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Development of a novel photocatalytic reaction system for oxidative decomposition of volatile organic compounds in water with enhanced aeration

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Abstract

A novel photocatalytic reaction system, composed of solution and gas spaces that are divided by a thin Teflon film and titanium(IV) oxide (TiO_2)-coated mesh or cloth, for the treatment of contaminated aqueous solutions was developed to be operated with enhanced aeration without bubbling of air in the solution. First, the photocatalytic activities of TiO_2 particles immobilized on two kinds of support material, stainless steel mesh (SSM) and fiberglass cloth (FGC), were investigated for photocatalytic oxidation of 2-propanol, as a model volatile organic compound, dissolved in aerated aqueous solution. The TiO_2 particles immobilized on both support materials exhibited photocatalytic activity to oxidize 2-propanol into acetone and carbon dioxide (CO_2), and the activity levels of the TiO_2 particles immobilized on the two kinds of support materials were comparable. Presumably due to the presence of a small amount of metal species originating in SSM that might work as reduction catalysts, molecular hydrogen (H_2) was also liberated on the TiO_2-immobilized SSM. Results of analysis of weight loss after photoirradiation suggested that the stability of the TiO_2-immobilized FGC was better than that of the TiO_2-immobilized SSM. On the basis of these results, FGC was employed in construction of a photocatalytic reactor equipped with an oxygen (O_2)-permeable Teflon membrane in order to make oxygen pass from a gas space to a solution space and to keep the surface of the immobilized TiO_2 photocatalyst, facing an aqueous solution containing volatile organic compounds, saturated with dissolved O_2. From the results of photocatalytic oxidative decomposition of 2-propanol, it was clarified that the surfaces of TiO_2 particles could be sufficiently supplied with O_2 from the gas space through the membrane to accelerate the oxidation.

Keywords: Titanium(IV) oxide; Supported photocatalysts; Oxygen-permeable membrane; Photocatalytic oxidation; Volatile organic compounds; Aqueous solution

1. Introduction

Volatile chlorinated organic compounds (VCOCs) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) have been widely used as solvents in industrial processes. As a result of their leakage from, for example, underground storage tanks and disposed plastics, soil or ground water has often become contaminated with VCOCs. This has become a serious problem recently, because these chemicals are toxic, often carcinogenic, and persistent in the environment. Conventional methods for removal of VCOCs from water using adsorbents, such as granular activated carbon (GAC), are effective for reducing the concentrations of VCOCs, but further treatment is required for recovery of GAC-adsorbing toxic organic compounds.

Photocatalytic oxidation is an alternative method for purifying water through decomposition of organic contaminants into carbon dioxide (CO_2) and mineral acids such as hydrogen chloride (HCl). There have been many studies on photoinduced decomposition of a wide range of organic compounds, including VCOCs, nonionic surfactants and aromatic compounds, in aqueous solutions using titanium(IV) oxide (TiO_2) as a photocatalyst [1–8]. Photocatalytic decomposition by TiO_2 is thought to be initiated usually by either direct [9,10] or hydroxyl radical ($^\bullet OH$)-mediated [4–6] positive hole (h^+) transfer to organic molecules, and as a counterpart of the redox reaction, conduction band electrons (e^-) are consumed by reaction with molecular oxygen (O_2) dissolved in the reaction solution [7]. To accelerate oxidation, efficient scavenging of e^- by O_2 is necessary. However, since the concentration of dissolved O_2 in an aqueous solution is limited (ca. 1 mmol dm^{-3}), recombination of e^- and h^+, which leads to low catalytic efficiency, is one of the

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problems in TiO_2 photocatalytic reactions operated in aqueous solutions. Bubbling of air through an aqueous solution is the simplest way to supply a sufficient amount of O_2 and thereby suppress e^-–h^+ recombination, but this method cannot be used in the case of VCOCs because of their volatilization to open air. An alternative method to remediate contaminated water by a TiO_2 photocatalyst is to decompose gaseous VCOCs which are expelled from the aqueous solution by air [11]. However, it has been shown that VCOC degradation in a gas-phase photocatalytic reaction produces unfavorable by-products such as dichloroacetyl chloride and phosgene, which are well-known highly toxic compounds [12,13]. It has been also reported that accumulation of chloroacetic acid on surfaces of TiO_2 particles results in a decrease in the photocatalytic activity of the catalyst when used in air [14,15].

Reactors with suspensions of TiO_2 particles have been used in most studies to clarify the reaction mechanism and to establish a method of complete mineralization of organics in an aqueous solution into carbon dioxide (CO_2) [1–6]. However, a suspension system is not practical because filtration is required to recover the catalyst from the reaction mixture. To overcome this problem, two methods for continuous use without removal from cycle to cycle have been proposed: a method using TiO_2 pellets [7] and a method in which TiO_2 particles are immobilized on various supports [8]. However, there are various problems in these methods, such as decrease in effective surface area, appreciable loss of TiO_2 from the supports, decrease in adsorption of organic substances on the surfaces of TiO_2 particles, and mass transfer limitations.

Our interest has, therefore, been focused on the development of a system for efficient photodegradation of aqueous VCOCs using an active immobilized TiO_2 photocatalyst. In this study, we investigated the photocatalytic activities of TiO_2 particles immobilized on two kinds of support, and we developed a new photocatalytic reaction system in which O_2 molecules can be supplied to the surfaces of TiO_2 particles used as photocatalysts from the gas phase through an O_2-permeable membrane to accelerate the oxidation of organic pollutants without the requirement of air bubbling to induce volatilization of organic compounds into open air.

2. Experimental

2.1. Materials

Degussa P25 TiO_2 powder was supplied from Nippon Aerosil. Based on the results of analysis of percent proportion of the most intense XRD peaks of anatase ((1 0 1), $2\theta = 25.3^\circ$) and rutile ((1 1 0), $2\theta = 27.5^\circ$) [16], the TiO_2 powder is composed of 83% anatase and 17% rutile. Its BET surface was calculated to be 50 $m^2\,g^{-1}$ by nitrogen adsorption at 77 K. A stainless steel mesh (SSM, 144 holes cm^{-2}, 0.2 mm in thickness) and fiberglass cloth (FGC, Central Glass EGW 110TH-153 (1 0 4), 0.24 mm in thickness) were used as supports of TiO_2 particles. Laboratory-grade water was prepared using a Milli-Q pure water system (Yamato-Millipore). Titanium(IV) tetra-2-propoxide ($Ti(O^iPr)_4$, Wako Pure Chemical), 2-propanol (Wako), and acetic acid (Wako) were used without further purification.

2.2. Immobilization of TiO_2 particles on SSM and FGC

To a 50 cm^3 portion of 2-propanol, $Ti(O^iPr)_4$ (0.94 g) was added dropwise with vigorous stirring in open air. After agitation overnight at ambient temperature, a slightly turbid solution thus obtained was diluted with 60 cm^3 of 2-propanol. Then 3.88 g of TiO_2 powder was added, and the resulting suspension was stirred for several hours to obtain a homogeneous dispersion. The dispersion was applied onto the SSM and FGC heated at ca. 350 K using a spray bottle followed by heat treatment at 473 K for 1 h in air. The amount of TiO_2 particles used in all experiments for which results are reported in this paper ranged from 7 to 10 mg cm^{-2} of the support material, SSM or FGC.

2.3. Photoirradiation under static conditions

The TiO_2-immobilized SSM or FGC (0.7 cm × 2.0 cm) and an aqueous 2-propanol (0.25 vol.%) solution (5 cm^3) were placed in a glass tube (transparent at >300 nm, 18 mm in diameter and 180 mm in length), and they were photoirradiated by a high-pressure mercury arc (Eiko-sha, 400 W) in air at 298 K. The TiO_2-coated faces of the SSM and FGC were kept perpendicular to the light beam. After irradiation for 1 h, a portion (0.2 cm^3) of the gas phase of the sample was withdrawn with an air-tight syringe and subjected to gas chromatography (GC) of molecular hydrogen (H_2) and carbon dioxide (CO_2) using a Shimadzu GC-8A gas chromatograph equipped with MS-5A (for H_2) and Porapak-Q (for CO_2) columns and a TCD detector. The yield of acetone was also measured by GC using a Shimadzu GC-14B gas chromatograph equipped with a PEG-20M column and an FID detector.

2.4. Photooxidation using a reactor equipped with an oxygen-permeable membrane

A schematic view of the reaction apparatus used for photocatalytic oxidation of organic contaminants in water using a TiO_2-immobilized FGC and an O_2-permeable membrane is shown in Fig. 1. The reactor consisted of an upper chamber and a lower chamber separated by a Teflon membrane (0.025 mm in thickness, ca. 9 cm in diameter): the upper chamber, made from Teflon, was used for circulation of the reaction solution (solution space), and the lower chamber, made from stainless steel, was used for gas supply, O_2, Ar, or air (gas space). TiO_2 (ca. 350 mg)-immobilized FGC (ca. 8 cm in diameter) was placed on the Teflon membrane so that the loaded TiO_2 photocatalyst could be supplied with O_2 from the gas space through the Teflon membrane. A

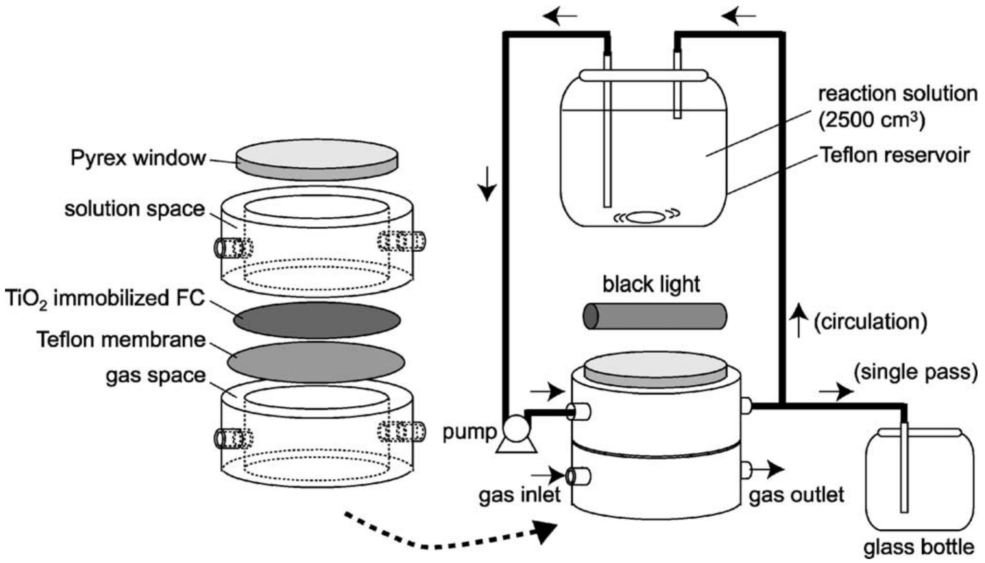

Fig. 1. Schematic illustration of the photocatalytic oxidation system with a reactor equipped with an O_2-permeable membrane.

peristaltic pump (Cole Palmer Masterflex 7553-70) was used to supply the solution space of the reactor with an aqueous 2-propanol solution from a Teflon reservoir (2500 cm^3). Photoirradiation was performed through a Pyrex window (8 cm in diameter) fixed on the top of the liquid space. Two sets of experiments were conducted using this reactor. In one set of experiments (circulation system), aqueous 2-propanol (18 $mmol\,dm^{-3}$) deaerated by bubbling with Ar was circulated at a flow rate of 140 $cm^3\,min^{-1}$, and photoirradiation was performed using a black light (Toshiba, 3.0 $mW\,cm^{-2}$ at 360 nm). A portion (0.2 cm^3) of the reaction solution in the reservoir was withdrawn every hour and subjected to GC to determine the amount of produced acetone. During the experiment, the solution in the reservoir was magnetically stirred (ca. 500 rpm) to maintain homogeneity. Gases supplied to the gas space were changed from Ar to O_2 or from O_2 to Ar. In another set of experiments (single pass system), aerated aqueous 2-propanol (2.5 $mmol\,dm^{-3}$) was supplied to the reactor at a flow rate of 55 $cm^3\,min^{-1}$, and the drainage from the outlet of the reactor was collected in a glass bottle and was analyzed every hour. A xenon (Xe) arc (300 W, Ushio) was employed as a light source. During the experiment, air or Ar was continuously supplied to the gas space at ambient pressure. Concentrations of dissolved O_2 in the solution after passing through the reactor were also monitored by a TOA-DKK DO55G dissolved oxygen meter.

3. Results and discussion

3.1. Photocatalytic activities of TiO_2 particles loaded on SSM and FGC

Photoinduced oxidation of 2-propanol in an aerated aqueous solution was conducted as a test reaction of photoactivities of the TiO_2-coated SSM and FGC. Table 1 shows the amounts of products and percent proportions of TiO_2 remaining on the supports after photoirradiation for 1 h. TiO_2 particles immobilized on both supports showed activity for photooxidation of 2-propanol, and acetone was produced as a main product along with liberation of an appreciable amount of CO_2, which might be produced by further oxidation of acetone [17]. There was almost no formation of these products without photoirradiation of a TiO_2-coated support or with irradiation in the absence of a TiO_2 photocatalyst; a negligible amount of acetone was detected following irradiation in the absence of TiO_2. Due to the difficulty in precisely controlling the amount of TiO_2 loaded, there was an obvious difference between the amounts of TiO_2 particles immobilized on the SSM and FGC, and an exact comparison of the activities was not possible. However, in a semi-quantitative sense, the amounts of acetone and CO_2

Table 1
Photocatalytic activity for oxidation of aqueous 2-propanol by immobilized TiO_2 particles on various supports

Support	W_{TiO_2} [a] (mg)	R_{ac} [b] ($\mu mol\,h^{-1}$)	R_{CO_2} [c] ($\mu mol\,h^{-1}$)	R_{H_2} [d] ($\mu mol\,h^{-1}$)	ΔW [e] (%)
Blank[f]	–	0.02	0	0	–
SSM[g]	14	0.53	0.13	0.07	21
FGC[h]	10	0.48	0.10	0	11

[a] Total amount of TiO_2 immobilized on the support.
[b] Rate of acetone production.
[c] Rate of CO_2 liberation.
[d] Rate of H_2 liberation.
[e] Percent weight loss of immobilized TiO_2 after photoirradiation for 1 h.
[f] Photoirradiation without a catalyst.
[g] Stainless steel mesh.
[h] Fiberglass cloth. Catalyst: Degussa P25 immobilized on 1.4 cm^2 of SSM or FGC.

produced by them were comparable, suggesting that the microenvironments of the loaded TiO_2 were almost the same. Notably, a small amount of molecular hydrogen (H_2) was detected on the TiO_2-immobilized SSM, while no H_2 liberation was observed when the TiO_2-immobilized FGC was used as a photocatalyst. Since the surfaces of TiO_2 particles have poor ability to reduce protons (H^+) to liberate H_2 [18,19], certain metal species in the SSM might participate in the observed H_2 liberation, i.e., metal species may work as active sites for reduction of H^+ with photoexcited electrons in TiO_2. Control of photocatalytic activities by metal species dissolved from the support materials is now under investigation.

Thus, FGC seems to be better than SSM for evaluation of the photocatalytic ability of oxidation without any other side-reactions. Another advantage of FGC as a support is that the stability of TiO_2 loaded on FGC is greater than that of TiO_2 loaded on SSM; the FGC support could retain about 90% of the TiO_2 particles, while less than 80% of the TiO_2 particles remained on the SSM under the present reaction conditions (Table 1). On the basis of these results, TiO_2-immobilized FGC was used in further experiments.

3.2. Photooxidation of 2-propanol using a reactor equipped with an oxygen-permeable membrane in a closed circulation mode

In order to confirm the effect of O_2 permeation through a Teflon membrane, photooxidation of 2-propanol in a deaerated aqueous solution using the reactor equipped with the membrane was performed while keeping the gas space filled with Ar or O_2. The reaction solution was circulated in this system at a flow rate of 140 $cm^3\,min^{-1}$ during the experiment (see Fig. 1). Fig. 2 shows time courses of acetone production when the atmosphere in the gas space was switched from Ar to O_2 (upper) or from O_2 to Ar during photoirradiation. In the dark, without photoirradiation, negligible acetone production was observed, as expected, when the gas space was filled with Ar. On the other hand, a detectable amount of acetone was produced under ultraviolet light irradiation even though O_2 content in the system was negligible, but the total yield of acetone was saturated after ca. 2 h irradiation. The production of a small amount of acetone under an Ar atmosphere is attributable to the oxidation of 2-propanol by positive holes (h^+) along with the formation of Ti^{3+} species by trapping of electrons (e^-) at defective sites in TiO_2 [20–22]. The reason for an appreciable induction period of the acetone production was ambiguous. As discussed in a previous report [22], such accumulation of e^- was also observed by photoirradiation to a deaerated aqueous TiO_2 suspension containing methanol and triethanolamine in the absence of a reduction catalyst such as platinum. The formation of Ti^{3+} is also supported by the change in color from white to pale blue during the photoirradiation. It has been reported that P25 TiO_2 contains ca. 50 $\mu mol\,g^{-1}$ of sites to become Ti^{3+} by photoirradiation, suggesting that ca. 10 μmol of acetone is produced on the assumption that two Ti^{3+} sites are produced along with one molecule of acetone. Additional Ti^{3+} in TiO_2 originating from $Ti(O^{i}Pr)_4$ may account for the remaining amount of acetone produced.

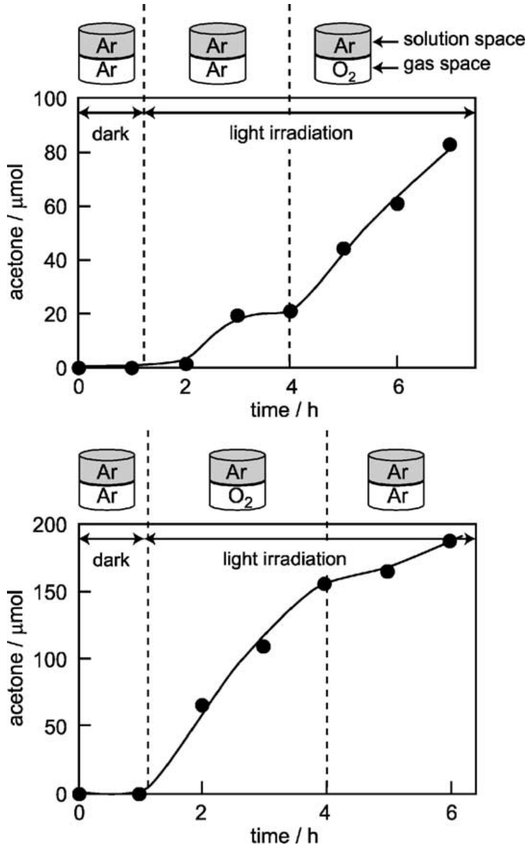

Fig. 2. Photooxidation of 2-propanol dissolved in a deaerated aqueous solution using the reactor shown in Fig. 1. The reaction solution was circulated at a flow rate of 140 $cm^3\,min^{-1}$.

The most striking feature in these plots is that just switching the atmosphere in the gas space changes the rates of acetone production; rates of acetone production in the presence of O_2 in the gas space were about three times higher than those in the presence of Ar. These results suggest that the photocatalyst in the solution space can be supplied with O_2 from the gas space through the Teflon membrane to enhance photooxidation of aqueous 2-propanol.

Table 2 summarizes the results of amounts of acetone produced and amount of 2-propanol consumed in a deaerated aqueous 2-propanol solution in the presence of air, Ar, or O_2 in the gas space after photoirradiation for 1 h. Photoirradiation induced production of acetone regardless of the kind of gas supplied to the gas space. In the presence of O_2 (air or O_2) in the gas space, the amounts of acetone produced were considerably greater than those in the absence of O_2 (Ar atmosphere). Moreover, the amount of acetone produced and the amount of 2-propanol consumed more than doubled when air was substituted by pure O_2 in the gas space, i.e., the presence of O_2 in the gas space is responsible for the

Table 2
Variation in amounts of acetone produced and 2-propanol consumed in the presence of various gases in the gas space[a]

Gas phase[b]	P_{ac}[c] (μmol)	C_{pr}[d] (μmol)	$C_{\mathrm{pr}}/P_{\mathrm{ac}}$
Ar	3.2	–[e]	–[e]
Air	8.5	10.2	1.2
O_2	18.4	55.6	3.0

[a] All reactions were carried out in a reactor equipped with an O_2-permeable membrane (Fig. 1) for 1 h. Catalyst: TiO_2 (Degussa P25, ca. 350 mg) immobilized on FGC (ca. 50 cm^2). The reaction solution was deaerated with Ar before photoirradiation.

[b] Gases supplied to the gas space.

[c] Amount of acetone produced.

[d] Amount of 2-propanol consumed.

[e] Not measured.

increase in photooxidation of reactants in an aqueous solution and the photoactivity depends on the concentration of O_2 in the gas space. Another point worth consideration is that the ratio of 2-propanol consumption to acetone production increased with increase in concentration of O_2 in the gas space. This might be due to the enhancement of further oxidation of acetone to yield CO_2 (see Table 1) with a high concentration of O_2 in the gas space.

When similar experiments were conducted using a 20 times thicker Teflon membrane (0.5 mm), there was no appreciable dependence of photocatalytic activity on the atmosphere of the gas space, and a change in the color of FGC from white to blue was observed even when O_2 was supplied to the gas space. This indicates that mass transfer of O_2 from the gas space is dominated by the thickness of the Teflon membrane. The coefficient of permeability of O_2 through Teflon, polytetrafluoroethylene, is $3.7 \times 10^{-7}\,cm^3\,(STP)\,cm^{-2}\,cm\,s^{-1}\,MPa^{-1}$ [23]. Assuming a pressure difference of 0.1 MPa (ca. 1 atm) between solution and gas spaces, the amounts of O_2 that permeate through 50 cm^2 membranes of 0.025 and 0.5 mm in thicknesses are ca. 120 and 6 $\mu mol\,h^{-1}$, respectively. Thus, the fact that there was no effect on photocatalytic oxidation when the thicker membrane was used is reasonable. The dependence of thickness is now being investigated in detail, and the results will be reported elsewhere.

3.3. Photooxidation of 2-propanol using a reactor equipped with an oxygen-permeable membrane in a single-pass mode

In view of the practical application of decomposition of VCOCs dissolved in water, a single-pass (flow) system, in which the reaction solution is supplied without circulation, is preferable to a circulation (batch) system shown above. Moreover, in order to clarify the effect of the O_2-permeable membrane employed in the present reactor on the purification of actual contaminated water, it is necessary to confirm the advantage of the use of an O_2-permeable membrane in the photocatalytic decomposition of organic compounds in an aerated (not deaerated) solution. Thus, photooxidation of 2-propanol in an aerated, i.e., air-saturated, aqueous solution was performed using a single-pass system. Fig. 3 shows variation in the amounts of acetone produced and concentrations of dissolved O_2 in the reaction solution after passage in the reactor versus photoirradiation time. As can be clearly seen in the time courses of acetone production, the level of photooxidation activity in the presence of air in the gas space was more than 1.5 times higher than that in the presence of Ar. It is also notable that no appreciable decrease in the concentration of dissolved O_2 was observed when the gas space was filled with air, while the O_2 concentration was decreased when air in the gas space was substituted by Ar owing to the consumption by the reaction. (Probably due to the further oxidation to give CO_2 as discussed in the preceding section, the molar amount of O_2 consumed exceeded that acetone produced. However, since we did not analyze the amount of CO_2 in this system, it is not discussed here.) These results indicate that the O_2-permeable membrane is effective for enhancement of aeration of the reaction solution, leading to an increase in photocatalytic activity even when the reaction solution contains dissolved O_2 before passage in the reactor. The pass length in the present experiments was only 8 cm, and it is expected that the longer the pass is, the more significant will be the effect of the O_2-permeable membrane.

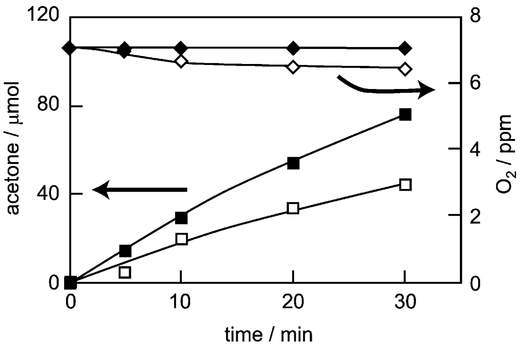

Fig. 3. Variation in amounts of acetone produced and concentration of dissolved O_2 after passage through the reactor at a flow rate of 55 $cm^3\,min^{-1}$ as a function of photoirradiation time. Ar (open symbols) or O_2 (filled symbols) was supplied to the gas space during the experiment. Squares and diamonds show amounts of acetone produced and O_2 dissolved, respectively.

4. Conclusions

The present study has shown for the first time that enhancement of aeration by an O_2-permeable membrane can increase photocatalytic activity for the decomposition of organic compounds in an aqueous solution [24]. The advantage of this system for application of photodegradation of aqueous VCOCs is that it does not require air bubbling, which causes unfavorable volatilization into open air. In this study, we used only 2-propanol as a model compound, and reaction conditions such as thickness of the membrane, flow rate of air (or O_2) and thickness of the reaction solutions were not optimized. Further studies using VCOCs and an O_2-permeable membrane with a large permeability coefficient other than a Teflon membrane, e.g., a silicone membrane, are now under way.

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