# A $TiO_2$-Suspended Continuous Flow Photoreactor System Combined with the Separation of $TiO_2$ Particles by Coagulation for the Photocatalytic Degradation of Dibutyl Phthalate

Kiyoshi Hasegawa,* Tomonori Ito, Miyoko Maeda, and Shigehiro Kagaya
*Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930-8555*

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A $TiO_2$-suspended continuous flow photoreactor system combined with the separation of $TiO_2$ particles by coagulation was applied for the photocatalytic degradation of dibutyl phthalate (DBP). The system enabled the efficient degradation of DBP and the continuous discharge of transparent water.

$TiO_2$ photocatalyst can oxidize water pollutants to $CO_2$, $H_2O$, and inorganic ions.[1] Earlier studies were conducted by suspending fine $TiO_2$ particles in aqueous solutions containing contaminants. However, difficult separation of the particles after the degradation of the pollutants turned toward the use of $TiO_2$-immobilized materials.[2–8] A membrane-coated type,[2,3] powder-coated-type,[4,5] a fixed bed-type,[6,7] a fluidized bed type,[8] and a optical fiber-type[9] photoreactors have been suggested, however, their efficiency has been often said to be lower than the photoreactors using suspended $TiO_2$ particles because of small liquid–solid contact area of the immobilized $TiO_2$.[8,10,11]

The development of new separation systems of the suspended $TiO_2$, which has large liquid–solid contact area, can be expected to overcome the defect of the $TiO_2$-supported photoreactors. According to the idea, we have recently found the fundamental conditions for the separation of $TiO_2$ from the aqueous suspensions by coagulation.[12] Thereafter Uchida et al.[13,14] have reported the agglomeration of $TiO_2$ suspension induced by ultrasonic irradiation in the presence of glass beads and proposed a combined process between photocatalytic oxidation and the ultrasonic irradiation for treating surfactant-containing wastewater. At present, the process is a batch-type. To aim at large-scale treatment of water contaminants, the construction of a continuous flow system is favored. This paper describes a $TiO_2$-suspended continuous flow photoreactor system combined with the separation of $TiO_2$ particles by coagulation for the photocatalytic degradation of endocrine-disrupting DBP.

Degussa P-25 $TiO_2$ was obtained from Nippon Aerosil Co. Its crystal structure is mainly anatase-type (ca. 70%) and the primary particle diameter is in the range of 15–40 nm. A basic aluminum chloride, $(Al_2(OH)_nCl_{6-n})_m$, (PAC) solution (10%)[12] was commercially available from Tada Chemical Industry Co.

Figure 1 shows the continuous flow photoreactor system. It is comprised of a reservoir, a Pyrex tube photoreactor spiraled doubly around a 400 W high-pressure mercury lamp (Riko UVL-400HA), a coagulation tank, and a solid–liquid separation tank in which an inner column is vertically inserted. Inner volume of the three cylindrical Pyrex tanks is 10.7 L and their sizes are 31 cm height and 21 cm i.d. The spiral tube, which has 0.7 cm i.d., 21 cm height and 286 $cm^3$ volume, is rounded 24 times apart 1.7 cm for an inner column and 4.0 cm for an outer column from a water jacket wall of the lamp. The outer wall of the tube is surrounded with a reflecting stainless steel foil. The quantity of the light ($I_0$) entered the tube was measured with potassium tris(oxalato)ferrate (III) actinometry. $I_0$ was estimated to be $8.50 \times 10^{16}$ and $4.42 \times 10^{16}$ photons $cm^{-3}$ $s^{-1}$ for 290 nm $< \lambda <$ 500 nm and for 290 nm $< \lambda <$ 400 nm ($I_0$ absorbed by $TiO_2$), respectively.

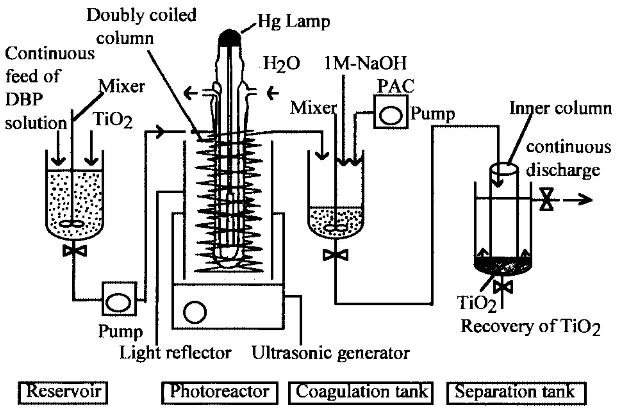

**Figure 1.** Continuous flow phtoreactor system.

The effect of the flow rate of $TiO_2$ suspension on the degradation of DBP was examined with the reservoir and the photoreactor. $TiO_2$ (2.5 g) was added to a 5 L aqueous solution of DBP (5 μM (1.39 mg $L^{-1}$), 10 μM, or 15 μM) and the suspension was mechanically stirred in the dark for 30 min at 25 °C to reach adsorption equilibrium concentration of DBP ($C_0$). It was flowed through the spiraled tube at various flow rates with a peristaltic pump under irradiation with and without ultrasonic irradiation (120 W, 38 kHz, EYELA MUS-10). Two $cm^3$ of the suspension was withdrawn from the outlet of the spiraled tube at timed intervals and $TiO_2$ was filtered through a syringe equipped with a disposal filter. The outlet concentration ($C_t$) of DBP was measured by HPLC with a UV/vis detector at 224 nm using an ODS column and a mobile phase ($CH_3CN$ (80%) + $H_2O$ (20%)). The penetration of light into the $TiO_2$ suspension was estimated with the actinometer by varying the length of the quartz cell filled with the suspension that was set toward the lamp apart 4 cm from the water jacket.

The effect of the flow rate on the separation of $TiO_2$ was examined with the reservoir, the coagulation, and the separation tanks. Ten litters of the suspension without DBP was continuously flowed into the coagulation tank to which a 1.5–2.5% PAC solution was added dropwise while the pH of the suspension was adjusted to 8.0–8.2[12] by adding 1 M aqueous NaOH with stirring at 900 rpm. After 5 L of the suspension was reserved, it was fed into the inner column of the separation tank by gravity at various flow rates. The influent was transferred into the outer column through the lower gap of the inner column and the water level was gradually raised. The transmittance of the supernatant solution was measured at 400 nm and the ratio of the height of the flocks to that of the separation tank (height ratio) was measured.

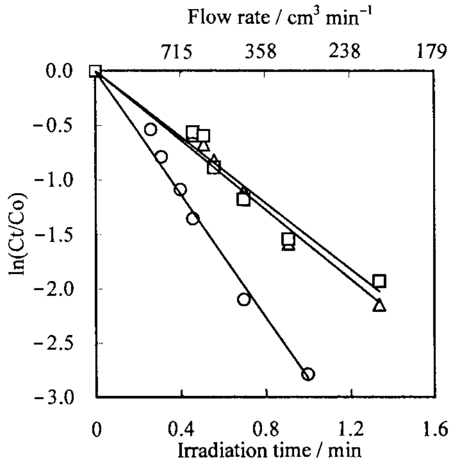

**Figure 2.** Effect of the flow rate (irradiation time) on the degradation of DBP. (○) 5 μM, (△) 10 μM, (□) 15 μM.

Continuous flow operation of the degradation of DBP combined with the separation of $TiO_2$ was performed with 30 L of DBP (5 μM) at the flow rate of 88 $cm^3$ $min^{-1}$.

Figure 2 shows the effect of the flow rate on the degradation of DBP. At a constant flow rate, $C_t$ was kept almost constant and it decreased with decreasing the flow rate. The irradiation time was estimated by dividing the inner volume of the spiraled tube by the flow rate. The degradation follows a first-order reaction kinetics to the concentration of DBP.

$$-\ln(C_t/C_0) = k_{obs}\, t$$

where $k_{obs}$ is the observed first-order rate constant, and t is the irradiation time. Table 1 lists the kinetic parameters and an apparent quantum yield ($\phi_{app}$), which is defined as the ratio of the number of DBP molecules degraded to the number of photons absorbed by $TiO_2$ (290 nm < $\lambda$ < 400 nm). It is remarkable that $\phi_{app}$ of 0.095 was obtained even under strong irradiation at the concentration of 15 μM because $\phi_{app}$ decreases with increasing light intensity.[9] The penetration experiment of light allowed us to estimate that about 75% of incident photons was absorbed in passing through the $TiO_2$ suspension in the tube. High $\phi_{app}$ may be ascribed to the facts that the transmitted photons can be reabsorbed by the reflection of the stainless steel foil and the DBP solution initially entered in the tube is not substantially mixed with that subsequently entered in the tube. Ultrasonic irradiation helped efficient dispersion of the $TiO_2$ particles, however, it did not almost accelerate the degradation of DBP. Many $TiO_2$-immobilized photoreactors have been suggested. The representatives whose $\phi_{app}$ have been reported are an annular reactor[2] (0.012), a spiral reactor[4] (0.022), a screening reactor[6] (<0.005), and a fiber-optic reactor[9] (0.010–0.042). Although target pollutants are different from each other and from DBP, $\phi_{app}$ of the $TiO_2$-immobilized photoreactors appears to be low compared with that obtained by our flow photoreactor.

**Table 1.** Kinetic parameters and quantum yield.

| Concentration / μM | $k_{obs}$ / $min^{-1}$ | $r_0$ / μM $min^{-1}$ | $t_{1/2}$ /min | Apparent quantum Yield, $\phi$ |
|---|---|---|---|---|
| 5 | 2.82 | 11.9 | 0.25 | 0.060 |
| 10 | 1.58 | 11.9 | 0.44 | 0.068 |
| 15 | 1.51 | 15.1 | 0.46 | 0.095 |

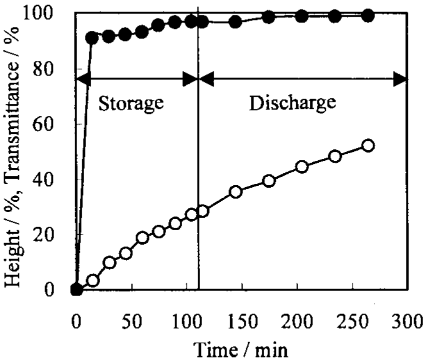

**Figure 3.** Changes in the transmittance of the supernatant solution(●) and the height ratio of the flocks with time(○). PAC : concentration = 1.5%, flow rate = 1.6 $cm^3$ $min^{-1}$.

In the separation tank, the separation of $TiO_2$ by the coagulation proceeded smoothly with decreasing flow rate and the transmittance of the effluents were 95% and 98% at the flow rate of 487 and 88 $cm^3$ $min^{-1}$, respectively. Therefore, the continuous flow operation was performed at 88 $cm^3$ $min^{-1}$. Figure 3 shows the change in the transmittance of the supernatant solution and the height ratio of the flocks with time. The transmittance increases rapidly and reaches 99.5% after 150 min of the discharge. The coagulation started in the inner column of the separation tank and the flocks sedimented almost in the outer column. The inner column was used to suppress the disturbance of the flocks caused by the pulsation of the influent. After a series of the operations, the flocks were taken out with a bottom cock open. After washing the flocks with 6M HCl[12] and subsequent centrifugation at pH = 6.6 (isoelectric point of $TiO_2$), $TiO_2$ can be satisfactorily reused as a photocatalyst (recovery: 70%, activity: 79%).

The continuous flow photocatalysis system would be promising for the treatment of water contaminants. The optimization of the process is under study.

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