

Photocatalytic decomposition of estrogens in aquatic environment by reciprocating immersion of TiO₂-modified polytetrafluoroethylene mesh sheets

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Abstract

Photocatalytic decomposition of 17 β -estradiol (E2) and estron (E1) in aqueous solutions was carried out by use of TiO₂ photocatalysts immobilized on polytetrafluoroethylene (PTFE) mesh sheets and irradiated with black fluorescent lamps. The TiO₂-modified PTFE mesh sheets were stacked in a 0.5 l (1 l = 1 dm³) or 5 l beaker and were reciprocally immersed in the range of 2–4 cm at the rate of 5–120 rpm. The first-order rate constant of E2 decomposition (initial concentration, 250 μ g l⁻¹) was proportional to the ratio of the surface area of the TiO₂-modified PTFE mesh sheets to the volume of the treated water. It was also proportional to the square root of the reciprocation rate of the TiO₂-modified PTFE mesh sheets, which was mainly due to mass-transfer limited condition. In addition, it was increased with increasing temperature, which was explained by the change of diffusion rate of E2 in water. About 90% of E1 in a practical discharged water was decomposed by using the 5 l reactor in 4 min with good reproducibility. Based on the results, application of this system to purification of discharged water at a sewage treatment plant could be expected.

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1. Introduction

Natural estrogens of 17 β -estradiol (E2) and estron (E1) are basic female sex hormones, and they are well-known to exhibit estrogenic activities potently even at a very low concentration [1]. They are present at a considerable concentration in aquatic environments because they are excreted in the urine of females [2]. E1 exhibits estrogen activity as much as \sim 0.3 times of the most potent E2. Recently, however, they have been problematic because they were detected at high concentrations in a discharged water from a sewage treatment plant [3]. This is because the removing rates of E2 and E1 in a sewage treatment plant were less than that of the other endocrine-disrupting chemicals (EDCs) [4,5]. It might be a significant problem if the concentrations of E2 and E1 become higher than allowed levels in the aquatic environment.

We have been studying TiO₂ photocatalysis in order to decompose EDCs [6–9]. Tanizaki et al. [10] also decom-

posed E2 by use of TiO₂ photocatalysts immobilized on the quartz beads. It is well-known that most organic compounds are oxidized to CO₂ by TiO₂ photocatalysis because photo-generated holes exhibit strong oxidizing power [11]. We previously reported a relatively fast reaction rate (a first-order rate constant of ca. 0.033 min⁻¹) obtained for the decomposition of E2, bisphenol-A and 2,4-dichlorophenol (2,4-DCP). In these studies, the TiO₂-modified polytetrafluoroethylene (PTFE) mesh sheets were stacked in glass cylinder and illuminated with black fluorescent lamps, in which the solution was circulated by use of a rotary pump [9]. Also, when the TiO₂-modified PTFE mesh sheets were attached to a bar-rotator in a fan-type arrangement being rotated, the higher first-order rate constant of ca. 0.050 cm⁻¹ was obtained for the decomposition of E2 and 2,4-DCP. In this case, the reaction rate was limited by the mass transfer of EDCs to the TiO₂ surface [9].

In order to increase the decomposition efficiency, we recently developed a reciprocation technique of TiO₂-modified PTFE mesh sheets. The reciprocation technique of the PTFE mesh sheets has an advantage, that a smaller resistance of water was received during motion than the rotation

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technique, so that a more effective decomposition of EDCs is expected. In the present work, we investigated the decomposition of E2 and E1 by utilizing the reciprocation technique. As a result, we could purify a discharge water (51) from a sewage treatment plant in a few minutes.

2. Experimental

E2 and E1 were purchased from Wako Pure Chemical Industries Ltd. The aqueous solutions of E2 and E1 were prepared with distilled water. The TiO₂-modified PTFE mesh sheets (PFG-SW20H) were obtained from Nitto Denko Co. TiO₂ photocatalysts, grain diameter of 0.007–0.5 μm, were immobilized to the PTFE mesh sheet by 20–450 g/m².

Details of the reactor are described as follows: TiO₂-modified PTFE mesh sheets (1 mm square openings, open ratio of ca. 49%) were horizontally stacked at a given interval by use of acrylic rods in a 0.51 glass beaker. The solution was illuminated with four black fluorescent lamps (Type FL 15 BL-B, 15 W, National Co.). The light intensity was 1.2 mW cm⁻², which was measured by use of a UV radiometer (UVR-36, Topcon Co.) at the center of the beaker. The TiO₂-modified PTFE mesh sheets were reciprocally immersed at an amplitude of 2–4 cm, and at the rate of 5–60 rpm by using a wheel and a motor (US590-501C and 5GU3.6KB, Oriental motor Co.).

On the other hand, 25 sheets of the PTFE mesh modified with TiO₂ were arrayed horizontally at 10 mm intervals in a 5 l glass beaker (180 mm diameter), as shown in Fig. 1. The solution was illuminated with eight black fluorescent lamps (15 W). The UV-light intensity was 1.2 mW cm⁻² at the center of the beaker. The TiO₂-modified PTFE mesh

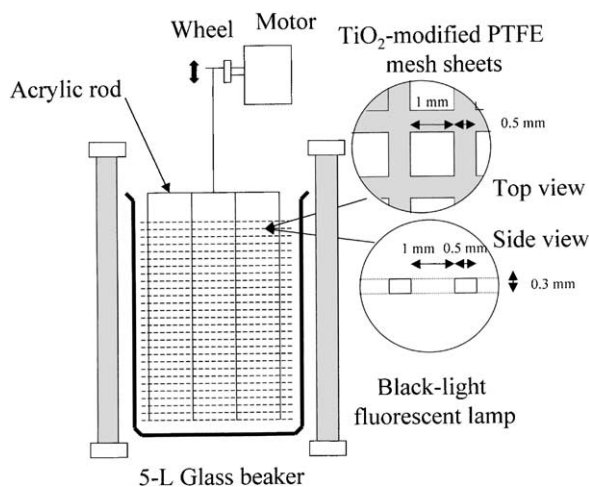


Fig. 1. Schematic illustration of the 5 l reactor. Twenty five sheets of TiO₂-modified PTFE mesh sheets were arrayed horizontally at 10 mm intervals by use of acrylic rods in a 5 l glass beaker (180 mm diameter). The solution was illuminated with eight black fluorescent lamps (Type FL15 BL-B, 15 W, National Co.). The TiO₂-modified PTFE mesh sheets were reciprocated at a width of 4 cm and at the rate of 60–120 rpm.

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The concentrations of the E2 and E1 were evaluated by two methods. The concentration of E2 (>1 μg l⁻¹) was evaluated with a high-performance liquid chromatograph (HPLC) equipped with a fluorescence spectrometer, whose details were described in the previous paper [9]. The concentration of E1 (>1 μg l⁻¹) was also evaluated with HPLC equipped with an absorption spectrometer (detection wavelength was 220 nm). The concentrations of E2 and E1 below 1 μg l⁻¹ were evaluated by radioimmunoassays (RIA) [12].

3. Results and discussion

3.1. Dependence of E2 decomposition rate on the ratio of surface area of the TiO₂-modified PTFE mesh sheets to water volume

TiO₂-modified PTFE mesh sheets were horizontally arrayed at 5, 10 or 20 mm intervals by use of acrylic rods in the 0.51 reactor. The ratios of the surface area of the sheets (S_{TiO_2}) to the volume of the treated water (V_{water}) were fixed as 1.0, 0.50, and 0.25 cm² ml⁻¹ for the mesh intervals of 5, 10, and 20 mm, respectively. Fig. 2 shows the time course of the concentration changes of E2 (initial concentration of 250 μg l⁻¹) at 20 °C. The TiO₂-modified PTFE mesh sheets were reciprocated at the width of 2 cm and rate of 60 rpm. As a result, the E2 concentration was decreased in the dark. This was explained by the adsorption on the TiO₂ surface of the PTFE mesh sheets. Under UV-light illumination, the E2 concentration was decreased more rapidly than in the dark. The semi-logarithmic plots of the concentration of E2 as a function of the UV illumination time showed a nearly linear slope, indicating that the reaction followed an apparent first-order kinetics. This should be due to the mass-transfer limited condition caused by the low concentration of E2 in the aqueous solution. Incidentally, the E2 concentration did not change under UV illumination without the TiO₂-modified PTFE mesh sheet.

The first-order rate constants of the photocatalytic decomposition of E2 were plotted against the ratio of S_{TiO_2} to V_{water} in Fig. 3. As a result, they were proportional to the ratio of S_{TiO_2} to V_{water} . This result indicates that the arranged TiO₂-modified PTFE mesh sheets were irradiated sufficiently with black fluorescent lamps. The E2 would be decomposed to CO₂ completely [7].

3.2. Dependence of E2 decomposition rate on the reciprocation rate of the TiO₂-modified PTFE mesh sheets

As shown in Fig. 2, the reaction was proceeded under mass-transfer limited condition due to the low concentration of E2 in the aqueous solution. In order to verify this, the reciprocation rate was changed from 5 to 60 rpm. The value of the Reynolds number (Re) at 60 rpm was estimated to be

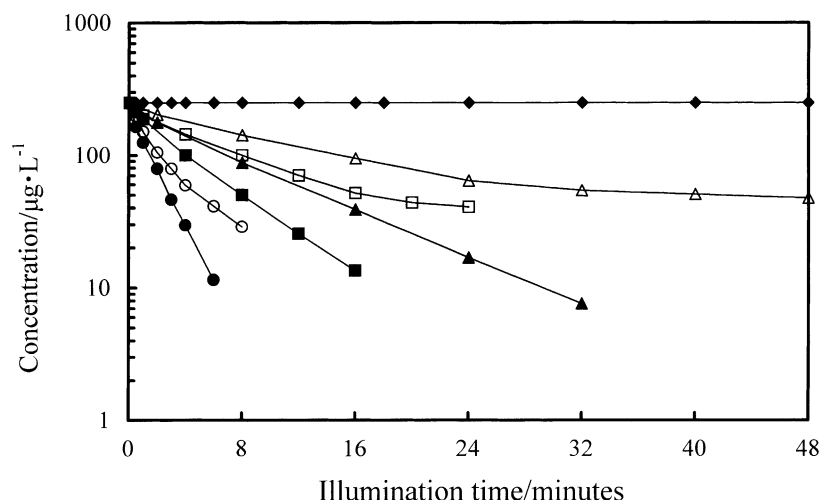


Fig. 2. Decomposition of E2 by the TiO_2 -modified PTFE mesh sheets (stacked interval of 5 mm) at 20°C under UV light (1.2 mW cm^{-2}); the ratio of the surface area of the TiO_2 -modified PTFE mesh sheets (S_{TiO_2}) to the volume of treated water (V_{water}); (●) 1.0; (■) 0.50; (▲) 0.25 $\text{cm}^2\text{ ml}^{-1}$ under UV light, and (○) 1.0; (□) 0.50; (△) 0.25 $\text{cm}^2\text{ ml}^{-1}$ in the dark; (◆) without mesh sheet.

50, which was calculated from $Re = dv/\nu$, where d is the cross-sectional diameter (0.1 cm), v the fluid velocity of the solution (4.0 cm s^{-1} at 60 rpm) and ν the kinematic viscosity of the solution ($0.008\text{ cm}^2\text{ s}^{-1}$). Thus, a laminar flow was assumed in the solution. The mass transfer is assumed to be proportional to the one-third power of the flux of the solution in the case of laminar flow [13]. The other experimental conditions were as follows: the sheets were stacked at a 5 mm interval, the ratio of $S_{\text{TiO}_2}/V_{\text{water}}$ was $1.0\text{ cm}^2\text{ ml}^{-1}$, the E2 initial concentration was $250\text{ }\mu\text{g l}^{-1}$, the temperature of water was 20°C , and the UV light intensity was 1.2 mW cm^{-2} . As a result, the first-order rate constant was proportional to a square root of the reciprocation rate (Fig. 4). The value of the power of the reciprocation rate was larger than the theoretical one. Incidentally, we previously reported that the first-order rate constant was proportional to one-third power of the reciprocation rate in the case of 2,4-DCP [14]. The difference in the present case might be probably due to the difference in the adsorption between E2 and 2,4-DCP on the

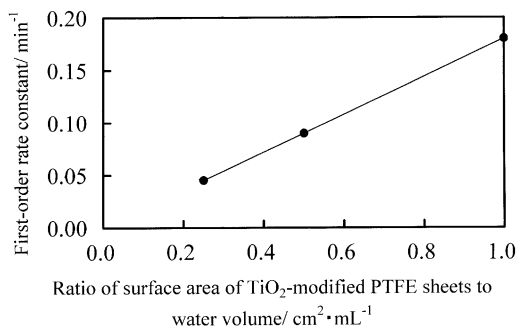


Fig. 3. Dependence of first-order rate constant of the photocatalytic decomposition of E2 on the ratio of S_{TiO_2} to V_{water} . These plots were derived from Fig. 2.

TiO_2 photocatalyst [9]. E2 was adsorbed to a greater extent than 2,4-DCP on TiO_2 . As E2 was adsorbed much more than 2,4-DCP when the reciprocation rate of the TiO_2 -modified PTFE mesh sheets became fast, the photocatalytic decomposition of E2 was enhanced more than that of 2,4-DCP.

3.3. Effect of temperature

The rate constant of E2 decomposition was changed by temperature of the treated solution. Fig. 5 shows the decomposition of E2 as a function of the UV illumination time at 10, 20, and 30°C in a 0.51 beaker. E2 decomposition was carried out with the following condition: initial concentration: $250\text{ }\mu\text{g l}^{-1}$; UV light intensity: 1.2 mW cm^{-2} ;

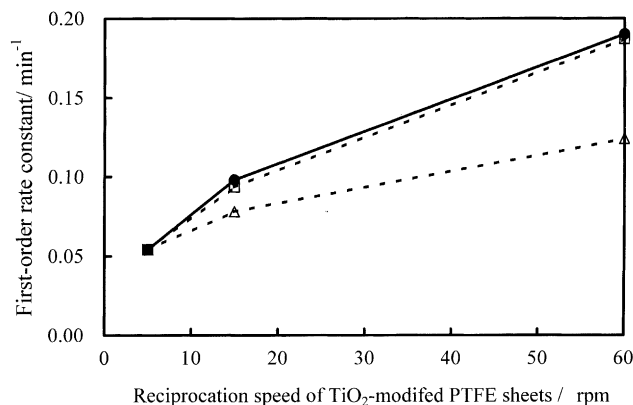


Fig. 4. Dependence of first-order rate constant of the photocatalytic decomposition of E2 on the reciprocation rate of TiO_2 -modified PTFE mesh sheets (mesh interval, 5 mm; ratio of S_{TiO_2} to V_{water} , $1.0\text{ cm}^2\text{ ml}^{-1}$; initial E2 concentration, $250\text{ }\mu\text{g l}^{-1}$; water temperature, 20°C ; UV light intensity, 1.2 mW cm^{-2}). The first-order rate constant of the experiment result (●), in the case of proportion to the square root (□) and one-third power (△) of the reciprocation rate.

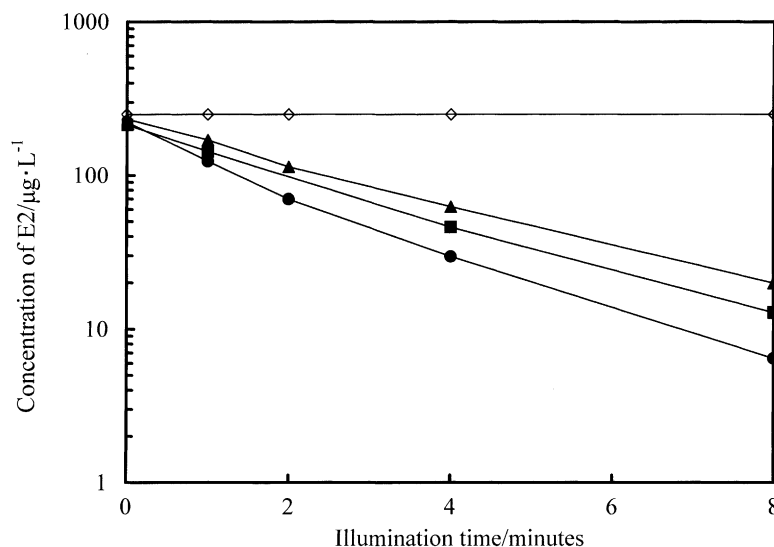


Fig. 5. Temperature dependence of E2 decomposition rate at the TiO₂-modified PTFE mesh sheets at (●) 30; (■) 20; (▲) 10 °C and (◇) without mesh sheet (mesh interval, 5 mm, reciprocation rate, 60 rpm; ratio of S_{TiO_2} to V_{water} , 1.0 cm² ml⁻¹; UV light intensity, 1.2 mW cm⁻²).

reciprocation rate of the TiO₂-modified PTFE mesh sheets: 60 rpm; arranged interval of sheets: 5 mm; ratio of ($S_{\text{TiO}_2}/V_{\text{water}}$): 1.0 cm² ml⁻¹. The first-order rate constant was found to increase with increasing temperature.

The temperature effect was considered to be caused by the mass transfer of the compounds to the TiO₂ surface [15]. This effect was analyzed based on a conventional fluid mechanics as follows. The mass transfer is assumed to be proportional to the one-third power of flux of the solution in the case of laminar flow [13]. Mass-transfer rate being dimensionless is expressed with Nusselt number as

$$Nu = 1.85 \left(\frac{Re Sc d}{L} \right)^{1/3} \quad (1)$$

where Sc is the Schmidt number (ν/D), L the length of reaction part (in this case, 0.3 mm thickness of the TiO₂-modified PTFE mesh sheet) and D the diffusion constant. First-order rate constant is given as

$$k = \frac{D}{d} Nu \quad (2)$$

Therefore, first-order rate constant could be expressed as follows:

$$k = \frac{1.85 \nu^{1/3} D^{2/3}}{(dL)^{1/3}} \quad (3)$$

The diffusion constant increases with increasing temperature, in general. The first-order rate constant is proportional to the diffusion constant of the solution to the two-third power.

We obtained the first-order rate constants of 0.16, 0.20, and 0.24 min⁻¹ at 10, 20, and 30 °C, respectively (Fig. 5). Two-third power of the diffusion constants were 5.6×10^{-4} , 6.9×10^{-4} , and 8.3×10^{-4} cm^{4/3} s^{-2/3} at 10, 20, and 30 °C,

respectively. Thus, the rate constants were found to be proportional to the calculated value of the two-third power of the diffusion constants.

3.4. Decomposition of E1 and E2 in discharged water

For applying this system to the practical water treatment with a large volume, we used the 5 l reactor (Fig. 1) and the solution containing E1 (concentration, 250 µg l⁻¹). The TiO₂-modified PTFE mesh sheets were reciprocated at the width of 4 cm and at the rate of 60 rpm. As shown in Fig. 6(a), about 98% of the initial E1 was decomposed under UV light for 16 min. The semi-logarithmic plots of the concentration of E2 as a function of the UV illumination time showed a nearly linear slope, so that the reaction followed an apparently first-order kinetics. The first-order rate constant of the photocatalytic decomposition of E1 was ca. 0.12 min⁻¹.

Fig. 6(b) shows the time course of the concentration changes of E2. The TiO₂-modified PTFE mesh sheets were reciprocated at the width of 4 cm and at the rate of 120 rpm (15 °C). E2 was decomposed in a similar way to E1. The first-order rate constant of the photocatalytic decomposition of E2 was also ca. 0.15 min⁻¹. Although the reciprocation rate and water temperature were different for decomposition of E1 and E2, almost the same value of decomposition rate was obtained. As mentioned above, this is explained by the fact that the first-order rate constant of E2 decomposition was proportional to the square root of the reciprocation rate of the TiO₂-modified PTFE mesh sheets ($1/\sqrt{2}$ times by the change from 120 to 60 rpm). This was also proportional to the two-third power of the diffusion constant (1.1 times by the change of temperature from 15 to 20 °C). Incidentally, adsorption behavior of E1 and E2 on the sample sheets was

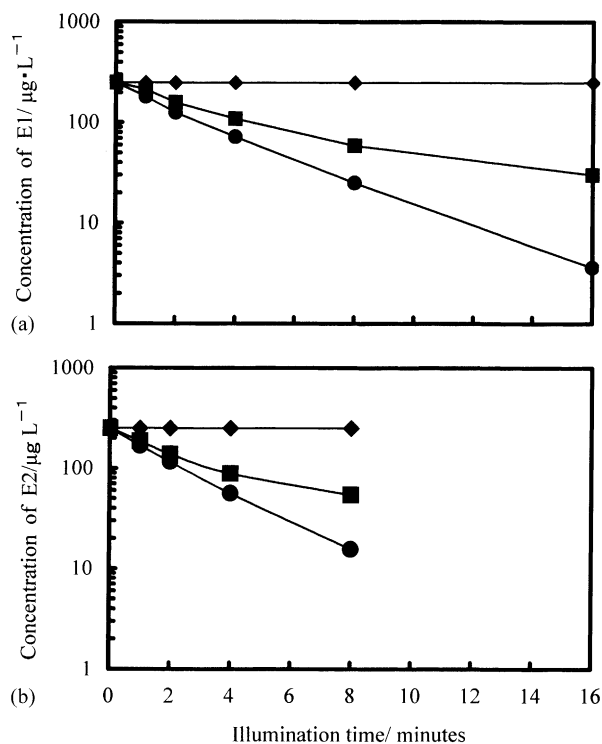


Fig. 6. Photocatalytic decomposition of E1(a) and E2(b) in the 51 reactor: (●) UV illumination; (■) no illumination; (◆) UV illumination without sheets (initial concentration, $250 \mu\text{g l}^{-1}$; UV light intensity, 1.2 mW cm^{-2} ; mesh interval, 10 mm, ratio of S_{TiO_2} to V_{water} , $0.5 \text{ cm}^2 \text{ ml}^{-1}$; reciprocation rate, 60 rpm for E1 and 120 rpm for E2; water temperature, 20°C for E1 and 15°C for E2).

similar to each other. Thus, if E2 is decomposed at the similar decomposition rate constant as E1 by photocatalysis, the value of 0.15 min^{-1} could be converted to $\sim 0.12 \text{ min}^{-1}$. This indicates that our system could be explained by the conventional fluid mechanics model, and the motion of reciprocation was effective for decomposition of EDCs at very low concentrations in aqueous solutions.

3.5. Treatment of discharged water from sewage treatment plant

Finally, we tried treatment of discharged water from Kitano sewage treatment plant at the Tama River near Tokyo. Concentrations of E1 and E2 in the discharged water were 140 and 15 ng l^{-1} , respectively, which were evaluated by RIA method. The discharged water was treated in the 51 reactor at 15°C . The TiO_2 -modified PTFE mesh sheets were reciprocated at the width of 4 cm and at the rate of 120 rpm. The solution was illuminated with eight 15 W black fluorescent lamps. As shown in Fig. 7, under UV illumination with the TiO_2 -modified PTFE mesh sheets, about 90% of the initial E1 was decomposed after 4 min. We replaced the solution of the 51 reactor after 16 min and then repeated these experiments. As a result, similar results were obtained for the concentration change of E1 at least four

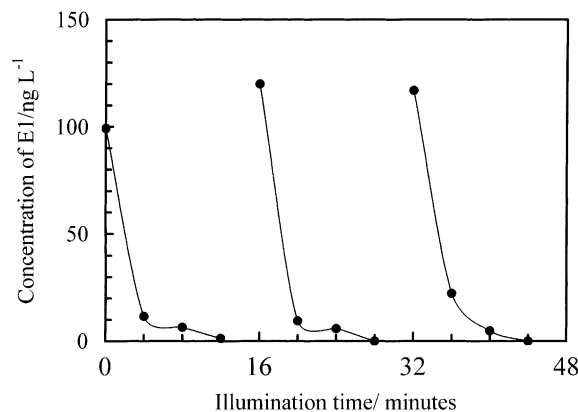


Fig. 7. Concentration change of E1 in a discharged water from a sewage treatment plant during photocatalysis. The measurement was repeated three times (UV light intensity, 1.2 mW cm^{-2} ; reciprocation rate of the TiO_2 -modified PTFE mesh sheets, 120 rpm; mesh interval, 10 mm; ratio of S_{TiO_2} to V_{water} , $0.5 \text{ cm}^2 \text{ ml}^{-1}$; water temperature, 15°C).

times. This reproducibility was attributed to regeneration of the TiO_2 -modified PTFE mesh sheets under UV illumination by TiO_2 photocatalysis. If the experiment was done in the dark, the reproducibility should not be obtained because, the surface of TiO_2 was covered with component of the discharged water.

4. Conclusions

E2 and E1 in aqueous solution (initial concentrations, $250 \mu\text{g l}^{-1}$) were decomposed relatively quickly by use of the TiO_2 -modified PTFE mesh sheets under relatively weak UV illumination (1.2 mW cm^{-2}). The first-order rate constant of decomposition of E2 was proportional to the square root of the reciprocation rate of the TiO_2 -modified PTFE mesh sheets and corresponded to two-third power of the diffusion constant. For example, the first-order rate constants of ca. 0.15 min^{-1} was obtained for E2 at 120 rpm at 15°C and that of ca. 0.12 min^{-1} was obtained for E1 at 60 rpm at 20°C by using a 51 reactor (Fig. 1).

Samples of discharged water from Kitano sewage treatment plant in the Tama River near Tokyo were successfully treated by this method. We could decompose repeatedly $\sim 90\%$ of E1 in a discharged water by using the 51 reactor in 4 min. By the reciprocation technique of the PTFE mesh sheets, we expect to purify the discharged water at a sewage treatment plant effectively with a relatively small energy in a short time.

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