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Photocatalytic degradation of cetylpyridinium chloride over titanium dioxide powder

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Abstract

The photocatalytic degradation of cetylpyridinium chloride (CPC) over titanium dioxide photocatalyst was investigated. The effects of various parameters, such as the pH, concentration of surfactant, amount of semiconductor, particle size, light intensity, etc., were observed and are discussed. The photocatalytic degradation of CPC follows pseudo-first-order kinetics and the rate constant was determined using the expression

Rate constant $k = 2.303 \times$ slope

The final products of degradation were characterized and a tentative mechanism was proposed for the photocatalytic degradation of cetylpyridinium chloride. ©1997 Elsevier Science S.A.

Keywords: Photocatalysis; Surfactant degradation; Titanium dioxide

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1. Introduction

The extensive use of surfactants for domestic and industrial purposes poses a severe problem of environmental pollution, since these compounds do not degrade very rapidly. In particular, cationic surfactants undergo slow biodegradation due to their bactericidal nature and are more toxic than other surfactants with respect to plants and animals [1,2]. There is a pressing need to provide a method for the treatment of wastewater which is of low cost and not too time consuming. Recently, several reports by Hidaka et al. [3–6] on the photocatalytic degradation of cationic surfactants have been published, but no attention has been paid to the photocatalytic degradation of surfactants such as cetylpyridinium chloride (CPC). Therefore the present work was undertaken.

2. Experimental details

A stock solution of CPC was prepared by dissolving 0.05 g of surfactant in 1 l of doubly distilled water. This surfactant solution was poured into four beakers. To the first and second beakers, 0.30 g of TiO_2 (without further purification) was added. The first and third beakers were exposed to light from a 1000 W halogen lamp (OKANO, Japan), and the second and fourth beakers were placed in the dark. The reaction takes place only in the presence of semiconductor and light, i.e. in the first beaker, demonstrating that the reaction is photocatalytic and not chemical (thermal and/or photochemical).

The progress of the reaction was observed using the orange G active substance (OAS) method [5]. A 0.1% solution of orange G (1.5 ml), 2.5 g of sodium chloride and 5 ml of CH_3COOH/CH_3COONa buffer solution (pH 3.5) were added to 5 ml of exposed solution. The solution was extracted with chloroform by vigorous shaking for about 3 min. The absorbance of the chloroform layer was measured spectrophotometrically at 420 nm at different time intervals; this provides the amount of unreacted CPC.

3. Results and discussion

A plot of log(OD) (OD, optical density) vs. time was measured to be a straight line. This indicates that the photocatalytic degradation of CPC follows pseudo-first-order kinetics. The rate constants of the reaction were determined using the expression

$$\text{Rate constant } k = 2.303 \times \text{slope} \tag{1}$$

The results of a typical run are presented graphically in Fig. 1.

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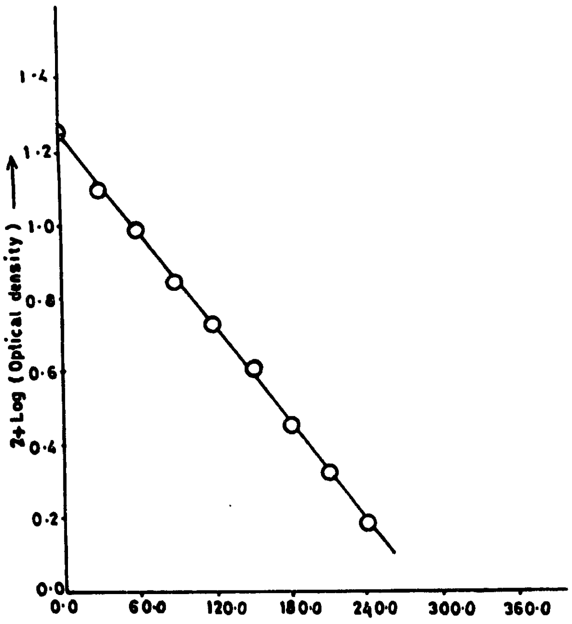

Fig. 1. A typical run.

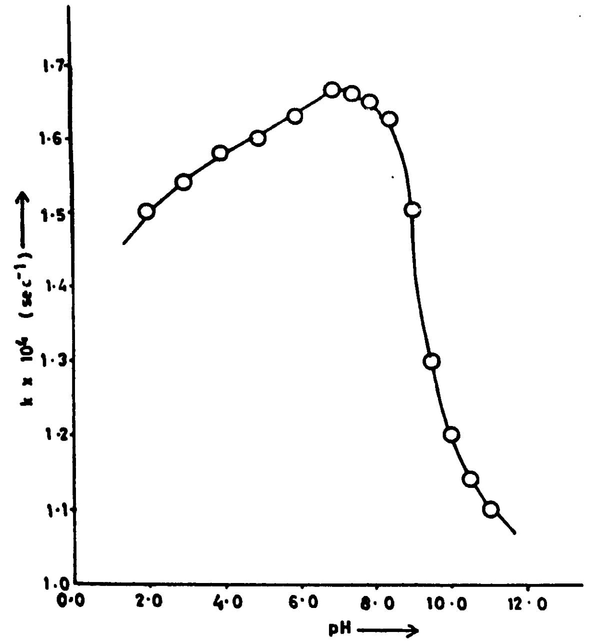

Fig. 2. Effect of pH.

3.1. Effect of pH

The pH of the medium is expected to affect the rate of photocatalytic degradation of CPC, and hence the photodegradation rate of CPC was investigated at different pH values. The results are given in Fig. 2. It is clear from Fig. 2 that the maximum rate is observed when the medium is neutral. In both alkaline and acidic media, the rate of photodegradation of CPC decreases. This may be explained on the basis that the titanium dioxide surface contains positively charged $^+OH_2$ groups in acidic medium. This positively charged surface of the TiO_2 particles will cause repulsion of the positively charged (cationic) surfactant entity

$$Ti\text{–}^+OH_2 \overset{\text{Repulsion}}{\Leftrightarrow} [CPC]^+$$

This will retard the approach of cetylpyridinium ions towards the TiO_2 surface, thus causing a corresponding decrease in the rate of photodegradation.

On the other hand, the surface of titanium dioxide will be negatively charged in alkaline medium due to O^- on the surface. This negatively charged surface will strongly adsorb CPC due to coulombic attraction

$$Ti\text{–}O^- \overset{\text{Attraction}}{\rightarrow\leftarrow} [CPC]^+$$

The attack of reactive $OH^\bullet$ radicals (formed via electron–hole pairs) will be checked and lowered. This will cause a corresponding decrease in the reaction rate.

3.2. Variation of pH with time

The pH values of the reaction mixtures were observed at different time intervals during the continuous exposure of solutions with different initial pH values. The results are reported graphically in Fig. 3. The pH of the reaction mixture changes on exposure and approaches pH 8.5 for solutions in the pH range 7.0–11.0. Solutions in the pH range 4.0–6.0 show a similar behaviour, but the pH approaches a value of 7.3–8.0. In contrast, in strongly acidic solutions with lower pH values (pH 2.0–3.0), OH_3^+ decreases strongly, thus indicating that the cationic surfactant CPC is photodegraded to a limited extent only in this range. Hidaka et al. [3] have observed that TiO_2 has an isoelectric point at pH 5.3. The present results are not in agreement with this observation; rather the curves of pH vs. time approach pH 8.5 in the present case.

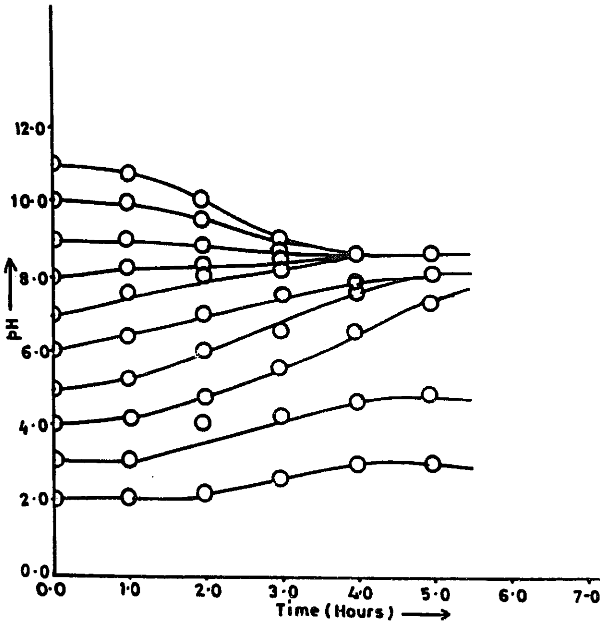

Fig. 3. Variation of pH with time.

3.3. Effect of concentration of surfactant

The effect of the concentration of the cationic surfactant CPC on the rate of photocatalytic degradation was observed by taking solutions of different initial concentration and keeping all the other factors identical. The results are reported in Table 1. As the concentration of CPC is increased above 2.94×10^{-5} M, up to 1.47×10^{-4} M, the rate of reaction decreases. At higher concentrations, the decomposition of CPC is so slow that no change in the concentration of unreacted CPC is observed. The concentration of unreacted CPC remains virtually constant even after about 4 h of irradiation for solutions with concentrations above the critical micelle concentration (CMC), i.e. 9.0×10^{-4} M. This suggests that the photodegradation of the cationic surfactant CPC must be carried out in solutions with concentrations below the CMC value.

The CPC micelle will have a positive surface potential denser than that of the surfactant molecule. This will restrict the approach of this micelle to the TiO_2 surface, and hence no reaction will be observed even on long-term exposure. Therefore it is necessary to keep the concentration of surfactant below the CMC value for efficient photocatalytic degradation. In other words, CPC cannot be photodegraded easily once it acquires a micellar structure.

The maximum was obtained at a CPC concentration of 2.94×10^{-5} M. The decrease in the rate of reaction with an increase in the concentration of the surfactant above this value can be explained by the fact that a larger concentration of surfactant will hinder the movement of surfactant towards the TiO_2 surface.

3.4. Effect of amount of semiconductor

Keeping all other factors identical, the effect of the amount of titanium dioxide (semiconductor) was observed. The results are given in Table 2. The data observed may be explained on the basis that, in the initial stage, even a small addition of semiconductor will increase the rate of reaction as the exposed surface area of the semiconductor increases; however, after a certain amount (0.30 g) of semiconductor has been added, the rate of reaction is not affected by further additions since, at this limiting amount, the surface at the bottom of the reaction vessel is completely covered with semiconductor. Any further increase in the amount of semiconductor will only increase the thickness of the layer of the semiconductor at the bottom of the vessel and not the exposed surface area.

Therefore it may be concluded that this limiting value will depend on the geometry of the reaction vessel. This was confirmed in an experiment in which reaction vessels of different dimensions were used. It was observed that the limiting value was shifted to a higher range for larger vessels, whereas a decrease in limiting value was observed for smaller vessels.

Table 1
Effect of the concentration of the surfactant (TiO_2 = 0.30 g; pH 7.0; temperature, 303 K; intensity, 65.0 mW cm^{-2})

[CPC] $\times10^5$ (M)	$k\times10^4$ (s^{-1})
1.47	1.13
2.94	1.67
4.41	1.66
5.88	1.65
7.35	1.60
8.82	1.58
10.29	1.57
11.76	1.56
13.23	1.51
14.70	1.50

Table 2
Effect of the amount of the semiconductor ([CPC] = 2.94×10^{-5} M; pH 7.0; temperature, 303 K; intensity, 65.0 mW cm^{-2})

Amount of TiO_2 (g)	$k\times10^4$ (s^{-1})
0.10	1.42
0.15	1.50
0.20	1.56
0.25	1.65
0.30	1.67
0.35	1.67
0.40	1.68

Table 3
Effect of the particle size ([CPC] = 2.94×10^{-5} M; TiO_2 = 0.30 g; intensity, 65.0 mW cm^{-2}; pH 7.0; temperature, 303 K)

Particle size (μm)	$k\times10^4$ (s^{-1})
0.8	1.67
1.6	1.50
2.4	1.42
3.2	1.26
4.0	1.20

3.5. Effect of particle size

The effect of particle size on the rate of reaction was investigated by taking semiconductor particles of different sizes. The results are reported in Table 3. As indicated by the data in Table 3, the rate of reaction increases with decreasing particle size of the semiconductor. This increase in rate may be explained on the basis of the increased surface area of the photocatalyst as the particle size is reduced.

3.6. Effect of light intensity

The effect of a variation in light intensity on the rate of the reaction was investigated and the results are summarized in Table 4. An increase in light intensity increases the rate of reaction. With an increase in the light intensity, the number of photons striking the semiconductor per unit area of the semiconductor powder increases. A linear behaviour is observed between the light intensity and the rate of reaction.

Table 4
Effect of the light intensity ([CPC] $=2.94\times10^{-5}$ M; $TiO_2=0.03$ g; pH 7.0; temperature, 303 K)

Light intensity (mW cm^{-2})	$k\times10^4$ (s^{-1})
15.0	0.42
25.0	0.66
35.0	0.82
45.0	1.32
55.0	1.44
65.0	1.67

Table 5
Effect of the sensitizer ([CPC] $=2.94\times10^{-5}$ M; pH 7.0; $TiO_2=0.30$ g; intensity, 65.0 mW cm^{-2})

Sensitizer	λ_{max} (nm)	$k\times10^4$ (s^{-1})
-	-	1.67
Methylene blue	661	1.69
Brilliant blue R	585	1.72
Pyronine B	533	2.10
Congo red	497	2.34
Potassium ferrocyanide	422	6.39

3.7. *Effect of sensitizer*

The effect of sensitizers on the rate of reaction was observed and the results are given in Table 5. A sensitized TiO_2 photocatalyst is more efficient than a non-sensitized catalyst. This may be attributed to the fact that sensitizer molecules absorb light radiation of higher wavelength and transfer its energy to the semiconductor particle, thus making it more active. All five sensitizers were effective in increasing the photocatalytic activity of semiconductor titanium dioxide, with the following order of efficiency: $K_4Fe(CN)_6>$ Congo red > pyronine B > brilliant blue R > methylene blue > non-sensitized. This trend can be related to λ_{max}, since as λ_{max} decreases the rate of photodegradation increases. This is due to the fact that sensitizers with lower λ_{max} will absorb radiation of higher energy.

4. Mechanism

On the basis of the experimental observations, the following tentative mechanism has been proposed for the photocatalytic degradation of CPC

$$SC\xrightarrow{h\nu}SC^* \tag{2}$$

$$SC^*\rightarrow e^-(CB)+h^+(VB) \tag{3}$$

$$h^+ + H_2O\rightarrow H^+ + OH^{\bullet} \tag{4}$$

$$C_{21}H_{38}N^+Cl^- + OH^{\bullet}\rightarrow CO_2+H_2O+N_2+Cl^- \tag{5}$$

The semiconductor is excited by the absorption of light radiation. The excited semiconductor produces electrons in the conduction band and holes in the valence band. The holes are trapped by surface hydroxyl groups yielding adsorbed $OH^{\bullet}$ radicals. The $OH^{\bullet}$ radicals attack CPC and gaseous products are obtained.

The aromatic ring seems to be the primary target for the attack of $OH^{\bullet}$ radicals as cationic surfactants containing aromatic groups are easily photodegraded. The aromatic moiety yields some hydroxyl groups containing radicals which are further oxidized. Carbon dioxide is detected as one of the products of the photodegradation of CPC by its usual test with barium hydroxide. The participation of $OH^{\bullet}$ radicals as the reactive oxidizing species is confirmed by the observation of the rate of photocatalytic degradation of CPC in the presence of the $OH^{\bullet}$ radical scavenger, isopropanol, where the rate of reaction is reduced almost to zero.

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