

Photocatalytic degradation of pentachlorophenol in aqueous solution employing immobilized TiO₂ supported on titanium metal

Jarnuzi Gunlazuardi^{a,*}, Winarti Andayani Lindu^b

^a Department of Chemistry, University of Indonesia, Kampus Baru UI-Depok 16424, Indonesia

^b Center for Research and Development of Isotopes and Radiation Technologies, National Nuclear Energy Agency, Jakarta, Indonesia

Received 19 September 2003; received in revised form 23 December 2004; accepted 5 January 2005

Available online 30 January 2005

Abstract

A study on photocatalytic degradation of pentachlorophenol (PCP) in aqueous solution employing immobilized TiO₂ on titanium metal has been conducted. TiO₂ film was prepared via a deep coating in a sol–gel system of titanium (IV) bis (ethyl acetoacetato)-diisopropoxide precursor, followed by calcinations at 525 °C. Two catalysts sheets (5 cm × 5 cm, each) were put in a batch reactor containing 10 ppm PCP and irradiated by a UV black light. The occurrence of PCP degradation was indicated by decrease in pH, increase of conductivity, and formation of chloride ion. Moreover, the UV spectra observation indicate that the degradation of PCP solely by UV light (photolysis) was observed due to in part dechlorination of PCP molecules, while aromatic moiety remained. The aromatic intermediate could be further degraded in the presence of TiO₂ and UV light (photocatalysis). The determination of intermediate degradation products by HPLC revealed that oxalic acid was detected consistently.

© 2005 Elsevier B.V. All rights reserved.

Keywords: PCP; Immobilized TiO₂; Photocatalytic degradation; Aromatic moiety; Chloride ion

1. Introduction

Pentachlorophenol, PCP, has been extensively used for wood preservation and biocide. This compound is carcinogenic and toxic to plants, animals, and human even at low concentrations [1]. PCP is also known as an environmental precursor for the formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), which are more harmful [2].

Recent studies indicate that advance oxidation processes such as sonication, ionising radiation, combination of UV and ozone or hydrogen peroxide are able to destroy environmentally persistent pollutants, due to their ability to generate the highly oxidizing species, •OH radical. Interestingly, •OH radical is also generated at the surface of TiO₂ when being irradiated with UV light [3–8].

Titanium dioxide (TiO₂) when being irradiated with light of wavelength (λ) \leq 415 nm produce excited-state electron and hole pairs, which are able to initiate various chemical reactions. Titanium dioxide as photocatalyst has been proposed to solve various environmental problems. It has been shown to be useful for elimination of microorganisms such as bacteria and viruses, for odour control, and degrading organic pollutants such as pesticides and phenol [9–13]. The degradation of PCP under UV light employing TiO₂ slurry to mineralize PCP producing formic and acetic acid as intermediate compounds has been examined successfully [14]. The use of slurry catalysts, however, creates a great technical problem in retrieving the catalyst from the treated water. In response to the retrieving problem many researchers have introduced an immobilized catalyst. In this paper, we report our investigation of photocatalytic degradation of PCP in aqueous solution using TiO₂ immobilized on titanium metal and under black light irradiation in a batch system.

* Corresponding author. Tel.: +62 217270027; fax: +62 217270012.
E-mail address: jarnuzi@makara.cso.ui.ac.id (J. Gunlazuardi).

2. Material and methods

2.1. Materials

TiO₂ catalyst was prepared by calcinations of sol-gel film produced from titanium (IV) bis (ethyl acetoacetato)-diisopropoxide (TAA) precursor at 525 °C. Based on X-ray diffraction data, the crystal structures was determined and predominantly was found to be in the anatase form. Scanning electron microscopy data revealed that the thickness of the film was 24.7 μm, and seem to be porous. The TAA and pentachlorophenol (PCP) 86% were purchased from Aldrich. The PCP was used after purification. Other chemicals such as ethanol, isopropyl alcohol, acetonitrile, petroleum benzene (60–80 °C), acetone, phosphoric acid, nitric acid, and oxalic acid were obtained from Merck, methanol and acetonitrile were HPLC grade.

2.2. Photocatalytic reactor

Photocatalytic reactor was constructed from a Pyrex vessel (25 cm × 11 cm × 7 cm), and two catalysts sheets (5 cm × 5 cm), were placed in it. Two of 10 W UV black light lamps (TOKI, Japan), were positioned 8 cm above Pyrex vessel (Fig. 1). The intensity of UV light was measured by UV ray radiometer. At the initial experiment the intensity were 1.9, 2.3 and 1.9 mW/cm² at the left, centre and right of reactor respectively and at the last experiment the intensity were 1.4, 1.8 and 1.5 mW/cm² at the left, centre and right of reactor respectively.

2.3. Chemical analysis

Determination of PCP residue was performed by HPLC, Shimadzu model LC-9A equipped with UV detector at 215 nm, and C-18 phenomenex column. The mobile phase was 90% methanol in phosphate buffer (pH 3.4) with the flow rate 1 mL/min. On the other hand, intermediate organic acids were determined by same instrument, but the UV detector was set at 210 nm, applying shodex KC-811 column,

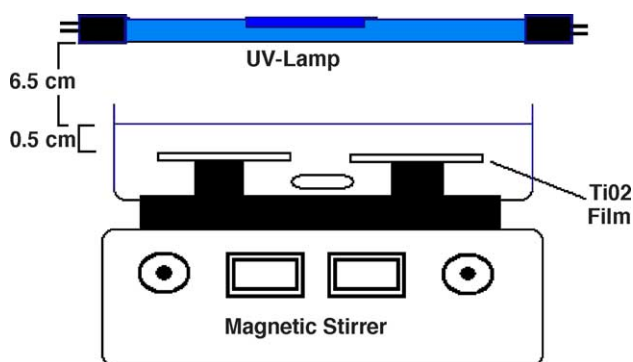


Fig. 1. Schematic of the photocatalytic reactor, comprised of a 2 × 10 W black light UV lamp (Toki, Japan), a Pyrex glass vessel equipped with magnetic bar and two catalyst sheets, and a magnetic stirrer.

and 0.005% phosphoric acids as the mobile phase with the flow rate were 1 mL/min.

The UV spectra of PCP solutions before and after irradiation were measured on Hewlett Packard Model 8453 Diode Array Spectrophotometer. Chloride ion concentrations were monitored by ferric thiocyanate methods, which was measured by UV-vis Spectrophotometer at 460 nm. Digital pH meter and conductometer were used to measure the pH and conductivity of the solution.

2.4. Methods of irradiation

Irradiation of 10 ppm PCP in aqueous solution were conducted at pH 6 for 15 min, 30 min, 1, 2, 4, 6, 8, 10, 13, and 16 h. During irradiation the solution of PCP was homogenized with magnetic stirrer.

3. Results and discussions

3.1. The pH, conductivity, and chloride ion concentration of the treated water

It is widely accepted that photocatalytic oxidation of organic compounds may produce carbon dioxide, mineral acid, and water. It can be inferred that pH will decrease during the course of reaction while chloride ion will evolve. It is apparent that before complete mineralization occurs, some intermediate may be produced.

The change of pH and conductivity during the photocatalytic of PCP in aqueous solution are displayed in Figs. 2 and 3. Fig. 2 shows that under the dark experiment, pH and conductivity of the solution was not changed during 16 h observation, even in the presence of TiO₂. When UV black light without TiO₂ is applied, the pH of the solution was decreased as the irradiation time increased, due to photolysis.

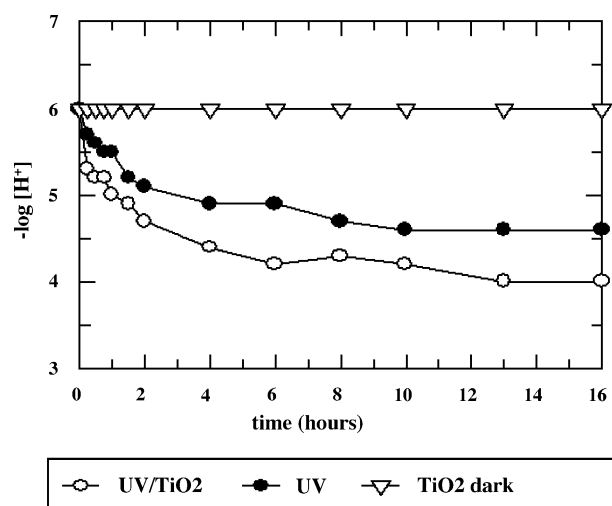


Fig. 2. The change in pH value during the photocatalysis, photolysis, and control experiment of 10 ppm pentachlorophenol.

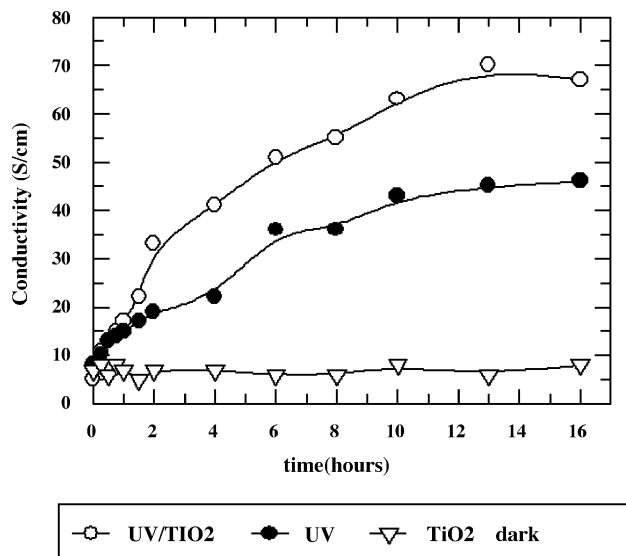


Fig. 3. The change in conductivity during photocatalysis, photolysis, and control experiment of 10 ppm pentachlorophenol.

The decrease of pH was much faster when immobilized TiO₂ on titanium metal was placed in the solution and UV black light was turned on, due to photocatalysis.

Fig. 3 shows that conductivity of the solution was increased when UV light was exposed to the solution. The increase of conductivity was much faster when UV light was applied in the presence of TiO₂. Apparently photolysis may cause a dechlorination process, which produce proton and chloride ion. Moreover, under the photocatalysis the dechlorination was much enhanced followed by breaking down the aromatic moiety.

The confirmation of chloride evolution was illustrated in Fig. 4, whereas under control experiments (in the dark) no chloride ion in the solution was observed. During long irradiation periods (16 h irradiation), under solely UV irradiation,

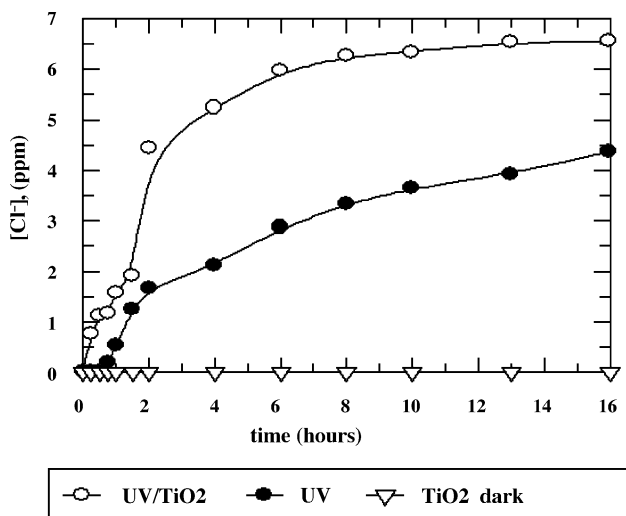


Fig. 4. Chloride ion evolution during photocatalysis, photolysis, and control experiment of 10 ppm pentachlorophenol.

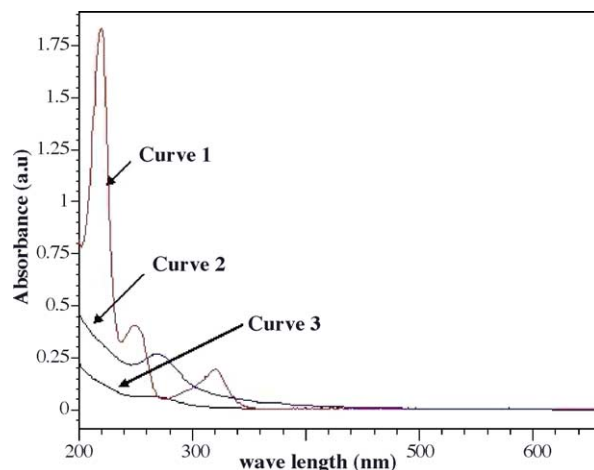


Fig. 5. The UV-vis spectra of PCP solution (10 ppm, initial pH=6) after 16 h experiments (curve 1=PCP unirradiated, curve 2=PCP irradiated by UV but without TiO₂, curve 3=PCP irradiated by UV in the presence of TiO₂).

dechlorination of apparently three atomic chlorine were observed, most probably due to direct photolysis. While in the presence of TiO₂ film and UV light, the dechlorination of PCP molecules were faster than direct photolysis. It seems that the photocatalytic degradation lead to complete dechlorination after 8 h irradiation.

3.2. UV spectra profile of aqueous PCP during treatments

The UV spectra profiles of PCP solution are displayed in Fig. 5. Initial PCP solution shows three absorbance bands at 220, 250 and 320 nm (curve 1). After 16 h irradiation of PCP solely by UV (photolysis) showed a new absorbance band at 270 nm (curve 2). When the solution was being irradiated in the presence of TiO₂ film, all the absorbance bands were almost completely disappear (curve 3). More detail observation of the absorbance bands were presented in Fig. 6, which shows plots of absorbance at different wavelength versus irradiation time. Upon UV irradiation, the absorbance of 220, 250 and 320 nm gradually decreased with increase in irradiation time. The PCP solution which was irradiated by UV in the absence of TiO₂ catalyst (photolysis) showed absorbance peak at 270 nm which increased gradually in line with irradiation time and no more change in absorbance after irradiated for more than 4 h. A different profile was observed at the PCP solution, when it was irradiated by UV in the presence of TiO₂ catalyst (photocatalysis). In the photocatalysis, at early irradiation time, the absorbance of 270 nm did increase and reach maximum at 4 h but then decreased and disappeared after 13 h. It can be inferred that the transformation of PCP solely by UV light (photolysis) was observed due to dechlorination and/or modification of PCP molecules, while the aromatic ring were remained. The aromatic intermediate could be further degraded in the presence of TiO₂ and UV light (photocatalysis).

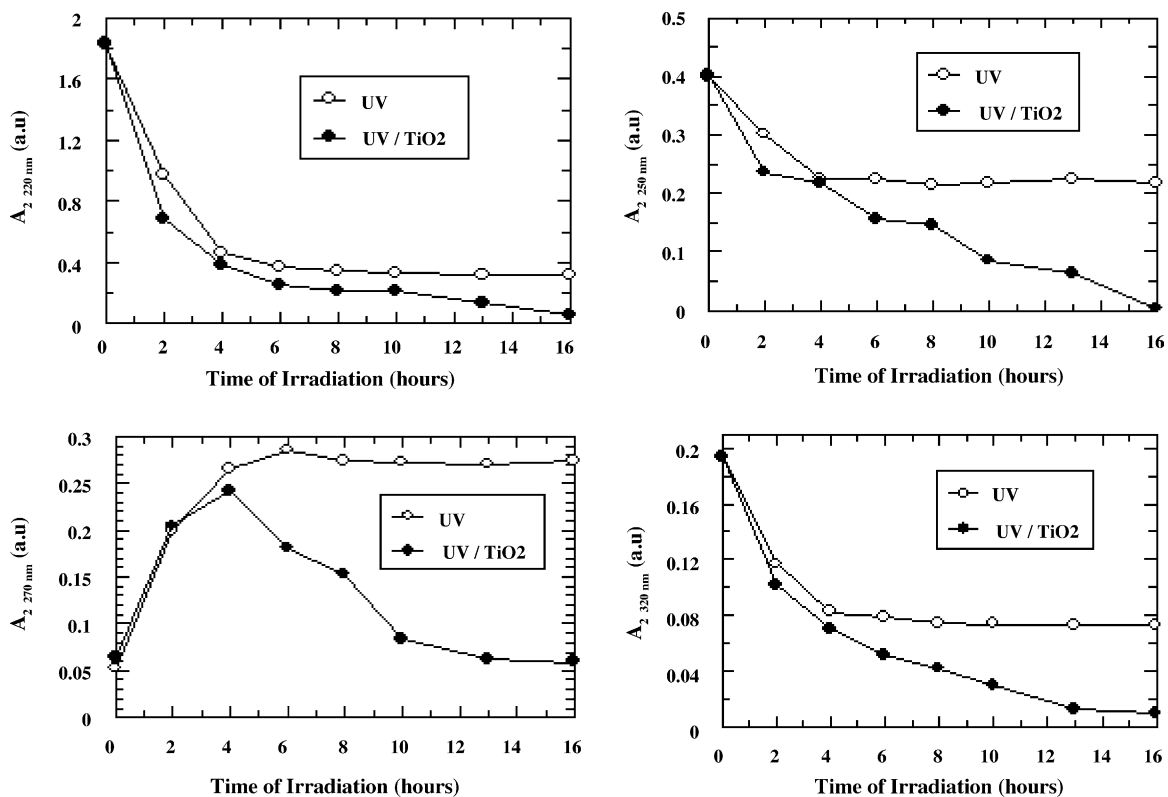


Fig. 6. The absorbance values, at different wavelength, of aqueous PCP during irradiation vs. irradiation time.

3.3. Degradation products

3.3.1. Degradation products of photolysis

Fig. 7 shows plots of the decay of PCP without the application of TiO_2 , the evolution of chloride ion and aromatic intermediate. Irradiation of solution containing 10 ppm PCP at pH 6, by solely UV light, resulted a rapid initial decrease in the concentration of PCP. Although significant levels of chloride ion were formed but aromatic intermediates were remained and no oxalic acid was detected. In the direct photolysis, photon energy of the UV light may promote the non-bonding electron either of oxygen or chlorine origin and lead

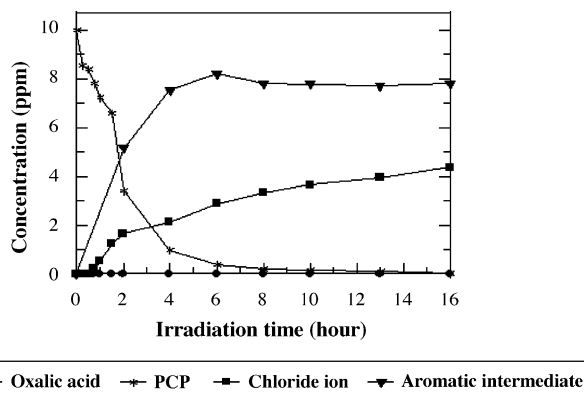


Fig. 7. Time course of the decay of PCP and formation of intermediate compound during photolysis.

to an alteration of its chemical bonding with carbon atom in the aromatic ring. The bonding alteration may cause chemical reaction that convert PCP to other molecules. As a result the PCP concentration dropped rapidly and at the same time the evolution of chloride ion and aromatic intermediate were observed. This might indicate that the photolysis was partially able to facilitate a detachment of the chlorine atoms, most probably three of the five in the PCP, but not powerful enough to break down the aromatic ring or further oxidation to a simple molecule. Therefore, no oxalic acid was detected during this experimental condition.

3.3.2. Degradation products of photocatalysis employing TiO_2 film catalyst

Fig. 8 shows the time course of PCP decay and evolution of its intermediate compounds. Compared to the photolysis, in the presence of TiO_2 or photocatalysis, the concentration of PCP was more sharply decreased and more significant levels of chloride ions are generated. At the initial irradiation time, the aromatic intermediate are generated, but later on the concentration of aromatic intermediate in the solution decreased gradually and disappeared after irradiation more than 10 h. The measurement of degradation products by HPLC revealed that oxalic acid was detected consistently. It seemed that complete mineralization of PCP was observed after irradiation for 16 h.

It is well understood that hydroxyl radical is generated upon proper photon illumination to TiO_2 photocata-

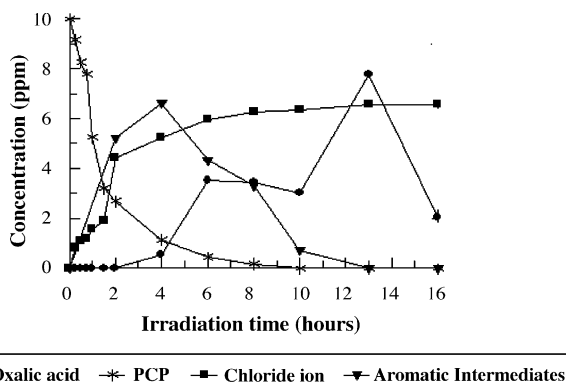


Fig. 8. Time course of PCP decay and formation of intermediate compound during photocatalysis on TiO₂ film.

lyst. The hydroxyl radical is a powerful oxidizing species, having potential oxidation of approximately 2.8 volt (versus NHE), which may lead to complete mineralization. Mills and Wang [15] reported that $\bullet\text{OH}$ attacks the phenyl ring in 4-chlorophenol to produce intermediates such as 4-chlorocatechol, benzoquinone, and hydroquinone, prior to complete degradation. While, Theurich et al. [14] reported that further oxidation of the mentioned intermediates produce more simple intermediates, likely aliphatic compounds, before complete mineralization to end products of carbon dioxide, water and mineral acid. Their reports very much concur to our observation during photocatalysis treatment. In essence, during the course, there was an aromatic intermediate evolution, which in turn disappears to give oxalic acid. In general, the attack of $\bullet\text{OH}$ radical to PCP may replace chlorine atoms, producing more hydroxyl functional groups that can be oxidized to aldehyde and/or further oxidation to open up the aromatic ring. The opening up of the aromatic ring may produce organic dicarboxylic acids, such as oxalic acid, before complete mineralization.

4. Conclusion

The degradation of pentachlorophenol solely by UV light (photolysis) was observed due to dechlorination of pentachlorophenol molecules, and aromatic intermediate remained. The aromatic intermediate could be further degraded

in the presence of TiO₂ (anatase) supported on titanium and UV light (photocatalysis). Both in photolysis and photocatalysis the dechlorination event were evidenced. The complete mineralization of PCP was observed after 16 h irradiation.

References

- [1] W.J. Hayes, E.R. Laws, Handbook of Pesticide Toxicology, Classes of Pesticides, vol. 3, Academic Press, 1991, pp. 1206–1216.
- [2] M.E. Harnly, M.E. Petreas, J. Flattery, L.R. Goldman, Polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran contamination in soil and home-produced chicken eggs near pentachlorophenol sources, Environ. Sci. Technol. 34 (2000) 1143–1149.
- [3] L.K. Weavers, N. Malmstadt, M.R. Hoffmann, Kinetics and mechanism of pentachlorophenol degradation by sonication, ozonation, and sonolytic ozonation, Environ. Sci. Technol. 34 (2000) 1280–1285.
- [4] J. Wu, F. Xingwang, H. Yongke, L. Jun, Oxidative decomposition of pentachlorophenol in aqueous solution, Rad. Phys. Chem. 54 (4) (1998) 411–415.
- [5] N. Getoff, Radiation-induced degradation of water pollutants-state of art, Rad. Phys. Chem. 47 (4) (1996) 581–593.
- [6] G. Ruppert, R. Bauer, UV-O₃, UV-H₂O₂, UV-TiO₂ and the photofenton reaction comparison of advanced oxidation processes for waste water treatment, Chemosphere 28 (8) (1994) 1447–1454.
- [7] A.L. Linsebigler, L. Guangquan, J.T. Yates Jr, Photocatalysis on TiO₂ surfaces: principles, mechanism, and selected results, Chem. Rev. 95 (1995) 735–758.
- [8] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental application of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.
- [9] A. Fujishima, K. Hashimoto, T. Watanabe, TiO₂ Photocatalysis Fundamentals and Applications, BKC, Inc., Japan, 1999.
- [10] K. Sunada, Y. Kikuchi, K. Hashimoto, A. Fujishima, Bactericidal and detoxification effects of TiO₂ thin film photocatalysts, Environ. Sci. Technol. 32 (5) (1998) 726–728.
- [11] A. Topalov, D.M. Gabor, J. Csanadi, Photocatalytic oxidation of the fungicide metalaxyl dissolved in water over TiO₂, Wat. Res. 6 (1999) 1371–1376.
- [12] E. Pramauro, A.B. Prevot, M. Vincenti, G. Brizzolesi, Photocatalytic degradation of carbaryl in aqueous solutions containing TiO₂ suspensions, Environ. Sci. Technol. 31 (1997) 3126–3131.
- [13] G. Mills, R. Hoffmann, Photocatalytic degradation of pentachlorophenol on TiO₂ particles: identification of intermediates and mechanism of reaction, Environ. Sci. Technol. 27 (1993) 1681–1689.
- [14] J. Theurich, M. Lindner, D.W. Bahnemann, Photocatalytic degradation of 4-chlorophenol in aerated aqueous titanium dioxide suspensions: a kinetic and mechanistic study, Langmuir 12 (1996) 6368–6376.
- [15] A. Mills, J. Wang, Photomineralisation of 4-chlorophenol by TiO₂ thin films, J. Photochem. Photobiol. A: Chem. 118 (1998) 53–63.