

Photocatalytic Water Treatment and Purification

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Semiconductor photocatalysis is a possible alternative to conventional water treatment technologies and, titanium dioxide (TiO_2), is the most widely employed semiconductor material for aqueous applications. When TiO_2 is illuminated with light of $\lambda < 400$ nm, an electron is promoted from the valence band to the conduction band of the semiconducting oxide to give an electron/hole pair. In electrochemical terms, the valence band potential is positive enough to generate hydroxyl radicals at the surface and the conduction band potential is negative enough to reduce molecular O_2 . The hydroxyl radical is a powerful oxidising agent and attacks organic pollutants present at or near the surface of the TiO_2 resulting in their complete oxidation to CO_2 , if allowed to proceed to completion.

In this work, nanoparticle TiO_2 was immobilized onto supporting substrates i.e. glass, ITO glass and titanium metal, using dip coating or, in the case of electrically conducting supports, an electrophoretic coating procedure. Immobilised catalyst films were then tested for their efficiency in the photocatalytic degradation of organic chemical contaminants and for the disinfection of water containing microbiological pathogens. Organic chemical pollutants investigated included 17 β -oestradiol, atrazine, and formic acid as a model pollutant. Microorganisms investigated included *E.coli*, *Clostridium perfringens*, and *Cryptosporidium parvum*. More recent work on disinfection has compared UVA and UVA-photocatalytic efficiency in real water taken from a catchment in Northern Ireland.

Where the supporting substrate was electrically conducting the samples were used in photoelectrolytic cells where the application of an external electrical bias was employed to increase the rate of the degradation. Furthermore, these photoanode materials were employed in a two compartment photogalvanic cell for the simultaneous degradation of organic contaminants and the recovery of dissolved metal ions. A number of different photoreactor configurations were employed in this work.

Experiments had shown that photocatalysis was effective for the destruction of the parent compounds i.e. 17- β -oestradiol, oestriol and oesterone. However, perhaps more important, is the removal of the oestrogenic activity. To this end experiment were undertaken to determine the “oestrogenic activity”, following photocatalytic treatment, using a yeast screen bioassay. In this work the TiO_2 (*Degussa P25*) was immobilized onto Ti-alloy using an electrophoretic coating method (Byrne et al. 1998). Photocatalysis was effective for the removal of the oestrogenic activity of 17- β -oestradiol under UVA illumination. Further work also demonstrated the effective destruction of the oestrogenic activity of oestrone and 17- α -ethinyl oestradiol (Coleman et al, 2004). These experiments clearly demonstrate that TiO_2 photocatalysis is a promising technology for the treatment of water contaminated with endocrine disrupting chemicals.

Work was also undertaken to monitor the genotoxicity of intermediate breakdown products of p-nitrophenol during photocatalytic degradation. A commercial toxicity bioassay (Vitotox test kit) was used to determine toxicity. The parent PNP was analysed by HPLC and it was shown that the degradation of the parent PNP was faster than the reduction in genotoxicity during photocatalytic degradation, as a result of the formation of genotoxic intermediates (Sekler et al, 2004).

Experiments were undertaken in a customised stirred tank photoreactor to investigate the use of electrochemically assisted photocatalysis (EAP) using formic acid as a model pollutant under either UVA or UVB irradiation. It was found that EAP did not increase the rate of oxidation of formic acid where the dissolved O₂ concentration was greater than 20% under conditions of good mass transfer. The use of a UVB source as compared to a UVA source resulted in a significant increase in the rate of oxidation and increased apparent quantum yields (McMurray et al, 2005). The photocatalytic degradation of the herbicide atrazine was also compared under UVA and UVB irradiation. The maximum apparent quantum yield for the photocatalytic degradation was higher under UVB (0.59%) compared to UVA (0.34%) (McMurray et al, 2006).

Photoanodes were incorporated into a two compartment photoelectrochemical cell for the simultaneous photocatalytic oxidation of formic acid in the anode compartment and the electrochemical reduction of Cu²⁺ on a copper mesh counter electrode in the cathode compartment (Byrne et al, 2002). The anode and cathode compartments were separated by an anion exchange membrane. The difference between the conduction band potential and the reduction potential of the Cu²⁺ ions is the driving source for this “photogalvanic” cell. Cu metal was recovered with a high faradaic efficiency (95.5%) and formic acid was degraded. The initial incident photon to current conversion efficiency (IPCE) of the system (using two 9 W blacklight lamps) was 9.5%. This type of system could be used for the remediation and recovery of metals from plating waste streams under solar illumination.

More recent work has concentrated on the photocatalytic disinfection of microorganisms in real water using UVA illumination. This work is aimed at the development of photocatalytic systems for water disinfection in developing regions where access to clean drinking water is limited. Results show that the rate of UVA and UVA - photocatalytic disinfection of *E.coli* is reduced in real or natural water as compared to distilled water, however, the rate of photocatalytic disinfection is greater than that found with UVA alone in both cases. Work is ongoing to determine the salient parameters in real water which affect the rate of photocatalytic disinfection under UVA illumination and to design an optimal reactor for solar water disinfection, taking into account the synergistic effects of UV, heat and UV-photocatalysis.

Acknowledgements: The authors wish to thank the EC for funding EVKI-CT-2000-00069-PEBCAT and FP6-2004-INCO-DEV-031650-SODISWATER; Degussa and Millennium for supplying free samples of TiO₂; Philips, Netherlands, for supplying free UV lamps; DEL for funding PhD students, and the engineering technical staff for reactor construction.

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