

Fundamental Study on the Photocatalytic Degradation of Organics in Industrial Waste Water with the Presence of Titanium Dioxide

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As part of fundamental studies on the degradation of the organic compounds in industrial waste water, the photocatalytic degradation properties of the organic compound by means of the UV/TiO₂ degradation process have been investigated. The test organic compound of acetic acid was chosen in this study. The testing of photocatalytic degradation were performed under various operation conditions such as TiO₂ dosages, initial concentration of the organic, the aqueous pH's, etc. The effects of various parameters on the short time activity of the present acetic acid-UV/TiO₂ system could be demonstrated from this investigation.

Keywords: Photocatalytic degradation, Titanium dioxide, Total organic carbon, Acetic acid

Introduction

Photocatalytic degradation of organics in waste water has been investigated for these two decades [1, 2]. However, most of these studies have been concerned with directly harmful organics in comparatively dilute solution. In recent years, chemical oxygen demand, COD, in municipal as well as industrial waste water have been aimed at several ppm or less in Japan, this becoming strict year by year. It seems still important that fundamental aspects of the photocatalytic degradation of organics are understood in the complex system such as industrial waste water.

As part of fundamental studies of the photocatalytic degradation of organics in aqueous medium, test organic of acetic acid was mineralized in aqueous TiO₂ suspension with the help of UV irradiation.

Experimental

Materials

Photocatalyst TiO₂ used in this investigation was obtained from Ishihara Sangyo Co., Japan (Ishihara ST-01). The average diameter of the Ishihara ST-01 sample is around 7 nm [data from the manufacturer].

Acetic acid (99.0 %, Nakalai tesque Co., Japan) was selected as the test organic compound to be mineralized in this study. The organic sample was used without further purification. As an inorganic oxidant, hydrogen peroxide, H₂O₂, was chosen to examine the influence on the mineralization efficiency of the organic compound tested. Other reagents included KNO₃ as a supporting electrolyte, KOH and HNO₃ as pH regulators.

Methods

The experiments were performed in a cylindrical photoreactor made of glass. The inner diameter is 60

mm, about 500 mm in height, and 2.7 mm in thickness. Eight 20 W black lights (FL20S-BLB, Toshiba Co., Japan) were positioned around the photoreactor. At a distance of 1.0 m, the light intensity yielded 31 μW cm⁻¹ in the wavelength of 300-450 nm (352 nm of peak wavelength) [data from the lamp's manufacturer]. From this value, the light intensity in W cm⁻¹ on the surface of the black light was calculated as 310 mW cm⁻¹ using the equation, $\ln E_{e,0} = 2 \ln r + \ln E_{e,r}$, where $E_{e,0}$ and $E_{e,r}$ represent the light intensity at distance 0 cm and r cm, respectively [3]. The average distance between the light and the reactor surface is 8 cm. The water-cooled coil was used to keep at a given temperature.

The aqueous solution including a given amount of acetic acid and the pH regulator was put into the photoreactor, before a given amount of TiO₂ was suspended in the solution. This TiO₂ suspension was ultrasonically dispersed for 10 min to obtain good dispersion. Air was bubbled from the bottom part of the cylindrical reactor, and the suspension was stirred using magnetic stirrer. After a given time, about 10 ml of the suspension was pipetted out for sampling, filtered using PTFE membrane filter, and then the filtrate was subject to the measurement of total organic carbon (TOC) by TOC-5000A (Shimadzu Co, Japan).

Results and discussion

Effect of TiO₂ dosage

Figure 1(a) shows the effect of TiO₂ dosage on the mineralization of acetic acid. The initial concentration of carbon derived from acetic acid in the aqueous solution, expressed as TOC₀, is a constant of 30 ppm, and the initial pH of the aqueous TiO₂ suspension is 4.0. Total organic carbon, which is presented in normalized concentration of TOC/TOC₀, is decreased with increasing UV-irradiation time, resulting from decomposition of acetic acid. In addition, the rate of

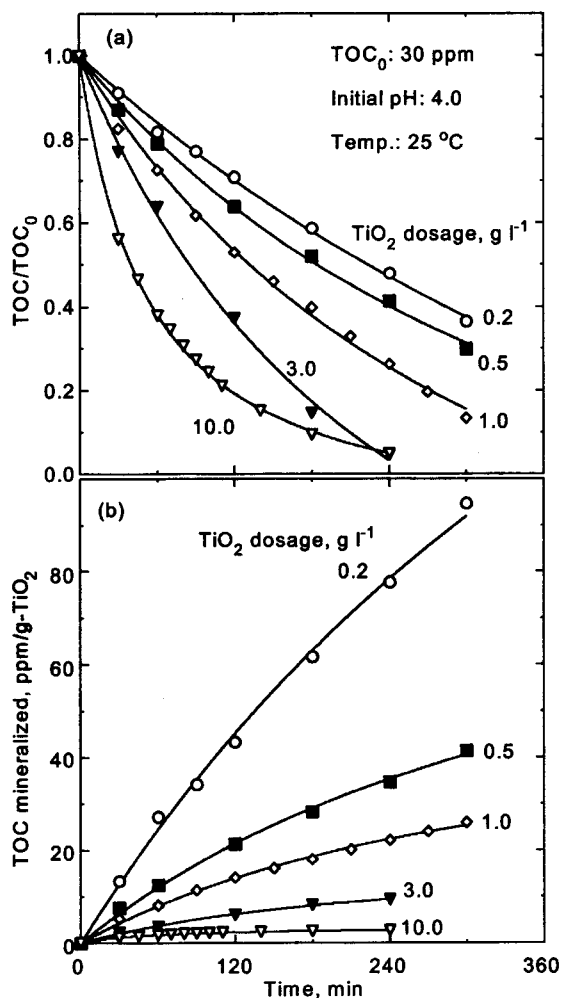


Figure 1. Time variation in normalized concentration of TOC/TOC_0 , (a), and TOC mineralized in the TiO_2 suspension, (b), at various TiO_2 dosages, an initial pH of 4.0, and 10 mM KNO_3 .

mineralization in this photocatalyzed system appears to increase as the TiO_2 dosage increases. In Figure 1(b), the reduction of TOC per a unit weight of TiO_2 is presented as a function of irradiation time. Obviously, the efficiency of mineralization per weight decreases as the TiO_2 dosage increases. The measurement of transmittance of the TiO_2 suspension using UV spectrophotometer and a 1-cm quartz cell indicated that the percent transmittance of the suspension at a wavelength of 352 nm containing 0.2, 0.5, 1.0, 3.0, and 10.0 g l⁻¹ TiO_2 is 10.5, 2.9, 0.5, 0, and 0 %, respectively. In consequence, the UV light does not transmit into the center of the photoreactor when the TiO_2 dosage increases. This seems to be attributed to the decrease in efficiency of the present photocatalyzed system.

In photocatalytic degradation, TiO_2 dosage appears to be an important parameter. Many extensive studies have been carried out so far [4, 5, 6, 7]. However, the optimal catalyst dosage reported was widely different for different photocatalyzed systems. It is even for the

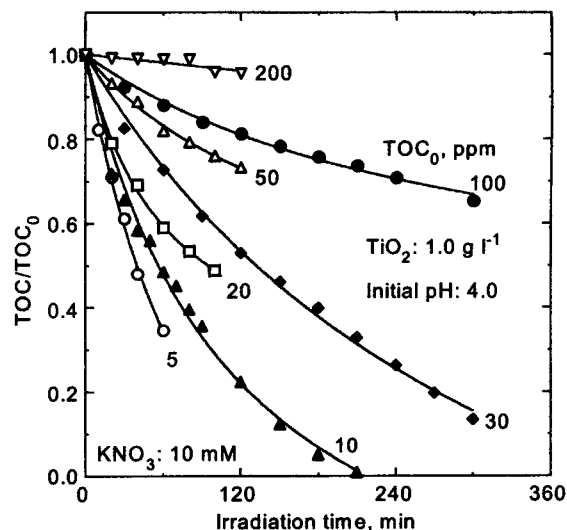


Figure 2. Time variation in TOC/TOC_0 at various levels of TOC_0 and at pH 4.0 (25 °C)

same catalyst that a big difference in optimal catalyst dosage has been reported. In this study, general conclusion might be that the efficiency of the mineralization rather than the mineralization rate is concerned to the transmittance of the photocatalyst suspension; the efficiency of the mineralization per a unit weight of catalyst is decreased as its dosage is increased.

Effect of initial concentration of organic

Figure 2 presents the TOC/TOC_0 vs. irradiation time plot at various levels of the initial TOC concentration. The initial pH of the aqueous suspension is a constant of 4.0. As can be seen from Figure 2, the mineralization rate expressed in TOC/TOC_0 appears to increase as TOC_0 decreases. At 5 ppm of TOC_0 , 65 % of TOC is mineralized after 60 min, whereas only 1-2 % at 200 ppm of TOC_0 . It seems that in terms of percent efficiency the present photocatalyzed system works well in the low concentration range of TOC.

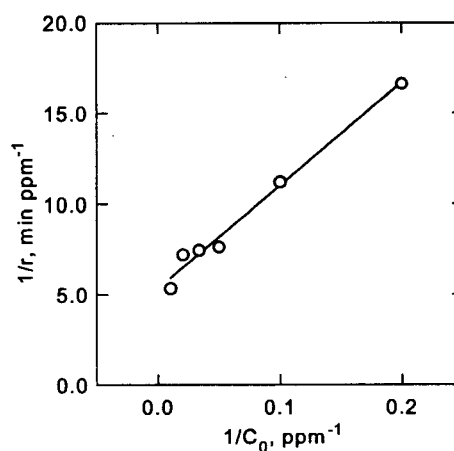


Figure 3. Plot of $1/r$ vs. $1/C_0$.

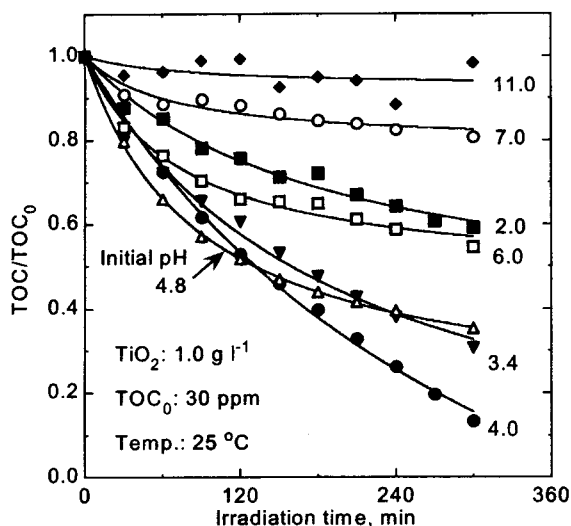


Figure 4. Time variation in normalized concentration of TOC/TOC₀ at various initial pH's of the aqueous TiO₂ suspension and 10 mM KNO₃

In the heterogeneous system of photocatalysis, the reaction rate in a solid-liquid interface is interpreted, based on the Langmuir-Hinshelwood (L-H) kinetic model. According to the model, the relationship between the initial reaction rate (r) and the initial concentration (C_0) can be expressed as

$$\frac{1}{r} = \frac{1}{k_a} + \frac{1}{k_a K C_0} \quad (1)$$

where k_a is the apparent reaction rate constant, K , the adsorption constant [1]. In Figure 3, the $1/r$ vs. $1/C_0$ plot is presented, after r is determined using the linear plots of TOC vs. irradiation time within 90 min at various initial concentrations (not indicated). As in Figure 3, linear relationship between $1/r$ and $1/C_0$ is obtained. From this result, it might be clarified that the mineralization of acetic acid in the present system occurs in the solid-liquid interface region.

Effect of pH

In Figure 4, time variation in mineralization of TOC at various initial pH's is presented. As can be seen from Figure 4, the mineralization rate of acetic acid is strongly affected by initial pH of the aqueous suspension. The initial mineralization rate of TOC seems to be maximal in the weak acidic pH range around 4.8, and an increase as well as a decrease in pH brings about the reduction in the initial mineralization rate.

In the L-H model, the relationship among the irradiation time, t , the TOC concentration, C , and the apparent first-order rate constant, k' , can be expressed as

$$\ln\left(\frac{C_0}{C}\right) = k't \quad (2)$$

Figure 5 shows the plot of $\ln(C_0/C)$ vs. t using the

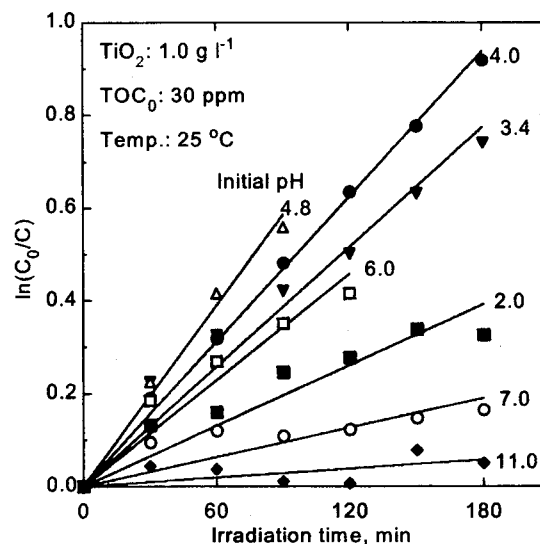


Figure 5. Plot of $\ln(C_0/C)$ vs. t .

data presented in Figure 4. The plotted data were sorted under the condition where the irradiation time is within 180 min and the change in aqueous pH is less than a unit and half. As can be seen from Figure 5, good linear relation between $\ln(C_0/C)$ and irradiation time can be obtained. The least-square regression analysis of the straight lines presented in Figure 5 gives respective k' values, and they are plotted in Figure 6; this figure may clearly indicate that the apparent first-order rate constant is maximal at around pH 4.8.

Regarding the effect of pH, many intensive studies have been conducted [e.g., 8, 9, 10, 11, 12, 13, 14]. The pH of the catalyst suspension influences the degradation rate in different ways, according to the photocatalyzed system and photoreactor. As the empirical result in the present photocatalyzed system, in Figure 6 the amount of TOC adsorbed onto the TiO₂ surface, Γ , is presented as a function of pH. Γ appears to reach a maximum in

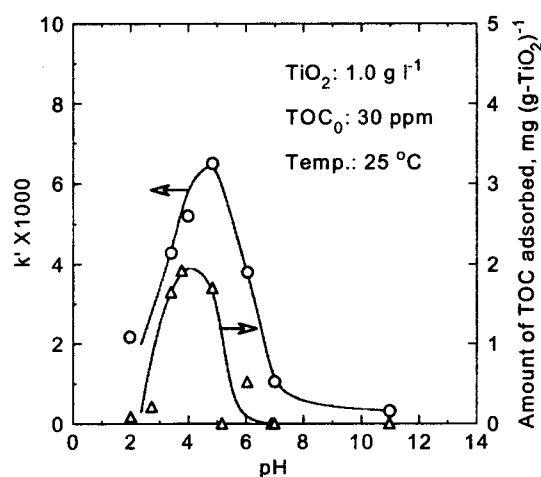


Figure 6. Apparent rate constant, k' , and amount of TOC adsorbed onto TiO₂ as a function of initial pH of the aqueous TiO₂ suspension.

the weak acidic pH range. In addition, a decrease and an increase in pH apart from this pH range leads to a decrease in Γ . In this way, Γ seems to be correlated to the mineralization rate, and hence k' . In the alkaline pH range beyond 7, negatively-charged acetate ion is predominant, and the TiO_2 surface has a negative charge because the IEP of the Ishihara ST-01 catalyst is supposed to be in the pH range of 6.0-6.4 [15]. Consequently, in this alkaline pH range, coulombic repulsion seems to prevent acetate ion from adsorbing in the TiO_2 -water interface region where the photocatalytic reaction takes place. In the weak acidic pH range, the TiO_2 surface is charged positively, whereas acetate species exist in the form of acetate ion. Electrostatic attraction between acetate species and the TiO_2 surface may enhance the adsorption of acetate onto TiO_2 , which causes the maximum in k' . On the other hand, since in the strong acidic pH range acetate species exist in the form of neutral acetic acid molecule, there is no contribution between acetate and the TiO_2 surface; this results in the low Γ , and hence k' . However, further detailed investigations with respect to the influence of pH from the viewpoints of surface chemical aspects would be needed using a variety of organic compounds, semi-conductive photocatalysts, and photocatalyzed reaction systems.

Effect of ionic strength

Figure 7 shows the TOC/TOC_0 vs. irradiation time plot at two different levels of KNO_3 concentration (ionic strength). The rate of mineralization tends to decrease as the ionic strength of the catalyst suspension increases.

As to the influence of the ionic strength and/or of the electrolyte concentration on the photocatalytic degradation of the organic compounds, Wenhua et al. [16] have examined the effect of 10 mM of some electrolytes on the degradation of aniline in the UV- TiO_2

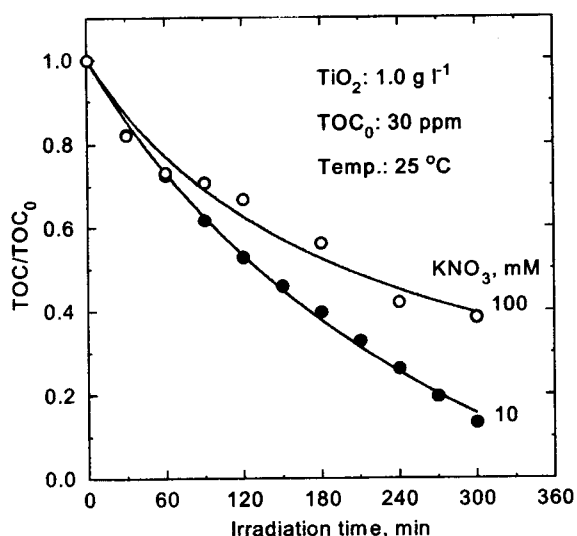


Figure 7. TOC/TOC_0 as a function of irradiation time at two different concentrations of KNO_3 .

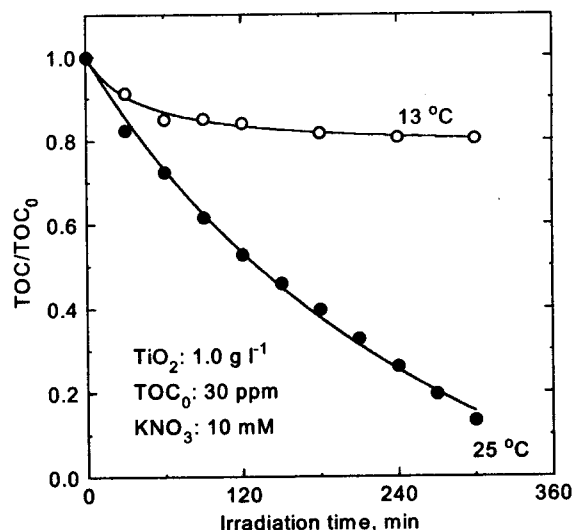


Figure 8. TOC/TOC_0 as a function of irradiation time at two different temperatures.

system. It has been pointed out that the electrolyte addition has no significant effect on the reaction rate. Dionysiou et al. [15] have investigated the influence of KNO_3 addition on the degradation of 4-chlorobenzoic acid (4-CBA), and have reported that no significant difference in time that requires perfect degradation of 4-CBA is observed although the increase in ionic strength in the solution leads to an decrease in the adsorption density of 4-CBA just before UV irradiation. In this study, negatively charged acetate and nitrate ions are competitively adsorbed on the catalyst surface. This might be attributed to the decrease in the mineralization of acetic acid at the higher ionic strength.

Effect of temperature

Figure 8 shows the TOC/TOC_0 vs. irradiation time plot at two different levels of temperature. The rate of mineralization at 13 °C seems to be somewhat lower than that at 25 °C.

The activation energies of degradation of organic compounds in a variety of catalyzed systems are supposed to range from 4 to 50 kJ mol^{-1} in the respective catalyzed systems from Arrhenius plot analysis [e.g., 17, 18]. The result obtained in this investigation concerning the influence of temperature might be consistent with those in the above publication; an increase in temperature brings about enhance of the mineralization.

Effect of H_2O_2 addition

To enhance the rate of mineralization, oxidant is widely utilized in the photocatalyzed system. In this investigation, the efficacy of H_2O_2 was examined.

Figure 9 shows the effect of H_2O_2 addition on the mineralization reaction of acetic acid at two different

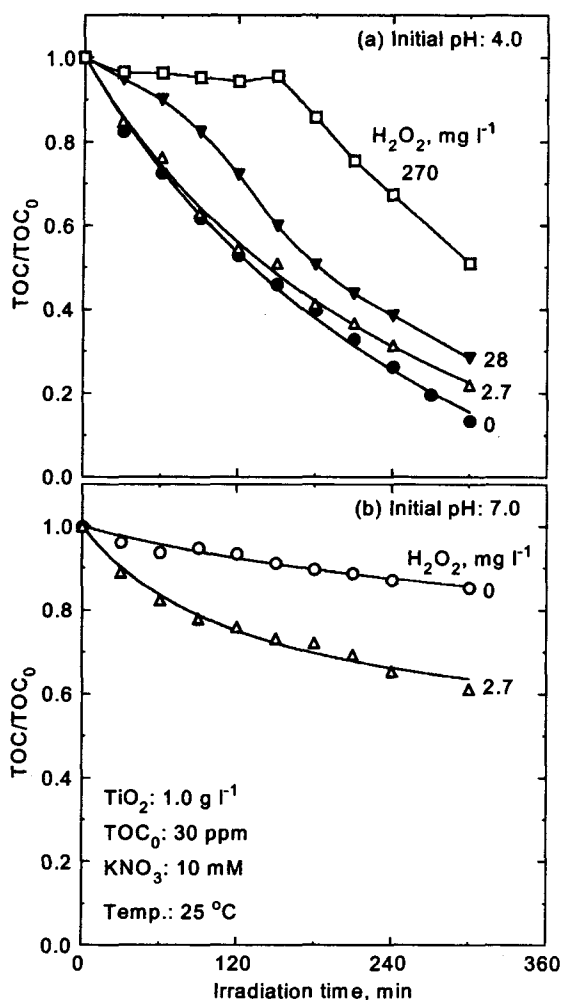


Figure 9. TOC/TOC₀ as a function of irradiation time at various additions of H₂O₂; (a) pH 4.0 and (b) pH 7.0

initial pH's of (a) 4.0 and (b) 7.0. As can be seen from Figure 9, it should be noted that the influence of H₂O₂ on the mineralization at pH 4.0 is reverse to that at pH 7.0, that is, that the mineralization at pH 4.0 is suppressed by the addition of H₂O₂ whereas that at pH 7.0 is enhanced.

As to the influence of H₂O₂, it has been reported that this oxidant normally acts as an activator for the mineralization of a variety of organic compounds in the respective photocatalyzed systems [2]. However, the excess of H₂O₂ suppresses the mineralization rate due partly to the consumption of the OH radical by H₂O₂ itself [19, 20, 21], resulting in the presence of optimum H₂O₂ concentration range for rapid degradation. In the present system, it is at pH 7 that H₂O₂ plays as an activator for mineralizing acetate species. Conversely, at pH 4, added H₂O₂ inhibits the mineralization of acetic acid. Since the mineralization reaction is of complexity and of heterogeneity, detailed mechanisms should be discussed in the further investigations.

Conclusions

In this study, the test organic compound of acetic acid was decomposed in the UV-TiO₂ system. The results obtained were discussed from the viewpoint of surface-chemical analysis. The pH of the aqueous catalyst suspension in the present system appears to be most sensitive among the parameters tested. It means that the importance of the interfacial phenomena in the catalyst-water, such as surface charge of the catalyst, adsorption and its pH-dependence of the organic to be decomposed, could be demonstrated.

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