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Photocatalytic water treatment on immobilized TiO_2 combined with ozonation

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Abstract

The degradation of acetic acid, monochloroacetic acid and dimethyl-2,2,2-trichloro-1-hydroxyethylphosphonate (DEP) by ozonation on illumination was enhanced considerably by the incorporation of photocatalyst. This effect was smaller for the degradation of phenol. However, intermediate organic acids formed during the degradation of phenol disappeared rapidly with the incorporation of photocatalyst. It is suggested that the effect of the photocatalyst is larger on the degradation of hydrophilic compounds than aromatic compounds.

Keywords: Ozone; Phenol; Photocatalyst; UV

1. Introduction

Photocatalytic water treatment has been studied for approximately two decades [1,2]. Recently, the possibilities of practical application have attracted the interest of industry [3]. The photocatalytic method, a mild method of water treatment, has been considered for application to wastewater containing low concentrations of pollutants using illumination by low intensity light, such as sunlight. It may also be used as a pretreatment before biological treatment [4–6], or as a secondary or tertiary treatment [7]. In this respect, the photocatalytic method differs from other photochemical methods, such as UV/H_2O_2 and UV/O_3 [8], which are used for rapid treatment and can be applied to wastewater containing higher concentrations of pollutants [9]. In a previous paper [10], we reported that ozone pretreatment improves considerably the photocatalytic degradation of several pollutants. In this paper, we report the effect of the combination of photocatalyst and ozone.

2. Experimental section

TiO_2 was immobilized by the following method. One part by weight of 51%–57% sodium silicate solution was diluted by adding three parts of deionized water, and was then mixed with five parts of TiO_2 powder. The mixture was coated on the inner surface of a glass tube, vertically cut in half to facilitate the coating of TiO_2. The coated tube was dried at room temperature for about 12 h, and then further at 120 °C. The dried tubes were calcined at 500 °C for 1 h. The details of the immobilization procedure and the characteristics of coated TiO_2 will be reported elsewhere. The TiO_2 used was TP-2 (Fujititan Co.) (anatase). Its characteristics have been described previously [11].

A round glass bottle in which the TiO_2-coated tube was installed was used as a reactor. Sample solution (150 ml) was added to the reactor. A 6 W low-pressure mercury lamp was placed in the centre of the bottle. The lamp was protected from the solution by a quartz tube. Ozone was bubbled from the bottom and the solution was stirred magnetically. The light intensity was in the range 13–42 mW cm^{-2} on the surface of the quartz tube, decreasing from the central part to the tip of the lamp. A Sasakura Ozonemaster OM-0.5 was used to generate ozone at a rate of 0.5 g h^{-1}. The concentration of ozone dissolved in water after equilibrium was reached was 16.8 mg l^{-1}, which was measured by iodometry. The analyses of the organic acids were performed by a Yokokawa ion chromatograph IC7000 equipped with a suppressor of background conductivity.

3. Results and discussion

Acetic acid was degraded by four different combinations of UV and O_3, namely UV, UV/TiO_2, UV/O_3 and $UV/TiO_2/$

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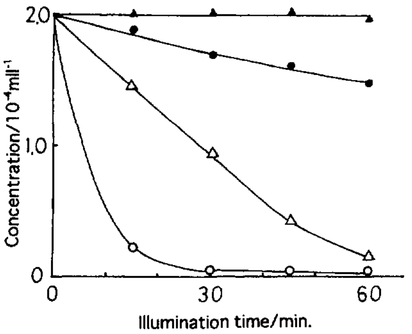

Fig. 1. Degradation of acetic acid by the combination of photocatalyst and ozone: ○, UV/TiO$_2$/O$_3$; △, UV/O$_3$; ●, UV/TiO$_2$; ▲, UV.

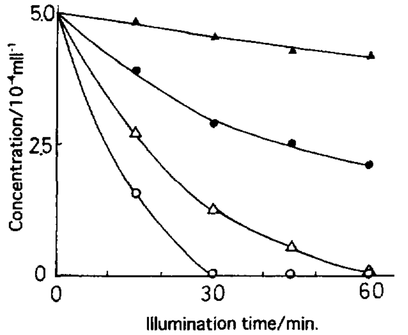

Fig. 2. Degradation of monochloroacetic acid by the combination of photocatalyst and ozone (symbols the same as in Fig. 1).

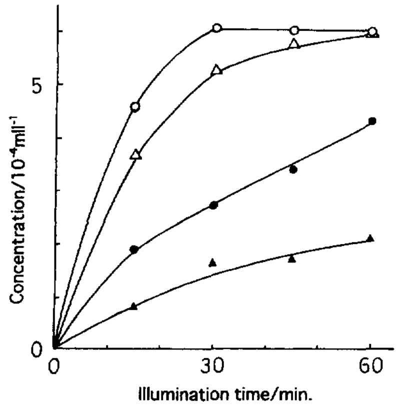

Fig. 3. Formation of Cl$^-$ from the degradation of DEP (2×10^{-4} mol l^{-1}) by the combination of photocatalyst and ozone (symbols the same as in Fig. 1).

O$_3$ (Fig. 1). Degradation of acetic acid by UV alone is negligible. This is because acetic acid absorbs very little at 254 nm, which is the principal emission line of the low-pressure mercury lamp. UV/TiO$_2$ degrades acetic acid slightly. UV/O$_3$ is slightly more efficient than UV/TiO$_2$. Bubbling air into the solution does not accelerate the degradation by UV/TiO$_2$ appreciably, in agreement with the results reported in Ref. [12], suggesting that the role of O$_3$ is not simply to increase the concentration of oxygen dissolved in the solution. The combination of UV/O$_3$ and photocatalyst, i.e. UV/TiO$_2$/O$_3$, exhibits considerably higher degradation efficiency.

Similar results are obtained for monochloroacetic acid (Fig. 2). However, the effect of UV/TiO$_2$/O$_3$ is not as large as in the case of acetic acid. For the insecticide dimethyl-2,2,2-trichloro-1-hydroxyethylphosphonate (DEP), the effect of UV/TiO$_2$/O$_3$ is apparently even smaller (Fig. 3). Since the disappearance of DEP is so rapid, the formation rate of Cl$^-$ was measured instead of the disappearance rate. The effect of UV/TiO$_2$/O$_3$ is even smaller on phenol, which is a common pollutant in surface water (Fig. 4). However, the effect of UV/TiO$_2$/O$_3$ is larger for the elimination of total organic carbon (TOC) than for the disappearance of phenol (Fig. 4). Therefore it can be concluded that UV/TiO$_2$/O$_3$ is more effective on the degradation of the intermediate compounds than on the disappearance of phenol. This trend was shown more clearly by measuring the evolution of intermediate compounds. Four organic acids (formic acid, acetic acid, glycoxylic acid and glycolic acid) were identified as intermediates during the degradation of phenol, of which formic acid was formed in the largest concentration. Fig. 5 shows that these intermediate organic acids are formed most rapidly by O$_3$/TiO$_2$/UV and disappear likewise with the

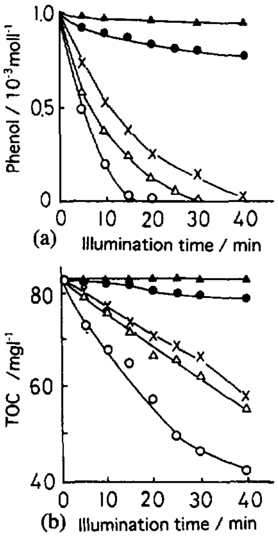

Fig. 4. Degradation of phenol (a) and TOC elimination (b) by the combination of photocatalyst and ozone (×, O$_3$; other symbols the same as in Fig. 1).

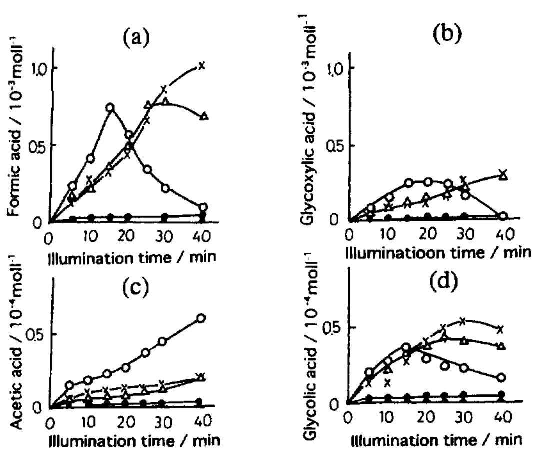

Fig. 5. Evolution of intermediate organic acids during the degradation of phenol (10^{-3} mol l^{-1}) (symbols the same as in Fig. 4): (a) formic acid; (b) glycoxylic acid; (c) acetic acid; (d) glycolic acid.

exception of acetic acid. Although acetic acid is more stable than the other organic acids, it also degrades on long-time illumination. The most rapid degradation of the intermediate compounds by $O_3/TiO_2/UV$ explains the greatest TOC elimination rate produced by this combination.

In a previous paper [10], we made the assumption that pretreatment by O_3 leads to the formation of hydrophilic compounds as intermediates, which are more degradable by UV/TiO_2 than by O_3. This assumption was supported by separate experiments on the degradation of acetic acid and methanol by ozonation and photocatalyst. Acetic acid was one of the major intermediates from the ozonation of agrochemicals reported previously [10,13]. Acetic acid (10^{-3} mol l^{-1}) and methanol (2.5×10^{-3} mol l^{-1}) are degraded by less than 10% after 2 h by ozonation, whereas they are degraded by 65% and 90% respectively after 2 h photocatalytic treatment under the experimental conditions described in Ref. [10]. In addition to the above, the effect of charge separation due to electron acceptance by O_3 is also in evidence. The mechanism of this effect can be represented as follows

$$TiO_2 \xrightarrow{h\nu} h^+ + e^-$$

$$e^- + O_3 \rightarrow O_3^-$$

$$O_3^- \rightarrow O_2 + O^-$$

$$O^- + H_2O \rightarrow OH^- + {}^{\cdot}OH$$

$$h^+ + OH^- \rightarrow {}^{\cdot}OH$$

Since this process involves the combination of UV, O_3 and TiO_2, the actual mechanism may be more complicated [8]. In this simultaneous combination, the charge separation is considered to be the most effective process for promoting the photocatalytic degradation, although the contribution of additional OH radicals formed via electron acceptance by O_3 is not clear. In this respect, the present method is advantageous over the pretreatment method reported previously [10].

Contrary to the general notion that the photocatalytic process is slow and can only be used for solutions of low concentration, it has been shown in this study that the photocatalytic method combined with ozonation provides rapid degradation. It may find potential application for the treatment of wastewater containing high concentrations of pollutants. Further research using additional pollutants is under way in our laboratory.

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