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Journal of Molecular Catalysis A: Chemical 104 (1996) L197–L199

JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

Letter

Photocatalytic degradation of mixed surfactants and some commercial soap/detergent products using suspended TiO_2 catalysts

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Received 26 May 1995; accepted 25 September 1995

Abstract

Photocatalytic degradation of binary and ternary mixtures of three surfactants, viz., dodecylbenzene sulphonic acid, sodium salt (DBS), cetylpyridinium chloride (CPC) and Triton X-100 (TX-100) has been examined. Indian origin TiO_2 powder was used as photocatalyst in addition to Degussa P-25 TiO_2. These studies were also extended to some commercial soap/detergent formulations. Both surfactant mixtures and commercial formulations photodegrade with comparable efficiency under these conditions.

Keywords: Surfactants; Degradation; Photocatalysis; Titanium dioxide

1. Introduction

Destruction of organic pollutants using UV/sunlight and a suitable photocatalyst such as titanium dioxide has been demonstrated to have great potential to emerge as an alternative water treatment technologies [1]. Surfactants pose severe ecological problem as their biodegradation is slow. Hidaka et al. [2–11] have shown earlier that various surfactants chosen from anionic, cationic and non-ionic classes can be effectively destroyed using aerated aqueous TiO_2 suspensions and UV light illumination. We recently reported [12] studies on adsorption and photocatalytic degradation of DBS, CPC and TX-100 as single components using modified TiO_2 catalysts.

Many commercial soap/detergent products contain two or more surfactants (even up to five) depending on the requirement of the objects to be cleaned. Therefore, it is important to examine the photocatalytic degradation of surfactant mixtures. In this study we report the results of photocatalytic degradation of binary and ternary mixtures of surfactants (DBS, CPC and TX-100) using Degussa P-25 and indian origin TiO_2 powder catalysts. We also examined degradation of aqueous solutions of Liril toilet soap, Rin detergent powder, Sunsilk hair shampoo and laboratory-made metal cleaner using P-25 TiO_2 which exemplify practical situations.

2. Experimental

A typical photolysis experiment included determination of the amount of surfactant disappeared

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1381-1169/96/$09.50
SSDI 1381-1169(95)00259-6

due to photocatalytic degradation from the change in chemical oxygen demand (COD) [13] shown by reacted solutions. Each COD determination was repeated twice and average values were considered for rate parameter estimations. For selected cases, UV–Vis and HPLC determinations were also carried out. All the test aliquots were first made free of catalyst by filtering (Millipore, 0.2 μ) before performing analytical determinations. An annular immersion well photoreactor (SAIC, India) consisting of a 400 W medium pressure Hg lamp (365 nm and 5×10^{19} photons/s) was used for irradiation experiments. P-25 TiO_2 catalyst was a gift from Degussa Inc. USA. TiO_2 (SD) is commercially available in India (S.D. Lab.Chem). The TiO_2 (SD) powder had received a reduction pretreatment in H_2 atmosphere (670 K, 8–10 h) and was characterized to contain a few paramagnetic impurities [14]. A total of 500 cm^3 of aqueous surfactant or soap/detergent solution was used for each experiment. The density of the catalyst suspensions was 0.4 mg/cm^3. Air was pumped through these stirred suspensions using aerator pump. Certain control experiments such as in dark and in presence of light without catalyst were carried out.

3. Results and discussion

The surfactants DBS, CPC and TX-100 adsorb on both P-25 TiO_2 and TiO_2 catalysts using their ionic/polar functional groups [12]. At equilibrium in dark, only about 25–45% of the initial concentration of these surfactants is adsorbed onto these catalysts. Adsorption of DBS, CPC and TX-100 on the surface of catalysts would involve molecules only and not their micelles as their chosen concentrations were below their respective critical micellization concentration.

Photocatalytic degradation of surfactants proceeds gradually when the two essential reaction components viz., TiO_2 catalyst and UV illumination are provided. UV–Vis spectra of the photodegraded surfactant solutions showed gradual disappearance of the peaks ($\lambda_{max} = 225$–250 nm) due to aromatic rings of DBS, CPC and TX-100. Further, HPLC chromatograms of the reacted surfactant solutions clearly demonstrated the photodegradation of these surfactants as well as the degradation of intermediates formed during the course of the reaction. We did not proceed further to identify these intermediates.

The chemical oxygen demand determined over a period of 6 to 18 h showed gradual decrease from its initial value. The $\log[(COD)_t]$ versus time of irradiation plots for the photodegradation of the chosen surfactants and commercial soap/detergent products were linear suggesting that the photodegradation reaction approximately follows first-order kinetics. The percent COD removed, first-order rate constants (k) and half-value periods ($t_{0.5}$) for different surfactants, their binary and ternary compositions and some soap/detergent commercial products are presented in Table 1. Rate constants were estimated [15] from the slopes ($-k/2.303$) of the log[COD] versus time plots; while $t_{0.5}$ values were deduced from $0.693/k$. The data shown against Experiment Nos. 1, 2, 3 and 9 in Table 1 were taken from our previous report [12]. It can be seen that binary and ternary mixtures of the chosen surfactants along with the commercial products can be destroyed (90–98% COD removed in 12–18 h) effectively using both P-25 TiO_2 and TiO_2 (SD) catalysts. The P-25 TiO_2 catalyst causes photodegradation of surfactants and commercial products with an average rate constant of 3.21×10^{-3} min^{-1} ($t_{0.5} = 216$ min), while TiO_2 (SD) catalyst performs better with a slightly higher average rate constant i.e., 3.50×10^{-3} min^{-1} ($t_{0.5} = 198$ min). The related $t_{0.5}$ values suggest that the pollutant load can be brought down to half of initial value in about 3–4 h. Comparing the data of experiments No. 1 and 8, we understand that the presence of hardness causing ions in water such as Mg^{2+} is deleterious for the photodegradation reaction of surfactants. The fact that rate constants for all the cases are comparably similar within a maximum scatter of 40% relative to the average rate constant suggests that the TiO_2 photocatalysis may be regarded as indiscriminate and can be applied to

Table 1
Photocatalytic degradation parameters for the destruction of surfactant mixtures and commercial formulations

Expt. No.	Catalyst	Reactant [$(COD)_0$]	Time (h)	% COD (ppm)	$k \times 10^3$ (min^{-1})	$t_{0.5}$ (min)
1	TiO_2 (SD)	D (82.3)	6	85.2	4.30	161
2	TiO_2 (SD)	C (83.4)	6	73.0	3.50	198
3	TiO_2 (SD)	T (71.1)	6	74.3	4.72	147
4	TiO_2 (SD)	DC (171)	18	98.0	3.42	202
5	TiO_2 (SD)	CT (211.2)	18	97.0	3.27	212
6	TiO_2 (SD)	DT (172.4)	18	98.7	3.69	144
7	TiO_2 (SD)	DCT (289.5)	18	96.0	2.58	268
8		D (82.3) ($MgSO_4$)	10	93.5	2.58	268
9	P-25	D (82.3)	6	78.0	3.70	187
10	P-25	DC (171.0	18	97.3	2.58	268
11	P-25	CT (211.2)	18	94.0	3.34	207
12	P-25	DT (172.4)	18	91.5	2.53	274
13	P-25	DCT (289.4)	18	95.0	3.20	216
14	P-25	Liril (100)	12	94.0	3.07	226
15	P-25	Rin (100)	12	93.0	3.21	216
16	P-25	Sunsilk (100)	12	96.0	3.84	180
17	P-25	Metal Cleaner (100)	12	95.0	3.42	202

D = DBS, C = CPC, T = TX-100; [$(COD)_0$] = initial COD in ppm.

treat surfactant mixtures as well as commercial soap/detergent products.

Acknowledgements

We thank Professor P. Natarajan (Director, C.S.M.C.R.I) for encouraging us to perform this work.

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