

Effect of pH, charge separation and oxygen concentration in photoelectrocatalytic systems: active chlorine production and chlorate formation

Huseyin Selcuk^{a*}, Marc A. Anderson^b

^a*Environmental Engineering Department, Engineering Faculty, Pamukkale University, Kinikli, Denizli, Turkey
Tel. +90 (536) 666-4552; email: selcukh@pamukkale.edu.tr*

^b*Environmental Chemistry and Technology Program, University of Wisconsin-Madison,
660 N. Park Street, Madison, WI 53706, USA; email: nanopor@facstaff.wisc.edu*

Received 14 October 2004; accepted 25 October 2004

Abstract

In this study, photoanodic chlorine generation and chlorate formation were investigated using a nanoporous TiO₂ photo-electrode under an illumination intensity of 7.4 mW/cm² UV and biased at +1.0 V vs. SCE. Chlorine formation increased over time finally reaching a steady-state concentration of 42 mg/l in 45 min. On the other hand, chlorate formation was observed after only 5 min irradiation and increased over time. The effect of pH, oxygen concentration and charge separation on chlorine generation and chlorate formation was also investigated. Chlorine production was practically constant over a pH range of 4.0–8.0, but decreased slightly at higher pH values. Chlorate production could be detected at pH values ≥ 7.0 . A significant effect of oxygen concentration on chlorate formation was observed. Chlorate was significantly reduced under nitrogen gas. Chlorine production in the separated photoanode compartment was about 10 fold higher than that in a combined photoanode–cathode system.

Keywords: Chlorine production; Chlorate formation; Photoanode; Photoelectrocatalytic treatment; Titanium dioxide

*Corresponding author.

Presented at the Seminar in Environmental Science and Technology: Evaluation of Alternative Water Treatment Systems for Obtaining Safe Water. Organized by the University of Salerno with support of NATO Science Programme. September 27, 2004, Fisciano (SA), Italy.

1. Introduction

Photocatalysis is a promising advanced oxidation technology for the treatment of waters. Among many catalysts, titanium dioxide (TiO_2) is the most widely used photocatalyst in drinking water due to its stability in aqueous solution and its ability to oxidize many organics to CO_2 [1–4] as well as eliminate microorganisms in water [5]. The oxidation mechanism of the TiO_2 photocatalytic process is based on the formation of the photo-excited electrons and holes that are created when TiO_2 is illuminated with light having greater than band-gap energy. The electron and hole pairs that are generated take part in the oxidation and reduction reactions respectively (Fig. 1).

Many studies have attempted to improve this photocatalytic treatment process [6–8]. One of the most promising mechanisms for improvement has been the separation of the electron and hole thereby reducing charge recombination, and allowing these active species to take part in subsequent redox reactions at the surface of the catalyst [9,10]. In 1972, Fujishima and Honda were the first scientists to employ the separation of charge technique. Subsequent studies using TiO_2 coated electrodes under a biasing potential have been referred to as photoelectrocatalytic (PEC) processes. It has been generally found that

by applying an external potential one increases the efficiency of TiO_2 by decreasing the recombination rate of the electron and hole [11]. Subsequently, some researchers applied PEC process for the treatment and disinfection of water and they reported higher efficiencies that would otherwise be accomplished using the standard TiO_2 /UV process [12–15]. Later developments have made it easier to separate electrons and holes reactions in PEC systems (Fig. 2) [16,17]. By separating the photoanodic compartment from the cathode one can easily determine which reactions take place on the photoanode vs. the photocathode. In our case here, chloride oxidation yielding chlorine species takes place in the photoanode compartment [18].

Chlorination is still the most widely employed and economical method for the disinfection of cooling, swimming pool and drinking waters. However, the formation of disinfection by-products represents an undesirable side of this disinfection process [19–21]. In this study, we measure the formation of chlorate in the photoanode compartment during the photoelectrocatalytic (PEC) production of chlorine. The PEC system was also used to evaluate the effect of pH, oxygen concentration and charge separation on the chlorine generation and chlorate formation.

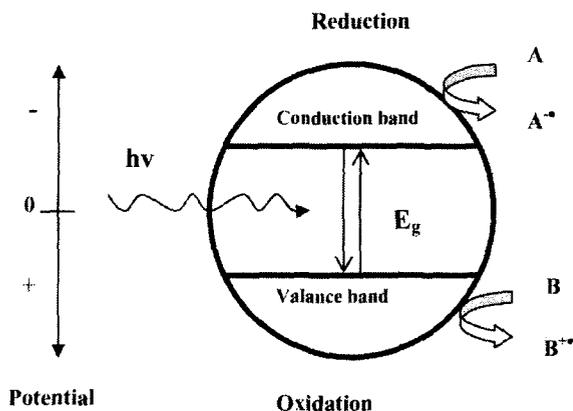


Fig. 1. Oxidation and reduction in the photocatalytic process (A, reducible and B, oxidizable species).

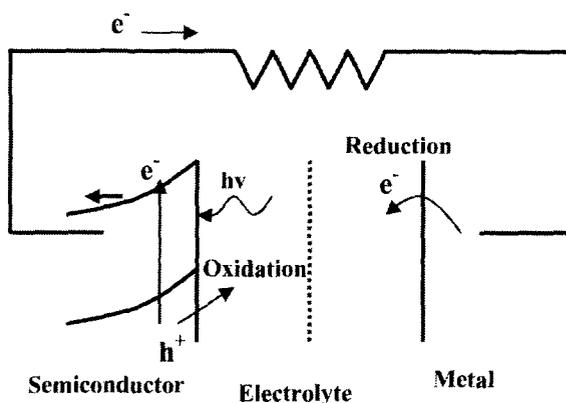


Fig. 2. Charge separation in the PEC system.

2. Materials and methods

2.1. Photoelectrodes

Titanium (IV) isopropoxide (Aldrich, Wisconsin, USA) was used as a precursor for preparing TiO_2 colloidal suspensions. Previous experimental procedures were used for the preparation and dialyzing of suspension, immobilization of TiO_2 and coating of TiO_2 photoelectrodes [22].

2.2. PEC experiments

PEC experiments were conducted in a two-compartment reactor isolated by a Nafion 117 membrane (Fig. 3). A Princeton Applied Research (PAR) potentiostat, model 6310 was used to bias the TiO_2 photoanode against perforated platinum foil used as counter electrode and a saturated calomel electrode (SCE) as a reference. 1 V vs. SCE applied potential which was previously found to be optimum potential in the PEC system [15,16,

22], was used in all PEC experiments. All experiments were carried out utilizing 100 ml test solutions in each compartment and the experiments were conducted at room temperature ($20 \pm 2^\circ\text{C}$). The photoactive area of the photoanode was 20 cm^2 and was illuminated by a 450W Xe-Hg arc lamp Oriel, model 6262 UV light source with wavelength range of 300–388. The light intensity on electrode surface was 7.3 mW/cm^2 as measured with an IL 1400A model International Light Inc. Photometer. The pH of the solution was measured with a double-junction combination electrode (Orion Model 81-72BN) connected to a Fisher Scientific Accumet 50 pH meter. Nafion 117 membrane was removed for non separated experiments. Dissolved oxygen (DO) that was measured by DO meter (Great Lakes Instruments, Model 867) was around 31 mg/l when oxygen was bubbled into the solutions. To understand the effect of oxygen, nitrogen was bubbled through the solution until oxygen concentration decreased under 0.4 mg/l.

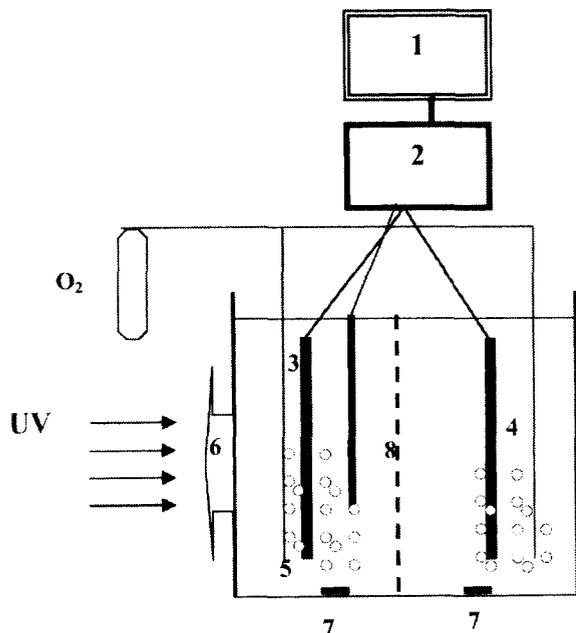


Fig. 3. PEC reactor systems: 1, computer; 2, potentiostat; 3, working TiO_2 photoelectrode; 4, counter electrode (Pt foil); 5, reference electrode (SCE); 6, quartz glass; 7, stirring bar, 8, Nafion 117 membrane.

2.3. Blank experiments

Photocatalysis: The photocatalytic (PC) experiment was carried out using a TiO_2 electrode in 100 ml chloride test solutions by illuminating the photoanode cell without bias. Neither chlorine generation nor chlorate formation was observed over a 45 min reaction period.

Electrolysis: To investigate mere electrolysis on both chlorine generation and chlorate formation, the electrochemical experiments were performed by biasing a TiO_2 anode with a potential of 1.0 V vs. SCE without UV illumination. A 100 ml test solution containing $1.0 \times 10^{-2} \text{ M NaCl}$ was used in each compartment. Samples were taken from the photoanode compartment for analytical measurements. Neither chlorine nor chlorate could be detected in the 45 min electrolysis period.

2.4. Analytical measurements

Chlorine analysis. The concentration of active chlorine was determined by a DPD (N,N,-diethyl-

p-phenylenediamine) colorimetric standard method [23], at an absorbance of 512 nm using a Hewlett Packard spectrophotometer, model HP 8452A in a 10 mm quartz cell.

Chlorate and chloride measurements. A Dionex ion chromatograph (DX-600) equipped with a AG9-HC anion column and an AG9-HC guard column with a 500 μ l loop was employed to determine chlorate and chloride concentrations. A carbonate eluent (9 mM sodium carbonate) was used for both chlorate and chloride analysis.

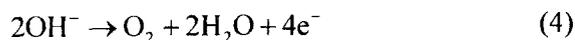
3. Results and discussions

3.1. Chlorine generation and chlorate formation

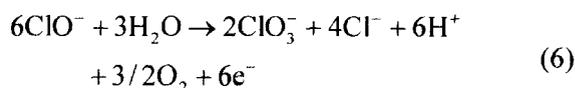
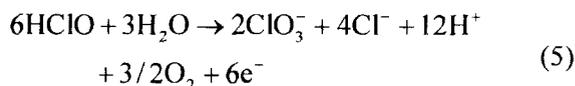
Chloride is a negatively charged ion and can adsorb on the positively charged photoanode where it may also be subsequently oxidized by photogenerated holes yielding the oxidized product — chlorine (Cl_2). This Cl_2 species spontaneously reacts with water yielding other active aqueous chlorine species, hypochlorous acid (HOCl), and hypochlorite ion (OCl^-) as described in Eqs.(1)–(3)



Besides the chloride oxidation reaction [Eq. (4)], oxygen is also evolved on the photocathode. As a result, in the separated photoanode cell, the pH of the solution decreases during PEC treatment.



On the other hand, chlorate may form by anodic oxidation of OCl^- and/or HOCl in the electrochemical process as explained with the Eqs. (5) and (6).



To determine if the PEC system can generate chlorine and/or chlorates, a solution containing 10^{-2} M NaCl at pH 8.0 was oxidized under an external biasing potential of 1.0 V vs. SCE. The variation in pH, chlorine and chlorate concentration was followed over time. As can be seen in Fig. 4, pH decreased over the reaction period due to the evolution of oxygen [Eq. (4)] and reached a pH of 3 in the photoanodic compartment after the 45 min reaction time. Chlorine production was observed after 5 min and increased over time until reaching a steady-state condition after 45 min. A constant concentration of 42 mg/l of active chlorine was obtained after 45 min. These results indicate that the chlorine photolysis side reaction [Eqs. (7) and (8)] seems to play a role in this process limiting the maximum concentration of chlorine [24,25].

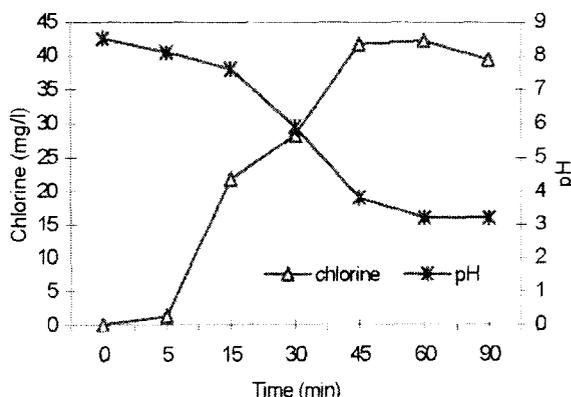


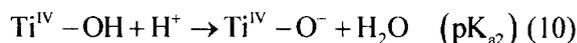
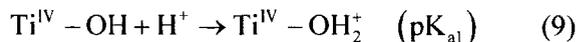
Fig. 4. Chlorine production and variation of pH at the photoanode cell.



Like chloride anion, ClO^- is also a negatively charged anion and its attraction on the positively charged photoanode surface was higher than that from the neutral HOCl. Hence, ClO^- likely plays the most important role in chlorate formation. The relative amount of each of Cl_2 , HOCl, and OCl^- free chlorine species forms is pH and temperature dependent. At room temperature Cl_2 has an important contribution under very acidic conditions and the HClO species predominates at $3.3 < \text{pH} < 7.5$. The OCl^- anion is the main species at $\text{pH} > 7.5$. Chlorate formation was observed after 10 min and increased sharply in 30 min reaction period due to the increasing OCl^- concentration at these high pH values. In prolonged reaction period, chlorate concentrations was almost the same due to the lowering of the OCl^- concentration with the decreasing pH in the photoanode compartment. In this compartment, a pH value of 3.1 was almost constant over the prolonged reaction time. At this pH value, Cl_2 is the most important chlorine species and it has no effect on the chlorate formation. Thus constant chlorate formation was attributed to the low pH value in the photoanode compartment.

3.2. Effect of pH

The adsorption of negatively charged organics and inorganics on the TiO_2 surface is a necessary prerequisite for the oxidation of these substances due to the surface oriented nature of the PC process. Adsorption onto the TiO_2 surface depends both on the nature of the surface and the physical chemical nature of the solution. The TiO_2 surface can acquire negatively or positively charged sites according to the pH of the aqueous medium. The pH value at which the number of the positively and negatively charged surface sites are equal is defined as the point of zero charge value (pH_{pzc}). The polarity of the TiO_2 surface has been expressed by Eqs. (9) and (10):



When $\text{pH} < \text{pH}_{\text{pzc}}$ the surface of TiO_2 is positively charged and this condition attracts negatively charged anions such as Cl^- and OCl^- . When pH is higher than the pH_{pzc} of TiO_2 , the surface of TiO_2 is negatively charged, causing electrostatic repulsion between negative ions and the TiO_2 surface. In the photoanode pH is not stable and decreases over time due to Eq. (4). Thus, a complementary PEC experiment was also performed under controlled pH value of 8.0. By controlling pH in photoanode, one affects chlorine production slightly. Chlorate formation under a controlled pH of 8.0 was much higher than that found without controlling pH (Fig. 5). This result may be attributable to the high ClO^- level at a pH value of 8.0.

Taking this into account, PEC experiments were carried out under different initial pH conditions. These results are shown in Fig. 6. Even though the pH_{pzc} of TiO_2 is around $\text{pH} = 5.9$, a constant active chlorine production was achieved (around 40 mg/l) in the range of pH 3.2–8.0. This production decreased sharply at initial $\text{pH} > 8.0$. The results are attributed to the positively applied potential on the photoanode that changes the

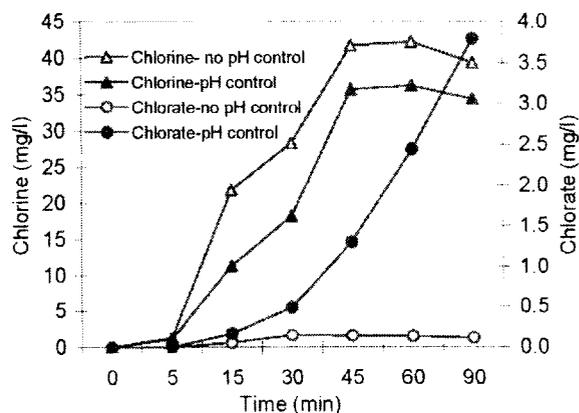


Fig. 5. pH control and its effect on the chlorine production and chlorate formation.

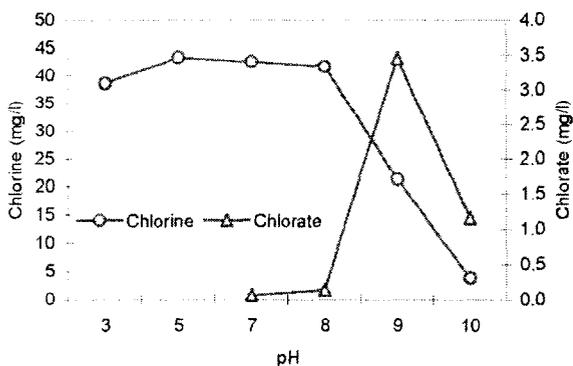


Fig. 6. Effect of initial pH on the generation of chlorine and formation of chlorate.

charge of TiO_2 coated photoanode and improves adsorption over a large pH range. Beyond this pH, the adsorption of Cl^- is unfavorable, which diminishes the rate of the oxidation reaction. On the other hand, Nowell and Hoigne [25] have reported that the photolysis of OCl^- is higher than HOCl , which leads to a high rate of chlorine photolysis at $\text{pH} > 7$ [25]. Above $\text{pH} = 8.0$, OCl^- is the predominant chlorine species in water. Consequently, the strong effect of pH on chlorine formation may be attributable in relation to the effect of pH on the zeta potential of TiO_2 and also in part to the high photolysis rate of chlorine at higher pH values.

The highest chlorate concentration was found at an initial pH of 9.0. Even though chlorine generation is very low at $\text{pH} = 10.5$, significant chlorate formation was observed at this pH, probably due to the high concentration of OCl^- species that increases chlorate formation. Chlorate formation decreased with decreasing initial pH values and at an initial pH of 7.0 chlorate formation was not significant (0.064 mg/l). Furthermore, chlorate concentrations were under the detection limits (0.025 mg/l) at initial pH values < 7.0 .

3.3. Effect of oxygen

In the PC processes, oxygen is an electron acceptor. On the other hand, photoexcited

electrons can be transferred to the cathode side in PEC systems. In the photoanode compartment, some species in the aqueous phase such as H_2O , OCl^- or Cl^- can react with the photoexcited hole resulting in oxygen evolution in the PEC process [Eqs. (4)–(6)]. In this study, beyond the anodic oxidation of OCl^- or Cl^- and water, the adsorbed hydroxide ion may also yield an electron yielding an atomic oxygen species on the photoanode. This atomic oxygen may subsequently react with oxygen and play a role in the formation of ozone (O_3) as illustrated by Eqs. (11) and (12) [26].



In the presence of chloride, chlorate may also form in the photo-anode compartment as a result of ozone and chloride reactions [27]. Possible adverse health effects from chlorate are not well established to date. The World Health Organization gives no guideline value for drinking water, however, it does suggest that chlorate should be kept as low as possible until more toxicological information is available. In Switzerland, the drinking water standard for chlorate is 200 mg/l [19].

To understand the effect of supplied and/or generated oxygen on chlorine and chlorate formation, two complementary PEC experiments (Table 1, experiments 2 and 3) were performed in the absence of oxygen bubbling in photoanode compartment at initial pH of 8.0. Here we employed a chloride containing sample that had been degassed with nitrogen until oxygen concentration decreased to under 0.4 mg/l. In the first experiment, the top of the reactor was closed to inhibit air penetration and the experiment was carried out stirring the solution without oxygen or nitrogen bubbling. A second PEC experiment was performed under nitrogen bubbling for initially degassed sample. As shown in Table 1, an insignificant increase ($< 5\%$) in chlorine production was observed without using oxygen in photoanode chamber that housed the

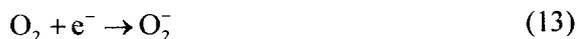
Table 1
Effect of oxygen and charge separation on the chlorine production and chlorate formation

Experiments	Reactor	Gas	Initial pH	Chlorate (mg/l)	Chlorine (mg/l)
1	Separated	Oxygen bubbling	8.0	0.141	41.7
2	Separated	Previously oxygen removed	8.0	0.068	43.4
3	Separated	Nitrogen bubbling	8.0	0.035	42.4
4	Separated	Oxygen bubbling	3.2	nd	4.2
5	Combined	Oxygen bubbling	3.2	nd	38.6
6	Combined	Oxygen bubbling	8.0	0.428	3.3

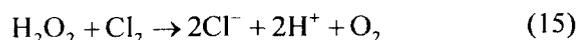
chlorine concentration of 41.7 mg/l. A significant oxygen effect was observed on the chlorate formation with chlorate decreasing to about 52% of its concentration in the first experiment after removing oxygen and 75% in the second experiment which was performed for initially degassed sample under nitrogen.

3.4. Effect of charge separation

PEC experiments using a solution containing 10^{-2} M NaCl at pH 3.2 were performed under an external biasing potential of 1.0 V vs. SCE over a 45 min reaction period with and without separating the anode and cathode compartments (Table 1, experiments 4 and 5). Chlorine generation was found to be 4.2 mg/l without separation and 39 mg/l in the separated photoanode cell. It is well known that hydrogen peroxide formation can occur on the cathode surface via reduction of oxygen as follows [28]:



H_2O_2 can react chlorine reducing this species to chloride as explained with the following equation [29]:



Thus, a high chlorine concentration in the separated photoanode cell was attributable to the

inhibition of the quenching of chlorine with H_2O_2 in the PEC system.

To further investigate the effect of separating anode and cathode compartments on the formation of chlorate, we used the combined photoanode–cathode configuration and performed the experiment at an initial pH value of 8.0. At this pH, we had previously found significant chlorate formation (0.141 mg/l) in the separated photoanode cell (Table 1, experiment 1). We now observed that the chlorate concentration increased to 0.428 mg/l in this combined photoanode–cathode system (Table 1, experiment 6) 3-fold higher than that in the separated system. pH change was insignificant in combined system while it decreased over time and reached around 3.0 in the photoanode cell. Consequently higher chlorate formation in non separated system was attributed to the high pH values in the non separated system.

4. Conclusions

Chlorine generation and chlorate formation was studied using a PEC treatment system under different conditions and the following conclusions may be drawn:

1. A PEC experiment was employed at initial pH of 8.0. The pH in the photoanode compartment decreased over time yielding a value of 3.2 after 45 min of reaction time. A constant concentration of 42 mg/l of active chlorine was achieved after 45 min in the photoanode chamber while chlorate concentration was found to be 0.141 mg/l after

45 min but slightly decreasing over time. A complementary PEC experiment was performed under a controlled pH of 8.0. Chlorine production was almost the same while chlorate formation was found to be 1.3 mg/l and increased over time probably due to the high ClO^- levels at a constant pH of 8.0.

2. Chlorine generation was also investigated under different initial pH values. A constant active chlorine production was achieved (around 40 mg/l) in the pH range of 3.2–8.0. This production decreased sharply at initial pH > 8.0. Chlorate formation was observed at initial pH values <7.0 and increased with increasing pH up to 9.0. Subsequently chlorate concentrations decreased due to reducing levels of chlorine production at these higher pH values.

3. The effect of oxygen on chlorine generation was not significant. On the other hand, its effect was more significant with respect to chlorate production with chlorates decreasing about 52% by removing oxygen and 75% under nitrogen.

4. Two different PEC (separated and combined photoanode-cathode) configurations were also used to investigate charge separation on the chlorine generation and chlorate formation. Chlorine generation (4.2 mg/l) in the combined photoanode-cathode system was 10 fold lower than that (39 mg/l) in the separated photoanode cell. On the other hand, chlorate concentrations of 0.428 mg/l, observed in the combined system at initial pH = 8.0 was around 3 times higher than that measured in the separated photoanode side under same initial concentration.

Acknowledgement

The authors gratefully thank J.J. Sene and M.V.B Zanoni for their help in using the PEC system and in making chlorine measurements respectively. In this study, the author, Huseyin Selcuk, was supported by University of Wisconsin-Madison, Water Chemistry Department. The contribution of the referees (John Byrne and Miray Bekbolet) to improve this work is appreciated.

References

- [1] M. Bekbolet and G. Ozkosemen, *Water Sci. Res.*, 33 (1996) 189–194.
- [2] B.R. Eggins, F.L. Palmer and J.A. Byrne, *Water Res.*, 31 (1997) 1223–1226.
- [3] H. Freudenhammer, D. Bahnemann, L. Bousselmi, S.U. Geissen, A. Ghrabi, F. Saleh, A. Si-Salah, U. Siemon and A. Vogelpohl, *Water Sci. Tech.*, 35 (1997) 145–159.
- [4] D. Chen and A.K. Ray, *Water Res.*, 32 (1998) 3223–3334.
- [5] P.S.M. Dunlop, J.A. Byrne, N. Manga, and B.R. Eggins, *J. Photochem. Photobiol. A*, 148 (2002) 355–363.
- [6] W. Xi and S.U. Geissen, *Water Res.*, 35 (2001) 1256–1262.
- [7] J.C. Lee, M.S. Kim and B.W. Kim, *Water Res.*, 36 (2002) 1776–1782.
- [8] G.S. Shaphard, S. Stockenstrom, D. deVilliers, W.J. Engelbrecht and G.F. Wessels, *Water Res.*, 36 (2002) 140–146.
- [9] A. Fujishima and K. Honda, *Nature*, 238 (1972) 37–38.
- [10] K. Rajeshwar, L.M. Peter, A. Fujishima, D. Meissner and M. Tomkiewicz, *Photoelectrochemistry. Electrochemical Society Publisher Press*, Pennington, NJ, 1997.
- [11] D.H. Kim and M.A. Anderson, *Environ. Sci. Technol.*, 28 (1994) 479–483.
- [12] I.M. Buterfield, P.A. Christensen, A. Hamnett, K.E. Shaw, G.M. Walker and S.A. Walker, *J. Appl. Electrochem.*, 27 (1997) 385–95.
- [13] R. Pelegrini, J. Reyes, N. Duran, P.P. Zamora, A.R. and De Andrade, *J. Appl. Electrochem.*, 30 (2000) 953–958.
- [14] J.C. Harper, T.A. Egerton, T.P. Curtis and J. Gunlazuardi, *J. Appl. Electrochem.*, 31 (2001) 623–628.
- [15] H. Selcuk, J.J. Sene, M. Bekbolet, H.Z. Sarikaya and M.A. Anderson, *J. Appl. Electrochem.*, 34 (2004) 653–658.
- [16] H. Selcuk J.J. Sene and M.A. Anderson, *J. Chem. Technol. Biotechnol.*, 78 (2003) 979–984.
- [17] H. Selcuk, J.J. Sene, H.Z. Sarikaya, M. Bekbolet and M.A. Anderson, *Wat. Sci. Technol.*, 49 (2004) 153–158.
- [18] M.V.B. Zanoni, J.J. Sene, H. Selcuk and M.A. Anderson, *Environ. Sci. Technol.*, 38 (2004) 3203–3208.

- [19] U. von Gunten, *Water Res.*, 37 (2003) 1469–1487.
- [20] S.W. Krasner, W.H. Glaze, H.S. Weinberg, D.A. Daniel and I.M. Najm, *J. AWWA*, 87 (1993) 71–83.
- [21] W.R. Haag and J. Hoigne, *Ozone Sci. Technol.*, 6 (1984) 103–114.
- [22] H. Selcuk, J.J. Sene, M.V.B. Zanoni, H.Z. Sarikaya and M.A. Anderson, *Chemosphere*, 54 (2004) 969–974.
- [23] *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Association, APHA/AWWA/WPCF, Washington, DC, 1998.
- [24] G.V. Buxton, C.L. Greenstock, W.P. Helman and A.B. Ross, *J. Phys. Chem. Ref Data*, 17 (1988) 513–886.
- [25] L.H. Nowell and J. Hoigne, *Water Res.*, 26 (1992) 593–598.
- [26] L.M.D. Silva, L.A.D. Faria and J.F.C. Boodts, *Electrochim. Acta*, 48 (2003) 699–709.
- [27] J. Hoigne, H. Bader, W.R. Haag and J. Stachelin, *Water Res.*, 19 (1985) 993–1004.
- [28] P. Clechet, C. Martelet, J.R. Martin and R. Olier, *Electrochim. Acta*, 24 (1979) 457–461.
- [29] S. Batterman, L. Zhang and S. Wang, *Water Res.*, 34 (2000) 1652–1658.