Electrolyte-promoted Easy Separation of Suspended TiO_2 Particles with a Solids Retaining Type Centrifuge in Combination with Photoreactor to Degrade Dibutyl Phthalate

Kiyoshi Hasegawa,* Tomonori Ito, Wakako Nakamura, Machi Nagai, and Shigehiro Kagaya
Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930-8555

(Received March 18, 2003; CL-030240)

Adjustment of a TiO_2 suspension containing electrolytes to the isoelectric point (IEP) enabled easy separation of fine particles of TiO_2 by a solids-retaining type centrifuge, which was combined with a batch photoreactor. Optimum separation conditions and reusability of the recovered TiO_2 for the degradation of dibutyl phthalate (DBP) were examined. For synthesized waste water samples (5 μM DBP in tap and well water), suspended TiO_2 was easily separated without addition of electrolytes after degradation of DBP.

Many photoreactors using TiO_2 as a photocatalyst have been suggested to degrade water pollutants.[1] Although a TiO_2 suspension method is said to be more efficient than a TiO_2- immobilized method due to large liquid–solid contact area,[2–4] it is difficult to separate the fine particles after the degradation of the pollutants. Coagulation,[5] ultrasonic irradiation,[6,7] cross-flow microfiltration,[8] and foam flotation[9] methods have been suggested to overcome this defect. However, they have some problems to be solved for waste water treatment. The major concerns are as follows: the coagulation and the foam flotation require processes of regenerating active TiO_2 from a coagulant-bound flock and an ionic surfactant-bound foamate; the ultrasonic irradiation to agglomerate TiO_2 on glass beads is time-consuming; and the cross-flow microfiltration requires back flushing of the membrane by water after each experiment.

We have recently succeeded in degrading DBP and continuously separating TiO_2 particles with a continuous flow photoreactor combined with coagulation using basic aluminum chloride as a coagulant.[10] However, the method generated large amounts of flock and required acid washing to regenerate active TiO_2. To operate known TiO_2-suspended flow and batch photoreactors effectively, one must develop easy separation and reuse methods of TiO_2 which are applicable to waste water treatment.

Thus, we suggest an electrolyte-promoted separation of suspended TiO_2 particles with a solids retaining type centrifuge in combination with a batch photoreactor to degrade DBP. This paper describes possible separation conditions of TiO_2 in an aqueous solution of electrolytes and in tap and well water, reusability of the recovered TiO_2, and the effect of the electrolytes on the DBP degradation.

Figure 1 shows a batch photoreactor system combined with the centrifuge with a 2L rotor (Kokusan Co. H-610), which was operated at a speed of 16000 r.p.m. (28930 × *g*). The quantity of the light absorbed by suspended TiO_2 (4 g in 8 L of water) in the photoreactor was estimated to be 1.97×10^{19} photons s^{-1} by potassium tris(oxalato)ferrate (III) actinometry. Degussa P-25 TiO_2 (Nippon Aerosil Co., primary particle diameter: 15–40 nm) was used.

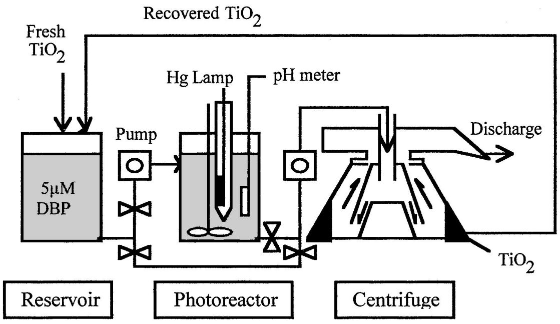

Figure 1. A batch photoreactor system combined with a continuous high-speed centrifuge.

The effect of the electrolyte on the centrifugation of TiO_2 particles was examined by combining the reservoir with the centrifuge. TiO_2 (4.0 g) was added to an 8 L aqueous solution of 1 mM ($1\,M=1\,mol\,dm^{-3}$) Na_2SO_4. The pH of the suspension was adjusted to 6.5 (isoelectric point (IEP) of TiO_2: 6.4–6.6[8], 6–7[11]) with 1 mM NaOH. The suspension was flowed into the centrifuge at a given rate with a peristaltic pump. Then the transmittance of the discharge was measured at 400 nm. The centrifugation of TiO_2 suspended in tap[12] and well[12] water, in which environmental electrolytes are dissolved, was performed without adding any electrolytes. Figure 2 shows the effect of Na_2SO_4 on the centrifugation of TiO_2, where the residence time was estimated by dividing the volume of the rotor by the flow rate. In the absence of Na_2SO_4, more than 14.5 minutes residence (flow rate: $138\,mL\,min^{-1}$) of the TiO_2 suspension was necessary to obtain a transparent discharge (T=95%). However, in a 1 mM Na_2SO_4 solution, the necessary residence time was shortened by 7.1 times (residence time=2.06 min, flow rate= $973\,mL\,min^{-1}$, T=98%). At the IEP, since the TiO_2 particle surface is occupied by dominant neutral groups, (TiOH), and minimal charged species such as $TiOH_2^+$ and TiO^-, electrostatic repulsion among the particles decreases. Addition of Na_2SO_4 neutralizes the charged species and is expected to decrease the thickness of the electrochemical double layer (EDL) of the particles, resulting in the least repulsion among particles and the highest rates of coagulation. The idea is based on that of O'Shea et al.,[11] who explained why the coagulation rate of TiO_2 was the fastest at the IEP in the presence of electrolytes such as organic and inorganic ions.

Figure 3 shows the centrifugation of TiO_2 with and without electrolytes at the flow rate of $973\,mL\,min^{-1}$ at pH 6.5. Good separation of TiO_2 particles was also attained for water containing 1 mM NaCl ($58.4\,mg\,L^{-1}$) and $CaCl_2$ ($111\,mg\,L^{-1}$) as well as 1 mM Na_2SO_4 ($142\,mg\,L^{-1}$) and even for well[12] and tap[12] water whose amounts of the electrolytes are about 50% and 30% of that in 1 mM Na_2SO_4, respectively. In many cases, since the concentration of electrolytes in industrial waste water

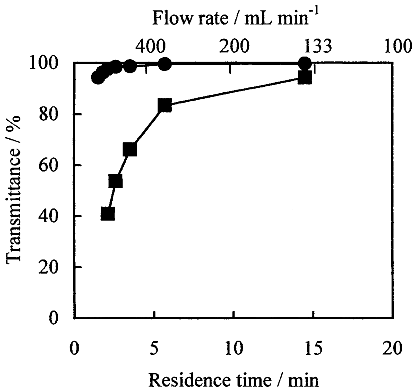

Figure 2. Effect of Na_2SO_4 on the centrifugation of TiO_2. ●: Na_2SO_4, ■: without Na_2SO_4, $[TiO_2] = 0.50\,g\,L^{-1}$, $[Na_2SO_4] = 1\,mM$, pH 6.5, Centrifuge : 16,000 r.p.m.

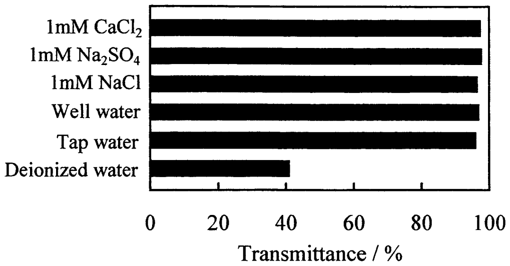

Figure 3. Centrifugation of TiO_2 with and without electrolytes. $[TiO_2] = 0.50\,g\,L^{-1}$, pH = 6.5, flow rate = $973\,mL\,min^{-1}$, Centrifuge : 16,000 r.p.m.

is higher than those in original well and river water, the coagulation of TiO_2 will occur more readily.

For the TiO_2 suspension containing 1 mM Na_2SO_4 flowing at the rate of $783\,mL\,min^{-1}$, continuous operation of 1315 L (28 h) was possible until the wet volume of the separated particles occupied about 50% of the volume of the rotor; above this volume, the transmittance of the discharge decreased below 95%. The use of a rotor larger than 2 L, decrease in the concentration of TiO_2, and alternating use of several centrifuges will further increase the treatment amount of TiO_2 suspension.

To apply the electrolyte-promoted TiO_2 separation method to waste water treatment, one must confirm that the activity of TiO_2 is not largely decreased by added or naturally contained electrolytes. The effect of the electrolytes on the degradation of DBP was examined by combining the reservoir with the photoreactor. TiO_2 (4.0 g) was added to an 8 L aqueous solution of DBP (5 μM($1.39\,mg\,L^{-1}$)) containing 1 mM Na_2SO_4 and the suspension was mechanically stirred in the dark for 30 min at 25 °C to reach the adsorption equilibrium concentration of DBP (C_0). The mixture was transferred into the photoreactor and irradiated with a 400 W high-pressure mercury lamp. The concentration (C_t) of DBP was measured with HPLC according to the reported method.[10] Reusability of the TiO_2 recovered from the centrifuge was examined by using the suspension instead of fresh TiO_2 particles. Figure 4 shows the effect of Na_2SO_4 (1 mM) on the photocatalytic degradation of DBP and on the reusability of the recovered TiO_2. All the degradation in the presence of Na_2SO_4 follows a first-order kinetics to the concentration of DBP ($-\ln(C_t/C_0) = k_{obs}\,t$) just as in the absence of Na_2SO_4, where k_{obs} is the observed first-order rate constant and t is the irradiation time. Table 1 lists the kinetic parameters and the apparent quantum yield (ϕ_{app}) in 5% degradation of DBP. The drop was nearly zero in the first reuse, but increased to 21% in the second reuse. Therefore, TiO_2 could be reused once without decrease in activity in a 1 mM Na_2SO_4 solution in which the particles can be separated with a centrifuge.

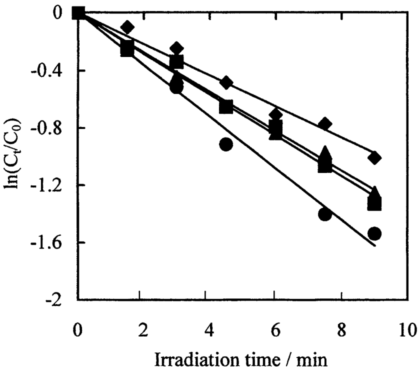

Figure 4. Effect of Na_2SO_4 and recovered TiO_2 on the degradation of DBP. ●: without Na_2SO_4, ▲: 1 mM Na_2SO_4, ■: first reuse, ◆: second reuse; $[TiO_2] = 0.50\,g\,L^{-1}$, [DBP] = 5 μM.

Table 1. Kinetic paremeters for the degradation of DBP

Condition	k_{obs} /min^{-1}	r_0 /μM min^{-1}	$t_{1/2}$ /min	Apparent quantum yield, ϕ/(%)
Without Na_2SO_4	0.180	0.900	3.85	0.36
1 mM Na_2SO_4	0.137	0.685	5.06	0.28
First reuse	0.142	0.710	4.88	0.28
Second reuse	0.108	0.540	6.42	0.22

Continuous separation conditions (pH, flow rate, and electrolytes) of TiO_2 suspended in electrolyte solutions and in well and tap water were found. The activity of TiO_2 was not largely decreased in electrolyte solutions and the recovered TiO_2 could be reused once without decrease in activity. The electrolyte-promoted centrifugal separation method would be applicable to the separation and reuse of TiO_2 suspension after degradation of water pollutants.

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12 Analysis of well water ($mg\,L^{-1}$): $[Na^+]=4.7$, $K^+=0.7$, $Ca^{2+}=11.9$, $Mg^{2+}=2.0$, $Cl^-=4.6$, $SO_4{}^{2-}=7.9$, $HCO_3{}^-=39.4$; Tap water ($mg\,L^{-1}$): $[Na^+]=1.9$, $K^+=0.5$, $Ca^{2+}=7.8$, $Mg^{2+}=1.0$, $Cl^-=3.3$, $SO_4{}^{2-}=9.0$, $HCO_3{}^-=18.9$.

Published on the web (Advance View) June 17, 2003; DOI 10.1246/cl.2003.596