Journal of Photochemistry and Photobiology A: Chemistry 151 (2002) 201–205

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photo-oxidation of dissolved cyanide using TiO_2 catalyst

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Received 26 March 2002; accepted 7 April 2002

Abstract

Catalytic oxidation of free cyanide using TiO_2 and UV radiation was investigated. The cyanide photo-oxidation rate was determined for different initial cyanide concentrations, pH, catalyst form, sparged gas, and temperature; and followed pseudo-first-order kinetics with respect to cyanide concentration. The TiO_2 catalyzed UV–O_2 reaction resulted in twice the oxidation rate of free cyanide, however, the rate appeared to be independent of oxygen partial pressure (0.2–1.0 atm) at the gas flow rates studied. An increase in temperature from 20 to 35 °C did not influence the rate of cyanide oxidation.

Keywords: Photodegradation; Cyanides; Hazardous waste; Titanium dioxide

1. Introduction

The presence of free and complex cyanides in industrial effluents is a problem of major concern owing to the well-known toxicity of these species for living organisms, even at low concentrations. Of particular concern is the discharge of large volumes of cyanide-contaminated wastewater from gold cyanidation plants. At present most of the world's gold production is achieved using cyanide leaching because of its simplicity and high efficiency. Ore containing only a few ppm of gold can be solubilized with aqueous solutions of sodium or calcium cyanide at pH 10–12 either by agitation leaching of finely ground material or heap leaching of crushed product. In some cases gold recovery can reach 98–99% after leaching at ambient temperature for 24–48 h.

Dissolved cyanides can be removed from solution by physical, chemical, and biological methods. The physical methods are based on ion exchange, adsorption (mainly on activated carbon) and flotation–foam separation. Biological treatment involves biodegradation and is limited to low concentrations of cyanides. The chemical methods typically involve oxidation of cyanide by reagents such as SO_2-air, chlorine, permanganate, hydrogen peroxide, air and/or ozone. Photocatalytic oxidation over metal oxides, mainly TiO_2, has also been proposed as a possible option for cyanide elimination [1,2].

Hidaka et al. reported photodegradation of CN^- in industrial wastewater using suspended TiO_2 as a catalyst [3]. The evolution of CO_2, consumption of O_2, evolution of N_2, and formation of the OCN^- intermediate ions were examined quantitatively. The catalytic activity of Degussa P-25 catalyst and Wako TiO_2 (rutile) were examined. Irradiation was carried out in both a small reactor ($V = 50\,cm^3$), and in a large reactor ($V = 5\,dm^3$). The CN^- solution was photodegraded using 546 ppm of TiO_2 catalyst in an alkaline environment (initially pH = 12). The effect of different amounts of TiO_2 catalyst was examined for the 500 ppm solution. The optimum amount of TiO_2 was found to be $1\,g/dm^3$ [3]. The photocatalytic oxidation of cyanide using Degussa P-25 catalyst was investigated by Pollema et al. [4]. It was confirmed that cyanide was first oxidized to cyanate and further through nitrite to nitrate [4].

Mihaylov et al. investigated photocatalytic oxidation of cyanide in the presence of TiO_2 (anatase and rutile), ZnS, ZnO, CdS, V_2O_5, SiO_2 and Fe_2O_3 [2]. Only TiO_2 and ZnO yielded satisfactory results. In most systems cyanide was also volatilized as HCN. The amount of HCN volatilized is a function of the pH of the solution and the surface area of the catalyst, and generally increases with decreasing pH and increasing surface area [2].

Frank and Bard reported photo-oxidation of cyanide in the presence of TiO_2 in both anatase and rutile forms [5,6]. The reaction was studied for several cyanide concentrations using a 450 W xenon lamp, 2500 W mercury–xenon lamp and direct (unfocused) sunlight. Under all conditions the reaction

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PII: S1010-6030(02)00151-X

proceeded at a measurable rate resulting in ONC^- as the final product of oxidation. They anticipated further oxidation of ONC^-, but found no evidence of other products [6].

Our paper presents experimental results for the photocatalytic oxidation of free cyanides in an aqueous suspension of titanium dioxide. The influence of pH, initial cyanide concentration, gas type (composition), temperature and catalyst form was investigated.

2. Experimental

Powdered anatase from Sigma and rutile from Alfa Aesar were used. The specific surface area was 8.6 m^2/g for anatase and 6.9 m^2/g for rutile as determined by the Brunauer–Emmett–Teller method using nitrogen and the Quantasorb apparatus [7].

Easily separable titanium photocatalyst was prepared by chemical deposition of titanium dioxide on glass microspheres [8]. The bulk density of the microspheres was 0.4 g/cm^3. The percentage of TiO_2 deposited on glass microspheres was 0.1–0.5 by weight, as determined by the complexing TiO_2–H_2O_2 colorimetric method [8].

The experimental set-up is shown in Fig. 1. A Heraeus photochemical reactor equipped with 150 W medium pressure mercury lamp was used for UV irradiation of NaCN solutions. Reference cyanide solution ($C_o = 8\ g/dm^3$) in distilled water was prepared. The reaction vessel was filled with distilled water (800 cm^3), the pH was adjusted with NaOH to value of 10 or 12, and 0.8 g of titanium dioxide was added. The aqueous titanium dioxide suspension was stirred and gas was sparged. After 10 min, 2 or 10 cm^3 of the reference cyanide solution was added ($C_o = 20$ or $100\ mg/dm^3$), and the reaction mixture was irradiated for 60 min. Either air, oxygen or argon was sparged through the solution at a rate of 10 or 20 dm^3/h. The gas phase leaving the reaction environment was directed to a 0.5 M NaOH solution for absorption. The cyanide degradation reactor was carried out at 20 and 35 °C. The pH and the CN^- concentration were monitored on-line using pH and ion-selective electrodes. The cyanide solution was circulated with a peristaltic pump at a rate of 300 cm^3/min through a cell in which the electrodes were placed. The data were collected every minute and the solution retention time was approximately 3 min.

Additionally, cyanide concentration was determined spectroscopically at 580 nm, based on cyanogen chloride reaction with pyridine and then with barbituric acid, according to the Polish Norm (PN-80/C 04603.01) procedure.

3. Results and discussion

The rate of cyanide degradation for different forms of titanium dioxide is contrasted to the rate in the absence of catalyst in Fig. 2. More favorable removal kinetics was obtained for powdered anatase or anatase supported on glass hollow microspheres than for powdered rutile. After 60 min irradiation of an aqueous solution, initially containing 20 mg/dm^3 of CN^-, a substantial amount of free cyanides had been eliminated for suspended anatase, supported anatase, and

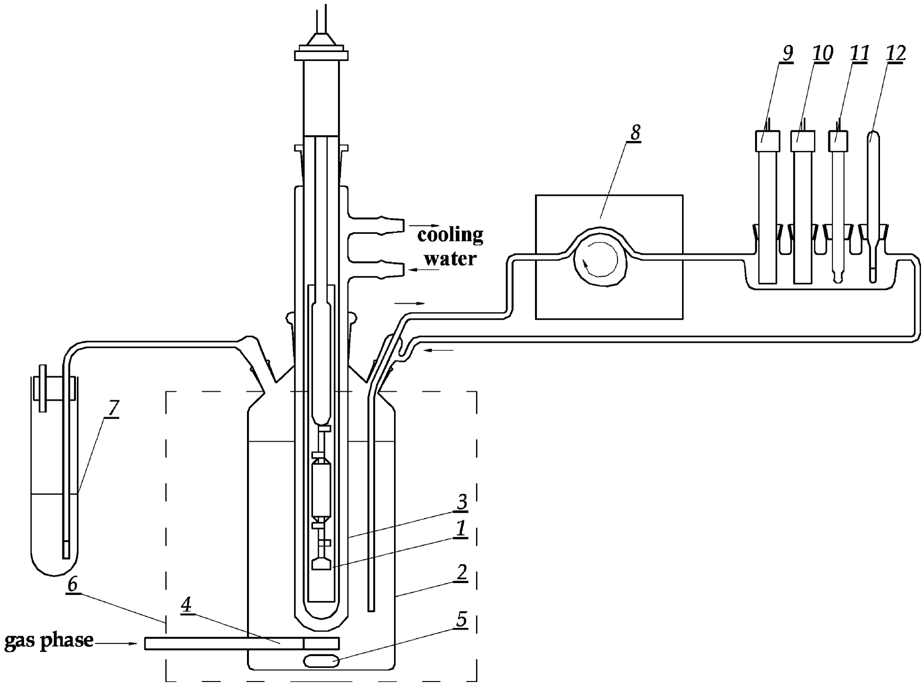

Fig. 1. Experimental set-up used for elimination of free cyanides from aqueous solutions: (1) Heraeus medium pressure mercury lamp; (2) glass reactor; (3) UV lamp cooling system; (4) sparged gas system; (5) magnetic stirrer; (6) thermostat; (7) NaOH solution; (8) peristaltic pump; (9) ion-selective electrode; (10) reference electrode; (11) pH electrode; (12) thermometer.

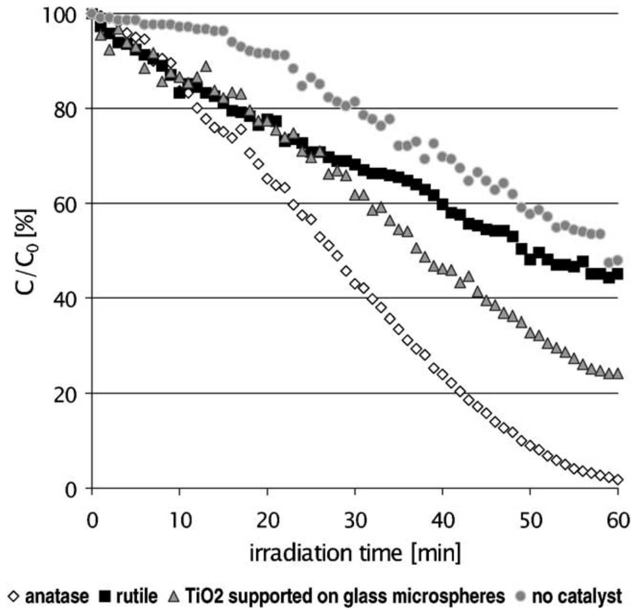

Fig. 2. Impact of catalyst type on elimination of free cyanides from aqueous solution at pH = 12.

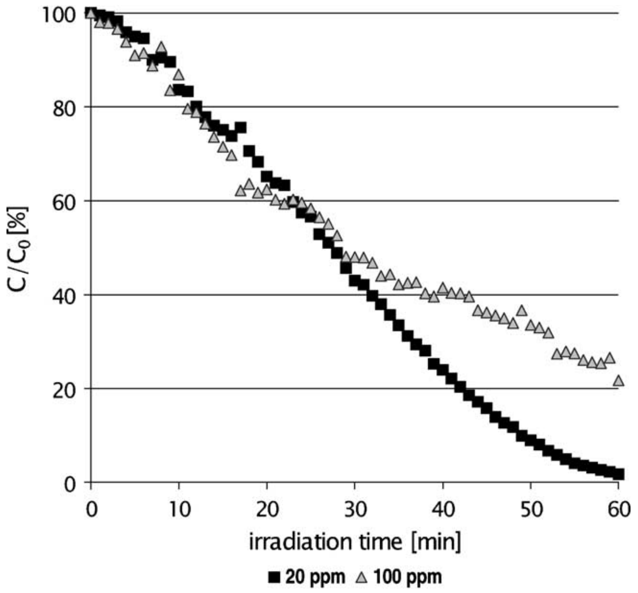

Fig. 3. The influence of initial cyanides concentrations on the elimination rate at pH = 12 in the presence of suspended anatase ($c_{\mathrm{TiO_2}} = 1\,\mathrm{g/dm^3}$) and O_2 sparged at 20 $\mathrm{dm^3/h}$.

suspended rutile. The effectiveness of each catalyst after 1 h reaction is shown by the data presented in Table 1. It is evident, that anatase is the most effective (97% removal) followed by supported anatase (75% removal) and then rutile (55% removal). The results suggest that commercial anatase and anatase supported on glass hollow microspheres were most effective for photocatalytic degradation of free cyanide.

At the beginning of the reaction a similar decrease of cyanide concentration was observed for the supported anatase and rutile. But after 30 min irradiation the activity of rutile dropped, probably due to an irreversible dehydroxylation of the catalyst surface. As a consequence, impaired potential for O_2 adsorption reduced the photoactivity, an explanation given earlier by Palmisano et al. [9]. On the other hand, the lower performance of the supported anatase compared to the same amount of the unsupported powdered anatase can be explained to be due to the much smaller overall TiO_2 content on the glass microspheres (up to 0.5 wt.%).

Frank and Bard, in their investigations reported weak oxidation of CN^- at best in the absence of a photocatalyst (<1% of the free CN^- was destroyed) [5]. However, the results of Pollema et al. showed otherwise. After 2 h irradiation of a 5 μg/ml cyanide solution, with pH adjusted to 10 and saturated with O_2, a complete loss of cyanide was observed. Our results confirm cyanide degradation in the UV–O_2 system. In the absence of titanium dioxide, 46% of the free cyanide was eliminated after 60 min. irradiation at pH = 12.

The influence of the initial cyanide concentration on the efficiency of cyanide destruction is shown in Fig. 3. The reaction was carried out at two initial CN^- concentrations:

Table 1
Effects of catalyst form, sparging gas, initial CN^- concentration, temperature and pH on photo-oxidation rate of CN^-

Catalyst form	Catalyst loading ($\mathrm{g/dm^3}$)	Initial amount of cyanide ($\mathrm{mg/dm^3}$)	Gas phase	Gas flow rate ($\mathrm{dm^3/h}$)	Temperature (°C)	pH	k_1 ($\mathrm{min^{-1}}$)
–	–	20	Oxygen	20	20	12	0.006
Anatase	1	4	Oxygen	20	20	12	0.112
Anatase	1	20	Air	20	20	10	0.021
Anatase	1	20	Air	20	20	12	0.023
Anatase	1	20	Oxygen	10	20	12	0.027
Anatase	1	20	Oxygen	20	20	10	0.030
Anatase	1	20	Oxygen	20	20	12	0.028
Anatase	1	100	Oxygen	20	20	12	0.020
Anatase	1	20	Oxygen	20	35	12	0.028
Rutile	1	20	Oxygen	20	20	12	0.012
TiO_2 supported on glass microspheres	0.005	4	Oxygen	20	20	12	0.015
TiO_2 supported on glass microspheres	0.005	20	Oxygen	20	20	12	0.016

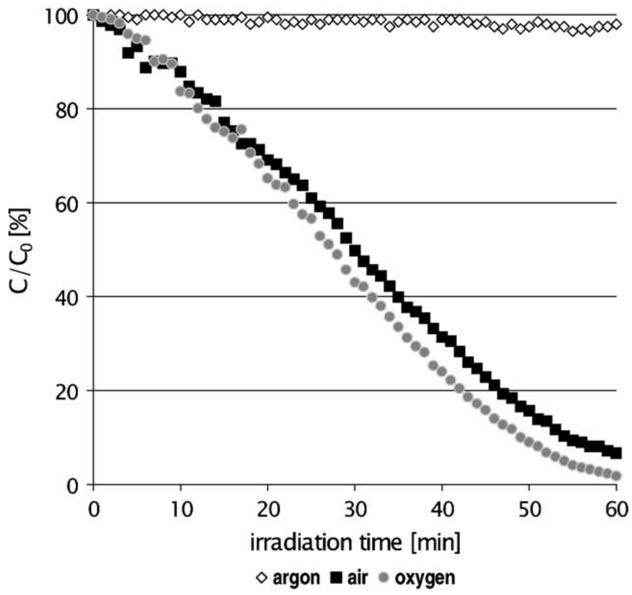

Fig. 4. The influence of air, oxygen and argon on eliminations of cyanides; initial cyanide concentration: 20 mg/dm^3; pH = 12; gas flow rate: 20 dm^3/h; photocatalyst: suspended anatase ($c_{\mathrm{TiO_2}} = 1$ g/dm^3).

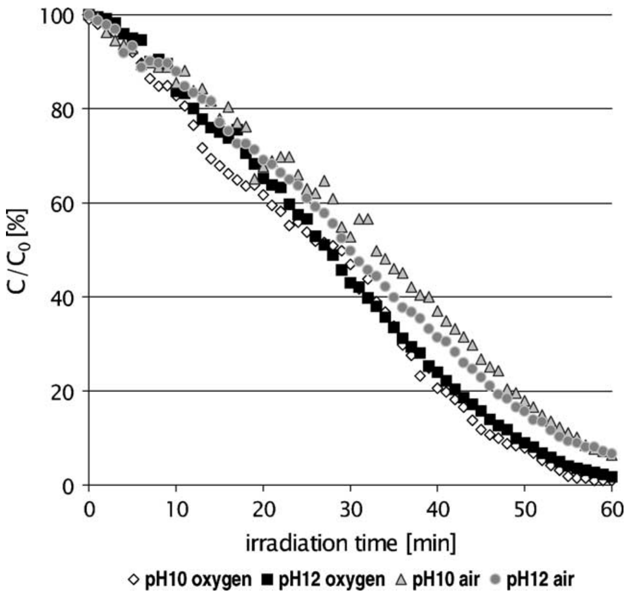

Fig. 5. Free cyanides elimination from aqueous solutions at different pH for air and oxygen; 20 mg/dm^3 initial cyanide concentration; pH = 12; 20 dm^3/h gas flow rate; suspended anatase ($c_{\mathrm{TiO_2}} = 1$ g/dm^3).

20 and 100 ppm. Nearly all free cyanides were removed after 60 min irradiation for the lower cyanide concentration (20 ppm). The same time of irradiation resulted in elimination of approximately 80% in the case of the solution initially containing 100 ppm of sodium cyanide. Our results confirm data from the literature regarding the pseudo-first-order kinetics when the cyanide concentration decreases. The first-order rate constants, obtained under different experimental conditions, are presented in Table 1. The data in Table 1 reveal that for a constant amount of anatase, pH value and temperature, smaller rate constants were obtained for air than for oxygen. Similar results were obtained by Pollema et al. in photocatalytic oxidation of 10 μg/ml cyanide solution using Degussa P-25 catalyst [4].

The influence of oxygen concentration on the rate of cyanide degradation in the UV–TiO$_2$ system is presented in Fig. 4. As expected, free cyanide was not destroyed after 60 min irradiation in the absence of oxygen. In order to obtain the deoxygenated solution, argon was sparged through a titanium dioxide (suspended anatase) aqueous suspension for 30 min before irradiation and than during processing at a flow rate of 20 dm^3/h. It is evident that, not much difference in the rate was observed for air and oxygen at an initial cyanide concentration of 20 ppm.

Also the oxidation rate of cyanide did not depend on the alkalinity of the reaction environment, see Fig. 5. No difference in the oxidation efficiency at pH 10 and 12 for either air or oxygen was observed. Peral et al. reported, that the amount of photo-oxidized free cyanide decreased when the pH was changed from 10.5 to 13 [10]. Such a behavior was explained by the increasing negative charge on TiO$_2$ particles in more alkaline environment as the result of competitive adsorption of OH$^-$ which limited the access of CN$^-$ ions to the TiO$_2$ surface [10].

The change of temperature from 20 to 35 °C did not influence the oxidation rate in the presence of titanium dioxide, see Fig. 6. The impact of temperature in the range 25–55 °C on CN$^-$ photo-oxidation was investigated by Peral et al. [10]. The degradation efficiency increased only from 74.8% at 25 °C to 75.8% at 35 °C, i.e. the results are similar to our data. Peral et al. calculated an activation

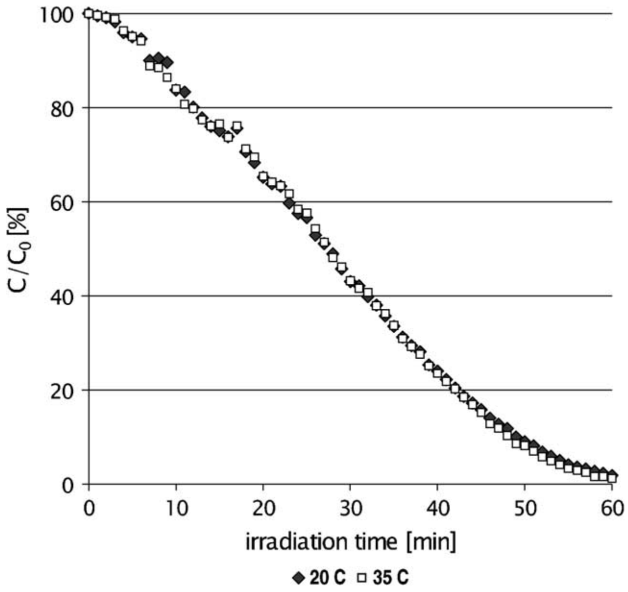

Fig. 6. The influence of temperature on kinetics of cyanide elimination for oxygen and argon; initial cyanide concentration: 20 mg/dm^3; pH = 12; gas flow rate: 20 dm^3/h; suspended anatase ($c_{\mathrm{TiO_2}} = 1$ g/dm^3).

energy of 5.5 kJ/mol. Such a low value is characteristic for a fast electron transfer reaction.

In all our runs the amount of stripped HCN was $<0.05\%$ of the total, initial cyanide amount as determined by analysis of the 20 ml NaOH absorption solution.

4. Conclusions

- Presence of TiO_2 as a catalyst in the UV–O_2 reaction system allowed for twice the degradation rate of free cyanides.
- The reaction order with respect to free cyanide concentration seemed to change depending on the initial cyanide concentration. The initial cyanide concentration affected the rate of oxidation in the UV–TiO_2–O_2 system.
- The increase of processing temperature from 20 to 35 °C (which can correspond to seasonal wastewater temperature changes) did not influence the extent of cyanide degradation.
- The extent of cyanide elimination was independent of whether air or oxygen was used for a gas flow rate of 20 dm^3/h.
- During all experiments, despite changing processing conditions, practically no HCN was released to the gas phase, which is essential for safety reasons.

Acknowledgements

This work was supported by the Technical University of Gdansk under Contract No. 014694/096 and Contract No. 014694/100; and the US Department of Energy Award No. DE-FC26-01NT41064.

References

[1] V. Augugliaro, V. Loddo, G. Marci, L. Palmisano, M.J. Lopez-Munoz, Photocatalytic oxidation of cyanides in aqueous titanium dioxide suspensions, J. Catal. 166 (1997) 272–283.
[2] B.V. Mihaylov, J.L. Hendrix, Comparative catalytic activity odf selected metal oxides and sulfides for the photo-oxidation of cyanide, J. Photochem. Photobiol. A: Chem. 72 (1993) 173–177.
[3] H. Hidaka, T. Nakamura, A. Ishizaka, M. Tsuchija, J. Zhao, Heterogeneous photocatalytic degradation of cyanide on TiO_2 surfaces, J. Photochem. Photobiol. A: Chem. 66 (1992) 367–374.
[4] C.H. Pollema, J.L. Hendrix, Photocatalytic oxidation of cyanide to nitrate at TiO_2 particles, J. Photochem. Photobiol. A: Chem. 66 (1992) 235–244.
[5] S.N. Frank, A.J. Bard, Heterogeneous photocatalytic oxidation of cyanide ion in aqueous solution at TiO_2 powder, J. Am. Chem. Soc. 99 (1977) 303–304.
[6] S.N. Frank, A.J. Bard, Heterogeneous photocatalytic oxidation of cyanide and sulfite in aqueous solution at semiconductor powders, J. Phys. Chem. 81 (15) (1977) 1484–1488.
[7] A. Zaleska, J. Drelich, J.D. Miller, J. Hupka, Adsorption isotherms of methoxychlor on TiO_2 as photocatalyst, in: Proceedings of Third International Symposium on Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids, 9–16 August 1998, Toruń, Poland, 1998, pp. 295–296.
[8] J. Rzechuła, A. Zaleska, J. Hupka, J. Drelich, J.D. Miller, Surface characteristic of microsphere-supported TiO_2 photocatalyst, in: Proceedings of Third International Symposium on Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids, Toruñ, Poland, August 9–16 1998, pp. 297–298.
[9] L. Palmisano, M. Schiavello, A. Sclafani, G. Martra, E. Borello, S. Coluccia, Photocatalytic oxidation of phenol on TiO_2 powders, a fourier transform infrared study, Appl. Catal. B: Environ. 3 (1994) 117–132.
[10] J. Peral, J. Munoz, X. Domenech, Photosensitized CN^- oxidation over TiO_2, J. Photochem. Photobiolog. A: Chem. 55 (1990) 251–257.