Korean J. Chem. Eng., **20**(5), 862-868 (2003)

Removal of Paraquat in Aqueous Suspension of TiO_2 in an Immersed UV Photoreactor

Joon-Chul Lee*, Moon-Sun Kim, Chul Kyung Kim, Chan-Hwa Chung, Sung M. Cho, Gui Young Han, Ki June Yoon and Byung-Woo Kim†**

*Department of Chemical Engineering, KAIST, Daejeon 305-701, Korea
**Division of Chemistry & Applied Chemistry, Mokwon University, Daejeon 302-729, Korea
Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea
(*Received 25 October 2002 • accepted 19 May 2003*)

Abstract−Experiments were performed to investigate the effect of operating parameters on the photodegradation efficiency of paraquat in a TiO_2-suspended photoreactor with immersed UV lamps. TiO_2 particles were prepared by a hydrothermal method. The removal rate of paraquat in the reactor was 0.54 mg/*l*/h with only air-sparging. The removal rate in 24 h with both the UV radiation and air-sparging was 50% higher than that with only the UV radiation. Variations of the paraquat concentration at the UV intensities of 4 and 8 W/m^2 decreased slowly with time, but that at 12 W/m^2 decreased more rapidly. The removal efficiency at the air-sparging flow rate of 1 *l*/min increased as a UV light intensity increased. pH value in the reactor at the UV intensity of 12 W/m^2 decreased with time until 12 h and then increased with time over 12 h.

Key words: Suspended TiO_2, Photocatalyst, Paraquat, Hydrothermal Method, Immersion-Type Reactor

INTRODUCTION

With industrial advances, the chemical and bacteriological contamination of water streams has become an issue of a worldwide concern. Several treatment methods of waste water have been reported to remove toxic or volatile organic compounds which are xenobiotic [Valladares, 1995; Pozzo et al., 1997; Lindner et al., 1997; Choi et al., 2000; Molinari et al., 2000]. The decomposition of organic compounds such as residual pesticides in the environment using a titanium dioxide (TiO_2) as a photocatalyst has gathered much attention due to easy handling and its high efficiency [Tennakone and Kottegoda, 1996; Kuo and Lin, 2000].

The TiO_2/UV process has been known to have many advantages: in particular, a large number of organic compounds dissolved or dispersed in water can be mineralized; the photodegradation is relatively high if large surface areas of the photocatalyst are available; TiO_2 is inexpensive and can be recycled on a technical scale; UV lamps emitting in the spectral region required to initiate the photocatalytic oxidation are easily available in various sizes or shapes. Furthermore, surface modification of the photocatalyst to increase the UV light absorption efficiency as well as doping process of transition metal-ion to utilize the visible light like free sunlight instead of expensive UV light, have enhanced the commercial applications of photocatalyst to water purifications [Legrini et al., 1993]. Although the efficiency of the photo-process due to a hole-electron recombination can slightly be reduced, the doping of TiO_2 with transition metal ions makes the amount of adsorbed visible light enhanced, and the doping effect of the metal ions increases with the low field of light intensity.

The well-known principle of photo-oxidation is that UV illumination onto a photocatalyst excites to produce electron and hole pair (e^-/h^+) with high-energy state, which migrate to the particle surface and initiate a wide range of chemical redox reactions [Hoffmann et al., 1995]. The valence band potential (+2 eV) is positive enough to generate hydroxyl radicals at the surface and the conduction band potential (−0.2 eV) is sufficiently negative to reduce molecular oxygen. The hydroxyl radical is used as a powerful oxidizing agent to convert organic pollutants into CO_2 and less toxic by-products.

Paraquat dichloride has been extensively used as a herbicide and its residues in the environment have been a potential health hazard. There have been some reports that photodegradation of paraquat by using titanium dioxide in recent years. Tennakone and Kottegoda [1996] reported that 50 mg paraquat/*l* was decomposed in aqueous solutions, when in contact with TiO_2 affixed on a polymer film on irradiation for 6 h with a 400 W medium-pressure mercury lamp. It was found that paraquat could be mineralized to CO_2, NH_3, HCl and small quantities of NO_2^-/NO_3^- by solar or artificial irradiation of contaminated water in the presence of TiO_2-coated film.

Many studies related to the photodegradation using aqueous suspended TiO_2 particles have been performed recently [Ollis, 1985; Matthews, 1986; Matsunaga and Okochi, 1995; Martyanov and Savinov, 1997]. However, these many studies involve the problem to be yet resolved, namely, the exponential decrease of radiation availability due to the absorbance of UV radiation by particles themselves.

In this study, the effect of photo-oxidation parameters on the paraquat removal has been investigated in a photoreactor with suspended TiO_2 particles, where UV lamps were immersed at the regular spatial intervals to enhance the light availability and TiO_2 particles were prepared by a hydrothermal method to enhance their photoactivity.

EXPERIMENTAL

1. Materials

Paraquat dichloride(1-1'-dimethyl-4,4'bipyridinium dichloride, purity>99%, Aldrich Chem Co., USA) was used without further

†To whom correspondence should be addressed.
E-mail: bwkim@skku.ac.kr

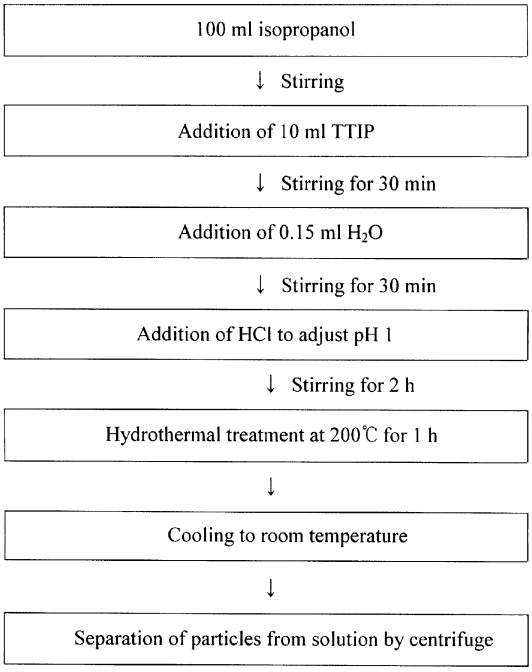

Fig. 1. Preparation procedure of TiO_2 by a hydrothermal method.

purification. The reactor wall made of polypropylene was used in the experiment because paraquat has self-attaching property on glass [Tennakone and Kottegoda, 1996].

TiO_2 as a photocatalyst was prepared by such a hydrothermal method as shown in Fig. 1 to increase the photoactivity [Lee et al., 2002; Cho et al., 2002].

Titanium-tetraisopropoxide (TTIP, 99.99%), ethyl alcohol, and isopropanol (Junsei Chemical Co Ltd., Japan) were used as the TiO_2 source and the solvent, respectively. Distilled water and hydrochloric acid (35%, Junsei Chemical Co Ltd., Japan) were used to induce the hydrolysis in the mixture. In the hydrothermal method, 10 ml TTIP was dissolved in 100 ml isopropanol and then 0.15 ml water and a few drops of about 1.0 ml of 9.6 N HCl were added. In fact, in order to synthesize the TiO_2 as a powder form, the stoichiometric amount of water needed is 2.5 ml for 10 ml TTIP. The mixture was heated up in an autoclave to 200 °C at a rate of 5 °C/min, and then the temperature was kept constant for 1 h. The TTIP was hydrolyzed with OH groups in the mixtures of water and isopropanol during the heat treatment at 20 atm. A very small amount of precipitate formed during the process, while it was almost invisible, was removed by centrifuge. The synthesized colloidal particles were used as a photocatalyst. The average diameter, the BET surface area, and the density of TiO_2 particles are 40±10 nm, 70±10 m^2/g, and 3.89 g/cm^3 at 20 °C, respectively. The crystal structure of prepared TiO_2 particles was shown to be the anatase type in a previous study [Lee et al., 2002].

2. Analysis

The photodegradation of the paraquat in the solution was determined colorimetrically at 600 nm by the dithionite method [Pope and Benner, 1974] using a UV spectrophotometer (UV-160A, Shimazu Co, Japan). Intermediate formation in the photo-reaction was analyzed by using an IC (Ion Chromatograph, Waters, Alltech Associates, Inc., Illinois, U.S.A.), a GC (Gas Chromatograph, M-600D, Younglin Co., Korea), and an LC-Mass Spectrometer (1100 series, Agilenp Co., California, U.S.A.). Ionized compounds in 5 ml samples from the reactor solution were measured at regular intervals. Gases produced during the photoreaction were analyzed by a GC, where a column of carboxen-1004 and helium as a carrier gas were used. The 5 ml gas, which was sampled by using an injector from a sealed photo-reactor, was analyzed according to the following procedures. The measurement with an HPLC was performed by using a 150×3.2 mm I.D. column filled with Nucleosil 100-3 C_{18} with the particle size of 3 μm.

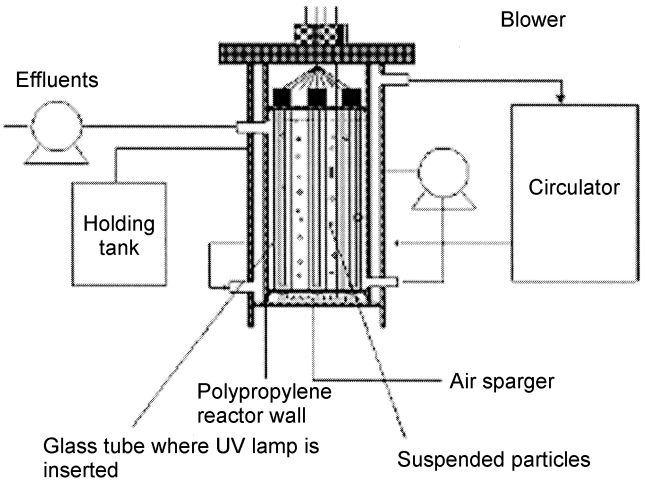

Fig. 2. Schematic diagram of a photoreactor with suspended TiO_2.

3. Methods

The experimental setup for the study is shown in Fig. 2, with a reactor volume of 1 liter. Experiments were performed in an immersion-type reactor equipped with an external water jacket to keep a constant temperature, and low-pressure mercury lamps of 6 W (Germicidal lamp; Shin-an Co., Korea) were used as the UV radiation source.

The energy spectrum of UV light was measured with a monochromator (404VM, Acton Research Co, MA, USA). The major peak wavelength occurs at 254 nm (in the UV-C), as in the usual anatase type of TiO_2 in various studies of photocatalytic decomposition [Mazzarino et al., 1999; Shiraishi et al., 1999], which has a stronger effect than that with UV-A lamps (λ: ~380 nm).

Air-sparging into the reactor was performed by a blower to supply oxygen for the enhancement of photooxidation. Air was dispersed at the flow rate of 1 *l*/min by using an air diffuser and the initial concentration of paraquat was 100 mg/*l*.

RESULTS AND DISCUSSION

1. Relationship of Photon Rate Dependent on the Number of Immersed UV Lamps

Light intensity of UV has been reported to be an important parameter affecting the photoactivity [Lindner et al., 1997; Martyanov and Savinov, 1997; Mazzarino et al., 1999]. The relationship of the photon rate with the number of inserted lamps is shown in Fig. 3.

The reactor was designed with nine pieces of lamp at the max-

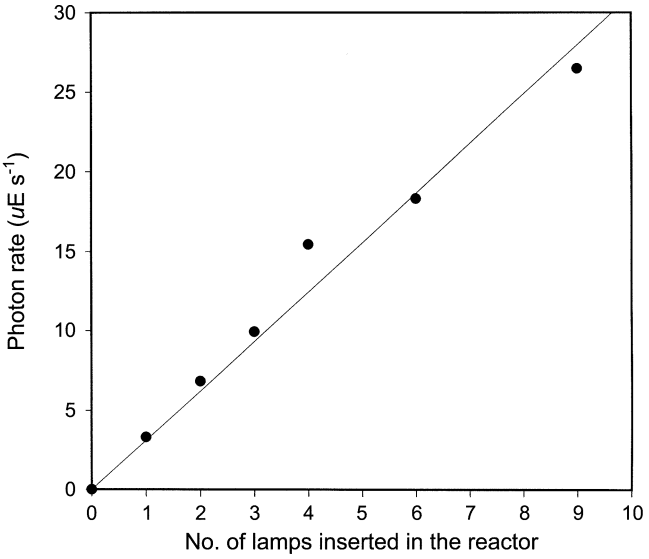

Fig. 3. Variation of photon rate with respect to the number of immersed lamps in the reactor.

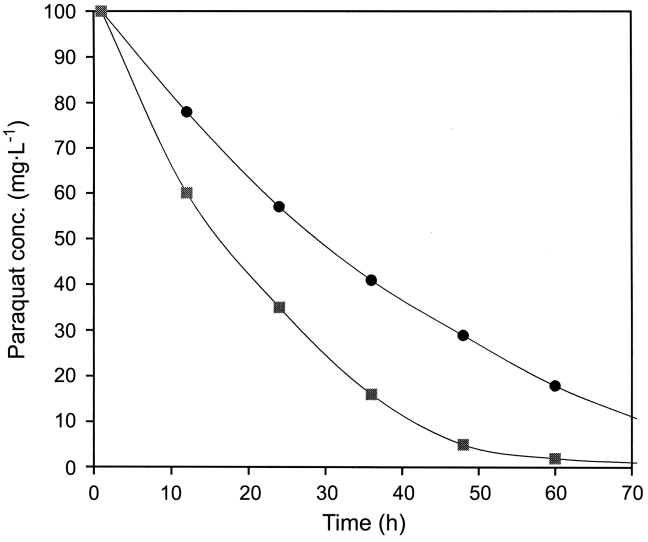

Fig. 5. Effect of the air-sparging on paraquat degradation in the absence of TiO_2 particles at UV light intensity of 36 W/m^2 (●: without air-sparging, ■: with air-sparging at 1 L/min).

imum. The photon rate of UV light was determined by an actinometry method using potassium ferrioxalate [Braum et al., 1991], where photon rate is calculated as the ratio of absorbed photons on the control surface during photocatalysis. The photon rate increased linearly as the number of the lamps increased from 1 to 9 pieces, where photon rates were 6.8, 15.5, 18.6, and 25.2 $\mu E \cdot s^{-1}$, respectively, where 2, 4, 6, and 9 lamps were inserted in the reactor.

2. Air-Stripping Effect on the Paraquat Removal in the Absence of UV Radiation

To investigate the effect of stripping due to the air-sparging, an experiment was performed with only air-sparging, without both the UV radiation and suspended TiO_2. The variation of paraquat concentration with time is shown in Fig. 4; the air-sparging into the reactor at the flow rate of 1 *l*/min was performed by a blower.

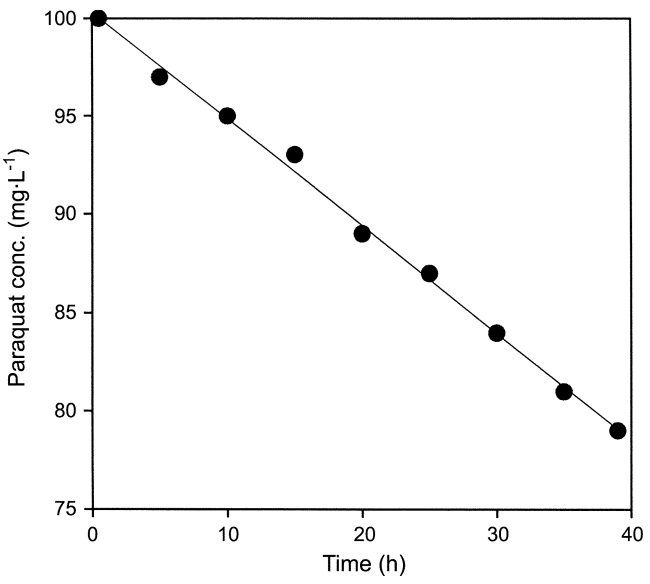

Fig. 4. Effect of the air-sparging (1 L/min) on paraquat degradation in the absence of both the UV radiation and TiO_2 particles.

The initial concentration of paraquat in the reactor was 100 mg/*l*. The paraquat concentration using the reactor with only air-sparging was 97, 93, and 70 mg/*l* in 5, 15, and 35 h, respectively. The concentration decreased linearly with time and the stripping rate was 0.54 mg/l/h, which was estimated as the amount of paraquat removed in unit volume per unit time. Complete removal of paraquat required about over 180 h in this manner.

3. Effect of Air Sparging on the Photodegradation of Paraquat in the Presence of UV Radiation

To investigate air sparging effect on the photodegradation of paraquat in the presence of the UV radiation, the experiment was conducted with/without air-sparging at the UV radiation intensity of 36 W/m^2 in the absence of TiO_2 particles. Fig. 5 shows the difference of the removal rates with the air-sparging and without the air-sparging, in the presence of the UV radiation in both cases.

Paraquat concentrations in the presence of only the UV radiation were 57, 41, and 10 mg/*l* in 24, 36, and 72 h, respectively. The concentrations with the air-sparging in the presence of the UV radiation were 35, 16, and 1 mg/*l* in 24, 36, and 72 h, respectively. The removal rate in the latter case was 50% higher in 24 h than that in the former case. The air-sparging effect on the paraquat removal in the photoreactor could have resulted from the oxygen increase.

4. Effect of UV-Light Intensity on the Photodegradation of Paraquat

The effect of UV-light intensity on the photodegradation in the presence of 0.1 g TiO_2/*l* was investigated by increasing the number of the UV lamps with the major peak wavelength at 254 nm in the absence of air-sparging (Fig. 6).

The initial concentration of paraquat in the reactor was 100 mg/*l*. The paraquat concentration at UV light intensities of 4 and 8 W/m^2 decreased slowly with time. However, the paraquat concentrations at the UV light intensity of 12 W/m^2 decreased rapidly as 38, 20, 12 mg paraquat/*l* in 16, 24, and 40 h, respectively. The removal rates

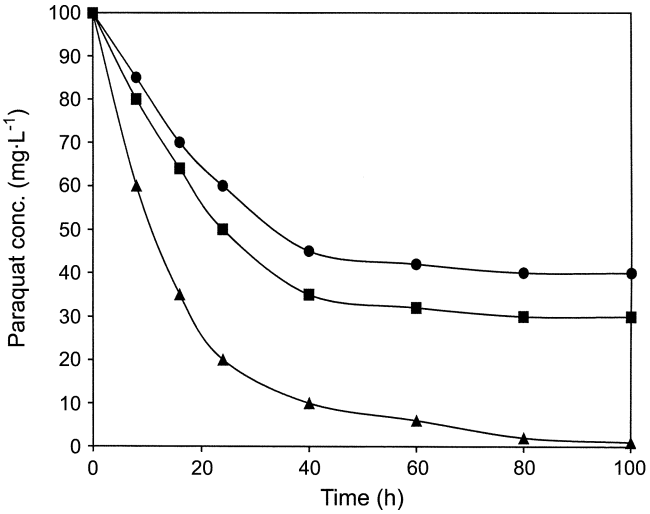

Fig. 6. Effect of UV-light intensity on paraquat degradation in the absence of the air-sparging with 0.1 g TiO_2/L (●: 4, ■: 8, and ▲: 12 W/m^2).

in 40 h were 1.4, 1.6, and 2.2 mg/*l*/h at the UV light intensities of 4, 8, and 12 W/m^2, respectively. If the reaction rate is an apparent first order, the rate constant (K) were 0.021, 0.026, and 0.053 h^{-1} at the UV light intensities of 4, 8, and 12 W/m^2, respectively.

5. Paraquat Removal and pH Variation with UV Light Intensity in the Presence of Air-Sparging

The variation of paraquat concentration with the UV light intensity in the presence of both air-sparging and TiO_2 particles is shown in Fig. 7.

The removal efficiency increased with UV-light intensity at air-sparging rate of 1 *l*/min and TiO_2 concentration of 0.1 g/*l*. The required times for 90% removal of paraquat were 18, 12, and 3 h at the UV light intensities of 12, 24, and 36 W/m^2, respectively.

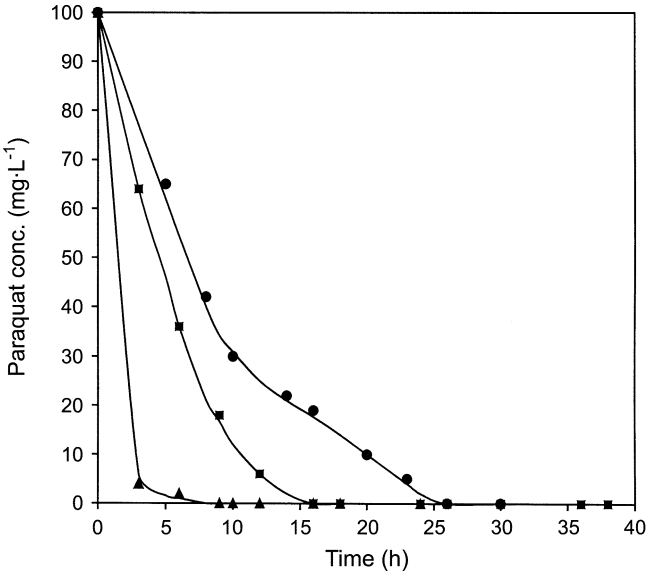

Fig. 7. Effect of UV-light intensity on paraquat degradation at 0.1 g TiO_2/*l* in the presence of the air-sparging (●: 12, ■: 24, and ▲: 36 W/m^2).

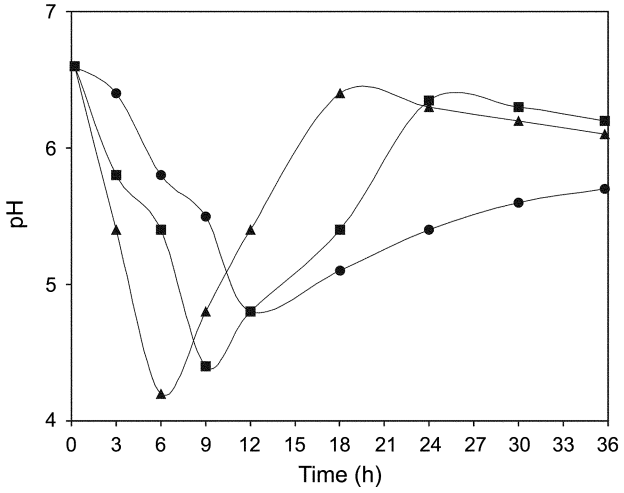

Fig. 8. pH variation with UV-light intensity at 0.1 g TiO_2/*l* in the presence of the air-sparging (●: 12, ■: 24, and ▲: 36 W/m^2).

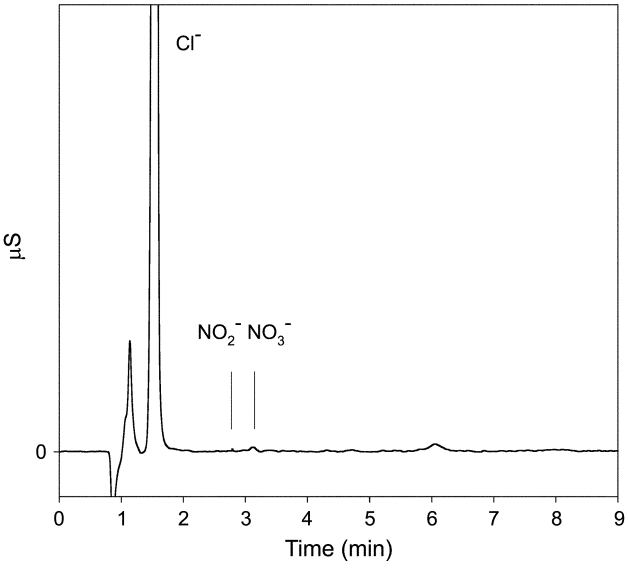

Fig. 9. Ion chromatogram of the by-products during the photodegradation of paraquat.

The pH value in the solutions varied during the paraquat photodegradation (Fig. 8). The time when a minimum pH value occurred was shortened as 12, 9, and 6 h as the UV-light intensity increased from 12, through 24, to 36 W/m^2.

By-products such as NO_3^-, NO_2^-, and HCl during the photodegradation of paraquat in 6 h were analyzed by an IC (Ion Chromatography) as shown in Fig. 9. The pH value decreased in the initial stage of the photodegradation due to the formation of acidic compounds (NO_3^-, NO_2^-, HCl); however, the pH value increased as a basic ammonium compound formed gradually. Tennakone and Kottgoda [1996] reported that by-products during the overall photooxidation of paraquat were as follows:

$$C_{12}H_{14}Cl_2N_2+nOH\cdot \rightarrow 12CO_2+(NH_4^+, NO_3^-, NO_2^-, HCl, H_2O) \quad (1)$$

Fig. 10 shows the production of the gases such as N_2, O_2, and

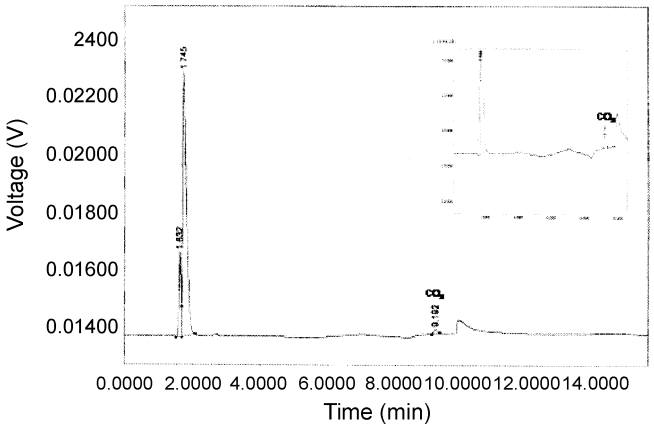

Fig. 10. Gas chromatogram of gases from the photodegradation of paraquat in the existence of both the UV radiation and TiO_2 particles.

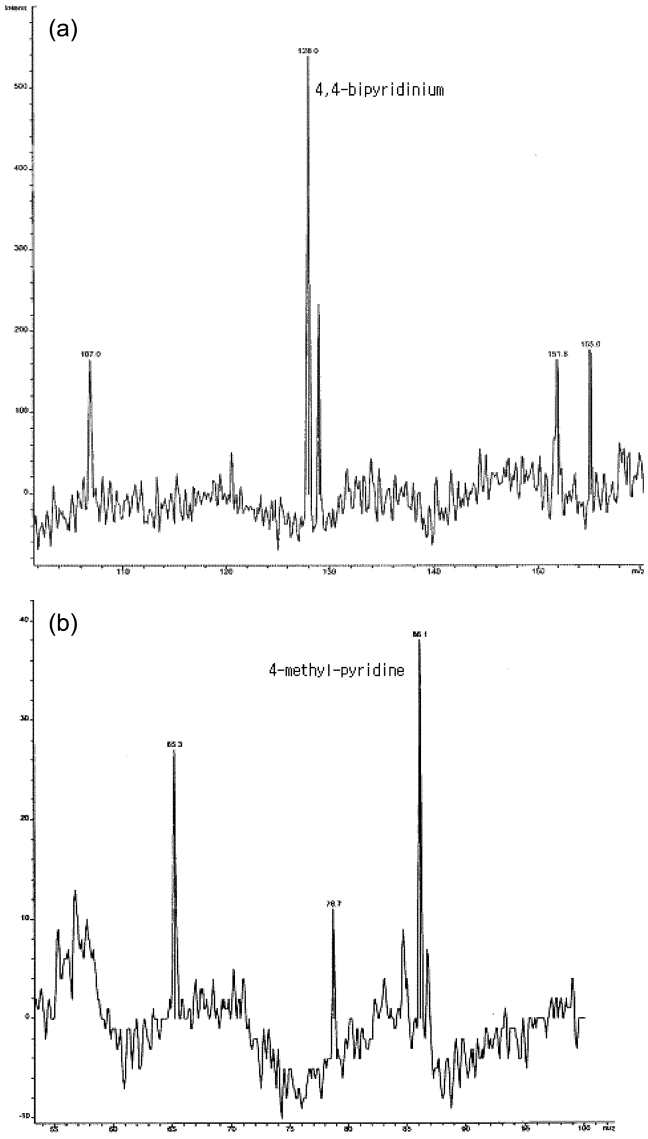

Fig. 11. Liquid chromatograms of derivative compounds formed during the paraquat photodegradation. (a) 4,4-bipyridinium and (b) 4-methyl-pyridine.

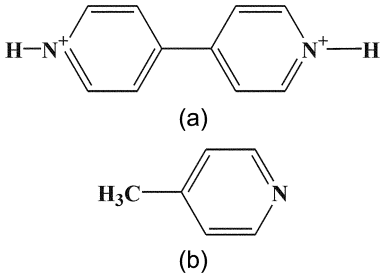

Fig. 12. Chemical structure of derivative compounds formed during the paraquat photodegradation (a) 4,4-bipyridinium and (b) 4-methyl-pyridine.

CO_2 corresponding with the chromatographic peaks at 1.587, 1.707, and 9.131 min. The total amount of CO_2 measured was larger than the stoichiometric amount reported by Tennakone and Kottegoda [1996], since other carbon sources in contaminated water were also photodegraded to CO_2.

Fig. 11 shows the derivative compounds formed during the photodegradation of paraquat in the reactor with TiO_2/UV, which were analyzed by the LC-MS (Liquid Chromatograph-Mass Spectrometer). Two kinds of compounds derived from the paraquat degradation in 1 h were identified as 4,4-bipyridinium(a) and 4-methyl-pyridine(b). Their structures are shown in Fig. 12, the molecular weights of which were 158 and 93.

The initial photocatalytic reaction rate with respect to initial organic concentration follows the Langmuir-Hinshelwood type of relationship, which is expressed as the following equation [Davis, 1994; Fernandez et al., 1995; Herrmann et al., 1997].

$$r_0 = kKC/(1+KC) \quad (2)$$

where k is the true reaction rate constant dependent on various parameters such as the mass of catalyst, the flux of efficient photons and the coverage in oxygen, K is the adsorption equilibrium constant, and C is the initial concentration of the target organic compound. The initial concentration of 100 mg paraquat/*l* decreased to 98 mg paraquat/*l* by a 48 h adsorption, namely, 2 mg paraquat/l was adsorbed in equilibrium at 0.1 g TiO_2/*l*, whose specific surface area is 70±10 m^2/g. The adsorption equilibrium constant (K) was estimated as 0.02, although paraquat is a strong adsorbent. The expression of Eq. (2) describes a first-order reaction at low substrate concentrations. Since the initial concentration is as low as 100 mg paraquat/*l*, the term KC in the denominator can be neglected with respect to unity, and then the reaction rate becomes an apparent first order [Fernandez et al., 1995].

$$r_0 = -dC/dt = kKC = K_a C \quad (3)$$

where K_a is the apparent rate constant of the pseudo-first order. The integral form of the rate equation is

$$\ln(C/C_o) = K_a t \quad (4)$$

The relationship between ln (C/C_o) and time (t) in the presence of the UV radiation and air-sparging is shown in Fig. 13. The slopes of the straight lines representative of apparent rate constant (K_a), are 0.007, 0.032, and 0.085/h with only air-sparging, only the UV radiation, and both the UV radiation and air-sparging, respectively.

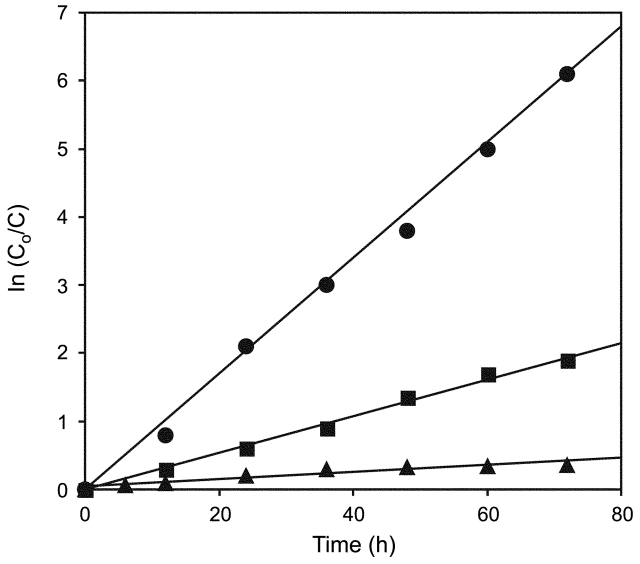

Fig. 13. Variation of paraquat concentration plotted in accordance with in the Langmuir-Hinshelwood kinetics in the existence of both the UV radiation and air-sparging (●: both the UV radiation and air-sparging, ■ : only UV radiation, and ▲ : only air-sparging).

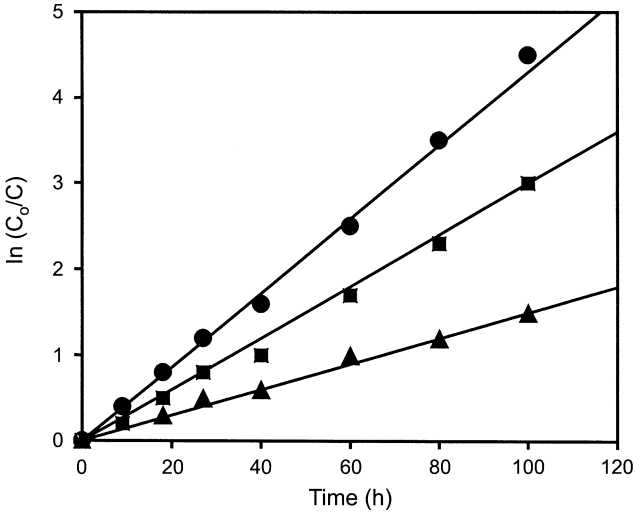

Fig. 14. Variation of paraquat concentration dependent with the number of inserted UV lamps plotted in the Langmuir-Hinshelwood kinetics (number of the inserted UV lamps; ▲ : 1, ■ : 2, and ●: 4).

The plot of $\ln(C/C_o)$ vs t was observed to be linear in three cases, and the air-sparging is one of important parameters to determine the degradation rate of paraquat [Chen et al., 1999; Wu et al., 2000; Boukas and Mantzouridou, 2001; Neves et al., 2001].

Fig. 14 shows the variation of paraquat concentration represented as the Langmuir-Hinshelwood model, which is dependent on the number of inserted UV-lamps. The apparent rate constant (K_a) increased as 0.016, 0.030, and 0.043/h as the number of inserted lamps in the reactor increased from 1, through 2, to 4 pieces.

CONCLUSIONS

Experiments were performed to investigate the parameters for the removal of paraquat dissolved in an immersion-type photoreactor with suspended TiO_2 particles, where they were prepared by a hydrothermal method. The required time for 90% removal of paraquat was 18, 12, and 2 h at the UV light intensities of 12, 24, and 36 W/m^2, respectively. The removal rates of paraquat in 0.1 g TiO_2/*l* at the UV intensity of 36 W/m^2 increased from 1.8 to 2.7 mg/*l*/h when the air-sparging flow rate of 1 *l*/min was given, while the removal rate was 0.54 mg/*l*/h in the reactor with only air-sparging.

The variation of paraquat concentration with time, dependent on the existence of UV radiation and air sparging, showed agreement with the Langmuir-Hinshelwood kinetics.

REFERENCES

Boukas, T. and Mantzouridou, F., "Effect of the Aeration Rate on Pullulan Production and Fermentation Broth Rheological Properties in an Airlift Reactor," *J. Chem. Technol. Biotechnol.*, **76**, 371 (2001).

Braun, S. S., Maurette, M. T. and Oliveros, E., "Photochemical Technology," John Wiley & Sons Inc., New York, U.S.A., 153 (1991).

Chen, J. Y., Wen, C. M. and Chen, T. L., "Effect of Oxygen Transfer on Lipase Production by Acinetobacter Radioresistens," *Biotechnol. Bioeng.*, **62**(3), 311 (1999).

Cho, Y. S., Seo, K. W., Ahn, Y. C. and Chung, Y. S., "Preparation of BaO-PbO-Nd_2O_3-TiO_2 Powders by Hydrothermal Synthesis," *Korean J. Chem. Eng.*, **19**(4), 688 (2002).

Choi, Y. S. and Kim, B. W., "Photocatalytic Disinfection of *E coli* in a UV/TiO_2-Immobilised Optical-Fiber Reactor," *J. Chem. Technol. Biotechnol.*, **75**, 1145 (2000).

Davis, A. P., "Photocatalytic Oxidation of Organic Contaminants in Process Engineering for Pollution Control and Waste Minimization," Marcel Dekker Inc., New York, U.S.A., 377 (1994).

Fernandez, A., Lassaletta, G., Jimenez, V. M., Justo, A., Gonzalez-Elipe, A. R., Hermann, J. M. and Tahiri, H., "Preparation and Characterization of TiO_2 Photocatalysts Supported on Various Rigid Supports (Glass, Quartz and Stainless Steel): Comparative Studies of Photocatalytic Activity in Water Purification," *Appl. Catal.*, **B 7**, 49 (1995).

Herrmann, J. M., Tahiri, H., Ait-Ichou, Y., Lassaletta, G., Gonzalez-Elipe, A. R. and Fernanez, A., "Characterization and Photocatalytic Activity in Aqueous Medium of TiO_2 and Ag-TiO_2 Coating on Quartz," *Appl. Catal.*, **B 13**, 219 (1997).

Hoffmann, H. R., Martin, S. T., Choi, W. and Bahnemann, D. W., "Environmental Applications of Semiconductor Photocatalysis," *Chem. Rev.*, **95**, 69 (1995).

Kuo, W. S. and Lin, Y. T., "Photocatalytic Oxidation of Xenobiotics in Water with Immobilized TiO_2 on Agitator," *J. Environ. Sci. Health*, **B 35**(1), 61 (2000).

Lee, J. C., Kim, M. S. and Kim, B. W., "Removal of Paraquat Dissolved in a Photoreactor with TiO_2 Immobilized on the Glass-Tube of UV Lamps," *Wat. Res.*, **36**, 1776 (2002).

Legrini, O., Oliveros, E. and Braun, A. M., "Photochemical Processes for Water Treatment," *Chem. Rev.*, **93**, 671 (1993).

Lindner, M., Theurich, J. and Bahnemann, D. W., "Photocatalytic Degradation of Organic Compounds: Accelerating the Process Efficiency," *Wat. Sci. Technol.*, **35**(4), 79 (1997).

Martyanov, N. and Savinov, E. N., "Mineralization of Organic Compounds in Photochemical and Photocatalytic Systems: Comparative

Analysis for the Example of Methylviologen Photooxidation," *Catal. Today*, **39**, 197 (1997).

Matsunaga, T. and Okochi, M., "TiO_2-mediated Photochemical Disinfection of *Escherichia coli* Using Optical Fibers," *Environ. Sci. Technol.*, **29**, 501 (1995).

Matthews, R. W., "Photo-Oxidation of Organic Material in Aqueous Suspensions of Titanium Dioxide," *Water. Res*., **20**, 569 (1986).

Mazzarino, I., Piccinini, P. and Spinelli, L., "Degradation of Organic Pollutants in Water by Photochemical Reactors," *Catal. Today*, **48**, 315 (1999).

Molinari, R., Mungari, M., Drioli, E., Paola, A. D. and Loddo, V., "Study on a Photocatalytic Membrane Reactor for Water Purification," *Catal. Today*, **55**, 71 (2000).

Neves, J. M., Teixeira, J. A., Simoes, N. and Mota, M., "Effect of Airflow Rate on Yields of Steinernema Carpocapse Az 20 in Liquid Culture in an External-Loop Airlift Bioreactor," *Biotechnol. Bioeng*., **72**(3), 369 (2001).

Ollis, D. F., "Contaminant Degradation in Water," *Environ. Sci. Technol.*, **19**, 480 (1985).

Pope, J. D. and Benner, J. E., "Colorimetric Determination of Paraquat Residues in Soil and Water," *J. AOAC*, **57**(1), 202 (1974).

Pozzo, R. L., Baltanas, M. A. and Cassano, A. E., "Supported Titanium Dioxide as Photocatalyst in Water Decontamination: State of the Art," *Catal. Today*, **39**, 219 (1997).

Shiraishi, F., Toyoda, K. and Fukinbara, S., "Photolytic and Photocatalytic Treatment of an Aqueous Solution Containing Microbial Cells and Organic Compounds in an Annular-Flow Reactor," *Chem. Eng. Sc*., **54**, 1547 (1999).

Tennakone, K. I. and Kottegoda, R. M., "Photocatalytic Mineralization of Paraquat Dissolved in Water of TiO_2 Supported on Polythene and Polypropylene Films," *J. Photochem. Photobiol*., **A 93**, 79 (1996).

Valladares, J. E., "A New Photocatalytic Reactor for the Photodegradation of Organic Contaminants in Water," Ph.D. Thesis, Western Ontario University, Canada (1995).

Wu, Z. L., Yuan, Y. J., Xing, Y. and Hu, Z. D., "Study on Volumetric Oxygen Transfer Coefficient of the Simulated Plant Cell Two-Phase Culture System," *Chem. Eng. Technol*., **23**(12), 1111 (2000).