Rate parameter independence on the organic reactant: a study of adsorption and photocatalytic oxidation of surfactants using MO_3–TiO_2 ($M \equiv Mo$ or W) catalysts

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Abstract

The adsorption of dodecylbenzene sulphonic acid sodium salt (DBS), cetylpyridinium chloride (CPC) and triton X-100 (TX-100) in aqueous solution on to TiO_2, MoO_3–TiO_2 and WO_3–TiO_2 photocatalysts has been studied. The sulphite group in DBS, the pyridinium ion in CPC and the ethoxyl group in TX-100 fix these surfactant molecules to the catalyst surface, leaving the hydrocarbon chains perpendicular to the surface plane of the catalyst. Irradiation of these surfactants in the presence of the above photocatalysts caused their degradation into carbon dioxide. After a 6 h irradiation period, over 80% reduction in chemical oxygen demand relative to its initial value was achieved. The first-order rate constants (k) and dark absorption equilibrium constants (K) were compared. It was found that k corresponds to a reaction step wherein surfactant molecules do not participate.

Keywords: Titanium dioxide; Photocatalysis; Oxidation; Surfactants; Adsorption

1. Introduction

Surfactants pose severe ecological problems as their biodegradation is often very slow. Anionic, cationic and nonionic surfactants can be destroyed using aerated aqueous TiO_2 suspensions [1–10] and UV light irradiation. It has been confirmed that such photocatalytic oxidation (PCO) reactions are mediated by hydroxyl radicals [7]. A survey of the available literature on the TiO_2-catalysed photodegradation of various surfactants revealed that (i) in general, anionic surfactants are easier to degrade, while any side-chains present react slower than the aromatic groups, (ii) the pseudo-first-order rate constant for CO_2 evolution is an order of magnitude higher than that of O_2 consumption [5], suggesting a parallel mechanism to be operative in which the extra CO_2 is evolved, (iii) the first-order rate constant for dearomatization of the surfactants is several orders of magnitude higher than that of CO_2 evolution and does not show any dependence on the structure of the surfactant [7] and (iv) the greater the mole number of ethoxyl groups in a non-ionic surfactant, the lower is the degradation rate [8]. These photodegradation kinetics were explained using the linear transform of the Langmuir–Hinshelwood (LH) kinetic

model, which yields the rate constant k relevant to illuminated conditions:

$$\frac{1}{r} = \frac{1}{kKC} + \frac{1}{k} \tag{1}$$

where r is the rate of photocatalytic degradation, C is the concentration of the reactant and K is the adsorption coefficient. Since the intercept values of such linear plots for a good number of organic compounds are comparable, the independence of the rate parameter on the organic reactant was interpreted earlier [11]. Because the LH kinetic model assumes solute adsorption, a wide range of reaction rates may be expected from the differences in adsorption coefficients of different solutes on a given semiconductor surface. The adsorption of these organic compounds may be influenced by illumination and the photoeffect (photoadsorption and photodesorption) may be manifested in the value of K deduced from the slopes of LH plots. Adsorption of oxygen and other substrates on metal oxides is sometimes dramatically enhanced during photolysis [12] and can thus deviate considerably from the adsorption isotherms measured in the dark. Therefore a direct comparison of K derived from Eq. (1) and rate constants would be rather inappropriate. Such a comparison, however, necessitates K being obtained from dark adsorption studies. The limitations inherent in an LH-

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type kinetic analysis applied to TiO_2-catalysed photodegradation are discussed by Cunningham and Al-Sayyed [13].

In this paper we undertook studies on the dark adsorption of anionic, cationic and non-ionic surfactants on three different titania catalysts and examined the photodegradation kinetics with reference to these adsorption parameters. It emerged that the first-order rate constants correspond to a reaction step which does not include surfactant molecules as reactants. The rate-limiting reaction appeared to be the photogeneration of hydroxyl radicals.

2. Experimental details

2.1. Materials

Titanium dioxide (anatase) powder was procured from SD Lab. Chem., India. The preparation and characterization (X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron paramagnetic resonance (EPR)) of MO_3-TiO_2 (M = Mo or W) catalysts was reported earlier [14]. The Brunauer-Emmett-Teller (BET) surface areas ($m^2\ g^{-1}$) of these catalysts were 10.45 (TiO_2, T), 9.10 (MoO_3-TiO_2, MT) and 9.90 (WO_3-TiO_2, WT). The bulk TiO_2 phase contains some metal ion impurities such as Co^{2+}, Fe^{3+}, Cu^+ and Mo^{5+}. These catalysts were first sieved (300 mesh) to remove particles of size greater than 50 μm and then used in adsorption and photocatalytic experiments. Dodecylbenzene sulphonic acid sodium salt (DBS; Aldrich, 1.2 mM critical micellization concentration (c.m.c.)), cetylpyridinium chloride (CPC; E-Merck, 0.90 mM c.m.c.) and triton X-100 (TX-100; Ubichem., 10 ethoxyl units, 0.24 mM c.m.c.) were used.

2.2. Adsorption experiments

The adsorbents were T, MT and WT. Stock solutions of DBS, CPC and TX-100 in doubly distilled water were used. The absorption maxima (λ_{max}, UV–visible, 160 Shimadzu) were observed for DBS at 224 nm ($\epsilon = 3.04 \times 10^3\ mol^{-1}\ dm^3$, for CPC at 214 nm ($\epsilon = 2.40 \times 10^3\ mol^{-1}\ dm^3$) and 259 nm ($\epsilon = 2.72 \times 10^3\ mol^{-1}\ dm^3$) and for TX-100 at 230 nm ($\epsilon = 48.50\ mol^{-1}\ dm^3$) and 275 nm ($\epsilon = 66.6\ mol^{-1}\ dm^3$). The suspensions of catalyst powders in surfactant solutions were allowed to equilibrate for 2 h (although sorption appeared to reach saturation in 30 min) in the dark under constant stirring at 25 °C at their natural pH. The amount of surfactant adsorbed on the catalyst was deduced from the absorption readings of the equilibrated solutions (the catalysts were removed by filtration using 0.5 μm Millipore filters). Three types of adsorption experiments were conducted. (i) A fixed amount of catalyst (0.02 g) was suspended in 25 cm^3 of aqueous solution of surfactant with various initial concentrations (105–250 ppm DBS, 110–250 ppm CPC and 25–150 ppm TX-100, all below their respective c.m.c. levels); this gave the data needed for obtaining adsorption iso-

therms. (ii) Various amounts of catalyst powder were suspended in 25 cm^3 of DBS (175 ppm), CPC (180 ppm) or TX-100 (100 ppm); the density of the suspension varied between 0.2 and 0.8 mg cm^{-3}. (iii) The pH of the surfactant solutions (25 cm^3 of 175 ppm DBS, 180 ppm CPC or 100 ppm TX-100) was varied from 4.0 to 8.2 in chosen steps.

2.3. Photocatalytic oxidation experiments

A typical photocatalytic oxidation experiment involved the irradiation (400 W medium pressure Hg lamp, 5×10^{19} photons s^{-1}, peak emission at 365 nm, Annular Immersion Well Photoreactor, SAIC, India) of equilibrated aqueous suspensions of surfactant (500 cm^3 of 50 ppm) and titania catalyst powder (0.2 g). Air was bubbled through the suspensions using an aerator pump. Control experiments in the dark and in the presence of light but without any catalyst were carried out. Aliquots (15 cm^3) of the photoreacted suspensions were collected at chosen intervals of irradiation time and the extent of degradation of the surfactant was obtained by determining the chemical oxygen demand (COD) of the photodegraded solutions. This determination included the digestion of 10 cm^3 of the sample using $K_2Cr_2O_7$ in H_2SO_4 medium and subsequent titration. Fractions of some of these aliquots were also used for the high performance liquid chromatography (HPLC) determination (Millipore Waters Instrument, Bondapak C_{18} column) of surfactant degradation. For comparison we also examined the degradation of DBS with Degussa P-25 TiO_2 and the degradation of DBS at concentrations higher than its c.m.c. level using the TiO_2 (SD) catalyst. The CO_2 evolved in the photocatalytic oxidation experiments on the surfactants and the fraction of mineralized CO_2 in the final test solutions were determined as described earlier [14].

3. Results and discussion

3.1. Dark adsorption studies

About 25%–43% of the initial concentration of each surfactant is adsorbed on to the T, MT and WT catalysts at equilibrium in the dark (Table 1). The quantity of adsorbed surfactant remained invariant at a suspension density greater than 0.6 mg cm^{-3}. Further, the quantity of adsorbed DBS decreased (from 34% to 24%), that of CPC increased (from 28% to 38%) and that of TX-100 remained unchanged when the suspensions were gradually made alkaline. This result is consistent with pH-dependent Ti-OH_2^+ (in acidic media) and Ti-O^- (in alkaline media) surface species and their interaction with the anionic, cationic and non-ionic surfactants.

Adsorption isotherms (plots of $1/X$ vs. $1/C_{eq}$) of DBS, CPC and TX-100 for each of the catalysts T, MT and WT are shown in Fig. 1. The linearity of these plots in the equilibrium concentration ranges 84–178 ppm (DBS), 100–180 ppm (CPC) and 50–150 ppm (TX-100) confirms the Langmuir-

Table 1

Adsorption data for DBS, CPC and TX-100 as a function of pH and density of suspensions. Adsorbents were T, MT and WT catalysts. Adsorption parameters were deduced from Fig. 1

Surfactant	Catalyst	Adsorbed surfactant (ppm)							Adsorption parameters	
		pH			Density (mg cm⁻³)				X_m (ppm mg⁻¹)	K (10^{-3} ppm⁻¹)
		4.0	6.2	8.0	0.2	0.4	0.6	0.8		
DBS	T	59.5	56.0	42.0	21.0	31.5	56.0	56.0	4.87	5.86
(175 ppm)	MT	59.0	49.0	42.0	28.0	38.5	59.5	59.5	5.26	6.08
	WT	63.0	56.0	45.5	31.5	42.0	63.0	63.0	5.00	8.88
CPC	T	50.4	57.6	64.8	25.2	39.6	57.6	57.6	4.16	9.60
(180 ppm)	MT	54.0	61.2	68.4	28.8	43.2	61.2	61.2	4.34	10.00
	WT	54.0	57.6	64.8	21.6	36.0	54.0	54.0	4.08	7.26
TX-100	T	36.0	36.0	36.0	15.5	21.6	36.2	36.2	66.66	0.14
(100 ppm)	MT	36.0	36.0	36.0	15.0	26.0	36.3	36.3	75.00	0.10
	WT	25.5	25.5	25.5	15.3	21.5	26.0	26.0	66.66	0.13

type adsorption–desorption model. The adsorption parameters X_m and K values (Table 1) were obtained by fitting the data to the LH adsorption isotherm

$$\frac{1}{X} = \frac{1}{X_m K C} + \frac{1}{X_m} \qquad (2)$$

where X is the amount of surfactant adsorbed, C is the equilibrium concentration of surfactant in the bulk solution phase, X_m is the limiting amount of surfactant that can be taken up by unit mass of adsorbent and K is the dark adsorption constant. It is evident from a comparison of the K values that the adsorbent–surfactant interaction is stronger in the order CPC > DBS ≫ TX-100. The values of K for TX-100 are nearly two orders of magnitude lower. The X_m value for any surfactant is found to be approximately the same on all three titania catalysts. This may be attributed to the comparable BET surface areas of the T, MT and WT catalysts.

The adsorption of DBS, CPC and TX-100 on the surface of the catalyst can be expected to involve surfactant molecules only (and not their micelles), as the chosen concentrations were below their respective c.m.c. levels. By substituting the X_m value of DBS (5.00 ppm mg⁻¹ or 1.435×10^{-5} mol), Avagadro's number N (6.023×10^{23}) and the surface area S of the catalyst T (10.45 m² g⁻¹ or 10.45×10^{18} nm² g⁻¹) into $S = X_m N a$ (where a is the area of the unsolvated surfactant molecule), the value of a can be deduced as 10 Å². However, if we assume that the DBS molecule is lying flat on the catalyst surface, it should occupy about 62 Å². Therefore the DBS molecule is not adsorbed flat but uses its sulphite group (SO_3^-), the three oxygen atoms of which act as "bite" atoms to hold the rest of the DBS molecule perpendicular to the surface. The area of the triangle formed by the sulphite oxygen atoms is approximately equal to 7–8 Å², which agrees roughly with the area deduced above. A similar calculation using the X_m value of CPC (the resultant a value is 15.0 Å²) revealed that CPC too is adsorbed using its pyridinium cation ($C_5H_5N^+$), while its aliphatic side-chain (cetyl group) is projected perpendicular to the surface. Similarly, the X_m value

of TX-100 (66 ppm mg⁻¹) yielded the value of a as 17.0 Å², supporting the adsorption of the TX-100 molecule via the end ethoxyl group ($-CH_2OH$).

3.2. Photocatalytic oxidation

Both the TiO_2 catalyst and UV illumination are essential for the photodegradation of these surfactants. The UV–visible spectra of the photodegraded surfactant solutions showed the gradual disappearance of the peaks due to the aromatic rings of DBS, CPC and TX-100. These data indicate that the dearomatization of these surfactants was nearly complete within 30–60 min. Further, a stack plot of HPL chromatograms (Fig. 2) of the reacted surfactant solutions (only that of DBS is shown) clearly demonstrates the photodegradation of these surfactants accompanied by the formation and degradation of intermediates. It may be noted that DBS, with a retention time of 2.0–2.1 min, still persisted even after 6 h irradiation. Further, the intermediates (aldehyde and carboxylics) that built up till 30 min appear to be involved in the photodegradation simultaneously with DBS until 3 h. Again after 3 h the degradation of DBS becomes predominant, leading to the build-up of an intermediate compound with a retention time of 1.5 min (compare chromatograms at 3 h and 4 h).

As these surfactants photodegraded to evolve CO_2 along with some intermediates which presumably contain fewer carbon atoms than the parent surfactant molecule, the COD decreased with the time of irradiation. The variation in COD as a function of irradiation time due to photodegradation of DBS, CPC and TX-100 using the T, MT and WT catalysts is presented in Table 2. Prior to commencing UV illumination of any TiO_2–surfactant suspension, the reactor contents were maintained under constant stirring for 2 h in order to fully establish an adsorption–desorption equilibrium (see Table 1; about 25%–45% of the initial concentration of these surfactants is adsorbed). However, the COD readings after a 15 min UV illumination period indicated significant re-entry of the surfactant (in this case the estimation of surfactants in the
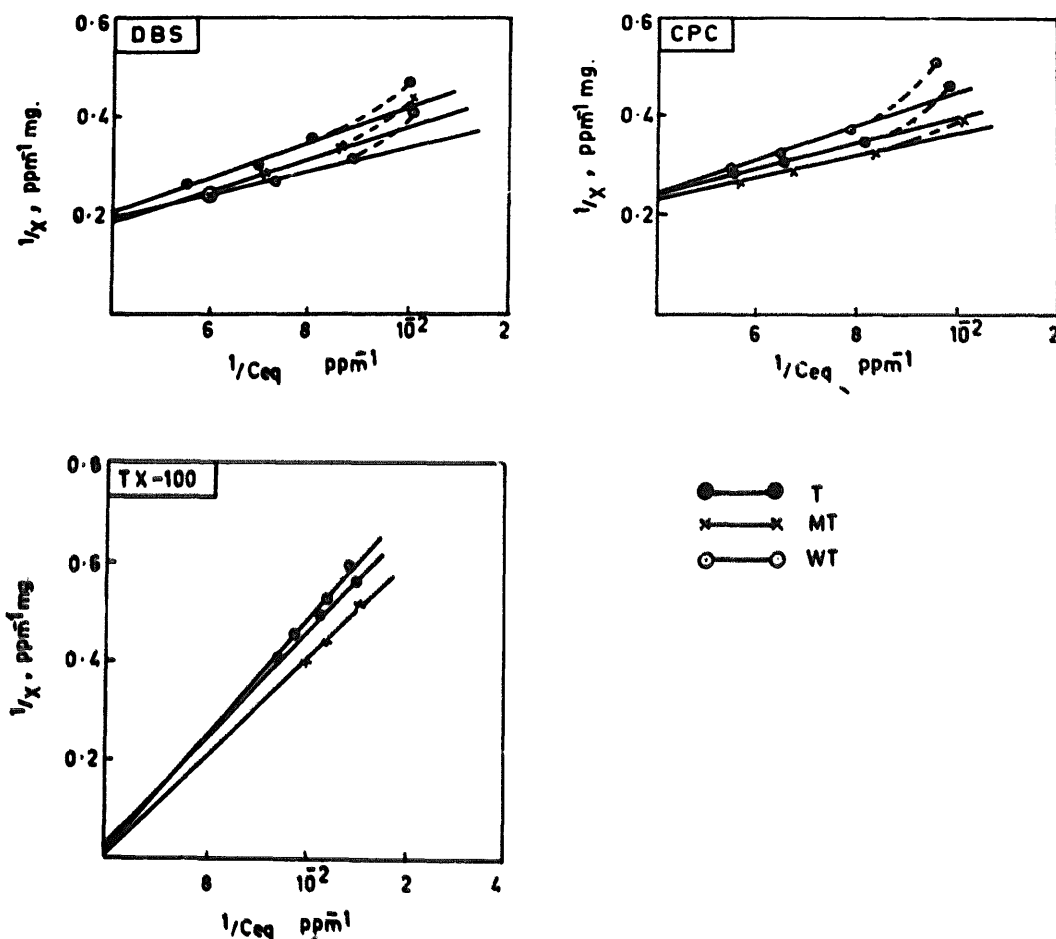
Fig. 1. Langmuir adsorption isotherms for adsorption of DBS, CPC and TX-100 on T (●), MT (×) and WT (○) catalysts.

bulk solution phase indicated the adsorbed amounts of surfactants to be between 12% and 28%) into the bulk solution phase even under the initial weak UV flux of the lamp soon after it was switched on. Apparently, photodesorption of the surfactant occurs at the illuminated TiO₂-surfactant solution interface simultaneously with photodegradation of the sur-

factants, as illustrated by the HPL chromatogram of the 15 min test sample (see Fig. 2). The photodesorptive effect was large (the COD value 15 min after illumination and the initial COD value differed by less than 3%) over the P-25 TiO₂ catalyst. This catalyst adsorbed about 25% of the initial concentration of surfactant in the dark. It can be seen from Table
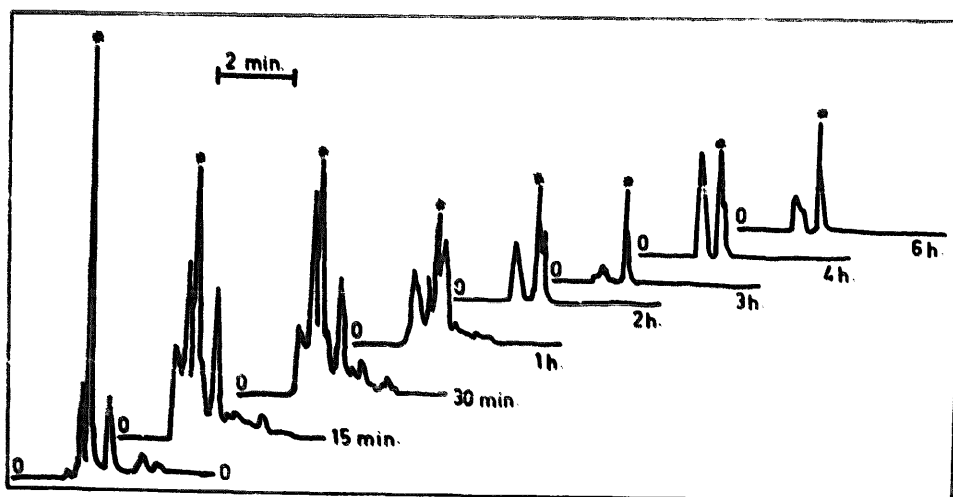

Fig. 2. Stack plot of HPL chromatograms of photoreacted DBS solutions as a function of irradiation time. The catalyst employed was TiO₂ (T). The peaks marked * correspond to DBS.
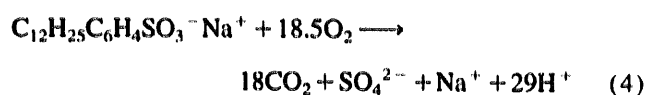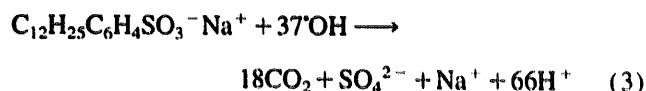
Table 2
Variation in COD (initial COD levels are given in parentheses) as a function of irradiation time during photocatalytic oxidation of surfactants using TiO_2 catalysts

Surfactant	Catalyst	COD, (ppm)						
		Time t (min)						
		15	30	60	120	180	240	360
DBS	T	71.1	56.9	44.7	34.5	24.4	18.3	12.2
(82.3 ppm)	MT	68.1	54.9	41.6	28.4	20.3	16.2	11.2
	WT	63.0	52.8	40.6	34.5	19.3	14.2	10.2
	P-25	80.3	70.0	54.9	44.7	--	30.5	18.3
DBS	T	589.3	526.2	467.5	414.5	–	321.0	235.7
(658.3 ppm)								
CPC	T	70.5	58.6	52.8	42.7	34.5	28.3	24.2
(89.4 ppm)	MT	65.0	55.9	48.8	38.6	30.5	24.4	18.3
	WT	67.0	58.0	50.8	40.8	32.5	26.5	22.3
TX-100	T	62.0	54.9	46.7	38.6	32.5	26.4	18.3
(71.1 ppm)	MT	61.0	51.0	43.7	34.5	26.4	20.3	14.3
	WT	63.7	57.0	51.0	40.0	34.5	28.4	21.3

2 that on average about 85% DBS at an average rate (r_a) of 0.21 ppm min^{-1}, 75% CPC at $r_a = 0.16$ ppm min^{-1} and 75% TX-100 at $r_a = 0.15$ ppm min^{-1} can be photodegraded in a 6 h period using the T, MT and WT catalysts. About 78% DBS could be degraded using P-25 TiO_2 at an approximate rate of 0.13 ppm min^{-1}. When [DBS] was greate. than the c.m.c. level, the initial COD (658.36 ppm) could be brought down

to 236 ppm in 6 h, which is equivalent to 64% COD removal at a rate of 0.89 ppm min^{-1} using the TiO_2 (SD) catalyst. We obtained 2.17×10^{-3} mol CO_2 from the photodegradation of 50 ppm DBS (1.44×10^{-4} mol) using the WT catalyst, which theoretically should have yielded 2.59×10^{-3} mol CO_2 (Eqs. (3) and (4)). This means that about 84% of the expected yield was realized experimentally, which is also in close agreement with the amount of DBS degraded using the titania catalysts. Similar calculations were applied to the other surfactants as well and it was found that the amount of surfactant degraded and the yield of CO_2 agreed within $\pm 3\%$–5%.

$$C_{12}H_{25}C_6H_4SO_3^-Na^+ + 37^\cdot OH \longrightarrow$$
$$18CO_2 + SO_4^{2-} + Na^+ + 66H^+ \quad (3)$$
$$C_{12}H_{25}C_6H_4SO_3^-Na^+ + 18.5O_2 \longrightarrow$$
$$18CO_2 + SO_4^{2-} + Na^+ + 29H^+ \quad (4)$$

The $\log(COD_t)$ vs. irradiation time plots (Fig. 3) for the photodegradation of these surfactants using the T, MT and WT catalysts were found to be linear, thus establishing that the photodegradation of the surfactants approximately follows first-order kinetics. The rate constants (k) evaluated from the slopes of these plots ($-k/2.303$) and the half-value periods ($t_{0.5} = 0.693/k$) are presented in Table 3. The adsorption equilibrium constant values K are repeated from Table 1. It may be noticed that the first-order rate constants were
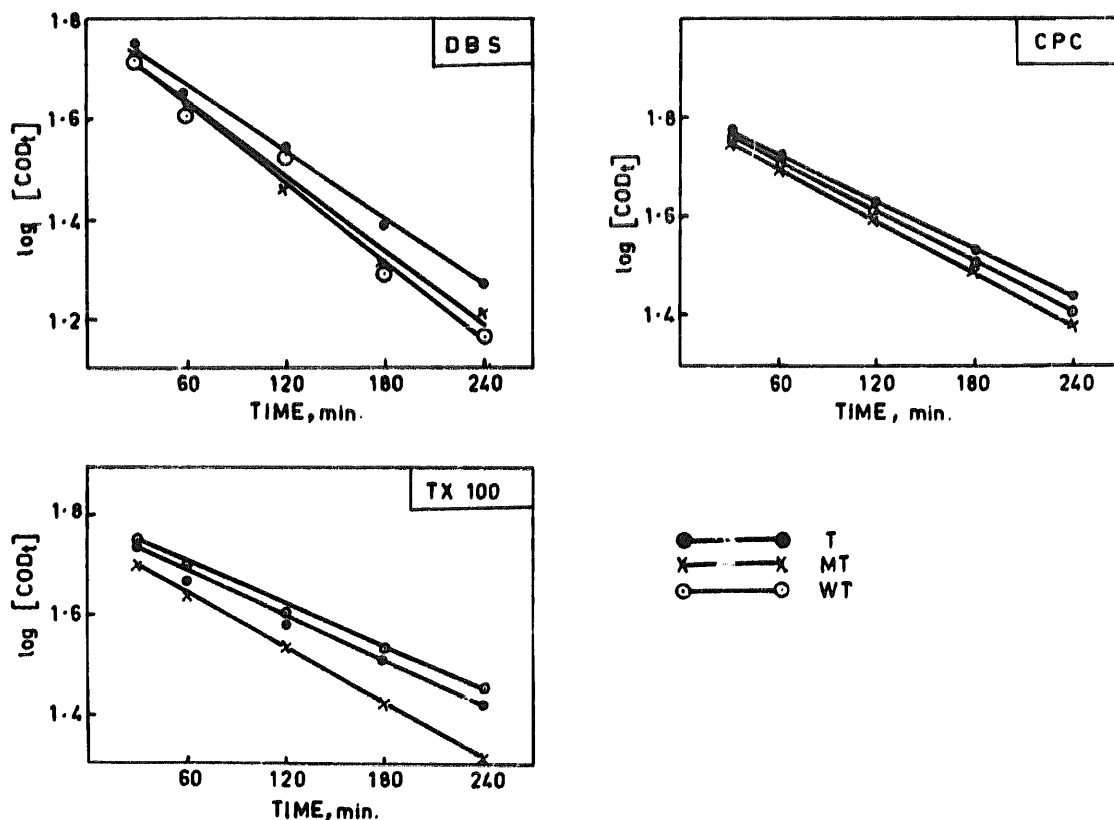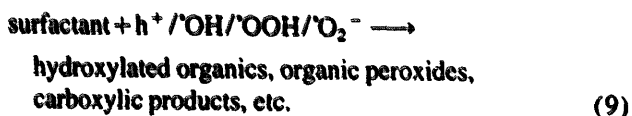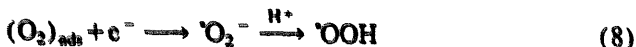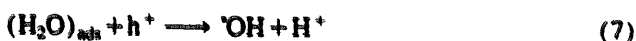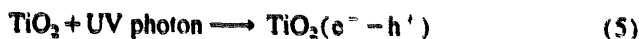

Fig. 3. Log(COD_t) vs. irradiation time plots for photocatalytic degradation of DBS, CPC and TX-100 using T (●), MT (×) and WT (○) catalysts.

Table 3

Rate constants (k), half-value periods ($t_{0.5}$) and adsorption equilibrium constants (K)

Surfactant	Catalyst	k (10^{-3} min^{-1})	$t_{0.5}$ (min)	K (10^{-3} ppm^{-1})
DBS	T	4.30	161	5.86
	MT	4.68	148	6.08
	WT	4.99	139	8.88
CPC	T	3.49	198	9.60
	MT	3.93	176	10.20
	WT	3.82	181	7.26
TX-100	T	4.72	147	0.139
	MT	4.66	149	0.102
	WT	4.49	154	0.130

not significantly different (average $k = 4.342 \pm 0.75$ min^{-1}). The half-value periods for a particular surfactant on all three catalysts may be averaged to 150 min (DBS), 185 min (CPC) and 150 min (TX-100). This implies that cationic surfactants degrade slowly. The rate constant for the degradation of DBS using the P-25 TiO$_2$ catalyst is 3.70×10^{-3} min^{-1} ($t_{0.5} = 187$ min). This performance is comparable with that of the T, MT and WT catalysts. For [DBS] greater than the c.m.c. level the rate constant is 2.20×10^{-3} min^{-1} ($t_{0.5} = 315$ min). These data suggest that the corresponding micelles are difficult to degrade.

The TiO$_2$ catalysts absorb UV photons to produce electron–hole pairs (Eq. (5)) which may be competitively trapped by adsorbed H$_2$O, OH, O$_2$ and surfactant molecules as shown in Eqs. (6)–(9), although some of them may be destroyed via recombination processes.

$$TiO_2 + UV \text{ photon} \longrightarrow TiO_2(e^- - h^+) \qquad (5)$$

$$(OH)_{ads} + h^+ \longrightarrow \cdot OH \qquad (6)$$

$$(H_2O)_{ads} + h^+ \longrightarrow \cdot OH + H^+ \qquad (7)$$

$$(O_2)_{ads} + e^- \longrightarrow \cdot O_2^- \xrightarrow{H^+} \cdot OOH \qquad (8)$$

$$surfactant + h^+ / \cdot OH / \cdot OOH / \cdot O_2^- \longrightarrow$$

hydroxylated organics, organic peroxides, carboxylic products, etc.   (9)

The highly reactive $\cdot$OH, $\cdot$O$_2^-$ and $\cdot$OOH radicals also react with adsorbed surfactant molecules to yield intermediate species such as hydroxylated organics (e.g. phenols), organic peroxides, carboxylic products, etc. (see Eq. (9)). Hidaka et al. [7] have proposed a general mechanism for the photodegradation of DBS wherein some of the intermediates are detected.

The Langmuir–Hinshelwood type of kinetic analysis assumes the transformation of adsorbed species as the rate-limiting reaction; thus the rate constant can be expected to show a dependence on the concentration (surface coverage) and mode of adsorption governed by the chemical nature of the adsorbed solute species and the specific surface area of

the catalyst. It is found from Table 3 that although the values of K change between 1.0×10^{-2} and 1.0×10^{-4} ppm^{-1} for all the titania catalyst–surfactant systems, the rate constants are comparable. Further, even though the large X_m value for TX-100 compared with that for DBS or CPC (see Table 1) signifies a greater surface coverage with TX-100, the relevant rate constants did not differ in expected magnitude (the large surface coverage implies a higher rate constant). It may be noted that the specific surface areas of the T, MT and WT catalysts are comparable. The data in Table 3 suggest a rate-determining step that does not include surfactant molecules as reactants. Such a reaction step may be the photogeneration of $\cdot$OH/$\cdot$O$_2^-$/$\cdot$OOH radicals (Eqs. (6)–(8)), which presumably shows a dependence on the state and extent of surface hydration/hydroxylation/oxygen adsorption of the catalyst. This may be the light-driven generation of OH radicals as also suggested by Turchi and Ollis [11]. In view of this, the conclusion about rate parameter independence on the organic reactant made by Turchi and Ollis [11] is further substantiated experimentally for the case of surfactants also.

4. Conclusions

Substantial amounts (75%–85%) of the surfactants studied can be photodegraded using TiO$_2$ catalysts and UV light. These surfactants are adsorbed on the TiO$_2$ catalysts using their ionic or polar functional groups. The adsorbent (TiO$_2$)–adsorbate (surfactant) interaction is stronger for the cationic and anionic surfactants and weaker for the non-ionic surfactant. The photocatalytic degradation of these surfactants proceeds according to first-order kinetics. The first-order rate constants are independent of the dark adsorption constants (K) and surface coverage of the surfactants. These first order-rate constants correspond to the photogeneration of reactive radicals ($\cdot$OH, $\cdot$O$_2^-$ or $\cdot$OOH radicals) and not to their subsequent attack on adsorbed surfactant molecules.

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