that the hydrophilic functions bearing atoms with the greatest negative charge in the MEL structure adsorbed on the positive hydrophilic TiO_2 surface (Fig. 3a). The $^{\bullet}OH$ radicals generated by the valence band holes through photooxidation of surface-bound hydroxyl groups and/or water molecules oxidatively attack the organic substrate at or close to the TiO_2 surface [36], while the photogenerated conduction band electrons can also reductively degrade the TCB substrate by electron attachment to the phenyl ring [37–39]. These two events, which likely occur either sequentially or concurrently, lead to the photodegradation of TCB in competition with photodegradation of the MEL biosurfactant. On the other hand, the TCB remains hydrophobically

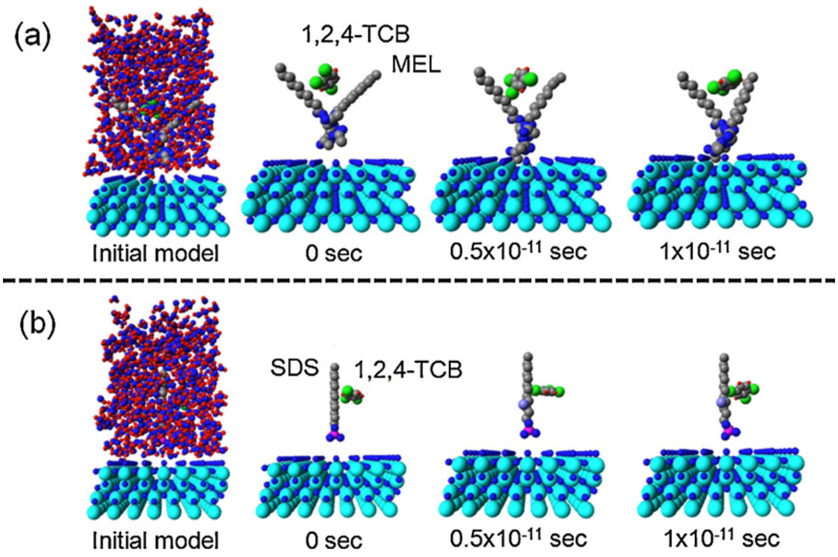

Fig. 2. Cartoons illustrating the interactions between the surfactants, the 1,2,4-trichlorobenzene substrate and the TiO_2 surface calculated using molecular dynamics simulation using Lennard–Jones and Coulomb potential parameters. The water molecules are only shown for the initial model. Note the differences of approaches of the surfactants toward the metal-oxide particle surface as a function of time.

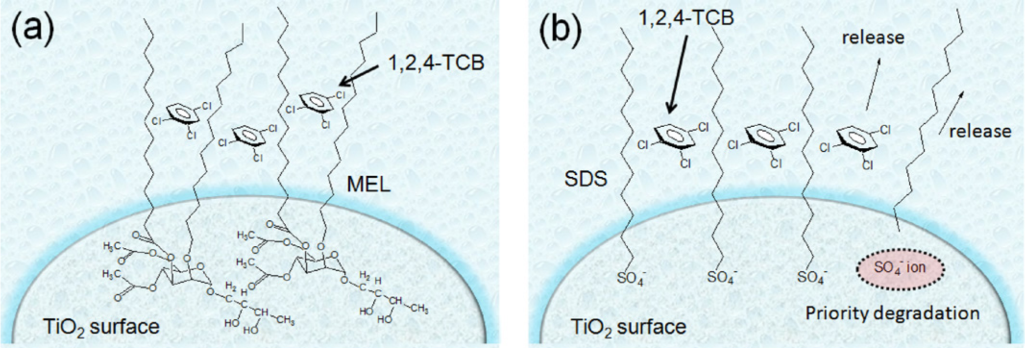

Fig. 3. Proposed detailed adsorption model of the (a) MEL biosurfactant, and (b) of the SDS surfactant on the TiO_2 particle surface; also shown are the 1,2,4-trichlorobenzene (TCB) molecules.

attached to the alkyl chain of SDS near the TiO_2 surface (Fig. 3b). Initial priority photodegradation of SDS occurs on the surface by the detachment of the sulfate moiety ($–OSO_3{}^-$) from the hydrophilic metal-oxide surface leading to the release of the alkyl chain along with the TCB substrate thereby obviating any oxidative or reductive degradation of the chlorinated aromatic pollutant in the SDS dispersion.

3.2. Photo-degradation and -dechlorination of TCB

The photodegradation of TCB occurring either oxidatively and/or reductively was monitored by the disappearance of the aromatic absorption feature at 226 nm for irradiation times 0, 30, 60, 120, 200 and 300 min. Results are illustrated in Fig. 4a. Degradation of TCB occurred via first-order kinetics with $k = 9.6 \pm 0.6 \times 10^{-3}\,\text{min}^{-1}$ and $10.4 \pm 1.2 \times 10^{-3}\,\text{min}^{-1}$ monitored by UV/vis spectral and GC methods, respectively, in the MEL-containing media, and $k = 1.0 \pm 0.1 \times 10^{-3}\,\text{min}^{-1}$ and $0.78 \pm 0.09 \times 10^{-3}\,\text{min}^{-1}$ by UV/vis and GC methods, respectively, in the presence of the SDS surfactant. The accord between the photodegradation dynamics (Fig. 4a) for a given surfactant system demonstrates that the UV/vis spectral method can be used to quantify the dynamics under certain circumstances. In the MEL case, the photodegradation of TCB was nearly 100% complete after irradiation for 300 min. By contrast, only about 22% of the TCB degraded in the dispersion containing the SDS anionic surfactant, under otherwise identical conditions of UV irradiation for 300 min. Clearly, the photodegradation of TCB improved nearly tenfold when adding the biodegradable MEL surfactant to the contaminated dispersion. An additional advantage is that both the MEL biosurfactant and the TCB substrate degraded competitively on the TiO_2 surface. Naked MEL is completely mineralized in an aqueous TiO_2 dispersion to CO_2 by UV irradiation for 320 min [22]. Control experiments demonstrated that in the absence of the biosurfactant less than 3% of the TCB degraded within 5 h of UV illumination; without TiO_2 and TCB no MEL degraded under the same experimental conditions. Results clearly demonstrate that photodegradation of TCB in the presence of the SDS surfactant was not very efficient. Formation of $SO_4{}^{2-}$ ions through desulfonation of SDS (not shown) was nearly 92% complete after irradiation for only 120 min, which confirms the notion that degradation of the SDS surfactant through desulfonation was competitively faster than degradation of the TCB system. This confirms the earlier observations of Fabbri et al. [7] who reported that the presence of SDS inhibited the photodegradation of a somewhat hydrophobic substrate such as trichlorophenol.

The time profiles for the formation of Cl^- ions through dechlorination of TCB in the presence of the MEL biosurfactant and the SDS surfactant are reported in Fig. 4b. Although the extent of dechlorination was ~90% in the presence of MEL and only ca. 5% with SDS after 300 min of UV irradiation, the first-order kinetics of formation of Cl^- ions, $k = 8.5 \pm 0.6 \times 10^{-3}\,\text{min}^{-1}$ with MEL, were nearly identical with the corresponding photodegradation kinetics ($k = 9.6 \pm 0.6 \times 10^{-3}\,\text{min}^{-1}$), whereas with SDS present Cl^- ion formation kinetics ($k = 0.23 \pm 0.04 \times 10^{-3}\,\text{min}^{-1}$) were nearly 4-fold slower than degradation of TCB ($k = 1.0 \pm 0.1 \times 10^{-3}\,\text{min}^{-1}$). Again, addition of the MEL biosurfactant impacted favorably on the dechlorination process, making the dechlorinated substrates (benzene and/or phenols) degradable by microorganisms – clearly this would not be the case in the presence of SDS since much of the TCB remained intact (ca. 78% after 5 h of irradiation). In the presence of SDS at a concentration of 8 mM (i.e. at the cmc of SDS), no photodegradation of TCB occurred as evidenced by both UV/vis spectral monitoring and GC techniques.

ESI-mass spectral results of hydrophobic intermediate species extracted from the aqueous media with hexane during the photodegradation of TCB in MEL/TiO_2 and SDS/TiO_2 dispersions

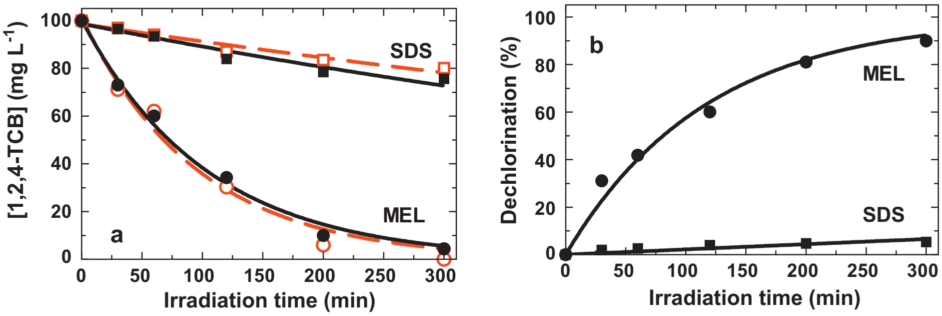

Fig. 4. (a) Photodegradation of 1,2,4-trichlorobenzene (TCB) in aqueous TiO_2 dispersions in the presence of MEL and SDS surfactants; solid lines: concentration changes monitored by UV/vis spectral methods; dashed lines: concentration changes monitored by gas chromatographic methods. (b) Photoassisted dechlorination of TCB in aqueous TiO_2 dispersions in the presence of MEL and SDS surfactants.

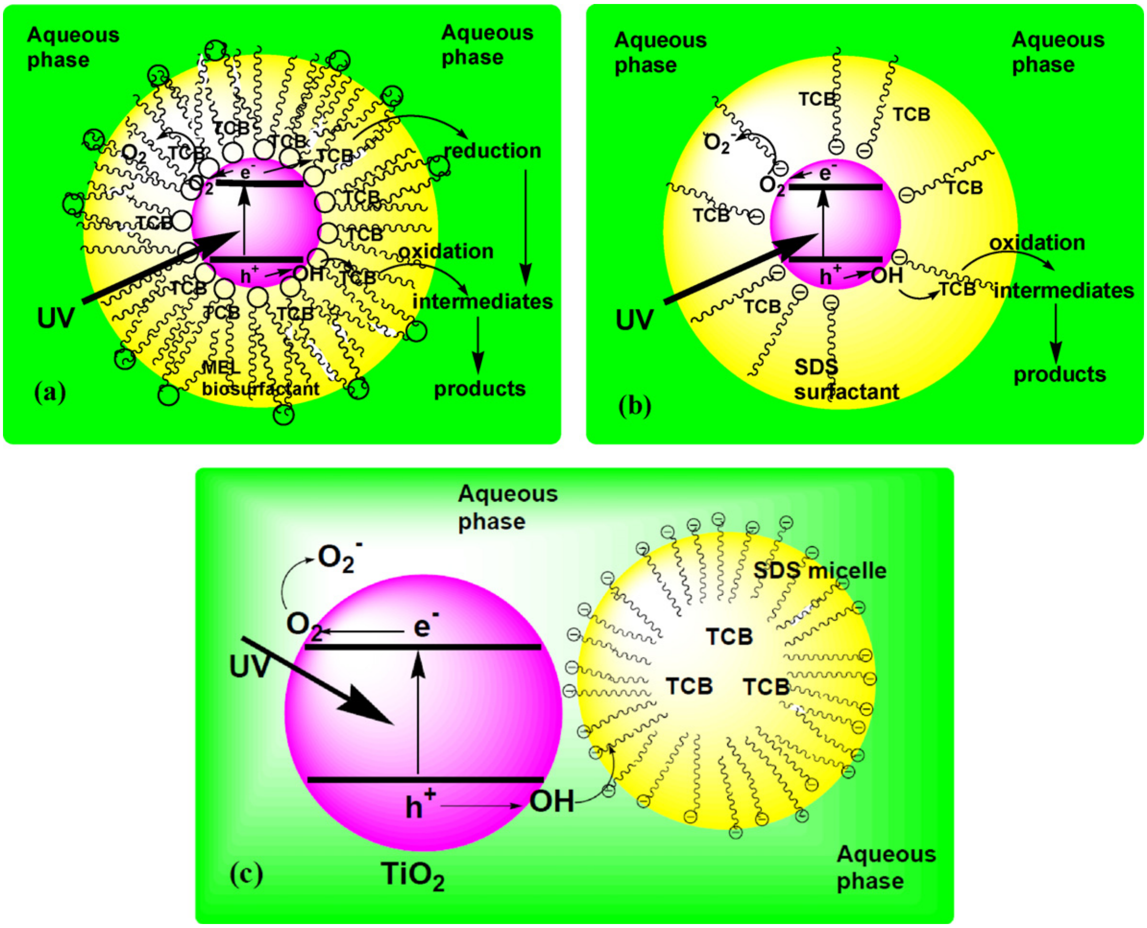

Fig. 5. Cartoons that conceptualize the initial events in the photodegradation of TCB in MEL/TiO_2 and SDS/TiO_2 dispersions: (a) for a MEL surfactant concentration of 200 mg L^{-1} (ca. 0.3 mM); (b) for a SDS surfactant concentration of 200 mg L^{-1} (0.69 mM; i.e. below cmc of 8 mM); and (c) for a SDS surfactant concentration at the cmc of 8 mM.

showed no presence of chlorinated species. By contrast, the mass spectra of the species remaining in the aqueous media displayed a multitude of very complex peak patterns that eluded a clear identification of the hydrophilic intermediates and byproducts.

We showed earlier [22] that the oxygen atoms in the MEL structure are the positions of closest approach of the biosurfactants to the TiO_2 metal-oxide surface and thus the most likely sites of adsorption as illustrated in Fig. 3a. The highest frontier orbital electron densities in the MEL structure were those of the carbonyl carbons and most likely susceptible to attack by the $^{\bullet}OH$ radicals, leading to the degradation of the MEL surfactant with $k_{deg} = 13 \pm 1 \times 10^{-3}\ min^{-1}$ [22].

Results of the molecular dynamics simulations and the proposed adsorption model illustrated in Figs. 2 and 3, together with the photodegradation dynamics of TCB in MEL/TiO_2 and SDS/TiO_2 dispersions allow making some mechanistic inferences with respect to initial events under our experimental conditions reported above. As depicted in Fig. 5a, the MEL surfactant adsorbs onto the TiO_2 surface forming aggregated pseudo-micellar type structures with the hydrophobic TCB trapped close to the surface. Subsequent to UV irradiation and photogeneration of valence band holes and conduction band electrons, which ultimately lead to formation of surface $^{\bullet}OH$ radicals by oxidation of surface-bound OH^-groups and water molecules and to formation of superoxide radical anions through electron scavenging by the ubiquitous adsorbed molecular oxygen, competitive oxidation of the TCB with the MEL surfactant molecules yields a multitude of hydrophilic intermediates in the aqueous phase. In parallel with the oxidative process and in competition with electron scavenging by O_2, electron attachment onto the aromatic ring [37] of TCB can also lead to degradation reductively through dechlorination and to formation of phenyl-type radicals, which upon reaction with water molecules also yield hydrophilic intermediates not unlike those produced by the oxidative pathway.

Fig. 5b illustrates the events inferred to take place in SDS/TiO_2 dispersions when the concentration of SDS (0.69 mM) is well below its cmc of 8 mM. While some SDS molecules do approach the TiO_2 surface, the hydrophobicity of the TCB molecules keeps the latter away from the hydrophilic particle surface such that both the oxidative and reductive pathways for the degradation of TCB are limited by the oxidative degradation of the SDS surfactant leading to desulfonation. Nonetheless, some degradation of TCB does occur albeit mostly by the oxidative pathway as dechlorination by the electron reductive pathway is likely impeded by the negatively charged head groups of the anionic SDS surfactant. By contrast, at the SDS concentration of its cmc (8 mM) the hydrophobic TCB molecules are trapped in the hydrophobic core of the SDS micelles (Fig. 5c), which impede the TCB from getting close to the particle surface and thus be degraded oxidatively and/or reductively as attested by the experimental lack of photodegradation and photodechlorination of the TCB substrate under these conditions.

4. Concluding remarks

The initial adsorption of the MEL and SDS surfactants that occurs in the dark on the TiO_2 surface was more extensive for the MEL (ca. 68%) relative to adsorption of SDS (ca. 4%). The adsorptive power of

MEL on the TiO_2 surface was clearly greater than that of SDS, such that many more TCB molecules were subsumed by this biosurfactant allowing the hydrophobic substrate to come into closer contact with the TiO_2 surface than is the case with the SDS surfactant.

The attractive characteristics of the microorganisms-produced MEL biosurfactant in photo-assisted redox reactions can be summarized thus: (i) strong adsorption of the MEL on the TiO_2 surface and (ii) trapping of the hydrophobic TCB pollutant into its long alkyl chains which leads to significant degradation of the pollutant in relatively short times, as evidenced by both experimental results and molecular dynamics simulations. The enhancement of the photo-degradation and -dechlorination of the TCB hydrophobic pollutant, whether oxidatively and/or reductively, was clearly demonstrated upon the addition of MEL to the hydrophilic aqueous titania dispersions. Even if the MEL biosurfactant remained after the photodegradation of TCB, unlike the SDS surfactant, natural microorganisms can easily biodegrade the biosurfactant. Wastewater treatments with metal oxides such as the highly hydrophilic TiO_2 are therefore limited in their photodegradation of hydrophobic pollutants, an issue that can be best resolved by the presence of biodegradable surfactants.

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