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Decomposition of endocrine-disrupting chemicals in water by use of TiO_2 photocatalysts immobilized on polytetrafluoroethylene mesh sheets

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Abstract

We examined the photocatalytic decomposition of 17β-estradiol (E2), bisphenol-A (BPA), and 2,4-dichlorophenol (2,4-DCP) in aqueous solutions by use of TiO_2 particulate photocatalysts immobilized on polytetrafluoroethylene (PTFE) mesh sheets and black-light fluorescent lamps. These organic compounds are known to be endocrine-disrupting chemicals (EDCs). These EDCs absorb little of the light from black-light fluorescent lamps. The TiO_2-modified PTFE mesh sheets were stacked with 5 mm gaps in a 2-l glass cylinder in which the solution was circulated by use of a rotary pump. In the case of this reactor, a first-order rate constant of ca. $0.033\,\mathrm{min}^{-1}$ was obtained at 10 °C for all of the compounds (initial concentration was $90\,\mu\mathrm{g\,l}^{-1}$ each). This relatively fast reaction rate was obtained repeatedly in cycling tests under UV illumination. The TiO_2-modified PTFE mesh sheets were attached to a bar-rotator in a fan-type arrangement being rotated at 60 rpm. In the case of the latter reactor, a higher first-order rate constant (ca. $0.050\,\mathrm{min}^{-1}$) was obtained for the decomposition of both E2 and 2,4-DCP. The apparent mass-transfer rate of the EDCs to the TiO_2 was able to be increased by a factor of ca. 4.5 by use of the latter reactor (i.e. with rotation of the PTFE mesh sheets themselves) compared to the use of the former reactor (conventional circulation of the aqueous solution only). Based on these results, we conclude that this rotation technique of the TiO_2-modified PTFE mesh sheets has the potential to become one of the most effective and efficient procedures for the removal of EDCs from water.

Keywords: Titanium dioxide; Photocatalyst; Decomposition; 17β-estradiol; Bisphenol-A; 2,4-dichlorophenol; Endocrine-disrupting chemicals; Polytetrafluoroethylene; Mesh sheet; Rotation; Rate constant; Mass transfer

1. Introduction

It has been pointed out that the existence of several types of pollutant chemicals in the environment can possibly result in the abnormal growth of wildlife [1,2]. For example, 17β-estradiol (E2), which is a female sex hormone and is contained in urine, is considered to be an endocrine-disrupting chemical (EDC). E2 possibly causes the abnormal growth of carp in the Tama River near Tokyo [3]. The concentration of E2 detected in a tributary of the Tama River near Tokyo reached $0.041\,\mu\mathrm{g\,l}^{-1}$, according to the Ministry of the Environment of Japan [4]. At that value, E2 has been shown experimentally to exhibit some estrogenic activity for human estrogen receptors [5]. In addition, bisphenol-A (BPA) has been regarded as an EDC ever since Krishnan et al. [6] discovered an abnormal increase in the growth of yeast cells in polycarbonate flasks. BPA was generated during the decomposition of the polycarbonate flasks. Besides, 2,4-dichlorophenol (2,4-DCP) is a well-known intermediate in the manufacture of dyes.

According to the Ministry of Construction of Japan, these EDCs are not removed completely by conventional treatment, for example, activated sludge, during sewage treatment. In fact, an average of 24% of the E2 originally contained in raw sewage remains after treatment and is released to the environment [7]. In order to avoid increasing the amounts of EDCs released as far as possible, an alternative method to remove EDCs from water is urgently required.

Recently, TiO_2 photocatalysts have been gaining attention for their strong photo-induced oxidation power. Almost all environmental chemicals, even those that are toxic at low concentration, can be decomposed to carbon dioxide by TiO_2 photocatalytic reactions [8–11]. Since increased quantum efficiencies of TiO_2 photocatalytic reactions can be obtained under lower-intensity UV light [9], UV light intensities much smaller than that of solar-light are necessary in order remove such small amounts of EDCs [12–15]. Thus, we employed the relatively low-intensity black-light fluorescent lamps in the present study.

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Conventionally, TiO_2 suspensions have been used to decompose EDCs [12–19]. In practice, however, an immobilized TiO_2 system is required in order to avoid the need to remove TiO_2 nanoparticles from the treated water. One possible problem with an immobilized system is that the effective TiO_2 surface area is typically substantially lower as compared with that in the case of TiO_2 suspensions. Thus, the reaction rates may be impractically low for treating large amounts of solution. Therefore, methods of enhancing the mass transfer to the TiO_2 surface are important for developing TiO_2-immobilized reactors.

To solve this problem, we constructed a new immobilized TiO_2 system as well as a second system involving rotating porous photocatalysts. Therefore, we used TiO_2-modified PTFE mesh sheets, because PTFE has long-term stability against TiO_2 photooxidation. The mesh sheets were attached to a single bar-rotator in order to be rotated in the solution. As a result, E2, BPA, and 2,4-DCP in aqueous solutions were decomposed more quickly than in the conventional case, in which the aqueous solution is pumped through the mesh sheets with a rotary pump. As these EDCs absorb little of the light from black fluorescent lamps, photo-sensitized oxidation of EDCs on the TiO_2 surface did not occur. To remove EDCs efficiently at sewage plants, the mass-transfer factor is very important in scaling up the photocatalytic reactor to a practical size. An analysis of the results from the viewpoint of fluid mechanics was carried out.

2. Experimental

E2 was purchased from Wako Pure Chemicals Industries, Ltd. BPA and 2,4-DCP were purchased from Tokyo Kasei Kogyo Co., Ltd. The aqueous solutions of E2, BPA and 2,4-DCP were prepared with distilled water.

The TiO_2-modified PTFE mesh sheets (PFG-S20, Nitto Denko Co.) are made up of strands that are 0.30 mm thick and 0.5 mm wide, with 1 mm square openings (49% open ratio; see inset in Fig. 2). The bare PTFE mesh sheets were also obtained from Nitto Denko Co.

Details of the type I reactor are as follows: 72 of the TiO_2-modified PTFE mesh sheets were arrayed horizontally at 5 mm intervals by use of acrylic rods in a 2-l glass cylinder (84 mm diameter), as shown in Fig. 1. A 2-l portion of the solution was poured into a measuring cylinder. The ratio of the apparent surface area of the TiO_2-modified PTFE mesh sheets to the volume of the test solution was $1.0\,\mathrm{cm^2\,ml^{-1}}$. The solution was illuminated with two 15 W black fluorescent lamps (Type FL15 BL-B, National Co.). The light intensity was $0.24\,\mathrm{mW\,cm^{-2}}$, measured by use of a UV radiometer (UVR-36, Topcon Co.) at the center of the glass cylinder. The solution was circulated at $340\,\mathrm{ml\,min^{-1}}$ with a rotary pump (Type PA-25A, 7520-10, Cole-Parmer Instrument Co.).

Details of the type II reactor are as follows: 16 of the TiO_2-modified PTFE mesh sheets ($58 \times 150\,\mathrm{mm^2}$) were attached vertically radiating out from the central shaft of a bar-rotator. They were then placed vertically in a 2-l beaker ($\phi = 125\,\mathrm{mm}$) as shown in Fig. 2. The ratio of the apparent surface area of the TiO_2-modified PTFE mesh sheets to the water volume was $0.35\,\mathrm{cm^2\,ml^{-1}}$. A 2-l portion of the solution was poured into the beaker. Two black-light fluorescent lamps were employed, and the TiO_2-modified PTFE mesh sheets were rotated at 60 rpm with a motor. The illumination intensity was also $0.24\,\mathrm{mW\,cm^{-2}}$.

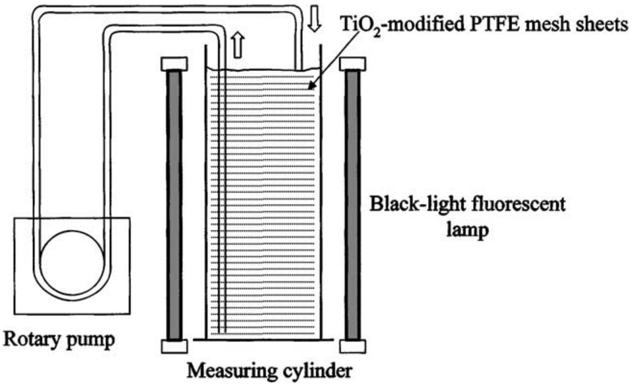

Fig. 1. Schematic illustration of the type I reactor. The 72 TiO_2-modified PTFE mesh sheets were stacked with 5 mm gaps in a 2-l glass cylinder ($\phi = 84\,\mathrm{mm}$) in which the solution was circulated at $340\,\mathrm{ml\,min^{-1}}$ by use of a rotary pump (see text).

The initial concentration of the compounds was $90\,\mu\mathrm{g\,l^{-1}}$, unless otherwise noted. The concentrations of the compounds in the test solutions were evaluated with a high-performance liquid chromatograph (HPLC) equipped with an ODS column (a reversed-phase TSK gel ODS-80Ts $250 \times 4.6\,\mathrm{mm^2}$ ID column) at 40 °C. The eluent was acetonitrile–water (1:1) with a flow-rate of $1.0\,\mathrm{ml\,min^{-1}}$. This was combined with a UV absorption detector (UV-8020, Tosoh Co.; flow-cell volume, $10\,\mu\mathrm{l}$) or a Hitachi F2000 fluorescence spectrometer with a micro-flow-cell volume of $18\,\mu\mathrm{l}$. UV–visible absorption spectra and diffuse

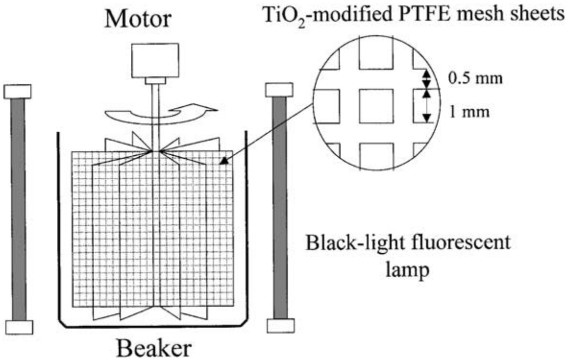

Fig. 2. Schematic illustration of the type II reactor. The 16 TiO_2-modified PTFE mesh sheets ($58 \times 150\,\mathrm{mm^2}$) were attached vertically radiating out from the central shaft of a bar-rotator in a 2-l beaker ($\phi = 125\,\mathrm{mm}$), being rotated at 60 rpm with a motor (see text). A magnified image of the PTFE mesh sheet is shown in the inset.

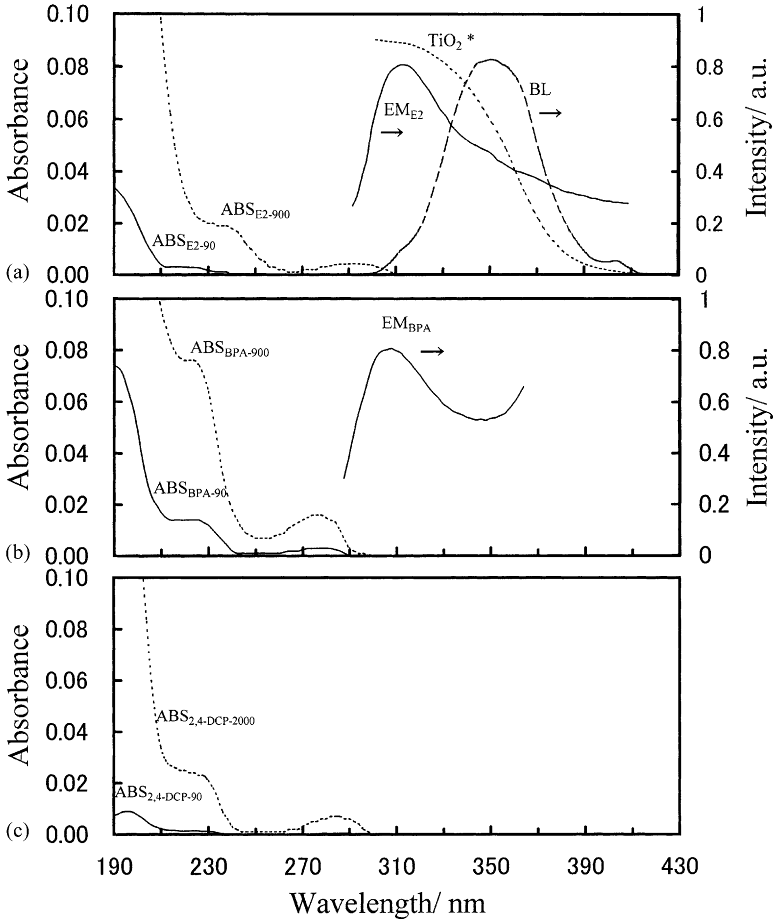

Fig. 3. Absorption spectra of E2 ($ABS_{E2\text{-}90}$, $ABS_{E2\text{-}900}$), BPA ($ABS_{BPA\text{-}90}$, $ABS_{BPA\text{-}900}$) and 2,4-DCP ($ABS_{2,4\text{-}DCP\text{-}90}$, $ABS_{2,4\text{-}DCP\text{-}2000}$); fluorescence emission spectra of E2 (EM_{E2}) and BPA (EM_{BPA}); a spectrum of the black fluorescent lamp used (BL); and a diffuse reflectance spectrum of the TiO_2-modified PTFE mesh sheet (TiO_2). The absorbance of the diffuse reflectance spectrum (∗) is presented with a scale of arbitrary units. The abbreviations $ABS_{E2\text{-}90}$ and $ABS_{E2\text{-}900}$ represent the absorption spectra obtained for solutions with concentrations of 90 and 900 $\mu g\,l^{-1}$ of E2, respectively, and so forth. The excitation wavelength to obtain EM_{E2} was 250 nm, while that to obtain EM_{BPA} was 240 nm.

reflectance spectrum were recorded on a UV-3100 spectrophotometer (Shimadzu Co.). Based on the absorption and fluorescence spectra of the EDCs (Fig. 3), the excitation and emission wavelengths were 278 and 307 nm, respectively, for the detection of E2; 275 and 309 nm for the detection of BPA; and the absorption wavelength was 195 nm for the detection of 2,4-DCP.

3. Results and discussion

3.1. Decomposition of E2, BPA, and 2,4-DCP by use of the type I reactor

As shown in Fig. 4(a), the concentration of E2 did not change under UV illumination without the TiO_2-modified PTFE mesh sheet. On the other hand, the E2 concentration was decreased by 85% with the TiO_2-modified PTFE mesh sheets in the dark after reaching absorption equilibrium for 1 h. Under UV illumination with the TiO_2-modified PTFE mesh sheets, 98% of the initial E2 was decomposed after 1 h. The semi-logarithmic plots of the concentration of E2 as a function of the UV illumination time had a nearly linear slope, the reaction following apparent first-order kinetics. This should be because of the mass-transfer limited condition caused by the low concentration of E2 in the aqueous solution. The first-order rate constant of the photocatalytic decomposition of E2 was ca. 0.033 $\min^{-1}$. King reported that E2 (conc., 0.03–3 × 10^{-6} M) was decomposed in 3.5 h at a TiO_2-immobilized Ti–6Al–4V stainless steel plate with a 150 W Xe lamp at an intensity of 8×10^{-8} einstein s^{-1} cm^{-2} [20]. In this case, however, the treated solution volume was very small (only 8 ml); in addition, the light source is inappropriate for practical application (i.e. large water volumes).

Fig. 4(b) and (c) show the time course of the concentration changes of BPA and 2,4-DCP, respectively. These two compounds showed behavior similar to that observed for E2, not only in the dark but also under UV illumination. Interestingly, the first-order rate constants of the photocatalytic decomposition of BPA and 2,4-DCP were also

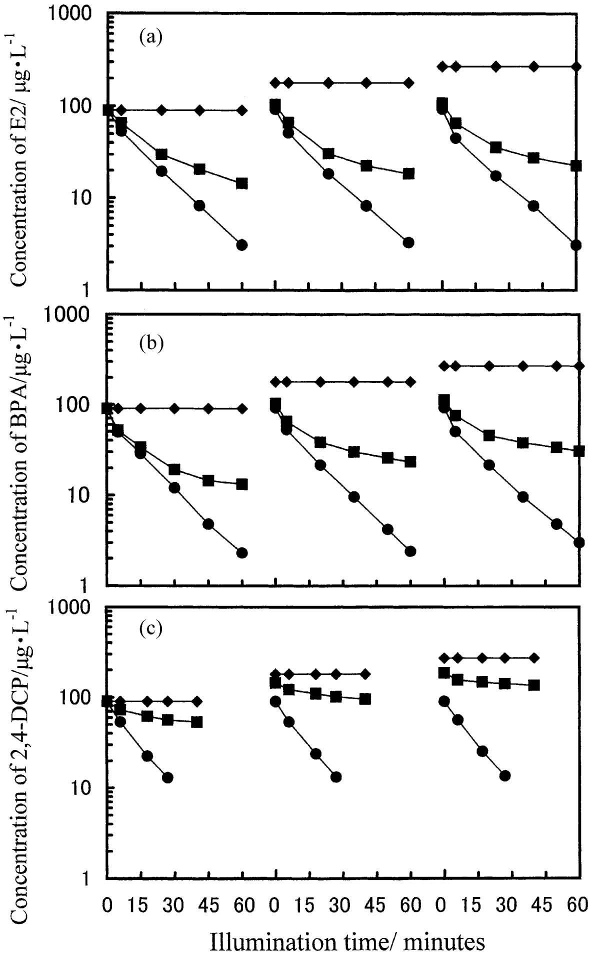

Fig. 4. Photocatalytic decomposition of (a) E2, (b) BPA, and (c) 2,4-DCP by use of the type I reactor ((●) UV illumination; (■) no illumination; (◆) UV illumination without sheets). The initial concentration was 90 μg l^{-1}; the UV light intensity was 0.24 mW cm^{-2}. Cyclability was examined twice for each reactant. See text for further details.

ca. 0.033 min^{-1}. In addition, the TiO_2-modified PTFE mesh sheets could also be used repeatedly for BPA and 2,4-DCP under UV illumination.

In the case of using a low-intensity light source, it often takes a longer time to decompose EDCs than in the case of a high-intensity light source. For example, our group has reported that BPA in TiO_2 suspensions in aqueous solution (P-25, 1 g l^{-1}; BPA conc., 40 mg l^{-1}; volume, 40 ml) can be decomposed in 20 h under UV illumination at 10 mW cm^{-2} intensity [16]. 2,4-DCP in TiO_2-suspended aqueous solution (TiO_2 powder 1.4 g l^{-1}, 2,4-DCP conc., 3×10^{-4} M; volume, 100 ml) can be decomposed in 3 h under illumination from a 5.8 W low-pressure mercury lamp, 0.5 mW cm^{-2} intensity at 254 nm [17], and in 3.6–54 h under illumination from a 100 W low-pressure mercury lamp [18]. In contrast, we found that BPA and 2,4-DCP in aqueous solution were also decomposed quickly by using the TiO_2-modified PTFE mesh sheets and a low-intensity light source, similar to the result observed for E2.

3.2. *Cycling tests by use of the type I reactor*

We introduced an additional amount of E2 (180 μg) into the glass cylinder after 1 h and then repeated these experiments several times. As a result, the adsorption behavior in the dark became worse, while almost the same decomposition rate was obtained as that obtained in the first experiment under UV illumination. We repeated this experiment one more time after a 1 h duration of the second experiment (totally ~2 h). Also, the adsorption behavior became much worse in the dark. However, almost the same decomposition rate was obtained under UV illumination as those obtained in the first and second experiments. The TiO_2-modified PTFE mesh sheets could be repeatedly used under UV illumination. These results can be explained by assuming that the adsorption sites were not regenerated in the dark, while they were regenerated under UV illumination by TiO_2 photocatalysis.

3.3. *Adsorption on the TiO_2-modified PTFE mesh sheets*

These three EDCs were well adsorbed on the TiO_2-modified PTFE mesh sheets in the dark. In order to know whether these EDCs are adsorbed on the TiO_2 or on the PTFE substrate, the adsorption properties were investigated as follows. A 30 cm^2 portion of the TiO_2-modified PTFE mesh sheet or of the bare PTFE mesh sheet was used in a sample bottle (ϕ = 18 mm). A 30 ml solution of either E2 or 2,4-DCP (conc., 250 μg l^{-1} each) was poured into the sample bottle. The solution was stirred with a magnetic stirrer in the dark for 10 min.

Table 1 shows the relationship between the concentrations of E2 or 2,4-DCP after 10 min with the use of the TiO_2-modified PTFE mesh sheet or with the use of the bare PTFE mesh sheet. The values in parentheses show the ratios of the concentration after 10 min to the initial concentration. Neither E2 nor 2,4-DCP were adsorbed on the bare PTFE mesh sheet, while 2,4-DCP as well as E2 were adsorbed on the TiO_2-modified PTFE mesh sheet. The ratio of adsorption for 2,4-DCP was 0.44. The ratio for E2 was 0.80. These results indicate that E2 and 2,4-DCP were adsorbed on the TiO_2 photocatalysts but not on the PTFE substrate. E2 was adsorbed to a greater extent than

Table 1
Adsorption characteristics for E2 and 2,4-DCP on TiO_2-modified PTFE mesh sheet

PTFE mesh sheet	17β-Estradiol (μg/l)[a]	2,4-Dichlorophenol (μg/l)[a]
PTFE photocatalytic mesh sheet	140 (0.44)[b]	49 (0.80)[b]
PTFE mesh sheet without photocatalysts	250 (0)[b]	250 (0)[b]

[a] Solution concentration after 10 min in the dark; initial concentration 250 μg/l.

[b] Adsorption ratio: (initial concentration − concentration of solution after 10 min)/initial concentration.

2,4-DCP on TiO_2. The good repeatability of the results for the TiO_2-modified PTFE mesh sheets under UV illumination is clearly seen in Fig. 4. It reflects the self-cleaning effect of TiO_2 photocatalysis. The TiO_2 surface is regenerated by photocatalytic reaction. Since the PTFE mesh sheets are not decomposed by TiO_2 photocatalysis, the long-term stability is promising. This means that a practical system without troublesome maintenance can be realized with the use of the TiO_2-modified PTFE mesh sheets.

It should be noted that TiO_2 absorbs much light from the black fluorescent lamp in contrast to the EDCs, which absorb little, as shown in Fig. 3. Thus, the photo-sensitized oxidation of E2 adsorbed on the TiO_2 surface can probably be neglected.

3.4. *Decomposition of E2 and 2,4-DCP with the type II reactor*

The results obtained by use of the type I reactor followed apparent first-order kinetics and exhibited the same reaction rate for all three compounds. These photocatalytic reactions are expected to proceed under a mass-transfer limited condition, caused by the low concentration of the compounds in aqueous solution. In order to promote the mass transfer of the compounds to the TiO_2 surface, we designed another reactor, in which TiO_2-modified PTFE sheets were attached to a bar-rotator, which was rotated with a motor, as shown in Fig. 2.

Fig. 5 shows the concentration changes of E2 and 2,4-DCP, respectively, as a function of the UV illumination time at 10 °C. The concentrations of both E2 and 2,4-DCP were decreased to some extent in the dark. These decreases in the dark are caused by the adsorption on the TiO_2 surface of the PTFE mesh sheets, as described previously. The semi-logarithmic plots of the concentrations of E2 and 2,4-DCP as a function of the UV illumination time exhibited a nearly linear slope. Ninety percent of both E2 and 2,4-DCP disappeared after 20 min. The first-order rate constants for the decomposition of E2 and 2,4-DCP were both ca. $0.050\,\mathrm{min}^{-1}$, which is significantly larger than those obtained with the type I reactor.

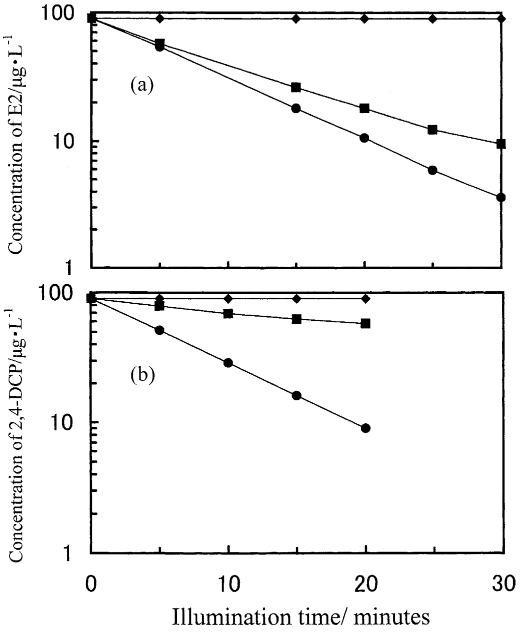

Fig. 5. Photocatalytic decomposition of (a) E2 and (b) 2,4-DCP by use of the type II reactor ((●) UV illumination; (■) no illumination; (◆) UV illumination without sheets). The initial concentration was $90\,\mu g\,l^{-1}$; the illumination intensity was $0.24\,mW\,cm^{-2}$.

3.5. *Comparison of the two reactors*

Let us consider the reaction rates obtained with the two reactors. The value of the ratio of the apparent surface area of the TiO_2-modified PTFE mesh sheets to the volume of test solution was ca. $0.35\,cm^2\,ml^{-1}$ in the case of the type II reactor. This was ∼1/3 times smaller than that in the case of reactor I (ca. $1.0\,cm^2\,ml^{-1}$). Nevertheless, the first-order rate constant of ca. $0.050\,min^{-1}$ increased by a factor of ca. 1.5 in the case of the type II reactor compared to that (ca. $0.033\,min^{-1}$) in the case of the type I reactor. In a preliminary experiment, the reaction rate increased with increasing TiO_2 surface area under these experimental conditions, so that the reaction rate per unit TiO_2 area can be estimated to have became ca. 4.5 times higher in the case of the type II reactor than that in the case of the type I reactor. This result indicates that the EDCs contact the TiO_2 photocatalysts more efficiently by rotation of the TiO_2-modified PTFE mesh sheets themselves rather than by simple solution convection.

This enhancement effect was analyzed based on a conventional model of fluid mechanics, as follows. The mass transfer is assumed to be proportional to the flux of the solution to the one-third power in the case of laminar flow [19]. The solutions in both reactors were considered to undergo mass transfer via laminar flow. The value of the Reynolds number (*Re*) was ca. 138 in the case of the type II reactor, calculated from $Re = d \times v/\nu$, where d is the cross-sectional diameter (0.1 cm), v is the fluid velocity of the solution ($18\,cm\,s^{-1}$) and ν is the kinematic viscosity of the solution ($0.013\,cm^2\,s^{-1}$). The flux of the solution was $340\,\mu l\,min^{-1}$ in the case of the type I reactor, which was equal to $0.1\,ml\,s^{-1}\,cm^{-2}$-sheet. In the case of the type II reactor, the volume of the solution was 2-l, and the rotation rate was 60 rpm. The flux of the solution was 2-l s^{-1} (=60 rpm × 2-l min^{-1}), which was equal to ca. $22\,ml\,s^{-1}\,cm^{-2}$-sheet [=2-l s^{-1}/(5.8 × $15\,cm^2$-single sheet)]. Thus, the increased flux of the solution should contribute ca. six times [=($22\,ml\,s^{-1}\,cm^{-2}$-sheet/$0.1\,ml\,s^{-1}\,cm^{-2}$-sheet)$^{1/3}$] to the mass-transfer process. On the other hand, the increasing ratio of the sheet area in the solution was ca. 1/3 (=$0.35\,cm^2\,ml^{-1}$/$1.0\,cm^2\,ml^{-1}$). Therefore, the increase of the actual reaction rate was expected to be a factor of ca. 2 (=1/3 × 6), although a value of 1.5 was obtained experimentally. The ratio was probably overestimated because the calculation assumed no movement of the solution itself, although in fact the solution does rotate together with the rotation of the sheets to some extent. If the flux of the solution in the type II reactor is assumed to decreased by a factor of 2, the value of the enhancement ratio is coincident with the experimental one. We are now developing a new reactor to further enhance the removal rate of EDCs in practice [21].

4. Conclusions

E2, BPA, and 2,4-DCP in aqueous solution (initial concentrations, 90 μg l^{-1}) were decomposed relatively quickly by use of the TiO_2-modified PTFE mesh sheets under relatively weak UV illumination (0.24 mW cm^{-2}). The same first-order rate constant of ca. 0.033 min^{-1} was obtained for all the EDCs examined in the case of the type I reactor (Fig. 1). On the other hand, in the case of the type II reactor (Fig. 2), the first-order rate constant increased to ca. 0.050 min^{-1}. These results indicate that the apparent mass-transfer rate of the EDCs to the TiO_2 could be improved ca. 4.5 times by rotating the PTFE mesh sheets themselves. The TiO_2-modified PTFE mesh sheets could be used repeatedly under UV illumination. Since the TiO_2-modified PTFE mesh sheets have sufficient open area, we can expect to obtain a greater reaction rate as well as to purify a greater amount of water. We are developing a new enlarged reactor with a greater number of sheets, a much increased sheet size and/or a more powerful rotation motor. Improvement and optimization of the reactor is now in progress [22].

Acknowledgements

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