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Light flux and light flux density dependence of the photomineralization rate of 2,4-dichlorophenol and chloroacetic acid in the presence of TiO_2

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Abstract

An examination of the effects of the variation of the light flux and light flux density over wide ranges on the photomineralization rates r_i of 2,4-dichlorophenol and monochloroacetic acid by TiO_2 in aqueous suspension reveals that r_i depends on the product of the light flux (to the first power) and the light flux density (to the power 0.0 and −0.5 at low and high light flux densities respectively).

Keywords: Light flux; Light flux density; Photomineralization

1. Introduction

The removal of organochlorine compounds from surface water by photochemical methods is of current interest. The aim is to mineralize these materials ultimately to chloride ion and carbon dioxide [1]. While direct UV light has been used, often in conjunction with the presence of ozone [2–4] or hydrogen peroxide [2–4], particular effort is currently being devoted to the investigation of the use of semiconductor photocatalysts [1,5], especially TiO_2 [6]. Despite the very large number of papers on the general kinetics of photomineralization, there have been few studies devoted to the dependence of the mineralization rate on the so-called intensity of irradiation I_a [7–16]. Systems which have received particularly detailed attention are those based on the photomineralization of phenol [7] and propan-2-ol [8], and brief references to the effects of I_a have been reported for the TiO_2-senzitized photolysis of 3-chlorophenol [9], 4-chlorophenol [10,11], 3-methylphenol [12], dichloroacetic acid [13], salicylic acid [14], pentachlorophenol [15] and Reactive Black 5 [16].

The photomineralization rate can be given by [1,7]

$$r=\frac{\gamma K_{O_2}[O_2]I_a{}^m K_S[S]}{(1+K_{O_2}[O_2])(1+K_S[S])} \qquad (1)$$

where I_a is the light flux (often called the light intensity) absorbed (in photons s^{-1}), m is an exponent with a value of unity at low light flux, but falling to 0.5 at high light flux, and K_{O_2} and K_S are the adsorption coefficients of oxygen and the organic substrate S on the TiO_2 surface. Experimental results have matched Eq. (1) [7-16], but Eq. (1) does not deal with one factor, namely the area undergoing irradiation. In the majority of reported experiments, the irradiated area was left unchanged, being given by the geometry of the reactor, whilst the light flux was varied. Moreover, Eq. (1) cannot account for the focusing of a given light beam. Thus, for a given light flux, the question arises as to whether r_i remains constant or changes significantly at high light flux density (denoted ϕ_{LFD}) (quanta s^{-1} cm^{-2}).

In our experiments with model systems TiO_2–water–2,4-dichlorophenol and TiO_2–water–chloroacetic acid, we have addressed these questions by:

(1) a systematic variation of the light flux I_a;
(2) a systematic variation of the area undergoing irradiation (at a constant light flux, but varying the light flux density ϕ_{LFD});
(3) the use of higher light flux densities than the maximum used hitherto (i.e. 2×10^{18} photons s^{-1} cm^{-2} [8]).

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2. Experimental details

2.1. Chemicals

All solutions were prepared using doubly distilled water. Titanium dioxide was purchased from Fluka (Germany), perchloric acid and potassium chloride from Fisons (UK), 2,4-dichlorophenol and chloroacetic acid from Reanal (Hungary), anhydrous sodium sulphate, iron(III) chloride, potassium oxalate and 1,10-phenanthroline hydrate from BDH (UK) and oxygen and high purity argon from B.O.C. (UK). High performance liquid chromatography (HPLC) grade hexane was purchased from Aldrich. The chemicals were used without further purification.

2.2. Instrumentation

UV–visible spectra were taken using a Perkin–Elmer 552 UV–visible spectrophotometer. The irradiations were carried out using an Illuminator 6000 xenon lamp (Eurosep Instruments, France) which features four apertures delivering different light flux outputs. Gas chromatography (GC) measurements were carried out with a Pye–Unicam 204 instrument equipped with a Carbowax 20 column and flame ionization detector. The chloride ion concentration was measured with a Russell 96-6179B combined chloride ion-selective electrode connected to a Thurlby 1503 millivoltmeter. The kinetic results obtained by ion-selective electrode, GC and UV–visible spectrophotometry were in accordance with each other. The centrifuge used to separate titanium dioxide from the solutions was a DuPont S1 instrument. The disc-shaped photoreactor was made of Pyrex glass, with a diameter of 5.5 cm, a thickness of 1.5 cm and a volume of 40 cm^3. The Pyrex glass cut out UV light below 320 nm. The sonicator from Sonicor Instrument Co. (Copiague, USA) had a power of 160 W.

2.3. Procedures

The 2,4-dichlorophenol solution was prepared to a concentration of 0.001 M (163 ppm). Its pH was adjusted to 3.0 with perchloric acid. The chloroacetic acid solution was also prepared to a concentration of 0.001 M (94.5 ppm). Its pH was 3.2 due to the dissociation of chloroacetic acid. To 40 cm^3 of stock solution was added 40 mg TiO_2 (0.1%). After 15 min of sonication, the solution containing suspended TiO_2 was purged for 10 min with argon or oxygen prior to irradiation; purging was continued during irradiation to maintain the suspension of TiO_2. The irradiated solution was then centrifuged and filtered through a Millipore filter of pore size 0.2 μm. UV–visible spectra were taken, and a 10 cm^3 sample was used to determine the chloride ion concentration. The ionic strength of the sample was adjusted to 0.1 M using 0.2 cm^3 of sodium nitrate solution (5.0 M) in the form of an ionic strength adjustor solution provided by Russell. The remaining irradiated solution (30 cm^3) was extracted by hexane, and the extract was dried with anhydrous sodium sulphate and analysed by GC.

The light fluxes of the four outputs from the Illuminator 6000 were measured by potassium trisoxalatoiron(III) actinometry according to Hatchard and Parker [17]. The calibration curve for the combined chloride ion-selective electrode was constructed using 10^{-2}, 10^{-3}, 10^{-4}, 5×10^{-5}, 2×10^{-5} and 10^{-5} M potassium chloride solutions, their ionic strength being adjusted to 0.1 M with 5.0 M $NaNO_3$ solution. The time response of the electrode was studied; since a generally stable value was achieved within 1 min, all millivolt values were taken 60 s after immersing the electrode in the solutions.

The area of cross-section of the light beam was determined by placing Kodak photographic paper in the light path, followed by measurement of the blackened area.

3. Results and discussion

3.1. Effects of sonication, pH and oxygen bubbling

In our initial experiments, the effects of sonication, pH and purging gas were checked. As can be seen in Table 1, both sonication and a decrease in pH from its natural value to 3.0 increased the photodecomposition rate of 2,4-dichlorophenol. The presence of oxygen also enhanced the photomineralization rate compared with an inert atmosphere, so that all subsequent experiments were carried out after 15 min of sonication, at pH 3.0 with oxygen bubbling constantly through the reactor.

3.2. Effects of light flux I_a and light flux density ϕ_{LFD}

The rate of chloride ion formation was measured during variation of the light flux and irradiated area between 5.46×10^{16} and 4.2×10^{17} photons s^{-1} and 0.071 and 22 cm^2 respectively. The calculated light flux densities and associated apparent quantum yields ϕ_{app} [18] are summarized in Tables 2 and 3. Inspection of the data in Table 2 shows that, when the maximum (constant) output (i.e. light flux) of the lamp was focused, the photomineralization rate (and hence the apparent quantum yield ϕ_{app}) decreased (while the total light flux remained unchanged). This decrease is probably a consequence of the enhanced electron–hole recombination.

The mineralization rate was divided by the irradiated area A to yield normalization, i.e. to ensure that the rates obtained were for irradiations carried out with

Table 1
Effects of pH, gaseous atmosphere and sonication on the photomineralization rate of 2,4-dichlorophenol (10^{-3} M) in the presence of TiO_2

Experiment	Purging gas	pH	Sonication	Light flux (10^{16} quanta s^{-1})	A (cm^{-2})	dC/ dt (10^{-5} M h^{-1})
1	Oxygen	Natural	No	42.0	0.3	1.2
2	Oxygen	3.0	No	42.0	0.3	1.6
3	Oxygen	3.0	Yes	42.0	0.3	3.2
4	Argon	3.0	Yes	42.0	0.3	1.3

Table 2
Effects of light flux (I_a) and light flux density (ϕ_{LFD}) on the photomineralization rate of 2.4-dichlorophenol in the presence of TiO_2 (pH 3.0)

Experiment	I_a (10^{16} photons s^{-1})	A (cm^2)	ϕ_{LFD} (10^{16} photons cm^{-2} s^{-1})	dC/ dt (10^{-5} M h^{-1})	ϕ_{app} (10^{-4})
1	5.46	22.0	0.25	0.27	3.31
2	5.46	22.0	0.25	0.25	3.09
3	15.2	22.0	0.69	0.91	4.02
4	15.2	22.0	0.69	0.92	4.05
5	19.5	7.07	2.76	0.96	3.28
6	42.0	6.16	6.82	2.25	3.58
7	42.0	4.34	9.68	2.54	4.06
8	26.6	0.64	41.8	1.34	3.38
9	26.6	0.407	65.4	1.28	3.21
10	42.0	0.407	103	2.58	4.11
11	42.0	0.407	103	2.88	4.59
12	42.0	0.300	139	2.60	4.15
13	42.0	0.300	139	2.62	4.18
14	42.0	0.300	139	2.80	4.46
15	42.0	0.300	139	3.20	5.08
16	42.0	0.181	232	2.02	3.22
17	42.0	0.181	232	2.45	3.90
18	42.0	0.071	592	2.26	2.00
19	42.0	0.071	592	1.44	2.30

Table 3
Effects of light flux (I_a) and light flux density (ϕ_{LFD}) on the photomineralization rate of monochloroacetic acid in the presence of TiO_2 (pH 3.2)

Experiment	I_a (10^{16} photons s^{-1})	A (cm^2)	ϕ_{LFD} (10^{16} photons cm^{-2} s^{-1})	dC/ dt (10^{-5} M h^{-1})	ϕ_{app} (10^{-4})
1	2.19	22.0	0.10	0.10	3.03
2	6.46	22.0	0.29	0.30	3.08
3	10.4	12.6	0.82	0.62	3.97
4	30.5	12.9	2.36	1.56	3.43
6	30.5	4.71	6.48	1.55	3.41
7	30.5	1.58	19.3	1.48	3.25
8	30.5	0.636	48.0	1.22	2.69
9	30.5	0.342	89.2	1.68	3.70
10	30.5	0.238	128	2.29	5.02
11	30.5	0.212	144	2.40	5.26
12	30.5	0.196	156	0.83	1.82
13	30.5	0.126	242	1.18	2.59
14	30.5	0.071	430	0.92	2.01

an area of 1.0 cm^2 in each case. In Fig. 1, the normalized photomineralization rate and the apparent quantum yield are plotted against the light flux density. As far as the normalized photomineralization rate is concerned, the pattern expected from previous studies using phenol [7] and propan-2-ol [8] can be seen: at low light flux density, the normalized decomposition rate is a linear function, whereas at high light flux density, a square root dependence is observed. The light flux density is equivalent to the light flux in these experiments, because the irradiated area is the same. However, when this is not so, both the quantum yield and light flux should

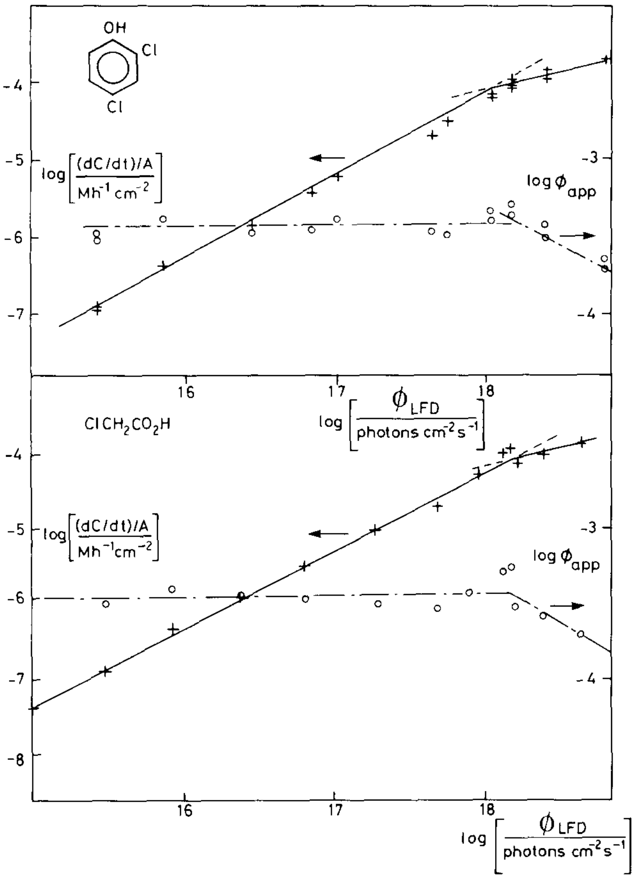

Fig. 1. Dependence of the normalized mineralization rate (full line) and quantum yield (broken line) of 2,4-dichlorophenol and monochloroacetic acid on the light flux density.

be taken into account, since the effect of irradiation is proportional to the product of the quantum yield and the light flux. When the quantum yield at low light flux density is constant, any increase in the light flux brings about a linearly proportional increase in the photomineralization rate; however, when the quantum yield is given as

$$\phi_{\mathrm{app}} = k\phi_{\mathrm{LFD}}^{-0.5} \qquad (2)$$

i.e. a decreasing function of the light flux density, the increase in the light flux is partly offset by the decreasing quantum yield. Thus the photomineralization rate is no longer linearly dependent on the light flux. We can write

$$r_{\mathrm{i}} = K\phi_{\mathrm{app}}I_{\mathrm{a}} \qquad (3)$$

and

$$\phi_{\mathrm{app}} \approx \phi_{\mathrm{LDF}}^{\;b} \qquad (4)$$

where $b = 0$ and -0.5 at low and high light flux densities respectively. Since $\phi_{\mathrm{LFD}} = I_{\mathrm{a}}/A$, we can write

$$r_{\mathrm{i}} = K\left(\frac{I_{\mathrm{a}}}{A}\right)^{b} I_{\mathrm{a}} = \frac{K}{A^{b}} I_{\mathrm{a}}^{\,1+b} \qquad (5)$$

If A is constant, Eq. (5) is equivalent to Eq. (1), but Eq. (5) stresses that r_{i} is influenced by the light flux not only directly, but also indirectly via the dependence of the quantum yield on the light flux density.

4. Conclusion

It is reasonable to complement Eq. (1) with an additional factor referring to the function $\phi_{\mathrm{app}}(\phi_{\mathrm{LFD}})$

$$r_{\mathrm{i}} = \frac{\gamma K_{\mathrm{O_2}}[\mathrm{O_2}]K_{\mathrm{S}}[\mathrm{S}]}{(1+K_{\mathrm{O_2}}[\mathrm{O_2}])(1+K_{\mathrm{S}}[\mathrm{S}])}\,\phi_{\mathrm{LFD}}^{\;b}I_{\mathrm{a}} \qquad (6)$$

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